Coupling of Rotation and Translation in Molecular Fluids

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Two types of correlation function which depend on rotation–translation coupling in a structured molecular fluid are studied. First are investigated the correlation functions of Berne and Montgomery for a fluid of rough spheres (*a*) by direct computation and (*b*) by computer simulation for nitrogen. Secondly it is proposed that rotation–translation coupling can also be investigated in terms of total velocity autocorrelation functions. A decoupled approximation for this function is developed within the model framework of itinerant oscillation/liberation and its limitations are studied.

In this paper we develop two types of correlation function which depend upon rotation–translation coupling in a structured molecular fluid. First we examine the coupled rotation–translation correlation functions for a fluid of rough spheres, calculated recently by Berne and Montgomery;[1] secondly we calculate the total velocity autocorrelation function for an atom within the model framework of itinerant oscillation/libration.

For a fluid of rough spheres, Berne and Montgomery used approximate methods to calculate the coupled correlation functions

$$C_l(\boldsymbol{q};t) = \langle P_l[\boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)]\exp[(i\boldsymbol{q}\cdot\Delta\boldsymbol{r}(t)]\rangle, l = 1, 2, \ldots, \quad (1)$$

where $P_l(x)$ is the Legendre polynomial of order l, $\boldsymbol{\mu}$ is a unit vector embedded in the molecule, $\boldsymbol{q}$ is the scattering wave vector and $\Delta\boldsymbol{r}(t) = \boldsymbol{r}(t) - \boldsymbol{r}(0)$ the displacement in time t. The $C_l(\boldsymbol{q};\ t)$ were Fourier transformed and the resulting spectra compared with those calculated in the uncoupled approximation

$$C_l^{(u)}(\boldsymbol{q};t) = \langle P_l[\boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)]\rangle\langle\exp[i\boldsymbol{q}\cdot\Delta\boldsymbol{r}(t)]\rangle \quad (2)$$

used almost universally in the theory of neutron scattering.[2] It was found[1] that the maximum deviation between $C_l(\boldsymbol{q};t)$ and $C_l^{(u)}(\boldsymbol{q};t)$ occurs for wavenumbers commonly found in thermal neutron scattering, and it was pointed out that the effect of the coupling would increase for structured molecules as opposed to rough spheres. In their work, Berne and Montgomery adopt three levels of approximation (apart from their model): (i) the Chandler binary collision approximation;[3] (ii) a second order expansion for the Laplace transform of the free particle rotation–translation correlation function; (iii) a partial curtailment to first order of approximation (ii) in obtaining $\hat{C}_l(\boldsymbol{q};p)$, the Laplace transform of $C_l(\boldsymbol{q};\ t)$. In our approach we dispense with approximation (iii), *i.e.*, we keep to second order in (ii) in our calculation of

$\hat{C}_l(q;p)$. The resulting ratio $C_l(q;t)/C_l^{(u)}(q;t)$ is then calculated for several values of the roughness and mass distribution parameters used by Berne and Montgomery. We also simulate and compare the correlation functions $C_1(q;t)$, $C_1^{(u)}(q;t)$ for nitrogen, using a molecular dynamics algorithm based on atom–atom interactions of Lennard-Jones type.

The present authors have demonstrated[4,5] how Mori 3-variable theory with its associated model of itinerant oscillation/libration can help to describe rotational and translational motions in molecular fluids. In the later part of this paper we begin to study how this model may cope with rotational–translational coupling. We show that although it is difficult to treat the coupling of spin angular velocity with linear velocity, the model does allow coupling between angular velocity and reorientation, which can be examined in terms of cylindrical probability density functions. Taking the analogy of eqn (1) and (2) we derive expressions for

$$\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle \text{ and } \langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\rangle\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle.$$

ROTATIONAL—TRANSLATION COUPLING IN A FLUID OF ROUGH SPHERES

Berne and Montgomery characterize a rough sphere fluid by the following parameters:[1]

(i) κ, a loading parameter which specifies the mass distribution in the sphere. κ takes values 0, $\frac{2}{5}$ and $\frac{2}{3}$, when the mass is distributed entirely in the centre, uniformly or entirely on the surface of the sphere, respectively.

