

A parameter-free description of the kinetics of formation of loop-less branched structures and gels

Francesco Sciortino,^{ab} Cristiano De Michele,^{ab} Silvia Corezzi,^{bc} John Russo,^{*a} Emanuela Zaccarelli^{ab} and Piero Tartaglia^{ad}

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We study, *via* Brownian dynamics simulation, the kinetics of formation of branched loop-less structures for a mixture of particles with functionalities of two and three, the three-functional ones providing the branching points in the resulting network. We show that for this system, by combining the appropriate Smoluchowski rate equations, including condensation and fragmentation terms, with the thermodynamic perturbation theory of Wertheim, it is possible to provide a parameter-free description of the assembly process, even in the limit of irreversible aggregation (low T). Our work provides evidence of a connection between physical and chemical gelation in low-valence particle systems, properly relating aging (or curing) time with temperature.

1. Introduction

Irreversible aggregation is the process by which particles stick together, driven by attraction energies u_0 much larger than the thermal energy $k_B T$. The aggregate often results in a fractal structure, whose dimension is controlled by the kinetics of the process.¹ Irreversible aggregation takes place not only in colloidal systems but also in molecular ones, when molecules with a finite functionality f react together, progressively forming larger and larger clusters, ending in a spanning structure.² In this last case, the process is named chemical gelation (or condensation). During irreversible aggregation, bonds – once formed – never break, and the final structure of the aggregates results from a delicate balance between the cluster-size dependence of the diffusion process and the probability of irreversible sticking. Recently, due to its importance in biological, technological and biomedical applications, the physics behind the formation of *equilibrium* branched structures and networks, starting from monomeric unassembled initial states, is receiving considerable interest.^{3–9} In reversible aggregation, bond-breaking events are possible and the equilibrium state is characterized by a distribution of clusters (which can even be of infinite size, *i.e.* percolating) which continuously restructure themselves on a time scale controlled by the bond lifetime. Theoretical studies are searching for a general approach to describe both the thermodynamics and the kinetic processes leading to self-assembly over the whole range of densities and temperatures,^{10–12} attempting to extend to equilibrium branched systems the work developed in recent decades for the case of self-assembling equilibrium polymers and

worm-like micelles.^{13–15} Numerical studies of the self-assembly of patchy¹⁶ and functionalized particles are also contributing to the quest for the essential features behind the formation of equilibrium branched structures and gels. Off-lattice models for thermoreversible gels have been recently introduced,^{17–21} confirming that the formation of equilibrium branched (and percolating) structures is favored by the limitation in the maximum number of possible inter-particle bonds (which in analogy with the functionality in chemical gels we also call f), *i.e.* by the limitation of the valence, brought by directional interactions (*e.g.* dipolar²² or quadrupolar²³) or by localized patchiness. For particles exhibiting a small number of independent patchy interactions, fundamental progress has been made based on the Wertheim theory.^{24–26} For small f values,^{9,19} the Wertheim theory predicts quite accurately the T and ρ dependence of the equilibrium bond probability and the region of gas–liquid instability in the T – ρ plane, confined at very small densities.¹⁹

In a recent work, some of us have discussed the possibility of connecting time in irreversible aggregation to temperature in equilibrium clustering, based on the behavior of a specific model of ellipsoidal particles interacting *via* localized interactions, explicitly designed to model chemical gelation.^{27,28} Here we study in detail the aggregation process of a binary mixture of bi- and tri-functional colloidal spherical particles over a wide range of densities. Differently from the previous case, the thermodynamic equilibrium properties of this model can be calculated analytically without fitting parameters,⁹ providing a test-case for the ideas proposed in ref. 28. We further merge the description of the aggregation kinetics modeled *via* Smoluchowski equations (incorporating breaking terms) with the Wertheim equilibrium liquid approach to provide a parameter-free description of the kinetics of cluster formation in the presence of branching. Our work shows that for a realistic model of functionalized (or patchy) particles, theoretical predictions are able to describe with great accuracy the aggregation process of limited-valence particles over a wide range of densities and temperatures.

