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HIGHLIGHT

# Chemical and physical aggregation of small-functionality particles

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The number of potentially relevant materials resulting from the aggregation of elementary units with a finite functionality continues to increase. The growth of branched clusters and networks may proceed through the formation of reversible (*physical*) or irreversible (*chemical*) bonds. The kinetics of bond formation is sensitive both to the intrinsic rate of the bonding process, controlled by the chemistry of the system, and to the encounter rate of clusters, controlled by cluster diffusion. In this Highlight we review a series of our recent numerical simulation studies designed to investigate the connections between chemical and physical aggregation and the crossover from a chemically controlled to diffusion-controlled regime. It is shown that in the chemically controlled limit, it is possible to formally correlate elapsed time during irreversible aggregation with equilibrium temperature in reversible aggregation. The diffusion-controlled regime sets in well-beyond percolation and the effect of diffusion can be described by introducing a single additional time scale, related to the average diffusion time. This concept can be readily generalized to interpret the experimental data.

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## I. Introduction

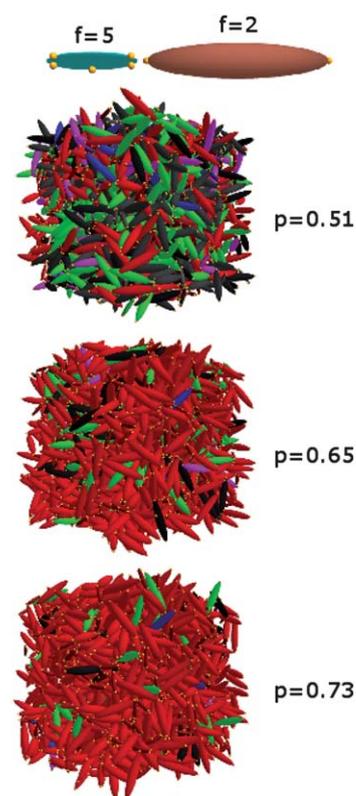
Several natural and synthetic materials, as well as biological structures, result from the aggregation into branched clusters or into a network of elementary units with a finite functionality, *i.e.* with a fixed number of bonding sites. This process, known under the names of polymerization, self-assembling, aggregation or clustering depending on the context, is receiving considerable attention in two fast-growing fields: supramolecular chemistry<sup>1–3</sup> and collective behavior of patchy and functionalized colloidal particles,<sup>4,5</sup> among the most promising building blocks of new materials. The process of formation of an extended three-dimensional network of bonds connecting independent molecules, proteins or colloidal particles is named gelation and the resulting material a gel.<sup>6–8</sup> At the gel point, an infinite (percolating) network of bonded particles first appears, which provides elasticity to the system and prevents it from flowing; yet, the system is not dynamically arrested on a mesoscopic length scale, and hence, glassy behaviour is not fully established.

In many cases of interest the elementary units (whether they are molecules or colloids) are particles with a small functionality. Two aspects of the aggregation process of small-functionality particle systems are the focus of this Highlight: (A) the nature of the bonding process (reversible or irreversible) and (B) the nature of the kinetics of aggregation (chemically or diffusion-controlled).

(A) Aggregation processes can be classified on the basis of the strength of the attraction between bonding sites, quantified by the ratio between the bond energy

$u_0$  and the thermal energy  $k_B T$  (where  $k_B$  is the Boltzmann constant and  $T$  is the temperature): for covalent bonds (strong attraction strength,  $u_0/k_B T \gg 1$ ), bond formation is irreversible (*chemical bonding*) and the number of bonds continuously grows with time. The aggregation proceeds *via* the build up of larger and larger clusters until an extensively bonded gel is formed. In the case of weak attraction strength ( $u_0/k_B T \sim 1$ ), bonds break and reform (*physical bonding*) while their number progressively reaches the thermodynamic equilibrium value, and fluctuates around it. The temperature at which reversible aggregation takes place controls the equilibrium extent of bonding (measured by the fraction of bonded sites). High values of  $T$  correspond to cluster fluid phases, low values of  $T$  to extensively connected gels. If the condition  $u_0/k_B T \sim 1$  is not met, and  $T$  is significantly smaller than the attraction strength, then the process of reversible aggregation turns into an irreversible one, since the thermal energy is not able to break bonds any longer. Starting from a monomeric state, the fraction of bonded sites progressively increases, and the system visits a sequence of states in time which may bear some relation to the states that are explored in equilibrium at different  $T$  values, from a high to lower values. This establishes a connection between physical and chemical aggregates, when the systems are formed by similar particles, which we will address in this Highlight.

(B) The process of bonding elementary units with a finite functionality requires as a first step that the system's constituents diffuse through random movements such



**Fig. 1** Graphical representation of the model particles (reactive sites are shown as yellow spheres on the surface of the hard-core ellipsoid), and snapshots of an irreversibly aggregating binary mixture at three values of the extent of aggregation  $p$ , beyond percolation. The percolating cluster (colored in red) progressively incorporates all particles in the system. Figure redrawn from ref. 31.

that when they come into contact, a reaction may be triggered. Therefore, the kinetics of aggregation is sensitive both to the encounter rate of clusters bearing the reactive sites and to the intrinsic rate of the chemical reaction process between clusters at contact. According to the relative importance of these two factors, the aggregation process is said to take place in the *chemically controlled* or in the *diffusion-controlled* limit. In the first case, diffusion is efficient and the rate of aggregation is controlled by the chemical mechanism at the basis of bonding. Many of these reactions occur in low viscosity solutions in which the aggregation product does not significantly limit the transport properties of reactants. In the second case, the encounter between clusters proceeds much slower than the bonding step and the aggregation is dominated by transport limitations. Such reactions are commonly found in



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biochemical processes such as protein aggregation, enzyme catalysis, and complexation in cells.<sup>9</sup> It often happens that a transition from the chemically controlled to diffusion-controlled limit occurs gradually as the aggregation product decreases the diffusivities in the system. Many thermoset materials of widespread use such as epoxy resins are the result of polymerization reactions where such crossover takes place.<sup>10</sup> In supramolecular chemistry the analogue is a so-called isodesmic polymerization.<sup>11</sup> Analytic solutions for the evolution of the cluster size distribution and the corresponding number of bonds with time are available for the chemically controlled case (under the hypothesis of the absence of bond loops in the aggregates of finite size),<sup>12,13</sup> but these solutions cannot describe efficiently the kinetics of aggregation when the diffusion contribution to the rate is not negligible. In general, the final structure of the aggregates results from a delicate balance between the cluster size dependence of the diffusion process and the probability to stick.

