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Kinetic glass transition in a charge–polydisperse colloidal fluid

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ABSTRACT: The time dependence of the density autocorrelation function in a model of a charge-stabilized charge-polydisperse colloidal suspension is calculated by using Brownian Dynamics simulations. Particular attention is paid to the different behaviour of high and low charge particles in the charge-polydisperse fluid near the kinetic glass transition. It is shown that the ratio of the corresponding diffusion constants varies considerably in the vicinity of the glass transition. The results are briefly discussed in the light of recent experiments in dense colloidal fluids.

I. INTRODUCTION

Charge-stabilized or sterically-stabilized colloidal particles in a liquid solvent can exhibit both crystalline and amorphous solid phases [1,2]. Recently, extensive dynamical light scattering experiments on colloidal suspensions [3] have revealed that the colloidal fluid undergoes a glass transition, signalled by a non-decaying density autocorrelation function over experimentally accessible time intervals ("structural arrest").

In this paper, we report results from a Brownian Dynamics simulation of the glass transition in a colloidal system. In particular, we calculate the long time behaviour of the density autocorrelation function evolving from the Brownian-motion-like short time dynamics. Within a time step Δt that is small compared to the typical time scale of the colloidal particles, the displacement of the colloidal particle j is given by [4]

$$\vec{r}_j(t+\Delta t) - \vec{r}_j(t) = \frac{1}{\xi}\vec{F}_j(t)\Delta t + (\Delta\vec{r})_R + O((\Delta t)^2) \qquad (1).$$

Here, ξ is the solvent friction, taken to be independent of particle configuration, thus neglecting hydrodynamic interactions. The direct force $\vec{F}_j$ stems from the colloid-colloid-interaction

$$\vec{F}_j = -\vec{\nabla}_j \sum_{i \neq j} V_{ij}(\mid \vec{r}_i - \vec{r}_j \mid) \qquad (2)$$

where V_{ij} is the interparticle potential. Furthermore, the random displacement $(\Delta\vec{r})_R$ is sampled from a Gaussian distribution of zero mean and variance $< (\Delta\vec{r})_R^2 >= 6k_BT\Delta t/\xi$, T being the temperature. The basic equation for Brownian Dynamics (BD) should be contrasted with usual Molecular Dynamics (MD), where the short time expansion is

$$\vec{r}_j(t+\Delta t) - \vec{r}_j(t) = \vec{v}_j(t)\Delta t + \frac{1}{2m}\vec{F}_j(t)(\Delta t)^2 + O((\Delta t)^3) \qquad (3)$$

m being the particle mass and $\vec{v}_j$ the velocity. Note that the velocities enter as independent statistical variables in the MD-case in contrast to the BD-case. Eq.(3) corresponds to atomic dynamics instead of irreversible colloidal dynamics. Nevertheless it is useful to compare the time dependence of the correlation function generated by (1) and (3). Indeed, this comparison was extensively made in a recent work by Roux and the authors [5]. Similarities and differences between Newtonian and Brownian Dynamics were found near the glass transition. The latter occurs at nearly the same temperature and, in both cases, the structural arrest is finally destroyed by thermal activated hopping processes, even in the BD-case where any phonon-assistance is missing. On the other hand, there is no clear separation of time scales in the decay of the density autocorrelation function in the BD-case and no evidence of β-relaxation. α-relaxation does occur but with a Kohlrausch-exponent significantly larger than in the MD-case. Thus the difference in the *short* time dynamics (1) versus (3) has an important influence on the *long* time dynamics and one should be cautious in interpreting glass transition data from colloidal systems within the framework of models and theories which are valid only for reversible MD.

In this article, we use the same model as in [5], but here we focus on the effect of *polydispersity* of a colloidal suspension on the dynamics near the kinetic glass transition. Polydispersity is an intrinsic and inevitable feature in any real colloidal suspension. For a charge-stabilized system, polydispersity in charge masks any polydispersity in size [6], so we only consider this kind of polydispersity. We find that the dynamics of low charge and high charge particles is different, especially near the glass transition.

