Vibrational dephasing and frequency shifts of polyatomic molecules in solution

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A theory for the effects of repulsive and spatially slowly varying attractive forces on the vibrational frequency and dephasing of polyatomic molecular liquids is developed. Thermodynamic state dependence of these features is of particular interest because of the competition between the two types of forces. Solvent shifts of vibrational lines are computed. Proper separation of the rapidly and slowly varying branches of the intermolecular potentials leads to a separation of time scales that allows the dephasing relaxation to be computed using a combination of binary collision and mean field ideas. The question of homogeneous versus inhomogeneous broadening of the isotropic Raman line is addressed. The theory is applied to several polyatomic fluids with special emphasis on the isothermal density dependence of the spectral features. Agreement with experiment is good. The slowly varying attractive forces are found to play a significant role in determining the Raman linewidth for all the systems studied. Comparison with previous theories is made.

I. INTRODUCTION

The dephasing of molecular vibrations in condensed phases has been the subject of intense theoretical and experimental study in recent years.\textsuperscript{1,2} Features of interest include the solvent, temperature, and density dependence of the dephasing rate in associated and non-associated fluids. The isothermal density dependence is a particularly useful and sensitive probe of liquid state structure and dynamics.\textsuperscript{3} Although a few specific systems appear to be well understood, a global understanding of the dependence of the dephasing process on solvent, thermodynamic state, and molecular parameters is lacking. However, a number of theoretical and experimental studies seem to have established that population (energy) relaxation and resonance transfer are generally not significant pathways for the dephasing of high frequency modes. Therefore, the present study is based on the assumption that the "pure dephasing" processes which modulate the vibrational frequency in an adiabatic manner are important.

An enormous number of theories have been proposed to treat various aspects of the dephasing phenomena.\textsuperscript{1,4} Essentially all are based on a weak coupling approximation in either the cumulant expansions or frequency (perturbative Mori theory) domains. Most treatments involve only a single physical mechanism for phase modulation. These include the motional narrowed repulsive force (collisional) process,\textsuperscript{4,5} static environment (inhomogeneous) dephasing,\textsuperscript{17} vibration–rotation coupling,\textsuperscript{18} and exchange dephasing.\textsuperscript{6,7} The only quantitative theories are based on the motional narrowed repulsive force mechanism. Fischer and Laubereau\textsuperscript{9} have developed a simple independent binary collision theory, while Oxtoby has constructed a hydrodynamic theory.\textsuperscript{4} Oxtoby has shown the two approaches are very similar.\textsuperscript{10} In addition, molecular dynamics simulations\textsuperscript{9,20} on liquid nitrogen have been performed using the quantum perturbation theory formulas. The general conclusions reached were that the dephasing process is very sensitive to the details of the interaction potentials, and attractive forces (e.g., dispersion, quadrupolar) play a significant role but do not lead to inhomogeneous broadening of the vibrational line. The question of inhomogeneous broadening has been a subject of recent debate.\textsuperscript{21,22} In the case of hydrogen–bonded liquids its importance is well established.\textsuperscript{23} Recently, Harris and co-workers\textsuperscript{24,25} have used picosecond pulse techniques in conjunction with spontaneous Raman scattering experiments to study the inhomogeneous broadening of symmetric methyl proton stretches in nonassociated liquids. Such an approach allows the direct measurement of the inhomogeneous contribution to the Raman linewidth, and these workers conclude that the methyl proton vibrations exhibit significant inhomogeneous broadening. On an empirical basis, they propose that the inhomogeneous contribution is related to the isothermal compressibility of the fluid.\textsuperscript{26} Subsequently, Oxtoby\textsuperscript{27} has questioned their interpretation of the experimental results, and proposed an alternative explanation unrelated to the inhomogeneous broadening mechanism.

We believe the effect of relatively slowly varying forces on the dephasing process, and its relation to the question of inhomogeneous broadening, has not been properly addressed. In addition, a unified quantitative theory that simultaneously predicts the role of repulsive (collisional), vibration–rotation, and attractive forces in determining the density, temperature, and solvent dependence of the dephasing of polyatomic molecules in liquids does not exist. Our goal is to develop such a theory, within the weak coupling regime, in the hope that it will provide a framework for understanding the wide variety of experimental observations. In particular, we construct a theory of the solvent induced vibrational frequency shift, and use it to elucidate the dynamic role of the slowly varying attractive forces. We find there is a delicate competition between the various dephasing mechanisms which can lead to great variety of qualitative behavior.

As we will show, this competition is the cause of the interesting behavior observed by Schindler and Jonas\textsuperscript{28}
in their high pressure studies of isobutylene (CH₃)₂C=CH₂. For this liquid, the dephasing rate associated with the CH₃-C stretching motion increases with increasing pressure. However, the C=CH₂ vibrational mode has a rate which decreases with increasing pressure. At a rough level of description, it is not difficult to understand these differing trends. To begin, one must appreciate that dephasing is controlled by the size and time scales for the solvent induced fluctuating forces imposed on the vibrational degrees of freedom (see Sec. II, below). In a liquid, the amplitude and frequencies for these fluctuations increase with increasing density provided their wavelengths are small compared to molecular dimensions. However, they decrease with increasing density or pressure if the relevant length scale is larger than a molecular diameter. Hence, for example, imagine that a particular vibrational mode is coupled to the surrounding liquid by both spatially slowly varying interactions (in the WCA sense), and by quickly varying repulsions. The amplitude and frequencies of the repulsive fluctuating forces will increase with density in a way roughly proportional to the collision frequency. The amplitude of the fluctuating forces associated with the relatively slowly varying interactions, however, will decrease with increasing density in a way roughly proportional to the compressibility. In general, both of these effects will be mixed together, and usually the repulsions are large enough to dominate the competition and a net increase in dephasing is observed with increasing density. However, as we will show, for isobutylene (and other systems, too), the relatively large Raman activity of the C=CH₂ mode in conjunction with the relatively large compressibility of isobutylene allows the slowly varying dispersive interactions to dominate in this case, and the dephasing rate decreases with increasing density.

The remainder of the paper is structured as follows. In Sec. II, we discuss our general approach and the specific physical mechanisms to be treated. The question of Raman line shape and homogeneous versus inhomogeneous broadening is addressed. Section III develops our theory of the frequency shift and dephasing process for the conceptually simple case of a diatomic solute dissolved in a solvent composed of structureless spherical particles. As illustrative examples, calculations are presented for nitrogen dissolved in solvents composed of nearly spherical molecules. The theory is generalized to polyatomic fluids in Sec. IV. In Sec. V the generalized theory is applied to a number of polyatomic systems with special emphasis on the thermodynamic state dependence of the frequency shift and dephasing rate. We also contrast our results with other available theories. The paper is closed in Sec. VI with a discussion of the significance of our work and its relevance to related problems. The Appendix is used to sketch the normal mode analysis pertinent to our polyatomic applications.

II. GENERAL APPROACH

A. Basic theory

The starting point for a theory of a fundamental vibrational transition in the weak coupling regime has been discussed many times extensions to treat overtone or hot bands is straightforward. Neglecting energy relaxation and resonance transfer, the line shape (normalized to the initial value (f(t))) due to liquid induced frequency fluctuations is given by the Fourier transform of

$$\langle e^{i\omega_0 t} e^{i\int_0^t dt'\Omega(t')} \rangle,$$

where \(\omega_0\) is the gas phase transition frequency and

$$\Delta\Omega(t) = V(t) - V_{\text{eq}}(t).$$

In the above equations, \(\Omega(t)\) is the instantaneous shift in vibrational frequency induced by the solvent, and \(V(t)\) is the unperturbed vibrational matrix element of the interaction Hamiltonian coupling the vibration to the "bath" of classical translational and rotational degrees of freedom. The time dependence of \(\Omega(t)\) arises from the classical bath dynamics of rigid molecules, and the pointed bracket \(\langle \cdots \rangle\) denotes an equilibrium ensemble average over the initial conditions associated with the bath coordinates. Equation (2.1) is exact through second order in the vibration-bath interaction and we consider only the weak coupling limit defined by truncating a cumulant expansion of Eq. (2.1) at second order:

$$\langle QQ(t)\rangle = \text{Re} \, \text{exp} \left[ i(\omega_0 + \langle \Omega \rangle) t - \int_0^t dt' \langle \omega(t) - \omega(t') \rangle \right],$$

where

$$\Delta\Omega = \Omega - \langle \Omega \rangle.$$
B. Role of various interaction mechanisms

To make further progress it is necessary to consider the specific types of interactions that can contribute to the force $F$. We consider three physically distinct classes. First, $\delta V/\delta q_j|_0$ can be resolved into an atom–atom force contribution by employing the standard relation between the normal coordinate of interest and atomic displacements. The vibrational energy is then modulated through the change in intermolecular interaction energy due to the translational motion of atomic sites. If we neglect the nonpairwise decomposable effects due to the dependence of the interaction energy on the collective normal coordinate, then one can employ the well-known interaction site model of polyatomic fluids. In dense nonassociated fluids, the equilibrium structure and molecular motions are dominated by the harshly repulsive branch of the potential [i.e., reference potential $u_{\text{ref}}(v)$] which serves to define molecular shape. Furthermore, these interactions can be related to a corresponding hard sphere reference system. Consequently, the atom–atom effects can be treated as arising solely from the corresponding hard core interactions. We refer to this contribution to the force along the normal coordinate as $F_n$.

Second, vibration–rotation coupling will be present if the moments of inertia change during a molecular vibration, leading to a force of the form

$$F_{\text{VR}} = -\sum_{a=1}^{3} \left( I^{-1}_a \frac{\partial I_a}{\partial q} \right) \frac{\partial \beta}{\partial I_a} ,$$

(2.7)

where the sum is over the three principal moments of inertia and $I_a^2/2 I_a$ is the angular kinetic energy for rotation about the $a$th axis of the vibrationally rigid molecule.

Finally, because molecular properties such as the polarizability and dipole moment can fluctuate during a molecular vibration, $\delta V/\delta q$ can have a part that is determined directly by this variation. In the site–site interaction language such a contribution arises from the $Q$ dependence of the Lennard–Jones coupling parameters. However, these interactions do not affect the local structure (i.e., how molecules pack) of the liquid. Therefore, they have a negligible effect on the repulsive atom–atom reference potentials, but do modify the relatively slowly varying part. We refer to this contribution to the force along the normal coordinate as $F_A$, where the subscripts $A$ anticipate the fact that in most cases the slowly varying interactions will be associated with attractive forces.

The role and form of the relatively slowly varying attractions discussed above should be contrasted with the point of view adopted by Oxtoby and co-workers. There, the attractions due to London dispersion forces were defined as the literal extrapolation of the standard asymptotic $R^6$ interaction. With this separation of the potential, large effects on the dephasing rate were attributed to dispersion forces. In addition, large cross correlations between the attractive dispersion forces and the Lennard–Jones atom–atom interactions were found, along with a short attractive force correlation time of less than a picosecond. Thus there is no clear separation of time scales between the attractive and basically repulsive force fluctuations. (It should be noted that these workers made no attempt to optimize the potential separation. Their aim was to demonstrate that both the repulsive and attractive interactions play an important role in the dephasing process.) We believe such an approach is misguided because it fails to separate the rapidly and slowly varying parts of the potential in a useful manner, and neglects the well established fact that the local structure of fluids is determined by harsh repulsions which are insensitive to relatively slowly varying multipole interactions. When artificially extrapolated to small distances, the spatial variation of the $R^{-6}$ potential is comparable to that of the repulsions and the existence of cross correlations and sub-picosecond correlation times is understandable. But it has little to do with the approach we take in this article.

