Connecting Irreversible to Reversible Aggregation: Time and Temperature

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We report molecular dynamics simulations of a gel-forming mixture of ellipsoidal patchy particles with different functionality. We show that in this model, which disfavors the formation of bond-loops, elapsed time during irreversible aggregation — leading to the formation of an extended network — can be formally correlated with equilibrium temperature in reversible aggregation. We also show that it is possible to develop a parameter-free description of the self-assembly kinetics, bringing reversible and irreversible aggregation of loopless branched systems to the same level of understanding as equilibrium polymerization.

Several natural and synthetic materials, as well as biological structures, result from the self-assembly of elementary units into branched aggregates and networks [1, 2]. This self-assembly process is receiving considerable attention in two fast-growing fields: supramolecular chemistry [1, 2] and collective behavior of patchy and functionalized particles [3, 4], among the most promising building blocks of new materials [5, 6]. 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 [7, 8, 9]. 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) can be used to classify aggregation into two broad categories: for strong attraction strength (chemical case [7, 8, 9, 10]), bond formation is irreversible and the number of bonds continuously grows with time. In the case of weak attraction strength (physical case [11]), bonds break and reform while the number of bonds progressively reaches its equilibrium value. In the latter case, the final structure of the system can in principle be predicted with equilibrium statistical mechanics methods.

The value of the ratio $U_0/k_B T$ separates the two classes. Conceptually, any model of physical aggregation may be turned into a chemical model by studying its properties following a quench to $k_B T \ll U_0$. Similarly, applying temperatures comparable to the bond energy turns an irreversible aggregation model into a physical one. The idea of a close connection between irreversible and reversible aggregation is already contained in the early mean-field theoretical work of Stockmayer [11], considering the Smoluchowski’s kinetic equations solved in the limit of absence of closed bonding loops. In Stockmayer’s calculations, at any time $t$ during chemical aggregation, the distribution of clusters of finite size $k (N_k(t))$ is identical to that found following equilibrium statistical mechanics prescriptions, i.e., by maximizing the entropy with the constraint of a fixed number of bonds. The $N_k$ are commonly referred to as Flory–Stockmayer (FS) distributions. Later on, Van Dongen and Ernst [12] confirmed that the FS distributions are also solutions of the Smoluchowski’s equations when bond-breaking processes are accounted for. According to these theoretical works — based on kinetic equations derived in the limit of reaction-controlled rates (as opposed to diffusion-controlled) — a system forming progressively larger and larger loopless branched aggregates 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 $p$ (the extent of reaction in chemical language) provides the connection between $t$ during reversible or irreversible aggregation and $T$ in equilibrium. Van Dongen and Ernst predictions have never been tested experimentally or numerically to assess their limit of validity.

