Polymerization with Freezing

E. Ben-Naim[1] and P. L. Krapivsky[2]

[1] *Theoretical Division and Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

[2] *Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215, USA*

Irreversible aggregation processes involving reactive and frozen clusters are investigated using the rate equation approach. In aggregation events, two clusters join irreversibly to form a larger cluster, and additionally, reactive clusters may spontaneously freeze. Frozen clusters do not participate in merger events. Generally, freezing controls the nature of the aggregation process, as demonstrated by the final distribution of frozen clusters. The cluster mass distribution has a power-law tail, $F_k \sim k^{-\gamma}$, when the freezing process is sufficiently slow. Different exponents, $\gamma = 1,\ 3$ are found for the constant and the product aggregation rates, respectively. For the latter case, the standard polymerization model, either no gels, or a single gel, or even multiple gels may be produced.

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I. INTRODUCTION

Aggregation is a fundamental irreversible process in which physical objects merge irreversibly to form larger objects. Aggregation has numerous applications ranging from astronomy where planetary systems form via collisions of planetesimals, to atmospheric science [1, 2], to chemical physics where polymeric chains chemically bond and form polymeric networks or gels [3–5], to computer science [6–8].

The standard framework for modeling aggregation is as follows. Initially, the system consists of a large number of identical molecular units ("monomers"). A cluster ("polymer") is composed of an integer number of monomers, termed the cluster mass. In each aggregation event, a pair of clusters merges, thereby forming a larger cluster whose mass equals the sum of the two original masses.

When the number of aggregation events is unlimited, the system condenses into a single cluster. However, in most practical applications, other processes intervene well before that, and as a result, the final state has multiple clusters, rather than a single condensate. For example, fragmentation of large clusters into smaller clusters is one mechanism that may counterbalance aggregation and prevent condensation.

In this study, we focus on another control mechanism: freezing. We use the generic term freezing to describe situations where there are two types of clusters: reactive clusters that participate in aggregation events and passive clusters that do not participate in aggregation events.

In particular, we consider the case where reactive clusters have a finite lifetime. In our model, reactive clusters spontaneously turn into frozen clusters. Spontaneous freezing can occur via various mechanisms. For instance, the environment may contain "traps" that absorb the diffusing polymers. In this situation, the reactive clusters are the free (mobile) polymers and the frozen clusters are the polymers adsorbed to the trap surface. Another example is a system of linear polymers with reactive end monomers. In a merging event, two different chains chemically bond via the end monomers, while in a freezing event, the two end monomers of the same chain bond to form a ring. Rings can no longer participate in aggregation events. Thus, in this case the linear polymers are reactive and the ring polymers are frozen.

In aggregation with freezing, it is natural to consider the initial condition where there are reactive clusters only. Of course, the system ends with frozen clusters only. Of special interest is the final mass distribution of frozen clusters. In this study, we address the two classical aggregation rates.

First, we study the simplest aggregation process where the aggregation rate is independent of the cluster mass. We find that the mass distribution of reactive clusters decays exponentially with the cluster mass. In general, the mass density of frozen clusters also decays exponentially with the cluster mass. However, when the freezing rate is very small, there is a power-law behavior, $F_k \sim k^{-1}$, over a substantial range of masses.

Second, we consider the case where the aggregation rate is proportional to the product of the masses, a process that is widely used to model polymerization and gelation. We find that when the freezing rate exceeds a certain threshold, no gels form, while when the freezing rate is below this threshold, at least one gel forms. Interestingly, the number of gels produced fluctuates from realization to realization. For supercritical freezing rates, the mass distribution of frozen clusters decays exponentially, while below this threshold, it decays algebraically, $F_k \sim k^{-3}$ [9].

