

## Methods for experimentally determining the angular velocity relaxation in liquids\*

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It is shown that the angular velocity autocorrelation function for symmetric top molecules can in principle be determined from infrared and Raman band shapes, and from thermal neutron scattering when the molecular tumbling rate is slow compared with the relaxation of angular momentum. The theory is compared with molecular dynamics studies on a liquid crystal and an isotropic liquid.

### INTRODUCTION

The infrared and Raman spectra of a symmetric top molecule are related to the orientational dynamics of the molecule.<sup>1</sup> If  $\mathbf{u}$  is the unit vector specifying the orientation of the top axis, then

$$I_l(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle P_l[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle \quad (1)$$

are respectively for  $l=1$  and  $2$  the normalized line shapes of the infrared and Raman spectra.  $P_l(x)$  is the  $l$ th order Legendre polynomial.

In this short note we shall show that

$$\langle \omega_1(0) \cdot \omega_1(t) \rangle = 2[l(l+1)]^{-1} \int_{-\infty}^{+\infty} d\omega e^{i\omega t} \omega^2 I_l(\omega), \quad (2)$$

where  $\omega_1(t)$  is the component of the angular velocity  $\omega(t)$  perpendicular to the initial orientation of the top axis,  $\mathbf{u}(0)$ . This formula is derived under the condition that  $\mathbf{u}(t)$  changes very little on the time scale characterizing the decay of  $\omega(t)$ . This condition should be met in a variety of liquid systems. It is then possible by measuring  $\omega^2 I_l(\omega)$  spectroscopically to determine the angular velocity correlation function, a property that would otherwise be very difficult to measure.

In addition to deriving Eq. (2) we show in the appendix how incoherent and coherent neutron scattering can also be used to determine the angular velocity autocorrelation functions.

Anderson and Ullman<sup>2</sup> have used orientational relaxation measurements to study angular velocity correlations in a variety of experimental systems. Their discussion relates  $\langle \omega(0) \cdot \omega(t) \rangle$  specifically to the dipolar orientation correlation function  $\langle \cos\theta_i(t) \cos\theta_i(t+\tau) \rangle$ , where  $\theta_i$  is the angle between the  $i$ th molecular dipole and an external field. Furthermore, their discussion assumes that the three cartesian components of the angular velocity decay at identical rates. However, in many systems of physical interest (e.g., liquid crystals), it is to be expected that the component of  $\omega$  parallel to  $\mathbf{u}$  will decay on a time scale far different

from the other components of  $\omega$ . The present discussion allows for this anisotropy.

Litovitz *et al.*<sup>3</sup> use Eq. (2) to deduce from their experiments the angular velocity correlation function.

Molecular dynamics studies of a liquid crystal and an isotropic liquid confirm Eq. (2). This gives us confidence that the angular velocity correlation function can be measured in this manner.

### THE DERIVATION OF EQ. (2)

It should be noted that the Fourier transform of the function

$$\psi_l(t) \equiv (-d^2/dt^2) \langle P_l[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle \quad (3)$$

is the measurable quantity

$$\omega^2 I_l(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \psi_l(t). \quad (4)$$

From the definition of  $\psi_l(t)$ , the spherical harmonic addition theorem, and the Hermitian property of the Liouville operator, it is easy to show that

$$\psi_l(t) = \left\langle \frac{4\pi}{2l+1} \sum_{m=-l}^{+l} [iLY_{lm}(\mathbf{u})]^* e^{iLt} [iLY_{lm}(\mathbf{u})] \right\rangle, \quad (5)$$

where  $\mathbf{u}$  is the initial orientation of the symmetric top axis, and where  $[Y_{lm}(\mathbf{u})]$  are the normalized spherical harmonics. The operator  $iL = \{, H\}$  has the property that

$$iLY_{lm}(\mathbf{u}) = i\omega \cdot \mathbf{I}Y_{lm}(\mathbf{u}), \quad (6)$$

where  $\omega$  is the angular velocity and  $\mathbf{I}$  is the angular momentum operator  $[-i(\mathbf{u} \times \nabla_{\mathbf{u}})]$ :

