Reversible gels of patchy particles

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ABSTRACT

In the last years a significant progress in the understanding of the aggregation properties of patchy colloidal particles and of the process of formation of equilibrium gels has taken place. We discuss here how the number of patches (a variable which can be experimentally controlled in current synthesis procedures) affects the equilibrium phase diagram and the relative stability against decomposition into two phases with different colloidal concentration, the analog of the gas–liquid phase separation in simple liquids. For small number of patches, the liquid phase exists as an equilibrium state down to small temperatures, giving rise to empty liquids and equilibrium gels. Finally, we discuss the connection between irreversible and reversible gelation in this class of colloidal systems proposing a conceptual link between elapsed time during the aggregation kinetics and temperature in thermodynamic equilibrium.

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1. Introduction

A significant change in colloidal science is taking place these days. Colloids are turning aspherical, asymmetric, patterned [1]. Chemists and material scientists are starting to gain control on the shapes [2] and on the local properties of the colloidal particles. Hard cubes, tetrahedra, cones, rods as well as composed shapes of nano or microscopic size have made their appearance in the labs, and will hopefully become available in bulk quantities in the near future. Patterning of the surface properties of these particles [3–5] is adding extra directions to the anisotropy axis space envisioned by Glotzer and Solomon [1]. Patches on the particle surface can be functionalized with specific molecules [6,7] (including DNA single strands) [8,9] to create hydrophobic or hydrophilic areas, providing specificity to the particle–particle interaction [10,11]. These new particles can be used as building blocks for nano and microscale self-assembly of new materials [12–14] and share conceptual similarities with supramolecular chemistry [15–18], where thermoreversibile or self-healing materials can be tuned at the molecular level: specific examples include thermoreversible rubber [19], oligo(amido-amine)s hydrogels [20] and self-healing liposome gels [21]. In the same way as sterically stabilized colloids have become the ideal experimental model system for investigating the behavior of hard-spheres and simple liquids, the new physico-chemical techniques will soon make available to the community colloidal analogs of several molecular systems.

An interesting class of patchy particles is that of colloids which, thanks to the selectivity of the patch–patch interaction, have a fixed valence (defined as the maximum number of bonded nearest neighbors) [3–5]. These colloidal particles, which mimic the corresponding atomic and molecular systems, are the subject of this contribution.

The study of simple models of fixed valence colloidal particles has indeed recently been the focus of several investigations [22–27], encompassing both the thermodynamic and dynamic collective behavior of the system, as well as its out-of-equilibrium dynamics. In this process, novel concepts like the so-called *empty liquids* (i.e. liquids composed by very long chains of particles interconnected by rare branching points [25], resulting in a very small overall density), the equilibrium gels, the analogy between colloidal gels and network forming liquids, the connection between chemical and physical gels, have been proposed and developed. In this article we will attempt to review these concepts and possible experimental studies which may provide a realization of these behaviors.

The numerical studies of simple and well defined models presented here can also be relevant to the ongoing debate on the thermodynamic signatures associated to the percolation transition in association polymer systems. Indeed, contradicting views have been expressed on the order of the sol–gel transition, arising from different approximations for the infinite cluster structure [28–30].

2. Phase behavior of limited valence particles

Spherical particles, in the presence of isotropic attractive interactions, usually show a gas–liquid critical point, characterized by a critical density ρ_c and a critical temperature T_c. In colloidal

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solutions, in which attraction is often induced by depletion forces, such critical point is metastable, i.e. located in the region where the thermodynamic stable phase is a crystal. Below T_c the solution becomes cloudy and it separates into two phases, one rich in colloidal particles (the liquid phase) and one poor in colloidal particles (the gas phase). In the liquid phase, particles tend to minimize their energy, which is equivalent to maximize the number of nearest neighbor particles, i.e. particles sitting close to the minimum of the potential well. Since interactions are usually short-ranged (i.e. the interaction range is smaller than the particle size), this is equivalent to maximize the number of contacts. As a consequence, each particle tends to be surrounded by about twelve neighbors (a number fixed by geometrical constraints) and the coexisting liquid is a rather dense state. At low T (i.e. such that $k_B T$ is smaller than the interaction energy strength ϵ, with k_B the Boltzmann constant) this dense state behaves as a glass, in which particle motion is hampered both by the crowding and by the difficulty to overcome the bonding potential energy. In this sense, a dynamic arrest at low densities can be obtained only through a phase separation process [31].

