On the effects of translation–rotation coupling on hydrodynamic diffusion tensors[a)]

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In recent theoretical investigations of hydrodynamic interactions in dilute solutions of spherical Brownian particles,[1,2] we have observed that translation–rotation coupling plays a fundamental and somewhat unexpected role. In this note we point out several approaches to this problem and their surprising consequences.

Consider a model of rotational relaxation in solution making the assumption that the velocities $\mathbf{u}_i$ of all particles are zero (i.e., a lattice of rotors). By well known hydrodynamic techniques, the rotational *self* diffusion tensor satisfying stick boundary conditions is found to lowest order in the inverse interparticle separation to be

$$\mathbf{u}_i=0:\ (\mathbf{D}_R)_{11}=\frac{kT}{\zeta_{R1}}\left\{\mathbf{I}-\frac{3a_1^3a_2}{4r^4}[\mathbf{I}-\hat{\mathbf{r}}^2]\right\},\quad \zeta_{R1}=8\pi\eta a_1^3. \tag{1}$$

A similar calculation of the translational *self* diffusion tensor,[3] for a nonrotating model (all angular velocities Ω_i zero) yields

$$\boldsymbol{\Omega}_i=0:\ (\mathbf{D}_T)_{11}=\frac{kT}{\zeta_{T1}}\left\{\mathbf{I}-\frac{3a_1a_2^3}{4r^4}[\mathbf{I}+4\hat{\mathbf{r}}^2]\right\},\quad \zeta_{T1}=6\pi\eta a_1. \tag{2}$$

In contrast, the hydrodynamic solution for two bodies simultaneously rotating and translating gives[2] to lowest order

$$(\mathbf{D}_T)_{11}=\frac{kT}{\zeta_{T1}}\left\{\mathbf{I}-\frac{15a_1a_2^3}{4r^4}\hat{\mathbf{r}}^2\right\}, \tag{3}$$

$$(\mathbf{D}_R)_{11}=\frac{kT}{\zeta_{R1}}\left\{\mathbf{I}-\frac{15a_1^3a_2^3}{4r^6}[\mathbf{I}-\hat{\mathbf{r}}^2]\right\}, \tag{4}$$

differing from (1) and (2) above in the distance dependent corrections to the usual Stokes–Einstein terms. Equations (1) and (2), correctly derived for models with frozen translational or frozen rotational degrees of freedom, none the less incorrectly represent the effects of hydrodynamic interaction that would be observed in a real solution. Felderhof[4] has recently noted the discrepancy between Eqs. (2) and (3), but without suggesting an explanation.

The difference between Eqs. (1), (2) and (3), (4) is due to hydrodynamic coupling between translational and rotational motions. For spherical particles, this effect occurs only in multiparticle systems. That is, a single sphere subject to a force (torque) executes only translational (rotational) motion—unlike a propeller, for example. However, a translating particle will exert both a force and a torque on a second particle within its velocity field. These effects[5] cannot be neglected in a discussion of diffusion in many particle systems.

This is manifested in the generalized Einstein relation[6] satisfied by (3) and (4)

$$\begin{pmatrix}\mathbf{D}_T & \mathbf{D}_{TR}\\ \mathbf{D}_{TR}^{+} & \mathbf{D}_R\end{pmatrix}=kT\begin{pmatrix}\boldsymbol{\zeta}_T & \boldsymbol{\zeta}_{TR}\\ \boldsymbol{\zeta}_{TR}^{+} & \boldsymbol{\zeta}_R\end{pmatrix}^{-1},$$

$$\mathbf{D}_T=kT(\boldsymbol{\zeta}_T-\boldsymbol{\zeta}_{TR}\boldsymbol{\zeta}_R^{-1}\boldsymbol{\zeta}_{RT})^{-1}, \tag{5}$$

$$\mathbf{D}_R=kT(\boldsymbol{\zeta}_R-\boldsymbol{\zeta}_{RT}\boldsymbol{\zeta}_T^{-1}\boldsymbol{\zeta}_{TR})^{-1}, \tag{6}$$

Equations (1) and (2) correspond and are obtained when the coupling terms $\boldsymbol{\zeta}_{TR}$, $\boldsymbol{\zeta}_{RT}$ in (5) and (6) are neglected.

