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Linking self-assembly, rheology, and gel transition in attractive colloids

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Synopsis

We propose a microscopic framework based on nonequilibrium statistical mechanics to connect the microscopic level of particle self-assembly with the macroscopic rheology of colloidal gelation. The method is based on the master kinetic equations for the time evolution of the colloidal cluster size distribution, from which the relaxation time spectrum during the gelation process can be extracted. The relaxation spectrum is a simple stretched-exponential for irreversible diffusion-limited colloidal aggregation gelation, with a stretching exponent $d_f/3$, where d_f is the mass fractal dimension. As opposed to glassy systems, the stretched-exponential relaxation does not result from quenched disorder in the relaxation times, but from the self-assembly kinetics in combination with the fractal character of the process. As the master kinetic equations for colloidal aggregation do not admit bond-percolation solutions, the arrest mechanism is driven by the interconnection among fractal clusters when excluded volume becomes active, i.e., at sufficiently high packing of clusters. The interconnections between rigid clusters decrease the soft modes of the system and drive a rigidity-percolation transition at the cluster level. Using the Boltzmann superposition principle, the creep and the full rheological response can be extracted for both irreversible and thermoreversible colloidal aggregation. In the case of thermoreversible gelation, the attraction energy is finite and plays the role of the control parameter driving a nonequilibrium phase transition into a nonequilibrium steady-state (the gel). A power-law spectrum coexisting with a stretched-exponential cut-off is predicted leading to power-law rheology at sufficiently high frequency. Our theory is in good agreement with experimental data of different systems published by other authors, for which no theory was available. © *2014 The Society of Rheology.* [http://dx.doi.org/10.1122/1.4878838]

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I. INTRODUCTION

In general, gelation processes differ depending upon the nature of the intermolecular bonds [Herrmann (1986); Corezzi *et al.* (2012)]: Chemical gels are realized by covalent bonding, whereas physical gels are formed through self-assembly via noncovalent bonds. These include van der Waals dispersion forces, hydrogen bonds electrostatic and entropic forces, etc. In both cases, however, the resulting final solid is amorphous (noncrystalline) with marked structural heterogeneity and mesoscopic spatial patterns which depend on the molecular geometry and on the bonding as well. Gels must hence be distinguished from glasses formed by homogeneous liquids states by supercooling at the glass transition [Debenedetti (1996)]. In this case, the intermolecular attraction forces can be very weak, while a major role is played by crowding and caging mechanisms [Götze and Sjögren (1992)], i.e., by repulsive interactions.

It is well established that in chemical gelation the elastic moduli at the transition exhibit power-law rheology, $G' \sim G'' \sim \omega^n$, where the power exponent n can be related to the formation of a percolating cluster at the transition, and to the fractal dimensionality of the latter [Winter and Chambon (1986); Chambon and Winter (1987)]. The underlying relaxation spectrum is a decreasing power-law function $H \sim \tau^{-n}$. This may be a consequence of the power-law density correlations, typical of second-order phase transitions like percolation [Stauffer and Aharony (1991)]. Hence, this scheme makes a close connection between percolation and rheology for chemical gels. Recently, it has been recognized [Winter (2013)] that the relaxation spectrum of soft glasses can also be represented in terms of power-laws. However, in this case the power-law exponent is positive with the spectrum broadening toward long relaxation times, which is just the opposite than chemical gelation.

Physical gels, that is, colloidal gels formed by attractive Brownian particles, do not exhibit a clear connection between the microscopic self-assembly of the particles and the macroscopic rheology [Poon and Haw (1997); Trappe and Sandkühler (2004); Romer *et al.* (2000); Segrè *et al.* (2001); Trappe *et al.* (2001); Zaccarelli (2007); Lu *et al.* (2008); Buzzaccaro *et al.* (2007); Solomon and Varadan (2001); Tanaka *et al.* (2005); Gibaud and Schurtenberger (2009); Eberle *et al.* (2011)]. Numerous models explaining gelation and dynamical arrest in attractive colloidal suspensions have been presented so far. These models include percolation [Binder and Kob (2011)], diffusion-limited cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA) [Poon and Haw (1997)], and spinodal decomposition [Lu *et al.* (2008)]. A review has been given some time ago by Zaccarelli (2007). No consensus has been reached so far, neither in terms of the dynamical arrest mechanism, nor in terms of the rheological response. Both simulations [Del Gado *et al.* (2003); Bergenholtz *et al.* (2003)] and experiments [Segrè *et al.* (2001); Shih *et al.* (1987); Sandkühler *et al.* (2004)] have shown the absence of percolation features in the dynamics at the gel transition. It appears that for low to moderate interparticle attractions, the arrest mechanism shares some similarities with the glassy dynamics of supercooled liquids [Segrè *et al.* (2001)]. The main difference is that in supercooled liquids the dynamical arrest occurs at the atomic/molecular level, whereas at the colloidal gelation the dynamical arrest occurs on the much larger (mesoscopic) length-scale of colloidal clusters. Various proposals have emphasized the cluster-glass or cluster-jamming transition as a viable scenario for colloidal gelation [Trappe *et al.* (2001); Kroy *et al.* (2004); Zaccone *et al.* (2009)]. Rheological studies have shown the absence of clear power-law behavior at the colloidal gelation transition [Trappe and Weitz (2000); Laurati *et al.* (2009)], where the moduli exhibit a very weak rise with the frequency, rather than the power-law seen in chemical gelation. In contrast to these studies, a more recent experimental work [Eberle *et al.* (2011); Eberle *et al.* (2012)] has

reported signatures of power-law rheology in colloidal gelation over a frequency of about one order of magnitude. The nanoparticles ($\sim$20 nm) in these studies were much smaller than in the study of Laurati *et al.* (2009).

At first, it may appear intuitive to presume a close connection between chemical and colloidal gelation where chemical aggregation may be envisioned as the limiting case for a high attraction energy. However, an important difference lies in the self-assembly kinetics: Colloidal aggregation is typically controlled by diffusive transport for large molecules/particles whereas chemical gelation is controlled by the bond-formation rate [Coresszi *et al.* (2012)], at least away from the glass transition [Zaccone and Terentjev (2013)] of the polymer. Another important difference is given by the anisotropic character of the covalent bond in chemical gelation which may impose not only bond-stretching constraints but also bond-bending (angular) constraints [Zaccone (2013)] in the deformation of a cluster. Colloidal gelation bonds, on the other hand, are generally isotropic. These are important considerations that will affect the deformation behavior considerably.

Recently, we have presented a new approach that starts from the microscopic level of self-assembly kinetics [Zaccone *et al.* (2011b); Zaccone *et al.* (2013)]. We work with a model of Brownian aggregation where the clustering kinetics can be evaluated approximately for colloidal bonds. The cluster mass distribution (CMD) is then used to derive an analytical form for the relaxation time distribution and, ultimately, the full rheological spectrum. This method provides a bottom-up approach to connect self-assembly and rheology. The proposed nonequilibrium statistical mechanics framework leads to rationalize the different colloidal and chemical gelation scenarios into a single picture. A first comparison of this theory with experimental data on the complex viscosity near the gelation point has met with gratifying success [see the discussion of Fig. 8 of Zaccone *et al.* (2013)]. Here, we extend this bottom-up approach much further to include the creep behavior, the linear viscoelasticity, and the dynamic rheology. Hence, our entirely kinetic model can now be compared to the experimental rheology data taken from literature. In particular, we compare our theoretical deductions to the data provided by Eberle *et al.* (2012) who worked with a system of spheres with very short range attraction. In this system, the gelation is located above the spinodal decomposition thus justifying an entirely kinetic approach. It is then interesting to compare theory to the data of Laurati *et al.* (2009) related to a colloidal suspension in which gelation was induced by depletion forces with a much longer range.

This paper is organized as follows: First, the cluster size distribution is derived in Sec. II based on different mechanisms of self-assembly kinetics leading to gelation (DLCA, RLCA, aggregation with breakup in the early stage, reversible cluster-aggregation and chemical gelation). For these cases, in Sec. III, the relaxation time spectrum is calculated. In Sec. IV. the dynamical arrest mechanism in colloidal gelation is discussed and in Sec. V. The rheological properties of the irreversible colloidal gelation are derived in an analytical manner. Furthermore, the low-shear viscosity divergence at the gelation transition is discussed in Sec. VI, followed by the microscopic theory of the rheology of thermoreversible colloidal gelation (Sec. VII). The results converge to a broader discussion about rheological classification of liquid-solid transitions in soft material in Sec. VIII, followed by the Conclusion (Sec. IX). Additional information will be given in the Appendix.

II. FROM SELF-ASSEMBLY TO THE CLUSTER SIZE DISTRIBUTION

Our starting point is the self-assembly process whereby colloidal/physical or chemical bonds can form with binding energy V and may also breakup due to thermal motion. The

aggregation leads to formation of clusters with mass k and linear size R_k according to the general master kinetic equation [Krapivsky *et al.* (2010)]

$$\dot{c}_k = \frac{1}{2} \sum_{i,j=1}^{i+j=k} K_{ij}^+ c_i c_j - c_k \sum_{i=1}^{\infty} K_{ik}^+ c_i - K_k^- c_k + \sum_{i=k+1}^{\infty} K_{ik}^- c_i, \tag{1}$$

where c_i is the number concentration of clusters with i particles in each of them. K_{ij}^+ is the rate of association between two clusters, one with mass i and the other with mass j to form a cluster of mass k, while K_{ik}^- is the rate of dissociation of a i aggregate into two clusters k and $i - k$. The first term expresses the "birth" of clusters with mass k, the second expresses the "death" of clusters with mass k due to aggregation with another cluster. The last two terms express the death and birth of k-clusters due to cluster breakup, respectively.

