Chapter 9

Time-Dependent Properties of Condensed Media

BRUCE J. BERNE†

† Alfred P. Sloan Foundation Fellow.

I. Introduction

A large number of experimental methods are currently used to probe the dynamics of molecular motions in solids, liquids, and gases. All of these experimental methods share one characteristic in common. They all use as a probe an external field that is weakly coupled to the system and they all study the response of the physical system to the probe. Line-shape studies of infrared and Raman spectra (Van Kranendonk, 1952), studies of the shape of the spectral density function obtained from light- and neutron-scattering experiments (Blume, 1965; Egelstaff, 1965, 1967; Pines and Nozieres, 1966; Sjolander, 1964) line-shape studies in nuclear magnetic resonance (Abragam, 1961), and electron spin resonance spectroscopy (Slichter, 1963), as well as studies of static and frequency-dependent transport coefficients (De Groot and Mazur, 1962), are some of the probes that fall in this category. These experiments can be divided into two groups according to whether the probe is mechanical or thermal. For example, light scattering falls into the first category, whereas the measurements of the thermal conductivity falls into the second. The reason for making this division is based on the fact that the response of a system to mechanical probes is much easier to treat than its response to thermal probes. The interaction between a mechanical probe and the physical system can be described by an interaction Hamiltonian, whereas thermal-probe-system interactions must be handled differently.

The basic theoretical problem is to describe the response of an equilibrium system to a weak force field, mechanical or thermal in nature. The solution to this problem is by now well known and there exist many

excellent reviews on the subject (Gordon, 1968; Helfand, 1960; Kadanoff and Martin, 1963; Kubo, 1961; Martin, 1968, 1965; Mazur, 1966; Zwanzig, 1965). In this section, we will review the theory.

The major conclusions of this theory, which is known as linear response theory, can be simply stated as follows. Whenever two systems are weakly coupled to one another, such as when radiation is weakly coupled to matter, or when molecular vibrations are weakly coupled to molecular motion, it is only necessary to know how both systems behave in the absence of the coupling in order to describe the way in which one system responds to the other. Furthermore, the response of one system to the other is completely describable in terms of time correlation functions of dynamical properties.

Time-dependent correlation functions have been familiar for a long time in the theory of noise and stochastic processes. In recent years, they have become very useful in many areas of statistical physics and spectroscopy. Correlation functions provide a concise method for expressing the degree to which two dynamical properties are correlated over a period of time. Because the response of a system to a specific weak probe is directly related to a correlation function, many experiments have been devised to determine specific correlation functions. Only a few such experiments will be mentioned here. The interested reader should consult the excellent reviews on the subject.

The most important experiment for the determination of the dynamics of molecular motion is thermal neutron scattering. A complete determination of the differential scattering cross section for the scattering of neutrons from liquids completely determines the Van Hove scattering function (Van Hove, 1954). This function is related through a space–time Fourier transform to the autocorrelation function of the number density at two different space–time points in the liquid. In principle, this function contains all relevant information concerning the structure and dynamics of liquids that is necessary to describe liquid equilibrium and transport properties. There are still many experimental difficulties preventing the complete realization of this experimental program.

With the advent of lasers, light scattering has become a convenient and powerful tool for the determination of liquid properties (Fabilinsky, 1968; Pecora, 1964). Brillouin-scattering experiments involve the spectral resolution of light scattered at various angles from a liquid or solid system. The differential scattering cross section obtained from this inelastic light-scattering experiment is directly related to the long-wavelength, low-frequency behavior of the Van Hove scattering function. It supplements

the information gained from neutron-scattering experiments but is not capable of giving short-wavelength, high-frequency information. Nevertheless, it is useful for the determination of hydrodynamic and transport properties (Dubin *et al.*, 1967; Mountain, 1966), and recently it has been shown how it can be used to determine rate constants of very fast chemical reactions (Berne and Frisch, 1967; Berne and Pecora, 1968; Blum and Salzburg, 1968).

The shape of the vibration-rotation bands in infrared-absorption and Raman-scattering experiments on diatomic molecules yields a great deal of information about molecular reorientation in solids, liquids, and gases (Gordon, 1968; Van Kranendonk, 1952). Another experimental method that has been used to determine orientational correlations in macromolecular systems is based on measurements of the time dependence of the depolarization of fluorescence. From these measurements, rotational diffusion coefficients and the shape of the rotating macromolecule can be determined (Perrin, 1926).

There are several compelling reasons to interpret experiments in terms of correlation functions. The most important among these is that the results of several different experiments can often be correlated and used to clarify the basic underlying dynamical processes. For example, infrared absorption and Raman spectroscopy, as well as dielectric relaxation and the depolarization of fluorescence, provide information about the same mechanical property. These different measurements can be used to construct a picture of the particular dynamical processes involved. Furthermore, correlation functions provide a useful link between theory and experiment. Any theoretical model that stands up to an exhaustive comparison with the full experimental time dependence of time correlation functions reflects more strongly on the nature of the liquid state than does one that only gives the transport coefficients. Thus, a set of quite different experiments can be used to test a given model of a liquid and to assess the validity of certain *ad hoc* assumptions which are usually unavoidable.

It can be stated that time correlation functions have done for the theory of time-dependent process what partition functions have done for equilibrium theory. The time-dependent problem has become well defined, but no easier to solve. One now knows which correlation function corresponds to a given time-dependent phenomenon. Nevertheless, it is still extremely difficult to compute the correlation function. This is analogous to equilibrium theory when one knows that, to compute a thermodynamic property of a system, one must evaluate a well-defined partition function—a very difficult task.

At present, the complete time dependence of only a few time correlation functions have been determined experimentally. Furthermore, the theory of time-dependent processes is such that we know in principle which experiments can be used to determine specific correlation functions. In addition, we know certain general properties of these correlation functions. However, one of the major difficulties encountered in developing a theory of time correlation functions arises from the fact that there seems to be, at least at present, no simple way of bypassing the complex many-body dynamics in a realistic fashion. Consequently, both theoretically and experimentally there are difficult obstacles impeding progress toward a satisfactory understanding of the dynamics of liquids, solids, and gases.

In the case of fluids, digital computers have recently been employed to cope with the mathematical difficulties encountered above. Molecular dynamics studies, as these studies are now called, provide a brute force solution to the N-body problem. The canonical equations of motion for a large assembly of atoms or molecules are solved subject to periodic boundary conditions. These studies are carried out, as will be explained, in such a way that averages can be evaluated. Among other things, time correlation functions are computed. According to Zwanzig (1965), such studies provide what is probably the most detailed "experimental information currently available about dynamical processes in liquids." These studies are to be regarded as experiments which probe time correlation functions. They provide the raw data against which various dynamical theories of the liquid state can be checked. Such studies provide insight into the microscopic dynamical behavior of real diatomic liquids for both experimentalists and theoreticians alike.

There have been a number of attempts to calculate time correlation functions on the basis of simple models. Notable among these is the non-Markovian kinetic equation, the memory-function equation for time correlation functions first derived by Zwanzig (1961). This approach is reviewed in this chapter, its relation to other methods is pointed out, and its applicability extended to other areas. The results of this theory are compared with the results of molecular dynamics.

Linear response theory is reviewed in Section II in order to establish contact between experiment and theory. In Section III, the memory-function equation is derived and the general properties satisfied by the time correlation function and the memory function are discussed. In Section IV, computer experiments are reviewed. In Section V and VI, time correlation functions are calculated on the basis of specific models.

II. Linear Response Theory

A. Linear Systems

When a system of molecules interacts with a weak field, the interaction Hamiltonian can often be expressed as

$$\mathscr{H}'(t) = -\int_v d^3r\, \hat{B}(\mathbf{r})F(\mathbf{r}, t), \tag{2.1}$$

where $\hat{B}(\mathbf{r})$ is the dynamical operator

$$\hat{B}(\mathbf{r}) = \frac{1}{2}\sum_{m=1}^{N} [\hat{B}_m, \delta(\mathbf{r} - \mathbf{r}_m)]_+ \tag{2.2}$$

so that

$$\mathscr{H}'(t) = -\frac{1}{2}\sum_{m=1}^{N} [\hat{B}_m, F(r_m, t)]_+; \tag{2.3}$$

$\hat{B}_m$ is a property of the mth particle located at the position $\mathbf{r}_m$; and $\frac{1}{2}[\alpha, \beta]_+$ represents the symmetrized product

$$[\alpha, \beta]_+ = [\alpha\beta + \beta\alpha].$$

The operators $\hat{B}_m$ and $\hat{\mathbf{r}}_m$ represent properties of the system and are consequently Hermitian. The symmetrized product of two Hermitian operators is a Hermitian operator. Thus, $\hat{B}(\mathbf{r})$ is Hermitian. In (2.1), $F(\mathbf{r}, t)$ is the applied field that acts on the system at the space–time point $(\mathbf{r}, t)$. This form of the interaction potential between a system and a weak probe is actually quite ubiquitous. Consider, for example, how a system of molecules interacts with a weak radiation field in the dipole approximation. Then,

$$\mathscr{H}'(t) = -\int d^3r\, \mathbf{M}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}, t), \tag{2.4}$$

where $\mathbf{E}(\mathbf{r}, t)$ is the electric field at the space–time point $(\mathbf{r}, t)$ with polarization $\boldsymbol{\epsilon}$ and $\mathbf{M}(\mathbf{r})$ is the electric polarization operator at the point $\mathbf{r}$,

$$\mathbf{M}(\mathbf{r}) \equiv \frac{1}{2}\sum_{m=1}^{N} [\boldsymbol{\mu}_m, \delta(\mathbf{r} - \mathbf{r}_m)]_+.$$

Here, $\boldsymbol{\mu}_m$ is the electric dipole operator and $\mathbf{r}_m$ is the center-of-mass position of molecule M. The interaction Hamiltonian can also be written

as

$$\mathscr{H}'(t) = -\frac{1}{2}\sum_{m=1}^{N} [\boldsymbol{\mu}_m \cdot \mathbf{E}(\mathbf{r}_m, t) + \mathbf{E}(\mathbf{r}_m, t) \cdot \boldsymbol{\mu}_m].$$

There is a completely analogous development for a system of nuclear spins interacting with a time-dependent magnetic field.

It is convenient to assume from the outset that in the absence of the probing field F the expectation value of the observable $\hat{B}$ is zero. In the presence of the probe F, $\langle B\rangle$ is in general nonzero, because the system is "driven" by the force F. This also applies to other properties of the system that in the absence of the probe are expected to be zero. The perturbation thus "induces" certain properties of the system to take on nonzero expectation values. If the perturbation is sufficiently weak, it produces a linear response in the system. In the linear regime, doubling the magnitude of F simply doubles the magnitude of the induced responses. A simple example of linear response is Ohm's law,

$$\mathbf{J} = \sigma \cdot \mathbf{E},$$

according to which, the current induced in a medium is linear in the electric field $\mathbf{E}$ (although not necessarily in the same direction as $\mathbf{E}$, because of possible anisotropies in the conductivity tensor σ).

The expectation value of property $\hat{B}$ at the space–time point $(\mathbf{r}, t)$ depends in general on the perturbing force F at all earlier times t' and at all other points $\mathbf{r}'$ in the system. This dependence springs from the fact that it takes the system a certain time to respond to the perturbation; that is, there can be a time lag between the imposition of the perturbation and the response of the system. The spatial dependence arises from the fact that if a force is applied at one point of the system it will induce certain properties at this point that will perturb other parts of the system. For example, when a molecule is excited by a weak field, its dipole moment may change, thereby changing the electrical polarization at other points in the system.

Another simple example of these nonlocal changes is that of a neutron which when introduced into a system produces a density fluctuation. This density fluctuation propagates to other points in the medium in the form of sound waves.

It is consequently quite natural to write

$$\langle B(\mathbf{r}, t)\rangle = \int_{-\infty}^{t} dt' \int d\mathbf{r}'\, \Phi_{BB}(\mathbf{r}, \mathbf{r}'; t, t')F(\mathbf{r}', t'), \tag{2.5}$$

where it is assumed that the force has been turned on in the past. Note that the induced response $\langle B(\mathbf{r}, t)\rangle$ is linear in the applied force F, and furthermore depends on the values F at all earlier times t', and at all points in the system. Causality is built into the above equation since the response follows and does not precede the application of the force. The function $\Phi_{BB}(\mathbf{r}, \mathbf{r}'; t, t')$ is called the "aftereffect function" because it relates the response $\langle B(\mathbf{r}, t)\rangle$ at the space–time point $(\mathbf{r}, t)$ to the disturbance at the space–time point $(\mathbf{r}', t')$. Note that the response to a delta-function field,

$$F(\mathbf{r}, t) = \delta(\mathbf{r} - \mathbf{r}_0)\,\delta(t - t_0),$$

is

$$\langle B(\mathbf{r}, t)\rangle = \Phi_{BB}(\mathbf{r}, \mathbf{r}_0; t, t_0)\eta(t - t_0),$$

where $\eta(t)$ is the Heaviside function. Thus, $\Phi_{BB}(\mathbf{r}, \mathbf{r}_0, t, t_0)$ is the response, $\langle B(\mathbf{r}, t)\rangle$, to a unit delta-function pulse applied at the space–time point $(\mathbf{r}_0, t_0)$. If in the absence of the perturbation the system is a large, uniform system in thermodynamic equilibrium, then the response should be invariant to an arbitrary shift in the origin of the space–time coordinate system by $(\mathbf{a}_0, \tau_0)$. Consequently, for such systems the condition

$$\langle \mathbf{B}(\mathbf{r} + \mathbf{a}_0, t + \tau_0)\rangle = \langle B(\mathbf{r}, t)\rangle$$

must hold. This condition can only be met if the aftereffect function has the form

$$\Phi_{BB}(\mathbf{r}, \mathbf{r}_0; t, t_0) = \Phi_{BB}(\,|\,\mathbf{r} - \mathbf{r}_0\,|\,, t - t_0). \tag{2.6}$$

Thus, the response of a spatially uniform system in thermodynamic equilibrium is always characterized by translationally invariant and temporally stationary aftereffect functions. This chapter is restricted to a discussion of systems that prior to an application of an external perturbation are uniform and in equilibrium. The condition expressed by Eq. (2.6) must be satisfied. Caution must be exercised in applying linear response theory to problems in double-resonance spectroscopy where nonequilibrium initial states are prepared. Having dispensed with this *caveat*, we adopt Eq. (2.6) in the remainder of this chapter.

The response can be written as

$$\langle B(\mathbf{r}, t)\rangle = \int_{-\infty}^{t} dt' \int d\mathbf{r}'\, \Phi_{BB}(\mathbf{r} - \mathbf{r}', t - t')F(\mathbf{r}', t'). \tag{2.7}$$

Once the aftereffect function has been determined, the response to any form of $F(\mathbf{r}, t)$ can be predicted. The aftereffect function is an intrinsic dynamical property of the system, which is independent of the precise magnitude and form of the applied force, and which succinctly summarizes the way in which the constituent particles in a many-body system cooperate to give the observed response of the system to the external perturbation.

That the aftereffect function $\Phi_{BB}(\mathbf{r}, t)$ is a real function of the space–time coordinates $(\mathbf{r}, t)$ can be deduced from the fact that, since B is an observable, the response $\langle B(\mathbf{r}, t)\rangle$ to a real force must be real.

The force $F(\mathbf{r}, t)$ is in general a very complicated real function of the position and time. Any such force can be regarded as a superposition of monochromatic components,

$$F_{k\omega} \exp -i[\mathbf{k} \cdot \mathbf{r} - \omega t]\, e^{\varepsilon t}, \qquad \varepsilon > 0.$$

The factor $e^{\varepsilon t}$ has been introduced so that the field vanishes in the infinite past. Since the response is linear in the force, it suffices to compute the response of the system to each one of the monochromatic waves separately and then to superpose the results to find the total response. Therefore, without loss of generality we consider only the response to a single monochromatic force. Introducing the above force into Eq. (2.7) yields

$$\langle B(\mathbf{r}, t)\rangle = \chi_{BB}(\mathbf{k}, \omega)F_{k\omega} \exp -i[\mathbf{k} \cdot \mathbf{r} - \omega t], \tag{2.8}$$

where $\chi_{BB}(\mathbf{k}, \omega)$ is the frequency- and wave-vector-dependent complex susceptibility governing the linear response of $\langle B(\mathbf{r}, t)\rangle$ to the monochromatic perturbation. The susceptibility is obviously the Fourier–Laplace transform of the aftereffect function,†

$$\chi_{BB}(\mathbf{k}, \omega) = \lim_{\varepsilon \to 0+} \int_0^\infty dt \int d\mathbf{r}\, \Phi_{BB}(\mathbf{r}, t) \exp i[\mathbf{k} \cdot \mathbf{r} - \omega t]\, e^{-\varepsilon t} \tag{2.9}$$

Since the aftereffect function is a real function of $(\mathbf{r}, t)$, the susceptibility can be written in terms of its real and imaginary parts, $\chi'_{BB}(\mathbf{k}, \omega)$ and $\chi''_{BB}(\mathbf{k}, \omega)$, respectively,

$$\chi_{BB}(\mathbf{k}, \omega) = \chi'_{BB}(\mathbf{k}, \omega) + i\chi''_{BB}(\mathbf{k}, \omega). \tag{2.10}$$

† The limit $\varepsilon \to 0+$ is imposed to ensure convergence of the integral.

Comparison of Eqs. (10) and (11) yields

$$\chi'_{BB}(\mathbf{k}, \omega) = \lim_{\varepsilon \to 0} \int_0^\infty dt \int d\mathbf{r}\, \Phi_{BB}(\mathbf{r}, t) \cos[\mathbf{k} \cdot \mathbf{r} - \omega t] e^{-\varepsilon t}$$
$$\chi''_{BB}(\mathbf{k}, \omega) = \lim_{\varepsilon \to 0} \int_0^\infty dt \int d\mathbf{r}\, \Phi_{BB}(\mathbf{r}, t) \sin[\mathbf{k} \cdot \mathbf{r} - \omega t] e^{-\varepsilon t}. \tag{2.11}$$

The field applied to the system must in general be real, so that the full monochromatic force should be the superposition

$$\tfrac{1}{2}\{F_{k\omega} \exp -i[\mathbf{k} \cdot \mathbf{r} - \omega t] + F^*_{k\omega} \exp i[\mathbf{k} \cdot \mathbf{r} - \omega t]\} e^{\varepsilon t} \tag{2.12}$$

and the total response is the superposition of responses from each component, or

$$\langle B(\mathbf{r}, t)\rangle = \tfrac{1}{2}[\chi_{BB}(\mathbf{k}, \omega) F_{k\omega} \exp -i[\mathbf{k} \cdot \mathbf{r} - \omega t] + \chi_{BB}(-\mathbf{k}, -\omega) F^*_{k\omega} \exp i[\mathbf{k} \cdot \mathbf{r} - \omega t]]. \tag{2.13}$$

The following properties follow directly from these definitions:

$$\begin{aligned} &\text{(i)} && \chi'_{BB}(-\mathbf{k}, -\omega) = \chi'_{BB}(\mathbf{k}, \omega) \\ &\text{(ii)} && \chi''_{BB}(-\mathbf{k}, -\omega) = -\chi''_{BB}(\mathbf{k}, \omega) \\ &\text{(iii)} && \chi^*_{BB}(\mathbf{k}, \omega) = \chi_{BB}(-\mathbf{k}, -\omega). \end{aligned} \tag{2.14}$$

These properties result from the fact that the sine and cosine are respectively odd and even functions of their arguments. Condition (iii) can also be deduced directly from Eq. (2.13) by demanding that the induced response be real (that is, $\langle B\rangle = \langle B\rangle^*$). Condition (iii) allows Eq. (2.13) to be expressed as

$$\langle B(\mathbf{r}, t)\rangle = \operatorname{Re} \chi_{BB}(\mathbf{k}, \omega) F_{k\omega} \exp -i[\mathbf{k} \cdot \mathbf{r} - \omega t]. \tag{2.15}$$

The response of the system to the external monochromatic perturbation of Eq. (2.12) is accompanied by the absorption and emission of energy. This follows because, under the influence of the external perturbation, the system changes state. The difference between the energy absorbed and emitted is the energy dissipation. The energy dissipated per second per unit volume, $Q(\mathbf{k}, \omega)$, can be related to a susceptibility of the system. The time rate of change of the system's energy is simply $\partial \hat{H}'/\partial t$, where H' is given by Eq. (2.1); $Q(\mathbf{k}, \omega)$ is obtained from the expectation value of $\partial \hat{H}'/\partial t$ by averaging it over one period of the monochromatic field. Thus,

$$Q(\mathbf{k}, \omega) = (\omega/2\pi V) \int_0^{2\pi/\omega} dt \int_v d\mathbf{r}\, \langle B(\mathbf{r}, t)\rangle (\partial F/\partial t)(\mathbf{r}, t). \tag{2.16}$$

Substitution of Eq. (2.13) results in

$$Q(\mathbf{k}, \omega) = +\frac{\omega}{2} \chi''_{BB}(\mathbf{k}, \omega) \,|\, F_{k,\omega} \,|^2, \tag{2.17}$$

where V is the volume of the system.

The imaginary part of the susceptibility, $\chi''_{BB}(\mathbf{k}, \omega)$, is therefore related to the net energy dissipated per unit time by the system. It is obvious that all real processes are always accompanied by some energy dissipation, so that $Q(\mathbf{k}, \omega) \geq 0$. It then follows from Eq. (2.17) that

$$\chi''_{BB}(\mathbf{k}, \omega) = \begin{cases} >0, & \omega > 0, \\ <0, & \omega < 0. \end{cases} \tag{2.18}$$

The susceptibility can in principle be determined in the following way. A force

$$F(\mathbf{r}, t) = F_{k\omega} \cos[\mathbf{k} \cdot \mathbf{r} - \omega t]$$

is switched on and the response $\langle B(\mathbf{r}, t)\rangle$ is measured as a function of time. From Eq. (2.15), it is seen that

$$\langle B(\mathbf{r}, t)\rangle = F_{k\omega}\{\chi'_{BB}(\mathbf{k}, \omega) \cos[\mathbf{k} \cdot \mathbf{r} - \omega t] + \chi''_{BB}(\mathbf{k}, \omega) \sin[\mathbf{k} \cdot \mathbf{r} - \omega t]\}.$$

If phase-sensitive detection is used, then χ'_{BB} can be found from the part of $\langle B\rangle$ that oscillates in phase with the applied field (dispersion) and and χ''_{BB} can be found from the part of $\langle B(\mathbf{r}, t)\rangle$ that oscillates 90° out of phase with the applied field (absorption). In practice, it is unnecessary to measure both χ' and χ'', and a determination of one member of the pair uniquely determines the other. This relationship will be discussed later.

B. The Statistical Theory of the Susceptibility

There are a number of different ways to determine the quantum-mechanical formulae for the susceptibilities $\chi_{BB}(\mathbf{k}, \omega)$. Perhaps the simplest and most elegant procedure is due to Kubo (1961). We follow a different procedure here.

The total Hamiltonian of our system $\hat{H}$ consists of two parts: $\hat{H}_0$, the unperturbed Hamiltonian of the system, and $\hat{H}'(t)$, the perturbation,

$$\hat{H}'(t) = -\int_V d\mathbf{r}\, \hat{B}(\mathbf{r}) F(\mathbf{r}, t). \tag{2.19}$$

This perturbation, as we have seen, can also be written as

$$\hat{H}'(t) = -\frac{1}{2}\sum_m [\hat{B}_m, F(\mathbf{r}_m, t)]_+. \tag{2.20}$$

Since the responses that we are trying to calculate are linear in the force, it suffices to develop $F(\mathbf{r}_m, t)$ in a Fourier series and then to compute the response to each term separately. The total response is found by superposing each of these terms. Thus, without loss of generality we consider only the response to the simple Hamiltonian,

$$\hat{H}'(t) = -\frac{1}{2}\sum_m \{[\hat{B}_m, \exp -i\mathbf{k}\cdot\mathbf{r}_m]_+ F_{k\omega} e^{i\omega t} + [\hat{B}_m, \exp i\mathbf{k}\cdot\mathbf{r}_m]_+ F^*_{k\omega} e^{-i\omega t}\}$$

or

$$\hat{H}'(t) = -[\hat{B}_{-k} F_{k\omega} e^{i\omega t} + \hat{B}_k F^*_{k\omega} e^{-i\omega t}]. \tag{2.21}$$

The operator $\hat{B}_k$ is

$$\hat{B}_k = \frac{1}{2}\sum_m [\hat{B}_m, \exp i\mathbf{k}\cdot\mathbf{r}_m]_+. \tag{2.22}$$

From the definition of $\hat{B}_k$, it should be noted that $\hat{B}_k$ and $\hat{B}_{-k}$ are Hermitian conjugates. According to the golden rule of time-dependent perturbation theory, the probability per unit time $W_{\mathrm{i}\to\mathrm{f}}(\mathbf{k}, \omega)$ that the field $F(\mathbf{k}, \omega)$ induces a transition in the system from the initial state $|\, i)$ to the final state $|\, f)$ is given by

$$W_{\mathrm{i}\to\mathrm{f}}(\mathbf{k}, \omega) = (2\pi/4\hbar^2)\,|\, F_{k\omega}\,|^2\,|\,(i\,|\, B_{+k}\,|\, f)\,|^2\,\delta(\omega - \omega_{\mathrm{fi}}), \tag{2.23}$$

where $\hbar\omega_{\mathrm{fi}} \equiv E_{\mathrm{f}} - E_{\mathrm{i}}$ and the delta function conserves energy. In a sense, the external field transfers momentum $\hbar\mathbf{k}$ and energy $\hbar\omega$ to the system in the transition. The probability that the system is initially in the state $|\, i)$ is simply the Boltzmann factor $\varrho_{\mathrm{i}} = Q^{-1}\exp(-\beta E_{\mathrm{i}})$. The probability per unit time that the probe will transfer momentum $\hbar\mathbf{k}$ and energy $\hbar\omega$ to the system regardless of the initial and final states is

$$P(\mathbf{k}, \omega) = (2\pi/4\hbar^2)\,|\, F_{k\omega}\,|^2 \sum_{\mathrm{if}} \varrho_{\mathrm{i}}\,|\,(i\,|\, B_{+k}\,|\, f)\,|^2\,\delta(\omega - \omega_{\mathrm{fi}}). \tag{2.24}$$

There is a corresponding inverse process in which the system makes a transition from the state $|\, f)$ to the state $|\, i)$ thereby giving momentum $\hbar\mathbf{k}$ and energy $\hbar\omega$ to the probe. In this process, the system suffers a momentum change $-\hbar\mathbf{k}$ and an energy change $-\hbar\omega$ with a probability per unit time

$$W_{\mathrm{f}\to\mathrm{i}}(-\mathbf{k}, -\omega) = (2\pi/4\hbar^2)\,|\, F_{k\omega}\,|^2\,|\,(f\,|\, \hat{B}_{-k}\,|\, i)\,|^2\,\delta(\omega - \omega_{\mathrm{fi}}). \tag{2.25}$$

The probability per unit time that the system will transfer momentum $\hbar\mathbf{k}$ and energy $\hbar\omega$ to the probe regardless of the initial state is consequently

$$P(-\mathbf{k}, -\omega) = (2\pi/4\hbar^2)\,|\, F_{k\omega}\,|^2 \sum_{\mathrm{if}} \varrho_{\mathrm{f}}\,|\,(f\,|\, B_{-k}\,|\, i)\,|^2\,\delta(\omega - \omega_{\mathrm{fi}}). \tag{2.26}$$

It should be noted that $W_{\mathrm{f}\to\mathrm{i}}(-\mathbf{k}, -\omega) = W_{\mathrm{i}\to\mathrm{f}}(\mathbf{k}, \omega)$. This follows directly from the fact that the operator $\hat{B}_k$ is the Hermitian adjoint of $\hat{B}_{-k}$. The transition probabilities $P(\mathbf{k}, \omega)$ and $P(-\mathbf{k}, -\omega)$ are in general unequal, as can be seen by a comparison of Eqs. (2.24) and (2.26). In fact, since $\varrho_{\mathrm{f}} = \varrho_{\mathrm{i}}\exp(-\beta\hbar\omega_{\mathrm{fi}})$, it is clear from the properties of the delta function that Eq. (2.26) is

$$P(-\mathbf{k}, -\omega) = (2\pi/4\hbar^2)\,|\, F_{k\omega}\,|^2\, e^{-\beta\hbar\omega} \sum_{\mathrm{if}} \varrho_{\mathrm{i}}\,|\,(f\,|\, B_k\,|\, i)\,|^2\,\delta(\omega - \omega_{\mathrm{fi}}); \tag{2.27}$$

$\hat{B}_{-k}$ and $\hat{B}_k$ are Hermitian conjugates, so that

$$|\,(f\,|\, \hat{B}_{-k}\,|\, i)\,|^2 = |\,(i\,|\, \hat{B}_{+k}\,|\, f)\,|^2. \tag{2.28}$$

Substitution of this into Eq. (2.27) and subsequent comparison with Eq. (2.24) yields

$$P(-\mathbf{k}, -\omega) = e^{-\beta\hbar\omega} P(\mathbf{k}, \omega). \tag{2.29}$$

This equation expresses the well-known condition of *detailed balance*, according to which every transition out of a microscopic state of a system in equilibrium is balanced on the average by a transition into that state. This condition is sufficient for the maintenance of thermodynamic equilibrium. Equation (2.29) demonstrates that the system absorbs more energy per unit time than it emits. It can be concluded that there is a net energy dissipation from the external field with a consequent production of heat.

The above transition probabilities can be written in terms of one-sided time correlation functions. For this purpose, we define the dynamical form factor $S_B(\mathbf{k}, \omega)$ as

$$S_B(\mathbf{k}, \omega) = 2\pi \sum_{\mathrm{if}} \varrho_{\mathrm{i}} \,|(i \mid B_{+k} \mid f)|^2\, \delta(\omega - \omega_{\mathrm{fi}}). \tag{2.30}$$

It follows from Eqs. (24), (26), and (29) that

$$\begin{aligned} P(\mathbf{k}, \omega) &= (1/4\hbar^2) \mid F_{k\omega} \mid^2 S_B(\mathbf{k}, \omega) \\ P(-\mathbf{k}, -\omega) &= (1/4\hbar^2) \mid F_{k\omega} \mid^2 S_B(-\mathbf{k}, -\omega) \end{aligned} \tag{2.31}$$

and

$$S_B(-\mathbf{k}, -\omega) = e^{-\beta\hbar\omega} S_B(\mathbf{k}, \omega). \tag{2.32}$$

Equation (2.32) expresses the condition of detailed balance.

From the physical interpretation of $P(\mathbf{k}, \omega)$ and $P(-\mathbf{k}, -\omega)$ as absorption and emission rates, it is clear that the power dissipated per unit time and per unit volume $Q(\mathbf{k}, \omega)$ is

$$Q(\mathbf{k}, \omega) = \hbar\omega[P(\mathbf{k}, \omega) - P(-\mathbf{k}, -\omega)], \tag{2.33}$$

which can be written as

$$Q(\mathbf{k}, \omega) = (\omega/4\hbar)[S_B(\mathbf{k}, \omega) - S_B(-\mathbf{k}, -\omega)] \mid F_{k\omega} \mid^2. \tag{2.34}$$

Comparison with Eq. (2.17) shows that

$$\chi''_{BB}(\mathbf{k}, \omega) = (1/2\hbar)[S_B(\mathbf{k}, \omega) - S_B(-\mathbf{k}, -\omega)]. \tag{2.35}$$

There are a variety of ways of expressing this result. From the condition of detailed balance, it should be noted that

$$[S_B(\mathbf{k}, \omega) \pm S_B(-\mathbf{k}, -\omega)] = [1 \pm e^{-\beta\hbar\omega}] S_B(\mathbf{k}, \omega). \tag{2.36}$$

From this equation, it follows that

$$[S_B(\mathbf{k}, \omega) - S_B(-\mathbf{k}, -\omega)] = \tanh(\beta\hbar\omega/2)[S_B(\mathbf{k}, \omega) + S_B(-\mathbf{k}, -\omega)] \tag{2.37}$$

$$[S_B(\mathbf{k}, \omega) - S_B(-\mathbf{k}, -\omega)] = [1 - e^{-\beta\hbar\omega}] S_B(\mathbf{k}, \omega). \tag{2.38}$$

Let us study the dynamical form factors $S_B(\mathbf{k}, \omega)$ and $S_B(-\mathbf{k}, -\omega)$ before returning to $\chi''_{BB}(\mathbf{k}, \omega)$.

According to the definition of $S_B(\mathbf{k}, \omega)$ given in Eq. (2.30),

$$S_B(\mathbf{k}, \omega) = 2\pi \sum_{\mathrm{if}} \varrho_{\mathrm{i}} \mid (i \mid B_k \mid f) \mid^2 \delta(\omega - \omega_{\mathrm{fi}}).$$

The delta function can be expressed in the integral representation

$$\delta(\omega - \omega_{\mathrm{fi}}) = (1/2\pi) \int_{-\infty}^{+\infty} dt \exp(i(\omega - \omega_{\mathrm{fi}})t)$$

Thus

$$S_B(\mathbf{k}, \omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \sum_{\mathrm{if}} \varrho_{\mathrm{i}} \mid (i \mid \hat{B}_k \mid f) \mid^2 e^{i\omega_{\mathrm{if}} t}. \tag{2.39}$$

The spectral density function is consequently the time Fourier transform of the function

$$\varphi_{BB}(\mathbf{k}, t) = \sum_{\mathrm{if}} \varrho_{\mathrm{i}} \mid (i \mid \hat{B}_k \mid f) \mid^2 e^{i\omega_{\mathrm{if}} t} \tag{2.40}$$

This formula can be written in the following forms:

$$\begin{aligned} \varphi_{BB}(\mathbf{k}, t) &= \sum_{\mathrm{if}} \varrho_{\mathrm{i}} \exp(iE_{\mathrm{i}}t/\hbar)(i \mid \hat{B}_k \mid f) \exp(-iE_{\mathrm{f}}t/\hbar)(f \mid B_{-k} \mid i) \\ &= \sum_{\mathrm{if}} \varrho_{\mathrm{i}}(i \mid \exp(i\hat{H}_0 t/\hbar)\, \hat{B}_k \exp(-i\hat{H}_0 t/\hbar) \mid f)(f \mid B_{-k} \mid i). \end{aligned}$$

In the first formula, we used the fact that $\hat{B}_k$ and $\hat{B}_{-k}$ are Hermitian conjugates [so that $(i \mid \hat{B}_k \mid f)^* = (f \mid \hat{B}_{-k} \mid i)$] and the definition $\hbar\omega_{\mathrm{if}} = E_{\mathrm{i}} - E_{\mathrm{f}}$. The second formula follows from the fact that the states $|i)$ and $|f)$ are energy eigenstates of the Hamiltonian $\hat{H}_0$. Now, it should be recalled that in the Heisenberg picture of quantum mechanics the basis states are time-independent, and the dynamical operators contain all the time dependence. Operators depend on the time in such a way that the arbitrary operator $\hat{A}(t)$ at time t is generated from its form at time t' by a unitary transformation with the propagator $\exp[i\hat{H}_0(t - t')/\hbar]$, so that

$$\hat{A}(t) = \exp[i\hat{H}_0(t - t')/\hbar]\, \hat{A}(t') \exp[-i\hat{H}_0(t - t')/\hbar].$$

It is easy to show that this operator satisfies the Heisenberg equation of motion

$$\frac{d}{dt} \hat{A}(t) = \frac{1}{i\hbar} [\hat{A}(t), H_0]_-.$$

Thus, it is easily seen that

$$\varphi_{BB}(\mathbf{k}, t) = \sum_{\mathrm{if}} \varrho_{\mathrm{i}}(i \mid \hat{B}_k(t) \mid f)(f \mid B_{-k}(0) \mid i)$$

where $\hat{B}_k(t)$ and $\hat{B}_{-k}(0)$ are the operators $\hat{B}_k$ and $\hat{B}_{-k}$ at times t and 0 respectively in the Heisenberg picture. The right-hand side of this equation is simply the equilibrium average value, $\langle B_k(t)B_{-k}(0)\rangle$, since the sum is just the trace, $\mathrm{Tr}[\hat{\varrho}\hat{B}_k(t)\hat{B}_{-k}(0)]$, where $\hat{\varrho}$ is the equilibrium density matrix. Thus, the function $\varphi_{BB}(\mathbf{k}, t)$ is

$$\varphi_{BB}(\mathbf{k}, t) = \langle B_k(t)B_{-k}(0)\rangle. \tag{2.41}$$

This function is a quantum-mechanical, one-sided time correlation function of the property B_k. It follows from Eq. (2.39) that

$$S_B(\mathbf{k}, +\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle B_k(t)B_{-k}(0)\rangle. \tag{2.42}$$

In a completely analogous manner, it can be shown that

$$S_B(-\mathbf{k}, -\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle B_{-k}(0)B_k(t)\rangle. \tag{2.43}$$

These functions differ in the order in which $B_{-k}(0)$ and $B_k(t)$ appear. Since $B_{-k}(0)$ and $B_k(t)$ do not generally commute, it follows that $\langle B_{-k}(0)B_k(t)\rangle$ and $\langle B_k(t)B_{-k}(0)\rangle$ are not equal.

From Eqs. (2.32) and (2.43),

$$[S_B(\mathbf{k}, \omega) \pm S_B(-\mathbf{k}, -\omega)] = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle [B_k(t), B_{-k}(0)]_{\pm}\rangle, \tag{2.44}$$

where $[\,.\,,\,.\,]_+$ denotes the anticommutator and $[\,.\,,\,.\,]_-$ the commutator. Let us now return to Eq. (2.35). The imaginary part of the susceptibility can be expressed in the alternate forms

$$\chi''_{BB}(\mathbf{k}, \omega) = \hbar^{-1} \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle \tfrac{1}{2}[B_k(t), B_{-k}(0)]_-\rangle, \tag{2.45a}$$

or

$$\chi''_{BB}(\mathbf{k}, \omega) = \hbar^{-1} \tanh \tfrac{1}{2}\beta\hbar\omega \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle \tfrac{1}{2}[B_k(t), B_{-k}(0)]_+\rangle, \tag{2.45b}$$

or

$$\chi''_{BB}(\mathbf{k}, \omega) = \hbar^{-1}(1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle B_k(t)B_{-k}(0)\rangle, \tag{2.45c}$$

Also, the transition probabilities can be expressed as

$$\begin{aligned} P(\mathbf{k}, \omega) &= (1/4\hbar^2) \mid F_{k\omega} \mid^2 \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle B_k(t)B_{-k}(0)\rangle \\ &= (1/4\hbar) \mid F_{k\omega} \mid^2 \chi''_{BB}(\mathbf{k}, \omega)/(1 - e^{-\beta\hbar\omega}) \\ P(-\mathbf{k}, -\omega) &= (1/4\hbar^2) \mid F_{k\omega} \mid^2 \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle B_{-k}(0)B_k(t)\rangle \\ &= (1/4\hbar) \mid F_{k\omega} \mid^2 \chi''_{BB}(\mathbf{k}, \omega)/(e^{\beta\hbar\omega} - 1) \end{aligned} \tag{2.46}$$

The functions that appear in the integrals,

$$\begin{aligned} \Phi_{BB}(\mathbf{k}, t) &= \langle i/\hbar[B_k(t), B_{-k}(0)]_-\rangle \\ C_{BB}(\mathbf{k}, t) &= \langle \tfrac{1}{2}[B_k(t), B_{-k}(0)]_+\rangle, \end{aligned} \tag{2.47}$$

are respectively called the *aftereffect function*† and the *autocorrelation function of the process* B_k.

---

† The aftereffect function can also be written as

$$\Phi_{BB}(\mathbf{k}, t) = \int_0^{\beta} d\lambda \langle (\exp \lambda\hat{H}_0)\dot{B}_{-k}(0)(\exp - \lambda\hat{H}_0)B_k(t)\rangle. \tag{2.47a}$$

This can be demonstrated by expanding the average,

$$\langle \exp(\lambda\hat{H}_0)\dot{\hat{B}}_{-k}(0) \exp(-\lambda\hat{H}_0)\hat{B}_k(t)\rangle = \sum_{\mathrm{if}} \varrho_{\mathrm{i}} \exp[\lambda(E_{\mathrm{i}} - E_{\mathrm{f}})](i \mid \dot{B}_{-k}(0) \mid f)(f \mid B_k(t) \mid i).$$

Since $\dot{B}_{-k} = (1/i\hbar)[B_{-k}, \hat{H}]_-$, it follows that

$$(i \mid \dot{B}_{-k} \mid f) = (1/i\hbar)(E_{\mathrm{f}} - E_{\mathrm{i}})(i \mid B_{-k} \mid f).$$

Consequently, the integral on the right-hand side of Eq. (2.47a) is

$$\sum_{\mathrm{if}} \varrho_{\mathrm{i}}\{[\exp \beta(E_{\mathrm{i}} - E_{\mathrm{f}})] - 1\}(i \mid B_{-k}(0) \mid f)(f \mid B_k(t) \mid i).$$

Now,

$$\varrho_{\mathrm{i}}\{[\exp \beta(E_{\mathrm{i}} - E_{\mathrm{f}})] - 1\} = \varrho_{\mathrm{f}} - \varrho_{\mathrm{i}},$$

so that the integral is $\langle \tfrac{1}{2}[B_k(t), B_{-k}(0)]_-\rangle$. This proves that

$$\Phi_{BB}(\mathbf{k}, t) = \int_0^{\beta} d\lambda \langle (\exp \lambda\hat{H})\dot{B}_{-k}(0)(\exp - \lambda\hat{H})B_k(t)\rangle.$$

Note that

$$(\exp \lambda\hat{H})\dot{B}_{-k}(\exp - \lambda\hat{H}) = \dot{B}_{-k}(-i\hbar\lambda),$$

so that

$$\Phi_{BB}(\mathbf{k}, t) = \int_0^{\beta} d\lambda \langle \dot{B}_{-k}(-i\hbar\lambda)B_k(t)\rangle.$$

The integral is called the Kubo transform (1961) of the time correlation function.

The Fourier transform $G_{BB}(\mathbf{k}, \omega)$ of the autocorrelation function $C_{BB}(\mathbf{k}, t)$,

$$2\pi G_{BB}(\mathbf{k}, \omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t} C_{BB}(\mathbf{k}, t), \tag{2.48}$$

plays a very important role in linear response theory. It should be noted that the imaginary part of the susceptibility is

$$\chi''_{BB}(\mathbf{k}, \omega) = 2\pi\hbar^{-1} \tanh(\beta\hbar\omega/2) G_{BB}(\mathbf{k}, \omega) \tag{2.49}$$

and consequently,

$$Q(\mathbf{k}, \omega) = (\omega\pi/\hbar) \tanh(\beta\hbar\omega/2) \mid F_{k\omega} \mid^2 G_{BB}(\mathbf{k}, \omega). \tag{2.50}$$

The power dissipation is linearly related to $G_{BB}(\mathbf{k}, \omega)$, which consequently is called the *power spectrum* of the process $\hat{B}_k$. It is noteworthy that the energy dissipated by a system when it is exposed to an external field is related to a time correlation function, $C_{BB}(\mathbf{k}, t)$, that describes the detailed way in which spontaneous fluctuations regress in the equilibrium state. The result embodied in Eq. (2.50) is called the *fluctuation dissipation theorem* (Callen and Welton, 1951). It is a direct consequence of this theorem that weak force fields can be used to probe the dynamics of molecular motion in physical systems. A list of experiments together with the time correlation functions that they probe is presented in Table I. An experiment that determines $Q(\mathbf{k}, \omega)$ determines $G_{BB}(\mathbf{k}, \omega)$ and consequently, through Fourier inversion, $C_{BB}(\mathbf{k}, t)$:

$$C_{BB}(\mathbf{k}, t) = (\hbar/\pi) \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, Q(\mathbf{k}, \omega) \coth(\beta\hbar\omega/2)/\omega \mid F_{k\omega} \mid^2. \tag{2.51}$$

$C_{BB}(\mathbf{k}, t)$ can also be determined from a measurement of either $P(\mathbf{k}, \omega)$ or $P(-\mathbf{k}, -\omega)$.

The one-sided correlation function $\langle B_k(t) B_{-k}(0)\rangle$ could have been determined instead of $C_{BB}(\mathbf{k}, t)$. From Eqs. (2.17) and (2.45c),

$$\langle B_k(t) B_{-k}(0)\rangle = (\hbar/\pi) \int_{-\infty}^{-\infty} dt\, e^{-i\omega t} Q(\mathbf{k}, \omega)/\omega[1 - e^{-\beta\hbar\omega}] \mid F_{k\omega} \mid^2. \tag{2.52}$$

This kind of investigation is becoming very common.

In the classical limit ($\hbar \to 0$), Eq. (2.49) reduces to

$$\chi''_{BB}(\mathbf{k}, \omega) = (\beta\pi\omega/KT) G^{\mathrm{cl}}_{BB}(\mathbf{k}, \omega), \tag{2.53}$$

TABLE I

Some Experimental Probes of Time Correlation Functions

Experimental measurement	Dynamical quantity	Time correlation function
Self-diffusion coefficient	$\mathbf{V}$, c.m. velocity of tagged molecule	$\langle \mathbf{V}(0) \cdot \mathbf{V}(t)\rangle$
Rotational diffusion coefficient	$\mathbf{\Omega}$, angular velocity about molecular c.m.	$\langle \Omega_\alpha(0)\Omega_\beta(t)\rangle$
Infrared absorption	$\mathbf{u}$, unit vector along molecular transition dipole	$\langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle$
Raman scattering: depolarization of fluorescence	$\mathbf{u}$	$\langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$
Spin-rotation relaxation time	$\mathbf{J}$, angular momentum about molecular c.m.	$\langle \mathbf{J}(0) \cdot \mathbf{J}(t)\rangle$
NMR line-shape	M_x, x component of the magnetization of the system	$\langle M_x(0) M_x(t)\rangle$
Mossbauer line shape	$\mathbf{r}_l$, position of lth nucleus	$(1/N) \sum_{l,l'}^{N} \langle \exp[-i\mathbf{k} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{k} \cdot \mathbf{r}_l(t)]\rangle$
Neutron scattering	$\mathbf{r}_l$, position of lth nucleus in fluid	$(1/N) \sum_{l,l'}^{N} \langle \exp[-i\mathbf{k} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{k} \cdot \mathbf{r}_l(t)]\rangle$
		$(1/N) \sum_{l,l'}^{N} \exp[-i\mathbf{k} \cdot \mathbf{r}_l(0)] \sum_{j=1}^{N} \exp[i\mathbf{k} \cdot \mathbf{r}_j(t)]\rangle$
Brillouin scattering: polarized scattering	α_l^f; trace of the polarizability tensor of molecule	$(1/N) \langle \sum_{j,l}^{N} \alpha_l^f(0) \alpha_j^f(t) \exp[i\mathbf{k} \cdot [\mathbf{r}_j(t) - \mathbf{r}_l(0)]]\rangle$
Brillouin scattering: depolarized scattering	xyth element of polarizability tensor of molecule	$(1/N) \langle \sum_{l,l'}^{N} \alpha_{xy}^{ll}(0) \alpha_{xy}^{ll}(t) \exp[i\mathbf{k}[\mathbf{r}_j(t) - \mathbf{r}_l(0)]]\rangle$

where

$$2\pi G^{\mathrm{cl}}_{BB}(\mathbf{k}, \omega) = \lim_{\hbar\to 0} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} C_{BB}(\mathbf{k}, t) \tag{2.54}$$

is the correspondence rule limit of the power spectrum of the quantum-mechanical time correlation function. The classical time correlation function $C^{\mathrm{cl}}_{BB}(\mathbf{k}, t)$ is defined as

$$C^{\mathrm{cl}}_{BB}(\mathbf{k}, t) = \int d\mathbf{\Gamma}_0 f^{(N)}(\mathbf{\Gamma}_0) B_{-k}(\mathbf{\Gamma}_0) e^{iLt} B_k(\mathbf{\Gamma}_0). \tag{2.55}$$

This formula is explained in the ensuing paragraphs.

Consider an isolated classical system of f degrees of freedom. The instantaneous mechanical state of the system is completely specified by f coordinates $q_1, \ldots, q_f$ and f conjugate momenta $p_1, \ldots, p_f$. This state is represented by a point, the phase point, in a $2f$-dimensional Cartesian hyperspace with f coordinate and f momentum axes. This space is called phase space or gamma space. As time progresses, the state changes accordingly to the canonical equations of motion,

$$\dot{q}_i = \partial H/\partial p_i, \qquad \dot{p}_i = -\partial H/\partial q_i, \qquad i = 1, \ldots, f,$$

where H is the Hamiltonian of the system,

$$H = T(p_1, \ldots, p_f) + V(q_1, \ldots, q_f),$$

with T the kinetic energy and V the potential energy. The $2f$ canonical equations of motion are first order in the time. Consequently, these equations can be solved if the state $(q_1(t), \ldots, q_f(t), p_1(t), \ldots, p_f(t))$ is known at some time t. Let Γ_t be the state or phase point of the system at time t and $\Gamma_{t+\tau}$ be the state at time $t + \tau$. Then,

$$\Gamma_{t+\tau} = \Gamma(\Gamma_t, \tau).$$

This last equation merely states the fact that the state at time $t + \tau$ is uniquely determined by the state at time t and by the time τ. Thus, corresponding to the state or phase point Γ_t there is a trajectory in Γ-space, i.e., $\Gamma_{t+\tau} = (\Gamma_t, \tau)$. This is illustrated for a system of one degree of freedom in Fig. 1.

Consider an arbitrary mechanical property, say

$$B_k(\Gamma) = \sum_{m=1}^{f} B_m(q_m, p_m) \exp ikq_m,$$

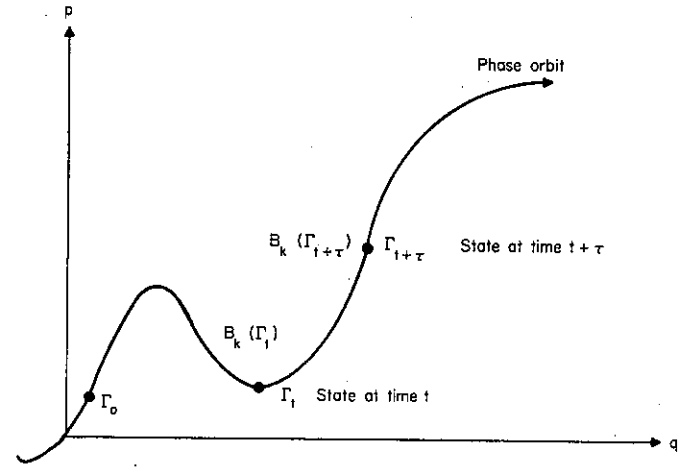

FIG. 1. A typical phase-space trajectory. The mechanical property $B_k(\Gamma)$ varies along this trajectory.

where B_m depends only on the coordinates and momenta of the mth degree of freedom. If the state Γ is specified, then $B_k(\Gamma)$ can be computed. Given the state Γ_t, the property $B_{-k}(\Gamma_t)$ is determined and, moreover, since the orbit is uniquely specified, $B_k(\Gamma_t)B_k(\Gamma_{t+\tau})$ depends only on the state Γ_t and τ. The property B_k will have a complicated time dependence unless it is a constant of the motion, such as the total energy. This time dependence often looks like a noise pattern (imagine the intensity of sound coming from a tin roof during a rainstorm); see Fig. 2.

A measure of the correlation between the property B_k at one time and at a time τ later is given by the time correlation function,

$$\langle B_{-k}(0)B_k(\tau)\rangle_0 = \lim_{T\to\infty} (1/T) \int_0^T dt\, B_{-k}(\Gamma_t)B_k(\Gamma_{t+\tau}). \tag{2.56}$$

This is a time average. Usually, there exist a characteristic time τ_c, called the correlation time, having the property that for $\tau \gg \tau_c$ the above time correlation function becomes independent of τ (see Fig. 3).

There is an alternative way to compute correlation functions. Following Gibbs, we set up an ensemble at $t = 0$ that satisfies the known constraints on the system of interest. Suppose for simplicity that this is an equilibrium ensemble, and, more specifically, a canonical ensemble. Then the fraction of the ensemble in the neighborhood $d\Gamma_0$ of the point Γ_0 is

$$f^{(N)}(\Gamma_0)\, d\Gamma_0 = Q_N(\beta, V)^{-1} e^{-\beta H(\Gamma_0)} d\Gamma_0,$$

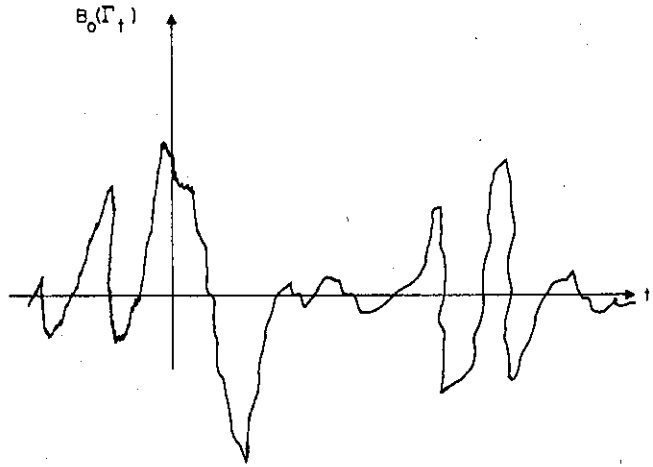

FIG. 2. The time dependence of a specified mechanical property $B_0(\Gamma)$, corresponding to the trajectory in Fig. 1, looks like a noise pattern.

where Q_N is the classical canonical partition function. The average of the product $B_{-k}(\Gamma_0)B_k(\Gamma_t)$ over this distribution function is†

$$C_{BB}(\mathbf{k}, t) = \int d\Gamma_0 f^{(N)}(\Gamma_0)B_{-k}(\Gamma_0)B_k(\Gamma_t) = \langle B_{-k}(0)B_k(t)\rangle. \quad (2.57)$$

Instead of writing down equations of motion for the state Γ_t, we can derive equations of motion for an arbitrary property $A(\Gamma_t)$ which depends

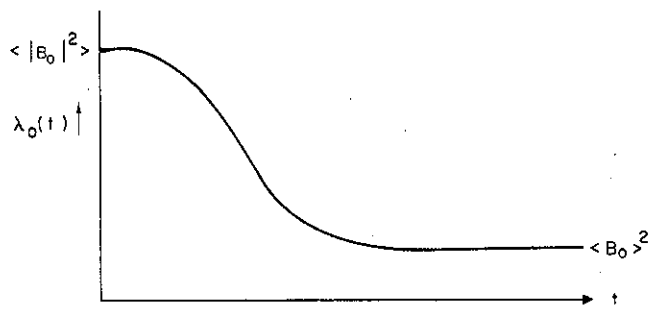

FIG. 3. The time correlation function of the property $B_0(\Gamma)$, $\lambda_0(t)$: $\lambda_0(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, B_0(\Gamma_t)B_0(\Gamma_{t+\tau})$.

† If the ergodic hypothesis is valid then the time average and the micro-canonical ensemble average are identical.

on the time implicitly. Note that

$$\frac{dA}{dt}(q_1, \ldots, p_f) = \sum_{i=1}^{f}\left[\frac{\partial A}{\partial q_i}\frac{\partial q_i}{\partial t} + \frac{\partial A}{\partial p_i}\frac{\partial p_i}{\partial t}\right].$$

Substitution from the canonical equations for $\dot{q}_i$ and $\dot{p}_i$ leads to the equation

$$dA/dt = \{A, H\}, \quad (2.58)$$

where $\{G, F\}$ is the Poisson bracket of G and F and is defined as

$$\{G, F\} = \sum_{i=1}^{f}\left[\frac{\partial G}{\partial q_i}\frac{\partial F}{\partial p_i} - \frac{\partial G}{\partial p_i}\frac{\partial F}{\partial q_i}\right].$$

We now define the Liouville operator L such that

$$iL = \{\cdot, H\}. \quad (2.59)$$

iL acts on an arbitrary function such that

$$iLF = \{F, H\}.$$

The Liouville operator L turns out to be Hermitian, as we will see later. From Eq. (2.58), it follows that

$$dA/dt = iLA, \quad (2.60)$$

which has the easily verified formal solution

$$A(\Gamma_t) = e^{iLt}A(\Gamma_0). \quad (2.61)$$

The operator e^{iLt} is a propagator or time displacement operator. It is unitary, as we shall see, and has the property that when it acts on $A(\Gamma_0)$ it transforms it to $A(\Gamma_t)$. Thus, we see that the correlation function $C_{BB}(\mathbf{k}, t)$ can be expressed as

$$C_{BB}(\mathbf{k}, t) = \int d\Gamma_0 f^{(N)}(\Gamma_0)B_{-k}(\Gamma_0)e^{iLt}B_k(\Gamma_0). \quad (2.62)$$

This is identical to Eq. (2.55).

C. Spectroscopic Line Shapes

To illustrate how the preceding formalism is generally used, we apply it to the solution of a well-known problem. Let us derive an analytic expression for the Doppler broadening in the dipole approximation. The Hamiltonian that describes the interaction between radiation of polariza-

tion ϵ and matter in the dipole approximation was discussed in the first section of this chapter:

$$H'(t) = -\int d\mathbf{r}\,[\epsilon \cdot \mathbf{M}(\mathbf{r})]E(\mathbf{r}, t), \tag{2.63}$$

with

$$\mathbf{M}(\mathbf{r}) = \tfrac{1}{2}\sum_j [\boldsymbol{\mu}_j, \delta(\mathbf{r} - \mathbf{r}_j)]_+,$$

where $\boldsymbol{\mu}_j$ is the dipole operator, and $\mathbf{r}_j$ the center-of-mass position of molecule m. From our preceding analysis, we see that the crucial quantum-mechanical autocorrelation function is $\langle \epsilon \cdot \mathbf{M}_{+k}(t)\mathbf{M}_{-k}(0) \cdot \epsilon\rangle$.

For convenience, we define an absorption cross section $\sigma_{\text{abs}}(\mathbf{k}, \omega)$ such that this cross section, multiplied by the incident radiation energy flux $c\,|E_{k\omega}|^2/8\pi$, is the energy dissipated per unit time, $Q(\mathbf{k}, \omega) = \omega\chi''_{MM}(\mathbf{k}, \omega)\,|E_{k\omega}|^2/2$. Consequently,

$$\sigma_{\text{abs}}(\mathbf{k}, \omega) = (4\pi\omega/c)\chi''_{MM}(\mathbf{k}, \omega). \tag{2.64}$$

From Eqs. (2.63) and (2.45c), we see that the time correlation function is related to $\sigma_{\text{abs}}(\mathbf{k}, \omega)$ through the equation

$$\frac{\hbar c\sigma_{\text{abs}}(\mathbf{k}, \omega)}{4\pi\omega[1 - e^{-\beta\hbar\omega}]} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle[\epsilon \cdot \mathbf{M}_k(t)][\epsilon \cdot \mathbf{M}_{-k}(0)]\rangle;$$

since it is the absorption cross section that is measured or more precisely, it is the absorption coefficient $\alpha(\mathbf{k}, \omega) = V^{-1}\sigma(\mathbf{k}, \omega)$, which is usually measured (from Beer's law, $\Phi(x) = I(0)e^{-\alpha(\omega)x}$), it is convenient to define the spectrum (Gordon, 1968) as

$$I(\mathbf{k}, \omega) = \frac{3\hbar c\alpha(\mathbf{k}, \omega)}{4\pi\omega[1 - e^{-\beta\hbar\omega}]} = \frac{3}{2\pi V}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle\epsilon \cdot \mathbf{M}_k(t)\epsilon \cdot \mathbf{M}_{-k}(0)\rangle. \tag{2.65}$$

The one-sided correlation function that determines the spectrum is

$$\varphi_{MM}(\mathbf{k}, t) = \epsilon \cdot \langle\mathbf{M}_k(t)\mathbf{M}_{-k}(0)\rangle \cdot \epsilon, \tag{2.66}$$

where

$$\mathbf{M}_k = \sum_{j=1}^{N} \boldsymbol{\mu}_j \exp i\mathbf{k} \cdot \mathbf{r}_j.$$

In the electronic absorption spectroscopy of atoms in gases, it is often a very good approximation to ignore correlations between dipole moments on different atoms; then

$$\varphi_{MM}(\mathbf{k}, t) = \sum_{j=1}^{N} \epsilon \cdot \langle\boldsymbol{\mu}_j(t)[\exp i\mathbf{k} \cdot \mathbf{r}_j(t)]\boldsymbol{\mu}(0)[\exp -i\mathbf{k} \cdot \mathbf{r}_j(0)]\rangle \cdot \epsilon.$$

The translational motion of the molecules is classical in usual gas-phase studies. Furthermore, the translational motion of an atom is, to a very good approximation, independent of the internal electronic motions, so that it is permissible to write

$$\varphi_{MM}(\mathbf{k}, t) = \sum_{j=1}^{N} \epsilon \cdot \langle\boldsymbol{\mu}_j(t)\boldsymbol{\mu}_j(0)\rangle \cdot \epsilon\langle\exp i\mathbf{k} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\rangle.$$

If all of the absorbing and emitting particles are identical and the gas is isotropic,

$$\varphi_{MM}(\mathbf{k}, t) = \tfrac{1}{3}NF_s(\mathbf{k}, t)U(t), \tag{2.67}$$

where

$$F_s(\mathbf{k}, t) \equiv \langle\exp i\mathbf{k} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]\rangle_{\text{cl}} = \langle\exp -i\mathbf{k} \cdot \mathbf{r}(0)\exp i\mathbf{k} \cdot \mathbf{r}(t)\rangle$$

describes the translational diffusive motion of a typical atom, and

$$U(t) = \langle\boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\rangle$$

describes the dipolar motion $\boldsymbol{\mu}$ of a typical atom. For ordinary temperatures, the system is in the ground electronic state, $|0)$, so that

$$U(t) = \sum_f |(f|\boldsymbol{\mu}|0)|^2 \exp -\gamma_f|t| \exp -i\omega_{f0}t,$$

where $|f\rangle$ is any excited electronic state connected to the ground electronic state by the transition dipole moment, ω_{f0} is the energy of the transition, and γ_f is the spontaneous emission rate.

