LETTERS TO THE EDITOR

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COMMUNICATIONS

Single particle and collective orientational relaxation in an anisotropic liquid near the isotropic–nematic transition

A. Perera, S. Ravichandran, and M. Moreau
Laboratoire de Physique Théorique des Liquides,[a)] Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

B. Bagchi
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560 012, India

We report molecular dynamics simulation results for the single particle and collective orientational correlations for Gay–Berne fluid of anisotropy parameters $\kappa=3$ and $\kappa'=5$. The following significant results are reported. (i) The decay of collective orientational relaxation of rank two is found to slow down appreciably while approaching the isotropic–nematic (I–N) transition. It eventually becomes even slower than the single particle orientational relaxation of rank one. Surprisingly, even the latter shows a marked slowing down near the I–N transition. (ii) Analysis of the long-time behavior shows a breakdown of the rank dependence predicted by the Debye law in the same region. (iii) An analysis of the memory functions of the orientational time-correlation functions shows that for the collective relaxation surprisingly approaches a Markovian behavior near the I–N transition. © *1997 American Institute of Physics.* [S0021-9606(97)51403-6]

I. INTRODUCTION

Fluids exhibiting liquid crystalline phases are of particular interest to study the interplay between single and collective orientational dynamics at the molecular level. Particularly, in the vicinity of the isotropic to nematic phase transition region, it is well known that long-range orientational correlations play an important role, and their growth will eventually destabilize the isotropic phase.[1] The dynamics of this growth at very large fluctuation lengths is dominated by defects and domain walls and this appears now to be relatively well understood in terms of scaling and phase ordering kinetics.[2,3] But at the molecular level a theoretical description is still pending. Allen and Frenkel[4] have studied, by molecular dynamics, a system of hard ellipsoids and shown that the dynamics in the vicinity of the I–N transition is dramatically influenced by the growth of orientational correlations. As far as we know, this is the first microscopic evidence of such dynamical effects. While a considerable amount of work has been done in theoretical investigation of the orientational microscopic dynamics in dense liquids, these investigations are often restricted or applicable to small anisotropies.

From the point of view of microscopic approach, one can address several questions concerning the dynamics in the vicinity of the I–N transition. For example, is the Debye law of rotational diffusion still applicable in this vicinity? What is the validity of the phenomenological models such as the extended Gordon model or the Langevin model?[5] How many relaxation times are necessary to describe the single particle

and collective orientational motions of highly anisotropic molecules? Answers to these questions are now urgently needed because new experimental techniques such as the transient grating optical Kerr effect technique[6] now allow accurate measurements at faster time scales, thus allowing detailed probe of molecular motions hitherto impossible. The separation of different time scales such as those of director fluctuations from the faster molecular motion is also now measurable.[7,8]

From the theoretical point of view, dynamics of the I–N pretransitional behavior poses interesting problems because one needs to take into account the intermolecular correlations, both spatial and orientational, that arise at high density.[9–11] In the absence of any detailed microscopic theories, computer simulations of simple model systems can be particularly useful in providing valuable insight.

The Gay–Berne (GB) fluid[12] has been extensively studied recently by computer simulations.[13] While the GB model may not be the best or the only choice of the anisotropic potential, the modified version[14] of the potential does exhibit surprisingly rich liquid crystalline phases such as nematic and various smectic phases. In addition, the model is sufficiently general and allows one to study the role of anisotropy and the influence of the attractive part of the potential. In this Communication we shall focus on the GB model with anisotropy parameters $\kappa=3$ and $\kappa'=5$ for which the isotropic–nematic transition has been reported at $\rho^*=0.323$ for the isotherm $T^* = 1.25$.[13] We report here first- and second-rank orientational time correlation functions defined for the single particle as

$$C_l^{(s)}(t) = \frac{\langle P_l(\hat{\mathbf{e}}_i(0) \cdot \hat{\mathbf{e}}_i(t))\rangle}{\langle P_l(\hat{\mathbf{e}}_i(0) \cdot \hat{\mathbf{e}}_i(0))\rangle}, \tag{1}$$