$$I^2 Y_{lm}(\mathbf{u}) = l(l+1) Y_{lm}(\mathbf{u}),$$

$$I_z Y_{lm}(\mathbf{u}) = m Y_{lm}(\mathbf{u}).$$

It is clear that any rotation about an axis parallel

to  $\mathbf{u}$  should produce no change in  $Y_{lm}(\mathbf{u})$  so that

$$\mathbf{u} \cdot \mathbf{I} Y_{lm}(\mathbf{u}) = 0. \tag{7}$$

This enables us to write Eq. (6) as

$$iL Y_{lm}(\mathbf{u}) = i\omega_{\perp} \cdot \hat{\mathbf{I}} Y_{lm} \tag{8}$$

where  $\omega_{\perp}$  is the component of  $\omega$  perpendicular to  $\mathbf{u}$ . [ $\omega_{\perp} = \omega - (\mathbf{u} \cdot \omega)\mathbf{u}$ ]. The operator  $e^{iL t}$  has the effect of displacing its operand to time  $t$ . Substitution of Eq. (8) into Eq. (5) yields

$$\psi_l(t) = \left\langle \omega_{\perp}^i(o) \omega_{\perp}^j(t) \left\{ \frac{4\pi}{2l+1} \sum_{m=-l}^l [I_i Y_{lm}(\mathbf{u})]^* e^{iL t} \times [I_j Y_{lm}(\mathbf{u})] \right\} \right\rangle, \tag{9}$$

where  $i$  and  $j$  denote the cartesian components and repeated indices indicate summation.

If we now assume that  $\mathbf{u}(t)$  varies very slowly compared to  $\omega(t)$ , it is permissible to replace  $\mathbf{u}(t)$  by  $\mathbf{u}(o)$  in Eq. (9)

$$\psi_l(t) \approx \left\langle \omega_{\perp}^i(o) \omega_{\perp}^j(t) \left\{ \frac{4\pi}{2l+1} \sum_{m=-l}^l [I_i Y_{lm}(\mathbf{u})]^* [I_j Y_{lm}(\mathbf{u})] \right\} \right\rangle. \tag{10}$$

This function can be evaluated by first calculating the conditional average

$$\langle \omega_{\perp}^i(o) \omega_{\perp}^j(t) \rangle_{\mathbf{u}},$$

where the subscript indicates that the average is done in an ensemble for which  $\mathbf{u}(0)$  is fixed at  $\mathbf{u}$ . This function is a second rank symmetric tensor. By symmetry this tensor can be written as

$$\langle \omega_{\perp}^i(o) \omega_{\perp}^j(t) \rangle_{\mathbf{u}} = a(t) \delta_{ij} + b(t) [u_i u_j - \frac{1}{3} \delta_{ij}]. \tag{11}$$

The trace of the tensor gives

$$a(t) = \frac{1}{3} \langle \omega_{\perp}(o) \cdot \omega_{\perp}(t) \rangle_{\mathbf{u}},$$

whereas the scalar product with  $u_i u_j$  gives

$$a(t) + \frac{2}{3} b(t) = \langle [\mathbf{u} \cdot \omega_{\perp}(o)] [\mathbf{u} \cdot \omega_{\perp}(t)] \rangle_{\mathbf{u}} = 0,$$

where the zero follows from the fact that  $[\mathbf{u} \cdot \omega_{\perp}(o)] = 0$ .

Substituting of Eq. (11) into Eq. (10) then yields

$$\psi_l(t) = \left\langle \frac{1}{2} \omega_{\perp}(o) \cdot \omega_{\perp}(t) \left\{ [4\pi/(2l+1)] \sum_m [I_j Y_{lm}(\mathbf{u})]^* \times [I_j Y_{lm}(\mathbf{u})] \right\} \right\rangle.$$

