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Dielectric Constant of Rare-Gas Mixtures*

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The calculation of the frequency-dependent dielectric constant of a binary mixture of rare-gas atoms is discussed. This macroscopic property reflects the fact that when two unlike rare-gas atoms undergo a collision, a dipole moment is formed. The problem is formulated in terms of response theory, which relates the dielectric constant to an integral of a correlation function, and the lowest-order contribution is explicitly calculated using the same empirical expression for the dipole moment as was used by Levine and Birnbaum.

1. INTRODUCTION

During the collision between unlike rare-gas atoms a dipole moment is formed. The macroscopic manifestation of this fact is described by a dielectric constant. It is the aim of this paper to set up the problem of calculating the frequency-dependent dielectric constant for such a system using a time-correlation function theory[1] and then to calculate the lowest-order contribution.

The experimental situation has been summarized in a recent paper by Levine and Birnbaum[2] who also calculated classically an expression for the frequency-dependent absorption coefficient by adopting a simple model for the collision process between two unlike rare-gas atoms. Levine[3] has given the quantum-mechanical extension of their calculation. Their results are in good agreement with the limited experimental data available in spite of the simplicity of the model. Of several ways one can approach the problem of calculating a dielectric constant, they consider the auxiliary problem of treating the gas mixture in thermal equilibrium with a blackbody radiation field and then use Kirchhoff's law to relate the absorption coefficient $\alpha(\omega)$ to the power per unit frequency per unit volume due to spontaneous emission $I(\omega)$ and the energy density of the radiation field [see Eq. (2.1) of Ref. 2]. By assuming that the index of refraction is unity they can determine the dielectric constant. Their problem reduces to the calculation of $I(\omega)$, which is done classically by using kinetic theory to compute an expression for the number of collisions of a given type and using the Larmor power formula of classical electromagnetic theory to describe the radiation emitted during each collision of this type. Then the final result is obtained by averaging over all types of collisions. In the quantum-mechanical calculation of Levine[3] the golden rule of time-dependent perturbation theory is used to calculate the spontaneous emission. Again Kirchhoff's law is used to relate this expression to the absorption coefficient as is derived in Appendix A. The reader is referred to their work for a detailed discussion of the model and of the experimental agreement.

A completely different approach is used in this paper, which in the biased view of the authors has some distinct advantages. The linear response of a system to an external time-dependent electric field has been discussed by Kubo[1] who related the transport coefficients to time-correlation functions; in particular, the dielectric constant is related to a transform of the dipole-dipole correlation function. The task is to use the microscopic dynamics appropriate to the model being considered to evaluate this correlation function and then to use some well-known transform relations to obtain the real and imaginary parts of the dielectric constant in terms of which the index of refraction and absorption coefficient are given. This method has the advantage of starting with an expression for the quantity of interest which is generally valid and then introducing in a straightforward way the model and a systematic approximation procedure suited to the model. In our calculation the form for the dipole moment is the one used by Levine and Birnbaum and by calculating the lowest-order contribution to the correlation function we find an expression in this order for the dielectric constant. The real part of the dielectric constant is seen to be essentially unity which in Refs. 2 and 3 had to be assumed. This fact enables one to obtain a simple relation between the imaginary part of the dielectric constant and the absorption coefficient. The resulting expression agrees with those of Levine and Birnbaum[2] and Levine.[3] It must be stated that it was not obvious to the authors when they performed this calculation that the two methods would lead to the same results. In the calculations of Levine and Birnbaum the energy density for a blackbody radiation field enters through Kirchhoff's law which in the classical calculation of Levine and Birnbaum is taken to be the Rayleigh-Jeans function and in the quantum calculation of Levine is taken to be the Planck function. In the correlation function calculation the blackbody radiation field never enters the discussion. However, it will be pointed out at the relevant point in the text how the quantum correlation function differs from the classical one in a way which has an effect similar to that of changing the form of the energy density.

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[1] For a review of correlation-function theory see R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965); R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[2] H. B. Levine and G. Birnbaum, Phys. Rev. **154**, 86 (1967).

[3] H. B. Levine, Phys. Rev. **160**, 159 (1967).

In Sec. 2 the general approach will be introduced and the application to our specific problem will be discussed. The expression for the correlation function valid in lowest order is obtained with most of the details given in Appendix B. The explicit form assumed for the dipole moment is introduced in Sec. 3 and the appropriate quantum-mechanical correlation function is evaluated. In Sec. 4 the real and imaginary parts of the dielectric constant are evaluated and the absorption coefficient obtained with some of the details relegated to Appendix C. The classical limit is also taken. A brief outline of the classical calculation of the correlation function is given in Sec. 5 and a comparison with the expression given by Levine and Birnbaum is made as they obtained a slightly different quantity. In Sec. 6 a discussion of the results is given.

2. GENERAL PROBLEM

Consider the electric vector $\mathbf{E}$ of a plane wave polarized in the z direction and propagating in the x direction, which is expressed as

$$E_z(x,t)=E_0\exp[i(\omega t-kx)], \tag{1}$$

where for a homogeneous, isotropic, and nonmagnetic material describable by a complex dielectric constant ϵ, the relation between ω and k is given by

$$k^2=\epsilon\omega^2c^{-2}. \tag{2}$$

Introducing the index of refraction n and the attenuaattenuation constant κ by $\epsilon^{1/2}=n-i\kappa$, k is given as

$$k=(\omega/c)[n-i\kappa]. \tag{3}$$

The average Poynting vector as a function of position is

$$S_x(x)=S_x(0)e^{-(2\omega\kappa/c)x}, \tag{4}$$

so that the absorption coefficient $\alpha(\omega)$ is

$$\alpha(\omega)=2\omega\kappa/c. \tag{5}$$

From the above it is evident that a knowledge of the dielectric constant determines both the index of refraction and the absorption coefficient.

