

Vibrational relaxation in supercritical fluids near the critical point

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We present a theory for the temperature and density dependence of the vibrational lifetime T_1 and the vibrational line position ν of a solute in a supercritical solvent, both close to and far from the critical point. The theory is based on the relation between a classical force correlation function and T_1 and ν . The force correlation function is determined from density functional theory, and can be expressed in terms of the solvent structure factor and the solute–solvent direct correlation function, thereby allowing physical properties in the region of large critical fluctuations to be described by various phenomenological scaling laws. The theory has been used to investigate recent experiments on the density dependence of the lifetimes and frequencies of the asymmetric CO stretching mode of $W(\text{CO})_6$ in supercritical ethane. Near the critical point, the experimental data are essentially independent of the density over a fairly broad range of densities. This behavior is ascribed to the existence of long-range correlations in the fluid mixture near the critical point. Such correlations, manifested in the divergence or vanishing of thermodynamic quantities, are shown to essentially eliminate the density dependence in the static and dynamic correlation functions that enter the theory. Because it is the anomalous thermodynamics near the critical point that ultimately governs changes in T_1 and ν , the results are not dependent on specific intermolecular interactions. The lack of a theoretical dependence on specific intermolecular interactions is supported by experiments that display the same behavior for various solute/solvent systems. © 1997 American Institute of Physics. [S0021-9606(97)52443-3]

I. INTRODUCTION

Vibrational relaxation—the loss of vibrational energy from an initially excited vibrational mode of a molecule—is of fundamental importance to solution phase chemistry. Among other things, it can influence the rates of chemical reactions, and it is involved in processes such as electron transfer.¹ The development of infrared picosecond laser sources has made it possible to measure the vibrational relaxation of molecules in liquids directly.² Such studies have recently demonstrated that the temperature dependence of vibrational relaxation can be strongly influenced, not only by thermal fluctuations, but also by the change in liquid density that accompanies a temperature change.³ An understanding of vibrational relaxation, therefore, requires knowing how it depends both on density at fixed temperature and on temperature at fixed density. Supercritical fluids (SCF's) are probably the ideal environment in which to explore such questions, since their temperature and density can be varied independently. Because SCF's have widespread applications in industry, their study is also important in its own right.⁴

Although there have been experimental and theoretical studies of vibrational energy transfer in supercritical fluids (I_2 in Xe, for instance⁵), such studies have, until recently, been confined to temperatures and/or densities distant from the corresponding critical values. Since vibrational relaxation is driven by the fluctuations of the medium, and since the neighborhood of the critical point is highly nonuniform, the possibility of observing novel vibrational phenomena in this

region of the phase diagram is especially strong.

These expectations are borne out by recent infrared vibrational experiments from this laboratory on the vibrational dynamics of carbonyl moieties dissolved in supercritical solvents, which have produced some intriguing results.⁶ One set of experiments records the absorption frequencies ν of the asymmetric CO stretching mode of dilute $W(\text{CO})_6$ in SCF solvents such as carbon dioxide, ethane, and fluoroform. The other monitors the lifetimes, T_1 , of the same mode under the same conditions. Both ν and T_1 are measured over a wide range of densities ρ at fixed temperatures T of the solvent. The measurements are made close to and away from the critical point of the solvent (ρ_c, T_c). For values of ρ and T distant from ρ_c and T_c , ν and T_1 decrease smoothly with density at fixed temperature. This is the behavior that one might have anticipated: increasing the density increases the contributions to the vibrational potential from attractive solute–solvent interactions, which tend to shift absorption frequencies toward the red.⁷ Increasing the density also increases the magnitude and frequency of the fluctuating forces experienced by the CO stretch, which increases the probability of dissipative exchange of excess vibrational energy, and so decreases lifetimes.

Something rather unexpected occurs in the neighborhood of the critical point, however; when $T \approx T_c$ and ρ ranges between about 0.73 and 1.2 ρ_c (these ranges vary somewhat from solvent to solvent: the quoted value refers to ethane), both ν and T_1 cease to change with density. On the face of it, there is no obvious reason why this should happen. If anything, given the anomalous thermodynamics near the critical point,⁸ rather more dramatic changes to these properties might have been expected. To be sure, there are extended

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regions of uniform density near the critical point that could, in principle, provide the kind of constant solvent environment necessary to eliminate the density dependence of ν and T_1 . But such regions fluctuate across a wide range of length scales, so the *measured* values of ν and T_1 , which represent spatial and temporal averages of local properties, are likely to be quite different.

One possible rationalization of these observations is that something akin to condensation takes place, in which molecules of the solvent form stable, relatively long-lived shells around the solute. Thus, changing the bulk density at constant temperature would have essentially no effect on the solute's immediate surroundings. This is essentially the "clustering" phenomenon often invoked in the literature on supercritical mixtures.⁴ Whether a clustering mechanism is necessary to explain the experimental data, or other mechanisms can be responsible for the lack of density dependence near the critical point, is the question we shall attempt to answer theoretically in this paper.

As discussed in the following section, our approach is elaborated around a model of vibrational relaxation that starts from a forced harmonic oscillator representation of the vibrational mode of $\text{W}(\text{CO})_6$. An important ingredient of the theory is the evaluation of a time-dependent force correlation function using density functional methods. This approach is useful in immediately allowing the measurable properties of the system to be expressed in terms of thermodynamic functions that can be studied in both critical and noncritical limits. The objective here is less to achieve quantitative agreement with the experimental data than to provide a framework for identifying the physical phenomena that might be responsible for anomalous behavior. To this end, the method ensures that the effects of critical fluctuations can be incorporated into the theory through well-known thermodynamic scaling relations. The results are rather surprising. Near the critical point, as a result of the divergence of the correlation length of the density fluctuations, all of the factors that could potentially lead to density-dependent frequencies and lifetimes, including the direct correlation function, scale out of the problem. Thus, despite the expected importance of short distance effects in controlling vibrational relaxation, it is the universal critical properties of the medium that seem ultimately to be responsible for what is observed. Experiments with other solute/solvent combinations, which exhibit the same behavior, suggest that this may, in fact, be the case.⁶ Specific solute-solvent clustering need not be invoked in order to reproduce the observed vibrational anomalies near the critical point.

