

## Anomalous diffusion in the nematic phase of thin disks

A. Alavi and D. Frenkel

*FOM-Instituut voor Atoom en Molecuulfysica, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*

(Received 13 September 1991)

We report molecular-dynamics simulations of the anisotropic diffusion of infinitely thin platelets in the nematic phase. Our simulations are used to distinguish between the predictions of two different theories. The first theory, based on a mapping of the nematic phase of ellipsoidal particles on the hard-sphere fluid, predicts that both the longitudinal and transverse diffusion constants decrease monotonically with increasing density. This is in stark contrast to a scaling argument which suggests that the transverse diffusion constant of platelets in the nematic phase in fact *diverges* with increasing density. Our simulations support the scaling argument.

PACS number(s): 61.20.Ja, 61.30.By, 64.70.Md

Anisotropic short-time diffusion is a characteristic feature of the fluid phases of anisometric molecules. Such behavior is a consequence of the locally anisotropic environment of such molecules, where motion in certain directions (referred to as molecular axes) is favored over motion in other directions. For molecules with pronounced anisometry, and at sufficiently high densities, not only is the local molecular environment anisotropic, but globally certain symmetries may be broken, leading to anisotropic fluid phases with overall orientational order. Nematic order in systems composed of prolate or oblate ellipsoids is an example of such orientational order. In such phases, the long-time diffusion is anisotropic with respect to the axis that characterizes the molecular alignment.

A simple theory of the closely related problem of the anisotropic viscosity in perfectly aligned phases of ellipsoidal molecules was proposed some time ago by Baalss and Hess [1]. Recently, Hess, Frenkel, and Allen [2] extended this theory to describe diffusion in more realistic models of liquid crystals. In the modified version of the theory, the condition of perfect orientational alignment has been relaxed. In the theory of Ref. [2], the diffusion coefficients  $D_{\perp}$  and  $D_{\parallel}$  for diffusion perpendicular and parallel to the nematic director are related to the *isotropic* diffusion coefficient  $D_0$  of a system of spherical molecules via an approximate affine transformation which maps the system of ellipsoidal molecules onto the corresponding system of spherical ones. This theory accounts adequately for the diffusion coefficients in the nematic phase of a variety of systems of ellipsoidal molecules with aspect ratios in the range  $\frac{1}{10} \leq a/b \leq 10$  where  $a/b$  is the ratio of the major to minor axes.

However, such a theory which related anisotropic diffusion to a reference system of spherical molecules may be expected to break down in cases where the molecular anisotropy is extreme. A case in point is a system of infinitely thin platelets ( $a/b \rightarrow \infty$ ), which are objects with zero volume. This system orders into a nematic phase at a density  $\rho B_2 \approx 4$  ( $B_2 = d^3 \pi^2/16$ ) [3], where  $d$  denotes the diameter of a platelet. For such platelets this nematic phase is stable at all finite densities with  $\rho B_2 \geq 4$  (and

therefore its nematic order parameter can be made arbitrarily close to 1), in contrast to molecules with finite proper volume which freeze at high enough densities. In this nematic phase, a naive application of the Hess theory predicts that  $D_{\perp}$  behaves as [4]

$$D_{\perp} = \left(\frac{3}{2}\right)^{1/3} D_0(\rho) \rho^{2/3}, \quad (1)$$

where  $D_0(\rho)$  is the (known) hard-sphere diffusion coefficient. In Enskog theory this diffusion coefficient behaves as

$$D_0 \sim 1/\rho g(\sigma), \quad (2)$$

where  $g(\sigma)$  denotes the value at contact of the radial distribution function of a hard-sphere system at density  $\rho$ . Since the volume fraction of a system of infinitely thin platelets is zero, the corresponding hard-sphere fluid is always in the limit of vanishing density, for which  $g(\sigma) = 1$  [5]. The predicted behavior of  $D_{\perp}(\rho)$  of platelets in the Hess theory is therefore

$$D_{\perp} \sim \rho^{-1/3}. \quad (3)$$

In other words, the transverse diffusion coefficient is expected to drop with increasing density. As we shall show below, the prediction for the density dependence of the diffusion constant of platelets, based on Eqs. (1) and (3), is wrong quantitatively and, more interestingly, qualitatively. The fact that this should be so can be anticipated from a simple scaling argument. Consider an assembly of smooth hard platelets of diameter  $d$  at a density  $\rho$  in which the system is in the nematic phase. The transverse diffusion coefficient for such a system can be estimated from a knowledge of the initial slope of the velocity autocorrelation function (VACF) (assuming that this function decays exponentially with time). This slope is given by