II. THE MASTER EQUATIONS

We analyze the stochastic process of aggregation with freezing using the rate equation approach. Let us first consider the evolution of reactive clusters. In aggregation processes, two reactive clusters of masses i and j

merge to form a larger reactive cluster of mass $i+j$. The aggregation rate $K(i,j)$ is a function of the two cluster masses. The freezing process is random: reactive clusters may spontaneously freeze with a constant rate. This freezing rate f_k may be mass-dependent. Therefore, the mass distribution $R_k(t)$ of reactive clusters of mass k at time t evolves according to the generalized Smoluchowki equation

$$\frac{dR_k}{dt} = \frac{1}{2}\sum_{i+j=k} K(i,j)R_iR_j - R_k\sum_{i=1}^{\infty} K(i,k)R_i - f_kR_k. \quad (1)$$

The first two terms account for gain and loss of clusters of mass k, and the last term accounts for loss due to freezing. This master equation assumes perfect mixing as the probability of finding two clusters at the same position is a product of the probabilities of finding each of the clusters independently at the same position. We restrict our attention to the natural case of monodisperse initial condition, $R_k(0) = \delta_{k,0}$.

The mass distribution of frozen clusters $F_k(t)$ is coupled to the mass distribution of reactive clusters according to the rate equation

$$\frac{dF_k}{dt} = f_kR_k. \quad (2)$$

It is simple to check that the total mass density $\sum_k k(R_k + F_k) = 1$ is conserved by the evolution equations (1)–(2). Initially, there are no frozen clusters so $F_k(0) = 0$. Eventually, all clusters become frozen, so the final mass distribution $F_k(\infty)$ of frozen clusters is of particular interest.

The master equations (1)–(2) are sets of infinitely many coupled nonlinear differential equations, and they are generally unsolvable. Even in the absence of freezing, these equations are solvable only for special aggregation rates [1, 6, 10]. The three classical solvable cases are the constant rate $K(i,j) = \text{const.}$, the sum rate $K(i,j) = i+j$, and the product rate $K(i,j) = ij$. These cases represent natural aggregation processes. Mass independent aggregation rates correspond to an aggregation process where two clusters are chosen randomly to merge. Aggregation rates proportional to the product of the two cluster masses correspond to polymerization processes where two monomers are picked randomly to form a chemical bond; consequently, their respective clusters are merged. The sum rate is a hybrid between the two as it is an aggregation process where a randomly chosen monomer bonds with a randomly chosen polymer. In this study, we focus on the two most widely used cases of constant and product aggregation rates.

III. CONSTANT AGGREGATION RATE

First, we discuss how the constant aggregation rate relates to polymerization in the presence of traps. To treat this problem formally, one should write down the master equations with inhomogeneous densities and add diffusion terms. Then, one should study these equations in the trap-free region subject to the absorbing boundary conditions imposed by the traps. This approach is not practical and the reaction-rate approach provides a powerful alternative [11–15]. The reaction-rate approach is roughly speaking an effective-medium theory that ignores the complicated influence of each trap on the diffusion of particles and instead, represents this influence by averages. The reaction-rate approach was used by Smoluchowski to compute the aggregation rate $K(i,j)$ for Brownian particles. Assuming that merging happens immediately upon collision, and that particles are spherical and have radii R_i and R_j and diffusion coefficients D_i and D_j, Smoluchowski obtained

$$K(i,j) = 4\pi(D_i + D_j)(R_i + R_j). \quad (3)$$

Stokes' law shows that the diffusion coefficient of a Brownian particle is inversely proportional to its radius, $D_k \sim 1/R_k \sim k^{-1/3}$, and therefore the Brownian kernel becomes

$$K(i,j) \propto \left(i^{-1/3} + j^{-1/3}\right)\left(i^{1/3} + j^{1/3}\right). \quad (4)$$

Here, we ignored the overall multiplicative factor as it is irrelevant for the current discussion.