The above is valid independent of the details of the microscopic system as long as it can be described by a nontensorial uniform dielectric constant. To relate the dielectric constant to the microscopic dynamics, it is written in terms of the susceptibility $\chi(\omega)$ as

$$\epsilon=1+4\pi\chi, \tag{6}$$

where $\chi(\omega)$ is the coefficient which relates the polarization $\mathbf{P}$ to the local electric field $\mathbf{E}$ as

$$\mathbf{P}=\chi\mathbf{E}. \tag{7}$$

The nature of the systems of interest allows us to equate the local field with the external field and hence to use the expression for $\chi(\omega)$ derived by Kubo[1] which is

$$\chi(\omega)=\int_0^\infty dt\, e^{-i\omega t}\Phi(t,\beta). \tag{8}$$

$\Phi(t,\beta)$ is the correlation function associated with the response of the z component of the dipole moment per unit volume to an external time-dependent electric field along the z direction. The quantum-mechanical expression for $\Phi(t,\beta)$ is

$$\Phi(t,\beta)=(i/\hbar V)\int_0^\beta d\lambda\, \mathrm{Tr}\{\rho[H,M_z(-i\hbar\lambda)]M_z(t)\}, \tag{9}$$

where $M_z(\tau)$ is the Heisenberg operator,

$$M_z(\tau)=e^{iH\tau/\hbar}M_ze^{-iH\tau/\hbar}, \tag{10}$$

β is the reciprocal of the product of the Boltzmann constant with the Kelvin temperature, ρ is the canonical ensemble, V is the volume of the system, $\mathbf{M}$ is the total dipole-moment operator, and H is the Hamiltonian of the system in the absence of an external field.

At this point we introduce the detailed nature of the system. We consider a system of N_A atoms of species A and N_B atoms of species B confined to the volume V. The species are assumed to be in the gaseous phase. It is assumed that the atoms have no permanent dipole moment and a negligible polarizability and that the only dipoles present are those which are induced during the collisions of unlike molecules. The Hamiltonian for the system is assumed to be of the form

$$H=H_0+V_{AA}+V_{BB}+V_{AB}, \tag{11}$$

where

$$H_0=\sum_{i=1}^{N_A}\frac{p_i^2}{2m_A}+\sum_{i=1}^{N_B}\frac{p_i^2}{2m_B}\equiv H_A{}^0+H_B{}^0, \tag{12a}$$

$$V_{AA}=\sum_{i<j}^{N_A}V_A(|\mathbf{r}_i-\mathbf{r}_j|), \tag{12b}$$

$$V_{BB}=\sum_{i<j}^{N_B}V_B(|\mathbf{r}_i-\mathbf{r}_j|), \tag{12c}$$

and

$$V_{AB}=\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}V_{AB}(|\mathbf{r}_i-\mathbf{r}_j|). \tag{12d}$$

The total dipole moment M_z is given by the following sum:

$$M_z=\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\mu_{zij}(\mathbf{r}_i-\mathbf{r}_j), \tag{13}$$

where an explicit functional dependence of the dipole moment $\boldsymbol{\mu}(\mathbf{r})$ on the nuclear separation between an A and a B atom will be assumed in the next section.

Introducing the quantum-mechanical Liouville operator L defined by

$$L\equiv[H,\ ], \tag{14}$$

Eq. (9) can be rewritten as

$$\Phi(t,\beta)=\frac{i}{\hbar V}\,\mathrm{Tr}\left\{\rho\left[L\left(\int_0^\beta d\lambda e^{\lambda L}M_z\right)\right]e^{iLt/\hbar}M_z\right\}, \tag{15}$$

and since $iL/\hbar$ is the Heisenberg time derivative operator one can write

$$\Phi(t,\beta)=(1/V)\langle(d\tilde{M}_z/dt)M_z(t)\rangle, \tag{16}$$

where $\tilde{M}_z$ is known as the Kubo transform, and is defined by

$$\tilde{M}_z\equiv\int_0^\beta d\lambda e^{\lambda H}M_z e^{-\lambda H}. \tag{17}$$

The form of Eq. (16) will aid in a later comparison with the classical calculation.

It is possible to perform the λ integral in Eq. (15) and when one introduces explicitly the form for the canonical ensemble

$$\rho=Z^{-1}e^{-\beta H}, \tag{18}$$

where

$$Z=\mathrm{Tr}e^{-\beta H}, \tag{19}$$

one is led to the following expression for $\Phi(t,\beta)$:

$$\Phi(t,\beta)=(i/Z\hbar V)\;\mathrm{Tr}\{[M_z,e^{-\beta H}]e^{iLt/\hbar}M_z\}. \tag{20}$$

Expression (20) may be used as a starting point for an approximation scheme similar to that developed by Fano[4] in his discussion of pressure broadening. The substitution of Eq. (20) in Eq. (8) leads to an expression for the susceptibility in terms of the resolvent operator. The Liouville operator can be split into a free-particle part and an interaction part, and then an expansion similar to that given by Fano will lead to a density expansion for the susceptibility. The lowest-order approximation which is calculated in this paper is obtained by neglecting the interparticle interactions. A similar assumption is made by Levine and Birnbaum when they introduce the straight-line trajectory approximation.

Let us now discuss this lowest-order approximation. Neglecting the interparticle interactions and using the free-particle representation to expand the trace in Eq. (20), we can write $\Phi(t,\beta)$ as

$$\Phi(t,\beta)=\frac{i}{Z\hbar V}\sum_{\{\mathbf{k}\}}D\{\mathbf{k}\}, \tag{21}$$

where $D\{\mathbf{k}\}$ is given by

$$D\{\mathbf{k}\}=\langle\{\mathbf{k}\}|\sum_{i,j}^{N_A}\sum_{m,n}^{N_B}[\mu_{zim},\,e^{-\beta H_0}]e^{iL_0t/\hbar}\mu_{zjm}|\{\mathbf{k}\}\rangle, \tag{22}$$

and $|\{k\}\rangle$ by

$$|\{\mathbf{k}\}\rangle=\prod_i^{N_A}|k_i\rangle\prod_j^{N_B}|k_j\rangle, \tag{23}$$

with $|k_i\rangle$ plane-wave states.

