Mode coupling theory for molecular liquids: What can we learn from a system of hard ellipsoids?

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Molecular fluids show rich and complicated dynamics close to the glass transition. Some of these observations are related to the fact that translational and orientational degrees of freedom couple in nontrivial ways. A model system which can serve as a paradigm to understand these couplings is a system of hard ellipsoids of revolution. To test this we compare at the ideal glass transition the static molecular correlators of a linear A-B Lennard–Jones molecule obtained from a molecular dynamics simulation with a selected fluid of hard ellipsoids for which the static correlators have been obtained using Percus–Yevick theory. We also demonstrate that the critical non-ergodicity parameters obtained from molecular mode coupling theory for both systems show a remarkable similarity at the glass transition, provided the aspect ratio is chosen properly. Therefore we conclude that a system of hard ellipsoids can indeed be used to understand part of the essential behaviour of such a simple molecular system like the A-B Lennard-Jones molecules in the vicinity of the ideal glass transition.

I. INTRODUCTION

When a fluid is driven towards a glass transition either by quenching down the temperature (super-cooling) or by increasing the density a critical slowing down of the dynamics occurs without a diverging length scale in the system. However there are only a few systems where the full dynamics of the glass transition is understood in detail and where it is possible to make predictions for the critical density and temperature for the ideal glass transition from a microscopic theory. Systems where such a transition is well understood are colloidal suspensions. Their liquid state is well described by a hard sphere system and the static structure factor calculated by Percus–Yevick approximation has been used as an input for the mode coupling theory (MCT) to calculate the dynamics near the ideal glass transition. Within idealized MCT this transition takes place at a critical temperature $T_c$ or a critical density $\rho_c$ at which a breaking of ergodicity occurs. For a simple glass former like a colloidal system the mode coupling equations describe the dynamics in great detail, explain why the transition is dominated by the cage effect and their solutions are in good agreement with experimental data.

Most glass formers do not have such a simple structure like hard spheres. A real glass former is usually a molecular system and shows a wide variety of additional structure in the dynamics (multiple microscopic peaks, fast and slow $\beta$ peaks, $\alpha, \alpha'$ peaks) where a detailed understanding is lacking so far. A large part of this additional structure is caused by the coupling of translational and orientational degrees of freedom. There are different possibilities to get a deeper insight into such couplings. The first possibility to study the relaxation in the super-cooled regime is to model a specific glass former as accurately as possible using model potentials, and then to perform computer simulations. This has been done, e.g. for water, for silicate glass or for a linear A-B molecule.

A second possibility to get insight into the statics as well as in the dynamics of a glass former is to study model systems which are as simple as possible but keep the essential mechanism – in our case the interplay between translational and rotational degrees of freedom. Such a model system which can be used is a system of hard ellipsoids of revolution.

The aim of this paper is to answer the question how far a system of hard ellipsoids can help to understand basic mechanisms present in molecular glass formers. We therefore compare in detail the static structure of the translational and orientational degrees of freedom obtained from a molecular dynamics simulation for an A-B-Lennard Jones molecule with results for hard ellipsoids of revolution. Using the static correlators as an input into the mode coupling equations we also compare the results for the critical non-ergodicity parameters with each other.

II. MODE-COUPLING EQUATIONS

As a first step towards finally calculating the full dynamics we want to test for both systems the occurrence of ergodicity breaking. Therefore the MCT– equations are solved in the limit $t \rightarrow \infty$ The non-ergodicity parameters are given by $(F(q,m))_W = \lim_{t \rightarrow \infty} S_W(q,m,t)$ where $S_W(q,m,t)$ is the time dependent tensorial density correlation function. The indices $l,l'$ and $m$ refer to expansion coefficients of a product of spherical harmonics $Y_l^m(\Omega)$ and $Y_{l'}^{m'}(\Omega')$. Since we have used the q-frame representation for the correlators, i.e. $q$ has been chosen along the z–axis, the correlators are...
diagonal in $m$ and $m'$ and are real. The reader should also note that the existence of a rotational axis of symmetry of the species of both systems allows to use the spherical harmonics, only. Using the results from ref. [8] and [10,11] one finds the molecular MCT–equations for these parameters:

$$ F(q, m) = \left[ S^{-1}(q, m) + S^{-1}(q, m) \mathcal{K}(q, m; \{ F(q, m) \}) \right]^{-1} S^{-1}(q, m) $$

where the matrix elements of the functional $\mathcal{K}(q, m; \{ F(q, m) \})$ are given by:

$$ \mathcal{K}(q, m; \{ F(q, m) \}) = \sum_{\alpha=T, R} \sum_{\alpha'=T, R} q_{\alpha}^q(q) \left( \left[ m(q, m; \{ F(q, m) \}) \right]^{-1} \right)^{\alpha\alpha'}_{\alpha'\alpha} q_{\alpha'}^q(q) $$

with the MCT–polynomial:

$$ (m(q, m; \{ F(q, m) \}))^{\alpha\alpha'}_{\alpha'\alpha} = m_{\alpha}^{\alpha'}(q, m; \{ F(q, m) \}) $$

$$ = \frac{1}{2N} \sum_{q_{1}q_{2}} \sum_{l_{1}l_{2}} V_{l_{1}l_{2}}^{\alpha\alpha'}(q, m, l_{1}; m_{2}) $$

$$ = F_{l_{1}l_{2}}(q_{1}, m_{1})F_{l_{2}l_{2}}(q_{2}, m_{2}) $$

and

$$ q_{\alpha}^q(q) = \begin{cases} \frac{q}{\sqrt{(l+1)}} & \alpha = T \\ \frac{q}{\sqrt{l(l+1)}} & \alpha = R \end{cases} $$

