Gelation in Model Colloid–Polymer Mixtures

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Mode coupling theory (MCT) is used to model gel formation in mixtures of colloidal particles and nonadsorbing polymer. The polymer induces an effective, short-range attraction among the colloids, which is modeled by a depletion attraction of the Asakura–Oosawa form. This enables the MCT to be solved analytically for dilute systems, leading to a prediction, free of adjustable parameters, of the location of the gel boundary in the phase diagram. For concentrated systems, a simple mapping is suggested that makes a previous theory for Yukawa interactions applicable to colloid–polymer mixtures. The results are compared against Monte Carlo simulations and experiments on model systems. Excellent agreement is observed at high colloid concentrations, where the theory predicts melting of glassy structures on addition of small amounts of polymer. Further addition of polymer causes gelation, in semiquantitative accord with experimental data at moderate to high colloid concentrations. However, at lower concentrations the theory is unable to capture the onset of transient gelation.

1. Introduction

Aggregation in an otherwise stable colloidal dispersion can be induced by adding a sufficient amount of nonadsorbing polymer. For small polymer–colloid size ratios, the main effect is well-known: entropy dictates that volumes between colloidal particles separated by distances less than roughly twice the polymer radius of gyration, r_g , are depleted of polymer, causing an osmotic imbalance to which the colloidal particles respond by spending more time in close proximity to one another. This effect can be approximately accounted for by viewing the mixture as a one-component system in which the colloids interact via an effective attraction mediated by the polymer, as suggested first by Asakura and Oosawa (AO)^{1,2} and later by Vrij.³

Colloid–polymer mixtures that in large fulfill the fairly restrictive requirements of the AO theory have been realized in practice.⁴ Sterically stabilized poly(methyl-methacrylate) (PMMA) spheres behave as near-perfect hard spheres when dispersed in *cis*-decalin,⁵ which is a slightly-better-than- θ solvent at room temperature for free polystyrene polymer. The phase diagrams of this model colloid–polymer mixture have been studied systematically and in great detail as functions of polymer concentration and polymer–colloid size ratio;^{6–10} these

studies confirmed the sensitivity of the phase behavior to the size disparity between the colloids and polymer coils noted in earlier work^{11–14} and further revealed, among several factors, the role of polymer partitioning and three-phase coexistence. In the absence of polymer, the phase diagram conforms to that of hard-sphere dispersions.¹⁵ Crystals begin to nucleate in the fluid at a colloid volume fraction $\phi \approx 0.494$, leading to completely crystalline samples beyond $\phi \approx 0.545$. However, homogeneous nucleation of crystals ceases at $\phi \approx 0.58$, which has been interpreted as being caused either by a glass transition^{16,17} or by free energy effects modulated by the size polydispersity of the synthetic colloids.¹⁸ On addition of nonadsorbing polystyrene, the fluid–crystal coexistence region expands dramatically for small values of ξ , the polymer–colloid size ratio,^{6,7} whereas for somewhat larger ξ the phase diagrams qualitatively resemble those familiar from simple liquids.⁷

Equilibrium statistical mechanical theories^{11,19–21} and computer simulations^{22,23} capture nearly all the features of the experimental phase diagrams. However, a sufficient dosage of low molecular weight polymer (such that ξ is small) suppresses crystallization, leaving instead what appears to be incompletely equilibrated solids,^{6,9} including

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(1) Asakura, S.; Oosawa, F. *J. Chem. Phys.* **1954**, *22*, 1255.

(2) Asakura, S.; Oosawa, F. *J. Polym. Sci.* **1958**, *33*, 183.

(3) Vrij, A. *Pure Appl. Chem.* **1976**, *48*, 471.

(4) Poon, W. C. K. *J. Phys.: Condens. Matter* **2002**, *14*, R859.

(5) Auer, S.; Poon, W. C. K.; Frenkel, D. *Phys. Rev. E*, in press.

(6) Poon, W. C. K.; Selfe, J. S.; Robertson, M. B.; Ilett, S. M.; Pirie, A. D.; Pusey, P. N. *J. Phys. II (Paris)* **1993**, *3*, 1075.

(7) Ilett, S. M.; Orrock, A.; Poon, W. C. K.; Pusey, P. N. *Phys. Rev. E* **1995**, *51*, 1344.

(8) Poon, W. C. K.; Pirie, A. D.; Haw, M. D.; Pusey, P. N. *Physica A* **1997**, *235*, 110.

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

(10) Poon, W. C. K.; Pham, K. N.; Egelhaaf, S. U.; Pusey, P. N. *J. Phys.: Condens. Matter* **2003**, *15*, S269.

(11) Gast, A. P.; Hall, C. K.; Russel, W. B. *J. Colloid Interface Sci.* **1983**, *96*, 251.

(12) Gast, A. P.; Hall, C. K.; Russel, W. B. *Faraday Discuss.* **1983**, *76*, 189.

(13) Gast, A. P.; Russel, W. B.; Hall, C. K. *J. Colloid Interface Sci.* **1986**, *109*, 161.

(14) Vincent, B.; Edwards, J.; Emmett, S.; Croot, R. *Colloids Surf.* **1988**, *31*, 267.

(15) Pusey, P. N.; van Megen, W. *Nature* **1986**, *320*, 340.

(16) Pusey, P. N.; van Megen, W. *Phys. Rev. Lett.* **1987**, *59*, 2083.

(17) van Megen, W.; Pusey, P. N. *Phys. Rev. A* **1991**, *43*, 5429.

(18) Auer, S.; Frenkel, D. *Nature* **2001**, *413*, 711.

(19) Lekkerkerker, H. N. W.; Poon, W. C. K.; Pusey, P. N.; Stroobants, A.; Warren, P. B. *Europhys. Lett.* **1992**, *20*, 559.

(20) Warren, P. B.; Ilett, S. M.; Poon, W. C. K. *Phys. Rev. E* **1995**, *52*, 5205.

(21) Ramakrishnan, S.; Fuchs, M.; Schweizer, K. S.; Zukoski, C. F. *J. Chem. Phys.* **2002**, *116*, 2201.

(22) Meijer, E. J.; Frenkel, D. *J. Chem. Phys.* **1994**, *100*, 6873.

(23) Dijkstra, M.; Brader, J. M.; Evans, R. *J. Phys.: Condens. Matter* **1999**, *11*, 10079.

gels, where one expects fluid–crystal coexistence from equilibrium theory. Intriguingly, similar observations have been made for several different colloidal systems, suggesting that gelation may be a universal phenomenon for colloidal dispersions. There is mounting experimental support^{9,10,24–27} that the gelation transition (at least at moderate to high packing fractions) coincides with the transition where bonding between colloids first sets in, in which the bonds originate from the intercolloidal attraction. It is prudent to distinguish between the physical *particle* gels discussed here, in which the bond between pairs of particles is significantly reversible, and chemical gels held together by covalent bonds that are effectively permanent.

In this work, we set out to construct a theory of gelation specifically for colloid–polymer mixtures in which the colloids interact via the AO depletion potential. The phenomena to be explained by such a theory include the following. Gelation occurs along a rather sharp boundary in the phase diagram, the location of which does not depend on how the samples are prepared. Even samples at low ϕ can exhibit gelation,^{28,29} though the behavior at low concentrations may be more complex than a pure gelation mechanism as seen at higher concentrations.⁴ Visual observation and dynamic light scattering measurements demonstrate that the particle dynamics slows markedly on traversing the gel boundary, giving a nonfluctuating component in the scattered intensity.^{9,10,30–32} Qualitatively similar observations have been made at the hard-sphere glass transition.^{16,17}

Gelling samples show a maximum in the intensity at small wavevectors in time-resolved static light scattering.^{8,33–35} This peak shrinks before finally arresting. This process has been linked to the growth of particle clusters, with the peak position indicative of the mean cluster size plus the region depleted of particles surrounding the growing cluster.^{35,36}

Additional studies have noted distinct types of dynamics in samples where crystallization is suppressed. At the onset of crystallization suppression at low ϕ , the dynamics is akin to the nucleation and growth and spinodal decomposition processes that signal a fluid–fluid phase separation.³⁷ At high enough particle and/or polymer concentrations, the dynamics is arrested for some time in a gel state before slow restructuring leads to loss of mechanical stability and a rapid collapse to form an

amorphous sediment.^{25,31,38} For this reason, these structures are also known as transient gels.^{35,37} Rheological measurements on colloidal gels yield a plateau in the elastic shear (storage) modulus at small frequencies,^{39,40} one of the defining characteristics of solids. This low-frequency plateau value of the storage modulus has been found to grow as a power law of particle concentration and attraction strength.⁴¹

Previous studies have shown that the so-called idealized mode coupling theory (MCT), developed originally to describe glass formation in atomic liquids,^{42–44} can deliver on some, albeit not quite all, of the requirements for a gel theory just mentioned.^{45–50} The theory requires as input information the equilibrium microstructure that reflects short-range attractions among particles. In fact, such short-range attractions are, according to the theory, the ultimate cause of gelation at low concentrations, which is very different from the cage effect thought to be responsible for glass formation at higher concentrations.^{17,43,44,51} As is now widely recognized, short-range attractions are ubiquitous to colloids,⁵² which may explain why colloidal gels are ubiquitous.