^aDipartimento di Fisica, Università di Roma 'La Sapienza', Piazzale A. Moro 2, I-00185 Roma, Italy

^bCNR-INFN SOFT, Università di Roma 'La Sapienza', Piazzale A. Moro 2, I-00185 Roma, Italy

^cDipartimento di Fisica, Università di Perugia, Via A. Pascoli, I-06100 Perugia, Italy

^dCNR-INFN SMC, Università di Roma 'La Sapienza', Piazzale A. Moro 2, I-00185 Roma, Italy

II. Theory and simulations

The aggregation kinetics have often been formally modeled in terms of Smoluchowski rate equations, including condensation and fragmentation terms, where the relative weight of diffusion and binding enters *via* the expression of the bonding rate constants.^{29–31} The equations provide the time evolution of the number $N_k(t)$ of clusters of size k observed at time t , assuming an expression for the rate constant of bonding k_{bond}^{ij} and breaking k_{break}^{ij} for all the different cluster sizes i and j . For a one-component system of particles of functionality f (the generalization to a binary mixture of particles with different functionalities is straightforward and it is omitted for clarity's sake – it is enough to replace f in the results with the system's average functionality \bar{f}), assuming equal reactivity of all sites, the evolution of N_k is given by

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k} \left(\frac{k_{\text{bond}}^{ij}}{V} N_i N_j - k_{\text{break}}^{ij} N_{i+j} \right) - \sum_{j=1}^{\infty} \left(\frac{k_{\text{bond}}^{kj}}{V} N_k N_j - k_{\text{break}}^{kj} N_{k+j} \right) \quad (1)$$

where V is the volume, k_{bond}^{ij} is the rate of forming a cluster of size $i+j$ joining two clusters of size i and j , k_{break}^{ij} is the rate of breaking a cluster of size $i+j$ into two clusters of size i and j . The expressions for k_{bond}^{ij} and k_{break}^{ij} incorporate the physics of the aggregation process. Under the strong assumptions that the bond-formation contribution to the rate is dominant compared to that of diffusion, and that particles with functionality f form loop-less clusters, it is possible to provide explicit expression for k_{bond}^{ij} and k_{break}^{ij} and to solve eqn (1) analytically. It is important to stress that these two assumptions are not trivial at all and somehow depend on the microscopic dynamics and on the range of the site–site interaction. Indeed, only when the site–site interaction is short-ranged, the probability that two sites on distinct clusters feel each other, in the absence of any activation barrier, is particularly small. As a consequence the time requested to form a bond between two nearby clusters can be significantly longer than the time requested for two clusters of any size to diffuse over distances comparable to the inter-cluster distances, and the size dependence of the diffusion coefficient can be removed in the expressions for k_{bond}^{ij} and k_{break}^{ij} . Regarding the absence of bond-loops in the aggregates, we note that both the fact that a small fraction of particle orientations allows the particles to bond and the fact that the average functionality is very small are important elements favoring the formation of loop-less aggregates.^{9,32} Specificity in the bond interaction and limited valence are thus crucial for the validity of the above assumptions, according to which k_{bond}^{ij} is proportional to the number of distinct ways a cluster of size i can bond a cluster of size j , and k_{break}^{ij} is proportional to the number of distinct ways a cluster can break into two clusters of size i and j , the coefficients of proportionality $k_{\text{bond}}^{\text{site}}$ and $k_{\text{break}}^{\text{site}}$ being respectively the rate constants of forming and breaking a single bond.²⁹ Specifically, one has

$$k_{\text{bond}}^{ij} = k_{\text{bond}}^{\text{site}} \sigma_i \sigma_j$$

where $\sigma_i \equiv (f-2)i+2$ is the number of unreacted sites on a cluster of size i , and

$$k_{\text{break}}^{ij} = k_{\text{break}}^{\text{site}} \frac{\omega_i \omega_j}{\omega_{i+j}} \sigma_i \sigma_j$$

where

$$\omega_i = \frac{(fi-i)!}{(fi-2i+2)! i!}.$$

The solution of eqn (1), with initial conditions $N_k(0) = N\delta_{k1}$ (*i.e.*, N monomers at time $t=0$) and the Flory post-gel assumption, first provided by van Dongen and Ernst,²⁹ is

$$N_k(t) = N \frac{f[1-p(t)]^2}{p(t)} [p(t)[1-p(t)]^{f-2}]^k \omega_k \quad (2)$$

where $p(t)$ – the time-dependent bond probability (number of formed bonds over the maximum possible number of bonds) – satisfies

$$\frac{dp}{d(tk_{\text{break}}^{\text{site}})} = -p \left[1 - \rho f \frac{k_{\text{bond}}^{\text{site}}}{k_{\text{break}}^{\text{site}}} \frac{(1-p)^2}{p} \right] \quad (3)$$

with $\rho = NV$ the particle number density.

