

Density dependence of vibrational energy relaxation rates in supercritical solution: A hydrodynamic model

V. B. Nemtsov,^{*,†} I. I. Fedchenia, A. V. Kondratenko,[†] and J. Schroeder

*Abteilung für Spektroskopie und Photochemische Kinetik, Max-Planck-Institut für Biophysikalische Chemie,
Am Fassberg, D-37077 Göttingen, Germany*

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An approximate expression describing the density dependence of vibrational energy relaxation rates in fluids in terms of thermodynamic and transport parameters of the fluid is developed on the basis of a classical statistical mechanical theory of vibrational energy relaxation of highly excited molecules in polyatomic solvents. The energy relaxation rate is expressed via the friction coefficient, which describes the interaction between solute oscillator and solvent molecules. The corresponding force-force time correlation function is expressed in terms of the dynamic structure factor of the solvent and the force of interaction between solute and solvent molecules. Approximating the dynamic structure factor appropriately leads to expressions for the density dependence of vibrational relaxation rates in terms of thermophysical solvent parameters. Using these expressions the density dependence of vibrational relaxation rates in supercritical ethane and propane both in the vicinity of the critical point and far from it are evaluated and compared with measured relaxation rates obtained under the same physical conditions. [S1063-651X(99)15710-6]

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I. INTRODUCTION

The increasing importance of supercritical fluids in chemical processes such as extraction and waste disposal techniques has initiated numerous studies on more fundamental aspects of chemical reaction kinetics in fluid media. Among these systematic investigations of the density dependence of vibrational energy transfer from highly excited species to a fluid solvent medium are of particular importance, as this process plays a central role as a competing energy degrading process in essentially every thermally, chemically, or photochemically activated reaction. The density range covered and accuracy achieved in such experiments [1–4] nowadays allows us to test different theoretical models. Of particular interest for the practitioner would be model descriptions that in addition to density and temperature of the fluid require as input only basic physical fluid parameters to estimate the energy transfer rate constant.

The time scale of vibrational energy transfer can be characterized by the corresponding vibrational energy relaxation time or its inverse, the relaxation rate, which according to the Landau-Teller model [5] is proportional to the friction coefficient. This coefficient is expressed by the time correlation function of the microscopic force exerted on the solute oscillator by the solvent molecules. This force correlation function can be calculated approximately by a variety of methods such as those based on the Gaussian model for the force correlation function [6] or on other models using short-time expansions of the time correlation function [7]. In one recent approach the microscopic forces are replaced by macro-

scopic forces defined with the help of density functional theory [3], though the appearance of the dynamic structure factor in such an approach seems to be unphysical. One may obtain the correct relation for the time correlation function of the microscopic force via the dynamic structure factor and the above mentioned force.

The important role of local density in vibrational relaxation was discussed for the case of supercritical fluids in a recent paper [2]. In the supercritical state density fluctuations are very significant, of course, and may be described with the help of the dynamic structure factor. It appears that Hills [8] was the first to employ the dynamic structure factor to calculate vibrational relaxation rates via the time correlation function of the potential of interaction between solute and solvent molecules. In contrast to his work we shall apply the dynamic structure factor to calculate the “force-force” time correlation function.

In the present work we shall derive a representation of the friction coefficient of the solute oscillator in terms of the dynamic structure factor of the solvent and the interaction forces between oscillator and atoms of solvent molecules. This representation is based on a general expression for the friction coefficient in form of the force correlation function. By using approximate expressions for the dynamic structure factor we derive equations for the friction coefficient for the supercritical fluid both in the vicinity of the critical point and far from it. These relations enable us to evaluate the density dependence of the relaxation rate using experimental data for thermodynamic and transport properties for ethane [9] and propane [10,11].

II. GENERAL EXPRESSION FOR THE FRICTION COEFFICIENT

In this section we shall derive a general expression for the friction coefficients in terms of the dynamic structure factor. To proceed, we start from a classical expression for the rate

^{*}Author to whom correspondence should be addressed. Electronic address: root@bgtu.minsk.by

[†]Permanent address: Belarussian State Technological University, Sverdlova St., 13^a, Minsk 220630, Belarus.

coefficient of vibrational energy relaxation K_C [12,13] in terms of the time correlation function of the rate of vibrational energy \dot{E} change of the excited molecule

$$K_C = \int_0^\infty \langle \dot{E}(t)\dot{E}(0) \rangle dt / (\langle E^2 \rangle - \langle E \rangle^2), \quad (1)$$

where $\dot{E} = dE/dt$, and the angular brackets denote Gibbs canonical averaging over the bath.

The transfer of energy E of the excited molecule to the solvent bath is caused by the interaction between atoms of the solute and the solvent molecules. The rate of energy change is defined by

$$\dot{E}(t) = \sum_{\alpha=1}^n \mathbf{v}_\alpha(t) \cdot \mathbf{F}_\alpha(t). \quad (2)$$

Here \mathbf{v}_α is the vibrational velocity of the atom α , \mathbf{F}_α is the force exerted on atom α by the solvent, and n is the number of atoms in the solute.

Taking into account relation $\langle E^2 \rangle - \langle E \rangle^2 = ck_B T^2$ and Eq. (2) we can write

$$K_C = (ck_B T^2)^{-1} \int_0^\infty \left\langle \sum_{\alpha=1}^n \sum_{\beta=1}^n \mathbf{v}_\alpha(t) \mathbf{v}_\beta(0) : \mathbf{F}_\alpha(t) \mathbf{F}_\beta(0) \right\rangle dt, \quad (3)$$

where k_B is the Boltzmann constant and T is the temperature, c is the thermal capacity of the solute molecule, and the colon denotes the dyadic inner product.

The expression in Eq. (3) may be represented in normal coordinates q_α and normal forces Q_α of the solute molecule. This results in

$$K_C = (ck_B T^2)^{-1} \times \int_0^\infty \left\langle \sum_{\alpha=1}^{3n-6} \sum_{\beta=1}^{3n-6} \dot{q}_\alpha(t) \dot{q}_\beta(0) Q_\alpha(t) Q_\beta(0) \right\rangle dt, \quad (4)$$

where $3n-6$ is the number of vibrational degrees of freedom for a nonlinear solute molecule. If one assumes that coupling between different normal modes is weak and can be neglected, the rate K_C is simply

$$K_C = (ck_B T^2)^{-1} \int_0^\infty \left\langle \sum_{\alpha=1}^{3n-6} \dot{q}_\alpha(t) \dot{q}_\alpha(0) Q_\alpha(t) Q_\alpha(0) \right\rangle dt. \quad (5)$$

