Mol. Cryst. Liq. Cryst. 1995, Vol. 262, pp. 491–497
Reprints available directly from the publisher
Photocopying permitted by license only

ORIENTATIONAL DEPENDENCE OF THE SELFDIFFUSION TENSOR AND RELAXATION TIME SPECTRA FOR NEMATIC PHASE OF HARD ELLIPSOID PARTICLES

V.S.VIKHRENKO, V.B.NEMTSOV and G.S.BOKUN
Belarussian State Technological University,
Minsk, 220 630, Belarus

Abstract The tensors of friction coefficients and relaxation times are calculated in the Enskog approximation at fixed orientation of a target particle. The angular dependence of the latter makes possible to introduce the velocity relaxation time spectra. So the Enskog theory originally operating with a single relaxation time allows to incorporate the whole spectrum when the selfdiffusion coefficients are considered.

THEORETICAL BACKGROUND

Recent progress in molecular dynamics simulations of a hard ellipsoids fluid[1-4] stimulated their theoretical investigations. The ideas of local orientational ordering and coupling between the two relaxation times[3,5] were useful for understanding of the selfdiffusion phenomena in such systems. It seems worthwhile to develop these ideas further.

The procedures that have led to the selfdiffusion tensor expression in the Enskog approximation are well documented.[6-10] This expression can be written as

$$\bar{\mathbf{D}}_1(\mathbf{e}_1) = (\beta m)^{-1}\bar{\tau}(\mathbf{e}_1), \tag{1}$$

$$\bar{\tau}^{-1}(\mathbf{e}_1) = m\bar{\varsigma}(\mathbf{e}_1) = \frac{2\bar{\rho}}{\sqrt{\beta m}}\int d\mathbf{e}_1\int d\mathbf{k}f(\mathbf{e}_1)g_c(\mathbf{e}_1,\mathbf{e}_2,\mathbf{k})(J\ /\ B)\mathbf{k}\mathbf{k}, \tag{2}$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature, $\bar{\rho}$ is the number density, m is the particle mass, $\mathbf{e}_1$ and $\mathbf{e}_2$ are the unit vectors along the symmetry axes of the two particles, $\mathbf{k}$ is the outward directed unit normal to the surface of particle 1 at the point where it touches the particle 2, J is the surface-to-angle Jacobian, B is the rotational-to-translational energy transfer function.[8]

For the one-particle distribution function we adopt the Mayer-Saupe exponential form

$$\begin{aligned} &f(\mathbf{e}_j) = A\exp(cP_2(x_j)), \\ &P_2(x) = (3x-1)/2, \qquad x_j = \mathbf{n}\cdot\mathbf{e}_j, \qquad j = 1,2, \end{aligned} \tag{3}$$

where the force constant c is self-consistently determined to reproduce the desired order parameter and $\mathbf{n}$ is the unit vector along the axis of orientational order of the system (director).

The usual practice [4,5,10] is to approximate the two-particle correlation function $g_c(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k})$ by its average value according to Song and Mason.[11]

Unlike the previous investigations expressions (1) and (2) do not contain averaging over orientations of particle 1. So the tensors of selfdiffusion $\tilde{\mathbf{D}}_1$, relaxation times $\tilde{\tau}$ and friction coefficients $\tilde{\varsigma}$ are determined as functions of the angle θ between the director $\mathbf{n}$ and the symmetry axis of particle 1. The usual diffusion tensor $\tilde{\mathbf{D}}$ is calculated as the mean value of $\tilde{\mathbf{D}}_1$ over the angle θ.

The transition from $\tilde{\varsigma}$ to $\tilde{\tau}$ and $\tilde{\mathbf{D}}_1$ includes a nonlinear inversion operation. So the results of averaging over θ before ($<\tilde{\varsigma}>$) and after ($<\tilde{\tau}>$) the inversion are not equivalent to each other ($m<\tilde{\tau}>\neq<\tilde{\varsigma}>^{-1}$). Nonspherical particle Brownian motion representations, hydrodynamical analogies and computer simulations clearly indicate that the averaging procedure should be applied after the inversion operation. This point of view requires the full revision of the existing scheme of the selfdiffusion tensor calculation. But for the case when reorientational motion of particles is almost immeasurably slow [2] one can prove calculations [7] for the center of mass velocity autocorrelation function for the fixed orientation of the nonspherical particle and as a consequence expressions (1) and (2) have become proved.

