Translational correlation function of interaction-induced dipoles in dense media

Zygmunt Gburski,[a] Jannis Samios, and Thomas Dorfmüller

Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld 1, Postfach 8648, West Germany

The time-correlation functions associated with the translational motions of the dipole—induced by permanent multipoles of an arbitrary order $1 = 1,2,3,...$—in a dense fluid have been calculated analytically assuming the isotropic diffusion mechanism. The correlation functions obtained from this model have been compared with the available results of the molecular dynamics simulations in liquid N_2 ($T = 75.5$ K, $\rho = 0.814$ g cm^{-3}) and CS_2 ($T = 298$ K, $\rho = 1.26$ g cm^{-3}) and appear to reflect the proper time scale of the relaxation process.

I. INTRODUCTION

The far-infrared absorption spectra of nonpolar molecules are caused by induced dipoles due to intermolecular interactions.[1]

These spectra reflect the relaxation of fluctuations in the local structure in a fluid.

The interaction-induced total dipole moment $M(t)$, and its correlation function $C(t) = <M(0) \cdot M(t)>$ directly depend upon intermolecular coordinates (reciprocal orientations and intermolecular separations). This is an important difference to allowed transitions (IR, Raman) which reflect only indirectly the influence of intermolecular interactions. The total correlation function $C(t)$ can be decomposed into a sum

$$C(t) = C_2(t) + C_3(t) + C_4(t) \qquad (1.1)$$

of its separate, n-body contributions $C_n(t)$ ($n = 2,3,4$). In other words, the induced spectrum $I(\omega)$ [Fourier transform of $C(t)$] may be represented by a power series expansion in density:

$$I(\omega) = I_2(\omega) \cdot \rho^2 + I_3(\omega) \cdot \rho^3 + I_4(\omega) \cdot \rho^4 , \qquad (1.2)$$

where $I_n(\omega)$ is the spectrum [Fourier transform of $C_n(t)$] due to n-body correlations in the fluid.

In a dilute gas, only binary interactions are important, and to a good approximation $C(t) = C_2(t)$, but as the density increases, the three-body term $C_3(t)$, eventually $C_4(t)$, becomes more pronounced.

Even though in the dense fluid the experimental spectrum $I(\omega)$ is not immediately related to any particular component correlation functions $C_n(t)$, this decomposition is helpful in understanding how the dynamical modes probed by far-infrared spectroscopy vary with density.

What is more important, the correlation functions $C_n(t)$ can be separately simulated via molecular dynamics (MD) experiments.

If accessible,[26] these functions may be used as very sensitive probes of different aspects of molecular motions and the dynamics of local structure in fluid. There are only two MD simulations of $C_n(t)$ in molecular liquids; the first by Steele[2]

for nitrogen, the second one by Samios *et al.*[3] for CS_2. The most important result of both simulations is a clear time-scale separation between the rapidly decaying $C(t)$ and its n-body components $C_n(t)$. The functions $C_n(t)$, taken separately, display a rather long time decay, at least one order longer than $C(t)$. The total correlation function decays so fast, because a great deal of almost exact cancellations occurs between the positive $C_2(t)$, $C_4(t)$ and the negative $C_3(t)$.

Although it does emerge from MD simulations that it is the time behavior of the various $C_n(t)$ which primarily determines the time plot of $C(t)$, the theoretical treatment of the separate components $C_n(t)$ is in its infancy. In this paper we make a step in this direction, by attempting to understand the contrasting behavior (slow and structureless decay) of the translational component of the pair correlation function $C_2(t)$. We explore a common assumption of decoupling of the translational and rotational motions of molecules. Thus $C_2(t)$ becomes a product $C_2(t) = C_{tr}(t) C_{rot}(t)$ of the corresponding translational $C_{tr}(t)$ and rotational $C_{rot}(t)$ correlation functions.

Assuming translational diffusion to be the mechanism by which the local structure of the fluid is changing, we were able to derive an analytical formula for $C_{tr}(t)$. The influence of the atomic diffusion on the depolarized Rayleigh scattering from argon in DID approximation has been pointed out by Ladd *et al.*,[4] also see further application by Madden and Cox.[5] The model is tested vs MD results for liquid N_2 and CS_2.

II. THE THEORETICAL CORRELATION FUNCTION

Absorption of radiation at angular frequency ω is measured by the absorption coefficient $A(\omega)$. An isolated molecule in the gas phase experiences only the electric field E_0 of the exciting radiation, and in this case one can derive a rigorous theoretical relationship between $A(\omega)$ and the spectral intensity $I(\omega)$, which is the Fourier transform, or power spectrum, of the dipole moment autocorrelation function $C(t)$. In the classical limit, the standard linear response calculation yields

$$A(\omega) = \frac{4\pi^2\beta}{3CV_0} \omega^2 I(\omega) , \qquad (2.1)$$

[a] Permanent address: Department of Physics, Silesian University, Uniwersytecka 4, 40-007, Katowice, Poland.

where V_0 is the sample volume, c is the speed of light, $\beta = (kT)^{-1}$ (k-Boltzmann constant), and

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} C(t)e^{-i\omega t}dt, \qquad (2.2)$$

where

$$C(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle . \qquad (2.3)$$

In Eq. (2.3) the angular brackets denote an equilibrium ensemble average in the absence of the radiation field, $\mathbf{M}$ is the total dipole moment of the system.

When one considers the absorption of light by the molecule of a liquid, however, one finds that the simple relationship (2.1) no longer holds. This is because each absorbing unit now no longer experiences only the field $\mathbf{E}_0$, but also the fluctuating electric fields generated by the time-dependent dipoles that $\mathbf{E}_0$ induces neighboring molecules.