In addition we suppose that coupling between velocities and forces is weak, and that therefore it is possible to approximately uncouple the correlation function into the product of correlation functions of velocities and forces:

$$K_C = (ck_B T^2)^{-1} \int_0^\infty \sum_{\alpha=1}^{3n-6} \langle \dot{q}_\alpha(t) \dot{q}_\alpha(0) \rangle \langle Q_\alpha(t) Q_\alpha(0) \rangle dt. \quad (6)$$

If we assume the same approximations also hold for ordinary velocities and forces we obtain the expression

$$K_C = (ck_B T^2)^{-1} \int_0^\infty \sum_{\alpha=1}^n \langle \mathbf{v}_\alpha(t) \mathbf{v}_\alpha(0) \rangle : \langle \mathbf{F}_\alpha(t) \mathbf{F}_\alpha(0) \rangle dt. \quad (7)$$

In the case of a spherically symmetric potential and vibrational velocities we can further simplify and obtain K_C for one vibrational mode as

$$K_C = (ck_B T^2)^{-1} \int_0^\infty \langle \mathbf{v}(t) \mathbf{v}(0) \rangle \langle F(t) F(0) \rangle dt. \quad (8)$$

Taking into account the relations

$$\langle \mathbf{v}(t) \mathbf{v}(0) \rangle = m^{-1} k_B T \operatorname{Re} e^{i\omega t} \quad \text{and} \quad c = k_B$$

we obtain the Landau and Teller expression for the rate of vibrational relaxation [5,14,15],

$$K_C = \zeta(\omega)/m, \quad (9)$$

where $\zeta(\omega)$ is the friction coefficient and m the reduced mass of the oscillator. So the friction coefficient is defined in terms of the force time correlation function

$$\zeta(\omega) = \beta \int_0^\infty \langle F(t) F(0) \rangle \cos \omega t dt, \quad \beta = (k_B T)^{-1}. \quad (10)$$

Returning to the general case, it is necessary to consider the friction tensors

$$\zeta_{\alpha\alpha}(\omega) = \beta \int_0^\infty \langle \mathbf{F}_\alpha(t) \mathbf{F}_\alpha(0) \rangle \cos \omega t dt, \quad (11)$$

$$\zeta_{\alpha\beta}(\omega) = \beta \int_0^\infty \langle \mathbf{F}_\alpha(t) \mathbf{F}_\beta(0) \rangle \cos \omega t dt. \quad (12)$$

These tensors arise from Eq. (3) by assuming that there are no correlations between velocities and forces. Then the integrand in Eq. (3) may be written as

$$\begin{aligned} & \sum_{\alpha=1}^n \sum_{\beta=1}^n \langle \mathbf{v}_\alpha(t) \mathbf{v}_\beta(0) : \mathbf{F}_\alpha(t) \mathbf{F}_\beta(0) \rangle \\ &= \beta^{-1} \sum_{\alpha=1}^n \langle \mathbf{v}_\alpha(t) \mathbf{v}_\alpha(0) \rangle : \gamma_{\alpha\alpha}(t) \\ &+ \beta^{-1} \sum_{\alpha \neq \beta} \sum \langle \mathbf{v}_\alpha(t) \mathbf{v}_\beta(0) \rangle : \gamma_{\alpha\beta}(t), \end{aligned} \quad (13)$$

where

$$\gamma_{\alpha\alpha}(t) = \beta \langle \mathbf{F}_\alpha(t) \mathbf{F}_\alpha(0) \rangle \quad \text{and} \quad \gamma_{\alpha\beta}(t) = \beta \langle \mathbf{F}_\alpha(t) \mathbf{F}_\beta(0) \rangle \quad (14)$$

are force correlation functions that allow the determination of the friction tensors. These are also significant for other problems in chemical kinetics, e.g., $\gamma_{\alpha\alpha}(t)$ and $\gamma_{\alpha\beta}(t)$ are important in the theory of chemical reaction rates in condensed phases [16]. In our case the coupling between different velocities \mathbf{v}_α and \mathbf{v}_β (in other words, coupling between different modes) dictates the correlations between forces \mathbf{F}_α

and \mathbf{F}_β exerted on different atoms α and β by solvent molecules. On the basis of Eqs. (11) and (12) we may calculate the coupling mentioned above from the difference between friction tensors $\zeta_{\alpha\alpha}$ and $\zeta_{\alpha\beta}$. This coupling originates from the interaction of the excited molecule with the solvent.

Let us denote with γ and δ the atoms in solvent molecule i . Then we shall denote as $\mathbf{B}^\alpha = \sum_{i,\gamma} \mathbf{B}(|\mathbf{r}_{\alpha\gamma i}|)$ the force acting on atom α due to interaction with atoms γ belonging to the i th solvent molecule. Here $\mathbf{r}_{\alpha\gamma i}$ is the vector connecting atoms α and γ . It should be noted that α also may be considered as the index of the vibrational mode of the excited molecule. Then \mathbf{B}^α must be considered as the relevant generalized force. Now we calculate the force correlation function in form of the dyadic

$$f_{\alpha\alpha}(t) = \langle \mathbf{B}^\alpha(t) \mathbf{B}^\alpha(0) \rangle \quad (15)$$

using the identities

$$\mathbf{B}^\alpha(t) = \sum_{i,\gamma} \mathbf{B}(|\mathbf{r}_{\alpha\gamma i}|) = \sum_{i,\gamma} d\mathbf{r} \delta(\mathbf{r} - \mathbf{r}_{\alpha\gamma i}) \mathbf{B}(|\mathbf{r}|)$$

and

$$\mathbf{B}^\alpha(0) = \sum_{j,\delta} \mathbf{B}(|\mathbf{r}_{\alpha\delta j}|) = \sum_{j,\delta} d\mathbf{r}' \delta(\mathbf{r}' - \mathbf{r}_{\alpha\delta j}) \mathbf{B}(|\mathbf{r}'|), \quad (16)$$

where $\delta(\mathbf{r})$ is the Dirac δ function. Then we introduce microscopic densities of particle numbers by means of the relations

$$\rho_\alpha(\mathbf{r}, t) = \sum_{\gamma i} \delta[\mathbf{r} + \mathbf{r}_\alpha(t) - \mathbf{r}_{\gamma i}(t)], \quad (17)$$

$$\rho_\alpha(\mathbf{r}', 0) = \sum_{\delta j} \delta[\mathbf{r}' + \mathbf{r}_\alpha(0) - \mathbf{r}_{\delta j}(0)],$$

realizing that

$$\mathbf{r}_{\alpha\gamma i} = \mathbf{r}_{\gamma i} - \mathbf{r}_\alpha, \quad \mathbf{r}_{\alpha\delta j} = \mathbf{r}_{\delta j} - \mathbf{r}_\alpha,$$

where \mathbf{r}_α , $\mathbf{r}_{\gamma i}$, and $\mathbf{r}_{\delta j}$ are the positions of atom α , γi , and δj with respect to the laboratory fixed reference frame. In this case the force correlation function is given by