Equilibrium (*i.e.*, $dp/dt=0$) imposes a relation between the bonding and breaking coefficients $k_{\text{bond}}^{\text{site}}$ and $k_{\text{break}}^{\text{site}}$ controlled by the equilibrium ($t \rightarrow \infty$) value of p , p_{eq}

$$\rho f \frac{k_{\text{bond}}^{\text{site}}}{k_{\text{break}}^{\text{site}}} = \frac{p_{\text{eq}}}{(1-p_{\text{eq}})^2} \quad (4)$$

The solution of eqn (3) with $p(0)=0$ and $p(\infty)=p_{\text{eq}}$ is

$$p(t) = p_{\text{eq}} \frac{1 - e^{-\Gamma t}}{1 - p_{\text{eq}}^2 e^{-\Gamma t}} \quad (5)$$

with $\Gamma = \rho f k_{\text{bond}}^{\text{site}} (1-p_{\text{eq}})^2 / p_{\text{eq}}$ or, by virtue of eqn (4), $\Gamma = k_{\text{break}}^{\text{site}}$.

In the limit of absence of breaking processes ($k_{\text{break}}^{\text{site}} \rightarrow 0$ or equivalently $p_{\text{eq}} \rightarrow 1$) – irreversible aggregation – the time-dependent solution $N_k(t)$, expressed in terms of p is still given by eqn (2), while the time evolution of p , eqn (5), with the initial condition $p(0)=0$ reduces to

$$p(t) = \frac{f \rho k_{\text{bond}}^{\text{site}} t}{1 + f \rho k_{\text{bond}}^{\text{site}} t} \quad (6)$$

The analytic solution (eqn (2)) of the Smoluchowski equations is particularly interesting, since the time dependence of $N_k(t)$ is entirely contained in $p(t)$ – therefore, the cluster size distribution only depends on the value of the bond probability. At each time t during the equilibration process, in which $p(t)$ progressively increases from zero to p_{eq} , the cluster size distribution is predicted to be identical to that observed in equilibrium when the temperature T is such that the equilibrium bond probability $p_{\text{eq}}(T)$ assumes the value $p(t)$. This means that the aging dynamics takes place along a sequence of equilibrium states and the progression of time can be properly seen as a progressive thermalization of the system toward equilibrium. This is still valid also in the case of a quench performed to such a low T that breaking processes become impossible and irreversible aggregation takes place at all times.

To test these predictions, we perform Brownian dynamics simulations³³ of a binary mixture of 2835 particles with

functionality $f = 2$ and 165 particles with $f = 3$ (average functionality $\bar{f} = 2.055$) at several ρ and T values, a model whose equilibrium properties have been well characterized recently.⁹ Particles are hard spheres of diameter $\sigma = 1$ whose surface is decorated by two or three interacting sites. Sites on different particles interact *via* a square-well potential of depth $u_0 = 1$ and interaction range $\delta = 0.119\sigma$. The high- T limit of this model is the hard-sphere fluid. On cooling, particles bond to each other, forming polydisperse clusters which then percolate and assemble, on further cooling, into a network of long-living bonds. Due to the negligible presence of rings of bonds, the distribution of cluster sizes in equilibrium is quite accurately described by the Flory–Stockmayer statistics,⁹ *i.e.*, by eqn (2) with $p(t)$ substituted with p_{eq} . The phase diagram of the system includes a region of thermodynamic instability at small densities, due to the onset of gas–liquid separation, and a percolation line defined by the value $p_{\text{eq}} = 0.9256$.⁹ We study the evolution of the system at constant ρ , after a T -jump (taking place at $t = 0$) starting from a high- T unbonded configuration. We average over ten independent realizations to decrease the statistic error. Temperature is measured in units of u_0 (Boltzmann constant $k_{\text{B}} = 1$), while time is measured in reduced units, such that $t = 1$ corresponds to the time requested to diffuse a particle diameter (so as to eliminate any trivial dependence on the T -dependence of the bare diffusion coefficient or, equivalently, of the solvent viscosity). Since the site–site interaction potential is of a square-well form, there is no ambiguity on the number of bonds in the system (proportional to the potential energy) and hence it is straightforward to evaluate from the simulation data the time dependence of the bond probability $p(t)$, to be compared with the theoretical predictions.