Recently, it has been shown that the reduction of the valence provides an effective method to reduce the density of the liquid phase at coexistence [22,25,26]. Indeed, when valence is small there is no energetic gain in generating dense configurations, since already with a small number of neighbors all possible bonds are satisfied. Hence, on progressively decreasing the valence one expects that ρ_c also decreases. At coexistence, along the liquid branch, the number of contacts is of the order of the valence and hence, the number of neighbors is smaller than in the isotropic case. As a result, the density of the coexisting liquid is significantly smaller than the one found in the case of spherically interacting particles and crowding can not be responsible any longer for the slowing down of the dynamics upon cooling. Dynamic arrest is not driven by packing but only by the presence of a (percolating) network of bonded particles which provides elasticity to the system. The network restructures itself on a timescale fixed by the bond lifetime. When the lifetime of the bond exceeds the experimental observation time, the system becomes a non-ergodic state in which particles occupy only a minor fraction of the total volume, i.e. a gel [32]. The main idea is thus that small valence is an essential condition for generating arrested states at low T (or equivalently strong interaction strengths) which are not arrested by packing, as in molecular and colloidal glasses, but by the formation of an extensive and percolating network of contacts which occupies only a small fraction of the sample volume. The finite energy of the interaction guarantees that the network structure is not permanently frozen (as in chemical gelation) but it can restructure itself, on a time scale which can be tuned at will externally. In addition, for valences approaching two, the coexisting liquid density vanishes. Such low-density liquid states have been named *empty liquids* [25].

2.1. Wertheim theory

A formal evaluation of the gas–liquid coexistence curve for the case of particles with fixed valence has been provided by the Wertheim theory [33,34]. The free-energy calculation has been developed for a model of patchy particles interacting under the assumption of single-bond per patch. This condition guarantees that the valence is encoded in the chemistry of the particle. The single-bond per patch condition can be realized either by creating chemically-different regions of the particle surface (the patches) sufficiently small to shield the attraction from other neighbors when two patches are in contact, or by functionalizing the particle with groups which act under a lock-and-key paradigm (as in the case of complementary single strand DNA sequences). In the

Wertheim approach, the free energy is written as sum of a reference free energy (usually the hard-sphere free-energy) and a bonding contribution F_{bond}, which is expressed as a function of the bond probability p_b (the fraction of bonds over the total number of possible bonds) and the particle valence, or functionality, f. The latter can be treated as a continuous variable, by attributing to it the meaning of average valence of the system [25] (see also Ref. [35]). Values of f between two and three can be realized for example in binary mixtures of bi and three-functional particles with different relative concentrations [25]. In the formulation of Ref. [36], the bond free energy density of a system of f-functional particles is

$$\frac{\beta F^{bond}}{V} = \rho \ln(1 - p_b)^f + \frac{1}{2}\rho f p_b \tag{1}$$

where $\beta = 1/k_B T$, $\rho = N/V$ is the particle number density. The T and ρ dependence of p_b is given by

$$\frac{p_b}{(1 - p_b)^2} = \rho e^{-\beta \mathcal{F}_b} \tag{2}$$

where $\mathcal{F}_b$ is the patch–patch bond free-energy, i.e. the free energy difference between the bonded and the unbonded state for a pair of particles. The Wertheim theory provides an expression for $\mathcal{F}_b$ which depends only on the potential parameters and on the reference fluid radial distribution function. The interesting point to notice is that, independently of the model (which only enters in $\mathcal{F}_b$), all systems with the same p_b and the same f will be characterized by the same free energy. This suggests that f discriminates between different class of particles, or equivalently, that particles with the same f will be represented by the same phase diagram in the p_b–ρ plane [37]. Solving the Wertheim theory for particles of different valence, one indeed finds that both T_c and ρ_c decrease with decreasing f, both approaching zero when $f \to 2$, as shown in Fig. 1. A similar trend characterizes the density of the coexisting liquid.

In essence, the Wertheim theory confirms that for small values of f there is a wide window of densities, delimited on one side by the coexisting liquid density and on the other side by packing (excluded volume) constraints, where it is possible to cool the system down to very small T without encountering any phase separation. Since excluded volume (caging) does not prevent the system to explore configurational space, particles can easily explore different bonding patterns and find the equilibrium state on a time-scale essentially controlled by the lifetime of the bonds. The sigmoidal shape of p_b vs T, resulting from Eq. (2), suggests that almost fully bonded states ($p_b \to 1$) can be accessed by the system at finite T.
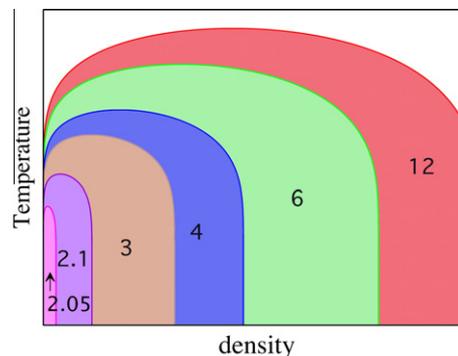
Fig. 1. Valence dependence of the gas–liquid coexistence region for particles with limited valence (whose value is written inside the curves). For spherically interacting particles, the gas–liquid coexistence is very wide in densities, since in the liquid state particles are surrounded by about twelve neighbors. For particles with limited valence, the liquid branch of the coexistence is located at a density significantly smaller than the isotropic case, approaching zero as the valence approaches two.

