Nonergodic states of charged colloidal suspensions: Repulsive and attractive glasses and gels

Hajime Tanaka,[1] Jacques Meunier,[2] and Daniel Bonn[2,3]

[1]*Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan*
[2]*Laboratoire de Physique Statistique, Ecole Normale Supérieure, 24 rue Lhomond, 75005 Paris, France*
[3]*Van der Waals-Zeeman Institute, Valckenierstraat 65, 1018XE Amsterdam, The Netherlands*

Two types of isotropic disordered nonergodic states exist in colloidal suspensions: glasses and gels. The difference between the two is that the nonergodicity, or elasticity, of gel stems from the existence of a percolated network, while that of glass stems from caging effects. Despite this clear difference in the origin of nonergodicity, it is not straightforward to distinguish the two states in a clear manner. Taking a Laponite suspension as an explicit example, we propose a general phase diagram for charged colloidal systems. It follows that a transition from the glass to the gel state can be induced by changing the interparticle interactions from predominantly repulsive to attractive. This originates from the competition between electrostatic Coulomb repulsion and van der Waals attraction. If the repulsion dominates, the system forms a Wigner glass, while in a predominantly attractive situation it forms a gel. In the intermediate region, where both repulsive and attractive interactions play roles, it may form an attractive glass.

I. INTRODUCTION

Both colloidal gels and glasses are interesting solid (or jammed [1–3]) states of soft condensed matter with static elasticity. They are similar in the sense that both are in a nonergodic disordered state [4]. The difference between gel and glass is rather clear in their ideal limits. The elasticity of gel stems from percolated infinite network [5], while that of glass stems from caging effects [6]. A gel is inhomogeneous over the characteristic length scale of the network, ξ, and has a hierarchic structural organization, while a glass is essentially homogeneous for interparticle distances $\bar{l}$, a few times larger than the radius. Despite this clear difference in the ideal limits, it may not be straightforward to distinguish them experimentally [7].

As an explicit example, we consider here suspensions of charged colloidal clay particles, Laponite. In suspension, when the particle concentration exceeds a few percent, Laponite forms a very uniform, isotropic soft solid state. The isotropic nonergodic state has recently attracted considerable attention. It has been proposed to be a colloidal glass [7–10], but is also very often called a colloidal gel [11–18], a situation that is quite confusing. In particular, the kinetics of "solidification" or jamming should be called "aging" for glasses, but "gelation" for gel formation. These two processes are physically quite different. At the same time, however, both processes can be characterized by the appearance of elasticity and nonergodicity.

In this paper, we consider the differences and similarities between glasses and gels, and how we can distinguish the two states, employing Laponite suspensions as a concrete example.

II. CLASSIFICATION OF DISORDERED STATES OF COLLOIDAL SUSPENSIONS

Before starting the discussion, we need to make clear definitions of the various nonergodic and ergodic states observed in colloidal suspensions (see also Fig. 1).

A. Classification of nonergodic disordered states in colloidal suspensions

1. Attractive gel

We define gel as a multicomponent fluid, which satisfies the following requirements.

(i) It is in a nonergodic disordered state.

(ii) At least one of its components forms an infinite elastic network and thus is percolated mechanically. For the network to be elastic on a typical observation time scale, the necessary condition is that the lifetime of junction point is sufficiently long, or $E/k_BT \gg 1$ (where E is the depth of the attractive potential) [19].

(iii) The characteristic length of the network between the two adjacent junctions, ξ, is much larger than the size of the colloids.