For a freely moving gas molecule, $\mathbf{r}(t) - \mathbf{r}(0) = \mathbf{v}t$, so that

$$F_s(\mathbf{k}, t) = \langle\exp i\mathbf{k} \cdot \mathbf{v}t\rangle = \int d^3v\, f(\mathbf{v})\exp i\mathbf{k} \cdot \mathbf{v}t,$$

where $f(\mathbf{v})$ is the Maxwell velocity distribution. Carrying out the average yields

$$F_s(\mathbf{k}, t) = \exp[-k^2\langle v^2\rangle t^2/6],$$

where $\langle v^2\rangle$ is the mean-square velocity. Consequently,

$$\varphi_{MM}(\mathbf{k}, t) = \tfrac{1}{3}N\sum_f |(f|\boldsymbol{\mu}|0)|^2 \exp[-\gamma_f|t| - i\omega_{f0}t - k^2\langle v^2\rangle t^2/6]$$

Now, for visible light, $k = 2\pi/\lambda \sim 10^5$ Å^{-1} and for a room-temperature gas $\langle v^2\rangle \sim 10^{10}$, so that $F_s(\mathbf{k}, t)$ decays on a time scale of 10^{-10} sec. The radiation damping term decays on the order of 10^{-8} to 10^{-9} sec.

Consequently, $\exp -\gamma_f |t|$ can be ignored in this simple discussion. The absorption spectrum is simply the time Fourier transform of this function, i.e., the power spectrum. Then,

$$I(\mathbf{k}, \omega) = \left(\frac{N}{V}\right) \sum_f |(f|\mu|0)|^2 S_s(\mathbf{k}, \omega - \omega_{f0}), \tag{2.68}$$

where

$$S_s(\mathbf{k}, \omega - \omega_{f0}) = (M\beta/2\pi k^2)^{1/2} \exp\{-[\beta M(\omega - \omega_{f0})^2/2k^2]\}.$$

Here, $\mathbf{k}$ and ω are the wave vectors and frequencies of the exciting light (visible), so that $\omega = ck$. Thus, we predict that there will be a sequence of absorption lines of Gaussian shape centered on each allowed transition. Moreover, the widths of the absorption line to state $|f)$ will be

$$\langle(\omega - \omega_{f0})^2\rangle^{1/2} = \omega_{f0}\,(k_B T/Mc^2)^{1/2}.$$

Thus, the width of the lines will be different and will increase linearly with (temperature)$^{1/2}$. This is the ordinary Doppler effect.†

The same kind of argument can be used to show that the line shape for a specific vibrational transition $0 \to 1$ is determined by the time correlation function

$$C_{MM}(\mathbf{k}, t) = \tfrac{1}{3}NF_s(\mathbf{k}, t)U(t)$$

$$U(t) = \sum_{\nu=1}^{n} |\partial\mu/\partial Q_\nu|^2 \,|Q^\nu_{0,1}|^2 \,[\exp -\gamma_\nu |t| - i\omega_{0,\nu}t]\,\langle \mathbf{u}_\nu(0)\cdot\mathbf{u}_\nu(t)\rangle \tag{2.69}$$

where $F_s(\mathbf{k}, t)$ was defined previously, Q^ν is the vibrational displacement in the νth normal mode, Q^ν_{01} is the vibrational matrix element of Q^ν between the states $|0)$ and $|1)$, $\mu(Q_1, \ldots, Q_n)$ is the dipole moment of the molecule averaged over the ground electronic state, $(\partial\mu/\partial Q_\nu)_0$ is the derivative of μ with respect to Q_ν evaluated at $Q_1, \ldots, Q_n = 0$, $\omega_{0\nu}$ is the vibrational quantum of the νth mode, γ_ν is the radiation damping rate plus the collisional vibrational relaxation rate in the νth mode, and $\mathbf{u}_\nu$ is a unit vector specifying the orientation of the transition dipole of the νth mode expressed in the spacefixed coordinate system. For example, in a heteronuclear diatomic molecule there is only one vibrational mode and $\mathbf{u}$ points along the molecular axis. Then $\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ reflects the reorientation of the diatomic molecule. The spectrum of a diatomic molecule is

† The same result can be obtained from the Doppler shift $\omega = \omega_{f0}[1 + \hat{\mathbf{k}}\cdot\mathbf{v}/c]$. Then, $(\omega - \omega_{f0})c/\omega_{f0} = \mathbf{k}\cdot\mathbf{v}/|\mathbf{k}|$. From the Maxwell distribution of velocities, $\langle(\omega - \omega_{f0})^2\rangle = \frac{1}{3}\langle v^2\rangle\omega_{f0}^2 = (k_B T/Mc^2)\omega_{f0}^2$.

then (Gordon, 1968)

$$I(\mathbf{k}, \omega) = (N/V)\,|(\partial\mu/\partial Q)_0|^2\,|Q_{0,1}|^2 \times \int_{-\infty}^{+\infty} dt\, e^{i(\omega-\omega_0)t}\, e^{-\gamma|t|}\langle\mathbf{u}(t)\cdot\mathbf{u}(0)\rangle F_s(\mathbf{k}, t).$$

Generally, a normalized spectrum $\hat{I}(\mathbf{k}, \omega)$ is defined such that

$$\hat{I}(\mathbf{k}, \omega) = I(\mathbf{k}, \omega)/\textstyle\int_{\text{band}} d\omega\, I(\mathbf{k}, \omega);$$

then

$$\hat{I}(\mathbf{k}, \omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{i(\omega-\omega_0)t}\, e^{-\gamma|t|}\langle\mathbf{u}(t)\cdot\mathbf{u}(0)\rangle F_s(\mathbf{k}, t); \tag{2.70}$$

$F_s(\mathbf{k}, t)$ can often be set equal to one because, for infrared, $k(=2\pi/\lambda)$ is very small, leading to a very narrow Doppler width. Moreover, $10^3\ \text{sec}^{-1} \le \gamma \le 10^9\ \text{sec}^{-1}$, whereas $\langle\mathbf{u}(t)\cdot\mathbf{u}(0)\rangle$ relaxes on a time scale of 10^{-12} sec. Then

$$\hat{I}(\mathbf{k}, \omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{i(\omega-\omega_0)t}\langle\mathbf{u}(t)\cdot\mathbf{u}(0)\rangle \tag{2.71}$$

and $\langle\mathbf{u}(t)\cdot\mathbf{u}(0)\rangle$ can be determined by Fourier inversion of spectral lines (Gordon, 1968).

Spectral line shapes were first expressed in terms of autocorrelation functions by Foley (1946) and Anderson (1949). Van Kranendonk gave an extensive review of this work and attempted to compute the dipolar correlation function for vibration rotation spectra in the semiclassical approximation. The general formalism in its present form is due to Kubo (1961). Van Hove related the cross section for thermal neutron scattering to a density autocorrelation function (Van Hove, 1954). Singwi and Sjolander (1960) applied this kind of formalism to the shape of Mössbauer lines, and recently Gordon (1968) has rederived the formula for the IR band shapes and has constructed a physical model for rotational diffusion. There also exists an extensive literature in magnetic resonance, where time correlation functions have been used for more than two decades (Abragam, 1961).

D. Relaxation Times

Relaxation times can be expressed in terms of time correlation functions (Abragam, 1961; Slichter, 1963). Consider, for example, a system A which is weakly coupled to a bath B. Let $\mathscr{H}_A$, $\mathscr{H}_B$, and $\mathscr{H}_{AB}$ be the Hamiltonians of the system A and of the bath B and the interaction

Hamiltonian between the system and the bath. Let $|\, i(a))$ and $|\, i(b))$ be eigenstates of A and B respectively such that

$$\mathscr{H}_A \,|\, i(a)) = \varepsilon_i(a) \,|\, i(a)) = \hbar\omega_i(a) \,|\, i(a))$$
$$\mathscr{H}_B \,|\, i(b)) = \varepsilon_i(b) \,|\, i(b)) = \hbar\omega_i(b) \,|\, i(b));$$

where $\varepsilon_i(a)$ and $\varepsilon_i(b)$ are energy eigenvalues. The transition rate for the system A to make a transition $|\, i(a)) \to |\, f(a))$ while the bath B makes the transition $|\, i(b)) \to |\, f(b))$ is, according to the golden rule of time-dependent perturbation theory,

$$W_{i(a),i(b)\to f(a),f(b)} = (2\pi/\hbar^2) \,|\, (i(a), i(b) \,|\, \mathscr{H}_{AB} \,|\, f(a), f(b)) \,|^2 \times \delta(\omega_{\mathrm{fi}}(a) + \omega_{\mathrm{fi}}(b)), \tag{2.72}$$

where $\omega_{\mathrm{fi}}(a) = \omega_{\mathrm{f}}(a) - \omega_{\mathrm{i}}(a)$ and likewise for $\omega_{\mathrm{fi}}(b)$. The delta-function ensures that energy is conserved in the transition; that is, if A decreases in energy, the bath must correspondingly increase in energy by absorption. The transition rate for the system making a transition from $|i(a)) \to |\, f(a))$ independent of the bath is determined by averaging over an ensemble of baths. If this rate is called $R_{i(a)\to f(a)}$, then

$$R_{i(a)\to f(a)} = \sum_{i(b),f(b)} \varrho_{i(b)} W_{i(a),i(b)\to f(a),f(b)},$$

where $\varrho_{i(b)} = \exp[-\beta\varepsilon_i(b)]/Q_b$. Then

$$R_{i(a)\to f(a)} = \frac{2\pi}{\hbar^2} \sum_{i(b),f(b)} \varrho_{i(b)} \,|\, (i(a), i(b) \,|\, \mathscr{H}_{AB} \,|\, f(a), f(b) \,|^2 \times \delta(\omega_{\mathrm{fi}}(a) + \omega_{\mathrm{fi}}(b)).$$

Now, for a number of cases of chemical and physical interest the interaction Hamiltonian can be written as $\mathscr{H}_{AB} = -\hat{F}_A\hat{F}_B$, where $\hat{F}_A$ and $\hat{F}_B$ are independent properties of the system and the bath. Then $(i(a), i(b) \,|\, \hat{F}_A\hat{F}_B \,|\, f(a), f(b)) = (i(a) \,|\, \hat{F}_A \,|\, f(a))\,(i(b) \,|\, \hat{F}_B \,|\, f(b))$. It follows that

$$R_{i(a)\to f(a)} = (2\pi/\hbar^2) \,|\, (i(a) \,|\, \hat{F}_A \,|\, f(a)) \,|^2 \sum_{i(b),f(b)} \varrho_{i(b)} \,|\, (i(b) \,|\, \hat{F}_B \,|\, f(b)) \,|^2 \times \delta(\omega_{\mathrm{fi}}(a) + \omega_{\mathrm{fi}}(b)). \tag{2.73}$$

This last formula can be related to the time correlation function of the bath property $\hat{F}_B$ as follows. The delta-function can be written as

$$\delta(\omega_{\mathrm{fi}}(a) + \omega_{\mathrm{fi}}(b)) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp i[\omega_{\mathrm{fi}}(a) + \omega_{\mathrm{fi}}(b)]t.$$

Substituting this formula into Eq. (2.73),

$$R_{i(a)\to f(a)} = (2\pi/\hbar^2) \,|\, (i(a) \,|\, \hat{F}_A \,|\, f(a)) \,|^2 S_B(-\omega_{\mathrm{fi}}(a)), \tag{2.74}$$

where

$$S_B(-\omega_{\mathrm{fi}}(a)) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{i\omega_{\mathrm{fi}}(a)t} \langle F_B(0) F_B(t)\rangle.$$

Let us now drop the labels for the bath and the system. Then the transition rate for a system to make a transition from $|\, i) \to |\, f)$ when it is in contact with a reservoir is

$$R_{i\to f} = (2\pi/\hbar^2) \,|\, (i \,|\, \hat{F}_A \,|\, f) \,|^2 S_B(-\omega_{\mathrm{fi}}), \tag{2.75}$$

where $S_B(\omega_{\mathrm{fi}})$ is the spectral density of the bath at the frequency necessary for the systems transition,

$$S_B(-\omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle F_B(0) F_B(t)\rangle.$$

The spectral density measures, in a way, the density of pairs of states in the bath that are connected by F_B and match the energy change of the system ($\hbar\omega_{\mathrm{fi}}$). If there are no such states available, then the system cannot make the transition $|\, i) \to |\, f)$. The reverse transition is simply

$$R_{\mathrm{f}\to\mathrm{i}} = (2\pi/\hbar^2) \,|\, (i \,|\, \hat{F}_A \,|\, f) \,|^2 S_B(\omega_{\mathrm{fi}}),$$

where

$$S_B(\omega_{\mathrm{fi}}) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{-i\omega_{\mathrm{fi}}t} \langle F_B(0) F_B(t)\rangle = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{i\omega_{\mathrm{fi}}t} \langle F_B(t) F_B(0)\rangle.$$

It is easy to show by using techniques leading to Eq. (2.32) that

$$S_B(-\omega) = e^{\beta\hbar\omega} S_B(\omega); \tag{2.76}$$

consequently,

$$R_{\mathrm{i}\to\mathrm{f}} = e^{-\beta\hbar\omega_{\mathrm{fi}}} R_{\mathrm{f}\to\mathrm{i}}. \tag{2.77}$$

This last formula implies that at any temperature the bath is more likely to absorb energy from the system than to give energy to the system. This is entirely in accord with what was said in Section II,B. Thus, if the system is a radiation field and the bath a system that we are interested

in observing, it is more likely for the radiation field to lose energy than to gain energy; that is, it is more likely for the bath to absorb than emit.

An example is the vibrational relaxation (Berne *et al.*, 1967b, 1968a) of a molecule from a state $|n+1)$ to a state $|n)$. The system is then the vibrational coordinate Q and the bath is all other degrees of freedom. The Hamiltonian can be written as

$$\mathscr{H}_{AB} = -fQ,$$

where

$$f = -\partial V/\partial Q - 2\varepsilon_{\mathrm{ROT}}/r_0,$$

where $F = -\partial V/\partial Q$ is the force acting on the vibrational displacement when the oscillator is at its equilibrium separation r_0, and $\varepsilon_{\mathrm{ROT}}$ is the rotational kinetic energy of the rotor. The term $2\varepsilon_{\mathrm{ROT}}/r_0$ arises from the centrifugal distortion of the molecule. The rate for the transition $|n+1) \to |n)$ is

$$R_{n+1\to n} = (2\pi/\hbar^2)\,|Q_{n+1,n}|^2\,(1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{i\omega_0 t}\langle f(t)f(0)\rangle,$$

where $Q_{n+1,n}$ is the vibrational matrix element, $|Q_{n+1,n}|^2 = (n+1)\hbar/2\mu\omega_0$, so that

$$R_{n+1\to n} = [(n+1)/2\mu\hbar\omega_0]\int_{-\infty}^{+\infty} dt\,(\exp i\omega_0 t)$$
$$\times\langle F(t) + 2\varepsilon_{\mathrm{ROT}}(t)/r_0][F(0) + 2\varepsilon_{\mathrm{ROT}}(0)/r_0]\rangle. \qquad (2.78)$$

If there is no Q dependence in the potential, the only source of vibrational relaxation is through the centrifugal distortion. Then,

$$R_{n+1\to n} = [(n+1)/2I\hbar\omega_0]\int_{-\infty}^{+\infty} dt\, e^{i\omega_0 t}\langle\varepsilon_{\mathrm{ROT}}(t)\varepsilon_{\mathrm{ROT}}(0)\rangle.$$

Consequently, $R_{n+1\to n}$ will then be given only in terms of the rotational-kinetic-energy time correlation function.

E. Thermal Transport Processes and Stochastic Processes

The previous subsections have been devoted to an exposition of linear response theory. It was shown how line shapes and relaxation times can be related to time correlation functions. These phenomena share one characteristic in common. They all involve mechanical perturbations

which can consequently be accounted for in a Hamiltonian. In this section, an example will be given of how thermal perturbations such as temperature gradients or concentration gradients can be treated. There are a variety of ways to treat this problem. Luttinger (1964) has invented fictitious mechanical perturbations that give rise to thermal transport. The advantage of this procedure is that the perturbations can be incorporated in a Hamiltonian and the preceding results of this chapter can be used. The disadvantage is that the fictitious perturbations do not correspond to experiments done in the laboratory. Luttinger's method is perhaps the most elegant that has been applied to the study of thermal transport processes. Helfand (1960) has developed a more direct approach to this problem, one that is close in spirit to the theory of Brownian motion, and stays close to actual laboratory experiments. In order to understand the Helfand approach, it is useful to know the main ingredients of the theory of random processes. Moreover, a study of random processes will pave the way to a better understanding of the next few sections. For this reason, we begin this section with a brief introductory review of the important features of random processes (Chandrasekhar, 1945; Feller, 1966; Rice and Gray, 1965).

Let $y(t)$ be a variable that does not depend on the time in a predictable way. We call y a stochastic or random process. Examples of stochastic processes are the number of raindrops hitting a metal roof at any given time, or the position of a colloidal (Brownian) particle as it wanders through the solvent. A stochastic process can be classified according to its representation and its order. If the random variable can take on only discrete values, then the representation of the process is said to be discrete. whereas if the variable can take on a continuum of values, the process said to be continuous. Only continuous processes are considered here.

All relevant information about the process $y(t)$ is contained in the hierarchy of probability distributions

$$P_n(y_1, t_1; \cdots; y_n, t_n)\,dy_1 \cdots dy_n$$
$$= \mathrm{Prob}\{y_1 \le y(t_1) \le y_1 + dy_1; y_2 \le y(t_2) \le y_2 + dy_2; \cdots; y_n \le y(t_n) \le y_n + dy_n\};$$

$P_n\,dy_1 \cdots dy_n$ is the joint probability that the random variable $y(t)$ has a value between y_1 and $y_1 + dy_1$ at time t_1, a value between y_2 and $y_2 + dy_2$ at time t_2, and in like manner for times t_3 on up to t_n. We call P_n the nth-order distribution function. These probability densities have the

following properties:

$$P_n(y_1, t_1; \cdots ; y_n, t_n) \geq 0, \tag{2.79a}$$

$$\int dy_1 P_1(y_1, t_1) = 1, \tag{2.79b}$$

$$\int \cdots \int dy_{l+1} \cdots dy_n P_n(y_1, t_1; \cdots ; y_n, t_n) = P_l(y_1, t_1 ; \cdots ; y_l, t_l), \tag{2.79c}$$

$$P_n(y_1, t; y_2, t; y_3, t_3; \cdots ; y_n, t_n) = P_{n-1}(y_1, t; y_3, t_3; \cdots ; y_n, t_n)\, \delta(y_1 - y_2). \tag{2.79d}$$

From (2.79c), it follows that all higher-order distribution functions imply all lower-order distribution functions.

A process is called a pure random process if

$$P_n(y_1, t_1; \ldots ; y_n, t_n) = \prod_{j=1}^{n} P_j(y_j, t_j) \tag{2.80}$$

because successive values of y are uncorrelated. All relevant information about $y(t)$ is contained in the first-order distribution function.

A random process is called a Markov process if the process is completely specified by the second-order distribution function $P_2(y_1, t_1; y_2, t_2)$. For the purposes of this discussion, it is necessary to define the conditional probability $K_1(y_1, t_1 \mid y_2; t_2)\, dy_2$ that $y(t)$ is found between y_2 and $y_2 + dy_2$ at the time t_2 if y has the value y_1 at t_1. Then,

$$P_2(y_1, t_1; y_2, t_2) = P_1(y_1, t_1) K_1(y_1, t_1 \mid y_2, t_2). \tag{2.81}$$

To be consistent with the properties of P_n, K_1 must have the properties

$$K_1(y_1, t_1 \mid y_2, t_2) \geq 0, \tag{2.82a}$$

$$\int dy_2 K_1(y_1, t_1 \mid y_2, t_2) = 1, \tag{2.82b}$$

$$\int dy_1 P_1(y_1, t_1) K_1(y_1, t_1 \mid y_2, t_2) = P_1(y_2, t_2). \tag{2.82c}$$

If periodicities are excluded,

$$\lim_{|t_2 - t_1| \to \infty} K_1(y_1, t_1 \mid y_2, t_2) = P_1(y_2, t_2). \tag{2.82d}$$

Higher-order transition probabilities can be defined. For example, $K_{n-1}(y_1, t_1; \cdots ; y_{n-1}, t_{n-1} \mid y_n, t_n)\, dy_n$ represents the probability that $y(t)$ will be between y_n and $y_n + dy_n$ at time t_n given that $y(t)$ had the values $y_1, \ldots, y_{n-1}$ at the times $t_1, \ldots, t_{n-1} (< t_n)$). Then,

$$P_n(y_1, t_1; \cdots ; y_n, t_n) = P_{n-1}(y_1, t_1; \cdots ; y_{n-1}, t_{n-1}) \times K_{n-1}(y_1, t_1; \cdots ; y_{n-1}, t_{n-1} \mid y_n, t_n). \tag{2.83}$$

A random process is a Markov process if

$$K_{n-1}(y_1, t_1; \cdots ; y_{n-1}, t_{n-1} \mid y_n, t_n) = K_1(y_{n-1}, t_{n-1} \mid y_n, t_n); \qquad t_{n-1} < t_n. \tag{2.84}$$

A Markov random variable is such that, if its value is known at time t_{n-1}, the value of the variable at time t_n is completely independent of its values at times prior to t_{n-1}. Then, from Eq. (2.83),

$$P_n(y_1, t_1; \cdots ; y_n, t_n) = P_{n-1}(y_1, t_1; \cdots ; y_{n-1}, t_{n-1}) K_1(y_{n-1}, t_{n-1} \mid y_n, t_n).$$

Iteration yields

$$P_n(y_1, t_1; \cdots ; y_n, t_n) = P_1(y_1, t_1) K_1(y_1, t_1 \mid y_2, t_2) \cdots K_1(y_{n-1}, t_{n-1} \mid y_n, t_n). \tag{2.85}$$

For a Markov process, it follows from property (2.79c) and Eq. (2.85) that

$$P_2(y_1, t_1; y_3, t_3) = \int dy_2 P_3(y_1, t_1; y_2, t_2; y_3, t_3)$$

or

$$P_1(y_1, t_1) K_1(y_1, t_1 \mid y_2, t_2) = \int dy_2 P_1(y_1, t_1) K_1(y_1, t_1 \mid y_2, t_2) K_1(y_2, t_2 \mid y_3, t_3).$$

Cancellation of $P_1(y_1, t_1)$ yields Markov's integral equation,

$$K_1(y_1, t_1 \mid y_3, t_3) = \int dy_2 K_1(y_1, t_1 \mid y_2, t_2) K_1(y_2, t_2 \mid y_3, t_3). \tag{2.86}$$

A random process is Markovian if and only if it satisfies Markov's integral equation. A Markov process is a second-order stochastic process.

A random process is *stationary* if

$$\begin{aligned} P_1(y_1, t_1) &= P_1(y_1), \\ P_2(y_1, t_1; y_2, t_2) &= P_2(y_1, y_2; t_2 - t_1), \\ P_n(y_1, t_1; y_2, t_2; \cdots ; y_n, t_n) &= P_n(y_1, y_2, t_2 - t_1; \cdots ; y_n, t_n - t_1). \end{aligned} \tag{2.87}$$

If the statistical process is invariant to a shift in the time origin, then the process is stationary. Fluctuations in a system in thermodynamic equilibrium are examples of stationary stochastic processes. For a stationary process, the transition probability satisfies the condition

$$K_1(y_1, t_1 \mid y_2, t_2) = K(y_1 \mid y_2; t_2 - t_1). \tag{2.88}$$

For a continuous, stationary Markov process, Markov's integral equation becomes

$$K_1(y_1 \mid y; t) = \int dy_0\, K_1(y_1 \mid y_0; t_0) K_1(y_0 \mid y; t - t_0). \tag{2.89}$$

The integrand is simply the conditional probability distribution for the transition from the initial state y_1 to the intermediate state y_0 in the time t_0, and then from this intermediate state to the final state y in the remaining time, $t - t_0$. The integral over all intermediate states then gives the conditional probability for the transition from y_1 to y in the time t.

Any distribution can be fully characterized if all of its moments are known. The $(n + m)$th moments of $P_2(y_1, t_1; y_2, t_2)$ are

$$\mu_{n,m}^{(n+m)} = \int dy_1 \int dy_2\, (y_1 - \langle y_1 \rangle)^n (y_2 - \langle y_2 \rangle)^m P_2(y_1, t_1; y_2, t_2). \tag{2.90}$$

Consider the second moments. There are three, $\mu_{20}^{(2)}$, $\mu_{02}^{(2)}$, and $\mu_{11}^{(2)}$. The moments $\mu_{20}^{(2)}$ and $\mu_{02}^{(2)}$ are mean-square deviations and are equal if the process is stationary; $\mu_{11}^{(2)}$ is an autocorrelation function of y,

$$\mu_{11}^{(2)}(t_1, t_2) = \int dy_1 \int dy_2\, (y_1 - \langle y_1 \rangle)(y_2 - \langle y_2 \rangle) P_2(y_1, t_1; y_2, t_2). \tag{2.91}$$

The normalized autocorrelation function of y is

$$C(t_1, t_2) = \mu_{11}^{(2)}(t_1, t_2) / [\mu_{02}^{(2)} \mu_{20}^{(2)}]^{1/2}. \tag{2.92}$$

If the process is stationary, then $C_1(t_1, t_2) \equiv C(t_2 - t_1)$.

If the distribution functions $P_1, \ldots, P_n$ have a Gaussian form, then it can be proved that the stationary process $y(t)$ is Markovian if and only if the time correlation function $C(t)$ is an exponential function of the time, i.e., $C(t) = e^{-\gamma|t|}$. This is known as Doob's theorem.

In many cases, the random process can be multidimensional. For example, the position of a Brownian particle is specified by three coordinates. All of the concepts presented here can be generalized to multidimensional processes. The interested reader should consult the many excellent references on this subject.

In this chapter, our primary goal is to compute autocorrelation functions. For this purpose, it is necessary to determine the second-order distribution function $P_2(y_1, t_1; y_2, t_2)$. Moreover, our interest is restricted to systems that are in statistical equilibrium so that the fluctuations are stationary stochastic processes. The process is often assumed to be Markovian; however, there is no compelling argument to support this assumption in many cases. The first- and second-order stationary distribution functions of fluctuations can be determined from the equilibrium ensemble distribution for a classical system.

Let y be a dynamical property of a classical system. Then y depends on the microscopic state (or phase point) Γ of the system, $y = y(\Gamma)$. The ensemble average of the property y is

$$\langle y \rangle = \int d\Gamma\, f^{(N)}(\Gamma, t) y(\Gamma),$$

where $f^{(N)}(\Gamma, t)$ is the phase-space distribution function at time t. Since this chapter is concerned with equilibrium ensembles, we may take $f^{(N)}(\Gamma, t)$ in any equilibrium ensemble. For convenience, choose $\langle y \rangle = 0$, so that y represents a fluctuation.

The probability $P_1(y_1)\, dy_1$ of finding $y(\Gamma)$ between y_1 and $y_1 + dy_1$,

$$P(y_1)\, dy_1 = \text{Prob}\{y_1 \le y(\Gamma) \le y_1 + dy_1\},$$

is found by integrating $f_{\text{eq}}^{(N)}(\Gamma_0)$ only over those regions of Γ-space for which $y_1 \le y(\Gamma) \le y_1 + dy_1$, or

$$P(y_1)\, dy_1 = \int d\Gamma\, f_{\text{eq}}^{(N)}(\Gamma), \qquad \{y_1 \le y(\Gamma) \le y_1 + dy_1\}.$$

Now consider the integral

$$F_1(y') = \int d\Gamma\, \eta(y' - y(\Gamma)) f_{\text{eq}}^{(N)}(\Gamma),$$

The last integral contains the step function

$$\eta(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0. \end{cases}$$

This integral is the probability of finding a value of the property $y(\Gamma)$ smaller than or equal to y'.

It follows that

$$P(y_1)\, dy_1 = F_1(y_1 + dy_1) - F_1(y_1), \tag{2.93}$$

so that

$$P(y_1) = dF(y_1)/dy_1 = \int d\Gamma\, \delta(y_1 - y(\Gamma)) f_{\text{eq}}^{(N)}(\Gamma).$$

This last formula follows from the fact that the derivative of the step function is the delta-function. Consequently, the first-order distribution function of the fluctuation y is

$$P(y_1) = \langle \delta(y_1 - y(\Gamma)) \rangle. \tag{2.94}$$

The probability $P_2(y_1, y_2; t)\, dy_1\, dy_2$ of finding $y(\Gamma_0)$ between y_1 and $y_1 + dy_1$ and $y(\Gamma_t) = e^{iLt} y(\Gamma_0)$ between y_2 and $y_2 + dy_2$ is found by integrating $f_{\text{eq}}^{(N)}(\Gamma_0)$ only over those regions of Γ space for which the following inequalities are valid

$$y_1 \leq y(\Gamma_0) \leq y_1 + dy_1, \qquad y_2 \leq y(\Gamma_t) \leq y_2 + dy_2.$$

This integral is determined in a completely analogous manner,

$$P_2(y_1, y_2; t) = \int d\Gamma_0\, \delta(y_1 - y(\Gamma_0))\, \delta(y_2 - y(\Gamma_t)) f_{\text{eq}}^{(N)}(\Gamma_0). \tag{2.95}$$

The second-order distribution function is consequently the ensemble average

$$P_2(y_1, y_2; t) = \langle \delta(y_1 - y(\Gamma_0))\, e^{iLt}\, \delta(y_2 - y(\Gamma_0)) \rangle. \tag{2.96}$$

The first- and second-order distribution functions obviously have the properties that

$$\int dy_1\, P_1(y_1) = 1, \qquad \int dy_1 \int dy_2\, P_2(y_1, y_2; t) = 1; \tag{2.97a}$$

$$\int dy_1\, P_2(y_1, y_2; t) = P_1(y_2), \qquad \int dy_2\, P_2(y_1, y_2; t) = P_1(y_2), \tag{2.97b}$$

$$P_2(y_1, y_2; 0) = P_1(y_1)\, \delta(y_1 - y_2); \tag{2.97c}$$

$$P_2(y_1, y_2; \tau) = P_2(y_2, y_1; -\tau). \tag{2.97d}$$

Properties (a)–(c) are direct consequences of Eqs. (2.93) and (2.95). Property (d) follows from the Hermitian property of the Liouville operator (see the next section).

A number of other properties of these probability distribution functions follow directly from Eqs. (2.94) and (2.96) and the character of

$y(\Gamma)$. Suppose, for example, that $y(\Gamma)$ has even signature under time reversal; that is,

$$y(r^{(N)}, -\mathbf{p}^{(N)}) = y(r^{(N)}, \mathbf{p}^{(N)}).$$

Then, transforming the integrals in Eq. (2.95) such that $\mathbf{p}^{(N)} \to -\mathbf{p}^{(N)}$ and recognizing that $iL \to -iL$ under this transformation, one sees that

$$P_2(y_1, y_2; t) = \int d\Gamma_0\, \delta(y_1 - y(\Gamma_0))\, e^{-iLt}\, \delta(y_2 - y(\Gamma_0)) f_{\text{eq}}^{(N)}(\Gamma_0),$$

which becomes, after an integration by parts,

$$P_2(y_1, y_2; t) = P_2(y_2, y_1; t). \tag{2.98}$$

This equality expresses the well-known property of detailed balance for time-even properties in an equilibrium system.

The transition probability $K_1(y_1 \mid y_2; t) = P_2(y_1, y_2; t)/P_1(y_1)$ satisfies the properties

$$\int dy_1\, K_1(y_1 \mid y_2; t) = P(y_2), \tag{2.99a}$$

$$\int dy_2\, K_1(y_1 \mid y_2; t) = 1 \qquad \text{(normalization)} \tag{2.99b}$$

$$P_1(y_1) K_1(y_1 \mid y_2; t) = P_1(y_2) K_1(y_2 \mid y_1; t) \qquad \text{(detailed balance)} \tag{2.99c}$$

$$K_1(y_1 \mid y_2; 0) = \delta(y_1 - y_2). \tag{2.99d}$$

The characteristic function of the joint probability distribution $P_2(y_1, y_2; t)$ is

$$G_2(K_1, K_2; t) = \int dy_1 \int dy_2 \exp[-i(K_1 y_1 - K_2 y_2)] P_2(y_1, y_2; t). \tag{2.100}$$

Substitution of Eq. (2.96) for the stationary ensemble leads to the interesting result

$$G_2(K_1, K_2; t) = \langle e^{-iK_1 y(\Gamma_0)} e^{iLt} e^{iK_2 y(\Gamma_0)} \rangle = \langle e^{-iK_1 y(0)} e^{iK_2 y(t)} \rangle \tag{2.101}$$

According to Eq. (2.101), the characteristic function of the second-order stationary distribution function P_2 is a stationary time correlation function. It is quite possible to derive memory-function equations for the characteristic function of the second-order distribution function

$P_2(y_1, y_2; t)$ (see next section). This development will not be pursued here, despite its utility in deriving kinetic equations corresponding to different physical models.

It is a very difficult matter to compute the second-order distribution function. Nevertheless, it is often possible to compute or experimentally determine the moments $\mu_{nm}^{(n+m)}$ of this distribution function. There exists an approximate method for finding $P_2(y_1, y_2; t)$ based on the tenets of information theory (Rice and Gray, 1965). For this purpose, we define the entropy (the basic measure of a distribution function) as

$$S[P_2] = -\int dy_1 \int dy_2\, P_2(y_1, y_2; t) \ln P_2(y_1, y_2; t). \tag{2.102}$$

According to information theory, if a certain set of moments of P_2 is known, then that P_2 is optimum that maximizes $S[P_2]$ subject to the known moments. Suppose we only known the moments $\mu_{20}^{(2)}$, $\mu_{02}^{(2)}$, and $\mu_{11}^{(2)}(t)$. The moment $\mu_{11}^{(2)}(t)$ is a stationary time correlation function and can consequently be determined experimentally as indicated in the preceding sections. The moments $\mu_{20}^{(2)}$ and $\mu_{02}^{(2)}$ can often be computed from statistical mechanics. The only thing that is assumed known about P_2 is

$$\begin{aligned}
\mu_{20}^{(2)} &= \int dy_1 \int dy_2 [y_1 - \langle y_1\rangle]^2 P_2(y_1, y_2; t),\\
\mu_{02}^{(2)} &= \int dy_1 \int dy_2\, [y_2 - \langle y_2\rangle]^2 P_2(y_1, y_2; t),\\
\mu_{11}^{2)} &= \int dy_1 \int dy_2\, [y_1 - \langle y_1\rangle][y_2 - \langle y_2\rangle] P_2(y_1, y_2; t),\\
\mu_{00}^{(0)} &= \int dy_1 \int dy_2\, P_2(y_1, y_2; t) = 1.
\end{aligned} \tag{2.103}$$

Now we must find the function P_2 that maximizes $S[P_2]$ subject to the four previous constraints. This problem can be solved by the method of Lagrange's undetermined multipliers. When y_1 varies between $-\infty$ and $+\infty$, $P_2(y_1, y_2; t)$ turns out to be

$$\begin{aligned}
P(y_1, y_2; t) = {} & \{2\pi\langle \delta y_1^2\rangle[1 - \psi^2(t)]^{1/2}\}^{-1}\\
& \times \exp\{-(\delta y_1^2 + \delta y_2^2 - 2\delta y_1\, \delta y_2\, \psi(t))/2\langle \delta y_1^2\rangle[1 - \psi^2(t)]\}
\end{aligned} \tag{2.104}$$

Integration of this distribution function over y_2 yields

$$P(y_1) = [2\pi\langle \delta y_1^2\rangle]^{-1/2} \exp(-\delta y_1^2/2\langle \delta y_1^2\rangle). \tag{2.105}$$

The transition probability $K_1(y_1, y_2; t)$ is then

$$\begin{aligned}
K_1(y_1, y_2; t) = {} & \{2\pi\langle \delta y_1^2\rangle[1 - \psi^2(t)]\}^{-1/2}\\
& \times \exp\{-[\delta y_2 - \delta y_1\, \psi(t)]^2/2\langle \delta y_1^2\rangle[1 - \psi(t)]^2\}.
\end{aligned} \tag{2.106}$$

In all of these formulas, $\delta y_1 = y_1 - \langle y_1\rangle$, $\delta y_2 = y_2 - \langle y_2\rangle$, and $\psi(t) = \langle \delta y_1\, \delta y_2\rangle / \langle \delta y_1^2\rangle$ is the normalized autocorrelation function of the property δy. Consequently, if all that is known are the moments in Eq. (2.103), the optimal distribution function P_2 is the Gaussian distribution of Eq. (2.106). So far, we have not specified that the process is Markovian. According to Doob's theorem (Feller, 1966), it would only be meaningful to assume that y is a Markov process in this approximation if $\psi(t)$ is exponential. It should be noted that this transition probability satisfies all of the conditions of Eq. (2.99).

Equations can be derived for the time evolution of the transition probability. Before describing these equations, it is instructive to consider the case of self-diffusion. For this purpose, consider a monatomic fluid, like liquid argon, in thermodynamic equilibrium. Let us suppose that all of the particles in the neighborhood of the point $\mathbf{r}_0$ at the time $t = 0$ are tagged. These tagged particles diffuse away from the point $\mathbf{r}_0$ in the course of time.

The fraction of these tagged particles that are found in the neighborhood d^3r of the point $\mathbf{r}$ at time t is simply the transition probability $K_1(\mathbf{r}_0 \mid \mathbf{r}; t)\, d^3r$. The random process is the position of a tagged molecule and this process is stationary because the system is in thermodynamic equilibrium. It is customary to call this transition probability $G_s(\mathbf{r} - \mathbf{r}_0, t)$. Note that

$$\begin{aligned}
G_s(\mathbf{r} - \mathbf{r}_0; t) &\equiv K_1(\mathbf{r}_0 \mid \mathbf{r}; t);\\
G_s(\mathbf{r} - \mathbf{r}_0; 0) &= K_1(\mathbf{r}_0 \mid \mathbf{r}; 0) = \delta(\mathbf{r} - \mathbf{r}_0);
\end{aligned} \tag{2.107}$$

G_s represents the probability that a particle starting at $\mathbf{r}_0$ at the initial instant will move to a point in the neighborhood of $\mathbf{r}$ by the time t. This function is called the Van Hove self space–time correlation function.

If $|\mathbf{R}| = |\mathbf{r} - \mathbf{r}_0|$ is a macroscopic distance and t is a macroscopic time, then $G_s(\mathbf{R}, t)$ will satisfy the diffusion equation, i.e.,

$$\frac{\partial G_s(\mathbf{R}, t)}{\partial t} = D\nabla_R^2 G_s(\mathbf{R}, t),$$

where D is the self-diffusion coefficient (see Section V,A). Moreover, it is obvious that the diffusion equation is applicable, since G_s represents the manner in which the concentration of tagged molecules changes in time at each point in space. This equation must be solved subject to the initial condition $G_s(\mathbf{R}, 0) = \delta(\mathbf{R})$. The solution is

$$G_s(\mathbf{R}, t) = [4\pi Dt]^{-3/2} \exp(-R^2/4Dt) \tag{2.108}$$

for t long compared to collision times. The mean-square displacement of a particle is

$$\langle R^2(t)\rangle = \langle[\mathbf{r}(t) - \mathbf{r}_0]^2\rangle = \int d^3R\, R^2 G_s(\mathbf{R}, t).$$

From Eq. (2.108), it follows that

$$\langle[\mathbf{r}(t) - \mathbf{r}_0]^2\rangle = 6Dt. \tag{2.109}$$

Consequently, the self-diffusion coefficient D is

$$D = \lim_{t\to\infty} \{\langle[\mathbf{r}(t) - \mathbf{r}_0]^2\rangle/6t\}. \tag{2.110}$$

This relationship was originally derived by Einstein. The Einstein formula can be expressed in terms of a time correlation function. It should be noted that

$$\mathbf{r}(t) - \mathbf{r}_0 = \int_0^t dt_1\, \mathbf{V}(t_1)$$

and

$$[\mathbf{r}(t) - \mathbf{r}_0]^2 = \int_0^t dt_2 \int_0^t dt_1\, \mathbf{V}(t_1) \cdot \mathbf{V}(t_2),$$

where $\mathbf{V}(t_1)$ is the velocity of the tagged molecule at time t_1. It follows that

$$\langle[\mathbf{r}(t) - \mathbf{r}_0]^2\rangle = \int_0^t dt_2 \int_0^t dt_1\, \langle\mathbf{V}(t_1) \cdot \mathbf{V}(t_2)\rangle.$$

The limits of integration can be separated into two regions, $t_1 \leq t_2$ and $t_1 \geq t_2$, so that

$$\langle[\mathbf{r}(t) - \mathbf{r}_0]^2\rangle = 2\int_0^t dt_2 \int_0^{t_2} dt_1\, \langle\mathbf{V}(0) \cdot \mathbf{V}(t_2 - t_1)\rangle,$$

where the fact that $\mathbf{V}$ is a stationary variable in an equilibrium ensemble has been used. Transforming to the new variables t_2, $\tau = t_2 - t_1$, we see after an integration by parts that

$$\langle[\mathbf{r}(t) - \mathbf{r}_0]^2\rangle = 2\int_0^t d\tau (t - \tau)\, \langle\mathbf{V}(0) \cdot \mathbf{V}(\tau)\rangle. \tag{2.111}$$

Substitution of this result into the Einstein equation yields a formula for the diffusion coefficient,

$$D = \tfrac{1}{3} \lim_{t\to\infty} \int_0^t dt\, [1 - (\tau/t)]\langle\mathbf{V}(0) \cdot \mathbf{V}(\tau)\rangle.$$

If the integrals exist for all times t, it follows that

$$D = \tfrac{1}{3} \int_0^\infty dt\, \langle\mathbf{V}(0) \cdot \mathbf{V}(\tau)\rangle. \tag{2.112}$$

Consequently, the self-diffusion coefficient is the time integral of the velocity autocorrelation functions. This is one example of the by now well-known result that linear thermal transport coefficients are proportional to the time integrals of the autocorrelation function of their corresponding fluxes. Such relations are called Kubo relations (1961). This derivation is a specific example of Helfand's derivation (1960) of the Kubo relations. This method consists in: (1) determining the macroscopic transport equations (hydrodynamics), (2) deriving the Einstein relation for the transport coefficients, (3) deducing the Kubo relation from the Einstein relation. For the details, the interested reader should consult Helfand's paper (1960).

Let us now return to the general theory of stochastic processes. Equations can be derived for the time evolution of the transition probability $K_1(y_1 \mid y_2; t)$ for two limiting cases: (a) the process y is subject to small, frequent changes, (b) the process y is subject to large, impulsive changes. It is instructive to review these two cases. For more details, the reader should consult the extensive literature on this subject (Rice and Gray, 1965).

In the former case, case (a), it is assumed that the changes in the random variable y are small compared to typical values of y, and that these changes occur on a time scale of order τ_c. Moreover, it is assumed that the distribution function varies on a time scale of order τ_r which is very long compared to τ_c. Consequently, changes in $K_1(y_1 \mid y_2; t)$ are the result of many very small changes in the process y. It is then reasonable to assume that there exists a time τ such that

$$\tau_c \ll \tau \ll \tau_r.$$

An example of such a process is the random walk, or diffusion process. In this process, the random variable is the net displacement of a particle after a time t. The net displacement is the superposition of a large number

of insignificant small changes in the instantaneous position of the particle. The small changes take place on a time scale of order τ_c and K_1 changes on a much longer time scale τ.

Markov's integral equation for a stationary Markov process is

$$K_1(y_1 \mid y; t+\tau) = \int dy_2\, K_1(y_1 \mid y_2; t) K_1(y_2 \mid y; \tau). \tag{2.113}$$

This equation is valid for all τ. The right-hand side of this equation is determined from the transition probabilities for going from y_1 to the intermediate point y_2 in the time t and then from y_2 to the final point y in the time τ. If τ is very small, then by hypothesis there will be very small changes in the random variable, so that y must be close to y_2. Let Δy represent the small difference between y and y_2, i.e., $\Delta y = y - y_2$. Then Eq. (2.113) becomes

$$K_1(y_1 \mid y; t+\tau) = \int d(\Delta y)\, K_1(y_1 \mid y - \Delta y; t)\, \psi(y \mid \Delta y; \tau), \tag{2.114}$$

where

$$\psi(y \mid \Delta y; \tau)\, d(\Delta y) \equiv K_1(y - \Delta y \mid y; \tau)\, d(\Delta y) \tag{2.115}$$

is the probability of a change Δy during the time interval τ starting from $y - \Delta y$. The left-hand side of this equation can be expanded around $\tau=0$ and the integrand can be expanded around $\Delta y = 0$, so that

$$\begin{aligned} K_1(y_1 \mid y; t) &+ \tau(\partial/\partial\tau) K_1(y_1 \mid y; t) + \cdots \\ &= \int d(\Delta y)\, \{K_1(y_1 \mid y; t)\psi(y \mid \Delta y; \tau) \\ &\quad - \Delta y(\partial/\partial y) K_1(y_1 \mid y; t)\psi(y \mid \Delta y; \tau) \\ &\quad + \tfrac{1}{2}(\Delta y)^2(\partial^2/\partial y^2) K_1(y_1 \mid y; t)\psi(y \mid \Delta y; \tau) + \cdots\}. \end{aligned} \tag{2.116}$$

If the time τ is chosen such that $\tau_c \ll \tau \ll \tau_r$, the left-hand side of this equation can be truncated at the second term. The right-hand side can be simplified by introducing the moments of the distribution function $\psi(y \mid \Delta y; \tau)$,

$$\int d(\Delta y)\, (\Delta y)^n \psi(y \mid \Delta y; \tau) = \langle \Delta y^n(\tau) \rangle_y. \tag{2.117}$$

It should be noted that these moments are conditional on the initial value of the random variable y. For example, $\langle \Delta y^2(\tau) \rangle_y$ is the mean-square displacement of the random variable in the time τ given that it had the value y at the initial instant. Moreover, the distribution function

$\psi(y \mid \Delta y; \tau)$ is normalized, i.e., $\langle \Delta y(\tau)^0 \rangle_y = 1$. Combining these results Eq. (2.116) becomes

$$\begin{aligned} K_1(y_1 \mid y; t) &+ \tau(\partial K_1(y_1 \mid y; t)/\partial t) \\ &= \sum_{n=1}^{\infty} [(-1)^n/n!](\partial^n/\partial y^n)\langle \Delta y^n(\tau) \rangle_y K_1(y_1 \mid y, t) + K_1(y_1 \mid y; t). \end{aligned}$$

If we divide through by τ and take the limit $\tau \to 0$ such that $\tau \gg \tau_c$,

$$\begin{aligned} &\partial K_1(y_1 \mid y; t)/\partial t \\ &\quad = \lim_{\substack{\tau \to 0 \\ \tau \gg \tau_c}} \sum_{n=1}^{\infty} ((-1)^n/n!)(\partial^n/\partial y^n)(\langle \Delta y^n(\tau) \rangle_y/\tau) K_1(y_1 \mid y; t). \end{aligned} \tag{2.118}$$

Before investigating the time dependence of the conditional moments, it should be noted that in order for Eq. (2.118) to be useful the time τ cannot appear explicitly. The time τ will disappear from the equation if the first m moments are proportional to τ, whereas the higher moments depend on higher powers of τ. Then, writing,

$$\lim_{\substack{\tau \to 0 \\ \tau \gg \tau_c}} \langle \Delta y^n(\tau) \rangle_y/\tau = \begin{cases} a^{(n)}(y), & n = 1, \ldots, m, \\ 0, & n = m+1, \ldots, \end{cases} \tag{2.119}$$

the equation then becomes

$$\frac{\partial K_1}{\partial t} = \sum_{n=1}^{m} ((-1)^n/n!)(\partial^n/\partial y^n) a^{(n)}(y) K_1. \tag{2.120}$$

This equation is called the generalized Fokker–Planck equation. It can be generalized to the case where y has more than one component.

Equation (2.120) describes the time evolution of the transition probability for a Markov process y. To get some idea about the time dependence of the moments $\langle \Delta y^n(\tau) \rangle_y$, let us use the Gaussian transition probability of Eq. (2.106). Since the process is Markovian, Doob's theorem requires that $\psi(\tau) = e^{-\gamma|\tau|}$, where $\gamma = 0(\tau_r^{-1})$. Since $\tau \ll \tau_r$, it is legitimate to substitute $\psi(\tau) \cong 1 - \gamma\tau$, where $\gamma = \dot{\psi}(0)$ is the initial slope of the normalized correlation function, so that

$$\begin{aligned} K_1(y_1 \mid y_2; \tau) &\simeq [4\pi\langle \delta y_1^2 \rangle \gamma\tau]^{-1/2} \\ &\quad \times \exp\{-[(\delta y_2 - \delta y_1)(1 - \gamma\tau)]^2/4\langle \delta y_1^2 \rangle [\gamma\tau]\}. \end{aligned} \tag{2.121}$$

For simplicity, take $\langle y \rangle = 0$. Then $K_1(y \mid y + \Delta y; \tau)$ is

$$K_1(y \mid y + \Delta y; \tau) = [2\pi\langle y^2 \rangle \gamma\tau]^{-1/2} \exp\{-[\Delta y + y\gamma\tau]^2/4\langle y^2 \rangle \gamma\tau\}.$$

It follows that

$$\langle \Delta y^n(\tau)\rangle_y = [4\pi\langle y^2\rangle\gamma\tau]^{-1/2} \int d(\Delta y)\,(\Delta y)^n \exp\{-[\Delta y + y\gamma\tau]^2/4\langle y^2\rangle\gamma\tau\} \tag{2.122}$$

and it is easy to see that

$$\begin{aligned}\langle \Delta y(\tau)\rangle_y &= -y\gamma\tau,\\ \langle \Delta y^2(\tau)\rangle_y &= 2\langle y^2\rangle\gamma\tau + (\gamma y\tau)^2,\end{aligned} \tag{2.123}$$

and all higher moments depend on higher powers of τ. This approximate result gives us reason to truncate the generalized Fokker–Planck equation after the second term so that

$$\partial K_1/\partial t = -(\partial/\partial y)a^{(1)}(y)K_1 + \tfrac{1}{2}(\partial^2/\partial y^2)a^{(2)}(y)K_1. \tag{2.124}$$

This result is exact for the case of a Gaussian Markov process in which $\langle y\rangle = 0$. Substitution of the moments from Eq. (2.123) leads to the result

$$\partial K_1/\partial t = \gamma\langle y^2\rangle(\partial/\partial y)[\partial/\partial y + (1/\langle y^2\rangle)y]K_1, \tag{2.125}$$

which is the common form of the Fokker–Planck equation (Chandrasekhar, 1945; Feller, 1966; Rice and Gray, 1965). The general solution of this equation is the Gaussian transition probability of Eq. (2.106) with an exponential autocorrelation function, as expected. Suppose, for example, that we are interested in the momentum along the x direction. $P_x = MV_x$, of a heavy particle immersed in a bath of light particles, i.e., a Brownian particle (Chandrasekhar, 1945). It is quite natural to regard this velocity as a Gaussian random process because for a system in thermal equilibrium P_x is distributed according to a Gaussian distribution,† so that, no matter what the initial momentum is, $P_1(P_x)$ should tend toward a Gaussian distribution. If furthermore it is assumed that the momentum is Markovian, it follows that ($y \equiv P_x$)

$$\partial K_1/\partial t = \zeta(\partial/\partial P_x)[\partial/\partial P_x + \beta V_x]K_1, \tag{2.126}$$

where $\beta = 1/kT$, $\zeta = \gamma MkT = \psi(0)MkT$, and $\psi(t)$ is the normalized momentum autocorrelation function.

The opposite limiting case, case (b), in which there are large, impulsive changes in the random variable y, can be handled in a slightly different fashion. Again it is assumed that there exists a time τ_c, called the collision

† This is a plausible assumption.

time, which is the time between the impulsive changes in the variable y. It is assumed that during τ_c, K_1 changes very little, so that we can immediately write in place of Eq. (2.116)

$$K_1(y_1 \mid y; t) + \tau(\partial/\partial t)K_1(y_1 \mid y; t) + \cdots = \int dy_2\, K_1(y_1 \mid y_2; t)K_1(y_2 \mid y; \tau).$$

Since

$$\int dy_2\, K_1(y \mid y_2; \tau) = 1,$$

it follows that

$$\begin{aligned}\tau(\partial/\partial t)K_1(y_1 \mid y; t) = \int dy_2\, \{&K_1 \mid y_1 \mid y_2; t)K_1(y_2 \mid y; \tau)\\ &- K_1(y_1 \mid y; t)K_1(y \mid y_2; \tau)\} + O(\tau^2).\end{aligned} \tag{2.127}$$

Let us now define the transition rates

$$\begin{aligned}R(y_2 \mid y) &= \lim_{\tau\to 0,\tau\gg\tau_c} (1/\tau)K_1(y_2 \mid y; \tau)\\ R(y \mid y_2) &= \lim_{\tau\to 0,\tau\gg\tau_c} (1/\tau)K_1(y \mid y_2; \tau);\end{aligned} \tag{2.128}$$

$R(y_2 \mid y)$ is the rate of transition from y_2 to y, and $R(y \mid y_2)$ is the rate of transition from y back to y_2. They give the probability per unit time for specified transitions. When a system is in equilibrium, these two quantities are related by detailed balance if y is time even [see Eq. (2.99)]. If y is time odd, an analogous relation can be proven. If Eq. (2.128) is divided through by τ and the limit $\tau \to 0$ ($\tau \gg \tau_c$) is taken, it follows that

$$\begin{aligned}(\partial/\partial t)K_1(y_1 \mid y; t) = \int dy_2\, \{&K_1(y_1 \mid y_2; t)R(y_2 \mid y)\\ &- K_1(y_1 \mid y; t)R(y \mid y_2)\}.\end{aligned} \tag{2.129}$$

This equation has many applications in physics and chemistry. An equation of this kind is the basis of the kinetic theory of gases (Chapman and Cowling, 1939) where it is used to describe how momentum changes occur in gases due to collisions. In the kinetic theory, y represents the position and momentum of a molecule and it can be shown that the transition rate R is proportional to K_1. In this eventuality, the equation is called the Boltzmann equation.

In the previous analysis, Eq. (2.125) followed from the assumption that $\psi(y \mid \Delta y; \tau)$ is large for $\Delta y \simeq 0$ and small for $\Delta y \sim \langle y^2\rangle^{1/2}$, and Eq. (2.129) followed from the assumption that $R(y_2 \mid y)$ is uniform for a range of Δy from 0 to $\langle y^2\rangle^{1/2}$. It is possible to derive an equation for intermediate-type behavior. An example of such intermediate behavior

is that of a molecule moving in a liquid. The intermolecular potential consists of a strong repulsive region and a weak attractive region. A molecule will consequently move in a soft fluctuating force field between strong repulsive collisions. Its momentum will then change by frequent small amounts due to the soft force field and by large amounts due to the strong repulsive collisions. Consequently, it may be conjectured that the momentum of a molecule is a random process intermediate between the Fokker–Planck and Boltzmann limiting forms. Such a random process might well satisfy the equation

$$\begin{aligned}(\partial/\partial t)K_1(y_1 \mid y_2; t) = \int dy_2\, [&K_1(y_1 \mid y_2; t)R(y_2 \mid y) \\ &- K_1(y_1 \mid y; t)R(y \mid y_2)] - (\partial/\partial y)a^{(1)}(y)K_1(y_1 \mid y; t) \\ &+ \tfrac{1}{2}(\partial^2/\partial y^2)a^{(2)}(y)K_1(y_1, y; t)\end{aligned}$$

For this equation to be valid, it is necessary that the soft and hard changes in y occur on the same time scale. This approach was suggested by Rice and Allnatt, who applied a similar equation to the transport properties of liquids (see Rice and Gray, 1965). The equation is called the Rice–Allnatt equation.

Only the Fokker–Planck equation will be applied in later sections. This section is meant only as a survey of some of the key developments in the kinetic theory of liquids. The development of kinetic theory is based on a mixture of mechanical and statistical arguments. Some of these equations can be derived from first principles.

III. Time Correlation Functions and Memory Functions

A. The Hilbert Space of Dynamical Operators

Time correlation functions are of central importance in understanding how systems respond to weak probes in the linear approximation. According to the fluctuation dissipation theorem of the preceding chapter, spectroscopic line-shape studies reflect the detailed way in which dynamical variables relax in the equilibrium state. This fact has been exploited first in radiofrequency and microwave spectroscopy and more recently in Mössbauer, neutron, and infrared spectroscopy. It is the aim of statistical physics to predict the stationary and dynamical properties of many-body systems in equilibrium. For this purpose, it is often necessary to adopt simple models. Solids and gases are well understood because there

exist many very successful simple idealized models for these states of matter. On the other hand, liquids still remain something of a mystery. There is no simple model of the liquid state that accounts for the observed properties. Furthermore, no new phenomena have yet been predicted by models of the liquid state, as in the solid state. Liquids have been a challenge and embarassment to generations of outstanding physicists and chemists. In the last decade, a great deal of new information on liquids has been acquired, partly because of new techniques and partly because linear response theory provided a theoretical framework in which different measurements and ideas could be unified. This information is usually in the form of time correlation functions. Thus, it is not difficult to see why theoretists have attempted to construct models of condensed media that account for the dynamical bahavior of time correlation functions.

In this section, we will discuss the role of memory functions in the theory of time correlation functions (Berne *et al.*, 1966; Kubo, 1966; Mori, 1965a; Zwanzig, 1961).

Consider the arbitrary operators $\hat{\alpha}$ and $\hat{\beta}$. Let us define the scalar products of α and β, $\langle\alpha \mid \beta\rangle$, as

$$\langle\alpha \mid \beta\rangle = \mathrm{Tr}\{\tfrac{1}{2}[\hat{\alpha}^+, \hat{\beta}]_+\hat{\varrho}_{\mathrm{eq}}\} = \langle\tfrac{1}{2}[\alpha^+, \beta]_+\rangle \tag{3.1a}$$

$$\langle\alpha \mid \beta\rangle = \int d\Gamma f_{\mathrm{eq}}^{(N)}(\Gamma)\alpha^*(\Gamma)\beta(\Gamma) = \langle\alpha^*\beta\rangle, \tag{3.1b}$$

where $\hat{\alpha}^+$ is the Hermitian conjugate of the operator $\hat{\alpha}$. Equation (3.1a) is the quantum-mechanical ensemble average of $[\alpha^+, \beta]_+$. Equation (3.1b) is the classical equilibrium ensemble average of $\alpha^*\beta$. In Eqs. (3.1), $\hat{\varrho}_{\mathrm{eq}}$ and $f_{\mathrm{eq}}^{(N)}$ correspond to any equilibrium ensemble. The scalar products (3.1a) and (3.1b) each satisfy the conditions

(1) $\langle\alpha \mid \beta\rangle^* = \langle\beta \mid \alpha\rangle$.

(2) If $\alpha = c_1\alpha_1 + c_2\alpha_2$, where α_1 and α_2 are two arbitrary observables, and c_1 and c_2 are two arbitrary constants, then $\langle\beta \mid \alpha\rangle = c_1\langle\beta \mid \alpha_1\rangle + c_2\langle\beta \mid \alpha_2\rangle$.

(3) $\langle\alpha \mid \alpha\rangle \geqq 0$; the equality sign appears only if $\hat{\alpha} \equiv \hat{0}$.

From (1), we see that the norm, $\langle\alpha \mid \alpha\rangle^{1/2}$, of the property $\hat{\alpha}$ is real. Thus, $\langle\alpha \mid \alpha\rangle^{1/2}$ can be regarded as the "length" of the property $\hat{\alpha}$. A property whose norm is unity is said to be normalized. Two observables $\hat{\alpha}$ and $\hat{\beta}$ are said to be orthogonal if $\langle\alpha \mid \beta\rangle = 0$. It should be noted from (1) that $\langle\alpha \mid \beta\rangle$ need not be equal to $\langle\beta \mid \alpha\rangle$. Consider all bounded linear operators, together with the scalar product defined above. A Hilbert space of dynamical operators can be constructed. In this space, the $\hat{\alpha}$ is represented by the ket $\mid \alpha\rangle$.