Numerical simulations confirm that the ground state can be sampled, in finite size systems, at finite temperatures (see discussion in connection to Fig. 4 in the following). Thus a fully bonded network of flickering bonds can be sampled in equilibrium when the thermal energy is significantly smaller than the bond energy. Further cooling these almost fully bonded states will generate technically out-of-equilibrium states, but the aging dynamics will be essentially missing since structural and energetic properties of the aging systems are already close to the final equilibrium ones. This (low-density) quasi-equilibrium state of soft matter has been named *equilibrium gel* to stress the fact that despite the system is trapped in one of its multiple local minima, defined by the bonding pattern, no change of the gel mechanical and thermal properties with time will take place. The name *equilibrium gel* also stresses the difference with the most common colloidal gels, resulting from a gas–liquid phase-separation process interrupted by dynamical arrest or by diffusion limited cluster aggregation [38–40], as found in spherically isotropic potentials [32]. In the latter case, the gel state can not be approached continuously from the liquid state since gelation requires the crossing of the first-order gas–liquid transition line [31].

2.2. Connecting Wertheim theory to gelation through the Flory–Stockmayer (FS) theory

An interesting connection between the thermodynamic Wertheim theory and gelation is provided by the formal equivalence between Eq. (1) and the free energy of a system of non-interacting clusters distributed according to the Flory–Stockmayer (FS) theory [41,42], developed to model aggregation in chemical gelation. The FS theory provides expressions for the number density of clusters of n particles, ρ_n, as a function of the bond probability (the extent of the reaction in the FS language). For functionality f

$$\rho_n = \rho(1 - p_b)^f [p_b(1 - p_b)^{f-2}]^{n-1} \omega_n$$
$$\omega_n = \frac{f(fn - n)!}{(fn - 2n + 2)!n!} \tag{3}$$

where $\rho \equiv \sum_n n\rho_n = N/V$ is the total number density. This connection arises from the fact that Wertheim theory describes the system as a collection of loop-less independent clusters, the same approximation at the heart of the FS theory. As a result, the Wertheim theory can be complemented with the FS expression

$$p_b^p = \frac{1}{f - 1}. \tag{4}$$

to evaluate the location in the (T, ρ) plane of the percolation line p_b^p. The percolation line separates the fluid phase into two regions, one composed by a fluid of polydisperse loop-less finite size clusters and one where the system is still fluid, but an infinite spanning cluster of reversible bonds is present. On entering deeper and deeper in the percolating region, the fraction of particles belonging to the infinite cluster progressively increases, and the average size of the remaining finite-size clusters approaches one (indicating that the system is composed by an infinite cluster in equilibrium with a very low density gas of monomers). Loops of bonds in the infinite cluster are predicted to occur and accounted for by the Flory theory. This is known as the Flory post-gel assumption.

A summary of the specific features which characterize the phase diagram of small-valence patchy particles, as predicted by the Wertheim and FS theory for the one-component case $f = 3$, are reported in Fig. 2. The gas–liquid phase separation is confined to packing fractions $\phi = \frac{\pi}{6}\rho\sigma^3$, where σ is the diameter of the particles, smaller than 20%. The percolation line separates the cluster-fluid phase from the percolating one. The gas–liquid phase separation takes place in the percolating region. Close to the critical point, the two
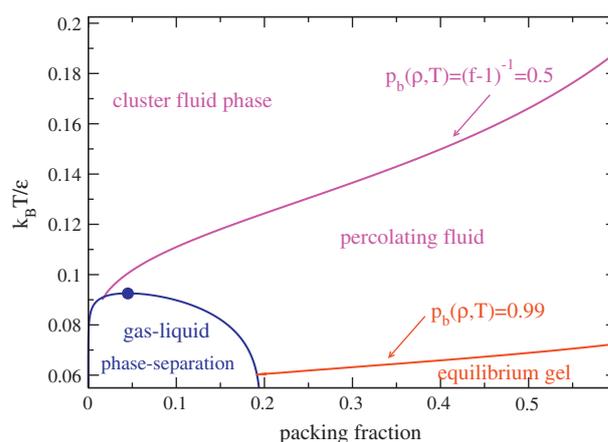

Fig. 2. Phase diagram, calculated for a model with $f = 3$ patches using the Wertheim and FS theories. Different loci are identified: the percolation line $p_b^p(\rho, T) = 0.5$, separating a fluid of clusters from a percolating fluid, the gas–liquid coexistence, the line where 99% of the bonds are formed. At low T, in the stable liquid region, the liquid behaves as an equilibrium gel.

coexisting phases are both percolating. For smaller T, only the liquid phase retains a percolating character. When the bond lifetime exceeds the observation time, the particle network formed by the system becomes persistent, and hence an equilibrium gel is found. The ideal gel transition thus would take place only at $T \to 0$, but an operative definition can be made in terms of a finite lifetime, as usually done for the glass transition. A reasonable guide of the gel line can be made by drawing an iso-p_b line at sufficiently large p_b value [43,44].