One is then confronted by a many-body problem for which only formal, or approximate, solutions exist. One such approximate treatment utilizes Lorentz's concept of the local field. This relates the average or local field $\mathbf{E}_l$ acting on an absorber in the condensed phase to $\mathbf{E}_0$ by an equation of the form

$$E_l^2 = \frac{(n^2 + 2)^2}{9n} E_0^2, \qquad (2.4)$$

where n is the refractive index of the sample. The quantity $\chi = (n^2 + 2)^2/9n$ defined in Eq. (2.4) is referred to as the Polo–Wilson factor.[6] Since the absorption is now proportional to E_l^2 rather than to E_0^2, Eq. (2.1) is replaced by the approximate relation

$$A(\omega) \cong \chi \frac{4\pi^2\beta}{3CV_0} \omega^2 I(\omega). \qquad (2.5)$$

For a nonpolar fluid the dipole moment $\mathbf{M}$ can be written as a sum of terms representing the induced dipoles of pairs of molecules, triplets, etc.
Thus

$$\mathbf{M} = \sum_{j>i} \boldsymbol{\mu}_{ij} + \sum_{k>j>i} \boldsymbol{\mu}_{ijk} + \cdots, \qquad (2.6)$$

where $\boldsymbol{\mu}_{ij}$ denotes the dipole moment that the isolated pair of molecules i and j induce in one another.

Only very rough estimates are at present available for the three-body term $\boldsymbol{\mu}_{ijk}$, and none of the treatments discussed attempt to take any account of these terms. The importance of three-body corrections in liquids is unclear, and remains an intriguing question.

In the pairwise-additive approximation the correlation function $C(t)$ becomes the sum of two-, three-, and four-body terms,

$$C(t) = \langle \sum_{i,j,k,l} \boldsymbol{\mu}_{ij}(0) \cdot \boldsymbol{\mu}_{kl}(t) \rangle$$

$$= \sum_{i,j} \langle \boldsymbol{\mu}_{ij}(0) \cdot \boldsymbol{\mu}_{ij}(t) \rangle$$

$$+ \sum_{i,j,k} \langle \boldsymbol{\mu}_{ij}(0) \cdot \boldsymbol{\mu}_{ik}(t) \rangle$$

$$+ \sum_{i,j,k,l} \langle \boldsymbol{\mu}_{ij}(0) \cdot \boldsymbol{\mu}_{kl}(t) \rangle, \qquad (2.7)$$

where i,j,k,l identify different molecules.

In this paper we focus on the first (two-body) term

$$C_2(t) = \sum_{i,j} \langle \boldsymbol{\mu}_{ij}(0) \cdot \boldsymbol{\mu}_{ij}(t) \rangle \qquad (2.8)$$

in Eq. (2.7) leaving the more elaborate three- and four-body terms for a further study.

As was shown by Joslin et al.,[7] the calculation of the correlation functions encountered in interaction-induced phenomena is considerably simplified if we work in terms of spherical tensors.

The spherical tensor components of the dipole $\boldsymbol{\mu}_2$ induced on a molecule, which we label 2, by the electric field generated by a neighboring molecule, labeled 1, are given by

$$\mu_{2,\nu} = -\alpha \nabla_\nu \phi(\mathbf{r}_{12}); \quad \nu = 0, \pm 1, \qquad (2.9)$$

where we have assumed that the molecular polarizability tensor $\boldsymbol{\alpha}$ is isotropic, i.e., $\boldsymbol{\alpha} = \alpha \mathbf{1}$ ($\mathbf{1} =$ unit vector), ∇_ν denotes a spherical component of the gradient operator $\nabla = \partial / \partial \mathbf{r}_{12}$ and $\phi(\mathbf{r}_{12})$ in the electrostatic potential. Neglecting the potential produced by the small induced moments themselves, we have

$$\phi(\mathbf{r}_{12}) = \sum_l \sum_{m=-l}^{+l} Q_{lm}^* (\omega_1) C_{lm}(\omega_{12}) r_{12}^{-(l+1)}. \qquad (2.10)$$

Here r_{12} and ω_{12} specify the magnitude and orientation, respectively, of the intermolecular vector $\mathbf{r}_{12}$, $c_{lm}(\omega_{12})$ denotes a Racah spherical harmonic, ω_1 specifies the orientation of molecule 1, and Q_{lm} denotes the mth component of the spherical permanent multipole moment tensor of order l.

Using the gradient formula, (viz. Ref. 8), the collision-induced pair dipole moment of molecules 1 and 2 is therefore

$$\mu_{12,\nu} = \mu_{1,\nu} + \mu_{2,\nu}$$

$$= \alpha \sum_{l,m} [(l+1)(2l+1)]^{1/2}$$

$$\times C_{(l+1,l+1;m,\nu,m+\nu)}$$

$$\times [Q_{lm}^*(\omega_1) + (-1)^{l+1} Q_{lm}^*(\omega_2)]$$

$$\times C_{l+1,m+\nu}(\omega_{12}) r_{12}^{-(l+2)}. \qquad (2.11)$$

If the system contains N molecules, there are $\frac{1}{2}N(N-1)$ molecular pairs and $C_2(t)$ becomes

$$C(t) = \frac{1}{2}N(N-1) \sum_\nu \langle \mu_{12,\nu}(0) \mu_{12,\nu}(t) \rangle$$

$$= C_{2A}(t) + C_{2B}(t), \qquad (2.12)$$

where

$$C_{2A}(t) = \frac{1}{2}N(N-1)\alpha^2 \sum_{l,l',m,m',\nu} K_{ll'mm'\nu} A_{ll'mm'\nu}, \qquad (2.13)$$

$$C_{2B}(t) = \frac{1}{2}N(N-1)\alpha^2 \sum_{l,l',m,m',\nu} K_{ll'mm'\nu} B_{ll'mm'\nu}, \qquad (2.14)$$

$$K_{ll'mm'\nu} = [(l+1)(2l+1)(l'+1)(2l'+1)]^{1/2}$$

$$\times C_{(l,1,l+1;m,\nu,m+\nu)} C_{(l',1,l'+1;m',\nu,m'+\nu)}. \qquad (2.15)$$

$$A_{ll'mm'\nu} = \langle \{ Q_{lm}[\omega_1(0)]Q^*_{l'm'}[\omega_1(t)] + (-1)^{l+l'+2}Q_{lm}[\omega_2(0)]$$