Consider now the dynamical operators $\hat{U}_1, \ldots, \hat{U}_N$. Suppose that these operators are chosen such that they have a norm of unity and are orthogonal,

$$\langle U_\lambda \mid U_\nu \rangle = \delta_{\lambda\nu}. \tag{3.2}$$

These properties are so chosen that their ensemble averages are zero,

$$\langle U_\nu \rangle = 0. \tag{3.3}$$

Let us further suppose that the operators $\{\hat{U}_\nu\}$ have the following form and properties:

$$\hat{U}_\nu = \sum_m \tfrac{1}{2}[\hat{U}_{\nu m}, \exp i\mathbf{k} \cdot \mathbf{r}_m]_+ = \hat{U}_\nu(\mathbf{k}), \tag{3.4}$$

where $\hat{U}_{\nu m}$ is the νth property of particle m and $\mathbf{r}_m$ is the center-of-mass position of particle m. The property $\hat{U}_{\nu m}$ is a single-particle property and consequently must be Hermitian. It should be noted that $\hat{U}_\nu(\mathbf{k})$ resembles $\hat{B}_k$ in Chapter 2. Because the single-particle properties $\{\hat{U}_{\nu m}\}$ are Hermitian, it follows that $\hat{U}_\nu(-\mathbf{k})$ is the Hermitian conjugate of $\hat{U}_\nu(\mathbf{k})$.

Observables can quite generally be classified as time-even or time-odd depending on whether they do or do not change sign on time reversal. All even time derivaties of the coordinates are even under time reversal, while all odd derivatives are odd under time reversal, Thus, the Hamiltonian is time-even, the angular momentum is time-odd, and the linear momentum is time-odd. Time-even properties are represented by real Hermitian operators, while time-odd properties are represented by imaginary Hermitian operators.

The operator $\hat{U}_{\nu m}$ has the property that

$$\hat{U}^*_{\nu m} = \gamma_\nu \hat{U}_{\nu m}, \tag{3.5}$$

where γ_ν is the signature of the property $\hat{U}_{\nu m}$ under time reversal. Thus, if $\hat{U}_{\nu m}$ is time-even, $\gamma_\nu = +1$, whereas if $\hat{U}_{\nu m}$ is time-odd, $\gamma_\nu = -1$. From the definition of $\hat{U}_{\nu m}$ and $\hat{U}_\nu$, it follows that

$$\hat{U}_\nu{}^* = \hat{U}_\nu{}^*(\mathbf{k}) = \gamma_\nu \hat{U}_\nu(-\mathbf{k}) = \gamma_\nu \hat{U}_\nu{}^+, \tag{3.6}$$

where $\hat{U}_\nu{}^+$ denotes the Hermitian conjugate of $\hat{U}_\nu$.

If will be useful to know how the properties $\hat{U}_1, \ldots, \hat{U}_N$ defined above behave under coordinate inversion $\hat{P}$, where

$$\hat{P}f(\mathbf{r}_1, \ldots, \mathbf{r}_j, \ldots) = f(-\mathbf{r}_1, \ldots, -\mathbf{r}_j, \ldots).$$

We will only consider the single-particle properties that have definite parity under inversion, such as the molecular dipole moment or momentum. Then,

$$\hat{P}\hat{U}_{\nu m}\hat{P}^{-1} = \varepsilon_\nu \hat{U}_{\nu m}, \tag{3.7}$$

where ε_ν is the signature of the single-particle property $\hat{U}_{\nu m}$ under coordinate inversion; that is, the parity of the operator. The signature $\varepsilon_\nu = +1$ if $\hat{U}_{\nu m}$ is symmetric and $\varepsilon_\nu = -1$ if $\hat{U}_{\nu m}$ is antisymmetric in the coordinates. Consequently,

$$\hat{P}\hat{U}_\nu\hat{P}^{-1} = \hat{P}\hat{U}_\nu(\mathbf{k})\hat{P}^{-1} = \varepsilon_\nu \hat{U}_\nu(-\mathbf{k}) = \varepsilon_\nu \hat{U}_\nu{}^+. \tag{3.8}$$

In the absence of external magnetic fields, or, for that matter, any external pseudovector field, the exact energy eigenstates of a system can only be degenerate with respect to the total angular momentum of the system. This source of degeneracy can be removed if we assume that the body is enclosed in a container with rigid walls. It is always possible in this case to choose the energy eigenstates to be real. Consider the matrix elements of $\hat{U}_\nu$ in this real energy representation. From Eq. (3.6), it is seen that

$$(n \mid \hat{U}_\nu{}^* \mid m) = \gamma_\nu (n \mid \hat{U}_\nu{}^+ \mid m). \tag{3.9}$$

Since the states are real,

$$(n \mid U_\nu{}^* \mid m)^* = (n \mid \hat{U}_\nu \mid m) = \gamma_\nu (n \mid \hat{U}_\nu{}^+ \mid m)^* = \gamma_\nu (m \mid \hat{U}_\nu \mid n).$$

The last equality follows explicity from the definition of the Hermitian conjugate, so that

$$(n \mid \hat{U}_\nu \mid m) = \gamma_\nu (m \mid \hat{U}_\nu \mid n). \tag{3.10}$$

The matrix $\hat{U}_\nu$ is seen to be symmetric or antisymmetric depending on its signature in time.

The classical counterpart properties to these,

$$U_\nu \equiv U_\nu(\mathbf{k}, \mathbf{r}, \mathbf{p}) = \sum_m U_{\nu m}(\mathbf{r}_m, \mathbf{p}_m) \exp i\mathbf{k} \cdot \mathbf{r}_m \tag{3.11}$$

have analogous characteristics. The coordinates $\mathbf{r}$ and $\mathbf{p}$ in U_ν stand for all of the coordinates and momenta in the system. The single-particle property U depends only on the degrees of freedom $(\mathbf{r}_m, \mathbf{p}_m)$ of particle m. We shall only consider properties $\hat{U}_\nu$ in which $\hat{U}_{\nu m}$ has definite time-

reversal symmetry and definite parity,

$$\begin{aligned} U_{\nu m}(\mathbf{k}, \mathbf{r}_m, -\mathbf{p}_m) &= \gamma_\nu U_{\nu m}(\mathbf{k}, \mathbf{r}_m, \mathbf{p}_m) \\ U_{\nu m}(\mathbf{k}, -\mathbf{r}_m, \mathbf{p}_m) &= \varepsilon_\nu U_{\nu m}(-\mathbf{k}, \mathbf{r}_m, \mathbf{p}_m). \end{aligned} \tag{3.12}$$

Furthermore, it should be noted that U_ν has the property that

$$\begin{aligned} U_\nu(\mathbf{k}, -\mathbf{r}, \mathbf{p}) &= \varepsilon_\nu U_\nu(-\mathbf{k}, \mathbf{r}, \mathbf{p}) = \varepsilon_\nu U_\nu^*(\mathbf{k}, \mathbf{r}, \mathbf{p}) \\ U_\nu(\mathbf{k}, \mathbf{r}, -\mathbf{p}) &= \gamma_\nu U_\nu(\mathbf{k}, \mathbf{r}, \mathbf{p}). \end{aligned} \tag{3.13}$$

The properties $\hat{U}_\nu$ obey the equations of motion

$$\partial U_\nu / \partial t = iLU_\nu, \tag{3.14}$$

where L is the Liouville operator:

$$\begin{aligned} iL\alpha &\equiv \{\alpha, \hat{H}\} \quad \text{(classical)} \\ iL\alpha &\equiv (1/i\hbar)[\alpha, \hat{H}]_- \quad \text{(quantum)}. \end{aligned} \tag{3.15}$$

The properties $\hat{U}_1, \ldots, \hat{U}_N$ can be represented by vectors $|\hat{U}_1\rangle, \cdots, |\hat{U}_N\rangle$ in the Hilbert space of dynamical operators defined in the beginning of this section. According to (3.1a),

$$\langle \alpha \mid L \mid \beta \rangle = \hbar^{-1} \operatorname{Tr} \tfrac{1}{2}\hat{\varrho}_{\text{eq}} \{\hat{\alpha}^+[\hat{H}, \hat{\beta}]_- + [\hat{H}, \hat{\beta}]_- \hat{\alpha}^+\}.$$

The trace can be expanded in the complete set of real energy eigenvectors of the Hamiltonian. Then,

$$\begin{aligned} \langle \alpha \mid L \mid \beta \rangle = \hbar^{-1} \sum_{\text{if}} \tfrac{1}{2}\varrho_i \{ &(i \mid \alpha^+ \mid f)(f \mid [\hat{H}, \hat{\beta}]_- \mid i) \\ &+ (i \mid [\hat{H}, \hat{\beta}]_- \mid f)(f \mid \hat{\alpha}^+ \mid i)\}. \end{aligned}$$

It should be noted that $(i \mid \hat{A} \mid f)$ is the *if* matrix element of an operator $\hat{A}$ in the energy representation. It is not a scalar product in the Hilbert space of operators. Since $(i \mid [\hat{H}, \hat{\beta}]_- \mid f) = (E_i - E_f)(i \mid \beta \mid f)$ and since $(i \mid \alpha^+ \mid f) = (f \mid \alpha \mid i)^+$ and $(f \mid \beta \mid i)^* = (i \mid \beta^+ \mid f)$, it follows that

$$\begin{aligned} \langle \alpha \mid L \mid \beta \rangle^* = \hbar^{-1} \sum_{\text{if}} \tfrac{1}{2}\varrho_i \{ &(i \mid \beta^+ \mid f)(f \mid [\hat{H}, \alpha]_- \mid i) \\ &+ (i \mid [\hat{H}, \alpha] \mid f)(f \mid \alpha^+ \mid i)\}, \end{aligned}$$

or

$$\langle \alpha \mid L \mid \beta \rangle^* = \langle \beta \mid L \mid \alpha \rangle. \tag{3.16}$$

Thus, the Liouville operator L is Hermitian in the space of linear operators.

An analogous proof can be carried through for the classical scalar product (3.1b). Note that

$$\langle \alpha \mid L \mid \beta \rangle^* = \int d\Gamma f_{\text{eq}}^{(N)}(\Gamma)\alpha(\Gamma)L^*\beta^*(\Gamma).$$

The operator iL is the linear differential operator of Eq. (2.93),

$$iL \equiv \{\cdot, \hat{H}\} = \sum_{j=1}^{N} \left[\mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{r}_j} + \mathbf{F}_j \cdot \frac{\partial}{\partial \mathbf{p}_j}\right]. \tag{3.17}$$

Substitution of L into $\langle \alpha \mid L \mid \beta \rangle$ and a subsequent integration by parts yields

$$\langle \alpha \mid L \mid \beta \rangle^* = \int d\Gamma f_{\text{eq}}^{(N)}(\Gamma)\beta^*(\Gamma)L\alpha(\Gamma) = \langle \beta \mid L \mid \alpha \rangle, \tag{3.18}$$

where it was assumed that the surface term is zero due to the presence of the distribution $f_{\text{eq}}^{(N)}$, which vanishes very quickly on the boundary of the accessible region of phase space. Since (3.1b) is the classical limit of (3.1a), Eq. (3.16) implies this result.

The time correlation function $\hat{C}_{\nu\mu}(t)$ is defined as

$$\hat{C}_{\nu\mu}(t) \equiv \langle U_\nu \mid e^{iLt} \mid U_\mu \rangle \equiv \langle U_\nu(0) \mid U_\mu(t) \rangle. \tag{3.19}$$

Corresponding to the two definitions of the scalar product, Eq. (3.1), there are the correlation functions

$$\hat{C}_{\nu\mu}(t) = \langle \tfrac{1}{2}[\hat{U}_\nu^+(0), \hat{U}_\mu(t)]_+ \rangle \tag{3.20a}$$

$$\hat{C}_{\nu\mu}(t) = \int d\Gamma_0 f_{\text{eq}}^{(N)}(\Gamma_0) U_\nu^*(\Gamma_0) e^{iLt} U_\mu(\Gamma_0). \tag{3.20b}$$

Equations (3.20a) and (3.20b) are the quantum and classical cross correlation functions of the properties U_ν and U_μ. They describe the correlation between $\hat{U}_\nu(0)$ and $\hat{U}_\mu(t)$ as a function of the time.

Consider the property $\hat{B}_k$ that we described in the last section: $\hat{B}_k$ has the property that

$$\langle \hat{B}_k \rangle = \operatorname{Tr} \hat{\varrho}_{\text{eq}} \hat{B}_k = 0.$$

Accordingly, the autocorrelation function of B_k was defined in the last section as

$$C_{BB}(\mathbf{k}, t) = \langle \tfrac{1}{2}[\hat{B}_{-k}(0), \hat{B}_{+k}(t)]_+ \rangle.$$

It can be concluded from the fact that $\hat{B}_k^+ = \hat{B}_{-k}$ that this autocorrelation function can be expressed as the scalar product

$$C_{BB}(\mathbf{k}, t) = \langle B_k \mid e^{iLt} \mid B_k \rangle,$$

where the definitions (3.20a) or (3.20b) apply in the quantum or classical limits. A ket $\mid U_i\rangle$ of norm 1 can be defined such that

$$\mid U_i\rangle = \langle B_k \mid B_k\rangle^{-1/2} \mid \hat{B}_k\rangle.$$

The time correlation function of this property is then related to $C_{BB}(\mathbf{k}, t)$ by

$$\hat{C}_{ii}(t) = \langle U_i \mid e^{iLt} \mid U_i\rangle = \langle B_k \mid B_k\rangle^{-1} C_{BB}(\mathbf{k}, t).$$

At $t = 0$, $C_{BB}(\mathbf{k}, 0) = \langle B_k \mid B_k\rangle$. Consequently,

$$\hat{C}_{ii}(0) = 1; \tag{3.21}$$

$\hat{C}_{ii}(t)$ is called a normalized autocorrelation function.

B. General Properties of Autocorrelation Functions

Theorem 1. Autocorrelation functions are stationary functions; i.e., $\langle U_\nu(t) \mid U_\nu(t+\tau)\rangle$ is independent of the time t.

Proof.

$$\begin{aligned} \mid U_\nu(t+\tau)\rangle &\equiv e^{iL(t+\tau)} \mid U_\nu\rangle, \\ \mid U_\nu(t)\rangle &= e^{iLt} \mid U_\nu\rangle, \\ \langle U_\nu(t) \mid &= \langle U_\nu \mid (e^{+(iL)t})^+ = \langle U_\nu \mid e^{-iLt}. \end{aligned}$$

This last result follows from the fact that the Liouville operator is Hermitian. Consequently,

$$\begin{aligned} \langle U_\nu(t) \mid U_\nu(t+\tau)\rangle &= \langle U_\nu \mid e^{-iLt} e^{iL(t+\tau)} \mid U_\nu\rangle \\ &= \langle U_\nu \mid e^{iL\tau} \mid U_\nu\rangle \\ &= \langle U_\nu(0) \mid U_\nu(\tau)\rangle. \end{aligned} \tag{3.22}$$

Q.E.D.

Stationarity follows from the fact that the time correlation functions are defined as averages over equilibrium (stationary) ensembles. In such ensembles, it *should not*, and, by our theorem, *does not* matter what time is chosen as the initial time.

Theorem 2. The autocorrelation function

$$\hat{C}_{\nu\nu}(t) \equiv \langle U_\nu \mid e^{iLt} \mid U_\nu\rangle$$

is a real, even function of the time, or

$$\hat{C}^*_{\nu\nu}(t) = \hat{C}_{\nu\nu}(t) = \hat{C}_{\nu\nu}(-t) \tag{3.23}$$

if U_ν has the properties described in Section III,A and there is no external magnetic field.

Proof. That $\hat{C}^*_{\nu\nu}(t) = \hat{C}_{\nu\nu}(-t)$ follows directly from the Hermitian property of the Liouville operator,

$$\begin{aligned} \hat{C}^*_{\nu\nu}(t) &= \langle U_\nu \mid e^{iLt} \mid U_\nu\rangle^* = \langle U_\nu \mid (e^{iLt})^+ \mid U_\nu\rangle \\ &= \langle U_\nu \mid e^{-iLt} \mid U_\nu\rangle = \hat{C}_{\nu\nu}(-t). \end{aligned}$$

As we have seen before, in the absence of an external magnetic field, the energy eigenstates can be chosen real. In this real representation, it follows that

$$\begin{aligned} \hat{C}_{\nu\nu}(t) = \tfrac{1}{2} \sum_{nm} \varrho_n \{ &(n \mid U_\nu^+ \mid m)(m \mid U_\nu \mid n) e^{i\omega_{mn}t} \\ &+ (n \mid U_\nu \mid m)(m \mid U_\nu^+ \mid n) e^{i\omega_{nm}t} \}. \end{aligned}$$

From Eq. (3.9), it is seen that

$$(n \mid U_\nu \mid m) = \gamma_\nu (m \mid \hat{U}_\nu \mid n), \qquad (n \mid U_\nu^+ \mid m) = \gamma_\nu (m \mid U_\nu^+ \mid n).$$

Consequently

$$\begin{aligned} \hat{C}_{\nu\nu}(t) = \tfrac{1}{2} \sum_{nm} \varrho_n \{ &\gamma_\nu\gamma_\nu (n \mid U_\nu \mid m)(m \mid U_\nu^+ \mid n) e^{-i\omega_{mn}t} \\ &+ \gamma_\nu\gamma_\nu (n \mid U_\nu^+ \mid m)(m \mid U_\nu \mid n) e^{-i\omega_{nm}t} \}. \end{aligned}$$

Since $\gamma_\nu^2 = 1$, the right-hand side is seen to be $C_{\nu\nu}(-t)$, so that

$$\hat{C}_{\nu\nu}(-t) = \hat{C}_{\nu\nu}(t).$$

Combining these results,

$$\hat{C}^*_{\nu\nu}(t) = \hat{C}_{\nu\nu}(t) = \hat{C}_{\nu\nu}(-t).$$

The classical argument is very similar. Instead of going through these arguments here, a similar classical proof which is given later (see Theorem 2, Section III,C) should make the argument transparent.

Theorem 3. The normalized autocorrelation function

$$\hat{C}_{\nu\nu}(t) \equiv \langle U_\nu \mid e^{iLt} \mid U_\nu \rangle$$

satisfies the inequality

$$-1 \leq \hat{C}_{\nu\nu}(t) \leq 1. \tag{3.24}$$

Proof. Consider the vectors $\mid \alpha \rangle$ and $\mid \beta \rangle$. According to the Schwartz inequality,

$$0 \leq \mid \langle \alpha \mid \beta \rangle \mid \leq [\langle \alpha \mid \alpha \rangle \langle \beta \mid \beta \rangle]^{1/2}.$$

Now, let

$$\mid \alpha \rangle = \mid U_\nu \rangle, \qquad \mid \beta \rangle = e^{iLt} \mid U_\nu \rangle.$$

Then, according to the Schwartz inequality

$$0 \leq \mid \langle U_\nu \mid e^{iLt} \mid U_\nu \rangle \mid = \mid C_{\nu\nu}(t) \mid \leq \langle U_\nu \mid U_\nu \rangle = 1,$$

thus proving our theorem.

A complex function of the time $F(t)$ is called positive-definite if and only if

$$\sum_{j,k=1}^{n} Z_j F(t_j - t_k) Z_k^* \geq 0 \tag{3.25}$$

holds for every choice of finitely many real numbers $t_1, \ldots, t_n$ and complex numbers $Z_1, \ldots, Z_n$.

According to Bochner's theorem (Feller, 1966), a continuous function $F(t)$ is the characteristic function of a probability distribution if and only if $F(t)$ is positive-definite and $F(0) = 1$.

Theorem 4. If the normalized autocorrelation function

$$\hat{C}_{\nu\nu}(t) \equiv \langle U_\nu \mid e^{iLt} \mid U_\nu \rangle$$

is continuous, then it is the characteristic function of a probability distribution $G_{\nu\nu}(\omega)$, or

$$\hat{C}_{\nu\nu}(t) = \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t} G_{\nu\nu}(\omega). \tag{3.26}$$

Proof. By hypothesis, $\hat{C}_{\nu\nu}(t)$ is continuous. By definition, $\hat{C}_{\nu\nu}(0) = 1$. Define a vector $\mid \alpha_n \rangle$ such that

$$\mid \alpha_n \rangle = \sum_{k=1}^{n} \mid U_\nu(t_k) \rangle Z_k$$

for every choice of the real numbers $(t_1, \ldots, t_n)$ and the complex numbers $(Z_1, \ldots, Z_n)$. It follows from the positivity of the norm of a vector that

$$\langle \alpha_n \mid \alpha_n \rangle = \sum_{j,k=1}^{n} Z_k^* \langle U_\nu(t_k) \mid U_\nu(t_j) \rangle Z_j \geq 0.$$

From the Theorem 1, we see that

$$\langle U_\nu(t_k) \mid U_\nu(t_j) \rangle = \langle U_\nu(0) \mid U_\nu(t_j - t_k) \rangle = \hat{C}_{\nu\nu}(t_j - t_k).$$

Thus, $\hat{C}_{\nu\nu}(t)$ is positive-definite and consequently satisfies all of the conditions for Bochner's theorem. It follows that $\hat{C}_{\nu\nu}(t)$ is the characteristic function of the probability distribution $G_{\nu\nu}(\omega)$. and the theorem is proved.

Any probability distribution $G_{\nu\nu}(\omega)$ by definition satisfies the condition

$$0 \leq G_{\nu\nu}(\omega). \tag{3.27}$$

The interesting thing to note is that $G_{\nu\nu}(\omega)$ is none other than the power spectrum of the time correlation function $C_{\nu\nu}(t)$. This has very important ramifications, as we shall see later. To summarize: Power spectra are everywhere positive and bounded, and furthermore, autocorrelation functions are bounded and have power spectra that can be regarded as probability distribution functions.

To make this kind of treatment plausible, consider the Fourier development of the vector $\mid U(t) \rangle$,

$$\mid U(t) \rangle = \int_{-\infty}^{+\infty} d\omega \mid U_\omega \rangle e^{-i\omega t}$$

where $\mid U_\omega \rangle$ is the amplitude of $\mid U(t) \rangle$ at the frequency ω. (In all rigor, this should be done with the Fourier–Stieltjes integral). Dotting the above into the Fourier development of $\mid U(t + \tau) \rangle$ yields

$$\langle U(t) \mid U(t + \tau) \rangle = \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega' \langle U_{\omega'} \mid U_\omega \rangle \times \exp[-i[\omega - \omega']t] \exp[-i\omega\tau]$$

According to Theorem 1, $\langle U(t) \mid U(t+\tau)\rangle$ is independent of t. Consequently,

$$\langle U_{\omega'} \mid U_\omega\rangle = \langle U_\omega \mid U_\omega\rangle\, \delta(\omega - \omega')$$

and

$$\hat{C}(t) = \int_{-\infty}^{+\infty} d\omega\, G(\omega) e^{-i\omega t} \tag{3.28}$$

with the power spectrum

$$G(\omega) = \langle U_\omega \mid U_\omega\rangle;$$

$G(\omega)$ is positive because the norm $\langle U_\omega \mid U_\omega\rangle$ is positive. From Eq. (3.28), we see that

$$\hat{C}(0) = 1 = \int_{-\infty}^{+\infty} d\omega\, G(\omega).$$

Therefore,

$$0 \leq G(\omega). \tag{3.29}$$

The Wiener–Khinchin theorem is a special case of Bochner's theorem applicable to time averages of stationary stochastic variables. Bochner's theorem enables the Wiener–Khinchin theorem to be applied to ensemble-averaged time correlation functions in quantum mechanics where it is difficult to think of properties as stochastic processes.

The power spectrum $G(\omega)$ of the normalized time correlation function $\hat{C}(t)$, like any distribution function, can be decomposed into a continuous and a discrete part, $G_c(\omega)$ and $G_d(\omega)$, respectively:

$$G(\omega) = G_d(\omega) + G_c(\omega). \tag{3.30}$$

The discrete part is of the form

$$G_d(\omega) = \sum_k P_k\, \delta(\omega - \omega_k), \qquad k = 1, \ldots . \tag{3.31}$$

Here, $\{\omega_k\}$ is a denumerable set of frequencies and $(P_k\}$ is the set of corresponding probabilities ($0 \leq P_k \leq 1$ and $0 \leq \sum_k P_k \leq 1$). It is assumed here that the continuous part of the spectrum, $G_c(\omega)$, is a continuous, well-behaved function of the frequency, although it is quite possible to find physical $G_c(\omega)$ that have singular points. From previous sections, it follows that $G(\omega)$ is even in ω.

The normalized time correlation functions can thus be decomposed

in a corresponding way,

$$\hat{C}(t) = \int_{-\infty}^{+\infty} d\omega\, G_d(\omega) e^{-i\omega t} + \sum_k P_k \cos \omega_k t. \tag{3.32}$$

In this case, $\hat{C}(t)$ does not have any long-time limit. If the spectrum is entirely continuous, then it follows from the lemma of Riemann–Lebesgue that $C(t)$ vanishes as $t \to \infty$. A system is irreversible if and only if all time correlation functions of properties $\hat{U}$ (with zero mean) vanish as $t \to \infty$. Consequently, irreversible systems must have continuous spectra. In finite isolated systems, the spectrum is discrete and

$$C(t) = \sum_k P_k \cos \omega_k t \tag{3.33}$$

is almost periodic. This is a consequence of Poincaré's theorem. In specialized cases, it can be shown that, in the thermodynamic limit, $N \to \infty$, $V \to \infty$ such that $N/V = \text{const}$, the discrete spectrum becomes continuous. Irreversibility enters in an asymptotic manner. This is a very important point.

Computer experiments on condensed media simulate finite systems and, moreover, use periodic boundary conditions. The effect of these boundary conditions on the spectrum of different correlation functions is difficult to assess. Before the long-time behavior of covariance functions can be studied on a computer, there are a number of fundamental questions of this kind that must be answered.

C. Projection Operators, Memory Functions, and Autocorrelation Functions

In the preceding subsection, it was shown that an arbitrary operator can be represented by a vector or ket in a space of linear operators. Consider the orthonormal operators $\hat{U}_1, \ldots, \hat{U}_N$ whose properties were defined previously. The projector onto the normalized vector $\mid U_\nu\rangle$ (representing the property $\hat{U}_\nu$ whose mean $\langle U_\nu\rangle$ is zero) is defined as

$$\hat{P}_\nu = \mid U_\nu\rangle \langle U_\nu \mid.$$

The necessary and sufficient conditions for $\hat{P}_\nu$ to be a projector is that it be Hermitian and idempotent. That $\hat{P}_\nu$ is idempotent follows from the fact that $\mid U_\nu\rangle$ is normalized,

$$\hat{P}_\nu^2 = \mid U_\nu\rangle \langle U_\nu \mid U_\nu\rangle \langle U_\nu \mid = \mid U_\nu\rangle \langle U_\nu \mid = \hat{P}_\nu.$$

That $\hat{P}_\nu$ is Hermitian follows from the definition of the scalar product. If $|\alpha\rangle$ and $|\beta\rangle$ are two arbitrary vectors in operator space, then

$$\langle\alpha|\hat{P}_\nu|\beta\rangle^* = \langle\alpha|U_\nu\rangle^*\langle U_\nu|\beta\rangle^* = \langle\beta|U_\nu\rangle\langle U_\nu|\alpha\rangle = \langle\beta|\hat{P}_\nu|\alpha\rangle; \tag{3.34}$$

$\hat{P}_\nu$ is Hermitian and consequently is a projection operator.

It is possible to derive an equation that describes the time evolution of the time correlation function $\hat{C}_{\nu\nu}(t)$, where $\hat{C}_{\nu\nu}$ stands for either the classical or quantum-mechanical autocorrelation function depending on the definition of the scalar product (3.1a) or (3.1b) adopted.

The equation of motion for the vector $|U_\nu(t)\rangle$ is, according to Eq. (3.15),

$$\partial|U_\nu(t)\rangle/\partial t = iL|U_\nu(t)\rangle. \tag{3.35}$$

Since $(1-\hat{P}_\nu)+\hat{P}_\nu$ is simply the identity operator, it can be substitued between iL and $|U_\nu(t)\rangle$ so that

$$\partial|U_\nu(t)\rangle/\partial t = iL\hat{P}_\nu|U_\nu(t)\rangle + iL(1-\hat{P}_\nu)|U_\nu(t)\rangle. \tag{3.36}$$

Since

$$\hat{C}_{\nu\nu}(t) = \langle U_\nu|\hat{P}_\nu|U_\nu(t)\rangle, \tag{3.37}$$

it should be noted that an equation for $\hat{C}_{\nu\nu}(t)$ can be derived by first operating on Eq. (3.36) with $\hat{P}_\nu$, and then dotting $\langle U_\nu|$ into the resulting equation. Following this procedure, we find

$$\partial\hat{C}_{\nu\nu}(t)/\partial t = \langle U_\nu|\hat{P}_\nu iL\hat{P}_\nu|U_\nu(t)\rangle + \langle U_\nu|\hat{P}_\nu iL(1-\hat{P}_\nu)|U_\nu(t)\rangle. \tag{3.38}$$

Now note that

$$\langle U_\nu|\hat{P}_\nu iL\hat{P}_\nu|U_\nu(t)\rangle = \langle U_\nu|iL|U_\nu\rangle\hat{C}_{\nu\nu}(t) = 0 \tag{3.39}$$

vanishes since $\langle U_\nu|iL|U_\nu\rangle$ vanishes. Then

$$\partial\hat{C}_{\nu\nu}(t)/\partial t = \langle U_\nu|iL(1-\hat{P}_\nu)|U_\nu(t)\rangle. \tag{3.40}$$

To complete the derivation, we must find how $(1-\hat{P}_\nu)|U_\nu(t)\rangle$ varies with time. For this purpose, operate on Eq. (3.36) with $(1-\hat{P}_\nu)$,

$$(\partial/\partial t)(1-\hat{P}_\nu)|U_\nu(t)\rangle = (1-\hat{P}_\nu)iL\hat{P}_\nu|U_\nu(t)\rangle + (1-\hat{P}_\nu)iL(1-\hat{P}_\nu)|U_\nu(t)\rangle. \tag{3.41}$$

Now note that

$$\begin{aligned}(1-\hat{P}_\nu)iL\hat{P}_\nu|U_\nu(t)\rangle &= iL|U_\nu\rangle\hat{C}_{\nu\nu}(t)\\ (1-\hat{P}_\nu)|U_\nu(0)\rangle &= (1-\hat{P}_\nu)|U_\nu\rangle = 0.\end{aligned} \tag{3.42}$$

The solution of Eq. (3.41) subject to Eq. (3.42) is

$$(1-\hat{P}_\nu)|U_\nu(t)\rangle = \int_0^t d\tau\,\exp[i(1-\hat{P}_\nu)L\tau]iL|U_\nu\rangle\hat{C}_{\nu\nu}(t-\tau). \tag{3.43}$$

Substitution of this into Eq. (3.40) yields

$$\frac{\partial}{\partial t}\hat{C}_{\nu\nu}(t) = -\int_0^t d\tau\,K_{\nu\nu}(\tau)\hat{C}_{\nu\nu}(t-\tau), \tag{3.44}$$

where

$$K_{\nu\nu}(\tau) = \langle iLU_\nu|\exp[i(1-\hat{P}_\nu)L\tau]|iLU_\nu\rangle; \tag{3.45}$$

$K_{\nu\nu}(\tau)$ is called the "memory function" and the equation for the time correlation function that we derived is called the memory-function equation. Note that the propagator in this equation contains the projection operator $\hat{P}_\nu$. This follows from Eq. (3.45). It should also be noted that the definition of the memory function depends strongly on which scalar product (3.1a) or (3.1b) is used.† Corresponding to definitions (3.1a) and (3.1b),

$$\langle\tfrac{1}{2}[(iLU_\nu)^+, \exp[i(1-\hat{P}_\nu)Lt]iLU_\nu)]_+\rangle, \tag{3.46a}$$

$$\int d\Gamma_0 f^{(N)}(\Gamma_0)(iLU_\nu(\Gamma_0))^*\exp[i(1-\hat{P}_\nu)Lt](iLU_\nu(\Gamma_0)), \tag{3.46b}$$

where the projection operator is so defined in each case that it is consistent with the definition of the scalar product adopted.

If the memory function $K_{\nu\nu}(t)$ is known, the memory-function equation can be solved for the autocorrelation function.

The memory function involves the operator $\exp[i(1-\hat{P}_\nu)Lt]$. Since the Liouville operator L and the projector $\hat{P}_\nu$ are Hermitian, $\hat{P}_\nu L$ and $L\hat{P}_\nu$ are Hermitian conjugates in operator space. If $|\alpha\rangle$ and $|\beta\rangle$ are arbitrary kets in operator space, it follows immediately that

$$\langle\alpha|\exp i(1-\hat{P}_\nu)Lt|\beta\rangle^* = \langle\beta|\exp -iL(1-\hat{P}_\nu)t|\alpha\rangle. \tag{3.47}$$

† If the dynamical operator $\hat{O}_\nu$ is a vector property, then the scalar product can be defined as (a) $\langle\boldsymbol{\alpha}|\boldsymbol{\beta}\rangle = \frac{1}{2}[\boldsymbol{\alpha}^+\cdot\boldsymbol{\beta}+\boldsymbol{\beta}\cdot\boldsymbol{\alpha}^+]$; (b) $\langle\boldsymbol{\alpha}|\boldsymbol{\beta}\rangle = \int d\Gamma\boldsymbol{\alpha}^*(\boldsymbol{\Gamma})\cdot\boldsymbol{\beta}(\boldsymbol{\Gamma})f^{(N)}(\boldsymbol{\Gamma})$. This is not necessary since the components can be handled independently.

The operator $1 - \hat{P}_\nu$ is a projector onto the subspace of operator space which is orthogonal to the vector $|U_\nu\rangle$. Thus, if $|G\rangle$ and $|F\rangle$ are two arbitrary vectors in operator space, it follows that

$$|g\rangle \equiv (1 - \hat{P}_\nu)|G\rangle, \qquad |f\rangle \equiv (1 - \hat{P}_\nu)|F\rangle \tag{3.48}$$

lie in the orthogonal subspace to $|U_\nu\rangle$. It will now be shown that the operator $(1 - \hat{P}_\nu)L$ is Hermitian in the orthogonal subspace of $|U_\nu\rangle$. The vectors $|f\rangle$ and $|g\rangle$ are arbitrary vectors in this subspace. Now, note that

$$\langle g|(1 - \hat{P}_\nu)L|f\rangle^* = \langle G|(1 - \hat{P}_\nu)^2 L(1 - \hat{P}_\nu)|F\rangle^*.$$

Since $(1 - \hat{P}_\nu)$ is a projector, it is idempotent, or $(1 - \hat{P}_\nu)^2 = (1 - \hat{P}_\nu)$. Consequently,

$$\begin{aligned}\langle g|(1 - \hat{P}_\nu)L|f\rangle^* &= \langle G|(1 - \hat{P}_\nu)L(1 - \hat{P}_\nu)|F\rangle^* \\ &= \langle F|(1 - \hat{P}_\nu)^+[(1 - \hat{P}_\nu)L]^+|G\rangle.\end{aligned}$$

Since both $(1 - \hat{P}_\nu)$ and L are Hermitian,

$$\begin{aligned}\langle g|(1 - \hat{P}_\nu)L|f\rangle^* &= \langle F|(1 - \hat{P}_\nu)L(1 - \hat{P}_\nu)|G\rangle \\ &= \langle f|(1 - \hat{P}_\nu)L|g\rangle.\end{aligned}$$

The last equality follows from the idempotency of $(1 - \hat{P}_\nu)$. Thus, $(1 - \hat{P}_\nu)L$ is Hermitian in the orthogonal subspace to $|U_\nu\rangle$. It follows that

$$\langle g|\exp i(1 - \hat{P}_\nu)Lt|f\rangle^* = \langle f|\exp -i(1 - \hat{P}_\nu)Lt|g\rangle. \tag{3.49}$$

It should be noted that the vector $|iLU_\nu\rangle \equiv iL|U_\nu\rangle$ is orthogonal to $|U_\nu\rangle$ since

$$\langle U_\nu|iL|U_\nu\rangle = 0.$$

Thus, $|iLU_\nu\rangle$ is a vector in the orthogonal subspace to $|U_\nu\rangle$ and

$$\langle iLU_\nu|\exp i(1 - \hat{P}_\nu)Lt|iLU_\nu\rangle^* = \langle iLU_\nu|\exp -i(1 - \hat{P}_\nu)Lt|iLU_\nu\rangle. \tag{3.50}$$

Consequently,

$$K_{\nu\nu}^*(t) = K_{\nu\nu}(-t). \tag{3.51}$$

D. General Properties of Memory Functions

Theorem 1. The memory function is a stationary function of the time.

Proof. Let the vector $|iLU_\nu(t+\tau)\rangle_P$ stand for

$$|iLU_\nu(t+\tau)\rangle_P \equiv [\exp i(1 - \hat{P}_\nu)L(t+\tau)]|iLU_\nu\rangle;$$

then,

$$|iLU_\nu(t)\rangle_P \equiv [\exp i(1 - \hat{P}_\nu)Lt]|iLU_\nu\rangle$$

and

$${}_P\langle iLU_\nu(t)| \equiv \langle iLU_\nu|[\exp i(1 - \hat{P}_\nu)Lt]^+,$$

so that

$$\begin{aligned}{}_P\langle iLU_\nu(t)|iLU_\nu(t+\tau)\rangle_P = \langle iLU_\nu|&[\exp i(1 - \hat{P}_\nu)Lt]^+ \\ &\times [\exp i(1 - \hat{P}_\nu)L(t+\tau)]|iLU_\nu\rangle.\end{aligned}$$

To prove the theorem, it must be shown that this is independent of t. Since $(1 - \hat{P}_\nu)L$ is Hermitian in the orthogonal subspace to $|U_\nu\rangle$, it follows that $[\exp i(1 - \hat{P}_\nu)Lt]^+ \to \exp -i(1 - P_\nu)Lt$ in the last equation, so that

$$\begin{aligned}{}_P\langle iLU_\nu(t)|iLU_\nu(t+\tau)\rangle_P &= \langle iLU_\nu|\exp i(1 - \hat{P}_\nu)L\tau|iLU_\nu\rangle \\ &= K_{\nu\nu}(\tau).\end{aligned} \tag{3.52}$$

It follows that both the autocorrelation function $\hat{C}_{\nu\nu}(t)$ and its associated memory function $K_{\nu\nu}(\tau)$ are stationary functions of the time.

Theorem 2. The memory function

$$K_{\nu\nu}(t) \equiv \langle iLU_\nu|\exp i(1 - \hat{P}_\nu)Lt|iLU_\nu\rangle$$

is a real, even function of the time, or

$$K_{\nu\nu}^*(t) = K_{\nu\nu}(-t) = K_{\nu\nu}(t), \tag{3.53}$$

if $|U_\nu\rangle$ has the properties described in Section III,A and there is no external magnetic field.

Proof. That $K_{\nu\nu}^*(t) = K_{\nu\nu}(-t)$ was established by the arguments leading to Eq. (3.51). A classical proof is presented here. By definition,

$$K_{\nu\nu}(t) = \int d\Gamma f_{\text{eq}}^{(N)}(\Gamma)(iLU_\nu)^*[\exp i(1 - \hat{P}_\nu)Lt](iLU_\nu).$$

From Eq. (3.13), we see that

$$U_\nu(\mathbf{k}, -\mathbf{r}, -\mathbf{p}) = \gamma_\nu \varepsilon_\nu U^*(\mathbf{k}, \mathbf{r}, \mathbf{p}).$$

It follows that

$$(iLU_\nu)_{k,-\mathbf{r},-\mathbf{p}} = \gamma_\nu \varepsilon_\nu (iLU_\nu)^*_{k,\mathbf{r},\mathbf{p}}.$$

Transforming variables $(\mathbf{r}_m, \mathbf{p}_m) \to (-\mathbf{r}_m, -\mathbf{p}_m) \to (-\mathbf{r}, -\mathbf{p})$ in the above integral leads to

$$K_{\nu\nu}(t) = (\gamma_\nu \varepsilon_\nu)^2 \int d\Gamma_0 f_{\text{eq}}^{(N)}(\Gamma_0)(iLU_\nu)[\exp i(1 - \hat{P}_\nu)Lt](iLU_\nu)^*.$$

Since $(1 - \hat{P}_\nu)L$ is Hermitian in the orthogonal subspace to $| U_\nu\rangle$ and $(\gamma_\nu \varepsilon_\nu)^2 = 1$, it follows that

$$K_{\nu\nu}(t) = \int d\Gamma\, d_{\text{eq}}^{(N)}(\Gamma_0)(iLU_\nu)^*[\exp -i(1 - \hat{P}_\nu)Lt](iLU_\nu) = K_{\nu\nu}(-t).$$

We have thus proved that

$$K^*_{\nu\nu}(t) = K_{\nu\nu}(t) = K_{\nu\nu}(-t).$$

Another proof can be given. It has already been shown that $\hat{C}_{\nu\nu}(t)$ is a real, even function of t. It has also been established that $\hat{C}_{\nu\nu}(t)$ satisfies the memory-function equation

$$\frac{\partial}{\partial t} \hat{C}_{\nu\nu}(t) = -\int_0^t dt\, K_{\nu\nu}(\tau)\hat{C}_{\nu\nu}(t - \tau).$$

It follows immediately that, if $\hat{C}_{\nu\nu}(t)$ is real, then $K_{\nu\nu}(t)$ must be real, and if $\hat{C}_{\nu\nu}(t)$ is an even function of t, $K_{\nu\nu}(t)$ must be even in t.

Theorem 3. The memory function

$$K_{\nu\nu}(t) \equiv \langle iLU_\nu \mid \exp i(1 - \hat{P}_\nu)Lt \mid iLU_\nu\rangle$$

satisfies the inequality

$$-\langle iLU_\nu \mid iLU_\nu\rangle \leq K_{\nu\nu}(t) \leq \langle iLU_\nu \mid iLU_\nu\rangle. \tag{3.54}$$

Proof. Define the vectors

$$| \alpha\rangle = | iLU_\nu\rangle, \qquad | \beta\rangle = [\exp i(1 - \hat{P}_\nu)Lt] \mid iLU_\nu\rangle.$$

Then, by Schwart'z inequality,

$$0 \leq | \langle \alpha \mid \beta\rangle \leq [\langle \alpha \mid \alpha\rangle \langle \beta \mid \beta\rangle]^{1/2},$$

it follows that

$$0 \leq | K_{\nu\nu}(t) | \leq \langle iLU_\nu \mid iLU_\nu\rangle.$$

Q.E.D.

Theorem 4. If the normalized memory function

$$\hat{K}_{\nu\nu}(t) = \langle iLU_\nu \mid \exp i(1 - \hat{P}_\nu)Lt \mid iLU_\nu\rangle / \langle iLU_\nu \mid iLU_\nu\rangle^{-1}$$

is a continuous function of the time, then it is the characteristic function of a probability distribution function $L_{\nu\nu}(\omega)$, or

$$\hat{K}_{\nu\nu}(t) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t} L_{\nu\nu}(\omega), \tag{3.55}$$

where $0 \leq L_{\nu\nu}(\omega)$.

Proof. By hypothesis, $\hat{K}_{\nu\nu}(t)$ is a continuous function of the time. By definition, $\hat{K}_{\nu\nu}(0) = 1$. Now define the vector

$$| \alpha_n\rangle_P = \sum_{k=1}^{n} |iLU_\nu(t_k)\rangle_P Z_k$$

for every choice of the real number $(t_1, \ldots, t_n)$ and the complex numbers $(Z_1, \ldots, Z_n)$. The ket $| \rangle_P$ was defined in Theorem 1 as

$$| iLU_\nu(t_k)\rangle_P \equiv [\exp i(1 - P_\nu)Lt_k] \mid iLU_\nu\rangle.$$

It follows from the positivity of the norm of $| \alpha_n\rangle$ that

$$\langle \alpha_n \mid \alpha_n\rangle = \sum_{j,k=1}^{n} Z_k^* \, {}_P\langle iLU_\nu(t_k) \mid iLU_\nu(t_j)\rangle_P Z_j \geq 0.$$

From Theorem 1 on the stationarity of the memory function, it follows that

$$\sum_{j,k=1}^{n} Z_k^* \hat{K}_{\nu\nu}(t_k - t_j) Z_j \geq 0,$$

and the normalized memory function $\hat{K}_{\nu\nu}(t)$ is positive-definite. Thus, $\hat{K}_{\nu\nu}(t)$ satisfies all the conditions of Bochner's theorem, $\hat{K}_{\nu\nu}(t)$ is the characteristic function of the probability distribution $L_{\nu\nu}(\omega)$. By definition, $0 \leq L_{\nu\nu}(\omega)$.

One interesting thing to note is that $L_{\nu\nu}(\omega)$ is none other than the "power spectrum" of the memory function,

$$L_{\nu\nu}(\omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{+i\omega t} \hat{K}_{\nu\nu}(t). \tag{3.56}$$

To summarize: The memory function is a real, even, bounded function of the time. Furthermore, the power spectrum of a memory function is everywhere positive and bounded, and can be regarded as a probability distribution function.

The power spectrum $L_{\nu\nu}(\omega)$ of the normalized memory function $\hat{K}_{\nu\nu}(t)$, like any distribution function, can be decomposed into a continuous and a discrete part, $L_c(\omega)$ and $L_d(\omega)$, respectively:

$$L_{\nu\nu}(\omega) = L_d(\omega) + L_c(\omega). \tag{3.57}$$

The discrete part is of the form

$$L_d(\omega) = \sum_k P_k\, \delta(\omega - \omega_k), \qquad k = 1, \ldots . \tag{3.58}$$

Here, $\{\omega_k\}$ is a denumerable set of frequencies and $\{P_k\}$ is the set of corresponding probabilities ($0 \leq P_k \leq 1$ and $0 \leq \sum_k P_k \leq 1$). It is assumed here that the continuous part of the spectrum, $L_c(\omega)$, is a continuous, well-behaved function of the frequency, although it is quite possible to find physical $L_c(\omega)$ that have singular points. From previous sections, it follows that $L_{\nu\nu}(\omega)$ is even in ω.

The normalized memory function can thus be decomposed in a corresponding way,

$$\hat{K}_{\nu\nu}(t) = \int_{\infty}^{+\infty} d\omega\, L_d(\omega) e^{i\omega t} + \sum_k P_k \cos \omega_k t. \tag{3.59}$$

In this case, $\hat{K}_{\nu\nu}(t)$ does not have any long-time limit. If the spectrum is entirely continuous, then it follows from the lemma of Riemann–Lebesgue that $\hat{K}_{\nu\nu}(t)$ vanishes as $t \to \infty$. A system is irreversible if and only if all memory functions of properties $\hat{U}$ (with zero mean) vanish as $t \to \infty$. Consequently, irreversible systems must have continuous spectra. In finite, isolated systems, the spectrum is discrete and

$$\hat{K}_{\nu\nu}(t) = \sum_k P_k \cos \omega_k t \tag{3.60}$$

is almost periodic. This is a consequence of Poincaré's theorem. In specialized cases, it can be shown that, in the thermodynamic limit, $N \to \infty$, $V \to \infty$ such that $N/V = \text{const}$, the discrete spectrum becomes continuous. Irreversibility enters in an asymptotic manner. This is a very important point.

E. Sum Rules and Dispersion Relations

The normalized autocorrelation function $\hat{C}_{\nu\nu}(t)$ satisfies the memory-function equation

$$\frac{\partial}{\partial t} \hat{C}_{\nu\nu}(t) = - \int_0^t d\tau\, K_{\nu\nu}(\tau) \hat{C}_{\nu\nu}(t - \tau). \tag{3.61}$$

According to this equation, $\hat{C}_{\nu\nu}(t)$ depends only on the values of the memory function $K_{\nu\nu}(\tau)$ for all time τ prior to t.

The power spectrum $G_{\nu\nu}(\omega)$ of $\hat{C}_{\nu\nu}(t)$ is, according to to Eq. (2.48),

$$2\pi G_{\nu\nu}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{+i\omega t} \hat{C}_{\nu\nu}(t).$$

The time correlation function $\hat{C}_{\nu\nu}(t)$ is a real, even function of the time. Consequently,

$$2\pi G_{\nu\nu}(\omega) = 2 \operatorname{Re} \int_0^{\infty} dt\, e^{-i\omega t} \hat{C}_{\nu\nu}(t).$$

The integral in this expression is the Laplace transform $\tilde{C}_{\nu\nu}(i\omega)$ of the normalized autocorrelation function $\hat{C}_{\nu\nu}(t)$, so that

$$\pi G_{\nu\nu}(\omega) = \operatorname{Re} \tilde{C}_{\nu\nu}(i\omega). \tag{3.62}$$

Let $\tilde{K}_{\nu\nu}(i\omega)$ represent the Laplace transform of the memory function,

$$\tilde{K}_{\nu\nu}(i\omega) = \int_0^{\infty} dt\, e^{-i\omega t} K_{\nu\nu}(t). \tag{3.63}$$

These Laplace transforms can be expressed as

$$\begin{aligned} \tilde{C}_{\nu\nu}(i\omega) &= C'_{\nu\nu}(\omega) + iC''_{\nu\nu}(\omega), \\ \tilde{K}_{\nu\nu}(i\omega) &= K'_{\nu\nu}(\omega) + iK''_{\nu\nu}(\omega), \end{aligned} \tag{3.64}$$

where the single prime denotes the real and the double prime denotes the imaginary parts of $\tilde{C}_{\nu\nu}(i\omega)$ and $\tilde{K}_{\nu\nu}(i\omega)$ respectively. Since $\hat{C}_{\nu\nu}(t)$ and $K_{\nu\nu}(t)$ are real, even functions of the time, it follows that

$$\begin{aligned} C'_{\nu\nu}(\omega) &= \int_0^{\infty} dt \cos \omega t\, \hat{C}_{\nu\nu}(t); & K'_{\nu\nu}(\omega) &= \int_0^{\infty} dt \cos \omega t\, K_{\nu\nu}(t), \\ C''_{\nu\nu}(\omega) &= - \int_0^{\infty} dt \sin \omega t\, \hat{C}_{\nu\nu}(t); & K''_{\nu\nu}(\omega) &= - \int_0^{\infty} dt \sin \omega t\, K_{\nu\nu}(t); \end{aligned} \tag{3.65}$$

$C'_{\nu\nu}(\omega)$ and $K'_{\nu\nu}(\omega)$ are real, even functions of ω, whereas $C''_{\nu\nu}(\omega)$ and $K''_{\nu\nu}(\omega)$ are real, odd functions of the frequency.

The Laplace transform of the memory-function equation is

$$i\omega\tilde{C}_{\nu\nu}(i\omega) - 1 = -\tilde{K}_{\nu\nu}(i\omega)\tilde{C}_{\nu\nu}(i\omega). \tag{3.66}$$

Solving for $\tilde{C}_{\nu\nu}(i\omega)$,

$$\tilde{C}_{\nu\nu}(i\omega) = 1/\{i\omega + \tilde{K}_{\nu\nu}(i\omega)\} = 1/\{i[\omega + K''_{\nu\nu}(\omega)] + K'_{\nu\nu}(\omega)\}. \tag{3.67}$$

From this, it follows that the power spectrum is

$$\pi G_{\nu\nu}(\omega) = C'_{\nu\nu}(\omega) = K'_{\nu\nu}(\omega)/\{[\omega + K''_{\nu\nu}(\omega)]^2 + [K'_{\nu\nu}(\omega)]^2\}. \tag{3.68}$$

The imaginary and real parts of $\tilde{K}_{\nu\nu}(i\omega)$ determine the shift and breadth of the power spectrum and consequently the line shape of spectral lines. Also,

$$C''_{\nu\nu}(\omega) = -[\omega + K''_{\nu\nu}(\omega)]/\{[\omega + K''_{\nu\nu}(\omega)]^2 + [K'_{\nu\nu}(\omega)]^2\}. \tag{3.69}$$

In the preceding sections, it was shown that

$$G_{\nu\nu}(\omega) = (1/2\pi)\int_{-\infty}^{\infty} dt\, e^{+i\omega t}\hat{C}_{\nu\nu}(t),$$

$$L_{\nu\nu}(\omega) = (1/2\pi)\int_{-\infty}^{\infty} dt\, e^{+i\omega t}\hat{K}_{\nu\nu}(t)$$

are probability distribution functions. These distribution functions are related to the real parts of $\tilde{C}_{\nu\nu}(i\omega)$ and $\tilde{K}_{\nu\nu}(i\omega)$,

$$\begin{aligned} G_{\nu\nu}(\omega) &= \pi^{-1}C'_{\nu\nu}(\omega), \\ L_{\nu\nu}(\omega) &= [\pi K_{\nu\nu}(0)]^{-1}K'_{\nu\nu}(\omega) = [\pi\langle iLU_\nu \mid iLU_\nu\rangle]^{-1}K'_{\nu\nu}(\omega). \end{aligned} \tag{3.70}$$

The moments of the probability distributions are defined as

$$\gamma_n = \int_{-\infty}^{+\infty} d\omega\, \omega^n G_{\nu\nu}(\omega); \qquad \mu_n = \int_{-\infty}^{+\infty} d\omega\, \omega^n L_{\nu\nu}(\omega). \tag{3.70a}$$

Since $G_{\nu\nu}(\omega)$ and $L_{\nu\nu}(\omega)$ are even functions of ω, the odd moments vanish. The even moments are

$$\begin{aligned} \gamma_{2n} &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} dt\, \omega^{2n} e^{+i\omega t}\hat{C}_{\nu\nu}(t) \\ &= (-1)^n \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, [(d^{2n}/dt^{2n})e^{+i\omega t}]\hat{C}_{\nu\nu}(t), \end{aligned}$$

or

$$\gamma_{2n} = (-1)^n \int_{-\infty}^{+\infty} dt[(d^{2n}/dt^{2n})\,\delta(t)]\hat{C}_{\nu\nu}(t) = [(-1)^n(d^{2n}/dt^{2n})\hat{C}_{\nu\nu}(t)]_{t=0}. \tag{3.71}$$

Since $\hat{C}_{\nu\nu}(t) = \langle U_\nu \mid e^{iLt} \mid U_\nu\rangle$, it follows that

$$\gamma_{2n} = (-1)^n\langle U_\nu \mid [iL]^{2n} \mid U_\nu\rangle = \langle [iL]^n U_\nu \mid [iL]^n U_\nu\rangle. \tag{3.72}$$

This latter result follows from the fact that L is a Hermitian operator. In a completely analogous manner, it can be shown that

$$\mu_{2n} = \langle [(1 - \hat{P}_\nu)iL]^n iLU_\nu \mid [(1 - \hat{P}_\nu)iL]^n iLU_\nu\rangle / \langle iLU_\nu \mid iLU_\nu\rangle. \tag{3.73}$$

These moment relations are called sum rules. They play a very important role in the theory of time-dependent processes.

The first few moments of $G_{\nu\nu}(\omega)$

$$\begin{aligned} \gamma_0 &= 1 \qquad \text{(normalization)}, \\ \gamma_2 &= \langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle, \\ \gamma_4 &= \langle U_\nu^{(2)} \mid U_\nu^{(2)}\rangle, \\ \gamma_6 &= \langle U_\nu^{(3)} \mid U_\nu^{(3)}\rangle, \end{aligned} \tag{3.74}$$

where $\mid U_\nu^{(n)}\rangle$ represents the nth derivative of the property $U_\nu^{(n)}$, i.e., $\mid U_\nu^{(n)}\rangle = (iL)^n \mid U_\nu\rangle$.

The first few moments of $L_{\nu\nu}(\omega)$ are

$$\begin{aligned} \mu_0 &= 1 \qquad \text{(normalization)}, \\ \mu_2 &= \langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle^{-1}[\langle U_\nu^{(2)} \mid U_\nu^{(2)}\rangle - \langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle^2], \\ \mu_4 &= \langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle^{-1}[\langle U_\nu^{(3)} \mid U_\nu^{(3)}\rangle - 2\langle U_\nu^{(2)} \mid U_\nu^{(2)}\rangle\langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle \\ &\qquad + \langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle^3]. \end{aligned} \tag{3.75}$$

To determine the explicit form of the moments μ_{2n}, it is necessary to use the properties of the projector $\hat{P}_\nu$. For example,

$$[i(1 - \hat{P}_\nu)L] \mid iLU_\nu\rangle = (iL)^2 \mid U_\nu\rangle - \mid U_\nu\rangle\langle U_\nu \mid (iL)^2 \mid U_\nu\rangle.$$

Since L is Hermitian, it follows that

$$\langle U_\nu \mid (iL)^2 \mid U_\nu\rangle = -\langle iLU_\nu \mid iLU_\nu\rangle = -\langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle,$$

so that

$$i(1 - P_\nu)L \mid iLU_\nu\rangle = \mid U_\nu^{(2)}\rangle + \mid U_\nu\rangle\langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle.$$

Consequently,

$$\begin{aligned}\langle i(1-P_\nu)LiLU_\nu \mid i(1-P_\nu)LiLU_\nu\rangle &= \langle U_\nu^{(2)} \mid U_\nu^{(2)}\rangle + \langle U_\nu^{(2)} \mid U_\nu\rangle\langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle \\ &\quad + \langle U_\nu \mid U_\nu^{(2)}\rangle\langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle + \langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle^2 \\ &= \langle U_\nu^{(2)} \mid U_\nu^{(2)}\rangle - \langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle^2. \end{aligned} \tag{3.76}$$

This last result follows from the fact that

$$\langle U_\nu \mid U_\nu^{(2)}\rangle = \langle U_\nu^{(2)} \mid U_\nu\rangle = -\langle U_\nu^{(1)} \mid U_\nu^{(1)}\rangle.$$

Comparison of Eqs. (3.74) and (3.75) allows the moments $\{\mu_{2n}\}$ of the memory function and the moments $\{\gamma_{2n}\}$ of the autocorrelation function to be related,

$$\begin{aligned}\mu_0 &= \gamma_0, \\ \gamma_2\mu_2 &= \gamma_4 - \gamma_2^2, \\ \gamma_2\mu_4 &= \gamma_6 - 2\gamma_2\gamma_4 + \gamma_2^2.\end{aligned} \tag{3.77}$$

Note that μ_{2n} depends on γ_{2n+2} and γ's of lower index.†

The functions $\hat{C}_{\nu\nu}(t)$ and $\hat{K}_{\nu\nu}(t)$ have the following even-power-series expansions:

$$\begin{aligned}\hat{C}_{\nu\nu}(t) &= \sum_{n=0}^{\infty} [(-1)^n/(2n)!\,]\gamma_{2n}t^{2n}, \\ \hat{K}_{\nu\nu}(t) &= \sum_{n=0}^{\infty} [(-1)^n/(2n)!\,]\mu_{2n}t^{2n},\end{aligned} \tag{3.78}$$

as is readily verified.

The complex Laplace transforms of $\hat{C}_{\nu\nu}(t)$ and $\hat{K}_{\nu\nu}(t)$ are defined as

$$\begin{aligned}\tilde{C}_{\nu\nu}(iz) &\equiv \int_0^\infty dt\, e^{-izt}C_{\nu\nu}(t), \\ \tilde{K}_{\nu\nu}(iz) &\equiv \int_0^\infty dt\, e^{-izt}K_{\nu\nu}(t),\end{aligned} \tag{3.79}$$

with the complex variable $z = x + iy$. It can be shown that $\tilde{C}_{\nu\nu}(z)$ and $\tilde{K}_{\nu\nu}(z)$ are analytic in the entire lower half of the complex z plane.

Let

$$\tilde{C}_{\nu\nu}(iz) = u(x, y) + iv(x, y); \tag{3.80}$$

$\tilde{C}_{\nu\nu}(iz)$ is analytic in a given region of the z plane if and only if

$$\partial u/\partial x = \partial v/\partial y \qquad \text{and} \qquad \partial v/\partial x = -\,\partial u/\partial y$$

† These moments are related as are the moments in cumulant expansions.

are satisfied in that region. These are the familiar Cauchy–Riemann conditions.

From Eqs. (3.79) and (3.80),

$$\begin{aligned}u(x, y) &= \int_0^\infty dt\hat{C}_{\nu\nu}(t) \cos xt\, e^{yt} \\ v(x, y) &= -\int_0^\infty dt\, \hat{C}_{\nu\nu}(t) \sin xt\, e^{yt}\end{aligned} \tag{3.81}$$

It follows that

$$\partial u/\partial x = -\int_0^\infty dt\, t\hat{C}_{\nu\nu}(t) \sin xt\, e^{yt} = \partial v/\partial y$$

$$\partial v/\partial x = -\int_0^\infty dt\, t\hat{C}_{\nu\nu}(t) \cos xt\, e^{yt} = -\,\partial u/\partial y.$$

Consequently, $\tilde{C}_{\nu\nu}(iz)$ is analytic only in those regions of the complex plane where these operations are valid—that is, in regions where the integrals are convergent. These integrals will converge when $y \leq 0$. Thus, $\tilde{C}_{\nu\nu}(iz)$ is analytic in the lower half-plane. Moreover, note that $|\tilde{C}_{\nu\nu}(iz)| \to 0$ if either $y \to -\infty$ or $x \to \pm\infty$. The latter result follows from the fact that the rapidly oscillating $\sin x$ and $\cos x$ wash out the integrals u and v. It follows that $|\tilde{C}_{\nu\nu}(iz)| \to 0$ as $|z| \to \infty$ for $y \leq 0$.

