

Letters to the Editor

THE Letters to the Editor section is subdivided into four categories entitled *Communications, Notes, Comments, and Errata*. The textual material of each Letter is limited to 950 words minus the following: (a) 200 words for each average-sized figure; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 January 1972 for a fuller description of Letters to the Editor.

Communications

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Spin-Rotational Relaxation in One Dimension: Angular Momentum-Orientational Correlation*

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Spin-rotational relaxation is generally accepted as an important spin-relaxation mechanism for both NMR¹ and ESR² in liquids. One usually uses the Hubbard model¹ which employs the rotational analog of the Langevin equation, for the calculation of angular momentum correlation functions.¹ That is, one examines the random time-dependent behavior of the spin-rotation interaction term (in units of \hbar): $\mathcal{H}_{SR} = \mathbf{J} \cdot \mathbf{C} \cdot \mathbf{S}$ where the molecular angular momentum \mathbf{J} and the orientation-dependent spin-rotation tensor \mathbf{C} are governed by rotational Brownian motion. In spherical tensor notation,³ $\mathcal{H}_{SR} = C^{(0)} \mathbf{J} \cdot \mathbf{S} + \sum_m C^{(2,m)} (S\mathbf{J})^{(2,-m)}$. In general one must calculate the correlation function $\langle \mathcal{H}_{SR}(t) \mathcal{H}_{SR}^*(t+\tau) \rangle$ to obtain spin-relaxation effects. One then finds that for the term involving the spherically symmetric part of \mathbf{C} or $C^{(0)} = \frac{1}{3} \text{Tr} \mathbf{C}$, the correlation function $\langle J_1(t) J_m(t+\tau) \rangle$ is needed, and it decays exponentially with time constant $\tau_J = \beta^{-1} = I/\beta'$, where β' is the friction constant. However, for the orientation-dependent portion of \mathcal{H}_{SR} one has to consider correlation functions of type¹: $\langle [J_{m'} \mathcal{D}_{0m'}^{L'}(\Omega)]_{t+\tau} [J_{k'} \mathcal{D}_{0k'}^{(L')}(\Omega)]_t \rangle$, i.e., one needs the joint correlation function for angular momentum and orientation. Since the six dimensional Markoffian conditional probability function in angular velocity and orientation is not known, the usual procedure is to treat the momentum and orientation parts as though they are independent. One then usually relies on the fact that, for Brownian motion, the orientational correlation time $\tau_{\theta,L} \gg \tau_J$, to justify this.

The problem of rotation about a fixed axis in space is, however, amenable to direct calculation. This is because the problem of noncommutation of rotational operators in three dimensional space no longer exists in one dimension. There is then a simple analogy between θ and $\dot{\theta}$ for this motion and x and \dot{x} for the translational motion of a Brownian particle. The joint conditional probability

density $P(\theta_0, \dot{\theta}_0 | \theta, \dot{\theta}, t)$ can then be written down as^{4,5}

$$P(\theta_0, \dot{\theta}_0 | \theta, \dot{\theta}, t) = P(\dot{\theta}_0 | \dot{\theta}, t) \sum_{n=-\infty}^{\infty} P_n(\theta_0, \dot{\theta}_0 | \theta, t) \times \exp \left[\frac{n^2 H^2}{2G} - \frac{inHS}{G} \right], \quad (1)$$

where

$$P(\dot{\theta}_0 | \dot{\theta}, t) = (2\pi G)^{-1/2} e^{-S^2/2G};$$

$$P(\theta_0, \dot{\theta}_0 | \dot{\theta}, t) = \sum_{n=-\infty}^{\infty} P_n(\theta_0, \dot{\theta}_0 | \dot{\theta}, t);$$

$$P_n(\theta_0, \dot{\theta}_0 | \theta, t) = (2\pi)^{-1} \exp \left[-\frac{1}{2} n^2 F + in(\theta - \theta_0) - in\dot{\theta}_0(1 - e^{-\beta t})/\beta \right].$$

Also $S = \dot{\theta} - \dot{\theta}_0 e^{-\beta t}$ and F, G , and H are given below.⁴ We have in this form already accounted for the periodicity in θ . It is thus possible to test a one dimensional model for the separability of θ and $\dot{\theta}$ in the correlation functions.

Before we proceed, it is instructive to take advantage of the analogy with one dimensional translational motion to note that for long times $\langle x\dot{x} \rangle_t = D$, which is obtained either by simply differentiating the Einstein relation, $\langle x^2 \rangle_t = 2Dt$ or from the general conditional probability.⁴ Actually we are interested in the decay with time of $\langle f(\theta)\dot{\theta} \rangle_t$, where $f(\theta)$ is a function periodic in θ . Here the averaging is just over the conditional probability function (i.e., just θ and $\dot{\theta}$). As a result of the periodicity, we shall find that there will be a slowly decaying term in D , which now is given by $D \equiv kT/\beta'$.