$$\times Q^*_{l'm'}[\omega_2(t)]\} C^*_{l+1,m+\nu}[\omega_{12}(0)]C_{l'+1,m'+\nu}[\omega_{12}(t)] \cdot r_{12}^{-(l+2)}(0)r_{12}^{-(l'+2)}(t)\rangle , \qquad (2.16a)$$

$$B_{ll'mm'\nu} = \langle \{ (-1)^{l'+1}Q_{lm}[\omega_1(0)]Q^*_{l'm'}[\omega_2(t)]$$

$$+ (-1)^{l+1}Q_{lm}[\omega_2(0)]Q^*_{l'm'}[\omega_1(t)]\} C^*_{l+1,m+\nu}[\omega_{12}(0)]\times C_{l'+1,m'+\nu}[\omega_{12}(t)]r_{12}^{-(l+2)}r_{12}^{-(l'+2)}(t)\rangle .$$

$$(2.16b)$$

In Eq. (2.16) there are two types of variables; the bimolecular variables r_{12}, ω_{12} which describe the mutual translation and orientation of two colliding molecules, and the monomolecular variables ω_1 and ω_2 which specify the rotation of each molecule.

In the correlation function $C_2(t)$, these two types of variables are coupled via the anisotropic part of the potential interaction, thus ruling out the possibility of a complete analytical calculation of $C_2(t)$.

Nevertheless, by noting the weak asymmetry of the small molecules considered here, we assume, in a first approximation, that the pair $U(\mathbf{r}_{12}, \omega_1, \omega_2)$ potential is isotropic.

Following the arguments presented by Joslin et al.,[7] we write the orientational dependence of the $Q_{lm}(\omega)$ explicitly as

$$Q_{lm}(\omega) = \sum_n D^{l*}_{mn}(\omega)Q_{ln} , \qquad (2.17)$$

where $D^l_{mn}(\omega)$ denotes a generalized spherical harmonic, and Q_{ln} is a body-fixed component of $\mathbf{Q}$. If the intermolecular potential is isotropic, i.e., depends only on r_{12} and not on ω_{12}, ω_1, ω_2, we generate the averages

$$\langle D^l_{mn}(\omega)\rangle = 0 \quad (l \neq 0) \qquad (2.18)$$

and

$$\langle D^{l*}_{mn}[\omega(o)]D^{l'}_{m'n'}[\omega(t)]\rangle = \delta_{ll'}\delta_{mm'}\delta_{nn'}(2l+1)^{-2}$$

$$\times \langle \sum_n D^l_{nn}[\delta\omega(t)]\rangle , \qquad (2.19)$$

with $\delta\omega(t)$ denoting the rotation needed to bring $\omega(0)$ into coincidence with $\omega(t)$.

As a consequence of Eq. (2.18), $C_{2B}(t) = 0$ for the isotropic intermolecular potential.

Defining $Q^{(l)^2} = \Sigma_n |Q_{ln}|^2$ and noting that[8]

$$\sum_\mu C^*_{l+1,\mu}[\omega_{12}(0)]C_{l+1,\mu}[\omega_{12}(t)] = P_{l+1}[\cos\theta_{12}(t)] ,$$

$$(2.20)$$

where $\theta_{12}(t)$ is the angle between $\mathbf{r}_{12}(0)$ and $\mathbf{r}_{12}(t)$, and $P_l[\cos\theta_{12}(t)]$ denotes the l th order Legendre polynomial, one then obtains

$$C_2(t) = \sum_l C^{(l)}_{tr}(t) \cdot C^{(l)}_{rot}(t) . \qquad (2.21)$$

The translation correlation function of order 1, $C^{(l)}_{tr}(t)$, is defined as

$$C^{(l)}_{tr}(t) = N(N-1)\alpha^2 Q^{(l)^2}(l+1)\langle P_{l+1}[\cos\theta_{12}(t)]$$

$$\times [r_{12}(0)r_{12}(t)]^{-(l+2)}\rangle \qquad (2.22)$$

and the rotational correlation function of order 1, $C^{(1)}_{rot}(t)$ is given by

$$C^{(l)}_{rot}(t) = \frac{1}{2l+1}\langle \sum_n D^l_{nn}(\delta\omega(t))\rangle . \qquad (2.23)$$

Since in the isotropic potential the molecules rotate freely (the angular momentum is conserved), $\langle \Sigma_n D^l_{nn}[\delta\omega(t)]\rangle$ can be calculated without further approximation. For a freely rotating spherical top we have[9]

$$C^{(l)}_{rot}(t) = \frac{1}{2l+1}\sum_{k=-l}^{+l}(1 - K^2\omega_0^2 t^2)\exp(-\tfrac{1}{2}K^2\omega_0^2 t^2) ,$$

$$(2.24)$$

where $\omega_0 = (kT/I)^{1/2}$ with I the molecular moment of inertia.

The two-body translational correlation function $C^{(l)}_{tr}(t)$ cannot be calculated so easily. In fact, the theoretical treatment of the separate components of the total correlation function $C(t)$ [see Eq. (1.7)] is in its infancy. It may therefore be useful at this stage to construct a simple model for $C^{(l)}_{tr}(t)$, not in the expectation that it will accurately represent the real dynamics but rather in order to test the possibilities and the limitations of a simple calculable model.

In the next section we calculate $C^{(l)}_{tr}(t)$ analytically, assuming that molecular center-of-mass translations in dense media proceed by a mechanism which can be approximated by the isotropic translational diffusion of the noninteracting hard spheres.

III. TRANSLATIONAL DIFFUSION OF THE INTERACTION-INDUCED MOLECULAR DIPOLES

In this section we explicitly calculate the two-body, translational correlation function $C^{(l)}_{tr}(t)$ given by Eq. (2.22), assuming that the molecular translational motions can be described by the diffusion equation. We assume no explicit interactions between the freely diffusing molecules. The calculation is done analytically.