$$f_{\alpha\alpha}(t) = \int d\mathbf{r} \int d\mathbf{r}' \langle \delta\rho_\alpha(\mathbf{r}, t) \delta\rho_\alpha(\mathbf{r}', 0) \rangle \mathbf{B}(\mathbf{r}) \mathbf{B}(\mathbf{r}'), \quad (18)$$

where $\delta\rho = \rho(\mathbf{r}, t) - \rho_0$ is the density fluctuation with respect to its equilibrium value ρ_0 . But the correlation of density fluctuation may be represented by the intermediate scattering function $F_{\alpha\alpha}(\mathbf{k}, t)$,

$$\langle \delta\rho_\alpha(\mathbf{r}, t) \delta\rho_\alpha(\mathbf{r}', 0) \rangle = \frac{n}{(2\pi)^3} \int F_{\alpha\alpha}(\mathbf{k}, t) e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k}, \quad (19)$$

where $\mathbf{R} = \mathbf{r}' - \mathbf{r}$, \mathbf{k} is a wave vector, and $n = N/V$ is the number density of the solvent (volume V of solvent contains N molecules). The function $F_{\alpha\alpha}(\mathbf{k}, t)$ is the atom-atom inter-

mediate scattering function because it is expressed in terms of the Fourier transformation of atomic density fluctuations

$$\rho_\alpha(\mathbf{k}, t) = \int e^{i\mathbf{k} \cdot \mathbf{r}} \delta\rho_\alpha(\mathbf{r}, t) d\mathbf{r}$$

by the relation

$$F_{\alpha\alpha}(\mathbf{k}, t) = N^{-1} \langle \rho_\alpha(\mathbf{k}, t) \rho_\alpha(-\mathbf{k}, 0) \rangle. \quad (20)$$

By substitution of Eq. (19) into Eq. (18) and by using the Fourier representations for forces $\mathbf{B}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r}')$ of the type

$$\mathbf{B}(\mathbf{r}) = (2\pi)^{-3} \int \mathbf{B}(\mathbf{k}') e^{-i\mathbf{k}' \cdot \mathbf{r}} d\mathbf{k}'$$

and after going through some simple transformation, we find the following theoretical expression for $\mathbf{f}(t)$:

$$f_{\alpha\alpha}(t) = \frac{n}{(2\pi)^3} \int d\mathbf{k} F_{\alpha\alpha}(\mathbf{k}, t) \mathbf{B}(\mathbf{k}) \mathbf{B}(-\mathbf{k}). \quad (21)$$

Finally, after Fourier transformation according to $\mathbf{f}_{\alpha\alpha}(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} \mathbf{f}_{\alpha\alpha}(t) e^{i\omega t} dt$ we obtain the following result for the friction coefficient:

$$\zeta_{\alpha\alpha}(\omega) = \beta n (2\pi)^{-3} \int d\mathbf{k} S_{\alpha\alpha}(\mathbf{k}, \omega) \mathbf{B}(\mathbf{k}) \mathbf{B}(-\mathbf{k}), \quad (22)$$

where

$$S_{\alpha\alpha}(\mathbf{k}, \omega) = (2\pi)^{-1} \int dt F_{\alpha\alpha}(\mathbf{k}, t) e^{i\omega t} \quad (23)$$

is the atom-atom dynamic structure factor.

Similarly, we now consider the friction tensor $\zeta_{\alpha\beta}$ accounting for the correlation between forces applied to different atoms (α and β) of the solute. In this case the force correlation function $\mathbf{f}_{\alpha\beta} = \langle \mathbf{B}^\alpha(t) \mathbf{B}^\beta(0) \rangle$ is determined as

$$f_{\alpha\beta} = \int d\mathbf{r} \int d\mathbf{r}' \langle \delta\rho_\alpha(\mathbf{r}, t) \delta\rho_\beta(\mathbf{r}', t) \rangle \mathbf{B}(\mathbf{r}) \mathbf{B}(\mathbf{r}'), \quad (24)$$

where $\delta\rho_\alpha$ and $\delta\rho_\beta$ are fluctuations in microscopic densities of particle numbers defined by Eq. (17). Then the correlation of density fluctuations is expressed in terms of the intermediate scattering function for different atoms $F_{\alpha\beta}(\mathbf{k}, t)$,

$$\langle \delta\rho_\alpha(\mathbf{r}, t) \delta\rho_\beta(\mathbf{r}', 0) \rangle = \frac{n}{(2\pi)^3} \int F_{\alpha\beta}(\mathbf{k}, t) e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k}. \quad (25)$$

$F_{\alpha\beta}(\mathbf{k}, t)$ is given by

$$F_{\alpha\beta}(\mathbf{k}, t) = N^{-1} \langle \rho_\alpha(\mathbf{k}, t) \rho_\beta(-\mathbf{k}, 0) \rangle. \quad (26)$$

The final result for the friction tensor, as in the case of $\zeta_{\alpha\alpha}$, can then be formulated as

$$\zeta_{\alpha\beta}(\omega) = \beta n (2\pi)^{-3} \int d\mathbf{k} S_{\alpha\beta}(\mathbf{k}, \omega) \mathbf{B}(\mathbf{k}) \mathbf{B}(-\mathbf{k}), \quad (27)$$

where

$$S_{\alpha\beta}(\mathbf{k}, \omega) = (2\pi)^{-1} \int dt F_{\alpha\beta}(\mathbf{k}, t) e^{i\omega t} \quad (28)$$

is the atom-atom dynamic structure factor for different atoms.

Next we consider more explicitly the structure of intermediate scattering functions. If \mathbf{R} , \mathbf{R}_i , and \mathbf{R}_j are center of mass coordinates of the solute and of solvent molecules (i and j), then

$$\mathbf{r}_\alpha = \mathbf{R} + \mathbf{d}_\alpha, \quad \mathbf{r}_{\gamma i} = \mathbf{R}_i + \mathbf{d}_{\gamma i}, \quad \mathbf{r}_{\delta j} = \mathbf{R}_j + \mathbf{d}_{\delta j},$$

where vectors \mathbf{d}_α , $\mathbf{d}_{\gamma i}$, and $\mathbf{d}_{\delta j}$ describe positions of atoms α , γ , and δ with respect to the center of mass of the solute and solvent molecules, respectively. Taking this into account we write explicit expressions for the intermediate scattering functions,

$$F_{\alpha\beta}(\mathbf{k}, t) = N^{-1} \left\langle e^{i\mathbf{k} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]} e^{-i\mathbf{k} \cdot [\mathbf{d}_\alpha(t) - \mathbf{d}_\beta(0)]} \times \sum_{\gamma i, \delta j} e^{-i\mathbf{k} \cdot [\mathbf{R}_i(t) - \mathbf{R}_j(0)]} e^{-i\mathbf{k} \cdot [\mathbf{d}_{i\gamma}(t) - \mathbf{d}_{j\delta}(0)]} \right\rangle, \quad (29)$$

$$F_{\alpha\alpha}(\mathbf{k}, t) = N^{-1} \left\langle e^{i\mathbf{k} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]} e^{-i\mathbf{k} \cdot [\mathbf{d}_\alpha(t) - \mathbf{d}_\alpha(0)]} \times \sum_{\gamma i, \delta j} e^{-i\mathbf{k} \cdot [\mathbf{R}_i(t) - \mathbf{R}_j(0)]} e^{-i\mathbf{k} \cdot [\mathbf{d}_{i\gamma}(t) - \mathbf{d}_{j\delta}(0)]} \right\rangle. \quad (30)$$