One way to prove the possible connections between chemical and physical aggregation and to look at how diffusion limitations interfere is to simulate model systems. Simulations offer the possibility to gradually switch from irreversible to reversible aggregation by changing the strength of the particle interactions. Also, through numerical investigation it is possible to develop a microscopic picture of how clusters diffuse and to devise a strategy to embed the effect of diffusion into an analytic description of the kinetics of aggregation. In this Highlight, we review a series of recent numerical studies specifically designed to evidence the analogies between reversible and irreversible gelation in small-functionality particles as well as to investigate the crossover from chemically controlled to diffusion-controlled aggregation.

## II. A model of chemical aggregation and its physical analogue

We have recently introduced a model for describing both the reversible and the irreversible aggregation process of a binary mixture of ellipsoidal particles, interacting *via* a small number of

short-ranged directional interactions.<sup>14,15</sup> The model represents two types of mutually reactive monomers as hard homogeneous ellipsoids of revolution whose surface is decorated by a given number of bonding sites in a predefined geometry (Fig. 1). Sites on particles of different types interact *via* an attractive potential that is modeled as a square-well of depth  $u_0$  and interaction range  $\delta$  much smaller than the particle size. In the numerical code, two sites, on particles of different type, form a bond if their distance becomes smaller than  $\delta$ . Clusters are defined as groups of bonded particles. The geometrical parameters of the particles are chosen to ensure that each site is engaged at most in one bond. As a reference case, we consider a 5 : 2 mixture of bifunctional and pentafunctional ellipsoids, in which the two types of reactive sites are initially present in equal number so that, in principle, there is the possibility to form a fully bonded state in which all the sites have reacted. Making use of an event-driven algorithm, the dynamic evolution of the system is studied starting from an initial configuration with no bonds between particles, at fixed  $T$ . The model offers the possibility to implement an irreversible (chemical) aggregation process as well as a reversible (physical) one: once a bond is formed, it is made irreversible by switching on an infinite barrier at distance  $\delta$  between the sites involved, which constrains the maximum distance between the two reacted sites to remain smaller than  $\delta$  and hence prevents bond breaking. Otherwise, there is a probability of breaking which depends on the relative value of the thermal energy  $k_B T$  compared to the energy barrier that must be overcome to escape the potential well,  $u_0$ .

Since the number of bonds in the simulation is measured without ambiguity, it is straightforward to evaluate the extent of aggregation  $p$  (or equivalently, the bond probability) as the number of bonds in the system over the maximum number of possible bonds. During irreversible aggregation,  $p$  increases monotonically with time, although the reaction never reaches its full extent. In the early stages of aggregation, particles are only connected into finite-size clusters (sol). The size of the clusters grows with time, progressively merging into an infinite (gel) cluster at the percolation transition when

the bond probability reaches a critical value  $p_{gel}$ . At longer times, a final state is approached where essentially all particles belong to the infinite cluster, even if a number of sites remain unbonded (Fig. 1). During reversible aggregation, instead, bonds form and break continuously with time (and  $p$  fluctuates) while the system evolves toward the equilibrium state, characterized by an average value  $p_{eq}(T)$  of the extent of aggregation. Note that while in chemical aggregation the temperature only controls the time scale of exploration of space (by modulating the average particle's velocity), and hence the rate of formation of new bonds but not their final number, in physical aggregation the temperature controls the average number of bonds at very long times, after the equilibration transient is over.

A mixture of ellipsoidal patchy particles is a very simple but effective coarse-grained model for aggregation, able to combine directional bonding, selectivity of interactions and asymmetry in shape, which are the key features of old and new-generation aggregating systems. The model has been realistically inspired by the three-dimensional step-growth polymerization that occurs at the molecular level, *e.g.* in epoxy-amine systems,<sup>16</sup> but can also be considered representative of associating polymers,<sup>17–19</sup> functionalized molecules<sup>20</sup> and, moving up in the length scale of the associated particles, of systems with bioselective interactions<sup>21,22</sup> and patchy colloids.<sup>5,23,24</sup> Small modification of the model can be implemented to model vitrimers dynamics.<sup>25</sup>

Most theoretical predictions for particle aggregation are derived under the assumptions that (i) all functional sites of a given type have equal and independent reactivity, (ii) the formation of bond loops within finite clusters (*i.e.* intra-cluster bonds connecting particles belonging to the same cluster) does not take place, and (iii) the bond-formation contribution to the rate is dominant as compared to that of diffusion, *i.e.* the aggregation process is chemically controlled. These conditions are commonly referred to as Flory–Stockmayer (FS) hypotheses. The first condition is encoded in the model by construction. The other two are not *a priori* implemented: these crucial conditions are highly non-trivial and somehow

depend on the functionality, the microscopic dynamics and the modeling of the site–site interaction. Concerning (ii), there is numerical evidence that the formation of bond loops is negligible when the average functionality is smaller than three,<sup>27</sup> and the no-loop condition is even more efficiently realized by adding anisotropy to the particle shape. The present model, whose average functionality is  $\bar{f} = 2.857$ , therefore disfavors the formation of loops in finite size clusters. The absence of loops is further driven by the elongated shape of the particles, the asymmetric location of the reactive sites on their surface and the excluded-volume effects. Concerning (iii), it should be noted that only when the bonding volume is small, the probability that two sites 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 distance and the cluster-size dependence of the diffusion coefficient can be neglected in the calculation of the rate constants. The choice of the packing fraction  $\phi$  is also relevant, since it impacts significantly on the particle mobility. Indeed, only when  $\phi$  is relatively small diffusion is not hampered by crowding and excluded-volume effects (caging). In the studied model, the chemically controlled limit of aggregation is favored by the short-range site–site interaction and by choosing  $\phi = 0.3$ , a value calibrated on a realistic mixture of epoxy-amine molecules in their initially fluid state. As a result, the connectivity properties of the chemical aggregation model have been compared in detail to the FS predictions, and the numerical data are found to be in very good agreement, without fit parameters, in a very wide range of  $p$ . The percolation threshold is found, as predicted by FS theory, at  $p_{\text{gel}} \approx 0.5$ , and the cluster size distribution observed in the simulations during the aggregation process coincides with the theoretical predictions up to  $p \approx 0.65$ , well beyond percolation. Furthermore,  $p(t)$  is well described, again for  $p \leq 0.65$ , by the kinetic equation derived for loopless chemically controlled aggregation. This agreement indicates that the model provides a close realization of the

