we obtain from the relation

$$\mu_p = \sigma/e[V_M'], \qquad (14)$$

$\mu_p(1394°C) = 0.25$ cm^2/V·sec. Using Eq. (13a) it is suggested that the mobility of holes in NiO at high temperature is given by

$$\mu_p = (5959/T) \exp(-0.37/kT) \, (\text{cm}^2/\text{V·sec}). \quad (15)$$

The measured Hall mobility in undoped NiO at 1000°C was found to be n type, 10^{-3} cm^2/V·sec [34] and 1.7×10^{-4} cm^2/V·sec.[40] These values are appreciably

[40] N. M. Tallan and D. S. Tannhauser, Phys. Letters 26, 136 (1968).

smaller than the value 0.143 cm^2/V·sec calculated from Eq. (15). The great discrepancy between the measured Hall mobility and the computed drift mobility was explained by van Daal and Bosman[34] on the basis of an interaction between the charge carriers and an induced magnetization. Tallan and Tannhauser[40] have attributed their observed dependence of the measured Hall mobility on charge-carrier concentration, the negative sign of the Hall mobility, and its small magnitude to a Hall mobility for holes that is orders of magnitude less than the drift mobility for holes, and suggested that this might be due to the localized nature of the holes at high temperatures.

Linear- and Angular-Momentum Autocorrelation Functions in Diatomic Liquids*

G. D. Harp† AND Bruce J. Berne

Department of Chemistry, Columbia University, New York, New York

(Received 18 March 1968)

The linear- and angular-momentum autocorrelation functions in liquid CO have been studied using computer-simulated molecular dynamics. The structure of these functions appears to be determined by the corresponding autocorrelation functions of the direction of the linear and angular momentum. The structure of the angular-momentum autocorrelation function is also shown to depend on the strength of the noncentral part of the pair potential used in the dynamics calculations. The assumptions that the linear and angular momenta are Gaussian random variables are examined and shown to be valid for the data presented.

I. INTRODUCTION

Despite recent advances in the theory of linear-transport phenomena in dense fluids, relatively little is known about the autocorrelation functions of the linear and angular momenta. In addition, aside from qualitative arguments, little can be said of the structure of the few autocorrelation functions which have been determined. One of the major difficulties encountered in developing a theory of autocorrelation 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.

Little if indeed anything has been reported about the full time evolution of the angular-momentum autocorrelation function of diatomic molecules in gases or liquids. This function plays a major role in determining the line shapes of NMR signals. The power spectrum of this function at the Larmour precession frequency of the nuclear spin determines the contribution of the nuclear-spin–rotation coupling to nuclear-spin–relaxation and thereby to the NMR line breadth.[1,2] Thus

NMR experiments can be used to probe isolated frequency components of this correlation function.

Thermal-neutron-scattering experiments offer in principle the most detailed experimental information about both the linear- and angular-momentum autocorrelation functions.[3] This information is very difficult to interpret owing to the extreme difficulty in separating the rotational from the translational motion of the molecules since rotations and translations are strongly coupled in most liquids. Recently, neutron-scattering experiments have been done on liquid argon,[4] and the linear-momentum correlations have been studied in detail.

The major source of information about the linear- and angular-momentum autocorrelation functions is provided by molecular-dynamics studies of polyatomic liquids. We are presently studying the coupling between translations and rotations in liquid CO and N$_2$. Many different intermolecular potentials are used. Without going into the details of these computations and without arguing as to the merits or weaknesses of the particular intermolecular potentials used in these studies, it is possible to make some fairly conclusive

[1] W. A. Steele, J. Chem. Phys. 38, 2411 (1963).
[2] J. S. Waugh, *Advances in Magnetic Resonance* (Academic Press Inc., New York, 1967), Vol. 3.

[3] P. A. Egelstaff, *Thermal Neutron Scattering* (Academic Press Inc., New York, 1965).
[4] B. Dasannacharya and K. Rao, Phys. Rev. 137, A417 (1965); K. Skold and K. Larsson, *ibid.* 161, 102 (1967).

statements about linear and angular momentum correlations in diatomic liquids.