If $P(\mathbf{R}, \mathbf{R}_0, t)$ is the conditional probability density that the intermolecular vector $\mathbf{r}_{12}$ has the value $\mathbf{R}$ at the time t if it has the value $\mathbf{R}_0$ at $t = 0$, and if $P(\mathbf{R}_0)$ is the probability density that $\mathbf{r}_{12}$ has value $\mathbf{R}_0$ at $t = 0$, then[16]

$$C^{(l)}_{tr}(t) \sim \int\int d^3\mathbf{R}_0\, d^3\mathbf{R}\, P(\mathbf{R},\mathbf{R}_0,t)P(\mathbf{R}_0)(RR_0)^{-(l+2)}$$

$$\times P_{l+1}[\cos\theta_{12}(t)] . \qquad (3.1)$$

In the integration (3.1) $R = |\mathbf{R}|$ and $R_0 = |\mathbf{R}_0|$ cannot take values below a lower limit d which is the minimum distance of approach of the molecular centers.

Since the medium is very large, homogeneous, and free of translational order, we have $P(\mathbf{R}_0) = 1/V_0$. In Legendre polynomial $P_{l+1}[\cos\theta_{12}(t)]$, $\theta_{12}(t)$ is the angle between $\mathbf{r}_{12}(0)$ and $\mathbf{r}_{12}(t)$, i.e., between $\mathbf{R}_0$ and $\mathbf{R}$. Using the spherical harmonics addition theorem[8] we may expand

$P_{1+1}[\cos\theta_{12}(t)]$ in terms of spherical harmonics $Y_{1+1,m}(\Omega_R)$, $Y_{1+1,m}(\Omega_{R_0})$ as follows:

$$P_{l+1}[\cos\theta_{12}(t)] = \frac{4\pi}{2l+3}\sum_{m=-l-1}^{l+1} y^*_{l+1,m}(\Omega_{R_0})$$

$$\times y_{l+1,m}(\Omega_R), \qquad (3.2)$$

where $\Omega_R = (\theta_R,\phi_R)$ and $\Omega_{R_0} = (\theta_{R_0},\phi_{R_0})$ are the polar angles of the vector $\mathbf{R}$ and $\mathbf{R}_0$, respectively. Thus, $C_{tr}^{(l)}(t)$ becomes

$$C_{tr}^{(l)}(t) \sim \sum_{m=-l-1}^{l+1} \int\int d^3\mathbf{R}_0\, d^3\mathbf{R}$$

$$\times P(\mathbf{R},\mathbf{R}_0,t)(RR_0)^{-(l+2)}$$

$$\times y^*_{l+1,m}(\Omega_{R_0})y_{l+1,m}(\Omega_R). \qquad (3.3)$$

The solution of the diffusion equation

$$\frac{\partial\psi(\mathbf{R},t)}{\partial t} = D\nabla^2\psi(\mathbf{R},t), \qquad (3.4)$$

where $\psi(\mathbf{R},0) = \delta(\mathbf{R}-\mathbf{R}_0)$, $\nabla = \partial/\partial\mathbf{R}$ is the gradient operator, and D is the translational diffusion coefficient, is given by

$$\psi(\mathbf{R},\mathbf{R}_0,t) = (4\pi Dt)^{-3/2}\exp[-(\mathbf{R}-\mathbf{R}_0)^2/4Dt]. \qquad (3.5)$$

In our case, $\mathbf{r}_{12}$ does not represent the radius vector of the molecule which diffuses relative to a fixed point, but the distance between two molecules which diffuse relative to each other. In other words, the vector $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ is a random variable being defined as the sum of the independent random variables $\mathbf{r}_2$ and $-\mathbf{r}_1$, each of which has a distribution which is a solution of the diffusion equation (3.4). Since the probability density of a random variable which is a sum of independent random variables has a Fourier transform that is a product of the Fourier transforms of the densities of the independent variables it is clear that the only change is the replacement of Dt by $2Dt$ in Eq. (3.5), leading to the expression

$$P(\mathbf{R},\mathbf{R}_0,t) = (8\pi Dt)^{-3/2}\exp[-(\mathbf{R}-\mathbf{R}_0)^2/8Dt]. \qquad (3.6)$$

The above expression can be expanded in terms of spherical harmonics by first using the Fourier integral expansion

$$\exp[-(\mathbf{R}-\mathbf{R}_0)^2/8Dt]$$

$$= (2Dt/\pi)^{3/2}\int d^3\kappa\,\exp(-2Dt\kappa^2)$$

$$\times\exp[(i\kappa\cdot(\mathbf{R}-\mathbf{R}_0)] \qquad (3.7)$$

and then replacing $\exp(-i\kappa\mathbf{R})$ and $\exp(-i\kappa\mathbf{R}_0)$ by their expansion of the form

$$\exp(i\kappa\cdot\mathbf{R}) = 4\pi(\pi/2\kappa R)^{1/2}\sum_{n=0}^{\infty}\sum_{\lambda=-n}^{+n}(i)^n y^*_{n\lambda}(\Omega_R)$$

$$\times y_{n\lambda}(\Omega_\kappa)J_{n+1/2}(\kappa R), \qquad (3.8)$$

where $\Omega_\kappa = (\theta_\kappa,\phi_\kappa)$ specifies the direction of κ and $J_{n+1/2}$ are Bessel functions.[11]

After Eqs. (3.7) and (3.8) are substituted in Eq. (3.6), one can perform the integral over Ω_κ by use of the orthogonality relation for spherical harmonics,

$$\int d\Omega\, y^*_{n\lambda}(\Omega)Y_{n'\lambda'}(\Omega) = \delta_{nn'}\delta_{\lambda\lambda'}. \qquad (3.9)$$

with the result

$$P(\mathbf{R},\mathbf{R}_0,t) = (RR_0)^{-1/2}\int_0^{\infty} d\kappa\,\kappa e^{-2Dt\kappa^2}$$

$$\times\sum_{n=0}^{\infty}\sum_{\lambda=-n}^{+n} y^*_{n\lambda}(\Omega_R)y_{n\lambda}(\Omega_{R_0})$$

$$\times J_{n+1/2}(\kappa R_0)J_{n+1/2}(\kappa R), \qquad (3.10)$$

because $d^3\kappa = \kappa^2 d\kappa\, d\Omega_\kappa$, in which $d\Omega_\kappa = \sin\theta_\kappa\, d\theta_\kappa\, d\phi_\kappa$. Substituting Eq. (3.10) into Eq. (3.3), taking into account the orthogonality properties of the spherical harmonics and the relations $d^3\mathbf{R} = R^2 dR\, d\Omega_R$, $d^3\mathbf{R}_0 = R_0^2 dR_0\, d\Omega_{R_0}$, it follows that

$$C_{tr}^{(l)}(t) \sim \int_0^{\infty} d\kappa\,\kappa e^{-2Dt\kappa^2}$$

$$\times\left[\int_d^{\infty} dR\, J_{l+3/2}(\kappa R)R^{-(l+1/2)}\right]^2. \qquad (3.11)$$

