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Diffusion-Localization and Liquid-Glass Transitions of a Colloidal Fluid in Porous Confinement

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1. Introduction

The properties of fluids adsorbed in porous media are of great interest for both technological applications and fundamental science. The effect of the confining matrix on the behaviour of the adsorbed fluid has been studied intensively during the last years both theoretically and in experiments [1]. It was only very recently, however, that a reliable theoretical framework, based on Mode Coupling Theory (MCT), was developed to study the dynamics of fluids in porous confinement [2]. Thus it is now possible to make quantitative predictions about the dynamical properties of simple model systems [2] and possibly more complicated interactions and matrix configurations.

The growing interest in soft matter in general and in colloidal systems in particular, motivates the study of the properties of colloidal fluids brought in contact with a soft porous matrix. The study of soft matter in confinement also has two more major advantages: First, the large size of the particles in colloidal suspensions allows direct imaging of the system through video and confocal microscopy, including tracking trajectories of particles [3]. Moreover, optical tweezers allow to fix particles at arbitrary positions, thus providing means to realize suitable matrix configurations. Second, theoretical modelling of complex macromolecular systems through effective potentials is meanwhile rather well established [4]. Hence, colloidal fluids in porous confinement offer an exciting opportunity to make direct contact between theory and experiments.

2. Model and Methods

In this contribution we study within the framework of MCT the glass transition of a simple model of colloidal fluid (Gaussian Core model) in a porous matrix. The matrix configurations are quenched from an equilibrium fluid composed of the same type of particles. The interaction between all particles (both fluid and matrix components) is described by the Gaussian potential [5]

$$u(r) = \varepsilon \exp(-(\sigma / r)^2)$$

where ε and σ provide the natural units of energy and distance of the model. We obtain the structural properties of the system by solving the Replica Ornstein-Zernike equations using the hypernetted chain closure relation. The reliability of the so obtained connected and blocked structure factors $S_c\ (k)$ and $S_b(k)$ has been checked against Monte Carlo simulations [6]. The latter structure factors, discretized on a grid of 200 points, are then used as input for MCT calculations.

3. Kinetic Diagram

The kinetic diagram of our system is shown in Fig. 1 for the same range of matrix-densities, ρ_m, and and fluid-densities, ρ_f, as investigated in Ref. 6. The “collective” glass transition lines (indicated by continuous lines) are obtained from the MCT solution for the infinite time limit $f_c(k)$ of the connected intermediate scattering function. Using the approach of Ref. 2 it is also possible to study the dynamics of tagged particles, described by the “self” part of the intermediate scattering function. The corresponding diffusion-localization lines are indicated in Fig. 1 as dashed lines.

Similar to the case of the confined hard-sphere system of Ref. 2, our model shows intriguing features, such as decoupling between collective and self dynamics and the appearance of continuous type A transitions. The shape of the transition lines is, however, peculiar. Only at lower T and very diluted conditions one recovers the shape of the kinetic diagram found for hard-spheres. As in the equilibrated system and in contrast with systems dominated by harsh repulsions, our model remains fluid at high fluid densities, giving rise to a distinct re-entrant behaviour.

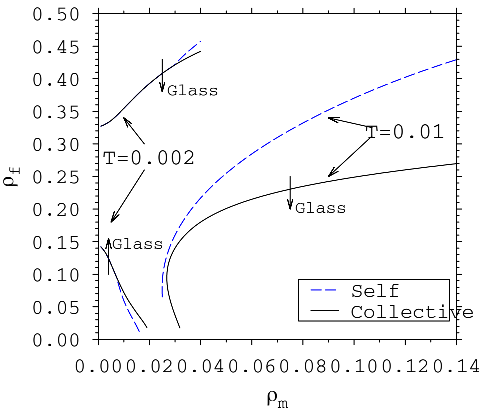

Fig. 1: MCT glass transition lines for the Gaussian Core model in confinement

4. Conclusion

The dynamics of soft matter in confinement, as studied through a recently developed MCT framework, combines general features found for models with harsh repulsions [2] (type A transitions, decoupling between diffusion and collective dynamics) and features of the corresponding equilibrium fluids (re-entrant behaviour). Extensive simulations for model colloidal fluids and experimental realizations of quenched-annealed colloidal systems are requested to test this fascinating scenario.

References

[1] L.D. Gelb et al., Rep. Prog. Phys. 62 (1999) 1573.
[2] V. Krakoviack, Phys. Rev. E 75 (2007) 031503; V.Krakoviack, arXiv:0901.3649
[3] E.R. Weeks and D.A. Weitz, Phys. Rev. Lett. 89 (2002) 095704.
[4] C.N. Likos, Phys. Rep. 348 (2001) 267.
[5] F.H. Stillinger, J. Chem. Phys. 65, (1976) 3968.
[6] D.F. Schwanzer, D. Coslovich, J. Kurzidim, G. Kahl, Mol. Phys. In press