(ii) the slip coefficient λ which varies between zero for a perfectly smooth sphere to unity for a perfectly rough sphere. If τ_v and τ_ω are the linear and angular velocity correlation times then τ_v/τ_ω is a strong function of λ but a weak function of κ.

Starting from the binary collision approximation, Berne and Montgomery obtain the relation

$$\hat{C}_l(\boldsymbol{Q};p) = \frac{\hat{C}_l^{(o)}[\boldsymbol{Q};\ p + \beta_l(Q)]}{1 - \beta_l(Q)\hat{C}_l^{(o)}[\boldsymbol{Q};\ p + \beta_l(Q)]}, \tag{3}$$

where $\boldsymbol{Q}$ denotes the dimensionless wave vector and $C_l^{(o)}(\boldsymbol{Q};p)$ the Laplace transform of the free particle rotation–translation correlation function. $\beta_l(\boldsymbol{Q})$ is defined by

$$\beta_l(Q) = \beta_\omega \left[\frac{l(l+1) + \left\{ \dfrac{(1+\lambda)\kappa + 1}{\lambda} \right\} Q^2}{l(l+1) + Q^2} \right],$$

where β_ω is the dimensionless relaxation time $1/\tau_\omega$. If $\beta_l \gg l$, then to second order

$$\hat{C}_l^{(o)}[\boldsymbol{Q};p + \beta_l(Q)] = \frac{1}{p + \beta_l(Q)} - \frac{l(l+1) + Q^2}{[p + \beta_l(Q)]^3}, \tag{4}$$

which when substituted directly into eqn (3) gives

$$\hat{C}_l(\boldsymbol{Q};p) = \frac{p^2 + 2\beta_l(Q)p + [\beta_l^2(Q) - l(l+1) - Q^2]}{p^3 + 2\beta_l(Q)p^2 + \beta_l^2(Q)p + \beta_l(Q)[l(l+1) + Q^2]}. \tag{5}$$

Eqn (5) is more complex than that quoted by Berne and Montgomery but its inverse transform $C_l(\mathbf{Q};\tau)$ may still be recovered analytically.[5] (τ here denoted dimensionless t.)

The time dependence of $C_l(\mathbf{Q};\tau)$ is illustrated for several parameter values in fig. 1. We see that for $Q = 1$ (i) the ratio $C_1(\boldsymbol{Q};\tau)/C_1^{(u)}(\boldsymbol{Q};\tau)$ always increases (from