A. Irreversible DLCA

If association is entirely controlled by diffusion, the rate of association in good approximation independent of the sizes of the two colliding clusters, $K_{ij}^+ = const$. Moreover, if the attractive binding well between two colloidal particles is virtually infinite or very deep $V/kT \gg 1$, dissociation is negligible at all levels, and $K_{ij}^- = 0$, for all i and j.

The approximation $K_{ij}^+ = const$, i.e., the collision rate independent of the cluster sizes, is a good assumption to describe Brownian diffusion-controlled aggregation where the dependence of the collision rate on the cluster size due to the cross section cancels mutually with the dependence due to the diffusion coefficient, which is the famous Smoluchowski diffusion-limited rate [Kaprivski *et al.* (2010)]. Hence, $K_{ij}^+ = const$ is an exact description of Brownian aggregation as long as the particles are nonfractal. With fractal clusters, a dependence of $K_{ij}^+ = const$ on the cluster size arises, which makes Eq. (1) no longer analytically solvable. Numerical solutions indicate that the resulting CMD differs from the one given by $K_{ij}^+ = const$, only in the fact that the primary particle and small aggregate concentrations are overestimated. However, the constant kernel approximation works well in reproducing the average part and large-mass limit of the CMD [Friedlander (2000)]. This is an important fact because the structural relaxation and rheological behavior close to the transition are controlled by the latter features of the CMD.

Under these assumptions, namely, $K_{ij}^+ = const$ and $K_{ij}^- = 0$, for all i and j, the analytical solution to Eq. (1) was found long ago by Smoluchowski and is given by the following exponential distribution [Kaprivski *et al.* (2010)]:

$$c_k = \frac{c_0 (\hat{t}/\theta)^{k-1}}{(1 + \hat{t}/\theta)^{k+1}}, \tag{2}$$

which gives the time evolution of the CMD during the self-assembly process. c_0 is the initial concentration of monomers (primary particles) forming the sol. $\hat{t}$ is the aggregation time, that is, the time elapsing from the moment at which the attraction between the particles is switched on. The characteristic aggregation time is $\theta = 1$ for irreversible diffusion-limited aggregation. $\theta > 1$ is due to either a repulsive barrier in the intermolecular interactions, such as an electric double layer repulsion, or can be due to the finite lifetime of single bonds, as discussed below. In the first case, θ is an Arrhenius *increasing* function of the energy barrier V_{max}, whereas in the latter case it is an

Arrhenius *decreasing* function of the binding energy V, cf. Eq. (16) in our previous contribution [Zaccone (2013)]. This analogy between aggregation with breakable bonds and reaction-limited cluster-cluster aggregation (RLCA) is further explored in Sec. II B.

B. Partly reversible colloidal aggregation and analogy with RLCA

Let us now consider the case where the only dissociation events which take place in the system are those involving the detachment of a single dangling particle from another particle or cluster of arbitrary size. In other words, breakup events leading to two fragments, each of them larger than one particle, are excluded. Hence, it should also be noted that linear particle chains do not break in this particular model, because this would lead to two fragments which are both larger than one particle. This assumption is physically justified if we consider that the breakup rate of a bond involving a dangling particle is much larger than the breakup rate of bonds involving two particles which are both multiply bonded to other particles. In the latter case, the effective attraction energy associated with the breaking bonds is the combined potential resulting from multiple bonds and the rate is exponentially lower. This effect is greatly amplified by the anharmonic character of the intermolecular potential. Hence in this model,

$$
\begin{aligned}
K_{ij}^+ &= const, \quad \forall \; i,j \\
K_{ij}^- &= \lambda K_{ij}^+, \quad \text{if} \;\; i = 1, \;\; \text{or} \;\; j = 1 \\
K_{ij}^- &= 0, \quad \text{if} \;\; i \neq 1, \;\; \text{or} \;\; j \neq 1.
\end{aligned}
\tag{3}
$$

Exact solutions are available for this model, in terms of the asymptotic ($k \gg 1$) cluster size distribution c_k. A nonequilibrium phase transition between a sol phase made of clusters, and a phase containing a giant cluster coexisting with small clusters, at $t \to \infty$, is found as a function of the parameter λ which represents the extent of breakup events. In particular, for $\lambda > 1$ no gel is formed, whereas gelation occurs for $\lambda < 1$, where λ is in units of c_0. The CMD has power-law form in both regimes. In the precritical sol regime, the power-law is accompanied by an exponential cut-off [Majumdar *et al.* (1998); Majumdar *et al.* (2000)]

$$
c_k(\hat{t} \to \infty) \sim k^{-3/2} e^{-k/k_c},
\tag{4}
$$

with the cut-off size k_c diverging as $\lambda \to 1^+$, according to [Majumdar *et al.* (1998); Majumdar *et al.* (2000)]

$$
k_c = \left\{ 2 \log(\lambda/\lambda_c) - \log[2(\lambda/\lambda_c) - 1] \right\}^{-1}.
\tag{5}
$$

Hence, close to the transition, the CMD is a simple power-law, $c_k \sim k^{-3/2}$.

Interestingly, this is exactly the same form of cluster-mass distribution observed in RLCA experiments [Lin *et al.* (1989)], even with the same power-law exponent $-3/2$. Hence, aggregation with partial bond-breakup and aggregation in the presence of a barrier are both described by the same scaling form of the CMD, Eq. (4). This observation lends further support to our previously reported analogy between reversible aggregation and RLCA [Zaccone *et al.* (2011b)]. The analogy is based on the fact that both thermal bond-breakup and the electrostatic energy barrier reduce the fraction of successful (bond-forming) collisions between particles/clusters. In both cases the probability of forming a stable, long-lived bond is controlled by a thermal activation process, with a characteristic

aggregation time $\theta \sim e^{V/k_B T}$, where V represents the finite depth of the bonding well in the case of partly reversible aggregation [Zaccone *et al.* (2013)], and the height of the electrostatic barrier in the case of RLCA, respectively.

The breakup rate K_{ij}^- of Eq. (3) is controlled by the Kramers escape rate of the individual particle detaching from the cluster, and hence, for a simple square-well attraction, $K_{ij}^- = (D/\delta^2) e^{-V/k_B T}$. Together with the condition $\lambda_c = 1$, in units of c_0, and with the assumption that the aggregation rate is diffusion-limited, $K_{ij}^+ = (8/3)k_B T/\mu$, with μ the solvent viscosity, this leads to a critical attraction energy

$$-V_c/k_B T \simeq \log \left[12(\delta/a)^2 \phi_0 \right], \tag{6}$$

where $\phi_0 = (4/3)\pi a^3 c_0$ is the solid volume fraction. This equation provides an estimate of the minimum attraction energy between two colloidal particles in order to have gelation at steady-state. It is approximately valid for dilute colloidal suspensions. For the colloidal system of [Eberle *et al.* (2011)], at $\phi_0 = 0.12$ and $\delta/a = 0.02$, Eq. (5) gives $V_c \simeq 7.4 k_B T$, which is not too far from the value $V_c \simeq 4.4 k_B T$ estimated by those authors. The case is different for the depletion induced colloidal system of Laurati *et al.* (2009) at $\phi_0 = 0.40$ and $c_p/c_p^* = 0.25$. The attraction range in this case is $\delta/a \approx 0.07$. The attraction energy at which the nonequilibrium gelation transition sets in, according to our formula Eq. (6), is $V_c \simeq 3.87 k_B T$. For this system, independent estimates of the critical attraction using, e.g., depletion attraction theory are not easily available, due to the relatively high volume fraction of the system.

An interesting related model is represented by the fully reversible aggregation process (sometimes used also in the context of reversible polymerization), where any bond inside any aggregate can breakup with the same constant rate. This is, again, an idealized model because with compact clusters, in reality, there would be a distribution of coordination numbers, leading to a distribution of dissociation rates. Nevertheless, it is instructive to briefly consider the outcome of this model with respect to the steady-state (gel or nongel). In this model $K_{ij}^- = const > 0$, $\forall$ i, j, and $K_{ij}^- = \lambda K_{ij}^+$, where λ is in units of c_0, as usual. A steady-state solution to Eq. (1) can be found by imposing that the steady-state satisfies detailed balance, $c_i c_j = \lambda c_{i+j}$, hence that the aggregation is at thermodynamic equilibrium (other nonequilibrium steady-states may still exist which do not satisfy detailed balance). The $\hat{t} = \infty$ solution in this case has the exponential form $c_k = \lambda b^k$, where b is also an algebraic function of λ. This shows that no gelation is possible in this case even in the $\hat{t} = \infty$ limit and regardless of the bonding energy. This model, which in contrast to those discussed in Sec. II A does not yield gelation under any conditions, might be applicable to systems for which equilibrium clusters have been observed experimentally [Stradner *et al.* (2004)].