Because  $\mathbf{I}$  is an Hermitian operator, this formula can be further evaluated in terms of  $I^2 Y_{lm}(\mathbf{u})$ , so that

$$\psi_l(t) = [l(l+1)/2] \left\langle \omega_{\perp}(o) \cdot \omega_{\perp}(t) \left\{ [4\pi/(2l+1)] \times \sum_m Y_{lm}^*(\mathbf{u}) Y_{lm}(\mathbf{u}) \right\} \right\rangle$$

which reduces to

$$\psi_l(t) = [l(l+1)/2] \langle \omega_{\perp}(o) \cdot \omega_{\perp}(t) \rangle$$

$$= [l(l+1)/2] \langle \omega(o) \cdot \omega(t) - [\mathbf{u} \cdot \omega(o)] [\mathbf{u} \cdot \omega(t)] \rangle. \tag{12}$$

$$[4\pi/(2l+1)] \sum_m Y_{lm}(\mathbf{u}) I^2 Y_{lm}(\mathbf{u}) = l(l+1) P_l(1) = l(l+1).$$

[The term in curly brackets is where  $P_l(1)$  follows from the spherical harmonic addition theorem.] Substitution of this equation into Eq. (4) followed by an inverse Fourier transform proves Eq. (2).

COMPARISON OF THEORY WITH MOLECULAR DYNAMICS

Two molecular dynamics<sup>4</sup> simulations were carried out for 256 molecules with cylindrical symmetry. Each molecule was envisioned as an ellipsoid of revolution with a major to minor axis ratio of 3.5. The interaction potential was taken to be of the pairwise additive Lennard-Jones (12-6) form. For each bimolecular interaction, the Lennard-Jones  $\sigma$  and  $\epsilon$  characterizing the interaction were dependent upon the relative orientation of the two molecules, and were calculated using a Gaussian overlap model discussed elsewhere.<sup>5</sup>

For discussion purposes, a value of unity may be assigned to the molecular mass, a scaled L-J  $\sigma$ , and a scaled L-J  $\epsilon$ . All other dimensions may be expressed in terms of these reduced quantities.

A Runge-Kutta-Gill procedure was used to integrate the equations of motion of the system with a reduced time increment of  $5 \times 10^{-3}$ . In one calculation, the initial conditions and equilibration procedure set a reduced temperature of 0.75, a reduced number density of 0.29, and induced a partial alignment of the molecules along a space fixed direction. The phase space trajectory was followed for 600 time steps (after equilibration), during which the system was found to maintain its orientational anisotropy. A more detailed study showed that this system is a nematic liquid crystal. The second calculation simulated an orientationally disordered system with a number density of 0.20 and a temperature of 1.00. The phase space evolution of this system was also followed for 600 time steps.

Figure 1 shows  $\langle P_l[\mathbf{u}(o) \cdot \mathbf{u}(t)] \rangle$  evaluated from the molecular dynamics data described above, for  $l=1$  and 2. Comparison with Fig. 2 shows that  $\mathbf{u}(t)$  changes very little in the time during which  $\omega_{\perp}(t)$  decays. Therefore, these systems satisfy the assumption made in Eq. (10). Plots of

$$- [2/l(l+1)] (d^2/dt^2) \langle P_l[\mathbf{u}(o) \cdot \mathbf{u}(t)] \rangle$$

are also shown in Fig. 2 for  $l=1$  and 2; these functions agree very closely with  $\langle \omega_{\perp}(o) \cdot \omega_{\perp}(t) \rangle$  for both the nematic and isotropic liquids. Thus, the relationship expressed by Eq. (2) is borne out by these molecular dynamics calculations.