In this work, we focus on developing a theory for gelation in colloid–polymer mixtures based on the idealized MCT. Model colloid–polymer mixtures provide perhaps the most stringent proving ground for a newly formulated theory aimed at phenomena related to short-range attractions, such as the MCT of colloidal gelation. The depletion potential for small polymers is well understood, and compared to other systems, for example, solutions of globular proteins, few parameters exist that are unknown or adjustable.

In what follows, we begin by briefly reviewing the dynamical behavior of colloids and the processes that may lead to the structural arrest that we believe is the cause of gelation. We then present a simple theoretical model for the equilibrium microstructure of colloids interacting via the depletion potential, followed by a description of the gel theory. Theoretical predictions for the phase behavior are subsequently tested by comparing with results from Monte Carlo simulations and experiments on well-characterized colloid–polymer mixtures. Part of the results in section 6.1.2(b) have been presented before in a brief report.⁹ As will be shown, the theory can be simplified such that analytical predictions are obtained that can be compared directly with experimental results. The simplified theory is limited to small size ratios ξ , but it is entirely free of adjustable parameters.

- (24) Verhaegh, N. A. M.; Asnaghi, D.; Lekkerkerker, H. N. W. *Physica A* **1999**, *264*, 64.
 (25) de Hoog, E. H. A.; Kegel, W. K.; van Blaaderen, A.; Lekkerkerker, H. N. W. *Phys. Rev. E* **2001**, *64*, 021407.
 (26) Puertas, A. M.; Fuchs, M.; Cates, M. E. *Phys. Rev. Lett.* **2002**, *88*, 098301.
 (27) Zaccarelli, E.; Foffi, G.; Dawson, K. A.; Buldyrev, S. V.; Sciortino, F.; Tartaglia, P. *Phys. Rev. E* **2002**, *66*, 041402.
 (28) Grant, M. C.; Russel, W. B. *Phys. Rev. E* **1993**, *47*, 2606.
 (29) Weeks, J. R.; van Duijneveldt, J. S.; Vincent, B. J. *Phys.: Condens. Matter* **2000**, *12*, 9599.
 (30) Verduin, H.; Dhont, J. K. G. *J. Colloid Interface Sci.* **1995**, *172*, 425.
 (31) Poon, W. C. K.; Starrs, L.; Meeker, S. P.; Moussaïd, A.; Evans, R. M. L.; Pusey, P. N.; Robins, M. M. *Faraday Discuss.* **1999**, *112*, 143.
 (32) Romer, S.; Scheffold, F.; Schurtenberger, P. *Phys. Rev. Lett.* **2000**, *85*, 4980.
 (33) Asnaghi, D.; Carpinetti, M.; Giglio, M.; Vailati, A. *Physica A* **1995**, *213*, 148.
 (34) Verhaegh, N.; van Duijneveldt, J. S.; Dhont, J. K. G.; Lekkerkerker, H. N. W. *Physica A* **1996**, *230*, 409.
 (35) Poon, W. C. K.; Haw, M. D. *Adv. Colloid Interface Sci.* **1997**, *73*, 71.
 (36) Haw, M. D.; Poon, W. C. K.; Pusey, P. N. *Phys. Rev. E* **1997**, *56*, 1918.
 (37) Poon, W. C. K.; Pirie, A. D.; Pusey, P. N. *Faraday Discuss.* **1995**, *101*, 65.

- (38) Starrs, L.; Poon, W. C. K.; Hibberd, D. J.; Robins, M. M. *J. Phys.: Condens. Matter* **2002**, *14*, 2485.
 (39) Patel, P. D.; Russel, W. B. *J. Colloid Interface Sci.* **1989**, *131*, 201.
 (40) Rueb, C. J.; Zukoski, C. F. *J. Rheol.* **1998**, *42*, 1451.
 (41) Trappe, V.; Weitz, D. A. *Phys. Rev. Lett.* **2000**, *85*, 449.
 (42) Bengtzelius, J.; Götze, W.; Sjölander, A. *J. Phys. C* **1984**, *17*, 5915.
 (43) Götze, W.; Sjögren, L. *Phys. Rev. A* **1991**, *43*, 5442.
 (44) Götze, W.; Sjögren, L. *Rep. Prog. Phys.* **1992**, *55*, 241.
 (45) Bergenholtz, J.; Fuchs, M. *Phys. Rev. E* **1999**, *59*, 5706.
 (46) Bergenholtz, J.; Fuchs, M. *J. Phys.: Condens. Matter* **1999**, *11*, 10171.
 (47) Bergenholtz, J.; Fuchs, M.; Voigtmann, Th. *J. Phys.: Condens. Matter* **2000**, *12*, 6575.
 (48) Dawson, K. A.; Foffi, G.; Fuchs, M.; Götze, W.; Sciortino, F.; Sperl, M.; Tartaglia, P.; Voigtmann, Th.; Zaccarelli, E. *Phys. Rev. E* **2000**, *63*, 011401.
 (49) Zaccarelli, E.; Foffi, G.; Dawson, K. A.; Sciortino, F.; Tartaglia, P. *Phys. Rev. E* **2001**, *63*, 031501.
 (50) Foffi, G.; McCullagh, G. D.; Lawlor, A.; Zaccarelli, E.; Dawson, K. A.; Sciortino, F.; Tartaglia, P.; Pini, D.; Stell, G. *Phys. Rev. E* **2002**, *65*, 031407.
 (51) van Megen, W.; Underwood, S. M. *Phys. Rev. E* **1994**, *49*, 4206.
 (52) Rosenbaum, D.; Zamora, P. C.; Zukoski, C. F. *Phys. Rev. Lett.* **1996**, *76*, 150.

2. Colloidal Dynamics

How do colloid dispersions differ from molecular systems with respect to particle interactions and dynamics? Consider a colloidal particle subjected temporarily to an external force, imparting an extra velocity; the velocity of the particle can relax quickly back to equilibrium by the rapid exchange of momentum with the surrounding solvent molecules. There is no need for the particle to exchange momentum with other colloidal particles: the velocity relaxes locally over a typical time ($\approx mD_0/k_B T$) that is short compared to the time scale required for the particle to significantly alter its position over distances comparable to its size ($\approx \sigma^2/D_0$), the structural relaxation time.⁵³ Here, m is the particle's mass, D_0 is the Stokes–Einstein diffusion coefficient, σ is the particle diameter, and $k_B T$ is the thermal energy.

Thus, the velocities of the colloidal particles are, under most circumstances, extraneous variables. It is both practical and possible to describe the statistics of colloidal displacements solely in terms of particle positions. In this reduced description, the only conserved variable is the concentration of the colloids: momentum and energy are continuously gained or lost through interactions with the solvent molecules. This means that local departures from the mean particle concentration, or fluctuations away from this value, must relax by cooperative motion. For instance, consider a subvolume where the concentration is higher than the mean value. This concentration fluctuation relaxes by particle diffusion driven by the local concentration gradient. This is a slow process because of hindrance by surrounding particles, and at not too low concentrations, particles must cooperate in order for relaxation to equilibrium to occur.

