Dynamical precursor of nematic order in a dense fluid of hard ellipsoids of revolution.

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We investigate hard ellipsoids of revolution in a parameter regime where no long range nematic order is present but already finite size domains are formed which show orientational order. Domain formation leads to a substantial slowing down of a collective rotational mode which separates well from the usual microscopic frequency regime. A dynamic coupling of this particular mode into all other modes provides a general mechanism which explains an excess peak in spectra of molecular fluids. Using molecular dynamics simulation on up to 4096 particles and on solving the molecular mode coupling equation we investigate dynamic properties of the peak and prove its orientational origin.

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If the temperature of a simple liquid is decreased or its density increased local correlations tend to grow. This tendency can be experimentally detected as a growing peak of the static structure factor $S_q$ at a wave vector $q = q_{\text{max}} = 2\pi/\Delta r_{\text{av}}$, where $\Delta r_{\text{av}}$ is an average nearest neighbor distance. The growth of the static structure factor at $q_{\text{max}}$ causes the dynamics to slow down on local length scales, a phenomenon known in neutron scattering experiments as de Gennes narrowing. Hansen and Verlet observed in simulations, that a large class of simple liquids crystallize, if the peak of the static structure factor at $q_{\text{max}}$ becomes larger than 2.80. The growing peak may therefore be interpreted as a precursor phenomenon of the first order crystallization transition. But since the local dynamics is slowing down, it seems that the crystalline minimum of the free energy is not reached during the time scale of the experiment. The system becomes supercooled and begins to exhibit the rich dynamics of supercooled liquids.

Dense fluids of hard spheres are a good experimental example, where this physics can be studied in great detail.

A simple example of a molecular liquid with translational and rotational degrees of freedom is obtained by deforming the hard spheres towards hard ellipsoids of revolution. They can be characterized by the diameter of the minor axes $d$ and the aspect ratio $X_0$. This is the relation between the major and minor axes of the ellipsoid. In the following discussion $d$ is always set to $d = 1$, i.e. length will be given in units of $d$, and we will address only prolate systems with aspect ratios larger than one. However we expect qualitatively similar results for oblate systems, replacing $X_0$ by $1/X_0$. If the aspect ratios of the ellipsoids are very large, the theory of Onsager (originally for hard spherocylinders) is valid. This theory predicts a weakly first order phase transition from an isotropic fluid to a nematic liquid upon increasing the packing fraction $\varphi = X_0 \rho \pi / 6$, with $\rho$ being the number density. Such a transition can be found from computer simulations for aspect ratios down to $X_0 \approx 2$. The weakly first order phase transition also has a precursor in the static structure. The autocorrelation function $S_{SS}(q \to 0)$ of the collective fluctuations of the second spherical harmonics, measuring the quadrupolar order of the molecules is strongly increasing, when the transition is approached. This value of the correlation function is proportional to the optical Kerr constant and related to the correlation function of the nematic order parameter. Theoretically it is possible to supercool also the weakly first order phase transition of the nematic instability although to our knowledge it has not been observed yet. The increase of $S_{SS}(q \to 0)$ when increasing the packing fraction towards the isotropic to nematic transition leads, analogous to the de Gennes narrowing phenomena, to a slowing down of the corresponding dynamic orientational correlation function.

In extreme cases such a collective mode can drive a glass transition.

Our molecular dynamics (MD) simulation is placed in the regime where an increase of the peaks of the static structure factor, and a formation of nematic ordered domains, are both present. This has been achieved by simulating a system of $N$ nearly hard ellipsoids with an aspect ratio of $X_0 = 1.8$, where $N$ has been chosen to be 4096 and 512. Nearly hard ellipsoids are defined by a pair potential $v(1,2) = 4\epsilon(s^{-12} - s^{-6} + \frac{1}{2})$ for $s < 2^{1/6}$, $v(1,2) = 0$ otherwise. Here $s = ((r_{12} - 2) - (\sigma(1,2) + d)/d$ is a scaled and shifted separation where the ‘diameter’ $\sigma(1,2)$ is a standard approximation to the contact distance of ellipsoids 1 and 2 at given relative orientation, and $r_{12}$ is the center-center distance. The potential is purely repulsive and varies quite strongly over a short range of interparticle separation; it has been used, for higher elongations $X_0$, in the study of nematic liquid crystals. We choose an energy parameter $\epsilon = 1$, and molecular mass $M = 1$. In each case the system was equilibrated at a temperature $k_B T = 1$, and then constant-energy molecular dynamics were carried out using timesteps in the range $\delta t = 0.003 – 0.005$; typical run lengths were $10^6$ timesteps.