II. THE MODEL

In order to model a charge-stabilized colloidal fluid, the interparticle potential in (2) is taken to be a natural generalization of the DLVO-type screened Coulomb-potential [7] to a charge-polydisperse situation [6]

$$V_{ij}(r) = U_0 \frac{a}{r} \frac{Z_i Z_j}{\bar{Z}^2} \exp(-\kappa \frac{r-a}{a}) \qquad (4).$$

Here U_0 and a set the natural energy and length scale of the colloidal particles. Together with ξ they define a natural time scale $\tau_B = \xi a^2/U_0$ and all quantities are from now on measured in these units. The corresponding reduced quantities are labelled by a star $*$. The decay parameter κ is chosen to be fixed ($\kappa \equiv 7$) for our simulation and the charges Z_i were sampled from a Schultz-distribution $P(Z)$. For $N = 500$ particles (we use this number throughout our study), the discrete charge distribution is illustrated in Fig.1, for a mean valence charge $\bar{Z}$ and a charge-polydispersity

$$p_Z = \frac{1}{\bar{Z}}\sqrt{\int_0^\infty P(Z)(Z-\bar{Z})^2 dZ} \equiv 0.5 \qquad (5).$$

The particles are grouped according to their charge and we have examined several regions separately. As indicated in Fig. 1, region (1) consists of particles labelled by numbers 1 – 150 which have low charges, whereas the 150 most highly charged particles, labelled by the numbers 350 – 500, belong to region (2).

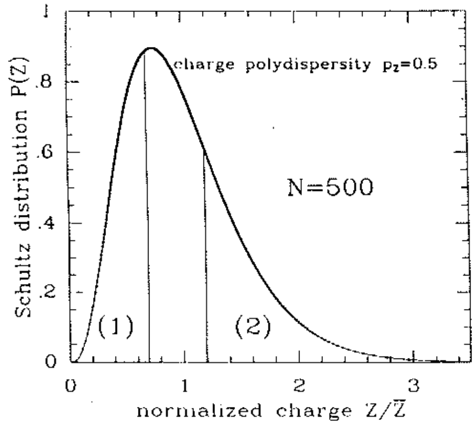

Fig. 1 *Schultz distribution of charges versus $Z/\overline{Z}$. The two different regions (1) and (2) of low charge and high charge particles are also indicated.*

We remark that, using the Gibbs-Bogoliubov inequality, the structural properties of a charge polydisperse fluid can be mapped onto those of a hard-sphere reference fluid [6]. For our parameters and a temperature $T^* \equiv k_B T/U_0 = 0.14$ the size-polydispersity of the equivalent hard-sphere system is $p_\sigma = 0.13$. In such a strongly polydisperse system, formation of an amorphous solid is favoured [8]. Correspondingly we did not find any crystallization during our simulations.

The finite time step Δt was chosen to be $0.003\tau_B$. Starting from the temperature $T^* = 0.45$, the system was cooled down to $T^* = 0.10$. The cooling rate was rather gentle and long equilibration runs were performed. Productions runs last about 2×10^5 time steps. Using several dynamical diagnostics, as described in Ref. [5], the kinetic glass transition temperature T_G^* was estimated to be $0.115 < T_G^* < 0.12$.

