another example, Hartree–Fock calculations[12] predict D_0 for HF ($R_e=1.733\ a_0$) as 0.161 a.u. (true value = 0.225 a.u.), while the Hartree–Fock calculations[13] for OH^- (interpolated to the $R=1.733\ a_0$ distance) predict 0.127 a.u. The difference between the two, assuming much of the error is common to both calculations and cancels, gives $\Delta=0.92$ eV, which means an error of 0.6×10^{-6} in $\sigma_{av}{}^d$.

In summary, Eq. (2) is shown to give reliable estimates for the average diamagnetic shielding at a nucleus in a molecule. The validity of Eq. (2) is related to the "isoelectronic principle" or the negligible change in dissociation energy with change in nuclear charge (total electrons and internuclear distances are kept constant). Equation (2) may be useful in extracting meaningful interpretations from chemical-shift data and also in assigning the signs of spin–rotation constants.

ACKNOWLEDGMENT

The support of the National Science Foundation is gratefully acknowledged.

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[12] P. E. Cade and W. M. Huo, J. Chem. Phys. **47**, 614 (1967).

[13] P. E. Cade, J. Chem. Phys. **47**, 2390 (1967).

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Molecular Reorientation in Liquids and Gases*

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In this paper two simple criteria for guessing the time-dependent orientational distribution function from the experimentally measured dipolar autocorrelation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ are examined. The first maximizes the information entropy of the distribution under the constraint imposed by the known $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$, and the second minimizes the mean-square difference between the distribution function and the equilibrium ($t\rightarrow\infty$) distribution under the same constraint. The accuracy of these criteria is tested on the results of computer studies of the rotational relaxation of diatomic liquids. The same general method is applied to the Van Hove self-correlation function, and to the center-of-mass velocity transition probability.

INTRODUCTION

The shape of the vibration–rotation bands in infrared absorption and Raman scattering experiments on polyatomic molecules dissolved in a host fluid have been used to determine the autocorrelation functions[1] $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ and $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$, where $\mathbf{u}$ is a unit vector pointing in the direction of the transition dipole of the corresponding band and $P_2(x)$ is the Legendre polynomial of index 2. These correlation functions measure the rate of rotational reorientation of the molecule in the host fluid. Consequently, the observed temperature and density dependence of these functions yield a great deal of insight into the mechanism of reorientation in solids, liquids, and gases. Moreover they have been used recently to explore the regression of fluctuations about the approach to equilibrium.

It would be very convenient to know how to predict Raman band shapes from ir band shapes and vice versa. This would provide insight into the paths by which spontaneous fluctuations from the approach to the equilibrium state decay.[2] It would, furthermore, be very useful for the determination of higher-order correlation functions such as $\langle P_n[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ which may be important for the discussion of higher-order radiative processes.

To make such a "prediction" we have to guess the distribution of $[\mathbf{u}(0)\cdot\mathbf{u}(t)]$ from one of its moments. In this paper we examine two simple criteria for guessing the distribution from $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ and therefore "predicting" Raman band shapes from observed ir band shapes. The first maximizes the information entropy of the distribution under the constraint imposed by the known $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$; the second minimizes the mean-square difference between the distribution and the equilibrium ($t\rightarrow\infty$) distribution under the same constraint.

We test the accuracy of these criteria on the results of computer studies[3] of the rotational relaxation of diatomic molecules, and also discuss the application of the general idea to Van Hove's self-correlation function $G_s(\mathbf{r}, t)$ and to the velocity transition probability.

MOLECULAR REORIENTATION IN DENSE MEDIA

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. (See

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[*] This work was supported in part by a grant from the Petroleum Research Foundation of the American Chemical Society.

[†] NASA predoctoral fellow.

[1] R. G. Gordon, J. Chem. Phys. **45**, 1649 (1966); **44**, 3083 (1966).

[2] R. G. Gordon, J. Chem. Phys. **47**, 1 (1967).

[3] G. D. Harp and B. J. Berne, "Linear and Angular Momentum Correlations in Diatomic Liquids," J. Chem. Phys. (to be published).

