Velocity correlations of two-dimensional hard needles from molecular dynamics

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We present velocity correlations of a two-dimensional system of perfectly smooth hard needles from molecular dynamics. In a nematic phase the autocorrelation velocity function (ACF) clearly separates into two domains with, first, a very quick decay and, then, a long-lasting exponential-like decay that pertains to several characteristic times of the fast decay. The latter one is strongly subjected to the order of the system. We demonstrate that the existence of two time scales corresponds to different relaxations of the transverse and longitudinal components of the ACF.

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Serving as a natural reference system hard core spheres have proved in the 1970s to be very helpful in studying liquids [1]. This approach has been extended with great success to utilize anisotropic bodies as hard ellipsoids [2] or spherocylinders [3] in the analysis of the basic properties of liquid crystals. Whereas spheres seem to be especially suitable for all computer simulations, hard anisotropic particles are not very convenient for molecular dynamics applications, hence the Monte Carlo (MC) method dominates. Nevertheless, molecular dynamics (MD) is indispensable to calculate the dynamical properties. In the study of liquid crystalline phases the efforts are mostly concentrated on obtaining diffusional properties. At the same time the diffusional features are a derivative of the behavior of the velocity autocorrelation function (ACF). This fact has been well appreciated in isotropic fluids, where the ACF decay has been extensively investigated [4]. According to the Enskog theory the ACF decays at short times exponentially (the deviations from this theory observed in simulation are due to the vortex flow and caging) and at longer times Alder *et al.* [5] have shown that the velocity correlations have long tails according to $t^{-n/2}$ (n is the dimensionality of the system). For the constituents that are anisotropic the description has been extended to include the rotational variables and applied, at the beginning, to hard needles. For this system Frenkel *et al.* presented in [6] a very detailed study of the ACFs properties together with the discussion of the diffusional properties. The three-dimensional (3D) needles, however, form only an isotropic phase. Theory and simulations for another system, hard ellipsoids [7,8], have revealed that the deviations of the MD translational diffusion from the Enskog predictions are qualitatively similar for both hard spheres and hard ellipsoids, whereas the rotational diffusion constant seems to be in agreement with the Enskog theory as long as the phase is isotropic [8]. In all the above cases the short-time behavior of ACFs is well reproduced by the Enskog theory. Long tails are more problematic.

Although the ACF is certainly being calculated in most of the MD runs for nematics made from hard bodies and from particles interacting via continuous potentials such as the Gay-Berne potential we have, surprisingly, found no data that had been reported on the ACF itself. In this paper we present now the velocity autocorrelation functions for the simplest nematic that is formed by 2D needles. We show that the decay of ACF takes place on two time scales and that the main contribution to ACF comes from the ability to transfer the momentum along the particle principal axis. In spite of the fact that the influence of the system order on the diffusional properties has been realized long ago [9], to our knowledge, this paper is the first presentation that clearly demonstrates the influence of the long-range orientational order on the ACFs features themselves.

We consider hard needles confined to a plane. Their kinetic energy is prescribed and the global momentum is put to zero. When at distance, they do not interact. Any needle can move freely, translationally as well as rotationally, until it encounters another particle. Then a collision takes place. We assume that this happens always when the end of one needle touches another needle at any point. On contrary 3D collisions are always side to side [6]. Moreover, in the 3D case the excluded volume is zero, whereas in 2D it becomes proportional to $4L^2\sin(\theta)$ (where θ is the contact angle between two needles and L is the half-length of the needle). The fact that the excluded volume is not zero results immediately in the possibility to obtain an ordered phase. The character of the phase transition differs from 3D liquid crystals. For 2D hard needles all available evidence [10] points towards the occurrence of a continuous disclination-unbinding transition of the Kosterlitz-Thoulesstype. Moreover, according to the findings of Frenkel *et al.* [10], the ordered phase of 2D hard needles does not exhibit true long-range order but quasi-long-range order, in which the order parameter vanishes in the thermodynamic limit and all the order parameter correlations decay algebraically. The global order parameter depends on the size of the system (on the total number of the particles, N) as $S \sim N^{-kT/2\pi K}$ [10], where K is the 2D Frank constant. It is important to realize here a second notion of the order parameter which represents the local strength of the anisotropic mean field. This local order is the factual parameter that influences the collision frequency and the velocity correlations and should not be dependent on the system size. Although a few hundreds of particles seems to be a reasonable choice for calculating the local order parameter, more investigations are needed to establish the right size of the area over which this parameter has to be evaluated.