The details of the above formalism are presented in Sec. II, while Sec. III discusses the results and conclusions.

II. THEORY

A. Lifetimes

Fermi's golden rule of time-dependent perturbation theory is the standard starting point for relating excited state lifetimes to various quantum mechanical averages.⁹ In particular, the vibrational lifetime, T_1 , can be shown to be in-

versely proportional to a dynamic force correlation function, as discussed, for instance, in Refs. 10 and 11. In this section, we sketch an alternative route to this result, based on path integrals, which we believe is somewhat more transparent, and possibly more easily extended to other situations.

We begin by representing the vibrational mode of the carbonyl by a harmonic oscillator of mass m and natural frequency ω , and its interactions with the solvent by a fluctuating force $F(t)$. This leads to the following Hamiltonian H for the system:

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 + F(t)x, \quad (1)$$

where p is the momentum of the oscillator and x its displacement from equilibrium. (For a molecule like $\text{W}(\text{CO})_6$, x represents the displacement of the normal coordinate.) The quantity of interest is the probability P_{mn} that the oscillator makes a transition from the m th excited vibrational state of the molecule to its n th excited state in the time t . This is proportional to the absolute square of the transition amplitude G_{mn} for this process, which can be written as¹²

$$G_{mn} = e^{iE_m t/\hbar} \int dx_a \int dx_b \phi_m(x_b) K(x_b, t; x_a, 0) \phi_n(x_a), \quad (2)$$

where E_m is the m th oscillator energy eigenvalue, $\phi_m(x)$ is the corresponding eigenfunction, defined by

$$\phi_m(x) = \frac{1}{\sqrt{2^m m!}} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} H_m(x\sqrt{m\omega/\hbar}) e^{-m\omega x^2/2\hbar}, \quad (3)$$

H_m is the Hermite polynomial of order m , \hbar is Planck's constant divided by 2π , and $K(x_b, t; x_a, 0)$ is the Feynman propagator, which has been determined exactly for the Hamiltonian of Eq. (1) as¹²

$$K(x_b, t; x_a, 0) = \sqrt{\frac{m\omega}{2i\pi\hbar \sin(\omega t)}} \exp(iS_{\text{cl}}/\hbar), \quad (4)$$

where S_{cl} is the classical action, given by

$$S_{\text{cl}} = \frac{m\omega}{2 \sin(\omega t)} [(x_a^2 + x_b^2) \cos(\omega t) - 2x_a x_b + x_b I_a + x_a I_b - I_{ab}], \quad (5a)$$

with

$$I_a = \frac{2}{m\omega} \int_0^t dt_1 F(t_1) \sin(\omega t_1), \quad (5b)$$

$$I_b = \frac{2}{m\omega} \int_0^t dt_1 F(t_1) \sin(\omega(t-t_1)), \quad (5c)$$

and

$$I_{ab} = \frac{2}{m^2 \omega^2} \int_0^t dt_1 \int_0^{t_1} dt_2 F(t_1) F(t_2) \sin(\omega(t-t_1)) \sin(\omega t_2). \quad (5d)$$

In the experiments described earlier,⁶ vibrational relaxation occurs from the first excited state of the carbonyl stretching mode, so for this case the required probability can be shown to be

$$P_{10} \propto |G_{10}|^2 = \frac{1}{m\hbar\omega} \exp\left\{-\frac{1}{m\hbar\omega} \int_0^t dt_1 \int_0^{t_1} dt_2 \times F(t_1)F(t_2)\cos(\omega(t_1-t_2))\right\} \times \int_0^t dt_1 \int_0^{t_1} dt_2 F(t_1)F(t_2)\cos(\omega(t_1-t_2)). \quad (6)$$

We shall assume that the coupling between the oscillator and reservoir is sufficiently weak that Eq. (6) can be approximated by

$$|G_{10}|^2 \approx \frac{1}{m\hbar\omega} \int_0^t dt_1 \int_0^{t_1} dt_2 F(t_1)F(t_2)\cos(\omega(t_1-t_2)). \quad (7)$$

This expression is now averaged over the quantum mechanical states of the bath, and the result rewritten in terms of a time-symmetrized anticommutator,¹¹ which yields

$$\langle |G_{10}|^2 \rangle = \frac{2}{m\hbar\omega} \frac{1}{1+e^{-\beta\hbar\omega}} \int_0^t dt_1 \int_0^{t_1} dt_2 \times \left\langle \frac{1}{2} [F(t_1), F(t_2)]_+ \right\rangle \cos(\omega(t_1-t_2)), \quad (8)$$

where $\beta = 1/k_B T$. Because of time translational invariance, Eq. (8) in turn becomes

$$\langle |G_{10}|^2 \rangle = \frac{2}{m\hbar\omega} \frac{1}{1+e^{-\beta\hbar\omega}} \int_0^t dt_1 (t-t_1) \times \left\langle \frac{1}{2} [F(t_1), F(0)]_+ \right\rangle \cos(\omega t_1) \quad (9a)$$

$$\equiv \frac{2}{m\beta\hbar\omega} \frac{1}{1+e^{-\beta\hbar\omega}} \times \int_0^t dt_1 (t-t_1) \zeta(t_1) \cos(\omega t_1), \quad (9b)$$

where Eq. (9b) defines a time-dependent quantum mechanical friction coefficient.¹¹ The rate of transition k_{10} between the excited and ground states can now be obtained as

$$k_{10} = \frac{2}{m\beta\hbar\omega} \frac{1}{1+e^{-\beta\hbar\omega}} \times \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt_1 (t-t_1) \zeta(t_1) \cos(\omega t_1) = \frac{2}{m\beta\hbar\omega} \frac{1}{1+e^{-\beta\hbar\omega}} \tilde{\zeta}'(\omega), \quad (10)$$

where $\tilde{\zeta}'(\omega)$ is the real part of the Fourier transform of $\zeta(t)$ evaluated at the frequency of the oscillator.