The integral in the brackets in Eq. (3.11) is equal to $d^{-(2l+1)}\kappa^{-1}J_{l+1/2}(d\kappa)$. When we set $x = d\kappa$ and take into account that $\int_0^{\infty} dx\, x^{-1}J_{l+1/2}^2(x) = (2l+1)^{-1}$, we obtain the simple expression for the normalized correlation function $\hat{C}_{tr}^{(l)}(t) = C_{tr}^{(l)}(t)/C_{tr}^{(l)}(0)$,

$$\hat{C}_{tr}^{(l)}(t) = (2l+1)\int_0^{\infty} dx\, x^{-1}J_{l+1/2}^2(x)$$

$$\times\exp(-2Dtx^2/d^2). \qquad (3.12)$$

Although the function $x^{-1}\exp(-2Dtx^2/d^2)J_{l+1/2}^2(x)$ in Eq. (3.12) behaves analytically for $x > 0$, the numerical integration of this function may create an error at the limit $x \to 0$. We show in the Appendix, that the formula (3.12) for $\hat{C}_{tr}^{(l)}(t)$ can be written in the form

$$\hat{C}_{tr}^{(l)}(t) = 1 - \frac{2l+1}{2}\int_1^{\infty} dx\, x^{-1}I_{l+1/2}(d^2x/4Dt)$$

$$\times\exp(-d^2x/4Dt), \qquad (3.13)$$

which is more convenient for the numerical integration; $I_{l+1/2}$ denotes the modified Bessel function.[11] Alternatively, for $t > 0$ the integral Eq. (3.12) can be expressed in terms of a series of hypergeometric functions $F(a,b;c;x)$:[12]

$$\hat{C}_t^{(l)}(t) = \frac{2l+1}{2^{2(l+1)}\Gamma(l+3/2)}\left(\frac{2Dt}{d^2}\right)^{-(l+1/2)}$$

$$\times\sum_{m=0}^{\infty}\frac{(-1)^m\Gamma(l+1/2+m)}{2^{2m}(m!)\Gamma(l+3/2+m)}$$

$$\times\left(\frac{2Dt}{d^2}\right)^{-m}F(-m,-l-1/2-m;l+3/2;1)$$

$$\qquad (3.14)$$

and finally converted into the closed form

$$\hat{C}_{tr}^{(l)}(t) = \frac{2l+1}{\sqrt{\pi}}\left(\frac{2Dt}{d^2}\right)^{-(l+1/2)}$$

$$\times\sum_{m=0}^{\infty}\left(-\frac{2Dt}{d^2}\right)^{-m}$$

$$\times\frac{1}{m!(2l+1+m)\prod_{\kappa=1}^{l+1}(l+m+\kappa)} \qquad (3.15)$$

which follows from the properties of the hypergeometric functions of special argument, namely $F(a,b; c; x = 1) = \Gamma(c)\Gamma(c - a - b)/\Gamma(c - a)\Gamma(c - b)$ where Γ denotes the Gamma function.[11]

It is evident from Eq. (3.12) or Eq. (3.15) that the time decay of $\hat{C}_{tr}^{(l)}(t)$ is governed by the ratio $d^2/2D$. In the case of simple liquids $D \approx 10^{-5}$ cm^2/s and $d \sim 10^{-8}$ cm, giving the relaxation time $\tau = d^2/2D \approx 10^{-11}$ s, at least an order of magnitude greater than that associated with the total correlation function $C(t)$. However, as already mentioned recent MD calculations[2,3] have demonstrated that $\hat{C}_{tr}^{(2)}(t)$, in fact, decays much more slowly than the total correlation function.

The model we discuss here qualitatively rationalizes this slow time behavior of $\hat{C}_{tr}^{(l)}(t)$. A further prediction can be made if we treat the molecules as rigid spheres of radius r. If we take $d = 2r$ and for D the Stokes formula for translational diffusion $D = KT/6\pi nr$, we find

$$\tau = d^2/2D = 9V_m\eta/KT, \qquad (3.16)$$

where $V_m = 4\pi r^3/3$ is the molecular volume and η is the viscosity of a fluid. The bigger the molecules involved are and the greater the viscosity is, the slower is the translational diffusion. This is expected to entail a slowing down of the decay of the translational correlation function.

The temperature dependence of τ is determined by the ratio $\tau(T) \sim \eta(T)/T$. To our knowledge, there are no systematic, experimental studies of the n dependence of the interaction-induced phenomena.

At long times $\hat{C}_{tr}^{(l)}(t)$ is proportional to $t^{-(1 + 1/2)}$ [see Eq. (3.15)] giving a cusped appearance to the two-body, translational spectrum $I_{tr}^{(l)}(w)$ in the low frequency region which is characteristic of the diffusional relaxation.

In Fig. 1 an example is displayed of the one dependence of $\hat{C}_{tr}^{(l)}(t)$ for a hypothetical liquid with $D = 3.0 \times 10^{-5}$ cm^2/s and $d = 4$Å.

The correlation function $\hat{C}_{tr}^{(l)}(t)$ decays faster for the higher-order than for the lower-order multipoles although the one dependence of $\hat{C}_{tr}^{(l)}(t)$ is not dramatic.

