Liquid-glass transition phase diagram for concentrated charge-stabilized colloids

S. K. Lai and W. J. Ma

Department of Physics, National Central University, Chung-li 320, Taiwan, Republic of China

W. van Megen and I. K. Snook

Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne, Victoria 3001, Australia

(Received 27 August 1996)

We model interactions between charged colloidal particles by the screened Coulomb potential, and employ the analytically solved static structure factor in conjunction with the idealized mode-coupling theory to determine the liquid-glass transition phase boundary. We find that the presence of an ionic screening has the consequence of revealing a subtle competition between the hard-core geometric factor and the charge-induced screening effect, resulting, for the strong screening case, in an extended charge-stabilized suspension and, for the weak screening case, in a more restrictive ergodic domain. [S1063-651X(97)09807-3]

The occurrence, in metastable liquid well above the calorimetric glass transition point, of a dynamical transition μ_c (which is the temperature for quenching or density for supercompressing), from ergodic to nonergodic behavior, has been the subject of considerable experimental and theoretical interest since it was first predicted by mode-coupling theory (MCT) [1]. The idealized version of MCT, which takes into account coupling of the density fluctuations only [2], is a formal generalization of the equilibrium kinetic theory of liquids and of the Vlasov plasma theory. This theory has been applied to different monatomic systems such as neutral hard spheres [3], charged hard spheres [4], Lennard-Jones atoms [5], and pure liquid metals [6]. Light [7] and neutron [8] scattering experiments on model colloids and a variety of molecular glass forming materials [9] suggest the existence of the predicted μ_c, and find compatibility with the scaling laws predicted by MCT despite the fact that, in many cases, the systems studied are far more complex than the one-component fluid for which the theory was developed. However, interpretation of both the experimental data and the theoretical predictions in terms of MCT is not without controversy [10].

In this paper we present a theoretical attempt to determine the liquid-glass transition boundaries for a system of hard-core particles with screened Coulomb interactions. This system is chosen because it represents a model for charge-stabilized colloidal suspensions, and it can, therefore, be realized experimentally. In addition, variation of the pertinent parameters, such as the number density, screening length, and coupling strength that determine the potential-energy function, gives a rich diversity of equilibrium phase behavior. At the same time, the interactions of these particles are sufficiently simple in that the parameters embodied in the MCT can be calculated directly.

Although a charge-stabilized suspension is implicitly a multicomponent system consisting of macroions of diameter σ and charge Ze, small counterions and co-ions, and solvent molecules, it can, in the coarse-grained view, be regarded as a one-component system of particles with the following general form of pair potential [11]:

$$\beta V(x) = \gamma_{\text{eff}} \frac{\exp(-kx)}{x}, \quad x > 1, \tag{1}$$

where the dimensionless length $x = r/\sigma$. Here β is the inverse temperature; $k = \kappa\sigma$, and κ is the inverse Debye screening length determined by the concentration of counterions and, in the presence of electrolytes, co-ions; γ_{eff} is the surface charge parameter, in general a function of k and of the volume fraction $\eta = \pi\sigma^3\rho/6$, ρ being the number density of macroions. An extensively studied γ_{eff} is the one-component macrofluid model of Derjaguin-Landau-Verwey-Overbeek (DLVO) [12] whose $V(x)$ exploits the large finite size of macroions. The attractive feature of this $V(x)$ is that static structure factor can be obtained analytically in the framework of the mean spherical approximation [13]. Here the static structure factor $S(q; \eta, k, \gamma)$, is characterized by three quantities: the η of macroions, the screening parameter k, and the surface charge parameter $\gamma_{\text{eff}} \equiv \gamma = \beta\pi\epsilon_0\epsilon\sigma\psi_0^2 e^k$ (where ϵ_0 is the electric permittivity of free space, ϵ is the dielectric constant of the solvent, and $\psi_0 = Ze/[\pi\epsilon_0\epsilon\sigma(2+k)]$ is the surface potential). Respectively, these parameters characterize the short-ranged hard-core, the intermediate-ranged screening, and the long-ranged charge-coupling effects in the system.

