Molecular linear velocity in dielectric and far-infrared spectroscopy

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In computer simulations of the molecular dynamics of liquid water from 1 bar, 293 K to 200 kbar, 1043 K, direct statistical correlation has been observed in the laboratory frame of reference between the molecular linear center of mass velocity $\mathbf{v}$ and (i) the dipole unit vector $\boldsymbol{\mu}$, and (ii) its time derivative. These results imply that dielectric relaxation and far-infrared absorption spectra are incompletely understood with theories which neglect cross correlations.

I. INTRODUCTION

Two of the most fundamental results in the theory of broad band spectroscopy[1-3] are that the dielectric loss and dispersion are related through a Fourier transform of the orientational autocorrelation function (acf)

$$C_\mu = \langle \boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)\rangle / \langle \mu^2\rangle \ ,$$

where $\boldsymbol{\mu}$ is the molecular dipole moment; and that the far-infrared absorption, the high-frequency adjunct of dielectric loss, is related to the rotational velocity acf

$$C_{\dot\mu} = \langle \dot{\boldsymbol{\mu}}(t)\cdot\dot{\boldsymbol{\mu}}(0)\rangle / \langle \dot\mu^2\rangle \ .$$

In order to interpret the dielectric and far-infrared absorptions of molecular liquids, theories of molecular dynamics are used to construct these correlation functions[4-7] usually in the time domain. It is almost universally assumed that the molecular linear velocity $\mathbf{v}$ plays no direct part in the dynamics leading to both time autocorrelation functions. This has been implicit in the theory of rotational diffusion since its inception.[8-10]

In this paper we provide the first evidence that this assumption is fundamentally false because the dipole unit vector and its time derivative have been observed in this work to be statistically correlated to $\mathbf{v}$ directly in the laboratory frame (x,y,z). In other words the time cross-correlation functions (ccf)

$$C_1 = \langle \boldsymbol{\mu}(t)\cdot\mathbf{v}(0)\rangle / \langle \mu^2\rangle^{1/2} \langle v^2\rangle^{1/2} \ ,$$

$$C_2 = \langle \dot{\boldsymbol{\mu}}(t)\cdot\mathbf{v}(0)\rangle / (\langle \dot\mu^2\rangle^{1/2}\langle v^2\rangle^{1/2})$$

exist directly in the laboratory frame for $t>0$ at state points from 1 bar, 293 K to 250 kbar, 1043 K in liquid water. Therefore it would be incomplete to interpret dielectric and far-infrared spectra without detailed consideration of cross-correlation functions. It follows that this is also true of all types of liquid-state spectra involving the orientation vector, such as infrared band-shape analysis,[11] light and neutron scattering,[12] and so on.[13] The most complete method of interpretation involves computer simulation which can be used self-consistently to produce experimental information for comparison[14] and to interpret this properly with the role of cross correlations fully recognized.

II. OUTLINE OF MOLECULAR DYNAMICS SIMULATION

The molecular dynamics of liquid water were simulated in this work with a site-site potential constructed of atom-atom terms and partial charges fully described elsewhere in the literature.[15] Simulations were made at a range of state points over a time segment of 6000 time steps of 0.5 fs each. The pressure in the simulation was computed for input temperature and molar volume, and the results are summarized in Table I. This shows that the potential behaves satisfactorily as regards pressure dependence up to 250 kbar in liquid water. The experimental pressure in Table I is derived from the literature.[16] We make no claim as to the ability of this potential to reproduce the various ice structures, however, and in this respect the MCY potential[17,18] is the most successful, as shown by the careful work of Morse and Rice.[19] However, the MCY potential produces a pressure which is far too high (8000 bar) at room temperature and molar volume.[14,18,20]

The new time cross-correlation functions reported in this work exist irrespective of the type of potential used and are fundamental, in other words, to liquid-state molecular dynamics in water. It is safe to infer that the same is true for all molecular liquids, i.e., cross-correlation functions of this type always exist in liquid-state molecular dynamics and affect the interpretation of spectral band shapes.

Each correlation function in this work was computed over 6000 timesteps of 0.5 fs dumped every second step into 3000 configurations. Running-time averages were computed over these configurations with an efficient algorithm which completed the computation in a few minutes of real time.

III. RESULTS AND DISCUSSION

Having reported a comparison with experimental thermodynamic data in Table I we report the major new results of this paper in Figs. 1 and 2, where illustrated is each component in the laboratory frame of the cross-correlation functions

$$C_{ij}^{(1)} = \langle \mu_i(t)v_j(0)\rangle / (\langle \mu_i^2\rangle^{1/2}\langle v_i^2\rangle^{1/2})$$

TABLE I. Comparison of computed and experimental pressures of liquid water. Note that the last point is at the critical point.