All of these studies show very clearly that there is an interval of time for which the velocity autocorrelation function is negative. The negative region indicates that on the average, a displacement of a molecule towards its near neighbors is followed by a displacement back towards its initial position. This is in agreement with molecular-dynamics studies on monatomic liquids.

Likewise, all of these studies show very clearly that in liquids for which the pair potential has a strongly noncentral character, there is an interval of time for which the angular-momentum autocorrelation function is negative, whereas in liquids for which the pair potential has a small noncentral component this correlation function remains positive and changes very little over the observed time interval. The negative region indicates that on the average, a molecule suffers a sufficiently strong collision with the cage formed by its nearest neighbors that the torque acting on it is large enough to reverse the direction of its angular momentum.

In this paper we investigate the degree to which changes in the linear and angular speed contribute to the over-all temporal behavior of the linear- and angular-momentum changes with time. The results of this study clearly show that it is the changes in the directions of these momenta and not the changes in their magnitudes which determine the structure of the auto-correlation functions.

Here, we also investigate to what extent it is accurate to consider the linear and angular momentum as Gaussian random processes. It is concluded that for the data presented this is a good approximation.

II. THE LINEAR- AND ANGULAR-MOMENTUM AUTOCORRELATION FUNCTIONS

The normalized linear and angular momentum auto-correlation functions, $\Psi(t)$ and $A_J(t)$ are, respectively, defined as

$$\Psi(t) = \langle \mathbf{p}(0) \cdot \mathbf{p}(t) \rangle / \langle p^2 \rangle,$$

$$A_J(t) = \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle / \langle J^2 \rangle,$$

where $\mathbf{p}(t)$ is the center-of-mass (c.m.), linear momentum and $\mathbf{J}(t)$ is the angular momentum about the c.m. of a molecule at time t. Here the angle brackets $\langle \ \rangle$ indicate an equilibrium ensemble average over the initial conditions. In all cases $\Psi(t)$ behaves just like the functions found for liquid argon even though there are molecular internal degrees of freedom in these liquids whereas in argon there are none.

To investigate further the behavior of these functions we have also computed the normalized linear- and angular-speed autocorrelation functions $\sigma(t)$, and

$\sigma_J(t)$ where

$$\sigma(t) = \langle \, | \, \mathbf{p}(0) \, | \, | \, \mathbf{p}(t) \, | \, \rangle / \langle p^2 \rangle,$$

$$\sigma_J(t) = \langle \, | \, \mathbf{J}(0) \, | \, | \, \mathbf{J}(t) \, | \, \rangle / \langle J^2 \rangle,$$

together with the corresponding directional correlation functions $D(t)$ and $D_J(t)$,

$$D(t) = \langle \mathbf{e}(0) \cdot \mathbf{e}(t) \rangle,$$

$$D_J(t) = \langle \mathbf{e}_J(0) \cdot \mathbf{e}_J(t) \rangle,$$

where $| \, \mathbf{p}(t) \, |$, $| \, \mathbf{J}(t) \, |$, $\mathbf{e}(t)$, and $\mathbf{e}_J(t)$ are, respectively, the magnitude of the linear and angular momenta and unit vectors pointing in the direction of the linear and angular momenta.

These functions are normalized; that is, they are initially unity. Their long-time limits are

$$\lim_{t \to \infty} \Psi(t) = \langle \mathbf{p} \rangle \cdot \langle \mathbf{p} \rangle / \langle p^2 \rangle = 0,$$

$$\lim_{t \to \infty} \sigma(t) = \{ \langle \, | \, \mathbf{p} \, | \, \rangle \}^2 / \langle p^2 \rangle = 8/3\pi,$$

$$\lim_{t \to \infty} D(t) = \langle \mathbf{e} \rangle \cdot \langle \mathbf{e} \rangle = 0,$$

$$\lim_{t \to \infty} A_J(t) = \langle \mathbf{J} \rangle \cdot \langle \mathbf{J} \rangle / \langle J^2 \rangle = 0,$$

$$\lim_{t \to \infty} \sigma_J(t) = \{ \langle \, | \, \mathbf{J} \, | \, \rangle \}^2 / \langle J^2 \rangle = \pi/4,$$

$$\lim_{t \to \infty} D_J(t) = \langle \mathbf{e}_J \rangle \cdot \langle \mathbf{e}_J \rangle = 0.$$

This springs from the fact that for very long times the value of the random variable in each correlation function becomes statistically independent of its initial value.

