Liquid-glass Transition in Charge-stabilized Colloidal Dispersions


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Abstract. We model the inter-colloidal interactions in a charge-stabilized colloidal dispersion by a hard-core Yukawa potential \( \phi(r) = \sigma_0 \gamma e^{-\kappa r}/r, r > \sigma_0 \) and apply the rescaled mean spherical approximation to calculate its static structure factor. In conjunction with the idealized mode-coupling theory, we determine the loci of the liquid-glass transition phase boundary for a salt-free suspension of charged colloids evaluated at different counter-ion environment (characterized by the \( \kappa \)) in terms of the macro-ion parameters: volume fraction \( \eta \), charge \( Z_0 \) and size \( \sigma_0 \). The calculated parametric phase diagrams are quite general since the results, with slight and straightforward modification, can be utilized to study the glass transition in a more realistic colloidal solution such as an aqueous monodisperse suspension of polystyrene charged spheres with an added electrolyte. Confining our discussion, then, to the simplest salt-free colloidal liquids, we extract from our analysis of the calculated liquid-glass transition boundaries some succinct features. Specifically, we show in this work that given a range of interaction \( \kappa = \kappa(\sigma_0) \leq 3.8 \), there is a possibility of observing the liquid=glass=liquid=glass (LGLG) re-entrant phenomenon in restrictive regions of the phase diagram \( \eta-\sigma_0 \) or \( \eta-Z_0 \) for a monodisperse charge-stabilized solution. However, as the \( \sigma_0 \) increases above a critical size, the LGLG re-entrant behavior vanishes. To delve into this re-entrant phenomenon, we compare, for a given \( \kappa \), the glassy Debye-Waller factor, static structure factor and their spatial counterparts for two cases—one for lower-\( Z_0 \) colloids at a high \( \eta \) and the other for higher-\( Z_0 \) colloids at a low \( \eta \). For the former, the glassification is basically driven by the geometric restriction while that, for the latter, it is mainly induced by the Coulomb force. We conclude from this comparison that under the same screening environment both the excluded volume and the electrostatic effects are equally effective in impelling a charge-stabilized colloidal dispersion to undergo a structural arrest configuration and hence the liquid-glass transition.

I. INTRODUCTION
Strongly charged colloidal particles are experimentally observed (1,2) to undergo crystallization at a lower volume fraction \( \eta (\lesssim 0.15) \) of macro-ions. Such phenomenon has been understood theoretically by the density functional theory (3-5) where the colloidal free energies separately of the crystalline and liquid phases were constructed in terms of their respective structures. In this connection the Ornstein-Zernike equation supplemented by the mean spherical approximation (MSA) closure has proved to be a competent tool if the evaluation of the equilibrium fluid structure is further augmented by the notion of size rescaling on macroparticles. Hansen and Hayter (6) were the first to apply this rescaling idea to study the static structure factor \( S(q) \) of micelle solutions measured at very low \( \eta (\approx 10^{-3}) \). By modeling the interactions between colloidal particles by the so-called Derjaguin-Landau-Verwey-Overbeek (DLVO) repulsive potential (7) for which the MSA analytical solutions (8) exist, they incorporated the rescaling concept in their theoretical study of micellar \( S(q) \) and found the calculated results agreeing excellently with measured data. For a dilute aqueous solution of charge-stabilized colloids, this rescaled MSA (RMSA) has achieved an impressive record in interpreting the colloidal \( S(q) \). In spite of this brilliant success of RMSA, comparatively less works are reported on applying the technique to more concentrated charged colloidal dispersions (\( \eta > 0.15 \)). Study on these latter dispersions is both an important and a worthwhile attempt since it affords an understanding of the mystery of the liquid-glass phase transformation whose occurrence was observed to fall into the range of \( \eta \gtrsim 0.2 \) (2,9). This paper reports calculations which show clearly that the RMSA is equally useful for charge-stabilized dispersions described by high concentrations (\( \eta > 0.15 \)). For concreteness, we shall employ the calculated \( S(q) \) in conjunction with the idealized mode-coupling theory (MCT (10)) to determine the liquid-glass transition boundaries under different screening conditions \( \kappa = \kappa_0 \), \( \kappa^{-1} \) being the Debye-Hückel screening length (to be defined below). It is shown in this work that the charge \( Z_0 \) carried by charged colloids is equally effective in inducing structural arrest and hence in manifesting the liquid-glass transition at a lower \( \eta \). In particular, we predict for the case of monodisperse charged colloids the LGLG re-entrant phenomenon. Quantitatively, we notice that, for any given \( \kappa \lesssim 3.8 \), the glass-liquid-glass (GLG) re-entrant behavior which extends from a higher \( \eta \) (and lower \( Z_0 \)) to a lower \( \eta \) (and higher \( Z_0 \)) or vice versa shrinks with increasing \( \kappa_0 \) and disappears above a critical size; the LGLG re-entrant behavior, on the other hand, vanishes for \( \kappa > 3.8 \). Nevertheless, the numerical data presented here are quite general; the results, with slight and straightforward modification, could be used to investigate the phase diagrams of a more realistic charge-stabilized colloidal solution such as a system of monodisperse polystyrene charged spheres both with and without electrolytes.