mean-field FS theory, in a wide range of  $p$  extending well beyond percolation. The departure from the FS predictions for  $p \geq 0.65$  are most likely to be ascribed to a progressive role of diffusion in the bonding rate.

It is worth noting that the range of  $p$  values in which agreement between simulations and FS predictions is realized depends on the functionality, and might change by changing the packing fraction. Indeed, the study of a similar model (a mixture of spherical particles with two and three patches) with  $\bar{f} = 2.055$  and  $\phi = 0.1$  shows that the agreement with the predictions remains valid during the whole aggregation process, up to the emergence of a fully bonded state.<sup>26</sup> In general, when the probability of forming closed bond loops in three-dimension is negligible the FS approach works very accurately both in the cluster phase (before percolation) and in the percolating region, up to an extent of aggregation which is controlled by the slowing down of the dynamics, and hence by diffusion.

### III. Connecting chemical and physical aggregation: time and temperature

#### A. Background

One may ask how different are the structure and connectivity properties of chemical and physical aggregation states. The idea of a close connection between irreversible and reversible aggregation is rather intuitive, and based on theoretical grounds. Is it correct? And to what extent? The idea is intuitive in that conceptually any model of physical aggregation may be turned into a chemical model by studying its properties following a quench to  $k_{\text{B}}T \ll u_0$ . Theoretically, a hint for the possible existence of a link between chemical and physical aggregates was formally anticipated by the early theoretical work of Stockmayer.<sup>28</sup> Indeed, Stockmayer assumed that at any time  $t$  during chemical aggregation, when the fraction of formed bonds is  $p$ , the concentrations  $c_k(p)$  of clusters of  $k$  particles 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 that 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. At the same time, Stockmayer also showed 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<sup>12</sup> extended the work of Stockmayer to the case in which bond-breaking processes are also possible. They were able to show analytically that in this reversible aggregation case the time-dependent solutions  $c_k(p(t))$  of the Smoluchowski's kinetic equations are formally identical to those obtained by Stockmayer in equilibrium at the extent of reaction  $p$ . The time dependence of  $p$  satisfies the equation

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

where  $k_{\text{bond}}^{\text{site}}$  and  $k_{\text{break}}^{\text{site}}$  are respectively the rate constants of forming and breaking a single bond,  $\rho = N/V$  is the particle number density and  $\bar{f}$  is the particle average functionality. The latter equation can be solved with  $p(0) = 0$  (*i.e.* starting from the absence of bonds) and  $p(\infty) = p_{\text{eq}}$ , providing an analytical expression of  $p(t)$  during a reversible aggregation process,

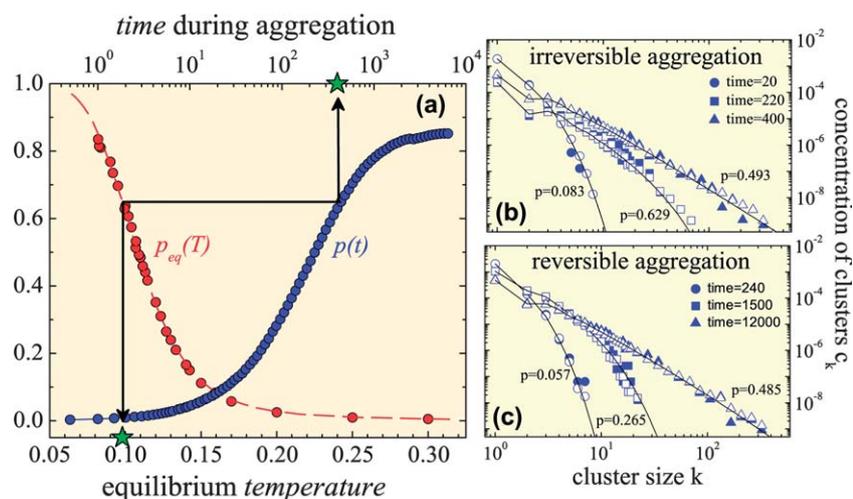
$$p(t) = p_{\text{eq}} \frac{1 - e^{-\Gamma t}}{1 - p_{\text{eq}}^2 e^{-\Gamma t}} \quad (2)$$

with  $\Gamma = \rho \bar{f} k_{\text{bond}}^{\text{site}} (1 - p_{\text{eq}}^2) / p_{\text{eq}}$ . In the limit of absence of breaking processes ( $k_{\text{break}}^{\text{site}} \rightarrow 0$  or equivalently  $p_{\text{eq}} \rightarrow 1$ ), when irreversible aggregation takes place, the cluster size distribution  $c_k(p(t))$ , expressed in terms of  $p$  retains the same form as in equilibrium, while the time evolution of  $p$  reduces to

$$\frac{dp}{dt} = \rho \bar{f} k_{\text{bond}}^{\text{site}} (1-p)^2 \quad (3)$$

whose solution with the initial condition  $p(0) = 0$  becomes

$$p(t) = \frac{\rho \bar{f} k_{\text{bond}}^{\text{site}} t}{1 + \rho \bar{f} k_{\text{bond}}^{\text{site}} t} \quad (4)$$



**Fig. 2** Results illustrating the connection between *time* during aggregation and *temperature* in equilibrium. (a) Red symbols show the  $T$  dependence of the fraction of bonds in the system at equilibrium, blue symbols the time evolution of the fraction of bonds during the aggregation process. At each time  $t$  of the aggregation, 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). The connectivity (and the structure) of the system in the two corresponding points (labeled by a star) is identical, and thus the aggregation process can be thought of as a sequence of equilibrium steps, in which the system is progressively cooled from high  $T$  (at short times) to low  $T$  (at large times). [Both  $T$  and  $t$  are in arbitrary units.] A demonstration is given in panel (b) and (c), respectively in the case of irreversible aggregation and in the case of reversible aggregation at  $T = 0.11$ . Solid symbols represent the cluster size distribution at different times during the aggregation process, open symbols the cluster size distribution obtained in equilibrium at the same fraction of bonds. Lines are the corresponding FS distributions.