In Appendix B it is shown that only those terms in Eq. (22) with $i=j$ and $m=n$ contribute and that each pair contributes the same. This allows the reduction of the correlation function to the form

$$\Phi(t,\beta)=N_AN_B\Phi_2(t,\beta), \tag{24}$$

with $\Phi_2(t,\beta)$ a two-particle correlation function given by

$$\Phi_2(t,\beta)=(i/\mathfrak{z}\hbar V)\;\mathrm{tr}\{[\mu_z(\mathbf{r}),e^{-\beta H_2}]\times e^{iH_2t/\hbar}\mu_z(\mathbf{r})e^{-iH_2t/\hbar}\}, \tag{25}$$

where relative and center-of-mass coordinates have been introduced with

$$\mathbf{r}=\mathbf{r}_i-\mathbf{r}_j, \tag{26}$$

$$H_2=(-\hbar^2/2m)\nabla_r^2, \tag{27}$$

$$m=m_Am_B/(m_A+m_B), \tag{28}$$

and

$$\mathfrak{z}=\mathrm{tr}e^{-\beta H_2}, \tag{29}$$

where tr stands for the trace over a complete set of single-particle states. Thus the problem has been reduced to that of evaluating $\Phi_2(t,\beta)$ which is equivalent to calculating the correlation function associated with the polarizability $\alpha_p(\omega)$ of a free particle of mass m and dipole-moment operator μ_z; i.e.,

$$\alpha_p(\omega)=V\int_0^\infty e^{-i\omega t}\Phi_2(t,\beta)dt, \tag{30}$$

where the average dipole moment is written as

$$\langle\mu_z\rangle_E=\alpha_pE. \tag{31}$$

The susceptibility is then that of a system of N_AN_B independent dipoles with dipole moment $\langle\mu_z\rangle_E$, so that

$$\chi=(N_AN_B/V)\alpha_p. \tag{32}$$

3. CALCULATION OF CORRELATION FUNCTION

On expanding the trace in Eq. (25), one obtains for $\Phi_2(t,\beta)$

$$\Phi_2(t,\beta)=(i/\hbar\mathfrak{z}V)\sum_{\mathbf{kq}}(e^{-\beta\epsilon(\mathbf{q})}-e^{-\beta\epsilon(\mathbf{k})})\times e^{i[\epsilon(\mathbf{q})-\epsilon(\mathbf{k})]t/\hbar}|\langle\mathbf{k}|\mu_z|\mathbf{q}\rangle|^2, \tag{33}$$

where the eigenstates are

$$|\mathbf{k}\rangle=V^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{34}$$

It is not possible to proceed further without an explicit form for μ_z. We shall adopt the expression used by Levine and Birnbaum[2,3] which is

$$\boldsymbol{\mu}=\mu_0\gamma\mathbf{r}e^{-\gamma^2r^2}, \tag{35}$$

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[4] U. Fano, Phys. Rev. **131**, 259 (1963).

so that the matrix element of μ_z is

$$\langle \mathbf{k}|\mu_z|\mathbf{q}\rangle=\frac{\mu_0\gamma}{V}\int\int\int e^{[i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}]}ze^{-\gamma^2r^2}dxdydz. \quad (36)$$

The x and y integrals are done at once by completing the square and the z integration is done the same way after an integration by parts and one finds

$$\langle \mathbf{k}|\mu_z|\mathbf{q}\rangle=\frac{-i\mu_0(\pi)^{3/2}(k_z-q_z)}{2\gamma^4V}\exp\left[-\frac{1}{4\gamma^2}|\mathbf{k}-\mathbf{q}|^2\right]. \quad (37)$$

On substituting Eq. (37) into Eq. (33) and replacing the sums by integrals in going to the usual large volume limit the resulting integral is

$$\Phi_2(t,\beta)=\frac{i}{V\hbar\mathfrak{Z}}\left(\frac{\mu_0}{\gamma^4 16\pi^{3/2}}\right)^2\int\int d\mathbf{q}d\mathbf{k}$$
$$\times\left[\exp\left(\frac{-\beta\hbar^2q^2}{2m}\right)-\exp\left(\frac{-\beta\hbar^2k^2}{2m}\right)\right]$$
$$\times\exp\left[\frac{i\hbar t}{2m}(q^2-k^2)\right](q_z-k_z)^2$$
$$\times\exp\left[-\frac{1}{2\gamma^2}|\mathbf{k}-\mathbf{q}|^2\right]. \quad (38)$$

The above integral can most conveniently be done by the change of variables

$$\mathbf{S}=\mathbf{q}+\mathbf{k} \quad \text{and} \quad \mathbf{W}=\mathbf{q}-\mathbf{k}. \quad (39)$$

The integrals are then elementary and the result is

$$\Phi_2(t,\beta)=\left(\frac{i\mu_0^2\beta m^4}{\hbar^4\gamma^8\mathfrak{Z}(32)V}\right)\left[\left(\frac{\beta m}{\gamma^2}+t^2+i\beta\hbar t\right)^{-5/2}\right.$$
$$\left.-\left(\frac{\beta m}{\gamma^2}+t^2-i\beta\hbar t\right)^{-5/2}\right]. \quad (40)$$

Since the terms in the brackets are complex conjugates, this insures the reality of $\Phi_2(t,\beta)$. The free-particle partition function $\mathfrak{Z}$ is $V[2\pi\beta\hbar^2m^{-1}]^{-3/2}$, which, together with Eq. (40), enables us to write the total correlation function from Eq. (24) as

$$\Phi(t,\beta)=C\left[\left(\frac{\beta m}{\gamma^2}+\frac{\beta^2\hbar^2}{4}+(t+\tfrac{1}{2}i\beta\hbar)^2\right)^{-5/2}\right.$$
$$\left.+\left(\frac{\beta m}{\gamma^2}+\frac{\beta^2\hbar^2}{4}+(t-\tfrac{1}{2}i\beta\hbar)^2\right)^{-5/2}\right], \quad (41)$$

where

$$C=\frac{in_An_B\mu_0^2(2\pi)^{3/2}}{\gamma^3\hbar(32)}\left(\frac{\beta m}{\gamma^2}\right)^{5/2}, \quad (41')$$

and n_A and n_B are the particle densities of the two species.