II. THEORY

In this section we introduce the effective one-component model previously developed by Belloni (11) and shown recently by Lai et al.(12-14) to be an adequate
model for studying the structures of concentrated charged colloidal liquids. In addition, we describe briefly the idealized MCT for the latter systems.

**A. Mean Spherical Approximation**

Consider the multicomponent coupled Ornstein-Zernike equations given by

\[ h_{ij}(r) = c_0(r) + \sum_{l=0} \rho_l \int h_{il}(|r - r'|) c_y(r') dr' \]  

(1)

where species \( i, j \) and \( l \) are defined as: \( i, j, l = 0 \) for macro-ions, \( i, j, l = 1 \) for counter-ions, and \( i, j, l = 2, 3, ... \) for other small ions. Here \( \rho_l \) is the number density for species \( l \); \( c_y(r) \) is the direct correlation function and \( h_{ij}(r) = g_{ij}(r) - 1 \) is the total correlation function which is defined in terms of the pair correlation function \( g_{ij}(r) \). Adelman (15) has shown that Eq. (1) can be contracted to an effective direct correlation function \( c_{00}^{\text{eff}}(r) \) whose Fourier transform \( \tilde{c}_{00}^{\text{eff}}(q) \) can be shown (11,12) to read

\[ \tilde{c}_{00}^{\text{eff}}(q) = \tilde{c}_{00}^{s}(q) + \sum_{i=1}^{\infty} \left( \tilde{c}_{00}^{s}(q) \right)^2 - \frac{[\alpha_0 + \sum_{i=1}^{\infty} \alpha_i \tilde{c}_{00}^{s}(q)]^2}{q^2 + \kappa^2} \]  

(2)

where \( \tilde{c}_{00}^{s}(q) \) is the short range component of \( \tilde{c}_{00}(q) \), \( \alpha_i^2 = 4 \pi L_B \rho_i Z_i^2 \), \( L_B \) and \( Z_i \) being the Bjerrum length and the charge of a macro-ion or small ion respectively, and \( \kappa^2 = \sum_{i=1}^{\infty} \alpha_i^2 \) is the Debye-Hückel screening parameter. Note that \( S(q) \) at this stage can already be calculated by the formula \( S(q) = S_{00}(q) = 1/[1 - \rho_0 \tilde{c}_{00}^{s}(q)] \) without invoking the MSA closure. There is, however, one interesting feature behind Eq. (2). If we carry out an inverse Fourier transform (see Lai and Wang (12) for mathematical details),

\[ c_{00}^{\text{eff}}(r) = -L_B Z_0^2 \frac{e^{-\kappa r}}{\kappa^2} = -\sigma_0^2 \frac{e^{-\kappa r}}{\kappa^2} \quad r > \sigma_0 \]  