With the proper perspective, it is clear that the relatively slowly varying attractive forces $F_A$ will generally relax on a time scale considerably longer than a picosecond. The relaxation should be of the order of a diffusion time, i.e., something like the time for a solvent molecule to diffuse a distance characteristic of the length scale of the relatively slowly varying interaction. For a dispersion like interaction this would be of the order of half a molecular diameter. Regardless of the specific relaxation time, since the repulsive atom–atom and vibration–rotation forces fluctuate on a collisional time scale, i.e., roughly 0.1 to 0.3 ps, the relatively slowly varying attractive force fluctuations are to a good approximation uncorrelated with the other force fluctuations. In addition, we make the simplifying assumption that the repulsive atom–atom and vibration–rotation force fluctuations are also uncorrelated. Such an approximation is not as well founded but should not lead to serious errors since for all the systems we have investigated, vibration–rotation coupling makes a small contribution to the overall rate. Consequently, the three relaxation mechanisms decouple

\begin{equation}
\langle \Delta F(t) \Delta F(t') \rangle = \langle \Delta F_A \Delta F_R(t) \rangle + \langle \Delta F_{\text{VR}} \Delta F_{\text{VR}}(t) \rangle + \langle \Delta F_A \Delta F_{\text{VR}}(t) \rangle .
\end{equation}

(2.8)

The idea of making the division and neglecting cross correlations is not new. It probably originates with Rice and co-workers who exploited the scheme in their studies of liquid state dynamics.

To compute the line shape, and hence dephasing rate, we must evaluate the time integral in Eq. (2.3). Since both the repulsive atom–atom and vibration–rotation force fluctuations decay on collisional time scales short compared to typical polyatomic dephasing times ($\tau_d \sim 1-4$ ps) we can invoke the standard Markov approximation for motionally narrowed lines

\begin{equation}
\int_0^t dt' \langle \Delta F_R \Delta F_R(t') \rangle = t \left[ \int_0^t \langle \Delta F_R \Delta F_R(t') \rangle dt' \right],
\end{equation}

(2.9)

and similarly for $F_{\text{VR}}$. However, the relatively slowly varying attractions should decay on a considerably
longer timescale, typically = 10 ps for polyatomic fluids (see Sec. III B). Thus, as far as phase relaxation is concerned, the attractive forces are approximately static, leading to the simple result

$$\int_0^t dt'(t-t')(\Delta F_A \Delta F_A(t')) = t^2(\langle \Delta F_A \rangle)^2/2.$$  \hspace{1cm} (2.10)

This approximation clearly breaks down if the dephasing time becomes very long. Such is the case, for example, in liquid nitrogen where $\tau_\text{e} = 150 \text{ ps}$ and other cryogenic diatomic liquids. For these systems, the detailed nature of the attractive force dynamics plays a crucial role (see Sec. III C for specific illustrative calculations). It should also be noted that in the static limit, truncation of the cumulant series at second order is no longer justified by the existence of a small expansion parameter. However, such a truncation can be rationalized by appealing to the common assumption that the frequency fluctuations associated with the long range slowly varying forces are nearly a Gaussian process.

Combining Eqs. (2.6), (2.9), (2.10) with Eq. (2.3), results in the isotropic Raman spectrum being shifted by $\langle \Omega \rangle$ from its gas phase maximum, and the line shape given by a convolution of Lorentzian and Gaussian functions, a so-called Voight line shape.

Before leaving this section, we note that the role of attractive force dynamics can be investigated by computing the effect on the line shape of a finite attractive force correlation time $T_A$. Following Kubo,\textsuperscript{34} we represent the attractive force time correlation function as

$$\langle \Delta F_A \Delta F_A(t) \rangle = \langle \Delta F_A \rangle^2 \exp(-t/T_A).$$ \hspace{1cm} (2.11)

The resulting line shape as a function of the correlation time can be determined, and the effect of a finite $T_A$ assessed (see Secs. III C and V C).

III. HOMONUCLEAR DIATOMIC IN A SIMPLE SOLVENT

For the sake of simplicity, we develop our theory of the frequency shift and dephasing process for the model problem of a homonuclear diatomic solute in a solvent composed of structureless spherical particles. (Throughout this section, the normal coordinate $Q$ is taken for convenience to be the diatomic bond length $|r_1 - r_2|$. In this case, the force along the normal coordinate $F = \partial V/\partial Q$ is identical to the force along the bond.) Generalization to the case of polyatomic molecules involves increased technical complexity but no fundamentally new concepts.

A. Frequency shifts

The modification of the vibrational transition frequencies of molecules dissolved in condensed phases has interested scientists for a long time\textsuperscript{34-37} and continues to be studied today.\textsuperscript{28,29,43} The effect of both solid\textsuperscript{28} and liquid\textsuperscript{29,34,36} state environments have been investigated. A rich variety of behavior has been found, but usually (though not always) the vibrational lines are red shifted with respect to their gas phase positions at atmospheric pressure. The response of the shift to change of solvent, temperature, and density is of particular interest and displays a wide range of trends. The application of pressure can lead to a further red shift, a blue shift, or a combination nonmonotonic behavior.\textsuperscript{28,34-36} Clearly, there is a delicate balance between the opposing effects of repulsive (blue shift) and attractive (red shift) interactions. Qualitative trends are a sensitive function of the quantitative magnitude of the competitive effects. Our goal is to understand these phenomena within a statistical mechanical framework, with special emphasis on the isothermal density dependence and the competition between the harmfully repulsive forces and the relatively slowly varying attractions. In addition, we find that knowledge of the form and magnitude of the attractive interaction effects on the frequency shift leads to a theory for their dynamic consequences.

1. Slowly varying attractions

For the case of a diatomic solute, the attractive force frequency shift $\langle \Omega_A \rangle$ is proportional to the force along the bond

$$\langle \Omega_A \rangle \approx \langle F_A \rangle.$$ \hspace{1cm} (3.1)

In general, the physical source of this force will be largely due to dispersive interactions and possibly (for polyatomic molecules) dipolar interactions if the vibration is strongly infrared active and the solvent has a large dipole moment. Equation (3.1) can be written as

$$\langle \Omega_A \rangle = \int dr F_A(r) \langle \rho_\text{r}(r) \rangle,$$ \hspace{1cm} (3.2a)

where

$$\rho_\text{r}(r; t) = \sum_j \delta (r_j(t') - r_j(t) - r).$$ \hspace{1cm} (3.2b)

Here, $\rho_\text{r}(r)$ is the density of solvent molecules a distance $r$ from the tagged solute. The solute and $jth$ solvent molecule position at time $t$ are $r_j(t)$ and $r_j(t)$, respectively. Because $F_A(r)$ is relatively slowly varying, the density dependence of $\langle \rho_\text{r}(r) \rangle$ can be approximated in Eq. (3.2a) by its long wavelength limit

$$\langle \rho_\text{r}(r) \rangle = \rho,$$ \hspace{1cm} (3.3)

where $\rho$ is the bulk solvent density. Such an approximation is in the spirit of the van der Waals equation of state which is known to be remarkably accurate for dense liquids.\textsuperscript{37} Combining Eqs. (3.2) and (3.3) we obtain

$$\langle \Omega_A \rangle = \rho C,$$ \hspace{1cm} (3.4)

where $C$ is a density independent constant that serves as a strength parameter for the attractive forces. We do not attempt to calculate $C$ from first principles, but determine its value empirically via the equation

$$\langle \Omega_A \rangle = \langle \Omega \rangle - \langle \Omega_R \rangle,$$ \hspace{1cm} (3.5)

where $\langle \Omega \rangle$ is the experimental frequency shift at a particular thermodynamic state, and $\langle \Omega_R \rangle$ is its repulsive force counterpart calculated theoretically (see below). The parameter $C$ is determined by a single experimental measurement, and any further density or temperature dependence is computed with no adjustable parameters.
2. Repulsive forces

As discussed in Sec. II, the atom–atom forces are dominated by the repulsive branch of the potential which is then related to a corresponding reference hard sphere interaction. The solvent-induced force between a pair of hard spheres (the solute diatomic) dissolved in a hard sphere solvent is determined by the slope of the two-point cavity distribution function. Numerical tables of this function have been published. Moreover, since the atom–atom repulsions are harsh, we follow Oxtoby and approximate \( \langle G_R \rangle \) by

\[
\langle G_R \rangle = \langle F_R \rangle / 4L ,
\]

where \( L \) is a characteristic range parameter for the repulsive interaction. Therefore, the repulsive frequency shift is given by

\[
\langle \Omega_R \rangle = \hbar^2 / 2 \Delta q \langle F_R \rangle ,
\]

\[
\Delta q = \Omega_\omega - \Omega_\rho + (\Omega_\omega - \Omega_\rho) / 4L ,
\]

where \( \Omega_\omega \) is the reduced mass and \( \omega \) is the harmonic frequency. The solvent-induced force along the bond \( \langle F_R \rangle \) is a sensitive function of solvent density, solute bond length, and solute atom and solvent hard sphere diameters.

It is instructive to contrast our microscopic calculation of the force along the bond with a macroscopic theory. One possible approach would focus on the reversible work for the solute diatomic to expand against a continuum solvent. Neglecting surface effects, one obtains

\[
dW = Fdl = \mu dV,
\]

\[ F = \mu (dV / dl) .
\]

The solvent-induced force is simply given by the pressure times the volume change with respect to bond length. This can be evaluated by employing the bulk hard sphere solvent pressure (e.g., from Carnahan–Starling formula) and computing the geometrical volume change factor. When this approach is compared to the microscopic calculation, one finds Eq. (3.8) overestimates the density dependence of the solvent-induced force (see Fig. 2). The major source of this discrepancy is probably due to the representation of the local solvent structure as an isotropic continuum. Such an approximation misses the geometrical interference and finite size effects present on a microscopic scale. These considerations should be kept in mind when assessing the merit of applying hydrodynamics to the calculation of microscopic forces.

B. Dephasing dynamics

The calculation of the three independent physical sources of phase modulation is developed for the diatomic in a spherical molecule solvent problem.

