

Hydrodynamic theory for vibrational relaxation in liquids

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Zwanzig and Bixon have introduced a hydrodynamic model for self-diffusion, in which a single tagged particle moves through a viscoelastic continuum. After a small error in their calculation is corrected, it is shown that the agreement between theory and molecular-dynamics calculations of the velocity autocorrelation function is improved. We apply a similar type of model to the vibrational relaxation (dephasing and population relaxation) of a diatomic molecule in a monatomic fluid. The quantitative agreement with expectations from experiment is poor, suggesting a breakdown of the approach at the high frequencies involved in vibrational motion; however, the qualitative predictions of the model may be useful in correlating experimental data on vibrational Raman line shapes. Furthermore, the results imply that vibrational relaxation experiments in liquids will provide nonhydrodynamic information on the poorly understood high-frequency viscoelastic properties of liquids.

I. INTRODUCTION

Molecular-dynamics calculations¹ have become an important source of data concerning the dynamical behavior of liquids. Since, at the present time, we lack a detailed molecular theory of relaxation phenomena in liquids, the interpretation of these data is based upon simplified models. One of the most interesting and intriguing has been proposed by Zwanzig and Bixon² who assume that the motion of a single atom through the liquid may be described by a Langevin equation whose friction coefficient is obtained by solving the hydrodynamic equations. Since molecular motions are extremely rapid, the hydrodynamic equations must be modified. The time scale of the atomic motion (for self-diffusion this is the ratio between the mass and the friction coefficient and is approximately 10^{-13} sec) is of the same order or longer than the time which a fluid molecule spends at a given quasilattice site; therefore the fluid responds elastically to the forces exerted on it by the moving atom.³ Phenomenologically, this is included by introducing complex (frequency-dependent) viscosities.^{3,4} Moreover, the molecular motion occurs on a time scale comparable to or faster than the time needed for sound to propagate over interatomic distances; hence the compressibility of the fluid, and the finite speed of sound, must be incorporated. Furthermore, the Zwanzig-Bixon theory assumes that the velocity, density, and pressure changes induced by a moving atom in the fluid are small enough that the hydrodynamic equations may be linearized with respect to them. Finally, temperature (or entropy) gradients are omitted. Once the idea of using hydrodynamics to compute the friction is accepted, these other assumptions seem entirely reasonable.

If the basic idea of the Zwanzig-Bixon model is correct, this obviously opens a very appealing possibility of calculating the role of the solvent in spectroscopic and chemical phenomena by assuming that the frictional force, which the solvent exerts on the moving atoms of the molecule of interest, is given by hydrodynamics. There is also a random force (to account for fluctuation) whose properties are given by the fluctuation-dissipation theorem.⁵ The solvent is specified by two generally unknown parameters, the relaxation times τ_s and τ_l of shear and "longitudinal" viscosity and by measurable quantities such as density, shear and bulk viscosity, and sound velocity. One can determine the parameters τ_s and τ_l by using hydrodynamic theory to evaluate certain observables and fitting to existing data. If a Gaussian approximation suffices, the structure factor for incoherent neutron scattering can be fit. Other possibilities are the use of the velocity or current autocorrelation functions provided by molecular-dynamics calculations. The self-diffusion coefficient cannot be used for this purpose since it is determined by the zero-frequency velocity autocorrelation function which does not depend on τ_s and τ_l ; it can be used, however, as an additional test of how well the hydrodynamic theory works for the solvent. The interaction between solute and solvent (in a dilute system) may then be described by the effective hydrodynamic radius of each atom in the solute molecule. This radius probably depends on both the atom and the solvent, but once these radii are determined by fitting some experimental data, the theory may be used for predictive purposes.

Given this prospect, we explore here the range of applicability and the limitations of the Zwanzig-Bixon hypothesis. An obvious reason for doubting

its validity comes from the commonly held opinion that the hydrodynamic equations describe collective motions of long wavelength and therefore are inapplicable to the motion of one atom. The above condition is *sufficient* for the hydrodynamic equations to hold,⁶ but it is not *necessary*; the equations may be valid for reasons which are not understood in terms of purely theoretical arguments. Thus it is important to determine whether the theory can consistently reproduce various observables. In this spirit Zwanzig and Bixon² have calculated the velocity autocorrelation function of a simple fluid. There is, however, a minor error in their formulae and the validity of their conclusions is thus uncertain. We show here that upon the removal of this error the agreement between calculated quantities and the molecular-dynamics result is improved.

Compared to vibrational motion, self-diffusion is slow; its characteristic time is of order 10^{-13} sec, while the frequency of vibration of a diatomic molecule is $(1-4) \times 10^{14}$ sec⁻¹. Zwanzig and Bixon have already noted that at very high frequencies (short times) the hydrodynamic theory breaks down; the power spectrum falls off as ω^{-2} and the correlation function has an unphysical cusp at $t=0$. It is not clear, however, whether this high-frequency breakdown occurs at values of the frequency of order 10^{14} , which would affect the ability of the theory to describe vibrational spectra, or at still higher frequencies, which would cause no harm. Recent experiments studying vibrational relaxation of molecules in liquids⁷ offer high-frequency data ($\sim 4 \times 10^{14}$ sec⁻¹) which we use to test the applicability of a hydrodynamical model in the 10^{14} sec⁻¹ frequency range. To do this we evaluate the vibrational line shape for spontaneous Raman scattering for nitrogen in inert liquids.^{7(b)} Since for this system population relaxation should be much slower than dephasing, the time associated with the width of the line shape is the same as the dephasing time,^{7(a)} and this provides us with an additional source of data. Since the only liquid for which we have reliable information concerning the relaxation times τ_s and τ_l is argon, we consider the vibrational line shape of N₂ in argon. This provides a very severe test of the theory since the nitrogen atom is rather small and the vibrational frequency is very high. It is just in this extreme situation that the theory may be anticipated to break down. Though there are no experimental data for this system, we expect its line shape to exhibit the same qualitative trends as that of N₂ in SF₆, CCl₄, CHCl₃, or SO₂,^{7(b)} since all these are inert solvents that have neither chemical affinity for N₂ nor intramolecular normal modes which are resonant with