and similarly for the analogous collective quantity

$$C_l^{(c)}(t) = \frac{\Sigma_j \langle P_l(\hat{\mathbf{e}}_i(0) \cdot \hat{\mathbf{e}}_j(t))\rangle}{\Sigma_j \langle P_l(\hat{\mathbf{e}}_i(0) \cdot \hat{\mathbf{e}}_j(0))\rangle}, \tag{2}$$

where $\hat{\mathbf{e}}_i$ is the unit orientation vector along the major axis of the ith molecule, and P_l is the Legendre polynomial of order l. The symmetry of the GB interaction imposes $C_1^s = C_1^c$. We find here that $C_2^{(c)}(t)$ decays slower than $C_1^{(s)}(t)$ when the density is increased towards the I–N transition density. This reflects the coupling of the collective motion with the single molecular motion as well as the increase of the collective orientational correlations near the I–N region. We show in Sec. II that this effect is linked to the growing orientational instability of the isotropic phase which is reflected by the divergence of the Kirkwood factor. Similar results were reported earlier by Allen and Frenkel for the case of hard ellipsoids.[4] In addition, we find here that the correlation times deviate strongly from the Debye law and that the relaxation of the collective orientational correlations becomes surprisingly Markovian near the I–N transition.

II. SIMULATION METHODS AND RESULTS

A system of 243 prolate Gay–Berne (GB) particles was studied using standard molecular dynamics (MD) techniques.[15] Both translational and rotational equations of motion were solved using leap-frog-type algorithm.[16] Our simulation results for various static and dynamic quantities were successfully checked for consistency against those obtained by de Miguel *et al.*[13] We have used the same simulation parameters as these authors, in particular the reduced time step Δt^* was taken to be 0.0015. We have concentrated on the isotherm $T^* = 1.25$ for which we found that the I–N transition takes place between $\rho^* = 0.323$ and $\rho^* = 0.331$, in good agreement with the previously reported results.[17]

Special attention was paid to extract accurately the long-time dynamics from the orientational correlation functions. For that purpose it was found that runs longer than those reported in Ref. 13 were required mainly close to the I–N transition region. For all the simulations reported here, equilibration runs were made over 10^5 steps and the trajectories were recorded during further 2×10^5 time steps. This allowed a thorough sampling of the time correlations which were necessary in order to isolate properly the exponential decay of the orientational time correlation functions at long times. Near $\rho^*=0.32$ the system has strong tendency to oscillate between the isotropic and the nematic phases, thus care was taken to discard any statistics related to the nematic phase. For densities between 0.25 and 0.32, the exponential decay of the orientational correlations sets in only after $t^* \geq 8$, which is already above the time scale reported in Ref. 13. For the case of the collective orientational correlation function $C_2^{(c)}(t)$, at least four independent runs were made
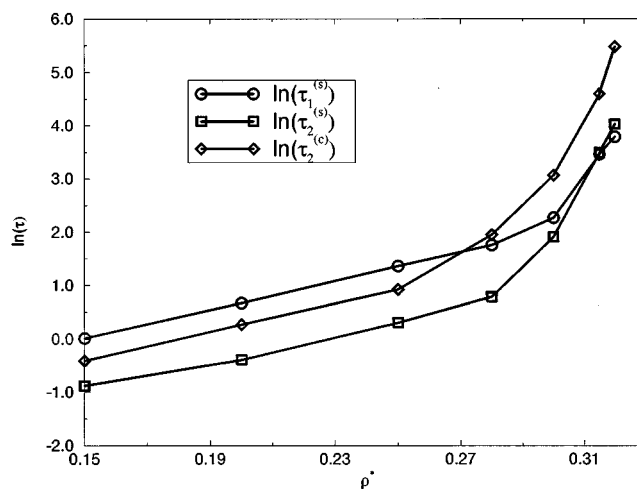

FIG. 1. Density dependence of the exponential decay times for single-particle orientation correlations $\tau_1^{(s)}$(circles) and $\tau_2^{(s)}$(squares) and for collective orientation correlations $\tau_2^{(c)}$ (diamonds). The line serves as a guideline for the eyes.