The curves in Figs. 1 and 2 correspond to the molecular-dynamics determination of $\Psi(t)$, $\sigma(t)$, and $D(t)$ for CO molecules interacting via:

(a) a Stockmayer potential.

(b) a center-of-mass Lennard-Jones (12–6) plus dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole potential (hereafter called the modified Stockmayer potential). Some of the details of the molecular-dynamics calculations for these potentials appear in the Appendix. The curves of Figs. 3 and 4 represent $A_J(t)$, $\sigma_J(t)$, and $D_J(t)$ for the same two potentials.

The Stockmayer potential for CO is very weakly angular dependent even at the liquid densities used for these calculations. On the other hand, the modified Stockmayer potential is strongly angular dependent. This is illustrated quite dramatically by our calculated values of the mean-square torque for the two potentials. The mean-square torque for the Stockmayer potential was found to be 6.7×10^{-31} (dyn·cm)^2 while the mean-
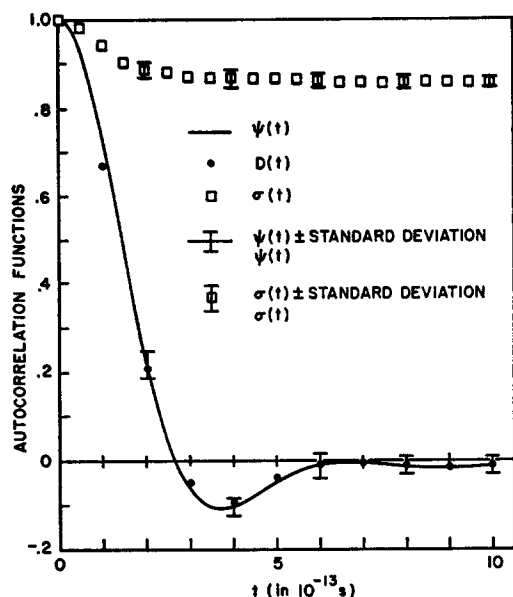
FIG. 1. Velocity autocorrelation functions for liquid CO using the Stockmayer potential.

square torque for the modified Stockmayer potential was found to be 3.6×10^{-27} (dyn·cm)^2. Note that for the weak noncentral (Stockmayer) potential $A_J(t)$ changes very little and is positive during the time it is observed, while for the strongly noncentral (modified Stockmayer) potential there is a region in which $A_J(t)$ is negative. This is a general observation we have made on the effect of strong vs weak angular potentials on the angular-momentum correlation function.

Note further in the modified Stockmayer simulation, how closely $D(t)$ resembles $\Psi(t)$ and $D_J(t)$ resembles
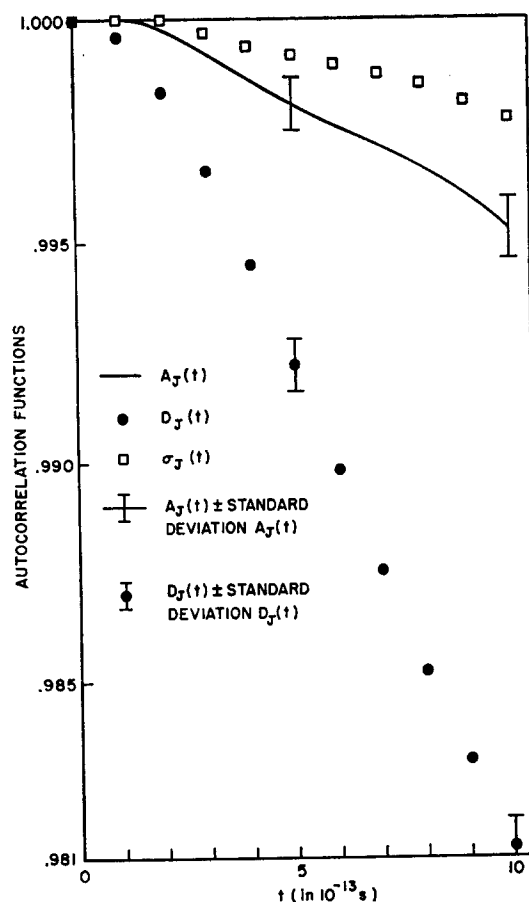