We note that to lowest order *only*, coupling effects may be neglected. That is

$$\mathbf{D}_T^{\circ}=kT(\boldsymbol{\zeta}_T^{\circ})^{-1}\quad \mathbf{D}_R^{\circ}=kT(\boldsymbol{\zeta}_R^{\circ})^{-1},$$

where

$$\mathbf{D}_T^{\circ}=kT\begin{pmatrix}\boldsymbol{\zeta}_{T1}^{-1} & \mathbf{T}_{12}^{xx}\\ \mathbf{T}_{21}^{xx} & \zeta_{T2}^{-1}\end{pmatrix}\qquad \mathbf{D}_R^{\circ}=kT\begin{pmatrix}\zeta_{R1}^{-1} & \mathbf{T}_{12}^{\Omega\Omega}\\ \mathbf{T}_{21}^{\Omega\Omega} & \boldsymbol{\zeta}_{R2}^{-1}\end{pmatrix}$$

$$\mathbf{T}_{12}^{xx}=(8\pi\eta r_{12})^{-1}[\mathbf{I}+\hat{\mathbf{r}}_{12}^2]\qquad \mathbf{T}_{12}^{\Omega\Omega}=-(16\pi\eta r_{12}^3)^{-1}[\mathbf{I}-3\hat{\mathbf{r}}_{12}^2].$$

In this limit, the usual Oseen tensor description of interactions between translating particles is recovered.

Finally it should be noted that both the translational motion and the rotational motion along the line of centers is precisely the same for the two cases, that is, for coupled and uncoupled rotations and translations, i.e.,

$$\hat{\mathbf{r}}\cdot(\mathbf{D}_T)_{11}\cdot\hat{\mathbf{r}}[\text{Eq. (2)}]=\hat{\mathbf{r}}\cdot(\mathbf{D}_T)_{11}\cdot\hat{\mathbf{r}}[\text{Eq. (3)}], \tag{7}$$

$$\hat{\mathbf{r}}\cdot(\mathbf{D}_R)_{11}\cdot\hat{\mathbf{r}}[\text{Eq. (1)}]=\hat{\mathbf{r}}\cdot(\mathbf{D}_R)_{11}\cdot\hat{\mathbf{r}}[\text{Eq. (4)}], \tag{8}$$

In this connection it should be noted that $(\mathbf{D}_T)_{12}$, and $(\mathbf{D}_R)_{12}$ are identical for the coupled and uncoupled cases.[2,3] The absence of the manifestation of translation–rotational coupling for motion *along the line of centers* is a consequence of symmetry in the flow and should persist to all orders in the interparticle separation. Accordingly the conventional procedures[7] for cal-

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culating the hydrodynamic effect on the rate of diffusion controlled reactions, which ignore rotations, are not in jeopardy.

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[3] J. L. Aguirre and T. J. Murphy, J. Chem. Phys. **59**, 1833 (1973).

[4] B. U. Felderhof, "Hydrodynamic interactions between two spheres," (preprint).

[5] Further discussion is given in J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics*, (Prentice-Hall, Englewood Cliffs, 1965).

[6] The generalized Einstein relation is derived by D. W. Condiff and J. S. Dahler, J. Chem. Phys. **44**, 3988 (1966).

[7] See P. G. Wolynes and J. M. Deutch, J. Chem. Phys. **65**, 450 (1976) and references cited therein.