Molar volume (cm^3/mole)	Temperature (K)	P experimental (bar)	P computed (bar)
18.0	293	1.0	-150 ± 200
18.0	373	1 000.0	1 515 ± 300
18.0	473	3 000.0	3 693 ± 600
18.0	673	7 500.0	8 773 ± 900
18.0	773	9 500.0	12 200 ± 1 000
18.5	1273	15 000.0	19 132 ± 1 500
56.8	647	221.0	300 ± 60
8.5	1043	250 000.0	599 610 ± 12 000

and

$$C_{ij}^{(2)} = \langle \dot{\mu}_i(t)v_j(0) \rangle / (\langle \dot{\mu}_i^2 \rangle^{1/2} \langle v_i^2 \rangle^{1/2})$$

at 250 kbar and 1043 K in the high-density water obtained experimentally by shock wave compression. Results are also available for the following states: 1 bar, 293 K; 15 kbar, 1273 K; 250 kbar, 1043 K. The acf's of center of mass velocity and rotational velocity were also computed. The cross correlation between the molecular linear velocity **v** and its own rotational velocity $\dot{\mu}$ is the stronger of the two ccf's, and both types of cross correlation increase in intensity with liquid density. The use of 6000 timesteps provides the necessary high-quality statistics with which to define the time dependence of each component.

As far as we are aware this is the first time that direct cross correlation has been observed between the molecular center of mass velocity **v** and the fundamental orientational vector μ and its time derivative, which underpin the interpretation of so much spectroscopic data in the literature. The theory of rotational diffusion and its many variations and derivatives takes no account of these direct and fundamental statistical correlations. This theory is often used, however, in the interpretation of
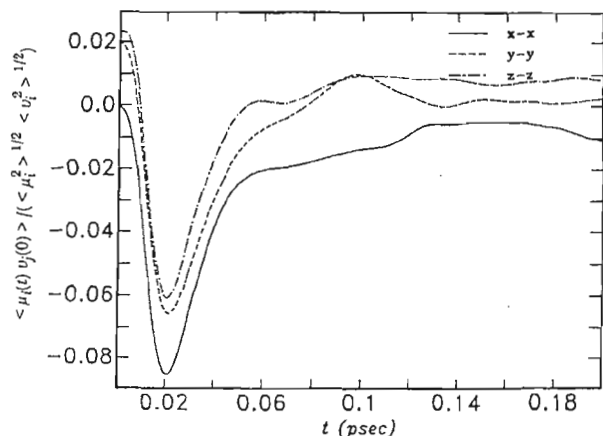
molecular dynamics and spectral band shapes, and such interpretations are now seen clearly to lead to false conclusions. This is because the theoretical assumptions are fundamentally incorrect in assuming implicitly that the intensity of the cross-correlation functions in Figs. 1 and 2 is zero for all t. Computer simulation therefore leads to a fundamentally more accurate appreciation of liquid-state molecular dynamics and the interpretation of spectral band shapes.

The origin of the new cross correlations in the laboratory frame must be sought in the fact that the total velocity of an atom in a molecule is

$$\mathbf{v}_a = \mathbf{v} + \tfrac{1}{2}\omega \times \mu , \tag{1}$$

where ω is the molecular angular velocity (note that molecular vibration has been neglected). Thus

$$\langle \mathbf{v}_a(t) \cdot \mathbf{v}_a(0) \rangle = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle + \langle \mathbf{v}(t) \cdot \omega(0) \times \mu(0) \rangle$$
$$+ \tfrac{1}{4} \langle \mu(t) \cdot \mu(0) \rangle \langle \omega(t) \cdot \omega(0) \rangle . \tag{2}$$

Therefore the central term on the right-hand side is the one observed in this work which measures the strength of rotation-translation coupling direct in the laboratory frame. A simple theory for the coupling term can be constructed from the linked Langevin equations

$$\dot{\mathbf{v}} = -\lambda_t \mathbf{v} - \lambda_{tr} \dot{\mu} + \mathbf{F} , \tag{3}$$

$$\ddot{\mu} = -\lambda_t \dot{\mu} - \lambda_{tr} \mathbf{v} + \mathbf{N} , \tag{4}$$

where λ_t, λ_r and λ_{tr} are friction coefficients. The second equation above is a Langevin equation direct in the rotational velocity, since it is possible in general to construct linked Langevin equations for any two fluctuating variables X and Y. Equations (1) and (2) are analytically soluble,[1] the cross-correlation function being described as

