

ance from the Science Research Council and the Institute of Petroleum Hydrocarbon Research Group.

<sup>1</sup> W. F. Sherman and P. P. Smulovitch, as yet unpublished work presented at the 10th European Molecular Spectroscopy Conference, Liege, September 1969.

<sup>2</sup> (a) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 296 (1950); (b) L. F. H. Bovey, *J. Opt. Soc. Am.* **41**, 836, (1951); (c) W. C. Price and W. F. Sherman, G. R. Wilkinson, *Proc. Roy. Soc. (London)* **A255**, 5 (1960); (d) W. Vedder and D. F. Hornig, *J. Chem. Phys.* **35**, 1560 (1961).

<sup>3</sup>  $\nu_T$  involves essentially a translatory motion of the  $\text{NH}_4^+$  ion, whereas  $\nu_R$  results from a rotatory type of motion, i.e., a torsional oscillation. These bands have been discussed in Ref. 2 and will be further discussed, together with their pressure dependence in Ref. 1.

<sup>4</sup> See, however, Ref. 1, where an extension of the notation of Z. Cihla (as quoted by Amat<sup>5</sup>) is used to describe this system.

<sup>5</sup> G. Amat, *Proc. Intern. Meeting Mol. Spectry.*, 9th, Madrid, 1969, 383 (1969).

<sup>6</sup> W. F. Sherman, *J. Sci. Instr.* **43**, 462 (1966).

<sup>7</sup> M. A. Cundill, Ph.D. thesis, London, 1968 (unpublished).

<sup>8</sup> J. C. Decius and D. J. Gordon, *J. Chem. Phys.* **47**, 1286 (1967).

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## Comments on the Coupling between Linear and Angular Momentum of Structured Molecules

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We consider systems of structured molecules which are capable of translational as well as rotational motion. Using symmetry arguments we show that the linear and the angular momentum of each molecule are statistically independent for systems which possess a center of symmetry. This result applies, in particular, to the case of Brownian rotors, and it implies that the Langevin equations for translational and rotational motion are uncoupled.

Several papers have appeared<sup>1,2</sup> which are concerned with the Brownian motion of a heavy structured molecule suspended in a solvent of lighter, also structured molecules. These investigations conclude that the Brownian motion of the COM of the heavy particle, and its rotation about the COM, are, in general, coupled. It is our contention that there is no such coupling for a very important class of systems, namely, systems of molecules which have a center of symmetry. Indeed, we shall show that in this case the linear and the angular momentum of any molecule are uncoupled.

The gist of our argument can be most easily presented as follows: Harris<sup>2</sup> derives Langevin equations for the COM linear momentum  $\mathbf{P}$  and the internal angular momentum  $\mathbf{L}$  of the Brownian particle in the form

$$(d\mathbf{P}/dt) + \xi_T \mathbf{P} + \xi_{TR} I_B^{-1} \mathbf{L} = \mathbf{f}, \quad (1a)$$

$$(d\mathbf{L}/dt) + \xi_R I_B^{-1} \mathbf{L} + \xi_{RT} \mathbf{P} = \mathbf{n}, \quad (1b)$$

$\mathbf{f}$  and  $\mathbf{n}$  are the dynamical fluctuating force and torque on the Brownian particle, respectively, and  $I_B$  is its moment of inertia. For simplicity, let us consider a fluid which is isotropic. Then the  $\xi$ 's are constant friction coefficients.

Now assume that the Brownian particle as well as the solvent molecules have a center of symmetry. Then Eqs. (1) must be invariant under a reflection through the origin. This transformation changes the sign of the linear momentum and the force, but it leaves unchanged the signs of the angular momentum, the torque, and the moments of inertia. Consequently, the coupling terms

in Eqs. (1) change sign, and thus, the coupling coefficients  $\xi_{TR}$  and  $\xi_{RT}$  must vanish. The argument applies as well if the system is not isotropic. In this case,  $\xi_T$  and  $\xi_R$  are tensors but  $\xi_{TR}$  and  $\xi_{RT}$  are pseudotensors which change sign under inversion. They must vanish if the system has a center of symmetry.

It is possible, and instructive, to generalize the above argument. Consider a homogeneous fluid of structured molecules. Let  $\mathbf{P}_1$  be the COM linear momentum of an arbitrary molecule 1, and  $\mathbf{L}_1$  its space-fixed angular momentum about the COM. For convenience we shall assume that the system is rotationally invariant, although this is not necessary. Instead of  $\mathbf{P}_1$  and  $\mathbf{L}_1$  we use the orthonormal properties

$$\mathbf{U}_1 = \mathbf{P}_1 / \langle P_1^2 \rangle^{1/2}, \quad (2a)$$

$$\mathbf{U}_2 = \mathbf{L}_1 / \langle L_1^2 \rangle^{1/2}, \quad (2b)$$

where the angle brackets indicate a canonical ensemble average. Now, let us define the time correlation matrix  $C_{ij}(t)$  by