The master equations with this complicated Brownian kernel have not been solved even in the case of pure aggregation. To simplify the analysis, Smoluchowski suggested to replace the Brownian kernel (4) by the constant kernel. These two kernels have one common feature—they both are invariant under the dilatation $K(ai,aj) = K(i,j)$. Therefore, one expects that both kernels lead to similar behaviors, and to a certain extent, i.e., as far as overall scaling properties are concerned, this approximation is sensible [10].

A straightforward extension of Eq. (3) gives the freezing rate

$$f_k = 4\pi\, n\,(D_k + D)(R_k + a) \quad (5)$$

where n is the density of traps that are assumed to be spheres of radius a and diffusion coefficient D. The clusters are usually polymers whose molecular weight is small compared to the size of the traps; hence $R_k \ll a$ and $D_k \gg D$. Therefore $f_k = 4\pi a n D_k$, yielding the mass dependence

$$f_k \propto k^{-1/3}. \quad (6)$$

Thus, a constant aggregation rate together with spontaneous freezing approximate aggregation of Brownian particles in the presence of traps. We stress that the use of a constant aggregation rate instead of (4) is an approximation.

A. Constant freezing rates

Since the constant aggregation rate merely sets the overall time scale, we may conveniently set its value

$K(i,j)=2$ without loss of generality. Let us first consider constant freezing rates, $f_k=\alpha$. The master equation (1) becomes

$$\frac{dR_k}{dt}=\sum_{i+j=k} R_iR_j-(2R+\alpha)R_k. \tag{7}$$

Here, we used the total density of reactive clusters, $R=\sum_k R_k$. In general, for mass-independent freezing rates, it is possible to eliminate the freezing term from the master equation by transforming the mass distribution $R_k=C_k\, e^{-\alpha t}$ and introducing the time variable

$$\tau=\frac{1-e^{-\alpha t}}{\alpha}\,. \tag{8}$$

The time variable τ grows from 0 to α^{-1} as the physical time increases from 0 to ∞. With these transformations, the governing equations for the densities C_k reduce to the pure aggregation case $dC_k/d\tau=\sum_{i+j=k}C_iC_j-2C\,C_k$ with the total density $C=\sum_k C_k$. We briefly recall how to solve these equations. The total density obeys $dC/d\tau=-C^2$ and subject to the initial condition $C(0)=1$, the total density is $C(\tau)=(1+\tau)^{-1}$. Let us now introduce the exponential ansatz $C(\tau)=A\,a^{k-1}$ with $A(0)=1$ and $a(0)=1$ to satisfy the initial conditions. Substituting this ansatz into the master equation and equating mass-independent and mass-dependent terms separately, yields $dA/d\tau=-2(1+\tau)^{-1}A$ and therefore, $A=(1+\tau)^{-2}$, and $da/d\tau=A$ leading to $a=\tau/(1+\tau)$. The well-known solution for the pure aggregation case is therefore

$$C_k(\tau)=\frac{\tau^{k-1}}{(1+\tau)^{k+1}}\,. \tag{9}$$

Thus, the mass distribution of reactive clusters reads

$$R_k(\tau)=(1-\alpha\tau)\frac{\tau^{k-1}}{(1+\tau)^{k+1}}\,. \tag{10}$$

The exponential mass dependence is as in the pure aggregation case. Also, the total density of reactive clusters is $R=(1-\alpha\tau)/(1+\tau)$ and as expected, the reactive clusters do eventually deplete $R(t=\infty)=R(\tau=1/\alpha)=0$.

The mass distribution of frozen clusters is found by integrating the equation $dF_k/d\tau=\alpha\, C_k$ with respect to time. Substituting (9), and using $d\tau/dt=(1-\alpha\tau)=e^{-\alpha t}$, the integration is immediate and

$$F_k(\tau)=\frac{\alpha}{k}\left(\frac{\tau}{1+\tau}\right)^k. \tag{11}$$

We see that in addition to the dominant exponential behavior, there is an additional algebraic prefactor. The total density of frozen clusters $F=\sum_k F_k$ is found by summation, $F(\tau)=\alpha\ln(1+\tau)$ and in particular, the final density of frozen clusters is $F(\infty)\equiv F(t=\infty)=\alpha\ln(1+1/\alpha)$. Also, the final mass distribution of frozen clusters is

$$F_k(\infty)=\frac{\alpha}{k}\left(\frac{1}{1+\alpha}\right)^k. \tag{12}$$

In general, the mass distribution decays exponentially, but there is a k^{-1} algebraic correction.