those of N₂ vibration. The qualitative trends expected for the data are a small band width of approximately 0.5 cm⁻¹, and a frequency shift between 2.5 and 6 cm⁻¹. Our calculations show that this qualitative behavior is not reproduced by the hydrodynamic theory. The calculated width is always substantially larger than that found in the existing data. It turns out that even using unreasonable values for the hydrodynamic parameters we cannot fit the width. Therefore, our conclusion is that at frequencies as high as 4×10^{14} sec⁻¹ the hydrodynamic theory breaks down. We must, however, emphasize that the case studied here is an extremely unfavorable situation, at very high vibrational frequency and small atomic size, and that the theory is potentially useful in other cases. On the other hand, the results make it clear that vibrational relaxation studies will, in fact, probe the poorly understood high-frequency viscoelastic properties of liquids, providing a nonhydrodynamic test of molecular-dynamics calculations. Hence, our results indicate that the vibrations of a diatomic molecule can act as a high-frequency probe of mechanical properties of a liquid which are not purely of hydrodynamic origin, a result which perhaps may be more interesting for our understanding of the dynamics of liquids than that which would be the case if the hydrodynamic theory worked well.

In Sec. II, we outline the hydrodynamic calculation of the friction coefficient of a sphere, correcting the minor error in the Zwanzig and Bixon work. We show in Sec. III that this correction improves the agreement between the calculated velocity autocorrelation function and that obtained from molecular dynamics. In Sec. IV we calculate the line shape for an oscillation in a hydrodynamic continuum and compare with experimental results for analogous systems. Sec. V suggests an application of the hydrodynamic approach to population relaxation, and Sec. VI presents a brief conclusion.

II. HYDRODYNAMIC MODEL

As we have already noted in the Introduction, it is assumed that the basic equation governing the motion of an atom in an inert fluid is the Langevin equation

$$m\ddot{\mathbf{r}}(t) + \int_{-\infty}^t \zeta(t-s)\dot{\mathbf{r}}(s)ds = \mathbf{f}(t) \quad (2.1)$$

Here m is the mass of the atom, $\mathbf{r}(t)$ is its position at time t , $\zeta(t)$ is the memory function for friction, and $\mathbf{f}(t)$ is a random force acting on the center of mass of the atom. This equation is exact but theoretical methods for the evaluation of $\zeta(t)$ are not yet available. Zwanzig and Bixon

assume that the friction coefficient is given by the equations of hydrodynamics. The atom moves with a time dependent velocity $\vec{u}(t)$, and the fluid exerts on its center of mass a force $\vec{F}(t)$. The friction coefficient is defined by

$$\vec{F}(\omega) = -\zeta(\omega)\vec{u}(\omega), \quad (2.2)$$

where the Fourier transform $f(\omega)$ of an arbitrary function $f(t)$ is

$$f(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} f(t) dt. \quad (2.3)$$

The linearized hydrodynamic equations may be solved easily by Fourier transformation: If the velocity of the atom is periodic with frequency ω , then the pressure, density, and velocity of the fluid is also a periodic function of the time. The total force on the atom may be obtained by an integration over its spherical surface

$$\vec{F}(\omega) = \oint dS \vec{\sigma} \cdot \vec{n}, \quad (2.4)$$

where \vec{n} is a unit vector normal to the surface of the atom and $\vec{\sigma}$ is the stress tensor

$$\vec{\sigma} = -P\vec{1} - (\frac{2}{3}\eta_s - \eta_v)\vec{\nabla} \cdot \vec{v}\vec{1} + \eta_s(\vec{\nabla}\vec{v} + \vec{v}\vec{\nabla}). \quad (2.5)$$

\vec{v} is the fluid velocity induced by the moving atom [with velocity $\vec{u}(t) = \vec{u}(\omega) \exp(-i\omega t)$]. The pressure is denoted by P , and η_s and η_v are the shear and bulk viscosities. Zwanzig and Bixon² used a positive sign in front of the η_v in their Eq. (28); this minor error introduces the term $-2\eta_v$ in the square parentheses in their Eq. (37). The correct equation for $\zeta(\omega)$ should not have this term. Obviously this error does not appear when the fluid is incompressible, because in this case the term $\vec{\nabla} \cdot \vec{v}$, where the sign error is initiated, is zero. The Zwanzig-Bixon equation thus has the correct behavior in the limit of an incompressible fluid. Anticipating some of our results we should mention that removal of this minor error improves slightly the agreement between the hydrodynamic theory and computer experiments.

To calculate the stress tensor in Eq. (2.5) we must first solve the hydrodynamic equations for the fluid pressure and velocity. A Fourier transform with respect to time gives the linearized Navier-Stokes equations in the form

$$-i\omega\rho(\omega) = -\rho_0\vec{\nabla} \cdot \vec{v}(\omega), \quad (2.6)$$

$$-i\omega\rho_0\vec{v}(\omega) = -\vec{\nabla}P(\omega) + (\frac{1}{3}\eta_s + \eta_v)\vec{\nabla}\vec{\nabla} \cdot \vec{v}(\omega) + \eta_s\nabla^2\vec{v}(\omega); \quad (2.7)$$

ρ_0 is the equilibrium density. These equations must be supplemented with an equation connecting the variation of pressure with density,

$$\vec{\nabla}P(\omega) = c^2\vec{\nabla}\rho(\omega); \quad (2.8)$$

c is the sound velocity.