If fluctuations become coupled such that the rate of relaxation of one hinges on the progress of others, we would expect the dynamics to slow dramatically. The so-called cage effect in concentrated colloidal dispersions (and dense molecular liquids) is an example of such correlation. Any given particle is temporarily confined to a cage of nearest neighbors, while the particle itself participates in the cages around other particles. Concentration fluctuations must therefore relax in a highly cooperative manner; a particle can escape its cage only if neighboring particles, themselves trapped in cages, can diffuse out of the way. Dynamic light scattering measurements of PMMA dispersions indicate that above a volume fraction of about 58% the particles become permanently trapped in their cages^{16,17,51} (while recent microscopic observations reveal additional complexities^{54,55}). The particles can only execute small-displacement motion within their cages, giving a finite short-time self-diffusion coefficient; the long-time self-diffusivity, however, essentially vanishes. Close to this critical volume fraction homogeneous nucleation of the equilibrium crystalline phase ceases.⁵⁶ The dynamically arrested state has been identified as a glass. This discovery was borne out of the close collaboration between experimentalists and theorists developing MCT of glassy dynamics.^{17,43,44,51}

Gels, on the other hand, do not require high particle concentrations to form. Typical for these systems is that short-range interparticle attractions cause aggregation to clustered structures, which remain intact over long

periods of time, apparently owing to the long-lived “bonds” that the attraction gives rise to. What remains to be answered is whether such aggregated dispersions constitute another example of systems with such a highly correlated dynamics that the long-time dynamics may come to a stop, and whether we can use the idealized MCT to describe such systems. Applicability of the theory would provide another example of a nonergodicity (or glass) transition in colloidal dispersions, this time driven by attractions and not by repulsions as in the cage effect. Verification of the central theoretical concept of a “bond-formation transition” would identify arrest of this local dynamical mechanism as one condition for colloidal gelation, while traditionally only mesoscopic concepts such as “percolation” or “diffusion-limited cluster aggregation” have been considered.

3. Depletion Interaction

For hard spheres in the presence of nonadsorbing polymer, Asakura and Oosawa^{1,2} and Vrij³ derived an effective sphere–sphere interaction potential (potential of mean force), given by

$$u(r) = \begin{cases} \infty & 0 < r < \sigma \\ -\Pi_p V_{\text{overlap}} & \sigma < r < \sigma(1 + \xi) \\ 0 & \sigma(1 + \xi) < r \end{cases} \quad (1)$$

where r is the center–center separation distance and Π_p is the osmotic pressure of a polymer solution in equilibrium with the mixture. V_{overlap} is the so-called overlap volume, which is given by

$$V_{\text{overlap}} = \frac{\pi}{6} \sigma^3 (1 + \xi)^3 \left(1 - \frac{3}{2} (r/\sigma)(1 + \xi)^{-1} + \frac{1}{2} (r/\sigma)^3 (1 + \xi)^{-3} \right) \quad (2)$$

In this model, a polymer coil is forbidden from coming closer than a distance of $\xi\sigma/2$ to the surface of a colloid, thus modeling the entropic cost of a real polymer coil approaching a hard surface. The parameter ξ is therefore a dimensionless measure of the polymer to colloid size ratio; in experiments, it can be estimated by $\xi = 2r_g/\sigma$, where r_g is the polymer's radius of gyration (see however, e.g., refs 20, 57, and 58). The polymer solution is taken to be ideal so that $\Pi_p = n_p^{(R)} k_B T$, where the polymer number density, $n_p^{(R)}$, must be interpreted as the number of polymer coils in the volume accessible to them;¹⁹ that is, the volume occupied by the colloidal particles and their associated depletion volumes must be subtracted from the total sample volume, leaving the free volume.^{7,19} This implies that the actual polymer number density in the mixture is given by $n_p = \alpha n_p^{(R)}$, where α is the free-volume fraction. A simple, approximate expression for α that depends only on ϕ and ξ has been suggested by Lekkerkerker et al.¹⁹ based on scaled-particle theory,

$$\alpha = (1 - \phi) \exp(-A\gamma - B\gamma^2 - C\gamma^3) \quad (3)$$

where $\gamma = \phi(1 - \phi)^{-1}$, $A = 3\xi + 3\xi^2 + \xi^3$, $B = 9\xi^2/2 + 3\xi^3$, and $C = 3\xi^3$.

As seen in Figure 1, where depletion potentials are shown for $\xi = 0.2$, the polymer concentration determines

(53) Pusey, P. N. In *Liquids, freezing and glass transition*; Hansen, J.-P., Levesque, D., Zinn-Justin, J., Eds.; North-Holland: Amsterdam, 1991.

(54) Kegels, W. K.; van Blaaderen, A. *Science* **2000**, *287*, 290.

(55) Weeks, E. R.; Crocker, J. C.; Levitt, A. C.; Schofield, A.; Weitz, D. A. *Science* **2000**, *287*, 627.

(56) van Megen, W.; Underwood, S. M. *Nature* **1993**, *362*, 616.

(57) Tuinier, R.; Vliegthart, G. A.; Lekkerkerker, H. N. W. *J. Chem. Phys.* **2000**, *113*, 10768.

(58) Fuchs, M.; Schweizer, K. S. *J. Phys.: Condens. Matter* **2002**, *14*, R239.

Figure 1. Depletion potential as a function of the dimensionless radial separation distance at a polymer–colloid size ratio of $\xi = 0.2$ and varying polymer volume fraction in the accessible volume, $\eta_p^{(R)}$, as labeled.

the strength of the attraction, whereas the range is determined by the relative size of the polymer, that is, the parameter ξ . For polymers that are small compared to the colloidal particles, the depletion potential is in good qualitative agreement with experimental measurements so long as the polymer concentration is not too high.^{59–61} Theory and simulations suggest that polymer–polymer interactions alter the depletion potential significantly.^{58,62,63} These works also provide a thorough discussion of the range of validity of the AO depletion potential for ideal and nonideal polymers. Here we restrict our attention to ideal polymers much smaller than the colloids, so that we expect the AO theory to provide a reasonably accurate effective colloid–colloid interaction. Note also that when $\xi < (2/\sqrt{3}) - 1 \approx 0.154$, there is no three-body (or higher) overlap between depletion zones, so that a description in terms of an effective *pair* potential is exact.

For $\xi < 0.1$, a rather good approximation to the full depletion potential, eqs 1 and 2, is given by

$$u(r) = -\eta_p^{(R)} k_B T \frac{3}{2} \frac{1 + \xi}{\xi^3} \left(\frac{r}{\sigma} - 1 - \xi \right)^2 \quad (4)$$

in the range $\sigma < r < \sigma(1 + \xi)$ (see the Appendix). Here $\eta_p^{(R)} = 4\pi n_p^{(R)} r_p^3/3$ is the polymer volume fraction in the free volume. This simple form of the depletion potential will enable us to give an analytic prediction of the MCT gel boundary at low ϕ without resorting to numerical work.

4. Equilibrium Structure

The gel theory that we propose in this work focuses on the relaxation of concentration fluctuations to equilibrium. For systems of monodisperse particles with short-range attractions, the equilibrium state is often one of fluid–crystal coexistence or fully crystalline. We shall overlook this fact out of necessity because the theory is not capable of describing the nucleation of crystals. Instead, we shall

take the “equilibrium” state as the disordered fluid even if it in reality is metastable and not the true equilibrium state.

The theory needs information about correlations among colloidal particles in these equilibrium fluid states, which nowadays can be calculated numerically.⁶⁴ The function we seek is the Fourier transform of the so-called direct correlation function, $c(k)$. It is a function of the wavevector k , as well as the particle concentration and the interaction potential, and is related to the familiar static structure factor, via $c(k) = (1 - S(k)^{-1})/n$. Here, n is the number density of the colloids, which, in dimensionless form, is $\phi = \pi n \sigma^3/6$, the colloid volume fraction.

To leading order in the concentration of colloids, $c(k)$ is given by a Fourier transform of $\exp(-u(r)/k_B T) - 1$,⁶⁵ which, for small polymer–colloid size ratios ($\xi \ll 1$), takes the form

$$c(\tilde{q}) \approx \frac{4\pi\sigma^3 K (\sin(b\tilde{q}) + \tilde{q} \cos(b\tilde{q}))}{b^2 \tilde{q} (\tilde{q}^2 + 1)} \quad (5)$$

where $\tilde{q} = k\sigma/b = q/b$ and

$$b = 3\eta_p^{(R)}(1 + \xi)/\xi^2 \quad (6)$$

$$K = \exp[3\eta_p^{(R)}(1 + \xi)/(2\xi)]$$

By defining the two parameters b and K in this manner, we observe that eq 5 is identical to an expression we have derived previously^{45,46} for the large wavevector asymptotic behavior of $c(q)$ for particles interacting via a hard core plus an attractive Yukawa tail, sometimes referred to as the hard-core attractive Yukawa (HCAY) system,⁶⁶ provided use is made of the mean spherical approximation (MSA). For HCAY systems, the interaction potential is given by

$$u(r) = \begin{cases} \infty & r < \sigma \\ -K \frac{k_B T}{r/\sigma} \exp[-b(r/\sigma - 1)] & r > \sigma \end{cases} \quad (7)$$

where the dimensionless parameters K and b determine the strength and range of the attraction, respectively.

