A molecular dynamics study of chemical gelation in a patchy particle model

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We report event-driven molecular dynamics simulations of the irreversible gelation of hard ellipsoids of revolution containing several associating groups, characterizing how the cluster size distribution evolves as a function of the extent of reaction, both below and above the gel point. We find that over a very large interval of values of the extent of reaction, parameter-free mean-field predictions are extremely accurate, providing evidence that in this model the Ginzburg zone near the gel point, where non-mean field effects are important, is very limited. We also find that the Flory's hypothesis for the post-gelation regime properly describes the connectivity of the clusters even if the long-time limit of the extent of reaction does not reach the fully reacted state. This study shows that irreversibly aggregating asymmetric hard-core patchy particles may provide a close realization of the mean-field model, for which available theoretical predictions may help control the structure and the connectivity of the gel state. Besides chemical gels, the model is relevant to network-forming soft materials like systems with bioselective interactions, functionalized molecules and patchy colloids.

I. Introduction

Irreversible polymerization is a mechanism of self-organization of molecules that proceeds *via* the formation of covalent bonds between pairs of mutually-reactive groups.[1–3] If monomers with functionality (number f of reactive groups on a monomer) greater than two are present, branched molecules grow by reactions and convert the system from a fluid of monomers into a well connected cross-linked network, giving rise to a chemical gelation process. At the gel point, a persistent network spanning the sample first appears; the system is then prevented from flowing, yet not arrested on a mesoscopic length scale. The development of a network structure results, for example, from step polymerization, chain-addition polymerization and cross-linking of polymer chains.[4,5] The same phenomenon is also observed in colloids and other soft materials when the thermodynamics and the molecular architecture favor the formation of a limited number of strong interactions (*i.e.*, with attraction strength much larger than the thermal energy) between different particles. Chemical gelation has been extensively studied in the past, starting from the pioneering work of Flory[1] and Stockmayer[6] who developed the first mean-field description of gelation, providing expressions for the cluster-size distribution as a function of the extent of reaction and the *critical* behavior of the connectivity properties close to gelation. More appropriate descriptions based on geometric percolation concepts have, in the late seventies, focused on the non-mean field character of the transition, which reveals itself near the gel point, extending to percolation the ideas developed in the study of the properties of systems close to a second-order critical point. Several important numerical studies,[7–18]—most of them based on simulations on lattice—have focused on the critical behavior close to the percolation point, providing evidence of the percolative nature of the transition and accurate estimates of the percolation critical exponents. As in critical phenomena, a crossover from mean-field to percolation behavior is expected close to the gel transition.[19] But, how the microscopic properties of the system control the location of the crossover (*i.e.*, how wide is the region where the mean-field description applies) and how accurate is the mean-field description far from the percolation point is not completely understood. Another important open question regards the connectivity properties of chemical gels well beyond percolation.[20] Even in the mean-field approximation, several possibilities for the post-gel solutions have been proposed, based on different assumptions on the reactivity of sites located on the infinite cluster.[20,21] Different propositions predict different cluster-size distributions above the gel point and a different evolution with time for the extent of reaction.

Here we introduce a model inspired by stepwise polymerization of bifunctional diglycidyl ether of bisphenol A (B particles in the following) with pentafunctional diethylenetriamine (A particles).[22] To incorporate excluded volume and shape effects, each type of molecule is represented as hard homogeneous ellipsoid of appropriate length, whose surface is decorated in a predefined geometry by f identical reactive sites per particle (see Fig. 1). In this respect, the model is also representative of colloidal particles functionalized with a limited number of patchy attractive sites,[23] where the selectivity of the interaction is often achieved building on biological specificity.[24–26] The off-lattice evolution of the system is studied *via* event-driven molecular dynamics simulations, using a novel code that specifically extends to ellipsoidal particles the algorithm previously designed for patchy spheres.[27] Different to previous studies, we do not focus on the critical properties close to the gel-point, but study in