Viscoelastic effects are included by allowing the shear and bulk viscosities to be frequency dependent; we follow Zwanzig and Bixon in taking a simple Maxwell form^{3,4}

$$\eta_s(\omega) = \eta_s^0(1 - i\omega\tau_s)^{-1} \quad (2.9)$$

and

$$\eta_l(\omega) \equiv \frac{4}{3}\eta_s(\omega) + \eta_v(\omega) \equiv \eta_l^0(1 - i\omega\tau_l)^{-1}. \quad (2.10)$$

The relaxation times τ_s and τ_l are physical constants connected to the rate of relaxation of shear and longitudinal modes and characterize the solvent. They must be determined by fitting some experimental data. η_s^0 and η_l^0 are zero-frequency shear and longitudinal viscosities, respectively, and $\eta_l^0 = \frac{4}{3}\eta_s^0 + \eta_v^0$. Equations (2.6)–(2.8) can be solved for the following boundary conditions at the surface of the sphere:

$$\sigma_{r\theta} = (\beta/R)(v_\theta - u_\theta) \quad (2.11)$$

and

$$v_r - u_r = 0. \quad (2.12)$$

Here, we use spherical coordinates with the origin at the center of the atom; \vec{u} is the velocity of the sphere and β is a constant. The case $\beta = 0$ corresponds to slip and $\beta = \infty$ to stick boundary conditions. The friction coefficient is found to be given by the following result:

$$\zeta(\omega) = (4\pi/3)\eta_s R X^2 [(1-Y)Q + 2(X-1)P], \quad (2.13)$$

with

$$X \equiv ik_t R, \quad (2.14)$$

$$Y \equiv ik_l R, \quad (2.15)$$

$$Q \equiv \frac{3}{\Delta} \left(3 - 3X + X^2 + \frac{X^2(1-X)}{2 + \beta/\eta_s} \right), \quad (2.16)$$

$$P \equiv - (3/\Delta) [Y^2 - 3Y + 3], \quad (2.17)$$

$$\Delta \equiv 2X^2(3 - 3Y + Y^2) + Y^2(3 - 3X + X^2) + \frac{3[X^2(1-X)(Y^2 - 2Y + 2)]}{2 + \beta/\eta_s}. \quad (2.18)$$

The quantities k_t and k_l are, respectively, wave vectors for the shear and longitudinal waves generated by the moving atom and R is the radius of the sphere. They are defined by

$$k_t = \pm \omega / (c^2 - i\omega\eta_t/\rho_0)^{1/2}, \quad (2.19)$$

$$k_l = \pm \omega / (-i\omega\eta_s/\rho_0)^{1/2}. \quad (2.20)$$

The signs in (2.19) and (2.20) are chosen to satisfy the boundary condition that the fluid is at rest an infinite distance from the sphere; this means that

the imaginary parts of k_t and k_i must be positive. We outline the derivation of these results in the Appendix, and have converted from the form used by Zwanzig and Bixon, which uses spherical Hankel functions, into a polynomial form [of the type used in Ref. 5(b)] which is more stable numerically, especially at the high frequencies that are of interest in parts of this paper. In this process we also show explicitly that the Zwanzig-Bixon result is equivalent, for the case of stick boundary conditions, to formulas derived by Bedeaux and Mazur⁸ and Chow and Hermans^{5(b)} in their work on Brownian motion [except of course for the minor error in ZB formula already mentioned above and an obvious sign misprint in the Chow and Hermans's Eq. (26)].

III. CALCULATION OF THE VELOCITY AUTOCORRELATION FUNCTION

Molecular-dynamics calculations¹ have determined the velocity autocorrelation function $C(t) \equiv \langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ for argon. This quantity is associated with the self-diffusion coefficient through the formula

$$D = \int_0^{\infty} dt \langle v_x(0)v_x(t) \rangle. \quad (3.1)$$

$C(\omega)$ can be evaluated from (2.1) using the fluctuation dissipation theorem⁵ extended to the situation at hand^{5,6}

$$\langle f(\omega)f(\omega') \rangle = kT \operatorname{Re} \zeta(\omega) \delta(\omega + \omega')/\pi. \quad (3.2)$$

The result is

$$C(t) = \frac{2}{\pi} kT \operatorname{Re} \int_0^{\infty} d\omega \frac{\cos \omega t}{[-i\omega m + \zeta(\omega)]}. \quad (3.3)$$

From (3.1) it is seen that the self-diffusion coefficient is $kT/\zeta(\omega=0)$.

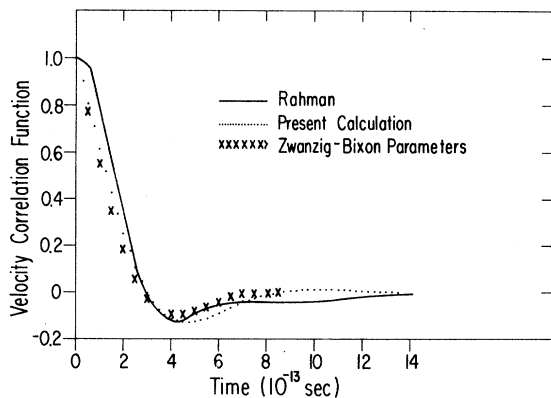


FIG. 1. Velocity correlation function, normalized to unity at zero time.

Figures 1 and 2 display the velocity autocorrelation function $C(t)$ and its Fourier transform $C(\omega)$, normalized so that $C(t=0) = C(\omega=0) = 1$. The dotted line has been computed with the following values for the parameters:

$$\begin{aligned} \text{atomic radius (slip)} R &= 1.70 \text{ \AA}; \\ \text{zero-frequency shear viscosity } \eta_s^0 &= 3 \times 10^{-3} \text{ P}; \\ \text{zero-frequency longitudinal viscosity} \\ \eta_l^0 &= 5.6 \times 10^{-3} \text{ P}; \end{aligned} \quad (3.4)$$

$$\text{longitudinal relaxation time } \tau_l = 2 \times 10^{-13} \text{ sec};$$

$$\text{shear relaxation time } \tau_s = 2.5 \times 10^{-13} \text{ sec};$$

$$\text{density } \rho_0 = 1.41 \text{ g/cm}^3;$$

$$\text{temperature } T = 76 \text{ }^\circ\text{K};$$

$$\text{self-diffusion coefficient } D = 1.63 \times 10^{-5} \text{ cm}^2/\text{sec};$$

$$\text{sound velocity } c = 6 \times 10^4 \text{ cm/sec}.$$

These are the data which fit the current-current correlation function given by the molecular-dynamics calculation of Ailawadi, Rahman, and Zwanzig.¹ Using their formula (38) for the friction coefficient (this formula has the minor error mentioned above) Zwanzig and Bixon² found that the best fit of the velocity autocorrelation function is obtained if the parameters are given other values than those which fit the current-current correlation function. These values are² $\eta_s^0 = 2.8 \times 10^{-3}$