$$1/\tau_{\perp} = - \frac{\langle \mathbf{v}_{\perp}^i \cdot \Delta \mathbf{v} \Gamma \rangle}{\langle \mathbf{v}_{\perp}^i \cdot \mathbf{v}_{\perp}^i \rangle}, \quad (4)$$

where  $\Gamma$  is the rate at which molecule  $i$  suffers collisions and  $\Delta \mathbf{v}$  is the velocity change per collision. Assume that the normal to the plane of molecule  $i$  is inclined at an angle  $\theta$  from the nematic director. A simple geometrical

construction shows that [3]

$$\theta \sim \frac{1}{\pi d^3 \rho}. \quad (5)$$

$\Gamma$ , the collision frequency, goes as

$$\Gamma \sim \rho v_c d^2, \quad (6)$$

where  $v_c$  is the average relative velocity of the platelets at contact.  $v_c$  contains contributions from the relative translations and rotations of the platelets. In the nematic phase,  $v_c$  is dominated by  $v_{\parallel}$  and rotations, and is only weakly dependent on density. Also  $|\Delta \mathbf{v}_{\perp}| \sim -\theta^2 v_{\perp}$ , since the impulse imparted at a rim-platelet collision is always perpendicular to the plane of the platelet which suffers the collision. (Note that  $v_{\perp}$  is the velocity *parallel* to the plane of the platelet.) In other words,

$$\langle v_{\perp}(0) \dot{v}_{\perp}(0^+) \rangle \sim -\langle v_{\perp}^2(0) \rangle \frac{1}{\rho^{*2}} \frac{\rho^*}{d}, \quad (7)$$

where the reduced density  $\rho^* = \rho d^3$  has been substituted in (7), and some numerical factors have been omitted. Hence integrating the VACF over all time we obtain

$$D_{\perp} \sim \rho^*. \quad (8)$$

Thus we arrive at the remarkable conclusion that the diffusion coefficient diverges with density. Physically this divergence can be understood simply as a consequence of the fact that as the density increases, the efficiency with which collisions can transfer momentum decreases (owing to the increased nematic order), so that the platelets are able to slide past each other with greater and greater ease. A similar scaling can be given for the longitudinal diffusion coefficient as well. In this case, a platelet must diffuse a distance of the order  $d$  parallel to its plane, before being able to move longitudinally an amount  $\delta r_{\parallel} \sim \theta d$ . Therefore

$$D_{\parallel} \sim \langle \delta r_{\parallel}^2 \rangle D_{\perp} / d^2 \sim \theta^2 D_{\perp} \sim 1 / \rho^*. \quad (9)$$

The corresponding Hess theory prediction for this diffusion coefficient is  $D_{\parallel} \sim 1 / \rho^{7/3}$ . In other words, while both theories predict a drop in  $D_{\parallel}$  with increasing  $\rho$ , the scaling argument predicts a much slower fall than the Hess theory. Indeed the difference in the exponents of  $\rho$  predicted by two theories for the longitudinal diffusion coefficient ( $\frac{4}{3}$ ) is the same as that predicted by the two theories for the transverse diffusion coefficient. Incidentally, a scaling argument similar to the one sketched above has been applied to diffusion in an isotropic system of infinitely thin needles. In the latter case, the scaling theory predicts a divergence of  $D$  with  $(\rho^*)^{1/2}$  [6].

We have carried out molecular-dynamics simulations of a system of infinitely thin platelets in the nematic phase in order to verify the unusual diffusive behavior predicted by the preceding scaling argument, particularly for the transverse diffusion coefficient. Recent simulations by Allen [7] of prolate and oblate ellipsoids in the nematic phase indicate a narrow range of densities, just beyond the isotropic-nematic transition, in which the longitudinal diffusion constant increases to a local maximum before decreasing. This behavior, however, can be explained qualitatively by the Hess theory. A monotonic increase of the diffusion constant in the nematic phase, predicted by the preceding scaling argument, however, has not been ob-

served thus far.