Factors $\exp\{i\mathbf{k} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]\}$, $\exp\{i\mathbf{k} \cdot [\mathbf{d}_\alpha(t) - \mathbf{d}_\beta(0)]\}$, and $\exp\{i\mathbf{k} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]\} \times \exp\{i\mathbf{k} \cdot [\mathbf{d}_\alpha(t) - \mathbf{d}_\alpha(0)]\}$ in Eqs. (29) and (30) describe the influence of the solute molecule on the dynamic structure factor of system. This influence is connected with the center of mass motion of the solute and with its intramolecular motion. But in the case of $F_{\alpha\alpha}$ at $t=0$ this factor equals 1. In the same way the sums in Eqs. (29) and (30) take into account the intramolecular and intermolecular motions of solvent particles.

In the case of a fluid without structured molecules the function $F(\mathbf{k}, t)$ becomes the ordinary intermediate scattering function such that

$$F(\mathbf{k}, 0) = \int S(\mathbf{k}, \omega) d\omega = S(\mathbf{k}), \quad (31)$$

where $S(\mathbf{k})$ is the traditional static structure factor [17]

$$S(\mathbf{k}) = 1 + n \int d\mathbf{r} [g(r) - 1] e^{i\mathbf{k} \cdot \mathbf{r}} \quad (32)$$

and $g(r)$ is the pair distribution function of the solvent. The friction coefficient in Eq. (22) may be considered as the drag coefficient for the generalized force between the vibrational coordinate of the solute and its bath partners. By using the atom-atom structure factor there is no need to assume that the probe molecule does not move as in Ref. [8]. It is not without interest that in our final formulas (22) the friction coefficient is separated into contributions arising from the

structure and the dynamics of the medium, and from interactions of the excited molecule with the medium.

III. MODELS FOR THE DYNAMIC STRUCTURE FACTOR OF SUPERCRITICAL FLUIDS

In order to estimate vibrational relaxation rates we need to employ a model for the dynamic structure factor. At first we shall consider the static structure factor. Setting $t=0$ in Eq. (30) we obtain the atom-atom structure factor

$$S_{\alpha\alpha}(\mathbf{k}) = (n^2 N)^{-1} \times \left\langle \sum_{\gamma i, \delta j} e^{-i\mathbf{k} \cdot [\mathbf{R}_i(0) - \mathbf{R}_j(0)]} e^{-i\mathbf{k} \cdot [\mathbf{d}_{i\gamma}(0) - \mathbf{d}_{j\delta}(0)]} \right\rangle, \quad (33)$$

where the factor n^{-2} (n is the number of atoms in a solvent molecule) is included in order to obtain the correct limit in the case of a monoatomic fluid when $\mathbf{d}_{i\gamma} = \mathbf{d}_{j\delta} = 0$. After separating the $i=j$ and $i \neq j$ terms we find the expression for $S_{\alpha\alpha}$ in the form of the sum of intramolecular and intermolecular contributions,

$$S_{\alpha\alpha}(\mathbf{k}) = S_{\text{intra}}(\mathbf{k}) + S_{\text{inter}}(\mathbf{k}), \quad (34)$$

where

$$S_{\text{intra}}(\mathbf{k}) = n^{-2} \left\langle \sum_{\gamma, \delta} e^{-i\mathbf{k} \cdot [\mathbf{R}_i(0) - \mathbf{R}_j(0)]} e^{-i\mathbf{k} \cdot (\mathbf{d}_{i\gamma} - \mathbf{d}_{j\delta})} \right\rangle, \quad (35)$$

$$S_{\text{inter}}(\mathbf{k}) = (n^2 N)^{-1} \sum_{i \neq j} \sum_{\gamma, \delta} \langle e^{-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} e^{-i\mathbf{k} \cdot (\mathbf{d}_{i\gamma} - \mathbf{d}_{j\delta})} \rangle, \quad (36)$$

and

$$\mathbf{d}_{i\gamma}(0) \equiv \mathbf{d}_{i\gamma}, \quad \mathbf{d}_{j\delta}(0) \equiv \mathbf{d}_{j\delta}, \quad \mathbf{R}_i(0) \equiv \mathbf{R}_i.$$

In the following we shall consider the rigid molecule approximation [17–19] such that

$$S_{\text{intra}}(\mathbf{k}) = \frac{1}{n^2} \sum_{\gamma, \delta} \frac{\sin kd_{\gamma\delta}}{kd_{\gamma\delta}} = \frac{1}{n^2} \left(n + \sum_{\gamma \neq \delta} \frac{\sin kd_{\gamma\delta}}{kd_{\gamma\delta}} \right), \quad (37)$$

where $\mathbf{d}_{\gamma\delta}$ is the distance between atoms γ and δ in the solvent molecule. This result is obtained after unweighted averaging over the orientation of a molecule. The intermolecular term is averaged over the angular pair distribution function $g(R_{12}, \omega_1, \omega_2)$, where ω_1 and ω_2 are orientations of two molecules and R_{12} is the distance between their centers of mass. Subtracting the term which corresponds to forward scattering and expanding $g(R_{12}, \omega_1, \omega_2)$ in spherical harmonics one can show [18,19] that

$$S_{\text{inter}}(\mathbf{k}) = \left(\frac{1}{n} \sum_{\gamma} \frac{\sin kd_{i\gamma}}{kd_{i\gamma}} \right)^2 (S_C(\mathbf{k}) - 1) + S_a(\mathbf{k}), \quad (38)$$

where S_C is the center of mass structure factor

$$S_C(\mathbf{k}) = 1 + n \int (g_C(\mathbf{R}) - 1) e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{R} \quad (39)$$

and $g_C(\mathbf{R})$ is obtained after averaging over orientations of two molecules, i.e., $g_C(\mathbf{R}) = \langle g(\mathbf{R}, \omega_1, \omega_2) \rangle_{\omega_1, \omega_2}$. The last term $S_a(\mathbf{k})$ is the so-called anisotropic part. It is small if the anisotropic part of the intermolecular interaction is weak. The expression for $S_{\alpha\alpha}(\mathbf{k})$ becomes simpler in the case of diatomic molecules or when a molecule may be modeled as a two-site object. The static structure factor then simply is given by [17]

$$S_{\alpha\alpha}(\mathbf{k}) = \frac{1}{2} \left[1 + \frac{\sin kd}{2kd} \right] + \left(\frac{\sin kd}{kd} \right)^2 (S_C(\mathbf{k}) - 1) + S_a(\mathbf{k}), \quad (40)$$

where d is the distance from the center of the solvent molecule to its site.