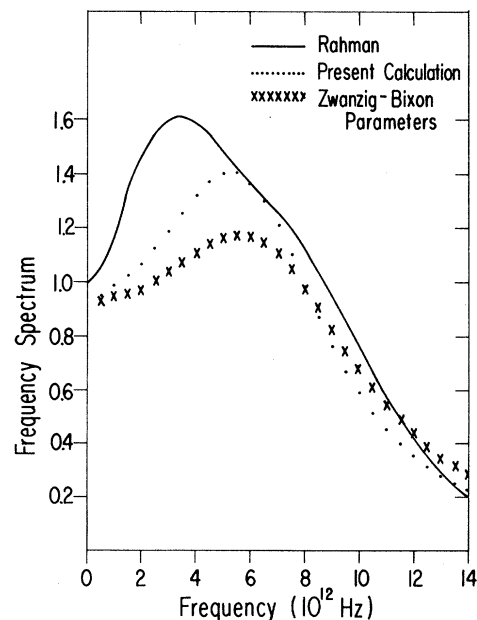


FIG. 2. Frequency spectrum of velocity correlation function, normalized to unity at zero frequency.

P , $\eta_i^0 = 5.5 \times 10^{-3} P$, $\tau_i = 1.8 \times 10^{-13}$ sec, and $\tau_s = 2.0 \times 10^{-13}$ sec. We see that our corrected formula, when used with these parameters gives a poorer fit of the data (see the crosses in Figs. 1 and 2) than in the case when we use the parameters [Eq. (3.4)] which also fit the current-current correlation function. However, the hydrodynamic theory, without adjustment of parameters, gives the correct location and depth of the minimum in the velocity autocorrelation function. Because of this fact and the need for a single set of parameters, the corrected formula is thus in better agreement with the molecular-dynamics calculations and, of course, this increases our confidence in the Zwanzig-Bixon theory.

IV. VIBRATIONAL RAMAN LINE SHAPE

It has already been noted by Zwanzig and Bixon² that the hydrodynamic theory has difficulties at high frequencies (short times) since $C(\omega) \sim \omega^{-2}$, which implies that $C(t)$ has an unphysical cusp at $t=0$. It is possible that these difficulties are important only at *very* high frequencies, higher than most frequencies at which molecular processes occur. For these processes the flaws of the model are not important. If the frequencies at which the hydrodynamic theory experiences difficulties are smaller than those involved in a given molecular process, the theory cannot describe the latter correctly.

Recent developments in spectroscopic techniques have enabled measurements of the dynamics of vibrational relaxation in liquids,⁷ providing information about vibrational line shapes, dephasing times, and population relaxation times. Since vibrational motion takes place at frequencies as high as 4×10^{14} sec⁻¹, a diatomic molecule can be viewed as a mechanical device which pounds the host liquid at this high frequency. The response of the host fluid consists in dissipating the energy of the diatomic, and the effect of this can be measured spectroscopically and can be computed from the hydrodynamic theory. This makes it possible to test how the theory works at very high frequencies.

To be specific, the correlation function is determined experimentally by measuring the intensity of both polarized $I_{||}(\omega)$ and depolarized $I_{\perp}(\omega)$ light scattering. It is given by

$$C(\omega) = \frac{I_{||}(\omega) - \frac{4}{3}I_{\perp}(\omega)}{\int_{-\infty}^{\infty} [I_{||}(\omega) - \frac{4}{3}I_{\perp}(\omega)] d\omega} \quad (4.1)$$

The approximations involved in deriving this formula are well known,⁹ and so is the connection between $C(\omega)$ and the infrared line shape. The

quantity $C(\omega)$ can be evaluated from hydrodynamic theory; such a calculation is provided for a hydrodynamic model that mimics the nitrogen molecule in liquid argon. Though we do not have experimental data for this system, data is available for N_2 in inert solvents such as SF_6 , CCl_4 , $CHCl_3$, and SO_2 . Some general features emerge that should be valid for N_2 in argon as well: (i) The line shape is quasi-Lorentzian. (ii) The width is of the order of 0.5 cm⁻¹. (iii) The frequency shift is of the order of 4 cm⁻¹. (iv) In all cases the shift is five or ten times larger than the width. (v) The shift is in all these cases negative (red shift).

Our model for the N_2 molecule is a cylinder with spherical extremities (Fig. 3) both of which vibrate along the cylinder axes with a frequency ω_0 . The radius R of the half-sphere, representing the nitrogen atom, is a parameter which is varied to fit the experimental data. Reasonable values for this parameter are of order 1.5 Å. The basis for letting R be a parameter, rather than choosing an *a priori* value for it, is that the boundary condition, in which R is involved, is thought of as an equivalent way of describing the effect of the long range, many-body interaction of the atom with the fluid. Thus R must be chosen so that the boundary condition best mimics the real interactions. The vibration of the diatomic molecule is simulated by letting the distance $\alpha(t)$ of Fig. 3 oscillate in time with frequency ω_0 . The force acting on the atoms is computed from hydrodynamics as follows. We assume that the motion of the fluid around the surface ABC is roughly the same as it would be if the center of mass of the sphere $ABCD$ oscillated with frequency ω_0 . As the molecule moves, the force is given by integrating the stress tensor in Eq. (2.4) over only half the surface of the sphere (the half containing points A, B, C). The resulting friction coefficient is half that obtained from Eq. (2.4). We have considered two other models: a dumbbell model and a pulsating

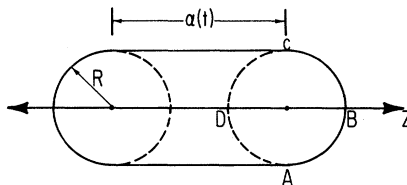


FIG. 3. Model assumed for the diatomic. $\alpha(t)$ is the internuclear distance and R the atomic radius.

sphere. The friction coefficient for a sphere whose radius oscillates with frequency ω_0 can be computed by the method described above and the result is $\zeta = 4\pi R^2 \rho_0 \omega_0 / k_1$. The qualitative conclusions obtained from these models are the same.