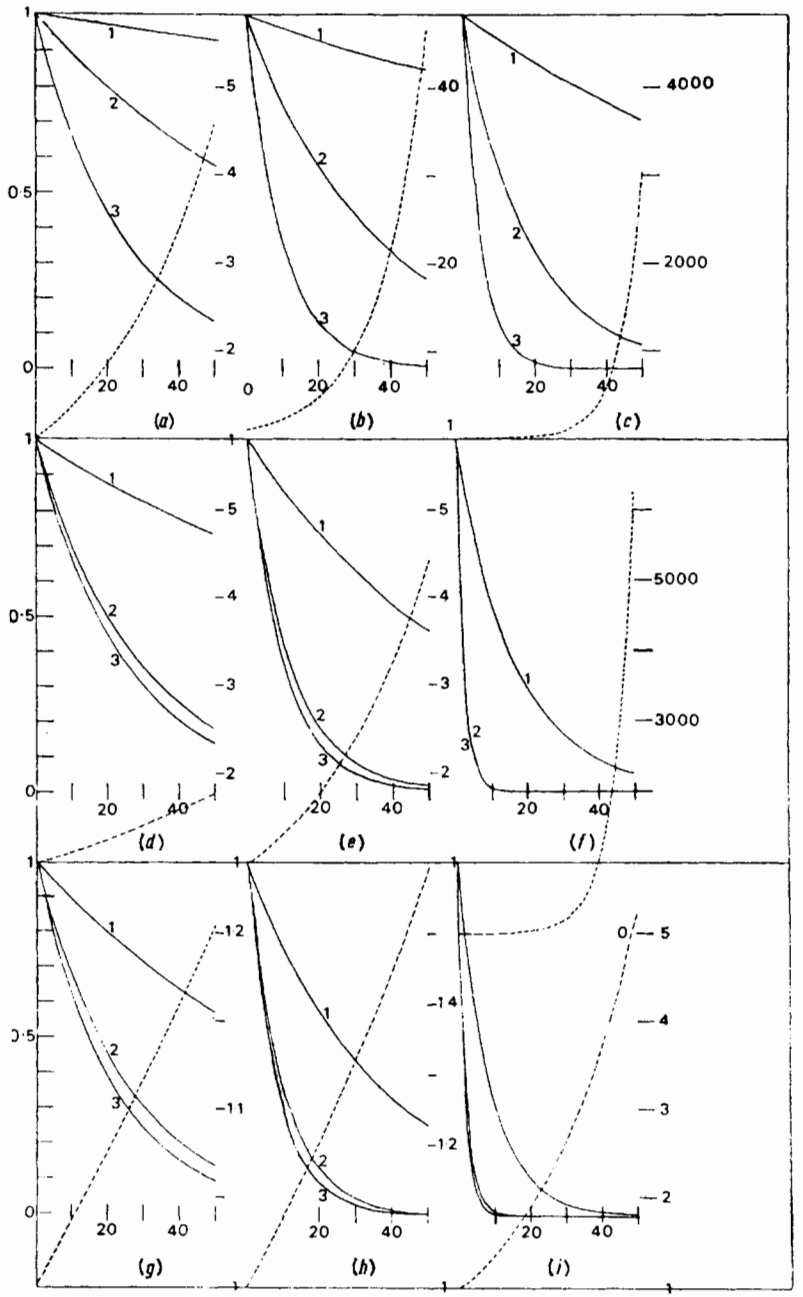

FIG. 1.—Correlation functions C_l plotted against τ. (1) $C_0(Q;\tau)$; (2) $C_1(Q;\tau)$; (3) $C_1(0;\tau)$. (- - - -) the ratio $C_1(Q;\tau)/C_1^{(u)}(Q;\tau)$ for $Q = 1$, $\kappa = 0.4$. (*a*) $\lambda = 0.1$, $\beta_\omega = 50$. (*b*) $\lambda = 0.1$, $\beta_\omega = 20$. (*c*) $\lambda = 0.1$, $\beta_\omega = 10$. (*d*) $\lambda = 0.5$, $\beta_\omega = 50$. (*e*) $\lambda = 0.5$, $\beta_\omega = 20$. (*f*) $\lambda = 0.5$, $\beta_\omega = 5$. (*g*) $\lambda = 1.0$, $\beta_\omega = 50$. (*h*) $\lambda = 1.0$, $\beta_\omega = 20$. (*i*) $\lambda = 1.0$, $\beta_\omega = 5$. λ is the roughness parameter, κ the mass distribution parameter of Berne and Montgomery.[1] The above parameters are in reduced units specified by these authors.

unity) with time; (ii) for fixed λ, the ratio increases more rapidly the smaller the value of β_ω; (iii) the ratio is greatest for small λ and least for λ approaching unity. Thus for given Q the coupling effect is small when β_ω is large and collisions are rough. It is greatest when slipping conditions are invoked in a dilute fluid where the angular velocity relaxes fairly slowly.