$$\langle \mathbf{v}(t) \cdot \dot{\mu}(0) \rangle = \frac{\langle v^2 \rangle}{(c-b^2)^{1/2}} \lambda_{tr} e^{-bt} \sin[(c-b^2)^{1/2}t]$$
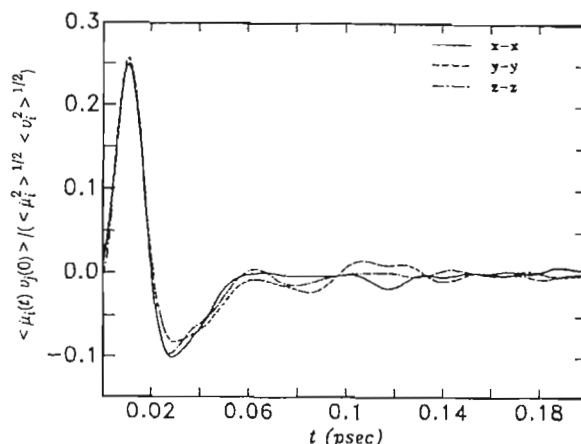
$$\text{if } c > b^2 , \tag{5}$$

FIG. 2. The diagonal elements of $\langle \dot{\mu}_i(t)v_j(0) \rangle / (\langle \dot{\mu}_i^2 \rangle^{1/2} \langle v_i^2 \rangle^{1/2})$ for water at 1 bar and 293 K ($ij = x,y,z$).

FIG. 1. The diagonal elements of $\langle \mu_i(t)v_j(0) \rangle / (\langle \mu_i^2 \rangle^{1/2} \langle v_i^2 \rangle^{1/2})$ for water at 1 bar and 293 K ($ij = x,y,z$).

$$\langle \mathbf{v}(t)\cdot\dot{\mu}(0)\rangle = \frac{\langle v^2\rangle}{(b^2-c)^{1/2}}\lambda_{tr}e^{-bt}\sinh[(b^2-c)^{1/2}t]$$

$$\text{if } c < b^2 , \quad (6)$$

where $b = 2(\lambda_t + \lambda_r)$ and $c = \lambda_t\lambda_r - \lambda_{tr}\lambda_{tr}$. Furthermore, the friction coefficients λ_t and λ_r can be found from the velocity and rotational velocity acf's individually. Therefore the new cross correlation of this work can be described approximately in terms of the new coupling parameter λ_{tr}. This depends on the nature of the molecule and on the thermodynamic state of the liquid. It is the analogy of the Debye relaxation time for rotation-translation coupling and can be used in the same way to characterize the molecular dynamics. It can be observed experimentally with a combination of tracer diffusion, far-infrared spectroscopy, and computer simulation.

The optimum fit to the computer simulation data at 1 bar and 296 K was found with the three friction coefficients $\lambda_t = 1.0$, $\lambda_r = 25.0$, and $\lambda_{tr} = 50.0$; and this is illustrated in Fig. 3. The simple theory reproduces reasonably accurate representations of the velocity and rotational velocity acf's together with the cross-correlation function, in terms of the three friction coefficients. For example, the translational velocity auto-correlation function becomes negative at about 0.04 psec, as found in the molecular dynamics simulations of water,[14,20] and the velocity-rotation cross correlation rises to a maximum of about 0.3 at ~ 0.02 psec, as found in Fig. 2. However, the theoretical curves have the usual limitations of an essentially Markovian treatment, for example, they cut the $t = 0$ axis with a finite slope. This can only be remedied through use of memory functions, but at the cost of analytical intractability and over parametrization. It is significant, however, that the *linked* Langevin equations produce a negative overshoot in both acf's as observed computationally. This is not possible with
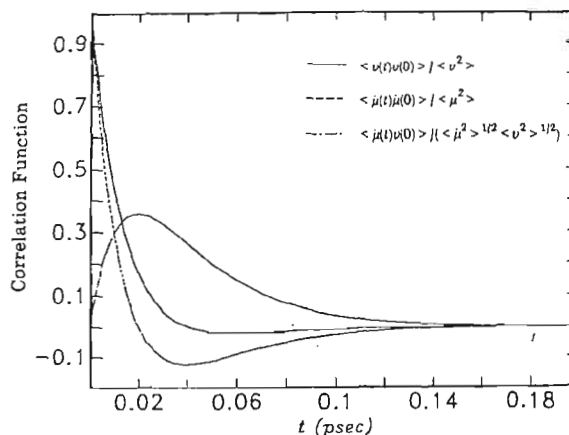

FIG. 3. Theoretical results for the velocity acf, the rotational velocity acf, and the cross-correlation function from the linked Langevin theory Eqs. (3) and (4). See text for the values of the parameters used.

decoupled Langevin equations, which produce simple exponentially decaying acf's if memory effects are neglected and give no result for the time cross-correlation function in the laboratory frame (x,y,z).

Finally we note the result

$$\langle\dot{\mu}(t)\cdot\mathbf{v}(0)\rangle = -\langle\mathbf{v}(t)\cdot\dot{\mu}(0)\rangle$$

from the simulation as required by independence of the time origin used in the expression, so that

$$\lambda_{rt} = -\lambda_{tr}$$

in Eqs. (3) and (4).

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