B. Slow freezing

The most interesting behavior occurs in the slow freezing limit: as $\alpha\to 0$, the final mass distribution becomes algebraic

$$F_k(\infty)\simeq \alpha\, k^{-1}. \tag{13}$$

This power law holds over a substantial mass range, $k\ll\alpha^{-1}$. Beyond this scale, the tail is exponential, $F_k(\infty)\simeq\alpha\, k^{-1}\, e^{-\alpha k}$.

The results in the slow freezing limit can be alternatively obtained using perturbation theory. Indeed, the modified time variable coincides with the original time variable, $\tau\to t$ as $\alpha\to 0$, and the pure aggregation results are recovered. In other words, the freezing loss term $-f_kR_k$ can be neglected in the master equation (1). Using this perturbation approach we address two related problems: general freezing rates and aggregation in low-dimensional systems.

Let us consider general mass dependent freezing rates f_k. Dropping the loss rate from the master equation, the reactive cluster density is as in the pure aggregation case $R_k=t^{k-1}(1+t)^{-k-1}$, given by Eq. (9). The mass distribution of frozen clusters is obtained by integrating Eq. (2)

$$F_k(t)=\frac{f_k}{k}\left(\frac{t}{1+t}\right)^k. \tag{14}$$

We see that the algebraic prefactor k^{-1} is generic. Therefore, the final mass distribution is

$$F_k(\infty)=k^{-1}\, f_k. \tag{15}$$

This behavior applies for masses below some threshold mass k_*, while the mass distribution sharply vanishes above the threshold. The threshold mass is estimated from mass conservation:

$$1=\sum_{k\geq 1}kF_k(\infty)\sim\sum_{k=1}^{k_*}f_k. \tag{16}$$

As argued above, for Brownian coagulation in the presence of traps, $f_k=\beta k^{-1/3}$. For slow freezing, $\beta\ll 1$, we conclude that the final mass distribution is algebraic, $F_k(\infty)\simeq\beta k^{-4/3}$, below the threshold mass $k_*\sim\beta^{-3/2}$.

The rate equation approach neglects spatial correlations as the probability of finding two clusters at the same position is represented by the product of the probabilities of finding each cluster separately at the same position. This mean-field approximation is valid only when the spatial dimension exceeds the critical dimension d_c [14, 15]. It is therefore interesting to study the behavior below the critical dimension.

We address here the Point Cluster Model (PCM) where the radii and the diffusion coefficients are both mass-independent. In this case $d_c = 2$. The lattice PCM is defined as follows: clusters occupy single lattice sites and hop to adjacent sites with rate D; if a reactive cluster hops onto a site occupied by another reactive cluster, both clusters merge. We assume that frozen clusters do not affect reactive clusters. The PCM without freezing can be solved exactly in one dimension. When all lattice sites are initially occupied by monomers, the density of reactive clusters of mass k is [16, 17]

$$R_k(t) = e^{-4Dt}\left[I_{k-1}(4Dt) - I_{k+1}(4Dt)\right] \tag{17}$$

where I_n is the modified Bessel function of order n. Here, we implicitly considered the slow freezing limit. The density of frozen clusters is found from $dF_k/dt = f_k R_k$, that is of course always valid. Using the identity $\int_0^\infty dx\, e^{-x}\left[I_{k-1}(x) - I_{k+1}(x)\right] = 2$, the final distribution of frozen clusters is

$$F_k(\infty) = (2D)^{-1} f_k. \tag{18}$$

Remarkably, the very same answer (18) is also found for the continuous version of the PCM. The mass distribution (18) holds up to a certain threshold mass. For example, for the constant freezing rate $f_k = \alpha \ll 1$ the threshold mass is $k_* \sim \sqrt{D/\alpha}$.