Let us consider some properties of this structure factor. In the limit $k \rightarrow 0$ due to relations $\lim_{k \rightarrow 0} \sin kd/kd = 1$ and $S_a(\mathbf{k}) = 0$ for $S_{\alpha\alpha}(\mathbf{k})$ one gets

$$S_{\alpha\alpha}(0) = 1 + n \int (g_C(R) - 1) d\mathbf{R} = \beta^{-1} n K_T, \quad (41)$$

where K_T is the isothermal compressibility. Correspondingly, $\lim_{k \rightarrow 0} S_{\text{inter}} = 1$ and $\lim_{k \rightarrow 0} S_{\text{intra}} = \frac{1}{2}$ (in the general case $\lim_{k \rightarrow 0} S_{\text{intra}} = 1/n$). It is very important that due to the molecular structure the function $S_C(\mathbf{k})$ is modulated by the factor $(\sin kd/kd)^2$.

Further let us consider $F_{\alpha\beta}(\mathbf{k}, t)$ at $t=0$, that is $S_{\alpha\beta}(\mathbf{k})$. On the basis of Eq. (29) for $F_{\alpha\beta}(\mathbf{k}, t)$ and Eq. (30) for $F_{\alpha\alpha}(\mathbf{k}, t)$ we can see that the difference between $S_{\alpha\beta}(\mathbf{k}, t)$ and $S_{\alpha\alpha}(\mathbf{k}, t)$ is connected with the term $\exp\{i\mathbf{k}\cdot[\mathbf{d}_\alpha(0) - \mathbf{d}_\beta(0)]\}$ containing the solute interatomic distance ($\mathbf{d}_\alpha - \mathbf{d}_\beta$). Averaging this factor over the molecular orientation we obtain the simple relation

$$S_{\alpha\beta}(\mathbf{k}) = \frac{\sin kb_{\alpha\beta}}{kb_{\alpha\beta}} S_{\alpha\alpha}(\mathbf{k}), \quad (42)$$

where $b_{\alpha\beta} = |\mathbf{d}_\alpha - \mathbf{d}_\beta|$. If atom α coincides with atom β ($b_{\alpha\beta} = 0$), we have $S_{\alpha\beta}(\mathbf{k}) = S_{\alpha\alpha}(\mathbf{k})$. At $k \approx \infty$ we obtain $S_{\alpha\beta}(\infty) = 0$ because $S_{\alpha\alpha}(\infty) = n^{-1}$. At $k \approx 0$ we find that $S_{\alpha\beta}(0) = S_{\alpha\alpha}(0)$. With increasing k the structure factor $S_{\alpha\beta}(\mathbf{k})$ decreases and becomes smaller than $S_{\alpha\alpha}(\mathbf{k})$. Therefore, one can expect that $\zeta_{\alpha\beta}$ is smaller than $\zeta_{\alpha\alpha}$.

In recent years the structure of supercritical liquids has been intensively investigated [20,21]. One important result emerging from these studies is that the static long-range structure of supercritical fluids may be described by the Ornstein-Zernike expression. Taking this observation into account, the static structure factor has the form [17,22]

$$S_C(k) = 1 + \frac{S_C(0) - 1}{1 + k^2 \xi^2}. \quad (43)$$

Here $S_C(0) = \beta^{-1} n K_T$ [17], K_T is the isothermal compressibility, ξ is the correlation length for density fluctuations. Not far from the critical point one has $S_C(0) \gg 1$, such that

$$S_C(k) = 1 + \frac{S_C(0)}{1 + k^2 \xi^2}. \quad (44)$$

In the following we shall use the inverse correlation length $b = \xi^{-1}$ such that Eq. (44) may be rewritten as

$$S_C(k) - 1 = \frac{S_C(0) b^2}{b^2 + k^2}. \quad (45)$$

If the fluid approaches the critical point correlation length ξ and isothermal compressibility diverge according to [22–24]

$$\xi = \xi_0 (|\Delta T|)^{-\nu}, \quad K = K_T^0 (|\Delta T|)^{-\gamma},$$

where $\nu = 0.630$, $\gamma = 1.2415$ are the universal exponents, ξ_0 and K_T^0 are critical amplitudes, $\Delta T = (T - T_C)/T_C$. The quantities ξ_0 and K_T^0 are system dependent [25]. Along the critical isotherm the correlation length and compressibility behave as

$$\xi \approx |\Delta \rho|^{-\nu/\beta}, \quad K_T \approx |\Delta \rho|^{-\gamma/\beta},$$

where $\Delta \rho = (\rho - \rho_C)/\rho_C$ and $\beta = 0.324$ is another universal exponent.

In the following we consider a fluid with structureless molecules. For modeling the dynamic structure factor we will use the short-time expansion of the intermediate scattering function, $F(\bar{k}, t)$, because this expansion corresponds to vibrational mode frequencies of the excited molecule. The short-time expansion written as a Taylor series has the form [26]

$$F(\bar{k}, t) = \omega^0(\bar{k}) - \frac{t^2}{2!} \omega^2(\bar{k}) + \frac{t^4}{4!} \omega^4(\bar{k}) + \dots, \quad (46)$$

where we have included only the first three terms relevant to our discussion. The coefficients are defined as moments of the dynamic structure factor

$$\omega^n(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \omega^4 S(\bar{k}, \omega) d\omega. \quad (47)$$