4. DIELECTRIC CONSTANT AND ABSORPTION COEFFICIENT

The frequency-dependent susceptibility is now obtained by substituting Eq. (41) into Eq. (8) which is shown in Appendix C to yield

$$\chi(\omega)=2C\left[-i\sinh\tfrac{1}{2}\beta\hbar\omega\int_0^\infty dt\right.$$
$$\times e^{-i\omega t}\left(\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+t^2\right)^{-5/2}+\int_0^{\beta\hbar/2}dy$$
$$\left.\times\{\cosh[\omega(y-\tfrac{1}{2}\beta\hbar)]\}\left(\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2-y^2\right)^{-5/2}\right]. \quad (42)$$

Writing the dielectric constant in terms of its real and imaginary parts,

$$\epsilon(\omega)=\epsilon'(\omega)-i\epsilon''(\omega), \quad (43)$$

one obtains, by combining Eqs. (6), (42), and (43),

$$\epsilon'(\omega)-1=8\pi C\left\{-\sinh\tfrac{1}{2}\beta\hbar\omega\int_0^\infty\frac{dt\,\sin\omega t}{(\beta m/\gamma^2+\frac{1}{4}\beta^2\hbar^2+t^2)^{5/2}}\right.$$
$$\left.+\int_0^{\beta\hbar/2}\frac{dy\,\cosh[\omega(y-\frac{1}{2}\beta\hbar)]}{(\beta m/\gamma^2+\frac{1}{4}\beta^2\hbar^2-y^2)^{5/2}}\right\} \quad (44)$$

and

$$\epsilon''(\omega)=8\pi C\sinh\tfrac{1}{2}\beta\hbar\omega\int_0^\infty\frac{dt\,\cos\omega t}{(\beta m/\gamma^2+\frac{1}{4}\beta^2\hbar^2+t^2)^{5/2}}. \quad (45)$$

It is to be noted that Eqs. (44) and (45) are direct expressions for the dielectric constant and do not rest upon the assumption that the index of refraction is unity.

The static dielectric constant can be obtained by setting $\omega=0$ in Eqs. (44) and (45) and one finds that

$$\epsilon(0)=\epsilon'(0)=1+4\pi C\beta\left(\frac{\beta m}{\gamma^2}\right)^{-5/2}$$
$$\times\left(1+\frac{1}{12}\frac{\gamma^2\hbar^2\beta}{m}\right)\left(1+\frac{\gamma^2\hbar^2\beta}{4m}\right)^{-2}, \quad (46)$$

which in the classical limit becomes

$$\epsilon_c'(0)=1+\frac{n_An_B\mu_0^2\beta(\pi)^{5/2}}{(2)^{3/2}\gamma^3}. \quad (47)$$

In the experimental situations for which Levine and Birnbaum[2] have fit their parameters, the static dielectric constant differs from unity by a term of order 10^{-9} which provides a justification for assuming the index of refraction is unity. Eq. (47) is in complete agreement with Levine,[3] who used Kramers-Kronig relations together with a knowledge of $\alpha(\omega)$ and the assumption of $n(\omega)=1$ to calculate $\epsilon(0)$.

The integral in Eq. (45) is related to a modified Bessel function of the second[5] kind which then gives for the imaginary part of the dielectric constant

$$\epsilon''(\omega)=\frac{8}{3}\pi C\left(\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2\right)^{-1}\omega^2$$

$$\times\sinh\tfrac{1}{2}\beta\hbar\omega\,K_2\left[\omega\left(\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2\right)^{1/2}\right]. \tag{48}$$

Let us go back to Eqs. (2), (3), and (5), which enable us to relate the index of refraction and the absorption coefficient to the real and the imaginary parts of the dielectric constant. These relations are

$$\epsilon'=n^2-\tfrac{1}{4}\alpha^2\omega^2/c^2 \tag{49a}$$

and

$$\epsilon''=\alpha nc/\omega. \tag{49b}$$

By combining Eqs. (48) and (49b) one obtains for $\alpha(\omega)$,

$$\alpha(\omega)=\frac{8\pi C}{3cn(\omega)}\left(\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2\right)^{-1}\omega^3$$

$$\times\sinh\tfrac{1}{2}\beta\hbar\omega\,K_2\left[\omega\left(\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2\right)^{1/2}\right], \tag{50}$$

and when $n(\omega)$ can be approximated by unity in Eq. (50) one recovers the result of Levine.[3] Making such an approximation and taking the classical limit of Eq. (50) one obtains for $\alpha(\omega)$

$$\alpha_c(\omega)=\frac{n_An_B\mu_0{}^2(\pi)^{5/2}(2)^{1/2}[(\beta m/\gamma^2)^{1/2}\omega]^4\,K_2[(\beta m/\gamma^2)^{1/2}\omega]}{12\gamma^2c(m/\beta)^{1/2}}. \tag{51}$$

5. CLASSICAL CALCULATION

Since the classical calculation is somewhat different in detail and a comparison with the quantum calculation and a comparison of the two with Levine and Birnbaum is desired, the classical calculation will be outlined in this section. To perform the classical calculation the only change needed in the previous sections is that the correlation function given by Eq. (16) is to be replaced by the corresponding classical expression which is

$$\Phi(t,\beta)=(\beta/V)\langle\dot{M}_z(0)M_z(t)\rangle. \tag{52}$$

By comparison of these two equations one sees that the essential structural difference is that the Kubo transform in Eq. (16) has been replaced by a simple factor of β and otherwise one has a classical statistical mechanics equilibrium average to calculate. It is this structural difference which is mysteriously equivalent to the change from the Rayleigh-Jeans distribution to the Planck distribution which was made by Levine[3] in performing the quantum calculation.