The equilibrium properties of this model are well described by the parameter-free Wertheim theory.⁹ Here we exploit the equilibrium condition expressed in eqn (4) to provide a connection between the kinetic approach of Smoluchowski and the theory-of-liquid approach based on the thermodynamic perturbation theory of Wertheim and develop a parameter-free description of the kinetics of the assembly process. Indeed, the Wertheim theory provides a parameter-free expression for $p_{\text{eq}}(T, \rho)$ and hence for the rhs of eqn (4), as

$$\frac{p_{\text{eq}}}{(1 - p_{\text{eq}})^2} = \rho f \Delta_{\text{W}}(\rho) (e^{\beta u_0} - 1) \quad (7)$$

where $\Delta_{\text{W}}(\rho)$ can be calculated analytically as integral of the Mayer function weighted by the hard-sphere reference radial distribution function (as discussed in detail – for the present model – in ref. 34). In terms of σ and δ one finds (indicating with $\phi = \pi\sigma^3\rho/6$ the packing fraction),

$$\Delta_{\text{W}} = \frac{\pi\delta^4(15\sigma + 4\delta)/30\sigma^2}{(1 - \phi)^3} \times \left[1 - \frac{5}{2} \frac{(3\sigma^2 + 8\delta\sigma + 3\delta^2)}{\sigma(15\sigma + 4\delta)} \phi - \frac{3}{2} \frac{(12\delta\sigma + 5\delta^2)}{\sigma(15\sigma + 4\delta)} \phi^2 \right] \quad (8)$$

This gives us the opportunity to predict the T and ρ dependence of the ratio between $k_{\text{bond}}^{\text{site}}$ and $k_{\text{break}}^{\text{site}}$ as

$$\frac{k_{\text{bond}}^{\text{site}}}{k_{\text{break}}^{\text{site}}} = \Delta_{\text{W}}(\rho) (e^{\beta u_0} - 1) \quad (9)$$

and, hence, except for a constant (which fixes the time scale and depends on the chosen particle dynamics) to provide a parameter-free description of the evolution of the entire aggregation process.

III. Results

Fig. 1 shows the time dependence of p following the T quench, starting from absence of bonds and approaching p_{eq} . Fig. 1(a) refers to the case of different values of T for the same ρ , while Fig. 1(b) refers to the case of different initial densities brought to the same final T . The simulation data are compared with the theoretical expressions, by only fitting the time-scale factor $k_{\text{break}}^{\text{site}}$, shown in the two insets. In both cases, eqn (5) provides an excellent description of the entire kinetic process. Since the breaking process is local and breaking requires only a potential energy fluctuation of the order of the well depth, $k_{\text{break}}^{\text{site}}$ does not depend on ρ but it depends on T as $k_{\text{break}}^{\text{site}} \sim \exp(-\beta u_0)$. Data shown in the insets of Fig. 1 fully confirm this expectation. Since aggregation takes place when $\beta u_0 \gg 1$, (indeed $T < 0.1$ in the investigated temperature region), the previous data and eqn (9)

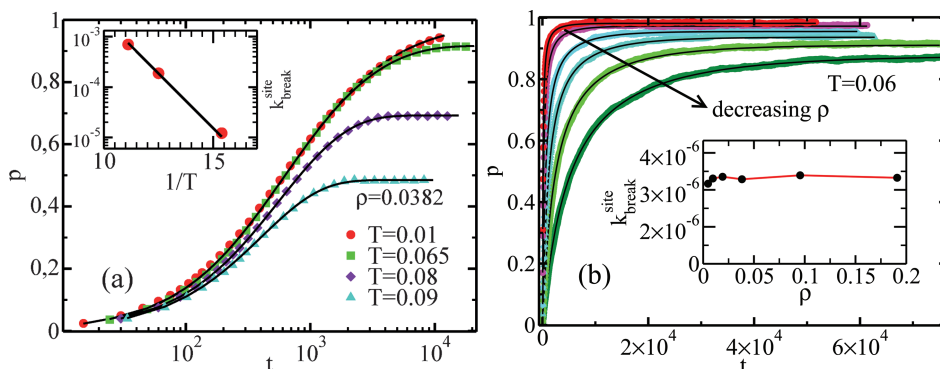


Fig. 1 (a) Evolution of the bond probability – for the case $\rho = 0.0382$ – at three different temperatures ($T = 0.09$, $T = 0.08$, $T = 0.065$) and for an irreversible aggregation case $T = 0.01$. Lines are solutions of the Smoluchowsky equations. The fitting constant is reported in the inset, suggesting that $k_{\text{break}}^{\text{site}} \sim \exp(-\beta u_0)$. (b) Evolution of the bond probability following a quench to $T = 0.06$ at several different densities. Lines are solutions of the Smoluchowsky equations for the reversible aggregation. The fitting constant is reported in the inset, suggesting that there is no significant density dependence in $k_{\text{break}}^{\text{site}}$.