2. Attractive and repulsive glass

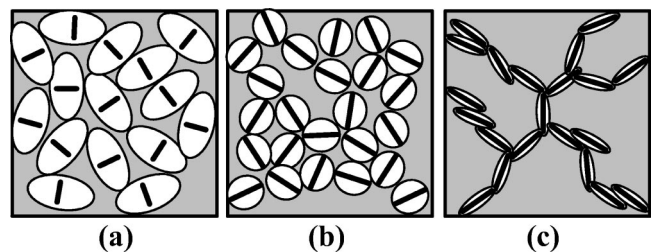Encompassing both attractive and repulsive glasses, we define colloidal glass as (i) a colloidal system in a noner-

FIG. 1. Schematic figures representing repulsive ("Wigner") colloidal glass (a), attractive glass (b), and gel (c). Each thick line represents a Laponite disk, while a white ellipsoid represents the range of electrostatic repulsions. In (a), long-range electrostatic repulsions dominate. In (b), attractive interactions affect the spatial distribution (i.e., the structure factor) but repulsive interactions still play the predominant role in the slow dynamics of the system. In (c), attractive interactions play a dominant role; a percolated network forms, which gives the system its elasticity.

godic disordered state, (ii) whose elasticity primarily originates from caging effects, and (iii) whose characteristic length scale is of the order of the interparticle distance $\bar{l}$; there is no static inhomogeneity beyond $\bar{l}$. The repulsive glass, the conventional glassy state of colloidal systems with hard-core repulsive interactions, is perhaps easier to understand than the attractive glass. If crystallization is avoided, above a certain volume fraction of particles the system will jam, i.e., reorganization of the structure becomes exceedingly difficult. The result is that the system will fall out of equilibrium: a glassy state is formed. An attractive glass should become possible if the depth of the attractive well E is in the order of k_BT and particle concentration ϕ is still high enough for the system to "jam." We underline therefore that even in "attractive glass," repulsive (steric) interactions play the main role, which makes it different from the gel state discussed above.

B. Ergodic states in colloidal suspensions

An ergodic-nonergodic transition in colloidal glass is usually called a liquid-glass transition. On the other hand, an ergodic-nonergodic transition in gel is called a sol-gel transition. Both transitions can be induced by changing the concentration of colloids, the interactions (e.g., by controlling the Debye screening length), and/or the temperature. This suggests that there may also be a significant difference even in the ergodic liquid state. A sol state would then be characterized by the presence of clusters with a finite lifetime and may consequently be inhomogeneous, which crucially differs from a homogeneous liquid state. This indicates the possibility of a liquid-to-sol transition in an ergodic regime.

III. SIMILARITIES AND DIFFERENCES BETWEEN GELS AND GLASSES

Gels and glasses are similar in their mechanical properties and dynamics. Density fluctuations in these systems consist of two modes: small-amplitude dynamically fluctuating and frozen-in components. In an ergodic state, the former is called (fast-)β mode while the latter is called α mode, using the terminology of dynamics of supercooled liquids [6]. Approaching the ergodic-nonergodic transition, the relaxation time of the α mode diverges, while that of the β mode is basically unchanged. Experimentally, the dynamical behavior of glasses and gels can be quite similar [4].

However, there are crucial differences. The gel intrinsically has a hierarchic structure. Its elementary mechanical unit consists usually of chainlike aggregates of particles and is therefore much larger than the particle size. On the other hand, the elementary mechanical unit of glass is a particle itself. Quite generally, the elasticity of a material is given by the following fundamental relation that holds for both repulsive and attractive systems:

$$G \sim k_BT_c/l^3, \tag{1}$$

where G is the elastic (shear) modulus, l is the characteristic length of the elementary mechanical unit, and T_c is the characteristic temperature above which the system loses the elas-

ticity. More strictly speaking, l gives the range of the elastic interactions. In general, glasses are much more rigid than gel for the same composition because l is much smaller for a typical glass than it is for a gel ($\xi \gg \bar{l}$).

For the colloidal systems we consider here, provided there is a significant difference in l between glasses and gels, it is straightforward to distinguish them in terms of the above general relationship. However, when l becomes comparable for glassy and gel states, it is difficult to distinguish them by mechanical measurements.