C. Aggregation with breakup in the early stage

Recently, we have shown that thermally activated breakup of colloidal dimers in the early stage of aggregation results in a slowing-down of the aggregation process with a finite aggregation time $\theta \sim e^{-V/k_B T}$, where V is the attraction energy between two particles. As shown earlier, instead of explicitly considering the two dissociation terms in the master equation, we can account for early stage dissociation in an effective way by replacing the association constant with an effective size-independent rate constant, K_{eff}, and dropping the breakup terms in the master equation. In the later stage of cluster-cluster aggregation, association is controlled by diffusion because breakup becomes less important

due to multiple bonds between particles in structures with $d_f \gtrsim 2$. Hence, the rate of association is in good approximation independent of the sizes of the two colliding clusters.

Analytical expressions for K_{eff} as a function of the relevant physical parameters, such as colloid size and attraction energy, can be found in Zaccone *et al.* (2013). The analytical solution for the CMD is thus given by the Smoluchowski expression, Eq. (2), with a finite aggregation time $\theta \sim e^{V/k_BT}$, where V represents the finite depth of the bonding well. In the work of Zaccone *et al.* (2013), we used the CMD and its time evolution to deduce analytical expressions for the viscosity and its divergence due to cluster close packing, from which also the gelation time can be obtained in analytical form.

D. Chemical gelation

All the above cases refer to systems where the aggregation rate K_{ij}^+ is basically independent of the size of the colliding clusters i and j. Only in RLCA a weak dependence $K_{ij}^+ \sim (ij)^{1/2}$ is necessary to account for partial interpenetrability of the clusters and leads to the power-law form of the CMD. The reason why the aggregation rate in the transport-dominated processes is either independent or weakly dependent on the cluster sizes resides in the mutual cancelation between the diffusive $\sim D_{ij} \sim (i+j)^{-1}$ contribution and the cross-section $\sim (i+j)$ contribution to the collision rate, leading to $K_{ij}^+ \sim (i+j) \cdot D_{ij} \sim const$.

If, instead, self-assembly is mediated by chemical reaction instead of transport, meaning that the time-scale of the chemical reaction is controlling, then the association rate is set by the reaction chemistry. Typically, the chemical reaction rate is proportional to the number f of reactive site per molecule, which is the valency or functionality of the molecule. Only branching reactions, $f > 2$, lead to gelation. If all reactive sites have the same reactivity, then the association rate is given by $K_{ij}^+ = [(f-2)i+2][(f-2)j+2] = (f-2)^2ij + 2(f-2)(i+j) + 4$.

Setting bond-dissociation to zero is a widely used approximation, given the high energy and thermal stability of covalent chemical bonds at ordinary T, hence $K_{ij}^- = 0$ for all i and j. Even so, however, there are no analytical solutions to Eq. (1) with this form for K_{ij}^+. The closest analytical solution known is the so-called product kernel $K_{ij}^+ \sim ij$, which corresponds to the limit $f \to \infty$. The analytical solution is well studied since the pioneering work of Ernst and van Dongen [van Dongen and Ernst (1985)], and predicts gelation, i.e., the formation of a percolating cluster, at a finite time $\hat{t}_c$. The asymptotic form of the CMD close to the transition is found to be

$$c_k(\hat{t} \to \hat{t}_c) \sim k^{-5/2}e^{-k/k_c}. \tag{7}$$

The derivation of this result, based on finding the generating function which reduces the problem to solving a Burgers equation, is nontrivial and can be found in the original contribution of van Dongen and Ernst (1985) or in Kaprivski *et al.* (2010). This form is very similar to the one found for partly reversible aggregation, Eq. (4), with only the power-law exponent being larger in this case. Also here k_c diverges as $\hat{t} \to \hat{t}_c$, and $c_k \sim k^{-5/2}$ right at the transition. As we are going to see below, this form for the CMD leads to a power-law distribution of relaxation times, which provides a qualitative theoretical foundation to power-law rheology of chemical gels.

E. Overview of the different models from the point of view of gelation

In Secs. II A–II D, we have discussed different models of self-assembly kinetics based on different choices for the assembly and disassembly rates, K^+ and K^-, which enter

Eq. (1). We have seen how models where all K^- are zero (no dissociation at all levels) always lead to gelation, irrespective of the aggregation mechanism (chemical or physical). When bonds are allowed to break, instead, the final steady-state may or may not be a gel depending on the ratio between K^- and K^+, which in turn depends on the attraction energy. Also, the occurrence of gelation depends on the location of the breakup events and on whether only a subset of bonds in the clusters (e.g., dangling bonds) are allowed to break. In Sec. III, we are going to formulate a model which connects the different self-assembly scenarios presented in Secs. II A–II D with the rheological response.

III. FROM THE SELF-ASSEMBLY KINETICS TO THE RELAXATION TIME SPECTRUM

For the different aggregation models presented in Sec. II, we now proceed to deduce the respective distribution functions of relaxation times, $H(\tau)$. These are based on the CMDs from the master kinetic equations governing the nonequilibrium self-assembly process. This is a crucial step toward deriving the rheological response as it provides a bridge between the molecular-level self-assembly process and the macroscopic response.

The relaxation time of a single cluster formed by k particles can be taken as the time needed to travel a distance equal to its linear size R_k

$$\tau(k) = R_k^2/D_k = R_k^2 \left(\frac{k_B T}{6\pi\mu R_k} \right)^{-1} = \frac{R_k^3}{k_B T/6\pi\mu}, \tag{8}$$

where μ is the solvent viscosity. The cluster radius is related to the number of particles k forming the cluster via the general fractal scaling relation $k = (R_k/a)^{d_f}$ [Stauffer and Aharony (1991); Poon and Haw (1997)] a is the radius of a primary colloid particle. The relaxation time of the cluster can thus be written as

$$\tau(k) = \frac{a^3 k^{3/d_f}}{k_B T/6\pi\mu} = \frac{a^2}{D_0} k^{3/d_f}, \tag{9}$$

where $D_0 = k_B T/6\pi\mu a$ is the diffusion coefficient of the primary colloid particle. From this equation, we get

$$k = \left(\frac{D_0}{a^2} \tau \right)^{d_f/3} = (\tau/\tau_0)^{d_f/3}, \tag{10}$$

and we recall that $\tau_0 = a^2/D_0$.

A. Irreversible DLCA

Upon replacing Eq. (10) in the CMD for DLCA, Eq. (2), we obtain the following expression for the relaxation-time distribution at a time t in the self-assembly process:

$$H(\tau, \hat{t}) \simeq \frac{(\hat{t}/\theta)^{(\tau/\tau_0)^{d_f/3}-1}}{\left[(\hat{t}/\theta) + 1 \right]^{(\tau/\tau_0)^{d_f/3}+1}}. \tag{11}$$

Using the standard algebraic relation $z^w = e^{w \log z}$, the above expression can be rewritten as

$$H(\tau,\hat{t}) \simeq \frac{(\hat{t}/\theta) + 1}{\hat{t}/\theta} e^{-(\tau/\tau_0)^{d_f/3} \cdot \log\left[(\hat{t}/\theta)^{-1} + 1\right]}. \tag{12}$$

Upon defining

$$\tau_c = \frac{\tau_0}{\left(\log\left[\left(\hat{t}/\theta\right)^{-1} + 1\right]\right)^{3/d_f}}, \tag{13}$$

the relaxation time distribution can be shown to be a stretched-exponential distribution

$$H(\tau,\hat{t}) \simeq \frac{(\hat{t}/\theta) + 1}{\hat{t}/\theta} e^{-(\tau/\tau_c)^{d_f/3}}. \tag{14}$$

Clearly, for a finite aggregation time θ this distribution goes to zero only at $\hat{t} \to \infty$, along with τ_c given by Eq. (13), while in the limit of fast aggregation with $\theta \to 0$, instantaneous gelation is recovered. Exactly the same relaxation time spectrum given by Eq. (11) applies also to the case of aggregation with bond-dissociation in the early stage discussed in Sec. II C. For irreversible DLCA gelation, where the attraction energy is virtually infinite, it is experimentally impossible to test these predictions because of the extremely fast gelation kinetics which defeats the current time-resolution of scattering and optical techniques.

B. Partly reversible colloidal aggregation

For colloidal aggregation in the presence of thermal breakage of dangling particles, the asymptotic formula for the CMD upon approaching the gelation transition in an experiment where the attraction energy is raised toward the transition, is given by Eq. (4). The time dependence of the CMD is difficult to be obtained but we can analyze the asymptotic limit of long aggregation time. In this case, we obtain the following relaxation time spectrum:

$$H(\tau) \simeq \left(\frac{\tau}{\tau_0}\right)^{-d_f/2} e^{-(\tau/\tau_c)^{d_f/3}}. \tag{15}$$

Right at the transition where $\tau_c \to \infty$, the power-law becomes dominant and we recover power-law critical behavior

$$H(\tau \to \tau_c) \simeq \left(\frac{\tau}{\tau_0}\right)^{-d_f/2}. \tag{16}$$

For the experiments of Eberle *et al.* (2011), where $d_f = 1.7$, this theory predicts a critical exponent $n = d_f/2 = 0.85$ which is in reasonable agreement with the experimental data. It is important to note that this critical behavior arises upon increasing the attraction energy between the particles, although in the absence of a standard bond-percolation transition at a finite aggregation time $\hat{t}$. The dynamical arrest mechanism is analogous to the fully irreversible diffusion-limited gelation case, only the scaling of CMD is different, power-law in this case, instead of exponential.