2.3. Comparison with simulations

A significant effort has been made in the last years to compare predictions of the Wertheim theory with accurate numerical simulations [25,26,45–47] to assess the quality of the theory and its predictive power. In all cases, simulations confirm the Wertheim predictions to a good extent. Bonding properties (i.e. the T and ϕ dependence of p_b) are rather accurate, and the agreement increases significantly when the valence is reduced below three. Indeed, when $f \to 2$, the typical liquid densities are rather small, excluded volume effects are properly captured by the reference system. In addition, when $f \to 2$, at low T the system is composed by rather long chains of bi-functional particles connecting the small concentration of multi-functional species which act as branching points in the system, as shown in Fig. 3. If the chains of bi-functional particles are characterized by a finite persistence length, then the probability of forming closed bond loops in three-dimensions is negligible and the Wertheim (or FS) theory becomes essentially exact. Only very close to percolation, i.e. when the average cluster size diverges, differences between the FS and the asymptotic percolation cluster size distributions can be observed. Different is the two-dimensional case where for entropic reasons bond loops are frequent and a strong disagreement between the Wertheim (or FS) theory and simulation data is observed [48].

As a comparison between theory and simulations we report in Fig. 4a the T and ϕ dependence of p_b for the case of a binary mixture of particles with two and three patches, resulting in an average valence $f = 2.055$. For this model the equilibrium phase diagram is found to be topologically similar to the theoretical one reported in Fig. 2, but with an extremely small critical density ($\rho_c \approx 0.005$) [49]. In addition, for this low average valence, the number of bond loops is always negligible, so that Wertheim and FS approaches work very accurately up to very large values of p_b.
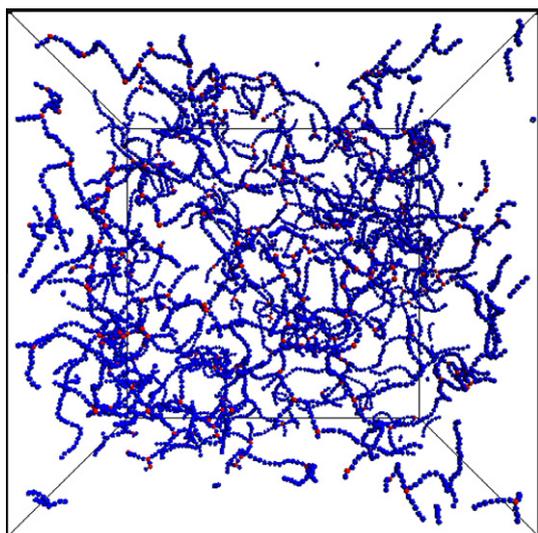
Fig. 3. Snapshot of a patchy particle system composed of 5670 bi-functional particles (the blue chain forming spheres) and 330 three-functional particles (the red branching points) in a (empty) liquid state. Here $k_BT/\epsilon = 0.05$, $\phi \equiv \pi\rho\sigma^3/6 = 0.005$ and $p_b = 0.97$ (see Ref. [49] for details). The average valence is $f = 2.055$.

Indeed, the peculiarity of such low-valence system is that percolation is only found for $p_b^p = 0.9256$. The cluster size distribution (Fig. 4b), both in the cluster phase (before percolation) and in the percolating region, are also very well predicted by FS theory. It is important to notice that $p_b \rightarrow 1$ both in theory and simulations at small T. This confirms that a reversible fully bonded network can spontaneously self-assemble in a density region where the system is always stable against gas–liquid decomposition. Hence, any further cooling of the system (for example to $T \ll 0.05$ in Fig. 4a) will only be accompanied by an increase of the bond lifetime, with no structural adjustments. The system is already very close to its ground state energy, since all possible bonds are formed. It is the stability of the structure and the possibility of controlling the network lifetime externally via a temperature variation which is the essence of the equilibrium gel state.

Finally, we note that in this class of models, we do not observe any detectable thermodynamic transition at the percolation line, despite the presence of cyclical structures in the infinite cluster.

3. Time and temperature: connecting physical and chemical gels

Studies reviewed in the previous section provide a clean theoretical approach for modeling the equilibrium properties of low-valence patchy particles. An interesting question concerns the relationship between physical (equilibrium or reversible) and chemical (irreversible) gels, when these are made by particles with similar values of functionality. In the chemical gel case bonding is irreversible and the final structure of the system is the result of a kinetic pathway, which depends in a fine way on the size dependence of the cluster diffusion coefficient as well as on the free-energy barriers that need to be overcome in order to form an (irreversible) bond. Chemical gelation can be thought of as an aggregation process in which the binding energy scale ϵ is much larger than the thermal energy k_BT and hence chemical gelation can be modeled, to a first approximation, as a temperature jump from high T (monomeric state) down to $T = 0$. We can then ask how different is the structure of an irreversible gel state, which is obtained at the end of the aging process through an instantaneous quench at low T, from the corresponding (i.e. same f) equilibrium gel structure. This question was raised in the context of ideal polymer chains (with $f = 2$) which can associate through sticky ends [50]. In Ref. [50] the number of loops was shown to be negligible at large system sizes, and the equilibrium polymerization process was found to be well described by mean-field theory. In addition, it was also found that the diffusion-limited case could be incorporated in the theoretical treatment, providing that a density-dependent association constant (used as a fit parameter) is used to rescale the data on the equilibrium case.