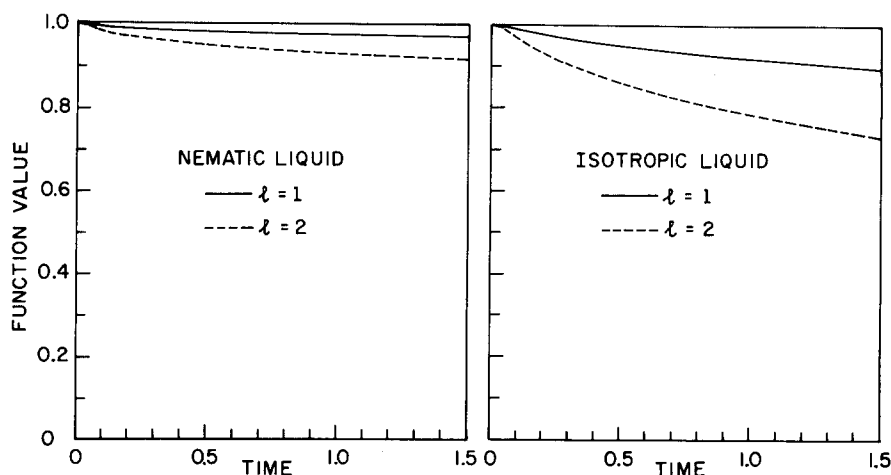


FIG. 1. Molecular dynamics calculation of  $\langle P_l[u(o) \cdot u(t)] \rangle$  for  $l=1, 2$ .

### CONCLUSION

It appears that infrared absorption spectroscopy, depolarized vibrational Raman scattering, pure rotational Raman scattering, and thermal neutron scattering experiments can be used to determine the angular velocity relaxation in dense systems where the rotational motions are hindered. This conclusion is supported by molecular dynamics studies on anisotropic liquids. Moreover, this idea has been used by Litovitz *et al.*<sup>3</sup> to determine  $\langle \omega_1(o) \cdot \omega_1(t) \rangle$  (by experiment) and by Anderson and Ullman<sup>2</sup> to calculate relaxation times for angular velocity correlations. Angular velocity fluctuations may play a very important role in molecular reorientation processes in dense media. Zwanzig and Nee<sup>6</sup> on the basis of a stochastic Liouville equation, and Harp and Berne<sup>7</sup> on the basis of molecular dynamics have suggested that the angular velocity correlation function can be regarded as the memory function of the orientational correlation functions  $\langle P_l[u(o) \cdot u(t)] \rangle$ . It would be interesting to pursue this idea using an experimentally determined  $\langle \omega_1(o) \cdot \omega_1(t) \rangle$ .

### ACKNOWLEDGMENTS

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### APPENDIX: THERMAL NEUTRON SCATTERING

In this section we consider thermal neutron scattering from an idealized solution in which:

- (a) The solute molecules are rigid symmetric

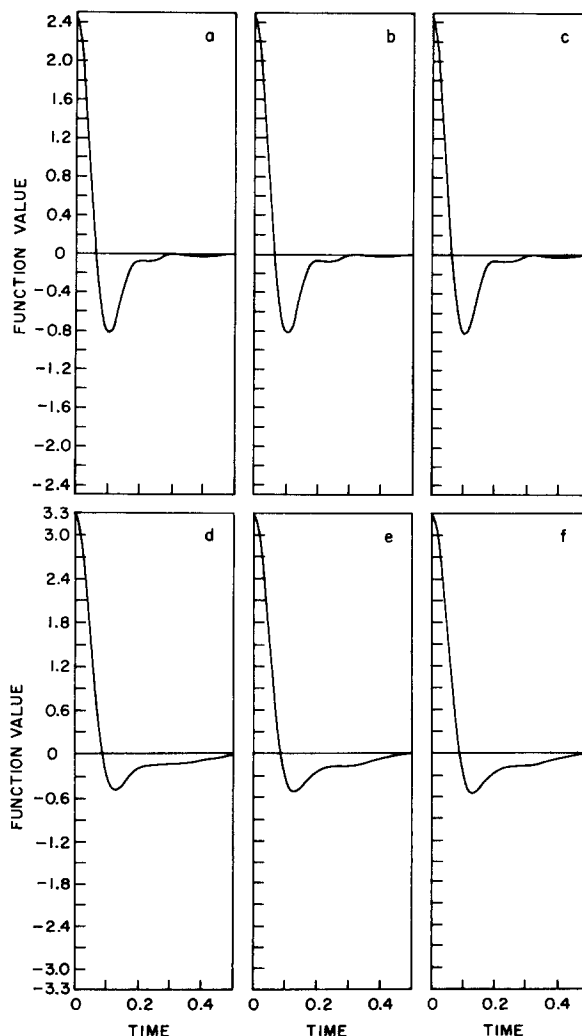


FIG. 2. Molecular dynamics calculations: (a)  $\langle \omega_1(o) \cdot \omega_1(t) \rangle$ , for a nematic liquid, where  $\omega_1(t) = \omega(t) - [\omega(t) \cdot u(o)]u(o)$ . (b)  $-\frac{d^2}{dt^2} \langle P_1[u(o) \cdot u(t)] \rangle$ , for a nematic liquid. (c)  $-(1/3) \frac{d^2}{dt^2} \langle P_2[u(o) \cdot u(t)] \rangle$ , for a nematic liquid. (d) Same as (a), but for an isotropic liquid. (e) Same as (b), for an isotropic liquid. (f) Same as (c), but for an isotropic liquid.

tops with principle axis  $u$ .