The vibrational lifetime T_1 is related to the rate of change of the average energy of the oscillator, which depends on k_{10} and the upward transition rate k_{01} . As shown by Bader and Berne,¹¹ this relationship is given by $T_1^{-1} = 2 \tanh(\beta\hbar\omega/2) \tilde{\zeta}'(\omega) / m\beta\hbar\omega$. The quantum mechanical friction coefficient is not easily determined, but for relaxation processes that proceed by the emission or absorption of a single reservoir phonon, it can be expressed in terms of a classical friction coefficient. For such processes, $\tilde{\zeta}'(\omega) = \beta\hbar\omega \coth(\beta\hbar\omega/2) \tilde{\zeta}'_{cl}(\omega)/2$, where $\tilde{\zeta}'_{cl}(\omega)$ is the classical counterpart of $\tilde{\zeta}'(\omega)$.¹³ Now in general, the excess vibrational energy of a high frequency mode of a polyatomic solute in a polyatomic solvent is most easily dissipated if it is transferred to other relatively high frequency vibrational modes on the solute or solvent. The relaxation to these modes (which typically are not thermally populated, and which consequently contribute little to the overall temperature dependence of vibrational relaxation) will, in addition, require the excitation of a small number of low frequency reservoir phonons to conserve energy overall. In the simplest case, only a single phonon is required for energy conservation. We shall assume, for convenience, that this is the relevant case for the experiments described here. [Our focus in this paper is primarily on the density dependence of lifetimes and frequencies, so the precise form of the temperature prefactor in Eq. (10) and related expressions is not of central importance. But it should be noted that multiphonon excitation can modify the temperature dependence of T_1 significantly—its study is currently under investigation.¹³] Within the one-phonon approximation, T_1 can be determined using the above expression for the friction coefficient, which in terms of a classical force autocorrelation function now becomes

$$T_1^{-1} = \frac{\beta}{m} \int_0^\infty dt \langle F(t)F(0) \rangle_{cl} \cos(\omega t). \quad (11)$$

The calculation of the lifetime is thus reduced to the problem of calculating $\langle F(t)F(0) \rangle$. This is a problem that immediately raises a number of difficult technical issues. For instance, it is clear from the experimental data that there is a significant degree of coupling between the slowly varying, long wavelength density fluctuations of the solvent and the high frequency, short distance oscillations of the solute, despite the apparently fundamental differences in character of vibrational and critical phenomena. It is far from clear, however, how this coupling occurs. Nor is it clear how, from a theoretical perspective, these two processes can be treated together when their characteristic time and length scales are so widely separated. Projection operator techniques or influence functional methods would seem to provide the natural framework within which to consider the problem, but neither is likely to be easy to implement here. Even if that were not the case, the results of such analyses would very likely involve parameters whose relationship to the actual properties of the system remained obscure.

On the other hand, molecular processes *have* been successfully described in terms of bulk properties. For instance,

the translational and rotational diffusion of individual molecules, which depend on local fluctuating forces, can be related to the viscous properties of the surrounding medium (represented as a continuum) using hydrodynamics. Such treatments lead to results such as the Stokes–Einstein and the Debye–Stokes–Einstein equations for translational and rotational diffusion, respectively. Indeed, vibrational relaxation itself has been studied by such methods, notably by Zwanzig¹⁴ in an early critique of the isolated binary collision model, in which he showed that the rate of transition of a molecule from its first excited vibrational states to the ground state can be described in terms of the solvent's self-diffusion coefficient. Related hydrodynamic models have been surveyed by Oxtoby¹⁵ in his review of vibrational population relaxation. Furthermore, it is often possible to extend the range of validity of relations that are expressed in terms of equilibrium structural or transport coefficients by replacing them with wave vector or frequency dependent analogs. In the context of vibrational relaxation, extensions of this kind have been developed by Metieu *et al.*,¹⁶ building upon the work of Zwanzig and Bixon¹⁷ on a hydrodynamic calculation of the velocity autocorrelation function. These considerations suggest that a fruitful approach to the calculation of $\langle F(t)F(0) \rangle$ might be (at least initially) to develop a largely thermodynamic or hydrodynamic description of the correlation function, and then subsequently (as needed) to include more and more molecular detail by the means discussed above.

To this end, we will regard F in Eq. (11) as a thermodynamic force, and determine it using density functional methods,¹⁸ the starting point of which is the following density functional expansion of the Helmholtz free energy:^{19,20}

$$\begin{aligned} \beta A[\rho_i(\mathbf{r})] = & \sum_i \int d\mathbf{r} \rho_i(\mathbf{r}) [\ln \rho_i(\mathbf{r}) / \rho_i^0 - 1] \\ & - \frac{1}{2} \sum_{i,j} \int d\mathbf{r} \int d\mathbf{r}' C_{ij}(\mathbf{r}-\mathbf{r}') \\ & \times \delta\rho_i(\mathbf{r}) \delta\rho_j(\mathbf{r}') + \dots, \end{aligned} \quad (12)$$

where $\rho_i(\mathbf{r})$ is the local density of the i th component at the point \mathbf{r} , ρ_i^0 is the mean density of that component, $\delta\rho_i(\mathbf{r})$ is the density fluctuation at \mathbf{r} , i.e., $\delta\rho_i(\mathbf{r}) = \rho_i(\mathbf{r}) - \rho_i^0$, and $C_{ij}(\mathbf{r}-\mathbf{r}')$ is the two-particle direct correlation function between components i and j located at positions \mathbf{r} and \mathbf{r}' . The right-hand side of Eq. (12) represents the first two terms of an infinite expansion in powers of the density fluctuation, the coefficients of which are multiparticle direct correlation functions. This expression for the free energy is most often used in studies of dense fluids,²¹ where density fluctuations are typically small, and the series may be safely truncated at second order. If density fluctuations are large, as is the case near a critical point, it is not entirely clear whether cubic and quartic contributions to (12) are important. However, since these contributions are associated with three- and four-body direct correlation functions, which are likely to be small, (12) may well be an adequate approximation even near the critical

point. In the absence of any definite information that would resolve this issue one way or the other, we use Eq. (12) as it stands.