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From the simulation the molecular density–density correlation functions $S_{ll}^m(q, t)$ are obtained.

$$S_{ll}^m(q, t) = \frac{1}{N} \langle \rho_{lm}^*(q, t) \rho_{lm}(q, 0) \rangle$$

(1)

The indices $l, l', m$ are the indices of the spherical harmonics, the brackets \langle ... \rangle denote a statistical average and $\rho_{lm}(q, t) = \sqrt{4\pi l^l} \sum_{n=1}^{N} \exp \{iL_{ln}(t)\} Y_{lm}(\Omega_n(t))$ is the time dependent tensorial density fluctuation, where $\vec{x}_n(t)$ and $\Omega_n(t)$ are position and orientation of the molecule $n$, respectively. We also have chosen a specific coordinate system, the q-frame, where the z-axis points along the wave-vector $\vec{q}$. In this particular coordinate system all correlation functions depend on $l$ and $l'$ and only on a single helicity index $m$ and on the absolute value $q = |\vec{q}|$. The static structure factors are the equal time correlation function and reads

$$S_{ll}^m(q) = \lim_{t \to 0} S_{ll}^m(q, t)$$

(2)

For all theoretical considerations shown in this work we truncate the correlation functions at $l_{max} = m_{max} = 2$.

The MD simulation is first used to generate the static structure factors. In Fig. 1 for a packing fraction of $\varphi = 0.575$, below any transition the $S_{00}^0(q)$ correlator is plotted together with the $S_{22}^0(q)$ correlator. The dense liquid manifests itself in the low compressibility $\kappa = \kappa_0 \lim_{q \to 0} S_{00}^0(q)$. $\kappa_0$ is the compressibility of an ideal gas. Important there is the well pronounced peak at $q = q_{max} = 6.5$, discussed above. This peak is the static manifestation of the cage formed by the nearest neighbors which is about to trap the particles. At higher densities it drives a glass transition. In the $S_{22}^0(q)$ correlator shown in the same plot an additional peak occurs at $q = 0$. The reader should also note that the peak at $q = 0$, which is a precursor of nematic order is accompanied by a second peak at $q \sim q_{max}$ and a third peak at about the same position as the third peak in $S_{00}^0(q)$. The half width of the peak at $q = 0$ is approximately unity $\Delta q \approx 1$ and indicates the formation of orientationally ordered domains with a diameter of $D = 2\pi/\Delta q \approx 6$. Such a domain formation is still far away from a true nematic transition. Yet, the $S_{22}^0(q)$ correlator reaches already a value of $1.9$ at $q = 0$. The static structure factors are used as input for the equations of the molecular mode coupling theory for the dynamic structure factors of supercooled molecular liquids. Some details of this theory and an application to dipolar hard spheres can be found in 13. For the comparison with the simulation it is important to remember, that the mode coupling theory of supercooled liquids overestimates the slowing down of structural relaxations upon decreasing the temperature or increasing the density 19-24. To allow for comparison with the simulations we have to rescale the packing fractions for the MMCT such, that the time scale of structural relaxations of the MMCT corresponds to the time scale of the structural relaxation in simulations.