(3)

we see immediately that setting \( c_{00}^{\text{eff}}(r) = -\beta \phi(r) \) with \( \beta = 1/(k_BT) \) and \( \phi(r) \) being the inverse temperature and the interparticle potential respectively, will cast the relation inversely in the form of an MSA closure for \( r > \sigma_0 \) if the hard-core condition \( \phi(r) = \infty \) for \( r < \sigma_0 \) is imposed. Such an identification is not only natural and has the advantage of utilizing the analytical \( S(q) \) solution (8). Of particular interest is the coupling parameter

\[ X = \cosh \left( \frac{\kappa}{2} \right) + U \left[ \frac{\kappa}{2} \cosh \left( \frac{\kappa}{2} \right) - \sinh \left( \frac{\kappa}{2} \right) \right] \]  

(4)

which not only depends on \( \kappa \) but also on \( \eta \) through \( U = (8 \zeta / \kappa^2 - 2 \nu / \kappa^2) \) in which \( \zeta = 3 \eta/(1 - \eta) \), \( \nu = (A_\eta + 2 \zeta)/[2(1 + \zeta) + A_\eta] \) and
\[ (\Lambda^{2} - \kappa^{2})[2(1 + \zeta) + \Lambda_{\sigma}]^2 = 96L_B\eta Z_0^2/\sigma_0 \]  
(5)

Given \( Z_0^2/\sigma_0, \kappa \) and \( \eta \), Eq. (5) has to be solved for \( \Lambda \sigma \) and hence \( \Lambda \) in Eq. (4). It is easy to show that \( X \to \exp(\kappa/2)/(1+\kappa/2) \) in the limit of \( \rho_0 \to 0 \) (the repulsive DLVO result). This would mean that the present model of Belloni is appropriate for the description of a charge-stabilized colloidal dispersion at finite concentration.

**B. Mode coupling theory**

We turn to introduce the MCT appropriate for a suspension of charge-stabilized colloids. Let us begin with the intermediate scattering function \( F(r,t) \) whose Fourier-Laplace transformed \( \hat{F}(q,z) \) can be shown to be related to the memory function \( \hat{M}(q,z) \) by

\[ \hat{R}(q,z) \equiv \frac{\hat{F}(q,z)}{S(q)} = \frac{1}{z + q^2 D_0/S(q) - \hat{M}(q,z)/S(q)} \]  
(6)

where \( D_0 \) is the Stokes-Einstein diffusion coefficient of a single particle. Spatially \( F(r,t) \) contains useful information on the local structure of macroparticles and temporally it describes a short-time decaying behavior representing a typical Brownian motion and a long-time slowly decaying relaxation representing a collective nonlinear coupling of macroparticles whose origin can be traced to the kind of cage and Feynman feedback effects. All these characteristics are embodied in the memory function \( \hat{M}(q,z) \). However, it was pointed out by Cichocki and Hess (17) that the memory function \( \hat{M}(q,z) \) in Eq. (6) is not an elementary quantity in the study of the dynamics of colloidal particles for its time evolution operator is not one-particle irreducible. By comparing the generalized dynamic viscosity within the contexts of a generalized Smoluchowski equation and of a Fokker Planck equation, Cichocki and Hess (17) (see also Ref. (19)) were able to derive an explicit formula relating the \( \hat{M}(q,z) \) to an irreducible memory function \( \hat{M}_0(q,z) \). In particular the latter can be written quite generally as \( \hat{M}(q,z) = \hat{M}_0(q,z) + \hat{M}_1(q,z) \) where \( \hat{M}_0 \) comprises all the contributions coming from the short-time dynamics and the \( \hat{M}_1(q,z) \) accounts for the long-time contributions including fully the slow structural motions. On approaching the glass phase at increased densities, the long-time contribution in \( \hat{M}(q,z) \) is manifestly dominant and it is a good approximation to write \( \hat{M}(q,z) \approx \hat{M}_1(q,z) \). It can be inferred from the works of Szamel and Löwen (18) and others (16,19,20) that there exists an idealized liquid-glass transition at a dynamical transition point which is determined by the following nonlinear vitrification equation