Let $\mathbf{D}_1$, τ, ς and $\mathbf{D}$ denote dimensionless quantities and

$$\varsigma = \frac{\rho g_c}{\sqrt{2\pi}} (a/b)^{2/3} \int d\mathbf{e}_2 \int d\mathbf{k} \left(J / b^2 B \right) f(\mathbf{e}_2) \mathbf{kk} \quad , \tag{4}$$

where a and b are the semiaxes perpendicular to and along the symmetry axis of the ellipsoid, respectively, $\rho = \tilde{\rho} / \tilde{\rho}_{cp,}$ ρ_{cp} is the close-packed density. Then one can write

$$\tilde{\mathbf{D}}_1 = \delta_D \mathbf{D}_1, \qquad \bar{\tau} = \delta_\tau \tau, \qquad \bar{\varsigma} = \delta_\varsigma \varsigma, \tag{5}$$

$$\mathbf{D}_1 = \tau = \varsigma^{-1} \quad , \tag{6}$$

where the dimensional multipliers are determined as:

$$\delta_D = \sigma / \sqrt{\beta m}, \quad \delta = \beta m \delta_D, \quad \delta_\zeta = \left(\beta / \delta_D \right)^{-1}, \quad \sigma^3 = 8ab^2. \tag{7}$$

For molecules of MBBA liquid crystal at T = 290K

δ_D= 7.4•10^{-8} m /c , δ_τ= 8.2•10^{-12} c , δ_ς=5.4 10^{-14} kg/c.

According to (6) the dimensionless tensors of selfdiffusion and relaxation times are equal to each other and to inverse of ς.

COMPUTATIONAL RESULTS

Some computational results are presented in Fig. 1 for the systems of prolate and oblate particles with semiaxes ratio 10:1 at ρ=0.5. Elements of tensor $\mathbf{D}_1$ (or τ) are represented in the body-fixed coordinate system.

The axis Z is directed along the particle symmetry axis, the axis X is perpendicular to the plane $(\mathbf{n},\mathbf{e}_1)$, and the axis Y is also perpendicular to the particle symmetry axis and lies in the plane $(\mathbf{n},\mathbf{e}_1)$.

There are five nonzero elements of the tensor $\mathbf{D}_1$: D_{1xx}, D_{1yy}, D_{1zz}, $D_{1yz}=D_{1zy}$. The figure demonstrates strong angular dependence of the elements. The angular dependences of the transversal mobilities D_{1xx} and D_{1yy} are very different for prolate particles and similar for oblate ones. These features are intuitively reasonable and can be explained by the ordering character in the systems.

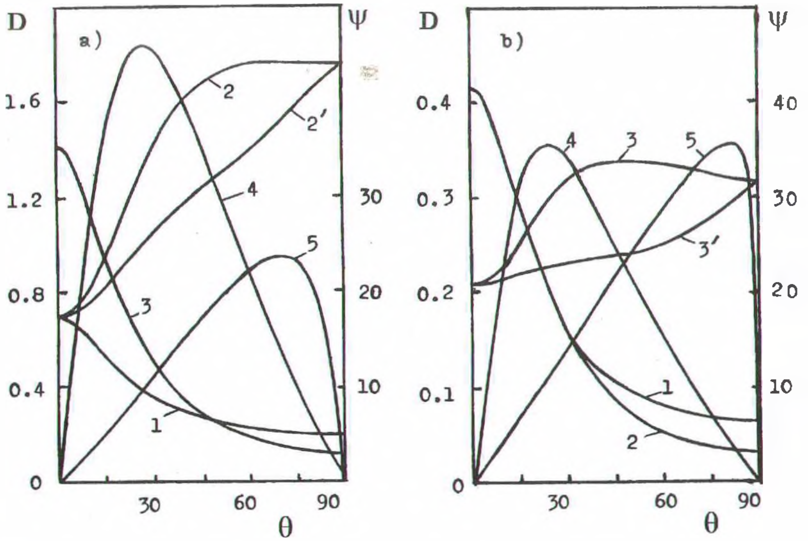

FIGURE 1 Angular dependence of the selfdiffusion tensor for prolate (a) and oblate (b) particles.