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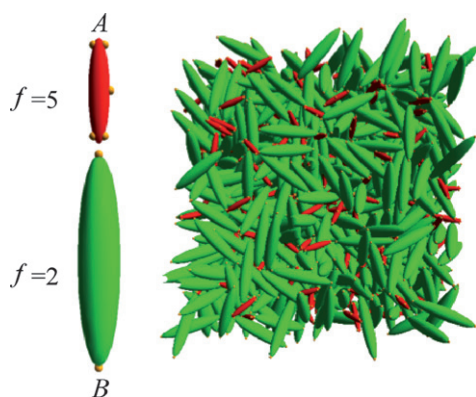
Fig. 1 Graphic description of the A and B particles (left) and snapshot of the simulated system (right). The centers of the small spheres locate the bonding sites on the surface of the hard-core particle.

detail the development of the irreversible gelation process and the properties of the cluster size distribution in the pre- and post-gelation regime.

We find that the dynamic evolution of the system produces an irreversible (chemical) gelation process whose connectivity properties can be described, in a very large window of the extent of reaction, with the Flory–Stockmayer (FS) predictions.[1,2,6] This offers to us the possibility to address, in a well controlled model, the kinetics of the aggregation and to evaluate the extent of reaction at which the breakdown of the Flory post-gel solution takes place.

II.   Method

We study a 5 : 2 binary mixture composed of $N_A = 480$ ellipsoids of type A and $N_B = 1200$ ellipsoids of type B, for a total of $N = 1680$ particles. A particles are modeled as hard ellipsoids of revolution with axes $a = b = 2\sigma$ and $c = 10\sigma$ and mass m; B particles have axes $a = b = 4\sigma$ and $c = 20\sigma$, mass $3.4m$. Simulations are performed at a fixed packing fraction $\phi = 0.3$. Five (two) sites are rigidly anchored on the surface of the A (B) particles, as described in Fig. 1. Sites on A particles can only react with sites on B particles. Every time, during the dynamic evolution, the distance between two mutually-reactive sites becomes smaller than a pre-defined distance $\delta = 0.2\sigma$, a new bond is formed between the particles. To model irreversible gelation, once a bond is formed, it is made irreversible by switching on an infinite barrier at distance $r^{ij}_{A_iB} = \delta$ between the sites i and j involved, which prevents both the formation of new bonds in the same sites and the breaking of the existing one. Hence, the newly formed bond cannot break any longer, and the maximum distance between the two reacted sites is constrained to remain smaller than δ. Similarly, the two reacted sites cannot form further bonds with available unreacted sites. The composition of the system and the particle functionality are such that the reactive sites of type A and B are initially present in equal number, $f_A N_A = f_B N_B$, which in principle allows the formation of a fully bonded state in which all the sites have reacted. This offers a way to properly define the extent of reaction as the ratio p between the number of bonds present in a configuration and the maximum number of possible bonds $f_A N_A$.

Between bond-formation events, the system propagates according to Newtonian dynamics at temperature $T = 1.0$. As in standard event-driven codes, the configuration of the system is propagated from one collisional event to the next one. Note that temperature only controls the time scale of exploration of space, by modulating the average particle's velocity. An average over 40 independent starting configurations is performed to improve statistics.

III.   Results

In the starting configurations no bonds are present by construction. As a function of time, the fraction p of formed bonds—a measure of the state of advancement of the reaction—increases monotonically, until most of the particles are connected in one single cluster (Fig. 2). As a result, p saturates around 0.86, despite the fact that an equal number of reactive sites of type A and B is initially present in the system.