1. Atom–atom repulsions

In the motional narrowing regime, the repulsive force contribution to dephasing is characterized by the rate

\[
\tau_\rho^2 = \frac{\langle \Delta q \rangle / \hbar^2}{\int_0^\infty dt \langle \Delta F_R \Delta F_R(t) \rangle} ,
\]

The integral of the force–force fluctuation time correlation function is calculated using the Enskog theory of hard sphere dynamics with geometrical corrections. Recall the standard result for a spherical particle of mass \( m \) in a solvent with particles of mass \( M \),

\[
\int_0^\infty dt \langle F(t) \rangle = 3 m h \tau_\rho^{-1} ,
\]

where \( F \) is the force exerted on the solute particle by the solvent, and \( \tau_\rho \) is the hard sphere Enskog collision time. In order to use this result, we must relate the force along the diatomic bond to the force on a single solute particle. We proceed in two steps. First the force on the two “atoms” of the bond are assumed to be uncorrelated:

\[
\int_0^\infty dt \langle \Delta F_R \Delta F_R(t) \rangle = 2 \int_0^\infty dt \langle \Delta \psi(t) \rangle .
\]

Here, \( f \) is the force exerted on a solute atom by the solvent along the bond direction. This reduction is consistent with our subsequent use of the binary collision Enskog result. Second, the force \( f \) is approximately related to the force \( F \) by introducing a steric factor \( \lambda \),

\[
\langle \Delta \psi(t) \rangle = \lambda^2 \langle F(t) \rangle ,
\]

where

\[
\lambda = \left[ 1 - \frac{r_s / 2 \bar{r}}{1 + (r_s / 2 \bar{r})} \right] ,
\]

Here, \( r_s \) is the solute bond length and \( \bar{r} = (\sigma_s + \sigma_a) / a \), where \( \sigma_s \) and \( \sigma_a \) are the solute atom and solvent hard sphere diameters, respectively. The correction factor is derived by considering the interaction of a diatomic and a single solvent sphere (see Fig. 1). It represents a mean force reduction factor due to the projection of the force between two hard spheres (solvent and one of the spheres defining the diatomic) along the direction defined by the bond. Equation (13.13) is obtained by averaging over relative solute–solvent orientations at contact:

\[
\lambda = \frac{\int_0^{2\pi} d\phi \int_0^{\phi_0} d\theta \sin \theta \cos \theta}{\int_0^{2\pi} d\phi \int_0^{\phi_0} d\theta \sin \theta} , \quad \phi_0 = \arctan \left( \frac{\sigma_s + \sigma_a}{2a} \right)
\]

\[
\phi_0 = \arctan \left( \frac{\sigma_s + \sigma_a}{2a} \right) .
\]
where \( \cos \theta = \gamma / \sqrt{2} \). Evaluation of the above integrals yields Eq. (3.13). Inclusion of this factor approximately incorporates the geometrical and finite size effects discussed in Sec. IIIA. It is a decreasing function of bond length in qualitative accord with a microscopic cavity distribution function calculation of the solvent induced force. It is not important for qualitative trends but necessary for accurate numerical estimates. (As such, it is analogous to the surface area exposure and slip or stick boundary condition factors that arise in the hydrodynamic theory. \(^4\)) Combining Eqs. (3.9)–(3.12) leads to the final result

$$
\tau^2 = 2(\Delta q / \hbar)^2 3k_B T/2 (1 + r_\mu / \overline{2}) \chi^2 \tau^2_{\text{E}}^2.
$$

(3.15)
The factor of \((1 + r_\mu / \overline{2}) / 2\) represents the fraction of total surface area exposed to the solvent by one of the sites of the diatomic solute. The collision rate should scale with this quantity. The frequency \(\tau^{2}_{\text{E}}\) is the hard sphere Enskog collision rate for a sphere of diameter \(\sigma_s\) at infinite dilution in a solvent of diameter \(\sigma_s\), and is given by

$$
\tau^{2}_{\text{E}} = \frac{1}{2} \overline{2} \gamma \frac{1}{2} \mu^2 \frac{1}{2} \gamma \frac{1}{2} \gamma \frac{1}{2} \gamma \frac{1}{2} \gamma
$$

(3.16)

where \(\overline{2} = m_s + M\),

and \(\gamma^2 \) is the contact value of the radial distribution function for a solute atom and the solvent. Generalizing the Carnahan–Starling formula to mixtures one obtains \(^{47}\)

$$
\gamma^2 = \frac{1}{2} (1 - \eta) \left\{ (1 - \eta) \left[ (\sigma_s / \overline{2}) (1 + 2 \eta) + (\sigma_s / \overline{2}) (1 - \eta) + \eta (\sigma_s / \overline{2})^2 \right] \right\}
$$

(3.17)

where \(\eta = \rho \sigma_s^2 / 6\).

The isothermal density dependence of \(\tau^2\) is of particular interest because of the sensitivity of liquid state properties to this variable. Clearly, Eq. (3.15) varies as an Enskog collision time in a manner similar to the Fischer and Laubereau independent binary collision theory. \(^5\) However, this dependence is somewhat weaker than the hydrodynamic theories, \(^4\) \(^6\) \(^7\) which vary as \(\eta \) or \(\rho \eta\), where \(\eta \) is the shear viscosity.

2. Vibration–rotation coupling

In the motional narrowing regime, the vibration–rotation coupling contribution to the dephasing rate of a diatomic molecule is given through quadratic order in the vibrational coordinate by

$$
\tau^2_{\text{R}} = (\Delta \hbar / \hbar)^2 (\Delta \hbar / \hbar)^2 \int_0^\infty dt \langle \Delta \hbar^2 \Delta \hbar^2 \rangle)
$$

(3.18a)

where

$$
\Delta \hbar = (\hbar_{11} - \hbar_{00}) - 3(\hbar_{11} - \hbar_{00}) / 2 \gamma,
$$

(3.18b)

and \(\Delta \hbar^2\) is the total angular momentum squared. The integral in Eq. (3.18) can be related to the angular momentum relaxation time \(\tau_J\) by assuming that the rotational motion is a Gaussian process. Such an approximation has been used by molecular dynamics and shown to be fairly accurate. \(^8\) By using it we can write \(^8\)

$$
\langle \Delta \hbar^2 \rangle / (\Delta \hbar^2) = [1 + A^2_J / 2],
$$

(3.19)

where

$$
A_J(t) = (\gamma \cdot J(t)) / (\Delta \hbar^2) = \exp(-t / \tau_J),
$$

(3.20)

and

$$
\tau_J = \int_0^\infty dt A_J(t).
$$

(3.21)

Using the standard relations \(\gamma(t) = 2(\hbar_\gamma \gamma)\) and \(\gamma(t) = 2\gamma(t)^2\) for classical rotation of linear molecules, along with Eqs. (3.16)–(3.21), one finds

$$
\tau^2_{\text{R}} = (\Delta R / \hbar)^2 (\hbar_\gamma / \gamma)^2 (\Delta \hbar / \hbar)^2.
$$

(3.22)

A similar result has been derived by Brueck. \(^1\) If available, the experimental \(\tau_J\) can be used to evaluate Eq. (3.22). Otherwise, we estimate its magnitude and density dependence from the rough hard sphere model \(^9\) of rotational motion in liquids. This theory, based on an independent binary collision approximation, predicts that

$$
\tau_J = \gamma \tau_S,
$$

(3.23)

where \(\tau_S\) is the molecular Enskog collision time and \(\gamma\) an adjustable parameter. According to Eq. (3.23), the vibration–rotation interaction contribution to the dephasing rate monotonically decreases with increasing density.

3. Slowly varying attractions

As discussed in Sec. II, the relatively slowly varying forces generate Gaussian inhomogeneous broadening of the form \(\exp(-t^2 / \sigma_\text{x}^2)\), where

$$
\sigma^2_x = [(\tau_{11} - \tau_{00}) / \hbar^2]^2 (\Delta \hbar^2 / \hbar^2).
$$

(3.24)

This can be rewritten as

$$
\sigma^2_x = [(\tau_{11} - \tau_{00}) / \hbar]^2 \int dt \int dt' \langle \rho_\gamma(t) \rho_\gamma(t') \rangle
$$

$$
\times F_\gamma(t') \langle \Delta \rho_\gamma(t) \Delta \rho_\gamma(t') \rangle / \langle \rho_\gamma(t) \rangle \langle \rho_\gamma(t') \rangle,
$$

(3.25)

where as before \(\rho_\gamma(t)\) is the density of solvent molecules a distance \(t\) from the tagged solute molecule, and \(\Delta \rho_\gamma(t) = \rho_\gamma(t) - \langle \rho_\gamma(t) \rangle\). The quantity in square brackets in Eq. (3.25) represents the solvent density fluctuations in the neighborhood of the solute relative to the mean density inhomogeneity \(\langle \rho_\gamma(t) \rangle\). Since \(F_\gamma(t)\) is supposed to be relatively slowly varying, we shall assume that the integrals in Eq. (3.25) are determined primarily by the relatively long wavelength density fluctuations. Therefore, we will estimate the integrals with a van der Waals or mean field approximation. In particular, when used in Eq. (3.25), we employ

$$
\langle \Delta \rho_\gamma(t) \Delta \rho_\gamma(t') \rangle / \langle \rho_\gamma(t) \rangle \langle \rho_\gamma(t') \rangle = \langle \rho_\gamma(t) \rangle / \langle \rho_\gamma(t') \rangle = (\delta \rho / \delta \rho) / \langle \chi \rangle / \langle \chi' \rangle = \chi / \chi',
$$

(3.26)

where \(\rho(t)\) is the pure solvent density at \(t\), and \(\chi\) is a parameter that should scale roughly with the number of nearest neighbors, but may be dependent on the details of the solvent–solute interaction. Because the compressibility \(\chi\) is a long wavelength property, an estimate based solely on the hard sphere model is inappropriate. The experimental value is used when avail-
able. Substituting Eq. (3.26) into Eq. (3.25) yields the result
\[
\tau_{A}^2 = \left(\frac{3}{X} \right) \left[ \int \mathrm{d}r (\rho_A(r)) (Q_{11} - Q_{00}/\hbar) F_A(r) \right]^2,
\]
\[
\tau_{A}^2 = \left(\frac{3}{X} \right) \tau_X^2 / N,
\]  
(3.27)
where the second equality follows from the definition of the attractive force contribution to the frequency shift [Eq. (3.2)]. Thus, we have related the attractive force line broadening to the attractive frequency shift previously determined, the experimental compressibility, and a parameter \( N \). Physically, the attractive force frequency shift is a measure of the total strength or magnitude of the slowly varying component(s) of the solvent induced force along the solute normal coordinate. The specific source (dispersion, induction, dipolar, etc.) of the slowly varying interactions is not the important feature in the determination of the observed spectral line shape. Of course, such a question is of interest, and the asymptotic formulas for the various electrostatic multipole interactions can be employed to qualitatively estimate their relative contributions. The compressibility factor can be interpreted as a measure of the distribution of local environments due to solvent number density fluctuations. More pictorially, it can be viewed as the response (long wavelength) of the surrounding solvent environment to the disturbance associated with the slowly varying attractive force solute-solvent coupling.

Of particular interest is the density dependence of the attractive force contribution. The linewidth appropriate for a Gaussian line shape is given by
\[
L_{W} = 2(2\ln 2)^{1/2} \tau_{A}^2 \propto (\rho_X)^{1/2},
\]  
(3.28)
where the proportionality follows from Eq. (3.4) and the assumed linear density scaling of \( N \). The above linewidth decreases with increasing density in contrast with the behavior of the repulsive collision mechanism. Consequently, the dephasing rate as inferred from the Raman linewidth will have a density dependence that reflects the competition between the rapidly and slowly varying forces. As in the case of frequency shifts, qualitative trends will depend on the quantitative relative magnitudes of the competing mechanisms.