The system comprising 800 hard particles with the periodic boundary conditions applied has been equilibrated by means of the MD technique. The simulation box is taken of

unit length and the half-length of the particles L ranges from 0.035–0.05 with the reduced density $\rho^*=4\rho L^2$ corresponding to values from the interval 4.0–8.0. As a starting velocity configuration we have used a random distribution of the linear and angular velocities adjusted to the chosen temperature $kT=2$. The equilibration runs have usually the length of $N_{\max}=10^5$ (125 col/particle) collisions for the isotropic phase and 1.6×10^5 (200 col/particle) for the densities from the nematic regime $\rho^*=7.0,8.0$. During these runs the system has evolved towards the state that corresponds to the equipartition theorem. The obtained characteristics of the linear and the angular velocities have been fitted to the Maxwellian distributions. In these fittings the temperatures obtained for each degree of freedom agree with the equipartition theorem with an error of about 2%. The order parameter remains at a constant level but exhibits the fluctuations usual for hard needles. Next we performed the production runs of 2×10^4 collisions, from which we collect the data for the autocorrelations. This number of collisions is sufficient to allow the ACF to drop almost to zero in the isotropic regime, but not in the nematic. In our simulations we have not come across large numbers of chattering collisions except for few subsequent collisions [11].

Autocorrelation functions are the statistical quantities that determine how long and in what form a trace of the initial value of the quantity A is being remembered over the passing time. They can be calculated as

$$C_A(t)=\frac{1}{\langle A(0)^2\rangle}\frac{1}{N}\sum_{i=1}^{N}[A_i(0)A_i(t)]. \tag{1}$$

In this work we focus on the ACFs, where A is assumed to be the linear or angular velocity. Also, because the particles are anisotropic in shape we will use a natural decomposition of the translational velocity $\mathbf{v}$ into the component that is parallel and perpendicular to the orientation $\mathbf{a}$ of the molecule at a starting time [6]. To these velocities two autocorrelation functions are associated: the longitudinal and the transverse ACF,

$$C_{\parallel}(t)=\frac{1}{\langle \mathbf{v}(0)^2\rangle}\frac{1}{N}\sum_{i=1}^{N}[\mathbf{v}_i(0)\cdot\mathbf{a}_i(0)\mathbf{v}_i(t)\cdot\mathbf{a}_i(0)], \tag{2}$$

$$C_{\perp}(t)=\frac{1}{\langle \mathbf{v}(0)^2\rangle}\frac{1}{N}\sum_{i=1}^{N}[\mathbf{v}_i(0)\cdot\mathbf{P}_i\cdot\mathbf{v}_i(t)]. \tag{3}$$

In Eq. (3) $\mathbf{P}_i$ is the projection tensor: $\mathbf{P}_i\equiv\mathbf{I}-\mathbf{a}_i(0)\mathbf{a}_i(0)$. From Eqs. (2) and (3) it can be easily seen that $C_{\parallel}$ and $C_{\perp}$ are normalized in such a way that their sum gives C_v. For perfectly smooth Maxwellian velocity distributions both $C_{\parallel}$ and $C_{\perp}$ at $t=0$ should be equal to 0.5.