Flory[1] and Stockmayer[6] laid out the basic relations between extent of reaction and resulting structure in step polymerizations, on the assumptions that all functional groups of a given type are equally reactive, all groups react independently of one another, and that ring formation does not occur in molecular species of finite size. Only when p exceeds a critical value p_c infinitely large molecules can grow.[1] In this respect the FS theory describes the gelation transition as the random percolation of permanent bonds on a loopless lattice.[28] The present model satisfies the conditions of equal and independent reactivity of all reactive sites. The absence of closed bonding loops in finite size clusters is not *a priori* implemented; as we will show in the following, however, such a condition—favored by the poor flexibility of the bonded particles and their elongated shape, the absence of an underlying lattice and the asymmetric location of the reactive sites—is valid in a surprisingly wide region of p values.

The FS theory predicts the p dependence of the cluster-size distribution in the very general case of a mixture of monomers bearing mutually reactive groups.[6] In the present case, the number n_{lm} of clusters containing l bifunctional particles and m pentafunctional ones can be written as:
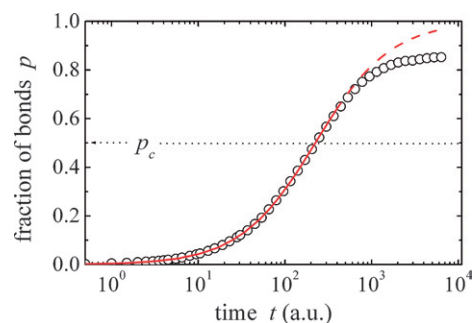

Fig. 2 Time dependence of the fraction of bonds p. Symbols: simulation results (averaged over 40 independent realizations). For the chosen stoichiometry, p coincides with the reacted fraction of A reactive sites, *i.e.* the A conversion, or equivalently with the reacted fraction of B sites, *i.e.* the B conversion. $p = 1$ would indicate that all possible bonding sites have reacted. Time is measured in arbitrary units. Line: $p(t) = kt/(1 + kt)$, with the fit-parameter k fixing the time scale. This functional form is expected when any pair of reactive groups in the system is allowed to react, but loops do not occur in finite size clusters.[21]
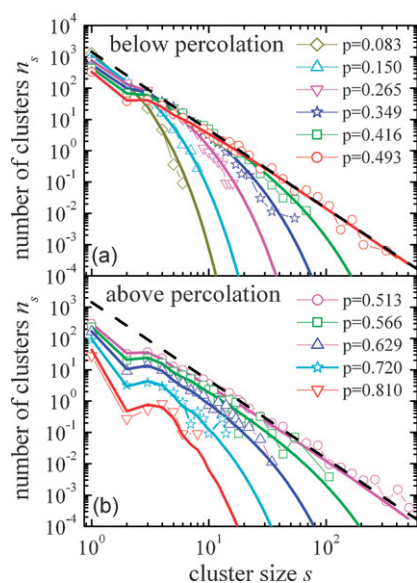
Fig. 3 Distribution of finite size clusters n_s for different fractions of bonds p (a) below and (b) above percolation. Points are simulation data and lines are the corresponding theoretical curves according to FS. The dashed line represents the power law $n_s \sim s^{-2.5}$.

$$n_{lm} = N_B N_A p^{l+m-1}(1-p)^{3m+2} w_{lm}$$
$$w_{lm} = \frac{(4m)!}{(l-m+1)!(4m-l+1)!m!} \tag{1}$$

and the number n_s of clusters of size s is obtained by summing over all contributions such that $l + m = s$, i.e., $n_s = \sum_{lm,l+m=s} n_{lm}$. As shown in Fig. 3a, on increasing p, the n_s distribution becomes broader and broader and develops a power-law tail. The theory predicts a gelation transition when $p_c = 1/\sqrt{(f_A-1)(f_B-1)} = 0.5$.[1,6] Even close to $p = 0.5$, the FS prediction—which conforms to the prediction of random percolation on a Bethe (loopless) lattice where $n_s \sim s^{-2.5}$ at the percolation threshold—is consistent with the numerical data. On further increasing p (Fig. 3b), the distribution of finite size clusters progressively shrinks, and only small clusters survive. Data show that eqn (1), with no fitting parameters, predicts rather well the numerical distribution at any extent of polymerization, both below and above the point where the system is expected to percolate, including details such that the local minimum at $s = 2$.

