Liquid-Glass Transition Phase Boundary for Monodisperse Charge-Stabilized Colloids in the Presence of an Electrolyte

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(Received 17 August 1998)

The idealized version of the mode-coupling theory which focuses on the nonequilibrium structural aspects of colloidal particles in glass formation is applied to determine the liquid-glass transition boundary for a suspension of monodisperse polystyrene charged spheres as a function of electrolyte concentration. Guided by previous studies of the liquid-fcc-bcc freezing transition, we employ the same macro-ion charge as that used in the latter and predict the colloidal liquid-glass transition loci in remarkably good agreement with measurements. [S0031-9007(99)09045-6]

There has been much interest in recent years in understanding the phase transition for colloidal dispersions. Such an increased interest arises partly from the impetus of experiments and partly from the successful formulation of microscopic theories [1,2] constructed from the areas of statistical mechanics, kinetic and hydrodynamic theories of liquids, and many-body theory. There are two general classes of colloidal suspensions for which improved experimental techniques have made significant impact. In one category, the colloidal particles are experimentally prepared to mimic a collection of neutral hard spheres suspending in a solvent in a sterically stabilized phase. A well-known example is the poly-(methyl methacrylate) (PMMA) particle core stabilized by a thin layer coating (≈ 10 nm) of poly-(12-hydroxystearic acid), and these colloidal particles are dispersed in a good solvent such as the decalin and tetralin [3]. Another category is electrostatically stabilized colloidal particles dispersed in an aqueous solution. These macroparticles are manifested by their surfaces distributing with headgroups which are capable of dissociating counterions in the dispersive medium to become strongly charged colloidal particles. Prototype examples are the aqueous solutions of spherical polymer colloids such as the latex particles made of polystyrene [4,5], PMMA [6], 1-1-dihydroperfluorobutylacrylate [7], etc. In both categories, measured phase diagrams for the liquid-crystal and liquid-glass transitions have been reported [4,5,8,9]. In this connection, it is of great theoretical interest to mention the celebrated density functional theory [10–12] which was applied to calculate the liquid-fcc-bcc freezing transition loci by matching the free energies of the equilibrium liquid and crystalline phases; the agreement between theory and experiments is reasonably good. In contrast, virtually no theoretical work on the colloidal liquid-glass transition phase diagrams is reported despite the fact that such experimental data have appeared for many years [4,5,9].

A first-principles determination of the colloidal liquid-glass transition phase diagram is a formidable task since, unlike crystalline solids, the glassy free energy is *a priori* unknown. Accordingly, a calculation of the liquid-glass transition boundary will have to be tackled somewhat differently. In this Letter, we report a microscopic theory which approaches this problem by delving into the nonequilibrium structural aspects of particles in glass formation. The physical significance of the theory leading to solidification can be visualized as follows. Let us imagine a tagged particle interacting with a certain number of its surrounding neighbors. At normal liquid density, the geometrical relation of any such cluster of particles can be physically dictated by the pair correlation function $g(r)$ or conceptually realized by the idea of a "potential mean force" [13]. This picture of a tagged particle coupled simultaneously with the local structure of particles (represented through the microscopic density) enters the density-density correlation function $F(r,t) = \langle \delta n(\mathbf{0},0) \delta n(\mathbf{r},t) \rangle$, where the $\langle \cdots \rangle$ is the usual ensemble average, and the $\delta n(\mathbf{0},0)$ and $\delta n(\mathbf{r},t)$ are the microscopic density fluctuations at the positions and times of the tagged particle and surrounding particles, respectively. Because of the rapid motion of the surrounding particles which behave in this case like a time-dependent potential barrier having a relatively short lifetime, the diffusive motion of the original particle is at any moment unaffected. The above-mentioned $g(r)$, though delineating the geometric feature absent for dilute gases, does not, however, really diminish the mobility of the tagged particle for the caged particles follow tacitly its motion. Pictorially, it is as if, in the course of diffusive motion, the tagged particle and the surrounding particles simply move together in a concerted unit. Accordingly, at the liquid density, we have $F(r,0) = \delta(r) + \rho_0 g(r)$, where ρ_0 is the equilibrium number density, and $F(r, t \to \infty) = 0$. As we approach the glass transition point at an increased density, the viscosity of the liquid increases dramatically, implying that the surrounding medium shows a slow structural relaxation. As a result, the tagged particle is trapped within a time-retarded cage. To diffuse away,