The remarkable result is that the evolution of  $c_k(t)$  is entirely contained in  $p(t)$ , *i.e.* the cluster size distribution only depends on the value of the extent of aggregation. The distribution of cluster sizes is predicted to be formally identical to that observed in a system in equilibrium at a  $T$  such that the extent of aggregation  $p_{eq}(T)$  is identical to  $p(t)$ . This amounts to formally establish a link between chemical and physical aggregation, through the following relationship for the extent of aggregation

$$p(t) = p_{eq}(T). \quad (5)$$

The aging dynamics following a temperature jump from high  $T$  (only monomers) to a finite  $T$  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 (Fig. 2). This is valid both when the system is quenched down to a  $T$  where equilibration is still possible and also in the case of a quench performed to such a low  $T$  that breaking processes become impossible and aggregation takes place irreversibly.

The thermodynamic theory of Wertheim,<sup>29,30</sup> developed to describe the behavior of associating liquids, provides a parameter-free expression for the  $T$  dependence of  $p_{eq}$ , through the independent bond mass-action law,  $p_{eq}/(1 - p_{eq})^2 = f \rho \exp(-\beta F_b)$ , where  $F_b$  is the bond free-energy, *i.e.* the free energy difference between the bonded and the un-bonded state for a pair of reactive sites.  $F_b$  can be evaluated from the potential parameters and the reference fluid radial distribution function. The interesting point to notice is that, independent of the model (which only enters in the details of the  $F_b$  calculation), the Wertheim theory can be complemented with the kinetic approach of Smoluchowski, *via* the equilibrium condition (*i.e.*  $dp/dt = 0$ ) which imposes the following relationship between the bonding and breaking coefficients  $k_{bond}^{site}$  and  $k_{break}^{site}$ ,  $\rho^2 f k_{bond}^{site} / k_{break}^{site} = p_{eq} / (1 - p_{eq})^2$ . As a result, the  $T$  dependence of the ratio between  $k_{bond}^{site}$  and  $k_{break}^{site}$  can be predicted, and hence, except for a constant which fixes the time scale and depends on the chosen particle dynamics, the evolution of the entire aggregation process can be described without free parameters.

It is worth stressing that all the above-mentioned predictions require the absence of bond loops within finite clusters and the absence of diffusional limitations.

## B. Simulation results

According to the theoretical work reviewed in the previous section – based on kinetic equations solved in the limit of chemically controlled rates and loop-less aggregation – a system forming progressively larger and larger branched aggregates, through either reversible or irreversible bonds, evolves in time *via* a sequence of states which are identical to the states explored in equilibrium at appropriate values of  $T$ . The equality in the fraction of formed bonds  $p$  provides the connection between *time* during reversible or irreversible aggregation and *temperature* in equilibrium. Numerical simulations of the binary mixture of reactive ellipsoids<sup>14,15</sup> have confirmed these theoretical predictions in a wide range of  $p$ , up to an extent of aggregation well beyond the emergence of a percolating cluster. In particular, the evolution of the same binary mixture of ellipsoids in time has been examined during irreversible aggregation and following several quenches from a very high temperature down to lower  $T$  values in conditions of reversible aggregation. The evolution of  $p(t)$  in time has been compared to the Van Dongen and Ernst predictions both for reversible and irreversible aggregation (eqn (2) and (4)), and the theoretical expressions very well represent the numerical data, except for  $p \geq 0.65$  in the irreversible case and for the lowest studied temperatures in the reversible case. Moreover, the connectivity properties of the system have been compared in thermal equilibrium and during aging, exploiting eqn (5). We have indeed compared  $c_k(t)$  at specific elapsed times  $t$  during the irreversible bonding process with the cluster size distribution of a system in equilibrium at a  $T$  corresponding to the same value of  $p$ . As shown in Fig. 2(b), the mapping in eqn (5) is confirmed. Similar comparison at several elapsed times during a reversible bonding process at finite  $T$ , starting from an un-bonded state, is shown in Fig. 2(c), demonstrating that both chemical and physical aggregation proceed along a

sequence of equilibrium states, accurately modeled by the FS distributions.

## IV. Modeling the crossover from chemically to diffusion-controlled aggregation

### A. Background

The binary ellipsoid model is a good candidate to study the role of cluster diffusion in controlling the late stages of the aggregation kinetics, since the effect of diffusion emerges well beyond percolation but still long before all possible bonds have been formed. Simulations have been scrutinized to gain insight into the origin of the crossover from chemically controlled to diffusion-controlled aggregation.<sup>31</sup> The present discussion will limit to the irreversible aggregation case.