COMPUTER SIMULATION

To simulate the motion of nitrogen molecules in the liquid state we have made use of the molecular dynamics algorithm developed originally by Tildesley and Streett. The algorithm solves the equations of motion of 256 particles under atom–atom interaction of Lennard-Jones type. At a dimensionless density of 0.643 and dimensionless temperature of 2.32 the pure orientational autocorrelation function $C_1(\mathbf{0};\tau) = \langle \boldsymbol{\mu}(\tau) \cdot \boldsymbol{\mu}(0) \rangle$, and the correlation functions $C_1(\boldsymbol{Q};\tau)$, $C_1^{(u)}(\boldsymbol{Q};\tau)$ were calculated.

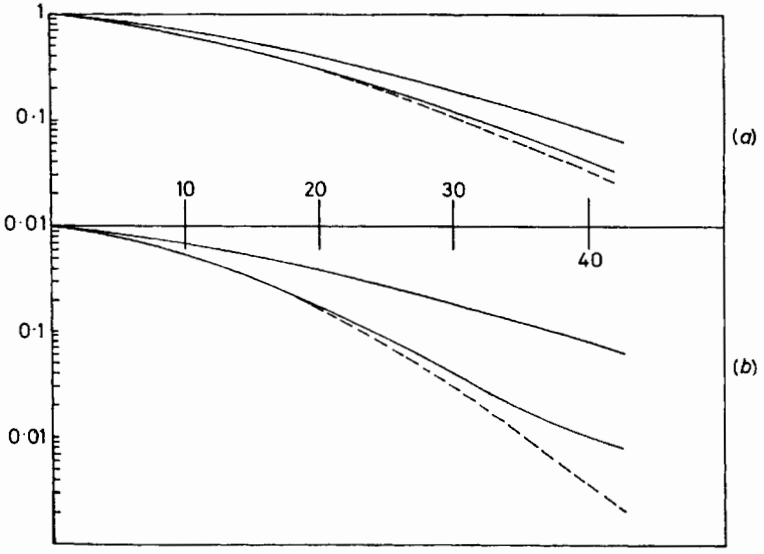

FIG. 2.—Simulated correlation functions for nitrogen at reduced density of 0.643, reduced temperature of 2.32. (*a*) Top to bottom: $C_1(\mathbf{0};\tau)$; $C_1(\boldsymbol{Q};\tau)$; $C_1^{(u)}(\boldsymbol{Q};\tau)$; $Q = 10$. (*b*) As (*a*), but $Q = 20$.

It was found that for $Q < 10$ the effect of rotation–translation coupling was small at the short times probed in the algorithm. The results for $Q = 10$ and $Q = 20$ are shown in fig. 2(*a*) and (*b*), respectively. These illustrate that the higher the wavenumber the more quickly $C_1(\boldsymbol{Q};\tau)$ decays relative to $C_1(\mathbf{0};\tau)$, a behaviour which is predicted by Berne and Montgomery's (and our) expression for $C_1(\boldsymbol{Q};\tau)$. We also find that the ratio $C_1(\boldsymbol{Q};\tau)/C_1^{(u)}(\boldsymbol{Q};\tau)$ increases steadily for high values of momentum transfer, again confirming the analytical trends of the rough-sphere model. Finally, we see that the autocorrelation $\langle \boldsymbol{\mu}(\tau) \cdot \boldsymbol{\mu}(0) \rangle$ in fig. 2 does not decay as a pure exponential, again in agreement with the rough-sphere $C_1(\mathbf{0};\ \tau)$ (except, of course, in the diffusion limit.)

ROTATION–TRANSLATION COUPLING IN FLUIDS OF STRUCTURED MOLECULES

Rather than consider the correlation function $C_1(\boldsymbol{q};t)$ an alternative and simple way of investigating the interplay between spin angular velocity and linear velocity

is to calculate the total velocity autocorrelation function for an atom. If $\boldsymbol{\mu}$ denotes a dipole of unit length then the total velocity $\boldsymbol{v}_a$ of an atom is

$$\boldsymbol{v}_a = \boldsymbol{v} + \tfrac{1}{2}\boldsymbol{\omega} \wedge \boldsymbol{\mu} \tag{6}$$