Using the theory of Sec. II B, we can also study how the maximum relaxation time τ_c depends on the attraction energy in an experiment where the gelation transition is driven

by increasing βV. The maximum cluster size in the system is given by Eq. (5) as a function of the attraction energy βV, upon replacing $\lambda = \left(16\pi\right)^{-1}\delta^{-2}a^{-1}e^{-\beta V}$ in Eq. (5)

$$k_c = 2\log\left[\frac{e^{-\beta(V-V_c)}}{2e^{-\beta(V-V_c)}-1}\right]^{-1}$$
$$\approx 4^{-1}(\beta V_c - \beta V)^{-1}, \tag{17}$$

where in the second approximate equality we have Taylor-expanded the denominator to first order about βV_c. Using Eq. (10), we then readily obtain the following formula for the divergence of the longest relaxation time in the system:

$$\tau_c \approx \tau_0 4^{-3/d_f}(\beta V_c - \beta V)^{-3/d_f}, \tag{18}$$

with a critical exponent $\simeq 3/2$ for most partly reversible colloidal systems.

Assuming that the attraction energy increases upon increasing T, as for thermoresponsive colloidal particles, we obtain $\tau_c \approx \tau_0 4^{-3/d_f}[\beta V(T) - \beta V_c(T_c)]^{-3/d_f}$, where the relation $\beta V(T)$ is specified by the chemistry used to induce attraction between the particles. For example, with colloidal particles coated with a thermoresponsive p-NIPAM shell, an analytical relation between βV and T is provided by Eq. (13) in the work of Zaccone *et al.* (2011b).

C. Chemical gelation

In this case, the time-dependent solution to the master kinetic equation Eq. (1) displays a genuine bond-percolation transition at a finite time $\hat{t}_c$, which is the time at which the CMD develops a power-law heavy-tail, instead of decaying exponentially with k. At this singular point, the second-moment of the CMD diverges, which is the signature of the formation of a system-spanning cluster. The CMD in the pregel is given by Eq. (7). Using Eq. (9) in Eq. (7), we obtain the following relaxation spectrum for chemical gelation in the limit of a large number of reactive groups per molecule ($f \to \infty$):

$$H(\tau) \simeq \left(\frac{\tau}{\tau_0}\right)^{-(5/6)d_f} e^{-(\tau/\tau_c)^{d_f/3}}. \tag{19}$$

Upon approaching the gel point, there is a shift from stretched-exponential to power-law dominance, and the relaxation spectrum at the transition becomes

$$H(\tau \to \tau_c) \simeq \left(\frac{\tau}{\tau_0}\right)^{-(5/6)d_f}. \tag{20}$$

This theory therefore predicts the correct qualitative behavior: The relaxation changes from stretched-exponential into power-law upon approaching the gel transition. However, the predicted power-law exponent appears to be too large if one considers that typical fractal dimensions for chemical gelation are around $d_f \simeq 2$. This problem is certainly due to the fact that this analytical result is valid in the limit of infinite reactive groups per molecule $f \to \infty$, whereas in reality this number is just somewhat larger than two. For finite f, however, there is no analytical solution to the master kinetic equation known, see our discussion in Sec. II E. A quantitative theory of chemical gelation based on nonequilibrium statistical mechanics is deferred until analytical solutions for the master kinetic equations with $2 < f < \infty$ will be found in future work.

IV. DYNAMICAL ARREST MECHANISM IN COLLOIDAL GELATION

A. Absence of percolation at finite time in colloidal aggregation

The stretched exponential format of $H(\tau)$ is a consequence of the CMD being a stretched-exponential [Eq. (2) can be easily put in stretched exponential form]. This is in analogy with the power-law rheology of chemical gels where the power-law form of the CMD at chemical gelation (due to a percolative phase transition) controls the power-law form of $H(\tau)$. There is a fundamental difference, however, between Brownian gelation and percolation processes: The Brownian CMD Eq. (2) evolves in time in a self-preserving way without developing any finite tail at $k \to \infty$ at any finite $\hat{t}$. The development of a finite tail in c_k at a finite $\hat{t}$ is a necessary condition for bond-percolation to occur, because it is the signature of the emergence of a giant percolating cluster. In the absence of this key feature, the self-assembly process leads to larger and larger clusters which grow indefinitely, though not to a giant percolating cluster which takes over all other clusters [Kaprivski *et al.* (2010)]. In the following, we describe the Brownian gelation process mathematically by combining the relaxation behavior for partly reversible colloidal aggregation found in Sec. III B, with concepts from rigidity percolation for the interconnection between fractal clusters at the gelation transition. The calculation will be done analytically for the case of irreversible aggregation or partly reversible in the early stage.

B. Colloidal gelation mechanism

The route by which a colloidal suspension turns into a solidlike colloidal gel has been the object of intense study. Although a conclusive unifying picture has not emerged yet, consensus has been gathered for few mechanisms which may be important in different regions of the attraction-density state diagram. At moderate to intermediate volume fractions, and mild attraction, aggregation occurs close to thermodynamic equilibrium and spinodal decomposition may well represent the driving force for local densification. A glasslike arrest then sets in within the dense domains leading to the final solidlike gel. This scenario is known as arrested spinodal decomposition [Lu *et al.* (2008); Gibaud and Schurtenberger (2009)].

Here, we focus on the fully nonequilibrium scenario of colloidal gelation, also known as "cluster-jamming." Here, the attraction is stronger (corresponding to deeper quenches well below the binodal/spinodal lines), the clusters are fractal, as is the case for Brownian self-assembly, and the mechanism is fully kinetic. Due to the fractal nature, clusters growth cannot continue indefinitely because the volume occupied by the clusters grows faster than the available space [Haw *et al.* (1995)]. Hence, at some point the spheres enclosing the clusters reach a random close packing limit $\tilde{\phi}_c$ at which the spatial separation between the clusters goes to zero and they can interconnect through the outermost particles on their respective surfaces (cluster jamming). This type of solidification mechanism has been demonstrated also for colloidal gelation under shear flow [Xie *et al.* (2010); Zaccone *et al.* (2011a)]. This condition defines the dynamical arrest at colloidal gelation which is schematically depicted in Fig. 1.

As this condition is reached, the characteristic aggregation time, obviously, must vanish. In the opposite limit of a perfectly fluid system one must recover the aggregation time θ as is determined by the diffusive collision dynamics. Hence, we can interpolate between the perfectly rigid limit, where the system has become solid and the aggregation time has become zero, and the perfectly fluid limit where the aggregation time is controlled by diffusive Smoluchowski dynamics, by considering an effective aggregation time
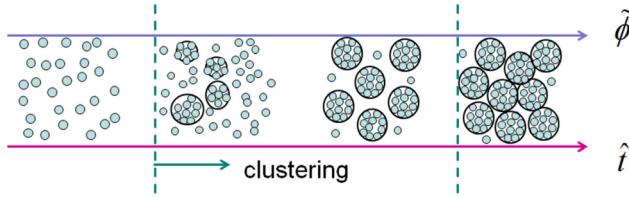
FIG. 1. Schematic representation of the kinetic self-assembly process leading to the formation of rigid fractal clusters. They eventually interconnect into a network through formation of intercluster bonds. The latter reduces the fraction of soft modes in the system and drive the final rigidity-percolation transition.

$$\theta_{\text{eff}} = \theta \cdot \psi. \qquad (21)$$

Here, ψ is a fluidity order parameter, which is $\psi = 1$ in a perfectly fluid system, and $\psi = 0$ in a perfectly rigid system. This identifies ψ with the fraction of soft modes, or floppy modes, in the system. We recall that a floppy mode is a global deformation mode of a particle assembly (i.e., a set of interparticle or intercluster displacements from the original or equilibrium positions) which can be excited with a vanishing applied stress. In a fluid all modes are soft, in that they can be excited with zero energy input, whereas in a solid there are no extended modes which can be excited without injecting energy into the system (of course there can be localized soft modes, with localized fluidlike behavior, which contribute to the viscous part of the response).

Upon approaching the random close packing condition, the rigid clusters form bonds with other rigid clusters, and the average number of bonds z per rigid building block (i.e., per cluster) becomes finite. While the clusters are internally rigid, the intercluster bonds are weaker (weak-link approximation), and therefore, it suffices to consider the intercluster bonds in the evaluation of the overall rigidity. The fraction of floppy modes is related to the bonding number via the mean-field Maxwell rigidity criterion, or one of its more modern rigidity-percolation versions [Thorpe (1983)]. According to Maxwell (1864), $\psi = (z_c - z)/z_c \sim (z - z_c)$, where $z_c = 2d = 6$ with central-force bonds in $d = 3$. According to rigidity-percolation theory, $\psi \sim (z - z_c) \sim (\tilde{\phi} - \tilde{\phi}_c)^\beta$, where β is a critical exponent [Jacobs and Thorpe (1995)], and $\tilde{\phi}_c \simeq 0.64$ is a random close packing limit for spherical-like clusters.

It should be emphasized that rigidity percolation is distinct from simple bond percolation and is a much more general phenomenon. Simple bond percolation is driven by one quantity, e.g., the fraction of bonds p, which is a scalar. However, the rigidity percolation is driven by the local force, which is a vector [Binder and Kob (2011)]. Therefore, it is expected and well established that bond percolation and rigidity percolation belong to different universality classes, and their respective thresholds are also very different [Binder and Kob (2011)]. There are several instances where the structural arrest is not strictly achieved through a bond-percolation transition, yet rigidity percolation provides a correct description of the emergence of rigidity. This has been shown, in particular, in the context of inorganic and semiconductor glasses [Thorpe (1983); Binder and Kob (2011)], and granular jamming [Zaccone and Scossa-Romano (2011)]. Hence, using $\psi \sim (\tilde{\phi} - \tilde{\phi}_c)^\beta$ in Eq. (11), we finally get

$$\theta_{\text{eff}} = \theta \cdot A (\tilde{\phi}_c - \tilde{\phi})^\nu, \qquad (22)$$

where A is a numerical constant.