An alternative derivation of Eq. (3.28) can be accomplished by rewriting Eq. (3.25) in terms of wavevector-\( k \) space integrations. A result of the form of Eq. (3.28) follows from assuming that the Fourier transform of the density-density fluctuation function can be evaluated in the \( k=0 \) (long wavelength) limit. Such an approach has been previously considered by Hills and Madden. The validity of this approximation rests on the assumption that \( F_A(r) \) is sufficiently slowly varying that its Fourier transform is localized near \( k=0 \). Because the structure factor is often a slowly varying function for small wave vectors, we estimate the small \( k \) structure factor with the \( k=0 \) limit. For the rapidly varying repulsive force case, this reduction is clearly not valid. In addition, the replacement of the density-density fluctuation function with the constraint of a solute molecule at the origin, by the corresponding pure solvent form, is not expected to be accurate because the integral [Eq. (3.25)] is sensitive to short wavelength (\( k \geq 2\pi/\sigma \)) variations.

The density scaling of Eq. (3.28) has been previously proposed on empirical grounds by George et al. (actually, these workers propose a scaling of the form \( \rho^3 \)). They also postulate that the inhomogeneous width is proportional to the mean intermolecular force the solvent exerts on the solute. This is not quite correct. Within a statistical mechanical framework, we have shown that the inhomogeneous broadening due to the relatively slowly varying forces (generally attractions) scales with the compressibility. However, we have also derived the proportionality constant, i.e., the attractive force frequency shift which depends on both intermolecular interactions and vibrational mode properties. The inhomogeneous broadening is related to only the mean force exerted along the vibrational coordinate by the relatively slowly varying attractions. The linewidth due to the harmonic repulsions is not simply related to the repulsive part of the force along the bond.

The physical argument employed to derive Eq. (3.26) can also be applied to estimate the attractive force correlation time. The attractive force time correlation function is given by
\[
\langle \Delta F_A(t) \Delta F_A(0) \rangle = \int \mathrm{d}t \int \mathrm{d}t' \langle \rho_A(r) \rangle F_A(r') \langle \rho_A(r) \rangle F_A(r') (\Delta \rho_A(r, 0) \Delta \rho_A(r', t))
\]
\[
\times F_A(r') \langle \Delta \rho_A(r, 0) \Delta \rho_A(r', t) \rangle / \langle \rho_A(r) \rangle^2.
\]  
(3.29)
where \( \Delta \rho_A(r, t) \) is the solvent density fluctuation a distance \( r \) from the tagged solute at time \( t \). As before, since the attractive forces are spatially slowly varying, we approximate the solvent density fluctuations in the neighborhood of the solute by their pure solvent counterparts
\[
\langle \Delta F_A(0) \Delta F_A(0) \rangle = \int \mathrm{d}t \int \mathrm{d}t' F_A(r) F_A(r') (\Delta \rho(r, 0) \Delta \rho(r', t))
\]
\[
= (2\pi)^4 \int \mathrm{d}k k^2 \exp(-k^2 D_t) \langle \hat{F}_A(k) \rangle^2.
\]  
(3.30)
The second line of Eq. (3.30) follows from transforming to wave-vector space and retaining only the self-part of the time-dependent structure factor of the pure solvent (the Vineyard approximation). The static structure factor is denoted as \( S(k) \) and \( D_t \) is the solvent diffusion constant. Since \( F_A(r) \) is considered slowly varying, its Fourier transform should be localized at relatively small \( k \leq \pi/\sigma \) wave vectors. Consequently, the time dependence of the attractive force fluctuations is approximately given by
\[
\langle \Delta F_A(0) \Delta F_A(0) \rangle = \exp(-k^2 D_t) \langle \hat{F}_A(k) \rangle^2,
\]  
(3.31)
where \( k_0 \) is of the order of \( \pi/\sigma \). Therefore, we estimate the attractive force correlation time as
\[
\tau_A = \sigma^2 / \pi^3 D_A,
\]  
(3.32)
which is typically of the order of 10–20 ps. Note that the correlation time varies with the length scale associated with the slowly varying interactions, i.e., the molecular diameter. Consequently, the attractive forces
TABLE I. Frequency shifts and linewidths for $N_2$ in nitrogen and carbon tetrachloride solvents. Attractive force linewidths are calculated in the static bath limit ($T_0 = \infty$) and are defined as $2/\Gamma(\hbar)T^2/2\kappa$, where $\kappa$ is the speed of light. The repulsive and vibration-rotation linewidths are $2\Gamma(\hbar)T^2/2\kappa$, respectively. All results are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$N_2/N_2$</th>
<th>$\langle \Omega \rangle^a$</th>
<th>$\langle \Omega \rangle^b$</th>
<th>$\Gamma_{\text{dim}}^c$</th>
<th>$\Gamma_{\text{HR}}^d$</th>
<th>$\Gamma_{\text{VR}}^e$</th>
<th>$\Gamma_{\text{VA}}^f$</th>
<th>$\Gamma_{\text{W}}$</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2/N_2$</td>
<td>1.84</td>
<td>-1.74</td>
<td>-9.4</td>
<td>0.069</td>
<td>0.015</td>
<td>0.27</td>
<td>0.32</td>
<td>0.067</td>
</tr>
<tr>
<td>$N_2$/CCl$_4$</td>
<td>3.2</td>
<td>-8.0</td>
<td>-19.8</td>
<td>0.43</td>
<td>0.24</td>
<td>0.88</td>
<td>1.29</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$^a$Calculated using Eq. (3.7).  
$^b$Calculated using Eq. (3.9) in conjunction with the experimental frequency shifts (Ref. 33 and 49) and the vibration-rotation line shift correction (Ref. 19).  
$^c$Calculated using Eq. (3.34) with $\bar{N} = 12$. The ionization energy (Ref. 55) and polarizability for nitrogen and carbon tetrachloride are 15.6 eV and 1.76 Å$^3$, and 11.47 eV, 10.4 Å$^3$ respectively.  
$^d$Calculated using Eq. (3.15).  
$^e$Calculated using Eq. (3.22).  
$^f$Calculated using Eq. (3.27) and (3.28) with $\bar{N} = 12$.

will generally relax more slowly as the polyatomic molecule becomes increasingly complex. However, in this same limit, the dephasing time often decreases. Hence, the separation of dephasing and attractive force relaxation time scales becomes more pronounced as the size of the polyatomic molecule increases. On the other hand, for low viscosity liquids composed of small molecules like $N_2$, the dephasing times can be very long, and attractive force correlation times will be relatively shorter. Hence, the contribution of the slowly varying attractions to the observed linewidth will be correspondingly smaller.

Finally, the overall line shape is given by the Fourier transform of

$$C(\omega) = \text{Re}\{\exp[i(\omega_0 + \langle \Omega \rangle)T - (\tau_{\text{HR}}^2 + \tau_{\text{VR}}^2)T^2/2\kappa^2]\}. \quad (3.33)$$

Such a line shape is referred to as a Voight profile, and numerical tables have been published. In all our applications we report only the spectral linewidth (full width at half height of the line), which is defined as twice the dephasing rate.

C. Applications

As illustrative examples, we apply the theory developed in Secs. III A and III B to two simple systems: pure liquid nitrogen at 76 K and nitrogen dissolved as an impurity in carbon tetrachloride at room temperature. High pressure data do not exist for these systems. Therefore we concentrate on calculating the frequency shift and Raman linewidth at a single thermodynamic state.

The results (for $\bar{N} = 12$) are displayed in Tables I and II, and Fig. 2. The nitrogen atom hard sphere diameter $a$

<table>
<thead>
<tr>
<th>$T_0$ (pa)</th>
<th>LW($N_2$)</th>
<th>LW($\text{CCl}_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.69</td>
<td>0.73</td>
</tr>
<tr>
<td>2</td>
<td>0.095</td>
<td>0.78</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.87</td>
</tr>
<tr>
<td>8</td>
<td>0.12</td>
<td>1.00</td>
</tr>
<tr>
<td>16</td>
<td>0.19</td>
<td>1.12</td>
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<tr>
<td>32</td>
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<td>1.21</td>
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<tr>
<td>64</td>
<td>0.26</td>
<td>1.26</td>
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<tr>
<td>128</td>
<td>0.29</td>
<td>1.28</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.32</td>
<td>1.29</td>
</tr>
</tbody>
</table>

was taken to be 3.34 Å, while the nitrogen and carbon tetrachloride molecular diameters are 3.77 and 5.16 Å, respectively, in accord with rough hard sphere calculations on these systems.\(^{46,52}\) The vibration–rotation contribution was calculated using Eq. (3.23) with the previously determined\(^{38}\) value of \(\gamma = 2.3\). The experimental compressibility, density,\(^{39}\) and frequency shifts\(^{35,40}\) were employed. Here, and throughout the paper, the repulsive force range parameter \(L\) is determined in the same manner discussed in Ref. 5. The shift in the line maximum due to the collapse of the rotational \(Q\)-branch structure was included in the usual manner.\(^{38}\) There are three important points concerning the liquid nitrogen results in Table I: First, the repulsive force frequency shift, atom–atom dephasing rate, and vibration–rotation linewidth contribution are in good agreement with molecular dynamics calculations. The simulation results are 2.03 cm\(^{-1}\) for the (exponential) repulsive frequency shift,\(^{29}\) 115 ps (neglecting the resonance coupling contribution) for the Lennard-Jones atom–atom dephasing rate\(^{19}\) (our result corresponds to 145 ps), and 0.02 cm\(^{-1}\) for the vibration–rotation linewidth.\(^{26}\) Second, the empirically determined attractive frequency shift is not in good agreement with an estimate based on the London dispersion formula
\[
\Omega_{\text{attr}} = h^2 \left( Q_{\text{L}} - Q_0 \right) \sum_{\alpha} a_{\alpha} \alpha / \beta ,
\]
where \(h\) is the ionization energy,\(^{55}\) \(\alpha\) the polarizability (1.76 Å\(^2\) and 10.4 Å\(^2\) for nitrogen and carbon tetrachloride respectively), \(\alpha'\) the polarizability derivative with respect to bond length (1.75 Å\(^2\) for \(N_2\)),\(^{56}\) \(\sigma\) the molecular diameter, and \(N\) the number of nearest neighbors. This is not surprising since the dispersion formula is an asymptotic result that cannot be expected to be reliable at close distances appropriate in a dense liquid. For liquid nitrogen, the extrapolated dispersion interaction significantly overestimates the magnitude of the attractive force. Third, the finite attractive force correlation time clearly plays a significant role since the overall dephasing time is very long for this system. An estimate based on Eq. (3.32) yields \(T_2 = 7\) ps. This leads to a Lorentzian line shape with a substantially decreased linewidth in accord with the familiar motional narrowing phenomena. However, as discussed previously, we believe subpicosecond correlation times and large cross correlations with the repulsive atom–atom force fluctuations are artifacts of the extrapolation of the dispersion forces to small distances.