The explicit expressions for the vertices $V^{\alpha\alpha'}$ for arbitrary $q$ can be found in ref. [8] and for the $q$-frame in ref. [10,11]. The vertices $V^{\alpha\alpha'}$ only depend on the static correlators $S_{l_{1}l_{2}}(q, m)$ and the direct correlation functions $c_{l_{1}l_{2}}(q, m)$ which are related to each other by the Ornstein–Zernike equation:

$$ S(q, m) = \left[ 1 - \frac{\rho}{4\pi} c(q, m) \right]^{-1} $$

where $\rho$ is the number density.

III. COMPARISON

For two particular systems the above equations have been solved. The first one is the diatomic linear A-B molecule of ref. [8] were the static correlators had been obtained by a molecular dynamics simulation. The parameters of the Lennard-Jones potentials had been chosen such that the diameter of atom A and B were equal to 1 and 0.95 (in Lennard-Jones units), respectively. Such an asymmetry is mainly needed to prevent crystallization. The distance between the two centers of the atoms was 0.5.

The second system is a fluid of prolate hard ellipsoids of revolution. Here the aspect ratio $X_0 = \frac{a}{b}$ which is the ratio between the major axis $a$ and the minor axis $b$ of the ellipsoids has to be chosen. If one wants to model the Lennard–Jones molecule by a hard ellipsoid the choice of the Lennard–Jones radii implies that $X_0 = 1.5$. Note that $X_0$ is not a fitting parameter. We also stress that the A–B molecules do not have a head–tail symmetry, in contrast to the ellipsoids. The value for $X_0$ is in a parameter range where no ordering due to a nematic phase is expected [12,13]. The static correlators are obtained using Percus–Yevick (PY) theory. Using PY theory automatically prevents crystallization since it is unable to yield a periodically ordered solution. PY, however, is in principle suited to study an orientational transition like an instability due to a nematic phase [13].

FIG. 1. Static structure factor for the A-B Lennard-Jones molecule (solid lines) at the glass transition $T_g = 0.475$ obtained from ref. [8]. The components of the static structure factor for the hard ellipsoid of revolution with an aspect ratio of $X_0 = 1.5$ and with, at the glass transition, a packing fraction of $\phi = 0.575$ are plotted with dashed lines. From up to down the $l=l'=0$, $m=0$, the $l'=m=0, l=2$ and the $l=l'=2, m=0$ components are shown.

In fig. [8] we have plotted with solid lines the three static correlators with $l = l' = 0; l = 0, l' = 2$ and $l = l' = 2$ for the Lennard–Jones system right at the
ideal glass transition \( T_c = 0.475 \) in L-J units and a density of \( \rho_c = 0.752 \). The first one \( (l = l' = 0) \) is the center of mass component. The second component with \( l = 0 \) and \( l' = 2 \) couples the two correlators for \( l = l' = 0 \) and \( l = l' = 2 \), whereas the third one, the "quadrupolar" correlator gives information on the orientational order of the system. In fig. 1 we have further plotted with dashed lines the same components for the system of hard ellipsoids at the critical density (packing fraction \( \phi_c = 0.575 \) or density \( \rho_c = \frac{\phi_c}{\pi X_0^2} = 0.732 \)) of the glass transition. Note the remarkable similarity with the exception of the \( q \rightarrow 0 \) behaviour where the simulation result has some shortcomings.

These static correlators were used to solve the equations \( (1)-(3) \) which are truncated at \( l_{\text{max}} = 2 \). As already mentioned above, the A–B molecules do not possess head–tail symmetry. Therefore the static correlators with \( l \) and/or \( l' \) odd do not vanish, in contrast to those for the ellipsoids. Accordingly these correlators were also taken into account when solving the MCT–equations for the A–B molecules. The resulting critical non-ergodicity parameters \( F_l' (q, m) \) are plotted in fig. 2 for the A-B LJ molecule with solid lines for the ellipsoids with dashed lines. It is clearly visible that the dominating contribution for the ergodicity breaking results from the first maximum \( (at \ q \approx 6.5 \frac{2 \pi}{a}) \) of the structure factor of the center of mass component \( (l = l' = 0) \). This is the manifestation of the cage effect.

**IV. CONCLUSION**

In conclusion, we have demonstrated that a system of hard ellipsoids of revolution is able to describe the static structure and the critical non-ergodicity parameters (for \( l \) and \( l' \) even) of a system of super-cooled diatomic molecules rather well, provided the aspect ratio is chosen properly. This result is not so obvious, since the static input into the MCT–equations for the diatomic molecules also includes the correlators with \( l \) and/or \( l' \) odd. Those correlators either equal one or zero in case of the head–tail symmetric ellipsoids. For atoms with aspect ratios \( X_0 \approx 1.5 \) the cage effect determines the glass transition. This relation however will change close to a nematic instability. On one particular example we have shown that the detailed relation between orientational and center of mass components and the detailed shape and even the exact symmetry of the two–particle potential seems only to have minor influence on the ergodicity breaking. Of course, it would be interesting to investigate how far more complex molecular systems can be modeled by hard ellipsoids. The full phase diagram for the glass transition of hard ellipsoids will be presented elsewhere [14].

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