The expression in eq 5 is tested in Figure 2 against (constant NVT) Monte Carlo simulations of 500 spheres interacting via the full depletion potential in eq 1 in a cubic simulation box with periodic boundary conditions. We choose to show the comparison with the static structure factor, $S(q) = (1 - nc(q))^{-1}$, instead of $c(q)$ because its behavior is likely more familiar and it varies over a smaller range of values at small q . In these simulations, the size ratio has been kept constant at the value 0.08. The systems simulated were verified to be single-phase fluids, but judging from the phase diagram for $\xi = 0.1$ ²³ (cf. also Figure 3), they are all close to the fluid–crystal coexistence boundary.

In all cases, we find that the behavior at large $q = k\sigma$ is reproduced, which implies that eq 5 captures the short-range or local structural correlations among the colloidal particles even though the approximate $c(q)$ was calculated in the limit $\phi \rightarrow 0$. This holds so long as $\xi \ll 1$ and the polymer concentration $\eta_p^{(R)}$ is not too low. Gelation occurs

(59) Rudhardt, D.; Bechinger, C.; Leiderer, P. *Phys. Rev. Lett.* **1998**, *81*, 1330.

(60) Bechinger, C.; Rudhardt, D.; Leiderer, P.; Roth, R.; Dietrich, S. *Phys. Rev. Lett.* **1999**, *83*, 3960.

(61) Crocker, J. C.; Matteo, J. A.; Dinsmore, A. D.; Yodh, A. G. *Phys. Rev. Lett.* **1999**, *82*, 4352.

(62) Fuchs, M.; Schweizer, K. S. *Phys. Rev. E* **2001**, *64*, 021514.

(63) Bolhuis, P. G.; Louis, A. A.; Hansen, J. P. *Phys. Rev. Lett.* **2002**, *89*, 128302.

(64) D’Aguanno, B.; Klein, R. In *Light scattering, principles and development*; Brown, W., Ed.; Oxford University Press: Oxford, 1996; pp 33–102.

(65) Hansen, J.-P.; McDonald, I. R. *Theory of simple liquids*; Academic Press: San Diego, 1986.

(66) Hagen, M. H. J.; Frenkel, D. *J. Chem. Phys.* **1994**, *101*, 4093.

Figure 2. The static structure factor as a function of the normalized wavevector $q = k\sigma$. The symbols are canonical Monte Carlo simulation results of spheres interacting via the depletion potential with $\xi = 0.08$, a fixed polymer concentration of $\eta_p^{(R)} = 0.15$, and varying colloid volume fraction; from top to bottom, $\phi = 0.1, 0.2, 0.3$, and 0.4 . The broken lines show the simple asymptotic result in eq 5, and the solid lines show the full MSA $S(q)$ for HCAY fluids using the mapping in eq 6. Note that the curves and data have been offset for clarity; they oscillate about unity in all cases.

Figure 3. Phase diagram for hard spheres interacting with an AO attraction at $\xi = 0.10$ from refs 23 and 73. Symbols for the various phase boundaries are given in the inset. The prediction of eq 8 is shown as the broken line, and the numerical calculation of the gel/glass boundary based on the mapping in eq 6 is shown as a solid line. The light gray region denotes nonergodic gel structures, and the dark gray areas denote regions of metastable fluid–fluid and crystal–crystal coexistence. The tie lines (not shown) between symbols are horizontal in this diagram.

when the interparticle attractions are strong (several $k_B T$), for which the simple formula in eq 5 accurately describes the local structural environment of any given particle so long as the system remains in a homogeneous (possibly metastable) fluid state.

The simple result in eq 5 is inaccurate for wavevectors around the primary peak of $c(q)$ or $S(q)$ near $q \sim 2\pi$, particularly at higher colloid volume fractions. A better, yet still simple, approximation is to exploit the correspondence with the asymptotics of the HCAY fluids within the MSA given in eq 6. Thus we take eq 6 to hold for any volume fraction, and we use the $c(q)$ for the HCAY

fluids known analytically within the MSA.^{67–69} This procedure amounts to a nontrivial renormalization of the HCAY parameters, such that the proper dilute limit of $c(q)$ is reproduced by the otherwise inaccurate MSA solution. Figure 2 shows that the mapping provided by eq 6 gives an improved overall representation of $S(q)$ compared to eq 5. The primary peak of $S(q)$ (and $c(q)$) is now accurately captured even at high colloid concentrations. A drawback of the mapping in eq 6 is that it does not reduce to the proper hard-sphere limit when $\eta_p^{(R)} \rightarrow 0$.

5. Gel Theory

In previous work, we have suggested the idealized MCT of glasses as a formalism for describing gel formation.^{9,10,45–47} Gelation within this framework hinges on short-range, local correlations, while the long-range (or small- q) structure is considerably less important. Whether this indeed is so has yet to be firmly established. The closely related glass formation has been studied in metastable Lennard-Jones liquids close to the spinodal line,⁷⁰ from which the small- q , critical correlations at least do not seem to preclude the structural arrest we believe is the cause also of gelation.

Let us attempt to discuss the content of bond formation according to MCT by comparing it with the familiar Smoluchowski theory of coagulation of charge-stabilized colloids.⁷¹ For the sake of simplicity, we restrict the discussion to low concentrations where only isolated pairs of particles need be considered. Two charged colloidal spheres interact via the DLVO (Derjaguin–Landau–Verwey–Overbeek) potential, which exhibits a deep and narrow primary minimum near contact as well as a repulsive barrier at somewhat larger separations, caused by the interplay between dispersion and screened Coulomb interactions. The aggregation is described as an activation problem, that is, whether the particle pair can overcome the repulsive barrier and enter the primary minimum near contact. The attraction strength here is of the order of some dozens of $k_B T$. In the Smoluchowski theory of aggregation (doublet formation in the present context), a nonequilibrium situation is postulated at the outset by the choice of the value of the radial distribution function $g(r)$ at contact, which differs from the value obtained from the interaction potential via equilibrium statistical mechanical averaging. While equilibrium theory predicts a finite, actually a rather high, contact value, for aggregation $g(r = \sigma+) = 0$ is enforced because two particles in contact are interpreted as a doublet and thus drop out of the description provided by $g(r)$. A nonequilibrium flux of particles forming doublets upon overcoming the barrier and reaching contact is established, while kinetic stabilization is regulated by the Coulombic barrier height.

This familiar Smoluchowski picture should be contrasted with the situation addressed in this paper: bond formation for dilute dispersions of particles interacting via the depletion interaction (or another short-range attraction) of only *moderate strength*. Since the attraction strength is of the order of a few $k_B T$, the loss of equilibrium cannot be assumed a priori, but the theory itself must deliver a criterion for when the attraction strength suffices for the formation of long-lived particle aggregates. Also, the absence of a repulsive barrier precludes kinetic stabilization. Thus the challenge is to find within an

(67) Waisman, E. *Mol. Phys.* **1973**, *45*, 1973.

(68) Høye, J. S.; Blum, L. *J. Stat. Phys.* **1977**, *16*, 399.

(69) Cummings, P. T.; Smith, E. R. *Chem. Phys.* **1979**, *42*, 241.

(70) Sastry, S. *Phys. Rev. Lett.* **2000**, *85*, 590.

(71) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal dispersions*; Cambridge University Press: Cambridge, 1989.

equilibrium statistical mechanics approach the threshold interaction beyond which the system falls out of equilibrium and where nonequilibrium types of approaches, such as diffusion-limited cluster aggregation, start to become meaningful. We propose to address this question using the MCT of nonergodicity transitions, within which, as a novel aspect, unexpected scenarios driven by short-range and medium-strength attractions have been discovered.^{9,10,45–48}

As shown by Poon and co-workers,^{6,7,31} a large portion of the composition plane in colloid–polymer mixtures with small ξ is occupied by samples showing nonequilibrium aggregation (including gelation) (cf. Figures 4 and 6 below). Therefore, in what follows, we attempt to construct a theory for gel formation for small values of the size ratio ξ . An added incentive for restricting the analysis to small ξ is that analytical progress toward a gel theory can be made. To this end, the asymptotic expression for $c(q)$ in eq 5, accurate for small ϕ and ξ and large q , is substituted in the MCT equations.^{42,44–47} We are now faced with some difficult integrations, which are normally performed numerically, but the simple form of eq 5 and the limit $\xi \ll 1$ allow us to complete them analytically.^{45,46} The result is that the long-time limit of the dynamic structure factor, $f(\vec{q})$, is controlled by a single, simple interaction parameter, $\Gamma = K^2\phi/b$.