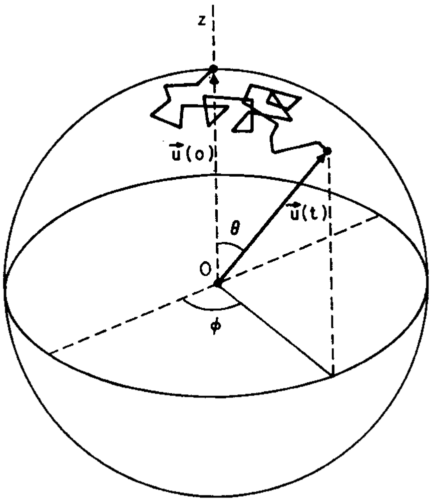

FIG. 1. The orientation of a molecule $\mathbf{u}(t)$ can be represented by a point on the surface of a unit sphere. As the molecule reorients, this point performs a random walk on this surface.

Fig. 1.) The initial orientation of a diatomic molecule $\mathbf{u}(0)$ can be represented by a point on the surface of this sphere, the location of which is uniquely specified by its polar and azimuthal angles θ and ϕ. The fraction of molecules which at a given time t are oriented in the direction of a solid angle $d\Omega$ is $P(\theta, \phi, t)d\Omega$. This fraction need not remain constant, however, since the molecules are being constantly reoriented due to interactions with their neighbors. After a time t has elapsed which is long compared to the orientational relaxation time, the distribution function $P(\theta, \phi, t)$ will be independent of its initial value and will tend to the uniform distribution, that is

$$\lim_{t\to\infty} P(\theta, \phi, t)d\Omega = d\Omega/4\pi.$$

The correlation functions $D(t) = \langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ and $D_2(t) = \langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ can be computed if the distribution function $P(\theta, \phi, t)$ is known since

$$D(t) = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \cos\theta P(\theta, \phi, t), \quad (1)$$

$$D_2(t) = \frac{1}{2}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta (3\cos^2\theta - 1) P(\theta, \phi, t). \quad (2)$$

All higher-order correlation functions

$$D_n(t) = \langle P_n[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$$

can likewise be computed.

We now assume that $D(t)$ is known, and we want to guess the probability distribution P. We do this first by maximizing the information entropy of the distribution[4]

$$S[P(\theta, \phi, t)] = -\int d\Omega P(\theta, \phi, t) \ln P(\theta, \phi, t) \quad (3)$$

subject to the constraints

$$P(\theta, \phi, t) \geq 0, \quad (4a)$$

$$\int d\Omega P(\theta, \phi, t) = 1, \quad (4b)$$

$$\int d\Omega \cos\theta P(\theta, \phi, t) = D(t), \quad (4c)$$

where (4a) and (4b) are the conditions that P be a probability distribution and (4c) the condition that P gives the right dipolar correlation function $D(t)$.

Ignoring (4a) for the moment and introducing (4b) and (4c) into the problem via Lagrange multipliers gives

$$\delta \int d\Omega [P \ln P - (\alpha+1)P - \beta \cos\theta P] = 0$$

or

$$\int d\Omega (\ln P - \alpha - \beta \cos\theta)\delta P = 0;$$

therefore

$$P(\theta, \phi, t) = \exp(\alpha + \beta \cos\theta). \quad (5)$$

This distribution satisfies the positivity condition (4a). The Lagrange multipliers α and β are determined from the constraints (4b) and (4c). From (4b) we see that

$$\int d\Omega \exp(\alpha+\beta\cos\theta) = 2\pi e^{\alpha}\frac{e^{\beta}-e^{-\beta}}{\beta} = 1$$

or

$$2\pi e^{\alpha} = \beta/(e^{\beta}-e^{-\beta}).$$

From (4c) it is found that

$$D(t) = \int d\Omega \cos\theta \exp(\alpha+\beta\cos\theta)$$

$$= 2\pi e^{\alpha}\left[-\frac{(e^{\beta}-e^{-\beta})}{\beta^2} + \frac{(e^{\beta}-e^{-\beta})}{\beta}\right]$$

or

$$D(t) = [-(1/\beta) + \coth\beta] = L_{\infty}(\beta). \quad (6)$$

$L_{\infty}(\beta)$ is the infinite-order Brilluoin function, plotted in Fig. 2. $\beta(t)$ can be determined from the known variation of $D(t)$ with time by inverting Eq. (6); this is best done numerically.