In order to evaluate the line shape, we must solve the Langevin equation for the model of Fig. 3:

$$m\ddot{x}(t) + m\omega_0^2 x(t) + \int_{-\infty}^t \tilde{\zeta}(t-s)\dot{x}(s) ds = f(t). \quad (4.2)$$

Here $x(t)$ is the amplitude of the oscillation about the equilibrium position, m is the atomic mass, and $\tilde{\zeta}(t-s)$ is the memory function. Again it should be emphasized that Eq. (4.2) is exact and follows from the generalized Langevin theory. However, techniques for the accurate evaluation of the memory function are not yet available, and this is, in part, the rationale for employing a hydrodynamic model. Likewise, the generalized Langevin theory also implies that the force constant $m\omega_0^2$ may be solvent, temperature, etc., dependent and, thereby, deviate from that of the free diatomic molecule. The value obtained in the liquid is $\langle b^2 \rangle / m \langle x^2 \rangle$, where the averages are to be taken in an ensemble having a single diatomic guest molecule in equilibrium with the host liquid.

For the model described in Fig. 3, the hydrodynamic approximation to the memory function has a Fourier transform which is one-half the value given by Eq. (2.13). Equation (4.2) can be solved to yield

$$\langle x(\omega)x(\omega') \rangle = \langle f(\omega)f(\omega') \rangle [G(\omega)G(\omega')], \quad (4.2')$$

with

$$G(\omega) = [m\omega_0^2 - m\omega^2 + i\omega\tilde{\zeta}(\omega)]^{-1}; \quad (4.3)$$

the spectral density of the force $\langle f(\omega)f(\omega') \rangle$ is given by the fluctuation-dissipation theorem^{5(b)} of Eq. (3.2). The vibrational line shape, defined by

$$C(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle x(0)x(t) \rangle e^{i\omega t} dt, \quad (4.4)$$

can be determined from Eq. (4.2') to give

$$C(\omega) \sim \text{Re}\tilde{\zeta}(\omega)G(\omega)G(-\omega). \quad (4.5)$$

Since $\tilde{\zeta}(\omega_0)/m$ is always much smaller than ω_0 and $\tilde{\zeta}(-\omega) = \tilde{\zeta}(\omega)^*$, it is easy to show that the line shape (4.5) is approximately Lorentzian,

$$C(\omega) \sim \frac{\text{Re}\tilde{\zeta}(\omega_0)}{[\omega - \omega_0 + \text{Im}\tilde{\zeta}(\omega_0)/2m]^2 + [\text{Re}\tilde{\zeta}(\omega_0)/2m]^2} \quad (4.6)$$

with the shift given by

$$S = -\text{Im}\tilde{\zeta}(\omega_0)/2m \quad (4.7)$$

and the half-width at half-height is

$$W = \text{Re}\tilde{\zeta}(\omega_0)/2m. \quad (4.8)$$

We have tested these formulas for data corresponding to the nitrogen molecule in liquid argon. We have varied the parameters β , R , τ_i , η_i^0 , τ_s , and η_s^0 to examine the extent to which the formula satisfies requirements (i)–(v) outlined at the beginning of this section. The parameter β was changed smoothly from stick ($\beta=0$) to slip ($\beta=\infty$) boundary conditions. As in the calculation of the velocity autocorrelation function, the variation in the nature of the boundary condition is not found to make much of a difference in the results for $C(\omega)$. In order for the theory to be consistent, the values of parameters yielding a good line shape should be close to those given by (3.4) which give a good representation of the current and velocity autocorrelation functions. Finally, we vary R , though it should be near the value 1.5 \AA in order for the theory to be considered satisfactory. We find that within these limits formula (4.5) cannot fit the observed behavior. For example, in all cases which we have considered, the dynamical frequency shift, arising solely from $\zeta(\omega)$, is much smaller than the line width, but the equilibrium shifts noted above probably provide the dominant portion of the experimental shift.^{7(b)} Moreover, for acceptable values of the parameters the line width is too large. The qualitative behavior predicted by Eqs. (4.7) and (4.8) is the following: The width and dynamical shift increase with η_i^0 , diminish as τ_i is increased and go up with R . The dynamic shift starts approaching the expected value (between -1 and -4 cm^{-1}) as the time τ_i becomes less than 0.5×10^{-13} sec (expected value about 2×10^{-13} sec), the radius is less than 0.75 \AA (expected value about 1.5 \AA), and η_i^0 larger than 7×10^{-3} P (expected values 5.6×10^{-3} P). For the values of the parameters for which the dynamic shift is forced to have the proper magnitude, the width is consistently too large (between 10 and 40 cm^{-1}). Attempts to get a reasonable value for the width (around 0.5 cm^{-1}) require anomalous values for parameters. (The dynamic shift becomes extremely low, but the static shift presumably rectifies this problem.)

It is thus obvious that the formula (4.5) cannot quantitatively fit, in a satisfactory manner, the line width of the vibrational, spontaneous Raman scattering spectrum. The problem is now to establish whether at least the qualitative predictions

of the model are correct.