(b) The solution is sufficiently dilute that the solute molecules scatter neutrons independently.

(c) The scattering from the molecules can be separated from the scattering from the solvent either for dynamic reasons or by virtue of the fact that the solvent, by design, is a weak scatterer, or relaxes on a different time scale than the solute.

Under these conditions it can be shown that the differential scattering cross section ( $d^2\sigma/d\epsilon d\Omega$ ) for thermal neutrons is determined solely by the temporal Fourier transform of the intermediate scattering function<sup>8</sup>

$$\Gamma(\mathbf{k}, t) = \left\langle \sum_{\alpha} \sum_{\beta} \alpha_{\alpha}^* \alpha_{\beta} e^{-i\mathbf{k} \cdot \mathbf{R}_{\alpha}(0)} e^{i\mathbf{k} \cdot \mathbf{R}_{\beta}(t)} \right\rangle, \quad (A1)$$

where  $\alpha_{\beta}$  and  $\mathbf{R}_{\beta}(t)$  are, respectively the scattering lengths and positions of the  $\beta$ th nucleus, and the sum goes over all nuclei in the molecule.

In an isotropic liquid it is a simple matter to show that

$$C(t) = - \left\{ \lim_{k \rightarrow 0} k^{-2} \ddot{\Gamma}(k, t) \right\} = \left\langle \sum_{\alpha\beta} \alpha_{\alpha}^* \alpha_{\beta} \mathbf{V}_{\alpha}(0) \cdot \mathbf{V}_{\beta}(t) \right\rangle, \quad (A2)$$

where  $\mathbf{V}_{\beta}(t)$  is the linear velocity of nucleus  $\beta$  at time  $t$ . Small angle neutron scattering therefore gives  $C(t)$ . [What is determined is

$$\lim_{k \rightarrow 0} (\omega^2/k^2) S(k\omega)$$

which is the Fourier transform of Eq. (A2).]

It is easy to see that Eq. (A2) can be expressed as

$$C(t) = \sum_{\nu} N_{\nu} I_{\nu} C_{\nu}(t) + \sum_{\nu\mu} N_{\nu} N_{\mu} I_{\nu\mu} C_{\nu\mu}(t), \quad (A3)$$

where  $\nu, \mu$  are labels for the  $\nu$ th and  $\mu$ th nuclei of which there are  $N_{\nu}$  and  $N_{\mu}$ , respectively in a molecule. The coefficients  $I_{\nu}$  and  $I_{\nu\mu}$  are proportional to the incoherent and coherent cross-sections

$$I_{\nu} = \langle |\alpha_{\nu}|^2 \rangle - |\langle \alpha_{\nu} \rangle|^2, \quad (A4)$$

$$I_{\nu\mu} = \langle \alpha_{\nu}^* \alpha_{\mu} \rangle,$$

where  $\alpha_{\nu}$  is the scattering length of nuclei  $\nu$ . The functions  $C_{\nu}(t)$  and  $C_{\nu\mu}(t)$  are

$$C_{\nu}(t) = \left\langle \frac{1}{N_{\nu}} \sum_{\alpha\beta\nu} \mathbf{V}_{\alpha}(0) \cdot \mathbf{V}_{\alpha}(t) \right\rangle, \quad (A5)$$

$$C_{\nu\mu}(t) = \left\langle \left( \frac{1}{N_{\nu}} \sum_{\alpha\beta\nu} \mathbf{V}_{\alpha}(0) \right) \cdot \left( \frac{1}{N_{\mu}} \sum_{\beta\delta\mu} \mathbf{V}_{\beta}(t) \right) \right\rangle$$