$$C_{ij}(t) = \langle \mathbf{U}_i(0) \mathbf{U}_j(t) \rangle, \\ = \langle \mathbf{U}_i | \exp(i\mathcal{L}t) | \mathbf{U}_j \rangle, \quad (3)$$

where  $\mathcal{L}$  is the Liouville operator. We use an obvious bracket notation, defined such that the scalar product,

$$\langle \mathbf{U}_i | \mathbf{U}_j \rangle \equiv \langle \mathbf{U}_i \cdot \mathbf{U}_j \rangle,$$

is simply the equilibrium ensemble average of  $\mathbf{U}_i \cdot \mathbf{U}_j$ . The dynamical coupling between the linear and angular

momentum is described by the function  $C_{12}(t) = C_{21}^*(t)$ , and we shall show that  $C_{12}(t) = 0$  for all times  $t$ . Namely, consider the transformation  $\{\mathbf{r}_i, \mathbf{P}_i\} \rightarrow \{-\mathbf{r}_i, -\mathbf{P}_i\}$  which inverts the signs of the positions and the linear momenta of all atoms in the system. Under this transformation,  $\mathbf{P}_1$  changes sign but  $\mathbf{L}_1$  does not, i.e.,

$$\mathbf{U}_1 \rightarrow -\mathbf{U}_1 \quad \text{and} \quad \mathbf{U}_2 \rightarrow \mathbf{U}_2. \quad (4)$$

Now if the Hamiltonian is invariant under inversion,

$$\mathcal{H}\{\mathbf{r}_i, \mathbf{P}_i\} = \mathcal{H}\{-\mathbf{r}_i, -\mathbf{P}_i\}, \quad (5)$$

both the canonical equilibrium distribution function and the Liouville operator are unchanged, and consequently,

$$C_{12}(t) = -C_{12}(t) = 0. \quad (6)$$

Again, as the reader will easily convince himself, the argument goes through as well if the system is not rotationally invariant.

To make contact with Langevin-type equations let us note an important result derived by Mori<sup>3</sup> and others. Mori has shown that the correlation matrix  $C_{ij}(t)$  generally satisfies the equation

$$\frac{d}{dt} C_{ij}(t) + \sum_{l=1}^2 \int_0^t d\tau K_{il}(\tau) C_{lj}(t-\tau) = 0, \quad (7)$$

where the memory function  $K(\tau)$  is given by

$$K_{ij}(\tau) = \langle \dot{\mathbf{U}}_i | \exp[i(1-\hat{P})\mathcal{L}\tau](1-\hat{P}) | \dot{\mathbf{U}}_j \rangle, \quad (8)$$

where  $\hat{P}$  is a projector onto the subspace of  $|U_1\rangle$  and  $|U_2\rangle$  which we can formally define by<sup>4</sup>

$$\hat{P} = \hat{P}_1 + \hat{P}_2 = |U_1\rangle\langle U_1| + |U_2\rangle\langle U_2|. \quad (9)$$

From (6) we then conclude that for all  $\tau$ ,

$$K_{12}(\tau) = K_{21}^*(\tau) = 0, \quad (10)$$

which can also be easily shown from Eq. (8).

The last few equations hold for any molecule. In the particular case of a heavy Brownian molecule 1,  $K_{ij}(\tau)$  contains the rapid microscopic processes due to collisions with light particles, and decays much faster than

$C_{ij}(t)$ . In this case, we can replace (7) by

$$\frac{d}{dt} C_{ij}(t) + \sum_{l=1}^2 \xi'_{il} C_{lj}(t) = 0 \quad (11a)$$

with

$$\xi'_{ij} = \int_0^\infty d\tau K_{ij}(\tau). \quad (11b)$$

This can easily be demonstrated by an expansion in terms of the mass ratio similar to the one performed by Lebowitz and Resibois.<sup>5</sup> It is well known that the resulting Eqs. (11) are entirely equivalent to the Langevin Eqs. (1). However, (10) again implies that in all systems with a center of symmetry, the coupling coefficients vanish:

$$\xi'_{12} = \xi'_{21} = 0. \quad (12)$$

We have thus shown that, in a homogeneous fluid, the linear and the angular momentum of structured molecules are statistically independent, if all the molecules possess a center of symmetry. While we have, for simplicity, only discussed the dot product correlation function  $\langle \mathbf{P}(t) \cdot \mathbf{L}(0) \rangle$ , the reader will readily convince himself that the same conclusions hold for the products of individual vector components of  $\mathbf{P}(t)$  and  $\mathbf{L}(0)$ .

We want to stress that our considerations do not rule out dynamical coupling between translational and rotational motion in collective excitations. These excitations are associated with a finite wave vector  $\mathbf{k}$  which breaks the homogeneity of the system. Then coupling will occur even if the Hamiltonian is symmetric under inversion. Moreover, in the presence of external fields there may indeed be this kind of coupling.

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<sup>4</sup> This form of the memory function equation differs from Mori's. Its development is presented in B. J. Berné and G. Harp, *Advan. Chem. Phys.* (to be published).

<sup>5</sup> J. L. Lebowitz and P. Resibois, *Phys. Rev.* **139**, A1101 (1965).