IV. PRODUCT AGGREGATION RATE

The product aggregation rate $K(i,j) = ij$ is equivalent to the Flory-Stockmayer gelation model [3, 4, 18]. In this model, any two monomers may form a chemical bond and when this happens the two respective polymers become one. Thus, the aggregation rate equals the product of the cluster masses. In this polymerization process, a polymer network ("gel") emerges in a finite time, and it is giant in the sense that it contains a finite fraction of the monomers in the system. Eventually it grows to engulfs the entire system. This gelation model is also the simplest mean-field model of percolation [19, 20].

As in the previous section, we analyze in detail mass-independent freezing rates, $f_k = \alpha$, for which the master equation (1) becomes

$$\frac{dR_k}{dt} = \frac{1}{2}\sum_{i+j=k} ijR_iR_j - mkR_k - \alpha R_k \tag{19}$$

where m is the total mass density of reactive clusters. If all clusters are finite in size then $m = M_1 = \sum_{k\geq 1} kR_k$ where $M_n = \sum_k k^n R_k$ is the general nth moment of the distribution. Again, we consider the monodisperse initial conditions $R_k(t) = \delta_{k,1}$ and $F_k(0) = 0$.

Low order moments of the mass distribution obey closed equations and thus, provide a useful probe of the aggregation dynamics. The total mass density of reactive clusters satisfies $dm/dt = -\alpha m$ reflecting the loss due to freezing, and therefore

$$m(t) = m(0)e^{-\alpha t}\,. \tag{20}$$

The total mass density decays exponentially with the physical time, or equivalently, linearly with the modified time, $m(\tau) = 1 - \alpha\tau$. Furthermore, the second moment includes in addition to the linear loss term, a nonlinear term that accounts for changes due to aggregation, $dM_2/dt = M_2^2 - \alpha M_2$. Solving this equation with arbitrary initial condition yields

$$M_2(t) = \alpha\left[\left(\frac{\alpha}{M_2(0)} - 1\right)e^{\alpha t} + 1\right]^{-1}. \tag{21}$$

Divergence of the second moment signals the emergence of a gel in a finite time, i.e., the occurrence of the gelation phase transition. Fixing the freezing rate, the initial conditions govern whether gelation does or does not occur: gelation occurs when the initial mass is sufficiently large, $M_2(0) > \alpha$, but otherwise there is no gelation. Conversely, fixing the initial conditions, gelation occurs only for slow enough freezing. For the monodisperse initial conditions, the critical freezing rate is $\alpha_c = 1$. When gelation does occur, the gelation time is

$$t_g = -\frac{1}{\alpha}\ln\left(1 - \frac{\alpha}{M_2(0)}\right). \tag{22}$$

The gelation point separates two phases. Prior to the gelation time, the system contains only finite clusters that undergo cluster-cluster aggregation. Past the gelation point, the gel grows via cluster-gel aggregation. We term these two the coagulation phase and the gelation phase, respectively. The above expressions for the first two moments are valid for the coagulation phase only.