In this Letter — stimulated by the renewed interest in reversible and irreversible self-assembly of nano- and micro-particles interacting via specific directional bonds [1, 2] — we provide a stringent test of the suggested connections between chemical and physical aggregation, and establish the limits of analytic description of the kinetics of formation of branched structures. We do so by extending a model for chemical gels, recently introduced [21], to the corresponding physical case by turning the attraction strength between bonding sites finite. The model, originally inspired by epoxy-amine step-polymerization [22], represents two types of mutually reactive molecules $A$ and $B$ as hard homogeneous ellipsoids of revolution whose surface is decorated in a predefined geometry by $f_A$ and $f_B$ identical reactive sites. The study of the chemical version of this model [21] showed that formation of closed bonding loops in finite size clusters is disfavored, possibly due to the non-spherical particle shape and the location of the reactive sites. Therefore,
it offers to us the possibility to carefully check the Stockmayer [14] and Van Dongen and Ernst [18] predictions. We can assess how closely — in the absence of loop formation — the chemical gelation process in a system of functionalized or patchy units, as well as the reversible evolution from a monomeric to an equilibrium bonded state, can be envisaged as a progressive sequence of equilibrium states, closely connecting it with $T$. We study via event-driven molecular dynamics simulations a binary mixture composed of $N_A = 480$ penta-functional ($f_A = 5$) ellipsoids of type $A$ and $N_B = 1200$ bifunctional ($f_B = 2$) ellipsoids of type $B$, so that the number $N_A f_A$ of $A$-type reactive sites equals the number $N_B f_B$ of $B$-type reactive sites. $A$-particles have mass $m$, revolution axis $a = 10\sigma$ and the other two axes $b = c = 2\sigma$; $B$-particles have mass $3.4m$, and axes $a = 20\sigma$, $b = c = 4\sigma$. Size- and mass-ratio are chosen to mimic the values of an epoxy-amine system [22]. The interaction potential is the hard ellipsoid potential $V_{HE}$ supplemented by site-site square-well attractive interactions $V_{SW}$ (of strength $u_0$, and width $\delta = 0.2\sigma$) between pairs of particles of different type. Our unit mass is $m$, the unit energy $u_0$. $T$ is measured in units of the potential depth (i.e., $k_B = 1$), time $t$ in units of $\sigma(m/u_0)^{1/2}$. The packing fraction is fixed at $\phi = 0.3$ and $T$ is varied from $T = 0.3$ to $T = 0.065$. Event-driven (newtonian) molecular dynamics simulations (in the NVT ensemble) are performed using a specifically designed code [23]. Two sites, on particles of different type, form a bond if their distance is closer than $\delta$. Clusters are defined as groups of bonded particles. The particle shape and the location of the attractive sites (see inset of Fig. 1) is such that each site is engaged at most in one bond, ensuring an unambiguous definition of the extent of reaction $p$ by the ratio between the number of bonds in the system and the maximum number of possible bonds (i.e., $N_A f_A$). Unless otherwise stated, we study the trajectory of the system in configuration space, starting from an initial configuration with no bonds between particles, at fixed $T$. During the simulation, bonds form and break continuously with time while the system evolves toward the equilibrium state, characterized by an equilibrium value $p_{eq}(T)$ of the extent of reaction. To improve the statistics we average over 11 different realizations for each studied $T$. Equilibrium results are obtained from the final part of the trajectories, after the equilibration transient is over.

Figure 1 shows $p_{eq}(T)$, for all $T$ values where equilibration was achieved within the allocated computational time (six months at low $T$). Within the range $0.2 > k_B T/u_0 > 0.08$ the system crosses from a monomeric state to a significantly bonded state, with more than 80% of the bonds formed. The sharp sigmoidal shape can be perfectly represented by the independent-bond mass-action law [24]

$$
\frac{p_{eq}}{(1 - p_{eq})^2} = e^{\beta(u_0 - T\Delta S)} \tag{1}
$$

where $u_0$ and $\Delta S$ describe, respectively, the energy and the entropy change associated to the formation of a single bond.

Figures 2(a)-(b) show the equilibrium structure of the system and the cluster size distribution $N_k$ at three different values of $T$, corresponding to $p_{eq}$ values below, at and above percolation (numerically located at $p_c = 0.505 \pm 0.007$ [21]). To describe the structure of the system we report the center-to-center pair distribution function $g_{BB}(r)$ for the $B$ particles. To quantify the $T$ dependence of $N_k$ we also report the number-($k_n$) and weight-average size ($k_w$) of the finite clusters (Fig. 2(c)). Data shown in Figs. 2(b)-(c) are very well described —without any fitting parameter— both below and above percolation by the FS predictions [15, 21] specialized to the $f_A=5$-$f_B=2$ case, confirming that bonding loops in finite size clusters can be neglected. Therefore, the model allows us to check, without fitting parameters, if the evolution of the system during equilibration and irreversible aggregation does follow a sequence of equilibrium steps, and in particular, how $t$ in chemical gelation can be associated to a corresponding equilibrium $T$. To this aim, we compare in Figs. 2(a)-(c) the equilibrium quantities with the corresponding quantities evaluated at selected elapsed times $t$ during the irreversible bonding process. The specific $t$ value is chosen in such a way that $p(t) = p_{eq}(T)$. For all these quantities, at each $t$, data are identical to those obtained in equilibrium at the same extent of reaction, demonstrating that the evolution of the system structure and connectivity during irreversible aggregation does follow a sequence of equilibrium states.