IV. AN EXPLICIT EXAMPLE: THE PHASE DIAGRAM OF LAPONITE SUSPENSIONS

Before discussing the phase behavior, we briefly describe Laponite. Laponite is a synthetic clay colloid with a disk shape; its diameter d is $\sim$30 nm and its thickness h is $\sim$1 nm. The density ρ_L is about 2.65 g/cm^3. Laponite suspensions are known to form a nematic phase above $\phi > 4$ wt % [20]. We limit our discussion here to the isotropic region.

The particles are negatively charged at pH$=10$; we consider only pH$=10$ here; the high pH ensures the chemical stability of the particles. The charge density is higher on the faces of a disk than its side, which may play an important role in gel formation. The number of surface charges on a face is the order of 10^3e. To control the interparticle interactions, one may add salt (NaCl) to the suspensions. Increasing the ionic strength I (increasing salt concentration ϕ_s) screens the Coulomb interactions between the disk. The interparticle electrostatic potential may be modeled by a Yukawa potential $\exp(-\kappa r)/r$, with κ being the inverse of the Debye screening length $l_D = \kappa^{-1}$. Here $\kappa = (\epsilon k_BT/2e^2)I^{1/2}$, with ϵ being the dielectric constant, e the electron charge, and k_B Boltzmann's constant. Thus, l_D is a decreasing function of the ionic strength I. Upon increasing I, the electrostatic potential is screened more strongly; eventually van der Waals attractions may prevail over the electrostatic repulsion, leading to the colloids sticking together, i.e., gel formation.

We will argue here that the competition between (anisotropic) long-range repulsions and van der Waals attractions induces the sequential transition between a repulsive glass, an attractive glass, and a gel in Laponite suspensions. Schematic drawings representing these three states are shown in Fig. 1.

Dependence of the composition of ergodic-nonergodic transition on the ionic strength

1. Colloidal glass

We previously proposed that the nonergodic state that forms at or below $I \approx 10^{-4}M$ is a colloidal Wigner glass [7,8], although the volume fraction is extremely low ($\phi \approx 0.01$), compared to "normal" (spherical) colloids for which glasses are obtained for $\phi \approx 0.5$. This can be attributed to the electrostatic interactions, since the particles are heavily

charged. This electrostatic repulsion leads to an effective volume fraction that is much larger than one would expect from their size alone.

The effective volume per particle can then be estimated as $(4/3)\pi d^2 l_D$ by adding the Debye length to the particle size. If this exceeds the volume per particle, which is estimated as $\pi d^2 h/\phi$, the free volume is not available and thus a glassy state can be formed. The volume fraction for the liquid-glass transition is given by $\phi_{eff} \approx 0.5$ and thus varies as $\phi_{lg} \sim h/l_D \propto I^{1/2}$. This means that if we add salt, we shift the liquid-glass transition to a higher volume fraction of particles. This is in strong contrast with gelation, for which adding salt shifts the sol-gel transition to lower volume fraction. Thus, we can check whether a system is glass or gel by simply looking at the sign of $d\phi_{lg}/dI$.

Measurement of the phase diagram in the volume fraction ϕ/ionic strength I plane allows us to locate the transition between liquid and glassy states. The experimentally determined volume fraction for which the glass forms ϕ_{lg} can then be compared with the above prediction: $\phi_{lg} \propto I^{1/2}$. This prediction was indeed confirmed experimentally for $I \leqslant 10^{-4}M$ by Levitz *et al.* [9], which strongly supports our previous proposal [7,8] that the Laponite system forms a colloidal glass stabilized by electrostatic repulsions for $I \leqslant 10^{-4}M$. The picture based on the electrostatic repulsion between the charged particles provides us with a picture of colloidal glass of relatively densely packed particles with an effective size determined by the Debye screening length.

For $\phi \sim 0.01$, the interparticle distance $\bar{l}$ is estimated to be in the order of 30 nm. Then the elasticity is estimated from Eq. (1) to be about 100 N/m^2, which is roughly the same order as the experimentally observed value. This also supports the picture that a Laponite suspension whose ionic strength is less than $I = 10^{-4}M$ is a glass-forming liquid.