Again in the lowest order one is able to reduce the problem to an effective single-particle problem in terms of the correlation function

$$\Phi_2(t,\beta)=\frac{\beta}{V^2\int d\mathbf{v}_0e^{-\beta mv_0{}^2/2}}\int\int d\mathbf{r}_0d\mathbf{v}_0$$

$$\times\dot{\mu}_z(0)\mu_z(t)e^{-\beta mv_0{}^2/2}, \tag{53}$$

where $\mathbf{v}$ is the classical velocity. By use of the same expression for the dipole moment, one has

$$\mu_z(t)=\mu_0\gamma(z_0+v_{0z}t)\exp[-\gamma^2(|\mathbf{r}_0+\mathbf{v}_0t|^2)] \tag{54}$$

and

$$\dot{\mathbf{u}}_z(0)=\mu_0\gamma[-2\gamma^2z_0(\mathbf{r}_0\cdot\mathbf{v}_0)+v_{0z}]e^{-\gamma^2r_0{}^2}. \tag{55}$$

Substituting Eqs. (54) and (55) into Eq. (53) one obtains

$$\Phi_2(t,\beta)=\frac{\beta\mu_0{}^2\gamma^2}{V^2(2\pi/\beta m)^{3/2}}\int\int d\mathbf{r}d\mathbf{v}$$

$$\times\exp\{-[(\tfrac{1}{2}\beta m+\gamma^2t^2)v^2+2\gamma^2(r^2+\mathbf{r}\cdot\mathbf{v}t)]\}$$

$$\times(z+v_zt)[-2\gamma^2z(\mathbf{r}\cdot\mathbf{v})+v_z], \tag{56}$$

where the subscript indicating the initial values has been dropped. The above can be integrated by repeated completion of squares and integration by parts to give

$$\Phi_2(t,\beta)=\frac{5(\pi)^{3/2}(\beta m/\gamma^2)^{5/2}\mu_0{}^2}{(2)^{3/2}\gamma mV}$$

$$\times\left[\frac{t}{(\beta m/\gamma^2+t^2)^{5/2}}-\frac{t^3}{(\beta m/\gamma^2+t^2)^{7/2}}\right]. \tag{57}$$

It is to be noted that the above correlation function differs from the one obtained by Levine and Birnbaum[2] since they calculated a slightly different quantity. It is possible to integrate Eq. (8) by parts and obtain an expression for $\chi(\omega)$ of the form [see Eqs. (7.1) and (7.2) of Ref. 2]

$$\chi(\omega)=\Phi_1(0)-i\omega\int_0^\infty dt\Phi_1(t)e^{-i\omega t}, \tag{58}$$

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[5] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964), Appl. Math. Ser. 55, pp. 376–9.

and it is the related correlation function $\Phi_1(t)$ which they calculated.

After substitution of Eq. (57) into Eq. (30) and several integrations by parts, the real and imaginary parts of the dielectric constant are now reduced to

$$\epsilon'(\omega)=1+C'\Bigg[3\left(\frac{\beta m}{\gamma^2}\right)^{-3/2}+\omega^2\left(\frac{\beta m}{\gamma^2}\right)^{-1/2} -2\int_0^\infty dt\omega\sin\omega t\left(\frac{\beta m}{\gamma^2}+t^2\right)^{-3/2} -\int_0^\infty dt\omega^3\sin\omega t\left(\frac{\beta m}{\gamma^2}+t^2\right)^{-1/2}\Bigg] \tag{59}$$

and

$$\epsilon''(\omega)=C'\Bigg[\int_0^\infty dt2\omega\cos\omega t\left(\frac{\beta m}{\gamma^2}+t^2\right)^{-3/2} +\int_0^\infty dt\omega^3\cos\omega t\left(\frac{\beta m}{\gamma^2}+t^2\right)^{-1/2}\Bigg], \tag{60}$$

where

$$C'=\frac{n_An_B\mu_0^2\pi^{5/2}}{2^{1/2}6m\gamma}\left(\frac{\beta m}{\gamma^2}\right)^{5/2}. \tag{60'}$$

Setting $\omega=0$ one recovers at once the result expressed in Eq. (47).

The integrals in Eq. (60) are given in Ref. 5 and one is led to

$$\epsilon''(\omega)=C'\left\{\frac{2\omega^2K_1[(\beta m/\gamma^2)^{1/2}\omega]}{(\beta m/\gamma^2)^{1/2}} +\omega^2K_0[(\beta m/\gamma^2)^{1/2}\omega]\right\}, \tag{61}$$

where K_0 and K_1 are modified Bessel functions of the zeroth and first kind. They are related by a recursion relation[5] which when used will yield

$$\epsilon''(\omega)=C'\omega^3K_2\left[\left(\frac{\beta m}{\gamma^2}\right)^{1/2}\omega\right], \tag{62}$$

which is in agreement with the classical limit of Eq. (48) and therefore leads also to Eq. (51).

6. CONCLUSIONS

The phenomenon of collision-induced absorption has been treated in this paper using the formal theory of linear transport processes which relates a linear transport coefficient, in this case the dielectric constant, to a transform of a time-correlation function which has come to be known as the Kubo formula. Both the quantum and classical lowest-order contributions to the dielectric constant of a rare-gas mixture were calculated using a simple model for the collision induced dipole moment. The same problem was recently discussed by Levine and Birnbaum[2,3] using a completely different approach.

It is felt that the main advantage of the approach taken in this work is that it is based on a general and rigorous first-principles expression for the dielectric constant and therefore lends itself to a systematic and straightforward approximation procedure such as a density expansion. In addition no further assumptions need be made outside of those which naturally arise in the statement of the model assumed. For example, nowhere in this paper was the assumption made that the index of refraction is unity, except when we wanted to make a comparison with Levine and Birnbaum. On the other hand their procedure assumes a value of unity for the index of refraction, which, of course, is a good assumption for the range of experimental situations of interest to them. It is not at all evident how one would modify their approach for the case where this assumption is not valid. To go to higher order using their technique it would be necessary to concern oneself with the very difficult problem of the emission of radiation from interacting particles. The higher-order approximations via the Kubo formula do not encounter such fundamental problems and this will be the subject of a future paper.

It is felt that the calculation in this paper also has another interest. It provides a rare example where a Kubo formula can be evaluated in a straightforward way. The more typical situation is to relate the Kubo expression to a function which satisfies an integral equation and the problem is to then solve this integral equation. (The reader is referred to the bibliography of Ref. 1 for a long list of such calculations.)