For nitrogen dissolved in carbon tetrachloride the empirically determined attractive force frequency shift is in rough agreement with the dispersion interaction estimate (but again the dispersion estimate is larger), and the finite attractive force correlation time has a non-negligible, but smaller, effect on the total linewidth (for this system \(T_2 = 14\) ps is a reasonable estimate). The isothermal density dependence of the frequency shift is shown in Fig. 2. As noted previously, the macroscopic calculation of the repulsive force frequency shift overestimates the density variation. Also, even though the repulsive force shift is rapidly varying over the liquid density region, the total shift is approximately constant: \(-6.8 \pm 0.1\) cm\(^{-1}\).

For both systems, the calculated linewidths are within a factor of 2 of the experimental values for reasonable values of \(T_2\). It should be noted that the vibration–rotation mechanism plays a fairly important role for these systems (~15% effect). Hence, the neglect of cross correlation between this mechanism and the repulsive atom–atom forces may lead to noticeable errors, which if accounted for could lead to a decrease of the linewidth.\(^{20}\)

### IV. GENERALIZATION TO POLYATOMICS

We now consider a generalization of the theory of vibrational frequency shifts and dephasing developed in Sec. III. Because our theory of the effects of the relatively slowly varying attractive forces ignores the detailed nature of the solute–solvent coupling, the treatment presented in Sec. III applies equally well to the polyatomic liquid case.

#### A. Frequency shift

We need only consider the modification of our \(ab\) initio calculation of the repulsive atom–atom part of the shift. The first step entails solving the normal mode problem for the particular molecule of interest. This allows the force along the normal mode coordinate \(Q_o\) to be related to forces on the atoms (or “sites”). Following the notation of Ref. 57 we have
\[
\eta_i = \sum_a a_{ia} Q_{ai} ,
\]
where \(\{\eta_i\}\) are the deviations of the molecular generalized coordinates from their equilibrium values and \(\{Q\}\) are the corresponding normal coordinates. Using this relation, we can write
\[
\langle F_b \rangle = \langle \text{d} V / \text{d} Q_a \rangle = \sum_i a_{ia} \langle \text{d} V / \text{d} \eta_i \rangle ,
\]
Similarly, since the atom–atom interactions are harsh repulsions, we can approximate \(\langle G_b \rangle\) by
\[
\langle G_b \rangle = -\sum_i \frac{1}{2 L_i} a_{ia} \langle \text{d} V / \text{d} \eta_i \rangle ,
\]
where as before \(L_i\) is a characteristic range parameter for the repulsive interaction.\(^{5}\) Equations (4.1) and (4.2) can be expressed in a form convenient for statistical mechanical calculation by relating the forces on atoms or sites to the forces along bonds (the term “bonds” is used generically to denote both bonded and nonbonded pairs of atoms or sites)
\[
\langle F_b \rangle = \sum_i a_{ia} \sum_q \left( \frac{\text{d} V}{\text{d} b} \cdot \frac{\text{d} b}{\text{d} \eta_q} \right)
\]
\[
= \sum_n c_b \langle F_b \rangle ,
\]
where \(b\) refers to a bond vector and \(\langle F_b \rangle\) is the hard sphere part of the solvent induced force along bond \(b\). The coefficients \(c_b\) are deduced from the normal coordinate analysis and the equilibrium molecular geometry. Similarly, Eq. (4.3) can be expressed in terms of forces along bonds as
\[
\langle Q_b \rangle = - \sum_b \frac{1}{2 \omega_b} c_b \langle F_b \rangle .
\]

(4.5)

The solvent induced forces between pairs of sites in a classical molecular liquid can be computed using the concept of cavity particles in conjunction with the interaction site model of fluids.\(^{29}\) For a polyatomic liquid this generally involves a multipoint cavity distribution function. These objects can be computed for dense fluids using the RISM integral equation\(^{24}\) and the Chandler–Frisch theory of liquids composed of flexible molecules.\(^{20}\) However, such a detailed description is probably not warranted because the frequency shift involves not only solvent induced forces but also the anharmonic bond shift \(Q_1 - Q_0\). The latter quantity is a property of the isolated molecule potential surface, which for polyatomic can be determined only from multiparameter fits of potential functions to spectroscopic data, a program carried out for very few systems. Consequently, \(Q_1 - Q_0\) is not available to high accuracy. Therefore, it seems appropriate to construct a simplified theory which is computationally easier to carry out, but still retains the essential physics of hard sphere packing.

Our simplified theory involves two basic approximations. First, we neglect the detailed molecular shape of solvent molecules by replacing them with appropriately chosen hard spheres. The diameter is chosen according to the rough hard sphere criterion of reproducing the experimental density dependence of the shear viscosity and/or diffusion constant.\(^{22}\) Second, the forces along the bonds are computed by imagining the bonds are "freely floating" in solution. That is, for the purpose of calculating a particular \(\langle F_b \rangle\), the full polyatomic solute molecule is replaced by the diatomic defining the bond. Such an approximation is exact in the asymptotic limits that all the other bond lengths go to zero and/or infinity. As such, the procedure can be viewed as an interpolation formula. Since we are ultimately most interested in the thermodynamic (density and temperature) dependence of the frequency shifts, we believe this "floating bond" algorithm is adequate. The calculation of the two point cavity distribution function for hard spheres dissolved in a hard sphere solvent was discussed in Sec. III.

The final quantities needed to compute the frequency shift are \(Q_1 - Q_0\) and \(Q_1^0 - Q_0^0\). The latter is easily deduced from the normal mode analysis. The former can be determined either experimentally or by constructing Morse potential bond models. The particular approach depends on the specific system (see Appendix and Sec. V).

B. Dynamics

1. Atom–atom repulsions

In the motional narrowing regime, the repulsive force contribution to dephasing is characterized by the rate \([\text{Eq. (2.2), (2.6), and (2.9)}]\)

\[
\tau_{\text{at}}^s = \hbar \gamma \int_0^t dt' \langle (Q_1 - Q_0) \Delta F_R(t) (Q_1^0 - Q_0^0) \Delta G_R(t) \rangle \times \langle (Q_1 - Q_0) \Delta F_R(t) + (Q_1^0 - Q_0^0) \Delta G_R(t) \rangle .
\]

(4.6)

Using Eqs. (47) and (48) we can rewrite this in terms of bond–bond force time correlation functions

\[
\tau_{\text{at}}^s = \langle (Q_1 - Q_0)/k \rangle \sum_b \sum_{i_b} \rho_{i_b} \int_0^t \langle \Delta F_{i_b} \Delta F_{i_b'}(t) \rangle dt ,
\]

(4.7)

where

\[
\rho_{i_b} = c_{i_b} + (Q_1^0 - Q_0^0)/2L_i (Q_1 - Q_0) c_{i_b} .
\]

(4.8)

In the spirit of our approach to the calculation of the hard sphere part of the frequency shift, we make a "dynamic floating bond" approximation. Unfortunately, unlike the equilibrium floating bond approximation, the dynamic analog does not interpolate between two exact limits. In particular, we assume the forces along different bonds are uncorrelated (and hence cross correlations do not contribute to \(\tau_{\text{at}}^s\)), and the remaining "diagonal" (in bond index) parts can be computed by literally taking the bond to be a diatomic molecule dissolved in a hard sphere solvent. An exception to the above rule occurs when the equilibrium force along two different bonds are identical due to the point group symmetry of the solute molecule (e.g., the two C–H bonds of isobutylene and acetone). For this special symmetry case, the cross correlations are retained and approximated by their diagonal counterpart. This approach is similar in spirit to the hydromechanical theory\(^{32}\) in that a certain class of cross correlations are neglected. However, instead of assuming that the forces on different atoms or sites are uncorrelated, we take bonds as the basic unit and neglect their cross correlations. The latter assumption is possibly more realistic and is in the spirit of our equilibrium theory. Under these assumptions, Eq. (4.8) becomes

\[
\tau_{\text{at}}^s = \langle (Q_1 - Q_0)/k \rangle \sum_b \rho_{i_b} \int_0^\infty dt \langle \Delta F_{i_b} \Delta F_{i_b}(t) \rangle ,
\]

(4.9)

where the prime on the summation is a reminder of the symmetry related caveat. The problem has now been reduced to computing the zero frequency part of the repulsive force–force time correlation function of a diatomic (bond) dissolved in a hard sphere solvent. This calculation was considered in Sec. III with the result given by Eq. (3.15) for a homonuclear diatomic. Generalization to a heteronuclear diatomic is straightforward, with the result

\[
\tau_{\text{at}}^s(b) = \sum_{\alpha = 1}^{\gamma} 2b_\alpha T m_\alpha(b) \lambda_\alpha(b) \left[ 1 + \cos \theta_\alpha(b) \right] ^2 ,
\]

(4.10)

where

\[
\lambda_\alpha(b) = \left[ 1 - \cos \theta_\alpha(b) \right] / \left[ 2 \left( 1 + \cos \theta_\alpha(b) \right) \right] ,
\]

\[
\cos \theta_\alpha(b) = \left[ r_\alpha(b)^2 + c_\alpha(b)^2 - d_\alpha(b)^2 \right] / 2r_\alpha(b) c_\alpha(b) ,
\]

\[
\sigma_\alpha(b) = \left[ c_\alpha(b) + s_\alpha(b) \right] / 2 ,
\]

\[
\gamma = 2b_\alpha + c_\alpha ,
\]

\[
\tau_{\text{at}}^s(b) = \left[ \pi \hbar \gamma T/2 \mu_\alpha(b) \right] ^1/2 p c_\alpha(b) d[\sigma_\alpha(b)] ,
\]

\[
\mu_\alpha(b) = m_\alpha(b) + M^\alpha .
\]

2. Vibration–rotation coupling

For an arbitrary polyatomic molecule, the vibration–rotation coupling contribution to the dephasing rate
is given by

$$\tau_{\text{VR}} = \frac{(Q_{11} - Q_{00})/\hbar^2}{3} \sum_{\alpha \neq \beta} \left\{ \int_0^\infty dt \langle \Delta J_\alpha^2 \Delta J_\beta^2(t) \rangle \right\},$$

(4.12)

where $\Delta J_\alpha^2 = J_\alpha^2 - (J_\alpha^2)_{eq}$, and $I_\alpha$ are the three independent moments of inertia. Because this mechanism is generally small for all the polyatomic systems studied in this paper the quadratic $G = \langle \Delta J^2 \Delta J^2 \rangle_{eq}$ term has been ignored. Further, a rough estimate of the remaining term will suffice. We neglect the detailed weighting associated with the moment of inertia tensor in Eq. (4.12), and approximate that equation by

$$\tau_{\text{VR}} \approx \frac{(Q_{11} - Q_{00})/\hbar^2}{\frac{1}{3} \sum_{\alpha \neq \beta} \int_0^\infty dt \langle \Delta J_\alpha^2 \Delta J_\beta^2(t) \rangle},$$

(4.13)

Finally, making the same assumptions employed in the derivation of Eq. (3.22), i.e., $\langle \Delta J_\alpha^2 \Delta J_\beta^2(t) \rangle = \langle \Delta J^2 \rangle$ $\times \exp(-2t/\tau_J)$, the above expression reduces to

$$\tau_{\text{VR}} = \left( \frac{Q_{11} - Q_{00}}{\hbar^2} \right) \cdot \left( \frac{1}{3} \sum_{\alpha \neq \beta} \int_0^\infty dt \langle \Delta J_\alpha^2 \Delta J_\beta^2(t) \rangle \right)^{-1/2},$$

(4.14)

where

$$\tau_{\text{VR}} = \frac{3}{I} \frac{\tau_J}{3},$$

(4.15)

and $\tau_J$ is given by Eq. (3.23).