Molecular-dynamics calculations have been carried out on a system of  $N = 500$  smooth, hard platelets, placed in a periodic truncated octahedral box. Only uniform platelets (moments of inertia  $I_{\perp} = Md^2/16$ ) were considered. Rotation around the molecular symmetry axis cannot relax and was therefore excluded. Technical details of implementing molecular-dynamics simulations of hard molecules have been given in [8]. Briefly, the platelets move ballistically between collisions. The outcome of a collision between a pair of platelets is determined entirely by the fact that the total linear and angular momentum is conserved during the collision, as is the kinetic energy, and by the fact that the impulse imparted at a rim-platelet collision is perpendicular to the plane of the platelet which suffers the collision, while during a rim-rim collision, no momentum is transferred tangential to either rim. Forthcoming collisions are detected by the method of Rebertus and Sando [9].

Molecular-dynamics calculations have been performed in the density range  $5 \leq \rho B_2 \leq 12$ , which corresponds to a regime with pronounced nematic order ( $0.92 < S < 0.99$ ) ( $S$  is the nematic order parameter, which was computed in the standard way [10]). Typical runs consisted of equilibration runs of  $5 \times 10^5$  collisions and production runs of a similar length. The temperature  $T$  was set such that  $k_B T = 1$ , giving an energy per platelet in reduced units of  $\frac{5}{2}$ . Runs at densities higher than  $\rho B_2 = 12$  were hampered by the necessity not only for larger system sizes but also for longer runs. The diffusion coefficients  $D_{\perp}$  and  $D_{\parallel}$  were determined by examining the long-time limit of the mean-square displacement curves.

In Fig. 1, we have plotted the diffusion coefficient  $D_{\perp}$  against  $\rho B_2$ , and in Table I we give the values for the diffusion coefficients  $D_{\parallel}$  and  $D_{\perp}$  at the densities studied. It is clear that the largest contribution to the diffusion constant comes from  $D_{\perp}$ , i.e., diffusion perpendicular to

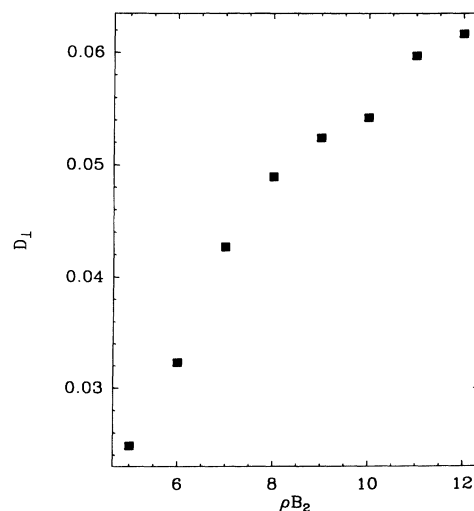


FIG. 1. Density dependence of the diffusion coefficient  $D_{\perp}$  of a system of infinitely thin, hard platelets in the nematic phase. The diffusion constant is expressed in reduced units  $d(k_B T / M)^{1/2}$ .

TABLE I. Summary of the density dependence of the order parameters  $S$  (column 2) and the diffusion coefficients  $D_{\perp}$  and  $D_{\parallel}$  (columns 3 and 4, respectively), expressed in units of  $d(k_B T/M)^{1/2}$ .

$\rho B_2$	$S$	$D_{\perp}$	$D_{\parallel}$
5	0.925	0.025	0.0037
6	0.952	0.032	0.0029
7	0.964	0.043	0.0021
8	0.973	0.049	0.0017
9	0.979	0.053	0.0016
10	0.982	0.054	0.0016
11	0.986	0.060	0.0015
12	0.987	0.062	0.0014

the nematic director, or equivalently, diffusion parallel to the plane of the platelets. Second,  $D_{\perp}$  increases with density, as had been anticipated earlier by the scaling arguments. At densities beyond  $\rho B_2=8$ ,  $D_{\perp}$  apparently increases approximately linearly with  $\rho B_2$ , a result also anticipated by the scaling argument. Further evidence for this linear increase can be obtained by examining the variation of  $D_{\perp}$  with  $S$ . Since  $S \sim 1 - 1/\rho^{*2}$ ,  $1/D_{\perp}^2$  plotted against  $S$  should in this case give a straight line, with an  $x$  intercept of 1. Such a plot is shown in Fig. 2, where it appears that at the highest densities studied we have entered this linear regime. Since longitudinal diffusion is expected to be 2 orders of magnitude slower than transverse diffusion, accurate determination of  $D_{\parallel}$  proved to be difficult. Nevertheless, inspection of the figures given for  $D_{\parallel}$  in Table I indicates, apparently, a roughly  $1/\rho^*$  dependence of  $D_{\parallel}$ —a result which is also consistent with the scaling predictions.