\footnote{1) Here we follow the work of Baur et al. (16) in our definition of the memory function \( \hat{M}(q,z) \). The difference between the latter and the one used by others (17,18) is a factor \( q^2 D_0 \) which can easily be identified.}
Here the solution \( f_c(q) = R(q,t \to \infty) \neq 0 \) is the glassy Debye-Waller factor, a non-ergodic state, whereas \( f(q) = 0 \) is the ergodic state. By making a two-mode approximation (16,18-21), the \( \tilde{\Gamma}(q,t) \) above can be put in a form suitable for numerical work:

\[
\tilde{\Gamma}(q,t) = \frac{D_0}{8q^2} \int_0^\infty dx \int_{|x-q|}^{x+i} dy \left( \frac{x^2 - y^2}{2q} \left[ c_{\text{eff}}^{(0)}(x) - c_{\text{eff}}^{(0)}(y) \right] \right)
\]

Given \( S(q) \), Eqs. (7) and (8) constitute two nonlinear coupled equations which we will solve iteratively for the loci of the liquid-glass transition (for technical details the interested readers should consult Lai et al. (22) for cases of atomic liquids).

### III. NUMERICAL RESULTS AND DISCUSSION

Figure 1(a) displays the \( \eta_c^{-\gamma_c} \) phase diagram for the colloidal dispersions calculated by solving Eqs. (7) and (8) self-consistently at \( \kappa = 2.65, 3.8, 4 \) and 7 in the increasing order of counter-ion screening. For convenience in discussion we have included in the same figure our previous results of \( \kappa = 3 \) and 6 (12). We emphasize that in all of these calculations we have (a) kept the charged colloidal particles in water and maintained the colloidal dispersion at room temperature, (b) considered monovalent counter-ions as the only source of screening small ions\(^2\) and (c) applied the condition of charge neutrality, \( \rho_1Z_1 = \rho_0Z_0 \), to the definition of \( \kappa \) to ensure that its value is consistent with that given by \( \kappa = \kappa/\sigma_0 \). As a consequence, the Z\(_0\) and \( \sigma_0 \) of macro-ions have to be adjusted (12). Figures 1(b) and 1(c) show the detailed change of \( \eta_c \) plotted against the \( Z_0^2/\sigma_0 \) and \( \sigma_0^2 \) separately, and, for completeness, we depict in Fig. 1(d) the relation of the last two quantities. We stress two main features—the first one is a general characteristic typical for the hard-core Yukawa potential while the second is the results on using the model of Belloni whose quantitative details are buried in the coupling constant \( \gamma \).

First, the ergodic region of the \( \eta_c^{-\gamma_c} \) phase diagram increases with increasing screening parameter \( \kappa \). This is physically comprehensible if we recall Eq. (3) and note for the increase in magnitude of \( Z_0^2/\sigma_0 \) with \( \kappa \), which is smaller at large \( \eta \) and becomes drastic at small \( \eta \) (see Fig. 7 in (12)). Since \( \gamma \propto (Z_0^2/\sigma_0)X^2 \) and \( X \), as

\[ \text{It is straightforward to generalize the calculation to studying charged colloidal dispersions subject to the influence of an electrolyte. This has in fact been done by Wang and Lai (14) in their studies of the liquid-glass transition phase boundary for a system of monodisperse polystyrene charged spheres in the presence of the electrolyte HCl.} \]
FIGURE 1. Phase diagrams of charge-stabilized colloidal dispersions determined by solving Eqs. (7) and (8) and plotted in terms of the coupling strength \( \gamma_c \) and macroion parameters: volume fraction \( \eta_c \), charge number \( Z_0^c \) and diameter \( \sigma_0^c \). The range of interaction is: \( \kappa = 2.65 \) (solid circles), 3 (open circles), 3.8 (open diamonds), 4 (solid triangles), 5 (solid diamonds), 6 (open triangles) and 7 (solid squares).