As alluded to previously, the kinetics of irreversible aggregation can be formally modeled in terms of the Smoluchowski's rate equations, especially for the case in which the rate of bond-breaking is zero.<sup>32</sup> The equations provide the time evolution of the concentrations  $c_k(t)$  of clusters of size  $k$  in the form

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} k_{\text{overall}}^{i,j} c_i c_j - \sum_{j=1}^{\infty} k_{\text{overall}}^{k,j} c_k c_j \quad (6)$$

where the first sum represents formation of  $k$ -mers by reactions between pairs of smaller clusters, and the second term represents their destruction through reactions with other clusters. The coagulation kernel  $k_{\text{overall}}^{i,j}$  represents the rate coefficient for a specific clustering mechanism between clusters of sizes  $i$  and  $j$ . It is assumed that both intrinsic chemical constraints and diffusional limitations to the bonding can be accounted for by an appropriate modeling of  $k_{\text{overall}}^{i,j}$ .<sup>32</sup> Solving eqn (6) provides a full description of the aggregation kinetics, as the time dependence of  $c_k(t)$  comes out to be complemented by the time dependence  $p(t)$  of the fraction of formed bonds (*i.e.* the extent of aggregation). In the experimental studies, on the other hand, often one searches for a simpler description which drops the information on the cluster size distribution, and focuses only on the experimentally more accessible time dependence of  $p$ . In the hypothesis that all sites have equal reactivity,

independent of the size of the cluster to which they are attached,  $p$  represents the bond probability (*i.e.* the probability that choosing a site at random in the system, it has reacted) and then it satisfies

$$\frac{dp}{dt} = k_{\text{overall}}(1-p)^2 \quad (7)$$

Different from eqn (3),  $k_{\text{overall}}$  is here an overall rate coefficient of forming a single bond which incorporates all information on the aggregation process and which can, in general, depend on  $p$ . Eqn (7) simply states that the probability to form a bond depends on the probability of encounter between two unreacted sites, independent of their spatial location or local environment. As previously discussed, in the simplest chemically controlled case,  $k_{\text{overall}}$  results to be constant and equal to  $k_c \equiv \bar{f} \rho k_{\text{bond}}^{\text{site}}$ . In this case, eqn (7) becomes coincident with eqn (3). The corresponding solution with  $p(0) = 0$  is given by eqn (4), or using the present notation,  $p(t) = k_c t / (1 + k_c t)$ .

In view of the experimental cases considered below, it is worth noting that more complex chemical mechanisms may be active in nature, and the description of such mechanisms, even under the chemically controlled assumption, may require more than one rate constant or may result in a variant of eqn (7). For example, reactions such as some epoxy-amine polymerizations have an autocatalytic nature and this fact, even assuming a simplified reaction scheme, leads to  $k_{\text{overall}} = k_{c1} + k_{c2}p$ , where  $k_{c1}$  and  $k_{c2}$  are constants related to the noncatalytic and autocatalytic pathways of reaction. Moreover, cases are not unusual where a phenomenological expression like

$$dp/dt = (k_{c1} + k_{c2}p^m)(1-p)^n \quad (8)$$

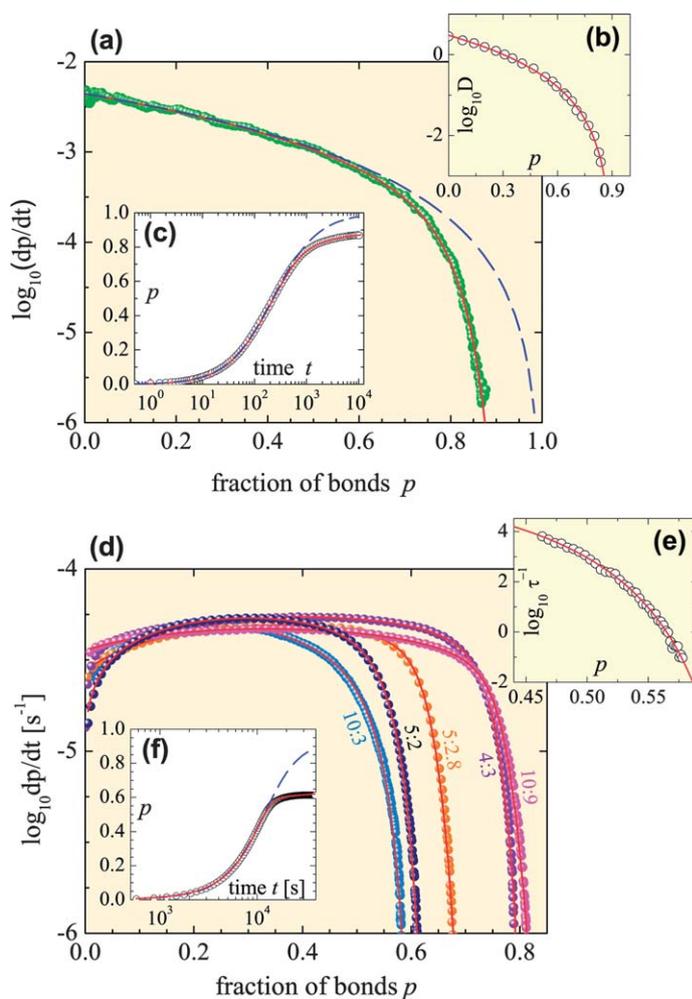
with  $m$  and  $n$  fractional exponents (known as Kamal equation<sup>33</sup>) is necessary to obtain a good description of the experimental data in the chemical regime. In general, how to best model throughout the aggregation process the time (or  $p$ ) dependence of the kernels  $k_{\text{overall}}^{i,j}$ , and  $k_{\text{overall}}$  in the description of eqn (7) is a non-trivial problem.

### B. Simulation results

As alluded to before, the early stages of irreversible aggregation of a mixture of

reactive ellipsoids are properly described by the chemical approximation, and up to  $p \approx 0.65$  eqn (3) is strictly obeyed. Beyond  $p \approx 0.65$ , deviations from the theoretical predictions are observed whose origin can be scrutinized by analyzing the numerical results. The investigation of the diffusion properties of the system as well as of the clusters as a function of their size, not possible experimentally, is the key to understand the failure of the chemically controlled approximation. For each value of  $p$ , the overall diffusion coefficient can be evaluated as  $D = \lim_{t \rightarrow \infty} \langle \Delta r^2(t) \rangle / 6t$ , where  $\langle \Delta r^2(t) \rangle$  is the mean squared displacement of all the particles in the system over the time period  $t$ . To provide an accurate determination of  $D$  which is not affected by the ongoing aggregation process we exploit the possibility offered by the numerical simulation of *freezing* the aggregation process, and to analyze the dynamics in a system of fixed cluster-size composition. More precisely, when during the simulation a given value of  $p$  is achieved, positions and velocities of all particles are copied and used to start a new simulation in which the bonding pattern is frozen by switching on an infinite barrier at distance  $\delta$  between each pair of mutually reactive sites. In this new simulation, the formed clusters remain free to move, while retaining their integrity (*i.e.* not binding to other clusters), and  $D$  is calculated from the long time limit of  $\langle \Delta r^2(t) \rangle$ , evaluated where a possible subdiffusive behavior is over and a linear increase in time is established. Note that the overall diffusion coefficient can also be written as  $D = \sum_k D_k k N_k / N$ , with  $D_k$  the average diffusion coefficient of clusters of size  $k$  and  $N_k$  the number of these clusters, in order to emphasize that the slowing down of the overall diffusion arises from two different mechanisms: the decrease of the diffusion coefficient of each cluster-size as well as the decrease in the number of diffusing clusters. Alternatively,  $D$  can also be split into two contributions coming from the particles that belong to the infinite cluster (gel) and from the remaining material (sol).