where $\boldsymbol{v}$ denotes the centre of mass velocity and $\boldsymbol{\omega}$ the angular velocity. Thus the autocorrelation function of $\boldsymbol{v}_a$ contains information on both linear and angular velocities. In fig. 3 we simulate for computer nitrogen the four autocorrelation functions for $\boldsymbol{v}_a$, $\boldsymbol{v}$, $\boldsymbol{\omega}$ and $\boldsymbol{\mu}$. The relation between the autocorrelations of $\boldsymbol{v}_a$ and $\boldsymbol{v}$ can easily be found if $\boldsymbol{\omega}$ is constrained to lie in a fixed direction. From eqn (6) we have

$$\langle \boldsymbol{v}_a(t) \cdot \boldsymbol{v}_a(0)\rangle = \langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(0)\rangle + \langle \boldsymbol{v}(t) \cdot \boldsymbol{\omega}(0) \wedge \boldsymbol{\mu}(0)\rangle + \tfrac{1}{4}\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle \tag{7}$$

since

$$\langle \boldsymbol{\omega}(t) \wedge \boldsymbol{\mu}(t) \cdot \boldsymbol{v}(0)\rangle = \langle \boldsymbol{v}(t) \cdot \boldsymbol{\omega}(0) \wedge \boldsymbol{\mu}(0)\rangle.$$

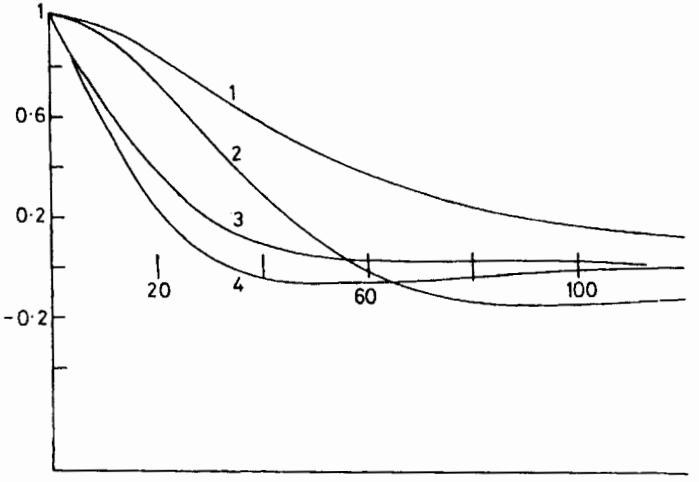

FIG. 3.—Simulated autocorrelation functions for nitrogen at reduced density of 0.643, reduced temperature of 2.32. (1) $\langle \boldsymbol{\omega}(\tau) \cdot \boldsymbol{\omega}(0)\rangle$. (2) $\langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(0)\rangle$. (3) $\langle \boldsymbol{\mu}(\tau) \cdot \boldsymbol{\mu}(0)\rangle$. (4) $\langle \boldsymbol{v}_a(\tau) \cdot \boldsymbol{v}_a(0)\rangle$

The central term in the right hand side of eqn (7) describes the effect of rotation–translation coupling and would vanish in a decoupled approximation; the third term describes the coupling of reorientation and spin angular velocity which vanishes only in the limit $t \longrightarrow \infty$.

We have shown elsewhere[4,5] how to calculate $\langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(0)\rangle$, $\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle$ and $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\rangle$ when $\boldsymbol{\mu}$ is embedded in an itinerant oscillator/librator, with $\boldsymbol{\omega}$ fixed in direction.* Below we show how to extend our previous analysis to calculate the cross-correlation $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle$. A direct calculation of the coupling term $\langle \boldsymbol{v}(t) \cdot \boldsymbol{\omega}(0) \wedge \boldsymbol{\mu}(0)\rangle$ will not be attempted here since it would involve modelling the collision dynamics (possibly along the lines of Berne and Montgomery.) An indirect approach involving Mori matrix theory is at present under investigation by one of us (A. R. D.). Here we content ourselves with the calculation of the decoupled approximation

$$\langle \boldsymbol{v}_a(t) \cdot \boldsymbol{v}_a(0)\rangle \approx \langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(0)\rangle + \tfrac{1}{4}\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle. \tag{8}$$