C. Relaxation spectrum upon approaching the liquid-solid transition

Upon placing Eq. (22) in Eq. (13) and linearizing the logarithm close to the transition, we get for the maximum cut-off time scale the following expression

$$\tau_c = \frac{\tau_0}{\theta \cdot A\big(\tilde{\phi}_c - \tilde{\phi}\big)^\nu}, \tag{23}$$

which correctly gives solidification $\tau_c \to \infty$ at the random close packing of clusters, $\tilde{\phi} \to \tilde{\phi}_c$.

The volume fraction occupied by the clusters $\tilde{\phi}$ is itself related to the self-assembly time $\hat{t}$, because this volume fraction grows along with self-assembly due to the fractal nature of the clusters [Haw *et al.* (1995)]. From our previous work [Zaccone *et al.* (2013)], we have the following approximate relation $(\hat{t}/\theta) \approx c\tilde{\phi}^{d_f/3}$, where c is a numerical prefactor. Using this relation, together with Eq. (23), in Eq. (12), we finally arrive at the relaxation time spectrum close to the transition

$$H\big(\tau, \tilde{\phi}\big) = H_0 \exp\left\{ -\left[\tau/s\big(\tilde{\phi}_c - \tilde{\phi}\big)^{-\nu}\right]^{d_f/3} \right\}, \tag{24}$$

where H_0 and s are numerical constants. H_0 is a numerical prefactor with dimensionality $k_B T/a^3$. This theoretical expression represents, to our knowledge, the first microscopic description of the relaxation time spectrum as a function of the underlying microscopic self-assembly process. In Sec. V, this expression is our starting point to derive the macroscopic rheological behavior of colloidal systems close to the gelation transition. Illustrative curves of $H(\tau)$ calculated according to Eq. (24) are shown in Fig. 2(a).

V. ANALYTICAL DERIVATION OF RHEOLOGY: IRREVERSIBLE COLLOIDAL GELATION

A. Relaxation modulus

We are now able to construct a bottom-up theory of rheology at the colloidal sol-gel transition. According to the Boltzmann's superposition principle, the constitutive stress-strain relation for a viscoelastic material is given as [Zener (1948)]

$$\sigma(t) = \int_0^\infty G(s)\dot{\gamma}(t - s)ds. \tag{25}$$

Within the Boltzmann framework, the overall material relaxation process is assumed to be the result of many independent exponential relaxations. Under this assumption, the time-dependent relaxation shear modulus can be expressed [Zener (1948)] in terms of the relaxation time spectrum $H(\tau)$, as a weighted time integral over all allowed relaxation modes for $\tau \leq \tau_c$

$$G(t) = G_e + \int_0^{\tau_c} \frac{1}{\tau} H(\tau) e^{-t/\tau} d\tau, \tag{26}$$

where G_e denotes the infinite-time value of the shear modulus, and $G_e > 0$ only for $\tilde{\phi} > \tilde{\phi}_c$, i.e., above the liquid-solid transition, while $G_e = 0$ below the transition. This is justified in view of the fact that G_e is finite only as long as the fraction of floppy modes is
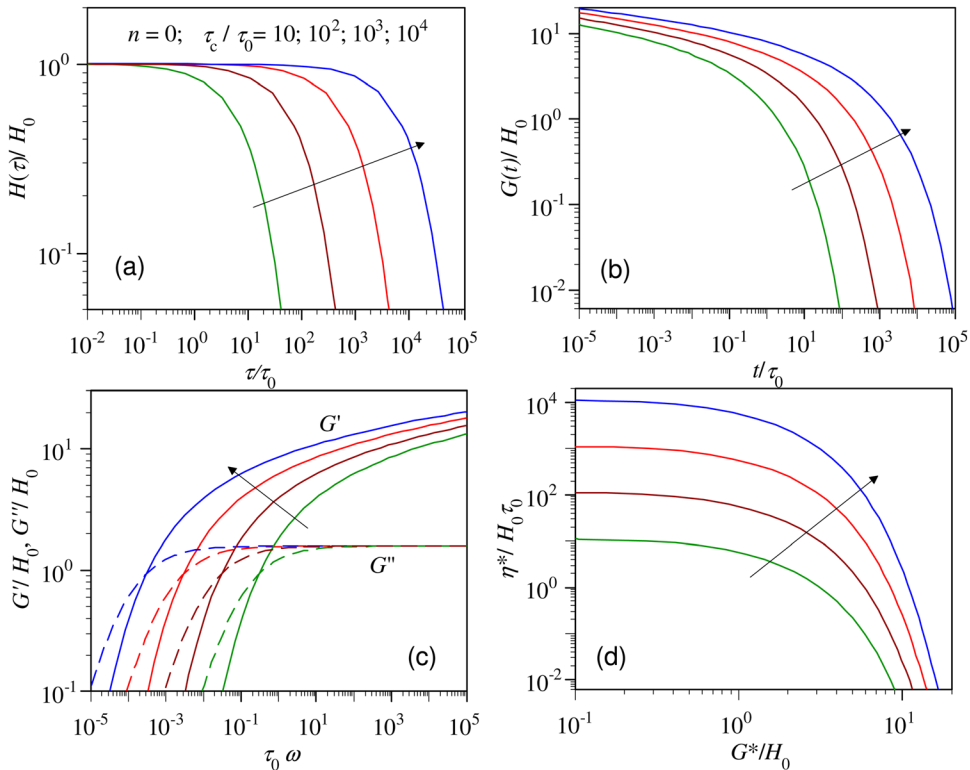
FIG. 2. Theoretical predictions for the limit of irreversible colloidal aggregation ($n = 0$). (a) Illustrative plots of the relaxation time spectrum, according to Eq. (14), as a function of the distance from the transition. (b) Relaxation modulus. (c) Frequency rheology according to Eq. (24) implemented in Eq. (30). (d) Plot of the complex viscosity as a function of the complex shear modulus. The exponent of the stretched-exponential is 0.8 in all cases, corresponding to $d_f = 2.4$. The arrow indicates in which order the ratio τ_c/τ_0 increases for the various curves.

zero, $\psi = 0$. Upon substituting Eq. (14) in Eq. (26), the integral cannot be done analytically. However, the expression in Eq. (8) can be very well approximated with the following function:

$$H(\tau) = H_0 e^{-1} \left[2 + \frac{1}{2} \left(1 - (\tau/\tau_c)^{d_f/3} \right)^2 - (\tau/\tau_c)^{d_f/3} \right], \tag{27}$$

with τ_c given as usual by Eq. (13). Now the integral can be evaluated analytically, which gives

$$G(t) \approx G_e + \frac{1}{2e} \left[5E_1(t/\tau_c) - 4E_{1+d_f/3}(t/\tau_c) + E_{1+2d_f/3}(t/\tau_c) \right], \tag{28}$$

where $E_n(x)$ denotes the exponential integral function of order n, defined as [Abramowitz and Stegun (1972)], $E_n(x) = \int_1^\infty t^{-n} e^{-xt} dt$. At the atomistic level, it rises at the transition point as $G_e \sim (z - z_c)$, where the negative term represents the contribution of nonaffine displacements [Zaccone and Scossa-Romano (2011)]. Predictions of relaxation modulus according to Eq. (28) are shown in Fig. 2(b).

As one can verify by plotting the function in the square bracket of Eq. (28), the behavior is dominated by the first term, the exponential-integral of order one: $E_1(t/\tau_c)$. The

latter can be approximated by a simpler function as $E_1(t/\tau_c) \approx e^{-t/\tau_c}\log[1 + (t/\tau_c)^{-1}]$. We therefore extract the following qualitative relaxation behavior

$$G(t) \approx G_e + \frac{5}{2e}E_1(t/\tau_c) \sim e^{-t/\tau_c}\log\left[1 + (t/\tau_c\})^{-1}\right]. \tag{29}$$

In the short-time limit, and close to the transition where τ_c diverges, $t \ll \tau_c$, $G \sim \log(\tau_c/t)$, and the relaxation is therefore *logarithmic*. In the opposite long-time limit and away from the transition, instead, the relaxation is mainly exponential, $G \sim e^{-t/\tau_c}$. The fact that the suspension of colloidal clusters displays logarithmic creep close to gelation is a signature of slow dynamics which suggests a similarity with glassy arrest in simple liquids. Experimental signatures of slow dynamics at the colloidal gelation transition with low to moderate attraction energy have been reported in the work of Segrè *et al.* (2001).