1 - αD_{1xx}, 2,2' - αD_{1yy}, 3,3' - γD_{1zz}, 4 - ξD_{1yz}, 5 - ψ.

a) $a = 10b$, $\alpha = 20$, $\gamma = 1$, $\xi = -20$;

b) $a = 0.1b$, $\alpha = 1$, $\gamma = 10$, $\xi = 1$.

Curves 5 in Fig.1 illustrate how the principal axes of the selfdiffusion tensor are oriented with respect to the body-fixed coordinate system:

$$2\psi = \mathrm{arctg}\left(2D_{1yy}/\left(D_{1yy}-D_{1zz}\right)\right). \qquad (8)$$

The principal axis Z lies between the directions $\mathbf{n}$ and $\mathbf{e}_1$ if $\theta<\pi/2$ and for $\theta\le\pi/3$ one can approximatelly find $\varphi\approx p\theta$ with p growing as ρ and the semiaxes ratio increase; p=0.08 for ρ=0.5, a=5b, and p=0.5 for ρ =0.6, a=0.1b. The coefficient p is appreciably higher for oblate ellipsoids at the same ρ and the semiaxes ratio.

Only those of the principal values of the tensor $\mathbf{D}_1$ are shown in Fig.1 (curves 2',3') that differ appreciably from its responsible diagonal elements in the body-fixed coordinate system XYZ. All stated about $\mathbf{D}_1$ is true for the relaxation times tensor τ .Three principal relaxation times vary in broad bonds and form relaxation time spectra (Fig.2). Distribution of states in time intervals was calculated as

$$\varphi_\alpha(\tau) = f(\mathbf{e}_1)\sin\,\theta\,/\,(d\tau_\alpha\,/\,d\theta),$$
$$\theta=\theta_\alpha(\tau),\qquad \alpha=x',y',z'. \tag{9}$$

There are two regions of high density in the spectra because the one-particle distribution function has a sharp maximum at θ = 0. This regions reveal themselves in the time dependence of the velocity autocorrelation functions.

When $\mathbf{D}_1$ was averaged over θ the results of Tang and Evans [5] for prolate ellipsoids were reproduced within 2 percent except for isotropic phase values at a=10b where our data were 5 percent lower than those of Tang and Evans.

The transversal (with respect to $\mathbf{n}$) element $D_\perp$ of $\mathbf{D}$ includes both D_{1zz} and D_{1xx},D_{1yy} approximately in equal parts due to the fact that $D_{1zz}\sin^2\theta$ is not very different from $D_{1xx},D_{1yy}\cos^2\theta$ at most probable small values of θ. Alternatively $D_{1yy}\sin^2\theta<<D_{1zz}\cos^2\theta$ at the same condition and the contribution of D_{1yy} to the longitudial element D_{II} does not exceed a few percent. So the time autocorrelation function of the transversal

velocity is characterized by two relaxation times whereas the longitudial velocity autocorrelation function has a single relaxation time.