The projection operator methods give the following formally exact expression for the dynamic structure factor [2]

$$\hat{R}(q,z) = -\frac{z + \hat{M}(q,z)}{z^2 - q^2/\beta m S(q; \eta, k, \gamma) + z\hat{M}(q,z)}, \tag{2}$$

where $\hat{R}(q,z) = i\int_0^\infty dt \exp(izt)R(q,t)$ is the Laplace transform of the normalized intermediate scattering function $R(q,t) = \langle \delta\rho^*(\mathbf{q},t)\delta\rho(\mathbf{q},0)\rangle/S(q; \eta, k, \gamma)$, $\delta\rho(q,t)$ being the number density fluctuations of wave vector q; $\hat{M}(q,z)$ is the memory function; and m is the mass of the particle. Central to the idealized MCT of the glass transition is to neglect the microscopic dynamics by taking the limit $z \to 0$, and to close Eq. (2) with an approximation $M(q,t) \approx \Lambda(q,t)$, where

$$\Lambda(q,t)=\frac{\rho}{8mq\beta\pi^2}\int_0^\infty dq'q'\int_{|q'-q|}^{|q'+q|}dq''q''\left(\frac{q'^2-q''^2}{2q}[c(q';\eta,k,\gamma)-c(q'';\eta,k,\gamma)]+\frac{q}{2}[c(q';\eta,k,\gamma)+c(q'';\eta,k,\gamma)]\right)^2$$

$$\times S(q';\eta,k,\gamma)S(q'';\eta,k,\gamma)R(q',t)R(q'',t), \tag{3}$$

$c(q;\eta,k,\gamma)=[S(q;\eta,k,\gamma)-1]/\rho S(q;\eta,k,\gamma)$ being the direct correlation function.

To determine the dynamical transition boundary $\mu_c=(\eta_c,k_c,\gamma_c)$ in MCT, we employ the analytical result for $S(q;\eta,k,\gamma)$ [13] and solve iteratively and self-consistently the dynamical nonlinear equation

$$\frac{f(q)}{1-f(q)}=\frac{\beta mS(q;\eta,k,\gamma)}{q^2}\Lambda(q,t\rightarrow\infty)\equiv\mathcal{F}_q(f(p)) \quad (4)$$

for (η_c,k_c,γ_c), which yields a nonzero Debye-Waller factor $f(q)=R(q,t\rightarrow\infty)$. Asymptotic solutions to the MCT equations near each dynamical transition point (η_c,k_c,γ_c) exhibit interesting and experimentally testable scaling properties. In particular, the dynamics over the mesoscopic time scale between the times characterizing the fast microscopic process and the slowest structural relaxation is governed by the so-called ''β-relaxation process.'' For this process the theory predicts factorization of $R(q,t)$ into temporal and spatial fluctuations. It can be shown [2] that near (η_c,k_c,γ_c) the temporal behavior of $R(q,t)$ is a scaled master function determined solely by a material-dependent parameter λ given by

$$\lambda=\frac{1}{2}\sum_{q,p',p''}\hat{l}_q^c[1-f(p')]^2[\partial^2\mathcal{F}_q/\partial f(p')\partial f(p'')]_T$$

$$\times[1-f(p'')]^2l_{\mathbf{p}'}^c l_{\mathbf{p}''}^c, \tag{5}$$

where $\mathcal{F}_q$ is defined in Eq. (4) and l_q^c (or $\hat{l}_q^c$) is the right-hand (or left-hand) eigenvector of the stability matrix $C_{qp}=[1-f(p)]^2\partial\mathcal{F}_q/\partial f(p)$.