One can show easily [26] that

$$\omega^0(\bar{k}) = S(\bar{k}), \quad \omega^2(k) = (k\nu_0)^2, \quad (48)$$

where $\nu_0 = \sqrt{1/\beta m_s}$ is the mean thermal velocity. The fourth moment is expressed by the high-frequency elastic constant $C_{11}(k)$ of the solvent [26]

$$\omega^4(k) = k^2 (k\nu_0)^2 C_{11}(k) / m_s n. \quad (49)$$

Here m_s is the solvent molecular mass and n is its number density. The elastic constant $C_{11}(k)$ is given by [26]

$$C_{11}(k) = 3nk_B T + \frac{n^2}{k^2} \int d\bar{r} g(r)(1 - \cos kZ) \frac{\partial^2 \varphi}{\partial z^2}, \quad (50)$$

where φ is the solvent-solvent pair potential and $g(r)$ is the corresponding pair distribution function. On the basis of the expansion Eq. (46) we extrapolate the time dependence of $F(k, t)$ to longer times with the help of the simple function

$$F(\bar{k}, t) = S(k) \cos \gamma \delta t / ch \gamma t. \quad (51)$$

Parameters γ and δ are determined by the requirement that this function has the same short-time expansion as Eq. (46). The extrapolating function $\cos \gamma \delta t / ch \gamma t$ was first suggested by Douglass [27] and then successfully used by many authors (see, for example, the list of references in [7]). Rewriting Eq. (46) in the form $F(k, t)/S(k) = 1 - At^2 + Bt^4$ and comparing with the short-time expansion of Eq. (51) results in

$$\gamma = \sqrt{A(C-1)/2}, \quad \delta = \sqrt{(5-C)/(C-1)}, \quad (52)$$

where

$$\begin{aligned} A &= (k\nu_0)^2 / 2S(k), & B &= k^2(k\nu_0)^2 C_{11}(k) / 24mnS(k), \\ C &= 6B/A^2. \end{aligned} \quad (53)$$

This leads to an expression for the dynamic structure factor in the form

$$S(k, \omega) = \pi^{-1} S(k) \int_0^\infty \frac{\cos \omega t \cos \gamma \delta t}{ch \gamma t} dt. \quad (54)$$

The integral in this formula can be calculated analytically to yield [28]

$$S(k, \omega) = \frac{S(k)}{\gamma} \frac{ch(\omega\pi/2\gamma)ch(\pi\delta/2)}{ch(\omega\pi/2\gamma) + \cos \pi\delta} \quad (55)$$

or, considering Eqs. (52) and (53), we obtain

$$S(k, \omega) = 2S(k) \sqrt{S(k)} \frac{ch(\omega\pi/2\gamma)ch(\pi\delta/2)}{ch(\omega\pi/2\gamma) + \cos \pi\delta}. \quad (56)$$

For $C > 5$ we get

$$S(k, \omega) = \frac{2S(k) \sqrt{S(k)}}{k\nu_0 \sqrt{C-1}} \frac{ch(\omega\pi/2\gamma)ch(\pi\delta/2)}{ch(\omega\pi/2\gamma) + \cos \pi\delta}, \quad (57)$$

where

$$\delta = \sqrt{(C-5)/(C-1)}. \quad (58)$$

Bear in mind that the Fourier component $\mathbf{B}(\mathbf{k})$ of the force $\mathbf{B}(r) = -\nabla \varphi(\mathbf{r})$ has the form

$$\mathbf{B}(\mathbf{k}) = i\mathbf{k}\varphi(\mathbf{k}),$$

where $\varphi(\mathbf{k})$ is the Fourier transform of the intermolecular solute-solvent potential $\varphi(\mathbf{r})$. For the case when the vector \mathbf{k} is directed along z axis we obtain

$$|B_z(k)|^2 = k^2 \varphi^2(k). \quad (59)$$

In this way, we find the general formula for the rate of vibrational energy relaxation

$$K_C = \frac{2\beta n}{\nu_0 m_0 (2\pi)^3} \int d\bar{k} \frac{s(k) \sqrt{s(k)}}{\sqrt{C-1}} k \phi^2(k) \frac{ch \frac{\omega\pi}{\gamma} ch \frac{\pi\delta}{2}}{ch \frac{\omega\pi}{\gamma} + ch \pi\delta} \quad (60)$$

Now let us consider the derivation of the calculated formula for the high-frequency elastic constant $C_{11}(k)$. For this end we will use the expression

$$\frac{d^2 \varphi}{dz^2} = \frac{1}{r} \frac{d\varphi}{dr} \sin^2 \theta + \cos^2 \theta \frac{d^2 \varphi}{dr^2}, \quad (61)$$

where θ is the angle between vector \bar{k} and \bar{r} . After integrating over the angle θ we obtain

$$\begin{aligned} C_{11}(k) &= \frac{3n}{\beta} + 2\pi n^2 \int_0^\infty dr r \varphi'(r) g(r) F_1(kr) \\ &\quad + 2\pi n^2 \int_0^\infty dr r^2 \varphi''(r) g(r) F_2(kr). \end{aligned} \quad (62)$$

Here, $\varphi'(r) = d\varphi/dr$, $\varphi''(r) = d^2\varphi/dr^2$,

$$F_1(kr) = \frac{4}{k^2} \left(\frac{1}{3} + \frac{\cos kr}{(kr)^2} - \frac{\sin kr}{(kr)^3} \right), \quad (63)$$

$$F_2(kr) = \frac{2}{k^2} \left(\frac{1}{3} + \frac{2 \sin kr}{(kr)^3} - \frac{\sin kr}{kr} - \frac{2 \cos kr}{(kr)^2} \right).$$

Below we will evaluate Eq. (62) for the Lennard-Jones potential on the basis of the Ornstein-Zernike expression for the pair distribution function with the help of Laplace method [29].

The Ornstein-Zernike formula for $g(r)$ is given by

$$\begin{aligned} g(r) &= 0 \quad \text{for } 0 \leq \xi^2 \leq \sigma_{LJ}, \\ g(r) &= 1 + \frac{e^{-rb} b^2 K_T}{4\pi\beta r} \quad \text{for } r > \sigma_{LJ}, \end{aligned} \quad (64)$$

where $b = 1/\xi$, and ξ is the correlation length for the density fluctuations. This leads to

$$\begin{aligned} C_{11}(k) &= 3n/\beta + \frac{12\varepsilon_{LJ} n^2 e^{-\alpha K_T \alpha^2}}{\beta(\alpha+7)(\alpha+13)} \\ &\quad \times [(19\alpha+91)f_2(\chi) - (\alpha+1)f_1(\chi)]. \end{aligned} \quad (65)$$

Here $\alpha = b\sigma_{LJ}$, $\chi = k\sigma_{LJ}$, and ε_{LJ} and σ_{LJ} are parameters of the Lennard-Jones potential

$$\varphi(r) = 4\varepsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r} \right)^{12} - \left(\frac{\sigma_{LJ}}{r} \right)^6 \right], \quad (66)$$

while the functions f_1 and f_2 are defined as

$$f_1(\chi) = \frac{4}{\chi^2} \left(\frac{1}{3} + \frac{\cos \chi}{\chi^2} - \frac{\sin \chi}{\chi^3} \right), \quad (67)$$

$$f_2(\chi) = \frac{2}{\chi^2} \left(\frac{1}{3} + \frac{2 \sin \chi}{\chi^3} - \frac{\sin \chi}{\chi} - \frac{2 \cos \chi}{\chi^2} \right).$$