The mass distribution of reactive clusters is found again by transforming the mass distribution $R_k = e^{-\alpha t}C_k$ and the time variable (8). With these transformations, the problem reduces to the no-freezing case, $dC_k/dt = \frac{1}{2}\sum_{i+j=k} ijC_iC_j - kMC_k$ with $m = Me^{-\alpha t}$. Using the variable $u(\tau) = \int_0^\tau M(\tau')d\tau'$ and the transformation $C_k = G_k\tau^{k-1}e^{-ku}$, the master equation reduces to a recursion equation for the *time-independent* coefficients G_k: $(k-1)G_k = \frac{1}{2}\sum_{i+j=k} ijG_iG_j$. This equation is solved using the generating function technique. The so-called "tree-function" $G(z) = \sum_k kG_k e^{kz}$ satisfies $dG/dz = G/(1-G)$ and the solution of this differential equation obeys $Ge^{-G} = e^z$. The coefficients $G_k = k^{k-2}/k!$ are found using the Lagrange inversion formula [21]. Hence, the mass distribution of reactive clusters is

$$R_k(\tau) = \frac{k^{k-2}}{k!}\,(1 - \alpha\tau)\,\tau^{k-1}\,e^{-k\,u}\,. \tag{23}$$

The corresponding generating function $\mathcal{R}(z) = \sum_{k=1}^{\infty} kR_k e^{kz}$ can be expressed in terms of the tree-function

$$\mathcal{R}(z) = \tau^{-1}(1-\alpha\tau)\, G(z + \ln\tau - u). \tag{24}$$

Explicitly, the tree function is $G(z) = \sum_{k\geq 1} \frac{k^{k-1}}{k!}\, e^{kz}$.

The mass distribution (23) is only a formal solution because the total mass density m and hence the variable u are yet to be determined. Prior to gelation, the solution can be obtained in an explicit form because the various variables are known. From the first moment (20) then $M = 1$ and therefore

$$u = \tau \tag{25}$$

for $t < t_g$. In this case, the mass distribution decays exponentially at large masses and the typical cluster mass is finite. When $\alpha > 1$, there is no gelation transition, and this behavior characterizes the mass distribution at all times. Otherwise, when gelation does occur, the gelation time (22) is simply $\tau_g = 1$. The gelation point is marked by an algebraic divergence of the mass distribution, $R_k(t_g) \sim (1-\alpha)k^{-5/2}$, for large k.

Using the explicit expression for R_k prior to gelation, we can calculate the mass distribution of the frozen clusters produced up to that point. Substituting (25) into the formal solution (23) and integrating $dF_k/dt = \alpha R_k$ over time using $d\tau/dt = e^{-\alpha t} = (1-\alpha\tau)$ yields the distribution $F_k(t_g)$ of frozen clusters produced prior to gelation ($t_g \equiv \infty$ for $\alpha > 1$)

$$F_k(t_g) = \begin{cases} \frac{\alpha}{k^2\cdot k!}\, \gamma(k,k) & \alpha \leq 1, \\ \frac{\alpha}{k^2\cdot k!}\, \gamma(k,k/\alpha) & \alpha \geq 1, \end{cases} \tag{26}$$

where $\gamma(n,x) = \int_0^x dy\, y^{n-1}\, e^{-y}$ is the incomplete gamma function. When $\alpha \geq 1$, this quantity equals the final distribution of frozen clusters, $F_k(\infty) = F_k(t_g)$. At large masses, the behavior is as follows

$$F_k(\infty) \simeq \begin{cases} \frac{1}{2}\cdot k^{-3} & \alpha = 1, \\ A(\alpha)\, k^{-7/2} \exp\left[-B(\alpha)k\right] & \alpha > 1, \end{cases} \tag{27}$$

where $A = (2\pi)^{-1/2}\alpha^2/(\alpha-1)$ and $B = \alpha^{-1} + \ln\alpha - 1$. These asymptotic results were obtained using the steepest descent method. Quantitatively, the mass distribution differs from that obtained for constant aggregation rates. However, qualitatively, there is a similarity: there is exponential decay above a critical freezing rate and algebraic decay at and below this critical freezing rate. For the constant aggregation rate, the critical freezing rate vanishes, but for the product aggregation rate the critical rate is finite.