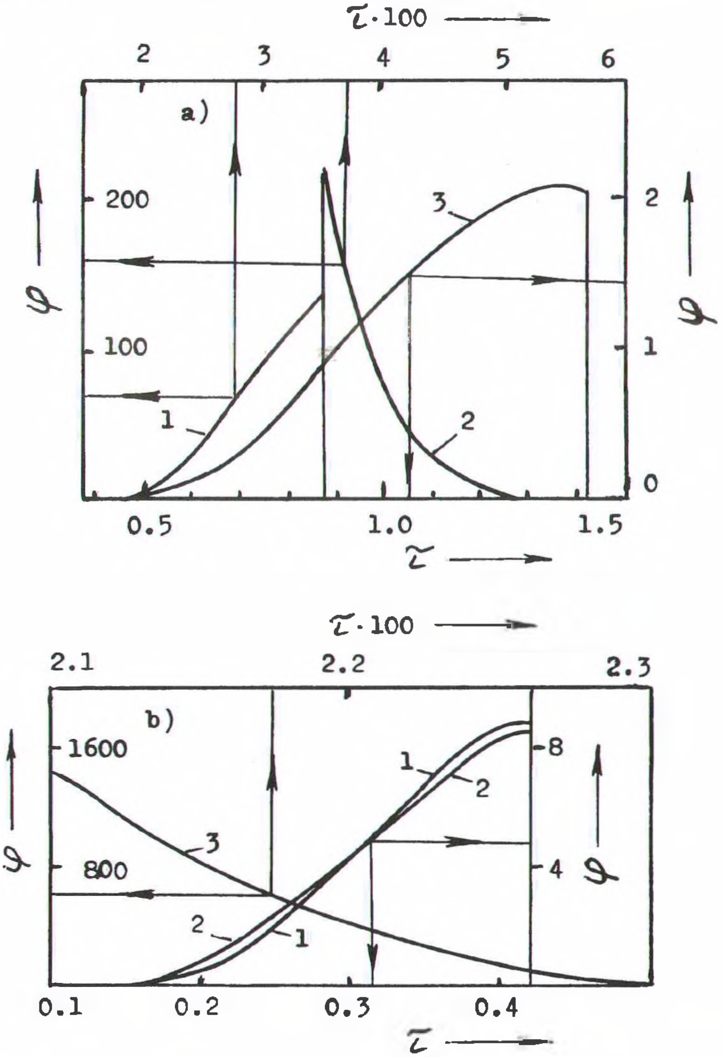

FIGURE 2 Normalized to unity relaxation time spectra for prolate (a) and oblate (b) particles.
1 - $\varphi_{x'}$, 2 - $\varphi_{y'}$, 3 - $\varphi_{z'}$.

For oblate ellipsoids our computations mainly overestimate the molecular dynamics data[2] for $D_\perp$ and underestimate those for $D_{\parallel}$ The difference between ours and molecular dynamics data does not exceed 40 percent except for D_{II} at a=0.1b and ρ= 0.5; 0.6 where the difference becomes equal to 80 and 140 percent, respectively. Probably the cage effect and chattering [12] are of great importance in these states.

For small values of the semiaxes ratio (≈3 - 4) one can not neglect reorientational motion of molecules and translational and rotational selfdiffusion cannot be investigated separately.

The Enskog approximation in representation cosidered produces the wide relaxation time spectrum and the problem arises how to incorporate this complicated spectral properties to calculate other transport coefficients of hard particle fluids.[4]

This work was supported by the Belarussian State Fundamental Research Fund.

REFERENCES

1. J.Talbot, M.P.Allen and G.T.Evans, D.Frenkel, D.Kivelson, Phys. Rev. A, 39, 4330 (1989).
2. M.P.Allen, Phys. Rev. Lett., 65, 2881.(1991).
3. S.Hess, D.Frenkel and M.P.Allen, Mol.Phys., 74, 765 (1991).
4. P.Bereolos, J.Talbot, M.P.Allen and G.T.Evans, J. Chem. Phys., 99, 6087 (1993).
5. S.Tang, G.T.Evans, J. Chem. Phys., 98, 7281 (1993).
6. D.K.Hoffman, J. Chem. Phys., 50, 4823 (1969).
7. D.Chandler, J. Chem. Phys., 60, 3500 (1974).
8. S.Jagannathan, J.S.Daller and W.Sung, J. Chem. Phys., 83, 1808 (1985).
9. V.B.Nemtsov, in: Thermophysics of Condensed Media: Struc-ture and Properties, (Minsk,1990), pp.38-48 (in Russian).
10. V.N.Kabadi and W.A.Steele, Ber. Bunsenges. Phys. Chem., 89, 9, (1985).
11. Y.Song and E.A.Mason, Phys. Rev. A, 41, 3121, (1990).
12. R.G.Cole and D.R.Evans, J.Chem.Phys., 82, 2061, (1965).