Journal of Engineering Physics and Thermophysics, Vol. 68, No. 5, 1995

STATISTICAL COMPUTATION OF TENSOR OF SELF-DIFFUSION COEFFICIENTS IN THE LIQUID-CRYSTAL NEMATIC PHASE

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UDC 548.0:532.783

Within the framework of the Enskog theory expressions are obtained for the tensors of the friction and self-diffusion coefficients in the ordered nematic phase of a system of nonspherical particles. Calculations of the tensor of the self-diffusion coefficients are performed; their comparison with the data of a computer experiment shows that the Enskog theory can be used to calculate the kinetic coefficients in such systems up to densities of 0.6–0.7 of the close-packing density.

The notion of molecules as rigid convex bodies plays an important role in the modern statistical theory of equilibrium and kinetic properties of molecular condensed systems due to the simplicity of describing intermolecular interaction in both computer simulation and analytical investigations. An important point is that in this case an effective basis approximation is formed for the actual interaction to be taken into account by the perturbation theory. An example of implementing this approach is provided by the construction of the quantitative theory of simple fluids consisting of spherically symmetric interacting particles [1].

In many works dealing with self-diffusion in a system of rigid spheres (see, for example, [2] and the literature cited there) it was found that up to very appreciable densities, $\rho \lesssim \rho_m$, the Enskog theory leads to results differing from the data of computer experiments by no more than 25%. The predictions of the Enskog theory in a system of rigid ellipsoids of revolution in an isotropic phase are less precise, and for not highly anisotropic particles (for a ratio of the ellipsoid semiaxes of 1:3) the deviation from the data of a computer experiment amounts to 60% [3].

To understand the processes occurring in liquid-crystal media, it is important to investigate the influence of anisotropy effects on the mobility of particles in an ordered phase. In what follows, within the framework of the Enskog approach, we establish expressions for the tensors of the friction and self-diffusion coefficients in a coordinate system moving with the particle and also for the principal values of the tensor of translational self-diffusion coefficients in both isotropic and ordered phases. We investigated the dependence of the self-diffusion coefficients on the relationships between the semiaxes of the particles – ellipsoids of revolution (elongated and flattened), and their orientation relative to the axis of orientational order and density.

1. Tensors of Friction and Self-Diffusion Coefficients. In a number of works on self-diffusion the Enskog approach is realized using the notion of time correlation functions (TCF). In this case the tensor of the self-diffusion coefficients is expressed by a time integral of the TCF for the velocity dyad of the particle mass center. Extending the computations performed in [4] to a system of nonspherical particles that comprise the anisotropic phase, we obtain the following relations for the tensor of the diffusion coefficients:

$$\mathrm{D}(\mathrm{e}_1) = (k_\mathrm{B}T/m)\,\tau(\mathrm{e}_1)\,, \tag{1}$$

$$\tau^{-1}(\mathrm{e}_1) = m^{-1}\zeta(\mathrm{e}_1) = (m/k_\mathrm{B}T)\,(N-1)\,\langle\, \mathrm{v}_1 T_{21} \mathrm{v}_1 \,\rangle_{(1)}\,. \tag{2}$$

The angle brackets indicate equilibrium Gibbs averaging over the phase space of the system excluding the configuration space of one of the particles. Expression (2) actually determines the tensor of the friction coefficients of a nonspherical particle; it is reasonable to calculate this tensor in a frame of reference fixed on the particle.

Belarus State Technological University, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 68, No. 5, pp. 743-749, September-October, 1995. Original article submitted January 18, 1994.

In an isotropic phase the system of the principal axes of the tensors $\mathbf{D}(\mathbf{e}_1)$, $\tau(\mathbf{e}_1)$, and $\zeta(\mathbf{e}_1)$ coincides with the system of the principal axes of a molecule modeled by a rigid ellipsoid of revolution with semiaxis a directed along the axis of its symmetry. The ordered phase is characterized by a lower symmetry, and such a coincidence is absent, while the principal values of tensors $\zeta(\mathbf{e}_1)$ and $\mathbf{D}(\mathbf{e}_1)$ depend on the orientation of the particle relative to the axis of orientational order.