For the limit

$$k_i R, k_i R \gg 1 \text{ and } \omega \tau_s, \omega \tau_i \gg 1 \quad (4.9)$$

we can show, using Eqs. (2.13)–(2.18) that

$$W \text{ (cm}^{-1}\text{)} = \frac{R^2}{3mc} \left[\rho_0 \alpha + 2 \left(\frac{\eta_s^0 \rho_0}{\tau_s} \right)^{1/2} \right] \quad (4.10)$$

$$S \text{ (cm}^{-1}\text{)} = \frac{R}{3mc} \left(\frac{R \eta_i^0}{2\alpha \omega \tau_i^2} + \frac{R(\eta_s^0 \rho_0 / \tau_s)^{1/2}}{\omega \tau_s} - \frac{4(\eta_s^0 \rho_0 / \tau_s)^{1/2} \alpha}{\omega} + \frac{\alpha^2 \rho_0}{\omega} \right) \quad (4.11)$$

for stick boundary conditions and

$$W \text{ (cm}^{-1}\text{)} = \frac{R^2}{3mc} (\rho_0 \alpha), \quad (4.12)$$

$$S \text{ (cm}^{-1}\text{)} = \frac{R}{3mc} \left(\frac{R \eta_i^0}{2\alpha \omega \tau_i^2} + \frac{\alpha^2 \rho_0}{\omega} - \frac{4\eta_s^0}{\omega \tau_s} \right) \quad (4.13)$$

for slip boundary conditions. Here we have defined

$$\alpha^2 \equiv C^2 + \eta_i^0 / \tau_i \rho_0. \quad (4.14)$$

The sign of the square root, when α is computed from (4.14), has to be taken such that the imaginary part of α is positive. Whether or not these formulas are qualitatively correct can be tested in several ways. Assuming that the radius of the nitrogen atom is independent of the solvent (since the radius appears in the boundary condition, which simulates the atom–fluid interaction, this may not be a very good assumption), we can vary the viscosities and the density by changing solvents or the temperature and the density. The dependence of width and dynamical shift on these two quantities is given by (4.10)–(4.13), and this dependence can be tested against the results of experiments. The same formulas make definite predictions about the isotope effect. For both stick and slip boundary conditions it is found that the width is inversely proportional to the mass of the atom in the diatomic and independent of ω_0 . The dynamic shift changes from one isotopic diatomic to another like $(m\omega_0)^{-1}$. It is possible that the hydrodynamic formulas, though inaccurate quantitatively, are still useful qualitatively by suggesting simple rules as those discussed above. Whether this is true or not will be clear only when more experimental data become available. Finally, we

should mention that using the friction coefficient obtained when the diatomic is viewed as a pulsating sphere or that obtained when the diatomic is considered to be made up of two independent spheres, leads to the same kind of discrepancy with the observed results.

Other models have been proposed for the vibrational line shape and vibrational relaxation of a diatomic in a liquid and they are reviewed in Ref. 9(b). Of these, Litovitz's model^{9(c)} has been used^{7(d),7(e)} for interpreting experimental data. If the atomic radii are considered adjustable functions of temperature, the model fits the data satisfactorily. It is interesting to note that molecular models, such as the one proposed by Litovitz and the hydrodynamic one, extract from the experimental data completely different information. While the molecular models relate characteristics of the intermolecular potentials and those of the distribution of the velocity to the line shape, the hydrodynamic one considers the diatomics to be mechanical devices which set the host fluid in motion. The spectroscopic quantities are thus a means of measuring high-frequency properties of the solvent. The two approaches are obviously complementary.

V. VIBRATIONAL ENERGY DECAY

One can, of course, use Eq. (4.2) to compute the relaxation time of vibrational energy. Recent experiments^{7(c)} show this time to be extremely long. We investigate here whether the hydrodynamic theory can predict such long relaxation times. To do this we must solve Eq. (4.2) with the condition that the average energy $\langle E(t) \rangle$ has a given value for $t=0$. In the relaxation problem, for short times, the friction coefficient contains transient effects which are not included in Eqs. (2.13)–(2.18). If we assume that these transients relax much faster than the vibrational energy, (2.13)–(2.18) may be used to study the long-time behavior of the vibrational relaxation. We also assume that the correlation function $\langle f(\omega)f(\omega') \rangle$ is given by the fluctuation–dissipation formula (3.2), although this may not be true for t close to $t=0$. With this assumption and using Laplace transform methods¹⁰ we obtain

$$\langle E(t) \rangle - E_{eq} = E_n \left\{ q(t)^2 + \frac{3}{2} [m\omega_0 G(t)]^2 + \frac{1}{2} [m\lambda(t)]^2 \right\}, \quad (5.1)$$

with

$$q(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{st} g(s) G(s) ds, \quad (5.2)$$

$$G(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{st} G(s) ds, \quad (5.3)$$

$$\lambda(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{st} s G(s) ds, \quad (5.4)$$

