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The Diffusion Theory for 2D Nematic of Hard Needles

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The Enskog type theory results of the diffusion coefficients are presented for a system of two-dimensional hard needles and they are confronted to the Molecular Dynamics simulation data. The theory reproduces well not only the basic features of the diffusion in the molecular frame, but also the values obtained after transformation to the laboratory frame.

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Keywords: diffusion; hard needles; nematic liquid crystals

I. INTRODUCTION

The diffusion problem is one of the most important subjects in the modern technology liquid crystals applications. The quality of the displays depends directly on the possibility of the molecular reorganizations which, among others, is governed by the diffusional properties. Theoretical investigations as well as computer simulation may provide then undeniable help in understanding complicated diffusional mechanisms in liquid crystals [1–3].

II. ENSKOG THEORY FOR TRANSLATIONAL DIFFUSIVITIES

Recently, in [4] we have showed that the Enskog theory of the autocorrelation functions provides predictions that are satisfactorily comparable to the simulation data. The framework of this theory has been taken from [5], where Frenkel and Maguire applied it to the isotropic phase of the three-dimensional hard needles. This theory assumes

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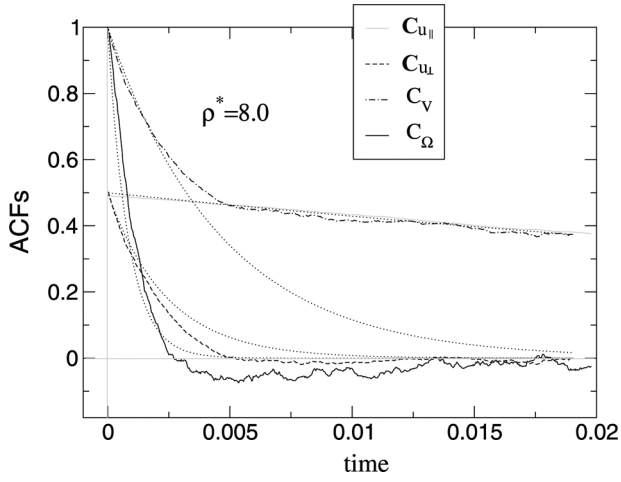

FIGURE 1 The concept of initial gradients. According to the theory, three of the velocity autocorrelations, $C_{\mathbf{u}_\perp}$, $C_{\mathbf{u}_\parallel}$ and C_Ω, can be described by single exponents, so in order to reconstruct the whole curves, it is sufficient to establish the values of initial gradients. Even in the case of C_v, which is a superposition of two exponents, the value of the initial gradient allows to describe the part of the curve at short times. The profiles are the examples of ACFs obtained from the Molecular Dynamics simulations for a system of 2D hard needles at the density $\rho^* = 8.0$ (nematic phase). They are compared to the Enskog theory predictions (the dotted curves). The reduced density is defined here as $\rho^* = L^2N/V$, where N is the number of the particles, V is the volume of the system and L is the length of the needle. Note that the autocorrelation functions $C_{\mathbf{u}_\perp}$ and $C_{\mathbf{u}_\parallel}$ are presented here as normalized to 0.5 at time = 0.

that the principal velocity autocorrelations are given by single exponents, so, in order to obtain main contribution to the real profiles, it is sufficient to establish initial gradients of the autocorrelation curves (see Fig. 1). As principal autocorrelations we understand the functions calculated in accordance to the molecular frame like the transversal ACF, $C_{\mathbf{u}_\perp}$, (i.e., the autocorrelation of the velocity perpendicular to the long axis of the system molecule), longitudinal, $C_{\mathbf{u}_\parallel}$, (i.e., the autocorrelation of the velocity along the main axis of the molecule) and the rotational ACF, C_Ω, (autocorrelation of the angular velocity Ω). Only the third one remains the same if we move the observer from the molecular to the laboratory frame. Laboratory frame has the privileged and important position, since almost all the experimental data is obtained within this particular geometry. Unfortunately, there is no straight correspondence between transversal and longitudinal autocorrelations in these both frames. Note that in the laboratory frame,

one can also use similar adjectives as longitudinal or transversal, according to the condition that the autocorrelations are obtained with respect to the director or the vector perpendicular to the director.

We propose a simple semi-empirical formula joinig the properties of the above autocorrelations in different frames. It is following:

$$C_n = \frac{1+\eta}{2\eta} C_{\mathbf{u}_\perp} + \frac{\eta-1}{2\eta} C_{\mathbf{u}_\parallel} \tag{1}$$

and

$$C_e = \frac{1+\eta}{2\eta} C_{\mathbf{u}_\parallel} + \frac{\eta-1}{2\eta} C_{\mathbf{u}_\perp}. \tag{2}$$

The autocorrelations on the right hand sides of (1) and (2) denote the values calculated in the molecular frame (parallel and perpendicular to the molecule), whereas the expressions on the left hand sides describe the autocorrelations in the laboratory frame (perpendcular and parallel to the director).