During a collision an impulsive force can only influence the longitudinal velocity $\mathbf{v}_{\parallel}$ of the particle whose end is active in the collision. For the other particle the gain (or loss) of momentum is always perpendicular to its own orientation. This feature is an effect of the needle geometry and of the assumption that the particles collide elastically. In an elastic collision only a part of momentum that is perpendicular to the surface at the point of contact can be exchanged. Velocities in the tangential plane remain unchanged so that one body slides freely on the surface of the other. As a result the influence on the change of $\mathbf{v}_{\parallel}$ depends on the mutual orientation of the colliding needles and is, simply, proportional to $\sin(\theta)$. It is a trivial conclusion then that if the needles are close to each other and the contact angle is small also the change of the longitudinal velocity is small. This observation entails the next conclusion that for dense systems the correlation functions $C_{\parallel}$ and C_v will depend strongly on the system organization. Indeed, looking at Fig. 1 one notices a significant change in the behavior of C_v in the isotropic and in the nematic phases. Whereas in the isotropic phase the function bears resemblance to a smooth exponentlike function, in the nematic phase one notices a clear separation into two regimes. At first, C_v quickly descends to the value around 0.4 and then decays slowly over a time interval 20 times larger (in the nematic phase) than the time of the fast decay. The connection of the two regimes reminds of a kink. Close examination reveals that this feature is present in both the nematic and the isotropic phases, i.e., the two-step character of the decay also pertains to the isotropic phase. A very similar effect of such a kink can be obtained just by adding two exponential decays with substantially different decay times. By fitting an exponent to the slow decay parts of C_v from Fig. 1 we can estimate the relaxation times for these curves as $\tau_{nem}\sim0.1$ in the nematic and $\tau_{is}\sim0.025$ in the isotropic phase. The presence of the orientational order has increased the relaxation time by a factor 4.

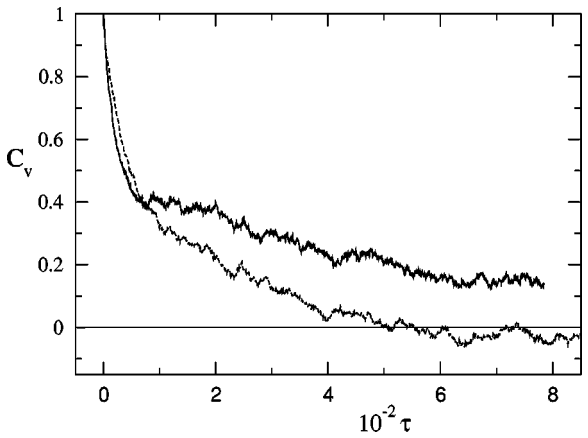

FIG. 1. Velocity autocorrelation $C_v(t)$: a dashed line is for the density $\rho^*=4.5$ (disordered state) and a solid line is for the density $\rho^*=8.0$ (nematic state).

Figure 2 shows an example of a general behavior of three ACFs, $C_{\parallel}, C_{\perp}$, and C_v for the density $\rho^*=8.0$ at which the system forms a nematic phase. There is a large difference between $C_{\parallel}$ and $C_{\perp}$. After the initial stage $C_{\perp}$ quickly drops to zero around the value 0.008 and stays at the null level experiencing strong fluctuations. At the same time the fluctuations are almost not present in $C_{\parallel}$. This is due to the fact that a change in the momentum of a colliding particle is prevailed by the component transverse to the needle. Since the longitudinal velocity change comes from a small fraction of the whole momentum exchanged, also its fluctuations are

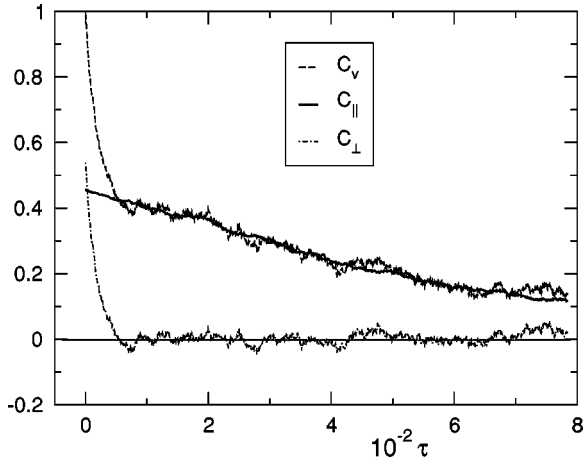

FIG. 2. Velocity autocorrelations in the nematic phase ($\rho^* = 8.0$)

small. Beyond the initial steep slope $C_\perp$ is always strongly fluctuating and $C_\parallel$ is always subjected only to tiny noise. The deviations of $C_\parallel$ and $C_\perp$ at $t=0$ from the value 0.5 are due to the velocity fluctuations present for a given starting configuration. Figure 2 allows one to distinguish two characteristic time scales for C_v: the first is given by the time after which $C_\perp$ relaxes to zero and the second is associated to the relaxation time of $C_\parallel$. The decay of $C_\parallel$ can be fitted well to a single exponent. This feature reminds of the behavior of $C_\perp$ of 3D system of infinitely thin disks [12]. More simulations have to be done to establish the true functional dependence. Both profiles, Figs. 1 and 2, are presented from single production runs.