The relation between chemical and physical gelation question could not be previously investigated for colloidal gels made by spherically interacting particles, due to the fact that gelation is always mediated by the gas–liquid phase separation. Indeed, in the isotropic potential case, the kinetics of the phase separation process dictates (via the spinodal and coarsening processes) the structure of the arrested system [51–53]. The diffusion limited cluster aggregation case (the extreme limit of a deep quench inside the unstable region) is illuminating in this respect, since it generates a fractal gel structure which results from the diffusion-limited or reaction-limited aggregation processes [38], a structure which is never encountered under equilibrium conditions.

On the contrary, for low valence systems phase separation is limited to small densities and hence it is quite interesting to discuss the possible analogies and differences between chemical and equilibrium gels in the absence of phase separation and to connect the knowledge of the equilibrium phase diagram with the irreversible gelation process. Since, as discussed previously, p_b is the scaling variable for the thermodynamics, the connection can be sought of as a relation between time in irreversible aggregation to (inverse) T in equilibrium clustering [54,55]. Indeed, during an irreversible aggregation process, p_b grows with time while for equilibrium gelation p_b grows with decreasing T. While irreversible polymerization proceeds, the system visits in time a sequence of
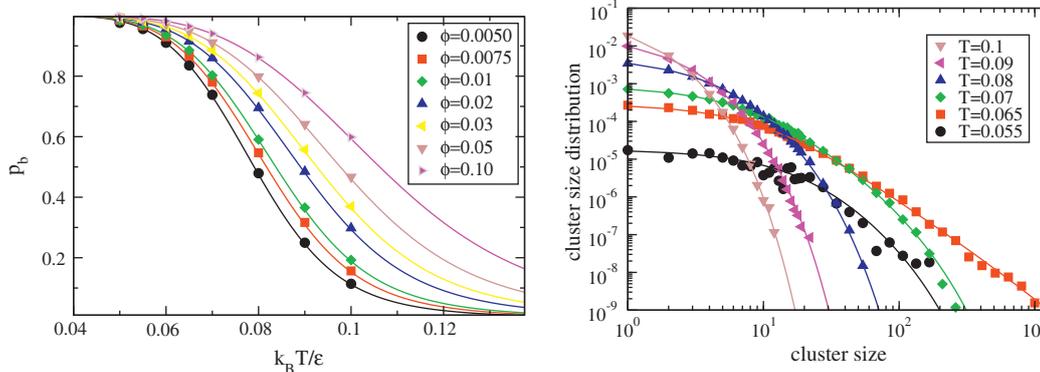
Fig. 4. (a) Parameter free comparison between the theoretical predictions for the T dependence of the bond probability and Monte Carlo results for a binary mixture of particles with two and three patches at $f = 2.055$, for several values of the packing fraction ϕ. (b) Parameter free comparison between the Flory–Stockmayer predictions for the cluster size distributions and corresponding Monte Carlo results. Data redrawn from Ref. [49].
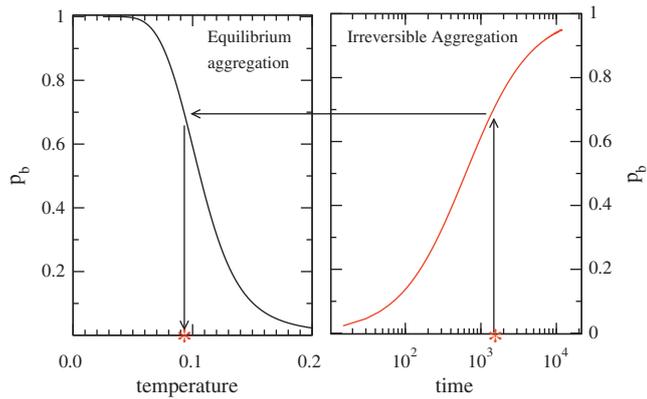
Fig. 5. Schematic cartoon illustrating the connection between time in irreversible aggregation and temperature in equilibrium. The left panel shows the T-dependence of the bond probability in equilibrium, the right panel the evolution of the bond probability following a quench to $T \to 0$, in the same system. Such a quench mimics the irreversible aggregation process. At each time following the quench, the reaction has proceeded establishing a certain fraction of bonds in the system. The same fraction of bonds is also found in the same system in thermal equilibrium at the corresponding T (indicated by the arrows). If the structure (and the connectivity) of the system in the two corresponding points (labeled by a star) are identical, then one can interpret the irreversible aggregation dynamics as a sequence of equilibrium steps, in which the system is progressively cooled from high temperature (short times) to low T (large times). Both T and t are in arbitrary units.

states (from the starting monomer solution to the extensively bonded gel) which may bear some relation to the states that are explored in equilibrium upon decreasing T, as schematically shown in Fig. 5.