The higher-order correlation functions such as $D_2(t)$ can now be found in terms of $\beta(t)$ and thereby in terms of $D(t)$. For example

$$D_2(t) = \frac{1}{2}\int d\Omega \exp(\alpha+\beta\cos\theta)(3\cos^2\theta - 1)$$

$$= 1 - [3/\beta(t)]L_{\infty}[\beta(t)]. \quad (7)$$

It is clear that maximizing the information entropy of a distribution subject to constraints gives in some sense the "smoothest" distribution consistent with

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[4] E. T. Jaynes, *Information Theory and Statistical Mechanics, Statistical Physics*, K. W. Ford, Ed. (W. A. Benjamin Inc., New York, 1963), 1962 Brandeis Lectures.

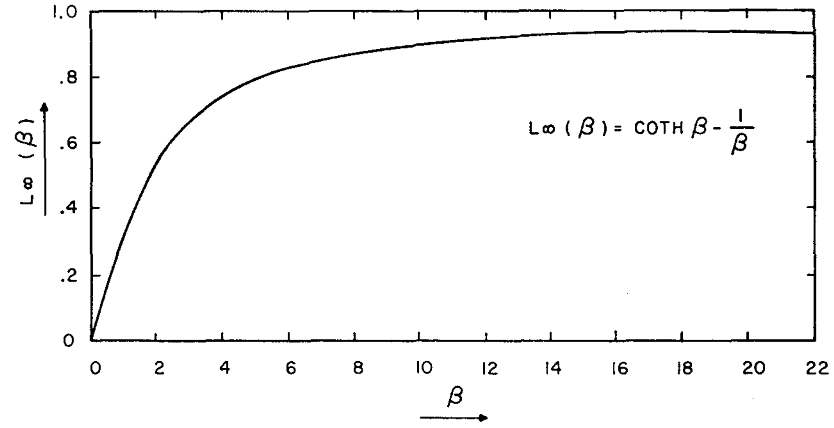

FIG. 2. The infinite-order Brillouin function.

those constraints.[4] There are, of course, other possible smoothness criteria. We can, for instance, look for the distribution which is closest to the uniform distribution, $P_0(\theta,\phi,t)=1/4\pi$, in the mean-square sense. The problem is then to minimize

$$I_2[P(\theta,\phi,t)]=\int d\Omega[P(\theta,\phi,t)-P_0(\theta,\phi)]^2, \quad (8)$$

subject to the constraints (4a), (4b), and (4c). We can take care of (4b) and (4c) with Lagrange multipliers. The problem then reduces to finding P such that

$$\int d\Omega(P-\alpha-\beta\cos\theta)\delta P\geq 0$$

for any variation δP consistent with (4a), that is, any variation δP which is ≥ 0 where P is zero and otherwise arbitrary. It is easy to see that the solution is

$$\begin{aligned} P&=\alpha+\beta\cos\theta && \text{for } \alpha+\beta\cos\theta\geq 0\\ &=0 && \text{otherwise.} \end{aligned} \quad (9)$$

The constants α and β have now to be chosen such (4b) and (4c) are satisfied. We find that when $|D(t)|\leq\frac{1}{3}$

$$P(\theta,\phi,t)=(1/4\pi)[1+3D(t)\cos\theta], \quad (10)$$

and when $D(t)\geq\frac{1}{3}$

$$\begin{aligned} P(\theta,\phi,t)&=\frac{[2-3D(t)+\cos\theta]}{9\pi[1-D(t)]^2}, && \theta\geq\cos^{-1}[3D(t)-2]\\ &=0, && \theta\leq\cos^{-1}[3D(t)-1], \end{aligned} \quad (11)$$

with $P(D,\theta)=P(-D,\pi-\theta)$ determining the corresponding formula when $D(t)\leq-\frac{1}{3}$.