To obtain the tensor of the diffusion coefficients $\mathbf{D}$, tensor $\mathbf{D}(\mathbf{e}_1)$ should be averaged over the particle orientations.

In order that expressions (1) and (2) be derived by the technique developed in [4], calculations should be performed in the system of the principal axes of tensor $\zeta(\mathbf{e}_1)$, subsequently representing this tensor in an invariant form. As a result, after the use of an explicit expression for the particle collision [5] operator T_{21}, we write relation (2) in the form

$$\zeta(\mathbf{e}_1) = \frac{\rho m^2}{k_B T} \int \ldots \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\omega_1\, d\omega_2\, d\mathbf{e}_2\, d\mathbf{S}\, f(\mathbf{e}_2) \times$$

$$\times\, \Phi(\mathbf{v}_1, \mathbf{v}_2, \omega_1, \omega_2)(\mathbf{v}_c \cdot \mathbf{k})\, H(\mathbf{v}_c \cdot \mathbf{k})\, \mathbf{v}_1\, \Delta\mathbf{v}_1 . \tag{3}$$

Here, ω_1, ω_2, $\mathbf{v}_1$, $\mathbf{v}_2$ are the angular and linear velocities of the centers of mass of the particles at the moment immediately preceding the collision between them; $\Delta\mathbf{v}_1$ is the change in the velocity of the center of mass of the first particle as a result of collision; $\mathbf{v}_c$ is the velocity of the point of contact of the first particle relative to the other directly before the collision; $\Phi(\mathbf{v}_1, \mathbf{v}_2, \omega_1, \omega_2)$ is the Maxwellian distribution normalized to unity; $H(\mathbf{v}_c \cdot \mathbf{k})$ is the Heaviside function ($H(x) = 0$, when $x < 0$, and $H(x) = 1$, when $x > 0$); and $d\mathbf{S}$ is a differential element of the surface of the excluded volume of two particles [6].

Expression (3) differs from that obtained in [7] by the absence of averaging over the orientations of the first particle.

Using Hoffman's procedure [8] for averaging over velocities, we obtain:

$$\zeta(\mathbf{e}_1) = 2\rho\sqrt{m k_B T} \int d\mathbf{e}_2 \int d\mathbf{k}\, f(\mathbf{e}_2)\, g_c(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k}) \times$$

$$\times\, [J(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k})/D(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k})]\, \mathbf{k}\,\mathbf{k}. \tag{4}$$

Here J is the Jacobian of the transition from integration over $d\mathbf{S}$ to integration over $d\mathbf{k}$ [9]; D is a quantity that characterizes the intensity of the momentum exchange between the particles on collision [5].

To perform averaging in (4), it is necessary to know the contact value of the correlation function $g_c(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k})$, which determines the probability density of the mutual arrangement of contacting particles. The amount of information concerning this function is extremely sparse, however, in a number of works [9-11] it is shown that the main orientational dependence is contained in the Jacobian J. The latter actually reflects the transition from integration with respect to the mutual arrangement of the centers of mass of contacting particles to integration with respect to the vector of the outward normal to the surface of the excluded volume that coincides with the vector $\mathbf{k}$ of the outward normal to the surface of the first particle at the point of its contact with the other particle. Therefore J includes a strong orientational dependence of the binary distribution function attributable to geometric factors. This makes it possible, as a first approximation, to replace the function $g_c(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k})$ by its value $\bar{g}_c$, averaged over the orientations of particles and determined from the thermal equation of state [12]:

$$\bar{g}_c = (1 - \gamma_1\eta + \gamma_2\eta^2)/(1 - \eta)^3 ,$$

$$\gamma_1 = (2 + 3\alpha - 3\alpha^2)/(1 + 3\alpha) , \quad \eta = (\pi/3\sqrt{2})\,\rho/\rho_c ,$$

$$\gamma_2 = (2 + 6.3648\alpha - 7\alpha^2)/(1 + 3\alpha) , \tag{5}$$

$$\alpha = \overline{R}S/3v = (1 + ((1 + \varepsilon)/\sqrt{\varepsilon}\,) \arcsin \sqrt{\varepsilon\,(1 + \varepsilon)}\,) \times$$

$$\times\, (1 + (\varepsilon\,(1 + \varepsilon))^{-1/2} \ln (\sqrt{\varepsilon} + \sqrt{1 + \varepsilon}\,))/4\,. \tag{6}$$