FIG. 3. Angular-momentum autocorrelation functions for liquid CO using the Stockmayer potential.
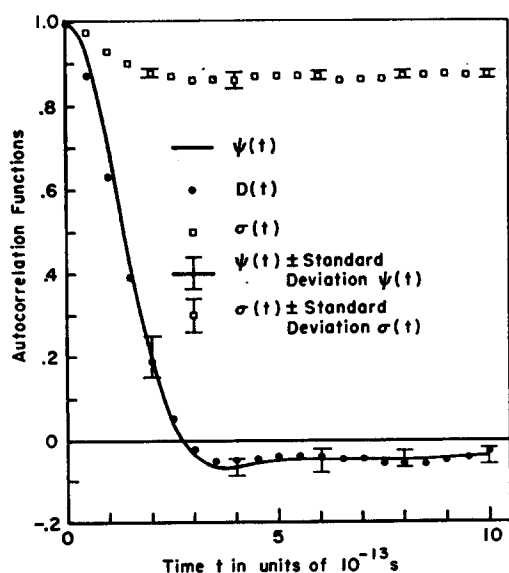

FIG. 2. Velocity autocorrelation functions for liquid CO using the modified Stockmayer potential.
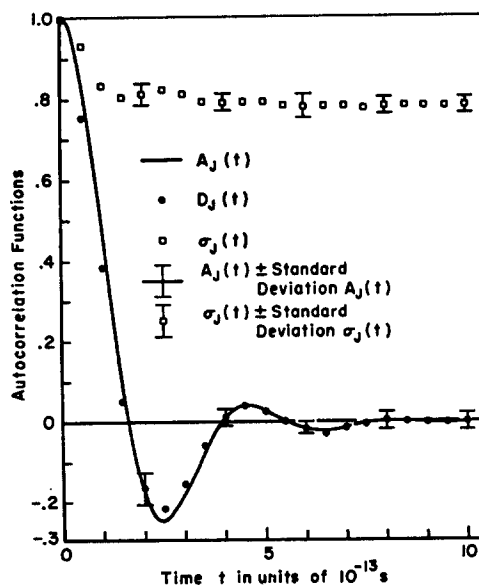

FIG. 4. Angular-momentum autocorrelation functions for liquid CO using the modified Stockmayer potential.
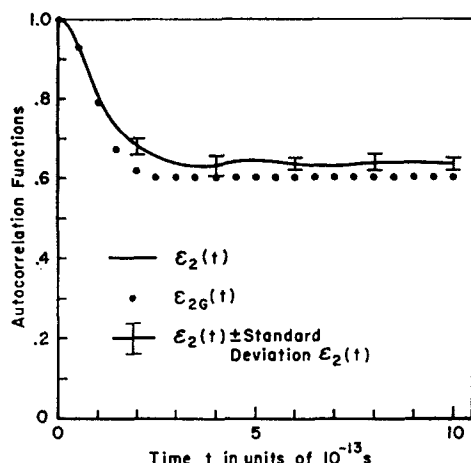
FIG. 5. The autocorrelation function $\mathcal{E}_2(t)$ from the modified Stockmayer simulation for liquid CO and the autocorrelation function $\mathcal{E}_{2G}(t)$ from the Gaussian approximation.