The effective potential $V^{(i)}(\mathbf{r})$ that determines the equilibrium density distribution $\rho_i(\mathbf{r})$ of the i th component is obtained from the requirement of the vanishing of the local chemical potential, which is the functional derivative of the free energy with respect to $\rho_i(\mathbf{r})$. This yields

$$\rho_i(\mathbf{r}) = \rho_i^0 \exp(-\beta V^{(i)}(\mathbf{r})), \quad (13)$$

where

$$\beta V^{(i)}(\mathbf{r}) \equiv - \sum_j \int d\mathbf{r}' C_{ij}(\mathbf{r}-\mathbf{r}') \delta\rho_j(\mathbf{r}'). \quad (14)$$

If $i=1$ denotes the solvent and $i=2$ the solute, and if, further, the solution is assumed to be infinitely dilute [as is the case in the experiments with $\text{W}(\text{CO})_6$], then the potential acting on the fixed solute at \mathbf{r} is simply

$$\beta V^{(2)}(\mathbf{r}) = - \int d\mathbf{r}' C_{21}(\mathbf{r}-\mathbf{r}') \delta\rho_1(\mathbf{r}'), \quad (15)$$

and the corresponding force [which we shall denote $\delta\mathbf{F}^{(2)}(\mathbf{r})$] is $-\partial V^{(2)}(\mathbf{r})/\partial\mathbf{r}$. The generalization of these results to time t involves the replacement of $\delta\rho_1(\mathbf{r})$ by $\delta\rho_1(\mathbf{r}, t)$. We now make the identification

$$\langle F(t)F(0) \rangle \equiv \frac{1}{3V} \int d\mathbf{r} \langle \delta\mathbf{F}^{(2)}(\mathbf{r}, t) \cdot \delta\mathbf{F}^{(2)}(\mathbf{r}, 0) \rangle, \quad (16)$$

where V is the volume of the system, and the integral over \mathbf{r} represents an average over all spatial locations of the fixed solute. Rewriting this expression in Fourier space, and substituting the result into Eq. (11), we can now show that

$$T_1^{-1} \propto T \int_0^\infty dt \cos(\omega t) \int d\mathbf{k} k^2 |\hat{C}_{21}(\mathbf{k})|^2 \hat{S}_1(\mathbf{k}, t), \quad (17)$$

where constants independent of density and temperature have been omitted. Here $\hat{C}_{21}(\mathbf{k})$ is the Fourier transform of the two-particle direct correlation function between solute and solvent, and $\hat{S}_1(\mathbf{k}, t)$ is the dynamic structure factor of the solvent, defined by

$$\hat{S}_1(\mathbf{k}, t) = \langle \delta\hat{\rho}_1(\mathbf{k}, t) \delta\hat{\rho}_1(-\mathbf{k}, 0) \rangle, \quad (18)$$

with

$$\delta\hat{\rho}_1(\mathbf{k}, t) = \frac{1}{(2\pi)^3} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \delta\rho(\mathbf{r}, t). \quad (19)$$

Equation (17) is the key relation between the excited state lifetime and measurable properties of the system. The integral over k in this relation has the range $0 \leq k \leq \infty$, so it would seem that both long and short distance contributions to T_1 have been incorporated into the theory. However, since the relation has been derived on the basis of a force that is thermodynamic in origin, there would probably be some inconsistency in allowing k to assume very large values. Accordingly, we introduce a cutoff Λ on the k integral, so that Eq. (17) is essentially restricted to relatively long wavelength

regimes. We shall later assign a definite value to λ using information about the thermodynamic properties of the system, specifically its correlation length.

In this context, we determine $\hat{S}_1(\mathbf{k}, t)$ from hydrodynamics as the solution to the coupled equations for the conservation of mass, momentum, and energy, which leads to⁸

$$\hat{S}_1(\mathbf{k}, t) = \hat{S}_1(\mathbf{k}) e^{-D_T k^2 t} \left[1 - \frac{1}{\gamma} \{ 1 - \cos(c_s k t) e^{-(\Gamma - D_T) k^2 t} \} \right]. \quad (20)$$

Here $\hat{S}_1(\mathbf{k})$ is the equilibrium structure factor of the solvent, which we approximate by the Ornstein–Zernike expression, given by⁸

$$\hat{S}_1(\mathbf{k}) = \frac{\rho_1 \kappa_T / \kappa_T^0}{1 + k^2 \xi^2}, \quad (21)$$

where ρ_1 is the number density of the solvent, κ_T is its isothermal compressibility, κ_T^0 is the isothermal compressibility of the ideal gas, and ξ is the correlation length of density fluctuations. Further, $\gamma \equiv C_p / C_V$ is the ratio of specific heats, D_T is the thermal diffusivity, c_s is the adiabatic sound velocity, and Γ is the sound attenuation constant, which in turn is given by $\Gamma = D_T(\gamma - 1) + (4\eta_s/3 + \eta_b)/\rho_m$, where η_s is the shear viscosity, η_b is the bulk viscosity, and ρ_m is the mass density. The second term in Eq. (20) accounts for acoustic phonons in the medium, and in light scattering experiments, it is associated with spectral peaks at frequencies of $\omega \pm c_s k$. In ethane, ω for the CO stretching frequency is on the order of 2000 cm^{-1} , so at long wavelengths it can be shown that $c_s k \ll \omega$. As a simplification, therefore, we set the term $\cos(c_s k t)$ in Eq. (20) to unity, which allows the dynamic structure factor to be written as

$$\hat{S}_1(\mathbf{k}, t) \equiv X - \frac{1}{\gamma} (X - Y), \quad (22)$$

where

$$X = \hat{S}_1(k) \exp[-t/\tau_1(k)], \quad (23a)$$

with $1/\tau_1(k) \equiv k^2 D_T$, and

$$Y = \hat{S}_1(k) \exp[-t/\tau_2(k)], \quad (23b)$$

with $1/\tau_2(k) = k^2 \Gamma$.