2. Colloidal gel

The transition line between fluid and nonequilibrium states changes dramatically for $I > 10^{-3}M$: the volume fraction separating the liquid and the nonergodic state decreases with an increase in I [11,21]. As already mentioned above, this suggests that the nonergodic state is a gel state: the more salt one adds, the easier it is to form a gel, i.e., gelation happens for a lower ϕ.

Mourchid *et al.* [11,21] studied the sol-gel transition in detail. They found ample evidence that suggests that the liquid-solid transition observed above $I \geqslant 10^{-3}M$ is the sol-gel transition.

(i) The viscosity diverges while approaching to the sol-gel transition composition ϕ_{sg} with an increase in ϕ at a constant ionic strength in a liquid domain as

$$\eta = \eta_{water}(1 - \phi/\phi_{sg})^{-\mu}, \tag{2}$$

where η_{water} is the viscosity of water and $\mu = 0.9$. This is a characteristic feature of sol-gel transition.

(ii) In the elastic region, the elastic modulus G' was found to increase with ϕ as
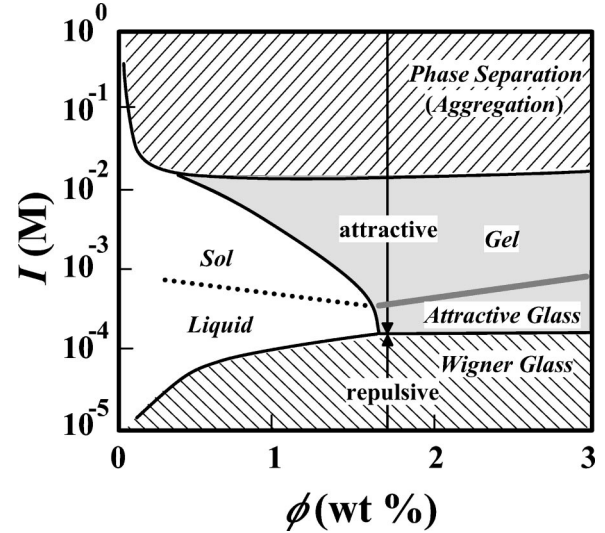

FIG. 2. Phase diagram of Laponite suspensions. Coexistence of phase separation and gelation is characteristic of a system that forms "physical" gel. Larger I means shorter κ, or the weaker electrostatic repulsion. Strictly speaking, this should be called a state diagram since a system is not in an equilibrium state.

$$G' = A(\phi - \phi_{sg})^v, \tag{3}$$

where $v = 2.35$. This is also a characteristic feature of the elastic behavior of gel.

3. Attractive glass?

In the intermediate region between $I = 10^{-3}M$ and $I = 10^{-4}M$, here is hardly any dependence on I of the threshold composition separating an ergodic from a nonergodic state (see Fig. 2); both attractive and repulsive interactions should be important, suggesting that this may be a region where an attractive glass forms.

4. Phase separation

At a very high ionic strength, a macroscopically homogeneous state becomes unstable and a system phase-separates possibly competing with gelation. Such behavior is also observed for suspensions of charged spherical colloids [22]. This competition between phase separation and gelation is generic to dynamically asymmetric mixtures such as polymer solutions and colloidal suspensions [23].