The static structure factors in dense liquids determine directly the microscopic frequencies measured in experiments of the respective dynamic structure factors. Neglecting the coupling to heat fluctuations in the liquid, the matrix of microscopic frequencies is given by

$$(\Omega(q)^2)^m_{ll'} = \left( q^2 \frac{k_B T}{M} + l(l+1) \frac{k_B T}{T} \right) \left( S^{-1}(q) \right)^m_{ll'}$$

(3)

where $I$ is the moment of inertia of the ellipsoid with respect to a rotation on one of the minor axes and $M$ the mass. For $l = l' = 0$ Eq. (3) describes the longitudinal (isothermal) phonon frequency with its linear dispersion for small $q$-values; $\Omega_{00}^2(q) = cq$ with the isothermal sound velocity of the liquid $c$. For $l, l' \neq 0$ and $q \to 0$ the static and dynamic structure factors become diagonal in $l, l'$ and independent of $m$ for short range interaction in general and the hard ellipsoids in particular. Therefore the microscopic frequencies in (3) reduce for $l, l' \neq 0$ and $q = 0$ to

$$\Omega(q)^2)^m_{ll'} = \left( l(l+1) \frac{k_B T}{T} \right) \frac{1}{\left( S(q = 0) \right)^m_{ll}} \delta_{ll'}$$

(4)

For the following it is important to note, that large values of the static structure factors lead to small microscopic frequencies and the corresponding slow modes have a strong intensity proportional to the corresponding static structure factor. This is the origin of the de Gennes narrowing phenomenon in the center of mass motion at wave vectors around $q = q_{max}$. The increase of the static structure factor $S_{22}^0(q = 0)$ shown in Fig. 1, will similarly yield, due to the relation $\Omega_{22}^2$, a slowing down of the corresponding optical $l = 2$ mode.

As soon as the structural relaxation becomes much slower than the microscopic motion, the microscopic frequencies become renormalized since the system is in a glassy state on the time scale of the microscopic motion. For molecular liquids also a splitting of the microscopic frequencies occur in addition to the renormalization due to rotation translation coupling 23. But the slowing down of the rotational mode due to the occurrence of locally ordered domains is preserved also under renormalization.
Nonlinear memory effects will couple all these modes. Therefore the described slow but intense modes will influence the spectra at different wave vectors and different rotation numbers \( l \) in the following way. The center of mass motion on a spatial scale of about \( \Delta r = 1/q_{\text{max}} \) will be the primary reason for a trapping of a particle in the cage of its nearest neighbor which leads to the bifurcation scenario described by MCT\(^2\). Indirectly, the precursor of nematic order seen in the static correlation function \( S_{22}^{0}(q) \) for \( q = 0 \) can support the tendency towards glass formation via the mentioned induced local spatial order, which is manifested as a peak in \( S_{2l}^{0}(q) \) at \( q \approx q_{\text{max}} \). The fact that there is a mode of strong oscillator strength and low frequency, \( S_{2l}^{0}(q \approx 0, t) \), can lead to a dynamic signature of this mode in other modes. It can be recognized by varying the inertia moment \( I \). If and only if an excitation in a density spectrum at some wave vector \( q \neq 0 \) is due to the rotational mode at \( q = 0 \), its position will shift according to Eq. (3) proportional to \( 1/\sqrt{I} \). The moment of inertia can be manipulated independently from the mass of the ellipsoids in the MD simulation and the numerical solution of the MMCT equations. Even extremely high values can be generated which can not be realized in a real systems.

In Fig. 3 the time dependent center of mass correlation function \( l, l' = 0 \) at \( q = q_{\text{max}} \) has been plotted. For the moment of inertia of an ellipsoid with homogeneous mass distribution \( I_{0} = (1 + X_{2}^{2})/20 \), we have fixed two densities \( \varphi_{\text{Sim}} = 0.66, \varphi_{\text{MMCT}} = 0.56 \) which lead to approximately the same time scale for the structural relaxation in the simulation and the numerical solution of the MMCT, respectively. Then, the moment of inertia was increased to 2.5, 10 and 25 times \( I_{0} \). The simulation and the theoretical calculation exhibit a shift to longer relaxation times, which are of the same order in both cases. In addition to a shoulder at longer times a plateau develops when the inertia moment is increased. This demonstrates clearly the considerable qualitative influence of the rotational motion on the center of mass motion. To study this effect and its dependence on wave vectors more quantitatively it is instructive to calculate the susceptibility spectrum \( \chi_{m}^{l, l'}(q, \omega) = \omega \phi_{m}^{l, l'}(q, \omega) \).