We shall first consider the limit $k\xi \ll 1$, which corresponds to the noncritical regime. The direct correlation function for a two-component mixture is not known in general, so in these calculations it is approximated by the direct correlation function of the binary hard sphere mixture, for which an analytic expression is available²² (although it is too lengthy to reproduce here). Hard sphere models are commonly used to represent dense liquids (where packing fractions are typically greater than about 0.3), but they have been successfully applied to less dense fluids as well.²³ Such models are therefore expected to provide a useful first approximation to $\hat{C}_{21}(\mathbf{k})$ for the entire range of experimental solvent densities (except, of course, near the critical point, where attractive interactions are important). We further approximate $\hat{C}_{21}(k)$ by $\hat{C}_{21}(0)$,

since $\hat{C}_{21}(k)$ at large k is small (it varies as $1/k^2$ when $k \gg 1$). No serious error appears to result from this approximation.²⁴

When these approximations are introduced into Eq. (17), the integrals there can be evaluated exactly, and the lifetime is found to be

$$T_1^{-1} \propto T \rho_1 \frac{\kappa_T}{\kappa_T^0} \hat{C}_{21}(0)^2 \Lambda^3 \left(Q_A - \frac{1}{\gamma} Q_A + \frac{1}{\gamma} Q_B \right), \quad (24a)$$

where ρ_1 is the solvent number density, and

$$Q_A = \frac{\bar{\Lambda}^2}{D_T(1 + \omega_1^2)} [R_1 + R_2 - R_3]. \quad (24b)$$

Here $\bar{\Lambda} = \Lambda \xi$, $\omega_1 = \omega \xi^2 / D_T$, and

$$R_1 = 1 - \frac{5}{3\bar{\Lambda}^2} \left[1 + \frac{3}{\bar{\Lambda}^2} \left\{ \frac{\tan^{-1} \bar{\Lambda}}{\bar{\Lambda}} - 1 \right\} \right], \quad (24c)$$

$$R_2 = \frac{5}{3\bar{\Lambda}^2} \left[1 + \frac{3}{4\sqrt{2}} \omega_2^{3/2} \{ \ln S_1 - 2 \tan^{-1} S_2 \} \right], \quad (24d)$$

$$R_3 = 1 - 5\omega_2^2 + \frac{5}{4\sqrt{2}} \omega_2^{5/2} [\ln S_1 + 2 \tan^{-1} S_2], \quad (24e)$$

with $\omega_2 = \omega / \Lambda^2 D_T$, and the functions S_1 and S_2 defined by $S_1 = (1 + \sqrt{2\omega_2 + \omega_2}) / (1 - \sqrt{2\omega_2 + \omega_2})$, and $S_2 = \sqrt{2\omega_2} / (\omega_2 - 1)$. Q_B is identical to Q_A except that Γ replaces D_T everywhere. Equation (24) determines T_1 for all ρ and T away from the critical point once the temperature and density dependence of quantities like κ_T , D_T , ξ , etc., are specified. (For the hard sphere model, the density dependence of the direct correlation function is, of course, known analytically.) As it turns out, there are no simple expressions for these thermodynamic functions, which must instead be described by phenomenological equations—typically involving 20 or more parameters obtained by fits to experimental data—that apply to individual solvents. Such equations have been obtained for the equilibrium and transport properties of ethane by Friend *et al.*²⁵ (similar equations are also available for CO_2 , but they are considerably more complicated²⁶). The calculations that lead to the equations for the equilibrium properties of the system typically begin by expressing the Helmholtz free energy of the system A as a series expansion in the density and temperature. The coefficients in the expansion are initially unknown, but they are later determined by fitting the properties derived from A to experimental data. Once the equation for A is established, all thermodynamic information about the system is immediately known. It then becomes possible to obtain, say, the compressibility, by taking derivatives of A with respect to the density at constant temperature. Knowledge of the compressibility in turn allows the correlation length ξ to be calculated, since $\kappa_T \propto \xi^2$. A similar approach is taken in calculating transport properties (viscosity, diffusivity, etc.), although here no general prescriptions are available for determining all such properties. The values of κ_T , D_T , ξ , etc., that are used in Eq. (24) at given values of the density and temperature have been

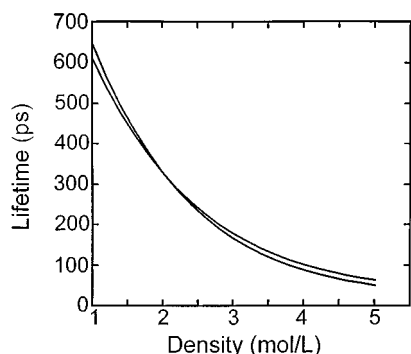


FIG. 1. The lifetime T_1 in picoseconds versus solvent concentration in mol/L for the temperatures $T=34\text{ }^\circ\text{C}$ and $T=50\text{ }^\circ\text{C}$ and densities between 1 and 5 mol/L. The curve with higher initial lifetime corresponds to the $T=34\text{ }^\circ\text{C}$ isotherm.

obtained in this way. However, the shear viscosity is one transport property that is not determined in these calculations, so we write it as $\eta_s = 3\eta_b/2$, an approximation that is sometimes used in the theory of liquids.²⁷

Several assumptions and approximations go into the determination of the above empirical equations, but the equations are deemed to be accurate across a wide range of temperatures and densities. The frequency ω is assigned the value $3.8 \times 10^{14}\text{ s}^{-1}$ (corresponding to an absorption energy of 2000 cm^{-1}). From the calculated values of ξ , the cutoff Λ is chosen to have the value $2 \times 10^8\text{ m}^{-1}$, which ensures that $\Lambda\xi < 1$ at all relevant temperatures and densities away from the critical point. The solvent diameter is taken to be 4.36 \AA (based on the Lennard-Jones parameter of Ref. 25), and the solute diameter is estimated to be 6.00 \AA .