We adopt the following simple model to elucidate the main point. For convenience we may think of the model as being that of an idealized liquid crystal where the molecular z' axis is fixed along the director and makes a

constant angle β with the lab z axis. Only $J_{z'}$ may be nonzero as a result of changes in angle θ about the z' axis. We also assume (in order to get nontrivial angular momentum-orientational correlation functions) that the z' axis is *not* a principal axis of \mathbf{C} (so $C'^{(2,\pm 1)} \neq 0$). Then in spherical tensor notation,

$$\mathcal{H}_{S-R}(t) = [C^{(0)} - 2(\frac{2}{3})^{1/2}C'^{(2,0)}]J_{z'} \sum_m \mathcal{D}_{0,m}^1(\Omega) S^{(1,m)} - 2^{1/2}C'^{(2,\pm 1)}J_{z'} \sum_m \mathcal{D}_{\pm 1,m}^1(\Omega) S^{(1,m)}, \quad (2)$$

where $\mathcal{D}_{-k,m}^L(\Omega) = \exp[ik\theta(t)]\mathcal{D}_{k,m}^L(0, \beta, 0)$. Here the prime on the $C'^{(2,m)}$ refers to a molecular axis system which includes z' as one of the axes. We thus need correlation functions of type:

$$G_{n,k}(t) = \langle [J_{z'}e^{i\theta}]_0 [J_{z'}e^{in\theta}]_t^* \rangle.$$

We obtain from Eq. (1) (and $\hbar J = I\dot{\theta}$) that

$$\langle J_{z'}e^{-in\theta} \rangle_t = (I/\hbar) [\dot{\theta}_0 e^{-\beta t} - inD(1 - e^{-\beta t})^2] \times \exp[-n^2F/2 - in(\dot{\theta}_0/\beta)(1 - e^{-\beta t}) - in\theta_0].$$

Then integrating with $[J_{z'}e^{i\theta}]_0$ over a Boltzmann distribution in θ_0 and over equal probabilities in θ_0 yields

$$G_{n,k}(t) = (IkT/\hbar^2) \{ \exp[(-n^2D/\beta)(\beta t - 1 + e^{-\beta t})] \times [e^{-\beta t} - (n^2D/\beta)(1 - e^{-\beta t})^2] \delta_{n,k}. \quad (3)$$

This function is approximated for $\beta t \gg 1$ and $\beta/n^2D \gg 1$ by

$$G_{n,k}(t) \cong (IkT/\hbar^2) [e^{-\beta t} - (n^2D/\beta) \exp(-n^2Dt)] \delta_{n,k}.$$

The spectral density

$$J(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} G(\tau) e^{-i\omega\tau} d\tau$$

from this approximate form (but actually accurate to the next order term in n^2D/β from the complete expression) is

$$J_{n,k}(\omega) \cong (IkT/\hbar^2) \beta^{-1} \{ 1 - n^2D[n^2D/(n^4D^2 + \omega^2)] \} \delta_{n,k}, \quad (4)$$

which is valid for $\omega^2 \ll \beta^2$. Note that for $n^4D^2 \ll \omega^2$,

$$J(\omega) \cong (IkT/\hbar^2) \beta^{-1} [1 - (n^4D^2/\omega^2)]$$

or essentially equivalent to the Hubbard-type result; but for $n^2D^2 \gg \omega^2$ we have $J(\omega) \cong (IkT/\hbar^2) \beta^{-1} (\omega^2/n^4D^2)$ which goes to zero as $\omega \rightarrow 0$ *unlike* the Hubbard-type result. This latter result is due to the fact that while the slowly decaying term in the approximate form of Eq. (3) has a coefficient smaller by n^2D/β than the main term, its slow decay relative to the main term means that it yields a very large (and negative) contribution to the time integral for $J(0)$.⁶

It is very likely that this type of interesting feature of the one dimensional case carries over into the three dimensional case, although the problems of noncommutativity make it difficult to analyze. Of course, for the isotropic term in $C^{(0)}$ (and $C'^{(2,0)}$ in the present case) no such problems can arise.

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¹ P. S. Hubbard, Phys. Rev. **131**, 1155 (1963).

² P. W. Atkins and D. Kivelson, J. Chem. Phys. **44**, 169 (1966); P. W. Atkins, Mol. Phys. **12**, 133 (1967).

³ We express irreducible tensor components in a form equivalent to that used by J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **39**, 326 (1963), e.g., we have incorporated a factor of $(-1)^m$ into the $C^{(2,m)}$.

⁴ S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943); cf. Eq. (178), the nonperiodic solution of Eq. (132). Here $F = (D/\beta)(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t})$, $G = (kT/I)(1 - e^{-2\beta t})$, and $H = D/(1 - e^{-\beta t})^2$.

⁵ This periodic solution is developed from the one dimensional nonperiodic form (Ref. 4) by methods analogous to those discussed by L. Dale Favro in *Fluctuation Phenomena in Solids*, edited by R. E. Burgess (Academic, New York, 1965), p. 82.

⁶ One can show $J(0) = 0$ identically to all orders in n^2D/β by summing the $\omega = 0$ Fourier transform of the series expansion of $G_{n,k}(t)$ as incomplete gamma functions using methods analogous to J. H. Freed, *NATO Summer School Lectures on ESR Relaxation in Liquids*, Norway, 1971 (Plenum, New York, to be published), Ch. VIII. *Added in proof*: This also follows more generally since (1) $G_{n,n}(t) \propto \langle \dot{F}_n^*(t) \dot{F}_n(t+\tau) \rangle$ with $F_n(t) = \exp[in\theta(t)]$ and (2) $\langle F_n^*(t) F_n(t+\tau) \rangle$ is bounded for all t ; cf. J. E. Anderson and R. Ullman, J. Chem. Phys. **55**, 4406 (1971) and R. Kubo, Rept. Progr. Phys. **29**, 253 (1966).

Statistical Mechanical Calculation of the Density Variation through a Liquid-Vapor Interface*

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Calculations of the density variation through a liquid-vapor interface based entirely or in part on thermodynamic concepts give monotonic functions even for conditions far from the critical point.¹ In contrast, investigations based on the statistical mechanical theory of molecular distribution functions suggest a density profile having oscillatory character.²

These investigations made use of the Born-Green³ integrodifferential equation for the density function but in no case was this equation actually solved for a particular model of the interface. This Communication is a preliminary report of the first such solutions obtained from the Born-Green equation.

Consider a one component system whose potential