APPENDIX A

Since Levine[3] did not derive his starting equation, Eq. (2.1), it was felt useful to include a derivation of it from Kirchhoff's law, which relates the absorption coefficient $\alpha(\omega)$ to the power due to spontaneous emission per unit frequency interval per unit volume $I(\omega)$ and the intensity of the blackbody radiation field $cu(\omega)$. This law has the form

$$\alpha(\omega)=I(\omega)/cu(\omega), \tag{A1}$$

where

$$u(\omega)=\frac{\hbar\omega^3}{\pi^2c^3[e^{\hbar\omega/kT}-1]}, \tag{A2}$$

and $I(\omega)$ is to be calculated here.

From Schiff[6] [Eq. (36-22)] the amount of energy emitted per unit volume per unit time involving spontaneous transitions from a higher-energy state b to a lower-energy state a, $I_{ab}(\omega)$, is given by

$$I_{ab}(\omega_{ab})=\frac{4\omega_{ab}^3}{Vc^3}|\langle M_z\rangle_{ab}|^2P_b\hbar\omega_{ab}, \tag{A3}$$

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[6] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1955), 2nd ed.

where P_b is the probability that the system is in state b and

$$\omega_{ab}=(\epsilon_b-\epsilon_a)/\hbar. \qquad (A4)$$

$I(\omega)$ may be obtained from Eq. (A3) by noting that many states a,b may have the same energy difference and $I(\omega)$ itself is a per unit frequency quantity. The resulting expression is

$$I(\omega)=\frac{4}{Vc^3}\sum_{a,b}\omega^3|\langle M_z\rangle_{ab}|^2P_b\omega_{ab}\delta(\omega-\omega_{ab}). \qquad (A5)$$

Now substitute Eqs. (A2) and (A5) into Eq. (A1) and obtain

$$\alpha(\omega)=\frac{4\pi^2}{Vch}\sum_{a,b}\omega_{ab}|\langle M_z\rangle_{ab}|^2P_b\,\delta(\omega_{ab}-\omega)\times(e^{\hbar\omega_{ab}/kT}-1). \qquad (A6)$$

The use of the canonical ensemble gives that

$$P_a=e^{-\hbar\omega_{ab}/kT}P_b, \qquad (A7)$$

so that one can write Eq. (A6) in the form used by Levine as his starting equation.

APPENDIX B

The correlation function of Eq. (20) will be reduced in this section to a two-particle correlation function involving an A and B atom multiplied by a factor of N_AN_B.

Introducing a complete set of intermediate states one writes Eq. (22) as

$$D\{\mathbf{k}\}=\sum_{\{\mathbf{q}\}}(e^{-\beta\epsilon\{\mathbf{q}\}}-e^{-\beta\epsilon\{\mathbf{k}\}})\exp\left[i(\epsilon\{\mathbf{q}\}-\epsilon\{\mathbf{k}\})\frac{t}{\hbar}\right]\times|\langle\{\mathbf{k}\}|M_z|\{\mathbf{q}\}\rangle|^2, \qquad (B1)$$

where M_z is the total dipole-moment operator. The product of the two sums contained in the M_z matrix elements may be split up into contributions where both terms involve the dipole-moment operator for the same A and B particles, the same A particles but different B particles, the same B particles but different A particles and different A and B particles. The resulting expression for $D\{\mathbf{k}\}$ may then be written as

$$D\{\mathbf{k}\}=\sum_{\{\mathbf{q}\}}(e^{-\beta\epsilon\{\mathbf{q}\}}-e^{-\beta\epsilon\{\mathbf{k}\}})\exp\left[i(\epsilon\{\mathbf{q}\}-\epsilon\{\mathbf{k}\})\frac{t}{\hbar}\right]\Big[\sum_{i,j}|\langle\{\mathbf{k}\}|\mu_{zij}|\{\mathbf{q}\}\rangle|^2+\sum_{\substack{ijm\\ i\neq m}}\langle\{\mathbf{k}\}|\mu_{zij}|\{\mathbf{q}\}\rangle\langle\{\mathbf{q}\}|\mu_{zmj}|\{\mathbf{k}\}\rangle$$
$$+\sum_{\substack{ijn\\ j\neq n}}\langle\{\mathbf{k}\}|\mu_{zij}|\{\mathbf{q}\}\rangle\langle\{\mathbf{q}\}|\mu_{zin}|\{\mathbf{k}\}\rangle+\sum_{\substack{i\neq m\\ j\neq n}}\langle\{\mathbf{k}\}|\mu_{zij}|\{\mathbf{q}\}\rangle\langle\{\mathbf{q}\}|\mu_{zmn}|\{\mathbf{k}\}\rangle\Big]. \qquad (B2)$$

The contributions from the last three terms will be shown to vanish.

Let us consider the contribution to the last term for given values of i, j, m and n. The matrix elements may be written as

$$\langle\{\mathbf{k}\}|\mu_{zij}|\{\mathbf{q}\}\rangle\langle\{\mathbf{q}\}|\mu_{zmn}|\{\mathbf{k}\}\rangle=\prod_{r=1}^{N_A}\delta(\mathbf{k}_r{}^A,\mathbf{q}_r{}^A)\times\prod_{s=1}^{N_B}\delta(\mathbf{k}_s{}^B,\mathbf{q}_s{}^B)\langle\mathbf{k}_i{}^A\mathbf{k}_j{}^B|\mu_{zij}|\mathbf{k}_i{}^A\mathbf{k}_j{}^B\rangle\times\langle\mathbf{k}_m{}^A\mathbf{k}_n{}^B|\mu_{zmn}|\mathbf{k}_m{}^A\mathbf{k}_n{}^B\rangle, \qquad (B3)$$

where $|\mathbf{k}_i\rangle$ are of the form

$$|\mathbf{k}_i\rangle=V^{-1/2}e^{i\mathbf{k}_i\cdot\mathbf{r}_i}. \qquad (B4)$$

Hence it follows that

$$\langle\mathbf{k}_i{}^A\mathbf{k}_j{}^B|\mu_{zij}|\mathbf{k}_i{}^A\mathbf{k}_j{}^B\rangle=V^{-2}\int\int d\mathbf{r}_i{}^Ad\mathbf{r}_j{}^B\mu_{zij}. \qquad (B5)$$

It is now assumed that μ_z is an odd function of the relative coordinates (z_i-z_j) and an even function of (x_i-x_j) and (y_i-y_j) which will make Eq. (B5) vanish.