Finally, we make a preliminary attempt towards a quantitative verification of the discussed model. Up to date, the
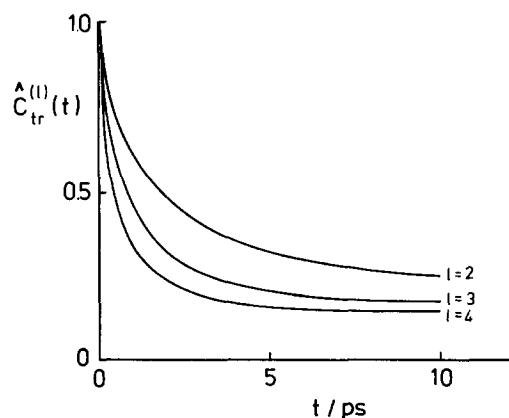
only available molecular dynamics estimations of the translational contribution to $C_2(t)$ in molecular liquids are due to Steele[2] for N$_2$ and Samios et al.[3] for CS$_2$. We must necessarily rely upon these results, although both molecules, being linear, are not ideal candidates for this purpose.

A. Liquid N$_2$

In deriving the formula (3.12) we ignored the anisotropy of the polarizability tensor α and wrote $\alpha = \alpha\mathbf{1}$ where $\mathbf{1}$ is the unit tensor. For a linear molecule α actually has the form $\alpha = \alpha[1 + \varkappa(3\mathbf{nn} - 1)]$ where $\mathbf{n}$ is a unit vector along the symmetric axis. The degree of anisotropy in α is measured by the dimensionless parameter $\varkappa = (\alpha_\| - \alpha_\perp)/3\alpha$; for N$_2$, $\varkappa = 0.133$.[8] Use of an anisotropic α is therefore expected to change the computed correlation function by at most 1%.

At both short and long range the N$_2$ intermolecular potential $U(\mathbf{r}_{12}, \omega_1, \omega_2)$ is anisotropic, and our use of the spherically symmetric potential $U(r_{12})$ introduces error of somewhat uncertain magnitude. However, it is now the consensus in the literature that the intermolecular potential in N$_2$ is indeed ony very slightly anisotropic. Both computer simulation[13] and neutron scattering[14] experiments have demonstrated that the equilibrium and the dynamical structure factor of liquid nitrogen at the triple point are almost identical to the structure factor of a system of spherical molecules. A computer simulation study[15] of orientational motions in fluids consisting of slightly elongated molecules shows that the orientational correlations between neighboring molecules are small. Moreover, a straightforward proof of the weak anisotropy of $U(r_{12})$ for N$_2$ can be deduced from Steele's computer simulation of $C_{2b}(t)^2$; the simulated $C_{2b}(t)$ is almost equal to zero, its contribution to the total $C_2(t)$ is of the order of a few percent. Summarizing, the two assumptions; the isotropy of the intermolecular potential and of the molecular polarizability seem to be fairly well fulfilled in the case of liquid nitrogen.

The molecular dynamics simulation of $\hat{C}_{tr}^{(2)}(t)$ for N$_2$ (the dominant induction mechanism is quadrupolar, so only $l = 2$ is involved) has been carried out[2] near the triple point, at $T = 75.5$ K at the density $\rho = 0.814$ g/cm^3. The intermolecular potential model used was that of Cheung and Powless[14] and consisted of a (diatomic) Lennard-Jones site–site interaction with site separation 1.09Å, $\epsilon/K = 35.3$ K and $\sigma = 3.315$ Å, plus an ideal quadrupole–quadrupole interaction.

Fortunately, Cheung and Pawles[16] simulated the diffusion coefficient of N$_2$ for the thermodynamic state point very close to that of Steele's; the density was $\rho = 0.827$ g/cm^3, the temperature $T = 71.6$ K and the calculated value of $D = 2.25 \times 10^{-5}$ cm^2/s. We accept this value of D as a representative for the state point ($\rho = 0.814$ g/cm^3, $T = 75.5$ K) as well, although the correct value of D at this point could be somewhat different, since $D = D(\rho,T)$. In the same paper,[16] the pair-correlation function $g_c(r)$ for the molecular centers of N$_2$ has been also simulated. $g_c(r)$ is a sharply peaked function, being practically zero for $r < \sigma$ reaching quickly a maximum at 1.25σ then slowly decreasing to 1.

For the distance of closest approach d we used a value of $d = \sigma = 3.315$ Å with a small error since the plot of $g_c(r)$ in

FIG. 1. The one dependence of the translational correlation function $\hat{C}_{tr}^{(l)}(t)$ for a hyphothetical liquid with $D = 3.0 \times 10^{-5}$cm^2/s and $d = 4.0$ Å.

Ref. 16 does not leave a room for any substantial manipulations of the value of d.

The simulated correlation function $\widehat{C}_{tr}^{(2)}(t)$ is compared in Fig. 2 with this theoretically calculated from the formula (3.12) for $D = 2.25 \times 10^{-5}$ cm^2/s and $d = 3.315$ Å.

A remarkable similarity between the simulated and calculated correlation function $\widehat{C}_{tr}^{(2)}(t)$ can be seen [$\widehat{C}_{tr}^{(2)}(t)$ has been simulated for times up to 0.6 ps, which is the limit up to which the data in Steele's[2] computer experiment can be considered to be reliable].

The discrepancies are quite large for short times, becoming gradually smaller at longer times. It should be pointed out that the diffusion equation is certainly valid for long times and may fail to describe the short-time details of molecular translation to a larger extent.[17] Therefore, while the general equation (2.22) for $C_{tr}^{(l)}(t)$ is correct for short as well as for long times, the special approach based on the diffusion equation to describe the translational motions puts a restriction to the validity of the theory at too short times. As a consequence, the model given here may be less accurate when it comes to predicting the spectral behavior of $I_{tr}^{(l)}(w)$ at the far wings.

B. Liquid CS$_2$

The two major assumptions; $\alpha = \alpha_1$ and $U(\mathbf{r}_{12}, \omega_1, \omega_2) = U(r_{12})$ are violated in the liquid carbon disulphide to a larger extent than in N$_2$. The molecule CS$_2$ is highly polarizable; $\kappa = (\alpha_\parallel - \alpha_\perp)/3 \, \alpha \approx 0.4$[8] comparing with $\kappa = 0.13$ for N$_2$.