$$G(s) = [ms^2 + m\omega_0^2 + s\tilde{\zeta}(s)]^{-1}, \quad (5.5)$$

$$g(s) = ms + \tilde{\zeta}(s). \quad (5.6)$$

Here the variable s is the Laplace transform variable. E_{eq} and E_n are the average energy of the oscillator in thermal equilibrium and the energy when the oscillator is in the n th vibrational quantum state. Assuming that $\tilde{\zeta}(t) = 0$ for $t < 0$ allows us to evaluate the Laplace transform $\tilde{\zeta}(s)$ from the Fourier transform $\tilde{\zeta}(\omega)$, given by (2.9)–(2.17), in a standard manner.¹⁰ The long-time behavior of $G(t)$, $\lambda(t)$, and $q(t)$ is determined by the asymptotic behavior of $G(s)$, $sG(s)$, and $g(s)G(s)$ around the singularities located in the semiplane corresponding to $\text{Re } s > 0$. To be more specific, exponential decay, for long times, may arise from poles or essential singularities in that semiplane.¹¹ In our computation we were not able to find any poles that would give the very long decay time observed experimentally. Introducing a second relaxation time in (2.2), i.e., a sum over two Maxwell terms, did not improve the situation. We are of the opinion that the simple hydrodynamic theory described above is not able to reproduce the long-time decay observed experimentally, though of course our failure to numerically find the poles is not absolute proof of their nonexistence. Qualitatively we interpret this failure in the following way: If the mechanism of relaxation is vibrational-to-translational energy transfer, then energy loss from diatomics produces a translationally hot-fluid molecule, of roughly 14 000 °K. Therefore, the vibrational relaxation of the diatomic puts the liquid out of local translational equilibrium by creating particles of extremely high velocity. The relaxation of these molecules to equilibrium may not be well described by the simple hydrodynamic model used here. Another less likely reason may be invoked, like the neglect of the hydrodynamic energy-density equation. By analogy with theories of vibrational relaxation in solids, it is to be anticipated that a proper theory of vibrational relaxation in liquids at least requires a coupling of the oscillator to local density fluctuations in the liquid, i.e., inhomogeneous terms involving $\rho(R)$ in (4.2) where R denotes the position of the oscillator (or its "surface").

VI. DISCUSSION

The idea² of describing the motion of an atom in a fluid by a Langevin equation, in which the friction kernel is determined from the Navier-Stokes equation for the viscoelastic compressible

fluid, is very appealing due to its simplicity and potential usefulness. Prior usage of hydrodynamic methods in the molecular theory of rotational line shapes¹² and polymer dynamics¹³ are an indication of what can be achieved along these lines. Since both the rotational motion and that of the long-wavelength modes of the polymer chain (which are of importance in polymer dynamics) are very slow, the success of hydrodynamic methods did not come as a great surprise. The merit of the Zwanzig-Bixon work is that it has shown that a hydrodynamic theory works reasonably well even for the rather fast motion of a diffusing atom. Their work clearly indicates that the theory would break down in the high-frequency limit and lead to unphysical behavior. However, it was not possible for them to assess whether the breakdown occurred at high frequencies, at which important physical processes take place, or at frequencies so high that the breakdown does not influence the ability of the theory to describe the experimentally accessible data. Our use of the hydrodynamic theory to analyze the spontaneous Raman-scattering line shape, reflecting phenomena occurring at frequencies as high as $4 \times 10^{14} \text{ sec}^{-1}$, indicates that the theory fails under these circumstances. No reasonable values of the parameters can give the correct order of magnitude for the linewidth. Our calculation does not, however, eliminate the hydrodynamic theory as a possible aid to the spectroscopists. Indeed, we have chosen conditions that are most difficult for the theory; small atomic radius and very large frequencies. It is possible that the theory will be useful for larger molecules with bulkier moving parts and slower motions. Moreover, lack of data prevent us from analyzing whether the qualitative features predicted by the theory for fast moving diatomics, such as the type of dependence on viscosity or density, are correct. The theory may be useful in this respect. Furthermore it is possible to numerically improve the predictions of the theory by using the moment expansion to generate a short-time expansion for the correlation function of interest, and the hydrodynamic theory to give the long-time behavior; then interpolations may be used to infer the behavior at all times.

The breakdown of hydrodynamic theory at high frequencies is not necessarily disappointing. It indicates that vibrational relaxation is a phenomenon which probes the quick, local motions around the guest molecules, rather than a very complicated way of inducing fast flows in fluids. It would, therefore, be very useful to experimentally consider a series of molecules with a range of vibrational frequencies to probe the high-frequency viscoelastic response of a liquid and to

compare with the high-frequency predictions of theories of liquid dynamics.

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APPENDIX

We give here some details concerning the solution of the viscoelastic linearized Navier-Stokes equations, for a compressible fluid set in motion by a sphere which moves with an arbitrary time-dependent velocity $\vec{u}(t)$ (no rotation is assumed). The calculation is straightforward but tedious and for this reason we present here more details than are given in the Zwanzig-Bixon paper. We also shown the equivalence of their formulas (in the case of stick boundary conditions) to those derived by Chow and Hermans^{5(b)} and Bedeaux and Mazur.⁸ From a numerical point of view the polynomial form in which the results are cast in Refs. 5(b) and 8 is more stable than the one using spherical Hankel functions.²

Taking the Fourier transform with respect to time, we use Eqs. (2.6)–(2.8) to eliminate the pressure and the density and obtain an equation for velocity. By using Helmholtz's theorem, we write the velocity as

$$\vec{v} = \vec{v}'' + \vec{v}' \quad (\text{A1})$$

Here \vec{v}'' is the gradient of an unknown function and \vec{v}' is the curl of an unknown vector whose divergence is zero. This permits us to separate the equation for the velocity into two independent equations:

$$(\omega^2/C_t^2)\vec{v}'' + \nabla^2\vec{v}'' = 0, \quad (\text{A2})$$

$$(\omega^2/C_t^2)\vec{v}' + \nabla^2\vec{v}' = 0. \quad (\text{A3})$$

Here

$$C_t^2 = C^2 - i\omega\eta_l/\rho_0, \quad (\text{A4})$$

$$C_t^2 = -i\omega\eta_s/\rho_0. \quad (\text{A5})$$

The physical meaning of \vec{v}'' and \vec{v}' becomes obvious if one takes the spatial Fourier transform. \vec{v}'' is along the \vec{k} vector (longitudinal) and \vec{v}' is perpendicular to it (transverse). The solutions for the vector Helmholtz equations (A2) and (A3)

are given on p. 1865 of Morse and Feshbach's book.¹⁴ The longitudinal component is

$$\vec{v}'' = \vec{P}_{01}^\sigma(\theta, \varphi) \frac{1}{k_l} \frac{d}{dr} [h_1(k_l r)] + \sqrt{2} \vec{B}_{01}^\sigma(\theta, \varphi) \frac{1}{k_l r} h_1(k_l r), \quad (\text{A6})$$

and the transversal one is

$$\vec{v}' = 2\vec{P}_{01}^\sigma(\theta, \varphi) \frac{1}{k_l r} h_1(k_l r) + \sqrt{2} \vec{B}_{01}^\sigma(\theta, \varphi) \frac{1}{k_l r} \frac{d}{dr} [r h_1(k_l r)]. \quad (\text{A7})$$