Figure 3 shows the dependence of the order parameter S on the density in the regime where the nematic phase sets in. This figure reproduces qualitatively the Monte Carlo data from [10], although our results are slightly shifted down with respect to the density. True comparison between our MD data and MC data from [10] cannot, however, be performed since the thermodynamic parameters used in these two studies are not compatible. The behavior of $C_\parallel$ and $C_\perp$ for different

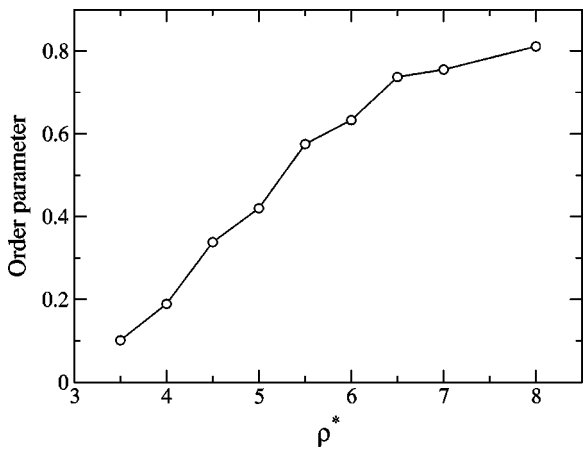

FIG. 3. Order parameter S for the simulations performed, averaged over several different states obtained during the equilibration runs.

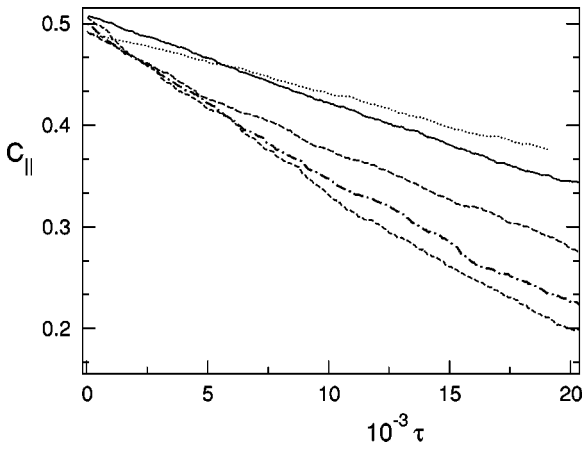

FIG. 4. Longitudinal velocity ACF $C_\parallel(t)$ as a function of time: dotted line $\rho^*=8$, solid line $\rho^*=7$, long-dashed line $\rho^*=6$, dash-dotted line $\rho^*=5$, short-dashed line $\rho^*=4$.

density parameters is presented in Figs. 4 and 5. According to these results $C_\parallel$ responds to the orientational order much stronger than $C_\perp$ and in somewhat opposite way. The values of $C_\parallel$ have a tendency to increase for more dense and more ordered systems whereas the values of $C_\perp$, quite differently, diminish, although very gently. Since in the isotropic phase the colliding molecules are not much restricted by the other particles $C_\parallel$ decays to zero on the time scale that is of the same order as for $C_\perp$. In Fig. 6 we present the angular velocity autocorrelation C_Ω. Very short ranges of this function can be fitted to one exponent, however, for the reasons given below, the overall behavior is by no means exponential. This is clearly seen for more dense systems. In the nematic phase C_Ω departs from an exponential behavior and even, after initial strong decay, gradually develops a negative part. This feature is reminiscent of the behavior of C_v in a hard sphere fluid [5] and has already been reported by Frenkel *et al.* [6] for $C_\perp$ and C_Ω of the 3D hard needles. Due to the argumentation of [6] such behavior is understandable if D_r scales as