Two different dipolar correlation functions determined from computer-simulated molecular-dynamics studies[3] of liquid CO are presented in Figs. 3 and 4. One corresponds to a strong and the other to a weak noncentral potential. The corresponding $D_2(t)$'s as predicted by Eqs. (7) and (11) are presented in Figs. 5 and 6. Note how closely information theory predicts the behavior of $D_2(t)$ for the strongly noncentral potential. On the other hand $D_2(t)$ as predicted by information theory for the weak noncentral potential is in poor agreement with experiment. It should be noted that in both cases information theory gives better agreement than the least-mean-square theory of Eq. (8). It seems clear that the information-theory ansatz, which is simpler, is also better.

The accuracy of these approximations is rather surprising, and we have no rational explanation. Nature

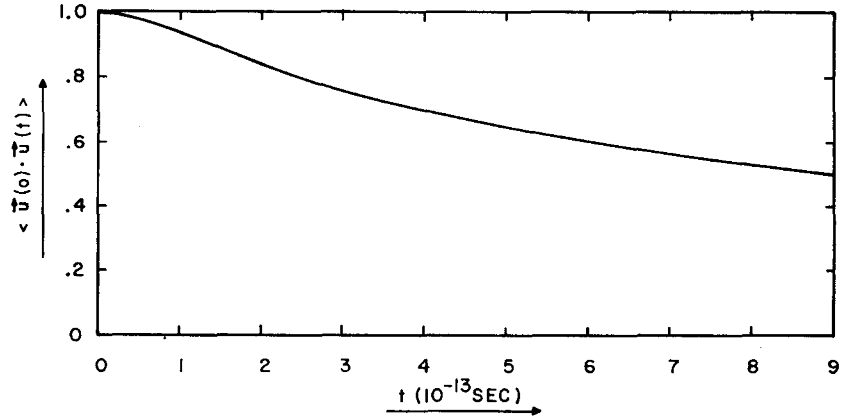

FIG. 3. The dipolar correlation function, $D(t)$ or $\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$, from a molecular-dynamics study of liquid CO at $T=67°$ and $\rho=0.8558$ g/cc in which the molecules interact through a Stockmayer potential plus a dipole–quadrupole and quadrupole potential.

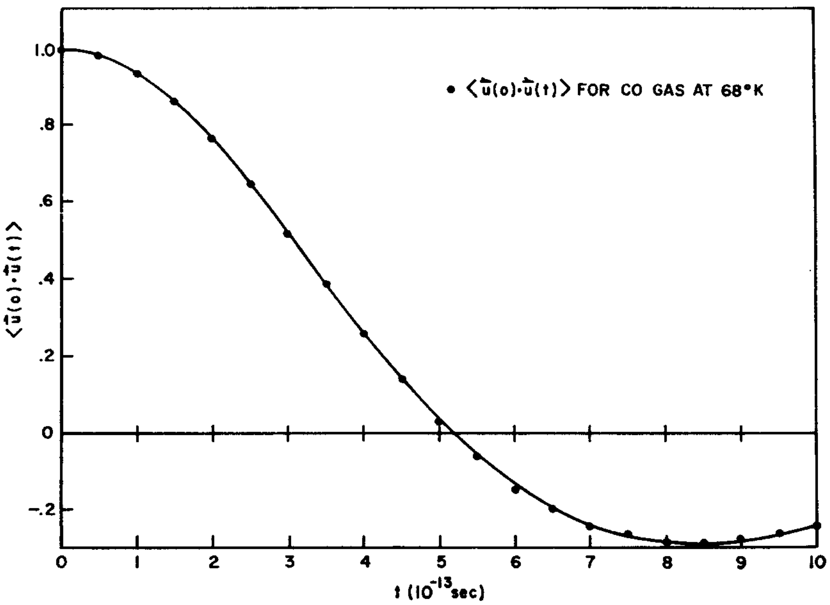

FIG. 4. The dipolar correlation function, $D(t)$ or $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$, from a molecular-dynamics study of liquid CO at $T=68°$ and $\rho=0.8558$ g/cc; the molecules interact through a Stockmayer potential. $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ for CO gas at 68°K is also plotted.

just seems to prefer smooth distributions. It seems fair to point out that the approximations are much better when the dipolar correlation function decays monotonically to zero then when it oscillates a bit. Our approximations predict that whenever $D(t)$ crosses zero, the distribution of $\mathbf{u}(t)$ becomes the uniform, equilibrium distribution, while in actuality $D(t)$ crosses zero because the molecules "collide" so infrequently that they can complete a number of rotational cycles before the orientations are randomized.

