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Localization and glass formation of fluids confined in porous matrices

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1. Introduction

Recently, the dynamics of colloids in porous media has been subject to a number of works. The slow dynamics is of particular interest, since the single-particle ("self") and the collective dynamics are influenced by the intricate interplay between confinement and connectivity of the surrounding medium. Recently, Krakoviack [1–3] combined mode-coupling theory (MCT) [4] with the replica Ornstein-Zernike (ROZ) formalism [5]. The resulting theory describes the glass formation process of a quenched-annealed (QA) mixture, i.e. of systems in which mobile fluid particles move in a matrix of immobile particles quenched from an equilibrium fluid. Based on the static structure factors of the system, the theory predicts the time dependence of the self and the (connected) collective intermediate scattering functions $F_s(k,t)$ and $F_c(k,t)$. The kinetic diagram of a simple hard sphere (HS) fluid in a HS matrix, evaluated using this new theory, contains a number of interesting features [1–3]: (i) two kinds of glass transitions, namely a transition of type B (abrupt occurrence of a long-time plateau) at low matrix packing fractions (φ_m) and a transition of type A (continuous rise of a long-time plateau) at large φ_m (ii) also for large φ_m a re-entrancy in the glass transition and (iii) a diffusion-localization transition restricted to the self dynamics (see thin lines in Fig. 1). MCT predicted similar complex features for other systems, which subsequently were found to exist (e.g. [6]).

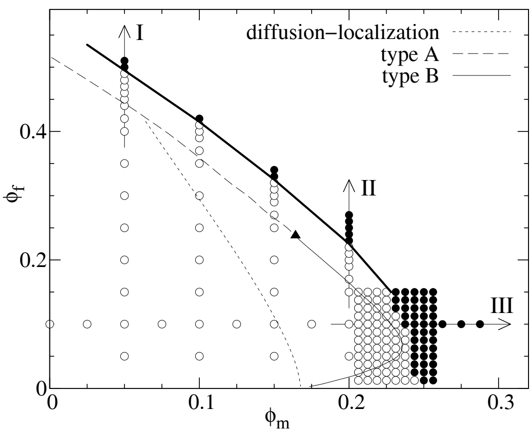

Fig. 1: Kinetic diagram of the HS QA system. White circles: equilibrated. Black circles: glassy. Thin lines: MCT transition lines [3]. Thick line: arrest line from simulations, defined via $\delta r^2(t)$.

2. Methods and Results

We put these theoretical predictions to a direct test using event-driven molecular dynamics [7]. We studied the system used by Krakoviack, i.e. a HS QA system in three dimensions, with the fluid and matrix particles having equal diameters and being monodisperse. For each state point, the mean squared displacement $\delta r^2(t)$ as well as $F_s(k,t)$ and $F_c(k,t)$ were monitored and averaged over multiple system realizations; the latter averaging is compulsory in the QA protocol to restore isotropy and homogeneity. Based on $\delta r^2(t)$, state points were classified either as equilibrated or as glassy (shown in Fig. 1). The so-defined arrest line resembles the ideal MCT glass line, with the notable exception that no re-entrant region is observed.

Detailed investigations on $F_c(k,t)$ and $F_s(k,t)$ along the paths labeled I and II in Fig. 1 revealed that this apparent discrepancy can be understood as a crossover from a glass transition to a diffusion-localization transition in the self dynamics: For path I we observe a type-B-like transition on the same time-scale for $F_c(k,t)$ and $F_s(k,t)$, which we find to be described semi-quantitatively by MCT [1]. For path II, however, $F_c(k,t)$ decays to zero in a type-A-like single-step transition, whereas $F_s(k,t)$ decays much slower than $F_c(k,t)$ in a two-step relaxation with a long-time plateau continuously rising from zero. We attribute the latter behavior to a type-A transition simultaneously occurring with diffusion-localization; this decoupling of $F_c(k,t)$ and $F_s(k,t)$ at high φ_m is indeed described by MCT [3].

To investigate the degree of universality of the predicted features, we solved the equations of the ROZ+MCT formalism for related purely-repulsive QA systems using the numerical procedure outlined in [2] and [3]. Specifically, we considered hard spheres with size ratio λ between the fluid and the matrix component (related e.g. to the system in [8]) and equal soft spheres interacting with inverse power law potentials of degree n. The topology of the kinetic diagrams of these systems was found to be very similar to the one shown in Fig. 1. In the HS systems the glass line shifts systematically to lower φ_m upon decreasing λ; in the soft-sphere systems the glass line shifts to larger φ_f upon decreasing n, and clearly a re-entrancy appears in the diffusion-localization line.

3. Conclusions

We showed that the self and collective dynamics in a QA model of a fluid in porous confinement exhibit a non-trivial and interdependent behavior. The slow dynamic features of this kind of systems, including the superposition of glass transitions and diffusion-localization transitions, are described in an idealized but coherent way by the mode-coupling theory put forward by Krakoviack [1–3]. We found that the theory predicts these non-trivial features also for other QA systems, and we therefore expect them be observed in suitable experimental setups.

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