$A_J(t)$. $\sigma(t)$ varies between its initial value of unity and its long time value of $8/3\pi$, and therefore, because of only a 13% change over the whole time axis contributes very little to the over-all time dependence of $\psi(t)$. Likewise, $\sigma(t)$ varies between 1 and its long-time value of $\pi/4$ and therefore, because of only a 21% change over the whole time axis, contributes very little to the over-all time dependence of $A_J(t)$. $D(t)$ and $D_J(t)$ are excellent approximations to $\Psi(t)$ and $A_J(t)$, respectively. We come to these conclusions on the basis of molecular dynamics. In a sense, this can be construed as an argument for a constant linear- and angular-speed approximation to the calculation of the linear- and the angular-momentum autocorrelation functions.

The Gaussian Approximation

It would be very convenient to know whether or not the linear and angular momenta can be accurately represented by stationary Gaussian random variables.
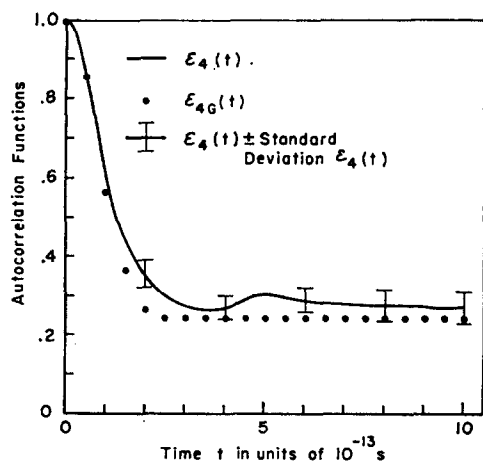

FIG. 6. The autocorrelation function $\mathcal{E}_4(t)$ from the modified Stockmayer simulation for liquid CO and the autocorrelation function $\mathcal{E}_{4G}(t)$ from the Gaussian approximation.
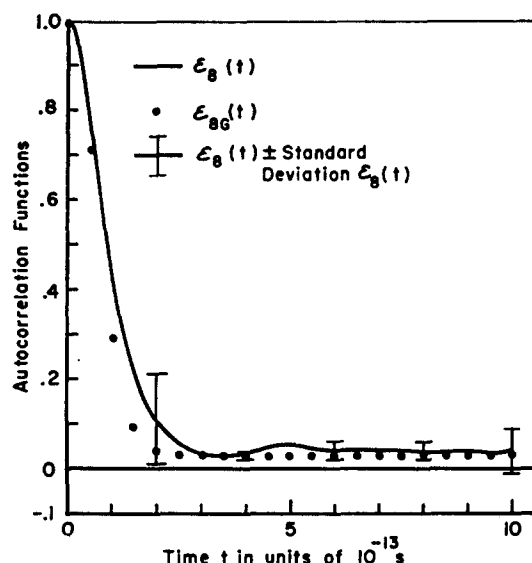

FIG. 7. The autocorrelation function $\mathcal{E}_8(t)$ from the modified Stockmayer simulation for liquid CO and the autocorrelation function $\mathcal{E}_{8G}(t)$ from the Gaussian approximation.

If the answer to this question is in the affirmative then the probability of finding a molecule at time t with a velocity $\mathbf{v}$ given that it was moving with velocity $\mathbf{v_0}$ at the initial instant $t=0$ is the Gaussian transition probability[5]

$$K(\mathbf{v}; t \mid \mathbf{v_0}; 0) = \left(\frac{M}{2\pi KT}\right)^{3/2} \{1 - \Psi^2(t)\}^{-3/2}$$

$$\times \exp\left\{-\tfrac{1}{2}(\beta M)\frac{[\mathbf{v} - \mathbf{v_0}\Psi(t)]^2}{[1 - \Psi^2(t)]}\right\}.$$