Equation (24) is shown in Fig. 1 for the temperatures $34\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$ and for densities in the range 1–5 mol/L. (For reference, the critical point of ethane occurs at $T=32\text{ }^\circ\text{C}$ and $\rho=6.9\text{ mol/L}$.) The plots in this figure are normalized so that at the lowest value of the solvent density used in the experiments (1 mol/L), the experimental and theoretical curves are roughly coincident.

The predicted decay curves of Fig. 1 are in general agreement with experimental trends observed for $\text{W}(\text{CO})_6$ in ethane and CO_2 in the range of densities below the critical density.⁶ As anticipated, the lifetimes decrease as the density is increased. However, the decrease with density is far steeper (by a factor of about 5 at 5 mol/L on the critical isotherm) than is seen experimentally. Possible reasons for this difference will be discussed later. If Eq. (24) is applied to the near critical region ($T \approx T_c$, $5 < \rho < 10\text{ mol/L}$), and to higher densities ($\rho > 10\text{ mol/L}$), the results are as shown in Fig. 2 for the two isotherms considered earlier. Expectedly, Eq. (24) breaks down in the immediate vicinity of the critical point, where it shows extrema that are reminiscent of the maximum and minimum seen in the P - V isotherms of the van der Waal's equation in the two-phase region of gas-liquid coexistence. Beyond $\rho \approx 11\text{--}12\text{ mol/L}$, T_1 decreases again, as in the experimental curve. The higher temperature isotherm falls essentially monotonically with density over

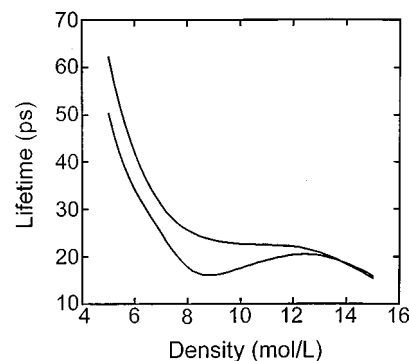


FIG. 2. The same two isotherms as in Fig. 1, with densities in the range 5–15 mol/L. The curve with the maximum and minimum in the critical region corresponds to the $T=34\text{ }^\circ\text{C}$ isotherm.

the entire density range 1–15 mol/L. At higher densities, away from the critical density, the two calculated isotherms decrease and have almost the same values. This is also in accord with experimental observations.⁶

To probe the critical region using our hydrodynamic approach, it is necessary to pass to the limit $k \ll 1$, $k\xi \rightarrow \infty$. Near the critical point, because of the divergence of the heat capacity C_p (and hence of γ), the second and third terms in Eq. (22) are small, so as a further simplification, they are neglected altogether. The resulting equation can be extended formally to the limit $k\xi \gg 1$ by using Kawasaki's mode-coupled expression for $\tau_1(k)$:²⁸

$$\frac{1}{\tau_1(k)} = \frac{k_B T}{8\pi\eta\xi^3} \left[1 + k^2\xi^2 + \left(k^3\xi^3 - \frac{1}{k\xi} \right) \tan^{-1}(k\xi) \right], \quad (25)$$

where η is the viscosity. Related “extended” hydrodynamic descriptions of the structure factor are known (e.g., Refs. 29 and 30). It is easy to show that when $k\xi \ll 1$, Eq. (25) reduces to the expression defined after Eq. (22).

Again, we approximate $\hat{C}_{21}(k)$ by its $k=0$ value (near the critical point, this is likely to be a less severe approximation than the corresponding approximation in the noncritical region), but we no longer evaluate it with the hard sphere model, which is inadequate near the critical point. Further, Eq. (25) shows that in the critical limit $1/\tau_1(k) \sim D_T \xi k^3$, while $\hat{S}_1(k) \sim \rho_1 \kappa_T / \kappa_T^0 k^2 \xi^2$, so that the lifetime becomes

$$T_1^{-1} \propto T \frac{\rho_1 \kappa_T / \kappa_T^0}{\xi^2} \hat{C}_{21}(0)^2 \int_0^\infty dt \cos(\omega t) \times \int d\mathbf{k} \exp(-D_T \xi k^3 t). \quad (26)$$

(More accurate representations of the structure factor are known near the critical point,³¹ but these do not alter the qualitative features of our model.) Without actually evaluating the integral in Eq. (26), we can draw the following conclusions: the correlation length ξ^2 is proportional to $\rho_1 \kappa_T / \kappa_T^0$, so the density dependence of T_1 resides in $\hat{C}_{21}(0)$ and the variable $D_T \xi$. In general, D_T is defined as $\lambda / \rho C_p$, where λ is the thermal conductivity and C_p is the constant

pressure heat capacity. On the critical isochore, both theory and experiment suggest that³² $\lambda \sim t^{-\gamma+\nu}$ and $C_p \sim t^{-\gamma}$, where $t \equiv |T - T_c|/T_c$, and γ and ν are universal exponents that have the values 1.24 and 0.63, respectively. On the critical isotherm, these relations are equivalent to $\lambda \sim (\Delta\rho)^{-(\gamma-\nu)/\beta}$ and $C_p \sim (\Delta\rho)^{-\gamma/\beta}$, where $\Delta\rho \equiv |\rho - \rho_c|/\rho_c$, and β is another universal exponent ($=0.324$).³² Hence $D_T \sim (\Delta\rho)^{\nu/\beta}$ along $T = T_c$. Since ξ also varies as $t^{-\nu}$ on the critical isochore, and therefore as $(\Delta\rho)^{-\nu/\beta}$ on the critical isotherm, $D_T \xi$ is either independent of the density, or at most weakly dependent on it (through a weak critical anomaly in the viscosity that is manifested asymptotically close to the critical point³²). Thus, in spite of the fact that the correlation length, the isothermal compressibility, and the thermal diffusivity all change rapidly with density near the critical point, the changes are mutually counterbalancing, with the result that they contribute very little to the density dependence of T_1 .