the tagged particle will have to push its way through via disturbing the surrounding medium. However, due to the sluggish motion of the latter, some of the disturbances propagate over larger distances and will act on the tagged particle at a later time. This kind of collective couplings constitutes a feedback effect. If the feedback effect lasts for a long time (occurring at a high enough density), a collective nonlinear coupling between the $\delta n(\mathbf{0}, 0)$ and the $\delta n(\mathbf{r}, t)$ will lead to a very slowly decaying component of $F(r, t \to \infty) \neq 0$. It is the simultaneous operation of the cage-diffusive and Feynman backflow effects that gives rise to the vitrification. The idealized mode-coupling theory (MCT), which will be elaborated further for a charged colloidal dispersion, incorporates these two effects and attributes them as the cause for glass transition. It thus appears that a MCT, to locate the liquid-glass transition boundary, needs the colloidal static structure factor $S(q)$ as an essential input.

A suspension of monodisperse charge-stabilized colloids consists of macro-ions, counterions, and co-ions, and these particles are dispersed in a dielectric continuum medium ϵ. In view of the large disparity in size of the macro-ions and small ions (counterions and electrolytes), it is a common practice in colloidal study to describe the multicomponent nature of a colloidal system by effectively one component macroparticles. Depending on the physical conditions, there are two generally used options. The first option confines the description to a system of weakly charged macro-ions which implies a weak correlation between the latter and small ions. For such a system, it can be shown that the interparticle interaction is described very well by the Derjaguin-Landau-Verwey-Overbeek (DLVO) [14,15] potential

$$\beta\phi_{00}(r) = \infty, \qquad r < \sigma_0,$$
$$\beta\phi_{00} = \frac{L_B(Z_0\Lambda_{\mathrm{DLVO}})^2 e^{-\kappa r}}{r}, \qquad r > \sigma_0, \tag{1}$$

where $\beta = 1/k_B T$ is the inverse temperature; $L_B = e^2\beta/4\pi\epsilon\epsilon_0$ is the Bjerrum length; $\kappa = (4\pi L_B \sum_{i=1} \rho_i Z_i^2)^{1/2}$ is the Debye-Hückel screening parameter in which ρ_i and Z_i are, respectively, the number density and charge for small ions (hereafter subscript 0 is reserved for macroparticles, 1 for counterions, and 2, 3, . . . for salts); $\Lambda_{\mathrm{DLVO}} = \exp(\varkappa/2)/(1 + \varkappa/2)$, where $\varkappa = \kappa\sigma_0$, σ_0 being the diameter of a spherical macro-ion; and Z_0 is the nominal macro-ion charge. Note that Eq. (1) is appropriate for the description of a dilute colloidal solution ($\rho_0 \to 0$).

The second option is a generalization of Eq. (1) to a finite ρ_0 and thus is more appropriate for general studies. It was shown in the literature [16,17] that, for pointlike small ions, such a model can be expressed analytically by an effective *direct correlation function:*

$$c_{00}^{\mathrm{eff}}(r) = -\frac{L_B(Z_0\Lambda)^2 e^{-\kappa r}}{r} \qquad r > \sigma_0. \tag{2}$$

Here, $\Lambda = \cosh(\varkappa/2) + U[(\varkappa/2)\cosh(\varkappa/2) - \sinh(\varkappa/2)]$, $U = (8\delta/\varkappa^3 - 2\nu/\varkappa)$ in which $\delta = 3\eta/(1 - \eta)$, $\nu =$

$(\Delta_\sigma/2 + \delta)/(1 + \Delta_\sigma/2 + \delta)$, and

$$\Delta_\sigma^2 = \varkappa^2 + 24\eta L_B(Z_0^2/\sigma_0)/(1 + \Delta_\sigma/2 + \delta)^2. \tag{3}$$

Given Z_0, σ_0, $\varkappa$, and $\eta = \pi\sigma_0^3\rho_0/6$, Eq. (3) has to be solved iteratively for Δ_σ and, hence, Λ. It is interesting to note that if one identifies $c_{00}^{\mathrm{eff}}(r) = -\beta\phi_{00}^{\mathrm{eff}}(r)$ and imposes the hard core condition $\phi_0^{\mathrm{eff}}(r) = \infty$ for $r < \sigma_0$, Eq. (2) is similar *in form* to the mean spherical approximation (MSA) closure, and the analytical solution [18] for $S(q)$ can thus be utilized. Since $\Lambda \to \Lambda_{\mathrm{DLVO}}$ in the limit of $\rho_0 \to 0$, the resulting $S(q)$ is appropriate for studying the structure of a colloidal dispersion at *any* finite concentration.