We have used only spherical harmonics of subscript 0, 1 since the velocities must be independent of φ . The spherical Hankel functions, e.g.,

$$h_1(k_l r) = j_1(k_l r) + i y_1(k_l r) = \left(\frac{\sin k_l r}{(k_l r)^2} - \frac{\cos k_l r}{k_l r} \right) - i \left(\frac{\cos k_l r}{(k_l r)^2} + \frac{\sin k_l r}{k_l r} \right), \quad (\text{A8})$$

are used to obtain outgoing wave solutions. To make the velocity decay to zero at infinity we must choose the sign in

$$k_l \equiv \pm \omega(C^2 - i\omega\eta_l/\rho_0)^{-1/2}, \quad (\text{A9})$$

$$k_t \equiv \pm (i\omega\rho_0/\eta_s)^{1/2}, \quad (\text{A10})$$

such that the imaginary parts of k_l and k_t are positive. Formulas for the vectors \vec{P}_{01}^σ and \vec{B}_{01}^σ are given on p. 1900 of Ref. 14, and various properties of the h_n functions are given on p. 437 of Ref. 15. (In Ref. 15 the spherical Hankel functions are called spherical Bessel functions of the third kind, and the one needed here is denoted $h_n^{(1)}$). A simple calculation then leads to

$$\vec{v}'' = [h_0(k_l r) - (2/k_l r)h_1(k_l r)] \cos\theta \vec{a}_r - [h_1(k_l r)/k_l r] \sin\theta \vec{a}_\theta, \quad (\text{A11})$$

$$\vec{v}' = \left(-h_0(k_l r) + \frac{h_1(k_l r)}{k_l r} \right) \sin\theta \vec{a}_\theta + \frac{2h_1(k_l r)}{k_l r} \cos\theta \vec{a}_r. \quad (\text{A12})$$

Here \vec{a}_r and \vec{a}_θ are unit vectors for spherical coordinates and

$$h_0(z) = (\sin z)/z - i(\cos z)/z. \quad (\text{A13})$$

Since there are various formulas which can be used to compute the derivatives of the Hankel functions in (A6) and (A7) various equivalent, but different looking, formulas can be generated for \vec{v}'' and \vec{v}' .

The general solution for the velocity is

$$\vec{v} = A_N \vec{v}^{\parallel} + A_L \vec{v}^{\perp}, \quad (\text{A14})$$

where A_N and A_L are constants to be determined from the boundary conditions (2.11) and (2.12). The result for A_N and A_L is given by Zwanzig and Bixon in terms of values of spherical Hankel functions on the surface,

$$A_N = 3h_2(k_t R) \left(h_0(k_t R) + 2h_0(k_t R)h_2(k_t R) + k_t R h_1(k_t R) \frac{[2h_2(k_t R) - h_0(k_t R)]}{2 + \beta/\eta_s} \right)^{-1}, \quad (\text{A15})$$

$$A_L = A_N h_2(k_t R)^{-1} \left(h_2(k_t R) - \frac{k_t R h_1(k_t R)}{2 + \beta/\eta_s} \right). \quad (\text{A16})$$

The only difference between (A15), (A16), and the

Zwanzig-Bixon result is that in our case β is divided by η_s . Practically, this is irrelevant since the values which are mostly used are either zero (slip) or infinite (stick). For intermediate values, however, the fact that β/η_s is complex and frequency dependent may be important.

To compute the total force on the surface of the sphere we use (2.4) and the fact that for symmetry reasons the resulting force is parallel to the velocity \vec{u} of the sphere. Hence, we obtain

$$F = 2\pi R^2 \int_0^\pi \sin\theta (\sigma_{RR} \cos\theta - \sigma_{R\theta} \sin\theta) d\theta. \quad (\text{A17})$$

The components of the stress tensor are computed from (A11), (A12), and (A14) to be

$$\begin{aligned} \sigma_{RR} &= \frac{\eta_s u}{R} \cos\theta \left\{ A_L \left[-\left(\frac{k_t}{k_t}\right)^2 k_t R h_1(k_t R) + \frac{12h_1(k_t R)}{k_t R} - 4h_0(k_t R) \right] + A_N \left(-\frac{12h_1(k_t R)}{k_t R} + 4h_0(k_t R) \right) \right\}, \\ \sigma_{R\theta} &= \frac{\eta_s u}{R} \sin\theta \left[A_L \left(\frac{6h_1(k_t R)}{k_t R} - 2h_0(k_t R) \right) + A_N \left(-\frac{h_1(k_t R)}{k_t R} + 2h_0(k_t R) + k_t R h_1(k_t R) \right) \right]. \end{aligned} \quad (\text{A18})$$

The result for the friction coefficient is

$$\zeta(\omega) = \frac{4}{3} \pi R \eta_s \left[A_L (k_t/k_t)^2 k_t R h_1(k_t R) + 2A_N k_t R h_1(k_t R) \right]. \quad (\text{A19})$$

This is slightly different from the Zwanzig-Bixon result, due to their use of a mistaken sign in the stress tensor.

Since spherical Hankel functions of complex argument contain exponentials that may become very large or very small and lead to numerical

errors, we use the following formulas:

$$X = ik_t R, \quad (\text{A20})$$

$$Y = ik_t R, \quad (\text{A21})$$

$$h_1(k_t R) = [ih_0(k_t R)/X](1 - X), \quad (\text{A22})$$

$$h_2(k_t R) = [h_0(k_t R)/X^2](-X^2 + 3X - 3), \quad (\text{A23})$$

to rewrite $\zeta(\omega)$ in the form given in the text [see Eqs. (2.13)–(2.18)].

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