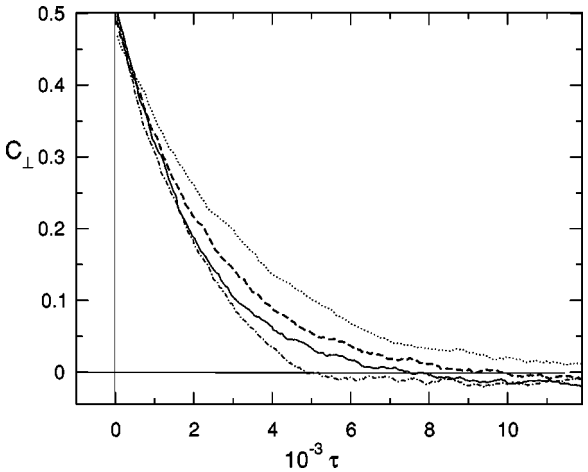

FIG. 5. Transverse velocity ACF $C_\perp(t)$ as a function of time: dash-dotted line $\rho^*=7$, solid line $\rho^*=6$, dashed line $\rho^*=5$, dotted line $\rho^*=4$.

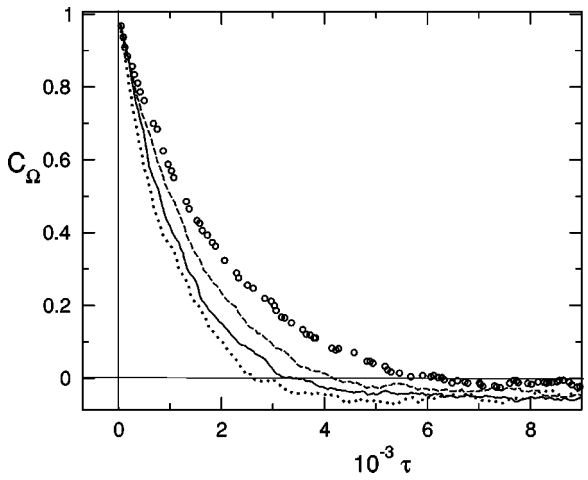

FIG. 6. Angular velocity ACF $C_\Omega(t)$ as a function of time: dotted line $\rho^*=7$, solid line $\rho^*=6$, dashed line $\rho^*=5$, circles $\rho^*=4$.

$$D_r \sim \frac{1}{\rho^{*2}}. \tag{4}$$

Assuming validity of the Enskog theory for the short-range decay, in which $C_\Omega(\tau)\sim\exp(-B\rho^*\tau)$, with B being the case specific constant, the contribution to D_r is scaled as $D_r \sim \int_0^\infty C_\Omega(\tau)d\tau \sim 1/\rho^*$. If Eq. (4) is to hold then C_Ω is expected to develop a negative portion whose integral over time will cancel a part of the Enskog theory contribution in such a way that the final result is proportional to $1/\rho^{*2}$. But for the isotropic and less ordered phases the negative part is not present. Since the scaling law (4) is supposed to hold in general, the above arguments may not be the only explanation or it is a part of a more general mechanism supporting Eq. (4). For a hard spheres gas, for instance, negative parts of the correlation function can be theoretically predicted within the ring approximation [4], an approach that takes into account recollisions. Here, in a so-called ring the tagged particle collides with a gas particle, undergoes a certain number of uncorrelated binary collisions, and at the end recollides with the original collision partner. For anisotropic particles recollisions are much more endemic, even up to chattering collisions with hundreds of events between only two bodies within very short time [11]. In general the dependence of C_Ω on density is similar as for $C_\perp$. The data presented in Figs. 4–6 are the results of averaging over ten equivalent configurations.

An interesting question is which factors determine the potential capability of hard particles of general shape to change their longitudinal velocity. It is obvious that not only is the shape anisotropy involved, but also the asphericity. An even more interesting question is how any plausible measure of the asphericity of the cores of the continuous potentials can be involved in the dynamical properties of realistic systems.

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