3.1. Bond probability as the link between irreversible and reversible gelation

A hint for the possible existence of a link between chemical and physical gels is already contained in the equivalence between the equilibrium cluster size distributions predicted by the Wertheim theory and by the gelation theory of FS. Such equivalence was formally anticipated by the early theoretical work of Stockmayer [42]. Indeed, Stockmayer showed that the distribution ρ_n of clusters of finite size n can be calculated following equilibrium statistical mechanics prescriptions, i.e., maximizing the entropy with the constraint of a fixed number of bonds. While this is not extensively discussed, the fact the FS distributions are the result of a maximum entropy constraint, suggests that these theoretical predictions may apply only to cases in which kinetic contributions are irrelevant. Indeed, Stockmayer also showed [42] that the very same distributions result from solving the Smoluchowski's kinetic equations when the rate of bond breaking is zero (irreversible aggregation) and the rate of bond formation is slaved to the chemical processes, i.e. depends only on the number of unreacted sites and not on the diffusion coefficient of the relative clusters.

Van Dongen and Ernst [56] extended the work of Stockmayer to the case in which also bond-breaking processes are possible. They were able to show that the solution of the Smoluchowski equations for the evolution of the cluster size distribution $\rho_n(t)$, with initial conditions $\rho_n(0) = \rho\delta_{n1}$ (i.e., only monomers at time $t = 0$) and the Flory post-gel assumption, is

$$\rho_n(t) = \rho[1 - p_b(t)]^f [p_b(t)[1 - p_b(t)]^{f-2}]^{n-1}\omega_n. \tag{5}$$

Remarkably, Eq. (5) is formally identical to that obtained by Stockmayer in equilibrium (Eq. (3)), with the only replacement of the equilibrium bond probability $p_{eq} \equiv p_b(T)$ with the time-

dependent bond probability $p_b(t)$, evolving during the aggregation process. Now the latter satisfies the equation,

$$\frac{dp_b}{d\left(tk_{break}^{site}\right)} = -p_b\left[1 - \rho f \frac{k_{bond}^{site}}{k_{break}^{site}} \frac{(1 - p_b)^2}{p_b}\right] \tag{6}$$

where k_{bond}^{site} and k_{break}^{site} are respectively the bond-forming and bond-breaking rates of a generic site. The latter equation can be solved with $p_b(0) = 0$ and $p_b(\infty) = p_{eq}$, providing an analytical expression of $p(t)$ during a reversible aggregation process,

$$p_b(t) = p_{eq}\frac{1 - e^{-\Gamma t}}{1 - p_{eq}^2 e^{-\Gamma t}} \tag{7}$$

with $\Gamma = \rho f k_{bond}^{site}\left(1 - p_{eq}^2\right)/p_{eq}$. In the limit of absence of breaking processes ($k_{break}^{site} \to 0$ or equivalently $p_{eq} \to 1$), when irreversible aggregation takes place, the cluster size distributions $\rho_n(t)$ are still expressed in terms of $p_b(t)$ by the same Eq. (5), while the time evolution of $p_b(t)$ with the initial condition $p_b(0) = 0$ reduces to

$$p_b(t) = \frac{f\rho k_{bond}^{site} t}{1 + f\rho k_{bond}^{site} t}. \tag{8}$$

We stress that the analytic solution for $\rho_n(t)$ (Eq. (5)) is obtained under two assumptions: (i) the bond-formation contribution to the rate is dominant as compared to that of diffusion, and (ii) that particles with functionality f form loop-less clusters. These two crucial assumptions are highly non trivial and somehow depend both on the microscopic dynamics and on the bonding volume. Indeed, only when the bonding volume is small (i.e. for short-range patch–patch interaction), the probability that two patches on distinct clusters will encounter, in the absence of any activation barrier, is small. Hence, 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 distances comparable to the inter-cluster distances and the size dependence of the diffusion coefficient can be neglected in the calculation of the rate constants.

The remarkable result of this approach is that, under these conditions, the evolution of the cluster size distribution $\rho_n(t)$ (Eq. (5)) is entirely contained in $p_b(t)$—therefore, the cluster size distribution only depends on the value of the bond probability. Hence, independently of the specific kinetic pathway, at each time t during the aggregation process, when $p_b(t)$ progressively increases from zero to the final equilibrium value p_{eq} following Eq. (7), or even under an irreversible aggregation process expressed by Eq. (8), the cluster size distribution is predicted to be formally identical to that observed in a system in equilibrium at a certain T such that its bond probability (at equilibrium) assumes the value $p_b(t)$.

This amounts to formally establish a link between chemical and physical gelation, under the assumptions discussed above, through the following relation for the bond probability (see Fig. 5),

$$p_b(t) = p_b(T). \tag{9}$$

In this way the aging dynamics can be interpreted as 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 valid both when the system is quenched down to a T where equilibration is still possible and, most importantly, 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.