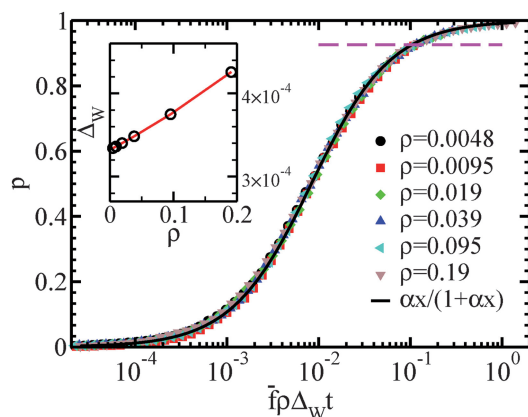


Fig. 2 Evolution of the bond probability $p(t)$ in an irreversible aggregation process (quench to $T = 0.01$) for several different starting densities ρ as a function of the variable $\bar{f}\rho\Delta_W t \equiv x$. The overlap of all set of data on the master curve $p = \frac{\alpha x}{1+\alpha x}$ (see eqn (6)) confirms that $k_{\text{bond}}^{\text{site}}(\rho)$ is indeed proportional to the Wertheim Δ_W (the proportionality constant is $\alpha \approx 120$). The dashed line indicates the percolation threshold $p = 0.9256$. The inset shows the density dependence of Δ_W (eqn (8)).

suggest that $k_{\text{bond}}^{\text{site}} \sim \Delta_W(\rho)$, *i.e.* does not depend on T and its only density dependence arises from Δ_W .

Fig. 2 shows the time evolution of $p(t)$ following a quench to a very small temperature, $T = 0.01$ – equivalent to an evolution process where bond-breaking events ($\sim \exp(-\beta u_0)$) are not encountered – *i.e.* the case of irreversible aggregation (chemical gelation) described by eqn (6). Data at different densities collapse on a master curve when reported as a function of $\bar{f}\rho\Delta_W t$, as predicted on the basis of eqns (6) and (9). Interestingly, the solution given by eqn (6) properly describes the evolution of the bonding probability even after the gel point, when a spanning cluster is present in the system.

A detailed analysis of the configurations allows us to test also the relevant theoretical prediction that the structure of the system during equilibration follows a sequence of equilibrium states. Fig. 3 shows the cluster size distribution N_k and the static structure factor S_q ³⁵ of the system in equilibrium at four distinct values of T and fixed ρ , and the corresponding quantities evaluated at selected times during the equilibration process. The

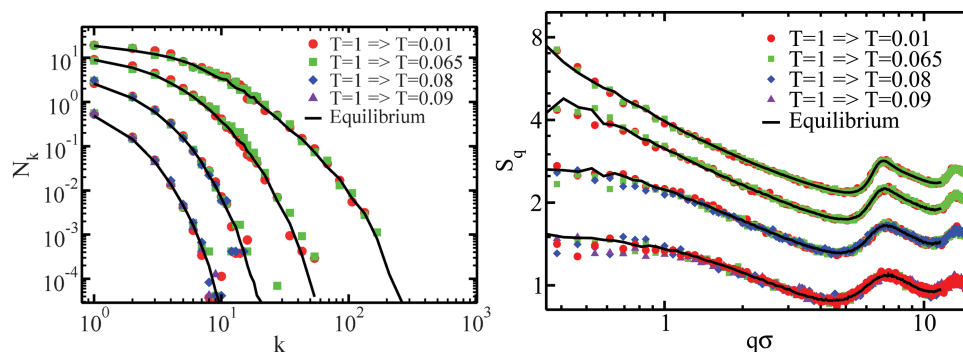


Fig. 3 Comparison between equilibrium (full lines) and aging (symbols) structural properties for $\rho = 0.0038$. The equilibrium data refer to $T = 0.1$, $T = 0.09$, $T = 0.08$ and $T = 0.07$. The aging data refer to different equilibration processes, always starting from the high temperature $T = 1$ where the system is composed only by monomers, to several different final temperatures indicated in the labels. Data refer to different times following the quench, t_w , chosen in such a way that $p(t_w) = p_{\text{eq}}(T)$. (Left) Cluster size distributions N_k . Data have been multiplied progressively by a factor 10 to avoid overlap of the different sets. (Right) Static structure factor S_q . Data have been progressively shifted by +1.