To compare with the mean-field prediction of gelation at $p_c = 0.5$, we examine the connectivity properties of the aggregates for each studied value of p, searching for the presence of clusters that are infinite under periodic boundary conditions. We find that configurations at $p = 0.497 \pm 0.008$ have not yet developed a percolating structure while configurations at $p = 0.513 \pm 0.007$ have. Hence, we locate the gel point at $p_c = 0.505 \pm 0.007$, in close agreement with the theoretical mean-field expectations. Beyond this point, the material that belongs to the infinite (percolating) network N_∞ constitutes the *gel*, while the soluble material formed by the finite clusters that remain interspersed within the giant network constitutes the *sol*. Fig. 4a shows that the fraction of gel $P_\infty = N_\infty/N$ and even its partition between particles of type A ($P_{A,\infty} = N_{A,\infty}/N$) and B ($P_{B,\infty} = N_{B,\infty}/N$)
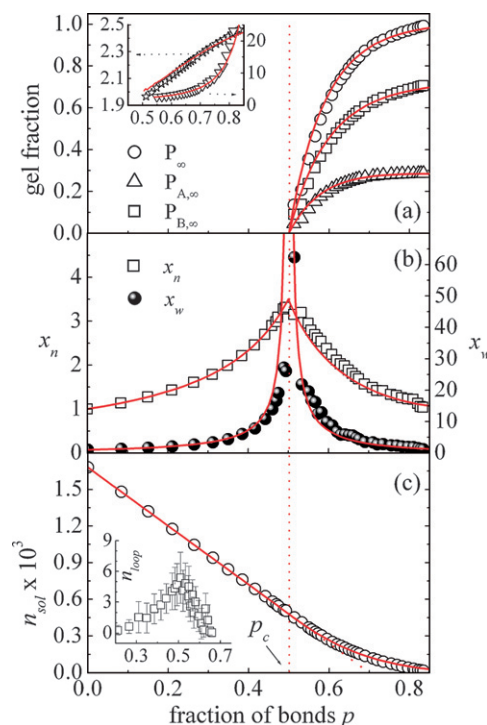

Fig. 4 (a) Gel fraction P_∞ and its partition between particles of type A ($P_{A,\infty}$) and B ($P_{B,\infty}$) *vs.* the fraction of bonds p (*i.e.* the extent of reaction in the system). The inset shows the proportion of B particles to A particles in gel ($N_{B,\infty}/N_{A,\infty}$ – left axis) and in sol ($N_{B,sol}/N_{A,sol}$ – right axis) *vs.* p. (b) Number- and weight-average cluster size (x_n and x_w) prior to gelation and for the sol after gelation *vs.* the fraction of bonds p. (c) Relation between the number of finite size clusters (molecules in the sol) n_{sol} and the fraction of bonds p. The inset shows the number of loops n_{loop} *vs.* p. In all panels, symbols are simulation results and solid lines are FS predictions.

calculated according to the FS theory,[29] properly represent the simulation results throughout the polymerization process. Indeed, the proportion of B particles to A particles in gel and in sol is a function of p (see inset). The relative amount of B particles in the sol ($N_{B,sol}/N_{A,sol}$) increases as a consequence of the preferential transfer of the A particles (having more reactive sites) to the gel, in a way that the fraction p_{sol} of sites B in the sol that have reacted (extent of reaction in the sol) differs from the total fraction p of sites B reacted (extent of reaction in the system). The constitution of the sol (Fig. 3b) results to be the same as that of a smaller system made of $N_{A,sol}$ particles of type A and $N_{B,sol}$ particles of type B reacted up to the extent p_{sol}.[1,30]