The corresponding transition probability for the angu-

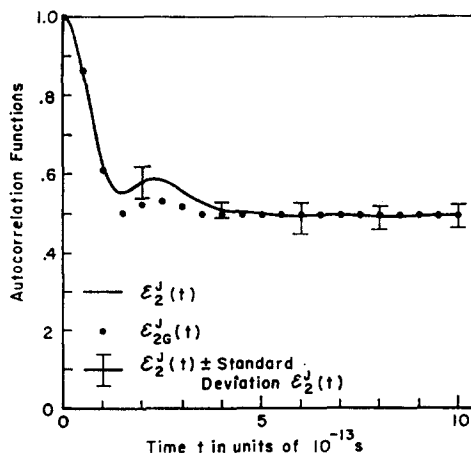FIG. 8. The autocorrelation function $\mathcal{E}_2^J(t)$ from the modified Stockmayer simulation for liquid CO and the autocorrelation function $\mathcal{E}_{2G}^J(t)$ from the Gaussian approximation.

[5] J. L. Doob, Ann. Math. **43**, 351 (1942).

lar momentum is similarly given by

$$K_J(\mathbf{J};t \mid \mathbf{J}_0;0) = \{2\pi IKT[1-A_J{}^2(t)]\}^{-1}$$

$$\times \exp\{-\beta[\mathbf{J}-\mathbf{J}_0 A_J(t)]^2/2I[1-A_J{}^2(t)]\}.$$

Thus all that one would be required to know in order to compute any autocorrelation function involving a higher power of $\mathbf{v}$ or $\mathbf{J}$ is $\Psi(t)$ or $A_J(t)$. For example the normalized translational kinetic-energy autocorrelation function $\mathcal{E}_2(t)$, where

$$\mathcal{E}_2(t) = \langle v^2(0)v^2(t) \rangle / \langle v^4 \rangle$$

can be determined in terms of $\Psi(t)$ from the Gaussian transition probability to be

$$\mathcal{E}_2\ (t) = \tfrac{3}{5}[1+\tfrac{2}{3}\Psi^2(t)].$$

The subscript G indicates that this is an approximate and as yet unverified result based on the Gaussian approximation. Similarly the normalized rotational kinetic-energy autocorrelation function $\mathcal{E}_2{}^J(t)$, where

$$\mathcal{E}_2{}^J(t) = \langle J^2(0)J^2(t) \rangle / \langle J^4 \rangle,$$

can be determined in terms of $A_J(t)$ from the Gaussian transition probability to be

$$\mathcal{E}_{2G}{}^J(t) = \tfrac{1}{2}[1+A_J{}^2(t)].$$

In like manner, the fourth-order correlation functions $\mathcal{E}_4(t)$ and $\mathcal{E}_4{}^J(t)$ and eighth-order correlation function $\mathcal{E}_8(t)$, which are defined as

$$\mathcal{E}_4(t) = \langle v^4(0)v^4(t) \rangle / \langle v^8 \rangle,$$

$$\mathcal{E}_4{}^J(t) = \langle J^4(0)J^4(t) \rangle / \langle J^8 \rangle,$$

$$\mathcal{E}_8(t) = \langle v^8(0)v^8(t) \rangle / \langle v^{16} \rangle,$$

can be determined in terms of $\Psi(t)$ and $A_J(t)$ from the Gaussian transition probabilities to be

$$\mathcal{E}_{4G}(t) = (1/945)[225+600\Psi^2(t)+120\Psi^4(t)],$$

$$\mathcal{E}_{4G}{}^J(t) = (1/384)[64+256A_J{}^2(t)+64A_J{}^4(t)],$$

$$\mathcal{E}_{8G}(t) = (1/36\ 465)[945+10\ 080\Psi^2+1844\Psi^4$$

$$+6912\Psi^6+384\Psi^8].$$

All even higher-order autocorrelation functions can be expressed as an even power series in $\Psi(t)$ or $A_J(t)$.