The Ornstein-Zernike structure factor may be represented by

$$S(\chi) = \frac{k_B T n K_T \alpha^2}{\alpha^2 + \chi^2} + \frac{\chi^2}{\alpha^2 + \chi^2}. \quad (68)$$

For calculating the correlation length, which appears in the structure factor and in $C_{11}(k)$ we will use the following formula [9]:

$$\xi = \xi_0 \left(\frac{P_c}{\Gamma_0 \rho_c^2} \right)^{\nu/\gamma} \left[\rho \left(\left(\frac{\partial P}{\partial \rho} \right)_T - \frac{T_r}{T} \left(\frac{\partial P}{\partial \rho} \right)_{T=T_r} \right) \right]^{\nu/\gamma}, \quad (69)$$

where ξ_0 and Γ_0 are the critical amplitudes which are system dependent. In addition, ν and γ are the critical exponents, P_c and ρ_c are the critical pressure and the critical density, respectively. The temperature T_r is so-called reference temperature, which may be put equal to $1.5T_c$ or $2T_c$ [9], where T_c is the critical temperature. The term with T_r in Eq. (69) is the background term which has to be subtracted from $\rho(\partial\rho/\partial P)_T$ to ensure that ξ becomes vanishingly small far away from the critical point.

IV. CALCULATION OF VIBRATIONAL ENERGY RELAXATION RATES AND ITS ANALYSIS

In the following we will compare our theoretical model with experimental results on the density dependence of the vibrational energy relaxation of azulene in supercritical fluids [1,2]. These experiments were done in fluid ethane and propane at temperatures close to (~ 3 K) and far above the critical temperature of the solvent. Relaxation rates were calculated for two kinds of solute-solvent potential, a repulsive and a Lennard-Jones potential as defined in Eq. (66).

A simple and analytically convenient expression for the repulsive potential is [30–32]

$$\varphi(r) = \varepsilon_{\text{rep}} e^{-r/\sigma_{\text{rep}}}, \quad (70)$$

where ε_{rep} and σ_{rep} are potential parameters, which for a sequence of fluids are given in [30,31]. These parameters differ from LJ parameter considerably, i.e., $\varepsilon_{\text{rep}} > \varepsilon_{\text{LJ}}$, $\sigma_{\text{rep}} < \sigma_{\text{LJ}}$. According to [32] $\sigma_{\text{rep}} = \sigma_{\text{LJ}}/l$, where l approximately equals 20. In what follows we will take $l = 20$.

The Fourier transformation of this potential is given by

$$\varphi(k) = 8\pi\varepsilon_{\text{rep}}\sigma_{\text{rep}}^3 / (1 + k^2\sigma_{\text{rep}}^2)^2 \quad (71)$$

and for $|B_z(k)|^2$ we obtain the expression

$$|B_z(k)|^2 = 64\pi^2\varepsilon_{\text{rep}}^2\sigma_{\text{rep}}^6 k^2 / (1 + k^2\sigma_{\text{rep}}^2)^4. \quad (72)$$

We note that the vector \vec{k} is directed along z axis.

The rate of vibrational energy relaxation for the repulsive potential is evaluated on the basis of Eq. (60) and is given by

$$K_C = \frac{\varepsilon_{\text{rep}}^2}{m_0} 64e^2\sigma_s^2\sqrt{\beta m_s}\beta n$$

$$\times \int_0^\infty \frac{d\chi \omega \chi \chi^3}{(l^2 + \chi^2)^4} \frac{S(\chi)\sqrt{S(\chi)}}{\sqrt{C(\chi)-1}} F(\omega, \chi). \quad (73)$$

Here $\chi = k\sigma_s$, σ_s is the LJ parameter for the solvent, m_s is the mass of the solvent molecule, $\beta = (k_B T)^{-1}$, m_0 is the reduced mass of the solute oscillator, and ω is some normal mode frequency of the solute. The function $F(\omega, \chi)$ has the form

$$F(\omega, \chi) = ch \frac{\pi \delta}{2} \frac{e^{-(\omega\pi/2\gamma)} + e^{-(3\omega\pi/2\gamma)}}{1 + e^{-(2\omega\pi/\gamma)} + 2e^{-(\omega\pi/\gamma)}} ch \pi \delta \quad (74)$$

for $e < 5$. For the case $c > 5ch(\dots)$ must be replaced with $\cos(e)$. It should be noted that due to the rapid convergence of the integral in Eq. (15) its upper limit was put to infinity. The parameter $\varepsilon_{\text{rep}}^2/m_0$ we will consider as a fitting parameter.

If solute-solvent interactions are described by a Lennard-Jones potential, the Fourier transformation is determined with the help of [33]

$$\frac{\Gamma(\nu+2)\sin\nu\pi/2}{2\pi^2 r^{\nu+3}} = - \lim_{\lambda \rightarrow 0} \frac{1}{(2\pi)^3} \int e^{i\pi\cdot\vec{r}-\lambda k^\nu} d\vec{k}, \quad (75)$$

where $\Gamma(x)$ is the γ function. Using this we obtain

$$\varphi(k) = 8\pi^2\varepsilon_{\text{LJ}}\sigma_{\text{LJ}}^6 \left(\frac{\sigma_{\text{LJ}}^6 k^9}{10!} - \frac{k^3}{4!} \right) \quad (76)$$

and the rate of relaxation is given by

$$k_C = \frac{\varepsilon_{\text{LJ}}^2}{m_0} \frac{\sqrt{\beta m_s} \pi^2 \sigma_{\text{LJ}}^2 \beta n}{9} \int_0^{\chi_0} d\chi \chi^3$$

$$\times \left(\frac{\chi^9}{151200} - \chi^3 \right)^2 \frac{S(\chi)\sqrt{S(\chi)}}{\sqrt{C(\chi)-1}} F(\omega, x), \quad (77)$$

where $\chi = k\sigma_{\text{LJ}}$, and the function $F(\omega, x)$ is determined as before. In this case, χ_0 (the upper limit of integration) is considered as a fitting parameter.

The correlation lengths are calculated by Eq. (69) with the help of tables of thermodynamic data [33]. The following values of parameters were used for ethane: $\xi_0 = 1.9 \times 10^{-10}$ m, $\Gamma_0 = 0.0563$ [9], $P_c = 4.871 \times 10^6$ Pa, $\rho_c = 206.7$ kg/m³; and for propane: $\xi_0 = 2 \times 10^{-10}$ m, $\Gamma_0 = 0.058$ [25], $P_c = 4.248 \times 10^6$ Pa, $\rho_c = 220.5$ kg/m³. In both cases the critical exponents are $\nu = 0.63$, $\gamma = 1.242$ [9]. The calculated values of ξ for ethane at 385 K and propane at 396.5 K and 372.5 K are shown in Fig. 1.