For small values of Γ , $f(\vec{q}) = 0$ for all wavevectors. Physically, this means that concentration fluctuations decay into equilibrium at long times, just as expected for a colloidal fluid. However, for $\Gamma \geq 3.02$ the solutions yield a nonzero $f(\vec{q})$, that is, the dynamics is arrested, which we interpret as a transition from a fluid to a glass or a gel. The transition occurs at $K_c^2\phi_c/b_c = 3.02$, where the subscript c denotes values of the parameters at the transition. With eq 6, we can translate this to a prediction for the fluid–gel boundary in the phase diagram of the colloid–polymer mixtures:

$$3.02 \approx \frac{K_c^2\phi_c}{b_c} = \frac{\xi^2\phi_c}{3\eta_{p,c}^{(R)}(1+\xi)} \exp[3\eta_{p,c}^{(R)}(1+\xi)/\xi] \quad (8)$$

Gel states with an arrested long-time dynamics are predicted when $K^2\phi/b \geq 3.02$. Gels can be destabilized and made into fluids in several ways. The parameter b ^{45,46} (cf. also section 6.2) is inversely related to bond length, such that increasing b decreases the bond length whereby the gel is destabilized. The parameter K (cf. eq 7) is a measure of the bond strength, and ϕ is expected to vary with the number of neighboring particles; decreasing either of these favors the fluid over the gel state. It is then the central contribution of MCT (applied here to low ϕ and large b) to attach a critical value, ≈ 3.02 , to this particular combination of the parameters. Note, however, that for high colloid concentrations and/or values of ξ exceeding roughly 0.1, a full numerical solution is required in place of eq 8.

6. Results and Discussion

In what follows, we test our theory by direct comparison with experiments and computer simulations at $\xi \sim 0.1$. For low ϕ , the simplifications made in the theory enable us to do this analytically, in the form of eq 8. For $\phi \sim 0.25$ and higher, the theory is solved numerically; however, with the mapping (eq 6) in hand, we require just solutions for the HCAY systems, which have been described previously^{45,46} and which are considerably simpler to generate in practice than solutions for systems of particles interacting via the full depletion potential. Predictions

for gel transitions in the phase diagrams of the HCAY fluids have been presented in refs 45 and 46. These were based on the mean spherical approximation and, as a consequence, should only be seen as qualitative for the HCAY (far more accurate results for Yukawa interactions are now available,⁵⁰ see also ref 72).

Note that the *raw* MCT prediction for the hard-sphere glass transition, $\phi_g^{\text{MCT}} \approx 0.516$,⁴² is about 10% lower than the value $\phi_g \approx 0.58$ measured from dynamic light scattering.^{15–17} Comparisons of MCT with light scattering experiments conducted around the hard-sphere glass transition have shown that the theory is within $\sim 15\%$ of the experimental data if the scaling $\phi = (0.58/0.516)\phi^{\text{MCT}}$ is used.^{43,44,51} We apply the same scaling in what follows. In terms of the absolute shift, $\phi - \phi^{\text{MCT}}$, the effect of the rescaling is large at high concentrations but rather modest at the low concentrations where the asymptotic result in eq 8 is applied.

6.1. Nonergodicity Transition. 6.1.1. Comparison with Simulations. Our calculations pertain to the AO model. No experimental system can be described *exactly* in this idealized way. (Thus, for example, even at the theta temperature, polymer coils still interact.) On the other hand, such an idealized system can be simulated to any desired degree of accuracy. We therefore turn first to set out our predictions in the context of simulations of the AO model.

The various phase boundaries of a system of particles interacting via a pair potential of AO type at $\xi = 0.1$ have been obtained using Monte Carlo simulations by Dijkstra et al.,²³ Figure 3. Their results reveal that the fluid–fluid critical point is metastable with respect to fluid–crystal coexistence and that a likewise metastable critical point exists at high ϕ associated with two face-centered cubic crystal structures.

The low- ϕ , analytic prediction for the gel boundary, eq 8, at $\xi = 0.1$ is plotted in Figure 3 as a broken line at low ϕ . It merges smoothly at about $\phi \approx 0.2$ with the numerical solution. This continuous line of nonergodicity transitions in Figure 3 may be viewed as consisting of two branches, one connecting smoothly to the hard-sphere glass transition at vanishing polymer concentration and a second connecting to the low- ϕ , particle-bonding limit described in the previous section. Somewhere along the curve, presumably close to the bend at $\eta_p^{(R)} \approx 0.15$, the character of the transition changes from glass formation to gelation, but for this value of ξ there is no abrupt transition from a glass at low polymer concentration to a gel at higher polymer concentration.

Note that the predicted nonergodicity transition line lies entirely within the equilibrium fluid–crystal coexistence region. This suggests that in experiments, the transition to nonergodicity may be associated with a *failure to crystallize*. Also, at low ϕ , the predicted gel boundary comes close to the metastable fluid–fluid binodal. The formation of long-lived bonds and fluid–fluid demixing may then interact strongly. It is difficult to say a priori how such interaction may show up in experiments; but at least the comparison with simulations should alert us to this possibility in interpreting experimental data.

6.1.2. Comparison with Experiments. Turning our attention to experimental data, we immediately face the problem of converting from the theoretical variable, $\eta_p^{(R)}$, based on the volume accessible to the polymer, to the mass concentration of polymer, c_p , based on the total sample volume, which is invariably used in experiments. To

Figure 4. Comparison of MCT predictions with the experimental phase diagram, in terms of the mass concentration of polymer c_p and the colloid volume fraction ϕ , determined by Poon and co-workers (ref 6) for $\xi = 0.08$. The analytical prediction in eq 8 is shown as broken lines, and the mapping onto the HCAY systems via eq 6 is shown as solid lines for two values of the polymer–colloid size ratio ξ .

convert from $\eta_p^{(R)}$ to c_p , note that the fraction of the total sample volume occupied by polymers can be written as $\eta_p = \alpha \eta_p^{(R)}$, where α is the free-volume fraction. Following previous work,^{7,19} we use an expression from scaled-particle theory for α that depends only on ϕ and ξ . The density of the polymer is taken as $3M_w/(4\pi r_g^3 N_A)$, where M_w is the polymer molecular weight and N_A is Avogadro's constant, giving $c_p = 3[\alpha \eta_p^{(R)}]M_w/(4\pi r_g^3 N_A)$.

Below, we compare our predictions with published experimental data obtained using PMMA colloids with added polystyrene dispersed in *cis*-decalin at room temperature with $\xi \sim 0.1$. We expect that this system⁴ can be reasonably well described by the AO model.

(a) Global Behavior. To date, the data set covering the widest range of colloid and polymer concentrations is that reported by Poon et al.⁶ at size ratio $\xi = 0.08$. Their data, reproduced in Figure 4, revealed that moderate concentrations of polymer broadened the equilibrium fluid–crystal coexistence region, which occurred at $0.5 < \phi < 0.55$ when no polymer was added. A glass transition was observed at $\phi = 0.58$ at zero polymer concentration. A small amount of polymer added to the pure hard-sphere glass led to crystallization. At the highest polymer concentrations investigated, the authors reported non-equilibrium, amorphous states that they called “gels”.

We have already seen that our theory predicts a nonergodicity boundary that is entirely buried within the equilibrium fluid–crystal coexistence region for an AO system at $\xi = 0.1$, Figure 3. This is consistent with the data in Figure 4, which show that at $\xi = 0.08$, all noncrystallizing samples (triangles = “gels” or diamonds = glass) are found within the region of the composition plane that should give fluid–crystal coexistence (squares) or fully crystalline (crosses) samples.

More detailed comparison with this set of data is hampered by a lack of information concerning the exact nature of the samples labeled “gels” in ref 6. We can nevertheless superimpose the predictions of our theory on the data, Figure 4. The MCT predictions are very sensitive to the value of ξ . Experimentally, the determination of this parameter is not precise (see the discussion in ref 6). We therefore show predictions for $\xi = 0.07$ and

Figure 5. Comparison of MCT predictions (continuous lines) in the colloid-rich part of the phase diagram of a colloid–polymer mixture at $\xi = 0.08$ with experimental data from Pham et al. (refs 9 and 10). The lines separate equilibrium states from nonergodic glass and gel states (repulsive and attractive glasses), respectively, in terms of the mass concentration of polymer c_p and the colloid volume fraction ϕ relative to the glass transition ϕ_g for three values of the polymer–colloid size ratio ξ . The symbols are experimental data (refs 9 and 10): ($\diamond$) fluid–crystal coexistence, (∇) fully crystalline dispersions, ($\bullet$) glass states, and ($\blacksquare$) gel states. The gray regions highlight where nonergodic states were observed experimentally. The theoretical transition lines are dashed very close to the hard-sphere glass transition, ϕ_g , because the HCAY mapping is unphysical close to this point.