The results of the molecular-dynamics simulations also provide an *a posteriori* justification for one ansatz in our scaling argument, namely, that the transverse VACF decays exponentially. We found this to be the case throughout the density range of interest.

In conclusion, what appears to be essential in the diffusion of hard smooth platelets in the nematic phase is that *topological* constraints force the molecules to move between the two (undulating) surfaces defined by neighboring platelets. This kind of motion is probably best described by the term “floundering.” We do not expect the results that we have obtained above to carry over directly to diffusion in nematic colloidal suspensions of thin, disk-

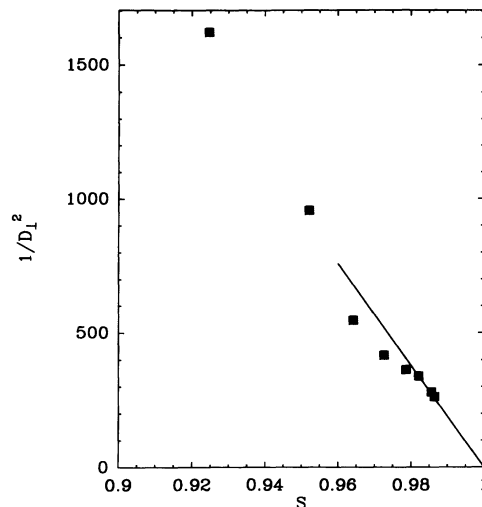


FIG. 2.  $1/D_{\perp}^2$  vs the nematic order parameter  $S$ . According to the theory of Ref. [2],  $1/D_{\perp}^2$  should diverge as  $[1/(1-S)]^{1/3}$ . In contrast, the scaling argument proposed in the text suggests that  $1/D_{\perp}^2 \sim (1-S)$ . The simulation data appear to confirm the latter prediction.

like particles. In the latter systems, the molecular motion is diffusive rather than ballistic, owing to the presence of viscous forces. This feature will change the qualitative dependence of  $D$  on  $\rho$ , in much the same way that the presence of a viscous solvent makes the Doi-Edwards predictions for the diffusion of rodlike polymers [11] different from the behavior predicted for rods that move ballistically [6]. Yet, the presence of solvent should not change the nature of the topological constraints that dominate the diffusion of disklike particles in a lyotropic nematic phase, even if the particles are no longer rigid. We therefore expect that the concept of floundering will apply in these systems as well. In the case of flexible platelets, floundering would correspond to a two-dimensional reptation.

We thank M. P. Allen and M. Doi for valuable suggestions and for a critical reading of the manuscript. A.A. acknowledges NATO/SERC for support and the FOM Institute for their hospitality. This work is part of the research program of FOM (Foundation for Fundamental Research on Matter), and is supported by The Netherlands Organisation for Scientific Research (NWO).

- [1] D. Baalss and S. Hess, Phys. Rev. Lett. **57**, 86 (1986).  
 [2] S. Hess, D. Frenkel, and M. P. Allen, Mol. Phys. **74**, 765 (1991).  
 [3] R. Eppenga and D. Frenkel, Mol. Phys. **52**, 1303 (1984).  
 [4] The factor  $\rho^{2/3}$  in Eq. (1) stems from a factor  $(1-S)^{-1/3}$  which occurs in the Hess theory, and the use of  $S \sim 1 - \rho^{-2}$ .  
 [5] Of course, the original Hess theory was not designed to describe the dynamics of infinitely thin platelets. Recently it has been suggested [S. Hess (private communication)] that, in the case of objects with zero proper volume, another mapping on the hard-sphere model could be more realistic. This would result in another prediction for the

- density dependence of the diffusion constants.  
 [6] D. Frenkel and J. F. Maguire, Mol. Phys. **49**, 503 (1983).  
 [7] M. P. Allen, Phys. Rev. Lett. **65**, 2881 (1990).  
 [8] M. P. Allen, D. Frenkel, and J. Talbot, Comput. Phys. Rep. **9**, 301 (1989).  
 [9] D. W. Rebertus and K. M. Sando, J. Chem. Phys. **67**, 2585 (1977).  
 [10] C. Zannoni, in *Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, New York, 1979).  
 [11] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford Science Pub., Oxford, 1986).