We turn next to a description of the MCT for a suspension of charge-stabilized colloids. Let us return to the $F(q, t)$ introduced above. Neglecting hydrodynamic interactions [19] and denoting the Laplace transform of a quantity $\Theta(q, t)$ by $\hat{\Theta}(q, z) = \int_0^\infty \exp(-zt)\Theta(q, t)\,dt$, one can show [20,21] that $\hat{F}(q, z)$ is related to the memory function $\hat{M}(q, z)$ by [22]

$$\hat{R}(q, z) \equiv \frac{\hat{F}(q, z)}{S(q)} = \frac{1}{z + q^2 D_0/S(q) - \hat{M}(q, z)/S(q)}, \tag{4}$$

where D_0 is the Stokes-Einstein diffusion coefficient of a single particle. Spatially $F(q, t)$ contains useful information on the local structure of macroparticles, and temporally it describes a short-time decaying behavior ($\tau_I \gg t \gg \tau_B$, where for typical aqueous colloidal dispersions $\tau_I \approx 10^{-3}$ s and $\tau_B \approx 10^{-8}$–10^{-9} s) representing a typical Brownian motion and a long-time slowly decaying dynamics ($t \gg \tau_I$) characterizing the kind of Feynman feedback effects where macroparticles manifest collective nonlinear couplings. All of these characteristics are buried in the memory function $\hat{M}(q, z)$. However, as pointed out by Cichocki and Hess [23], the $\hat{M}(q, z)$ in Eq. (4) is not an elementary quantity in the study of the dynamics of colloidal particles since its time evolution operator is not one-particle irreducible. To show this, Cichocki and Hess [23] compared the generalized dynamic viscosity within the context of a generalized Smoluchowski equation and of a Fokker Planck equation. Their analysis led them to an explicit formula between an irreducible memory function $\hat{\mathcal{M}}(q, z)$ and the $\hat{M}(q, z)$. In general, $\hat{\mathcal{M}}(q, z) = \Gamma_0(q, z) + \Gamma(q, z)$ in which Γ_0 is meant for all contributions yielding the short-time behavior, and $\Gamma(q, z)$ is the mode-coupling contribution including fully the slow structural motions. At high enough densities, the long-time part contributes dominantly and thus permits an approximation $\hat{\mathcal{M}}(q, t) \approx \Gamma(q, t)$. It can be inferred from the works of Szamel and Löwen [21], Baur *et al.* [20], and others [24,25] that an idealized liquid-glass transition exists and its dynamical transition point is determined by the following nonlinear vitrification equation:

$$\frac{f(q)}{1 - f(q)} = \frac{S(q)}{D_0 q^2} \Gamma(q, t = \infty) = \mathcal{F}_q[f(k)]. \tag{5}$$

Here, $f_c(q) = R(q, t \to \infty) \neq 0$ is the glassy Debye-Waller factor corresponding to the nonergodic state, whereas $f(q) = 0$ is the ergodic state. We note that $f(q)$ is a realistic function since it corresponds to the form factor for the elastic part of the coherent spectrum

in neutron scattering experiments and is thus observable. Dynamically, this function also accounts for the nondiffusive states as the liquid phase approaches the glassy region. By making a two-mode approximation [20,21,24–26], the $\Gamma(q, t)$ above can be derived to read

$$\Gamma(q, t) = \frac{\rho_0 D_0}{8q\pi^2} \int_0^\infty dx\, x \int_{|x-q|}^{|x+q|} dy\, y \left(\frac{x^2 - y^2}{2q} [c(x) - c(y)] + \frac{q}{2} [c(x) + c(y)] \right)^2 S(x)S(y)R(x, t)R(y, t), \quad (6)$$

where $\rho_0 c(q) = 1 - 1/S(q)$ is the direct correlation function. Given $S(q)$, Eqs. (5) and (6) constitute two nonlinear coupled equations which we will solve iteratively for the loci of the liquid-glass transition (for technical details, consult [27] for cases of atomic liquids).

It is clear that in order to study the liquid-glass transition phase diagram within the idealized MCT, one needs first to calculate $S(q)$. Here, we employ the effective one component model of Belloni [16], whose $S(q)$ can be computed from Eqs. (2) and (3) if the nominal charge Z_0 [28] of the macro-ion is known. In the absence of a reliable datum from experiment [29], we have thus fixed it by consultation of the papers of Salgi and Rajagopalan [11] and Choudhury and Ghosh [12] who both have calculated the liquid-crystal phase diagrams of Sirota et al. [4] using the density functional theory. It can be inferred from their literature that $Z_0 \approx 350e$ interprets very well the phase boundary for the liquid-crystal transition. Based on their results, we have set $Z_0 = 350e$ for the bare charge of a macro-ion. With the Z_0 fixed, $\sigma_0 = 91$ nm and $\varkappa$ calculated in terms of charges and number densities of counterions and electrolyte, we vary η to obtain different $S(q)$s by the analytical formula of Hayter and Penfold [18]. We should emphasize that in this paper the inherent deficiency of MSA which gives a negative $g(r)$ for the case of strongly coupled macro-ions near their contact distance will be handled by the rescaling method [17,30] [see, in particular, Fig. 1 in [17] for an assessment of $S(q)$]. To locate the liquid-glass transition loci, it then remains to solve iteratively Eqs. (5) and (6) and search η_c for the solution $f_c(q) \neq 0$ at each electrolyte concentration C_{HCl}. We give in Fig. 1 the loci of the liquid-glass transition phase diagram compared with those of measurements [4]. We stress two noticeable features.