$\xi = 0.08$. Our theory, which involves no adjustable parameter beyond ξ , gives a reasonable account of the region where noncrystallizing behavior was found over the whole composition plane.

Of course, while nonergodicity certainly implies non-crystallization, observation of the latter by itself does not constitute a test of our theory's correctness. More in-depth interaction between experiment and theory requires detailed knowledge of the nature of the various amorphous states. For this purpose, we turn to later experiments from the same group.

(b) High Colloid Volume Fractions. The behavior at high ϕ has been examined in detail recently,^{9,10} Figure 5. Glassy samples near the hard-sphere transition crystallize on addition of small amounts of low molecular weight polymer, while further addition of polymer at fixed colloid concentration leads again to structural arrest. This implies that there is a re-entrant glass transition on addition of polymer. The prediction of the MCT is in full accord with this finding. This was initially noted in the context of so-called sticky or adhesive spheres^{45,74,75} and the HCAY systems.^{45,46} Subsequent theoretical work on square-well fluids⁴⁸ confirmed the prediction of re-entry and clarified its connection to special singularities in the MCT equations.^{76,77}

(73) Brader, J. M.; Dijkstra, M.; Evans, R. *Phys. Rev. E* **2001**, *63*, 041405.

(74) Fabbian, L.; Götze, W.; Sciortino, F.; Tartaglia, P.; Thiery, F. *Phys. Rev. E* **1999**, *59*, R1347.

(75) Fabbian, L.; Götze, W.; Sciortino, F.; Tartaglia, P.; Thiery, F. *Phys. Rev. E* **1999**, *60*, 2430.

(76) Götze, W.; Haussmann, R. *Z. Phys. B: Condens. Matter* **1988**, *72*, 403.

(77) Götze, W. In *Liquids, freezing and glass transition*; Hansen, J.-P., Levesque, D., Zinn-Justin, J., Eds.; North-Holland: Amsterdam, 1991.

Physically speaking, the addition of small amounts of polymer induces a weak, short-range attraction among the colloids. As described elsewhere,^{4,45,48,74,75} particles respond by spending more time in closer-spaced configurations. As a result, the cage of neighbors that restricts the large-displacement particle motion in the hard-sphere glass state deteriorates such that holes are created, increasing the chance of liberating the entrapped particles. The glass can now only be realized by reinforcing the cage by inserting more particles, in effect sealing the leaks, that is, by increasing the colloid concentration; hence the glass transition line tends toward higher ϕ on addition of polymer at small ξ , in agreement with data reproduced here^{9,10} and other experiments^{6,78,79} and computer simulations.^{26,27} Equivalently, at fixed ϕ , addition of polymer first leads to a melting of the hard-sphere glass. Adding even more polymer, or, equivalently, deepening further the short-range interparticle attraction, leads to another structural arrest. This picture has been confirmed by simulations.^{26,27}

A quantitative comparison between our theory and the data of Pham et al.^{9,10} is shown in Figure 5, where theoretical predictions for three values of ξ are shown. Evidently, our theory, which has no adjustable parameter apart from ξ , is able to reproduce the re-entrant glass transition boundary to well within a factor of 2. The three theoretical plots also illustrate what is now well understood from the study in ref 48, namely, that on restricting the range of attraction (lowering ξ), a discontinuity appears in the glass transition line. For square-well particles, this occurs for well widths of about 4% of the particle diameter.⁴⁸ The mapping used here suggests that we may expect a discontinuity to occur for colloid–polymer mixtures with ξ in the range $0.08 < \xi < 0.1$; for results from another mapping see ref 80. Focusing on the plot for $\xi = 0.1$, we see that there is a smooth change along the boundary from a glass at low polymer content to gels at higher polymer loadings. However, for smaller polymers ($\xi = 0.07$ and 0.08) the change is discontinuous. Previous work^{76,81,82} predicts that samples in fluid states in close proximity to this discontinuity exhibit anomalous and extremely slow relaxations. The dynamic structure factor (or autocorrelation function) is predicted to assume a logarithmic dependence on time.^{48,74,75,81,82} A number of experimental systems have now been identified that exhibit this behavior.^{9,10,26,27,83–85}

(c) *Low Colloid Volume Fractions.* The nature of the noncrystallizing states labeled “gels” in Poon et al.⁶ (triangles, Figure 4) has been clarified in a subsequent publication on a similar system with a slightly smaller size ratio, $\xi = 0.06$. These data are reproduced in Figure 6. Sufficient polymer concentration suppresses crystallization at a nonequilibrium boundary, beyond which different types of aggregation behavior are observed. (Note that all samples beyond this boundary would have been labeled “gel” in the terminology used in ref 6 and Figure 4.) Immediately across the nonequilibrium aggregation boundary, disordered clusters of colloids are formed that rapidly settle under the influence of gravity to give

Figure 6. Comparison of MCT predictions with the experimental phase diagram, in terms of the mass concentration of polymer c_p and the colloid volume fraction ϕ , determined by Poon and co-workers (ref 31) for $\xi \approx 0.06$. The analytical prediction in eq 8, using $\xi = 0.057$ and $\xi = 0.06$, is shown as broken lines. The mapping onto the HCAY systems via eq 6 is shown as the solid line for $\xi = 0.057$. Also shown is the PRISM prediction for the metastable fluid–fluid spinodal with a cross marking the location of the critical point (refs 58 and 62).

amorphous sediments. Deeper inside this nonequilibrium region, a rigid gel forms, which settles suddenly after an induction time. Samples in this “transient gel” region exhibit not only a transient rigidity but also nonergodic dynamics, manifested as a nonfluctuating component in the dynamic light scattering speckle pattern.³¹ In fact, for intermediate wavevectors, the decay of the autocorrelation function is found to be very small compared to the static component.³¹

A finite rigidity and nonergodic dynamics^{45–47} are precisely the properties associated with the transitions predicted by MCT. One may therefore expect MCT to predict the onset of transient gelation in this system. However, as Figure 6 shows, our theory is in nearly quantitative accord with the nonequilibrium aggregation boundary, along which crystallization stops, instead of the transient gelation boundary. As before, the theoretical prediction is sensitive to the value of ξ , but even on treating ξ as a freely adjustable parameter, the theoretical line cannot be brought in agreement with the transient gelation boundary. On the other hand, a minor adjustment of ξ from 0.06, as quoted in the experimental study, to 0.057 leads to near-quantitative agreement with the experimentally observed onset of nonequilibrium effects that limit crystallization.

As seen in all the comparisons made here with experimental phase diagrams for small ξ , Figures 5 and 6, the theory consistently predicts the correct slope of the gel line for concentrations exceeding $\phi \approx 0.25$. In this concentration range, recent rheological measurements⁸⁶ also provide evidence for a slow structural process as predicted by the theory. But for lower concentrations, the theory is unable to capture the much higher polymer concentrations needed to induce transient gelation, calling for the need to explore alternative mechanisms.^{87,88}

We should point out that in colloid–polymer mixtures with small ξ , a metastable fluid–fluid (or “gas–liquid”)

(78) Bartsch, E.; Eckert, T.; Pies, C.; Silesu, H. *J. Non-Cryst. Solids* **2002**, *307–310*, 802.

(79) Eckert, T.; Bartsch, E. *Phys. Rev. Lett.* **2002**, *89*, 125701.

(80) Götze, W.; Sperl, M. *J. Phys.: Condens. Matter*, in press.

(81) Götze, W.; Sjögren, L. *J. Phys.: Condens. Matter* **1989**, *1*, 4203.

(82) Götze, W.; Sperl, M. *Phys. Rev. E* **2002**, *66*, 011405.

(83) Bartsch, E.; Antonietti, M.; Schupp, W.; Silesu, H. *J. Chem. Phys.* **1992**, *97*, 3950.

(84) Chen, W.-R.; Chen, S.-H.; Mallamace, F. *Phys. Rev. E* **2002**, *66*, 021403.