3.2. Simulation results

Numerical simulations of patchy particles have confirmed these theoretical predictions for models where bond loops are scarce. In particular, the aging behavior of the same binary mixture (with
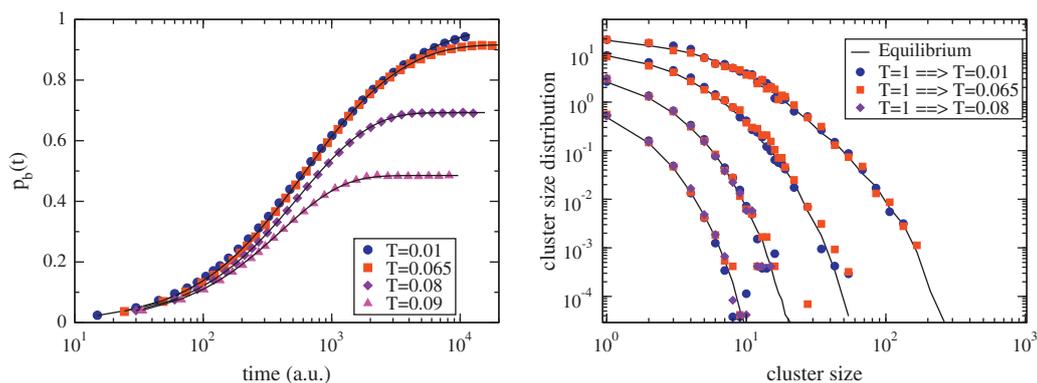
Fig. 6. Left panel: Evolution of the bond probability for the $f = 2.055$ binary mixture at fixed number density $\rho = 0.0382$ after several quenches from high $T = 1.0$ to a final T, as indicated in the label. Note that for the quench down to $T = 0.01$, the system never equilibrates, thus mimicking an irreversible gelation process. Symbols are Brownian dynamics simulation data, while solid lines are the analytic solutions of Eq. (6) [57]. Right panel: Comparison of the cluster size distributions calculated for an equilibrated system at a certain T with those calculated in an aging system after a certain t_w following a T quench. T and t_w are chosen in such a way that $p_b(T) = p_b(t_w)$, i.e. fulfilling Eq. (9). With this choice of T and t_w, the structure of the system during the aging dynamics is very similar to that occurring in equilibrium. Data redrawn from Ref. [57].

low average valence $f = 2.055$), whose equilibrium behavior was illustrated in Fig. 4, has been examined and compared to the equilibrium results. Indeed, the large value of the percolation threshold for the bond probability makes it an ideal candidate to test the theoretical predictions for the aging behavior. As previously alluded, the two theoretical assumptions at the heart of the theory remain valid during the whole aggregation process, up to the emergence of a fully bonded state. The aggregation kinetics has been followed via Brownian Dynamics simulations [57], in which the system is quenched from a high T down to very low ones for a series of densities (always outside the phase coexistence region). The evolution in time of $p_b(t)$ following several quenches has been compared to the Van Dongen and Ernst predictions (Eqs. (7) and (8)) both for reversible and irreversible aggregation, and the numerical results are found to be in very good agreement, as shown in Fig. 6(left panel), using as the only fit parameter the value of k_{break}^{site}.

Having established the functional form of $p_b(t)$, it is possible to compare the system properties to the corresponding equilibrium states, exploiting Eq. (9). Since $\rho_n(t)$ is only a function of $p_b(t)$, we can indeed compare it at specific waiting times with the cluster distribution of a system in equilibrium at a T corresponding to the same value of p_b. We find, as shown in Fig. 6(right panel), that indeed the mapping in Eq. (9) is confirmed. Thus the knowledge of $p_b(t)$ is sufficient to describe the full aggregation kinetics. Extending this concept to all static properties, like for example static structure factors or radial distribution functions, the structure of the system can also be predicted starting from the knowledge of the same quantity at equilibrium, as shown in Ref. [57].

4. Discussion and perspectives

In this article we have discussed the equilibrium and out-of-equilibrium behavior of patchy colloids, focusing on the case in which particles can form a limited number of bonds with their neighbors. We have shown that thermodynamic theories developed in the past to describe the behavior of associating liquids can be applied to predict the phase behavior of this class of systems, providing a clear reference frame for describing the system stability against phase separation and the properties of the liquid phase. The key result of this studies is that in limited valence systems phase-separation is confined in a very small region of densities, leaving a large window of densities where the liquid can be cooled to low T in an homogeneous state. Dynamics slow down only due to the increase of the bond lifetime τ_b which takes place on cooling, generating a network of bonded particles which can support shear and propagate elastic perturbations for times smaller than τ_b. In essence, small valence is a fundamental requisite to generate stable equilibrium gels.

We have also discussed the possible existence of a connection between physical and chemical gels for low-valence particles. This is made possible by the fact that when valence is small, closed loops of bonds are not very frequent and the fundamental assumptions of both the Wertheim and the FS theories are satisfied. Indeed, under the no-loop condition which can be realized by investigating systems in which the average valence is smaller than three or by adding anisotropy in the particle shape in order to disfavor multiple bond formation, theory is found to accurately describe the cluster size distribution and the presence of an infinite cluster at all state points, even beyond percolation [57].

The equivalence between the equilibrium Wertheim theory and the FS description for loop-less aggregating systems establishes a connection between equilibrium properties and the aggregation kinetics, suggesting that the formation of a branched network proceeds via a sequence of equilibrium steps. This occurs even in the deep quench limit where the system behaves as in an irreversible (or chemical) gelation, but still it is found to visit, as time proceeds, equilibrium states of lower and lower temperature. Under these conditions, the 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 [38]. Recently, it has been provided evidence that, for colloidal particles interacting via depletion interactions, the (reversible) aggregation process is driven by a phase-separation [31] and 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, and hence small valence is a pre-requisite for this mapping to hold. The reason for this, which has been investigated in the context of equilibrium properties [49,45], 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 shown [45] that systems with small average functionality have a negligible number of loops and fulfill rather

precisely 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 [58]. 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 patches must be small enough so that the time it takes two colloids to diffuse and reach a bonding-compatible relative distance is negligible as 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.