The evolution of the cluster size distribution can be quantified by the number- (x_n) and weight-average (x_w) cluster sizes of the sol, defined as $x_n = \sum_s s n_s / \sum_s n_s$ and $x_w = \sum_s s^2 n_s / \sum_s s n_s$. The numerical results and the FS theoretical predictions are shown in Fig. 4b. Both averages increase before gelation; then, they regress in the sol existing beyond the gel point, since large clusters are preferentially incorporated into the gel network. While x_n increases only slightly up to the gel point, never exceeding 3.5, x_w increases sharply in proximity of p_c as well as sharply decreases beyond this point, consistently with the fact that x_w is singular at percolation being dominated by large clusters. Again, simulation data agree very well with FS predictions. Discrepancies between theory and simulation—which reveal the mean-field character of

the FS theory—only concern the range of p very near p_c, suggesting that for this model the crossover from mean-field to percolation is very close to the gel point—*i.e.*, the Ginzburg zone[19] near the gel point, where non-mean field effects are important, is very limited. A finite-size study very close to the critical point would be requested to accurately locate the percolation point and the critical exponents, a calculation beyond the scope of the present work.

From a physical point of view, the change from mean-field to percolation universality class is rooted in the presence of bonding loops in the clusters of finite size, which pre-empts the possibility to predict the cluster-size distribution. The realistic estimate of the percolation threshold and the agreement between theory and simulation (Fig. 3) suggest that the present model strongly disfavors the formation of loops in finite clusters, at least for cluster sizes probed in this finite-size system. As a test, we evaluate the total number of finite (sol) clusters $n_{sol} = \sum_s n_s$ as a function of the extent of reaction. If finite clusters do not contain closed loops, n_{sol} equals the number of particles in the sol minus the number of bonds, since each added bond decreases the number of clusters by one. This applies equally to the system preceding gelation, or to the sol existing beyond the gel point. Thus, at $p < p_c$ (pre-gelation) the relation between n_{sol} and p is linear, *i.e.* $n_{sol} = N - 2N_B p$. At $p > p_c$ (post-gelation), n_{sol} can be calculated as $n_{sol} = N_{sol} - 2N_{B,sol} p_{sol}$, where n_{sol} is the number of particles in the sol fraction ($N_{B,sol}$ of which bear reactive sites of type B), and $p_{sol} \neq p$ is the reacted fraction of sites B in the sol. Hence, the relation between n_{sol} and p crosses to a nonlinear behavior, so that the number of clusters becomes one when $p = 1$. As shown in Fig. 4c, the number of finite clusters found in the simulation data conforms to the theoretical expectation for all p values, both below and above the gel point. Hence, as a first approximation, loops are only present in the infinite (percolating) cluster and do not significantly alter the distribution of the finite size clusters, both below and above percolation. The difference between n_{sol} found in simulation and the value predicted by the FS theory counts the number of loops in the sol, n_{loop}. Such a quantity is shown in the inset of Fig. 4c. The maximum value of n_{loop}, achieved for $p \sim p_c$, corresponds to 0.2% of the total number of bonds. This demonstrates that intramolecular bonds within finite clusters can be neglected, consistent with the Flory hypothesis for the post-gelation regime.[20] Fig. 4c also shows that the linear relation between n_{sol} and p is valid also after the gel point (up to $p \approx 0.6$). This finding is in full agreement with recent experimental studies[22,31,32] on the polymerization of bifunctional diglycidyl ether of bisphenol A with pentafunctional diethylenetriamine, also suggesting that the number of cyclic connections in the infinite cluster is negligible well above p_c.