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

(86) Prasad, V.; Trappe, V.; Dinsmore, A. D.; Segre, P. N.; Cipelletti, L.; Weitz, D. A. *Faraday Discuss.* **2003**, *123*, 1.

(87) Poon, W. C. K. *Faraday Discuss.* **2003**, *123*, 419.

(88) Kroy, K.; Poon, W. C. K.; Cates, M. E. To be submitted.

Figure 7. The localization length or root-mean-square displacement in the glass/gel state as a function of polymer concentration for three values of ξ .

binodal lies “buried” within the equilibrium fluid–crystal coexistence region. In Figure 6, we have also plotted the position of this boundary predicted by the PRISM theory of Fuchs and Schweizer^{58,62} for the system of ref 31. This metastable binodal lies right across the region where nonequilibrium behavior was observed. The possible interaction of fluid–fluid phase separation with gelation therefore complicates comparison with MCT theory.⁸⁷ Working with colloid–polymer mixtures with much smaller ξ ($\sim 10^{-2}$) should push the metastable fluid–fluid binodal to a position well beyond the onset of gelation.^{21,45} In the study of Ramakrishnan et al.²¹ for ξ below 0.03, for a range of colloid densities, a dramatic increase of the viscosity, hinting at nonergodicity transitions, was observed when adding polymer even before crystallization set in. Mapping the experimental system onto one of particles with a narrow square-well attraction, MCT calculations for the latter⁴⁷ gave nonergodic states at comparable attraction strengths.

6.2. Mechanical Properties. MCT not only predicts locations of glass and gel transitions in the phase diagram, it also produces predictions for some properties of the solid structures formed (and nearby fluid samples). In the glass, particles are confined to cages, but they are still able to explore the interior of the cages. Similarly, particles in gelled samples are strongly localized because of the effective particle–particle bonds that arise when the potential attraction is moderately strong and of short range. In analogy with Lindemann’s considerations for crystalline structures, a localization length can be defined as the root-mean-square displacement of particles in the noncrystalline solidlike structure.

Figure 7 shows the localization length r_s along the line of dynamical arrest as a function of $\eta_p^{(R)}$ and ξ . Turning on a weak, short-range attraction decreases the localization length slightly, indicating that in the glass state bordering the equilibrium crystal phase the particles become somewhat more confined as we add small amounts of polymer. This may be expected on physical grounds, because the particle concentration required to form the glass increases initially with increasing $\eta_p^{(R)}$. Overall, still, the localization length remains rather close to the value argued by Lindemann for the melting of a (crystalline) solid, namely, some 10% of the particle size.⁴² The rapid decrease of the localization length at somewhat higher polymer concen-

trations, however, is caused by the glass transition line meeting the gel transition line; that is, the dominant mechanism of structural arrest changes from caging to bonding. For sufficiently small values of ξ , somewhere between $0.08 < \xi < 0.1$, the change is discontinuous, and the localization length jumps from higher values in the glass to lower values in the gel. For somewhat larger values of ξ , there is a continuous, albeit abrupt, changeover from glass to gel. The typical localization length in the gel state is some fraction of ξ , indicating that bonds with lengths of the order of r_g are formed among particles. The asymptotic result $r_s/\sigma \approx 0.91\xi^2/(3\eta_{p,c}^{(R)}(1 + \xi))$ is shown as broken lines in Figure 7. It merges smoothly with the full numerical solution of the MCT using the mapping in eq 6 at intermediate polymer concentrations.

These striking changes in the local particle dynamics suggest corresponding effects in the bulk rheology.⁸⁹ Colloidal dispersions generally behave as liquids at low frequencies but assume progressively more solidlike character as the frequency is increased because relaxation by Brownian motion cannot keep up with the rate of deformation. On crossing a gel or glass transition, the long-time dynamics, corresponding to low frequencies, arrests such that shear perturbations cannot relax, and the system deforms instead in an elastic manner. The frequency-dependent storage or elastic shear modulus $G'(\omega)$, which vanishes in the low-frequency limit when the dispersion is in a fluid state, acquires a plateau at low frequencies.

The MCT connects the relaxation of fluctuations of the shear stress to concentration fluctuations such that the complex shear modulus $G^* = G' + iG''$ can be calculated. For glasses and gels, the theory predicts that $G = \lim_{\omega \rightarrow 0} G'(\omega) \neq 0$. In other words, were we to approach a glass transition from a metastable fluid state, G would be zero until crossing the glass transition when it would suddenly jump to a finite value. Entering the glass from an equilibrium crystalline phase, G would go from one finite value to another.

In Figure 8, the zero-frequency value of $G'(\omega)$, G , is shown as a function of $\eta_p^{(R)}$ and ξ along the glass and gel transition curves, two of which are shown in Figure 4. At low polymer concentration, the shear modulus is nearly constant at the hard-sphere glass value. For the shorter-range attractions, $\xi = 0.07$ and 0.08 , the shear modulus jumps to much larger values. The discontinuity arises because of the glass transition line being intercepted by the gel transition line. For somewhat longer-range attractions, $\xi = 0.10$, there is a steep but continuous increase of the shear modulus as the polymer concentration is increased.

The maximum in G in Figure 8 occurs around $\phi \approx 0.45$. It arises from the competition between particle packing and bond strength. At low polymer concentrations, the high particle concentration imparts elasticity; increasing polymer concentration leads to an increased elasticity because of the increasing bond strength, whereas at sufficiently high polymer loadings in the gel state the particle concentration is so low that the shear modulus eventually begins to decrease. At these lower particle concentrations, the asymptotic analysis supplies the analytic result $G\sigma^3/k_B T \approx 18.8(\eta_{p,c}^{(R)}(1 + \xi)/\xi^2)^3 \exp[-3\eta_{p,c}^{(R)}(1 + \xi)/\xi]$, which is shown in Figure 8 as broken lines.

(89) Gisler, T.; Weitz, D. A. *Curr. Opin. Colloid Interface Sci.* **1998**, 3, 586.

Figure 8. The zero-frequency shear modulus as a function of polymer concentration for three values of ξ along the glass and gel transitions lines, two of which are shown in Figure 4. Note that the particle concentration changes along the curves shown. The asymptotic result $G\sigma^3/k_B T \approx 18.8(\eta_{p,c}^{(R)}(1 + \xi)/\xi^2)^3 \exp[-3\eta_{p,c}^{(R)}(1 + \xi)/\xi]$ is shown as broken curves at high polymer concentration.

7. Conclusions

Building on the earlier studies^{45–50} that demonstrated the potential of MCT for understanding glass and gel transitions in colloidal systems, we have constructed a simple analytic theory of depletion-induced gelation based on accurate analytic approximations for the static structure of colloid–polymer mixtures. Many aspects of the nonequilibrium behavior of colloid–polymer mixtures can be explained, and even predicted, for small polymer–colloid size ratios, at least at high colloid concentrations. The systems acquire solidlike properties because of structural arrest either because of the cage effect (glasses) or because of particle bonding (gels). Bonding occurs for short-range attractions of moderate strength; for example, along the theoretical gel curve for $\xi = 0.08$ in Figure 4, the contact value of the depletion potential $u(\sigma) \approx -2.7k_B T$ when $\phi_c \approx 0.6$. Somewhat stronger attractions are required at lower concentrations, for example, $u(\sigma) \approx -3.8k_B T$ when $\phi_c \approx 0.17$.

The simplifications made in the theory produce analytical predictions at low to moderate colloid concentrations. But the theory appears to insist on associating these predictions with the observed boundaries of equilibrium behavior (viz., the limit of crystallization) rather than transient gelation, an aspect that warrants further study. Especially important would be dynamical studies to establish the dynamical anomalies accompanying local bonding. The connection between gelation and the metastable fluid–fluid binodal, the role of the small-angle scattering peak, and gel aging on longer time scales are examples of other topics that need be addressed in the future.

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Appendix

Asymptotic Solution of the (Idealized) Mode Coupling Theory for an AO-Model System. In this

appendix, we present a relatively detailed account of an asymptotic analysis of the direct correlation function that lets us construct a semianalytical solution of the MCT. The end result is a series of analytical formulas for the location of the gel transition boundary in the colloid–polymer phase diagram and also for some properties of the gel structures for small values of ξ . In addition, the analysis reveals a simple way to map the colloid–polymer state parameters onto the parameters of the HCAY fluid within the mean spherical approximation that can be used to model the behavior of more concentrated gels and glasses.