Consider the function $\tilde{C}_{\nu\nu}(iz')/(z' - \omega)$; this function has a simple pole at the point ω on the real axis and is analytic everywhere else in the lower half-plane. By Cauchy's integral theorem,

$$\int_C dz'\, [\tilde{C}_{\nu\nu}(iz')/(z' - \omega)] = 0 \tag{3.82}$$

where C is the contour of Fig. 4.

The integral can be expressed as the sum of integrals over the four regions C_1, C_2, C_3, C_4 of the contour,

$$\begin{aligned}&\int_{-R}^{\omega-\varrho} d\omega'\, [\tilde{C}_{\nu\nu}(i\omega')/(\omega' - \omega)] + \int_{\omega+\varrho}^{+R} d\omega'\, [\tilde{C}_{\nu\nu}(i\omega')/(\omega' - \omega)] \\ &\quad + \int_{C_2} dz\, [\tilde{C}_{\nu\nu}(iz)/(z - \omega)] + \int_{C_4} dz\, [\tilde{C}_{\nu\nu}(iz)/(z - \omega)] = 0.\end{aligned} \tag{3.83}$$

The first two integrals come from regions C_1 and C_3, the third integral comes from region C_2, and the fourth integral comes from region C_4. In the limit $R \to \infty$, $\varrho \to 0$, the integral over C_4 vanishes because

$$\lim_{|z|\to\infty} |\tilde{C}_{\nu\nu}(iz)| = 0; \qquad y \leq 0;$$

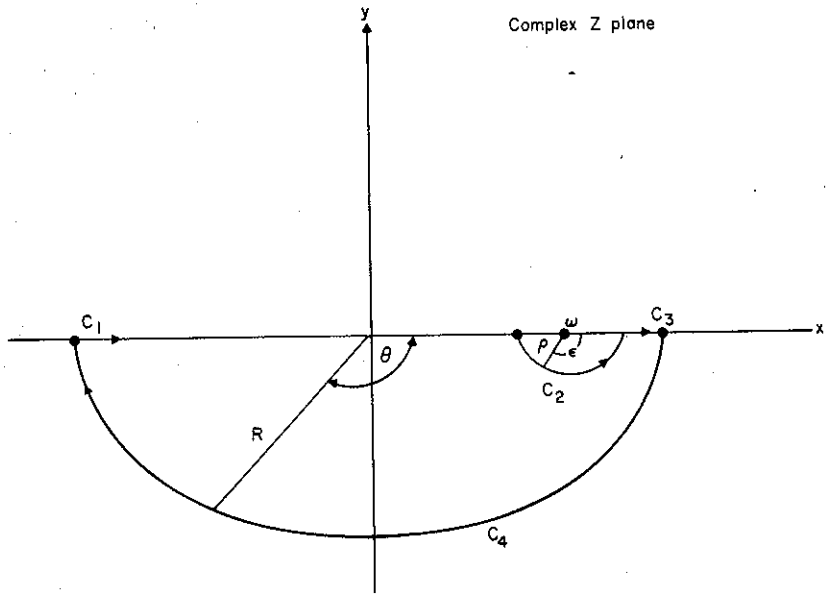

FIG. 4. The contour for the derivation of the Kramers–Kronig relations.

the integral over C_2 is, by the residue theorem, $-\pi i\tilde{C}_{\nu\nu}(i\omega)$, and the integrals over C_1 and C_3 together are the Cauchy principle part,

$$P\int_{-\infty}^{+\infty} d\omega'[\tilde{C}_{\nu\nu}(i\omega')/(\omega'-\omega)]$$
$$= \lim_{\varrho\to 0}\left[\int_{-\infty}^{\omega-\varrho} d\omega' + \int_{\omega-\varrho}^{+\infty} d\omega'\right]\tilde{C}_{\nu\nu}(i\omega')/(\omega'-\omega). \tag{3.84}$$

It thus follows that

$$\tilde{C}_{\nu\nu}(i\omega) = (1/\pi i)P\int_{-\infty}^{+\infty} d\omega'\,[\tilde{C}_{\nu\nu}(i\omega')/(\omega'-\omega)]. \tag{3.85}$$

The last integral can be written as

$$C'_{\nu\nu}(\omega) + iC''_{\nu\nu}(\omega)$$
$$= (1/\pi i)P\int_{-\infty}^{+\infty} d\omega'\,\{[C'_{\nu\nu}(\omega') + iC''_{\nu\nu}(\omega')]/(\omega'-\omega)\}.$$

The real and imaginary parts of this equation are

$$\begin{aligned} C'_{\nu\nu}(\omega) &= (1/\pi)P\int_{-\infty}^{+\infty} d\omega'[C''_{\nu\nu}(\omega')/(\omega'-\omega)],\\ C''_{\nu\nu}(\omega) &= -(1/\pi)P\int_{-\infty}^{+\infty} d\omega'[C'_{\nu\nu}(\omega')/(\omega'-\omega)]. \end{aligned} \tag{3.86}$$

The real and imaginary parts of $\tilde{C}_{\nu\nu}(iz)$ are therefore Hilbert transforms of each other. Since $C'_{\nu\nu}(\omega)$ and $C''_{\nu\nu}(\omega)$ are even and odd, respectively,

$$\begin{aligned} C'_{\nu\nu}(\omega) &= (1/\pi)P\int_{-\infty}^{+\infty} d\omega'[C''_{\nu\nu}(\omega')\omega'/\{(\omega')^2-(\omega^2)\}],\\ C''_{\nu\nu}(\omega) &= -(\omega/\pi)P\int_{-\infty}^{+\infty} d\omega'[C'_{\nu\nu}(\omega')/\{(\omega')^2-(\omega^2)\}]. \end{aligned} \tag{3.87}$$

In an identical fashion, it can be shown that

$$\begin{aligned} K'_{\nu\nu}(\omega) &= (1/\pi)P\int_{-\infty}^{+\infty} d\omega'[K''_{\nu\nu}(\omega')\omega'/\{(\omega')^2-\omega^2\}],\\ K''_{\nu\nu}(\omega) &= -(\omega/\pi)P\int_{-\infty}^{+\infty} d\omega'[K'_{\nu\nu}(\omega')/\{(\omega')^2-\omega^2\}]. \end{aligned} \tag{3.88}$$

From these relations, we see that the width and shift of the power spectrum and consequently spectroscopic lines are related through Kramers–Kronig dispersion relations.

F. The Modified Langevin Equation

The Langevin equation

$$M\dot{V}(t) = -M\beta V(t) + F(t) \tag{3.89}$$

is of central importance in the theory of Brownian motion. In this equation, V is velocity of the Brownian particle, M the mass, $M\beta$ the friction coefficient (often called ζ), and $F(t)$ the random force. The random force $F(t)$ is usually assumed to have the following properties:

(a) The stochastic process $F(t)$ is a stationary, Gaussian process.
(b) It has an infinitely short correlation time, so that its autocorrelation function is $\langle F(0)F(t)\rangle = 2\gamma\delta(t)$, where γ is a constant of proportionality.
(c) The motion of the Brownian particle is due to equilibrium thermal fluctuations of the bath in which it is moving.

Assumption (a) implies that $V(t)$ is a stationary, Gaussian process. The Langevin equation, when solved subject to assumption (b), yields the velocity autocorrelation function

$$\langle V(0)V(t)\rangle = \langle V^2\rangle e^{-\zeta|t|/M}. \tag{3.90}$$

Doob's theorem states that a Gaussian process is Markovian if and only

if its time correlation function is exponential. It thus follows that V is a Gaussian Markov process. From this and from Eqs (2.121) and (2.122), it follows that the probability distribution $P(V, t)$ in velocity space satisfies the Fokker–Planck equation,

$$(\partial/\partial t)P(V, t) = D_v(\partial/\partial V)[M\beta V + \partial/\partial V]P(V, t), \tag{3.91}$$

which is a diffusion equation in velocity space, where D_v is the diffusion constant in this space. D_v is related to the friction coefficient according to the equation

$$D_v = (1/M\beta)(\zeta/M)$$

Condition (c) requires that the stationary solution of the Fokker–Planck equation should be the Maxwellian distribution function which it is.

It is possible to show from the Langevin equation, Eq. (3.89), that the friction coefficient is itself related to the force autocorrelation function

$$\zeta = \beta \int_0^\infty dt\, \langle F(0)F(t)\rangle. \tag{3.92}$$

Furthermore, we see from condition (b) that the coefficient γ is simply related to ζ, $\zeta = \beta\gamma$.

The friction constant is consequently related to the time dependence of the random force in the equilibrium system.

The question immediately arises: How can we generalize the Langevin model to, say, the motion of an atom or a molecule in a liquid?

In addition, it is legitimate to ask whether there exists a generalized Langevin equation which describes the time evolution of properties $U_l(\mathbf{\Gamma})$ which were discussed previously. The answer is affirmative. It will be shown by arguments similar to those presented in the preceding sections that the correct generalization of the Langevin equation is

$$(\partial/\partial t) \mid U_l(t)\rangle = -\int_0^t d\tau\, K_{ll}(\tau) \mid U_l(t-\tau)\rangle + \mid F_l(t)\rangle, \tag{3.93}$$

where $F_l(t)$ is the "random force." Moreover, it will be shown that this random force has the following properties:

$$\langle F_l(t)\rangle = 0 \tag{3.94a}$$

$$\langle U_l(0) \mid F_l(t)\rangle = 0 \tag{3.94b}$$

$$K_{ll}(t) = \langle F_l(0) \mid F_l(t)\rangle. \tag{3.94c}$$

The last property has been called the "second fluctuation dissipation theorem" by Kubo (1966) (see also Mori, 1965b). According to this theorem, the kernel $K_{ll}(\tau)$ is entirely prescribed by the statistical properties of the "random force."

Taking the scalar product of the modified Langevin equation with $\langle U_l(0) \mid$ together with property (3.94b) yields the memory-function equation for $\hat{C}_{ll}(t) = \langle U_l(0) \mid U_l(t)\rangle$,

$$(\partial/\partial t)\hat{C}_{ll}(t) = -\int_0^t d\tau\, K_{ll}(\tau)C_{ll}(t-\tau). \tag{3.95}$$

Consequently, the kernel in the modified Langevin equation is simply the memory function of the memory-function equation [Eq. (3.44)]. Thus, the memory function $K_{ll}(\tau)$ is the autocorrelation function of the random force $\mid F_l(t)\rangle$.

If the random force has a delta-function correlation function, then $K_{ll}(t)$ is a delta-function, and the generalized Langevin equation reduces to the classical Langevin equation. The next obvious approximation to make is that $F_l(t)$ is a Gaussian Markov process. Then, $\langle F_l(0) \mid F_l(t)\rangle$ is exponential by Doob's theorem and $K_{ll}(t)$ is exponential. Then, $\hat{C}_{ll}(t)$ can be found. This approximation will be discussed at length in a later section. The main thing to note here is that the second fluctuation dissipation theorem provides an intuitive understanding of the memory function.

In order to derive the generalized Langevin equation, it is necessary to use some equations that were previously derived. From the Laplace transform of Eq. (3.43), we see that

$$(1 - \hat{P}_l) \mid \tilde{U}_l(s)\rangle = \{1/[s - i(1 - \hat{P}_l)L]\}iL \mid U_l\rangle\tilde{C}_{ll}(s), \tag{3.96}$$

where $\nu = l$. Here, $\tilde{C}_{ll}(s)$ is the Laplace transform of the time correlation function $\hat{C}_{ll}(t)$ and $\mid \tilde{U}_l(s)\rangle$ is the Laplace transform of $\mid U_l(t)\rangle$. Let us now define the property $\mid F_l(t)\rangle$ such that its Laplace transform is

$$\mid \tilde{F}_l(s)\rangle \equiv \{1/(s - i(1 - \hat{P}_l)L)\}iL \mid U_l\rangle, \tag{3.97a}$$

i.e.,

$$\mid F_l(t)\rangle \equiv [\exp i(1 - \hat{P}_l)Lt]iL \mid U_l\rangle. \tag{3.97b}$$

From Eq. (3.44), we see that the Laplace transform of the time correlation function $\hat{C}_{ll}(t)$ is

$$\tilde{C}_{ll}(s) = 1/[s + \tilde{K}_{ll}(s)], \tag{3.98}$$

where $\tilde{K}_{ll}(s)$ is the Laplace transform of the memory function. Substitution of Eqs. (3.97) (3.98) into Eq. (3.96) yields

$$(1 - \hat{P}_{ll}) \mid \tilde{U}_l(s)\rangle = \{1/[s + \tilde{K}_{ll}(s)]\} \mid \tilde{F}_{ll}(s)\rangle. \tag{3.99}$$

The left-hand side of this equation is $\mid \tilde{U}_l(s)\rangle - \mid U_l\rangle\langle U_l \mid \tilde{U}_l(s)\rangle$ or $\mid \tilde{U}_l(s)\rangle - \mid U_l\rangle \tilde{C}_{ll}(s)$. Substitution of Eq. (3.98) into this yields

$$\mid \tilde{U}_l(s)\rangle - \mid U_l\rangle\{1/(s + \tilde{K}_{ll}(s))\} = \{1/[s + \tilde{K}_{ll}(s)] \mid \tilde{F}_l(s)\rangle. \tag{3.100}$$

Multiplication by $s + \tilde{K}_{ll}(s)$ followed by obvious rearrangements yields

$$s \mid \tilde{U}_l(s)\rangle - \mid U_l\rangle = - \tilde{K}_{ll}(s) \mid \tilde{U}_l(s)\rangle + \mid \tilde{F}_l(s)\rangle.$$

Laplace inversion leads to the generalized Langevin equation (3.93),

$$(\partial/\partial t) \mid U_l(t)\rangle = - \int_0^t d\tau\, K_{ll}(\tau) \mid U_l(t - \tau) + \mid F_l(t)\rangle,$$

where $K_{ll}(\tau)$ is the memory function [Eq. (3.45)] and $\mid F_l(t)\rangle$ is the random force [Eq. (3.97)]. Note that $\mid F_l(0)\rangle = \mid \dot{U}_l\rangle$, so that

$$\begin{aligned}\langle F_l(0) \mid F_l(t)\rangle &= -\langle U_l \mid iL[\exp i(1 - \hat{P}_l)Lt]iL \mid U_l\rangle \\ &= K_{ll}(t).\end{aligned} \tag{3.101}$$

Furthermore,

$$\begin{aligned}\langle U_l \mid F_l(t)\rangle &= \langle U_l \mid [\exp i(1 - \hat{P}_l)Lt]iL \mid U_l\rangle \\ &= \langle U_l \mid iL + (1 - \hat{P}_l)iLiL + \cdots \mid U_l\rangle \\ &= 0.\end{aligned} \tag{3.102}$$

Furthermore, $\langle F_l(t)\rangle = 0$. Thus, we have derived the generalized Langevin equation and have shown, moreover, that the random force satisfies the conditions of Eq. (3.94).

G. Continued-Fraction Representation of Time Correlation Functions

The memory-function equation for the time correlation function of a dynamical operator U_l can be cast into the form of a continued fraction, as was first pointed out by Mori (1965b). We prove this in a different way than Mori. In order to proceed, it is necessary to define the set of

memory functions, $K_0(t), \ldots, K_n(t), \ldots$, such that

$$K_n(t) = \langle f_n \mid e^{iL_n t} \mid f_n\rangle, \tag{3.103}$$

where the quantities f_n and L_n are defined in terms of the Liouville operator $iL \equiv iL_0$ and the dynamical quantity $\hat{\alpha}_0 \equiv \hat{U}_l \equiv f_0$ as

$$\begin{aligned} iL_n &\equiv (1 - \hat{P}_{n-1})iL_{n-1}; \\ \mid f_n\rangle &\equiv (1 - \hat{P}_{n-1})iL_{n-1} \mid \alpha_{n-1}\rangle; \\ \mid \alpha_n\rangle &\equiv \langle f_n \mid f_n\rangle^{-1/2} \mid f_n\rangle; \\ \hat{P}_n &\equiv \mid \alpha_n\rangle\langle \alpha_n \mid. \end{aligned}$$

From these definitions, note that

$$\mid \alpha_0\rangle, \ldots, \mid \alpha_n\rangle, \ldots \quad \text{are orthonormal;} \tag{3.104a}$$

$$iL_n = (1 - P_{n-1})(1 - P_{n-2}) \ldots (1 - P_0)iL_0 = \Big[1 - \sum_{l=0}^{n-1} \hat{P}_l\Big]iL_0; \tag{3.104b}$$

$$\mid f_n\rangle = (1 - P_{n-1})iL_{n-1} \mid \alpha_{n-1}\rangle = \Big(1 - \sum_{l=0}^{n-1} \hat{P}_l\Big)iL_0 \mid \alpha_{n-1}\rangle. \tag{3.104c}$$

Therefore, $\mid f_n\rangle$ and $\mid \alpha_n\rangle$ are orthogonal to all vectors of lower index. Furthermore, $(1 - \sum_{l=0}^{n-1} \hat{P}_l)L_0$ is Hermitian in the subspace orthogonal to $\mid \alpha_0\rangle, \ldots, \mid \alpha_{n-1}\rangle$. With these definitions, we can prove the following theorem by mathematical induction:

Theorem. The set of memory functions $K_0(t), \ldots, K_n(t)$ obey the set of coupled Volterra equations such that

$$\partial K_{n-1}(t)/\partial t = - \int_0^t d\tau\, K_n(\tau)K_{n-1}(t - \tau), \qquad n = 1, \ldots, N. \tag{3.105}$$

Proof. That the theorem holds for $n = 1$ is easy to see. Note that $K_0(t)$ is simply the time correlation function

$$K_0(t) = \langle U_\nu \mid e^{iLt} \mid U_\nu\rangle = C_{\nu\nu}(t),$$

and consequently satisfies Eq. (3.44). Thus, if the kernel $K_1(t)$ is identical to the kernel $\langle iLU_\nu \mid \exp i(1 - \hat{P}_\nu)Lt \mid iLU_\nu\rangle$ of Eq. (3.44), then the theorem holds for $n = 1$. Note that

$$K_1(t) = \langle f_1 \mid \exp iL_1 t \mid f_1\rangle = \langle iLU_\nu \mid \exp i(1 - \hat{P}_\nu)Lt \mid iLU_\nu\rangle.$$

The theorem is consequently valid for $n = 1$.

Show $\langle f_n \mid iL_n \mid f_n\rangle =$

To proceed, we assume that the theorem is valid for n and deduce it for $n+1$,

$$\partial K_n(t)/\partial t = -\int_0^t dt\, K_{n+1}(\tau)K_n(t-\tau). \tag{3.106}$$

Here

$$K_n(t) = \langle f_n \mid e^{iL_n t} \mid f_n\rangle = \langle f_n \mid f_n\rangle\langle \alpha_n \mid e^{iL_n t} \mid \alpha_n\rangle$$
$$= \langle f_n \mid f_n\rangle \hat{K}_n(t). \tag{3.107}$$

The equation of motion for $e^{iL_n t} \mid \alpha_n\rangle = \mid \alpha_n(t)\rangle$ is

$$\partial/\partial t \mid \alpha_n(t)\rangle = iL_n \mid \alpha_n(t)\rangle. \tag{3.108}$$

This equation is analogous to Eq. (3.35). Note that

$$\hat{K}_n(t) = \langle \alpha_n \mid e^{iL_n t} \mid \alpha_n\rangle = \langle \alpha_n \mid \hat{P}_n \mid \alpha_n(t)\rangle.$$

Thus, to find the equation of evolution for $\hat{K}_n(t)$, operate on Eq. (3.108) with $\hat{P}_n$,

$$(\partial/\partial t)\hat{P}_n \mid \alpha_n(t)\rangle = \hat{P}_n iL_n \hat{P}_n \mid \alpha_n(t)\rangle + \hat{P}_n iL(1-\hat{P}_n) \mid \alpha_n(t)\rangle. \tag{3.109}$$

Following exactly the same reasoning that led to Eq. (3.44), we find that

$$(\partial/\partial t)\hat{K}_n(t) = \int_0^t d\tau\, \langle \alpha_n \mid iL_n e^{iL_{n+1}\tau} \mid iL_n\alpha_n\rangle \hat{K}_n(t-\tau). \tag{3.110}$$

Multiplication by $\langle f_n \mid f_n\rangle$ shows that $K_n(t)$ satisfies this equation. To complete our proof, we must show that the kernel above is identical to $-K_{n+1}(t)$, where

$$K_{n+1}(\tau) = \langle f_{n+1} \mid e^{iL_{n+1}\tau} \mid f_{n+1}\rangle. \tag{3.111}$$

This is readily proved by noting that L_n is Hermitian in the space orthogonal to $\mid \alpha_0\rangle, \ldots, \mid \alpha_{n-1}\rangle, \mid \alpha_n\rangle$ so that

$$\langle \alpha_n \mid iL_n\, e^{iL_{n+1}\tau} \mid iL_n\alpha_n\rangle = -\langle iL_n\alpha_n \mid e^{iL_{n+1}\tau} \mid iL_n\alpha_n\rangle.$$

Because of parity, $(1-\hat{P}_n)$ can be inserted in such a way that

$$\langle \alpha_n \mid iL_n e^{iL_{n+1}\tau} \mid iL_n\alpha\rangle = -\langle iL_n\alpha_n \mid (1-\hat{P}_n)\, e^{iL_{n+1}\tau}(1-\hat{P}_n) \mid iL_n\alpha_n\rangle.$$

Since $1-\hat{P}_n$ is Hermitian, it follows from the fact that $\mid f_{n+1}\rangle = (1-\hat{P}_n) \times iL \mid \alpha_n \mid \alpha_n\rangle$ that

$$\langle \alpha_n \mid iL_n e^{iL_{n+1}\tau} \mid iL_n\alpha_n\rangle = -\langle f_{n+1} \mid e^{iL_{n+1}\tau} \mid f_{n+1}\rangle = -K_{n+1}(\tau). \tag{3.112}$$

Thus,

$$(\partial K_n/\partial t)(t) = -\int_0^t d\tau\, K_{n+1}(\tau)K_n(t-\tau).$$

This proves the theorem.

Let $K_n(0) = \langle f_n \mid f_n\rangle = \Delta_n^2$. Taking the Laplace transform of $K_n(t)$ yields

$$\tilde{K}_n(s) = \Delta_n^2/[s + \tilde{K}_{n+1}(s)]$$

where $K_n(s)$ is the Laplace transform of $K_n(t)$. Iteration leads to

$$\tilde{C}_{vv}(s) = \cfrac{C_{vv}(0)}{s + \cfrac{\Delta_1^2}{s + \cfrac{\Delta_2^2}{s + \cfrac{\Delta_3^2}{s + \cdots \cfrac{\Delta_{n-1}^2}{s + \tilde{K}_n(s)}}}}} \tag{3.113}$$

with $\Delta_n^2 = \langle f_n \mid f_n\rangle$. In particular, $\Delta_1^2 = \langle \dot{U}_l \mid \dot{U}_l\rangle$ and $\Delta_2^2 = [\langle \dot{U}_l \mid \dot{U}_l\rangle/\langle \dot{U}_l \mid \dot{U}_l\rangle] - \langle \dot{U}_l \mid \dot{U}_l\rangle$. Continuation of this procedure leads to an infinite continued fraction. It is obvious that the precise definition of the quantities that appear in these formulae depends on the precise definition of the scalar product used. Moreover, this approach is easily extended to the multivariate processes.

H. A Relationship between Memory Functions and Time Correlation Functions

The memory function $K_{vv}(t)$ corresponding to the time correlation function $\hat{C}_{vv}(t) \equiv \langle U_v \mid e^{iLt} \mid U_v\rangle$ is a complicated function whose time dependence is determined by a propagator with a projection operator $\hat{P}_v = \mid U_v\rangle\langle U_v \mid$ in it,

$$K_{vv}(t) = \langle iLU_v \mid \exp i(1-\hat{P}_v)Lt \mid iLU_v\rangle.$$

It is possible to develop a relationship between this memory function and the time correlation function

$$\Phi_{vv}(t) = \langle iLU_v \mid e^{iLt} \mid iLU_v\rangle.$$

It is useful for this purpose to deal with the Laplace transforms of

$K_{vv}(t)$ and $\Phi_{vv}(t)$

$$\tilde{K}_{vv}(s) = \langle iLU_v \mid [s - i(1 - \hat{P}_v)L]^{-1} \mid iLU_v\rangle,$$
$$\tilde{\Phi}_{vv}(s) = \langle iLU_v \mid [s - iL]^{-1} \mid iLU_v\rangle.$$

Then, it is easy to see that

$$\tilde{K}_{vv}(s) - \tilde{\Phi}_{vv}(s) = \langle iLU_v \mid [s - i(1 - \hat{P}_v)L]^{-1} - [s - iL]^{-1} \mid iLU_v\rangle.$$

From the operator identity

$$1/A - 1/B = (1/A)(B - A)(1/B),$$

it follows that

$$[s - i(1 - \hat{P}_v)L]^{-1} - [s - iL]^{-1} = - [s - iL]^{-1}\hat{P}_v iL[s - i(1 - \hat{P}_v)L]^{-1}.$$

Substitution of this identity into the previous equation yields

$$\begin{aligned}\tilde{K}_{vv}(s) &- \tilde{\Phi}_{vv}(s)\\ &= - \langle iLU_v \mid [s - iL]^{-1} \mid U_v\rangle\langle U_v \mid iL[s - i(1 - \hat{P}_v)L]^{-1} \mid iLU_v\rangle.\end{aligned}$$

Now, the two terms on the right-hand side of this equation can be expressed in terms of $\tilde{\Phi}_{vv}(s)$ and $\tilde{K}_{vv}(s)$. Note that

$$\begin{aligned}&\langle U_v \mid iL[s - i(1 - \hat{P}_v)L]^{-1} \mid iLU_v\rangle\\ &\quad = - \langle iLU_v \mid [s - i(1 - \hat{P}_v)L]^{-1} \mid iLU_v\rangle\\ &\quad = - \tilde{K}_{vv}(s)\end{aligned}$$

and

$$\begin{aligned}&\langle iLU_v \mid [s - iL]^{-1} \mid U_v\rangle\\ &\quad \equiv \langle iL_vU \mid [s - iL]^{-1}[s - iL + iL](1/s) \mid U_v\rangle\\ &\quad \equiv (1/s)\langle iLU_v \mid U_v\rangle + (1/s)\langle iLU_v \mid [s - iL]^{-1} \mid iLU_v\rangle\\ &\quad \equiv 0 + (1/s)\tilde{\Phi}_{vv}(s).\end{aligned}$$

Substitution of these results leads to the result

$$\tilde{K}_{vv}(s) - \tilde{\Phi}_{vv}(s) = (1/s)\tilde{\Phi}_{vv}(s)\tilde{K}_{vv}(s)$$

or

$$\tilde{K}_{vv}(s) = [1 - (1/s)\tilde{\Phi}_{vv}(s)]^{-1}\tilde{\Phi}_{vv}(s) \tag{3.113a}$$

or

$$\tilde{\Phi}_{vv}(s) = [1 + (1/s)\tilde{K}_{vv}(s)]^{-1}\tilde{K}_{vv}(s). \tag{3.113b}$$

Thus, the memory function $K_{vv}(t)$ and the time correlation function $\Phi_{vv}(t)$ are related. This relationship will prove very useful in our discussion of long-time limits and the derivation of hydrodynamics.

I. Information Theory and the Memory Function

The normalized memory function $\hat{K}_{vv}(t)$ is the characteristic function of the probability distribution function $L_{vv}(\omega)$ (see Section III,D). According to Section III,E, the moments of this distribution are

$$\langle\omega^{2n+1}\rangle = 0, \qquad \langle\omega^0\rangle = 1, \qquad \langle\omega^2\rangle = \mu_2, \qquad \langle\omega^4\rangle = \mu_4,$$

where μ_2 and μ_4 are given in Eqs. (3.73) and (3.75).

It is often a very complicated problem to compute $L_{vv}(\omega)$ for a given many-body system. Nevertheless, it is often possible to compute or experimentally determine the moments μ_2, μ_4, etc. There then exists an approximate method for finding $L_{vv}(\omega)$. For simplicity, we approach this problem through information theory (Berne and Harp, 1970). For this purpose, we define the information measure of the distribution as

$$S[L_{vv}(\omega)] = - \int_{-\infty}^{+\infty} d\omega\, L_{vv}(\omega) \ln L_{vv}(\omega). \tag{3.114}$$

The measure $S[L_{vv}(\omega)]$ is called the entropy corresponding to the distribution $L_{vv}(\omega)$. According to information theory, if a certain set of moments of $L_{vv}(\omega)$ is known, that $L_{vv}(\omega)$ is optimum that maximizes $S[L_{vv}(\omega)]$ subject to the known moments. Suppose we know only

$$\langle\omega^0\rangle = 1 = \int_{-\infty}^{+\infty} d\omega\, L_{vv}(\omega) \qquad \text{(normalization)},$$
$$\langle\omega^2\rangle = \mu_2 = \int_{-\infty}^{+\infty} d\omega\, \omega^2 L_{vv}(\omega).$$

Then we must find that $L_{vv}(\omega)$ for which

$$\begin{aligned}&\delta S[L_{vv}(\omega)] = - \delta \int_{-\infty}^{+\infty} d\omega\, L_{vv}(\omega) \ln L_{vv}(\omega) = 0,\\ &\delta \int_{-\infty}^{+\infty} d\omega\, L_{vv}(\omega) = 0,\\ &\delta \int_{-\infty}^{+\infty} d\omega\, \omega^2 L_{vv}(\omega) = 0,\end{aligned} \tag{3.115}$$

are satisfied. This problem can be solved using Lagrange multipliers. The optimal $L_{\nu\nu}(\omega)$ turns out to be

$$L_{\nu\nu}(\omega) = [2\pi\mu_2]^{-1/2} \exp -(\omega^2/2\mu_2). \tag{3.116}$$

Since $\hat{K}_{\nu\nu}(t)$ is the characteristic function of this distribution, it follows that

$$\hat{K}_{\nu\nu}(t) = \int_{-\infty}^{+\infty} d\omega \exp[-i\omega t] K_{\nu\nu}(\omega) = \exp[-\mu_2 t^2/2]. \tag{3.117}$$

Information theory consequently leads to the normalized memory function, which is a Gaussian function of the time. Since the memory function $K_{\nu\nu}(t)$ is related to the normalized function $\hat{K}_{\nu\nu}(t)$, it follows that the memory function is

$$K_{\nu\nu}(t) = \langle \dot{U}_\nu \mid \dot{U}_\nu \rangle \exp[-\tfrac{1}{2}[\langle \dot{U}_\nu \mid \dot{U}_\nu \rangle / \langle \dot{U}_\nu \mid \dot{U}_\nu \rangle - \langle \dot{U}_\nu \mid \dot{U}_\nu \rangle] t^2]. \tag{3.118}$$

This approximation will be very useful in the following sections. It should be noted that higher-order moments could have been used to generate higher-order approximations.

This approach is not entirely satisfactory. From Eqs. (3.64) and (3.67), it is seen that, rigorously,

$$K'_{\nu\nu}(0) = \int_0^\infty dt\, K_{\nu\nu}(t) = \left[\int_0^\infty dt\, \hat{C}_{\nu\nu}(t)\right]^{-1}$$

Yet, from information theory,

$$K'_{\nu\nu}(0) = \pi \langle \dot{U}_\nu \mid \dot{U}_\nu \rangle L_{\nu\nu}(0) = \pi \langle \dot{U}_\nu \mid \dot{U}_\nu \rangle [2\pi\mu_2]^{-/12}.$$

In general, this interpolarive result is not identical with the rigorous result. Nevertheless, as we shall see in later sections, the information-theory result often is in good agreement with experiment. Needless to say, it would be better to use an optimization procedure that would simultaneously satisfy the moment theorems and give the correct $K'_{\nu\nu}(0)$. We have not been able to devise such a procedure.

Given an approximate $K_{\nu\nu}(t)$, such as Eq. (3.118), the memory-function equation [see Eq. (3.44)] can be solved for the autocorrelation function $\hat{C}_{\nu\nu}(t)$. The approximation used here only satisfies the first two sum rules. Nevertheless, if the information measure is maximized subject to higher-order moments, higher-order sum rules will be satisfied.

IV. Computer Experiments (Molecular Dynamics)

A. Introduction

Section II was devoted to an exposition of linear response theory. It was shown how weak probing fields can be used to determine time correlation functions. The fluctuation dissipation theorem enables us to determine which time correlation function corresponds to a specific probe. Unfortunately, only a few time correlation functions have been experimentally determined. There is, consequently, very little quantitative experimental information on the dynamics of molecular motions in liquids and gases.

The present status of the theory of time-dependent processes in liquids is the following. Experiments can be categorized in terms of the time correlation functions that are measured. Moreover, experiments can be designed to measure specific correlation functions. With regard to the time correlation functions themselves, certain general properties of these functions are known. However, because of the complexities of the N-body problem, the direct calculation of the full time dependence of these functions is, in general, an extremely difficult task. Only simple time correlation functions in the simplest systems (free rotor, particle in box, etc.) have yielded to analytical treatment.

The theory of time-dependent processes is analogous to the theory of equilibrium statistical mechanics, where equilibrium properties can be determined if certain multidimensional integrals involving the equilibrium ensemble distribution function of the system can be evaluated. In both cases, the physical and mathematical formulation is complete but the computation of physical properties is exceedingly difficult.

The dynamics of molecular motion in condensed media can be studied with high-speed digital computers. In the past decade, techniques have been developed which greatly expedite the computer simulation of many-body systems. There are several compelling reasons to make these studies:

1. To obtain a realistic and detailed picture of how individual molecules rotate and translate in classical fluids.
2. To examine in detail the structure of the most frequently encountered time correlation functions, such as those that determine transport coefficients and the absorption and scattering spectra of photons and neutrons, to name a few.

3. To examine the sensitivity of equilibrium properties and time correlation functions to the form of the intermolecular potential.

4. To test various stochastic assumptions that are often made about molecular motions.

Computer simulations are far superior to laboratory experiment for purpose since (1) the intermolecular potential is known and (2) it provides much more detailed information than can be obtained by any known experiment.

These computer "experiments" have provided insight into the microscopic dynamical behavior of real diatomic liquids for both the experimentalist and theoretician alike. Furthermore, it is hoped that these studies will motivate more realistic approximate theories of the liquid state and provide "experimental" data to test these theories. In addition, the methods employed illustrate the concepts of statistical mechanics in a very clear way. In the next subsection, a brief description of the method is presented.

B. Molecular Dynamics

Electronic computers have advanced to such a degree that Newton's equations of motion can now be integrated for a fairly large assembly of interacting particles. This method, which is now commonly called molecular dynamics, is particularly useful for the study of the condensed phases of matter.† The features common to all molecular dynamics experiments that have been done to date are the following:

(a) The systems are finite $N \leq 1000$.

(b) The interaction potential is pairwise additive

$$V(1, \ldots, N) = \sum_{i>j=1}^{N} \phi(r_{ij})$$

where the pair potential $\phi(r)$ has a finite range r_0 such that for $r > r_0$, $\phi(r) = 0$.

(c) Newton's equations of motion

$$m \frac{d\mathbf{v}_i}{dt} = -\sum_{j\neq 1} \frac{\partial}{\partial \mathbf{r}_i} \phi(r_{ij}); \qquad \mathbf{v}_i = \frac{d\mathbf{r}_i}{dt}$$

† This work has been renewed recently by Berne and Foster and will appear in the *Ann. Rev. Phys. Chem.* in 1971.

are solved by finite difference techniques with time steps t between 10^{-14} sec and 10^{-15} sec.

(d) The positions, velocities, and accelerations are stored on magnetic tape.

Computer experiments on equilibrium liquids all have, in addition, the following features in common:

(a) The N particles are contained in a cubic box of edge $L > r_0$,

(b) The initial state (initial positions and momenta) are sampled such that the momenta are distributed according to the Maxwell distribution at a given temperature and the positions are sampled such that the initial configuration is one corresponding to a quite large value of the Boltzmann factor $\exp[-[\beta V(1, \ldots, N)]]$; i.e. the system is in a probable state for a member of an equilibrium ensemble.

(c) The equations of motion are solved subject to periodic boundary conditions.

A number of comments are in order. N and V $(= L^3)$ are chosen to give the number density N/V of the physical system under study. The sampling of the configuration is quite complicated and we refer the reader to the literature for a more detailed discussion of this subject.

The equations of motion are solved subject to the initial state together with periodic boundary conditions: The latter means that if (x_i, y_i, z_i) is the position of particle i in the box, there are 26 periodic images at $(x_i \pm L, 0; y_i \pm L, 0; z_i \pm L, 0)$. The particles in the box interact with the periodic images within their range. These boundary conditions have the consequence that when a particle leaves the box through one side, its image enters through the opposite side, thus preserving the number of particles in the box. These conditions eliminate strong surface effects and essentially simulate an infinite system. Nevertheless, periodic boundary conditions have the following limitations:

(a) Because the number of particles in the box is constant it is impossible to study thermodynamic states in which thermal fluctuations have correlation lengths of the order of the box size as they do in the critical region.

(b) The time scale is limited to times shorter than L/c where c is the velocity of sound. For times longer than this a disturbance which arises in one region of the box can traverse the box and enter through the opposite side thus leading to spurious recurrences.

(c) The collective properties that can be studied are limited to discrete wave vectors

$$\mathbf{q} = \frac{2\pi}{L}\mathbf{n}$$

with minimum wave number

$$q = \frac{2\pi}{L}.$$

This limits the kinds of questions that can be investigated by molecular dynamics.

The computer output is then the sequence of states

$$\mathbf{\Gamma}_0, \ldots, \mathbf{\Gamma}_j, \ldots, \mathbf{\Gamma}_M.$$

through which the system passes in the course of time. Here $\mathbf{\Gamma}_j$ is the state of the system [all positions and momenta] after the jth time step; i.e. at time $t = j\,\Delta t$. The output is consequently a set of discrete points in phase space and M is the total number of iterations done in the computations.

The computer output may be regarded as a dynamical movie of the many body system and may be converted into an actual movie via computer animation techniques. This has been done by several investigators (Harp, Berne, Paskin, Rahman, and Fehder). Such sources present a particularly convenient way to present the enormous data in such a way that the viewer can get some insight into the dynamical behavior of molecules in condensed media. For example, as the strength of the noncentral potential is increased in polyatomic liquids, the movie shows how the rotational motions of molecules becomes more hindered. Such movies give the viewer an opportunity for discoveries by serendipity that exist in connection with laboratory experiments.

These solutions are checked for consistency in the following way:

(a) At intermediate times, say j, the velocities of the particles are reversed and the calculation proceeds j steps. The final state should rigorously coincide with the initial state (microscopic reversibility) and any deviation reflects roundoff error.

(b) The total energy and momentum are computed. Since these are constants of the motion any variation in the total energy and momentum reflects inaccuracies in the solution.

(c) The mean kinetic energy per particle is computed and its variation in time is monitored. This should fluctuate about the average desired "temperature." Any systematic drift in this quantity reflects the fact that the system is not at equilibrium.

(d) An order parameter

$$\zeta_k(t) = 1/N \sum_{i \neq j=1}^{N} \cos K x_{ij},$$

where K is a vector in the reciprocal lattice of the corresponding solid, is monitored. If this system is ordered $\zeta_k(t)$ should fluctuate around $N-1$ whereas if it is a liquid $\zeta_k(t)$ should fluctuate around zero.

It should be noted that if (a) checks out it does not, by itself, imply that the solution is accurate. The numerical algorithm may itself be reversible in time. All (a) does is check roundoff error. We regard (a) as an important check on the accuracy of the solution. Many of the studies reported here do not report the degree to which the constants of the motion are conserved so that we cannot always assess their trustworthiness. In every case, the temperature fluctuates around its equilibrium values. Likewise for the order parameter. All these systems are in equilibrium.

The computer generates the state $(\mathbf{\Gamma}_0, \ldots, \mathbf{\Gamma}_j, \ldots, \mathbf{\Gamma}_M)$ through which the system passes in the course of time so that any property $A(\mathbf{\Gamma}_t)$ can be determined at each of these states $(A_0, \ldots, A_j, \ldots A_M)$ where $A_j \equiv A(\mathbf{\Gamma}_j)$.

In classical statistical mechanics bulk properties of an isolated system are given by infinite time averages

$$\langle A \rangle = \lim_{T\to\infty} (1/T) \int_0^T dt\, A(\mathbf{\Gamma}_t),$$

where $\mathbf{\Gamma}_t$ is the state of the mechanical system at time t. In addition, the linear response of a system to "weak probes" is given in terms of time correlation functions

$$\langle A(0)A(t) \rangle = \lim_{T\to\infty} (1/T) \int_0^T dt\, A(\mathbf{\Gamma}_t) A(\mathbf{\Gamma}_{t+\tau}).$$

The computer, unfortunately generates a part of the phase orbit, and only discrete points at that. Thus the infinite time averages must be

replaced by the finite sums

$$\langle A \rangle = (1/M) \sum_{j=0}^{M} A_j$$

$$\langle A(0)A(t) \rangle = (1/M) \sum_{j=0}^{M-n} A_j A_{j+n} \qquad t = n\,\Delta t.$$

Averaging over finite rather than infinite times gives rise to errors in the computed averages. Zwanzig and Ailawadi (1969) estimated these errors on the basis of a Gaussian stochastic model of the fluctuations. They found that the errors grow with the time τ and with a decrease in M. They also found that the single particle (incoherent) properties can be determined with greater accuracy than the collective (coherent) properties.

Throughout this chapter, we will refer to the computer experiments on diatomic liquids done in our laboratory. This is only done for convenience.

V. Hydrodynamics and Generalized Hydrodynamics

A. Self-Diffusion in Classical Liquids

Many important properties of liquids, solids, and gases can be probed by absorption (Gordon, 1968; Harp and Berne, 1970), light-scattering (Mountain, 1970), and neutron-scattering spectroscopy (Egelstaff, 1965; Boutin and Yip, 1968). The cross sections for these processes are all related in part to the "self" intermediate scattering function $F_s(\mathbf{k}, t)$ (see Section VI)

$$F_s(\mathbf{k}, t) = (1/N) \left\langle \sum_{l=1}^{N} \exp[-i\mathbf{k} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{k} \cdot \mathbf{r}_l(t)] \right\rangle. \tag{5.1}$$

This is a one-sided quantum-mechanical time correlation function. We shall only be interested in its classical behavior.

Let $G_s(\mathbf{r}, t)$ denote the Fourier transform with respect to the vector $\mathbf{k}$ of $F_s(\mathbf{k}, t)$. Then,

$$G_s(\mathbf{r}, t) = (1/N) \left\langle \sum_{l=1}^{N} \delta(\mathbf{r} - [\mathbf{r}_l(t) - \mathbf{r}_l(0)]) \right\rangle; \tag{5.2}$$

$G_s(\mathbf{r}, t)$ is called the Van Hove self space–time correlation function

(Van Hove, 1954). From the properties of the delta-function, it clearly follows that $G_s(\mathbf{r}, t)$ is a probability distribution describing the event that a molecule is at the origin at time $t = 0$ and at the point $\mathbf{r}$ at the time t. Thus, $G_s(\mathbf{r}, t)$ is the probability distribution function characterizing a net displacement (or self-diffusion) of a particle in the time t [see Section II,E, where $G_s(\mathbf{r}, t)$ is discussed]. From Eq. (5.2), it should be noted that

$$G_s(\mathbf{r}, 0) = \delta(\mathbf{r}), \tag{5.3a}$$

$$\int d^3r\, G_s(\mathbf{r}, t) = 1, \tag{5.3b}$$

$$\int d^3r\, r^2 G_s(\mathbf{r}, t) = \langle \Delta r^2(t) \rangle, \tag{5.3c}$$

where $\langle \Delta r^2(t) \rangle$ is the mean-square displacement of a particle. According to Eq. (2.111),

$$\langle \Delta r^2(t) \rangle = 2 \int_0^t d\tau\, (t - \tau) \langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle, \tag{5.4}$$

where $\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle$ is the velocity autocorrelation function. Thus, it is quite obvious that $G_s(\mathbf{r}, t)$ contains complete information about the velocity correlation function.

An approximate $G_s(\mathbf{r}, t)$ can be determined by information theory (Jaynes, 1963) (see Section II,G). If only a small number of moments $\langle \Delta r^n(t) \rangle$ of $G_s(\mathbf{r}, t)$ are known, the "optimal" $G_s(\mathbf{r}, t)$ consistent with this incomplete knowledge is that $G_s(\mathbf{r}, t)$ that maximizes the "information entropy" and simoultaneously satisfies the known moments. Let us apply information theory to the simple case where all that is known is (5.3b) and (5.3c). For this purpose, define the information entropy

$$S[G_s] = -\int d^3r\, G_s(\mathbf{r}, t) \ln G_s(\mathbf{r}, t). \tag{5.5}$$

This entropy is to be maximized subject to the constraints (5.3a)–(5.3c). The optimal function turns out to be

$$G_s(\mathbf{r}, t) = [2\pi \langle \Delta r^2(t) \rangle / 3]^{-3/2} \exp -[r^2 / \tfrac{2}{3} \langle \Delta r^2(t) \rangle] \tag{5.6}$$

with

$$F_s(\mathbf{k}, t) = \exp -[k^2 \langle \Delta r^2(t) \rangle / 6].$$

(Higher moments could generate non-Gaussian corrections.)

This is the well-known Gaussian approximation for $G_s(\mathbf{r}, t)$ first proposed in connection with the random-walk problem. It was Vineyard

(1958) who first pointed out that $G_s(\mathbf{r}, t)$ is a Gaussian for (1) a freely-moving gas particle, (2) a particle diffusing according to the diffusion equation, (3) a particle vibrating in a harmonic lattice, and (4) the Brownian motion of a heavy particle in a bath of much lighter particles.

One of the great advantages of the Gaussian approximation is that it permits $G_s(\mathbf{r}, t)$ to be computed from a model of the velocity correlation function [see Eq. (5.4)]. Let us, therefore, explore some simple models for the velocity correlation function.

In the phenomenological theory of Brownian motion (Chandrasekhar, 1945), it is assumed that the random force in the Langevin theory, Eq. (3.93), is a Gaussian random process with a white spectrum. It follows that the velocity is a Gaussian Markov process which, by Doob's theorem, has an exponential correlation function, $\langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle = \langle v^2(0)\rangle \times e^{-\gamma|t|}$. Here, γ is called the friction coefficient. From the Kubo relation, Eq. (2.112), the friction coefficient γ and the self-diffusion coefficient are related ($D = \langle v^2\rangle/3\gamma = kT/M\gamma$). The corresponding mean-square displacement is

$$\begin{aligned}\langle \Delta r^2(t)\rangle &= 2\langle v^2\rangle[(t/\gamma) - (1/\gamma^2)(1 - e^{-\gamma|t|})] \\ &= 6Dt - (2\langle v^2\rangle/\gamma^2)(1 - e^{-\gamma|t|}).\end{aligned} \tag{5.7}$$

Thus,

$$\langle \Delta r^2(t)\rangle = \begin{cases} \langle v^2\rangle t^2, & t \ll 1/\gamma \\ 6Dt, & t \gg 1/\gamma. \end{cases}$$

The particle moves like a free particle ($\langle \Delta r^2(t)\rangle = \langle v^2\rangle t^2$) for a time small compared to $1/\gamma$, whereas for long times, it moves like a "random walker" or diffusing particle ($\langle \Delta r^2(t)\rangle^{1/2} \sim \sqrt{t}$). The Brownian motion theory, so far as is known, accounts correctly for the dynamical behavior of a large, heavy particle in a solvent of light particles. However, it fails to account for the motion of atoms and small molecules. Computer experiments show that $\langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle$ is much more complicated than an exponential, and moreover, that Eq. (5.7) is a good approximation only at short and long times. Before discussing how $\langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle$ and $F_s(\mathbf{k}, t)$ can be calculated for liquids, it is appropriate to discuss the long-time behavior from a formal point of view.

The long-time behavior of $G_s(\mathbf{r}, t)$ can be inferred from a macroscopic argument. Consider a small neighborhood around the origin of the coordinate system which is sufficiently large to contain many molecules but which is also infinitesimal on a macroscopic scale. At time $t = 0$, paint a small subset of the particles in this neighborhood. At time t, count the fraction of these particles that have diffused into the volume element $d^3\mathbf{r}$ centered on the point $\mathbf{r}$. To a good approximation, this fraction is $G_s(\mathbf{r}, t)\, d^3\mathbf{r}$ (the probability that a particle at $\mathbf{r} = 0$ at time $t = 0$ will diffuse into the neighborhood $d^3\mathbf{r}$ of $\mathbf{r}$ at t). For times t that are long on a microscopic time scale, it is expected that this experiment can be described by diffusion theory so that $G_s(\mathbf{r}, t)$ should satisfy the diffusion equation

$$(\partial/\partial t)G_s(\mathbf{r}, t) = D\nabla^2 G_s(\mathbf{r}, t), \tag{5.8}$$

where D is the self-diffusion coefficient and ∇ is the gradient operator with respect to $\mathbf{r}$. This equation should be solved subject to the boundary condition

$$G_s(\mathbf{r}, 0) = \delta(\mathbf{r}).$$

It is much easier to deal with the Fourier transform, $F_s(\mathbf{k}, t)$, of $G_s(\mathbf{r}, t)$ that satisfies the Fourier transform of the diffusion equation

$$(\partial/\partial t)F_s(\mathbf{k}, t) = -k^2 D F_s(\mathbf{k}, t) \tag{5.9}$$

together with the boundary condition $F_s(\mathbf{k}, 0) = 1$. The solution is

$$F_s(\mathbf{k}, t) = \exp -k^2 Dt, \tag{5.10}$$

which is the same as the long-time limit of Brownian theory. We shall now turn to a formal derivation of Eq. (5.9).

The function $F_s(\mathbf{k}, t)$ is a normalized time correlation function of the property $U_1 \equiv \exp[i\mathbf{k} \cdot \mathbf{r}]$,

$$\begin{aligned}F_s(\mathbf{k}, t) &\equiv \langle \exp[-i\mathbf{k} \cdot \mathbf{r}(0)] \exp[i\mathbf{k} \cdot \mathbf{r}(t)]\rangle \\ &\equiv \langle U_1 \mid e^{iLt} \mid U_1\rangle;\end{aligned} \tag{5.11}$$

consequently, $F_s(\mathbf{k}, t)$ obeys the memory-function equation,

$$\partial F_s(\mathbf{k}, t)/\partial t = -\int_0^t d\tau\, K_1(\mathbf{k}, \tau) F_s(\mathbf{k}, t - \tau), \tag{5.12}$$

where

$$K_1(\mathbf{k}, t) = \langle iLU_1 \mid \exp[i(1 - \hat{P}_1)Lt] \mid iLU_1\rangle$$

and

$$\hat{P}_1 \equiv \mid U_1\rangle\langle U_1 \mid = \mid \exp[i\mathbf{k} \cdot \mathbf{r}]\rangle\langle \exp[i\mathbf{k} \cdot \mathbf{r}] \mid.$$

From the properties of U_1, it is possible to show (see Section II) that

$F_s(\mathbf{k}, t)$ and $K_1(\mathbf{k}, t)$ are even functions of $\mathbf{k}$ and t. Since $iLU_1 = i\mathbf{k} \cdot \mathbf{v} \times \exp[i\mathbf{k} \cdot \mathbf{r}]$, it follows that

$$K(\mathbf{k}, t) = \mathbf{k} \cdot \langle \mathbf{v} \exp[i\mathbf{k} \cdot \mathbf{r}] \mid \exp[i(1 - \hat{P}_1)Lt] \mid \mathbf{v} \exp[i\mathbf{k} \cdot \mathbf{r}] \rangle \cdot \mathbf{k}$$
$$= \mathbf{k} \cdot \mathbf{D}_k(\tau) \cdot \mathbf{k}, \tag{5.13}$$

where $\mathbf{D}_k(\tau)$ is a tensor

$$\mathbf{D}_k(\tau) = \langle \mathbf{v} \exp[i\mathbf{k} \cdot \mathbf{r}] \mid \exp[i(1 - \hat{P}_1)Lt] \mid \mathbf{v} \exp[i\mathbf{k} \cdot \mathbf{r}] \rangle.$$

The memory-function equation becomes

$$(\partial/\partial t)F_s(\mathbf{k}, t) = -\int_0^t d\tau\, [\mathbf{k} \cdot \mathbf{D}_k(\tau) \cdot \mathbf{k}]F_s(\mathbf{k}, t - \tau). \tag{5.14}$$

This equation can be solved in terms of the Laplace transforms $\tilde{F}_s(\mathbf{k}, s)$ and $\tilde{\mathbf{D}}_k(s)$ of $F_s(\mathbf{k}, t)$ and $\mathbf{D}_k(\tau)$. Since $F_s(\mathbf{k}, t = 0) = 1$, [see Eq. (5.10)], it follows that

$$\tilde{F}_s(\mathbf{k}, s) = [s + \mathbf{k} \cdot \tilde{\mathbf{D}}_k(s) \cdot \mathbf{k}]^{-1}. \tag{5.15}$$

This should be compared with the Laplace transform of the solution to the diffusion equation, Eq. (5.10),

$$\tilde{F}_s(\mathbf{k}, s) = [s + k^2D]^{-1}.$$

Clearly, the exact function involves a complicated k- and s-dependent diffusion coefficient $\tilde{\mathbf{D}}_k(s)$. Our goal is to show under what circumstances the memory-function equation for $F_s(\mathbf{k}, t)$ reduces to the diffusion equation. Let us be guided by the properties of the solution to the diffusion equation,

$$F_s(\mathbf{k}, t) = \exp -k^2Dt. \tag{5.16}$$

The time dependence is always associated with the vector $\mathbf{k}$ in the combination k^2t. Let us therefore redefine the time scale to be (Zwanzig, 1964)

$$\tau = k^2t.$$

Then $F_s(\mathbf{k}, t)$ goes as $e^{-D\tau}$. Consider the double limit

$$\lim_{\substack{t\to\infty\ k\to 0\\ \tau=\text{const}}} \lim F_s(\mathbf{k}, t) = \lim_{\substack{t\to\infty\ k\to 0\\ \tau=\text{const}}} \lim e^{-D\tau} = e^{-D\tau} \tag{5.17}$$

Consequently, the decay of $\exp -k^2Dt$ does not change in this double limit. This limit selects out from the exact $F_s(\mathbf{k}, t)$ the small-k and long-time behavior, i.e., the hydrodynamic behavior where the distances are very large compared with molecular distances (k small) and the times are long compared with molecular times. To determine the small-k and long-t behavior of the exact $F_s(\mathbf{k}, t)$, we take the double limit of the inverse Laplace transform of Eq. (5.15), that is, of the exact $F_s(\mathbf{k}, t)$,

$$F_s(\mathbf{k}, t) = (1/2\pi i) \oint ds\, e^{st}/[s + \mathbf{k} \cdot \tilde{\mathbf{D}}_k(s) \cdot \mathbf{k}]. \tag{5.18}$$

Now we introduce the new time variable $\tau = k^2t$ and a corresponding new Laplace variable $s = k^2x$,

$$F_s(\mathbf{k}, t) = (1/2\pi i) \oint dx\, e^{x\tau}/[x + \mathbf{k} \cdot \tilde{\mathbf{D}}_k(k^2x) \cdot \mathbf{k}/k^2]. \tag{5.19}$$

We then take the double limit of this equation keeping τ fixed. Provided that $\tilde{\mathbf{D}}_k(s)$ is a continuous function of $\mathbf{k}, s$ (which we cannot prove), the limit gives

$$\lim_{\substack{t\to\infty\ k\to 0\\ \tau=\text{const}}} \lim F_s(\mathbf{k}, t) = (1/2\pi i) \oint dx\, e^{x\tau}/[x + \lim_{k\to 0} \mathbf{k} \cdot \tilde{\mathbf{D}}_k(k^2x) \cdot \mathbf{k}/k^2]$$
$$= \exp -[\lim_{s\to 0} \lim_{k\to 0} \mathbf{k} \cdot \tilde{\mathbf{D}}_k(s) \cdot \mathbf{k}/k^2]\tau. \tag{5.20}$$

Comparison with Eq. (5.17) shows that the self-diffusion coefficient is

$$D = \lim_{s\to 0} \lim_{k\to 0} \mathbf{k} \cdot \tilde{\mathbf{D}}_k(s) \cdot \mathbf{k}/k^2. \tag{5.21}$$

This expression for the self-diffusion coefficient is still not in a useful form because it depends on the projection operator. To shorten the notation, we define

$$\tilde{D}_k(s) = \mathbf{k} \cdot \tilde{\mathbf{D}}_k(s) \cdot \mathbf{k}/k^2. \tag{5.22}$$

In Section III,4, a relation was described between memory functions $K_{vv}(t)$ and corresponding time correlation functions. In our case, Eq. (3.113b) becomes

$$\tilde{\Phi}_{11}(\mathbf{k}, s) = \mathbf{k} \cdot \langle \mathbf{v} \exp i\mathbf{k} \cdot \mathbf{r} \mid (s - iL)^{-1} \mid \mathbf{v} \exp i\mathbf{k} \cdot \mathbf{r} \rangle \cdot \mathbf{k}$$
$$= \tilde{K}_{11}(\mathbf{k}, s)/[1 + (1/s)\tilde{K}_{11}(\mathbf{k}, s)] = k^2\tilde{D}_k(s)/[1 + (k^2/s)\tilde{D}_k(s)], \tag{5.23}$$

so that

$$(1/k^2)\tilde{\Phi}_{11}(\mathbf{k}, s) = (1/[1 + (k^2/s)\tilde{D}_k(s)])\tilde{D}_k(s). \tag{5.24}$$

It was assumed that $\tilde{\mathbf{D}}_k(s)$ and, consequently, $\tilde{D}_k(s)$ are continuous functions of $\mathbf{k}$ and s. This assumption is based on the fact that $\tilde{D}_k(s)$ is associated with a physical process, self-diffusion, and should therefore be mathematically well behaved. On the other hand, $(1/k^2)\tilde{\Phi}_{11}(\mathbf{k}, s)$ is not directly related to a physical process and consequently need not be well behaved. In fact, $(1/k^2)\tilde{\Phi}_{11}(\mathbf{k}, s)$ is not well behaved at $(k = 0, s = 0)$. This can be seen from the fact that the double limit $s \to 0$, $k \to 0$ depends on the order in which the limits are taken; note that

$$\lim_{k\to 0}\lim_{s\to 0} (1/k^2)\, \tilde{\Phi}_{11}(\mathbf{k}, s) = 0,$$

whereas

$$\lim_{s\to 0}\lim_{k\to 0} (1/k^2)\, \tilde{\Phi}_{11}(\mathbf{k}, s) = \lim_{s\to 0}\lim_{k\to 0} \tilde{D}_k(s) \neq 0. \tag{5.25}$$

From Eq. (5.21), it should be noted that the right-hand side of this equation is the self-diffusion coefficient. Thus,

$$D = \lim_{s\to 0}\lim_{k\to 0} \mathbf{k} \cdot \langle \mathbf{v} \exp[i\mathbf{k} \cdot \mathbf{r}] \mid (s - iL)^{-1} \mid \mathbf{v} \exp[i\mathbf{k} \cdot \mathbf{r}]\rangle \cdot \mathbf{k}/k^2. \tag{5.26}$$

In this limit, the exponentials $\exp(i\mathbf{k} \cdot \mathbf{r})$ can be replaced by unity. The scalar product then becomes

$$\langle \mathbf{v}(s - iL)^{-1}\mathbf{v}\rangle,$$

which is the Laplace transform of the tensor velocity correlation function $\langle \mathbf{v}(0)\mathbf{v}(t)\rangle$. The ijth element of this tensor is $\langle v_i e^{iLt} v_j\rangle$, where $(i, j = 1, 2, 3)$. Under the transformation $x_j \to -x_j$, $p_j \to -p_j$, $iL \to iL$,

$$\langle v_i e^{iLt} v_j\rangle = -\langle v_i e^{iLt} v_j\rangle = 0 \qquad (i \neq j).$$

Thus, $\langle \mathbf{v}(0)\mathbf{v}(t)\rangle$ is diagonal. Moreover, if the system is isotropic,

$$\langle v_1(0)v_1(t)\rangle = \langle v_2(0)v_2(t)\rangle = \langle v_3(0)v_3(t)\rangle = \tfrac{1}{3}\langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle,$$

so that

$$\langle \mathbf{v}(0)\mathbf{v}(t)\rangle = \tfrac{1}{3}\langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle \mathbf{U}, \tag{5.27}$$

where $\mathbf{U}$ is the unit tensor. Thus,

$$\langle \mathbf{v}[s - iL]^{-1}\mathbf{v}\rangle = \tfrac{1}{3}\langle \mathbf{v} \cdot [s - iL]^{-1}\mathbf{v}\rangle \mathbf{U}$$

Since $\mathbf{k} \cdot \mathbf{U} \cdot \mathbf{k}/k^2 = 1$, substitution of Eq. (5.27) into Eq. (5.26) yields

$$D = \lim_{s\to 0} \frac{1}{3} \langle \mathbf{v} \cdot \frac{1}{s - iL} \mathbf{v}\rangle. \tag{5.28}$$

The function $\langle \mathbf{v} \cdot [s - iL]^{-1}\mathbf{v}\rangle$ is the Laplace transform of $\langle \mathbf{v} \cdot e^{iLt}\mathbf{v}\rangle = \langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle$, so that,

$$D = \lim_{s\to 0} \tfrac{1}{3} \int_0^\infty dt\, e^{-st}\langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle. \tag{5.29}$$

This is just the formula that we derived in Section II,E. Here, we have shown that the memory-function equation reduces to the diffusion equation in the long-time, small-k limit and, moreover, the self-diffusion coefficient is given by the Kubo relation. This same approach can be applied to other properties to derive long-time equations like the Bloch equations or the hydrodynamic equations. We shall discuss the derivation of other such equations later. It should be noted, nevertheless, that if short-time behavior or large-k dependence is required, the memory-function equation and not its long-time limit should be used. In the ensuing paragraphs, we discuss approximations in the "nonhydrodynamic limit."