In Fig. 3 the susceptibility spectrum \( \chi_{00}^{m}(q, \omega) \) of the MMCT result and the simulation are shown for two different wave vectors. Note that there are no adjustable parameters. For both wave vectors the wave vector dependent position of the high frequency excitations agree very well. The splitting of the high frequency band, seen for \( q = 2.71 \) in the MMCT calculation and mentioned above is smeared out in the simulation. This may be understood as follows. Since we did not want to bias our calculation with a theory for the microscopic bare damping, we assumed a free oscillatory microscopic motion with frequencies given by (3). The effect of smaller damping can also be seen in the time dependent functions (see Fig. 3) as a tendency towards oscillation in the plateau regime of the MMCT results. By switching on a phenomenological microscopic constant damping term \( \nu_{m}^{l, l'} \) in the MMCT equations the split microscopic frequency can be forced to merge in one single excitation as in the simulation. In addition to the microscopic excitation an additional almost wave vector independent hump can be seen in the MD - and the MMCT result at about one decade below the microscopic frequency band, before the \( \alpha \) - relaxation peak starts to grow at smaller frequencies. This hump is due to the additional plateau in Fig. 3. But the positions of the peak do not agree very well quantitatively. The reason for this is not completely clear. The effect can partially be accounted for by the missing microscopic damping in the MMCT calculation, since the first minimum below the microscopic band in the simulation is already shifted to smaller frequencies because of damping. In addition, since the memory kernels in the MCT - equations, which generate the coupling between translational and rotational modes and therefore the hump, are approximate, only, we can in general not expect a quantitative agreement of both positions.

The variation of the peak position of the low lying excitation in the MMCT - result with changing the moment of inertia can be seen in Fig. 4. The susceptibility spectra \( \chi_{l, l'}^{m}(q_{\text{max}}, \omega) \) at the wave vector \( q_{\text{max}} = 6.5 \approx \) exhibit the anomaly between the structural relaxation peak and the microscopic excitations for all allowed combinations of \( l, l', m \), either as an additional peak or an additional shoulder. Especially in the \( l = l' = 2 \) susceptibility spectra a well pronounced peak can be identified, which shifts to lower frequencies for increasing moment of inertia \( I \) and is therefore influenced by the orientational motion. The \( l = l' = 0 \) spectrum demonstrates that this orientation anomaly is hybridized with the lowest of the split high frequency excitations for \( I = I_{0} \) and turns into a well defined shoulder for larger inertia moments. These features are present in the spectrum of the MMCT calculations and the MD - simulations for all susceptibilities \( \chi_{l, l'}^{m} \) with \( (ll'm) = (000), (200), (220), (221) \) and \( (222) \). We show some of them in Fig. 4. Since the MMCT calculations can be extended to longer times compared to the simulations, the quality of the spectra are better for the MMCT. But is is still possible to identify in Fig. 4 for all moments of inertia the position of the anomaly. To get better statistics, we average the value of the position \( \omega_{\text{pp}} \) over five spectra \( (ll'm) = (000), (200), (220), (221) \) and \( (222) \) and plot the results against \( 1/\sqrt{I} \) in Fig. 5. A well defined linear law through the origin is found. This proves our assertion that the orientational anomaly in the \( q = q_{\text{max}} \) spectra is due to the \( q = 0 \) anomaly in \( S_{22}^{0}(q = 0) \) as explained above.