The numerical results for the  $p$  evolution of  $D$  are well described by a power law  $D = D_0(p_0 - p)/p_0^\gamma$  with  $D_0$  the diffusion coefficient at  $p = 0$ ,  $\gamma$  the power-law exponent, and  $p_0$  the value of  $p$  where diffusion is expected to vanish. The best-fit value  $p_0 = 0.902 \pm 0.005$  indicates that



**Fig. 3** Rate of bond formation,  $dp/dt$ , as function of the fraction  $p$  of formed bonds. (a) The case of a binary mixture of ellipsoidal patchy particles with functionalities 2 and 5 in the stoichiometric ratio 5 : 2. Symbols are the simulation results. The dashed and solid lines represent eqn (7), respectively in the chemically controlled limit ( $k_{\text{overall}} = k_c$ ) and in the case including the effect of diffusion ( $k_{\text{overall}}$  given by eqn (10)). In the last case, the diffusion coefficient  $D(p)$  [shown in (b)] provides the relevant time scale entering in  $k_{\text{overall}}$ , leaving only one free fit-parameter. (c) Time dependence of the fraction of bonds  $p$ . Lines are solution of eqn (7) with the initial condition  $p(0) = 0$ , in the chemically controlled limit (dashed line; analytic solution given by eqn (3)) and in the case including the effect of diffusion (solid line; numerical solution). (d) The case of an epoxy-amine mixture (DGEBA, functionality = 2 and DETA, functionality = 5) at different values, as indicated, of the epoxy-amine molar ratio (and different  $T$  of reaction). Symbols are the experimental results, obtained by differential scanning calorimetry. The solid lines represent the best fit of eqn (8) in the case including the effect of diffusion ( $k_{\text{overall},1}$  and  $k_{\text{overall},2}$  given by eqn (11)). With  $k_{c1}$  and  $k_{c2}$  known from the early stages of polymerization, and the structural relaxation time  $\tau(p)$  measured by photon-correlation spectroscopy [shown in (e), for the reaction DGEBA/DETA 5 : 2 at  $T = 28$  °C], the fit procedure only adjusts two parameters,  $k_0$  and the fractional exponent  $\xi$ . (f) Time dependence of the fraction of bonds  $p$  for the system DGEBA/DETA 5 : 2 during reaction at  $T = 28$  °C. Lines are numerical solutions of eqn (8) with the initial condition  $p(0) = 0$ , in the chemically controlled limit (dashed line) and in the case including the effect of diffusion (solid line).

the arrest of the dynamics occurs before all available sites have reacted, *i.e.* that a fraction of unreacted sites exists in the arrested gel network. For all cluster sizes,  $D_k$  slows down by one order of magnitude during the aggregation process and tends to vanish at approximately the

same point as the overall diffusion coefficient.

Analysis of the simulation results also shows that when the chemical approximation starts to fail ( $p \sim 0.65$ ) most of the particles in the system belong to the gel, whose contribution to the diffusion can

be safely neglected since the gel always retains a subdiffusive motion (*i.e.* the mean squared displacement of the gel center of mass increases less than linearly in time) and the particles belonging to the network are always much more localized than the particles in clusters of finite size. The bulk diffusion process is thus associated with the sol phase. In particular, it is mostly controlled by the monomers, through their number and diffusivity. The number of monomers in the system exceeds the number of dimers and of clusters of any other size by more than one order of magnitude throughout the aggregation process and their diffusivity stays higher, providing a major contribution to the diffusion coefficient. On increasing  $p$  beyond  $p_{\text{gel}}$ , the number of monomers significantly drops but at a slower pace compared to larger clusters, quickly becoming the dominant particles in the sol. Hence, at large values of  $p$ , the percolating cluster coexists with sol particles, which are mostly found in monomers and very small aggregates. To provide a graphical visualization of the system structure and clustering in the region where the chemical approximation breaks down, Fig. 1 shows one configuration at  $p = 0.65$ . It appears clearly that the sol concentration is strongly suppressed and that only very small clusters are present in this region.

These results can be incorporated into a simple but effective modeling of the long time kinetics of aggregation, taking into account the effect of diffusional limitations. At the level of the less-demanding description of eqn (7), this corresponds to devise an expression of  $k_{\text{overall}}$  which captures both the properties of the chemical bonding act and the diffusive properties of the clusters to which the reactive sites are attached. Following the Rabinowitch model for small-molecule reactions,<sup>34</sup> we write

$$k_{\text{overall}}^{-1} = k_c^{-1} + k_{\text{diff}}^{-1} \quad (9)$$

where  $k_c$  is the intrinsic rate constant which is given by the chemistry of the system, and  $k_{\text{diff}}$  is the rate coefficient for a system with no chemical barriers where reactions occur upon collision of functional groups. This last coefficient depends on the diffusion time scale, which is expected to vary with  $p$ . Eqn (9) simply states that the time required to form a new

bond is the sum of the time required for two clusters of any size to approach each other plus the time required for the repeated collisions between nearby clusters to become fruitful to bond a reactive pair. The parallel sum of  $k_c$  and  $k_{\text{diff}}$  suggests that in the early stages of aggregation, when the system consists mainly of monomers and oligomers, the particle mobility is high and the aggregation proceeds in the absence of diffusional limitations ( $k_{\text{diff}} \gg k_c$ , hence  $k_{\text{overall}} \approx k_c$ ). However, on increasing the extent of reaction, the cluster-size dependence of the diffusion coefficient starts to limit the reactivity of unreacted sites, so that, for large values of  $p$ , the rate of aggregation is primarily determined by the mass transfer of the reactants ( $k_{\text{diff}} \ll k_c$ , hence  $k_{\text{overall}} \approx k_{\text{diff}}$ ).