The influence of the anisotropy of the polarizability tensor α on the two-, three-, and four-body components of $C(t)$ [see Eq. (2.17)] in liquid CS$_2$ has been studied[3] by a molecular dynamics simulations. It was found that the three- and four-body correlation functions are quite sensitive to the value of (20%–25%).

However, the two-body correlation function $C_2(t)$ depends only moderately on κ; the differences between $C_2(t)$ for $\kappa = 0$ and $\kappa = 0.4$ are about 1% for a short time ($t < 0.4$
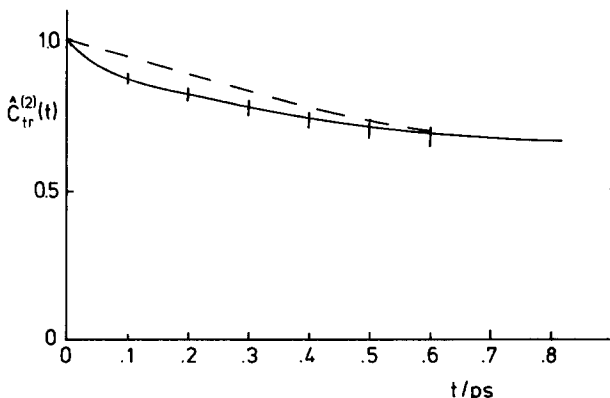
ps), up to 10% for $t \approx 1$ ps. Taking into account an electron-density map for CS$_2$,[18] a definite orientational dependence of the intermolecular potential $U(\mathbf{r}_{12}, \omega_1, \omega_2)$ must be expected.

Exploration of a less sweeping approximation $U(\mathbf{r}_{12}, \omega_1, \omega_2) = U(r_{12})$ introduces an error of uncertain magnitude, which cannot be objectively estimated at this stage. We can only guess that the anisotropy of $U(\mathbf{r}_{12}, \omega_1, \omega_2)$ might have a weaker impact on the translational motions [$C_{tr}(t)$], then on the molecular reorientations [$C_{rot}(t)$, $C_{2b}(t)$].

The molecular dynamics simulation of the interaction-induced phenomena in liquid CS$_2$($T = 298$ K, $\rho = 1.26$ g/cm^3, the atom–atom Lennard-Jones potential) has been recently reported.[3] For a linear molecule with the dominant quadrupole induction mechanism (CS$_2$), the formula (2.21) for $C_2(t)$ reduces to

$$\widehat{C}_2(t) = \widehat{C}_{tr}^{(2)}(t) \cdot \widehat{C}_{rot}^{(2)}(t), \qquad (3.17)$$

where $\widehat{C}_{rot}^{(2)}(t) = \langle P_2[\cos \theta_{12}(t)] \rangle$. Both $\langle P_2[\cos \theta_{12}(t)] \rangle$ and $\widehat{C}_2(t)$ have been simulated and $\widehat{C}_{tr}^{(2)}(t)$ obtained using Eq. (3.17).

The simulated translational diffusion coefficient is $D = 4.0 \times 10^{-5}$ cm^2/s, in a good agreement with the experimental value $D_{exp} = 4.2 \times 10^{-5}$ cm^2/s and with the previous molecular dynamics calculation.[19] In Ref. 19, $D = 3.85$ 10^{-5} cm^2/s for exactly the same potential and density, the only difference was a temperature $T = 298$ K in Ref. 3 and $T = 294$ K in Ref. 19.

We were not able to find for CS$_2$ convincing, preferable molecular dynamics results to make an unbiased choice of d, the closest distance between the molecular centers. Such a study would be of value in the discussed context. The *ab initio* calculations showed[18] that CS$_2$ is 6.9 Å long and 4.2 Å wide; the molecular centers separation can actually vary between those values, depending on the configuration of the neighboring molecules. What is really needed is an appropriate average of this separation over all possible configurations of molecules in dense media. Guided by some previous work,[5,10] we can roughly estimate the value of d with CS$_2$ model of a sphere of radius r, which has the same volume as a CS$_2$ molecule. It gives $r = 2.75$ Å and $d = 2, r = 5.5$ Å. Note that the value $d = 5.5$ Å is in excellent agreement with the neutron diffraction study of the structure of liquid CS$_2$.[21] They found a loose hexagonal arrangement as the most probable configuration in which the axis of any two molecules are preferentially oriented at $\approx 60°$ rather than parallel and perpendicular orientation of the crystalline form. The distance between intermolecular centers (C–C distance) is for this most probable configuration, $d = 5.55$ Å. The model correlation function $\widehat{C}_{tr}^{(2)}(t)$, calculated from Eq. (3.22) using $D = 4.0 \times 10^{-5}$ cm^3/s and $d = 5.5$ Å, is compared in Fig. 3 with that obtained from the molecular dynamics simulation.

Overall, the agreement is surprisingly good, given the number of assumptions of the model and its simplicity. However, before any definite conclusion about the quantitative validity of the discussed model can be drawn from Fig. 3, the influence of anisotropy of the intermolecular potential on $\widehat{C}_{tr}^{(2)}(t)$ has to be clarified. Also, the calculation of d should be established on a more firm basis.
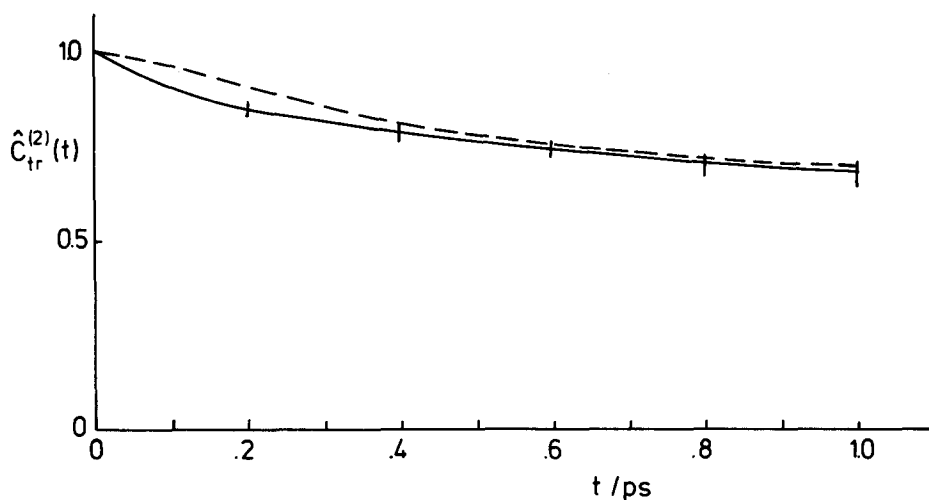