B. Oscillatory rheology

We can now derive the oscillatory rheology, which is given by the Fourier transform of Eq. (26) and by the Kramers-Kronig relation, leading to the storage and loss modulus [Ferry (1980)]

$$G'(\omega) = G_e + \int_0^{\tau_c} \frac{d\tau}{\tau}H(\tau)\frac{(\omega\tau)^2}{1 + (\omega\tau)^2},$$
$$G''(\omega) = \int_0^{\tau_c} \frac{d\tau}{\tau}H(\tau)\frac{\omega\tau}{1 + (\omega\tau)^2}. \tag{30}$$

Using our relaxation spectrum for Brownian gelation given by Eq. (14) in the above integrals, analytical expressions for $G'(\omega)$ and $G''(\omega)$ can be derived upon integration. The resulting expressions are somewhat lengthy, and they are reported in full in the appendix. For illustrative purposes, the rheological spectra are shown in Fig. 2(c). Here, we just show the leading terms which control the qualitative behavior

$$G'(\omega) \sim \log\left(1 + \omega^2\tau_c^2\right),$$
$$G''(\omega) \sim \tan^{-1}(\omega\tau_c). \tag{31}$$

As is evident from Fig. 2(c), at low extent of self-assembly the rheological response is Newtonian. As the self-assembly process evolves leading to larger volume fractions occupied by the clusters, G' and G'' tend to cross at increasingly lower frequencies, although no signature of power-law behavior is evident. At the transition, the crossing point gets shifted to vanishing frequency, while both moduli tend to flatten out at larger frequencies. All these features (absence of clear power-law rheology, crossing of the moduli, flattening at the transition) are reminiscent of those observed in experimental studies of colloidal gelation with finite attraction energy between the particles, such as the work of Trappe and Weitz (2000) and Laurati *et al.* (2009).

VI. LOW-SHEAR VISCOSITY DIVERGENCE AT THE GELATION TRANSITION

The low-shear viscosity is given by

$$\eta = \int_0^\infty G(t)dt = \int_0^{\tau_c} H(\tau)d\tau, \tag{32}$$

where Eq. (26) is used to be obtain the second equality. Upon inserting the relaxation time spectrum that we derived for Brownian gelation, Eq. (24), in the above Eq. (32), the simple integral gives

$$\eta \simeq s\left(\tilde{\phi}_c - \tilde{\phi}\right)^{-\nu d_f/3}. \tag{33}$$

Hence, our theory predicts a power-law divergence of the viscosity at the colloidal gelation transition, which provides a theoretical explanation to experimental observations [Trappe *et al.* (2001); Prasad *et al.* (2003)]. Interestingly, the power-law criticality is not a consequence of bond-percolation, as has been speculated many times in the past, but descends from rigidity percolation. The fraction of floppy modes in the system decreases due to the increasing number $zN/2$ of intercluster bonds formed due to the continuous fractal growth of the clusters.

The power-law exponent which controls the divergence of the viscosity at the colloidal gelation transition is proportional to both the power-law critical exponent β of rigidity percolation, and to the fractal dimension d_f which characterizes the fractal growth of the clusters, and inversely proportional to the space dimensionality. Physically, this means that the transition is steeper for larger fractal dimensions of cluster growth, because the relaxation spectrum is narrower, i.e., less "stretched," at a fixed $\tilde{\phi}$. Conversely, for lower d_f the relaxation spectrum is broader which leads to a smoother divergence of the viscosity.

VII. MICROSCOPIC THEORY OF RHEOLOGY: THERMOREVERSIBLE COLLOIDAL GELATION

A. Comparison with small amplitude oscillatory shear rheology (SAOS) data from the literature

We now consider the case of colloidal particles where the attraction energy can be controlled by means of chemical modifications of the particle surface. Typically, the attraction energy βV is a monotonic increasing function of T. The best data available are those of Eberle *et al.* (2011), who used a well characterized system of octadecyl silica nanoparticles. The octadecyl shell becomes increasingly more attractive as the temperature is raised in the system. The rheological response was studied at different temperatures across the gelation transition by means of small amplitude oscillatory shear rheology (SAOS). The latter was done at a small imposed stress amplitude (17.68 mPa) well within the linear response regime. As a consequence, hysteresis is expected to be negligible. The critical attraction energy at the gelation transition for a system at $\phi_0 = 0.12$ is about $4.4k_BT$, according to the experimental estimate of Eberle *et al.* (2011), and $\approx 7.4k_BT$ according to our estimate using our Eq. (6) above.

The oscillatory rheological response can be calculated using our theory, by implementing the relaxation spectrum $H(\tau)$ for reversible colloidal aggregation, given by Eq. (15) above, together with the cut-off relaxation time τ_c given by Eq. (18), in Eq. (30). Since βV as a function of T is not known in analytical form for this system, we take a power-law divergence $\tau_c \approx (T_c - T)^{-\nu}$, where ν is a fitting parameter. Eq. (30) with $H(\tau)$ given by Eq. (15) is not soluble analytically, therefore, we resort to the numerical discretization scheme of Winter and Mours (2006) to calculate the $G'(\omega)$ and $G''(\omega)$ spectra. It

should be noted that Eq. (15) is obtained from a model where all particles on the outer-most (surface) shell of the clusters are allowed to breakup with a finite breakup rate. In reality, of course, the distribution of breakup events is more random and the actual exponents may differ from those prescribed by Eq. (15). In the following, we will determine more realistic values of the exponents of Eq. (15) for thermoreversible gelation upon fitting experimental data from the literature.

To fit the SAOS data of Eberle *et al.* (2011), we therefore used the following expression, which is inspired by Eq. (15)

$$H(\tau \to \tau_c) = H_0 \left(\frac{\tau}{\tau_0} \right)^{-n} e^{-(\tau/\tau_c)^b}, \tag{34}$$

where n and b are fitted to the experimental data, together with the scale factor H_0. A typical spectrum, together with the set of rheological material functions, is shown in Fig. 3.

The comparison between theory and experiments is shown in Fig. 4. It is evident from the comparison that our theory is able to reproduce the transition from power-law rheology at high frequency into Newtownian limiting behavior in the limit of zero frequency. At low frequency some discrepancy between theory and experiments is evident, which may be due to the continuing aggregation of clusters in the experimental system as frequency is gradually increased in the sweep experiment. In practice, we believe that, at
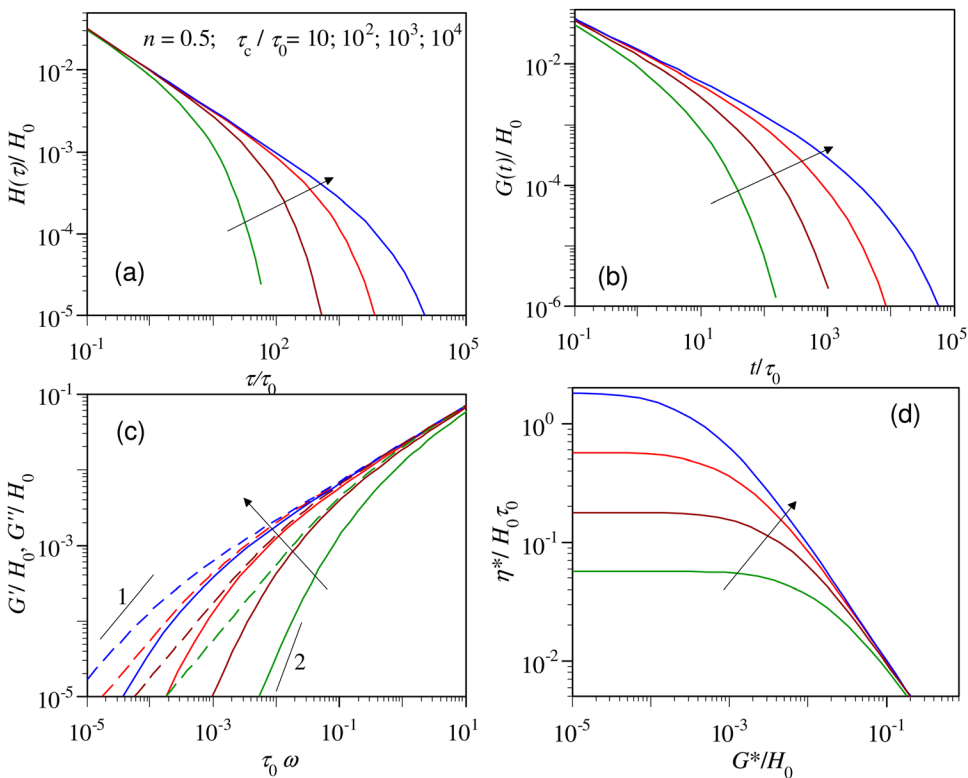

FIG. 3. Theoretical predictions for the limit of reversible colloidal aggregation with $n = 0.5$. (a) Illustrative plots of the relaxation time spectrum, according to Eq. (34), as a function of the distance from the transition. (b) Relaxation modulus. (c) Frequency rheology. (d) Plot of the complex viscosity as a function of the complex shear modulus. The exponent of the stretched-exponential is $b = 0.8$ in all cases, corresponding to $d_f = 2.4$. The arrow indicates in which order the ratio τ_c/τ_0 increases for the various curves.
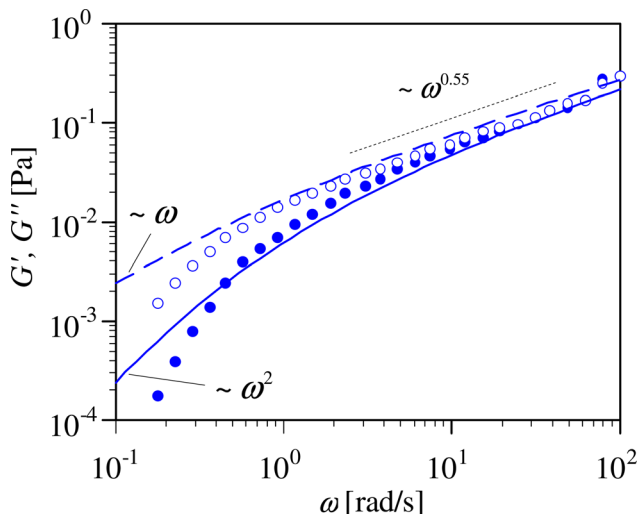
FIG. 4. Oscillatory rheology at the gelation transition of thermoresponsive colloidal particles. Continuous lines: Our theory using Eq. (34) in Eq. (30) with $H_0 = 0.01$ Pa and $\tau_c = 2$ s. Symbols: Experimental data of Eberle *et al.* (2011) at $T = 28.2\,°C$.