The position of nucleus  $\alpha$ ,  $\mathbf{R}^{\alpha}$ , can be expressed as

$$\mathbf{R}^{\alpha}(t) = \mathbf{R}(t) + \mathbf{r}^{\alpha}(t),$$

where  $\mathbf{R}(t)$  is the center of mass (COM) position of the molecule and  $\mathbf{r}^{\alpha}(t)$  is the relative position of the nucleus  $\alpha$  in the molecule. It follows that the linear velocity of the molecule is

$$\mathbf{V}_{\alpha}(t) = \mathbf{V}(t) + \boldsymbol{\omega}(t) \times \mathbf{r}^{\alpha}(t), \quad (A6)$$

where  $\mathbf{V}(t)$  is the velocity of the COM and  $\boldsymbol{\omega}(t)$  is the angular velocity of the molecule about its COM. The second term follows from the equation of motion ( $\dot{\mathbf{r}}^{\alpha} = \boldsymbol{\omega} \times \mathbf{r}^{\alpha}$ ). Substitution of Eq. (A6) into Eq. (A5) together with the assumption that the COM and relative motions of the molecule are independent, yields

$$C_{\nu}(t) = \psi_{\text{com}}(t) + \psi_{\mathbf{r}_{\text{e}1}}^{\nu}(t), \quad (A7)$$

$$C_{\nu\mu}(t) = \psi_{\text{com}}(t) + \psi_{\mathbf{r}_{\text{e}1}}^{\nu\mu}(t),$$

where

$$\psi_{\text{com}}(t) \equiv \langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle, \quad (A8a)$$

$$\psi_{\mathbf{r}_{\text{e}1}}^{\nu}(t) \equiv \langle \boldsymbol{\omega}_i(0) \{ \overline{\mathbf{r}(0) \cdot \mathbf{r}(t)}^{\nu} \delta_{ij} - \overline{r_i(t) r_j(0)}^{\nu} \} \boldsymbol{\omega}_j(t) \rangle, \quad (A8b)$$

$$\psi_{\mathbf{r}_{\text{e}1}}^{\nu\mu}(t) \equiv \langle \boldsymbol{\omega}_i(0) \{ \overline{\mathbf{r}(0)^{\nu} \cdot \mathbf{r}(t)^{\mu}} \delta_{ij} - \overline{r_i^{\nu}(t) r_j^{\mu}(0)} \} \boldsymbol{\omega}_j(t) \rangle, \quad (A8c)$$

where

$$\overline{r_i(t) r_j(0)}^{\nu} \equiv \frac{1}{N_{\nu}} \sum_{\alpha=1}^{N_{\nu}} r_i^{\alpha}(t) r_j^{\alpha}(0),$$

$$\overline{r_i^{\nu}(t) r_j^{\mu}(0)} \equiv \left[ \frac{1}{N_{\nu}} \sum_{\alpha\beta\nu} r_i^{\alpha}(t) \right] \left[ \frac{1}{N_{\mu}} \sum_{\beta\delta\mu} r_j^{\beta}(0) \right].$$

In the limit of slow rotations

$$\overline{r_i(t) r_j(0)}^{\nu} \cong \overline{r_i(0) r_j(0)}^{\nu} = \langle r_i r_j \rangle_{\nu}, \quad (A9)$$

$$\overline{r_i^{\nu}(t) r_j^{\mu}(0)} \cong \overline{r_i(0)^{\nu} r_j(0)^{\mu}} = \langle r_i \rangle_{\nu} \langle r_j \rangle_{\mu}.$$