shown above (Eqs. (4) and (5)), depends explicitly on \( Z_0^c/\sigma_0 \), it is natural to expect such a possible trend also for the dependence of \( \eta \) on \( \kappa \). Our conjecture is indeed confirmed by the change of \( \eta_c - \gamma_c \) curve given in Fig. 1(a). Second, we see from Figs. 1(c) and 1(d) that, for any \( \sigma_0 \) between \( \sigma_m \) and \( \sigma_M \), there exists a LGLG re-entrant behavior for \( \kappa \lesssim 3.8 \) (here, \( \sigma_m \) (\( \sigma_M \)) is a critical size above (below) which liquid = glass = liquid (glass = liquid = glass) behavior occurs) but the LGLG feature disappears for \( \kappa > 3.8 \). This is an interesting scenario for it means that given a range of interaction \( \kappa \lesssim 3.8 \), one may observe the liquid-glass transition in a monodisperse charge-stabilized colloidal suspension either for highly charged colloids at a lower \( \eta \) or for less highly charged colloids at a higher \( \eta \). Since
FIGURE 2. (a) Glassy Debye-Waller form factor $f_c(q)$ and (b) static structure factor $S(q)$ for charge-stabilized colloidal dispersions at $\eta_k=0.5$, $Z_0=114e$ (dashed curve) and $\eta_k=0.104$, $Z_0=552e$ (full curve). The corresponding quantities for (i) $\eta_k=0.104$ calculated without rescaling (see text) are denoted by solid circles and (ii) the neutral hard-sphere results (dot-dashed curves) are included for comparison.

the former is basically driven by strong electrostatic couplings which differs drastically from the latter hard-core effects, it would be instructive to compare the glassy Debye-Waller factor $f_c(q)$ for these two cases in order to gain insight into the mechanism of glassification. For concreteness, we display in Fig. 2(a) the two $f_c(q)$ for the case $\sigma_0 \approx 1407 \text{ Å}$ (the interception of the horizontal lines in Figs. 1(c) and 1(d)) calculated at $\kappa = 2.65$ (solid circles) and, to show their correspondence to $S(q)$, the latter is separately depicted in Fig. 2(b). As these figures dictate, the $f_c(q)$ and $S(q)$ curves show concerted oscillatory structures. Quantitatively, we may analyze these figures as follows. Let us start with a system of neutral hard spheres. Previous glass transformation studies (20,22) based on the MCT have propounded the hard-sphere particles to exhibit the structural arrest at the transition point $\eta_k = 0.516$ and have attributed the liquid-glass transition to be purely due to the excluded volume effects. For this system, the $f_c(q)$ is thus rather short-ranged (see Fig. 2(a)). Proceeding to charged colloids, first, for the less highly charged ones ($Z_0=115e$), the system is still driven predominantly by the geometric restriction and the $f_c(q)$ is thus still mainly of a shorter-range order. Physically, this will reveal as a “protrusion” of the glassy region as evidenced by the predicted liquid-glass
FIGURE 3. (a) Spatial critical amplitude $H(r)$ and (b) pair correlation function $g(r)$ for charge-stabilized colloids calculated at $\eta_c=0.5$ (dashed curve) and $\eta_c=0.104$ (full curve). The insert in (b) shows the Coulomb hole as discussed in text.