Equations (3) and (4) were solved iteratively using $S(q;\eta,k,\gamma)$ for parameters typically encountered in aqueous suspensions, namely, $T=298$ K, $\epsilon=78.3$, and $\sigma=5$ nm. The
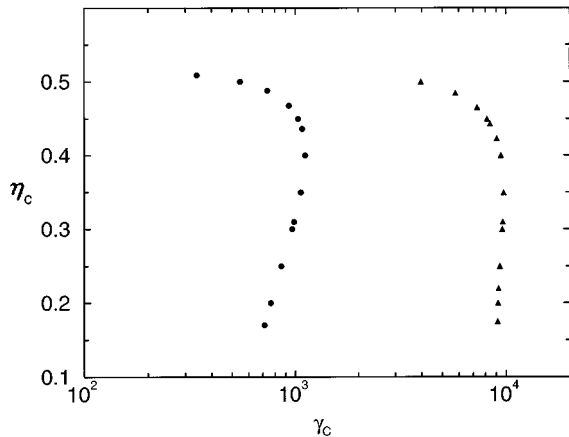
bifurcation of solutions $f(q)=0$, defining ergodic behavior, and $f(q)>0$, defining nonergodic behavior, gives the dynamical transition points (η_c,k_c,γ_c). In Fig. 1 we display the transition loci which separate the ergodic regime, $\eta-\gamma<\eta_c-\gamma_c$, from the nonergodic one, $\eta-\gamma\gtrsim\eta_c-\gamma_c$, for the cases of weak $(k=3)$ and strong $(k=6)$ screening. One notices immediately that the ergodic region in the weak screening environment is restrictive, whereas in the strong screening case the ergodic domain is comparatively more extensive. In both cases η_c decreases with increasing γ_c for $0.5>\eta\gtrsim0.4$, but, for $\eta<0.4$, γ_c is almost independent of η. The extent of the supercompressed regime can be understood by considering the physical significance of k. For given colloidal condition (β,σ,ϵ), the charge-induced coupling constant $\gamma\propto e^k/(1+k/2)^2$ is significantly larger for the strong screening case. In the absence of electrolytes, this latter case would correspond physically to an increase in screening by counterions (relative to the case $k=3$), and hence leads to more stable suspensions. Note that although also $\gamma\propto Z^2$, the detailed structures of the $\eta_c-\gamma_c$ characteristics have been considerably masked by the $e^k/(1+k/2)^2$ dependence, and are only weakly affected by Z^2. To pursue our study of the transition loci further, in Fig. 2 we depict the variation of η_c with the macroion charge Z_c [14]. There are two interesting aspects. The first aspect is the η_c-Z_c behavior for both screening cases which, in the range $0.5>\eta\gtrsim0.45$, have η_c-Z_c phase boundaries virtually the same but show different η_c-Z_c behavior for $\eta<0.45$. The former features manifests the hard-core geometric effect, whereas the second, in the absence of electrolytes, exhibits the change in ionic strength due to counterions which now play the role of charge stabilizing the macroparticles. The second aspect is

FIG. 1. Volume fraction η_c vs surface charge parameter γ_c for screening parameters $k=3$ (circles) and $k=6$ (triangles).
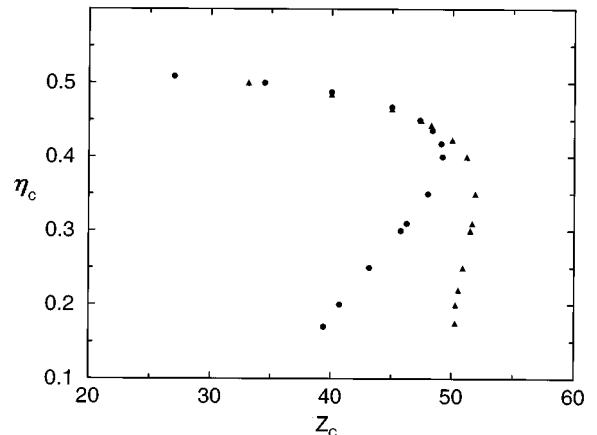

FIG. 2. Volume fraction η_c vs colloidal charge Z_c (in units of electronic charge) for screening parameters $k=3$ (circles) and $k=6$ (triangles).

the $k=3$ case which, for a given Z between $37e \lesssim Z \lesssim 49e$, predicts the existence of two η_c at whose places the colloidal suspension is seen to undergo a glass→liquid→glass transformation. This transformation property is reminiscent of the ''re-entrant'' behavior theoretically predicted for the colloidal crystal [15] and here, for a given macroion σ, is associated with the change in ρ of macroions. We should stress, however, that in view of the use of the DLVO-type potential the phase diagram depicted in Fig. 2 is somewhat qualitative. Thus, although the estimated transition loci occur in a reasonable parameter space, the quantitative details of the error of the estimation cannot be predicted at present.