These higher-order correlation functions play a large role in determining many different physical properties of polyatomic systems. For example the vibrational relaxation time can be expressed in terms of the rotational kinetic-energy autocorrelation function.[6] Similarly the line shape of the rotational Raman spectra of diatomic molecules is determined by the correlation function $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)] \rangle$,[7] where $\mathbf{u}$ is a unit vector
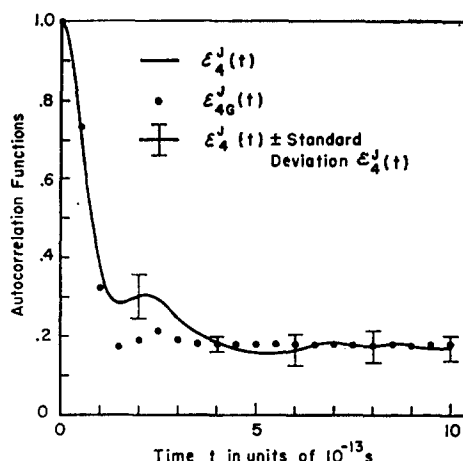
[6] B. J. Berne, J. Jortner, and R. G. Gordon, J. Chem. Phys. **47**, 1600 (1967); B. J. Berne, R. G. Gordon, and V. F. Sears, "Mechanisms of Vibrational Relaxation," *ibid.* (to be published).

[7] R. G. Gordon, J. Chem. Phys. **42**, 3658 (1965); **43**, 1307 (1965).

FIG. 9. The autocorrelation function $\mathcal{E}_4{}^J(t)$ from the modified Stockmayer simulation for liquid CO and the autocorrelation function $\mathcal{E}_{4G}{}^J(t)$ from the Gaussian approximation.

pointing in the direction of the molecular axis and $P_2(x)$ is the second-order Legendre polynomial. As is well known, the infrared spectrum of diatomic molecules has a band shape which can be expressed in terms of the autocorrelation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t) \rangle$.[7] Thus if $\mathbf{u}$ is a Gaussian random variable, the Raman band shape can be determined from the infrared band shape. There are many other illustrations of the importance of these higher-order correlations.

At this time the only experimental method for determining to what extent the Gaussian approximation adequately reflects the complicated motions in many-body systems is computer-simulated molecular-dynamics studies of polyatomic liquids. It is in principle possible by this method to determine the transition probabilities completely as a function of time. Although this will eventually be done, we have to date tested only the correlation functions $\mathcal{E}_2(t)$, $\mathcal{E}_4(t)$, $\mathcal{E}_8(t)$, $\mathcal{E}_2{}^J(t)$, and $\mathcal{E}_4{}^J(t)$. These functions were first computed from molecular dynamics and then compared with $\mathcal{E}_{2G}(t)$, $\mathcal{E}_{4G}(t)$, $\mathcal{E}_{8G}(t)$, $\mathcal{E}_{4G}{}^J(t)$ determined from the previous formulas using the correct $\Psi(t)$ and $A_J(t)$ from the dynamics. The results of these computations are presented in Figs. 5–9. These first few calculated moments indicate that the Gaussian transition probabilities for the linear and angular momentum may represent the dynamics fairly well. However it may not yet be concluded that the Gaussian approximation is actually correct, since the same test must be made on the corresponding higher moments, i.e., $\mathcal{E}_{12}(t)$, $\mathcal{E}_{12}{}^J(t)$, $\cdots$, etc. If the linear and angular momentum were truly Gaussian random processes than they are not Markovian. This follows from the facts that $\Psi(t)$ and $A_J(t)$ are not exponential with time—Figs. 2 and 4—and Doob's theorem[5] according to which a stationary Gaussian process is Markovian if and only if the autocorrelation function for the process is exponential in time.

ACKNOWLEDGMENT

APPENDIX

The molecular-dynamics calculations were carried out in a manner similar to that used by Rahman[8] in his original study of liquid argon. A finite number of molecules were assumed to interact pairwise through a given truncated intermolecular pair potential. In addition, the atoms on the same molecule were assumed to interact through a harmonic potential, $\frac{1}{2}K_v(r_i-\bar{r})^2$, where K_v is the ground-state vibrational force constant for the molecule, r_i is the internuclear separation for the ith molecule, and $\bar{r}$ is the ground-state vibrational equilibrium internuclear separation. The harmonic potential was added because the calculations were done in the Cartesian coordinates of the atoms forming the molecules. These atoms were originally separated by the equilibrium internuclear distance. They remained separated by this distance to within $\sim 10^{-4}$ Å throughout the course of the calculations. Therefore the results of these computations are essentially those for a system of rigid rotors.