The short-time behavior of the memory function $K_{11}(\mathbf{k}, t)$ is

$$K_{11}(\mathbf{k}, t) = \tfrac{1}{3}k^2\langle v^2\rangle - \tfrac{1}{2}t^2[\tfrac{2}{9}k^4\langle v^2\rangle^2 + \tfrac{1}{3}\langle a^2\rangle k^2] + \cdots. \tag{5.30}$$

To second order in $\mathbf{k}$, it can be shown that (Harp and Berne, 1970)

$$K_{11}(\mathbf{k}, t) \cong \tfrac{1}{3}\langle v^2\rangle k^2\psi(t) + O(k^4), \tag{5.31}$$

where $\psi(t)$ is the normalized velocity autocorrelation function. Thus, for sufficiently small values of k, $K_{11}(\mathbf{k}, t) \cong \tfrac{1}{3}\langle v^2\rangle k^2\psi(t)$ may be a good approximation to the memory function. To get some idea of the values of k for which this approximation may be useful, let us look at the coefficient of t^2 in Eq. (5.31). Note that the term of order k^4 can be neglected with respect to the term of order k^2 if k is such that

$$k^2\langle v^2\rangle \ll \tfrac{3}{4}\langle a^2\rangle/\langle v^2\rangle.$$

For liquid CO or N_2, this amounts to $k \ll 3 \times 10^8\ \mathrm{cm}^{-1}$. The interesting feature of this memory function is that it leads to a non-Gaussian behavior of the $F_s(\mathbf{k}, t)$ and thus provides an approximate method for exploring the non-Gaussian behavior. It should be noted that this memory function (1) gives the correct long-time limit, (2) gives the correct initial time

dependence of $\langle \Delta r^n(t) \rangle$ ony for $n = 1$, whereas the Gaussian approximation gives the correct long-time limit but also gives the correct short-time behavior of $\langle \Delta r^{2n}(t) \rangle$ for all n. Thus, both the diffusion approximation, $F_s(\mathbf{k}, t) = \exp -k^2Dt$, and Eq. (5.31) fail at short times.

Figure 5 gives $F_s(\mathbf{k}, t)$ for two different values of k. These functions were evaluated from computer experiments (Harp and Berne, 1970)

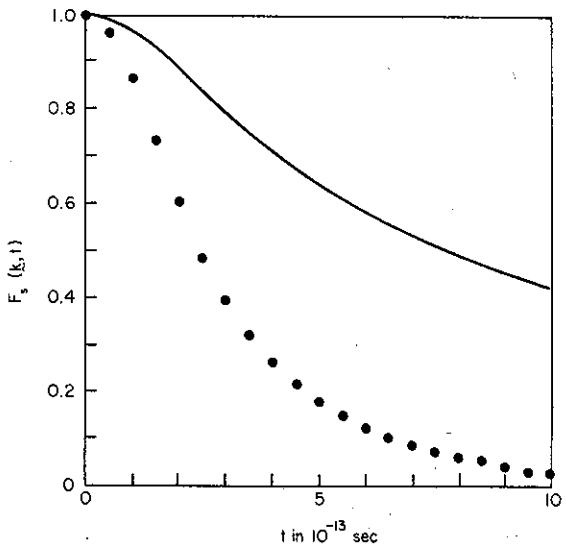

FIG. 5. Intermediate scattering function $F_s(\mathbf{k}, t)$ for the COM motion of CO molecules from computer experiments (modified Stockmayer simulation). (●) $k = 2$ Å^{-1}; (solid line) $k = 4$ Å^{-1}.

on liquid CO. The corresponding normalized memory functions for $F_s(\mathbf{k}, t)$ are presented in Fig. 6. These functions were evaluated from the same computer experiments. Note that, although the two scattering functions are quite different, their normalized memory functions are quite similar, as would be predicted by Eq. (5.31). Note further that these normalized memories resemble the velocity autocorrelation function for the same computer experiment. In addition, the approximate memory function, Eq. (5.31), is used to compute approximate intermediate scattering functions $F_s(\mathbf{k}, t)$. The results of this approximate theory are presented along with the corresponding experimental functions in Fig. 7. Note that this approximation is better than the Gaussian for intermediate values of k.

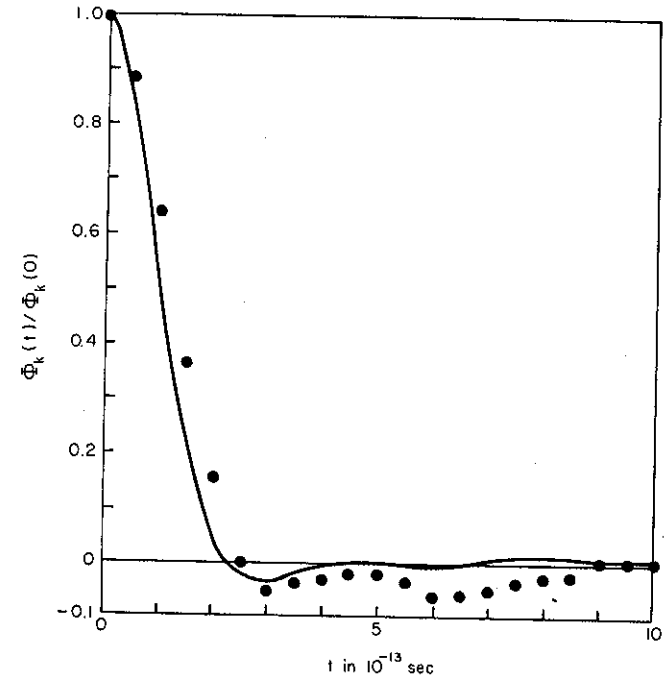

FIG. 6. The normalized memory function $\Phi_k(t)/\Phi_k(0)$ corresponding to the intermediate scattering functions of Fig. 5.

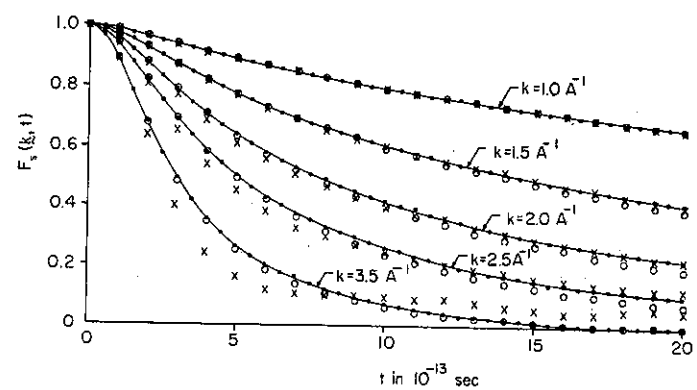

FIG. 7. Intermediate scattering functions $F_s(\mathbf{k}, t)$ for the COM motion of CO molecules from computer experiments on liquid CO (modified Stockmayer simulation) (dots) compared with the Gaussian approximation, Eq. (5.6) (circles), and the approximation specified by Eq. (5.31) (crosses).

B. The Density Correlation Function

Many important properties of liquids, solids, and gases can be probed by scattering photons or neutrons off the system in question. The differential scattering cross section in monatomic systems is related to the time Fourier transforms of the intermediate scattering functions $F_s(\mathbf{k}, t)$ [see Eq. (5.1)] and $F(\mathbf{k}, t)$,

$$F(\mathbf{k}, t) = N^{-1}\left\langle \sum_{l=1}^{N} \exp -i\mathbf{k} \cdot \mathbf{r}_l(0) \sum_{m=1}^{N} \exp i\mathbf{k} \cdot \mathbf{r}_m(t)\right\rangle; \tag{5.32}$$

$F_s(\mathbf{k}, t)$ and $F(\mathbf{k}, t)$ are one-sided quantum-mechanical time correlation functions. We shall be interested in the classical behavior of these functions. The differential scattering cross sections for photons and neutrons are linear combinations of the two spectral density functions

$$\begin{aligned} S(\mathbf{k}, \omega) &= (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{i\omega t} F(\mathbf{k}, t), \\ S_s(\mathbf{k}, \omega) &= (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{i\omega t} F_s(\mathbf{k}, t). \end{aligned} \tag{5.33}$$

The first function contributes to the coherent scattering and the second function contributes to the incoherent scattering of the neutrons. Neutron scattering and light scattering consequently probe the spontaneous fluctuations of the property

$$\varrho_k(t) = \sum_{l=1}^{N} \exp i\mathbf{k} \cdot \mathbf{r}_l(t), \tag{5.34}$$

which is the spatial Fourier transform of the number density at the position $\mathbf{r}$ in the fluid at time t, i.e., of $\varrho(\mathbf{r}, t) = \sum_{l=1}^{N} \delta(\mathbf{r} - \mathbf{r}_l(t))$. Thus, neutrons and photons probe the dynamics of "density fluctuations."

From the definition of $F(\mathbf{k}, t)$ it follows that

$$F(\mathbf{k}, t) = F_s(\mathbf{k}, t) + F_d(\mathbf{k}, t) = N^{-1}\langle \varrho_{-k}(0)\varrho_k(t)\rangle, \tag{5.35}$$

where $F_d(\mathbf{k}, t)$ is called the distinct intermediate scattering function (Van Hove, 1954) because it involves correlations between different (distinct) nuclei,

$$F_d(\mathbf{k}, t) = N^{-1}\left\langle \sum_{l \neq m=1}^{N} \exp[-i\mathbf{k} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{k} \cdot \mathbf{r}_m(t)]\right\rangle. \tag{5.36}$$

Let $G_d(\mathbf{r}, t)$ denote the Fourier transform with respect to the vector $\mathbf{k}$ of $F_d(\mathbf{k}, t)$. Then,

$$G_d(\mathbf{r}, t) = N^{-1}\left\langle \sum_{l \neq m=1}^{N} \delta(\mathbf{r} - [\mathbf{r}_m(t) - \mathbf{r}_l(0)])\right\rangle; \tag{5.37}$$

$G_d(\mathbf{r}, t)$ is called the Van Hove distinct space–time correlation function (Van Hove, 1954). It clearly follows from Eq. (5.37) that $\varrho G_d(\mathbf{r}, t)$ is the number density at the space–time point $(\mathbf{r}, t)$ given that a particle was at the origin at time $t = 0$ (the number density at point $\mathbf{r}$ is to be computed in such a way that the particle that was at the origin is excluded from the counting). Moreover, $\varrho G_d(\mathbf{r}, t)\, d^3\mathbf{r}/(N - 1)$ is the probability of finding a particle in the neighborhood $d^3\mathbf{r}$ of the point $\mathbf{r}$ at time t given that there was a different particle at the origin at time $t = 0$. Here, $\varrho G_d(\mathbf{r}, t)$ describes the correlated motion of two particles. It follows that $\varrho G_d(\mathbf{r}, 0)$ is the number density at the point $\mathbf{r}$ given that a particle is at the origin at the time $t = 0$. It also follows that $\varrho G_d(\mathbf{r}, 0)\, d^3\mathbf{r}/(N - 1)$ is the probability of finding a particle in the neighborhood $d^3\mathbf{r}$ of the point $\mathbf{r}$ given that a particle is at the origin in an equilibrium ensemble. Thus,

$$\varrho G_d(\mathbf{r}, 0) = \varrho g^{(2)}(\mathbf{r}), \tag{5.38}$$

where $g^{(2)}(\mathbf{r})$ is the pair correlation function and ϱ is the number density. In Fig. 8, the pair correlation function of CO determined from computer experiments is presented. The peaks correspond to the neighbor distributions (as is well known).

Vineyard made a valiant attempt to relate $G_d(\mathbf{r}, t)$ to $G_s(\mathbf{r}, t)$. According to Vineyard,

$$G_d(\mathbf{r}, t) = \int d^3\mathbf{r}'\, g^{(2)}(\mathbf{r}')G_s(\mathbf{r} - \mathbf{r}', t). \tag{5.39}$$

This is called the convolution approximation. Then

$$F_d(\mathbf{k}, t) = G(\mathbf{k})F_s(\mathbf{k}, t),$$

where $G(\mathbf{k})$ is the Fourier transform of the pair correlation function. From the convolution approximation,

$$F(\mathbf{k}, t) = F_s + F_d = \{1 + G(\mathbf{k})\}F_s(\mathbf{k}, t) = S(\mathbf{k})F_s(\mathbf{k}, t), \tag{5.40}$$

where $S(\mathbf{k}) = 1 + G(\mathbf{k})$. The spectral density $S(\mathbf{k}, \omega)$ is then

$$S(\mathbf{k}, \omega) = S(\mathbf{k})S_s(\mathbf{k}, \omega); \tag{5.41}$$

$S(\mathbf{k})$ is the ordinary structure factor that appears in X-ray and neutron scattering.

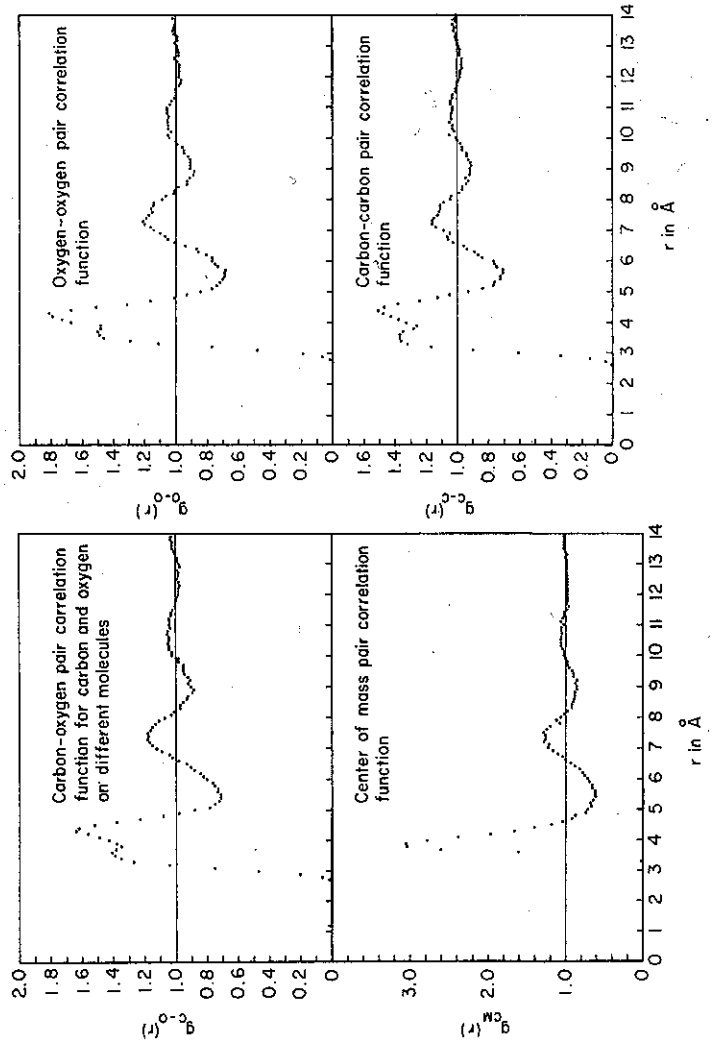

FIG. 8. Pair correlation functions for liquid CO (modified Stockmayer simulation) specifying the distribution of carbon with respect to carbon, $g^{(2)}_{C-C}(r)$; oxygen with respect to carbon, $g^{(2)}_{C-O}(r)$; oxygen with respect to oxygen, $g^{(2)}_{O-O}(r)$; and the COM with respect to the COM, $g^{(2)}_{cm}(r)$. Here, $\Delta r = 0.02$ Å.

In order to see why Vineyard proposed this approximation, let us write Eq. (5.39) as

$$\varrho G_d(\mathbf{r}, t)/(N-1) = \int d^3\mathbf{r}'\, \varrho g^{(2)}(\mathbf{r}')G_s(\mathbf{r}-\mathbf{r}', t)/(N-1).$$

The product $g^{(2)}(\mathbf{r}')G_s(\mathbf{r}-\mathbf{r}', t)/(N-1)$ can be interpreted as the conditional probability distribution that if a particle is at the origin at time $t = 0$ another particle will be at the point $\mathbf{r}'$ at $t = 0$ and will subsequently move to the point $\mathbf{r} - \mathbf{r}'$ at time t. Integrating over all points $\mathbf{r}'$ yields the conditional probability distribution that if a particle is at the origin at time $t = 0$ a different particle will be found at the point $\mathbf{r}$ at time t. This is simply $\varrho G_d(\mathbf{r}, t)/(N-1)$, the left-hand side of the equation. Implicit in this approximation is the assumption that the motion of a molecule starting at the point $\mathbf{r}'$ is not affected by the presence of a molecule at the origin at time $t = 0$. This assumed statistical independence leads to the factorization $[\varrho g^{(2)}(\mathbf{r}')/(N-1)]G_s(\mathbf{r}-\mathbf{r}', t)$. For paths in which $\mathbf{r}'$ is large, it is probably a good approximation, but for $\mathbf{r}'$ small, there must be large correlations which are neglected. Rahman tested this convolution approximation by computer experiments on liquid argon (Rahman, 1964). He concluded that the approximation is not valid as it stands, but can be improved if t is replaced by a specified function of the time. It remains to be shown why Rahman's modification of the Vineyard convolution approximation works. There is no explanation for this at the present time.

Light-scattering and neutron-scattering experiments probe different spectral regions of $S(\mathbf{k}, \omega)$. Thermal neutrons have wavelengths $\sim$1 Å, so that $k \sim 10^8$ cm^{-1}. On the other hand, visible photons have wavelengths $\sim$5000 Å, so that $k \approx 10^5$ cm^{-1}. Consequently, light scattering probes the small-k dependence (or hydrodynamic behavior) of $S(\mathbf{k}, \omega)$, whereas neutrons probe the large-k dependence (kinetic theory behavior) of $S(\mathbf{k}, \omega)$. Before discusing the high-$\mathbf{k}$ dependence of $S(\mathbf{k}, \omega)$ appropriate to neutron-scattering experiments, we shall discuss the behavior of $S(\mathbf{k}, \omega)$ for low k's. For this purpose, it is necessary to study the hydrodynamic equations.

C. Hydrodynamic Calculation of $S(\mathbf{k}, \omega)$

In this subsection, we present Mountain's calculation of $S(\mathbf{k}, \omega)$ in the hydrodynamic limit of a one-component fluid (Mountain, 1966, 1970). The equations of linear hydrodynamics are (Martin, 1968): the equation

of continuity (mass conservation)

$$\partial\varrho/\partial t + \varrho_0 \nabla \cdot \mathbf{v} = 0; \tag{5.42a}$$

the Navier–Stokes equation (conservation of linear momentum),

$$m\varrho_0\, \partial\mathbf{v}/\partial t = -\operatorname{grad} p + \eta_s \nabla^2\mathbf{v} + (\tfrac{1}{3}\eta_s + \eta_v)\nabla(\nabla \cdot \mathbf{v}); \tag{5.42b}$$

and the heat flow equation (conservation of energy),

$$\varrho_0 T_0\, \partial s/\partial t = \lambda\, \nabla^2 T. \tag{5.42c}$$

In these equations, ϱ is the number density, m is the mass of a molecule, $\mathbf{v}$ is the velocity field, p is the pressure, η_s is the shear viscosity, η_v is the bulk viscosity, s is the entropy density, λ is the thermal conductivity, and T is the temperature. Here, ϱ, $\mathbf{v}$, and T are fluctuations from the equilibrium density (ϱ_0), equilibrium velocity ($\mathbf{v} = 0$), and equilibrium temperature (T_0) at the space time point $(\mathbf{r}, t)$. These equations are closed by making the assumption of local thermodynamic equilibrium, according to which local thermodynamic variables are related to each other by the same equations as are the thermodynamic properties in an equilibrium system. Then,

$$\begin{aligned} \delta p &= (\partial p/\partial\varrho)_T\, \delta\varrho + (\partial p/\partial T)_\varrho\, \delta T, \\ \delta s &= (\partial s/\partial\varrho)_T\, \delta\varrho + (\partial s/\partial T)_\varrho\, \delta T, \\ \varrho &\equiv \delta\varrho, \qquad T \equiv \delta T. \end{aligned} \tag{5.43}$$

Equations of motion for ϱ_k, T_k, and $\mathbf{v}_k$ are obtained by Fourier transforming the hydrodynamic equations with respect to $\mathbf{r}$, and substituting the relations of Eq. (5.43). The correlation function $\langle \varrho_{-k}(0)\varrho_k(t)\rangle$ is then determined by solving these equations for $\varrho_k(t)$ in terms of $\varrho_k(0)$, multiplying by $\varrho_{-k}(0)$, and averaging over an equilibrium ensemble of initial conditions. It follows that

$$\langle \varrho_{-k}(0)\varrho_k(t)\rangle = \langle |\, \varrho_k(0)\, |^2\rangle \Psi\, (\mathbf{k}, t), \tag{5.44}$$

where, according to Eqs. (5.35) and (5.42),

$$\begin{aligned} \langle |\, \varrho_k(0)\, |^2\rangle &= NS(\mathbf{k}) \\ \Psi(\mathbf{k}, t) &= [1 - 1/\gamma] \exp[-k^2\lambda t/\varrho_0 C_p] \\ &\quad + [1/\gamma] \exp[-k^2\Gamma t]\{\cos(c_0 kt) + b(k) \sin(c_0 kt)\}. \end{aligned} \tag{5.45}$$

Here, $S(\mathbf{k})$ is the structure factor [$k \to 0$, $S(\mathbf{k}) \to$ isothermal compressibility], $\gamma = C_p/C_v$, with C_p and C_v the isobaric and isochoric heat capacities, c_0, is the adiabatic speed of sound, Γ is the acoustic attenuation coefficient

$$\Gamma = \tfrac{1}{2}[\tfrac{4}{3}\eta_s + \eta_v]/m\varrho_0 + (\lambda/\varrho_0 C_v)(\gamma - 1),$$

and

$$b(k) = [\Gamma + (\lambda/\varrho_0 C_p)(\gamma - 1)]k/c_0. \tag{5.45a}$$

Then the spectrum $S(\mathbf{k}, \omega)$ is

$$\begin{aligned} \frac{S(\mathbf{k}, \omega)}{NS(\mathbf{k})} &= (1 - \gamma)\frac{k^2\lambda/\varrho_0 C_p}{\omega^2 + (k^2\lambda/\varrho_0 C_p)^2} \\ &\quad + \frac{1}{\gamma}\left[\frac{k^2\Gamma}{(\omega + c_0 k)^2 + (k^2\Gamma)^2} + \frac{k^2\Gamma}{(\omega - c_0 k)^2 + (k^2\Gamma)^2}\right] \\ &\quad + \frac{b(k)}{\gamma}\left[\frac{c_0 k + \omega}{(\omega + c_0 k)^2 + (k^2\Gamma)^2} + \frac{c_0 k - \omega}{(\omega - c_0 k)^2 + (k^2\Gamma)^2}\right]. \end{aligned} \tag{5.46}$$

The last term is hard to observe. Now, $S(\mathbf{k}, \omega)$ consists of three bands: a central (Rayleigh) component and two shifted (Brillouin) components (see Fig. 9). The width of the Rayleigh component is $k^2\lambda/\varrho_0 C_p$ (the thermal diffusivity) and the width of the Brillouin components is $k^2\Gamma$, whereas

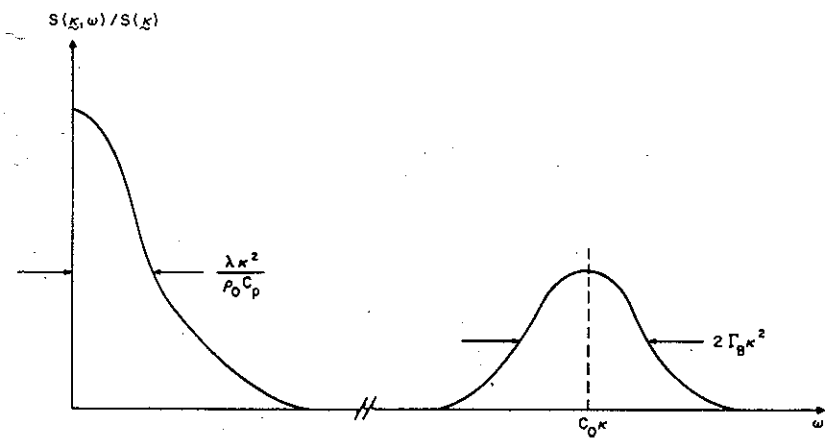

FIG. 9. Sketch (not to scale) of the spectrum of light scattered by a simple fluid. Since the spectrum is even in the frequency ω, only the positive ω axis is shown.

there positions are at $\pm c_0 k$. The ratio of the intensity of the Rayleigh components is $\gamma - 1$, the famous Landau–Placzek ratio.†

Thus, it can be concluded that the light-scattering spectrum from a one-component fluid can be used to measure the thermal diffusivity (from the width of the central component), adiabatic sound velocity (from the position of the Brillouin doublets), $\frac{4}{3}\eta_s + \eta_v$ (from the width of the Brillouin lines), and C_p/C_v (from the integrated intensities).

Recently, Fleury and Boon have studied the isotropic light-scattering spectrum from liquid argon (Fleury and Boon, 1969; McTague *et al.*, 1969). They find that their spectrum fits the hydrodynamic theory [Eq. (5.46)] quite well. The interested reader is referred to the extensive literature on light scattering.

This theory must be modified in order to account for the relaxation of molecular internal degrees of freedom (Mountain, 1970) and chemical reactions (Berne and Frisch, 1967, 1968; Berne and Pecora, 1969). Moreover, for mixtures, the hydrodynamic equations are more complex, but solvable (Mountain and Deutch, 1970).

D. A Derivation of Linear Hydrodynamics

In this subsection, an attempt will be made to show how the linear hydrodynamic equations of Section V,C can be derived from the formalism developed in the first few sections of this chapter. This derivation follows the same lines as the derivation of the equation of self-diffusion described in Section V,A. Space and time do not permit an extensive treatment of this problem. It suffices for our purposes to present the argument for one of the hydrodynamic equations. Our purpose is twofold: (1) to demonstrate that "hydrodynamic fluctuation" theory follows from statistical mechanics, and (2) to indicate how the hydrodynamic equations can be generalized to account for the high-k and ω dependence of $S(\mathbf{k}, \omega)$ in neutron scattering.

Consider the linearized Navier–Stokes equation, Eq. (5.42). Let $\mathbf{J}(\mathbf{k}, t)$ be the spatial Fourier transform of the velocity field $\mathbf{v}(\mathbf{r}, t)$. Then, taking the Fourier transform of Eq. (5.42b),

$$m\varrho_0(\partial/\partial t)\mathbf{J}(\mathbf{k}, t) = -i\mathbf{k}p(\mathbf{k}, t) - \eta_s k^2\mathbf{J}(k, t) + (\tfrac{1}{3}\eta_s + \eta_v)i\mathbf{k}(\mathbf{k}\cdot\mathbf{J}), \quad (5.47)$$

where $p(\mathbf{k}, t)$ is the Fourier transform of the pressure at $(\mathbf{r}, t)$. The

† The ration of the intensities of the central line to the total intensity of the Brillouin lines is $\gamma - 1$.

$\mathbf{J}(\mathbf{k}, t)$ can be separated into three orthogonal components, $J_{\parallel}(\mathbf{k}, t)$, $J_{\perp,1}(\mathbf{k}, t)$, and $J_{\perp,2}(\mathbf{k}, t)$, which are the components of the flux density parallel and perpendicular to the vector $\mathbf{k}$. From Eq. (5.47), it follows that

$$m\varrho_0(\partial/\partial t)J_{\parallel}(\mathbf{k}, t) = -i\mathbf{k}p(\mathbf{k}, t) - (\tfrac{4}{3}\eta_s + \eta_v)k^2 J_{\parallel}(\mathbf{k}, t) \quad (5.48a)$$

$$m\varrho_0(\partial/\partial t)J_{\perp,\alpha}(\mathbf{k}, t) = -k^2\eta_s J_{\perp,\alpha}(\mathbf{k}, t), \qquad \alpha = 1, 2. \quad (5.48b)$$

The Fourier transform of the equation of continuity is

$$(\partial/\partial t)\varrho_k(t) = -\varrho_0 ikJ_{\parallel}(\mathbf{k}, t), \quad (5.48c)$$

since the Fourier transform of $\nabla\cdot\mathbf{v}(\mathbf{r}, t)$ is $-i\mathbf{k}\cdot\mathbf{J}(\mathbf{k}, t)$ $[= -ikJ_{\parallel}(\mathbf{k}, t)]$. It can be concluded from the linearized hydrodynamic equations that the transverse current is coupled neither to the density ϱ_k nor the entropy s_k. Equation (5.48b) can consequently be solved independently of the other hydrodynamic equations,

$$J_{\perp,\alpha}(\mathbf{k}, t) = J_{\perp,\alpha}(\mathbf{k}, 0)\exp -k^2\nu t. \quad (5.49)$$

Here, $J_{\perp\alpha}(\mathbf{k}, 0)$ is the initial value of $J_{\perp,\alpha}$ and ν is the kinematic viscosity coefficient,

$$\nu = \eta_s/m\varrho_0. \quad (5.50)$$

The time correlation function of $J_{\perp,\alpha}$ is found by multiplying by $J_{\perp,\alpha}(-\mathbf{k}, 0)$ and averaging over the equilibrium ensemble. Because the fluid is isotropic, $J_{\perp,1}(\mathbf{k}, t)$ and $J_{\perp,2}(\mathbf{k}, t)$ have identical time correlation functions. We can thus drop the subscript α. Let $C_{\perp}(\mathbf{k}, t)$ stand for this normalized time correlation function; then

$$C_{\perp}(\mathbf{k}, t) \equiv \langle J_{\perp}^*(\mathbf{k}, 0)J_{\perp}(\mathbf{k}, t)\rangle/\langle J_{\perp}^*(\mathbf{k})J_{\perp}(\mathbf{k})\rangle. \quad (5.51)$$

Consequently, in the hydrodynamic limit (small k),

$$C_{\perp}(\mathbf{k}, t) = \exp -k^2\nu t. \quad (5.52)$$

It should be noted that the microscopic current density at the space–time point $(\mathbf{r}, t)$ is

$$\mathbf{v}(\mathbf{r}, t) = \sum_{j=1}^{N} \mathbf{v}_j\delta(\mathbf{r} - \mathbf{r}_j(t)), \quad (5.53a)$$

where $\mathbf{v}_j$ is the velocity and $\mathbf{r}_j$ is the position of the jth particle. It follows that

$$\mathbf{J}(\mathbf{k}, t) = \sum_{j=1}^{N} \mathbf{v}_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \quad (5.53b)$$

If the coordinate system is so defined that $\mathbf{k}$ points in the z direction, then

$$J_{\parallel}(\mathbf{k}, t) = \sum_{j=1}^{N} \dot{z}_j(t) e^{ikz_j(t)},$$
$$J_{\perp,1}(\mathbf{k}, t) = \sum_{j=1}^{N} \dot{x}_j(t) e^{ikz_j(t)}, \tag{5.54}$$
$$J_{\perp,2}(\mathbf{k}, t) = \sum_{j=1}^{N} \dot{y}_j(t) e^{ikz_j(t)}.$$

$C_{\perp}(\mathbf{k}, t)$ is a normalized time correlation function of the property

$$U_2 \equiv J_{\perp}(\mathbf{k})/\langle J_{\perp}(\mathbf{k}) \mid J_{\perp}(\mathbf{k})\rangle^{1/2}. \tag{5.55a}$$

It follows from Section III that $C_{\perp}(\mathbf{k}, t)$ obeys the memory-function equation

$$(\partial/\partial t) C_{\perp}(\mathbf{k}, t) = -\int_0^t d\tau\, K_{\perp}(\mathbf{k}, \tau) C_{\perp}(\mathbf{k}, t-\tau), \tag{5.55b}$$

where the memory function is

$$K_{\perp}(\mathbf{k}, t) \equiv \langle iLU_2 \mid \exp[i(1-\hat{P}_2)Lt] \mid iLU_2\rangle, \tag{5.55c}$$
$$\hat{P}_2 \equiv \mid U_2\rangle\langle U_2 \mid.$$

It follows from the properties of U_2 that $C_{\perp}(\mathbf{k}, t)$ and $K_{\perp}(\mathbf{k}, t)$ are even functions of $\mathbf{k}$ and t.

The memory-function equation can be solved in terms of the Laplace transforms $\tilde{C}_{\perp}(\mathbf{k}, s)$ and $\tilde{K}_{\perp}(\mathbf{k}, s)$ of $C_{\perp}(\mathbf{k}, t)$ and $K_{\perp}(\mathbf{k}, t)$. Since $C_{\perp}(\mathbf{k}, t = 0) = 1$, it follows from Eq. (5.55b) that

$$\tilde{C}_{\perp}(\mathbf{k}, s) = [s + \tilde{K}_{\perp}(\mathbf{k}, s)]^{-1}. \tag{5.56}$$

This should be compared with the Laplace transformation of the hydrodynamic equation Eq. (5.52),

$$\tilde{C}_{\perp}(\mathbf{k}, s) = [s + k^2\nu]^{-1}. \tag{5.57}$$

Clearly, the exact solution [Eq. (5.55b)] involves a complicated k- and s-dependent kinematic viscosity. Our goal is to show how the exact $C_{\perp}(\mathbf{k}, t)$ reduces to the hydrodynamic limit $\exp -k^2\nu t$. Let us be guided by the hydrodynamic correlation function

$$C_{\perp}(\mathbf{k}, t) = \exp -k^2\nu t.$$

As in the case of self-diffusion, the time dependence is always associated with the vector $\mathbf{k}$ in the combination k^2t. Let us again redefine the time scale to be (Zwanzig, 1964)

$$\tau = k^2 t. \tag{5.58}$$

Then, in the hydrodynamic limit, $C_{\perp}(\mathbf{k}, t) = e^{-\nu\tau}$. Consider the double limit

$$\lim_{\substack{t\to\infty \\ \tau=\text{const}}} \lim_{k\to 0} C_{\perp}(\mathbf{k}, t) = e^{-\nu\tau}. \tag{5.59}$$

Consequently, the decay of $\exp -k^2\nu t$ does not change in this double limit. Thus, we expect this limit to select out the proper small-k and large-t behavior (the hydrodynamic limit) of the exact correlation function.

The inverse transform of Eq. (5.56) is

$$C_{\perp}(\mathbf{k}, t) = (1/2\pi i)\left(\oint ds\, e^{st}/[s + \tilde{K}_{\perp}(\mathbf{k}, s)]\right). \tag{5.60}$$

Now we introduce the new time variable $\tau = k^2t$ and a corresponding new Laplace variable $s = k^2x$.

$$C_{\perp}(\mathbf{k}, t) = (1/2\pi i)\left(\oint dx\, e^{x\tau}/[x + (1/k^2)\tilde{K}_{\perp}(\mathbf{k}, s)]\right). \tag{5.61}$$

We now take the double limit of Eq. (5.59), keeping τ fixed. Provided that $(1/k^2)\tilde{K}_{\perp}(\mathbf{k}, s)$ is a continuous function of k and s at (0, 0), the limit yields

$$\lim_{\substack{t\to\infty \\ \tau=\text{const}}} \lim_{k\to 0} C_{\perp}(\mathbf{k}, t) = (1/2\pi i)\left(\oint dx\, e^{x\tau}/[x + \lim_{k\to 0} \tilde{K}_{\perp}(\mathbf{k}, k^2x)]\right)$$
$$= \exp[-\lim_{k\to 0} (1/k^2)\tilde{K}_{\perp}(\mathbf{k}, k^2x)\tau]. \tag{5.62}$$

Comparison with Eq. (5.59) shows that the kinematic viscosity is

$$\nu \equiv \lim_{k\to 0} (1/k^2)\tilde{K}_{\perp}(\mathbf{k}, k^2x).$$

Since continuity at (0, 0) is assumed (it cannot be proved),

$$\nu = \lim_{s\to 0} \lim_{k\to 0} (1/k^2)\tilde{K}_{\perp}(\mathbf{k}, s). \tag{5.63}$$

This expression can be put in a much more useful form. Consider the

functions

$$\tilde{\Phi}_\perp(\mathbf{k}, s) \equiv \langle iLU_2 \,|\, [s - iL]^{-1} \,|\, iLU_2\rangle,$$
$$\tilde{K}_\perp(\mathbf{k}, s) \equiv \langle iLU_2 \,|\, [s - i(1 - \hat{P}_2)L]^{-1} \,|\, iLU_2\rangle \tag{5.64}$$

where, from Eqs. (5.55a) and (5.54)

$$iLU_2 = \sum_{j=1}^{N} [\ddot{x}_j + ik\dot{x}_j\dot{z}_j]e^{ikz_j}/\langle J_2 \,|\, J_2\rangle^{1/2} \tag{5.65a}$$

where $\ddot{x}_j$ is the x component of the acceleration of particle j. For small k, the exponential $\exp ikz_j$ can be expanded and

$$iLU_2 = \left\{\sum_{j=1}^{N} [\ddot{x}_j + ik(\dot{z}_j\dot{x}_j + \ddot{x}_j z_j)] + O(k^2)\right\} \Big/ \langle J_2 \,|\, J_2\rangle^{1/2} \tag{5.65b}$$

It should be noted that, in the absence of external forces acting on the fluid, $\sum_{j=1}^{N} \ddot{x}_j = 0$, so that

$$iLU_2 = \left\{ik \sum_{j=1}^{N} (\dot{z}_j\dot{x}_j + \ddot{x}_j z_j) + O(k^2)\right\} \Big/ \langle J_2 \,|\, J_2\rangle^{1/2}. \tag{5.65c}$$

Thus,

$$\tilde{\Phi}_\perp(\mathbf{k}, s) = 1/m^2\{k^2\langle \sigma_{zx} \,|\, [s - iL]^{-1} \,|\, \sigma_{zx}\rangle + O(k^2)\}/\langle J_2 \,|\, J_2\rangle^{1/2} \tag{5.66a}$$

and

$$\tilde{K}_\perp(\mathbf{k}, s) = 1/m^2\{k^2\langle \sigma_{zx} \,|\, [s - i(1 - \hat{P}_2)L]^{-1} \,|\, \sigma_{zx}\rangle + O(k^2)\}/\langle J_2 \,|\, J_2\rangle^{1/2} \tag{5.66b}$$

where

$$\sigma_{zx} \equiv \sum_{j=1}^{N} m(\dot{z}_j\dot{x}_j + \ddot{x}_j z_j) = \sum_{j=1}^{N} [p_j^z p_j^x/m + F_j^x z_j] \tag{5.66c}$$

is the zxth component of the "stress tensor."

The functions $\tilde{\Phi}_\perp$ and $\tilde{K}_\perp$ are related to each other [see Eq. (3.13a)],

$$(1/k^2)\tilde{\Phi}_\perp(\mathbf{k}, s) = [1 + (1/s)\tilde{K}_\perp(\mathbf{k}, s)]^{-1}(1/k^2)\tilde{K}_\perp(\mathbf{k}, s). \tag{5.67}$$

The same considerations apply here as in self-diffusion [see the paragraph below Eq. (5.24)]. Then, since $\lim_{s\to 0}\lim_{k\to 0}(1/s)\tilde{K}_\perp(\mathbf{k}, s) = 0$, it follows from Eq. (5.67) that

$$\lim_{s\to 0}\lim_{k\to 0}(1/k^2)\,\tilde{\Phi}_\perp(\mathbf{k}, s) = \lim_{s\to 0}\lim_{k\to 0}(1/k^2)\tilde{K}_\perp(\mathbf{k}, s) \tag{5.68}$$

and from Eq. (5.63) that

$$\nu = \lim_{s\to 0}\lim_{k\to 0}(1/k^2)\Phi_\perp(\mathbf{k}, s)$$

or

$$\nu = \lim_{s\to 0}(1/m^2)\int_0^\infty dt\, e^{-st}\langle \sigma_{zx}(0)\sigma_{zx}(t)\rangle/\langle J_2 \,|\, J_2\rangle. \tag{5.69a}$$

The shear viscosity is thus

$$\eta_s = \lim_{s\to 0}(1/VkT)\int_0^\infty dt\, e^{-st}\langle \sigma_{zx}(0)\sigma_{zx}(t)\rangle \tag{5.69b}$$

This is the Kubo relation for the shear viscosity. Thus, we have shown that, in the long-time, small-k limit, the transverse current correlation function correctly reduces to the hydrodynamic limit with the shear viscosity given by the Kubo relation. The same conclusion would be reached for the remaining hydrodynamic variables. $S(\mathbf{k}, \omega)$ would reduce to Eq. (5.46) and the remaining transport coefficients would be given by their corresponding Kubo relations.

In the remaining part of this subsection, we investigate the opposite limit, where k and ω are quite large. For illustrative purposes, we consider only $C_\perp(\mathbf{k}, t)$. The memory function has the property that

$$K_\perp(\mathbf{k}, 0) = \langle iLU_2 \,|\, iLU_2\rangle \equiv \omega_t^2(k). \tag{5.70a}$$

According to Eq. (5.65a), this is

$$\omega_t^2(k) = \langle \,|\, \sum_{j=1}^{N} (\ddot{x}_j + ik\dot{x}_j z_j)\exp[ikz_j] \,|^2\rangle \Big/ \langle \,|\, \sum_{j=1}^{N} \dot{x}_j \exp[ikz_j] \,|^2\rangle. \tag{5.70b}$$

This moment can be written in terms of the pair potential $U(r)$, and the radial distribution function,

$$\omega_t^2(k) = k^2/m\beta + \langle(1 - \cos kz)\,\partial^2 U/\partial x^2\rangle/m. \tag{5.70c}$$

A normalized memory function $\psi_\perp(\mathbf{k}, t)$ can be defined as

$$K_\perp(\mathbf{k}, t) = K_\perp(\mathbf{k}, 0)\psi_\perp(\mathbf{k}, t) = \omega_\perp^2(k)\psi_\perp(\mathbf{k}, t), \tag{5.70d}$$

where $\psi_\perp(\mathbf{k}, 0) = 1$. The memory-function equation is then

$$\partial C_\perp(\mathbf{k}, t)/\partial t = -\,\omega_t^2(k)\int_0^t d\tau\, \psi_\perp(\mathbf{k}, \tau)C_\perp(\mathbf{k}, t - \tau). \tag{5.71}$$

Ailawadi (1969; Ailawadi *et al.*, 1971) has analyzed the time dependence of $C_\perp(\mathbf{k}, t)$ in much the same way that the velocity correlation function was investigated by previous investigators. They tried different functional forms for $\psi_\perp(\mathbf{k}, t)$. We only present one form here. We adopt the form suggested by information theory, according to which the optimal memory function corresponding to knowledge of the second moment of $\psi_\perp(\mathbf{k}, t)$ is [see Eq. (3.118)]

$$\psi_\perp(\mathbf{k}, t) = \exp -\tfrac{1}{2}t^2[\langle \dot{U}_2 \mid \dot{U}_2\rangle/\langle \dot{U}_2 \mid \dot{U}_2\rangle - \langle \dot{U}_2 \mid \dot{U}_2\rangle], \qquad (5.72)$$

where $\dot{U}_2 = iLU_2$ and $\ddot{U}_2 = (iL)^2U_2$. The coefficient of t^2 in the exponent involves equilibrium moments. They can be determined if the equilibrium three-particle distribution function is known (which is the case in only the rarest circumstances). The only option open to us is to evaluate these moments from computer experiment and compare the $C_\perp(\mathbf{k}, t)$ resulting from a solution of Eq. (5.71) with the computer-generated $C_\perp(\mathbf{k}, t)$. This is precisely what Ailawadi and Zwanzig (1969; Ailawadi *et al.*, 1971) did. Rahman (1967) computed $C_\perp(\mathbf{k}, t)$ for liquid argon at a series of large values of k. Ailawadi and Zwanzig then found the coefficient of t^2 in $\psi_\perp(\mathbf{k}, t)$ and compared the $C_\perp(\mathbf{k}, t)$ that resulted with Rahman's data. Their results are shown in Fig. 10. The qualitative agreement should be noted. They also tried other forms of the memory function $\psi_\perp(\mathbf{k}, t)$. Ailawadi and Zwanzig applied this philosophy to the calculation of the longitudinal current-density correlation function,

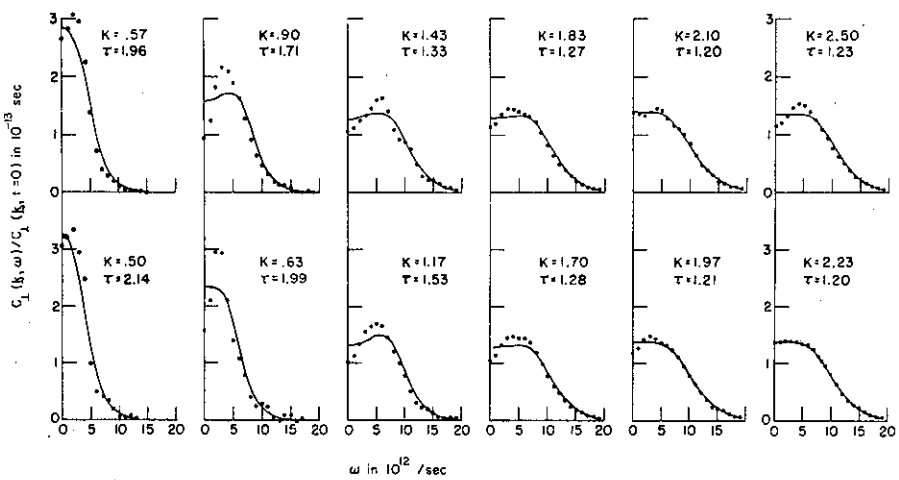

FIG. 10. The power spectrum of the normalized transverse-current correlation function for various values of $k \times 10^8$ cm^{-1} from computer experiments (solid line) and from the Gaussian memory function (dots).

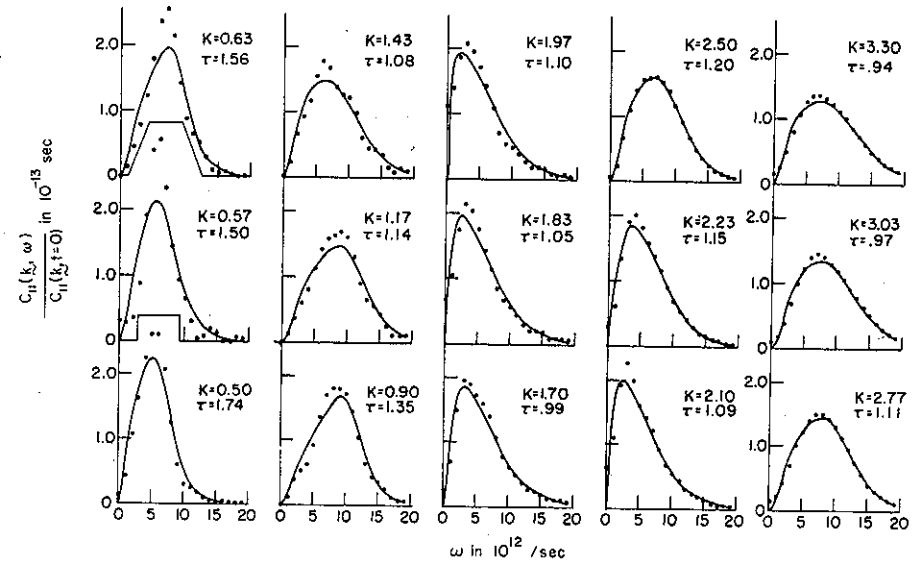

FIG. 11. The power spectrum of the normalized longitudinal current correlation function for various values of $k \times 10^8$ cm^{-1} from computer experiments (solid line), and from the Gaussian memory function (dots).

$$C_\parallel(\mathbf{k}, t) = \langle J_\parallel^*(\mathbf{k}, 0)J_\parallel(\mathbf{k}, t)\rangle/\langle \mid J_\parallel(\mathbf{k}, 0) \mid^2\rangle.$$

These results are presented in Fig. 11. Note the excellent agreement with the computer experiments.

It can be concluded that "generalized hydrodynamics" accounts for both the small-k, large-t, and the large-k, small-t limits of time correlation functions. This represents significant progress in the theory of fluids.

E. The Linear Momentum and Angular Momentum Autocorrelation Functions

The normalized velocity autocorrelation function $\psi(t)$ is

$$\psi(t) \equiv \langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle/\langle \mathbf{v}(0) \cdot \mathbf{v}(0)\rangle \equiv \langle \mathbf{p}(0) \cdot \mathbf{p}(t)\rangle/\langle \mathbf{p}(0) \cdot \mathbf{p}(0)\rangle, \quad (5.73)$$

where $\mathbf{v}$ and $\mathbf{p}$ are the center-of-mass velocity and momentum of a given molecule. This function reflects the single-particle dynamics of atoms in liquids, solids, and gases.

The full time dependence of $\psi(t)$ can in principle be obtained from the incoherent differential scattering cross section for thermal neutrons $[S_s(\mathbf{k}, \omega)]$ in the following way. From Eq. (5.11), we see that

$$-d^2F_s(\mathbf{k}, t)/dt^2 = \mathbf{k} \cdot \langle \mathbf{v} \exp -i\mathbf{k} \cdot \mathbf{r} \mid \exp iLt \mid \mathbf{v} \exp +i\mathbf{k} \cdot \mathbf{r} \rangle \cdot \mathbf{k}$$

It follows from the discussion in Section V,A that

$$-\lim_{k\to 0} (1/k^2)\ddot{F}_s(\mathbf{k}, t) = \tfrac{1}{3} \langle \mathbf{v}(0) \cdot \mathbf{v}(t)\rangle = \tfrac{1}{3} \langle v^2\rangle \psi(t).$$

The Fourier transform of this equation is

$$\lim_{k\to 0} (\omega^2/k^2)S_s(\mathbf{k}, \omega) = \tfrac{1}{3} \langle v^2\rangle G(\omega), \tag{5.74}$$

where $G(\omega)$ is the power spectrum of $\psi(t)$,

$$G(\omega) = \mathrm{Re}\,(1/\pi) \int_0^\infty dt\, e^{-i\omega t}\psi(t) = \mathrm{Re}\,(1/\pi)\tilde{\psi}(i\omega) \tag{5.75}$$

and $\tilde{\psi}(s)$ is the Laplace transform of $\psi(t)$. Thus, a measurement of $S_s(\mathbf{k}, \omega)$ from neutron scattering is sufficient for determining $G(\omega)$ and thereby $\psi(t)$.

The normalized velocity autocorrelation function contains all the information required for the computation of the coefficient of self-diffusion D, or, correspondingly, the friction coefficient $\gamma = kT/mD$. This follows from the Kubo relation

$$\begin{aligned} D = kT/m\gamma &= \lim_{s\to 0} \tfrac{1}{3}\langle v^2\rangle \tilde{\psi}(s) \\ &= \lim_{\omega\to 0} \tfrac{1}{3}\pi\langle v^2\rangle G(\omega), \end{aligned} \tag{5.76}$$

where $\psi(s) = \int_0^\infty dt\, e^{-st}\psi(t)$ and the last equality follows from Eq. (5.29). Substitution of Eq. (5.74) shows that D(or γ) can be determined directly from neutron scattering,

$$D = \lim_{\omega\to 0} \lim_{k\to 0} (\pi\omega^2/k^2)S_s(\mathbf{k}, \omega). \tag{5.77}$$

This should not be surprising, since $F_s(\mathbf{k}, t)$ contains $\psi(t)$ through $\langle \Delta r^2(t)\rangle$.

The memory-function equation for $\psi(t)$ is

$$\partial\psi(t)/\partial t = -\int_0^t d\tau\, K_\psi(\tau)\psi(t-\tau). \tag{5.78}$$

This is to be solved subject to the initial condition $\psi(0) = 1$. The Laplace transform of Eq. (5.78) yields the solution

$$\begin{aligned} \tilde{\psi}(s) &= 1/[s + \tilde{K}_\psi(s)] \\ \psi(t) &= (1/2\pi i)(\oint ds\, e^{st}[s + \tilde{K}_\psi(s)]), \end{aligned} \tag{5.79}$$

where $\tilde{K}_\psi(s)$ is the Laplace transform of $K_\psi(t)$. From Eq. (5.76), it follows that the friction coefficient γ, is

$$\gamma = \lim_{s\to 0} \tilde{K}_\psi(s). \tag{5.80}$$

Only for special cases can $\psi(t)$ or $K_\psi(t)$ be determined analytically. For example: for a free particle, $\psi(t) \equiv 1$; for a Brownian particle, $\psi(t) = e^{-\gamma|t|}$; and for a particle performing perfect harmonic motion of frequency ω_0, $\psi(t) = \cos \omega_0 t$. The models for which $\psi(t)$ has been computed exactly are (1) the classical motion of a particle in a box (Nossal, 1965), (2) the quantum-mechanical motion of a particle in a box (Kinsey *et al.*, 1969), the Brownian motion of a particle in a classical lattice of one, two, and three dimensions (Rubin, 1961), (4) the motion of a particle in a three-dimensional quantum harmonic lattice, and (5) the motion of a particle in a one-dimensional, many-body system of hard rods (hard spheres in one dimension) (Lebowitz, Percus, and Sykes, 1969).

The first thing that will be demonstrated in this section is how the exponential form of $\psi(t)$,

$$\psi(t) = e^{-\gamma|t|} = e^{-\zeta|t|/M}, \tag{5.81}$$

for the motion of a heavy particle (Brownian particle) of mass M in a fluid of light particles of mass m follows from the memory-function equation for $\psi(t)$. For simplicity, it is assumed that the B particle is identical in every respect to the solvent particles except that $M \gg m$. It follows from this assumption that the pair potential between a fluid and a Brownian particle is identical to the pair potential between two fluid particles, so that the mean-square force on the B particle is the same as the mean-square force acting on a fluid particle. The B particle will travel on the average with a much smaller velocity $\mathbf{V}$ than the fluid particles since $\langle V^2\rangle = 3kT/M$. It follows from these considerations that the Liouville operator L can be separated into a part L_f and a part L_B, where

$$\begin{aligned} iL_f &= \sum_{j=1}^{N} [\mathbf{v}_j \cdot \partial/\partial\mathbf{r}_j + \mathbf{F}_j \cdot \partial/\partial\mathbf{p}_j], \quad N \text{ fluid atoms}, \\ iL_B &= \mathbf{V} \cdot \partial/\partial\mathbf{R} + \mathbf{F}_B \cdot \partial/\partial\mathbf{P}, \end{aligned} \tag{5.82}$$

where $\mathbf{F}_j$ is the force on particle j (contains interactions with the B particle) and $\mathbf{F}_B$ is the force exerted on the B particle by the fluid particles. In an equilibrium system, the velocity $\mathbf{V}$ will fluctuate with a root-mean-square value proportional to $M^{-1/2}$. If we are only interested in fluctuations of this order, it follows that iL_B is of order $(m/M)^{1/2}$ compared with iL_f. Thus, in the limit of infinite mass for the B particle, the effects of iL_B are expected to be negligible compared to iL_f.

The memory function $K_\psi(t)$ for the B particle can be written as

$$\begin{aligned} K_\psi(t) &= \langle \mathbf{a} \mid \exp[i(1-\hat{P})Lt] \mid \mathbf{a}\rangle / \langle V^2\rangle \\ &= (3MkT)^{-1}\langle \mathbf{F}_B \mid \exp[i(1-\hat{P})(L_f+L_B)t] \mid \mathbf{F}_B\rangle, \end{aligned} \tag{5.83}$$

where $\mathbf{F}_B$ is the force acting on the B particle. This formula follows from Eq. (3.44).

The normalized velocity correlation function for a B particle is, according to the phenomenological theory of B motion,

$$\psi(t) = e^{-\zeta t/M},$$

where the friction constant ζ is determined from hydrodynamics (Chandrasekhar, 1945)

$$\zeta = 6\pi\eta_s a.$$

This is called the Stokes formula. Here, η_s is the shear viscosity of the fluid and a is the radius of the B particle. It should be noted that, if the radius of the B particle is held fixed, ζ does not change as $M \to \infty$. Consequently, in Brownian-motion theory the time dependence of a $\psi(t)$ is associated with the mass in the combination t/M. Let us redefine the time scale to be $\tau = t/M$. Then $\psi(t)$ goes as $e^{-\zeta\tau}$ Consider the double limit

$$\lim_{\substack{t\to\infty \\ \tau=\text{const}}} \lim_{M\to\infty} \psi(t) = e^{-\zeta\tau}. \tag{5.84}$$

The decay $e^{-\zeta t/M}$ does not change in this limit. Once again, we may determine the Brownian $\psi(t)$ from the exact $\psi(t)$ in Eq. (5.79),

$$\psi(t) = (1/2\pi i)\left(\oint ds\, e^{st}[s + \tilde{K}_\psi(s)]\right).$$

Now we introduce the new time variable $\tau = t/M$ and the new Laplace variable $x = Ms$. Then,

$$\psi(t) = (1/2\pi i)\left(\oint dx\, e^{x\tau}[x + M\tilde{K}_\psi(s)]\right). \tag{5.85}$$

Now we take the double limit of this equation, keeping τ fixed. Provided that $\tilde{K}\psi(s)$ is a continuous function of (s,M) at $(0, \infty)$, this limit gives

$$\lim_{\substack{t\to\infty \\ \tau=\text{const}}} \lim_{M\to\infty} \psi(t) = \exp -[\lim_{M\to\infty} M\tilde{K}_\psi(x/M)]\tau. \tag{5.86}$$

Comparison with Eq. (5.84) yields

$$\zeta = \lim_{M\to\infty} M\tilde{K}_\psi(x/M) = \lim_{s\to 0} \lim_{M\to\infty} M\tilde{K}_\psi(s). \tag{5.87}$$

The last equality follows from the assumed continuity of $\tilde{K}(s)$ at $s = 0$ (continuity has not been proved). This expression for the self-diffusion coefficient is still not in its most useful form because $\tilde{K}_\psi(s)$ depends on the projection operator.

Consider the function $\Phi_\psi(t)$,

$$\begin{aligned} \Phi_\psi(t) &= \langle \mathbf{a}(0)\cdot\mathbf{a}(t)\rangle / \langle v^2\rangle \\ &= \langle \mathbf{F}_B(0)\cdot\mathbf{F}_B(t)\rangle / 3MkT \\ &= \langle \mathbf{F}_B \mid \exp[i(L_f+L_B)t] \mid \mathbf{F}_B\rangle / 3MkT. \end{aligned} \tag{5.88}$$

The functions $\Phi_\psi(t)$ and $K_\psi(t)$ are related through their Laplace transforms [see Eq. (3.13a)]

$$M\tilde{\Phi}_\psi(s) = MK_\psi(s)/[1 + (1/s)\tilde{K}_\psi(s)], \tag{5.89}$$

where $\tilde{K}_\psi(s)$ is given explicitly in Eq. (5.83). Since both $\tilde{K}_\psi(s)$ and $\tilde{\Phi}_\psi(s)$ depend on the mass of the B particle only through L_B and the denominator $3MkT$, it follows that

$$\lim_{s\to 0} \lim_{M\to\infty} (1/s)\tilde{K}_\psi(s) = 0, \tag{5.90}$$

and consequently,

$$\lim_{s\to 0} \lim_{M\to\infty} M\tilde{K}_\psi(s) = \lim_{s\to 0} \lim_{M\to\infty} M\tilde{\Phi}_\psi(s). \tag{5.91}$$

Thus, the friction coefficient ζ is determined by the force autocorrelation function $\Phi_\psi(t)$. Combining Eqs. (5.87) and (5.91),

$$\zeta = \lim_{s\to 0} \lim_{M\to\infty} M\tilde{\Phi}_\psi(s). \tag{5.92}$$

Now, from Eq. (5.88), it follows that

$$M\tilde{\Phi}_\psi(s) = \frac{1}{3kT}\left\langle \mathbf{F}_B \,\middle|\, \frac{1}{s - i(L_f + L_B)} \,\middle|\, \mathbf{F}_B \right\rangle \tag{5.93}$$

The limit as $M \to \infty$ is consequently

$$\lim_{M\to\infty} M\tilde{\Phi}_\psi(s) = \frac{1}{3kT}\left\langle \mathbf{F}_\mathrm{B} \left| \frac{1}{s - iL_\mathrm{f}} \right| \mathbf{F}_\mathrm{B} \right\rangle. \tag{5.94}$$

This follows from the dependence of $\mathbf{F}_\mathrm{B}$ only on the pair potentials, and the dependence of L_B on $M^{-1/2}$. Thus, the friction constant is given by the formula

$$\zeta = \lim_{s\to 0} (1/3kT) \int_0^\infty dt \exp[-st]\langle \mathbf{F}_\mathrm{B} \cdot (\exp iL_\mathrm{f}t)\mathbf{F}_\mathrm{B}\rangle. \tag{5.95}$$

This formula was first derived by Kirkwood in an entirely different way. It is completely consistent with the exact treatment of Brownian motion first developed by Lebowitz and Rubin (1963).