Since $\boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0) = \cos[\theta(t) - \theta(0)]$, where $\theta(t)$ denotes the angular orientation of the dipole at time t, the required cross-correlation function is defined by

$$\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi} \omega\omega_0 \cos(\theta - \theta_0) p(\omega, \theta;\, t|\omega_0, \theta_0) p(\omega_0, \theta_0) \cdot \mathrm{d}\omega\, \mathrm{d}\omega_0\, \mathrm{d}\theta\, \mathrm{d}\theta_0 \tag{9}$$

* See appendix A.

where $p(\omega, \theta;\ t|\omega_0, \theta_0)$ denotes the joint conditional probability density function for $\omega(t)$ and $\theta(t)$ at time t, given that $\omega(0) = \omega_0$, $\theta(0) = \theta_0$, and $p(\omega_0, \theta_0)$ is the joint density for the initial distribution of ω and θ at time $t = 0$. Since ω and θ are statistically independent variables, and the initial distribution of ω may be assumed Maxwellian we may write

$$p(\omega_0, \theta_0) = \left(\frac{2\pi kT}{I}\right)^{-\frac{1}{2}} \exp\left[-\frac{\omega_0^2}{(2kT/I)}\right] p(\theta_0) \tag{10}$$

where the initial distribution $p(\theta_0)$ satisfies

$$\int_{-\pi}^{\pi} p(\theta_0)\, \mathrm{d}\theta_0 = 1, \tag{11}$$

but otherwise need not be specified for the purpose of our present calculations. The main problem here is to specify the joint conditional density in eqn (9). If $\theta(t)$ were the total angle swept out in time t then the joint conditional distribution could be taken as bivariate normal. Since $\theta(t)$ is restricted to the range $-\pi \leqslant \theta \leqslant \pi$, however, we require a cylindrical distribution whose marginal distribution for ω is normal and whose marginal distribution for θ is wrapped normal. We achieve this by generalizing a well-known result in the theory of wrapped distributions.[7] If x is a normally distributed random variable with mean $\langle x\rangle$ and variance $\sigma_x^2 = \langle (x - \langle x\rangle)^2\rangle$, then the corresponding wrapped variate $\tilde{x} = x(\mathrm{mod}\ 2\pi)$ has a density

$$p(\tilde{x}) = \frac{1}{2\pi}\left[1 + 2\sum_{n=1}^{\infty} \{\cos(n\langle x\rangle)\cos(n\tilde{x}) + \sin(n\langle x\rangle)\sin(n\tilde{x})\} \mathrm{e}^{-\frac{1}{2}n^2\sigma_x^2}\right].$$

Extending this result to the case of two normal variables, only one of which is wrapped, we obtain the expression

$$\begin{aligned} p(\omega, \theta;\ t|\omega_0, \theta_0) = \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} [&\mathrm{e}^{\mathrm{i}s\langle\omega\rangle - \frac{1}{2}s^2\sigma_x^2} \cdot \mathrm{e}^{-\mathrm{i}s\omega} \\ &+ 2\sum_{n=1}^{\infty} \{\cos(s\langle\omega\rangle + n\langle\theta\rangle)\cos(s\omega + n\theta) + \\ &+ \sin(s\langle\omega\rangle + n\langle\theta\rangle)\sin(s\omega + n\theta)\} \times \\ &\exp\{-\tfrac{1}{2}(s^2\sigma_\omega^2 + 2ns\cdot\mathrm{cov} + n^2\sigma_\theta^2)\}]\, \mathrm{d}s \end{aligned} \tag{12}$$