for each density in order to ensure proper convergence. The single and collective correlation functions for rank $l = 1,2$ are written as

$$C_l(t) = \delta C_l(t) + \alpha \exp(-t/\tau_l), \tag{3}$$

where $\delta C_l(t)$ is a time-short-ranged function (i.e., it decays faster than $1/t^2$) and the exponential decay time τ_l is determined by fitting numerically the long-time behavior of $C_l(t)$. The density dependence of single and collective decay times thus obtained is plotted in Fig. 1 as $\ln(\tau_l)$ vs ρ^*. One sees immediately that between $\rho^*=0.2$ and $\rho^*=0.26$ the Debye relation $[\tau_1^{(s)}/\tau_2^{(s)} = 3]$ is well-obeyed; but this relation breaks down after $\rho^*=0.28$. In addition to this, we see that the collective relaxation time $\tau_2^{(c)}$ also becomes greater than both the single relaxation times, the cross over occurring at $\rho^*=0.27$, and the difference grows faster for higher densities. We find it more appropriate to look at the relaxation time τ_l defined by Eq. (3) rather than the integrated time, $\tau_l = \int_0^\infty dt \, C_l(t)$, which is often used in the literature. The main reason for our choice is that the time correlation functions are not exponential at all time especially in the intermediate density range, and they do have a clear exponential decay as defined by Eq. (3) at longer times.

In order to understand the long-time dynamics, it is instructive to look at the time relaxation kernel as defined by the relation

$$\frac{\partial}{\partial t} C_l(t) = \int_0^t d\tau \, M_l(t-\tau) C_l(\tau). \tag{4}$$

In a purely diffusive regime $M_l(t)$ would simply become $\tau_l^{-1}\delta(t)$. The kernel $M_l(z)$ can be easily extracted from the Laplace transform of the above relation. One needs to take special care of the long-time decay so that the small z dependence of the Laplace transform $M_l(z)$ can be accurately analyzed. This might give valuable information of the existence of the scaling laws, if any, of $C_l(t)$ in the large time limit. We have found here no special scaling law, in the
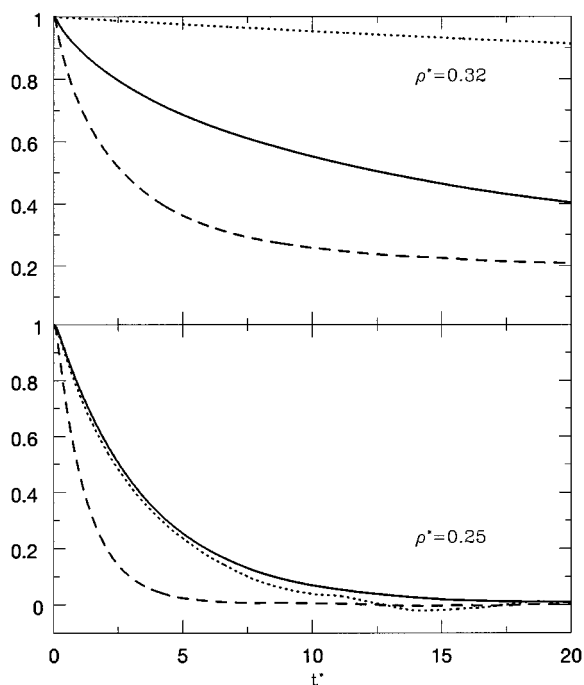
FIG. 2. Correlation functions $C_1^{(s)}(t)$ (solid line) and $C_2^{(s)}(t)$ (dashed line) for single-particle orientation, and $C_2^{(c)}(t)$ (dotted line) for collective orientations. Lower panel is for $\rho^*=0.25$ and upper panel for $\rho^*=0.32$.