As discussed at length in the previous sections and shown in Fig. 3a, the early time kinetics in this system is properly described within the chemically controlled regime, and the constant value of  $k_c$  is entirely determined by the early stage of aggregation. Concerning the  $p$  dependence of  $k_{\text{diff}}$ , it is reasonable to assume that the time scale  $k_{\text{diff}}^{-1}$  is associated with the average diffusion time scale  $D^{-1}$ , or equivalently, that  $k_{\text{diff}}$  varies with  $p$  in the same manner as the average diffusion coefficient  $D$  of the reacting entities,  $k_{\text{diff}}(p) \sim D(p)$ . With this ansatz, it is possible to write

$$k_{\text{overall}}^{-1} = k_c^{-1} + k_0^{-1} \left( \frac{p_0 - p}{p_0} \right)^{-\gamma} \quad (10)$$

where  $k_0$  is the proportionality constant between the diffusion rate coefficient and  $D/D_0$ , the normalized diffusion coefficient. Substitution of eqn (10) in eqn (7) yields a kinetic model that would account for chemically and diffusion-controlled regimes of the aggregation and also the crossover between the two, provided that the  $p$  dependence of  $D$  is known. The description of the entire kinetic process is then provided by only one additional parameter,  $k_0$ , the diffusion rate constant in the initially ( $p = 0$ ) unbonded state.

A comparison between the simulation data for  $dp/dt$  vs.  $p$  and eqn (7) [with  $k_{\text{overall}}(p)$  expressed by eqn (10)] offers a way to check the sustainability of a mean-field description, to test the quality of the approximation and, with the parameters  $p_0$  and  $\gamma$  known from  $D(p)$ , to extract the best value of  $k_0$ . The best-fit value is two

orders of magnitude larger than  $k_c$ , confirming the separation between the two kinetic regimes. The solid line in Fig. 3a demonstrates that the mean-field diffusion-controlled rate equation provides an excellent description of the entire kinetic process. The close agreement between simulation and diffusion-corrected modeling is further stressed in the inset of Fig. 3a, comparing the numerical solutions of eqn (7) with the initial condition  $p(0) = 0$  in the case  $k_{\text{overall}} = k_c$  and  $k_{\text{overall}}$  given by eqn (10).

### C. Comparison with experiments

The problem of describing the effects of diffusional limitations on the kinetics of aggregation in systems with a finite number of reactive sites has historically been addressed by studying polymerization. The case of epoxy resins is emblematic. The step-growth polyaddition reaction of an epoxy compound with a cure agent (e.g. an amino reagent) progressively changes an initially fluid small-molecule mixture into an insoluble network, which is typically solid. In the early stages the reactions are chemically controlled. At higher extents of reaction, the mobility of unreacted groups is more and more hindered due to cluster-size effects and the decreasing rate at which they diffuse within the system in turn decreases the rate at which they react. The resulting negative feedback between the physical process of diffusion and the chemical process of bonding brings both processes to vanishing levels, even if the reaction is not complete. With a good kinetic model, valid over the entire range of polymerization, it is possible to predict how the system will behave during the process and what its final condition will be, and consequently to optimize the processing conditions and control the performance of the final material. Many strategies to analyze the entire reaction kinetics have been employed, as reviewed in ref. 35.

The first experimental attempts to analyze the diffusion-controlled kinetics by replacing each chemical rate constant with an overall one built on the Rabino-witch model (eqn (9)) and by assuming proportionality between  $k_{\text{diff}}$  and the overall diffusion coefficient, date back many years ago.<sup>36–38</sup> The experimental approach, however, unavoidably suffers

from certain limitations, as it relies on the knowledge of the kinetic equation governing the chemically controlled limit of the reaction – which in most situations is complicated by autocatalytic terms, multiple-reaction effects, or is obtained on a semiempirical basis – and on the determination of the diffusion coefficient, which in most cases cannot be directly accessed and requires a non-trivial assumption on the way it is related to the relaxation time experimentally measured. These experimental limits are overcome by simulations, which now provide a useful reference. The approach discussed in the previous section and validated *via* the comparison with numerical data has been recently adapted to model diffusion-control in the experimental studies. As an example, Fig. 3b shows the rate of bond formation,  $dp/dt$ , as function of  $p$  for an epoxy-amine system with different proportions of the reagents, during reaction at a constant temperature. The chemically controlled regime is properly described by the Kamal equation,<sup>33</sup> containing the noncatalytic and autocatalytic chemical rate constants  $k_{c1}$  and  $k_{c2}$ . This equation, like the simplest eqn (3), always reaches  $dp/dt = 0$  at  $p = 1$ , significantly departing in the final stage of reaction from the experimental data (inset of Fig. 3). In this region the diffusion at molecular level is increasingly hindered, as also reflected in the marked increase of the structural relaxation time  $\tau$ , for example measured by dielectric<sup>39</sup> or photon-correlation spectroscopy,<sup>40–42</sup> and diffusion-corrected rate constants must be used. The lack of direct information about  $D(p)$  generally represents the greatest obstacle to follow the same strategy of description as emerges from the simulations. Knowledge of  $\tau(p)$  can be used to bypass this problem. In fact, the structural relaxation time  $\tau$  offers a measure of the ability of the molecules to rearrange their structure, also related to their ability to move through the sample, in a way that an increase of the time needed to relax corresponds to a decrease of the diffusion coefficient. In a simplistic approach,  $D$  has been assumed to be inversely proportional to  $\tau$ ,  $D \sim \tau^{-1}$ .<sup>37,38</sup> This assumption, which is referred to as Debye–Stokes–Einstein relationship, follows from two equations, both derived within the theory of macroscopic hydrodynamics. As such,  $D$  and  $\tau$  should refer