The second and third terms of Eq. (B2) contain a factor like

$$\langle\mathbf{k}_i{}^A\mathbf{q}_j{}^B|\mu_{zij}|\mathbf{k}_i{}^A\mathbf{k}_j{}^B\rangle=V^{-1}\int\int d\mathbf{r}_id\mathbf{r}_j\mu_z(\mathbf{r}_i{}^A-\mathbf{r}_j{}^B)\times\exp[i(\mathbf{k}_j{}^A-\mathbf{q}_j{}^B)\cdot\mathbf{r}_j{}^B], \qquad (B6)$$

which upon making the change of variables

$$\mathbf{u}=\mathbf{r}_i{}^A-\mathbf{r}_j{}^B \quad\text{and}\quad \mathbf{w}=\mathbf{r}_i{}^A+\mathbf{r}_j{}^B \qquad (B7)$$

can be rewritten

$$\langle\mathbf{k}_i{}^A\mathbf{q}_j{}^B|\mu_{zij}|\mathbf{k}_i{}^A\mathbf{k}_j{}^B\rangle=(\text{factor})\times\int d\mathbf{u}\mu_z(\mathbf{u}) \qquad (B8)$$

which has been argued above to vanish.

The expression for $D\{\mathbf{k}\}$ is therefore of the form

$$D\{\mathbf{k}\}=\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}D^{ij}\{\mathbf{k}\}, \qquad (B9)$$

where

$$D^{ij}\{\mathbf{k}\}=\sum_{\{\mathbf{q}\}}(e^{-\beta\epsilon\{\mathbf{q}\}}-e^{-\beta\epsilon\{\mathbf{k}\}})\exp\left[i(\epsilon\{\mathbf{q}\}-\epsilon\{\mathbf{k}\})\frac{t}{\hbar}\right]\times|\langle\{\mathbf{k}\}|\mu_{zij}|\{\mathbf{q}\}\rangle|^2. \qquad (B10)$$

Let us calculate a sample $D^{ij}\{\mathbf{k}\}$ by letting $i=1$ and $j=1$. This yields

$$D^{1,1}\{\mathbf{k}\}=\sum(e^{-\beta\epsilon\{\mathbf{q}\}}-e^{-\beta\epsilon\{\mathbf{k}\}})\exp\left[i(\epsilon\{\mathbf{q}\}-\epsilon\{\mathbf{k}\})\frac{t}{\hbar}\right]\prod_{i=2}^{N_A}\delta(k_i{}^A,q_i{}^A)\prod_{j=2}^{N_B}\delta(k_j{}^B,q_j{}^B)\,|\langle k_1{}^Ak_1{}^B|\mu_{z11}|\mathbf{q}_1{}^A\mathbf{q}_1{}^B\rangle|^2, \quad \text{(B11)}$$

and by summing over all $\{\mathbf{q}\}$ except $\mathbf{q}_1{}^A$ and $\mathbf{q}_1{}^B$ one reduces $D^{1,1}\{\mathbf{k}\}$ to

$$D^{1,1}\{\mathbf{k}\}=\prod_{i=2}^{N_A}\prod_{j=2}^{N_B}\exp\{-\beta[\epsilon(q_i{}^A)+\epsilon(q_j{}^B)]\}\sum_{\mathbf{q}_1{}^A,\mathbf{q}_1{}^B}[e^{-\beta[\epsilon(q_1{}^A)+\epsilon(q_1{}^B)]}-e^{-\beta[\epsilon(k_1{}^A)+\epsilon(k_1{}^B)]}]$$
$$\times\exp\{i[\epsilon(q_1{}^A)+\epsilon(q_1{}^B)-\epsilon(k_1{}^A)-\epsilon(k_1{}^B)]\}\,|\langle\mathbf{k}_1{}^A\mathbf{k}_1{}^B|\mu_{z11}|\mathbf{q}_1{}^A\mathbf{q}_1{}^B\rangle|^2, \quad \text{(B12)}$$

where

$$\epsilon(k_j{}^A)=\hbar(k_j{}^A)^2/2m_A. \quad \text{(B13)}$$

Upon writing the correlation function $\Phi(t,\beta)$ as

$$\Phi(t,\beta)=\sum_{i,j}\Phi_{i,j}, \quad \text{(B14)}$$

where

$$\Phi_{i,j}=\frac{i}{Z\hbar V}\sum_{\{k\}}D^{i,j}\{k\}, \quad \text{(B15)}$$

we have that

$$\Phi_{1,1}(t,\beta)=\frac{i}{\mathfrak{Z}_1{}^A\mathfrak{Z}_1{}^A\hbar V}\sum_{k_1{}^Aq_1{}^Ak_1{}^Bq_1{}^B}[e^{-\beta[\epsilon(q_1{}^A)+\epsilon(q_1{}^B)]}$$
$$-e^{-\beta[\epsilon(k_1{}^A)+\epsilon(k_1{}^B)]}]\exp\left\{\frac{it}{\hbar}[\epsilon(q_1{}^A)+\epsilon(q_1{}^B)\right.$$
$$\left.-(\epsilon(k_1{}^A)+\epsilon(k_1{}^B))]\right\}|\langle k_1{}^Ak_1{}^B|\mu_{z11}|q_1{}^Aq_1{}^B\rangle|^2, \quad \text{(B16)}$$

with $\mathfrak{Z}_1{}^A$ given by

$$\mathfrak{Z}_1{}^A=\sum_{k_1{}^A}e^{-\beta\epsilon(k_1{}^A)}. \quad \text{(B17)}$$

By inspection of (B15) we see that all $\Phi_{i,j}$ are identical in form so that we may write the desired result

$$\Phi(t,\beta)=N_AN_B\Phi_{1,1}(t,\beta)\equiv N_AN_B\Phi_2(t,\beta). \quad \text{(B18)}$$