V. APPLICATIONS

We now apply the theory developed in Secs. II–IV to four particular systems. The first two include the symmetric carbon stretching vibrations of isobutylene (C–C and C=C) and the C=O mode of acetone. Schindler and Jonas have accurately measured the frequency shift and Raman linewidth of these vibrations over a wide range of density and temperature. Very different behavior was observed for both the frequency shift and the dephasing rate as a function of density. The line shapes were significantly non-Lorentzian, and the line broadening and peak shifts appear to be strongly correlated. In particular, the C=C mode of isobutylene exhibits an increasing linewidth with increasing density, the C=O mode of acetone a decreasing linewidth, and the C=C stretch of isobutylene a nonmonotonic dependence. All three of these systems are far from the simple monotonically increasing dependence predicted by the binary collision and hydrodynamic theories. Consequently, these vibrations appear to be excellent examples of the competition between the effects of interactions and slow varying variations on the frequency shift and dephasing dynamics in dense liquid media. The second pair of systems studied are the symmetric CH$_3$ of methyl iodide and the C–H symmetric stretching mode of chloroform. Both have been previously analyzed in terms of the binary collision and/or hydrodynamic theories. Each exhibits monotonically increasing relaxation rates as a function of density. However, our analysis reveals that the slowly varying

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**TABLE III.** Isothermal compressibilities $\chi = \nabla \rho_0 / \nabla p_0$, where $\rho_0$ is in units of $10^3$ m$^3$/N. All values are appropriate to 1 atm. of pressure. Unless noted otherwise, all numbers for $\rho_0$ are taken from Ref. 53, Sec. F14.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T$ (K)</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>76</td>
<td>3.22</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>298</td>
<td>1.97</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>298</td>
<td>1.24</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>323</td>
<td>1.60</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>303</td>
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</tr>
<tr>
<td>CHCl$_3$</td>
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</tr>
<tr>
<td>(CH$_3$)$_2$CH$_2$I</td>
<td>298</td>
<td>3.25</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>293</td>
<td>1.10</td>
</tr>
<tr>
<td>C$_2$H$_5$I</td>
<td>293</td>
<td>0.94</td>
</tr>
<tr>
<td>C$_2$H$_5$Cl</td>
<td>293</td>
<td>0.49</td>
</tr>
<tr>
<td>C$_2$H$_5$Br</td>
<td>293</td>
<td>0.74</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>293</td>
<td>0.65</td>
</tr>
<tr>
<td>C(CH$_3$I</td>
<td>293</td>
<td>0.57</td>
</tr>
<tr>
<td>C(CH$_3)_2$I</td>
<td>293</td>
<td>2.27</td>
</tr>
<tr>
<td>C(CH$_3)_2$Cl</td>
<td>293</td>
<td>1.96</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>293</td>
<td>0.99</td>
</tr>
</tbody>
</table>

$^a$Calculated from $\chi = \nabla \rho_0 / \nabla p_0$ using the density data of Ref. 26.

$^b$Taken from Ref. 54, p. 48.

$^c$Calculated from equation of state given in Ref. 26.

$^d$Taken from Ref. 63.

$^e$Taken from Ref. 23.

$^f$Taken from Ref. 64.

---

The calculations are performed using the results of Secs. III and IV. The isothermal compressibility is taken as the experimental value (Table III). However, measurements of the density variation of the compressibility are scarce. For simplicity, and in the spirit of our approach to the calculation of the density dependent frequency shifts, we estimate the density variation of the compressibility from the van der Waals equation of state

$$\beta p = \beta p_{\text{HS}} - \beta p^3/2,$$

(5.1)

where $p_{\text{HS}}$ is the pressure of the corresponding hard sphere fluid, $\rho$ the density, and $b$ an adjustable parameter. The isothermal compressibility corresponding to Eq. (5.1) is given by

$$\chi = (\beta p / \beta \rho)^{1/2},$$

(5.2)

where $\chi_{\text{HS}}$ is calculated from the Carnahan-Starling equation of state as

$$\chi_{\text{HS}} = (1 - \eta)/(1 + 4\eta(1 - \eta) + \eta^2),$$

(5.3)

and $\eta = 5\rho a^3/6$ is the solvent packing fraction. The parameter $b$ is fixed by requiring Eq. (5.2) reproduces the
experimental compressibility at one atmosphere of pressure.

The parameter $\bar{N}$ appearing in the attractive force contribution to relaxation is not specified unambiguously by our theory. It should be of the order of the mean number of solvent molecules interacting with the solute via the slowly varying attractive interactions. Consequently, for a neat liquid and London dispersion type interactions, $\bar{N}$ is of the order of 12. In general, it could vary depending on the details of the specific solute–solvent interactions, and/or normal vibration amplitudes. Since $\bar{N}$ only affects the linewidth through the factor $\bar{N}^{-1/2}$, our results are not overly sensitive to its variation. Calculations are performed for several choices of this parameter.

A. Isobutylene and acetone

1. Frequency shift

We have considered the two symmetric stretches of isobutylene (C=C, C–C; see Fig. 3) and the C–O stretch of acetone. The normal mode analysis for these cases is briefly discussed in the Appendix. The equilibrium geometry (bond lengths and bond angles) for these molecules is well known.\(^{61}\) The anharmonic bond shift was estimated by constructing a Morse potential bond model and computing the relevant cubic potential parameters. A Morse bond model for the diatomic like carbon stretching vibrations of ethane and ethylene yield anharmonic bond shifts of $1.1 \times 10^{-3}$ and $0.9 \times 10^{-3}$ cm, respectively. For isobutylene the corresponding quantity is approximately $0.8 \times 10^{-3}$ cm for both the C=C and C–C modes. We have used the estimate of $1 \times 10^{-3}$ cm for isobutylene. In addition, the Morse potential bond analysis for the C=O mode of acetone yields results very similar to the isobutylene case. Therefore, for simplicity, we use the same anharmonic bond shift as stated above.

Results are displayed in Fig. 4 and Table IV, and are in excellent agreement with the experimental data. Recall the only adjustable parameter in our calculation is the attractive force strength parameter $C$. Its value is chosen to exactly reproduce the experimental frequency shift at atmospheric pressure (i.e., the lowest density data point). The density dependence is then computed with no adjustable parameters. It is interesting to note the very different behavior of the three modes. From Table IV, we see the quantitative source of the various trends. The C–C isobutylene mode has the largest repulsive interaction and the smallest attractive contribution. The former result is a consequence of the totally symmetric breathing structure of the C–C normal
TABLE IV. Frequency shifts for selected density states of the C≡C and C−C modes of isobutylene, and the C−O stretch of acetone. The temperature is 25°C in all cases. Frequencies are expressed in cm−1.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(\rho^2)</th>
<th>(\Omega_{\alpha\beta})</th>
<th>(\Omega_{\alpha\gamma})</th>
<th>(\Omega_{\alpha\delta})</th>
<th>(\Omega)</th>
<th>(\Omega_{\text{res}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
<td>0.744</td>
<td>2.05</td>
<td>−8.75</td>
<td>−7.4</td>
<td>−6.7</td>
<td>−6.7 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.828</td>
<td>2.69</td>
<td>−9.74</td>
<td>−7.05</td>
<td>−7.0</td>
<td>−6.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.867</td>
<td>3.97</td>
<td>−10.20</td>
<td>−7.13</td>
<td>−7.15</td>
<td>−6.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.919</td>
<td>3.78</td>
<td>−10.81</td>
<td>−7.63</td>
<td>−7.05</td>
<td>−6.55</td>
</tr>
<tr>
<td></td>
<td>0.954</td>
<td>4.35</td>
<td>−11.22</td>
<td>−6.9</td>
<td>−6.8</td>
<td>−6.55</td>
</tr>
<tr>
<td></td>
<td>0.978</td>
<td>4.70</td>
<td>−11.50</td>
<td>−6.8</td>
<td>−6.55</td>
<td></td>
</tr>
<tr>
<td>C−C</td>
<td>0.744</td>
<td>4.13</td>
<td>−3.13</td>
<td>−4.2</td>
<td>1.0</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.954</td>
<td>8.66</td>
<td>−4.02</td>
<td>4.64</td>
<td>4.65</td>
<td></td>
</tr>
<tr>
<td>C≡O</td>
<td>0.780</td>
<td>1.91</td>
<td>−24.71</td>
<td></td>
<td>−22.8</td>
<td>−22.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.944</td>
<td>3.32</td>
<td>−29.91</td>
<td></td>
<td>−26.6</td>
<td>−26.7</td>
</tr>
</tbody>
</table>

* Obtained from experimental density measurements (Refs. 26 and 38) and calculated rough hard sphere diameters of 4.9 Å for isobutylene (Ref. 26) and 4.55 Å for acetone.
* Calculated using Eqs. (4.30) and (4.30) and the appropriate values for \(\Omega_{\text{res}}\) and \(\Omega_{\text{res}}\) of 3.7 Å, while an atomic hard sphere diameter of 3.1 Å was used for the C≡O acetone bond.
* Calculated using Eq. (3.5).
* Calculated using Eq. (3.34) with \(N = 12\). The ionization energy of isobutylene was estimated to be 9.3 eV, the polarizability \(\beta\), and the polarizability derivatives are 1.9 Å² and 1.13 Å² for the C≡C and C−C modes, respectively.
* Experimental results of Refs. 26 and 38. Estimated experimental accuracies are as indicated.

mode which leads to a constructive interference between the solvent induced forces along the different bonds. For the C≡C mode the forces interfere destructively (See Appendix). The latter feature is consistent with the known ratio of the polarizability derivatives for the two isobutylene modes:25 \(\alpha_{CJC}/\alpha_{CJC} = 1.7\). In the case of acetone, the very large attractive forces are a consequence of the presence of both polarizability and large dipolar interactions.26 Figure 4 is a striking display of the sensitivity of the qualitative frequency shift trends on the relative magnitude and density dependence of the competing repulsive and attractive interactions.

As before one can estimate the red shift from "first principles" and compare it to the empirically determined value at 1 atm. In the case of isobutylene, only the dispersion interaction is important. We estimate the magnitude using the standard London formula [Eq. (3.34)] with the results shown in Table IV (for \(N = 12\)). The solvent dependence of the frequency shifts has been discussed previously23 using concepts motivated by our present work.

In closing this section we wish to emphasize that the success of our theory for the density dependence of the frequency shift, lends further concrete support for the physical picture of the role of slowly varying attractive forces developed in Secs. II and III. The dynamical manifestations of this picture should be equally accurate, and are investigated in the next section.

2. Dephasing and Raman linewidth

The vibration–rotation coupling was determined by computing the appropriate \(\partial \gamma / \partial Q\) using the normal mode analysis sketched in the Appendix. The angular momentum relaxation time is taken as \(\tau_L = 2.7 \tau_E\), where \(\tau_E\) is the molecular Enskog relaxation time. The latter estimate is consistent with the results (\(\gamma = 2–3\)) obtained on several systems using Chandler’s rough hard sphere theory.19 As previously noted, the final results are not very sensitive to this approximation because the vibration–rotation mechanism is a small effect (see Table V). Specific calculations were performed for \(N = 8\) and 12.