Also the equilibration process at finite $T$, i.e., when bond-breaking processes are included, proceeds along a sequence of equilibrium states described by the FS theory. Indeed, Fig. 3 shows $N_k(t)$ for several successive
times following a quench, in conditions of reversible aggregation, from a high-\(T\) unassembled state to a low-\(T\) assembled one. Data are compared — without fit parameters — with the corresponding equilibrium quantities, accurately modeled by the FS distributions. Similar agreement is observed for all the investigated equilibria, accurately modeled by the FS distributions. Similar parameters — with the corresponding equilibrium quantities, from a high-\(T\) unassembled state to a low-\(T\) assembled one. Data are compared — without fit parameters — with the corresponding equilibrium quantities, accurately modeled by the FS distributions. Similar agreement is observed for all the investigated equilibria, accurately modeled by the FS distributions.

Data in Fig. 3 show that the cluster size distribution during the kinetics of equilibration evolves via a sequence of FS distributions. Fig. 4 shows the associated time dependence of the bond probability \(p(t)\), following a \(T\)-jump starting either from a high-\(T\) unassembled state to a low-\(T\) assembled one. Data are compared — without fit parameters — with the corresponding equilibrium quantities, accurately modeled by the FS distributions. Similar agreement is observed for all the investigated equilibria, accurately modeled by the FS distributions.

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\[
p(t) = p_{eq} \frac{1 - \left( \frac{1-p(t)/p_{eq}}{1-p(0)/p_{eq}} \right) e^{-\Gamma t}}{1 - p_{eq}^2 \left( \frac{1-p(t)/p_{eq}}{1-p(0)/p_{eq}} \right) e^{-\Gamma t}} ,
\]

with \(\Gamma \equiv K_{site}^{breaking}(1 + p_{eq})/(1 - p_{eq})\), where \(K_{site}^{breaking}\) is the rate constant for breakage of a single bond. Since \(p_{eq}\) is known from Eq. 11 the entire equilibration dynamics in this aggregating branching system only depends on one parameter, \(K_{site}^{breaking}\), which fixes the time scale of the aggregation process. The theoretical expression very well represents the numerical data, except for the two lowest studied temperatures \((T \leq 0.07)\), at which extensively bonded states are reached \((p > 0.8)\). Such disagreement can be traced to a failure of the Flory post–gel assumption and/or to a progressive role of the size-dependence of the cluster mobility. The overall agreement between theory and simulation in Fig. 4 is further stressed by the \(T\) dependence of the single fit-parameter \(K_{site}^{breaking} \sim e^{-w_0/k_BT}/\sqrt{T}\), which as expected incorporates both an Arrhenius term and the thermal velocity component \(\sim \sqrt{T}\), entering the attempt rate of bond breaking.

The results of this study clearly indicate that the irreversible evolution of a system of patchy or functionalized...
particles, in which bonding loops can be neglected, can be put in correspondence with a sequence of equilibrium states. For this class of aggregating systems, it is thus possible to convert irreversible-aggregation time into an effective $T$ and to envisage the evolution of a chemical gel as a progressive cooling of the corresponding physical model. Elapsed time $t$ can be uniquely associated to an equilibrium $T$, recalling the concept of fictive $T$ in aging glasses \cite{25}. Equally important is the possibility of interpreting cases in which during the formation of a chemical gel the corresponding thermodynamic path crosses a thermodynamic instability line, e.g., the gas–liquid coexistence line \cite{3}, producing an inhomogeneous arrested structure. Such thermodynamic lines have been recently calculated with statistical mechanics methods and computer simulations \cite{8,26,27}. Thus, it will become possible to interpret the stability and structural properties of chemical gels by connecting them to the thermodynamic properties and to the phase diagram of the corresponding physical models.

Our study also demonstrates, for a realistic model of patchy particles, that the self-assembly kinetics of particles aggregating in loopless structures can be fully described—with no fitting parameters—by merging a thermodynamic approach providing $p_{eq}(T)$ (e.g., Eq. \ref{eq1}) with the Smoluchowski’s equations studied by Van Dongen and Ernst, thus bringing reversible and irreversible aggregation of loopless branched systems to the same level of understanding as the equilibrium polymerization case \cite{20}. This is made possible by the limited valence of the particles and by the specificity of the site-site interaction. The reduced valence, coupled to the non-spherical particle shape, contributes to disfavor the formation of closed bond-loops, while the specificity in the bonding interaction contributes to reduce the rate-controlling role of diffusion compared to the bonding process \cite{19}.

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