We also note that the two-particle Hamiltonian may be written in terms of the translational energy of the center of mass and the translational energy of a particle with reduced mass whose coordinate is the relative position. Since the dipole operator only depends on relative coordinates, it is easy to see that the center of mass will completely disappear from the problem leaving

$$\Phi_2(t,\beta)=\frac{i}{\mathfrak{Z}\hbar V}\sum_{\mathbf{kq}}(e^{-\beta\epsilon(\mathbf{q})}-e^{-\beta\epsilon(\mathbf{k})})$$
$$\times\exp\left\{\frac{it}{\hbar}[\epsilon(\mathbf{q})-\epsilon(\mathbf{k})]\right\}|\langle\mathbf{k}|\mu_z(\mathbf{r})|\mathbf{q}\rangle|^2, \quad \text{(B19)}$$

or writing this result in a representation independent form one has

$$\Phi_2(t,\beta)=\frac{i}{\mathfrak{Z}\hbar V}\operatorname{tr}\{[\mu_z,e^{-\beta H_2}]e^{itH_2/\hbar}\mu_ze^{-itH_2/\hbar}\}, \quad \text{(B20)}$$

where tr is the trace over a complete set of single-particle states for the effective one-particle problem.

APPENDIX C

The derivation of Eq. (42) will be given here. Upon substituting Eq. (41) into Eq. (8), one obtains

$$\chi(\omega)=C\int_0^\infty dt$$
$$\times e^{-i\omega t}\left\{\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+(t+\tfrac{1}{2}i\beta\hbar)^2\right]^{-5/2}-\text{c.c.}\right\}, \quad \text{(C1)}$$

where c.c. stands for complex conjugate. We now convert the integration of (C1) into integrals along straight-line contours in the complex plane by the substitutions $\tau=(t\pm\frac{1}{2}i\beta\hbar)$ in the first and second terms, respectively, thus obtaining

$$\chi(\omega)=Ce^{-\beta\hbar\omega/2}\left\{\int_{0+i\beta\hbar/2}^{\infty+i\beta\hbar/2}d\tau e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}\right.$$
$$\left.-\int_{0-i\beta\hbar/2}^{\infty-i\beta\hbar/2}d\tau e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}\right\}. \quad \text{(C2)}$$

Note that the integrand of the first term is analytic throughout the rectangle which is bounded on two sides by the positive real axis and the part of the imaginary axis from the origin to $\frac{1}{2}\beta\hbar$. The integrand of the second term is analytic over the mirror reflection of the real axis of the above described rectangle. Contour integrals around the respective rectangles for each of the two integrands will vanish so that (C2) may be written as

$$\chi(\omega)=-2C\sinh\tfrac{1}{2}\beta\hbar\omega\int_0^{\infty+i0}d\tau$$

$$\times e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}+C\left\{e^{-\beta\hbar\omega/2}\int_{0+i\beta\hbar/2}^{0}d\tau\right.$$

$$\times e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}-e^{\beta\hbar\omega/2}\int_{0-i\beta\hbar/2}^{0}d\tau$$

$$\left.\times e^{-i\omega\tau}\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+\tau^2\right]^{-5/2}\right\}. \quad (C3)$$

The above terms can now be combined into the form which is Eq. (42),

$$\chi(\omega)=-2C\sinh\tfrac{1}{2}\beta\hbar\omega\int_0^{\infty}dt$$

$$\times e^{-i\omega t}\left[\frac{\beta u}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2+t^2\right]^{-5/2}$$

$$-2C\int_0^{\beta\hbar/2}dy\cosh\omega(y-\tfrac{1}{2}\beta\hbar)$$

$$\times\left[\frac{\beta m}{\gamma^2}+\tfrac{1}{4}\beta^2\hbar^2-y^2\right]^{-5/2}. \quad (C4)$$

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New Approximation for the Calculation of Neutron Scattering from a Simple Liquid

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A conceptually simple and easily applied approximation is made for the Van Hove distribution function $G(\mathbf{R},t)$ of a classical liquid. This approximation gives a less rapid temporal decay of $G(\mathbf{R},t)$ than is found in the Vineyard convolution approximation. In addition, by requiring that the sum rules be satisfied, we find that for t smaller than about 0.5×10^{-13} sec the "correlations" in a liquid may be said to be increasing. Comparisons are made with recent neutron scattering experiments. There is fair agreement between the theoretical and experimental results.

I. INTRODUCTION

In 1954, in a study of neutron-diffraction phenomena, Van Hove introduced the time-dependent generalization of the equilibrium radial distribution function.[1] This function, denoted $G(\mathbf{R},t)$, represents the ensemble averaged time evolution of the spatial distribution of pairs of molecules in a liquid. $G(\mathbf{R},t)$, and its space and time transform $S(\boldsymbol{\kappa},\omega)$, contain a wealth of information concerning the properties of a liquid. For example, by use of the first Born approximation $S(\boldsymbol{\kappa},\omega)$ may be shown to be proportional to the probability of creating an excitation of momentum $\hbar\boldsymbol{\kappa}$ and energy $\hbar\omega$ in a scattering experiment.[1,2] As expected, then, $S(\boldsymbol{\kappa},\omega)$ appears in the theoretical expressions for the scattering of light[3,4] and neutrons[1,5] by a liquid.

There have been two approaches to the computation of $S(\boldsymbol{\kappa},\omega)$. In one, the hydrodynamic equations have been solved to find the time-dependent distribution functions. As might be expected, such analyses lead to quite good agreement between theory and observation in the hydrodynamic regime,[6] and even to agreement in the case of the long-time behavior probed by neutron-scattering experiments.[7,8] However, since a hydrodynamic theory avoids study of the microscopic dynamics of the liquid and uses only the coarse-grained hydrodynamic equations of motion, such an analysis is not capable of predicting the behavior of the liquid for short times.

In the other approach, attempts have been made to determine $G(\mathbf{R},t)$ by examining the microscopic behavior of the system.[9-15] Because of the complicated

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