According to the Enskog theory $C_{\mathbf{u}_\perp}$ and $C_{\mathbf{u}_\parallel}$ are single exponentials

$$C_{\mathbf{u}_\perp} = \exp\left(-\frac{t}{\tau_{\mathbf{u}_\perp}}\right),$$

$$C_{\mathbf{u}_\parallel} = \exp\left(-\frac{t}{\tau_{\mathbf{u}_\parallel}}\right),$$

so their inverse relaxation times are given by

$$\frac{-1}{\tau_\perp} = \left.\frac{dC_{\mathbf{u}_\perp}}{dt}\right|_{t=0} \quad \text{and} \quad \frac{-1}{\tau_\parallel} = \left.\frac{dC_{\mathbf{u}_\parallel}}{dt}\right|_{t=0}. \tag{3}$$

These formulas have allowed to calculate the following microscopic expressions [4]:

$$\left(-\frac{1}{\tau_\perp}\right)\langle \mathbf{v}_0^2 \rangle = -\left\langle \mathbf{v}_{ij} \cdot \mathbf{u}_j^\perp \Delta v (2 - \cos^2\alpha) \frac{dn}{dt} \right\rangle \tag{4}$$

and

$$\left(-\frac{1}{\tau_\parallel}\right)\langle \mathbf{v}_0^2 \rangle = -\left\langle \mathbf{v}_{ij} \cdot \mathbf{u}_j^\perp \Delta v \cos^2\alpha \frac{dn}{dt} \right\rangle. \tag{5}$$

In (4) and (5) $\langle \mathbf{v}_0^2 \rangle$ is the average of the particle velocity squares which corresponds to the particle mean kinetic energy of translational movement (the mass of the needle is assumed as 1); Δv corresponds to the exchange of the momentum during a binary collision. α is the angle

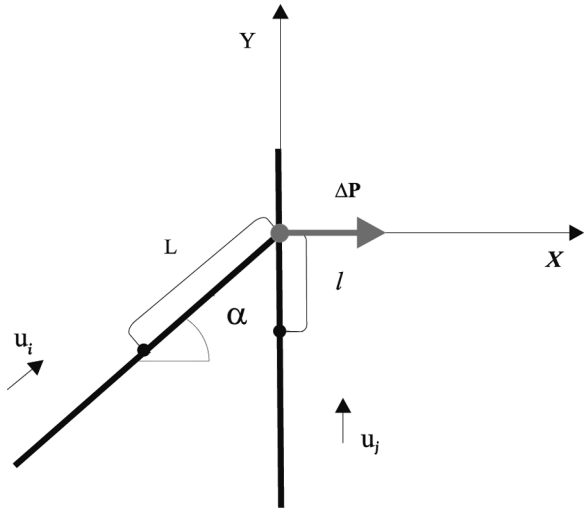

FIGURE 2 The geometry of collision between two hard needles. $\Delta\mathbf{P}$ is the vector of the momentum exchange.

between two colliding needles; $\mathbf{u}_j$ is the particle j orientation and $\mathbf{u}_j^{\perp}$ is the unit vector perpendicular to $\mathbf{u}_j$ along which the transfer of momentum $\Delta\mathbf{P}$ takes place (as shown by the grey arrow in Fig. 2). $\mathbf{v}_{ij}$ denotes the relative velocity of the particles "i" and "j".

The expression for the mean collision rate $\langle\frac{dn}{dt}\rangle$ has been derived in [4] as:

$$\left\langle \frac{dn}{dt} \right\rangle = \mathrm{d}\sqrt{\pi} \int_{-L}^{L} \int_{0}^{\pi} d\alpha dl f(\alpha) \sqrt{1 + \frac{m}{I} l^2 + \frac{m}{I} L^2 \sin^2 \alpha}. \tag{6}$$

Here d is the density, I the inertia moment of the needle, L half of the particle length and l is the distance from the centre of the needle to the point of contact (see Fig. 2). From this formula one can see that the expression for the dn/dt needed in (4) and (5) is the function which stands here after the integral sign.

If the orientational distribution function $f(\alpha)$ is known explicitely, then the integrals of (4) and (5) are easily calculated.