Now in a symmetric top molecule we expect that

$$\langle r_i \rangle_{\nu} = r_{\nu} u_i, \quad (A10a)$$

$$\langle r_i r_j \rangle_{\nu} = a_{\nu} \delta_{ij} + b_{\nu} [u_i u_j - \frac{1}{3} \delta_{ij}], \quad (A10b)$$

where  $r_{\nu}$  measures the assymetry of the distribution of the nuclei  $\nu$  along the principle axis  $u$ . Only if the distribution is completely symmetric about the COM, will  $r_{\nu}$  be zero. The coefficients  $a_{\nu}$  and  $b_{\nu}$  are found by contraction to be

$$a_{\nu} = \frac{1}{3} \langle r^2 \rangle_{\nu}, \quad (A11)$$

$$b_{\nu} = \frac{1}{3} \langle 3z^2 - r^2 \rangle_{\nu}.$$

These are like the independent elements of the mass quadrupole tensor. It thus follows that

$$\psi_{\mathbf{r}_{\text{e}1}}^{\nu}(t) = \langle \frac{1}{2} (r^2 + z^2) \rangle_{\nu} \langle \boldsymbol{\omega}_1(0) \cdot \boldsymbol{\omega}_1(t) \rangle + \langle (r^2 - z^2) \rangle_{\nu} \langle \boldsymbol{\omega}_u(0) \cdot \boldsymbol{\omega}_u(t) \rangle, \quad (A12a)$$

$$\psi_{\mathbf{r}_{\text{e}1}}^{\nu\mu}(t) = r_{\nu} r_{\mu} \langle \boldsymbol{\omega}_1(0) \cdot \boldsymbol{\omega}_1(t) \rangle. \quad (A12b)$$

Combining Eqs. (A3), (A8), and (A12) then gives

$$C(t) = A\psi_{\text{com}}(t) + B\langle\omega_1(o) \cdot \omega_1(t)\rangle + C\langle\omega_u(o) \cdot \omega_u(t)\rangle, \quad (\text{A13})$$

where the coefficients are

$$A \equiv \sum_{\nu} N_{\nu} I_{\nu} + \sum_{\nu\mu} N_{\nu} N_{\mu} I_{\nu\mu},$$

$$B \equiv \sum_{\nu} [N_{\nu} I_{\nu} \langle \frac{1}{2} (r^2 + z^2) \rangle_{\nu}] + \sum_{\nu\mu} N_{\nu} N_{\mu} I_{\nu\mu} r_{\nu} r_{\mu},$$

$$C \equiv \sum_{\nu} N_{\nu} I_{\nu} \langle (r^2 - z^2) \rangle_{\nu}.$$

It is usually true in a liquid that the relaxation time for  $\psi_{\text{com}}(t)$  is much longer than the relaxation time of the components of the angular velocity. In this eventuality it should be possible to separate the contribution of  $\psi_{\text{com}}(t)$  from Eq. (A13).

Equation (A13) simplifies considerably in several cases:

(a) Spherical molecules:  $r_{\nu} = 0$ ,  $\langle r^2 \rangle_{\nu} = 3\langle z^2 \rangle_{\nu}$ ,

$$\psi_{\text{rel}}^{\nu}(t) = \frac{2}{3} \langle r^2 \rangle_{\nu} \langle \omega(o) \cdot \omega(t) \rangle.$$

(b) Symmetric mass distribution along  $z$ .

$$\psi_{\text{rel}}^{\nu\mu}(t) = 0.$$

(c) Linear molecule:  $\langle x^2 \rangle_{\nu} = \langle y^2 \rangle_{\nu} = 0$ ;  $\langle r^2 \rangle_{\nu} = \langle z^2 \rangle_{\nu}$ ,

$$\psi_{\text{rel}}^{\nu}(t) = \langle r^2 \rangle_{\nu} \langle \omega_1(o) \cdot \omega_1(t) \rangle,$$

$$\psi_{\text{rel}}^{\nu\mu}(t) = r_{\nu} r_{\mu} \langle \omega_1(o) \cdot \omega_1(t) \rangle.$$

(d) Planar molecule (disc).

$$\psi_{\text{rel}}^{\nu}(t) = \langle r^2 \rangle_{\nu} \left\{ \frac{1}{2} \langle \omega_1(o) \cdot \omega_1(t) \rangle + \langle \omega_u(o) \omega_u(t) \rangle \right\},$$

$$\psi_{\text{rel}}^{\nu\mu} = 0.$$

Thus for slow molecular reorientations neutron scattering should be useful for finding the angular velocity correlation function. It is not difficult to work out other variations of the procedure.

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