As a further confirmation of the absence of closed loops we compare the time evolution of p with the prediction of the mean-field kinetic modeling of polymerization, based on the solution of the Smoluchowski coagulation equation.[33,34] For loopless aggregation, $p(t)$ is predicted to follow

$$p(t) = \frac{kt}{1 + kt}, \qquad (2)$$

where the fit-parameter k, which has the meaning of a bond kinetic constant, fixes the time scale of the aggregation process. The time evolution of p is found to perfectly agree with the

theoretical predictions[21] (see Fig. 2) up to $p \approx 0.6$, *i.e.* beyond p_c. While the prediction would suggest that $p(t \to \infty) = 1$ (dash line in Fig. 2), the simulation shows that the formation of a percolating structure prevents the possibility of completing the chemical reaction, leaving a finite number of unreacted sites frozen in the structure. As shown above (Fig. 3), even in this frozen state the cluster size distribution is provided by the Flory's post-gel hypothesis. Such a feature is not captured by the mean-field Smoluchowski equation in which spatial information in the kernels are neglected.

IV. Conclusions

A binary mixture of patchy hard ellipsoids undergoing chemical gelation displays a very large interval of the extent of reaction in which parameter-free mean-field predictions are extremely accurate. The connectivity properties of the model are properly described—without any fitting parameter—both below and above percolation by the mean-field loopless classical FS theory.[1,21] The mean-field cluster size distribution for the sol component is found to be valid for all values of the extent of reaction, both below and above the gel point, suggesting that for the present model, the Flory's hypothesis for the post-gelation regime properly describes the irreversible aggregation phenomenon, despite the explicit consideration of the excluded volume.

The absence of loops in finite size clusters, which is not assumed by the model, results from the specific geometry of the bonding pattern and by the presence of the excluded volume interactions, disfavoring the formation of ordered bonding domains. Hence, the geometry of the particles and the location of the reactive sites on them may play a significant role in the stabilization of the mean-field universality class with respect to the percolation universality class,[35] locating the crossover between the two classes[19] very close to the gel point. The present study shows that irreversibly aggregating asymmetric hard-core patchy particles, even if excluded volume effects are properly taken into account, may provide a close realization of the FS predictions in a wide range of p values. The model thus offers a starting point—for which theoretical predictions are available—for further investigations of the gelation process and for a more precise control over the structure and connectivity of the gel state. In particular, full and detailed structural information can be known along with the dynamics of the system, which may be potentially useful to investigate the relation between structural heterogeneity and heterogeneous dynamics,[32] and to shed light on the microscopic aspects of the dynamic crossover from short[36] to long relaxation times,[37] during irreversible polymerization.

While the structural properties are all well described by the FS theory, the evolution of the extent of reaction, modeled *via* the coagulation Smoluchowski equation, is properly described by the theory only in the pre-gelation region. After gelation, kinetic constraints due to the absence of mobility of the reactive sites anchored to the percolating cluster or to smaller clusters trapped inside the percolating matrix prevent the completion of the reaction and the extent of reaction freezes (to $p \approx 0.86$ in the present case) before reaching one (as eqn (2) would predict). A proper modeling of the long-time behavior will require the insertion of spatial information inside the kernels entering the Smoluchowski equation. The freezing of the extent of reaction at

long times correspondingly freezes the cluster-size distribution to that predicted by Flory for the reached p value.

In the present model, the entire polymerization process proceeds *via* a sequence of FS cluster-size distributions, determined by $p(t)$. Recently, it has been shown that the FS theory also properly describes equilibrium clustering in patchy particle systems when p is a function of temperature and density.[38] It is thus tempting to speculate that for loopless models, irreversible evolution can be put in correspondence with a sequence of *equilibrium* states, which could be sampled in the same system for finite values of the ratio between temperature and bonding depth. If this is indeed the case, chemical gelation could be formally described as a deep quench limit of physical gelation. This correspondence would facilitate the transfer of knowledge from recent studies of equilibrium gels[39,40] to chemical ones. Concepts developed for irreversible aggregation of colloidal particles, like diffusion- and reaction-limited cluster–cluster aggregation, could be connected to chemical gelation. Work in this direction is ongoing.

Acknowledgements

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