The inverse relaxation times for C_v and C_Ω are given in a similar manner ([4]):

$$\left(-\frac{1}{\tau_v}\right)\langle \mathbf{v}_0^2 \rangle = -\frac{\sqrt{\pi}\mathrm{d}}{2m} \frac{\sqrt{2kT}}{m} \frac{2kT}{m} \int_{-L}^{L} \int_{0}^{\pi} \frac{\sqrt{1 + \frac{m}{I}(l^2 + L^2 \sin^2 \alpha)}}{1 + \frac{mL^2}{2I} \sin^2 \alpha + \frac{m}{2I} l^2} f(\alpha) dl\, d\alpha \tag{7}$$

and

$$-\frac{1}{\tau_\Omega}\langle \mathbf{\Omega}_0^2 \rangle = -\frac{1}{4}\frac{2kT}{I}\sqrt{\frac{2kT}{m}}\pi^{-1/2}L^2 mI\mathrm{d}2\pi \times \int_{-L}^{L}\int_0^\pi \frac{\sin^2\alpha\sqrt{1+\frac{m}{I}(l^2+L^2\sin^2\alpha)}}{1+\frac{mL^2}{2I}\sin^2\alpha+\frac{m}{2I}l^2} f(\alpha)d\alpha dl. \quad (8)$$

Integrating both sides of (1) and of (2) with respect to time and using $D_\parallel = \int C_n\,dt$ and $D_\perp = \int C_e\,dt$ one gets:

$$D_\parallel = \frac{1+\eta}{2\eta}\tau_{\mathbf{u}_\perp} + \frac{\eta-1}{2\eta}\tau_{\mathbf{u}_\parallel} \quad (9)$$

and

$$D_\perp = \frac{1+\eta}{2\eta}\tau_{\mathbf{u}_\parallel} + \frac{\eta-1}{2\eta}\tau_{\mathbf{u}_\perp}. \quad (10)$$

In the expressions (9) and (10) there is one unknown parameter, η, which, as a matter of fact, is responsible for the coupling between velocity and orientational ordering fields.

This coefficient can be found using an additional condition as, for instance, for $R_2 = \frac{D_\parallel - D_\perp}{D_\parallel + D_\perp}$. In terms of the Enskog theory relaxation times it can be expressed as

$$R_2 = \frac{1}{\eta}\frac{\tau_{\mathbf{u}_\perp} - \tau_{\mathbf{u}_\parallel}}{\tau_{\mathbf{u}_\perp} + \tau_{\mathbf{u}_\parallel}}. \quad (11)$$

On the other hand, the affine model of diffusion for 2D case [6] provides that

$$R_2 = S\frac{Q^2-1}{Q^2+1}, \quad (12)$$

where the ratio $Q = length/width$ characterizes the shape anisotropy of the molecule and S is the order parameter. For infinitely hard needles R_2 becomes simply $R_2 = S$. Thus, one can relate the so far unknown coefficient η as:

$$\eta = \frac{1}{S}\frac{\tau_{\mathbf{u}_\perp} - \tau_{\mathbf{u}_\parallel}}{\tau_{\mathbf{u}_\perp} + \tau_{\mathbf{u}_\parallel}}. \quad (13)$$

The formula for η (13), together with the Enskog theory expressions for the relaxation times, shows that the coupling between the velocity and the orientational degrees of freedom is nontrivial. This conclusion

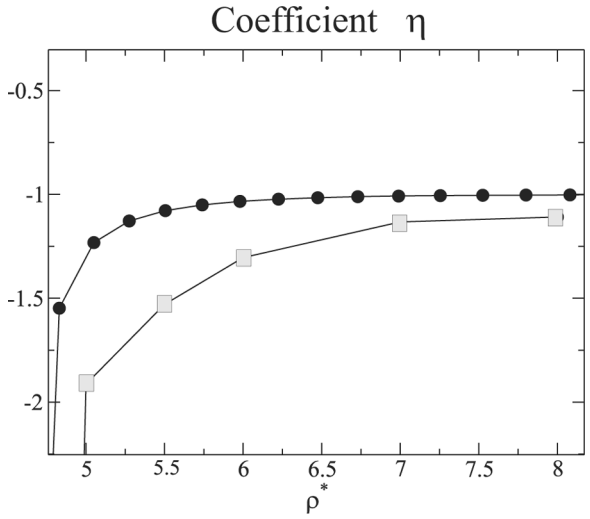

FIGURE 3 The coefficient η calculated according to the formula (13) on the basis of the theoretical relaxation times (the black circles) the MD data (the grey squares). The reduced density ρ^* is defined here as in Figure 1.

is similar to the results obtained for 3D nematic, which have been presented, for instance, in [1] by Tang and Evans for 3D ellipsoids. In this paper ([1]), using the friction matrix and the generalized Langevin equation, the authors have showed that the autocorrelations C_n and C_e can be really expressed as linear functions of $C_{\mathbf{u}_\parallel}$ and $C_{\mathbf{u}_\perp}$ but the needed proportionality factors exhibit a very complicated order parameter dependence.