Based on these considerations, we propose a phase diagram that should be generic to charged colloidal suspensions (when ordered states such as crystals and liquid crystals are not formed). The phase diagram specific to Laponite suspensions is schematically shown in Fig. 2. We point out that this phase diagram has common features to that of polymer-doped colloidal suspensions [24–27], which is schematically shown in Fig. 3. The primary difference between the two phase diagrams is the composition range: ϕ_{lg} exists even below 1% for Laponite suspensions, while it exists above 50% for polymer-doped colloidal suspensions.
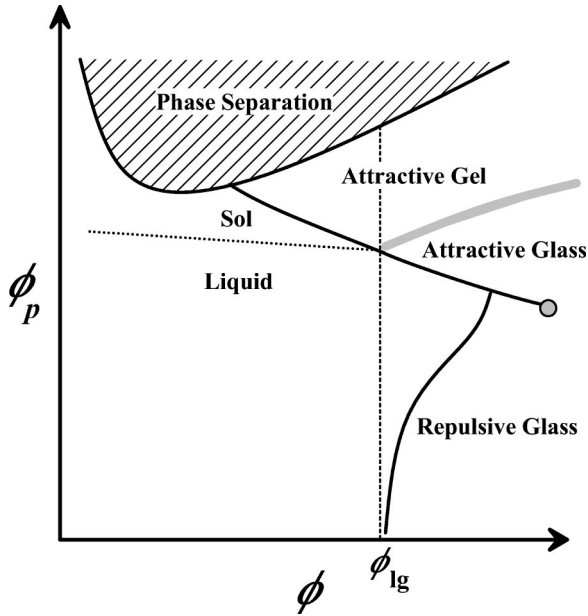
FIG. 3. Phase diagram of (uncharged) colloidal suspensions (see also Refs. [24–27]). Larger concentration of polymers ϕ_p means the stronger attractive interactions. The shaded circle represents the critical point of the repulsive glass-attractive glass transition. In this system, repulsive interactions are due to hard-core potentials. The absence of long-range repulsive interactions is a key factor creating the large difference in the phase diagram between Laponite suspensions and polymer-doped colloidal suspensions.

V. HOW CAN WE DISTINGUISH GLASSES AND GELS EXPERIMENTALLY?

An obvious difference between gels and glasses is structural: the static structure factor $S(q)$ should be significantly different, as is schematically shown in Fig. 4. Thus, $S(q)$, as measurable in scattering experiments, can be used as a fingerprint to distinguish gel from glass. For gels, there is no
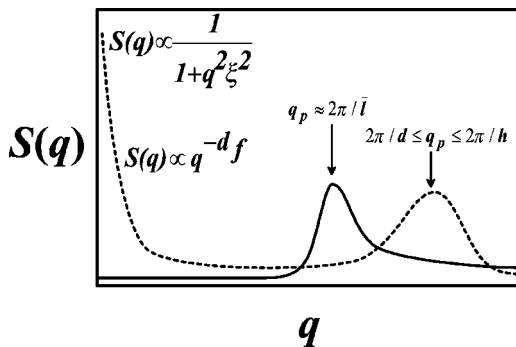

FIG. 4. Characteristic features of $S(q)$ for gel (dashed line) and glass (solid line). The peak at the high q side of gel may be located between $2\pi/d$ and $2\pi/h$ for a Laponite suspension. Here we note that an unstable gel (or phase-separating gel) should have a peak at the low q side that is followed by the power-law tail (instead of the Ornstein-Zernike-like behavior) [3], reflecting the existence of the characteristic size of the growing network structure. This is characteristic feature of spinodal decomposition [22,23].

distinct peak at the wave number corresponding to the inverse of $\bar{l}$ (the interparticle distance). Gel systems exhibit a peak at larger q, reflecting the short interparticle distance between aggregating particles, and also excess scattering at low q, reflecting the correlation of the concentration fluctuations associated with the network structure (see Fig. 4). For $q\xi < 1$, this excess scattering is described by the Ornstein-Zernike form for a stable gel as

$$S(q) \sim 1/(1+q^2\xi^2). \tag{4}$$

For $q\xi \gg 1 \gg qd$, there would be a power-law tail in the high q side of $S(q)$, reflecting the fractal nature of the network structure:

$$S(q) \sim q^{-d_f}, \tag{5}$$

where d_f is the fractal dimension [5].

For colloidal glasses, on the other hand, $S(q)$ should have a peak around $q=2\pi/\bar{l}$ and no characteristic features at lower q because of its homogeneity beyond the length scale of $\bar{l}$ (see Fig. 4).