transition point reducing to $\eta_c=0.5$. On expansion (in the sense of lowering the $\eta \propto \rho_0$) into the liquid phase the charged colloidal dispersion re-enters into the glassy phase at the lower $\eta_c=0.104$. On continuing expansion further, the system re-enters again into a liquid phase at a lower still $\eta_c=0.018$. Here, the lower-$\eta$ highly charged colloids reflect a change in localization mechanism which is manifested primarily by the electrostatic effect and secondarily by the hard-core factor. As a result, the Coulomb-dominated $f_c(q)$ displays a longer-range order. This latter feature can be realized more clearly by scrutinizing Fig. 3(a) for the spatial critical amplitude $H(r)$ which is the Fourier transform of $S(q)h_c(q)$ where $h_c(q) \propto [1 - f_c(q)]^2$. It is interesting to see that the colloidal $H(r)$ of the $\beta$-relaxation process (10) in the lower-$\eta$ highly charged colloids exhibits a “softening” in the local collective excitation. Similar characteristic is revealed in the pair correlation function $g(r)$ shown in Fig. 3(b); here the outward shift of $g(r)$ for the lower-$\eta$ case is consistent with the overall change in $f_c(q)$. We should emphasize at this point that in approaching to the lower $\eta$, the macro-ion charge $Z_0$ needs increased to strong enough (Coulombic) couplings to ensure structural arrest of charged colloidal particles (subject, in addition, to the self-consistent use of charge neutrality condition in the definition of counter-ions environment). Within the MSA closure, this increment of $Z_0$ would
quite often bring forth the annoying problem of an unphysical \( g(r) \), for the MSA closure is generally known to account poorly for short-range correlations particularly the \( g(r) \) near the contact distance \( r = \sigma_0^+ \) which may become negative even for \( \eta \) as large as 0.4 (12, 23). Such an inherent deficiency of the MSA was pointed out previously by Hansen and Hayter (6) when studying the \( S(q) \) of dilute \( (\eta < 0.1) \) highly charged micellar solutions and recently by Lai and Wang (12) when investigating the liquid-glass transition problem for concentrated \( (\eta > 0.2) \) charge-stabilized colloidal solutions. It turns out that this shortcoming of the MSA can be remedied in both cases by introducing the concept of Coulomb hole in close analogy to that used in the interacting many-electron theory (24). For the interacting electrons immersed in a positive uniform background, the Coulomb repulsion (and also the position correlations) between electrons induces for each electron a region of space unavailable for the other electrons to appear. Since the positively charged ions are playing the role as a background, any electron in its distribution with all other electrons is surrounded by a positive (Coulomb) hole. This scenario where an electron is accompanied by a positively charged hole is called the “quasiparticle” and is the basic entity that L.D. Landau (25) used in his formulation of the phenomenological Fermi liquid theory. For the case at hand, due to the strong Coulombic repulsion (relative to the thermal energy \( k_B T \)), there is less probability for two charged colloids to appear within a certain distance of each other (compare the two \( g(r) \) given in the insert of Fig. 3(b)). Thus, whereas in the interacting many-electron system the electrons are to be treated as Fermions (causing position correlations (24)) and be described using quantum mechanics, the case of macro-ions, however, are to be treated as purely classical particles. The RMSA technique previously proposed by Hansen and Hayter (6) to re-size the macro-ions at low density is actually founded on this similar physical picture. The method has been widely applied in different contexts to study the highly charged colloidal \( S(q) \). Now, in connection with this rescaling scheme, we should mention one more characteristic of the charged colloidal dispersion since it marks the basic difference between the RMSA and the Coulomb hole of quasiparticles. In the colloidal solution, although the macro-ions can be handled by the rescaling technique, such Coulomb restriction does not apply to describe the correlations between macro-ions and counter-ions for their charges are opposite in sign. As far as Coulomb correlations are concerned, the counter-ions can always enter the prohibited voids induced among the strongly charged macroparticles and manifest their attraction with them. This is the well-known problem of the non-additive radii correlations in the integral equation theory (26) and one should be on guard when implementing the size rescaling of macro-ions in particular within the multicomponent MSA closure. In the present work, the same problem, however, does not arise since the mathematical structure of the effective one component fluid model of Belloni naturally permits the non-additive radii prob-

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3) Incidentally, the equivalence between the Fermi liquid theory and the many electron theory discussed within the context of the electronic spin paramagnetic susceptibility is given recently (Lai, S.K., J. Non-Cryst. Solids 205/207, 342-346 (1996)).
lem to be resolved reasonably, albeit approximately (see Lai, Wang and Wang (13) for more details). All of our results given above have taken proper consideration of rescaling if \( g(r=\sigma_0^+)<0 \). In Fig. 3(a) we include, for comparison, the \( f_c(q) \neq 0 \) for the case \( \eta=0.104 \) obtained by solving Eqs. (7) and (8) without effecting the size rescaling on its associated \( g(r) \) whose \( S(q) \) is displayed as solid circles in Fig. 3(b); these figures illuminate the significant differences and hence the uncertainties in these two quantities. Note that the higher-\( \eta \) case does not need rescaling since \( g(r=\sigma_0^+) > 0 \).