In Figure 3 we present a comparison of the η values obtained from the MD simulations (the MD simulations details for hard needles has been given in [6]) and the theoretical Enskog-affine description. Taking into account the simplicity of the Enskog assumption that decays are single exponentials, it can be seen that these exponentials are really major contributions. From (13) it can be also seen that the formula for η is valid only in the nematic phase, when S is different from 0. At the isotropic-nematic transition η escapes into $-\infty$.

The figures of the principal diffusivities themselves, $D_\parallel$ and $D_\perp$, are given in Figure 4. A disagreement, which one observes in both figures at the nematic regime, is attributed to the fact that at longer times C_n is non-exponential and that this effect is eventually stronger than influence of the backscattering on the shape of C_e.

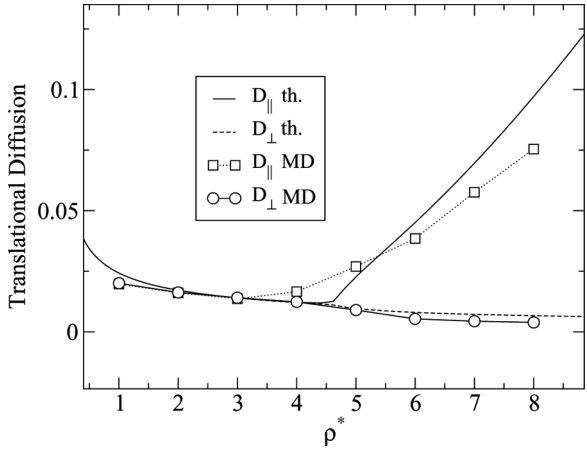

FIGURE 4 The translational diffusion coefficients $D_{\parallel}$ and $D_{\perp}$. Comparison of the Enskog-affine theory and the MD data. The symbols present the data from the Molecular Dynamics simulations and the solid lines come from the kinetic theory in which the orientational distribution function from the Onsager theory [7] has been used. The reduced density ρ^* is defined here as in Figue 1.

III. RESULTS: ROTATIONAL SELF-DIFFUSION

In Figure 5 we present the rotational diffusion coefficient obtained by the use of the theoretical Enskog-affine theory and the Molecular Dynamics. The results for D_{Ω} are not as good as for the diffusivities of translational movement. This, most probably, is an effect of the single collision assumption. Since the MD profiles for the angular velocity autocorrelation C_{Ω} even in the isotropic phase exhibit pronounced negative parts, this means that the secondary collisions play a very important role. These events (the secondary collisions), however, are beyond the scope of the Enskog approach, which, basing only on the exponential decays, is not capable to reproduce the negative parts of the autocorrelations. Nevertheless, the results of the theory predict the right order of the diffusion value, reconstructs its general character together with the dependence on the density. It can be observed that within the nematic phase the predictions of the Enskog theory, however slightly of smaller values, indeed follow the shape of the MD data.

IV. SUMMARY

Summing up, although the Enskog-type theory may not predict subtleties of the rotational diffusivities, yet the obtained values can be still

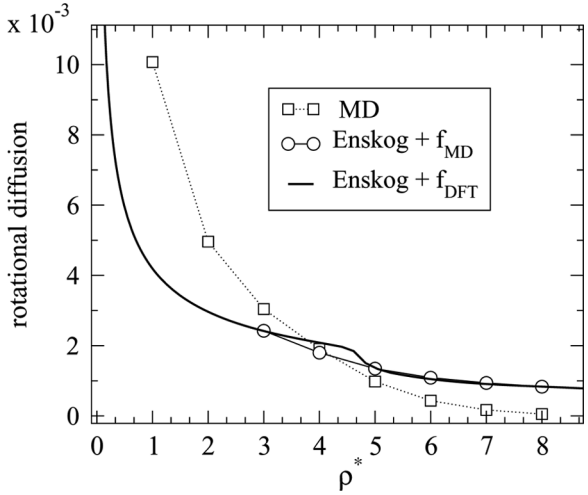

FIGURE 5 The rotational diffusion coefficient obtained within different methods. The squares correspond to the Molecular Dynamics data, the circles are the results of the Enskog theory with the application of the distribution function ODF from the MD simulations. The solid line is the outcome of the Enskog theory with the ODF from the Onsager approach [7]. The reduced density ρ^* is defined here as in Figure 1.

compared for different particles parameters and help to choose the ones which lead to better or more desirable characteristics. We believe that this prognosis is also true for more realistic 3D nematics.

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