The individual linewidths contributed by the three mechanisms are displayed in Table V for isobutylene and acetone at atmospheric pressure. In all cases the line shape is significantly non-Lorentzian, in agreement with the experimental observations. The overall linewidths are within a factor of 2 of the experimental values while the relative linewidths of the isobutylene modes are in rough agreement with the experimental values. Note that the repulsive force contribution to the linewidth is approximately the same for both the isobutylene modes. Given that the anharmonic bond shifts are equal for the two modes, this result agrees with the hydrodynamic theory prediction. Also, the C−C mode of isobutylene has an appreciable vibration–rotation contribution. This arises because of the relatively larger values of \(\partial \gamma / \partial Q\) for this mode and the "in phase" breathing structure of the C−C stretch. In addition, the C−C mode has a larger \(\partial \gamma / \partial Q\) for rotation about the twofold symmetry axis of the planar molecule. One expects a relatively longer relaxation time for this motion and hence a larger contribution to the dephasing.

The isothermal density variation of the linewidths is shown in Fig. 5. Aside from the specification of a single value of \(N\), this dependence is computed with no adjustable parameters. The theoretical results are in good agreement with the experiments. Note the similarity between the density dependence of the linewidths and frequency shifts (see Fig. 4). The resulting density behavior is a nontrivial result of the competition between the rapidly and slowly varying forces, which individually
TABLE V. Linewidth calculations (in cm\(^{-1}\)) for isobutylene and acetone at various density states and a temperature of 25° C. Notation is identical to Table I. Results for the attractive force linewidth and corresponding total linewidth are presented for two choices of the parameter \(N=6\) and 12. The last entry is for acetone at 50° C.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(\rho_o^a)</th>
<th>(LW_R^a)</th>
<th>(LW_{VR}^b)</th>
<th>(LW_A)</th>
<th>(LW)</th>
<th>(LW_{exp.}^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C==C</td>
<td>0.744</td>
<td>0.76 (0.07)</td>
<td>2.46 (1.74)</td>
<td>2.98 (2.22)</td>
<td>5.10 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.828</td>
<td>1.02 (0.05)</td>
<td>1.97 (1.39)</td>
<td>2.60 (2.05)</td>
<td>4.85 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.954</td>
<td>1.61 (0.03)</td>
<td>1.43 (1.01)</td>
<td>2.49 (2.13)</td>
<td>4.4 (0.05)</td>
<td></td>
</tr>
<tr>
<td>C==C</td>
<td>0.744</td>
<td>0.82 (0.40)</td>
<td>0.88 (0.62)</td>
<td>1.70 (1.50)</td>
<td>2.50 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.828</td>
<td>1.11 (0.30)</td>
<td>0.71 (0.50)</td>
<td>1.72 (1.58)</td>
<td>2.6 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.954</td>
<td>1.72 (0.19)</td>
<td>0.51 (0.36)</td>
<td>2.04 (1.98)</td>
<td>2.95 (0.05)</td>
<td></td>
</tr>
<tr>
<td>C==O</td>
<td>0.780</td>
<td>0.89 (0.40)</td>
<td>0.97 (3.50)</td>
<td>5.48 (4.02)</td>
<td>4.60 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.894</td>
<td>1.29 (0.03)</td>
<td>4.12 (2.91)</td>
<td>4.87 (3.67)</td>
<td>4.10 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.944</td>
<td>1.61 (0.02)</td>
<td>3.65 (2.58)</td>
<td>4.60 (3.55)</td>
<td>3.80 (0.05)</td>
<td></td>
</tr>
<tr>
<td>50° C</td>
<td>0.730</td>
<td>0.80 (0.05)</td>
<td>5.52 (3.88)</td>
<td>6.00 (4.29)</td>
<td>5.05 (0.05)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Calculated using Eqs. (4.39)–(4.11).
\(^b\)Calculated using Eqs. (3.23) and (4.14) with \(\gamma=1,7\).

The dependence of the dephasing rate on temperature is usually quite weak. This is a general feature of dense liquids. At constant density, the effective hard sphere diameter is a decreasing function of temperature (typically, \(\sigma/\sigma_0=10^{-3}\)). This causes the Enskog collision rate to decrease, and for the isobutylene and acetone systems the corresponding repulsive force dephasing rate decreases (see Table V). Schindler and Jonas have measured the temperature dependence of the dephasing rate in isobutylene and acetone. For each mode, the isothermal density variation is roughly temperature independent, while the absolute magnitude of the linewidths is an increasing function of temperature. This behavior is consistent with the increased compressibility (and hence, increased attractive force inhomogeneous linewidth) at higher temperatures, and is reproduced by our theory. This behavior should be contrasted with the constant density experimental temperature dependence for the chloroform and methyl iodide systems considered in the next section. For these liquids, the dephasing rate is practically temperature independent (at constant density), which is in accord with the far greater importance of the repulsive force mechanism as compared to the inhomogeneous attractive contribution (see Table VI). The calculations were performed utilizing the experimental frequency at each temperature in the manner discussed in Sec. II A. The temperature-dependent hard sphere diameter and experimental density and compressibility were employed. The change in magnitude of the dephasing rate of acetone for a change in temperature of 25 to 50° C is listed in Table V. Note that the experimental ratio of the linewidth at 50° C to that at 25° C is 1.10 ± 0.02, while the theory yields 1.10 and 1.08 for \(N=6\) and 12, respectively.

Finally, we have computed the solvent dependence of the dephasing rate of the C=C mode of isobutylene at atmospheric pressure. The parameters (rough hard sphere diameters and densities) and experimental frequency shifts used to compute the relaxation rates in the various solvents are taken from Table I of Ref. 39. We neglect the vibration-rotation contribution since it is small (see Table V). The inhomogeneous attractive force contribution is computed using the experimental

![Relative change in linewidth as a function of density for the isobutylene and acetone modes at 25° C. Experimental results (Ref. 36 and 38) are denoted by solid dots with vertical error bars. The solid curves are the theoretical calculations for two values of \(N\). The repulsive atom-atom contribution for the C=C mode of isobutylene is displayed as the dashed curve. The C==O acetone and C==C isobutylene modes have nearly identical repulsive force contributions.](image-url)
TABLE VI. Calculated frequency shifts (cm⁻¹) at atmospheric pressure and 30°C, and linewidths (cm⁻¹) for various density states at 30°C for the chloroform and methyl iodide systems. Notation is same as in Tables I and V.

<table>
<thead>
<tr>
<th></th>
<th>(\rho^a)</th>
<th>(\langle \Omega_{\text{R}} \rangle)</th>
<th>(\langle \Omega_{\text{L}} \rangle)</th>
<th>(\Gamma_{\text{exp}}^b)</th>
<th>(\langle \Omega_{\text{exp}} \rangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>0.819</td>
<td>17.0</td>
<td>-29.0</td>
<td>-27.0</td>
<td>-12.0</td>
</tr>
<tr>
<td>CH₃I</td>
<td>0.918</td>
<td>9.5</td>
<td>-16.5</td>
<td>-13.8</td>
<td>-7.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>(\rho^b)</th>
<th>(LW_{\text{exp}}^c)</th>
<th>(LW_{\text{VR}})</th>
<th>(LW_{\text{A}})</th>
<th>(LW)</th>
<th>(LW_{\text{exp}}^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>0.819</td>
<td>11.13</td>
<td>(\cdots)</td>
<td>5.15</td>
<td>13.26</td>
<td>7.85</td>
</tr>
<tr>
<td>(N = 6)</td>
<td>0.861</td>
<td>13.80</td>
<td>(\cdots)</td>
<td>4.68</td>
<td>15.35</td>
<td>9.42</td>
</tr>
<tr>
<td>(N = 12)</td>
<td>0.937</td>
<td>16.93</td>
<td>(\cdots)</td>
<td>4.24</td>
<td>17.98</td>
<td>11.23</td>
</tr>
<tr>
<td>(N = 12)</td>
<td>0.978</td>
<td>19.59</td>
<td>(\cdots)</td>
<td>3.94</td>
<td>26.40</td>
<td>12.09</td>
</tr>
<tr>
<td>CH₃I</td>
<td>0.918</td>
<td>6.43</td>
<td>0.33</td>
<td>2.26</td>
<td>7.52</td>
<td>4.35</td>
</tr>
<tr>
<td>(N = 6)</td>
<td>0.955</td>
<td>7.38</td>
<td>0.29</td>
<td>2.09</td>
<td>8.22</td>
<td>4.78</td>
</tr>
<tr>
<td>(N = 6)</td>
<td>1.008</td>
<td>9.07</td>
<td>0.23</td>
<td>1.87</td>
<td>9.68</td>
<td>5.61</td>
</tr>
</tbody>
</table>

*Calculated using the density data of Refs. 60 and 61 and rough hard sphere diameters of 4.58 Å for methyl iodide and 4.80 Å for chloroform (Ref. 39).

*Calculated using Eq. (3.34) and \(N = 12\). The ionization energy and polarizability (Ref. 39) of chloroform and methyl iodide are 11.42 eV, 8.25 Å³ and 9.54 eV, 7.3 Å³, respectively.

*Calculated by subtracting the gas phase (Ref. 62) and condensed phase (Refs. 60 and 61) values.

*Calculated using Eqs. (4.9)–(4.11) with atomic hard sphere diameters of 2.5 Å (hydrogen), 3.2 Å (carbon), 3.7 Å (methyl group), and 4.0 Å (iodine).

References 50 and 61.

The frequency shifts at atmospheric pressure were computed as described in Sec. IV. The results are displayed in Table VI. For simplicity, the C-H and CH₃-I bonds were modeled as homonuclear diatomics (with bond lengths of 1.09 and 2.1 Å, respectively, and atomic

frequency shifts in conjunction with Eq. (3.5), experimental compressibilities, and \(N = \rho_{\text{sol}} / \rho_{\text{solvent}}\), where \(\rho_s\) is the density of the solvent of interest. The results are displayed as a correlation plot in Fig. 6. For all cases the repulsive contribution to the linewidth was larger than in pure isobutylene, while the attractive inhomogeneous broadening was always smaller. The lack of a strong correlation should be judged in light of several factors. Accurate calculation of the solvent dependence is considerably more difficult than the thermodynamic state dependence of a single system because of the sensitivity to the specific nature of the repulsive and attractive interactions (e.g., dependence on molecular shape and anisotropy effects on \(N\)). In addition, the solvent variation of the dephasing is rather small. In our case, the experimental linewidths (excluding acetonitrile) vary only over the range 4.25–5.35 cm⁻¹, a 25% change. Our calculations reflect a similar insensitivity. This is a nontrivial result since the physical factors that enter the problem vary over a much wider range. For example, compressibility varies from 0.015 (C₂H₅Br) to 0.048 (C₂H₅I), while the attractive force frequency shift varies from -7.9 to -13.6 cm⁻¹. Any attempt to correlate the solvent scaling with viscosity, collision rate, compressibility, or other predictions of simple theories based on a single dephasing mechanism fails completely. Clearly, the solvent dependence is a complex phenomena that reflects the competing influences of the detailed repulsive and attractive solute-solvent interactions.