First, our salt-free result yields a transition $\eta_c = 0.175$ which is slightly less than the lowest glassy state $\eta_c = 0.2$ observed by Sirota et al. [4]. We believe that the magnitude of this η_c is reasonable since, for η immediately below, we see mixed crystalline phases of the fcc and bcc types followed by an equilibrium liquid phase ($\eta < 0.06$). Second, as the C_{HCl} concentration increases, our theoretical η_c increases monotonously, whereas experimentally η_c increases from $\eta_c = 0.2$ to values that fluctuate in the range $0.25 \lesssim \eta_c \lesssim 0.3$. Since

the glassy and fcc crystalline phases coexist around $\eta_c \approx 0.25$ for the major region $200 \leq C_{HCl} \leq 500$ μM in the phase diagram, the liquid-glass transition loci predicted here by the MCT is physically sound if one considers further the η_c results from the viewpoint that the theory has suppressed in the formulation the occurrence of any crystallization process [17,25].

It is remarkable that both the liquid-glass and the liquid-crystal transition loci were favorably reproduced using the same macro-ion charge $Z_0 = 350e$, although the underlying microscopic theories are rather different. It should be emphasized that our colloidal $S(q)$s were calculated for pointlike small ions. This, however, does not incur a large error in the liquid-glass transition boundary, for in the electrolyte concentration $0 \leq C_{HCl} \leq 700$ μM the screening length lies in the range $182 > \varkappa^{-1} > 70$ Å whose values are much larger than the size of small ions (typically 5–10 Å). To illustrate this point, we have followed the qualitative method of finite size treatment proposed by Belloni [16] and repeated a calculation for the case $C_{HCl} = 300$ μM in which the finite size of small ions is arbitrarily taken to be 5 Å. The predicted
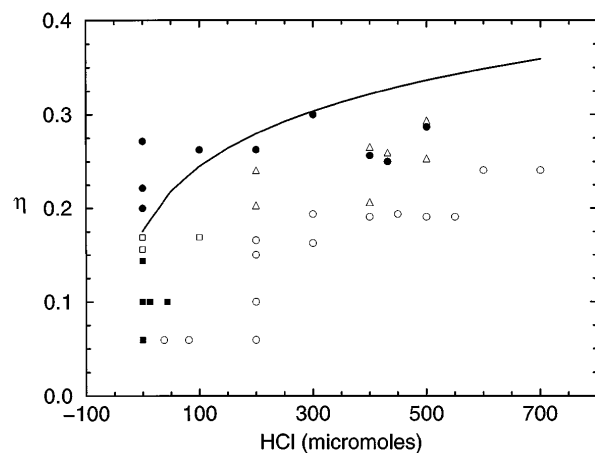

FIG. 1. Phase diagram for a suspension of monodisperse polystyrene charged spheres of size $\sigma_0 = 91$ nm immersed in methanol-water medium at room temperature calculated using the idealized MCT compared with data taken from small-angle, synchrotron x-ray scattering experiments [4]. Notations used are the following: solid squares, bcc crystal; open triangles, fcc crystal; open squares, fcc + bcc coexistence; closed circles, glass; open circles, liquid; full line, theory.

$\eta_c = 0.29957$ differs negligibly from the $\eta_c = 0.30365$ given in Fig. 1.

In conclusion, we have drawn attention to a microscopic theory which is useful for determining the liquid-glass phase diagram. Given a reliable means to evaluate the colloidal $S(q)$, the present method is a realistic approach to the study of the latter property. The method can be generalized straightforwardly to a multicomponent system, and used to investigate the charged colloidal liquid-glass transition phase diagrams of a more complex nature. For instance, the bidisperse charged polystyrene spheres at various number concentrations and for different size ratios were already reported experimentally in the literature [5,9]. To my knowledge, these data have not yet be explained theoretically.

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