OTHER CORRELATION FUNCTIONS

The Van Hove self-correlation function[5,6] $G_s(\mathbf{r}, t)$ specifies the probability of finding a particle at the space–time point $(\mathbf{r}, t)$ given that it was at the origin at the initial time $t=0$. This function plays a very important role in the scattering of thermal neutrons from gases, liquids, and solids.

Suppose that we are given the full time dependence of the mean-square displacement of a particle in an N-body system. This information can then be used to determine the best functional form of $G_s(\mathbf{r}, t)$ consistent with the known mean-square displacement, $\langle r^2(t)\rangle$, where

$$\langle r^2(t)\rangle = \int d^3r\, r^2 G_s(\mathbf{r}, t). \qquad (12)$$

The information entropy $S[G_s(\mathbf{r}, t)]$ is defined as

$$S[G_s(\mathbf{r}, t)] = -\int d^3r\, G_s(\mathbf{r}, t) \ln G_s(\mathbf{r}, t), \qquad (13)$$

where the square bracket indicates that the entropy is a functional of the distribution function $G_s(\mathbf{r}, t)$. $S[G_s(\mathbf{r}, t)]$ is to be maximized subject to the constraints

$$\int d^3r\, G_s(\mathbf{r}, t) = 1, \qquad (14a)$$

$$\int d^3r\, r^2 G_s(\mathbf{r}, t) = \langle r^2(t)\rangle, \qquad (14b)$$

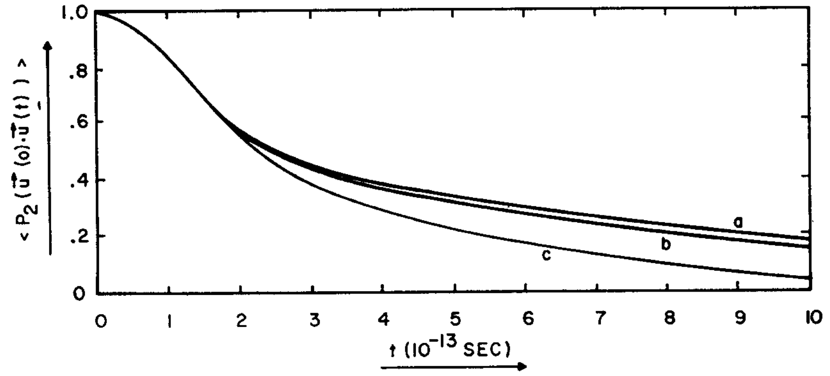

FIG. 5. $D_2(t)$ or $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ from the molecular-dynamics study cited in Fig. 3, curve a; $D_2(t)$ as predicted by Eq. (7), curve b; $D_2(t)$ as predicted by Eq. (8), curve c.

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[5] L. Van Hove, Phys. Rev. 95, 249 (1954).

[6] G. H. Vineyard, Phys. Rev. 110, 999 (1958).

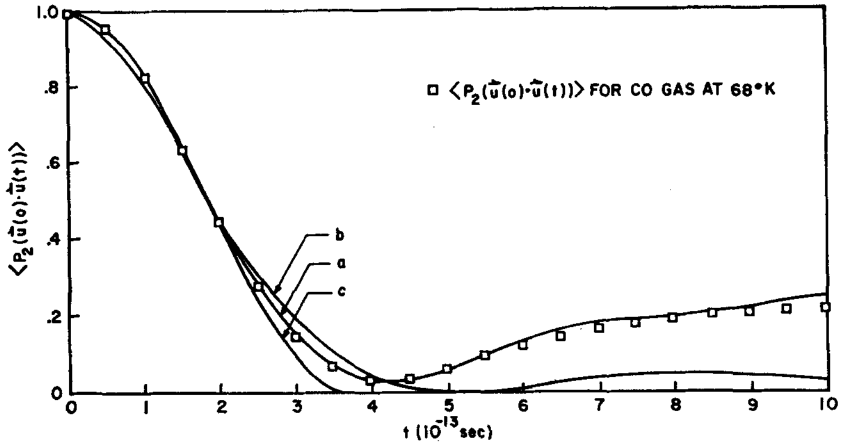

FIG. 6. $D_2(t)$ from the molecular-dynamics study cited in Fig. 4, curve a; $D_2(t)$ as predicted by Eq. (8), curve c. $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$ for CO gas at 68°K is also plotted.