Here the parameter α is defined in terms of the mean value of the particle surface curvature radius $\overline{R}$, the area of this surface S, and the particle volume v. These parameters are introduced in [13]; in the present article they are given in terms of the eccentricity $\varepsilon = (a/b)^2-1$. Expression (6) is valid for prolate ellipsoids of revolution ($a > b$). For oblate ellipsoids α has the same numerical value as for prolate ones with the same ratio between the major and minor semiaxes.

We take the orientation distribution function of the particles in the form [14]:

$$f\,(\mathbf{e}_j) = f\,(x_j) = A \exp\,(cP_2\,(x_j))\,, \quad x_j = \mathbf{n} \cdot \mathbf{e}_j\,, \quad j = 1\,,\,2\,, \tag{7}$$

where $P_2(x) = (3x^2-1)/2$ is a Legendre polynomial; A is a normalized constant; and c is a constant determined from the self-consistency condition:

$$\int\limits_{-1}^{1} P_2\,(x)\,f\,(x)\,dx = s\,. \tag{8}$$

Due to this condition, the constant c is a function of the thermodynamic parameters ρ and T, because the order parameter s depends on them. When $\tilde{\rho} \leq 0.7$, we can assume that $c \simeq 5s$ with an error not exceeding 10%, while the well-known Maier-Saupe distribution [14] employs $c = 6.81s$. When $\tilde{\rho} > 0.7$, the constant c increases rapidly, attaining the value $c = 68$ at $s = 0.98$.

Averaging according to (4) requires four-dimensional integration, so that a five-dimensional integral must be calculated to compute the self-diffusion coefficient with allowance for averaging over the orientations of the first particle. The use of symmetry properties makes it possible to develop an efficient scheme of numerical integration suitable for medium-class personal computers.

First of all, we note that J and D depend only on the mutual orientation of vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{k}$, and not on the orientation of these vectors relative to vector $\mathbf{n}$. Therefore, the result of integration in (4) with respect to vector $\mathbf{k}$ will depend only on the angle between the symmetry axes of the particles ($\mathbf{e}_1$ and $\mathbf{e}_2$ vectors). It is advisable to tabulate and use this result in further averaging over $\mathbf{e}_1$ and $\mathbf{e}_2$. Owing to this, as judged by the expenditures of computer time, the computation of the original five-dimensional integral is reduced to the computation of a small number of three-dimensional integrals.

2. Results of Computations and Their Analysis. Specific computations were performed for both prolate and oblate rigid ellipsoids of revolution with semiaxis ratios $a/b = 10$, 5, 3, 1/3, 1/5, and 1/10 for $\tilde{\rho} = 0.2-0.65$. These contain isotropic and ordered phases. Figure 1 presents the dependences of the dimensionless longitudinal $\tilde{D}_{\parallel}$ and transverse $\tilde{D}_{\perp}$ (with respect to the director $\mathbf{n}$) self-diffusion coefficients of particles in an orientationally-ordered phase and of the self-diffusion coefficient $\tilde{\mathbf{D}}$ in an isotropic phase on the density $\tilde{\rho}$. For transition to the physical dimension m^2/sec the components of tensor $\tilde{\mathbf{D}}$ should be multiplied by the dimensional factor δ:

$$\delta = \sigma\,\sqrt{k_{\mathrm{B}}T/m}\,. \tag{9}$$

The values of the components of the tensor $\tilde{\mathbf{D}}$ correspond to the data obtained in a computer experiment [15, 16] by the method of molecular dynamics, in which it was assumed that $m = 1$, $k_BT = 1$, and $\sigma = 1$. These data are also presented in Fig. 1. Comparing them with the results of statistical calculation, we find that the Enskog theory affords a good description of the behavior of the components of tensor $\tilde{\mathbf{D}}$ in the entire investigated range of densities of the system, including the transition from the isotropic to the ordered phase.