where the convariance term is defined by $\mathrm{cov} = \langle(\omega - \langle\omega\rangle)(\theta - \langle\theta\rangle)\rangle$. In terms of the normalized correlation functions $C_\omega(t)$ and $X_\omega(t)$ defined in Appendix A we have

$$\left.\begin{aligned} \langle\omega\rangle &= C_\omega(t)\cdot\omega_0, \\ \langle\theta\rangle &= \theta_0 + X_\omega(t)\cdot\omega_0, \\ \sigma_\omega^2 &= \frac{kT}{I}[1 - C_\omega^2(t)], \\ \sigma_\theta^2 &= \frac{kT}{I}\left[2\int_0^t X_\omega(\tau)\,\mathrm{d}\tau - X_\omega^2(t)\right], \\ \text{and } \mathrm{cov} &= \frac{kT}{I} X_\omega(t)[1 - C_\omega(t)]. \end{aligned}\right\} \tag{13}$$

Using eqn (10)–(13), the integration of eqn (9) is described in Appendix B. The final result is

$$\begin{aligned} \langle\boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)\boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle &= \frac{kT}{I}\left[C_\omega(t) - \frac{kT}{I}X_\omega^2(t)\right]\exp\left[-\frac{kT}{I}\int_0^t X_\omega(\tau)\mathrm{d}\tau\right] \\ &= \langle\boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)\rangle\left\{\langle\boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle - \left[\frac{kT}{I}X_\omega(t)\right]^2\right\}. \end{aligned} \tag{14}$$

This last relation enables us to examine the limitation of the decoupled approximation (8). The results of our investigations will appear in the Discussion Remarks section of the printed volume. As a final remark we note the interesting result that in analogy with eqn (1) and (2), for $t > 0$

$$\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle \neq \langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\rangle\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle.$$

APPENDIX A

If $C_\nu(t)$, $C_\omega(t)$ and $C_\mu(t)$ denote the normalized autocorrelation functions for $\boldsymbol{\nu}$, $\boldsymbol{\omega}$ and $\boldsymbol{\mu}$, then in terms of constants a, β, Γ defined in ref. (4) and (5) we have

$$\begin{aligned} C_\nu(t) &= \frac{m}{3kT}\langle \boldsymbol{\nu}(t) \cdot \boldsymbol{\nu}(0)\rangle \\ &= \frac{1}{1+\Gamma_\nu}\left[\left\{\cos \beta_\nu t + \left(\frac{\alpha_{\nu 1} + \Gamma_\nu \alpha_{\nu 2}}{\beta_\nu}\right)\sin \beta_\nu t\right\} e^{-\alpha_{\nu 1} t} + \Gamma_\nu e^{-\alpha_{\nu 2} t}\right]; \\ C_\omega(t) &= \frac{I}{kT}\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle \\ &= \frac{1}{1+\Gamma_\omega}\left[\left\{\cos \beta_\omega t + \left(\frac{\alpha_{\omega 1} + \Gamma_\omega \alpha_{\omega 2}}{\beta_\omega}\right)\sin \beta_\omega t\right\} e^{-\alpha_{\omega 1} t} + \Gamma_\omega\, e^{-\alpha_{\omega 2} t}\right]; \end{aligned}$$

and

$$C_\mu(t) = \langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)\rangle = \exp\left[-\frac{kT}{I}\int_0^t X_\omega(\tau)\, d\tau\right]$$

where

$$X_\omega(t) = \int_0^t C_\omega(\tau)\, d\tau.$$

k denotes Boltzmann's constant, T the absolute temperature, and m and I the mass and moment of inertia of the inner disc in the itinerant oscillator/librator.