FIG. 3. Memory kernels $M_l(z)$ associated with the orientation correlation functions. Symbols and conventions as in Fig. 2.

sense that in the limit $z \to 0$, $M_l(z) - M_l(0) \approx z^\gamma$, with $\gamma=1$ as from a Taylor expansion of $M_l(z)$. This is to be expected since we find that at long times $C_l^{(c)}(t)$ decay almost exponentially for all l values. The time-correlation functions are plotted in Fig. 2 for two densities, $\rho^*=0.25$ and $\rho^*=0.32$, chosen before and after the crossover as observed in Fig. 1. The corresponding memory functions are shown in Fig. 3. One sees clearly in Fig. 2 that at $\rho^*=0.32$ the orientational correlations decay much slower than for the case of $\rho^*=0.25$ and, in addition, that $C_2^{(c)}$ is dramatically slowed down. For the high density, the collective time correlations are found to decay exponentially at almost all times. As a consequence, one sees that the corresponding memory kernel $M_2^{(c)}(z)$ is just a constant, as might be expected from Eq. (3). However, it is clear that this Markovian behavior cannot be explained entirely in terms of Debye-type diffusion, since cooperative effects tend precisely to breakdown the Debye law at these densities. This non-Debye behavior is also apparent in the strong nonexponentiality observed at small times for the single particle correlations $C_1^{(s)}(t)$ and $C_2^{(s)}(t)$.

III. DISCUSSION AND CONCLUSION

Let us first summarize the main results of this Communication. We have performed MD simulations of orientational relaxation of a dense liquid of anisotropic molecules interacting via the Gay–Berne potential. Our aim was two-fold. First, we wanted to find the nature of orientational relaxation in dense anisotropic liquids. Second, we wanted to find the effects of the impending isotropic–nematic transition on the single particle and collective relaxations. It is found that the Debye model of rotational diffusion is not obeyed at
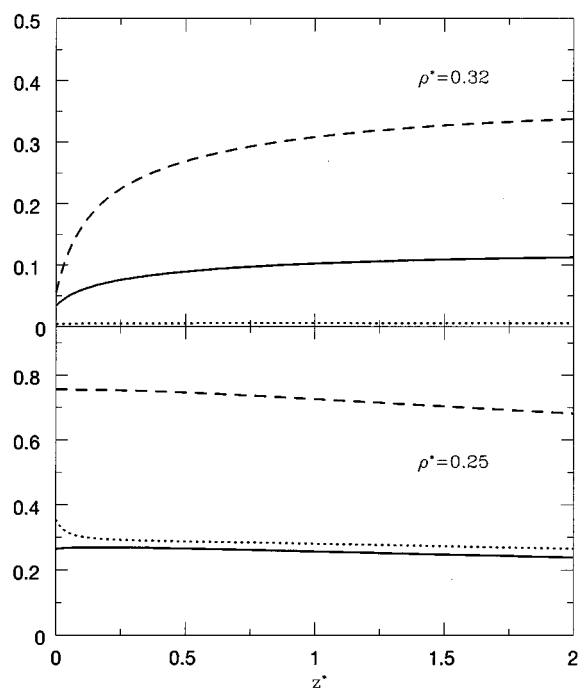
high densities, although the decay of the correlation functions are exponential. Another interesting result is that even the first-rank correlation function shows a significant slowing down as the I–N transition is approached.

The breakdown of the Debye mechanism can only be explained by the cooperative molecular motions due to the increase of orientational long-range order. This effect can be explained semiquantitatively by using a molecular hydrodynamic theory where the effects of interactions are included through a mean-field potential. However, the behavior of the first-rank correlation function is hard to explain by using such a simple theory. We are not aware of any theoretical discussion on this point.

It is the existence of long-range orientational order that give the I–N transition its weak first-order character. This is certainly linked to the appearance of small prenematic domains in the I–N region, whose growth leads to an increase of the relaxation time of the underlying dynamical processes. Such dynamics have been studied recently by Fayer et al.,[6,18] both experimentally through fast optical Kerr affect and theoretically through modified Landau–de Gennes-type approach. What is observed in thermotropic liquid crystals and in the I–N pretransition region, is a fast *universal* relaxation linked to intradomain orientational motion, and slower relaxation due to domain motion which is temperature dependant. The above-mentioned experiments might have probed dynamics beyond the linearized hydrodynamics regime and one perhaps requires a mode-coupling theory approach[19,20] to understand the experimental results of Fayer and co-workers. We are currently examining this problem.

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[a] Unité associée au C.N.R.S.

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