The ideas discussed in this review are promising for the prediction of the aggregation behavior of low-valence particles which could become the building blocks of tomorrow functionalized materials [1]. In addition to the simple spherical patchy particles discussed in this work, a few other similar systems have been tested in simulations against theory. In particular, extensive numerical work has tried to connect the behavior of chemical gelation observed in polymerizing systems to the concepts introduced for patchy particles. Building on experimental studies of step-polymerization of epoxy resins [59–61], a mixture of asymmetric ellipsoidal particles, respectively with valence five and two (with average valence 2.5), has been devised to study irreversible aggregation, as well as the link to reversible one. In a sequence of works [54,55,62], Corezzi et al. have shown that the theoretical framework described in this review holds also for these types of systems even beyond the percolation transition. However, given the fact that the average valence is not so low (as compared to the small-valence spherical colloid case addressed before) and consequently that $p_b^p \simeq 0.5$, clear deviations are observed when the final state is extensively bonded ($p_b \gtrsim 0.8$) [55]. Taking into account that for late times a crossover from reaction-limited to a diffusion-limited growth takes place in the irreversible aggregation process, it was found that also the late-stage aggregation can be well described [62] by a proper rescaling of the bond-forming rate constant.

Another interesting system that is suitable to be studied within the theoretical framework reviewed here is that of DNA-coated particles. These particles have recently received considerable attention due to their prominent role as building blocks for nano and microscale self-assembly [8,63] and to the control that can be obtained experimentally [12–14]. In particular, a recent numerical study [64] has focused on the aggregation kinetics of a mixture of bi-functional and three-functional DNA-coated particles, with the same average functionality ($f = 2.055$) of the binary mixture of patchy particles discussed in the previous paragraphs (so that the percolation threshold for the two models is obviously the same). However, the bonding volume is very different for the two cases, because in the DNA constructs each particle is decorated with four DNA strands chosen to give complementary pairing between different arms. Nonetheless the comparison of the aging behavior of the system with the theoretical predictions discussed in Section 2 still provides an excellent agreement up to very large values of p_b as for the patchy spheres (although some adjustment of the bond-forming rate constant was needed for short times [64]).

These studies provide evidence that 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 (Fig. 5) in the equilibrium phase diagram. Hence, the concepts presented in this review can be in principle applied to all those systems where the self-assembly of low-valence elementary units leads to branched structures and networks. In particular, these ideas can be of relevance in the field of supramolecular chemistry [15–18] (e.g. thermoreversible or "self-healing" rubber [19]), which models self-assembly of large molecules, again interacting via strong directional forces, to produce materials with relevance in technological and biomedical applications. Other candidates for the applications of these ideas are gels whose viscoelastic properties can be tuned at the molecular level, by changing the number of bonding groups (i.e., in a certain sense, the valence) such as recently shown for oligo(amidoamine)s hydrogels [20] and self-healing liposome gels [21]. There is indeed a strong analogy, with the only difference in the length scale of the building blocks, between self-assembly of patchy colloids and supramolecular chemistry.

The concept developed here can be relevant also to describe self-assembly in magnetic nanoparticles, whose interactions are mainly controlled by strong dipolar interactions. The preferred dipolar orientation makes them suitable candidates for the formation of low-valence networks [65–68,46]. However, it is to bear in mind that experimental studies in two-dimensional low-valence systems might suffer from the presence of a large number of bond loops, favored in low dimensions [69,48]. Similarly, patchy particles with extended patches (such as Janus particles for example [70]) will also not be appropriate for these types of treatments, due to the large number of bonded neighbors per patch. However, the experimental control of the number and width of the patches decorating colloidal particles appears to be nowadays possible [71,72] so that the self-assembly of more elaborated Janus-like particles (like the triblock Janus [71]) could be studied along the same lines.

The existence of a time–temperature mapping can also be exploited to describe the behavior of systems with less characterized effective interactions. Recently, the case of an anisotropic colloidal clay (Laponite) which is known to undergo a subtle aging behavior [73] has been examined in these terms. The irreversible aggregation process taking place in the experimental system has been interpreted in the framework of a patchy disk model, connecting the theoretical equilibrium phase diagram with the experimental observations of a low-density phase separation process followed by the presence of an equilibrium gel state [74].

We finally note that an interesting case which has not been studied so far is that offered by the possibility that, during the formation of an irreversible 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. It is possible that the slow syneresis phenomena which characterize some gel systems could be interpreted as slow approach toward the equilibrium coexisting density. Limited-valence colloidal systems [4,5,71] can thus be excellent candidates for testing the analogies between equilibrium and aging properties and the connection between gel stability and colloidal gas–liquid phase separation.

Acknowledgments

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