For prolate ellipsoids of revolution ($a > b$) the results of the Enskog theory are virtually everywhere lower than the data or the computer experiment, with deviations reaching 30% at $a/b = 5$ and 36% at $a/b = 10$. In this case, the statistical theory affords a good reproduction of the anisotropy of the tensor of the self-diffusion

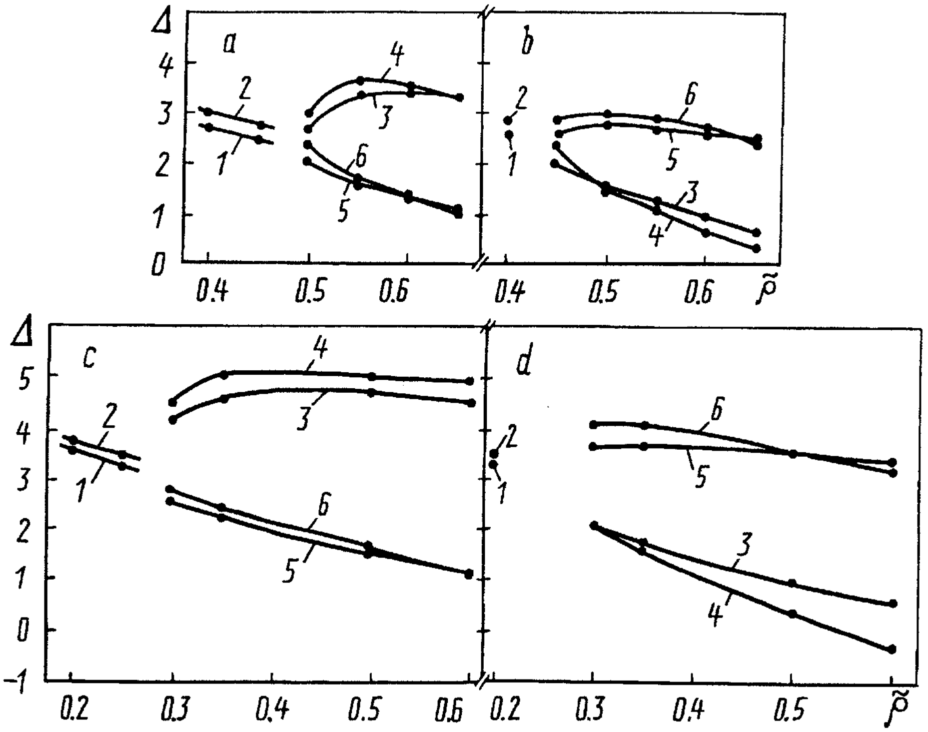

Fig. 1. Dependence of self-diffusion coefficients on density at $a = 5b$ (a), $0.2b$ (b), $10b$ (c), and $0.1b$ (d): 1, 3, 5) results of statistical theory; 2, 4, 6) computer experiment [15]; 1, 2) isotropic phase, $\Delta = \ln(100\tilde{D})$; 3-6) orientationally ordered phase; 3, 4) $\Delta = \ln(100\tilde{D}_{\parallel})$; 5, 6) $\Delta = \ln(100\tilde{D}_{\perp})$.

coefficients expressed by the ratio $\tilde{D}_{\parallel}/\tilde{D}_{\perp}$. Deviations of this ratio from the computer experiment, except for the point $a/b = 10$, $\tilde{\rho} = 0.6$, does not exceed 16%, while its absolute value changes from 2 to ~30.

For oblate ellipsoids ($a < b$) the agreement of the results of calculation of $\tilde{\mathbf{D}}$ with the computer experiment is less satisfactory, especially for large densities: $\tilde{\rho} = 0.5-0.65$. The same applies to the characteristic of the anisotropic properties of tensor $\tilde{\mathbf{D}}$.

The deterioration of the correspondence between the results of the statistical theory and computer experiment for oblate ellipsoidal particles can be understood if we take into account that the oblate particles have a larger cross-sectional area and smaller moment of inertia as compared with prolate particles of the same volume, and if the reorientation of particles is neglected in computations. The difference is also explained by the contribution of repeated collisions, which is ignored in the Enskog approximation. An additional source of the difference discussed is the lack of information about the distribution functions, especially the replacement of the anisotropic function $g_c(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k})$ by its averaged value $\bar{g}_c$. At the same time, the good agreement of the statistical computations with the computer experiment shows that $\bar{g}_c$, determined by the equilibrium properties of an isotropic phase, well approximates g_c also in an anisotropic phase.