We conclude this discussion of Brownian motion by describing how ζ can be determined by computer experiment. Since only L_f appears in the propagator of the time correlation function, the system should consist of a particle held fixed in the fluid (infinite mass). The fluid particles then

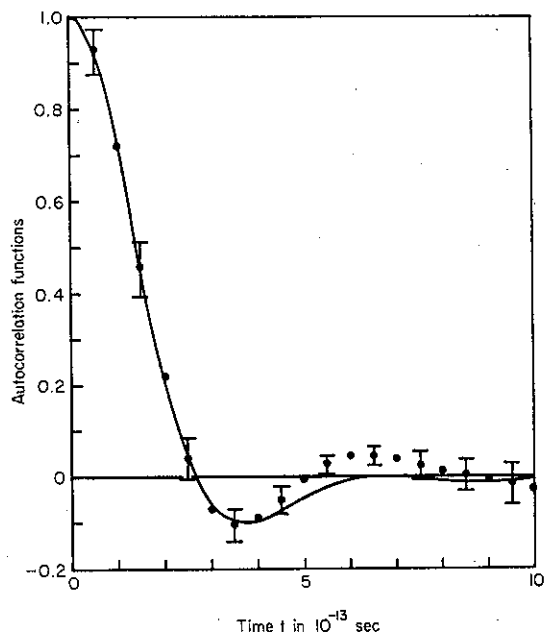

FIG. 12. The normalized velocity autocorrelation function for the COM motion of CO molecules from computer experiments (modified Stockmayer potential).

move in the central force of this fixed particle (which is identical to the fluid particles in all other respects). The total force exerted by the fluid particles on the fixed particle is $\mathbf{F}_\mathrm{B}$. The time correlation function of this force then is determined by the methods of Section IV,B. Then the friction coefficient is determined by integration. This coefficient is independent of the B-particle mass. Thus, for a B particle of finite mass, it is expected that $\psi(t) = e^{-\zeta t/M}$, with ζ determined by the computer experiment.

The normalized time correlation function $\psi(t)$ in liquids has (compared to B motion) a complicated non exponential dependence on time. One feature that is present in all computer experiments can be summarized as follows (Harp and Berne, 1970). There is an interval of time for which the center-of-mass velocity autocorrelation function is negative. See, for example, Figs. 12 and 13. The negative region indicates that, on the average, a displacement of a molecule toward its nearest neighbors is followed by a displacement back toward its initial position. The time at which $\psi(t)$ goes negative, t_-, can be approximately computed from the nearest-

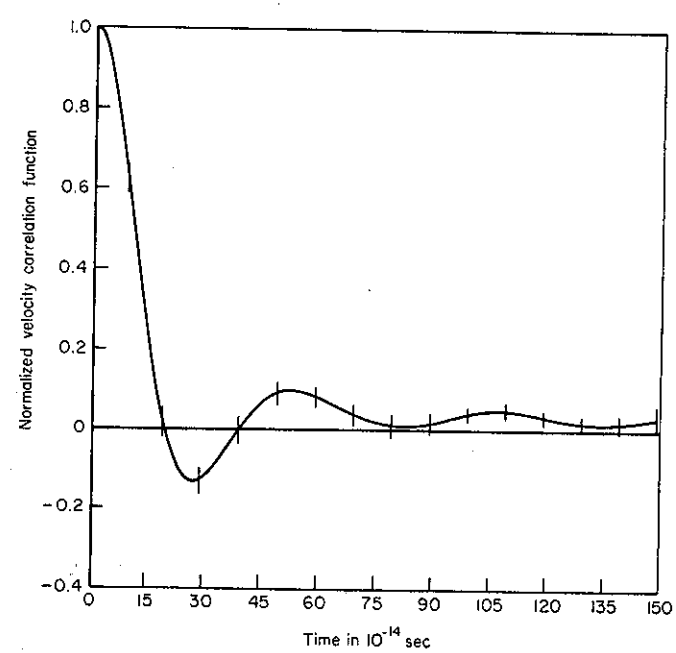

FIG. 13. The normalized velocity autocorrelation function (for 150 time origins) for a one-dimensional system of Lennard-Jones (6–12) particles.

neighbor distance l (position of first peak in the pair correlation function) the diameter of the molecules σ, and the root-mean-square velocity, $\langle v^2\rangle^{1/2}$. Then the velocity turning point $t_- \approx (l - \sigma)/\langle v^2\rangle^{1/2}$. Since $\psi(t)$ goes negative, the events leading to the decay of these functions are correlated. In other words, a molecule must retain some memory of its interactions for a finite time period. Later, we shall construct a theory for $\psi(t)$ that accounts for these empirical observations. It suffices to say that we have also determined $K_\psi(t)$ from our computer experiments. The normalized velocity correlation functions and their corresponding memory functions are presented in Figs. 14 and 15.

The center-of-mass velocity correlation function depends on changes in both the magnitude and the direction of the center-of-mass velocity. Therefore, it is interesting to determine which of these changes contributes most to the overall time dependence of $\psi(t)$. In order to investigate this problem, we have determined the correlation functions

$$\sigma(t) = \langle s(0)s(t)\rangle/\langle s^2\rangle, \qquad D(t) = \langle \mathbf{e}(0)\cdot\mathbf{e}(t)\rangle, \tag{5.96}$$

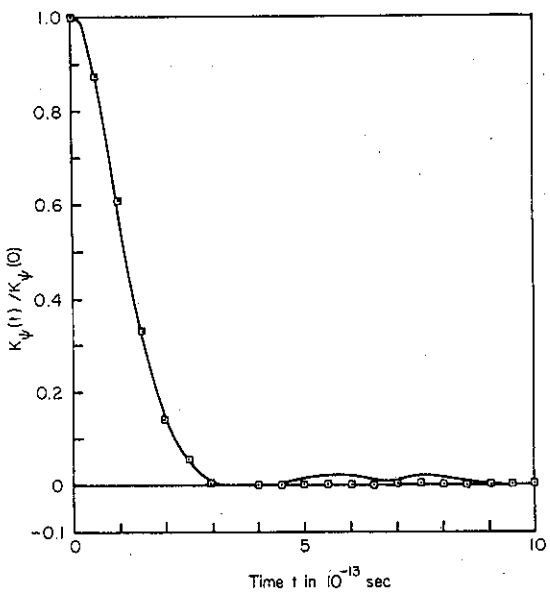

FIG. 14. The normalized memory function $K_\psi(t)/K_\psi(0)$ corresponding to the velocity autocorrelation function from computer experiments (solid line) and from the Gaussian II approximation (squares).

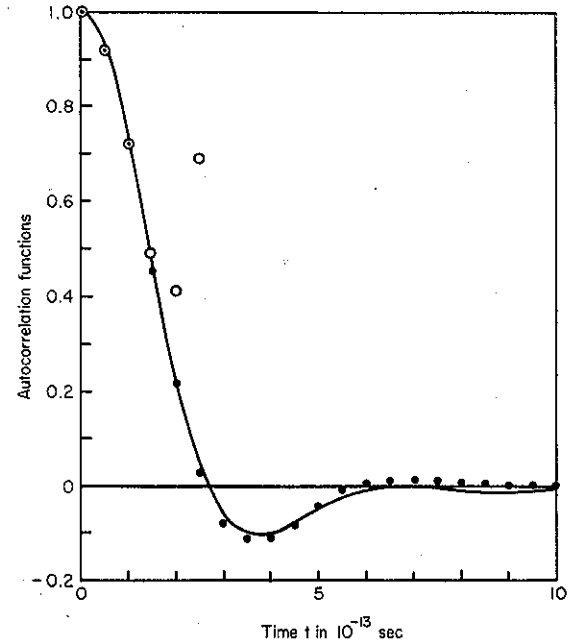

FIG. 15. The normalized velocity autocorrelation functions from the computer experiment (solid line), the Gaussian II memory function (solid dots), and the short time expansion corresponding to the memory functions in Fig. 14 (open dots): $\psi(t) = 1 - \frac{1}{2}(\langle a^2\rangle/\langle v^2\rangle)t^2 + \frac{1}{24}(\langle \dot{a}^2\rangle/\langle v^2\rangle)t^4$.

where $s(t) = |\mathbf{v}(t)|$ is the speed of the molecule at time t and $\mathbf{e}(t) = \mathbf{v}(t)/|\mathbf{v}(t)|$ is the direction of its velocity at the same time $[\mathbf{v}(t) = s(t)\mathbf{e}(t)]$. Now, $\sigma(t)$ and $D(t)$ have the following properties

$$\begin{aligned} &\lim_{t\to\infty} \sigma(t) = \langle s\rangle^2/\langle s^2\rangle = 8/3\pi, \qquad \sigma(0) = 1 \\ &\lim_{t\to\infty} D(t) = \langle \mathbf{e}\rangle\cdot\langle \mathbf{e}\rangle = 0, \qquad D(0) = 1. \end{aligned} \tag{5.97}$$

In Fig. 16 $\psi(t)$, $\sigma(t)$, and $D(t)$ are presented. It should be noted that $D(t)$ and $\psi(t)$ are indistinguishable within the errors (indicated by bars) of the computer experiment. This same conclusion obtains in all the liquids that we have studied by computer experiment. This conclusion might be useful since it indicates that $\Psi(t)$ can be determined from the theoretically simpler function $D(t)$.

The first attempt to account for the structure of a time correlation function using memory functions was in fact the attempt (Berne *et al.*, 1966)

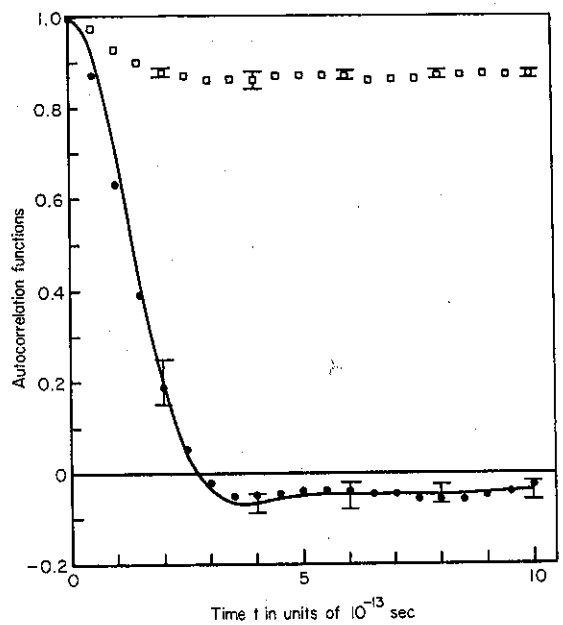

FIG. 16. The normalized velocity correlation function $\psi(t)$ (solid line), directional correlation function $D(t)$ (dots), and speed correlation function $\sigma(t)$ (squares) from computer experiment (modified Stockmayer simulation).

to determine the normalized velocity autocorrelation function $\psi(t)$ based on the simple ansatz that the memory function $K_\psi(t)$,

$$K_\psi(t) = \langle \mathbf{a} \mid \exp i(1 - \hat{P})Lt \mid \mathbf{a}\rangle / \langle v^2 \rangle,$$

depends on a single relaxation time, that is,

$$K_\psi(t) = (\langle a^2 \rangle / \langle v^2 \rangle) e^{-\alpha|t|} \tag{5.98}$$

Since this calculation serves as a prototype for much that has been done in the field of time correlation functions, it is useful to present this work in some detail. It should be kept in mind that precisely the same methods that are discussed in the remainder of this section have been applied by many investigators (Ailwadi, 1969; Ailwadi *et al.*, 1971; Akcasu and Daniels, 1970; Chung and Yip, 1969; Forster *et al.*, 1968a,b; Martin and Yip, 1968; Singwi and Tosi, 1967) to the computation of other correlation functions, i.e., $\langle \varrho_{-k}(0)\varrho_k(t)\rangle$, $C_\perp(\mathbf{k}, t)$, $C_\parallel(\mathbf{k}, t)$, $F_s(\mathbf{k}, t)$, $F(\mathbf{k}, t)$, and many others.

The exponential memory function satisfies the required condition that $K_\psi(0) = \langle a^2 \rangle / \langle v^2 \rangle$. This single-relaxation-time approximation corresponds to a stochastic model in which the fluctuating force has a Lorentzian spectrum. Thus, if the fluctuating force is a Gaussian Markov process, it follows that the memory function must have this simple form. Of course, it would be naive to assume that this exponential memory will accurately account for the dynamical behavior in liquids. It should be regarded as a simple model which has certain qualitative features that we expect real memory functions to have. It decays to zero and, moreover, is of a sufficiently simple mathematical form that the velocity autocorrelation function

$$\psi(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle / \langle v^2 \rangle$$

can be determined analytically from the memory-function equation. That the exponential form of the memory function can never be the exact memory function follows from the fact that it has odd derivatives at the initial instant, and furthermore, its moments, μ_{n2}, do not exist for $n \geqq 1$. The corresponding power spectrum of the velocity will be non-Lorentzian with finite moments γ_{2n} only for $n \leqq 1$. It should be noted that this non-Lorentzian power spectrum is a considerable improvement over more traditional theories according to which the power spectrum of the velocity is Lorentzian (cf. Brownian motion). A Lorentzian power spectrum has finite moments only for $n = 0$, whereas the exponential memory function leads to a velocity power spectrum which has finite moments for $n \leq 1$. It is therefore quite profitable to study the properties of the exponential memory.

To proceed, it is necessary to evaluate the single relaxation time α^{-1}, which appears in Eq. (5.98). This is easily accomplished as follows. The Laplace transform of Eq. (5.98) is

$$\tilde{K}_\psi(s) = \langle a^2 \rangle / \langle v^2 \rangle (s + \alpha). \tag{5.99}$$

From Eq. (5.80) it follows that

$$\gamma = kT/MD = \lim_{s \to 0} \tilde{K}_\psi(s) = (1/\alpha)\langle a^2 \rangle / \langle v^2 \rangle, \tag{5.100}$$

and the relaxation time α^{-1} can be determined from an experimental determination of the friction coefficient γ (or self-diffusion coefficient). It also follows from Eq. (5.76) that

$$1/\gamma = \lim_{s \to 0} \tilde{\psi}(s) = \int_0^\infty dt\, \psi(t). \tag{5.101}$$

Therefore,

$$\alpha = (\langle a^2\rangle/\langle v^2\rangle) \int_0^\infty dt\, \psi(t) \tag{5.102}$$

and the single-relaxation-time memory function is

$$K_\psi(t) = (\langle a^2\rangle/\langle v^2\rangle) \exp\left[-(\langle a^2\rangle/\langle v^2\rangle)t \int_0^\infty dt'\, \psi(t')\right]. \tag{5.103}$$

The velocity autocorrelation function can be obtained by substituting Eq. (5.99) into Eq. (5.79),

$$\psi(t) = (1/2\pi i) \oint ds\, e^{st}[(s + a)/s(s + a) + \langle a^2\rangle/\langle v^2\rangle)]$$

Laplace inversion then yields

$$\psi(t) = [1/(s_+ - s_-)][s_+ e^{s_- t} - s_- e^{s_+ t}], \tag{5.104a}$$

where $s_\pm$ are the roots of the equation $s^2 + \alpha s + \langle a^2\rangle/\langle v^2\rangle = 0$,

$$s_\pm = -\tfrac{1}{2}\alpha\{1 \pm [1 - 4\langle a^2\rangle/\langle v^2\rangle\alpha^2]^{1/2}\} \tag{5.104b}$$

Depending on the values of $\langle a^2\rangle$, $\langle v^2\rangle$, and γ, these roots can be complex. Explicity, if

$$D < 2(kT/M)/[\langle a^2\rangle/\langle v^2\rangle]^{1/2},$$

the roots will be complex and $\psi(t)$ will oscillate so that

$$\psi(t) = e^{-\alpha t/2}\{\cos(\tfrac{1}{2}\lambda\alpha t) + (1/\lambda)\sin(\tfrac{1}{2}\lambda\alpha t)\},$$

where

$$\lambda = [-1 + 4(\langle a^2\rangle/\langle v^2\rangle)(1/\alpha^2)]^{1/2}. \tag{5.105}$$

The power spectrum of the velocity correlation function is, consequently,

$$G(\omega) = (2/\pi)[s_+ s_-(s_+ + s_-)/(s_+^2 + \omega^2)(s_-^2 + \omega^2)], \tag{5.106}$$

and goes asymptotically as $1/\omega^4$. This is why γ_{2n} does not exist for $n \geq 1$. The exponential memory approximation is presented in Figs. 17 and 18.

This initial attempt to compute the time correlation function was followed by a study of the Gaussian memory function, with no significantly new results (Singwi and Tosi, 1967). The Gaussian memory,

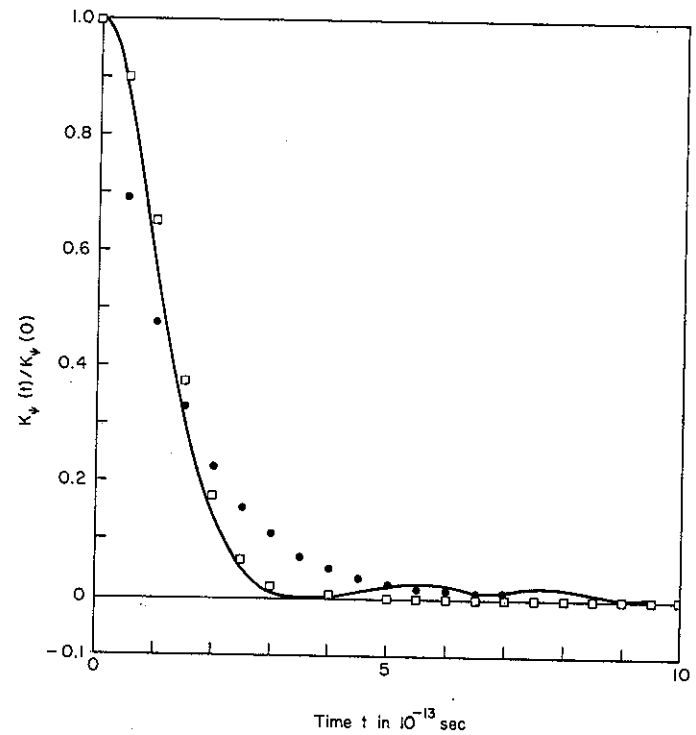

FIG. 17. The normalized memory function $K_\psi(t)/K_\psi(0)$ corresponding to the velocity correlation function from computer experiment (solid line), the exponential memory (dots), and Gaussian I approximation (squares).

adjusted to give the correct diffusion coefficient, is found in exactly the same way as the exponential memory. It turns out to be†

$$K_\psi(t) = (\langle a^2\rangle/\langle v^2\rangle) \exp -\left[(\pi/4)^{1/2}(\langle a^2\rangle/\langle v^2\rangle)t \int_0^\infty dt'\, \psi(t')\right]^2. \tag{5.107}$$

The major advantage of this memory function is that all of its moments are finite. The corresponding velocity correlation function cannot be determined analytically, but must be studied numerically. The results of this approximation appear elsewhere (Harp and Berne, 1970). There are alternative forms of the Gaussian memory function corresponding to $\psi(t)$. From the information-theory calculation of memory functions where only the first two moments are known, it follows that the optimal

† In the following discussion this is referred to as the Gaussian memory I approximation.

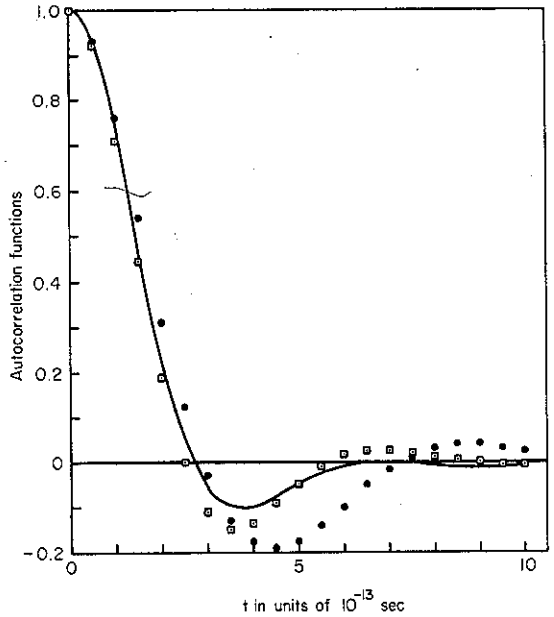

FIG. 18. The normalized velocity autocorrelation functions from the computer experiment (solid line), the Gaussian I memory function (squares), and the short-time expansion corresponding to the memory functions in Fig. 17 (solid dots).

memory function† is

$$K_{vv}(t) = \langle \dot{U}_v \mid \dot{U}_v \rangle \exp - \{\tfrac{1}{2}t^2[\langle \dot{U}_v \mid \dot{U}_v \rangle / \langle \dot{U}_v \mid \dot{U}_v \rangle - \langle \dot{U}_v \mid \dot{U}_v \rangle]\}. \tag{5.108}$$

In this approximation,

$$K_\psi(t) = (\langle a^2 \rangle / \langle v^2 \rangle) \exp - \{\tfrac{1}{2}t^2[\langle \dot{a}^2 \rangle / \langle a^2 \rangle - \langle a^2 \rangle / \langle v^2 \rangle]\}; \tag{5.109}$$

$\psi(t)$ and $K_\psi(t)$ corresponding to this approximation are presented in Figs. 14 and 15. This result can be applied to the calculation of $\psi(t)$ and to the calculation of the friction coefficients. The Laplace transform of $K_\psi(t)$ is such that

$$\lim_{s \to 0} \tilde{K}_\psi(s) = (\pi/2)^{1/2}\mu,$$

where

$$\mu = (\langle a^2 \rangle / \langle v^2 \rangle)[\langle \dot{a}^2 \rangle / \langle a^2 \rangle - \langle a^2 \rangle / \langle v^2 \rangle]^{-1/2}. \tag{5.110}$$

† In the following discussion this approximation is called Gaussian memory II.

Consequently, from Eq. (5.80), it follows that

$$\gamma = \tilde{K}_\psi(0) = (\pi/2)^{1/2}\mu.$$

This is a formula for a transport coefficient (γ) in terms of equilibrium moments. This illustrates a method for determining transport coefficients in terms of equilibrium moments.

Time correlation functions can also be computed from their continued-fraction representations by exploiting a hierarchy of approximations of the following kind. Suppose that the nth-order "random force" has a white spectrum. It follows that

$$K_n(t) = \lambda_n\, \delta(t), \qquad \tilde{K}_n(s) = \lambda_n. \tag{5.111}$$

It is obvious from Eq. (3.113) that this assumption allows the continued-fraction approximation to be truncated at the nth iterate so that

$$\tilde{C}_{vv}(s) = \cfrac{1}{s + \cfrac{\Delta_2^2}{s + \cfrac{\Delta_2^2}{s + \cfrac{\Delta_3^2}{\cfrac{\vdots}{s + \cfrac{\Delta_{n-1}^2}{s + \lambda_n}}}}}}. \tag{5.112}$$

The terms Δ_j^2 are well-defined equilibrium averages. On the other hand, λ_n depends on the integral

$$\lambda_n = \int_0^\infty dt\, K_n(t). \tag{5.113}$$

To proceed, it is necessary to evaluate this coefficient. One possible procedure is to use a measured value of the transport coefficient which is related to $\tilde{C}_{ll}(0)$ through a Kubo relation. Another possibility is to relate λ_n to the moments of $G_{vv}(\omega)$.

This method of approximation is applied to the velocity correlation function, although it can be applied to the other time correlation functions that have been discussed. For the purposes of this illustrative example, let us assume that the second-order random force has a white spectrum. Then, the continued-fraction representation of $\psi(s)$ is

$$\tilde{\psi}(s) = \cfrac{1}{s + \cfrac{\Delta_1^2}{s + \lambda_2}}. \tag{5.114}$$

Comparison with Eq. (296) shows that

$$\tilde{K}_\psi(s) = \Delta_1^2/(s + \lambda_2), \tag{5.115}$$

so that the memory function corresponding to the velocity correlation function is

$$K_\psi(t) = \Delta_1^2\, e^{-\lambda_2 t}. \tag{5.116}$$

This is just the single-relaxation-time memory with

$$\Delta_1^2 = \langle a^2\rangle/\langle v^2\rangle \tag{5.117}$$

and

$$\Delta_1^2/\lambda_2 = \gamma, \tag{5.118}$$

where γ is the friction coefficient. Consequently, the truncation of the continued-fraction expansion at K_2, leads to the simple exponential memory function that we described earlier, Eq. (5.98), and thereby to the corresponding time correlation function. This approximation can be carried through for higher-order truncations. For example, the truncation at $\tilde{K}_3(s)$ yields

$$\tilde{\psi}(s) = \cfrac{1}{s + \cfrac{\Delta_1^2}{s + \cfrac{\Delta_2^2}{s + \lambda_3}}}. \tag{5.119}$$

Δ_1^2 and Δ_2^2 are the well-defined equilibrium moments

$$\begin{aligned} \Delta_1^2 &= \langle f_1 \,|\, f_1\rangle = \langle a^2\rangle/\langle v^2\rangle, \\ \Delta_2^2 &= \langle f_2 \,|\, f_2\rangle = [\langle \dot{a}^2\rangle/\langle a^2\rangle - \langle a^2\rangle/\langle v^2\rangle], \end{aligned} \tag{5.120}$$

which have already been evaluated. The Laplace transform of the memory function is

$$\tilde{K}_\psi(s) = \cfrac{\Delta_1^2}{s + \cfrac{\Delta_2^2}{s + \lambda_3}}. \tag{5.121}$$

The friction coefficient γ is consequently

$$\gamma = \tilde{K}_\psi(0) = \Delta_1^2\lambda_3/\Delta_2^2. \tag{5.122}$$

The parameter λ_3 is consequently

$$\lambda_3 = (\langle v^2\rangle/\langle a^2\rangle)[(\langle \dot{a}^2\rangle/\langle a^2\rangle) - (\langle a^2\rangle/\langle v^2\rangle)]\gamma, \tag{5.123}$$

and can consequently be determined from the experimental value of the friction coefficient. It follows from Eq. (5.119) that

$$\tilde{\psi}(s) = [(s^2 + \Delta_2^2) + s\lambda_3]/[s(\Delta_1^2 + \Delta_2^2 + s^2) + \lambda_3(\Delta_1^2 + s^2)]. \tag{5.124}$$

This expression can be analytically inverted to yield the velocity autocorrelation function. The power spectrum $G(\omega)$ corresponding to this correlation function is

$$G(\omega) = (1/\pi)[\lambda_3\Delta_1^2\Delta_2^2/(\omega^2[\Delta_1^2 + \Delta_2^2 - \omega^2] + \lambda_3^2[\Delta_1^2 - \omega^2]^2)]. \tag{5.125}$$

This power spectrum falls off asymptotically as $1/\omega^6$ and has finite moments μ_{2n} for $n \leq 2$. A comparison of this approximation with experiment is presented in Fig. 19.

The normalized angular momentum autocorrelation function $A_J(t)$ is

$$A_J(t) \equiv \langle \mathbf{J}(0) \cdot \mathbf{J}(t)\rangle/\langle J^2\rangle, \tag{5.126}$$

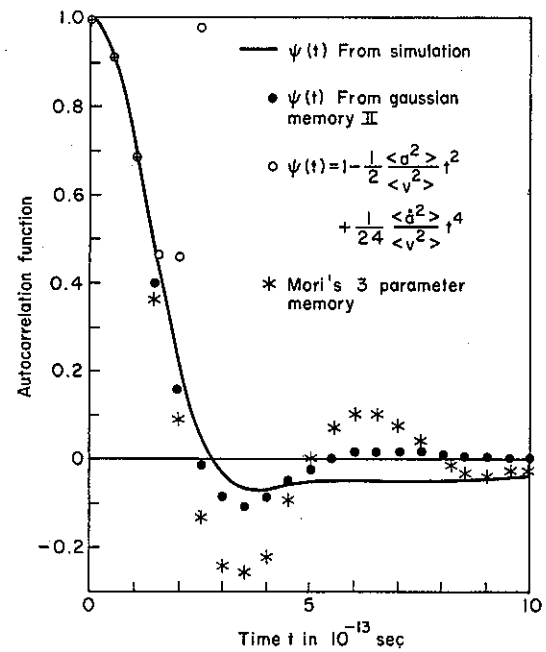

FIG. 19. The normalized velocity autocorrelation function from the computer experiment (modified Stockmayer simulation) and from the third iterate of the continued-fraction representation.

where $\mathbf{J}$ is the angular momentum of the diatomic molecule about its center of mass (COM). Prior to our computer experiments, little, if indeed anything, was known about the full time evolution of $A_J(t)$ in gases or liquids.

The full time dependence of $A_J(t)$ can in principle (but not generally in practice) be determined from NMR experiments. When the relaxation of nuclear spins is dominated by the coupling of the nuclear spins to the rotational motion of the molecules (a rotating molecule generates a magnetic field at the nucleus), the spin relaxation time is determined by the function $A_J(t)$. For nuclei with spin 1/2, the spin–rotation interaction leads to an interaction Hamiltonian $\mathscr{H}' = -c\hat{\mathbf{I}} \cdot \hat{\mathbf{J}}$, where $\hat{\mathbf{I}}$ and $\hat{\mathbf{J}}$ are respectively the nuclear and rotational angular momenta of the molecule and c is the spin–rotation coupling constant. When this is the major contribution to spin relaxation, the spin relaxation time T_I is (Abragam, 1961)

$$(1/T_I) = (2IkTc^2/3\hbar^2)\int_{-\infty}^{+\infty} dt\, e^{-i\omega_0 t}A_J(t) = (IkTc^2/3\pi\hbar^2)G_J(\omega_0). \quad (5.127)$$

This formula follows directly from Section II,D. Here, ω_0 is the Larmor precession frequency ($\omega_0 = \gamma H$), I is the moment of inertia of the diatomic molecule, and $G_J(\omega_0)$ is the power spectrum of the angular momentum. Thus, to find $A_J(t)$, it is necessary to determine $1/T_I$ as a function of the Larmor frequency ω_0; that is, a function of the Zeeman field H, and then to invert the Fourier transform. This is usually impossible to do for a liquid, for the following reason. In liquids, $A_J(t)$ decays on a time scale of order 10^{-12} sec, which is many orders of magnitude faster than typical precessional periods ($1/\omega_0 \sim 10^{-6}$ sec). Thus, the power spectrum $G_J(\omega_0)$ is, to excellent approximation, $G_J(0)$, a constant, for these frequencies. It is precisely because ω_0 can only be varied around such a small value ($\omega_0 \sim 10^{-6}\ \text{sec}^{-1}$) that $G_J(\omega)$ cannot be determined for all frequencies. We conclude that, in liquids, magnetic resonance is only capable of providing the integral

$$\int_0^\infty dt\, A_J(t) = (1/\pi)G_J(0).$$

This integral is also related to the rotational diffusion coefficient D_R, as we now show.

Consider the unit vector $\mathbf{u}(t)$ pointing in the direction of the molecular axis of a rigid rod at time t. The angle that this vector makes with $\mathbf{u}(0)$ is denoted by $\theta(t)$. According to Debye (1929) the rotational diffusion

coefficient, D_R is

$$D_R = \lim_{t\to\infty} \langle\theta^2(t)\rangle/4t. \quad (5.128)$$

The mean-square angular deviation $\langle\theta^2(t)\rangle$ can be found in the following way. Note that the following integral of the angular velocity $\boldsymbol{\omega}(t)$, $\int_0^t dt_1\, \boldsymbol{\omega}(t)$, is a vector whose magnitude is the angular displacement $\theta(t)$. The mean-square angular displacement can consequently be written in terms of this integral as

$$\langle\theta^2(t)\rangle = (1/I^2)\int_0^t dt_1 \int_0^{t_1} dt_2\, \langle \mathbf{J}(t_1)\cdot\mathbf{J}(t_2)\rangle,$$

where I is the moment of inertia of the molecule. The correlation function $\langle \mathbf{J}(t_1)\cdot\mathbf{J}(t_2)\rangle$ is a stationary, even function of the time—a result that follows from the fact that an equilibrium average is being taken,

$$\langle \mathbf{J}(t_1)\cdot\mathbf{J}(t_2)\rangle = \langle \mathbf{J}(0)\cdot\mathbf{J}(t_2 - t_1)\rangle;$$

then,

$$\langle\theta^2(t)\rangle = (2/I^2)\int_0^t dt_1 \int_0^{t_1} dt_2\, \langle \mathbf{J}(0)\cdot\mathbf{J}(t_2 - t_1)\rangle.$$

Introduction of the normalized stationary angular momentum correlation function $A_J(t)$ into this integral, followed by an integration by parts, yields

$$D_R = (\langle J^2\rangle/2I^2)\lim_{t\to\infty}\int_0^t dt'\, [1 - (t'/t)]A_J(t').$$

If the integral $\int_0^\infty dt\, tA_J(t)$ exists, then the above limit is

$$\begin{aligned} D_R &= (kT/I)\int_0^\infty dt\, A_J(t) = (kT/I)\tilde{A}_J(0) \\ &= (kT/\pi I)G_J(0) = kT/I\gamma_R, \end{aligned} \quad (5.129)$$

where the equilibrium mean-square angular momentum $2IkT$ has been used and $\tilde{A}_J(0)$ is the Laplace transform $\tilde{A}_J(s)$ of $A_J(t)$ at $s = 0$. The rotational friction coefficient γ_J is so defined that

$$D_R = kT/I\gamma_R. \quad (5.130)$$

The memory-function equation for $A_J(t)$ is

$$(\partial/\partial t)A_J(t) = -\int_0^t d\tau\, K_J(\tau)A_J(t-\tau). \quad (5.131)$$

This is to be solved subject to the initial condition $A_J(0) = 1$. The Laplace transform of Eq. (5.131) yields solution

$$\tilde{A}_J(s) = 1/[s + \tilde{K}_J(s)]$$
$$A_J(t) = (1/2\pi i)\left(\oint ds\, e^{st}[s + \tilde{K}_J(s)]\right). \tag{5.132}$$

From Eq. (5.129), it follows that the rotational friction coefficient γ_R is

$$\gamma_R = \lim_{s\to 0} \tilde{K}_J(s). \tag{5.133}$$

The detailed behavior of $A_J(t)$ has been determined analytically only for a few very special cases. For example; for a free rotor, $A_J(t) \equiv 1$; for a Brownian rotor, $A_J(t) = e^{-\gamma_R|t|}$, for a torsional harmonic oscillator of frequency ω_0, $A_J(t) = \cos \omega_0 t$, and for a Brownian torsional oscillator, $A_J(t)$ is a damped periodic function.

In the classical theory of rotational Brownian motion, it is assumed that the angular momentum $\mathbf{J}$ satisfies a Langevin equation

$$d\mathbf{J}/dt = -\gamma_R \mathbf{J} + \mathbf{N}(t),$$

where $\mathbf{N}$ is a random torque with properties analogous to the random force in translational B motion [see Eqs. (3.89)]. It follows from a solution of this equation that

$$A_J(t) = e^{-\gamma_R|t|} = e^{-\zeta_R|t|/I}$$

for the motion of a heavy rod of moment of inertia I in a fluid of much lighter molecules. This form of $A_J(t)$ can be deduced from the memory-function equation just as the translational Brownian result was deduced from its corresponding memory function in the previous subsection. The result of this analysis is

$$\zeta_R = \lim_{s\to 0} (1/2kT) \int_0^\infty dt\, e^{-st}\langle \mathbf{N}_B \cdot e^{iL_t t}\mathbf{N}_B\rangle. \tag{5.134}$$

That is, the friction coefficient is given by the correlation function of the torque $\mathbf{N}_B$ acting on a rigid rod held fixed in the fluid. This is analogous to the formula for ζ derived in the last subsection.

Prior to our computer experiments (Berne and Harp, 1970; Harp and Berne, 1970), little if indeed anything had been reported about the full time evolution of the angular momentum autocorrelation function of diatomic molecules in gases and liquids. In most discussions of spin relaxation, it was assumed that $A_J(t)$ was exponential. In our computer experiments, it was shown that in liquids $A_J(t)$ has a complicated nonexponential on the time. All of our computer studies show that in diatomic liquids with potentials that have a strong noncentral character there is an interval of time for which $A_J(t)$ is negative. This negative region indicates that on the average a molecule suffers a sufficiently strong collision with the cage of its nearest neighbors that the torque acting on it is large enough to reverse the direction of its angular momentum. The time at which $A_J(t)$ first goes negative in these cases is comparable to the corresponding time for $\psi(t)$. On the other hand, all of our studies show that, for potentials with weak noncentral character, $A_J(t)$ does not go negative. This complicated behavior of $A_J(t)$, although not known before, is quite expected. Since $A_J(t)$ goes negative, the events contributing to its decay are correlated. The memory function should then decay on the same time scale as $A_J(t)$. It suffices to say that we also determined $K_J(t)$ from computer experiments. Figures 20 and 21 show $A_J(t)$ and its corresponding memory functions.

$A_J(t)$ depends on changes in both the magnitude and direction of $\mathbf{J}$.

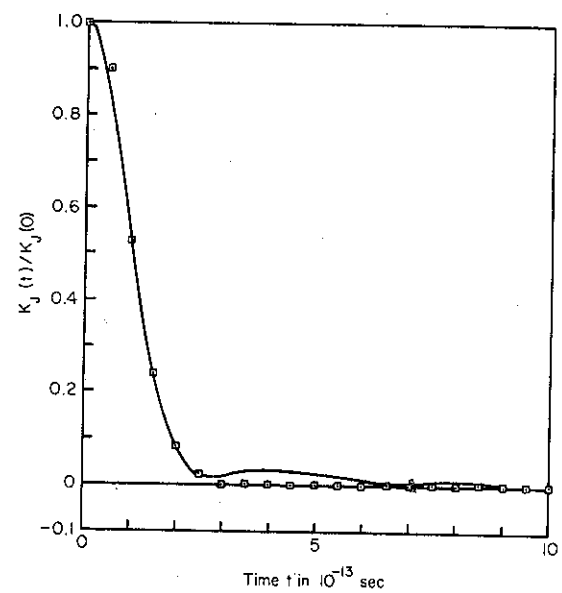

FIG. 20. The normalized memory function $K_J(t)/K_J(0)$ corresponding to the angular momentum autocorrelation function from computer experiment (modified Stockmayer potential) (solid line) and the Gaussian II approximation (squares).

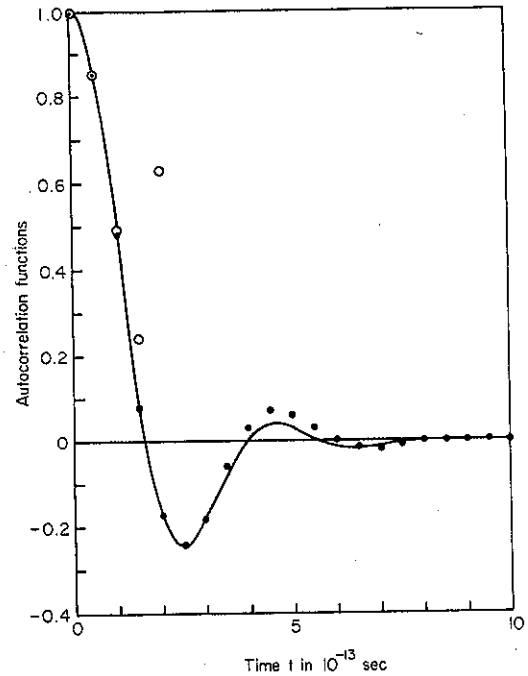

FIG. 21. The normalized angular momentum autocorrelation function $A_J(t)$ from computer experiment (solid line), the Gaussian II memory function (solid dots), and the short-time expansion corresponding to the memory functions in Fig. 20 (open dots): $A_J(t) = 1 - \frac{1}{2}(\langle N^2\rangle/\langle N^2\rangle)t^2 + \frac{1}{24}(\langle N^2\rangle/\langle J^2\rangle)t^2$.

As in the case of the linear center-of-mass velocity, we have determined the correlation functions

$$\begin{aligned} \sigma_J(t) &= \langle \omega(0)\omega(t)\rangle/\langle \omega^2\rangle, \\ D_J(t) &= \langle \mathbf{e}_J(0)\cdot \mathbf{e}_J(t)\rangle, \end{aligned} \tag{5.135}$$

where $\omega(t) = |J(t)|/I$ is the angular speed of the molecule at time t and $\mathbf{e}_J(t) = \mathbf{J}(t)/|\mathbf{J}(t)|$ is the direction of the angular velocity at time t. Here, $\sigma_J(t)$ and $D_J(t)$ have the following properties:

$$\begin{aligned} \lim_{t\to\infty} \sigma_J(t) &= \langle \omega\rangle^2/\langle \omega^2\rangle = \pi/4, \qquad \sigma_J(0) = 1 \\ \lim_{t\to\infty} D_J(t) &= \langle \mathbf{e}_J\rangle\cdot\langle \mathbf{e}_J\rangle = 0, \qquad D_J(0) = 1. \end{aligned} \tag{5.136}$$

In Fig. 22, $A_J(t)$, $J_J(t)$, and $D_J(t)$ are presented. It should be noted that

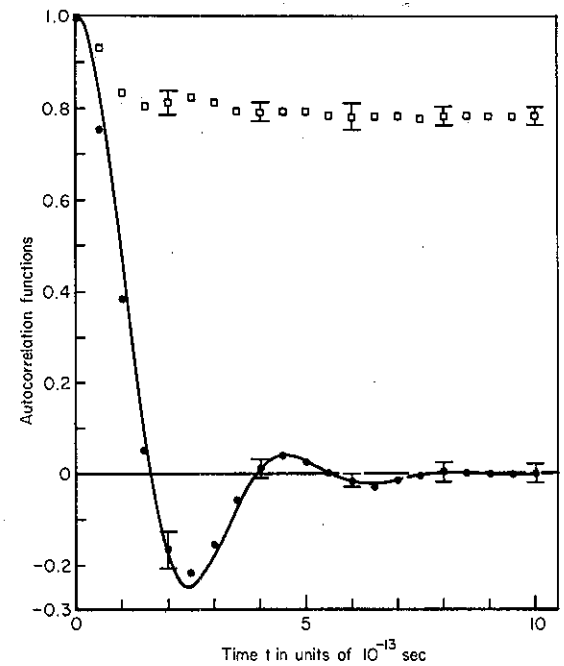

FIG. 22. The normalized angular momentum correlation function $A_J(t)$ (solid line), directional correlation function $D_J(t)$ (dots), and angular speed correlation function $\sigma_J(t)$ (squares), from computer experiment (modified Stockmayer simulation).

$A_J(t)$ and $D_J(t)$ are indistinguishable within the errors of the computer experiment.

The same methods can be used to compute the time correlation function $A_J(t)$ as were applied to the computation of $\psi(t)$ in the last section. We merely summarize the results here.

The exponential memory function

$$\begin{aligned} K_J(t) &= (\langle N^2\rangle/\langle J^2\rangle)\, e^{-\alpha_R|t|} \\ \alpha_R &= (\langle N^2\rangle/\langle J^2\rangle)(1/\gamma_R) = (\langle N^2\rangle/\langle J^2\rangle)\int_0^\infty dt'\, A_J(t'), \end{aligned} \tag{5.137}$$

where $\langle N^2\rangle$ is the mean-square torque acting on a molecule, leads to the normalized time correlation function

$$A_J(t) = [1/(s_+ - s_-)]\{s_+e^{s_-t} - s_-e^{s_+t}\}, \tag{5.138a}$$

where $s_\pm$ are the roots of the equation $s^2 + \alpha_R s + \langle N^2\rangle/\langle J^2\rangle = 0$.

Explicity, if

$$D_R > 2[kT/I]/[\langle N^2\rangle/\langle J^2\rangle],$$

the roots will be complex and $A_J(t)$ will oscillate. This is the case in liquids when the potential is strongly noncentral. According to our computer experiments, the inequality is satisfied. Then,

$$\begin{aligned} A_J(t) &= e^{-\alpha_R/t2}\{\cos[\lambda\alpha_R t/2] + (1/\lambda)\sin[\lambda\alpha_R t/2]\} \\ \lambda &= [4\langle N^2\rangle/\langle J^2\rangle\alpha_R{}^2 - 1]^{1/2} \end{aligned} \tag{5.138b}$$

The Gaussian memory function is

$$\begin{aligned} K_J(t) &= (\langle N^2\rangle/\langle J^2\rangle)\exp-\left[[\tfrac{1}{4}\pi]^{1/2}(\langle N^2\rangle/\langle J^2\rangle)t\int_0^\infty dt' A_J(t')\right]^2 \\ &= (\langle N^2\rangle/\langle J^2\rangle)\exp-[[\tfrac{1}{4}\pi]^{1/2}\langle N^2\rangle t/\langle J^2\rangle\gamma_R]^2 \end{aligned} \tag{5.139}$$

From information theory, when the first two moments of $K_J(t)$ are known, it follows that the optimal memory function is

$$K_J(t) = (\langle N^2\rangle/\langle J^2\rangle)\exp-\{\tfrac{1}{2}t^2[\langle \dot{N}^2\rangle/\langle N^2\rangle - \langle N^2\rangle/\langle J^2\rangle]\}. \tag{5.140}$$

The results of this approximation are presented in Figs. 19 and 20. This result can be applied to the calculation of the rotational friction coefficient in terms of equilibrium moments.

VI. Molecular Orientations in Gases and Liquids

A. Experimental Probes of Molecular Reorientations

Many experiments probe the dynamics of molecular rotational motions in solids, liquids, and gases. For example, neutron-scattering experiments probe both translational and rotational motions of molecules (Egelstaff, 1965, 1967; Sears, 1966a, b; 1967). The differential scattering cross section $(d^2\sigma/d\Omega\, d\omega)$ for a neutron of momentum $\hbar\mathbf{k}_0$ to be scattered into a solid angle $d\Omega$ with final momentum $\hbar\mathbf{k}_f$ and with energy change $\hbar\omega = \hbar^2(k_f{}^2 - k_0{}^2)/2m$ was determined by Van Hove to be

$$\begin{aligned} (d^2\sigma/d\Omega\, d\omega) &= \sum_{\alpha,\beta} (d^2\sigma/d\Omega\, d\omega)_{\alpha,\beta}, \\ (d^2\sigma/d\Omega\, d\omega)_{\alpha,\beta} &= (d^2\sigma/d\Omega\, d\omega)^{\text{inc}}_{\alpha,\alpha}\,\delta_{\alpha,\beta} + (d^2\sigma/d\Omega\, d\omega)^{\text{coh}}_{\alpha,\beta}, \\ (d^2\sigma/d\Omega\, d\omega)^{\text{inc}}_{\alpha,\alpha} &= N_\alpha(k_f/k_0)(a^\alpha_{\text{inc}})^2 S^{\alpha,\alpha}_s(\mathbf{k},\omega), \\ (d^2\sigma/d\Omega\, d\omega)^{\text{coh}}_{\alpha,\beta} &= (N_\alpha N_\beta)^{1/2}(k_f/k_0)(a^\alpha_{\text{coh}})^*(a^\beta_{\text{coh}})S^{\alpha,\beta}(\mathbf{k},\omega). \end{aligned} \tag{6.1}$$

Here, $(d^2\sigma/d\Omega\, d\omega)_\alpha$ is the differential scattering cross section for the scattering of the neutrons off nuclei of type α, of which there are N_α, the indices "inc" and "coh" denote incoherent and coherent scattering, a^α_{inc} and a^α_{coh} are the incoherent and coherent scattering lengths (properties of the nuclei) of nuclei of type α, $S^{\alpha,\alpha}_s(\mathbf{k},\omega)$ is the spectral density of the time correlation function $F^\alpha_s(\mathbf{k}, t)$ for nuclei α,

$$\begin{aligned} S^{\alpha,\alpha}_s(\mathbf{k},\omega) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, \exp[-i\omega t](N_\alpha)^{-1} \\ &\quad\times\left\langle\sum_{j=1}^{N}\exp[-i\mathbf{k}\cdot\mathbf{r}_j(0)]\exp[i\mathbf{k}\cdot\mathbf{r}_j(t)]\right\rangle \end{aligned} \tag{6.2}$$

and $S^{\alpha,\beta}(\mathbf{k},\omega)$ is the spectral density of $F^{\alpha,\beta}(\mathbf{k}, t)$ for nuclei of type α, β,

$$\begin{aligned} S^{\alpha,\beta}(\mathbf{k},\omega) &= (1/2\pi)\int_{-\infty}^{+\infty} dt\, \exp[-i\omega t](N_\alpha N_\beta)^{-1/2} \\ &\quad\times\left\langle\sum_{j=1}^{N_\alpha}\exp[-i\mathbf{k}\cdot\mathbf{r}_j(0)]\sum_{l=1}^{N_\beta}\exp[i\mathbf{k}\cdot\mathbf{r}_l(t)]\right\rangle \end{aligned} \tag{6.3}$$

To see how neutron scattering can be used to determine the dynamics of molecular rotation, we consider the case when the incoherent scattering lengths of all the different nuclei in the system are much larger than the coherent scattering lengths (i.e., hydrogen nuclei). Then, from Eq. (6.1),

$$\begin{aligned} (d^2\sigma/d\Omega\, d\omega) &\cong \sum (d^2\sigma/d\Omega\, d\omega)^{\text{inc}}_{\alpha,\alpha}, \\ (d^2\sigma/d\Omega\, d\omega)^{\text{inc}}_{\alpha,\alpha} &\cong N_\alpha(k_f/k_0)S^{\alpha,\alpha}_s(\mathbf{k},\omega). \end{aligned}$$

It follows that only $S^{\alpha,\alpha}_s(\mathbf{k},\omega)$ is determined. For simplicity, we consider only diatomic molecules. The position of a nucleus of type α in the jth molecule is

$$\mathbf{r}_j = \mathbf{R}_j + (\mu/m_\alpha)\boldsymbol{\rho}_j,$$

where $\mathbf{R}_j$ is the COM position of the molecule, μ is the reduced mass of the molecule, m_α is the mass of the nucleus of type α, and $\boldsymbol{\rho}_j$ is a vector whose direction represents the orientation of molecule j and whose magnitude is the interatomic separation. At sufficiently low temperatures, the overwhelming majority of molecules are in their ground vibrational states. It is then permissible to represent these molecules by rigid rotors so that $\varrho_j = a_0\mathbf{u}_j$, where a_0 is the equilibrium separation and $\mathbf{u}_j$ is the orientation of molecule j. Then,

$$\mathbf{r}_j = \mathbf{R}_j + (\mu/m_\alpha)a_0\mathbf{u}_i$$

and

$$F_s^{\alpha,\alpha}(\mathbf{k}, t) = (1/N) \sum_{j=1}^{N} \langle \exp[-i\mathbf{k} \cdot \mathbf{R}_j(0)] \exp[i\mathbf{k} \cdot \mathbf{R}_j(0)] \times \{\exp[-i\mathbf{k}' \cdot \mathbf{u}_j(0)] \exp[i\mathbf{k}' \cdot \mathbf{u}_j(t)]\}\rangle \tag{6.4}$$

where $\mathbf{k}' = (\mu a_0/m_\alpha)\mathbf{k}$. It is often a good approximation to decouple the center-of-mass motion from the reorientation (rel) motion:

$$F_s^{\alpha,\alpha}(\mathbf{k}, t) \cong F_s^{\text{com}}(\mathbf{k}, t) F_\alpha^{\text{rel}}(\mathbf{k}, t), \tag{6.5}$$

where

$$\begin{aligned} F_s^{\text{com}}(\mathbf{k}, t) &= (1/N) \left\langle \sum_{j=1}^{N} (\exp[-i\mathbf{k} \cdot \mathbf{R}_j(0)] \exp[i\mathbf{k} \cdot \mathbf{R}_j(t)] \right\rangle \\ F_s^{\text{rel}}(\mathbf{k}, t) &= (1/N) \left\langle \sum_{j=1}^{N} \exp[-i\mathbf{k}' \cdot \mathbf{u}_j(0)] \exp[i\mathbf{k}' \cdot \mathbf{u}_j(t)] \right\rangle \end{aligned} \tag{6.6}$$

The assumption that the translational and rotational motions are decoupled is expected to be good for nearly spherical molecules. For polymers, it may well be that there is significant coupling between these degrees of freedom. The coupling has its origin in the fact that a molecule may encounter less frictional drag when moving along one molecular axis then it does along another. For example, a long, cylindrical molecule will move more easily in a direction along its cylindrical axis then along a direction transverse to this axis. Since we are talking here about small molecules, this kind of coupling should be small. This approximation has been tested in our computer experiments, however, it is not appropriate to go into these details here.

$F_s^{\text{com}}(\mathbf{k}, t)$ can be computed by the methods described in Section V,A. The relative part can be computed in the following way. The Rayleigh expansion of a plane wave is

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l,m} (i)^l j_l(kr) Y_{l,m}(\Omega_r) Y_{l,m}^*(\Omega_k)$$

where $j_l(x)$ is a spherical Bessel function of the first kind, $\Omega_r = (\theta_r, \varphi_r)$ and $\Omega_k = (\theta_k, \varphi_k)$ are the orientations of the vectors $\mathbf{r}$ and $\mathbf{k}$ in a given Cartesian coordinate system, and $Y_{l,m}(\Omega)$ is a surface spherical harmonic. It follows that

$$F_{\text{rel}}^{\alpha}(\mathbf{k}, t) = \left\langle \left[4\pi \sum_{l,m} (-i)^l j_l^*(k') Y_{l,m}^*(\Omega_u(0)) Y_{l,m}(\Omega_k) \right] \times \left[4\pi \sum_{l'',m''} (i)^{l''} j_{l''}(k') Y_{l'',m''}(\Omega_u(t)) Y_{l'',m''}(\Omega_k) \right] \right\rangle, \tag{6.7}$$

where $\Omega_{\mathbf{u}}(t)$ specifies the orientation $\mathbf{u}(t)$ of the molecule at time t.

In order to evaluate the average indicated by the brackets, it is necessary to determine the joint probability distribution $P(\Omega_0, \Omega, t)$ of the orientation Ω_0 at time zero and the orientation Ω at time t. In the absence of an external orienting field, the orientations in an equilibrium ensemble must be randomly distributed so that

$$\int d\Omega_0 \int d\Omega\, P(\Omega_0, \Omega; t) = 1, \tag{6.8a}$$

$$\int d\Omega_0\, P(\Omega_0, \Omega; t) = P(\Omega) = 1/4\pi, \tag{6.8b}$$

$$\int d\Omega\, P(\Omega_0, \Omega; t) = P(\Omega_0) = 1/4\pi; \tag{6.8c}$$

(6.8a) is simply the normalization condition, whereas (6.8b) and (6.8c) reflect the fact that the orientations in an equilibrium ensemble are uniformly distributed at all times. Since the surface spherical harmonics form a complete orthonormal set, it is possible to expand the joint probability distribution $P(\Omega_0, \Omega; t)$ in this set,

$$P(\Omega_0, \Omega; t) = \sum_{l,m} \sum_{l',m'} B_{l,m}^{l',m'}(t) Y_{l,m}(\Omega_0) Y_{l',m'}^*(\Omega), \tag{6.9}$$

where the expansion coefficients are

$$\begin{aligned} B_{l,m}^{l',m'}(t) &= \int d\Omega_0 \int d\Omega\, P(\Omega_0, \Omega; t) Y_{l,m}^*(\Omega_0) Y_{l',m'}(\Omega) \\ B_{l,m}^{l',m'}(t) &= \langle Y_{l,m}^*(\Omega(0)) Y_{l',m'}(\Omega(t)) \rangle. \end{aligned} \tag{6.10}$$

From conditions (6.8a–c) and the rotational invariance of the equilibrium ensemble it follows that

$$\begin{aligned} B_{l,m}^{l',m'}(0) &= (1/4\pi)\, \delta_{l,l'}\, \delta_{m,m'}, \qquad B_{0,0}^{0,0}(t) \equiv 1/4\pi \\ B_{l,m}^{l',m'}(t) &= b_{l,m}(t)\, \delta_{l,l'}\, \delta_{m,m'}. \end{aligned} \tag{6.11}$$

From Eq. (6.10),

$$b_{l,m}(t) = \langle Y_{l,m}^*(\Omega(0)) Y_{l,m}(\Omega(t)) \rangle. \tag{6.12}$$

Thus, quite generally for an equilibrium ensemble,

$$P(\Omega_0, \Omega; t) = \sum_{l,m} \langle Y_{l,m}^*(\Omega(0)) Y_{l,m}(\Omega(t)) \rangle Y_{l,m}(\Omega_0) Y_{l,m}^*(\Omega). \tag{6.13}$$

The specific dynamics are contained entirely within the time correlation functions $\langle Y_{l,m}^*(\Omega(0)) Y_{l,m}(\Omega(t)) \rangle$.

The general form of the distribution function can be used to compute $F_\alpha^{\text{rel}}(\mathbf{k}, t)$. Then it follows that

$$F_\alpha^{\text{rel}}(\mathbf{k}, t) = 16\pi^2 \sum_{l,m} |j_l(k')|^2 |Y_{l,m}(\Omega_k)|^2 \langle Y_{l,m}^*(\Omega_u(0)) Y_{l,m}(\Omega_u(t))\rangle. \tag{6.14}$$

In the absence of an aligning field, $F(\mathbf{k}, t)$ and $F_s(\mathbf{k}, t)$ must be even functions of $\mathbf{k}$ and cannot therefore depend on the orientation of $\mathbf{k}$, i.e., Ω_k. It follows therefore that

$$F_\alpha^{\text{rel}}(\mathbf{k}, t) = (1/4\pi) \int d\Omega_k \, F_\alpha^{\text{rel}}(\mathbf{k}, t).$$

Now, substituting Eq. (6.14) into this, together with the orthonormality condition on $Y_{l,m}(\Omega_k)$, it follows that

$$F_\alpha^{\text{rel}}(\mathbf{k}, t) = 4\pi \sum_{l,m} |j_l(k')|^2 \langle Y_{l,m}^*(\Omega_u(0)) Y_{l,m}(\Omega_u(t))\rangle. \tag{6.15}$$

According to the spherical harmonic addition theorem,

$$P_l(\mathbf{u}(0) \cdot \mathbf{u}(t)) = [4\pi/(2l+1)] \sum_{m=-l}^{+l} Y_{l,m}^*(\Omega_u(0)) Y_{l,m}(\Omega_u(t)).$$

Therefore,

$$F_\alpha^{\text{rel}}(\mathbf{k}, t) = \sum_{l=0}^{\infty} (2l+1) |j_l(\mu k a_0/m_\alpha)|^2 \langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle. \tag{6.16}$$

It follows that the incoherent differential scattering cross section for neutrons is determined by $F_s^{\text{com}}(\mathbf{k}, t)$ and $\langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$. When $\mu a_0 k/m_\alpha$ is small, the sum is rapidly convergent and only the first two terms need be retained. Although we restricted our attention to the case of incoherent scattering, it is quite possible to treat other cases by these methods. The interested reader should have no trouble generalizing these results. The major point to be noted here is that neutron scattering can be used to determine orientational time correlation functions (Sears, 1966, 1967) $\langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$.

The correlation function $\langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$ can be determined spectroscopically. As was shown in Section II,C the infrared absorption coefficient $\alpha(\omega)$ of a system of heteronuclear diatomic molecules is

$$\begin{aligned} \alpha(\omega) &= (4\pi^2\omega/\hbar c)[1 - e^{-\beta\hbar\omega}]\varrho \hat{I}(\omega), \\ \hat{I}(\omega) &= (1/2\pi) \int_{-\infty}^{+\infty} dt \, e^{i(\omega-\omega_0)t} \langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle, \end{aligned} \tag{6.17}$$

and ω_0 is the vibrational frequency of the molecule. Fourier inversion of the normalized spectrum $\hat{I}(\omega)$ determines $\langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$. This kind of analysis has been carried through on the spectrum of a series of different molecules as a function of temperature and pressure (Gordon, 1968).