B. Methyl iodide and chloroform

For these systems, the anharmonic bond shifts \(Q_{11} - Q_{00}\) were calculated using Morse bond potentials. For chloroform a force constant, \(k\), of 2.5 \times 10⁻⁹ dyn/Å and Morse length parameter \(a\) equal to 2 Å⁻¹ were used²⁹ \(\left[Q_{11} - Q_{00} = 3 \alpha \pi / (2k\mu)^{1/2}\right]\), where \(\mu\) is the reduced mass. For methyl iodide, a value of 1.19 \times 10⁻¹⁰ cm was obtained using a bond dissociation energy of 56 kcal/mol²⁹ \(\left[Q_{11} - Q_{00} = 3 \hbar / (2\mu\alpha\beta)^{1/2}\right]\).

The frequency shifts at atmospheric pressure were computed as described in Sec. IV. The results are displayed in Table VI. For simplicity, the C-H and CH₃-I bonds were modeled as homonuclear diatomics (with bond lengths of 1.09 and 2.1 Å, respectively, and atomic

FIG. 6. Calculated solvent dependence of the C=C isobutylene linewidth at 20°C and atmospheric pressure. Results are displayed as a correlation plot of the experimental linewidth (Ref. 39) vs. the theoretical calculation. Estimated experimental uncertainties (Ref. 39) are denoted by the vertical lines. The numbers refer to the specific solvents: (1) CH₃CN, (2) C₂H₅Cl, (3) CH₃I, (4) C₂H₅Br, (5) C₂H₅I, (6) C₂H₅CH₂, (7) C₂H₅N, (8) C₂H₅, (9) C₂H₅Cl, and (10) CHCl₃.

hard sphere diameters of 3 and 3.8 Å, respectively) for the purpose of calculating the repulsive force frequency shifts. Selected linewidth results for the nearly Lorentzian lines are presented in Table VI. The vibration–rotation contribution for methyl iodide was computed using the experimentally measured \( \tau_2 \) (for this case \( \tau_2 = 2.9 \tau_1 \) at 1 atm) while for chloroform this mechanism is negligible because of the small moment of inertia change associated with the proton stretch. As before, the absolute magnitude of the dephasing rate is within a factor of 2 of the experimental value. Closer agreement would be fortuitous. For the repulsive force contribution, our results are in good agreement with the hydrodynamic theory concerning the relative importance of anharmonic bond shift contribution with respect to the harmonic part. However, our rates are smaller than those predicted by that theory (8.35 cm\(^{-1}\) for CH\(_2\)I and 26.6 cm\(^{-1}\) for CHCl\(_3\)). The cause of the difference is probably twofold: the use of the macroscopic viscosity yields an estimate of the collision rate which is typically a factor of 2 larger than that obtained from the hard sphere Enskog theory; the independent atom assumption probably overestimates forces by neglecting to project these forces along bonds.

The isothermal density variation of the linewidths is presented in Figs. 7 and 8. Note that the independent binary collision theory \( [LW - \tau_2^2(p)] \) predicts too rapid a density dependence, while the hydrodynamic theory \( [LW - \eta(p)] \) is even more quickly varying. The former behavior is a result of the neglect of the attractive force contribution, while the latter follows from the use of the macroscopic viscosity (which is more rapidly varying than the Enskog collision rate) in addition to the neglect of attractions. These observations, coupled with the good agreement of our theory with experiment, demonstrate that even for the more “traditional” systems that exhibit a monotonically increasing dephasing rate as a function of density, the role of the slowly varying attractive forces is non-negligible.

Finally, the sensitivity of our results to the static inhomogeneous broadening \( (T_\omega = \infty) \) assumption has been investigated using Eq. (2.11). Representative results are collected in Table VII. The chloroform and methyl iodide calculations are virtually independent of the attractive force correlation time (which should be an increasing function of density). The isobutylene results are not quite as insensitive, but certainly for \( T_\omega \geq 4 \) ps the qualitative trends are not changed. Indeed, since our theory for isobutylene underestimates the absolute magnitude of the dephasing rate by approximately a factor of 2, the actual dependence on \( T_\omega \) should be considerably less than seen in Table VII.

VI. DISCUSSION

A major emphasis of this work has been the role of relatively slowly varying forces, usually attractions, on
the vibrational frequency shift and dephasing rate of polyatomic molecules in dense liquids. Even though the relative force fluctuation are small (AF/kB) < 1 their effect on the dephasing process is significant because the mean attractive forces (F_a) can be large. It is these mean forces which are responsible for spectral red shifts. With the proper perspective, we believe the separation in time scales between the repulsive and attractive force fluctuations is generally valid. However, the quantitative value of the attractive force relaxation time is an open question. We have avoided addressing this problem by arguing that for polyatomic molecules, the dephasing time (as measured by Raman scattering) is short compared to the attractive force relaxation time. This allows the static, Gaussian inhomogeneous approach to the calculation of the effects of the attraction on the line shape. Even if T_o were comparable to T_a, the static approach would be qualitatively correct.

The theory of slowly varying forces developed here may be relevant to several other phenomena in condensed phases. The infrared and Raman absorption of small molecules dissolved as impurities in rare gas matrices often exhibit large spectral red shifts. Slowly varying dispersion and/or dipolar interactions may play an important role in these systems. Another class of experiments involves the electronic absorption of molecules dissolved in both liquid and solid media. Okamoto and Drickamer have made an extensive study of the solvent and pressure dependence of the Gaussian inhomogeneously broadened lines. These workers suggest a rough scaling of the width with the isothermal compressibility and attractive force parameters (which include both polarizability and dipole properties). Our theory may allow a quantitative explanation of these measurements. Finally, the density, temperature, and solvent dependence of vibrational second moment measurements should also be interpretable within our general framework.

In conclusion, we believe we have developed the first quantitative theory for the simultaneous influence of atom-atom repulsions, vibration-rotation coupling, and slowly varying attractions on the thermodynamic state dependence of the dephasing of polyatomic vibrations in dense liquids. The significant role played by the slowly varying attractive forces for the systems studied in this paper seems to be a general phenomena, not restricted to hydrogen bonded liquids or proton stretching vibrations. The presence of competing processes with very different thermodynamic state dependence precludes any simple scaling behavior of the dephasing rate based on a single mechanism. However, the sensitivity of the dephasing phenomena to the relative magnitudes of the repulsive and attractive forces holds the promise that thermodynamic state-dependent studies can lead to valuable insights concerning questions of structure and dynamics in dense liquids.

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APPENDIX

We sketched the normal mode analysis and anharmonic bond shift calculations for the carbon stretching vibrations of isobutylene (analysis of the C=O stretch of acetone is identical). There are three symmetric (A_t) carbon vibrations for the planar C=C isobutylene molecule: C=C stretch (1664 cm⁻¹), C-C stretch (804 cm⁻¹), and the CCC bond bend (378 cm⁻¹). For these vibrations, we can treat the protons as nonvibrating entities, and hence isobutylene can be characterized by four masses: C, CH₃, and 2 CH₂ sites. Furthermore, since we are not interested in the bond bending mode, and because it involves nonbonded interactions, we neglect the "springs" (i.e., vibrational interaction energy) coupling the two methyl groups and the methylene group with the methyl groups. Such a simplification makes little error because the energy associated with these springs is small and plays a minor role in determining the character of the C-C and C=C vibrations. The neglect of bond bending allows the problem to be reduced to only three relevant degrees of freedom, and two unspecified spring constants. If accurate values of anharmonic bond shift were available, then a more precise normal mode analysis may be warranted and could be easily accomplished.
Removing the center of mass translation, the secular determinant problem is solved in the usual way.\textsuperscript{57} The spring constant are chosen to reproduce the observed gas phase normal mode frequencies. Solution of the eigenvector problem allows the atomic coordinates (relative to equilibrium values) for the four masses to be expressed in terms of the normal mode coordinates (following notation of Ref. 57)

\begin{equation}
\eta_i = \sum_i \alpha_{ij} Q_j .
\end{equation}

The force exerted by the solvent along the normal coordinate $Q$ can then be written as

\begin{equation}
\frac{\delta V}{\delta Q} = \sum_i \alpha_{ij} \left( \frac{\delta Y}{\delta \eta_i} \right) .
\end{equation}

This can then be related to the forces along the bonds by expanding,

\begin{equation}
\frac{\delta V}{\delta \eta_i} = \sum_j \frac{\delta V}{\delta \eta_j} \frac{db_j}{dn_i} ,
\end{equation}

where $b_j$ is a bond vector (one H$_2$C=C bond and two C=CH$_2$ bonds), and we have neglected solvent induced forces along bond bending directions because the normal mode problem has been solved ignoring the change in vibrational energy associated with these motions. The numerical results of these calculations are

\begin{equation}
\langle \frac{\delta V}{\delta Q} \rangle = \langle F \rangle = \left( \frac{3}{4} \right) \sum_i c_i \langle F_i \rangle ,
\end{equation}

where

\begin{align}
c_1 &= 1.228, & \text{for} & \text{C=C mode} \\
c_2 &= 0.102, & \text{for} & \text{C--C mode} \\
c_3 &= c_4 = 0.251, & \text{for} & \text{C=C mode} \\
c_5 &= 0.747, & \text{for} & \text{C--C mode} ,
\end{align}

and $M$ is the mass of a methyl group with $\langle F \rangle$ and $\langle F_2 \rangle$ the solvent induced forces along the C=CH$_2$ and C=CH$_3$ bonds, respectively. Note that there is destructive interference between the solvent induced forces along the C=C and C=C bonds for the C=C mode. This arises because the atomic motions are out of phase, while the C=C stretch is a "breathing" mode (i.e., equilibrium molecular framework is totally preserved) and hence, the forces along the different bonds add constructively. As discussed in Sec. III, a similar analysis can be carried out for $\langle F \rangle = \langle \frac{\delta V}{\delta Q} \frac{\delta V}{\delta Q} \rangle$

The anharmonic bond shifts $Q_{11} - Q_{00}$ can be estimated by modeling the "spring" bond potential energy between sites as Morse functions. Relating the atomic displacements to the normal coordinates via the eigenvector transformation matrix, and expanding the potential energy through cubic order in the normal coordinates one obtains

\begin{equation}
V = \frac{1}{2} \sum_{i=1}^{3} \frac{\omega_i^2}{2} Q_i^2 + K_{11} Q_1^2 + K_{22} Q_2^2 + K_{12} Q_1 Q_2 + K_{33} Q_3^2 Q_2 + K_{31} Q_1 Q_2^2 ,
\end{equation}

where the subscripts 1 and 2 refer to the C=C and C--C modes, respectively. The cubic coefficients $K_{ij}$ can be computed from the normal mode expansion coefficients $a_{ij}$, the harmonic frequencies, and bond dissociation energies. First order quantum-mechanical perturbation theory yields

\begin{equation}
Q_{11} - Q_{00} = -6 C_{00} \hbar / 2 \omega_0^2 .
\end{equation}

Using average C-C and C=C bond energies\textsuperscript{39} for the dissociation constants leads to the numerical results discussed in Sec. V.
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