Thus, there are crucial differences in the characteristic features of $S(q)$ between gel and glass, which can be used as a fingerprint to distinguish gel and glass. Below we apply this criterion to reveal the nature of nonergodic states of Laponite suspensions.

A. Gel regime

For Laponite suspensions with $I \geq 10^{-3}M$ a clear q dependence of $S(q)$ indicative of the fractal structure was observed by Pignon *et al.* [12–14] and by Nicolai and Cocard [18]. Pignon *et al.* [12–14] determined the fractal dimension for Laponite suspensions at $I \geq 10^{-3}M$. Nicolai and Cocard measured the correlation length ξ. They found that it increases with the gelation time t_w and with I, but decreases with ϕ (see Fig. 5). All these features are consistent with the hypothesis that Laponite suspensions at $I \geq 10^{-3}M$ form a gel.

An additional observation by Nicolai and Cocard [18] is that, due to the increase in the correlation length, the intensity of the scattered light S also increases with t_w and with I (see Fig. 6). This constitutes, as we will see below, an important difference with glasses.

B. Glass regime

The nature of a nonergodic state below $I=10^{-3}M$ is subtler. A high q power-law tail in $S(q)$ suggestive of a fractal structure was reported around $I=10^{-4}M$ [16,17]. Hence, this nonergodic state was also believed to be a gel. However, we have recently shown that this q dependence of $S(q)$ around $I=10^{-4}M$ is spurious: it is due to incompletely dissolved aggregates of particles. These aggregates can be removed or destroyed simply by filtering the suspensions without affecting the elasticity. Hence the observed ''structure'' is not at the basis of the elasticity. A filtered sample exhibits no q dependence of $S(q)$ during the entire process of aging.
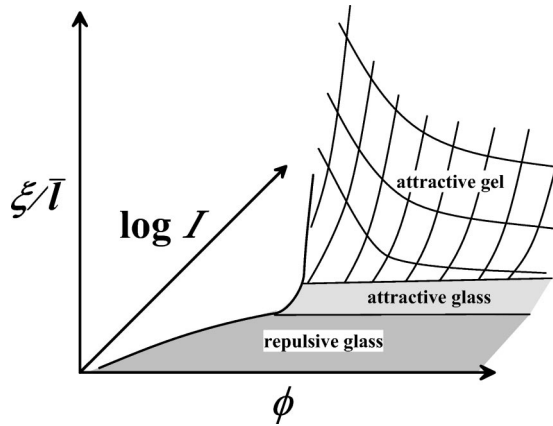
FIG. 5. Relationship among the characteristic length ξ scaled by $\bar{l}$, $\xi/\bar{l}$, the ionic strength I, and the volume fraction of colloid ϕ. In the repulsive glass regime, the characteristic length is primarily determined solely by ϕ, which is roughly equal to $\bar{l}$, while in the attractive gel regime it steeply increases with I.

This indicates that concentration fluctuations are not spatially correlated in the measured q range and that the system is homogeneous beyond the length scale of $\bar{l}$. Thus, we concluded that a nonergodic state at $I \sim 10^{-4}M$ is a Wigner glass. The absence of q dependence of $S(q)$ was also confirmed by Knaebel et al. [10].

Another characteristic feature of $S(q)$ of glass is in the high q region (see Fig. 4). Levitz et al. [9] found an amorphous peak around $q = 2\pi/\bar{l}$ in Laponite suspensions with low ionic strength, which supports that a Laponite suspension is a glass-forming liquid for $I \lesssim 10^{-4}M$. This picture
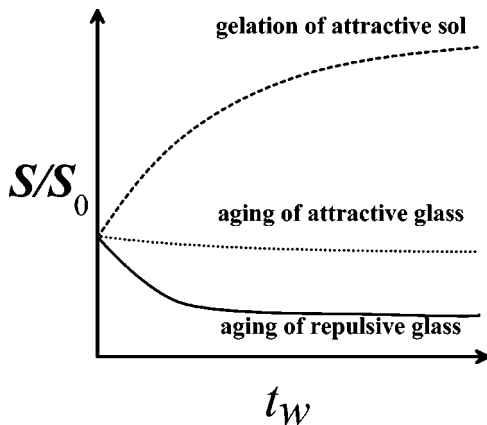