Another method for determining $\langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$ is through dielectric relaxation experiments. The linear response of an equilibrium system to a time-dependent electrical field is completely determined by the complex susceptibility, which, in this case, is the frequency-dependent dielectric constant $\varepsilon(\omega)$,

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega). \tag{6.18}$$

As was shown in Section II,B the imaginary part ε'' is related to the energy absorption and, moreover, gives that part of the polarization that is 90° out of phase with the applied (monochromatic field). Energy is absorbed when the permanent dipole moments of the molecules cannot reorient rapidly enough to follow the changing electric field. Debye showed that $\varepsilon''(\omega)$ could be related to the dynamics of molecular reorientations (Debye, 1929). In fact, $\varepsilon''(\omega)$ is related to the absorption coefficient $\alpha(\omega)$ (Gordon, 1968). The real part $\varepsilon'(\omega)$ describes that part of the response that is in phase with the applied field, and in fact determines the real part of the refractive index of the medium.

Glarum (1960) and Cole (1965) have independently formulated theories that give $\varepsilon(\omega)$ in terms of the time correlation function $D_1(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle$, where $\mathbf{u}$ is the direction of the permanent dipole $\boldsymbol{\mu}$

$$\left[\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}\right]^{-1} = 1 - \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty}\left[\frac{1}{i\omega\tilde{D}_1(i\omega) - 1} + 1\right], \tag{6.19}$$

and where $\tilde{D}_1(i\omega)$ is simply the Laplace transform of $D_1(t)$ with Laplace variable $s = i\omega$. Here, ε_0 is the static dielectric constant and ε_∞ is the high-frequency dielectric constant.

A measurement of $\varepsilon(\omega)$ can thus be used to extract $\tilde{D}_1(s = i\omega)$ and thereby $\langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle$ by Laplace inversion. It should be noted that the Laplace transform of $(dD_1(t)/dt)$ is $s\tilde{D}_1(s) - 1$, which appears in (6.19) for $s = i\omega$. Now, the memory-function equation for $D_1(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle$ is

$$\frac{\partial}{\partial t} D_1(t) = -\int_0^t d\tau \, K_D(\tau) D_1(t-\tau); \qquad D_1(0) = 1, \tag{6.20}$$

and consequently, the Laplace transform of the dipolar correlation function is

$$\tilde{D}_1(s) = 1/[s + \tilde{K}_D(s)]. \tag{6.21}$$

Substitution of this with $s = i\omega$ into Eq. (6.19) shows that

$$\left[\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_n - \varepsilon_\infty}\right]^{-1} = 1 - \frac{2\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty} i\omega[\tilde{K}_D(i\omega)]^{-1},$$

or

$$\left[\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon(\omega) - \varepsilon_0}\right] = \left(\frac{2\varepsilon_0 + \varepsilon_\infty}{2\varepsilon_0}\right)\frac{1}{i\omega}\tilde{K}_D(i\omega). \tag{6.22}$$

It can be concluded that dielectric relaxation can be used to measure the memory function $\tilde{K}_D(i\omega)$ that corresponds to $D_1(t)$,

$$\tilde{K}_D(i\omega) = \int_0^\infty dt \exp[-i\omega t]\langle \dot{\mathbf{u}} \mid \exp[i(1 - \hat{P}_u)Lt] \mid \dot{\mathbf{u}}\rangle \tag{6.23}$$

The correlation function $\langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$ can be determined from depolarized light scattering either from the vibration-rotation Raman spectrum or from the rotational Raman (Rayleigh wing). It can also be obtained for large molecules from the depolarization of fluorescence.

Light is scattered because it induces an oscillating dipole moment in the scattering system which then radiates (Fabilinsky, 1968). If the system contains molecules that are optically anisotropic, the polarization of the radiation can change due to the scattering event. It is no wonder then that light scattering should be related to the polarizability tensor α of the molecules ($\alpha \cdot \mathbf{E}_1$ is the induced dipole moment in a molecule due to the incident radiation field E_1). The polarizability tensor of a molecule in the ground electronic state can be expanded in the vibrational displacements Q^ν, $\nu = 1, \ldots, n$, of the n vibrational "normal" modes. In the space fixed coordinate system, this expansion is, for molecule j,

$$\alpha_j = \alpha_j^\circ + \sum_{\nu=1}^{n} \alpha_j^\nu Q_j^\nu, \tag{6.24}$$

where α_j° is the polarizability tensor for the molecule in its equilibrium configuration, and α_j^ν is proportional to the derivative of α_j with respect to the displacement Q_j^ν evaluated for ($Q_j^\nu = 0$, $\nu = 1, \ldots, n$). The polarizability tensor of molecule j can be divided into two parts: an isotropic part $\alpha_j\mathsf{I}$ and a traceless part β_j, so that

$$\alpha_j = \alpha_j\mathsf{I} + \beta_j, \qquad \alpha_j = \tfrac{1}{3}\,\mathrm{Tr}\,\alpha_j, \tag{6.25}$$

where I is the unit tensor. The same separation can be applied to α_j° and α_j^ν, so that

$$\begin{aligned} \alpha_j^\circ &= \alpha_j^\circ\mathsf{I} + \beta_j^\circ, \qquad & \alpha_j^\circ &= \tfrac{1}{3}\,\mathrm{Tr}\,\alpha_j^\circ; \\ \alpha_j^\nu &= \alpha_j^\nu\mathsf{I} + \beta_j^\nu, \qquad & \alpha_j^\nu &= \tfrac{1}{3}\,\mathrm{Tr}\,\alpha_j^\nu. \end{aligned} \tag{6.26}$$

It should be noted that α_j depends on the orientation of molecule j with respect to the laboratory fixed coordinate system. Since the trace is invariant to a rotation (unitary transformation), it follows that α_j°, α_j^ν are independent of the orientations of the molecule. On the other hand, β_j°, β_j^ν depend on the orientation angles. It follows that the isotropic parts of the polarizability tensor do not change the polarization of the light.

It can be shown (Gordon, 1968) that the differential scattering cross section $(d^2\sigma/d\Omega\, d\omega)$ describing the event that a photon is scattered from its initial direction of propagation $\mathbf{k}_i$ into the solid angle $d\Omega$ suffering a wave-vector change $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$ ($\mathbf{k}_f$ being the final wave vector of the photon) and a frequency change $\omega_f - \omega_i$, can be separated into two parts: a part $(d^2\sigma/d\Omega\, d\omega)_\parallel$ that gives the spectrum of scattered light with polarization in the same plane as the incident beam, and a part $(d^2\sigma/d\Omega\, d\omega)_\perp$ that gives the spectrum of scattered light with polarization perpendicular to that of the incident beam. In an isotropic system it is more convenient to define an isotropic cross section $(d^2\sigma/d\Omega\, d\omega)_{\mathrm{ISO}}$ such that

$$(d^2\sigma/d\Omega\, d\omega)_{\mathrm{ISO}} = (d^2\sigma/d\Omega\, d\omega)_\parallel - \tfrac{4}{3}(d^2\sigma/d\Omega\, d\omega)_\perp. \tag{6.27}$$

If the vibrational frequencies are well separated from each other, that is, if their separations exceed the breadth of the spectral bands, it is possible to define cross sections corresponding to each mode. It can then be shown that these cross sections for the scattering off a single molecule are

$$\begin{aligned} \lambda^4(d^2\sigma/d\Omega\, d\omega)^\circ_{\mathrm{ISO}} \propto (1/2\pi)\int_{-\infty}^{+\infty} dt \exp[-i\omega t]\langle \alpha_j^\circ(0)\alpha_j^\circ(t) \\ \times \exp[i\mathbf{k}\cdot(\mathbf{r}_j(t) - \mathbf{r}_j(0))]\rangle, \end{aligned} \tag{6.28a}$$

$$\begin{aligned} \lambda^4(d^2\sigma/d\Omega\, d\omega)^\circ_{\mathrm{ISO}} \propto (1/2\pi)\int_{-\infty}^{+\infty} dt \exp[-i\omega t]\langle \alpha_j^\nu(0)\alpha_j^\nu(t) \\ \times \exp[i\mathbf{k}\cdot(\mathbf{r}_j(t) - \mathbf{r}_j(0))]\rangle \exp[i\omega_\nu t], \end{aligned} \tag{6.28b}$$

$$\begin{aligned} \lambda^4(d^2\sigma/d\Omega\, d\omega)_\perp^\circ \propto (1/2\pi)\int_{-\infty}^{+\infty} dt \exp[-i\omega t]\langle \mathrm{Tr}\,\beta_j^\circ(t)\cdot\beta^\circ_j(0) \\ \times \exp[i\mathbf{k}\cdot(\mathbf{r}_j(t) - \mathbf{r}_j(t))]\rangle. \end{aligned} \tag{6.28c}$$

$$\lambda\!\!\!^{-4}(d^2\sigma/d\Omega\, d\omega)_\perp{}^\nu \propto (1/2\pi)\int_{-\infty}^{+\infty} dt\, \exp[-i\omega t]\langle \mathrm{Tr}\, \beta_j{}^\nu(t)\cdot\beta_j{}^\nu(0) \times \exp[i\mathbf{k}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))]\rangle \exp[i\omega_\nu t]. \tag{6.28d}$$

Here, $\lambda\!\!\!^{-}$ is the circular wavelength ($\lambda/2\pi$) of the scattered light, ω_ν is the frequency of the νth normal mode, $\mathbf{r}_j(t)-\mathbf{r}_j(0)$ is the displacement of the COM of molecule j in the time t, $\exp[i\mathbf{k}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))]$ gives rise to the velocity dependence (Doppler breadth) of each of the lines, and $\mathbf{k}=\mathbf{k}_f-\mathbf{k}_i$ specifies the momentum change $\hbar\mathbf{k}$ of the photon due to the scattering ($k=2k_i\sin\theta/2$, where θ is the scattering angle). Band (6.28a) is just the undisplaced line or Rayleigh line. Band (6.28c) is the pure rotational Raman line, which, for a diatomic molecule, consists of SQS bands. Band (6.28b) is the isotropic vibrational Stokes Raman scattering, and band (6.28b) is the depolarized vibration-rotation Raman band (which, in diatomic molecule, is simply made up of the well-known OQS bands).

For the purpose of analysis, it is convenient to define a normalized spectrum $\hat{I}(\mathbf{k},\omega)$ of a given band as

$$\hat{I}(\mathbf{k},\omega) = \lambda\!\!\!^{-4}(d^2\sigma/d\Omega\, d\omega)\Big/\int_{\text{band}} d\omega\, \lambda\!\!\!^{-4}(d^2\sigma/d\Omega\, d\omega), \tag{6.29}$$

where the integral simply goes over the specific band in question. Since the contributions (6.28a-d) are all Fourier transforms of time correlation functions, it follows that, for the prototype,

$$\lambda\!\!\!^{-4}(d^2\sigma/d\Omega\, d\omega) \propto \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\langle A^+(0)A(t)\rangle,$$

$$\int_{\text{band}} d\omega\, \lambda\!\!\!^{-4}(d^2\sigma/d\Omega\, d\omega) \propto \langle A^+(0)A(0)\rangle,$$

so that the normalized spectrum is the power spectrum of the normalized correlation function $\langle A^+(0)A(t)\rangle/\langle\,|\,A\,|^2\rangle$. That is,

$$\hat{I}(\mathbf{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\langle A^+(0)A(t)\rangle/\langle\,|\,A(0)\,|^2\rangle.$$

Thus, corresponding to (6.28b), for example, we have

$$\hat{I}^\nu_{\text{ISO}}(\mathbf{k},\omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, \exp[-i(\omega-\omega_\nu)t] \times \langle \alpha_j{}^\nu(0)\alpha_j{}^\nu(t)\exp[i\mathbf{k}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))]\rangle/\langle\alpha_j{}^\nu(0)\alpha_j{}^\nu(0)\rangle.$$

If light is scattered off an assembly of molecules in an isotropic system rather than off a single molecule, there will be a change in the formulas. Then,

$$\hat{I}^\circ_{\text{ISO}}(\mathbf{k},\omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\psi^\circ_{\text{ISO}}(\mathbf{k},t), \tag{6.30a}$$

$$\hat{I}^\nu_{\text{ISO}}(\mathbf{k},\omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{-i(\omega-\omega_\nu)t}\psi^\nu_{\text{ISO}}(\mathbf{k},t), \tag{6.30b}$$

$$\hat{I}_\perp{}^\circ(\mathbf{k},\omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\psi_\perp{}^\circ(\mathbf{k},t), \tag{6.30c}$$

$$\hat{I}_\perp{}^\nu(\mathbf{k},\omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{-i(\omega-\omega_\nu)t}\psi_\perp{}^\nu(\mathbf{k},t), \tag{6.30d}$$

where the ψ's are the normalized time correlation functions

$$\psi^\circ_{\text{ISO}}(\mathbf{k},t) = F(\mathbf{k},t)/S(\mathbf{k}), \tag{6.31a}$$

$$\psi^\nu_{\text{ISO}}(\mathbf{k},t) = F_s(\mathbf{k},t), \tag{6.31b}$$

$$\psi_\perp{}^\circ(\mathbf{k},t) = \left\{\left\langle\sum_{j,l=1}^N \mathrm{Tr}\,\beta_j{}^\circ(0)\cdot\beta_l{}^\circ(t)\exp[i\mathbf{k}\cdot(\mathbf{r}_l(t)-\mathbf{r}_j(0))]\right\rangle \Big/ \left\langle\sum_{j,l=1}^N \mathrm{Tr}\,\beta_j{}^\circ(0)\cdot\beta_l{}^\circ(0)\right\rangle\right\} \tag{6.31c}$$

$$\psi_\perp{}^\nu(\mathbf{k},t) = \left\{\left\langle\sum_{j=1}^N \mathrm{Tr}\,\beta_j{}^\nu(0)\cdot\beta_j{}^\nu(t)\right\rangle\Big/\left\langle\sum_{j=1}^N \mathrm{Tr}\,\beta_j{}^\nu(0)\cdot\beta_j{}^\nu(0)\right\rangle\right\}\times F_s(\mathbf{k},t). \tag{6.31d}$$

These formulas were written for a pure fluid of molecules, in which: $\alpha_j{}^\circ$ is assumed to be a property of each molecule, which is invariant in time; it is assumed that there is no correlation between the vibrational displacements on different molecules [$\langle Q_i{}^\nu(0)Q_l{}^{\nu'}(t)\rangle = 0$ for $j\neq l$ and all ν and ν']; and ω_ν contains an imaginary part corresponding to the vibrational lifetime of the νth mode due to collisions and radiation damping. It is often further assumed that the orientations on different molecules are uncorrelated, but this is not assumed here. Since the Fourier transforms of $F(\mathbf{k},t)$ and $F_s(\mathbf{k},t)$ are $S(\mathbf{k},\omega)$ and $S_s(\mathbf{k},\omega)$, respectively, it follows that

$$\begin{aligned}\hat{I}^\circ_{\text{ISO}}(\mathbf{k},\omega) &= S(\mathbf{k},\omega)/S(\mathbf{k}),\\ \hat{I}^\nu_{\text{ISO}}(\mathbf{k},\omega) &= S_s(\mathbf{k},\omega-\omega_\nu).\end{aligned} \tag{6.32}$$

Thus, the isotropic Rayleigh line shape is determined by $S(\mathbf{k},\omega)$, as was mentioned in the last section. Moreover, the isotropic Stokes scat-

tering from the νth mode provides information about the motion of individual molecules, the self-motion. In mixtures, it turns out that, bacause different molecules have different vibrational frequencies, the self-motion of the different components can be singled out so that $S_s(\mathbf{k}, \omega)$ for each kind of molecule can in principle be determined.

It follows from (6.30d) and (6.31d) that $\langle \mathrm{Tr}\, \beta^\nu(0) \cdot \beta^\nu(t)\rangle / \langle \mathrm{Tr}\, \beta^\nu(0) \cdot \beta^\nu(0)\rangle$ can be determined from the depolarized Stokes scattering from the νth mode. Usually, $F_s(\mathbf{k}, t)$ can be ignored since it is so slowly varying on the time scale of $\beta(t)$ that it can be taken as unity. Gordon (1968) has analyzed this correlation function in detail. For diatomic gases (there is only one mode), $\hat{I}_\perp^{\nu=1}(\mathbf{k}, \omega)$ contains the familiar O, Q, and S branches corresponding to vibration-rotation transitions. Gordon shows that for this case

$$\hat{I}_\perp^{\nu=1}(\mathbf{k}, \omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{-i(\omega-\omega_1)t} \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle, \tag{6.33}$$

where the superscript 1 indicates the only vibrational mode in the molecule. If correlations between orientations on different molecules can be neglected, it can be shown from Eqs. (6.30) and (6.31c) that

$$\hat{I}_\perp^{(0)} = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle, \tag{6.34}$$

which in diatomic gases gives the SOS bands. As the pressure is raised, the O, Q, and S bands merge into one broad band centered at ω_1, whereas the SOS bands collapse into one broad band at $\omega = 0$. This latter band is called the Rayleigh wing. This is easy to see: For a diatomic molecule, the most general traceless tensor β is $c(\mathbf{uu} - \frac{1}{3}\mathbf{u} \cdot \mathbf{u}\, \delta_{ij})$. Then,

$$\begin{aligned}
\mathrm{Tr}\, \beta(0) \cdot \beta(t) &= c^2 \sum_{i,j=1} [(u_i(0)u_i(t))(u_j(0)u_j(t)) - \tfrac{1}{3}u_i(0)u_j(0)\, \delta_{ij} \\
&\quad - \tfrac{1}{3}u_i(t)u_j(t)\, \delta_{ij} + \tfrac{1}{9}\, \delta_{ij}] \\
&= c^2[(\mathbf{u}(0) \cdot \mathbf{u}(t))^2 - \tfrac{1}{3}] \\
&= \tfrac{1}{6}c^2 P_2(\mathbf{u}(0) \cdot \mathbf{u}(t)), \\
\psi_\perp(\mathbf{k}, t) &= \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle F_s(\mathbf{k}, t).
\end{aligned}$$

The depolarization of fluorescence can be used to probe the dynamics of molecular reorientations of large molecules (Perrin, 1926). In these experiments, an assembly of molecules is exposed to a pulse of linearly polarized radiation [ϵ_i being the unit vector specifying the direction of polarization of the incident light, $\mathbf{E}_i(t)$] which is resonant with an electronic transition $|0) \to |f)$ in the molecule. The transition probability for a molecule j to make the transition $|0) \to |f)$ is proportional to $|(f|\, \mu_j \cdot \epsilon_i\, |0)|^2$, where μ_j is the dipole operator of molecule j. If the chromophor is rigid, the transition dipole $(f|\, \mu_j\, |0)$ will have a definite direction in the molecule and thus $(f|\, \mu_j \cdot \epsilon_i\, |0)$ will depend on the orientation of the molecule in the space fixed system. If the molecules are randomly oriented before the application of the pulse it will excite only those molecules with orientations such that the transition dipoles have a component along ϵ_i, and the orientational distribution of excited molecules will be

$$P(\Omega_0) \propto |\, \mu_{f0} \cdot \epsilon_i\, |^2 = \cos^2\theta \qquad (\epsilon_i \parallel z \text{ axis}),$$

θ being the angle between μ and $\hat{z}$. After the pulse is applied, the excited molecules will begin to fluorescence. The fluorescence may involve the same states $|f) \to |0)$ or there may first be a non radiative decay to a different state $|f')$ followed by the fluorescence from $|f') \to |0)$. The probability that the photon will be emitted with polarization ϵ_f will be proportional to $|(0|\, \mu_j \cdot \epsilon_f\, |f')|^2$. The state $|f')$ will have a finite lifetime $\tau_{f'}$ so that photons will not immediately be emitted. Moreover, the transition matrix element $(0|\, \mu_j\, |f')$ will in general lie in a different direction in the chromaphor's body-fixed frame than does $(f|\, \mu_j\, |0)$ (since the states $|f)$ and $|f')$ are different). Let us follow what happens to a molecule after it is excited. Before a photon is emitted, the molecule will rotate, and the transition dipole will reorient. The molecule can emit a photon of a given polarization, say ϵ_f, if its transition dipole at the instant of emission has a component along ϵ_f. Thus, the emitted flux of photons with given polarization should be modulated by the rotational motions of the molecules. Since the exciting pulse produces a $\cos^2\theta$ distribution of excited molecules, the fluorescent intensity will reflect how this non equilibrium distribution returns to the uniform (equilibrium) distribution.

Let $I_\parallel(t)$ and $I_\perp(t)$ be the intensities of fluorescence where the emitted photons have polarizations parallel to $\epsilon_i(\epsilon_f \parallel \epsilon_i)$ and perpendicular to $\epsilon_i(\epsilon_f \perp \epsilon_i)$, respectively. Then the polarization ratio $r(t)$ is defined as

$$r(t) = [I_\parallel(t) - I_\perp(t)]/[I_\parallel(t) + 2I_\perp(t)]. \tag{6.35}$$

For simplicity, we present the case where the fluorescence comes from the same state $|f)$ to which the molecule was excited. Then it can be shown that

$$r(t) = \tfrac{2}{5}\langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle, \tag{6.36}$$

where $\mathbf{u}$ is a unit vector pointing in the direction of the transition dipole $(f \mid \mu \mid 0)$. Let τ_f be the lifetime of the state $|f)$. Thus, if τ_f is very short compared with the correlation time of the reorientation, the molecules will have no time to rotate, and only polarized emission will be observed. On the other hand, if τ_f is long compared withthe correlation time of $\langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$, emission will take place only after the molecules have been reoriented and complete depolarization will result. In either of these extremes, the depolarization will not give useful information about the correlation function. Since $\tau_f \sim 10^{-8}$ sec for electronic transitions, and since typical orientational correlation times for small molecules are $\sim 10^{-11}$ sec, this experiment is not very useful for the determination of correlation functions in small molecules. On the other hand, molecules of large moment of inertia (polymers) have correlation times of order 10^{-8} sec and can clearly be studied. Experiments of this kind have been useful for determining the rotational diffusion coefficients and thereby, the size and shape of such molecules as myglobin (Tao, 1969).

It can be concluded that the dynamics of molecular rotations can be probed by a variety of spectroscopic methods. It is therefore quite important to investigate the properties of the correlation functions $\langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$ in different systems. Moreover, the results of one experiment may greatly aid in the analysis of another experiment. For example, $\langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$ and $\langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t))\rangle$ can be determined from absorption and light-scattering experiments and can then be applied to neutron-scattering experiments so that the translational correlation functions can be analyzed.

B. Free Rigid Rotors: Classical and Quantum Time Correlation Functions

Orientational correlation functions play an important role in absorption, Raman, Rayleigh, NMR, ESR, and neutron-scattering spectroscopy. Unfortunately, only a small number of such correlation functions have been determined analytically, and these correspond to very simple models. Ironically, much is known about the behavior of time correlation functions in condensed media (Berne & Forster, 1971). Computer simulations of monoatomic and diatomic classical liquids provide a complete development of the positions and momenta of the constituent particles of the liquid. Consequently, the time correlation functions

of any two mechanical properties can be determined. Since these machine studies determine only the classical correlation functions, they are often not directly applicable to quantum-mechanical, i.e., real systems. A number of approximations have been proposed to deduce the quantum-mechanical correlation function from the corresponding classical function. The accuracy of these approximations is rather difficult to assess. In the following (Kushick and Berne, 1970), we compare exact classical and quantum-mechanical behavior of some orientational time correlation functions that are frequently encountered in spectroscopic studies.

1. *The One-Dimensional Rigid Rotor*

Here, the normalized dipolar autocorrelation function for a classical and quantum-mechanical ensemble of one-dimensional rigid rotors is determined. Let $\mathbf{u}$ be a unit vector along the rigid rotor axis. Then

$$D_1^{\mathrm{cl}}(t) \equiv \langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle, \qquad D_1^{\mathrm{qm}}(t) \equiv \langle \tfrac{1}{2}[\mathbf{u}(0); \mathbf{u}(t)]_+\rangle \tag{6.37}$$

are respectively the classical and quantum-mechanical time correlation functions. The quantum-mechanical function involves the anticommutator $[\hat{\mathbf{a}}, \hat{\boldsymbol{\beta}}]_+ = \hat{\mathbf{a}} \cdot \hat{\boldsymbol{\beta}} + \hat{\boldsymbol{\beta}} \cdot \hat{\mathbf{a}}$. Since $\mathbf{u}(0)$ and $\mathbf{u}(t)$ are Hermitian operators, $D_1^{\mathrm{qm}}(t)$ is a real function of the time.

The one-dimensional rigid rotor is a rotor constrained to rotate in a given plane. For this case, $D_1^{\mathrm{cl}}(t)$ is easy to evaluate. For a free rotor, $\mathbf{u}(0) \cdot \mathbf{u}(t) = \cos \omega t$, where ω is the rotational velocity and ωt is the angle between $\mathbf{u}(0)$ and $\mathbf{u}(t)$. The distribution of angular velocities is $p(\omega) = (I/2\pi kT)^{1/2} \exp -(\beta I \omega^2/2)$. Consequently,

$$D_1^{\mathrm{cl}}(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle = \int_{-\infty}^{+\infty} d\omega\, p(\omega) \cos \omega t = \exp -\tau^2/2, \tag{6.38}$$

where $\tau = \langle \omega^2\rangle_{\mathrm{cl}}^{1/2} t$ is a reduced time, $\langle \omega^2\rangle_{\mathrm{cl}} = kT/I$ is the mean-square angular velocity, and I is the rotor's moment of inertia.

The corresponding quantum time correlation function is more difficult to evaluate. The Hamiltonian of the free one-dimensional rotor is $\hat{H} = (1/2I)\hat{J}_z^2$, where $\hat{J}_z$ is the angular momentum (perpendicular to the plane of rotation). The eigenvalues and corresponding eigenfunctions are $\varepsilon_m = \hbar^2 m^2/2I$, $\Phi_m(\varphi) = (2\pi)^{-1/2} e^{im\varphi}$ where $m = 0, \pm 1, \ldots$, and φ is the angle that specifies the orientation of the rotor in the plane of rotation. In the energy representation, $D_1^{\mathrm{qm}}(t)$ is

$$D_1^{\mathrm{qm}}(t) = \sum_{n,m} \varrho_n \mathbf{u}_{nm} \cdot \mathbf{u}_{mn} \cos \omega_{mn} t, \tag{6.39}$$

where ϱ_n is the Boltzmann factor $e^{-\beta\varepsilon_n}/Q$ and $\mathbf{u}_{nm}$ is the nmth matrix element of $\mathbf{u}$, where $\mathbf{u} = \mathbf{i}\cos\phi + \mathbf{j}\sin\phi$. Here, $\mathbf{i}$ and $\mathbf{j}$ are two basis vectors which span the space of the rotational plane. Evaluation of the matrix elements yields $\mathbf{u}_{nm}\cdot\mathbf{u}_{mn} = \frac{1}{2}[\delta_{n,m+1} + \delta_{n,m-1}]$. Then,

$$D_1^{\mathrm{qm}}(t) = \cos\omega_0 t \,\mathrm{Re} \sum_{n=-\infty}^{+\infty} Q^{-1}\exp[-\beta\hbar\omega_0 n^2]\exp[-2in\omega_0 t], \tag{6.40}$$

where $\omega_0 = \hbar/2I$. This function is periodic with period $2\pi/\omega_0$. This is the recurrence time for the quantum-mechanical time correlation function. In order to calculate $D_1^{\mathrm{qm}}(t)$, the two sums

$$\begin{aligned} \Gamma(t) &= \sum_{n=-\infty}^{+\infty} \exp[-\beta\hbar\omega_0 n^2]\exp[-i2n\omega_0 t] \\ Q(\beta) &= \sum_{n=-\infty}^{+\infty} \exp[-\beta\hbar\omega_0 n^2] = \Gamma(0) \end{aligned} \tag{6.41}$$

must be determined. For the purposes of comparing the classical and quantum time correlation functions, it is most convenient to evaluate the above sums using the Poisson summation formula (Abragam, 1961), according to which, if $F(x)$ is a good function and $G(y)$ is its Fourier transform, then

$$\sum_{m=-\infty}^{+\infty} F(\lambda m) = (1/\lambda)\sum_{n=-\infty}^{+\infty} G(n/\lambda). \tag{6.42}$$

Consider the function $F(x) = \exp -x^2$ and its corresponding Fourier transform $G(y) = \sqrt{\pi}\exp -\pi^2 y^2$. Therefore, by the Poisson summation formula

$$\sum_{m=-\infty}^{+\infty} \exp[-\lambda^2 m^2] = (\pi/\lambda^2)^{1/2}\sum_{n=-\infty}^{+\infty}(\exp -\pi^2 n^2/\lambda^2). \tag{6.43}$$

If we let $\lambda^2 = \beta\hbar\omega_0$, the left-hand side of the preceding equation is the partition function, so that

$$Q(\beta) = (\pi/\beta\hbar\omega_0)^{1/2}\sum_{n=-\infty}^{+\infty}\exp[-\pi^2 n^2/\beta\hbar\omega_0]. \tag{6.44}$$

The advantage of this formula is that it is rapidly convergent for high temperatures or small $\beta\hbar\omega_0$, whereas the original sum is not. Now, $(\pi/\beta\hbar\omega_0)^{1/2}$ is the classical partition function and the sum gives the quantum corrections to the classical partition function and consequently to the thermodynamic properties.

Consider the function $F(x) = \exp[-x^2 - 2\pi ixz]$ and its corresponding

Fourier transform $G(y) = (\pi)^{1/2}\exp[-\pi^2(y+z)^2]$. According to the Poisson summation formula,

$$\sum_{m=-\infty}^{+\infty}\exp[-\lambda^2 m^2]\exp[-\pi i 2\lambda m] = (\pi/\lambda^2)^{1/2}\sum_{n=-\infty}^{+\infty}\exp[-\pi^2(n/\lambda + z)^2].$$

If we let $\lambda^2 = \beta\hbar\omega_0$ and $z = \omega_0 t/\pi\lambda$, the left-hand side of this equation is $\Gamma(t)$ so that

$$\begin{aligned} \Gamma(t) = (\pi/\beta\hbar\omega_0)^{1/2}&\exp[-\omega_0^2 t^2/\beta\hbar\omega_0]\sum_{n=-\infty}^{+\infty}\exp[-\pi^2 n^2/\beta\hbar\omega_0] \\ &\times\exp[-2i\pi n\omega_0 t/\beta\hbar\omega_0]. \end{aligned} \tag{6.45}$$

From Eqs. (6.44) and (6.45), it is concluded that

$$\begin{aligned} D_1^{\mathrm{qm}}(t) &= \cos\omega_0 t\exp(-\omega_0^2 t^2/\beta\hbar\omega_0) \\ &\times\left\{\sum_{n=-\infty}^{+\infty}\exp(-\pi^2 n^2/\beta\hbar\omega_0)\exp(2-i\pi nt/\beta\hbar)\Big/\sum_{n=-\infty}^{+\infty}\exp(-\pi^2 n^2/\beta\hbar\omega_0)\right\}. \end{aligned}$$

Since $\omega_0/\beta\hbar = kT/2I = \frac{1}{2}\langle\omega^2\rangle_{\mathrm{cl}}$, the factor $\exp[-\omega_0^2 t^2/\beta\hbar\omega_0]$ is equal to $\exp -(\langle\omega^2\rangle_{\mathrm{cl}} t^2/2)$ or $D_1^{\mathrm{cl}}(t)$, and

$$\begin{aligned} D_1^{\mathrm{qm}}(t) &= D_1(t)\cos\omega_0 t \\ &\times\left\{\sum_{n=-\infty}^{+\infty}\exp[-\pi^2 n^2/\beta\hbar\omega_0]\exp[-2\pi int/\beta\hbar]\Big/\sum_{n=-\infty}^{+\infty}\exp[-\pi^2 n^2/\beta\hbar\omega_0]\right\}. \end{aligned} \tag{6.46}$$

The strong difference between the classical and quantum-mechanical correlation functions should be noted. The quantum-mechanical function is periodic with period $2\pi/\omega_0$. This has profound effects on the spectral line shapes that would be observed. Note that as $I \to \infty$, $\omega_0 = \hbar/2I \to 0$, the period $2\pi/\omega_0 \to \infty$, and $D_1^{\mathrm{qm}}(t) \to D_1^{\mathrm{cl}}(t)$. Another way of indicating this behavior is to say that as $\hbar \to 0$ (correspondence rule limit) the quantum time correlation function approaches its classical counterpart.

Let us express $D_1^{\mathrm{qm}}(t)$ in terms of the dimensionless time $\tau = \langle\omega^2\rangle_{\mathrm{cl}}^{1/2} t$ and in addition define the dimensionless parameter $x = \omega_0/\langle\omega^2\rangle_{\mathrm{cl}}^{1/2} = \hbar/(4IkT)^{1/2}$. Note that x is the ratio of the quantum of angular momentum, and $(IkT)^{1/2}$ the root-mean square classical thermal angular momentum, of the rotor. In terms of these reduced variables,

$$\begin{aligned} D_1^{\mathrm{qm}}(\tau) &= D_1^{\mathrm{cl}}(\tau)\cos x\tau \\ &\times\left\{\sum_{n=-\infty}^{+\infty}\exp[-\pi^2 n^2/2x^2]\exp[-\pi in\tau/x]\Big/\sum_{n=-\infty}^{+\infty}\exp[-\pi^2 n^2/2x^2]\right\}. \end{aligned} \tag{6.47}$$

The parameter x is small when the thermal angular momentum is large compared to the quantum of angular momentum. Thus, if τ is fixed and $x \to 0$, it follows that

$$\lim_{x\to 0} D_1^{\mathrm{qm}}(\tau) = D_1^{\mathrm{cl}}(\tau).$$

The classical limit is attained when $I\langle\omega^2\rangle_{\mathrm{cl}}^{1/2} \gg \hbar$. In these reduced variables, the recurrence time for $D_1(t)$ is $2\pi/x$.

Schofield (1960; Egelstaff, 1962; Egelstaff and Schofield, 1962) has proposed that the quantum-mechanical one-sided time correlation function $\langle A(0)A(t)\rangle_{\mathrm{qm}}$ can be approximated from the classical autocorrelation function from the equation

$$\langle A(0)A(t)\rangle_{\mathrm{qm}}^{\mathrm{SCH.}} = \langle A(0)A(t - i\hbar\beta/2)\rangle_{\mathrm{cl}}. \tag{6.48}$$

This approximate quantum-mechanical time correlation function satisfies the condition of detailed balance, but does not satisfy any sum rule. For example, at $t = 0$, the quantum-mechanical function should be $\langle A^2\rangle_{\mathrm{qm}}$, but the Schofield approximation leads to $\langle A(0)A(-i\hbar\beta/2)\rangle_{\mathrm{cl}}$.

Egelstaff (1961) showed that, if $y^2 = t^2 - i\hbar\beta t$, then another approximation to the one-sided function that satisfies the condition of detailed balance and in addition the above sum rule is

$$\langle A(0)A(t)\rangle_{\mathrm{qm}}^{\mathrm{EG.}} = \langle A(0)A(y)\rangle_{\mathrm{cl}}. \tag{6.49}$$

Let us compare these two approximations with the exact result in Eq. (6.47):

$$\begin{aligned} \langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle_{\mathrm{qm}}^{\mathrm{SCH.}} &= D_1^{\mathrm{cl}}(t - i\hbar\beta/2) = D_1^{\mathrm{cl}}(t)e^{i\omega_0 t}e^{\beta\hbar\omega_0/4}, \\ \langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle_{\mathrm{qm}}^{\mathrm{EG.}} &= D_1^{\mathrm{cl}}\left((t^2 - i\hbar\beta t)^{1/2}\right) = D_1^{\mathrm{cl}}(t)e^{i\omega_0 t}. \end{aligned} \tag{6.50}$$

Consequently, since $D_1^{\mathrm{qm}}(t)$ is the real part of the quantum one-sided correlation function, the Schofield and Egelstaff approximations become, in reduced coordinates,

$$\begin{aligned} D_1^{\mathrm{SCH.}}(\tau) &= \exp -(x^2/2)\, D_1^{\mathrm{cl}}(\tau)\cos x\tau, \\ D_1^{\mathrm{EG.}}(\tau) &= D_1^{\mathrm{cl}}(\tau)\cos x\tau. \end{aligned} \tag{6.51}$$

It should be noted that the Egelstaff correction is identical to the $\beta\hbar\omega_0 \to 0$ limit (that is, the high-temperature limit) of the full quantum-mechanical time correlation function for short times even though it does not predict the recurrence phenomena.

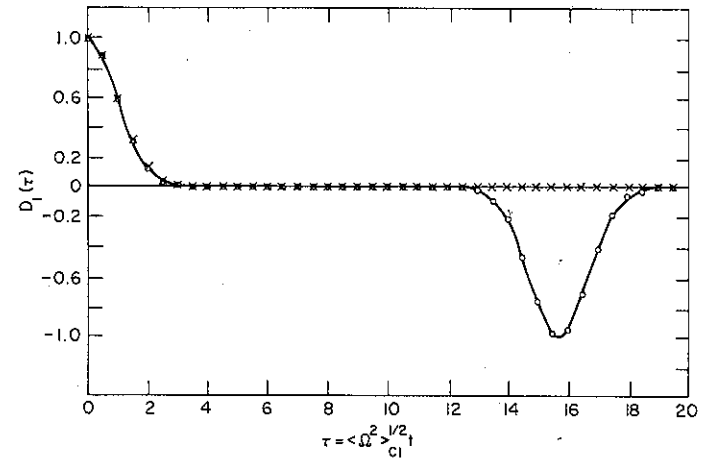

FIG. 23. The dipolar autocorrelation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ for a two-dimensional rigid rotor, (×) classical. Note the recurrence in the quantum-mechanical autocorrelation function (open dots).

These results are plotted in Figs. 23 and 24. It can be concluded that there are important differences between quantum and classical time correlation functions and, moreover, the Egelstaff and Schofield approximations are of limited utility.

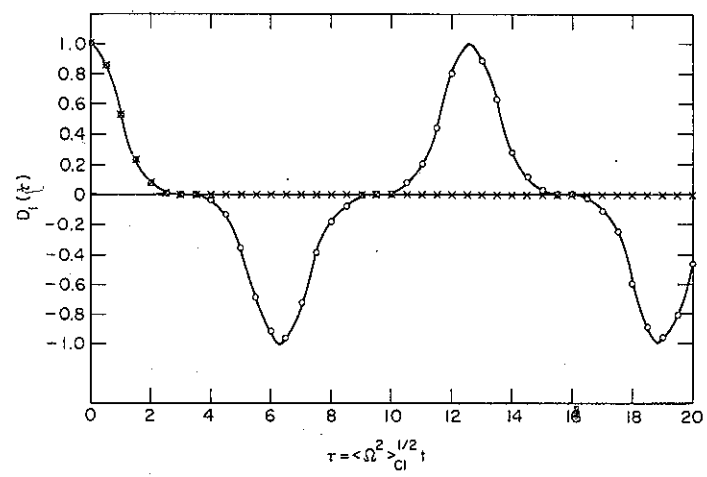

FIG. 24. The Egelstaff approximation to the quantum-mechanical time correlation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ for the two-dimensional rigid rotor, for $x = 0.5$ (Egelstaff). There is no recurrence, as there is in the exact quantum-mechanical expression (open dots).

2. *The Rigid Heteronuclear Diatomic Molecule*

$D_1^{\mathrm{cl}}(t)$ and $D_1^{\mathrm{qm}}(t)$ can be computed for a rigid molecule rotating in 3-space. Then,

$$D_1^{\mathrm{cl}}(\tau) = 2\int_0^\infty dz\, z \exp[-z^2] \cos z\tau, \tag{6.52}$$

where $\tau = (2kT/I)^{1/2}t$ is a dimensionless time. This integral cannot be evaluated analytically, but a numerical calculation of $D_1^{\mathrm{cl}}(\tau)$ is plotted in Fig. 25.

The corresponding quantum-mechanical time correlation function $D_1^{\mathrm{qm}}(t)$, is

$$D_1^{\mathrm{qm}}(t) = \mu^{-2}\,\mathrm{Re} \sum_{JM,J'M'} \varrho_{J'M'} \,|\, (J'M' \,|\, \boldsymbol{\mu} \,|\, JM) \,|^2 \exp[i(\omega_{JM} - \omega_{J'M'})t], \tag{6.53}$$

where $|\, JM)$ is the eigenket of the Hamiltonian $\hat{H} = (1/2I)\hat{J}^2$ corresponding to the eigenvalue $\varepsilon_{JM} = \hbar\omega_{JM} = J(J+1)\hbar^2/2I$, and $(JM \,|\, \boldsymbol{\mu} \,|\, J'M')$ is the transition dipole moment for the transition $|\, J'M') \to |\, JM)$. Substituting the known values of the matrix elements, together with the Boltzmann factor $\varrho_{J'M'} = (\exp - \beta\hbar\omega_{J'M'})/Q$ and the degeneracies $g_{JM} = 2J+1$ yields, after some manipulation,

$$D_1^{\mathrm{qm}}(t) = 2\sum_{J=0}^{\infty} (J+1)(\exp -(J+1)^2\beta\hbar\omega_0)/Q \times [\cosh[(J+1)\beta\hbar\omega_0] \cos[2(J+1)\omega_0 t]. \tag{6.54}$$

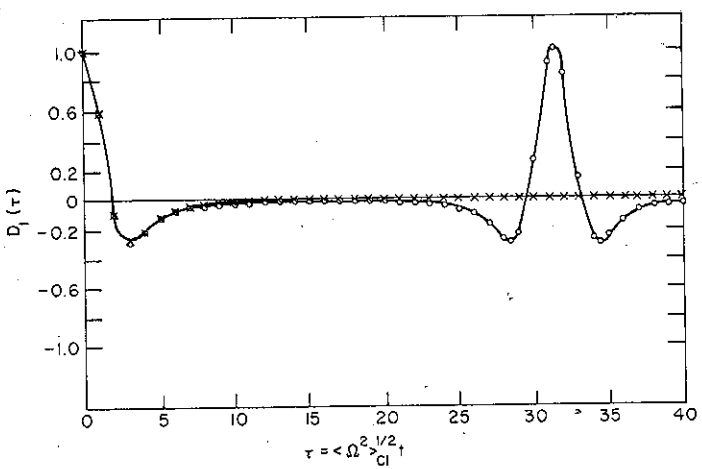

FIG. 25. The dipolar autocorrelation function $\langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle$ for a rigid heteronuclear diatomic molecule, (×) classical. Note the recurrence (open dots).

If we introduce the dimensionless variables $x^2 = I\omega_0^2/2kT = \beta\hbar\omega_0/4$, $\tau = \omega_0 t/x$, we have

$$D_1^{\mathrm{qm}}(\tau) = \frac{\sum_{J=0}^{\infty} 2(J+1)[\exp[-4(J+1)^2x^2] \cosh[4(J+1)x^2] \cos[2(J+1)x\tau]]}{\sum_{J=0}^{\infty} (2J+1) \exp[-4J(J+1)x^2]} \tag{6.55}$$

Here, the sums in the expression for $D_1^{\mathrm{qm}}(\tau)$ converge quickly enough to be calculated directly. The results of these calculations are plotted in Fig. 25.

As was observed before, the quantum-mechanical time correlation function is periodic with recurrence time π/x. Again the strong contrast with classical correlation functions should be noted.

Even in the high-temperature, high-moment-of-inertia limit, the difference between classical and quantum time correlation functions may be observable. The vibration-rotation spectrum is

$$\hat{I}(\omega) = (1/2\pi)\int_{-\infty}^{+\infty} dt\, e^{-i\omega t} e^{-|t|/\tau_{\mathrm{R}}} D_1^{\mathrm{qm}}(t) \tag{6.56}$$

where τ_{R} is the lifetime of the excited vibrational state. When collisions play no role in the lifetime, $1/\tau_{\mathrm{R}}$ is the spontaneous emission rate and is of order $\langle 10^{+3}\ \mathrm{sec}^{-1}$. Thus, if the recurrence time $\pi/\omega_0 = 2\pi I/\hbar$ ($\sim 10^{-12}$ sec) is small compared with τ_{R}, recurrences will be observable.

C. Effects of Collisions on Molecular Reorientations

The orientation of a diatomic molecule is specified by a unit vector $\mathbf{u}$ pointing along the molecular axis. Every orientation can be specified by a point on a unit sphere. As the molecule rotates, this point moves along a trajectory on the surface of the sphere. If the molecule rotates freely, the point $\mathbf{u}$ will complete a cycle with a frequency equal to the molecular rotational speed $|\,\boldsymbol{\omega}\,|$. If the molecule suffers collisions, then its motion is represented by jagged trajectories due to the change in its rotational velocity on collision. In dilute gases, collisions will be so infrequent that the point will travel on long arcs of great circles before suffering a collision and shifting to a new arc. As the density increases, the collisions will become so frequent that the point will perform a kind of Brownian motion on the surface of the unit sphere.

The following is a simple stochastic model for collisional reorientation which provides a great deal of insight into the mechanism of rotational motion (Gordon, 1965a, b):

1. A molecule undergoes free rotational motion until it is interupted by a hard-core collision of zero duration.
2. Collisions change the molecule's rotational velocity but do not change its orientation.
3. Successive hard-core collisions are uncorrelated, that is, the instants at which the collisions occur form a pure random process and the angular velocity changes produced by the collisions are uncorrelated.
4. Each collision radomizes the direction of the angular momentum.

It follows from these considerations that after n collisions which occur at the times $t_1, \ldots, t_n$ a molecule that rotates with the angular speeds $\omega_1, \ldots, \omega_{n+1}$ between these collisions will have

$$\mathbf{u}(0) \cdot \mathbf{u}(t)\,|_{n\ \mathrm{coll}} = \prod_{j=1}^{n+1} \cos \omega_j(t_j - t_{j-1}), \qquad t > t_n, \tag{6.57}$$

where $t_0 \equiv 0$ and $t_{n+1} \equiv t$. From condition 3, these collisions can occur at any time such that $0 \leq t_1 \leq t_2 \leq \cdots \leq t_{n+1} = t$. All possible choices of the collision times are equally probable, so that the average of Eq. (6.57) over all possible collision times given the sequence of rotational speeds is

$$\overline{\mathbf{u}(0) \cdot \mathbf{u}(t)}^n = \frac{n!}{t^n} \prod_{j=1}^{n+1} \int_0^{t_j} dt_{j-1} \cos \omega_j(t_j - t_{j-1}), \qquad t_{n+1} = t. \tag{6.58}$$

Now, the probability for n collisions in the time t is the Poisson distribution (collisions are independent and random)

$$P_n(t) = \frac{(\omega_0 t)^n}{n!} \exp -\omega_0 t, \tag{6.59}$$

where ω_0 is the gas kinetic collision frequency ($= 1/\tau$, τ being the average time between collisions). Then, averaging $\overline{\mathbf{u}(0) \cdot \mathbf{u}(t)}^n$ over $P_n(t)$ gives the correlation function $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle_{\{\omega_j\}}$, for a specific set of rotational speeds $\{\omega_1, \ldots, \omega_l, \ldots\}$,

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle_{\{\omega_l\}} = \sum_{n=0}^{\infty} \omega_0{}^n e^{-\omega_0 t} \prod_{j=1}^{n+1} \int_0^{t_{j+1}} dt_{j-1} \cos \omega_j(t_j - t_{j-1}). \tag{6.60}$$

This correlation function must now be averaged over the joint probability distribution of molecular speeds $P(\omega_1, \ldots, \omega_l, \ldots)$. According to condition 4, this joint probability factorizes,

$$P(\omega_1, \ldots, \omega_l, \ldots) = \prod_{j=1} P(\omega_j), \tag{6.61}$$

since the collisions randomize the angular velocities. Now, $P(\omega_j)$ is just the Maxwell distribution of speeds

$$P(\omega_j) = (I/2kT)\omega_j \exp[-\beta I \omega_j{}^2/2]. \tag{6.62}$$

This average is

$$\begin{aligned} D_1(t) &= \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle \\ &= \sum_{n=0}^{\infty} \omega_0{}^n \exp[-\omega_0 t] \prod_{j=1}^{n+1} \int_0^{t_j} dt_{j-1} \exp[-\omega_0(t_j - t_{j-1})] \\ &\quad \times \langle \cos \omega(t_j - t_{j-1}) \rangle \\ &= \sum_{n=0}^{\infty} \omega_0{}^n \prod_{j=1}^{n+1} \int_0^{t_j} dt_{j-1} \exp[-\omega_0(t_j - t_{j-1})] \langle \cos \omega(t_j - t_{j-1}) \rangle. \end{aligned} \tag{6.63}$$

Now, $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ for a free particle is

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \langle \cos \omega t \rangle. \tag{6.64}$$

This was computed in the previous section and is presented in Fig. 24. Equation (6.63) contains this function in combination with $e^{-\omega_0 t}$. Let us define the function $D_{10}(t)$,

$$D_{10}(t) \equiv e^{-\omega_0 t} \langle \cos \omega t \rangle.$$

Equation (6.63) then becomes

$$\begin{aligned} D_1(t) &= D_{10}(t) + \omega_0 \int_0^t dt_1\, D_{10}(t - t_1) D_{10}(t_1) \\ &\quad + \omega_0{}^2 \int_0^t dt_2\, D_{10}(t - t_2) \int_0^{t_2} dt_1\, D_{10}(t_2 - t_1) D_{10}(t_1) + \ldots. \end{aligned}$$

This can be iterated to give the integral equation

$$D_1(t) = D_{10}(t) + \omega_0 \int_0^t dt'\, D_{10}(t - t') D_1(t'). \tag{6.65}$$

Again we define the dimensionless variables $\tau = \langle \omega^2 \rangle_{\mathrm{cl}}^{1/2} t$, $\tau' = \langle \omega^2 \rangle_{\mathrm{cl}}^{1/2} t'$, and $w = \omega_0 / \langle \omega^2 \rangle_{\mathrm{cl}}^{1/2}$. Then

$$D_1(\tau) = D_{10}(\tau) + w \int_0^{\tau} d\tau'\, D_{10}(\tau - \tau') D_1(\tau') \tag{6.66}$$

The parameter w measures the ratio of collision frequency to rotational frequency at a given temperature and density. If w is very small, we expect to have free rotation, whereas if w is very large, we expect to see very little free motion. In fact, in this latter limit we expect to see Brownian rotations. This model cannot be computed analytically. In Fig. 26 this function is computed for different values of w. Note that, as w increases, $D_1(\tau)$ goes from the free-rotor to the Brownian-rotor model.

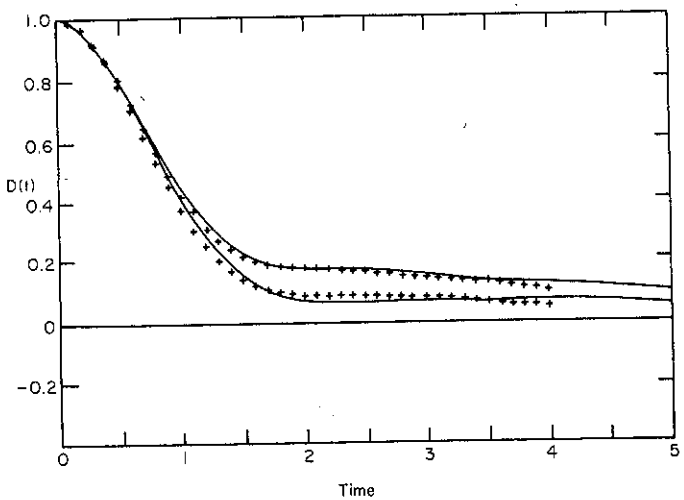

FIG. 26. The dipolar autocorrelation function $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ for CO in CCl_4 solution compared with the theoretical curve Eq. (6.66) (bottom curve), and in $CHCl_3$ solution compared with theory (top curve).

D. Information Theory of Orientational Distribution Functions

It would be very convenient if $\langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle$ for $l = 2, \ldots$ could be determined from knowledge of $\langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle$. If this could be done, it would then be possible, for example, to predict Raman band shapes from ir band shapes, or neutron-scattering cross sections from infrared spectroscopic data. In order to make these predictions, the distribution function of $\mathbf{u}(0)$ and $\mathbf{u}(t)$ has to be guessed from one or more of its known moments. In the following (Berne *et al.*, 1968), we shall make this guess by maximizing the information entropy of this distribution subject to the known (experimental) behavior of $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$.

First, suppose that a spherical surface of unit radius is drawn and the

center of this sphere is taken as the origin of a spherical polar coordinate system. Suppose further that $\mathbf{u}(0)$ the initial orientation of a diatomic molecule, is represented by the unit vector $\mathbf{z}$ along the positive Z axis of this system. As time progresses, $\mathbf{u}$ will move about on the surface of the sphere and at any particular instant of time t its orientation will be uniquely specified by its polar and azimuthal angles θ and ϕ. The actual path that $\mathbf{u}$ traces out on the surface will, in general, be very complicated due to the continual interaction of the diatomic molecule with its neighbors. Let $P(\theta, \phi; t)\, d\Omega$ be the probability at time t that $\mathbf{u}$ is oriented in the direction of the solid angle $d\Omega$. After a time t that is long compared to the orientational relaxation time, $P(\theta, \phi; t)$ will be independent of its initial value and will tend toward the uniform distribution, i.e.,

$$\lim_{t \to \infty} P(\theta, \phi; t) = 1/4\pi$$

The time correlation functions $\langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle$ can be computed provided $P(\theta, \phi; t)$ is known since

$$\langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle = \int d\Omega\, P(\theta, \phi; t) P_l(\cos\theta). \tag{6.67}$$

It is now assumed that $\langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ is known and we want to guess the probability distribution P. We do this by maximizing the information entropy $S[P]$ of the distribution P,

$$S[P] = -\int d\Omega\, P(\Omega; t) \ln P(\Omega; t) \tag{6.68}$$

subject to the constraints

$$P(\Omega; t) \geq 0, \tag{6.69a}$$

$$\int d\Omega\, P(\Omega; t) = 1, \tag{6.69b}$$

$$\int d\Omega\, P(\Omega, t) \cos\theta = \langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle, \tag{6.69c}$$

where (a) and (b) are the conditions that P be a probability distribution and (c) is the condition that P gives the right dipolar correlation function. Introducing Eq. (6.69) into the problem via Lagrange multipliers α and β gives

$$\begin{aligned} &\delta \int d\Omega [P \ln P - (\alpha + 1)P - \beta \cos\theta P] = 0, \\ &\int d\Omega [\ln P - \alpha - \beta \cos\theta]\, \delta P = 0, \end{aligned} \tag{6.70}$$

or

$$P(\Omega; t) = e^{\alpha+\beta\cos\theta} \tag{6.71}$$

This distribution automatically satisfies the positivity condition (6.69a). This distribution function can be expanded in Legendre polynomials,

$$P(\Omega; t) = e^{\alpha} \sum_{n=0}^{\infty} (2n+1) B_{n+1/2}(\beta) P_n(\cos\theta) \tag{6.72}$$

where

$$B_{n+1/2}(\beta) = (\pi/2\beta)^{1/2} I_{n+1/2}(\beta); \tag{6.73}$$

$I_{n+1/2}(\beta)$ is the modified spherical Bessel function of the first kind. The functions $B_{n+1/2}(\beta)$ can be determined from the recursion relations

$$\begin{aligned} B_{n+(1/2)}(\beta) &= g_n(\beta)\sinh\beta + g_{-n-1}(\beta)\cosh\beta \\ g_{n-1}(\beta) - g_{n+1}(\beta) &= [(2n+1)/\beta] g_n(\beta), \qquad n = 0, \pm 1, \pm 2, \ldots, \end{aligned} \tag{6.74}$$

with

$$g_0(\beta) = 1/\beta, \qquad g_1(\beta) = -1/\beta^2.$$

It is then easy to see that

$$\begin{aligned} B_{1/2}(\beta) &= \sinh\beta/\beta \\ B_{3/2}(\beta) &= -\sinh\beta/\beta^2 + \cosh\beta/\beta \\ B_{5/2}(\beta) &= (3/\beta^3 + 1/\beta)\sinh\beta - (3/\beta^2)\cosh\beta \\ B_{7/2}(\beta) &= [1/\beta^2 + 5/\beta^3 + 15/\beta^4]\sinh\beta - (3/\beta^3)\cosh\beta \end{aligned} \tag{6.75}$$

The Lagrange multipliers α and β are determined from the constraints (6.69b) and (6.69c). From (6.69a),

$$\int d\Omega\, P(\Omega; t) = 4\pi e^{\alpha} B_{1/2}(\beta) = 1,$$

or

$$e^{\alpha} = 1/4\pi B_{1/2}(\beta) \tag{6.76}$$

This result follows directly from the orthogonality relation on the Legendre polynomials,

$$\int d\Omega\, P_n(\cos\theta) P_m(\cos\theta) = [4\pi/2n+1)]\, \delta_{nm}. \tag{6.77}$$

From Eqs. (6.72) and (6.76),

$$P(\Omega; t) = [1/4\pi B_{1/2}(\beta)] \sum_{n=0}^{\infty} (2n+1) B_{n+1/2}(\beta) P_n(\cos\theta). \tag{6.78}$$

Consequently,

$$\langle P_l(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle = B_{l+1/2}(\beta)/B_{1/2}(\beta). \tag{6.79}$$

Constraint (6.69c) gives

$$\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle = \langle P_1(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle = B_{3/2}(\beta)/B_{1/2}(\beta). \tag{6.80}$$

From Eq. (6.75), we see that

$$\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle = [-1/\beta(t) + \coth\beta(t)] = L(\beta(t));$$

$L(\beta)$ is the well-known Langevin function from the theory of paramagnetism; $\beta(t)$ can be determined from the experimental dipolar correlation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$.

The higher-order correlation functions such as $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ can now be determined in terms of $\beta(t)$ and thereby in terms of $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$. For example,

$$\begin{aligned} \langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle &= B_{5/2}(\beta)/B_{1/2}(\beta) = [3/\beta^2 + 1] - (3/\beta)\coth\beta \\ &= 1 - (3/\beta(t))L(\beta(t)) \end{aligned} \tag{6.81}$$

and

$$\begin{aligned} \langle P_3(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle &= B_{7/2}(\beta)/B_{1/2}(\beta) \\ &= [1 + 15/\beta^2]\coth\beta - [1/\beta + 5/\beta^2 + 15/\beta^3]. \end{aligned} \tag{6.82}$$

Maximizing the information entropy of a distribution gives in some sense the "smoothest" distribution consistent with our available information on this distribution. We have tested the information-theory prediction of $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ from $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ for two different systems: the Stockmayer and modified Stockmayer simulations of CO. We have already seen that these two systems represent two extreme forms of molecular rotational motion. In the Stockmayer simulation, the molecules rotate essentially freely, whereas in the modified Stockmayer simulation, there is evidence for strongly hindered rotational motion. Figure 27 shows $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ from the Stockmayer simulation, and the experimental $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ and its information–theory prediction are presented in Fig. 28. In this particular instance, the information-theory prediction agrees with experiment only for short times, i.e., $t \lesssim 4.5 \times 10^{-13}$ sec. Figure 29 shows $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ from the modified Stockmayer simulation, and the experimental $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ and its in-

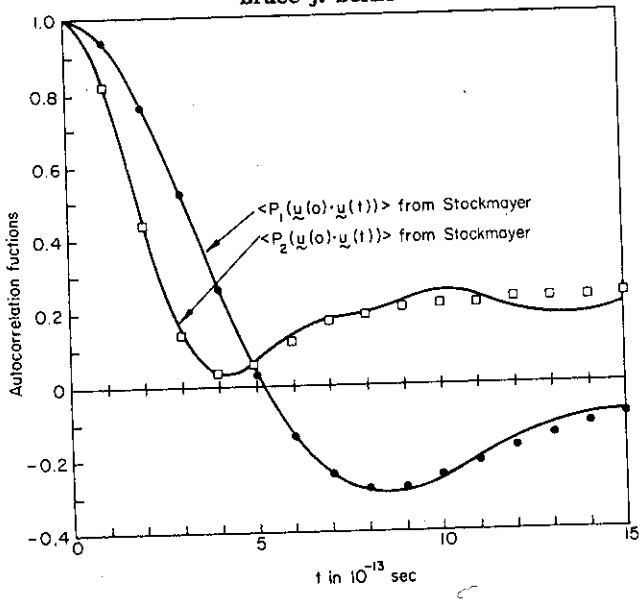

FIG. 27. Plot of $\langle P_1(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ (solid point) and $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ (square point) from the Stockmayer simulation (solid line) and from the gas phase for CO gas at 68°K.