In order to explore the practicability of the fluid-glass transition phase diagram shown in Fig. 1, we consider two recent experiments performed on charge-stabilized suspensions. The first one is the synchrotron small-angle x-ray-scattering experiment by Sirota et al. [16], who measured the static structure factors and phase diagram for a system of charged polystyrene spheres of diameter $\sigma=91$ nm immersed in the water-methanol solvent ($\epsilon=38$), as functions of concentration and of the range of the interaction. Their electrolyte-free results show a glass transition at $\eta_c=0.2$. The second one is the experiment of Härtl, Versmold, and Zhang-Heider [17] who, from static structure factors and intermediate scattering functions measured by light scattering on 500-nm poly-perfluorobutylacrylate particles suspended in water-glycerol mixtures, observed a liquid-glass transition at $\eta_c=0.22$. Since $S(q;\eta,k,\gamma)$ depends on the parameters (η,k,γ), it can be seen from Eq. (1) that there is a range of physical conditions yielding equivalent structures [18], provided (η,k,γ) are scaled properly. Thus, for given η and k, the surface charge parameter γ can be written as a function of three variables $\gamma(\sigma,\psi_0,\epsilon)=\beta\pi\epsilon_0\epsilon\sigma\psi_0^2 e^k$. For the two specific cases $\eta_c=0.2$ and 0.22 of interest here, we obtain, respectively, from Fig. 1 the values of the surface charge parameters γ_c (5 nm, 92.652 mV, 78.3) = 9162.44 and γ_c (5 nm, 92.955 mV, 78.3)=9222.46 for the case $k=6$. In accordance with the structural equivalents pointed out above, we may equate separately the experimental conditions γ_c (91 nm, ψ_0, 38) and γ_c (500 nm, ψ_0, 38) to the theoretical values for γ_c, 9162.44 and 9222.46, to deduce the corresponding values for ψ_0, respectively, for $\eta_c=0.2$ and 0.22. In this way we arrive at $\psi_0=31.2$ and 13.3 mV, and, by $\psi_0=Ze/[\pi\epsilon_0\epsilon\sigma(2+k)]$, respectively obtain the critical charges $Z_c=150e$ and $351e$. The same procedure when applied to $k=3$ for the case $\eta_c=0.2$ yields $Z_c=121e$. It is interesting to note that these values for Z_c, $150e$ and $121e$, respectively, for the cases $k=6$ and 3 span the value $Z_c=135e$ estimated by Sirota et al. [16]. In other words, the screening parameter k for the dispersion of charged polystyrene spheres, free of electrolytes, is approximately 4.5, and with $\sigma=91$ nm, will yield $\kappa^{-1}\approx 202$ Å, which is in reasonable order to 290 Å estimated from Ref. [16].

We now turn our attention to results of relevance of MCT. Figure 3 displays the $S(q_m)$ at the first peak position q_m plotted as a function of Z_c for different k. The kind of the cage effect mechanism manifested by dynamically interlocked clusters, each consisting of a central particle surrounded by neighboring particles, is qualitatively exhibited
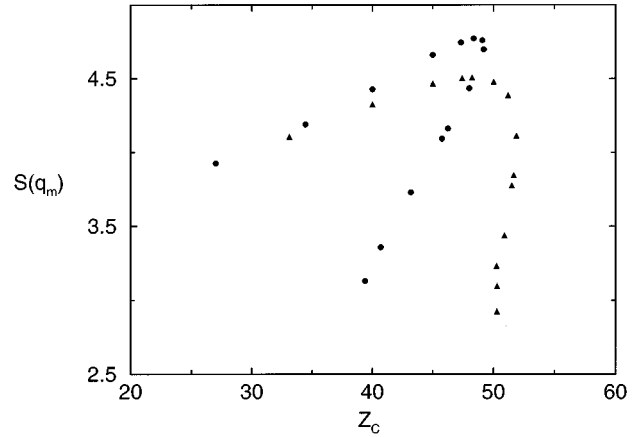

FIG. 3. Static structure factor $S(q_m)$ at the principal peak position q_m vs colloidal charge Z_c (in units of electronic charge) for screening parameters $k=3$ (circles) and $k=6$ (triangles).

by the dependence of $S(q_m)$ on Z_c. Note that $S(q_m)$ versus Z_c qualitatively mimics the η_c-Z_c transition phase boundary shown in Fig. 2.