The \( \chi_{22}^{l, l'}(q, \omega) \) susceptibility of the simulation shows an additional excitation compared to \( m = 0 \) or \( m = 2 \), which is not present in the version of MMCT used in this paper. This excitation is strongly wave vector dependent (see Fig. 5) and turns into a shoulder for the three smallest wave vectors. It therefore does not have the same origin as the orientation anomaly, which is almost wave vector independent. A possible explanation could be a coupling to
transverse phonon modes. Such a coupling to transverse phonon modes is expected from a more general version of
the MMCT. Unfortunately the allowed wave vector range of the simulation seems to be too small to test for the
linear dispersion $\omega_T = c_T q$. In conclusion we find for the spectra $\chi^{(0)}(q, \omega)$ and $\chi^{(2)}(q, \omega)$ a reasonably good agreement between the MMCT for
hard ellipsoids and simulations of this system. We can identify a dynamic anomaly which appears about one decade
below the microscopic excitations. This anomaly is due to the medium range nematic order which can be identified
by the $q = 0$ value of the static structure factor $S^{zz}(q = 0)$. In an analogous anomaly for dipolar hard spheres
due to medium range ferroelectric order could be identified. There it was argued that the anomaly behaves very much
like the well known Bose-peak phenomenon. Similar arguments can be applied to the anomaly caused by the medium
ranged nematic order, found here for hard ellipsoids.

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FIG. 1: For an aspect ratio of $X_0 = 1.8$, from a MD simulation of 4096 hard ellipsoids of revolution the $S_{00}(q)$ component (solid line) and the $S_{22}(q)$ (dashed line) components of the static structure are shown. The packing fraction was $\varphi = 0.575$ and is right at the glass transition from MMCT.

FIG. 2: For four different values of the moment of inertia $I_0$ (solid lines), $2.5 \times I_0$ (dotted lines), $10 \times I_0$ (dashed lines), $25 \times I_0$ (long dashed lines) the time dependent relaxation of $\phi^{0}_{00}(q = q_{\text{max}}, t) = S_{00}(q = q_{\text{max}}, t)/S_{00}(q = q_{\text{max}}, t = 0)$ has been plotted. The upper curves are shifted by 0.1 vertically and result from a numerical solution of the MMCT equations at $\varphi = 0.56$ and the lower curves are the result of a MD simulation with 4096 particles at $\varphi = 0.66$. 

FIG. 3: The susceptibility spectrum $\chi''(q,\omega)$ from simulation at packing fraction $\varphi = 0.66$ (solid line) and MMCT at packing fraction $\varphi = 0.56$ (dashed line) for two different wave vectors a) $q_1 \simeq 6.5$ and b) $q_2 \simeq 2.71$.

FIG. 4: Susceptibility spectra $\chi''(q_{\text{max}},\omega)$ at the wave vector $q_{\text{max}} \simeq 6.5$ from the solution of the MMCT at a packing fraction $\varphi = 0.56$. The plots for four values of the moment of inertia $I_0$ (solid lines), $2.5 \times I_0$ (dotted lines), $10 \times I_0$ (dashed lines), $25 \times I_0$ (long dashed lines) are shown.
FIG. 5: Susceptibility spectra $\chi''_{\text{mm}}(q_{\text{max}}, \omega)$ at the Debye wave vector $q_{\text{max}} \approx 6.5$ from the MD simulation at a packing fraction $\varphi = 0.67$. The plots for four values of the moment of inertia $I_0$ (solid lines), $2.5 \times I_0$ (dotted lines), $10 \times I_0$ (dashed lines), $25 \times I_0$ (long dashed lines) are shown.

FIG. 6: The average position of the anomaly in the five spectra $\chi''_{\text{mm}}(q, \omega)$ is plotted against $1/\sqrt{T}$. Shown are a) the results for the MMCT and b) the results for the simulation.
FIG. 7: Susceptibility spectra $\chi''_{22}(q, \omega)$ and $\chi''_{22}(q, \omega)$ from the simulation at small wave vectors $0.4 \leq q \leq 1.33$ and at $q = q_{\text{max}}$ and $\varphi = 0.69$. 