III. RESULTS

The static quantities, like $g(r)$, $S(k)$ etc. do not depend on the kind of dynamics (BD or MD) and were extensively studied in Refs. [5,6]. As regards dynamic features, let us first focus on the diffusion constants. In Table I, the diffusion constants for the lowly and highly charged particles of regions (1) and (2) (see Fig.1) are given for different temperatures. Far away from T_G^*, plots of $ln(D_1^*)$, $ln(D_2^*)$ versus $ln(T^* - T_G^*)$ are reasonably linear thus suggesting a power law behaviour

$$D_i^* = A_i(T^* - T_G^*)^{\gamma_i}, i = 1,2 \qquad (6).$$

We found $\gamma_1 = \gamma_2 \simeq 1.4$, the same exponent as for the total diffusion constant D^* [5] if T is not too close to T_G. However, as the glass transition is approached, the deviations from (6) become significant and D_1^* and D_2^* behave differently. This is shown in Table I by the ratio D_1^*/D_2^* which is nearly constant well above T_G^* and increases considerably near T_G^*. Therefore the low charge particles are much more mobile in the glass than the highly charged ones.

T^*	$D^* \times 10^3$	$D_1^* \times 10^3$	$D_2^* \times 10^3$	D_1^*/D_2^*
0.22	17	22	12	1.8
0.19	12	16	9	1.8
0.175	8.0	10	5.6	1.8
0.16	4.5	6.2	3.1	2.0
0.14	2.3	3.1	1.5	2.1
0.13	1.2	1.8	0.8	2.4
0.12	0.6	0.9	0.3	2.8
0.115	0.3	0.4	0.1	3.4
0.10	0.1	0.17	0.05	3.5

Table I: *Reduced diffusion constants D^*, D_1^*, D_2^* for different reduced temperatures T^*. The corresponding ratio D_1^*/D_2^* is also given.*

A similar difference in the dynamical behaviour of low and high charge particles becomes apparent in the self parts of the corresponding van Hove correlation functions given by

$$G_S^{(1)}(r,t) = \frac{1}{150} < \sum_{j=1}^{150} \delta(\vec{r} - \vec{r}_j(0) + \vec{r}_j(t)) > \qquad (7)$$

$$G_S^{(2)}(r,t) = \frac{1}{150} < \sum_{j=351}^{500} \delta(\vec{r} - \vec{r}_j(0) + \vec{r}_j(t)) > \qquad (8).$$

These functions are illustrated in Fig.2 for two temperatures a) above and b) below the glass transition. For $T > T_G$, the $G_S^{(i)}(r,t)$ tend rapidly to their hydrodynamic long time limit [9] governed by the diffusion constants D_1,

D_2, see Fig. 2a, whereas for $T \lesssim T_G$ the structure becomes frozen (Fig. 2b). Again, the low charge particles are less frozen and there is evidence for hopping processes over a typical interparticle spacing a since a shoulder is clearly visible at $r = a$ in $G_S^{(1)}(r,t)$ for large t. This hopping is much less frequent for the high charge particles. The same conclusion can be drawn from direct observation of particle trajectories.

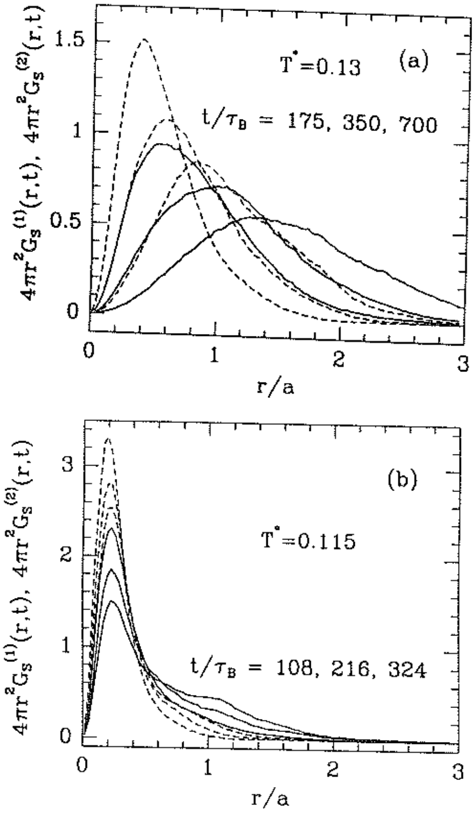

Fig. 2: *Self part of the van Hove functions for the low and high charge particles,* $G_S^{(1)}(r,t)$ *(solid lines),* $G_S^{(2)}(r,t)$ *(dashed lines), multiplied by* $4\pi r^2 a$ *versus reduced distance* r/a *for different times* t. *(a) Above the glass transition* $T^* = 0.13$. *(b) Below the glass transition* $T^* = 0.115$.