FIG. 2. Comparison of the simulated (taken from Ref. 2) and theoretical [formula (3.22) with $D = 2.25 \times 10^{-5}$ cm^2/s, $d = \sigma = 3.315$ Å] translational correlation function $\widehat{C}_{tr}^{(2)}(t)$ for liquid nitrogen at the temperature $T = 75.5$ K and density $\rho = 0.814$ g/cm^3. The vertical bars indicate the error due to change of d by $\pm 10\%$.

FIG. 3. Comparison of the simulated (taken from Ref. 3) and theoretical [formula (3.22) with $D = 4.0 \times 10^{-5}$ cm^2/s, $d = 5.5$ Å] translational correlation function $\widehat{C}_{tr}^{(2)}(t)$ for liquid carbon disulphide (CS$_2$) at the temperature $T = 298$ K and density $\rho = 1.29$ g/cm^3. The vertical bars indicate the error due to change of d by $\pm 10\%$.

IV. CONCLUSIONS

We have shown that if molecular translation is described by the diffusion equation the two-body correlation function $\widehat{C}_{tr}^{(l)}(t)$, associated with the pure translational motions of the dipole moment of a pair of interacting (via permanent multipoles of order l) molecules, decays very slowly in dense media. The relaxation time τ of $\widehat{C}_{tr}^{(l)}(t)$ in liquid phase is at least an order of magnitude greater than that associated with the correlation function of the total induced dipole moment which can be calculated from infrared band shape. The linear viscosity dependence of τ is predicted ($\tau \sim \eta$) and the temperature dependence of τ is governed by the ratio $\tau(T) \sim \eta(T)/T$.

The possibility to critically compare the present theoretical model with MD data set is limited. It would be useful to work with molecules belonging to the thetrahedral point group T_d. For reasons of symmetry the polarizability tensor α is isotropic for these molecules. Moreover, for some of those, the anisotropy of intermolecular potential is actually quite small.

To obtain $C_2(t)$ or possibly even $C_3(t)$, in the liquid phase, high-pressure far-infrared measurements of $A(\omega)$ as a function of density should be carried out.

There are a number of ways in which our present preliminary treatment could be improved and extended. They include:

(1) Inclusion of the anisotropy of the translational motions for a nonspherical molecule. This could be done by using, instead of Eq. (3.4), the anisotropic diffusion equation with the two $(D_{\parallel}, D_{\perp})$ or even three different diffusion coefficients. It may be essential for the study of interaction-induced phenomena in ordered liquids like, e.g., liquid crystals and polymers.

(2) Extension of the calculations we have carried out for $C_2(t)$, in view of estimating a translational contribution to the three- and four-body correlation functions $C_3(t)$ and $C_4(t)$.

(3) Inclusion of some nondiffusive modes (short-time correction). It is important to stress once more, that the proposed model must fail for very short time, because of the peculiar behavior of the factor $(8\pi Dt)^{-3/2}$ in the condition-

al probability (3.6) when the time gets short enough. The calculation of $C_{tr}^{(l)}(t)$ may be also improved by applying the more sophisticated theories of diffusion, such as that of Hwang and Freed,[22] where the dynamical effect of the mean force between the two diffusing molecules is explicitly taken into account.[25]

The proposed formalism might find some applications in NMR spectroscopy[23] and to the interpretation of the intermolecular light scattering.[24]

APPENDIX

We outline here the derivation of Eq. (2.13) of Sec. II. Differentiating the integral (2.12) in x with respect to t and then integrating over x gives

$$\frac{d\widehat{C}_{tr}^{(l)}(t)}{dt} = -\frac{(2l+1)}{2t} \times \exp(-d^2/4Dt)I_{l+1/2}(d^2/4Dt).$$

(A1)

Taking the Laplace transform of Eq. (A1) we have,

$$\widehat{C}_{tr}^{(l)}(z) = Z^{-1}\{1 - (2l+1)K_{l+1/2}[d(z/2D)^{1/2}] \times I_{l+1/2}[d(z/2D)^{1/2}]\},$$

(A2)

where

$$\widehat{C}_{tr}^{(l)}(z) = \int_0^\infty dt\, \widehat{C}_{tr}^{(l)}(t)e^{-zt}$$

and $K_{l+1/2}$ is the modified Bessel function.[11] The inverse Laplace transform of Eq. (A2) gives

$$\widehat{C}_{tr}^{(l)}(t) = 1 - \frac{2l+1}{2}\int_0^t dt'(t')^{-1} \times \exp(-d^2/4Dt')I_{l+1/2}(d^2/4Dt').$$

(A3)

After a simple transformation of the integration variables in the above integral, one can readily obtain the equivalent expressions for $\widehat{C}_{tr}^{(l)}(t)$;

$$\widehat{C}_{tr}^{(l)}(t) = 1 - \frac{2l+1}{2}\int_{\frac{d^2}{4Dt}}^\infty dx\, x^{-1}e^{-x}I_{l+1/2}(x),$$

(A4)

$$\widehat{C}_{\text{tr}}^{(l)}(t) = 1 - \frac{2l+1}{2}$$

$$\times \int_{1}^{\infty} dx\, x^{-1}\, e^{-xd^2/4Dt} I_{l+1/2}(xd^2/4Dt) .$$

$$(A5)$$

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[26] An accurate, high pressure measurement of $I(\omega)$ as a function of density would be necessary to obtain $I_n(\omega)$ ($n = 2, 3,$ and 4) experimentally.