APPENDIX B

INTEGRATION OF EQN (9)

This calculation is quite straightforward if the integrals are evaluated in a certain order. First, using the standard integral

$$\int_{-\infty}^{\infty} \cos(\alpha s + \beta) e^{-\frac{1}{2}(as^2 + 2bs + c)}\, ds = \sqrt{\frac{2\pi}{a}} \cos\left(\beta - \frac{\alpha b}{a}\right) e^{-\frac{1}{2}\left(c + \frac{\alpha^2 - b^2}{a}\right)},$$

eqn (12) may be written

$$\begin{aligned} p(\omega, \theta;\ t \mid \omega_0, \theta_0) &= \frac{1}{(2\pi)^{\frac{1}{2}}\sigma_\omega} \exp\left[-\frac{(\omega - \langle\omega\rangle)^2}{2\sigma_\omega^2}\right] \\ &\times \left[1 + 2\sum_{n=1}^{\infty} \cos n\left\{(\theta - \langle\theta\rangle) - \frac{\mathrm{cov}}{\sigma_\omega^2}(\omega - \langle\omega\rangle)\right\} e^{-\frac{1}{2}n^2\sigma_\theta^2(1-\rho^2)}\right] \end{aligned} \tag{B1}$$

where

$$\rho = \frac{\mathrm{cov}}{\sigma_\omega \sigma_\theta}.$$

Since

$$2\int_{-\pi}^{\pi} \cos(\theta - \alpha)\cos n(\theta - \beta) = \begin{cases} 0, & n > 1 \\ 2\pi\cos(\beta - \alpha), & n = 1 \end{cases}$$

it follows from eqn (B1) that

$$\int_{-\pi}^{\pi} \cos(\theta - \theta_0) p(\omega, \theta;\ t \mid \omega_0, \theta_0)\, \mathrm{d}\theta = \frac{1}{\sqrt{2\pi}\sigma_\omega} \exp\left[-\frac{(\omega - \langle\omega\rangle)^2}{2\sigma_\omega^2}\right] \times \cos\left[\frac{\mathrm{cov}}{\sigma_\omega^2}(\omega + \omega_0)\right] \mathrm{e}^{-\frac{1}{2}\sigma_\theta^2(1-\rho^2)},$$

which is independent of θ_0. Hence eqn (11) may be used to carry out the integration with respect to θ_0. Next, using the standard integral

$$\int_{-\infty}^{\infty} \omega \cos(\alpha\omega + \beta) \exp\left[-\frac{(\omega - \mu)^2}{2\sigma^2}\right] \mathrm{d}\omega = = \sqrt{2\pi}\sigma[\mu\cos(\alpha\mu + \beta) - \alpha\sigma^2 \sin(\alpha\mu + \beta)]\mathrm{e}^{-\frac{1}{2}\alpha^2\sigma^2}$$

we obtain

$$\int_{-\infty}^{\infty}\int_{-\pi}^{\pi} \omega \cos(\theta - \theta_0) p(\omega, \theta;\ t \mid \omega_0, \theta_0)\, \mathrm{d}\omega\, \mathrm{d}\theta = = \{C_\omega(t) \,.\, \omega_0 \cos[X_\omega(t)\omega_0] - \mathrm{cov} \,.\, \sin[X_\omega(t)\omega_0]\} \times \mathrm{e}^{-\frac{1}{2}\sigma_\theta^2}.$$

Finally we integrate with respect to ω_0 to obtain eqn (14), using the results

$$\left(\frac{2\pi kT}{I}\right)^{-\frac{1}{2}} \int_{-\infty}^{\infty} \omega^2 \cos(X\omega_0)\mathrm{e}^{-\omega_0^2 I/2kT}\, \mathrm{d}\omega_0 = \frac{kT}{I}\left(1 - \frac{kT}{I}X^2\right)\mathrm{e}^{-\frac{1}{2}kTX^2/I}$$

and

$$\left(\frac{2\pi kT}{I}\right)^{-\frac{1}{2}} \int_{-\infty}^{\infty} \omega_0 \sin(X_{\omega_0})\mathrm{e}^{-\omega_0^2 I/2kT}\, \mathrm{d}\omega_0 = \frac{kT}{I} \,.\, X\mathrm{e}^{-\frac{1}{2}kTX^2/I}.$$

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