Normal stress in a solution of a plane-polygonal polymer under oscillating shearing flow

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Polymer solutions exhibit fascinating rheological behavior; they are non-Newtonian fluids. In order to characterize such systems, one needs to know the normal stresses, in addition to the shear stress behavior which determines the viscosity in the linear region. Under shearing flow, normal stresses are second-order quantities which depend on velocity gradients at least quadratically. Relatively little theoretical work has been done on molecular theories of normal stress. Most existing calculations are for the simplified cases of either free draining molecules or preaveraged hydrodynamic interactions under static flow; they have been reviewed recently by Curtiss, Bird, and Hassager.[1]

Exactly soluble model polymer systems would be helpful in examining the mathematical approximations involved in other calculations. Paul and Mazo[2] have found an exact solution of Kirkwood's formalism of rheological processes for the model of a planar polygonal polymer. They calculated the normal stresses under an oscillating shearing flow among other transport processes. Recently, Curtiss, Bird, and Hassager[1] have also calculated normal stress differences for plane-polygons in the free draining limit by using a Giesekus type formula derived by them. Their result is different from that published by Paul and Mazo.[2] This difference has not previously been resolved. In this paper, we re-examine this question and repeat the calculation of Paul and Mazo according to Kirkwood's formalism. We find Eqs. (24)–(26) of Ref. 2 to be in error. The corrected normal stresses presented in the following agree with Curtiss *et al.*[1] in the free draining limit.

We will use the notation of Paul and Mazo.[2] The imposed shearing flow, in laboratory coordinates, is

$$\mathbf{v}^\circ = \epsilon(\mathbf{R}\cdot\hat{e}_y)\hat{e}_x\,, \tag{1}$$

$$\dot{\epsilon} = Re[\dot{\epsilon}_0 \exp(i\omega t)]\,. \tag{2}$$

Then the excess stress tensor due to the solute particle is

$$(\sigma-\sigma^\circ)_{ij} = -n\sum_l \langle(\mathbf{F}_l\cdot\hat{e}_i)(\mathbf{R}_l\cdot\hat{e}_j)\rangle\,, \tag{3}$$

where $\mathbf{F}_l$ is the force acting on the lth "pearl" at $\mathbf{R}_l$:

$$\mathbf{F}_l = -\zeta(\mathbf{v}_l^\circ-\mathbf{u}_l)-\zeta\sum_{s\neq l}\mathbf{T}_{ls}\cdot\mathbf{F}_s \tag{4}$$

$\mathbf{T}_{ls}$ is the Oseen tensor.

For a rigid ring, the velocity of an individual element $\mathbf{u}_l$ is $\mathbf{u}_l = \Omega\times\mathbf{R}_l$, where Ω is the angular velocity given by

$$\mathbf{\Omega} = \mathbf{\Omega}_0 - \mathbf{D}_R\cdot\nabla\ln f\,. \tag{5}$$

$\mathbf{\Omega}_0$ is the angular velocity that the polymer would have in the absence of Brownian motion, $\mathbf{D}_R$ is the rotation diffusion tensor, f is the distribution function for molecular orientation. An expansion of f in powers of the velocity amplitude, $\dot{\epsilon}_0$, has been given by Paul and Mazo.[2]

The calculation then involves collecting terms of the same power in $\dot{\epsilon}_0$ in Eq. (3). Some of the $\dot{\epsilon}_0$ dependence comes from the f in the averaging process, some comes from the f dependence of $\mathbf{F}_l$, through Eq. (4) and (5). Paul and Mazo's error occurs in missing one term of order $\dot{\epsilon}_0^2$ contributed by the $\mathbf{F}_l$ term in Eq. (3) for normal stresses. Omitting all the details, we present the corrected results. We have not recomputed the $\dot{\epsilon}_0^3$ terms in the shear stress, given in Ref. 2; we believe the linear (Newtonian) terms to be correct:

$$(\sigma-\sigma^0)_{xx} = \frac{nN\zeta R^2\dot{\epsilon}_0^2(\xi_A+\xi_B)}{210D_\parallel}\cdot\frac{\cos\omega t(\cos\omega t+\omega\tau\sin\omega t)}{1+\omega^2\tau^2} + \frac{nN\zeta R^2\dot{\epsilon}_0^2\xi_C}{280D_\parallel}\left[\frac{1}{1+\omega^2\tau^2}+\frac{(1+2\omega^2\tau^2)\cos 2\omega t-\omega\tau\sin 2\omega t}{(1+2\omega^2\tau^2)^2+\omega^2\tau^2}\right], \tag{6}$$