low frequencies, the time scale of the experimental measure is long compared to the aggregation time scale. Hence, we expect the CMD to be changing during the experiment, at least at low frequencies. However, based on the information that we can find in the original references, it is hard to provide a conclusive assessment. This is indeed a crucial unsettled aspect related to rheological characterization of aggregating colloids. This effect may also lead to violation of the Kramers-Kronig relation in the experimental response, whereas the theory does satisfy Kramers-Kronig and correctly recovers the limiting Newtonian behavior. Further experimental investigations are required in order to elucidate the role of continuing aggregation during the time frame of the oscillatory sweep experiment.

The values of the exponents used in the comparison of Fig. 4 are $n = 0.55$ and $b = 0.8$. From the comparison of the exact Eq. (15) and the semiempirical Eq. (34), we are led to the following generalized expression:

$$H(\tau \to \tau_c) = H_0 \left(\frac{\tau}{\tau_0} \right)^{-\alpha d_f} e^{-(\tau/\tau_c)^{\beta d_f/3}}, \qquad (35)$$

where $\alpha = 0$ for irreversible colloidal aggregation, while $\alpha = 1/2$ for the reversible aggregation model with breakup on the cluster surface. The data of Eberle *et al.* (2011) at the gelation transition are fitted with

$$\begin{aligned} \alpha &\simeq 0.31, \\ \beta &\simeq 1.3. \end{aligned} \qquad (36)$$

The α value falls well within the two values of α found for irreversible aggregation and the reversible aggregation models, and is somewhat closer to the latter limit.

Finally, we also compared our theory with experimental data obtained using polymer-colloid mixtures where the attraction is induced by the depletion effect of nonadsorbing polymers. The comparison using Eq. (34) is shown in Fig. 5. An excellent description of

the experimental response close to the gelation transition is provided with $n = 0.17$ and $b = 0.8$. This is consistent with a more strongly attractive/diffusion-controlled system, as now $\alpha \approx 0.06$. Further, $d_f \approx 2.8$ is appropriate for a practically nonfractal gel. This value of α is now much closer to zero, and we recall that $\alpha = 0$ represents the fully irreversible, and fully diffusion-controlled, limit. This difference between the data of Eberle et al. (2011) ($\alpha \approx 0.31$, closer to $\alpha = 1/2$ of reversible aggregation) and those of Laurati et al. (2009) ($\alpha \approx 0.06$, closer to fully irreversible diffusion-limited) may be ascribed to the fact that the polymer-depletion system has a longer range of attraction and larger particles, thus being closer to the fully diffusion-controlled limit $\alpha = 0$. The system of Eberle et al. (2009), on the other hand, with much smaller particles and short-range, moderate attraction, might be comparatively closer to a reaction-limited scheme where diffusion is less controlling and only a fraction of all interparticle or particle-cluster collisions lead to stable bonds due to thermal breakup.

B. Extracting the CMD from fitting the SAOS data

Let us consider the generalized relaxation-time spectrum, Eq. (35). Upon recalling the relation between the cluster mass k and the relaxation time τ, given in Eq. (10), it is possible to extract the CMD from the fitted relaxation-time spectrum. The CMD corresponding to the fitted spectrum Eq. (35), close to the transition takes the following form:

$$c_k \approx k^{-3\alpha} e^{-(k/k_c)^{\beta}}, \qquad (37)$$

where $k_c = (\tau_c/\tau)^{d_f/3}$, and we omitted numerical prefactors. Using the value of α that we determined from the fitting to the experimental data of Eberle et al. (2011), this analysis suggests that the actual solution to the full Eq. (1) with all terms taken into account, for the problem of thermoreversible gelation might be given semiempirically by the following CMD:
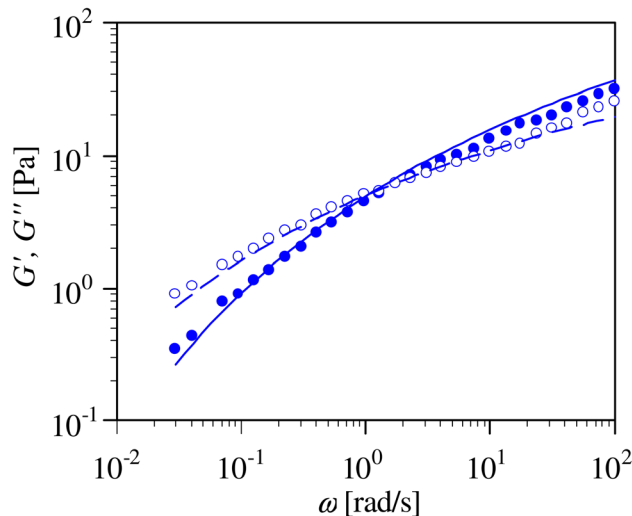

FIG. 5. Oscillatory rheology at the gelation transition of colloidal particles induced by polymer depletion attraction. Continuous lines: Our theory using Eq. (34) in Eq. (30) with $H_0 = 6.6$ Pa and $\tau_c = 1.55$ s. Symbols: Experimental data of Laurati et al. (2009).

$$c_k \approx k^{-0.93} e^{-(k/k_c)^{0.80}}, \tag{38}$$

with the associated relaxation-time spectrum

$$H(\tau) = H_0 \left(\frac{\tau}{\tau_0}\right)^{-0.31 d_f} e^{-(\tau/\tau_c)^{1.30 d_f/3}}. \tag{39}$$

For the data of Laurati *et al*. (2009), we obtain instead the following CMD at the transition:

$$c_k \approx k^{-0.18} e^{-(k/k_c)^{0.80}}. \tag{40}$$

Clearly, this form of the CMD, with a weak power-law, is very close to the purely stretched-exponential form that we recover in the fully irreversible diffusion-controlled limit, where $c_k \approx e^{-(k/k_c)^{\beta}}$.

VIII. RHEOLOGICAL CLASSIFICATION OF LIQUID-SOLID TRANSITION IN SOFT MATERIALS

In recent work [Winter (2013)], a criterion has been proposed in order to distinguish among different mechanisms of dynamical arrest based on the material function $H(\tau)$ which controls the creep and the rheological response. From the analysis of several experimental data sets on different materials, it has been established that power-law spectra which tend to narrow down toward large time scales $\sim \tau^n$ with $n < 0$ are representative of chemical gelation and bond-percolation processes [Winter and Chambon (1986)], whereas the opposite behavior, with $n > 0$, is characteristic of soft glassy materials [Siebenbürger *et al*. (2009)], in particular upon approaching the hard sphere glass transition. In the present study, we found a somewhat more complex relaxation time spectrum for Brownian fully irreversible gelation starting from the microscopic self-assembly of colloidal particles, that is, a purely stretched-exponential spectrum. Upon introducing the possibility that some bonds can be broken up by thermal energy (reversible or partly reversible aggregation), we have shown that power-laws are recovered although they still coexist with a stretched-exponential cut-off.

It is useful to consider the obtained spectrum in comparison with the above mentioned paradigms of chemical gelation and soft glass. The scenario is schematically depicted in Fig. 6. For fully irreversible diffusion-controlled gelation, close to the transition, the stretched-exponential spectrum exhibits a broad plateau (see also Fig. 2) which could be approximated by $n = 0$. This result suggests that fully irreversible diffusion-controlled colloidal gelation is a rheological midway between chemical gelation and glass transition and represents the bridge between those two limits. Reversible aggregation and gelation with finite attraction energy is instead much closer to chemical gelation and in general to a reaction-limited process because only a limited fraction of collisions leads to stable bonding due to thermal breakup.