We have calculated also the β-relaxation parameter λ which describes physically the temporal behavior of $R(q,t)$ near $(\eta_c,k_c\gamma_c)$. Our calculations show that λ varies mildly in magnitude for $0.5\gtrsim\eta_c>0.15$ due to numerical precision in achieving an equal eigenvalue one (typically we obtain 0.99545 ± 0.0044 for a total of 400 iterations). For $k=3$ and 6 they satisfy $\lambda=0.728\pm 0.02$ and $\lambda=0.719\pm 0.017$, respectively. These values differ from the $\lambda=0.76$ deduced from the dynamic data of Ref. [17] for charged polymer colloids having $\sigma=500$ nm and at $\eta_c=0.22$. One should note, however, that this empirically fitted large-λ value is physically unsound, since the magnitude lies close to the hard-sphere-like potential ($\lambda=0.772$ [6]). For lack of details on the Z_c of charged colloidal particles, we cannot proceed with our analysis.

In summary, we have proposed a tractable means to study the qualitative phase diagram for a liquid-glass transformation. This was done for a charge-stabilized colloidal dispersion using the DLVO-type static structure factor in conjunction with the idealized MCT. Our salt-free results indicate a more extended supercompressed suspension when the screening is effective. This implies an enhancement in charge-stabilizing tendency associated with the ionic strength of counterions. The potential application and importance of our calculations are further exploited by explicitly estimating the charges carried by macroions and by comparing with experimental polymer colloids the mode-coupling parameter λ near the same dynamical transition point. Our analysis shows that more quantitative works are necessary for a detailed comparison with experiments.

[1] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915 (1984).

[2] W. Götze, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991), p. 287; W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

[3] J. L. Barrat, W. Götze, and L. Latz, J. Phys. Condens. Matter **1**, 7163 (1989); M. Fuchs, I. Hofacker, and A. Latz, Phys. Rev. A **45**, 898 (1992).

[4] S. K. Lai and S. Y. Chang, Phys. Rev. B **51**, R12 869 (1995).

[5] U. Bengtzelius, Phys. Rev. A **34**, 5059 (1986); **33**, 3433 (1986).

[6] S. K. Lai and H. C. Chen, J. Phys. Condens. Matter **5**, 4325 (1993); **7**, 1499 (1995).

[7] W. van Megen and S. M. Underwood, Phys. Rev. E **49**, 4206 (1994); Y. Yang and K. A. Nelson, Phys. Rev. Lett. **74**, 4883 (1995).

[8] J. Wuttke, M. Kiebel, E. Bartsch, F. Fujara, W. Petry, and H. Sillescu, Z. Phys. B **91**, 357 (1993).

[9] For a recent review, see *Relaxation Kinetics in Supercooled Liquids—Mode Coupling Theory and its Experimental Tests*, edited by P. Nelson, special issue of Transp. Theory Stat. Phys. **24**, pp. 755–1268 (1995).

[10] X. C. Zeng, D. Kivelson, and G. Tarjus, Phys. Rev. Lett. **72**, 1772 (1994); W. Van Megen and S. M. Underwood, *ibid.* **72**, 1773 (1994); X. C. Zeng and D. Kivelson, Phys. Rev. E **50**, 1711 (1994); H. Z. Cummins and G. Li, *ibid.* **50**, 1720 (1994); R. Schmitz, J. W. Dufty, and P. De, Phys. Rev. Lett. **71**, 2066 (1993); J. Yeo, Phys. Rev. E **52**, 853 (1995); T. Odagaki, Phys. Rev. Lett. **75**, 3701 (1995).

[11] L. Belloni, J. Chem. Phys. **85**, 519 (1986).

[12] E. J. Verwey and J. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[13] J. B. Hayter and J. Penfold, Mol. Phys. **42**, 109 (1981).

[14] Strictly speaking, we should envisage this from the viewpoint of an effective charge that depends explicitly on η, since we are working on the concentrated colloidal suspensions. We refer interested readers to Ref. [11] for further details.

[15] S. Khan, Thomas L. Morton, and D. Ronis, Phys. Rev. A **35**, 4295 (1987).

[16] E. B. Sirota, H. D. Ou-Yang, S. K. Sinha, and P. M. Chaikin, Phys. Rev. Lett. **62**, 1524 (1989).

[17] W. Härtl, H. Versmold, and X. Zhang-Heider, J. Chem. Phys. **102**, 6613 (1995).

[18] I. K. Snook and J. B. Hayter, Langmuir **8**, 2880 (1992).