In summary, our strongly polydisperse system exhibits a behaviour intermediate between simultaneous structural arrest for both particle species at the same temperature and an ideal superionic conductor where the large (highly charged) particles are frozen and the small (lowly charged) ones remain completely mobile. The first case of simultaneous freezing was found, for instance, in MD-simulations of a binary alloy with a particle size ratio not too far from

1 [9]. On the other hand, a superionic-conductor-behaviour was investigated in the framework of mode coupling theory applied to strongly asymmetric two component mixtures [10].

Finally, in Fig.3, we show the normalized density autocorrelation function $F(k_0,t)/S(k_0)$ versus t for k_0 near the first peak in the static structure factor $S(k)$. This quantity is directly accessible in dynamic light scattering experiments. Comparing our data with the experimental results of [3] for a sterically-stabilized colloidal system, one finds qualitative agreement of the temperature dependence of the curves.

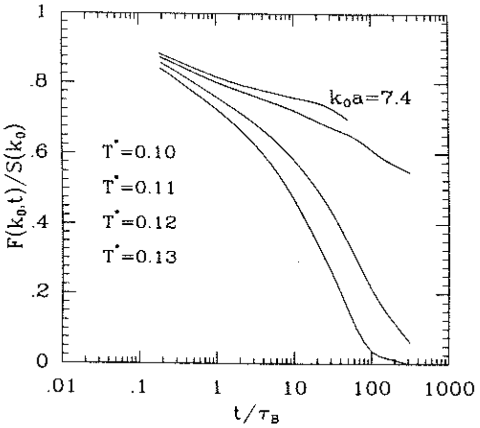

Fig. 3: *Coherent part of the normalized density autocorrelation function* $F(k_0,t)/S(k_0)$ *(for* k_0 *near the first peak of the static structure factor* $S(k)$*) versus time* t *on a logarithmic scale for 4 different temperatures* $T^* = 0.13, 0.12, 0.11, 0.10$. *The lowest curve corresponds to* $T^* = 0.13$.

At this point, two remarks are in order: Firstly, the kinetic glass transition, as detected by a different dynamic behaviour in $G_S(r,t)$ which provides a rather clearcut estimation of T_G (see again Figs. 2a,2b), is not associated directly with a plateau in $F_S(k,t)$. In MD, these two features coincide. There is no clearly visible separation of time scales in Fig.3 nor evidence of β-relaxation. This discussion is quite similar to that of $F_S(k_0,t)$ in [5]. Secondly, we remark that the absolute duration of the correlation functions shown in Fig.3 is longer by a factor of about 3 than the experimental data of Ref.[3], so that a more complete picture of the decay transient emerges.

IV. OUTLOOK

In the present work, the irreversible dynamics in a colloidal fluid was modelled in a rather simple way. Of course the true colloidal dynamics is more complicated. However the BD approach represents a more realistic description than reversible MD (3) where any solvent effect is completely neglected. The first improvement of our simple BD algorithm (1) would be to include solvent mediated hydrodynamic interactions by introducing a $3N \times 3N$ friction matrix depending on the positions of the colloidal particles, see e.g. [11]. An even more complicated algorithm based on Stokesian dynamics was proposed by Brady and Bossis [12]. In a concentrated charge-stabilized colloidal suspension, one can also question the pairpotential assumption (2). It may be relevant to treat the counterion cloud as a dynamical variable which leads to many-body effects. Our future work lies in this direction.

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