These considerations motivate us to draw a possible scenario to classify liquid-solid transitions in soft matter which is based on two key parameters: The bonding energy and the ratio of bond-formation rate to transport rate. The latter ratio controls the crossover between bond-percolating chemical gelation and colloidal gelation, based on the underlying self-assembly kinetics. This can be understood from the consideration of the microscopic aggregation rate K_{ij}^+ in Eq. (1). Bond-percolation solutions, with the emergence of a tail at $k \to \infty$ at a finite aggregation time, are admitted by the master equations, Eq. (1),
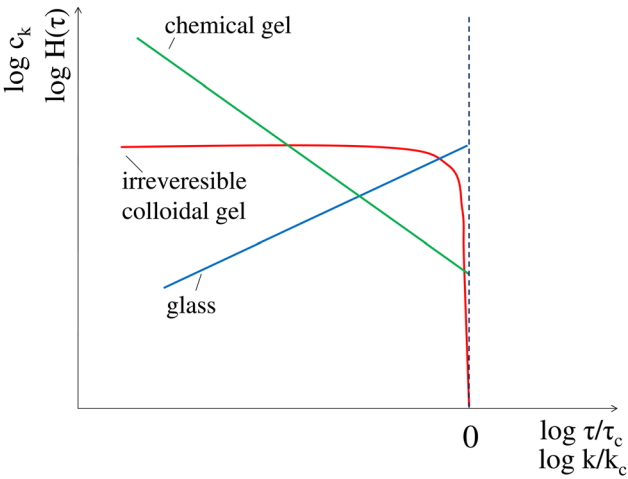
FIG. 6. Rheological classification of different mechanism for the liquid-solid transition in soft matter according to the qualitative form of the CMD and relaxation time spectrum. c_k denotes the distribution of cluster sizes k, $H(\tau)$ is the spectrum of relaxation times τ.

only with rates of the form $K_{ij}^+ = A + B \cdot ij + C \cdot (i+j)$, where B, $C > 0$ depend on the functionality f (number of reactive end-groups) of the molecules [Kaprivski *et al.* (2010)]. This form has full validity in the chemical regime where the assembly rate K_{ij}^+ is proportional to the number of end-groups on the colliding clusters. In the opposite limit where the assembly rate is entirely controlled by the diffusion transport [Kaprivski *et al.* (2010)], $K_{ij}^+ \sim (i+j) \cdot D_{ij} \sim const$ because $D_{ij} \sim (i+j)^{-1}$. With this form of K_{ij}^+ there is no bond-percolation solution [Kaprivski *et al.* (2010)], and the gelation process occurs following the scheme of Fig. 1. A schematic summary of the different gelation transition scenarios depending on the underlying microscopic collision-reaction and dissociation physics is shown in the table below, Table I. Hence, gelation through bond-percolation typically occurs when the self-assembly rate is a monotonic increasing function of the sizes of colliding clusters. This condition is satisfied when the aggregation rate is independent of diffusive transport and is controlled only by the functionality of the molecules and by the collision cross-section. This self-assembly process leads to clear power-law rheology with $n < 0$, which is rooted in the power-law form of the CMD at percolation. In the opposite limit of diffusion-limited self-assembly, there is no bond-percolation route to gelation, which proceeds, instead, via packing and interconnection of many rigid clusters (rigidity-percolation [Jacobs and Thorpe (1995)]), in the absence of a giant percolating cluster. In this case, $n = 0$ at the transition. Reversible colloidal gelation still

TABLE I. Summary of different chemical and colloidal gelation scenarios depending on the underlying microscopic association and dissociation kinetics.

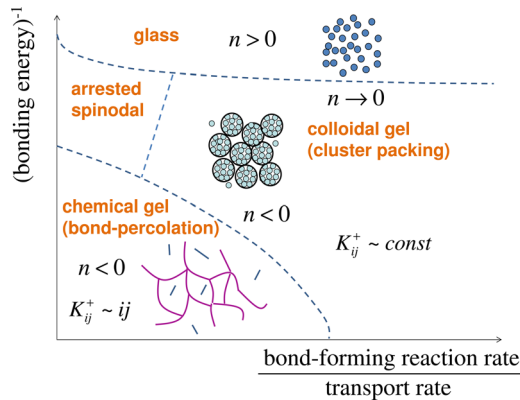| K_{ij}^- \ K_{ij}^+	$\sim const$	$\sim ij$	$Aij + B(i+j) + C$
~ 0	• Irreversible colloidal gelation	• Chemical gelation $f \to \infty$	• Chemical gelation $2 < f < \infty$
	• Power-law: No	• Power-law: Yes	• No solution so far
$\sim e^{-\beta V} K_{ij}^+$	• Reversible colloidal gelation	• Reversible chemical gelation $f \to \infty$	• Reversible chemical gelation $2 < f < \infty$
	• Power-law: Yes	• No solution so far	• No solution so far

FIG. 7. Hypothetical crossovers between different dynamical arrest mechanisms in soft matter.

occurs via interconnection of the clusters, but this time the process is no longer fully diffusion-controlled as the collision efficiency is lower than 1. We have shown in Sec. II B that this is a nonequilibrium phase transition where the finite attraction energy plays the role of the control parameter, and the CMD presents power-law form at criticality which leads to power-law rheology in the frequency spectrum.

This scenario is schematically summarized in the hypothetical state diagram of Fig. 7. The separation between different arrest mechanisms should be interpreted as gradual crossovers, not as actual state boundaries. The crossover between colloidal glass and colloidal gel has been discussed in Zaccone *et al.* (2009). Another important parameter which controls this crossover, besides the attraction energy, is the structural heterogeneity, related to the cluster size, which also controls the mechanical response. Clearly, the colloidal gelation process represents a continuous bridge between the two limits of chemical gelation and glass transition in terms of mechanical response. Of course, another crucial parameter which controls fluid-solid transitions in self-assembling colloids and polymers is the volume fraction. For example, volume fraction will significantly affect the crossover between the gelation and the glass transition, and it obviously controls the structural heterogeneity of an attractive colloidal system. Therefore, a complete state diagram would have to include the volume fraction as an additional axis in Fig. 7. However, our aim here is to isolate the effect of the interplay between attraction and transport, which has not been considered in previous works, to yield new insights.

IX. CONCLUSION

We developed a fully analytical, nonequilibrium statistical mechanics framework to connect the microscopic level of self-assembly and clustering, with the macroscopic rheology and relaxation at the colloidal gelation transition. The starting point is always the master kinetic equations for aggregation and breakup of clusters given a microscopic interaction between the particles. Colloidal gelation, even when reversible, always occurs far away from detailed balance, insofar the association rates are always larger then the fragmentation rates, and the colloidal gel represents a nonequilibrium steady-state which has nothing in common with equilibrium steady-states. With finite attraction energy between the particles, we have shown that gelation is a nonequilibrium phase transition with the attraction energy playing the role of the control parameter.

We then used these solutions of the master kinetic equations in terms of CMDs to calculate the relaxation time spectra from which the full rheological response can be

calculated using Boltzmann's superposition principle. In the limit of fully irreversible diffusion-controlled gelation, the relaxation spectrum is a simple stretched-exponential, with a stretching exponent which depends on the fractal dimension of the clusters. No power-law features are therefore found in the rheological response. When the attraction energy is finite, the CMD exhibits a power-law form, still coexisting with a stretched-exponential cutoff, but this time power-law rheology is recovered at sufficiently high frequency. The theory allows us to describe and rationalize experimental data from the literature where attraction is tuned either using a thermoresponsive shell [Eberle *et al.* (2011)] or by polymer-depletion [Laurati *et al.* (2009)].

This provides a theoretical explanation to previous experimental findings. Following a recent proposal for the rheological classification of liquid-solid transitions in soft matter based on the power-law exponent of the relaxation time spectrum [Winter and Chambon (1986)], $H(\tau) \sim \tau^n$, our model indicates that colloidal gelation can be represented by $n = 0$ in the fully irreversible diffusion-controlled limit, and by $n < 0$ for reversible aggregation, thus being an effective midway or bridge between chemical gelation, with $n < 0$, and glass transition $n > 0$.

Our method can be further developed in future studies to deal with more complex material-mediated chemistries [Di Michele *et al.* (2013); Di Michele *et al.* (2012)], and with field-induced assembly mechanisms such as shear-induced aggregation [Xie *et al.* (2010); Zaccone *et al.* (2011a); Wu *et al.* (2009)]. Also, it can be used to bridge chemical and colloidal gelation into a single framework. In industrial applications, it can be employed to extract the CMD of the self-assembly process from simple oscillatory rheology measurements.

ACKNOWLEDGMENT

APPENDIX: G' AND G'' EXPRESSIONS FOR IRREVERSIBLE COLLOIDAL SELF-ASSEMBLY

In this Appendix, we reported the full expression for the storage and loss moduli calculated using Eq. (14) in Eq. (20). For the storage modulus, we have

$$
G'(\omega) = G_e + \frac{1}{4e}\left[5\log\left(1 + \omega^2\tau_c^2\right) + 3\omega^2\tau_c^2\left(\frac{{}_2F_1\left[1,\dfrac{3+d_f}{3};\dfrac{6+d_f}{3};-\omega^2\tau_c^2\right]}{3+d_f} \right. \right.
$$
$$
\left. \left. - 8\frac{{}_2F_1\left[1,\dfrac{6+d_f}{6};2+\dfrac{d_f}{6};-\omega^2\tau_c^2\right]}{6+d_f} \right) \right],
\tag{A1}
$$

while for the loss modulus, we obtain

$$
G''(\omega) = \frac{1}{4e}\left[10\tan^{-1}(\omega\tau_c) + 6\omega\tau_c\left(-4\frac{{}_2F_1\left[1,\dfrac{3+d_f}{6};\dfrac{9+df}{6};-\omega^2\tau_c^2\right]}{3+d_f} \right. \right.
$$
$$
\left. \left. + \frac{{}_2F_1\left[1,\dfrac{1}{6}(3+2d_f);\dfrac{1}{6}(9+2d_f);-\omega^2\tau_c^2\right]}{3+2d_f} \right) \right].
\tag{A2}
$$

Here, $_2F_1[a, b; c; x]$ is the ordinary hypergeometric function of the variable x with arguments a, b, c [Abramowitz and Stegun (1972)]. In this equations, we have taken $H_0 = 1$ in units of $k_B T / a^3$.

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