By defining $x = r/\sigma$ and $\zeta = 1 + \xi$, we can express the depletion potential in the range $1 < x < \zeta$ as $u(x)/k_B T = -\eta_p^{(R)}[\zeta^3 - (3/2)x\zeta^2 + (1/2)x^3]/\xi^3$. Before proceeding, we make the following change of variables, $z = 1 + (x - \zeta)(\zeta - 1)^{-1}$, so that

$$u(z)/k_B T =$$

$$\begin{cases} \infty & (1 - \zeta)^{-1} < z < 0 \\ -\eta_p^{(R)}\left[\frac{3}{2}\zeta(1 - z)^2 - \frac{1}{2}(1 - z)^3\right]/\xi & 0 < z < 1 \\ 0 & 1 < z < \infty \end{cases} \quad (9)$$

For small values of ξ , the depletion attraction in the range $0 < z < 1$ has the limiting form

$$u(z)/k_B T \approx -\eta_p^{(R)}\frac{3}{2}\zeta(1 - z)^2/\xi \quad (10)$$

This approximate form preserves the continuity of the attraction at the well boundary so that it vanishes smoothly at $z = 1$. The Fourier transformed direct correlation function, $c(k)$, is of central importance to the MCT. We focus initially on systems that are dilute with respect to the colloidal spheres; that is, we restrict the analysis to the limit $\phi \rightarrow 0$, for which

$$c(k) = \frac{4\pi}{k} \int_0^\infty dr r \sin(kr) [\exp(-u(r)/k_B T) - 1] \quad (11)$$

in general, and

$$c(q) = \frac{4\pi\sigma^3}{q} \frac{\partial}{\partial q} \left(\frac{\sin(q\zeta)}{q} \right) + \frac{4\pi\sigma^3\xi}{q} e^s \int_0^1 dz (1 + \xi z) \sin(q + q\xi z) e^{-2sz} e^{sz^2} \quad (12)$$

for a colloid–polymer mixture at size ratio ξ in particular. In the last expression, $q = k\sigma$ is the dimensionless wavevector and $s = 3\eta_p^{(R)}\zeta/(2\xi)$.

We shall carry out an asymptotic analysis of the integral in eq 12 in order to extract the dominant term for large values of s and q . The reason for this is that we wish to focus on small values of ξ , leading to large values of s , and small, local length scales, which imply large q -values. The former is consistent with the approximation of the depletion attraction already made in eq 10, and the latter is justified by previous analyses that have shown that gel transitions can be captured using the MCT by only considering the local structure. Since s is of $\mathcal{O}(\xi^{-1})$, the dominant contribution to the integral comes from the small region $0 < z < \mathcal{O}(s^{-1})$ when $\xi \ll 1$, other contributions being exponentially small. Thus we linearize the last exponential in eq 12, which leads to a simpler expression given by

$$I(q) \approx \frac{4\pi\sigma^3\xi}{q} e^s \int_0^1 dz (1 + \xi z)(1 + sz^2) \sin(q + q\xi z) e^{-2sz} \quad (13)$$

where $I(q)$ denotes the integral in eq 12. This integral can be evaluated analytically, but we will only make use of the leading-order, large- q result, which in practice amounts to retaining unity in the polynomial part of the integrand in eq 13:

$$I(q) \approx \frac{4\pi\sigma^3\xi}{q} e^s \left(\frac{2s \sin(q) + q\xi \cos(q)}{(q\xi)^2 + (2s)^2} \right) \quad (14)$$

This expression can be cast in a more convenient form by introducing $b = 2s/\xi$, $K = e^s$, and the rescaled wavevector $\tilde{q} = q/b$, which leads to

$$I(\tilde{q}) = \frac{4\pi\sigma^3 K (\sin(b\tilde{q}) + \tilde{q} \cos(b\tilde{q}))}{b^2 \tilde{q} (\tilde{q}^2 + 1)} \quad (15)$$

Finally, the other contribution to the direct correlation function is seen to be negligible, so that $c(\tilde{q}) \approx I(\tilde{q})$. Figure 2, in which comparisons are made with Monte Carlo results for $S(q)$, demonstrates that this simple formula captures large- q correlations in the single-phase fluid irrespective of the particle concentration when $\xi = 0.08$ and $\eta_p^{(R)} = 0.15$.

Substituting this simple form of the direct correlation function in the MCT and using the same scaled variables predicts that the parameter

$$\Gamma = K^2 \phi/b \quad (16)$$

in the limit $b \rightarrow \infty$ is governed by the following equations:

$$\frac{f(\tilde{q})}{1 - f(\tilde{q})} = \frac{\Gamma}{\tilde{q}^2} \int d\tilde{\mathbf{k}} [\tilde{V}^s(\tilde{\mathbf{q}}, \tilde{\mathbf{q}} - \tilde{\mathbf{k}})^2 + \tilde{V}^s(\tilde{\mathbf{q}}, \tilde{\mathbf{k}})^2] f(\tilde{k}) f(|\tilde{\mathbf{q}} - \tilde{\mathbf{k}}|) \quad (17)$$

$$\tilde{V}^s(\tilde{\mathbf{q}}, \tilde{\mathbf{k}})^2 = \frac{3}{\pi^2} \frac{(\tilde{\mathbf{q}} \cdot \tilde{\mathbf{k}})^2}{\tilde{q}^2 k^2 (1 + k^2)} \quad (18)$$

Here, $f(\tilde{q})$ goes by several names, for example, the Debye–Waller factor, Edwards–Anderson parameter, or glass form factor;⁷⁷ it is the long-time limit of the intermediate scattering function, that is, the autocorrelation function accessible in dynamic light scattering experiments, and is defined as $f(q) = S(q, t \rightarrow \infty)/S(q)$. This set of equations can be solved self-consistently for $f(\tilde{q})$ by iteration. For small values of Γ , the iteration yields $f(\tilde{q}) = 0$, indicating that the autocorrelation function will decay to zero given sufficient time. However, for $\Gamma \geq \Gamma_c$ the resulting $f(\tilde{q})$ is

finite, which means that the autocorrelation function does not decay to zero at long times but instead reaches finite values given by $f(\tilde{q})$.

Since eqs 16–18 are identical to the equations obtained by a similar asymptotic analysis of the HCAY fluid using the MSA expression for $c(q)$,^{45,46} the results from that study are applicable also here. We find then that $\Gamma_c \approx 3.02$ and the path of the gel transition in the small- ϕ part of the phase diagram for sufficiently small values of ξ is given by eq 8. We emphasize that although the final equations can be cast in such a form that they are identical to those resulting from the HCAY fluid with the MSA $c(q)$, it does not immediately imply that the present analysis suffers from inaccuracies resulting from use of the MSA closure.

In reaching eq 8, we made the identifications stated in eq 6. The parameters K and b regulate the strength and the range of the attraction, respectively, of the HCAY fluid. This connection between the parameters of the colloid–polymer mixtures and the HCAY fluid was made in the joint limit $\phi \rightarrow 0$ and $\xi \rightarrow 0$. We can construct a simple model for the colloid–polymer mixtures by assuming this mapping to hold for any particle volume fraction. It is important to note that the mapping provided by eq 6 only applies approximately when the HCAY fluid is treated within the MSA theory.

We have previously determined the phase diagram and the gel properties for the HCAY fluids using the MSA $c(q)$.^{45,46} It is thus a simple matter to construct predictions, free of any adjustable parameters, for the colloid–polymer mixtures. The small-wavevector expansion of the form factor, $f(\tilde{q}) = 1 - \tilde{q}^2(r_s b/\sigma)^2$, defines the localization length, r_s , in the arrested structure. The HCAY analysis produced the prediction $r_s \approx 0.91\sigma/b$, which can be translated via eq 6 to a prediction for the colloid–polymer mixtures,

$$\frac{r_s}{\sigma} \approx \frac{0.91\xi^2}{3\eta_{p,c}^{(R)}(1 + \xi)} \quad (19)$$

Likewise, MCT links the arrested structure contained in $f(\tilde{q})$ to the zero-frequency shear modulus, $G = G'(\omega \rightarrow 0)$, which is finite for solid materials but vanishes for liquids. The (MSA) prediction for the HCAY fluid is $G \approx 0.0764 b_c \phi_c^2 K_c^2 k_B T / \sigma^3$, which gives us the following prediction for the colloid–polymer mixtures:

$$G \frac{\sigma^3}{k_B T} \approx 18.8 \left(\frac{\eta_{p,c}^{(R)}(1 + \xi)}{\xi^2} \right)^3 \exp[-3\eta_{p,c}^{(R)}(1 + \xi)/\xi] \quad (20)$$