where (14a) is the normalization condition and (14b) is the condition that $G_s(\mathbf{r}, t)$ must be consistent with the given correlation function $G_s(\mathbf{r}, t)$. As before this yields

$$G_s(\mathbf{r}, t) = \exp(-\alpha - \beta r^2), \qquad (15)$$

where α and β are Lagrange multipliers. Substitution of Eq. (15) into the constraints yields the values of α and β:

$$e^{-\alpha} = (\beta/\pi)^{3/2},$$

$$\beta(t) = \tfrac{3}{2}[\langle r^2(t)\rangle]^{-1},$$

so that

$$G_s(\mathbf{r}, t) = [\tfrac{2}{3}\pi\langle r^2(t)\rangle]^{-3/2} \exp[-r^2/\tfrac{2}{3}\langle r^2(t)\rangle]. \qquad (16)$$

The mean-square displacement can be expressed in terms of the normalized velocity autocorrelation function $\Psi(t) = \langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle / \langle v^2\rangle$ as

$$\langle r^2(t)\rangle = 2\langle v^2\rangle \int_0^t d\tau (t-\tau)\Psi(\tau).$$

Thus if $\Psi(t)$ is known, $\langle r^2(t)\rangle$ can be computed and $G_s(\mathbf{r}, t)$ determined.

Note that this result is the well-known Gaussian approximation[6] which has been used for many years in the theory of neutron scattering. It has been found that $G_s(\mathbf{r}, t)$ is to a good approximation Gaussian for short and long times but that for intermediate times there are non-Gaussian corrections.[7,8] To compute these corrections higher moments of r can be used. For example if $\langle r^4(t)\rangle$ is known and if $\langle r^4(t)\rangle \neq \tfrac{5}{3}[\langle r^2(t)\rangle]^2$ then the procedure used will predict non-Gaussian corrections.

The same procedure can be used to find the probability that an atom will have a velocity $\mathbf{v}$ at time t given that it had velocity $\mathbf{v}_0$ at time $t=0$, $K(\mathbf{v}, t \mid \mathbf{v}_0, 0)$. Since the joint probability of $(\mathbf{v}, t)$ and $(\mathbf{v}_0, 0)$, $P(\mathbf{v}, t; \mathbf{v}_0, 0)$, is

$$P(\mathbf{v}, t; \mathbf{v}_0, 0) = K(\mathbf{v}, t \mid \mathbf{v}_0, 0) f(\mathbf{v}_0), \qquad (17)$$

where $f(\mathbf{v}_0)$ is the Maxwell distribution function, it follows that the information entropy should be

$$S[P] = -\int d^3v \int d^3v_0 P(\mathbf{v}, t; \mathbf{v}_0, 0) \ln P(\mathbf{v}, t; \mathbf{v}_0, 0).$$

Then the maximum entropy occurs for

$$K(\mathbf{v}, t \mid \mathbf{v}_0, 0) = [m/2\pi kT(1-\Psi^2(t)]^{3/2}$$
$$\times \exp(-m/2kT)\{[\mathbf{v}-\mathbf{v}_0\Psi(t)]^2/[1-\Psi^2(t)]\}, \qquad (18)$$

which is the well-known Gaussian transition probability.[9] This transition probability has recently been tested in another publication and is found to represent the dynamics moderately well for all times. This distribution could be corrected by maximizing S subject to higher moments.[10]

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[7] R. C. Desai, J. Chem. Phys. **44**, 77 (1966).

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

[9] M. C. Wang and G. E. Uhlenbeck, Res. Mod. Phys. **17**, 323 (1945).

[10] B. O. Koopman (private communication) has shown that when dealing with distributions whose domain is unbounded in space, the highest moment used must be even to permit the existence of a distribution of maximum entropy.