FIG. 6. Temporal change in the scattering intensity normalized by that at $t_w = 0$, S/S_0 for Laponite suspensions. For gelation in the region of the attractive interaction S/S_0 increases with the waiting time t_w, reflecting the increase in the size of aggregates and the resulting increase in the correlation length. For the aging of the glassy state, S/S_0 decreases with time, reflecting an increase in the repulsive interaction (a decrease in the osmotic compressibility), which is induced by the cooperative redistribution of counter and salt ions and charged colloids.

is also supported by real-space electron microscopy observations by Mourchid et al. [11] that show that most of the particles are isolated and are well apart from each other.

Finally, the intensity of the scattered light S also decreases with t_w (see Fig. 6). For colloidal suspensions, the scattered intensity is proportional to the osmotic compressibility $\sim d\phi/d\Pi$, with Π the osmotic pressure. The decrease in scattering intensity signals a decrease in compressibility, consistent with the formation of a "solid like" glassy phase. Thus, the sign of $\partial S/\partial t$ can also be used as a fingerprint to distinguish glasses from gels. Direct measurement of the osmotic pressure [20] also clearly shows that the interaction between Laponite particles in this region of the phase diagram is strongly repulsive.

C. Attractive glass

Avery and Ramsay [17] show that although their samples become elastic, there is no gel-like structure for salinities up to $I \sim 10^{-3}M$. In addition, there is no evident increase in the scattering intensity during the aging and no clear q dependence in the high q region reminiscent of the fractal structure of gel. This indicates that we are dealing with a glassy state. The location of the liquid-glass transition line in phase diagram, however, disagrees with the assumption that it is a simple repulsive glassy state: at $I \sim 10^{-3}M$ the transition happens at much lower volume fractions than can be anticipated from $\phi_{lg} \propto I^{1/2}$. Therefore, this region of the phase diagram appears to be a glassy state, for which interparticle attractions are very important. We tentatively conclude that this region corresponds to an attractive glass (see Figs. 1 and 2), although further detailed study is necessary to confirm its existence and to elucidate the nature of the repulsive glass-attractive glass transition.

D. Suspensions and sols

An increase in the cluster size with I in a liquid state was also reported by Bakk et al. [28]. They also point out that particles may exist without aggregation without salt, or for $I = 10^{-4}M$. This indicates that an ergodic state at $I \lesssim 10^{-4}M$ is a liquid and "not" a sol, different from the case of $I \gtrsim 10^{-3}M$ described above. Nicolai and Cocard [18] have also reported excess scattering (i.e., the existence of clusters) in the liquid state at rather high salt. Therefore, a signature of the sol-gel transition may already be present at high salt even in the liquid phase, whereas the liquid-glass transition has no structural precursors in the liquid phase (see Fig. 2).

VI. SUMMARY

In summary, we have discussed the differences and similarities between glasses and gels and have proposed a general phase diagram for charged colloidal suspensions as a function of ionic strength. The phase diagram suggests the existence of a transition between repulsive and attractive glassy states, and between an attractive glass and a gel state. In addition, there may be a difference (and hence maybe a

transition) between a homogeneous liquid dispersion and a sol (in the sense of a precursor to the gel phase).

A repulsive glass-attractive glass transition in colloidal suspensions was recently reported in polymer-doped colloidal suspensions and has since then attracted considerable attention [24–27]. Our study suggests an interesting connection between the phase behavior of charged colloidal suspensions (see Fig. 2) and that of polymer-doped colloidal suspensions (see Fig. 3).

[1] A.J. Liu and S.R. Nagel, Nature (London) **396**, 21 (1998).

[2] V. Trappe, V. Prasad, L. Cipelletti, P.N. Serge, and D.A. Weitz, Nature (London) **411**, 772 (2001).