The center of mass of each molecule was initially placed in a cubic lattice system within a large cube whose dimensions were determined from the density and number of molecules to be followed. The molecular orientational angles were chosen randomly on a unit sphere. The relative and center-of-mass velocity components for each molecule were chosen by the Von Neumann[9] rejection method from Gaussian distributions appropriate to a preselected temperature. Periodic boundary conditions were imposed[10,8] and Hamilton's equations of motion for the interacting molecules were solved numerically using the method of Runga-Kutta Gill[11] with a step size in time of 5×10^{-15} sec. During the initial stages of the computation, if the temperature of the system fell outside a preselected range of temperatures, the velocities were changed accordingly. After the system had equilibrated, it was followed

for an additional 600 steps in time. During this period the positions, velocities, and accelerations were put on magnetic tape. The tape was later analyzed for the time-dependent and time-independent properties of the system. The time-dependent correlations were computed using an ensemble of 100 blocks of data as time origins.[8] Therefore each autocorrelation function represents the average of the appropriate dynamical information along $100N$ molecular trajectories, where N is the number of molecules followed.

The results presented here for CO were done at a density of 0.8558 g/cc. The equilibrium internuclear separation used was 1.1281 Å with a harmonic force constant of 1.9020×10^6 dyn/cm.[12] The Stockmayer intermolecular pair potential that was used is given by[13]

$$V_s(R,\theta_1,\theta_2,\phi)=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^6]$$
$$-(\mu^2/R^3)(2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\phi),$$

where R is the distance between the center of masses of the two molecules and θ_1, θ_2, and ϕ are the orientational angles of the two molecules with respect to a line joining their center of masses. The Stockmayer potential parameters used were $\epsilon=1.5172\times10^{-14}$ erg, $\sigma=3.585$ Å, and $\mu=0.1172$ D.[13] This simulation was done for 512 molecules and equilibrated at 69°K.

The modified Stockmayer pair potential that was used is given by

$$V(R,\theta_1,\theta_2,\phi)=V_S(R,\theta_1,\theta_2,\phi)$$
$$+(3\mu Q/4R^4)[\cos\theta_1(3\cos^2\theta_2-1)+\cos\theta_2(3\cos^2\theta_1-1)$$
$$-2\sin\theta_1\sin\theta_2\cos\phi(\cos\theta_2+\cos\theta_1)]$$
$$+(3Q^2/4R^5)[1-5\cos^2\theta_1-5\cos^2\theta_2-15\cos^2\theta_1\cos^2\theta_2$$
$$+2(\sin\theta_1\sin\theta_2\cos\phi-4\cos\theta_1\cos\theta_2)^2].$$

The quadrupole–dipole term used here differs by a factor of 2 from the usual definition of this term.[13] However, the effect of this difference on the over-all results is thought to be small. The same values of ϵ, σ, and μ that were used in the Stockmayer simulation were used here. The range of the intermolecular potentials in both simulations was 2.25σ. The value of Q used was 2.43×10^{-26} esu.[14] This simulation was done for 512 molecules and equilibrated at 67°K.

[8] A. Rahman, Phys. Rev. **136**, A405 (1964).

[9] H. Kahn, Atomic Energy Commission Rept. AECU-3259 (unpublished).

[10] B. J. Alder and T. E. Wainwright, in *Transport Processes in Statistical Mechanics*, I. Prigogine, Ed. (Interscience Publishers, Inc., New York, 1958).

[11] A. Ralston and H. Wilf, *Mathematical Methods for Digital Computers* (John Wiley & Sons, Inc., New York, 1966).

[12] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Co., Inc., New York, 1961), Vol. 1.

[13] J. Hirschfelder, C. Curtiss, and R. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

[14] T. Spurling and E. Mason, J. Chem. Phys. **46**, 322 (1967).