The direct correlation function at zero wave vector can be related rigorously to the thermodynamic properties of an infinitely dilute binary mixture. For instance, if the correlation function integral \bar{C}_{21} is defined as

$$\bar{C}_{21} = \int d\mathbf{r} C_{21}(\mathbf{r}) \equiv \hat{C}_{21}(0), \quad (27)$$

then from the fluctuation theory of Kirkwood and Buff,³³ using the results of McGuigan and Monson,³⁴ it is readily demonstrated that

$$\bar{C}_{21}^\infty = 1 - \frac{\bar{V}_2^\infty}{k_B T \kappa_T}, \quad (28)$$

where the \bar{V}_2 is the partial molar volume of the solute, κ_T is the isothermal compressibility of the solvent, and the superscript ∞ denotes the limit of infinite dilution. Now it is known that \bar{V}_2 diverges as κ_T near the critical point,³⁵ so from Eqs. (27) and (28) it follows that

$$\hat{C}_{21}(0) \rightarrow c, \quad T \rightarrow T_c, \quad \rho_1 \rightarrow \rho_c, \quad (29)$$

where c is some function that is expected to be at most weakly dependent on the density.

Thus, the lifetime is finally seen to be essentially density independent. Further, because the effect is attributed to the long-range correlations in the density fluctuations, similar behavior is expected of other solute-solvent combinations, irrespective of the character of their microscopic molecular interactions. In particular, no distinctions can be drawn between what have been referred to in the literature as attractive, repulsive, or weakly attractive mixtures,³⁶ since for all of them, \bar{V}_2 diverges in exactly the same way, aside from differences of sign. Indeed, at least two other systems, $\text{W}(\text{CO})_6$ /carbon dioxide and $\text{W}(\text{CO})_6$ /fluoroform, show qualitatively the same changes with density near the critical point as $\text{W}(\text{CO})_6$ /ethane.⁶ Moreover, within the present density functional formalism based on Eq. (12), the only difference between a one-component system and an infinitely dilute mixture is that $\hat{C}_{11}(\mathbf{k})$, rather than $\hat{C}_{21}(\mathbf{k})$, is used in the expressions for the lifetime. At zero wave vector, the limit-

ing form of this function near the critical point is also likely to be largely density independent. Thus the critical properties of pure fluids are also expected to be similar.

B. Frequency shifts

As stated earlier, the absorption frequency ν of the CO stretching mode of $\text{W}(\text{CO})_6$ in ethane changes with density in much the same way as the lifetimes: near the critical isotherm ν first decreases, then remains constant, then decreases again. At higher temperatures, ν simply decreases monotonically. The lack of density dependence of ν near the critical point has also been observed in supercritical CO_2 and supercritical fluoroform.⁶ The CO stretching mode of the solute rhodium dicarbonylacetoacetate in these solvents also behaves similarly.⁶ If the changes in ν with density are reexpressed in terms of the shifts $\Delta\nu$ of the fluid phase frequencies from a putative gas phase frequency ν_g (which could be identified, for instance, with the extrapolated zero density fluid frequency), the trends mentioned above are reversed. That is to say, along the critical isotherm, $\Delta\nu$ first *increases* with density, then remains constant, then increases again, while at higher temperatures, it simply increases monotonically.

From general considerations, it is clear that $\Delta\nu$ must depend on the average force along the vibrational coordinates of interest.⁷ The nature of this connection is hard to define when these coordinates involve collective motions, as is the case for polyatomics. Nevertheless, we shall assume that the fluctuating force $\delta\mathbf{F}^{(2)}(\mathbf{r})$ on the solute located at \mathbf{r} is related to the shift in frequency of the CO mode as a result of interactions with its surroundings. The average of this force is, of course, 0, so we define the frequency shift as

$$(\Delta\nu)^2 \propto \int d\mathbf{r} \langle \delta\mathbf{F}^{(2)}(\mathbf{r}) \cdot \delta\mathbf{F}^{(2)}(\mathbf{r}) \rangle. \quad (30)$$

Following the sequence of steps outlined earlier, Eq. (30) can be reduced to

$$(\Delta\nu)^2 \propto T^2 \int d\mathbf{k} k^2 |\hat{C}_{21}(k)|^2 \hat{S}_1(k), \quad (31)$$

which in turn becomes

$$(\Delta\nu)^2 \propto T^2 \rho_1 \frac{\kappa_T}{\kappa_T^0} \hat{C}_{21}(0)^2 \frac{1}{\bar{\Lambda}^2} \left(1 - \frac{3}{\bar{\Lambda}^2} + \frac{3}{\bar{\Lambda}^3} \tan^{-1} \bar{\Lambda} \right) \quad (32)$$

in the noncritical ($k\xi \ll 1$) limit, with $\bar{\Lambda} \equiv \Lambda\xi$ as before, and which becomes

$$(\Delta\nu)^2 \propto T^2 \frac{\rho_1 \kappa_T / \kappa_T^0}{\xi^2} \hat{C}_{21}(0)^2 \quad (33)$$

in the critical ($k\xi \gg 1$) limit.