to a macroscopic particle diffusing in a continuous medium, a limitation that should not be underestimated. Surprisingly, these equations are well verified in ordinary liquids and in many simple glass-formers, irrespective of the fact that they should be strictly valid for particles larger than the surrounding molecules. The existence of appreciable deviations, however, is well documented in high viscosity fluids and when these equations fail, their modification by the introduction of a fractional exponent correlates successfully the experimental data. In more general terms, the relationship between the overall diffusion coefficient of the molecules participating in the reaction and the structural relaxation time is better written as a fractional power law,  $D \sim \tau^{-\xi}$  with  $0 < \xi < 1$ , according to which, molecular diffusion diverges more slowly than the structural relaxation. With this refined assumption, it is possible to write, for each chemical rate constant

$$k_{\text{overall}}^{-1} = k_{\text{c}}^{-1} + k_0^{-1} \tau(p)^\xi \quad (11)$$

where  $k_0$  is the proportionality constant between the diffusion rate coefficient  $k_{\text{diff}}$  and  $\tau^{-\xi}$ . The solid lines in Fig. 3b are obtained by fitting to the experimental data the kinetic equation resulting from the substitution of eqn (11) into eqn (8), with the adjustment of only two parameters, *i.e.*  $k_0$  and the fractional exponent  $\xi$ . Relatively small values of this exponent ( $\xi < 0.5$ ) are typically found. With such values, the fit function is able to reproduce very well the behavior of  $p$  vs.  $t$  and  $dp/dt$  vs.  $p$  over the whole reaction range, describing a smooth transition from the chemical to the diffusion-controlled regime. On the other hand, the structural arrest is generally so rapid that an equally rapid evolution of the molecular diffusion coefficient ( $\xi = 1$ ) would make the fit function overestimate the reaction rate in the first part of the reaction, and to compensate afterwards, describing an all too abrupt deceleration in the final stage with a non-negligible deviation from the experimental data. The key to accurately reproduce the kinetics of reaction in the experimental case is to give up the common assumption that the relaxation rate provides a reasonable estimate of the diffusional rate. The agreement shown in Fig. 3b is significantly better than previous models, and has been similarly

obtained for a large number of systems over the entire range of polymerization, in a wide range of reaction temperatures,<sup>35</sup> thus providing experimental support to the numerical strategy of data analysis.

## V. Conclusions and perspectives

In this Highlight we have discussed the kinetics of aggregation of a mixture of asymmetric reactive ellipsoids, in which particles can form a limited number of bonds with their neighbors giving rise to a gelation process and finally an arrested dynamics. The key feature of this model is that bonding can be switched from the irreversible (chemical) to the reversible (physical) case.

Comparing the two modes of bonding, it was shown that there exist “corresponding states”, *i.e.* states characterized by identical cluster size distributions at a certain period of time during irreversible aggregation and at a certain  $T$  under equilibrium conditions, and the associated possibility to convert *time* during aggregation into an effective equilibrium *temperature*, envisioning aggregation as a progressive cooling of the corresponding physical model. The equality in the fraction of formed bonds  $p$  represents the condition of the corresponding states. The possibility of defining “corresponding states” allows one to make use of theories developed for equilibrium systems and of results derived using statistical mechanics methods and computer simulations, to describe irreversible aggregation phenomena, and *vice versa*.

During irreversible aggregation, the system evolves in a chemically controlled regime in the early stages and then progressively crosses to a diffusion-controlled regime. The effect of diffusion emerges only in the later stages of aggregation. It is interesting to discuss why the chemical limit works for such a long interval, well beyond percolation. At the basis of this behavior is the small value of the chemical rate constant. The origin of such a small value has to be found in the essence of the bonding interaction which, thanks to its short-range nature and localization, imposes by itself an entropic barrier to bond formation. Bonding indeed requires that two reactive sites become close to each other or, in

equivalent terms, that the two reacting clusters face each other with the right orientation. As a consequence, the time required for two clusters to diffuse and approach each other is significantly smaller than the time required to orient themselves in the right bonding geometry, thus establishing the chemical regime.

When diffusion becomes relevant – due to the general mechanism that the average distance between the unreacted sites progressively grows, coupled to the increased size of the diffusing clusters – the sol clusters which contribute to diffusion are mostly monomers, which progressively react with the infinite gel cluster determining the faster depletion of their concentration and a rapid decrease of the average diffusivity (by several orders of magnitude in a small range of the extent of aggregation). Such a decrease, in fact, is mostly driven by the progressive reduction in the number of clusters in the sol and, in the interesting kinetic region where diffusion effects are dominant, mainly due to the change in the number of monomers. The higher diffusivity of the monomers results in a progressive depletion of small clusters as compared to the predicted concentration in the reaction-limited case and to the breakdown of the time–temperature mapping. Discrepancies between the cluster size distribution observed in simulation and the one provided by the ideal kinetic theory of aggregation are therefore not easily dismissed as an effect associated with the omitted spatial information in the rate coefficients. Instead, they are likely to be associated with the diffusion-altered size-dependent reaction rates, which favor the depletion of faster, small clusters and the reduced production of slower, big clusters.

Finally, we have discussed how a simple modeling of the entire kinetics of aggregation accounting for the decrease of the system’s average diffusivity can be developed by introducing a single characteristic  $p$ -dependent time scale. Such modeling requires the simultaneous determination of the extent of reaction as a function of time  $p(t)$ , and of the diffusion coefficient as a function of the extent of reaction  $D(p)$ . The adjustment of only one constant parameter is sufficient to describe the entire evolution of  $p(t)$ , even in the last stages of aggregation, where a small number of finite clusters remain

interspersed within the frozen structure of the gel network. We believe these results will provide a useful guide for the interpretation of the kinetics in real systems. As a first example, we have discussed how the evidence derived from the analysis of the simulation data can help modeling the experimentally measured extent of reaction in epoxy-resin systems.

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