specific time value t_w is chosen in such a way that $p(t_w) = p_{\text{eq}}(T)$. In all cases, the equilibrium structure and connectivity of the system is perfectly reproduced during the equilibration process, confirming that in this system the equilibration process proceeds *via* a progressive thermalization of the configurations, in agreement with the theoretical predictions.

IV. Discussion and conclusions

The present study demonstrates that, for the case of aggregation processes in which bond-loops (in finite size clusters) can be neglected, a complete theoretical description of the kinetics of self-assembly can be obtained *via* a combined use of the Smoluchowski and of the Wertheim approaches. The formation of a branched network proceeds *via* a sequence of equilibrium steps, even in the deep quench limit, where the model behaves as in a irreversible (or chemical) gelation process. Hence, equilibrium properties of “physical” gels in which bond-loops can be neglected present strong analogies with the evolution and final configurations of “chemical” gels.

It is important to discuss the reasons behind the possibility of properly mapping equilibrium and aging properties, with the aim of assessing the conditions of validity of such a mapping. Indeed, the irreversible aggregation process of spherically interacting particles does not take place along a sequence of equilibrium steps, as clearly revealed by the fractal structure of the aggregates resulting from diffusion-limited or reaction-limited aggregation processes.¹ Recently, evidence has been provided that, for colloidal particles interacting *via* depletion interactions, the aggregation process is driven by a phase separation³⁶ and that the structure of the system is not homogeneous. The mapping discussed in this article holds only in the limit of loop-less aggregating clusters, and provided diffusion does not play a relevant role in the rate constants. This imposes a condition on the average valence of the particles, since it has been shown that the absence of loops is enhanced by the small valence. The reason for this, which has been investigated in the context of equilibrium properties,^{9,32} can be found in the different entropic cost of closing a loop of bonds, which becomes larger and larger on increasing the length of the bifunctional chains connecting the three-functional branching points. In particular it is shown³² that

systems with average functionality $\bar{f} \lesssim 2.8$ (as it is the case in this article) have a negligible number of loops and fulfil rather well the mean-field predictions. For higher valence systems the number of loops becomes non-negligible and deviations from the mean-field results are observed. The other important condition for the validity of the mapping is the possibility of neglecting the diffusional component in the aggregation and fragmentation rates, *i.e.* the so-called chemical limit of the aggregation process.³⁷ Here the chemical limit is set not by the presence of an activation energy for bonding (as in the case of most aggregation processes where the barrier arises from electrostatic repulsion) but again by an entropic barrier for bonding, set by the difficulty in interacting with the right orientation to form a bond. For this to happen the range of the attraction between sites must be small enough so that the time it takes two colloids to diffuse and reach a bonding-compatible relative distance is negligible compared to the time requested to collide with the correct orientation for bonding. In this case, the entropic search of the correct orientation for bonding is controlling the bonding rate constant. Once more, the validity of the chemical limit is enhanced by the small valence, which makes it harder to properly orient the colliding clusters for bond formation. Interestingly enough, in the present system such a condition remains valid even close to percolation and beyond. This apparently puzzling phenomenon can be tentatively rationalized by noting that the increased differences into diffusional times is contrasted by the progressive decrease in the number of unreacted sites, which determines an increase also in the time for successful bond formation.

The proposed mapping between equilibrium and aging properties in small valence systems makes it possible to convert aging (curing) time with an effective temperature and envisage the evolution of a chemical gel as a progressive cooling of the corresponding physical model, *i.e.*, as a progressive path in the phase diagram of the physical model. An interesting case is that offered by the possibility that during the formation of a chemical gel the corresponding thermodynamic path crosses the gas–liquid coexistence, resulting in an inhomogeneous arrested structure. The stability and structural properties of the final state of the chemical gels will be in this case connected to the thermodynamic properties and the phase diagram of the corresponding physical model. Small limited-valence colloidal systems³⁸ are thus excellent candidates for testing the analogies between equilibrium and aging properties and the connection between gel stability and colloidal gas–liquid phase separation.

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