[3] L. Cipelletti and L. Ramos, Curr. Opin. Colloid Interface Sci. **7**, 228 (2002).

[4] S.Z. Ren and C.M. Sorensen, Phys. Rev. Lett. **70**, 1727 (1993).

[5] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[6] E. Donth, *The Glass Transition* (Springer-Verlag, Berlin, 2001).

[7] D. Bonn, H. Kellay, H. Tanaka, G. Wegdam, and J. Meunier, Langmuir **15**, 7534 (1999).

[8] D. Bonn, H. Tanaka, G. Wegdam, H. Kellay, and J. Meunier, Europhys. Lett. **45**, 52 (1998).

[9] R. Levitz, E. Lecolier, A. Mourchid, A. Delville, and S. Lyonnard, Europhys. Lett. **49**, 672 (2000).

[10] A. Knaebel, M. Bellour, J.-P. Munch, V. Viasnoff, F. Lequeux, and J.L. Harden, Europhys. Lett. **52**, 73 (2000).

[11] A. Mourchid, A. Delville, J. Lambard, E. Lecolier, and P. Levitz, Langmuir **11**, 1942 (1995); A. Mourchid, A. Delville, and P. Levitz, Faraday Discuss. **101**, 275 (1995).

[12] F. Pignon, J.-M. Piau, and A. Magnin, Phys. Rev. Lett. **76**, 4857 (1996).

[13] F. Pignon, A. Magnin, and J.-M. Piau, Phys. Rev. Lett. **79**, 4689 (1997).

[14] F. Pignon, A. Magnin, J.-M. Piau, B. Cabane, P. Lindner, and O. Diat, Phys. Rev. E **56**, 3281 (1997).

[15] M. Kroon, G.H. Wegdam, and R. Sprik, Phys. Rev. E **54**, 6541 (1996).

[16] M. Kroon, W.L. Vos, and G.H. Wegdam, Phys. Rev. E **57**, 1962 (1998).

[17] R.G. Avery and J.D.F. Ramsay, J. Colloid Interface Sci. **109**, 448 (1986).

[18] T. Nicolai and S. Cocard, Langmuir **16**, 8189 (2000); Eur. Phys. J. E **5**, 221 (2001).

[19] In relation to this, we should mention "reconnectable gel," which is a gel in the sense that it has a percolated topological network, but it can flow by reconnecting the network. The network is "topological" but not "elastic" for this case. This is the case for the network whose junction point has a rather short lifetime due to the weakness of attractive interactions. We do not consider such a gel, since it is basically an ergodic system.

[20] S. Bhatia, J. Barker, and A. Mourchid, Langmuir **19**, 532 (2003).

[21] A. Mourchid, E. Lécolier, H. Van Damme, and P. Levitz, Langmuir **14**, 4718 (1998).

[22] L. Cipelletti, S. Manley, R.C. Ball, and D.A. Weitz, Phys. Rev. Lett. **84**, 2275 (2000).

[23] H. Tanaka, Phys. Rev. E **59**, 6842 (1999); H. Tanaka, J. Phys.: Condens. Matter **12**, R207 (2000).

[24] T. Eckert and E. Bartsch, Phys. Rev. Lett. **89**, 125701 (2002).

[25] K.N. Pham, A.M. Puertas, J. Bergenholtz, S.U. Egelhaaf, A. Moussaïd, P.N. Pusey, A.B. Schofield, M.E. Cates, M. Fuchs, and W.C.K. Poon, Science **296**, 104 (2002).

[26] F. Sciortino, Nat. Mater. **1**, 145 (2002).

[27] K.A. Dawson, Curr. Opin. Colloid Interface Sci. **7**, 218 (2002).

[28] A. Bakk, J.O. Fossum, G.J. da Silva, H.M. Adland, A. Mikkelsen, and A. Elgsaeter, Phys. Rev. E **65**, 021407 (2002).