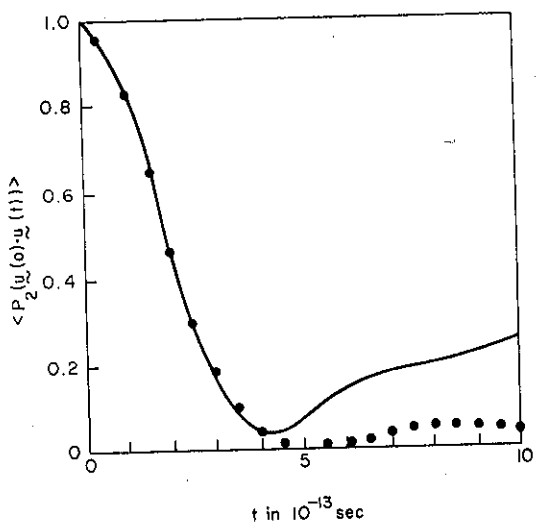

FIG. 28. Comparison of $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ from Stockmayer (solid line) and from information theory (solid points).

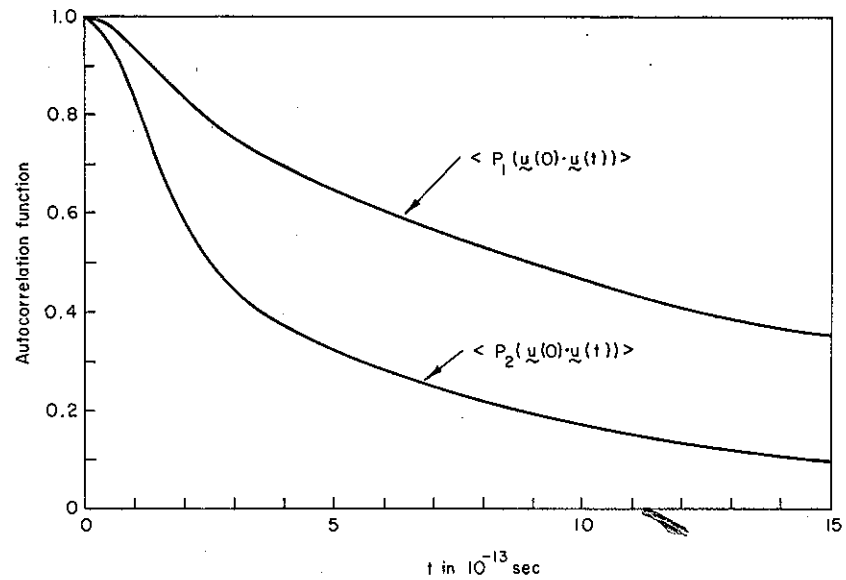

FIG. 29. Plot of $\langle P_1(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ and $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ from the modified Stockmayer simulation.

formation-theory prediction are presented in Fig. 30. Note that in this example the information-theory prediction is in excellent agreement with experiment for $t \leq 10^{-12}$ sec. This is a significant result, since in this particular instance, the decay of $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ is predominantly governed by intermolecular interactions and, hence, would be very difficult to calculate theoretically from first principles.

E. Rotational Brownian Motion

When the relative collision frequency w in Eq. (6.66) is large, molecules are so frequently jostled by collisions that they rarely can complete free rotational cycles. This is usually the case in liquids. Debye proposed a random walk theory of rotational reorientation of point dipoles in liquids (Debye, 1929). According to Debye, the joint probability $P(\Omega_0, \Omega; t)$ for a molecule to have the orientation Ω at time t and the orientation Ω_0 at $t = 0$ satisfies the equation

$$\frac{\partial}{\partial t} P = D_{\mathrm{R}}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]P, \qquad (6.83)$$

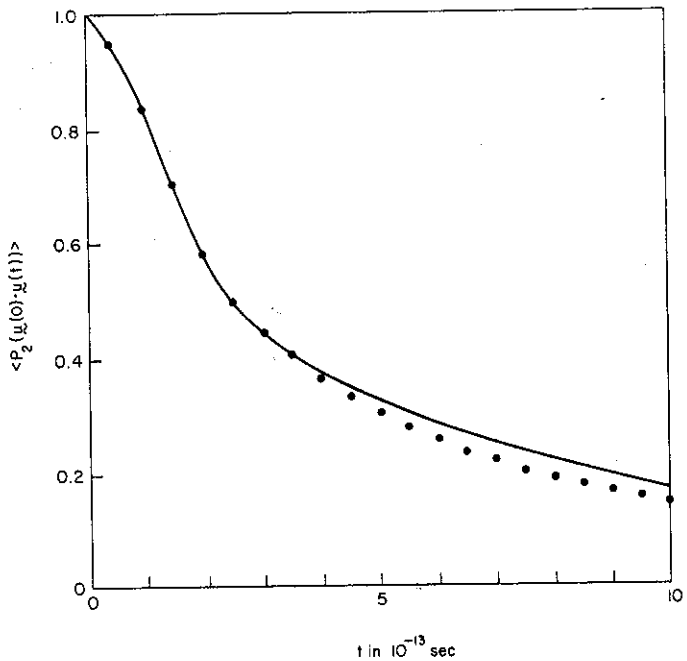

FIG. 30. Plot of $\langle P_1(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ and $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ from computer experiment (modified Stockmayer simulation) (solid line) and from information theory (dots).

where the angles θ and ϕ the specify orientation of the dipole at time t and D_R is the "rotational diffusion constant." The operator in parenthesis is simply the angular part of the Laplacian. From quantum mechanics, we know that this is identical to $-\hat{J}^2/\hbar^2$, where $\hat{J}$ is the angular momentum operator in the central force problem. Let us call the dimensionless angular momentum operator $\hat{I} = (1/\hbar)\hat{J}$. Then Debye's equation for isotropic rotational Brownian motion is

$$(\partial/\partial t)P(\Omega_0, \Omega; t) = -D_R\hat{I}^2P(\Omega_0, \Omega; t). \tag{6.84}$$

The total angular momentum operator $\hat{I}^2$ has the well-known surface spherical harmonics as eigenfunctions,

$$\hat{I}^2Y_{l,m}(\Omega) = l(l+1)Y_{l,m}(\Omega), \qquad \hat{I}_zY_{l,m}(\Omega) = mY_{l,m}(\Omega). \tag{6.85}$$

It is obvious, then, that Eq. (6.83) can be solved by expanding $P(\Omega_0, \Omega; t)$ in the surface spherical harmonics. In Section VI,A, it was shown that

the only expansion consistent with the system being in thermal equilibrium is

$$P(\Omega_0, \Omega; t) = \sum_{l,m} b_{l,m}(t)Y^*_{l,m}(\Omega)Y_{l,m}(\Omega_0) \tag{6.86}$$

where

$$b_{l,m}(t) = \langle Y^*_{l,m}(\Omega(0))Y_{l,m}(\Omega(t))\rangle$$

and where $b_{l,m}(0) = 1/4\pi$. Substitution of Eq. (6.86) into Eq. (6.84) yields

$$\sum_{l,m} Y^*_{l,m}(\Omega)Y_{l,m}(\Omega_0)\frac{\partial}{\partial t}b_{l,m}(t) \sum_{l,m} Y^*_{l,m}(\Omega)Y_{l,m}(\Omega_0)[-l(l+1)D_Rb_{l,m}(t)]$$

where the fact that $Y^*_{l,m}(\Omega)$ is an eigenfunction of $\hat{I}^2$ has been exploited. Taking the scalar product of this equation with $Y_{l,m}(\Omega)Y^*_{l,m}(\Omega_0)$ yields the equation for $b_{l,m}(t)$

$$(\partial/\partial t)b_{l,m}(t) = -l(l+1)D_Rb_{l,m}(t), \tag{6.87}$$

which has the solution [subject to the boundary condition $b_{l,m}(0)=1/4\pi$]

$$b_{l,m}(t) = (1/4\pi)\exp[-2(l+1)D_Rt]. \tag{6.88}$$

We have thus determined the joint probability

$$P(\Omega_0, \Omega; t) = (1/4\pi)\sum_{l,m} Y^*_{l,m}(\Omega)Y_{l,m}(\Omega_0)\exp[-l(l+1)D_Rt] \tag{6.89}$$

and the time correlation function

$$\langle Y^*_{l,m}(\Omega(0))Y_{l,m}(\Omega(t))\rangle = (1/4\pi)\exp - l(l+1)D_Rt] \tag{6.90}$$

for an equilibrium ensemble of isotropic Brownian rotors. Note that the time-dependent coefficient $b_{l,m}(t)$ does not depend on m, i.e., there is a $(2l+1)$fold degeneracy. This is because all space-fixed directions are equivalent in an isotropic system. If an external electric field is switched on, the degeneracy is lifted and $b_{l,m}(t)$ will also depend on m.

All of the experiments that have been discussed require time correlations like $\langle P_l(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ where $\mathbf{u}$ is the direction of the dipole moment $\mathbf{u}$. These functions can be computed in the following way. From the spherical harmonic addition theorem,

$$P_l(\mathbf{u}(0)\cdot\mathbf{u}(t)) = [4\pi/(2l+1)]\sum_{m=-l}^{+l} Y^*_{l,m}(\Omega(0))Y_{l,m}(\Omega(t)),$$

where the angles $\Omega(0)$ and $\Omega(t)$ specify the directions of $\mathbf{u}(0)$ and $\mathbf{u}(t)$. Thus,

$$\langle P_l(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle = [4\pi/(2l+1)]\sum_{m=-l}^{+l}\langle Y^*_{l,m}(\Omega(0))Y_{l,m}(\Omega(t))\rangle, \quad (6.91)$$

which, from Eq. (6.90), yields

$$\langle P_l(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle = \exp[-l(l+1)D_{\mathrm{R}}t]. \quad (6.92)$$

Debye's theory of isotropic rotational diffusion of point dipoles leads to the following results for:

1. Neutron scattering, Eq. (6.16):

$$F_\alpha^{\mathrm{rel}}(\mathbf{k},t) = \sum_{l=0}^{\infty}(2l+1)\,|j_l(\mu k a_0/m_\alpha)|^2\exp[-l(l+1)D_{\mathrm{R}}t]. \quad (6.93)$$

2. Infrared absorption, Eq. (6.17):

$$\langle P_1(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle = e^{-2D_{\mathrm{R}}t},$$
$$\hat{I}(\omega) = \frac{1}{\pi}\frac{2D_{\mathrm{R}}}{(\omega-\omega_0)^2+(2D_{\mathrm{R}})^2}. \quad (6.94)$$

3. Dielectric relaxation, Eq. (6.22):

$$\left[\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}\right]^{-1} = 1 - i\frac{\varepsilon_0}{2\varepsilon_0+\varepsilon_\infty}\left(\frac{\omega}{2D_{\mathrm{R}}}\right). \quad (6.95)$$

4. Raman scattering, Eqs. (6.33) and (6.34):

$$\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle = e^{-6D_{\mathrm{R}}t}$$
$$\hat{I}_\perp^{(1)}(\omega) = \frac{1}{\pi}\frac{6D_R}{[\omega-\omega_1]^2+[6D_R]^2} \quad (6.96)$$
$$\hat{I}_\perp^{(0)}(\omega) = \frac{1}{\pi}\frac{6D_R}{\omega^2+[6D_R]^2}$$

5. The depolarization of fluorescence, Eq. (6.36):

$$r(t) = \tfrac{2}{5}e^{-6D_{\mathrm{R}}t}. \quad (6.97)$$

In the event that a molecule is nonspherical, the Debye theory, which describes the rotational diffusion of isotropic (spherical) molecules, does not apply. The Debye theory has been generalized by Favro. This generalization is discussed in the remainder of this section. It should be noted that this development is completely analogous to the foregoing.

The problem of describing the rotations of rigid polyatomic molecules

has been solved completely. The orientation of a rigid body is specified with respect to a space-fixed Cartesian coordinate system by the three Eulerian angles α, β, γ. In terms of the molecular axes (or body-fixed axes), α and β are the azimuthal and polar angles of the body-fixed Z axis in the space-fixed frame and γ is the angle that specifies orientation of the molecule about its own z axis.

The Wigner rotation matrices $D^J_{M,K}(\Omega)[\mathbf{\Omega} = (\alpha,\beta,\gamma)]$ form a complete orthogonal set of functions which span the space of these Euler angles $\mathbf{\Omega}$. Any function of these angles can consequently be expressed as a linear combination of the rotation matrices. The transformation properties of the matrices under rotations are described in the books by Rose (1957) and Edmunds (1957). Only a few of their more important properties are summarized below:

$$D^{J*}_{M,K}(\Omega) = (-1)^{K-M}D^J_{-M,-K}(\Omega), \quad (6.98a)$$

$$\int d\Omega\, D^{J'*}_{M',K}(\Omega)D^J_{M,K}(\Omega) = [8\pi^2/(2J+1)]\,\delta_{J,J'}\,\delta_{M,M'}\,\delta_{K,K'}, \quad (6.98b)$$

$$D^J_{\alpha,\beta}(\Omega_0) = \sum_M D^J_{\alpha,M}(\Omega_t)D^{J*}_{\beta,M}(\delta\Omega(t)), \quad (6.98c)$$

$$D^J_{\alpha,\beta}(\Omega_t) = \sum_M D^J_{\alpha,M}(\Omega_0)D^J_{M,\beta}(\delta\Omega(t)), \quad (6.98d)$$

$$\sum_M D^{J*}_{M,K}(\Omega)D^J_{M,K'}(\Omega) = \delta_{K,K'}, \quad (6.98e)$$

$$\sum_K D^{J*}_{M,K}(\Omega)D^J_{M',K}(\Omega) = \delta_{M,M'}, \quad (6.98f)$$

where $d\Omega = d\alpha\, d(\cos\beta)\, d\gamma$. Property (a) follows from the symmetry properties of the rotation matrices. Property (b) expresses the orthogonality property. If a body with orientation Ω_0 is rotated through an angle $\delta\Omega_t$ to the new orientation Ω_t, then the rotation matrices transform under this rotation according to properties (c) and (d). Properties (e) and (f) express the completeness or closure relations of the Wigner rotation matrices.

These functions are very useful in both classical and quantum-mechanical studies of rotational motion. They have an added significance in quantum theory, where they are eigenfunctions of the total angular momentum L^2 and the angular momentum L_z^{S} and L_z^{B} around the space-fixed and body-fixed z axes, respectively:

$$\begin{aligned} L_z^{\mathrm{B}}D^J_{K,M}(\Omega) &= -i\hbar(\partial/\partial\gamma)D^J_{K,M}(\Omega) = -\hbar M D^J_{K,M}(\Omega)\\ L_z^{\mathrm{S}}D^J_{K,M}(\Omega) &= -i\hbar(\partial/\partial\alpha)D^J_{K,M}(\Omega) = -\hbar K D^J_{K,M}(\Omega)\\ L^2D^J_{K,M}(\Omega) &= J(J+1)\hbar^2D^J_{K,M}(\Omega). \end{aligned} \quad (6.99)$$

Let $K(\Omega, t \mid \Omega_0, 0)\, d\Omega$ be the transition probability that a molecule stating with orientation Ω_0 at the initial instant $t = 0$ will rotate in such a way that it will have an orientation within $d\Omega$ of Ω at time t. Since the functions $D^J_{K,M}(\Omega)$ span the space of all functions of Ω, then $K(\Omega, t \mid \Omega_0, 0)$ can be expanded in these functions as

$$K(\Omega, t \mid \Omega_0, 0) = \sum_{JMK} b^J_{K,M}(t) D^J_{K,M}(\Omega_0) D^{J*}_{K,M}(\Omega). \tag{6.100}$$

It is perhaps more transparent to determine the form of $K(\Omega, t \mid \Omega_0, 0)$ using the arguments that were developed in the sections on linear molecules. Let $P(\Omega, t)$ be the probability density for finding a molecule with orientation Ω at time t. Then $P(\Omega, t)$ can be expanded in the complete set $D^J_{K,M}(\Omega)$ as follows:

$$P(\Omega, t) = \sum_{J=0}^{\infty} \sum_{K,M=-J}^{J} a^J_{K,M}(t) D^{J*}_{K,M}(\Omega), \tag{6.101}$$

with the expansion coefficient $a^J_{K,M}(t)$.

$$a^J_{K,M}(t) = \int d\Omega\, P(\Omega, t) D^J_{K,M}(\Omega)[(2J+1)/8\pi^2]. \tag{6.102}$$

If the molecule has an orientation Ω_0 at $t = 0$, it follows that $K(\Omega, t \mid \Omega_0, 0) \equiv P(\Omega, t)$. In that case,

$$P(\Omega, 0) = \delta(\Omega - \Omega_0)$$

and

$$a^J_{K,M}(0) = [(2J+1)/8\pi^2] D^J_{K,M}(\Omega_0). \tag{6.103}$$

If $a^J_{K,M}(t)$ is expressed as $a^J_{K,M}(0) F^J_{K,M}(t)$, it follows that

$$K(\Omega, t \mid \Omega_0, 0) = \sum_{JKM} [(2J+1)/8\pi^2] F^J_{K,M}(t) D^{J*}_{K,M}(\Omega) D^J_{K,M}(\Omega_0). \tag{6.104}$$

In thermodynamic equilibrium, molecules are distributed with the random distribution $P(\Omega_0) = 1/8\pi^2$. Consequently, the joint probability distribution $P(\Omega, t; \Omega_0, 0)$ is simply $P(\Omega_0) K(\Omega, t \mid \Omega_0, 0)$ or

$$P(\Omega_0, \Omega; t) = 1/8\pi^2 \sum_{JKM} [(2J+1)/8\pi^2] F^J_{K,M}(t) D^{J*}_{K,M}(\Omega) D^J_{K,M}(\Omega_0). \tag{6.105}$$

In this case, it is a simple matter to determine the time-dependent functions $F^J_{K,M}(t)$ in terms of orientational time correlations functions.

Multiplication of Eq. (6.105) by $D^{J*}_{K,M}(\Omega_0) D^J_{K,M}(\Omega)$ followed by an integration over $d\Omega\, d\Omega_0$ with subsequent use of the orthogonality property Eq. (6.98b) yields

$$\langle D^{J*}_{K,M}(\Omega(0)) D^J_{K,M}(\Omega(t)) \rangle = [1/(2J+1)] F^J_{K,M}(t), \tag{6.106}$$

where the left-hand side is a time correlation function in an equilibrium or uniform ensemble. Consequently,

$$P(\Omega_0, \Omega; t) = \sum_{JKM} [(2J+1)/8\pi^2] \langle D^{J*}_{K,M}(\Omega(0)) D^J_{K,M}(\Omega(t)) \rangle \times D^{J*}_{K,M}(\Omega) D^J_{K,M}(\Omega_0) \tag{6.107}$$

for an equilibrium system. Note that this function is normalized, as it must be. This follows from the fact that $D^0_{0,0}(\Omega) = 1 = D^0_{0,0}(\Omega_0)$. If the molecule is linear and if the body-fixed z axis is along the molecular axis, then the orientation of the molecule in the space-fixed system is specified by α and β with $\gamma = 0$. In this case, $D^J_{K,M}(\alpha, \beta, 0) = D^J_{K,0}(\alpha, \beta, 0)$ and the joint probability distribution $P(\Omega, t; \Omega_0, 0)$ correctly reduces for linear molecules to Eq. (6.86).

This formulation is quite general. It is easy to specialize it to specific models. All that remains is to compute $F^J_{K,M}(t)$ or, equivalently, $\langle D^{J*}_{K,M}(\Omega(0)) D^J_{K,M}(\Omega(t)) \rangle$. For example, Favro has derived the rotational diffusion equation for an arbitrary rigid rotor,

$$(\partial/\partial t) P(\Omega, t) = -\hat{\mathbf{M}} \cdot \mathbf{D}_{\mathrm{R}} \cdot \hat{\mathbf{M}} P(\Omega, t), \tag{6.108}$$

where $\mathbf{M}$ is the dimensionless angular momentum operator and $\mathbf{D}_{\mathrm{R}}$ is the rotational diffusion tensor. This equation is simple if the body-fixed axes are chosen as the principal axes of the rotational diffusion tensor. In this case,

$$(\partial/\partial t) P(\Omega, t) = -[D_{aa} \hat{M}_a^2 + D_{bb} \hat{M}_b^2 + D_{cc} \hat{M}_c^2], \tag{6.109}$$

where the Euler angles (α, β, γ) define the rotation that carries the space fixed coordinate system into the principal axes of diffusion, a, b, c, fixed in the body, and $\hat{M}_a$, $\hat{M}_b$, and $\hat{M}_c$ are the dimensionless angular momentum operators along these principal axes. This equation cannot be solved exactly for the asymmetric rotor. Nevertheless, all time correlation functions with $J \leq 2$ can be determined. The solution is quite tedious. For the sake of simplicity we discuss the solution for the symmetric top. The symmetric top is a rigid Brownian rotor with two principal diffusion

coefficients equal, say $D_{aa} = D_{bb}$, then

$$\partial P(\Omega, t)/\partial t = -[D_{aa}[\hat{M}_a^2 + \hat{M}_b^2] + D_{cc}\hat{M}_c^2]P. \tag{6.110}$$

Since $M^2 = M_a^2 + M_b^2 + M_c^2$ it follows that

$$\partial P(\Omega, t)/\partial t = -[D_{aa}\hat{M}^2 + (D_{cc} - D_{aa})\hat{M}_c^2]P, \tag{6.111}$$

$\hat{M}_c$ is the angular momentum operator about the symmetric top's symmetry axis or z axis and M^2 is the total angular momentum. It should be noted that this reduced to Eq. (6.84) when $D_{aa} = D_{bb} = D_{cc}$. From Eq. (6.99)

$$\begin{aligned}&[D_{aa}\hat{M}^2 + (D_{cc} - D_{aa})\hat{M}_c^2]D^{J*}_{K,M}(\Omega)\\ &\quad = [D_{aa}J(J+1) + (D_{cc} - D_{aa})M^2]D^{J*}_{K,M}(\Omega)\end{aligned}$$

Consequently the Wigner rotation matrices are eigenfunctions of the diffusion operator. Thus if $P(\Omega, t)$ is expanded in $D^{J*}_{K,M}(\Omega)$ [Eq. (5.128)], the diffusion equation becomes

$$\begin{aligned}&\sum_{JKM} (\partial/\partial t)a^J_{K,M}(t)D^{J*}_{K,M}(\Omega)\\ &\quad = -\sum_{JKM} a^J_{K,M}(t)[D_{aa}J(J+1) + (D_{cc} - D_{aa})M^2]D^{J*}_{K,M}(\Omega).\end{aligned} \tag{6.112}$$

Taking the scalar product of this equation with $D^J_{K,M}(\Omega)$ yields

$$\frac{\partial}{\partial t} a^J_{K,M}(t) = -[D_{aa}J(J+1) + (D_{cc} - D_{aa})M^2]a^J_{K,M}(t), \tag{6.113}$$

whose solution is

$$a^J_{K,M}(t) = a^J_{K,M}(0) \exp -[J(J+1)D_{aa} + M^2(D_{cc} - D_{aa})]t. \tag{6.114}$$

Comparison of this with Eq. (6.104) shows that

$$F^J_{K,M}(t) = \exp -[J(J+1)D_{aa} + M^2(D_{cc} - D_{aa})]t. \tag{6.115}$$

From Eq. (6.106), it follows that

$$\begin{aligned}&\langle D^{J*}_{K,M}(\Omega(0))D^J_{K,M}(\Omega(t))\rangle\\ &\quad = [1/(2J+1))] \exp -[J(J+1)D_{aa} + M^2(D_{cc}D_{aa})]t\end{aligned} \tag{6.116}$$

and

$$\begin{aligned}P(\Omega_0, \Omega; t) = \sum_{JKM} &1/8\pi^2[(2J+1)/8\pi^2]D^{J*}_{K,M}(\Omega)D^J_{K,M}(\Omega_0)\\ &\times \exp -[J(J+1)D_{aa} + (D_{cc} - D_{aa})M^2]t.\end{aligned} \tag{6.117}$$

These are the orientational time correlation functions and the joint probability distribution for the symmetric top Broronian rigid rotor.

For a freely-rotating molecule, it should be noted from Eq. (6.98d) that

$$\langle D^{J*}_{K,M}(\Omega(0))D^J_{K,M}(\Omega(t))\rangle = \sum_{M'} \langle D^{J*}_{K,M}(\Omega_0)D^J_{K,M}(\Omega_0)D^J_{M',M}(\delta\Omega(t))\rangle, \tag{6.118}$$

where a molecule with initial orientation Ω_0 rotates freely through an angle $\delta\Omega(t)$ to the new orientation $\Omega(t)$. For a free rotor, $\delta\Omega(t)$ depends only on the angular velocities about the three principal axes of rotation and the time. Consequently, an average over an initial uniform distribution $P(\Omega_0) = 1/8\pi^2$ can be performed, so that, for a free rotor,

$$\langle D^{J*}_{K,M}(\Omega(0))D^J_{K,M}(\Omega(t))\rangle = \frac{1}{2J+1}\langle D^J_{M,M}(\delta\Omega(t))\rangle, \tag{6.119}$$

where the latter average is over a Maxwell distribution of angular velocites about the body-fixed axes. These averages have been explicitly computed (St. Pierre and Steele, 1969; Fixman and Rider, 1969). They are carried out in an analogous way to Eq. (6.52) of this section. From Eq. (6.106), we see that

$$F^J_{K,M}(t) = \langle D^J_{M,M}(\delta\Omega(t))\rangle. \tag{6.120}$$

Suppose that a correlation function of some vector property that lies fixed within the molecule is needed. As the molecule rotates, this vector will change its orientation in the laboratory or space-fixed coordinate system. This is important, for example, if the vector is a transition dipole moment $\boldsymbol{\mu}$; then absorption and fluorescence of light will depend on the reorientation of $\boldsymbol{\mu}$ in the laboratory frame.

Generally, the vector $\boldsymbol{\mu}$ is known in Cartesian form,

$$\boldsymbol{\mu} = \begin{pmatrix}\mu_x\\ \mu_y\\ \mu_z\end{pmatrix}.$$

It is easier to solve problems of this kind if the vector is in spherical vector from μ_S, where

$$\boldsymbol{\mu}_S = \begin{pmatrix}\mu_1\\ \mu_0\\ \mu_{-1}\end{pmatrix} = \begin{pmatrix}-(\mu_x + i\mu_y)/\sqrt{2}\\ \mu_z\\ (\mu_x + i\mu_y)/\sqrt{2}\end{pmatrix}.$$

This is most easily done (Rose, 1957) by applying the unitary transformation U so that

$$\mu_S = \mathsf{U} \cdot \mu,$$

where

$$\mathsf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & -i & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & -i & 0 \end{pmatrix}.$$

The spherical vector μ_S can be transformed from body-fixed $\mu_S{}^B$ to space-fixed $\mu_S{}^S$ coordinate axes by the unitary matrix $\mathbf{D}(\Omega)$,

$$\mu_S{}^S = \mathbf{D}(\Omega) \cdot \mu_S{}^B,$$

where $\mathbf{D}$ is a 3×3 unitary matrix with matrix elements

$$\mathbf{D}(\Omega) = \begin{pmatrix} D^1_{1,1}(\Omega) & D^1_{1,0}(\Omega) & D^1_{1,-1}(\Omega) \\ D^1_{0,1}(\Omega) & D^1_{0,0}(\Omega) & D^1_{0,-1}(\Omega) \\ D^1_{-1,1}(\Omega) & D^1_{-1,0}(\Omega) & D^1_{1,-1}(\Omega) \end{pmatrix} \tag{6.121}$$

and where Ω is the orientation in Eulerian angles of the body-fixed axes with respect to the space-fixed axes.

In general, the vector μ^B does not point along any of the principal axes of the molecular frame. Suppose μ^B is characterized by the polar and azimuthal angles (θ, ϕ) relative to the molecular z axis. Then the body-fixed spherical components of $\mu^B{}_S$ are

$$\mu_S{}^B = \mu \begin{pmatrix} D^{1*}_{1,0}(\theta, \phi) \\ D^{1*}_{0,0}(\theta, \phi) \\ D^{1*}_{-1,0}(\theta, \phi) \end{pmatrix}$$

Suppose that at time $t = 0$ the body-fixed axes have an orientation Ω_0 with respect to the space-fixed system. Then the spherical dipole moment in the space-fixed system at $t = 0$, $\mu_S{}^S(0)$, is

$$\mu_S{}^S(0) = \mathbf{D}(\Omega_0) \cdot \mu_S{}^B. \tag{6.122}$$

Likewise, if the molecular orientation is Ω_t at time t, the spherical dipole moment in the space-fixed system at time t, $\mu_S{}^S(t)$, is

$$\mu_S{}^S(t) = \mathbf{D}(\Omega_t) \cdot \mu_S{}^B. \tag{6.123}$$

If should be noted that the dot product of a pair of vectors is invariant to a unitary transformation; consequently, the projection of the Cartesian

vector $\mu(t)$ on $\mu(0)$ in the laboratory frame is equal to the scalar product of the spherical vectors,

$$\begin{aligned} \mu(0) \cdot \mu(t) &= \sum_{n=1}^{-1} \mu_n^{S*}(0)\mu_n{}^S(t) \\ &= \mu_1^{S*}(0)\mu_1{}^S(t) + \mu_0^{S*}(0)\mu_0{}^S(t) + \mu_{-1}^{S*}(0)\mu_{-1}^S(t). \end{aligned}$$

When Eqs. (6.121)–(6.123) are substituted into this, it is found that

$$\mu(0) \cdot \mu(t) = \mu^2 \sum_{KMM'} D^{1*}_{K,M'}(\Omega_0) D^1_{K,M}(\Omega_t) D^1_{M',0}(\theta, \phi) D^{1*}_{M,0}(\theta, \phi). \tag{6.124}$$

Consequently, the dipolar correlation function is

$$\langle \mu(0) \cdot \mu(t) \rangle = \mu^2 \sum_{KMM'} \langle D^{1*}_{K,M}(\Omega_0) D^1_{K,M}(\Omega_t) \rangle D^1_{M',0}(\theta, \phi) D^{1*}_{M,0}(\theta, \phi). \tag{6.125}$$

At $t = 0$, it is easy to show that $\langle \mu(0) \cdot \mu(0) \rangle = 1$. This follows from the orthogonality of the $\mathbf{D}$ matrices.

The correlation function that appears in this formula can be evaluated using the joint probability distribution for an equilibrium ensemble given by Eq. (6.105). Then,

$$\langle D^{1*}_{K,M'}(\Omega(0)) D^1_{K,M}(\Omega(t)) \rangle = \tfrac{1}{3} F^1_{K,M}(t)\, \delta_{M,M'}, \tag{6.126}$$

so that

$$\begin{aligned} \langle \mu(0) \cdot \mu(t) \rangle &= \tfrac{1}{3}\mu^2 \sum_{K,M} F^1_{K,M}(t) \mid D^1_{M,0}(\theta, \phi) \mid^2 \\ &= \mu^2 \sum_{K,M} \langle D^{1*}_{K,M}(\Omega(0)) D^1_{K,M}(\Omega(t)) \rangle \mid D^1_{M,0}(\theta, \phi) \mid^2 \end{aligned} \tag{6.127}$$

It should be noted that this function depends on the position of μ^B in the body-fixed frame. If the molecule is linear $D^J_{M,0}(0, 0, 0) = \delta_{M,0}$ and

$$\langle \mu(0) \cdot \mu(t) \rangle = \tfrac{1}{3}\mu^2 \sum_K F^1_{K,0}(t) = \mu^2 \sum_K \langle D^{1*}_{K,0}(\Omega(0)) D^1_{K,0}(\Omega(t)) \rangle.$$

Substitution of Eq. (6.98d), with subsequent use of the orthogonality relation, yields, for a linear molecule,

$$\langle \mu(0) \cdot \mu(t) \rangle = \mu^2 \langle D^1_{0,0}(\delta\Omega(t)) \rangle = \mu^2 \langle P_1(\cos\theta(t)) \rangle, \tag{6.128}$$

where $\theta(t)$ is the angle between $\mu(0)$ and $\mu(t)$. This is an obvious result, but serves as a useful consistency check.

In the general case, the time correlation functions $\langle D^{1*}_{K,M}(\Omega(0)) \times D^{1}_{K,M}(\Omega(t))\rangle$ must be determined. For the rotational Brownian motion of a symmetric top,

$$\langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle = \mu^2 \sum_{M=-1}^{+1} |D^1_{M,0}(\theta,\phi)|^2 \times \exp[-2D_{a,a}t]\exp[-M^2(D_{c,c}-D_{a,a})t], \quad (6.129)$$

For a spherical-top molecule, $D_{cc} = D_{aa} = D_{\mathrm{R}}$, and

$$\langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle = \mu^2 e^{-2D_{\mathrm{R}}t}. \quad (6.130)$$

It is often necessary to consider time correlation functions of real, symmetrical Cartesian tensors (3×3 matrix). For example, we saw that the depolarized component of the light-scattering spectrum is determined by the time correlation function

$$C_\perp(t) = \langle \mathrm{Tr}\, \boldsymbol{\beta}^*(0)\cdot\boldsymbol{\beta}(t)\rangle$$

where $\boldsymbol{\beta}$ is a real, symmetrical, traceless tensor

$$\boldsymbol{\beta} = \boldsymbol{\alpha} - \alpha_{\mathrm{I}}\mathbf{I}$$

which involves the polarizability tensor $\boldsymbol{\alpha}$ of the molecule in the laboratory frame. In this section, our aim will be to evaluate this time correlation function.

Let $\mathbf{T}^{\mathrm{BF}}$ and $\mathbf{T}^{\mathrm{SF}}$ stand for the symmetric Cartesian tensor

$$\mathbf{T} = \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{xy} & T_{yy} & T_{yz} \\ T_{xz} & T_{yz} & T_{zz} \end{pmatrix} \quad (6.131)$$

in the body-fixed and space-fixed coordinate systems. In the body-fixed system, the matrix elements are properties of the molecule, such as, for example, the polarizabilities or moments of inertia along different directions in the molecule. It is often convenient to choose a body-fixed coordinate system that diagonalizes $\mathbf{T}^{\mathrm{BF}}$. This is always possible, since a real, symmetric tensor is a Hermitian matrix. The axes of this coordinate system are called principal axes. Then,

$$\mathbf{T}^{\mathrm{BF}} = \begin{pmatrix} T^{\mathrm{BF}}_{xx} & 0 & 0 \\ 0 & T^{\mathrm{BF}}_{yy} & 0 \\ 0 & 0 & T^{\mathrm{BF}}_{zz} \end{pmatrix}. \quad (6.132a)$$

This tensor simplifies considerably when the body possesses elements of symmetry:

1. *Symmetrical-top molecule*: $T^{\mathrm{BF}}_{xx} = T^{\mathrm{BF}}_{yy} \equiv T_\perp$; $T^{\mathrm{BF}}_{zz} \equiv T_\parallel$:

$$\mathbf{T}^{\mathrm{BF}} = \begin{pmatrix} T_\perp & 0 & 0 \\ 0 & T_\perp & 0 \\ 0 & 0 & T_\parallel \end{pmatrix}. \quad (6.132b)$$

2. *Spherical-top molecule*: $T^{\mathrm{BF}}_{xx} = T^{\mathrm{BF}}_{yy} = T^{\mathrm{BF}}_{zz} = T^{\mathrm{BF}}$:

$$\mathbf{T}^{\mathrm{BF}} = \begin{pmatrix} T & 0 & 0 \\ 0 & T & 0 \\ 0 & 0 & T \end{pmatrix} \quad (6.132c)$$

As the molecule reorients, the space-fixed tensor $\mathbf{T}^{\mathrm{SF}}$ changes. Since what is required is the space-fixed tensor (molecular properties are probed in the laboratory or space-fixed system), we must study how $\mathbf{T}$ transforms under rotations. Note that

$$\mathbf{T}^{\mathrm{SF}}(\Omega) = \mathbf{R}^{-1}(\Omega)\cdot\mathbf{T}^{\mathrm{BF}}\cdot\mathbf{R}(\Omega),$$

where $\mathbf{R}(\Omega)$ is the rotation operator, which has the effect of rotating the body-fixed axes into the space-fixed axes, and Ω is the set of Euler angles that specify the body-fixed coordinate system with respect to the space-fixed system. In what follows, we merely summarize the solution to this problem. We can transform this matrix equation into the spherical basis by applying the similarity transformation with the matrix $\mathbf{U}$. Then,

$$\mathbf{U}\mathbf{T}^{\mathrm{SF}}(\Omega)\mathbf{U}^{-1} = [\mathbf{U}\mathbf{R}^{-1}\mathbf{U}]\cdot[\mathbf{U}\mathbf{T}^{\mathrm{BF}}\mathbf{U}^{-1}][\mathbf{U}\mathbf{R}\mathbf{U}^{-1}]$$

or

$$\mathbf{S}^{\mathrm{SF}}(\Omega) = \mathbf{D}(\Omega)\mathbf{S}^{\mathrm{BF}}\mathbf{D}^{-1}(\Omega),$$

where $\mathbf{S}^{\mathrm{SF}}$ and $\mathbf{S}^{\mathrm{BF}}$ are the spherical tensors corresponding to $\mathbf{T}^{\mathrm{SF}}$ and $\mathbf{T}^{\mathrm{BF}}$, and $\mathbf{D}$ is the Wigner rotation matrix of Eq. (6.121),

$$\mathbf{D}(\Omega) = \begin{pmatrix} D^1_{1,1}(\Omega) & D^1_{1,0}(\Omega) & D^1_{1,-1}(\Omega) \\ D^1_{0,1}(\Omega) & D^1_{0,0}(\Omega) & D^1_{0,-1}(\Omega) \\ D^1_{-1,1}(\Omega) & D^1_{-1,0}(\Omega) & D^1_{-1,-1}(\Omega) \end{pmatrix}.$$

Consequently, $\mathbf{S}^{\mathrm{SF}}(\Omega)$ depends on products of $D^1_{K,M}(\Omega)$. To simplify this result, these products are expanded in terms of $D^2_{K,M}$ with the

Clebsch–Gordon coefficients as expansion coefficients. This is a rather elaborate proceedure. We merely present the results in a form which the reader will have no trouble using. For this purpose, we define a set of spherical components as

$$\begin{aligned} T_I &\equiv \tfrac{1}{3}[T_{xx} + T_{yy} + T_{zz}], \\ T_{\pm 2} &\equiv \tfrac{1}{2}[T_{xx} - T_{yy}] - iT_{xy}, \\ T_{\pm 1} &\equiv \mp[T_{zx} \pm iT_{zy}], \\ T_0 &\equiv (2/\sqrt{6})[T_{zz} - \tfrac{1}{2}(T_{xx} + T_{yy})]. \end{aligned} \tag{6.133a}$$

These equations can be solved for $T_{ij}(i, j = x, y, z)$,

$$\begin{aligned} T_{xx} &= T_I - (1/\sqrt{6})T_0 + (T_{+2} + T_{-2})/2 \\ T_{yy} &= T_I - (1/\sqrt{6})T_0 - (T_{+2} + T_{-2})/2, \\ T_{zz} &= T_I + (2/\sqrt{6})T_0, \\ T_{xy} &= (T_{+2} - T_{-2})/2i, \\ T_{zx} &= (T_{+1} - T_{-1})/2, \\ T_{zy} &= (T_{+1} + T_{-1})/2i. \end{aligned} \tag{6.133b}$$

Thus, the symmetrical tensor T is completely specified by T_I, $T_{\pm 1}$, $T_{\pm 2}$, and T_0. In the body-fixed system, T^{BF} is diagonal, so that $T_{ij}^{\mathrm{BF}} = 0\ (i \neq j)$ and

$$\begin{aligned} T_I^{\mathrm{BF}} &= \tfrac{1}{3}[T_{xx}^{\mathrm{BF}} + T_{yy}^{\mathrm{BF}} + T_{zz}^{\mathrm{BF}}], \\ T_{\pm 2}^{\mathrm{BF}} &= \tfrac{1}{2}[T_{xx}^{\mathrm{BF}} - T_{yy}^{\mathrm{BF}}], \\ T_{\pm 1}^{\mathrm{BF}} &= 0, \\ T_0^{\mathrm{BF}} &= (2/\sqrt{6})[T_{zz}^{\mathrm{BF}} - \tfrac{1}{2}(T_{xx}^{\mathrm{BF}} + T_{yy}^{\mathrm{BF}})], \end{aligned} \tag{6.133c}$$

so that

$$\mathsf{T}^{\mathrm{BF}} = \begin{pmatrix} T_I^{\mathrm{BF}} - (1/\sqrt{6})T_0^{\mathrm{BF}} + (T_{+2}^{\mathrm{BF}} + T_{-2}^{\mathrm{BF}})/2 & 0 & 0 \\ 0 & T_I^{\mathrm{BF}} - (1/\sqrt{6})T_0^{\mathrm{BF}} - (T_{+2}^{\mathrm{BF}} + T_{-2}^{\mathrm{BF}})/2 & 0 \\ 0 & 0 & T_I^{\mathrm{BF}} + (2/\sqrt{6})T_0^{\mathrm{BF}} \end{pmatrix}. \tag{6.134}$$

The problem to be solved is the following: Knowing T^{BF}, find T^{SF}. The solution is simply stated in terms of the spherical components

T_I, T_0, $T_{\pm 1}$, $T_{\pm 2}$. It can be shown that T_n^{SF} and T_n^{BF} are related by

$$\begin{aligned} T_I^{\mathrm{SF}} &= T_I^{\mathrm{BF}}, \\ T_n^{\mathrm{SF}} &= \sum_{n'=-2}^{+2} D_{n,n'}^2(\Omega) T_{n'}^{\mathrm{BF}}, \qquad n, n' = 0, \pm 1, \pm 2, \end{aligned} \tag{6.135a}$$

where the set T_n^{SF} is given in Eq. (6.133c), and where Ω specifies the orientation of the space-fixed with respect to the body-fixed axes. The resulting T_n^{SF} are used in conjunction with Eq. (6.133b) to determine T^{BF}. From Eq. (6.135a), we see that

$$\begin{aligned} T_I^{\mathrm{SF}} &= T_I^{\mathrm{BF}}, \\ T_0^{\mathrm{SF}}(\Omega) &= D_{0,0}^2(\Omega) T_0^{\mathrm{BF}} + [D_{0,2}^2(\Omega) + D_{0,-2}^2(\Omega)] T_2^{\mathrm{BF}}, \\ T_{\pm 1}^{\mathrm{SF}}(\Omega) &= D_{\pm 1,0}^2(\Omega) T_0^{\mathrm{BF}} + [D_{\pm 1,2}^2(\Omega) + D_{\pm 1,-2}^2(\Omega)] T_2^{\mathrm{BF}}, \\ T_{\pm 2}^{\mathrm{SF}}(\Omega) &= D_{\pm 2,0}^2(\Omega) T_0^{\mathrm{BF}} + [D_{\pm 2,2}^2(\Omega) + D_{\pm 2,-2}^2(\Omega)] T_2^{\mathrm{BF}}. \end{aligned} \tag{6.135b}$$

From Eq. (6.133b), it is easily seen that the matrix elements $T_{i,j}^{\mathrm{BF}}$ depend on the orientation of the molecule through the Wigner function $D_{K,M}^2(\Omega)$, since they are linear combinations of $T_n^{\mathrm{SF}}(\Omega)$.

Let us compute time correlation functions of the form $\langle T_n^{\mathrm{SF}*}(0) T_m^{\mathrm{SF}}(t)\rangle$. From Eq. (6.135a), it follows that

$$\langle T_n^{\mathrm{SF}*}(0) T_m^{\mathrm{SF}}(t)\rangle = \sum_{lj} \langle D_{nl}^{2*}(\Omega(0)) D_{mj}^2(\Omega(t))\rangle T_l^{\mathrm{BF}*} T_j^{\mathrm{BF}}. \tag{6.136}$$

It was already shown that in an equilibrium ensemble

$$\langle D_{nl}^{2*}(\Omega(0)) D_{mj}^2(\Omega(t))\rangle = \langle D_{nj}^{2*}(\Omega(0)) D_{nj}^2(\Omega(t))\rangle\, \delta_{nm}\, \delta_{lj}, \tag{6.137}$$

so that

$$\langle T_n^{\mathrm{SF}*}(0) T_m^{\mathrm{SF}}(t)\rangle = \sum_j \langle D_{nj}^{2*}(\Omega(0)) D_{nj}^2(\Omega(t))\rangle\, |\, T_j^{\mathrm{BF}}\, |^2\, \delta_{nm} \tag{6.138}$$

Let us now form the traceless tensor Γ,

$$\Gamma = \mathsf{T} - T_I \mathsf{I}, \tag{6.139}$$

whose elements Γ_{ij} can be written in terms of T_I, T_0, $T_{\pm 1}$, $T_{\pm 2}$ from Eq. (6.133b). Let us in fact compute the time correlation function

$$C_\perp(t) = \langle \mathrm{Tr}\, \Gamma^{\mathrm{SF}*}(0) \cdot \Gamma^{\mathrm{SF}}(t)\rangle \tag{6.140}$$

of this tensor. This can be expanded as

$$C_\perp(t) = \sum_{ij} \langle \Gamma_{ij}^{\mathrm{SF}*}(0)\Gamma_{ji}^{\mathrm{SF}}(t)\rangle. \tag{6.141}$$

From Eqs. (6.133b), (6.141), and (6.138), we see that

$$\begin{aligned}
\left.\begin{aligned}\langle\Gamma_{xx}^{\mathrm{SF}*}(0)\Gamma_{xx}^{\mathrm{SF}}(t)\rangle\\ \langle\Gamma_{yy}^{\mathrm{SF}*}(0)\Gamma_{yy}^{\mathrm{SF}}(t)\rangle\end{aligned}\right\} &= \tfrac{1}{6}\langle T_0^{\mathrm{SF}}(0)T_0^{\mathrm{SF}}(t)\rangle + \tfrac{1}{4}[\langle T_{+2}^{\mathrm{SF}*}(0)T_{+2}^{\mathrm{SF}}(t)\rangle \\
&\quad + \langle T_{-2}^{\mathrm{SF}*}(0)T_{-2}^{\mathrm{SF}}(t)\rangle], \\
\langle\Gamma_{zz}^{\mathrm{SF}*}(0)\Gamma_{zz}^{\mathrm{SF}}(t)\rangle &= \tfrac{2}{3}\langle T_0^{\mathrm{SF}*}(0)T_0^{\mathrm{SF}}(t)\rangle, \\
\langle\Gamma_{xy}^{\mathrm{SF}*}(0)\Gamma_{xy}^{\mathrm{SF}}(t)\rangle &= \tfrac{1}{4}[\langle T_{+2}^{\mathrm{SF}*}(0)T_{+2}^{\mathrm{SF}}(t)\rangle + \langle T_{-2}^{\mathrm{SF}*}(0)T_{-2}^{\mathrm{SF}}(t)\rangle], \\
\left.\begin{aligned}\langle\Gamma_{zx}^{\mathrm{SF}*}(0)\Gamma_{zx}^{\mathrm{SF}}(t)\rangle\\ \langle\Gamma_{zy}^{\mathrm{SF}*}(0)\Gamma_{zy}^{\mathrm{SF}}(t)\rangle\end{aligned}\right\} &= \tfrac{1}{4}[\langle T_{+1}^{\mathrm{SF}*}(0)T_{+1}^{\mathrm{SF}}(t)\rangle + \langle T_{-1}^{\mathrm{SF}*}(0)T_{-1}^{\mathrm{SF}}(t)\rangle].
\end{aligned} \tag{6.142}$$

Substitution into Eq. (6.141) yields the result

$$C_\perp(t) = \sum_{n=-2}^{+2} \langle T_n^{\mathrm{SF}*}(0)T_n^{\mathrm{SF}}(t)\rangle. \tag{6.143}$$

From Eq. (6.138), it follows that

$$C_\perp(t) = \sum_{n,j=-2}^{2} \langle D_{n,j}^{2*}(\Omega(0))D_{n,j}^{2}(\Omega(t))\rangle \mid T_j^{\mathrm{BF}}\mid^2. \tag{6.144}$$

This equation can be simplified considerably when the molecules have symmetry elements. For example:

1. *Symmetrical-top molecule*:

$$T_{\pm2}^{\mathrm{BF}} = 0; \qquad T_{\pm1}^{\mathrm{BF}} = 0; \qquad T_0^{\mathrm{BF}} = (2/\sqrt{6})(T_\parallel - T_\perp)$$

and

$$C_\perp(t) = \tfrac{2}{3}\mid T_\parallel - T_\perp\mid^2 \sum_{n=-2}^{2} \langle D_{n,0}^{2*}(\Omega(0))D_{n,0}^{2}(\Omega(t))\rangle. \tag{6.145a}$$

2. *Spherical-top molecule*:

$$T_{\pm2}^{\mathrm{BF}} = T_{\pm1}^{\mathrm{BF}} = T_0^{\mathrm{BF}} = 0, \qquad C_\perp(t) \equiv 0 \tag{6.145b}$$

In Section E, it was shown that a symmetrical-top Brownian rotor has the time correlation function

$$\langle D_{n,0}^{2*}(\Omega(0))D_{n,0}^{2}(\Omega(t))\rangle = \tfrac{1}{5}\, e^{-6D_\perp t} \tag{6.146}$$

so that, for the symmetrical-top,

$$C_\perp(t) = \tfrac{2}{3}\mid T_\parallel - T_\perp\mid^2 \exp(-6D_\perp t). \tag{6.147}$$

This function depends on the anisotropy of the axially symmetrical tensor T^{BF}.

In the case of light scattering, the relevant tensor is the polarizability tensor α, and the time correlation function that is needed is

$$\begin{aligned}
\psi_\perp(\mathbf{k}, t) &= \frac{\langle \mathrm{Tr}\, \beta^*(0)\cdot\beta(t)\rangle}{\langle \mathrm{Tr}\, \beta^*(0)\cdot\beta(0)\rangle} F_s(\mathbf{k}, t) \\
&= \sum_{j,n=-2}^{+2} \langle D_{n,j}^{2*}(\Omega(0))D_{n,j}^{2}(\Omega(t))\rangle \mid \alpha_j\mid^2 F_s(\mathbf{k}, t).
\end{aligned} \tag{6.148}$$

For the symmetrical-top Brownian rotor (example is tabacco mosaic virus) (Dubin *et al.*, 1967)

$$F_s(\mathbf{k}, t) = e^{-k^2Dt},$$

[see Eq. (5.10)] and, from Eq. (6.143),

$$\psi_\perp(\mathbf{k}, t) = \exp -[6D_\perp + k^2D]t, \tag{6.149}$$

so that the normalized spectrum is

$$\hat{I}_\perp(\mathbf{k}, \omega) = \frac{1}{\pi}\frac{[6D_\perp + k^2D]}{[\omega - \omega_0]^2 + [6D_\perp + k^2D]^2}. \tag{6.150}$$

The strength with which this band occurs is determined by the anisotropy factor $\mid \alpha_\parallel - \alpha_\perp\mid^2$. These methods can be applied to more complicated systems.

Acknowledgments

The work reported here was supported by grants from The Petroleum Research Fund of the American Chemical Society, the National Science Foundation, and the Alfred P. Sloan Foundation. Without the cooperation of the staff and the free use of the facilities of the Columbia University Computer Center this work could never have been undertaken.

References

Abragam, A. (1961). "The Principles of Nuclear Magnetism." Oxford Univ. Press, New York and London.

Alder, B. J., and Wainwright, T. E. (1969). *J. Chem. Phys.* **31**, 459.

AILAWADI, N. (1969). Thesis, Univ. of Maryland.
AILAWADI, N., ZWANZIG, R., and RAHMAN, A. (1971). *Phys. Rev.* A (to be published).
AKCASU, A. Z., and DANIELS, E. (1970). *Phys. Rev.* **A2**, 962.
ANDERSON, P. W. (1949). *Phys. Rev.* **76**, 647.
BERNE, B. J. (1966). Lecture Notes.
BERNE, B. J., and FRISCH, H. L. (1967). *J. Chem. Phys.* **47**, 3675.
BERNE, B. J., and FRISCH, H. L. (1968). *J. Chem. Phys.* **49**, 2864.
BERNE, B. J., and HARP, G. D. (1970). *Advan. Chem. Phys.* **XXII**, 63.
BERNE, B. J., and PECORA, R. (1968). *J. Chem. Phys.* **50**, 783.
BERNE, B. J., BOON, J. P., and RICE, S. A. (1966). *J. Chem. Phys.* **45**, 1086.
BERNE, B. J., BOON, J. P., and RICE, S. A. (1967a). *J. Chem. Phys.* **47**, 2283.
BERNE, B. J., JORTNER, J., and GORDON, R. G. (1967b). *J. Chem. Phys.* **47**, 1600.
BERNE, B. J., GORDON, R. G., and SEARS, V. F. (1968a). *J. Chem. Phys.* **49**, 475.
BERNE, B. J., PECHUKAS, P., and HARP, G. D. (1968b). *J. Chem. Phys.* **49**, 3125.
BERNE, B. J., and FORSTER, D. (1971). *Ann. Rev. Phys. Chem.*
BLUM, L., and SALSBURG, Z. W. (1968). *J. Chem. Phys.* **48**, 2292.
BLUME, M. (1965). Symposium on Inelastic Scattering of Neutrons by Condensed Systems, Brookhaven Nat. Lab., September.
BOUTIN, H., and YIP, S. (1968). "Molecular Spectroscopy with Neutrons." M.I.T. Press, Cambridge, Massachusetts.
CALLEN, H. B., and WELTON, T. A. (1951). *Phys. Rev.* **83**, 34.
CHANDRASEKHAR, S. (1945). *Rev. Mod. Phys.* **15**, 1.
CHAPMAN, S., and COWLING, T. G. (1939). "The Mathematical Theory of Non-Uniform Gases." Cambridge Univ. Press, London and New York.
CHUNG, C. H., and YIP, S. (1969). *Phys. Rev.* **182**, 323.
COLE, R. H. (1965). *J. Chem. Phys.* **42**, 637.
DEBYE, P. (1929). "Polar Molecules." Dover, New York.
DE GROOT, S. R., and MAZUR, P. (1962). "Non-Equilibrium Thermodynamics." North-Holland Publ., Amsterdam.
DUBIN, S. B., LUNACEK, J. H., and BENEDEK, G. B. (1967). *Proc. Nat. Acad. Sci.* **57**, 1164.
EDMUNDS, A. R. (1957). "Angular Momentum in Quantum Mechanics," Princeton Univ. Press, Princeton, New Jersey.
EGELSTAFF, P. A. (1962). *Advan. Phys.* **11**, 203.
EGELSTAFF, P. A. (1961). "Inelastic Scattering of Neutrons in Solids and Liquids." I.A.E.A. Vienna.
EGELSTAFF, P. A. (1965). "Thermal Neutron Scattering." Academic Press, New York.
EGELSTAFF, P. A. (1967). "Introduction to the Liquid State." Academic Press, New York.
EGELSTAFF, P. A., and SCHOFIELD, P. (1962). *Nuc. Sci. Eng.* **12**, 260.
FABILINSKY, I. L. (1968). "Molecular Scattering of Light." Plenum Press, New York.
FAVRO, D. (1960). *Phys. Rev.* **119**, 53.
FLEURY, P., and BOON, J. P. (1969). *Phys. Rev.* **186**, 244.
FELLER, W. (1966). "An Introduction to Probability Theory," Vol. II. Wiley, New York.
FIXMAN, M., and RIDER, K. (1969). *J. Chem. Phys.* **51**, 2425.
FOLEY, H. M., (1946). *Phys. Rev.* **69**, 616.
FORSTER, D., MARTIN, P., and YIP, S. (1968a). *Phys. Rev.* **170**, 155.
FORSTER, D., MARTIN, P., and YIP, S. (1968b). *Phys. Rev.* **170**, 160.

GLARUM, S. H. (1960). *J. Chem. Phys.* **33**, 1371.
GORDON, R. G. (1965a). *J. Chem. Phys.* **42**, 3658.
GORDON, R. G. (1965b). *J. Chem. Phys.* **43**, 1307.
GORDON, R. G. (1968). *In* "Advances in Magnetic Resonance" (J. S. Waugh, ed.), Vol. 3, p. 1. Academic Press, New York.
HARP, G., and BERNE, B. J. (1970). *Phys. Rev.* **2A**, 975.
HELFAND, E. (1960). *Phys. Rev.* **119**, 1.
JAYNES, E. T. (1963). "Information Theory and Statistical Mechanics, Statistical Physics, 1962 Brandeis Lectures" (K. W. Ford, ed.). Benjamin, New York.
KADANOFF, L. P., and MARTIN, P. C. (1963). *Ann. Phys.* (*N.Y.*) **24**, 419.
KINSEY, J., DEUTCH, J., and SILBEY, R. (1969). *J. Chem. Phys.*
KUBO, R. (1961). "Lectures in Theoretical Physics," Vol. 1, pp. 120–203. Wiley (Interscience), New York.
KUBO, R. (1966). *Rep. Progr. Phys.* **29**, 255.
KUSHICK, J., and BERNE, B. J. (1970). *J. Phys. Chem.* (to be published).
LANDAU, L., and LIFSHITZ, E. M. (1959). "Fluid Mechanics." Addison-Wesley, Reading, Massachusetts.
LEBOWITZ, J., and RUBIN, R. (1963). *Phys. Rev.* **131**, 2381.
LEBOWITZ, J., PERCUS, J., and SYKES, B. (1969). *Phys. Rev.* **188**, 487.
LUTINGER, J. M. (1964). *Phys. Rev.* **135A**, 1505.
MARTIN, P. C. (1965). *In* "Statistical Mechanics of Equilibrium and Non-Equilibrium" (J. Meixner, ed.), p. 100. North-Holland Publ., Amsterdam.
MARTIN, P. C. (1968). *In* "1967 Les Houches Lectures," p. 39. Gordon and Breach, New York.
MARTIN, P., and YIP, S. (1968). *Phys. Rev.* **170**, 151.
MAZUR, P. (1966). "Cargese Lectures in Theoretical Physics." Gordon and Breach, New York.
MCCLUNG, R. E. D. (1969). *J. Chem. Phys.* **9**, 3842.
MCTAGUE, J. P., FLEURY, P. A., and DUPRÉ, D. B. (1969). *Phys. Rev.* **188**, 303.
MORI, H. (1965a). *Progr. Theoret. Phys.* **33**, 423.
MORI, H. (1965b). *Progr. Theoret. Phys.* **34**, 399.
MOUNTAIN, R. D. (1966). *J. Res. Nat. Bur. Std.* **70A**, 207.
MOUNTAIN, R. D. (1970). Chem. Rubber Co. Crit. Rev. Solid State 1:5–46.
MOUNTAIN, R. D., and DEUTCH, J. (1970). *J. Chem. Phys.*
NOSSAL, R. (1965). *J. Math. Phys.* **6**, 193.
PECORA, R. (1964). *J. Chem. Phys.* **40**, 1604.
PERRIN, F. (1926). *J. Phys. Radium* **7**, 390.
PINES, D., and NOZIERES, P. (1966). "The Theory of Quantum Liquids." Benjamin, New York.
RAHMAN, A. (1964). *Phys. Rev.* **136**, A405.
RAHMAN, A. (1967). *Phys. Rev. Lett.* **19**, 420.
RICE, S. A., and GRAY, P. (1965). "Statistical Mechanics of Simple Liquids." Wiley, New York.
ROSE, M. E. (1957). "Elementary Theory of Angular Momentum." Wiley, New York.
RUBIN, R. J. (1961). *J. Math. Phys.* **2**, 373.
SCHOFIELD, P. (1960). *Phys. Rev. Lett.* **4**, 39.
SCHOFIELD, P. (1961). "Inelastic Scattering of Neutrons in Solids and Liquids." IAEA, Vienna.

Sears, V. F. (1966a). *Can. J. Phys.* **44**, 1279.
Sears, V. F. (1966b). *Can. J. Phys.* **44**, 1299.
Sears, V. F. (1967). *Can. J. Phys.* **45**, 1.
Singwi, K. S., and Sjolander, A. (1960). *Phys. Rev.* **120**, 1093.
Singwi, K., and Tosi, S. (1967). *Phys. Rev.* **157**, 153.
Sjolander, A. (1964). "Phonons and Phonon Interactions" (T. A. Bak, ed.). Benjamin, New York.
Slichter, P. (1963). "Principles of Magnetic Resonance." Harper & Row, New York.
St. Pierre, A. G., and Steele, W. A. (1969). *Phys. Rev.* **184**, 172.
Tao, T. (1969). Theses, Columbia University.
Van Hove, L. (1954). *Phys. Rev.* **95**, 249.
Van Kranendonk, J. (1952). On the Theory of Pressure-Broadening and Pressure-Induced Absorption, Thesis, Univ. of Amsterdam, Amsterdam, Holland, December 17.
Verlet, L. (1967). *Phys. Rev.* **159**, 98.
Vineyard, G. (1958). *Phys. Rev.* **110**, 999.
Zwanzig, R. (1961). "Lectures in Theoretical Physics" Vol. 3, pp. 135–141. Wiley (Interscience), New York.
Zwanzig, R. (1964). *J. Chem. Phys.* **40**, 2527.
Zwanzig, R. (1965). *Ann. Rev. Phys. Chem.* **16**, 67.
Zwanzig, R., and Ailawadi, N. K. (1969). *Phys. Rev.* **182**, 280.