Equation (32) is shown in Fig. 3 for densities in the range 1–15 mol/L with the various thermodynamic and structural parameters of the model calculated as before. The general trends in the behavior of $\Delta\nu$ in the noncritical region are in qualitative agreement with the experimental data at low and high densities. In particular, they correctly predict

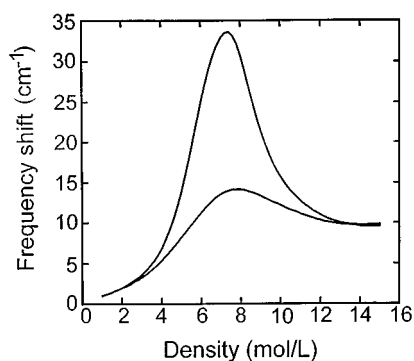


FIG. 3. The frequency shift $\Delta\nu$ in cm^{-1} versus solvent density in mol/L for the isotherms $T=34^\circ\text{C}$ and $T=50^\circ\text{C}$. The upper curve corresponds to the lower temperature isotherm and the lower to the higher temperature isotherm.

the magnitude of the total shift in frequency between the highest and lowest densities. However, the breakdown of the equation near the critical point is far more dramatic here than was the case for the lifetimes. Moreover, the higher temperature isotherm, which should have increased smoothly with density across the entire range of densities, does not do so when ρ is centered around the critical density. The temperature must be considerably higher ($>175^\circ\text{C}$) before the change of $\Delta\nu$ with ρ is monotonic. These results suggest that Eq. (32) accurately describes some, but not all, the contributions to the frequency shift from the various forces in the medium.

The study of the critical region requires the use of Eq. (33). As before, $\rho_1\kappa_T/\kappa_T^0$ scales as ξ^2 , and $\hat{C}_{12}(0)$ becomes nearly constant in the critical region. The equation, therefore, predicts (as observed) that $\Delta\nu$ is density independent near the critical point.

III. DISCUSSION

The foregoing results suggest that the changes in T_1 and ν near the critical point (or lack of change, to be more precise) are ultimately governed by the growth of critical fluctuations in the medium. Specific solute/solvent cluster formation, an appealing alternative scenario (discussed in the Introduction), is not required by the current theory to explain the observed trends in the vibrational data. At the same time, however, it is probably important to emphasize that the term cluster is not very well defined. Cluster is often taken to refer to the extended regions of uniform density that are understood to exist in the critical domain. Such clusters, strictly speaking, are not antithetical to our theory. But they do not seem to be quite the same objects that are often spoken of in the engineering and chemistry literature,^{4,36} which actually seem to be persistent structures with well-characterized geometric properties, like shape and average spatial extent. To this list of attributes should probably be added a residence time of the molecules in the cluster, since otherwise one would classify as clusters the coordination shells that surround individual molecules in a bulk fluid and whose existence is detected as peaks in a radial distribution function.

While the theoretical results presented here demonstrate that persistent structures are not required to explain the vibrational lifetime and line position experiments, they do not rule out the existence of such structures. Clusters may be involved in the explanation of other experimental observables, e.g., fluorescence peak shift measurements by Bennett and Johnston, which are also characterized by density independent properties near the critical point.³⁷ It should be possible to adapt the present density functional formalism to treat fluorescence problems, but the central quantity of interest there is a transition dipole moment correlation function, and not a force correlation function. So our present results have no direct bearing on the fluorescence data.

The structural integrity of persistent clusters is dependent on the attractive or repulsive character of the intermolecular interactions; indeed, so-called repulsive binary mixtures are not expected to form clusters. Therefore, repulsive mixtures, as well as pure fluids, would differ, spectroscopically, from attractive binary mixtures. But our theory suggests that such differences are unlikely to be observed in vibrational experiments because the lack of density-dependent vibrational observables near the critical point does not require the existence of solute/solvent clusters. Unfortunately, there appear to be few systems (other than rare gas mixtures) that qualify as true repulsive mixtures, and these do not exhibit the kinds of vibrational transitions that can be probed with vibrational spectroscopy. Pure fluids are difficult to study for other reasons, but a deuterio-substituted polyatomic in a large excess of the normal compound is very nearly a single-component system, so its critical behavior may provide a valuable test of the above ideas.

If hydrodynamics is found to provide a reasonable description of the process of vibrational relaxation near the critical point, this would suggest that the short distance events that must occur during the process are coupled to the modes of the medium, which are themselves influenced over large distances. In this view, the correlated regions in the solvent that surround isolated molecules of the solute can be thought of, crudely, as being solidlike³⁸—they are therefore expected to support low and high frequency oscillations. The intermolecular spacing within these regions determines the highest frequency (quasi-Debye) translational modes, as well as high frequency hindered rotations, or librations. Over distances up to the correlation length, translational and rotational modes may be highly extended instantaneous normal modes,³⁹ somewhat akin to the phonons of an amorphous solid, making the fluctuations experienced by the solute inherently different from those in a fluid far from the critical point, where the correlation length is small.

Away from the critical point, it seems clear that a hydrodynamic theory of vibrational relaxation is not wholly reliable, although there is nothing at present to indicate that the calculation of the dynamic force correlation function by density functional methods is necessarily a poor approximation—what appears to be needed are more accurate representations of both the two-particle direct correlation function and the dynamic structure factor. Such representations can be formulated (through memory function methods,

for instance³⁸), but they are unlikely to lead to analytical results. A microscopic theory of vibrational relaxation that is valid in the high k , short time limit may make our predicted lifetimes in the range 1–5 mol/L more quantitative. (It is possible that a quantum mechanical treatment is actually necessary to account properly for the participation of discrete high frequency modes of the solute and solvent.^{9,40}) Despite the shortcomings of the present approach away from the critical point, we have found that its predictions for the temperature dependence of the lifetime along a critical isochore are reasonably consistent with recently acquired experimental data. These results will be discussed in a subsequent publication.⁴⁰

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