At first, we discuss the numerical results for K_C derived from Eq. (73) using an Ornstein-Zernike structure factor and a repulsive exponential potential to describe solute-solvent interactions. Computed and experimental values [1,2] for K_C are presented in Figs. 2 and 3. The fitting parameter ε^2/m_0 equals 0.27671×10^{-12} J²/kg and 0.4744×10^{-12} J²/kg, respectively, corresponding to physically reasonable values.

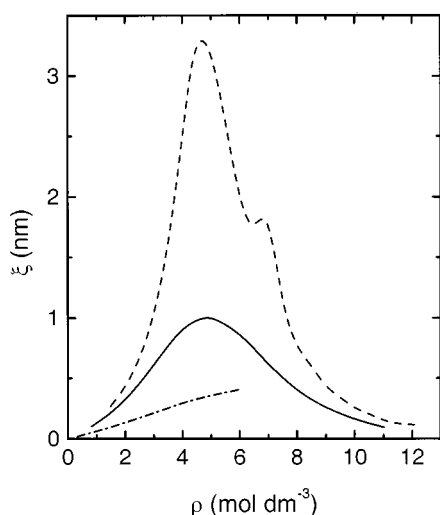


FIG. 1. Calculated density dependence of the correlation lengths. —, ethane at $T=385$ K; —, propane at $T=372.5$ K; ---, propane at $T=396.5$ K.

From these figures we can conclude that the rate of relaxation of our model increases almost linearly, whereas the experimental values at half the critical density show a slower increase of K_C with density. The linear $K_S(\rho)$ -dependence of our model, however, is in agreement with a theory that uses a different structure factor [8].

The linearity of the density dependence of K_C has a straightforward explanation. The contribution of the repulsive interaction in the integral Eq. (27) is dominant for large magnitudes of wave vectors (the repulsive forces are large for small distances). But in this region of wave vectors the structure factor goes to unity and the information about the density dependence contained in $S(k)$ and also in $C_{11}(k)$ is partially washed out.

In some sense the situation is better for cases when the solute-solvent interaction described by a Lennard-Jones potential is well beyond the critical density. Calculated

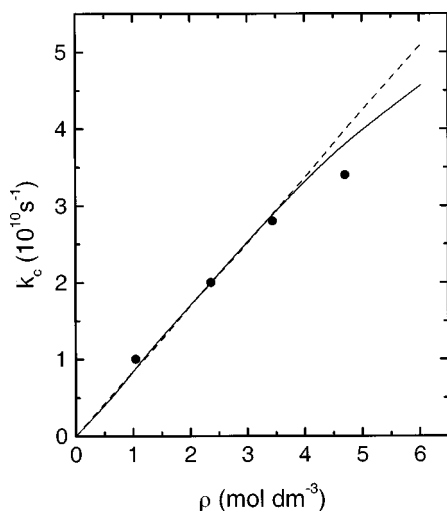


FIG. 2. Density dependence of the vibrational relaxation rate K_C for azulene in ethane at 385 K. ●, Experiment (Refs. [1,2]); —, calculation for the LJ potential; ---, calculation for the repulsive potential (with $\omega=3.56 \times 10^{13} \text{ s}^{-1}$ corresponding to the lower normal mode frequency of azulene).

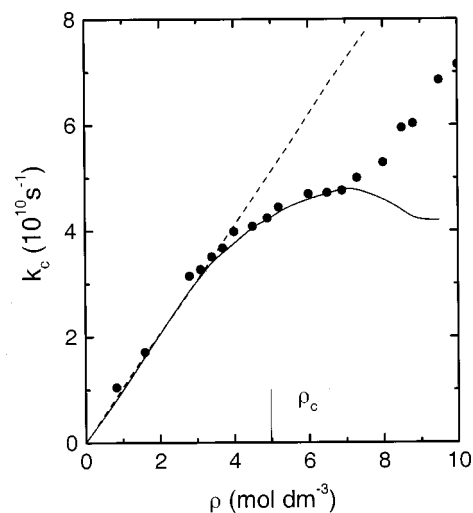


FIG. 3. As in Fig. 2 for azulene in propane at $T=396.5$ K.

K_C -values for ethane at $T=385$ K and for propane at $T=396.5$ K and $T=372.5$ K are plotted in Figs. 2–4 in comparison with experimental data [1,2]. Again we use the Ornstein-Zernike structure factor for these cases. The parameter ε^2/m_0 was put to $0.4639 \times 10^{-15} \text{ J}^2/\text{kg}$. Fitting at the upper limit of integration yields $x_0=8.10$ for ethane and $x_0=8.64$ for propane at 396.5 K and $x_0=8.75$ at 372.5 K.

We note that the agreement between the calculated values of the rate K_C and the experimental values is satisfactory beyond the critical density. At high densities the Ornstein-Zernike approximation breaks down, and therefore we are not able to give a description of the density dependence of K_C in this region on the basis of this approximation. The upper limit of integration of $\chi_0 \cong 8$ corresponds to a distance of $\chi=0.75\sigma_{LJ}$, which indicates that we take into account the local environment of an excited molecule, which plays a significant role in vibrational energy relaxation.

V. CONCLUSIONS

We have derived an expression for the vibrational relaxation rate of a vibrationally excited molecule in supercritical

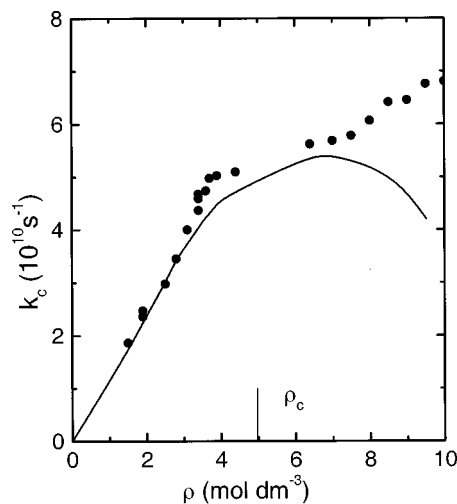


FIG. 4. As in Fig. 2 for azulene in propane at $T=372.5$ K.

solvents in terms of the dynamic structure factor of the solvent and the force describing the interaction between solute and solvent molecules. By using a hydrodynamic model for the dynamic structure factor we find a connection between the thermodynamic properties of the solvent and the rate of vibrational relaxation of the excited molecule. In addition, we establish a relation between the relaxation rate and the parameters of the solute-solvent interaction potential.

Calculations of vibrational relaxation rates of azulene in ethane and propane on the basis of a Lennard-Jones and an exponential repulsive potential permits us to reproduce the density dependence of the experimental rates in a quantitative

and qualitative way both far from and close to the solvent critical density.

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