An important property revealed in both the computer experiment and statistical computations is the presence of a maximum on the $\tilde{D}(\tilde{\rho})$ curves in the directions of the most favorable motion of particles. The structure of expression (4) for the tensor of the friction coefficients makes it possible to explain this effect by the competition of two factors. On the one hand, the contact value of the correlation function $\bar{g}_c$ increases with density (it changes from 2.7 at $\tilde{\rho} = 0.3$ to 5.1 at $\tilde{\rho} = 0.6$ for $a = 10b$). On the other hand, as the order parameter s increases (and, consequently, also the density ρ), the contribution of the integral of J/D over angular variables becomes smaller; this reflects the decrease in the resistance to the motion of particles due to the ordering of their orientations.

This effect is not observed for the components of the tensor of the self-diffusion coefficients in the directions of the greatest resistance to motion. Here, increased ordering does not decrease the resistance to particle motion, while a decrease in the mean angle between the axis of the particle and the direction $\mathbf{n}$ leads to an additional decrease in the contribution to the transverse component $\tilde{\mathbf{D}}$ owing to the motion of the particle along its own long axis. The dependences obtained in a statistical calculation for the tensor of the friction coefficients of the particle in its own frame of reference confirm this conclusion [17, 18].

The values of the self-diffusion coefficients found in an isotropic phase are in a good agreement with molecular-dynamic data, differing from them by about 20–25% for both prolate and oblate particles. These results are much better than the data of calculations made in [3], probably due to our use of the particle's own coordinate system to calculate the tensor of the friction coefficients. For a nonspherical particle this tensor is anisotropic in an isotropic phase as well.

At the time of preparing this article for publication, a work [19] appeared in which a statistical computation of the tensor of the self-diffusion coefficients of prolate particles was considered. The authors used the Mori method to write the evolution equations in terms of an extended set of variables. The resulting dependences were obtained in the Enskog approximation. Although the working formulas and the technique of calculation differ substantially from those considered in the present work, the discrepancy with our results does not exceed 2–3%, except for the data in an isotropic phase at $a/b = 10$, where the difference attains 5%. A system of oblate particles was not considered in [19].

We also note that in [19] the time correlation functions of the velocities include two terms corresponding to two different relaxation times. In our approach we have a continuous spectrum of relaxation times attributable to the dependence of the tensor of the friction coefficients on the particle orientation. Subsequent computation of the time correlation functions of the velocities of the particle involves averaging over the orientations of the particle, which reveals the regions of large and small relaxation times. Therefore, in this case as well the qualitative picture of the behavior of the time correlation functions is the same as that obtained by the method of molecular dynamics [15, 16].

The work was done with the support of the Fund for Fundamental Investigations of the Republic of Belarus.

NOTATION

N, the number of particles in system; V, volume occupied by system; a, b, semiaxes of ellipsoid of revolution; $v = 4/3\pi ab^2$, particle volume; m, particle mass; σ, diameter of spherical particle equal to the ellipsoid of revolution; $\rho = N/V$, particle number density; $\rho_m = \sqrt{2}/\sigma^3$, density in the state of close packing; $\tilde{\rho} = \rho/\rho_m$, dimensionless density; $\eta = \rho v$, packing coefficient; T, absolute temperature; k_B, Boltzmann's constant; $\mathbf{D}$, τ, ζ, tensors of the coefficients of self-diffusion, relaxation times, and friction; T_{21}, operator of binary collisions; $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{n}$, unit vectors along the axes of symmetry of two particles of system and axis of orientational order; $f(\mathbf{e})$, single-particle orientation distribution function; $g_c(\mathbf{e}_1, \mathbf{e}_2, \mathbf{k})$, contact value of the two-particle correlation function; s, order parameter; $\mathbf{k}$, unit vector of outward normal to surface of first particle.

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