Finally, we should elaborate further on the LGLG re-entrant behavior given in Figs. 1(b)-1(d). As pointed out above, our calculation predicts the LGLG re-entrant phenomenon for any \( \kappa \lesssim 3.8 \) and that this re-entrant characteristic disappears for \( \sigma_0 \) above a critical size \( \sigma_M \). Such a LGLG re-entrant behavior is not uncommon and has been predicted also for the extremely low-density Coulomb fluid at a sufficiently low temperature (27). In particular, the kind of the GLG re-entrant behavior below \( \sigma_M \) bears a close resemblance to a two-phase region whose occurrence is attributed in the equilibrium thermodynamic theory to the structure-independent energies (the self-interaction of macro-ions with their clouds of counter-ions) contributed negatively to the DLVO-based free energy (28). Perhaps, a more realistic aspect of the LGLG re-entrant phenomenon is its density dependence whose effect on the dynamical correlations has already been studied by computer simulation for an aqueous solution of charged rodlike macromolecules (29). Here, for spherical charged colloids, it is clearly seen that as the \( \kappa \) increases from 2.65 (solid circles) to 3 (open circles) (see Figs. 1(c) and 1(d)), the GLG supercooled liquid region decreases displaying a feature which can be interpreted in terms of the subtle competition between the hard core factor and the electrostatic factor comprising the strength of interaction (the \((Z_0 X)^2\) term) as well as the range of interaction (parameter \( \kappa \)). Generally, this GLG liquid domain below \( \sigma_M \) (bounded between \( \sigma_0=\sigma_m \) and the phase boundary) decreases with increasing \( \kappa \) until at \( \kappa \simeq 3.8 \) where all colloidal particles with a size \( \sigma_0=\sigma_M \approx 630 \) Å show a linearly decrease in the macro-ion charge \( Z_0 \) (reducing approximately from 350e to 160e) for \( \eta \) varies approximately from 0.15 to 0.4. It should be mentioned moreover that the magnitude of the critical point \( \sigma_M \) depends sensitively on the screening parameter \( \kappa \). It would be interesting if all of these predictions can be verified experimentally. In summary, we should reiterate that by imposing the condition of charge neutrality on the macro-ions and counter-ions so that the \( \sigma_0 \) and \( Z_0 \) are adjusted to ensure self-consistency in the definition of \( \kappa \), we are in fact working on an extensive phase diagram of the charge-stabilized colloidal dispersion possessing any \( \sigma_0 \) and \( Z_0 \). With slight and straightforward modification, the results can be applied to study more realistic colloidal liquids such as a monodisperse solution of polystyrene charged spheres with added salts as reported recently by Lai et al. (13,14).

**IV. CONCLUSION**
The RMSA in conjunction with the idealized MCT is applied to locate the liquid-glass transition phase boundary for a hard-core Yukawa potential widely used in the colloidal community to model charge-stabilized colloids. It is found that in going from weak-to-strong counter-ion screening the ergodic region of the \( \eta - \gamma \) phase diagram increases. This is a general feature of the hard-core Yukawa potential and is independent of any model employed, either the DLVO or the Belloni model. Within the context of the Belloni model applied to quantify \( \gamma \), our calculations based on the MCT predict the (salt-free) case \( \gamma \approx 3.8 \) marking the inception of the LGLG re-entrant behavior. To scrutinize the re-entrant phenomenon more closely, we examine the \( f_c(q) \), \( S(q) \) and their spatial counterparts and conclude from our analysis that in a given screening condition both the geometric restriction and the Coulombic coupling are equally effective in driving the charge-stabilized colloids to a structurally arrested phase and hence in manifesting the idealized liquid-glass transition. A remarkable feature of the LGLG re-entrant behavior predicted here is that, for any \( \gamma \lesssim 3.8 \), there exists two critical sizes, \( \sigma_m \) and \( \sigma_M \), demarcating the LGLG characteristic which vanishes for any \( \gamma > 3.8 \).

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