At the gelation transition a giant cluster that contains a fraction of the mass in the system emerges. Past the gelation point, two aggregation processes occur in parallel: in addition to cluster-cluster aggregation, the giant cluster grows by swallowing finite clusters. Now, reactive clusters consist of finite clusters (the "sol") with mass $s = M_1$, and the gel with mass g. The total mass density is $m = s + g$. These three masses are coupled via the evolution equations

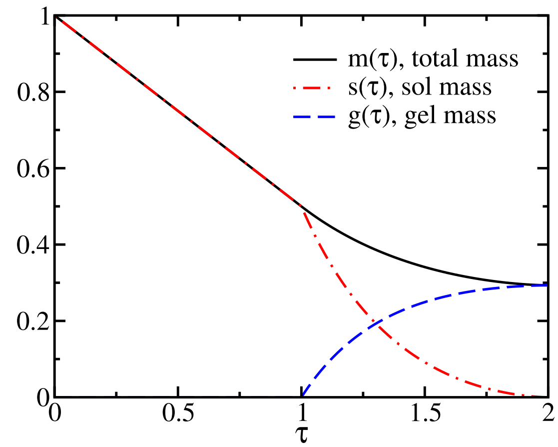

FIG. 1: The total mass, the sol mass, and the gel mass versus the modified time τ for $\alpha = 1/2$.

$$\frac{dm}{dt} = -\alpha\, s, \tag{28a}$$

$$\frac{ds}{dt} = -\alpha\, s - \frac{s(m-s)}{1 - s\tau e^{\alpha t}}. \tag{28b}$$

The initial conditions are $m(t_g) = s(t_g) = 1-\alpha$. The first equation reflects that as long as the gel remains reactive, mass may be converted from the reactive state to the frozen state via freezing of finite clusters. The second equation follows from $ds/dt = -\alpha M_1 - g\, M_2$, obtained by summing (19). The second moment is written explicitly, $M_2 = \mathcal{R}_z(z=0) = s/(1 - s\tau e^{\alpha t})$, using the aforementioned identity $G'(z) = G/(1-G)$. The initial conditions are $m(t_g) = s(t_g) = 1-\alpha$. Once these equations are solved, the solution (23) becomes explicit. We analyze this equation using perturbation theory in the limits $\alpha \uparrow 1$ and $\alpha \downarrow 0$ as detailed in Appendix A. For general freezing rates, we solve these equations numerically (Fig. 1).

In addition to the freezing of the finite clusters, the gel itself may freeze. One way to characterize the gel by its maximal possible size $g_{\max} = \lim_{t\to\infty} g(t)$. The limiting behaviors are as follows (see Appendix A)

$$g_{\max} \to \begin{cases} 1 - \frac{\pi^2}{6}\alpha & \alpha \downarrow 0, \\ C(1-\alpha)^2 & \alpha \uparrow 1, \end{cases} \tag{29}$$

with $C = 1.303892$. The maximal gel size decreases as the freezing rate increases. Just below the critical freezing rate, the gel is very small as its size shrinks quadratically with the distance from the critical point $g \sim (1-\alpha)^2$; perturbation analysis shows that this behavior is generic and not limited to the maximal gel size. Therefore, freezing is a mechanism for controlling the gel

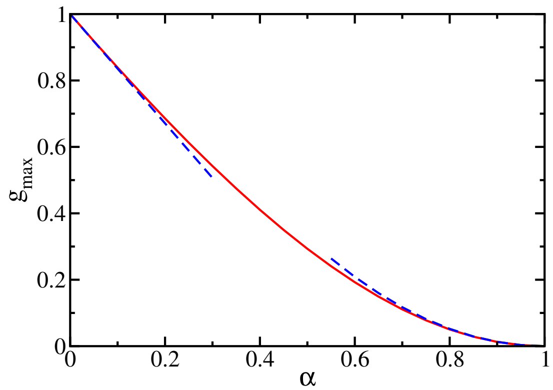

FIG. 2: The maximal gel mass $g_{\rm max}$ versus the freezing rate α (solid line). Perturbation theory results are shown using dashed lines.

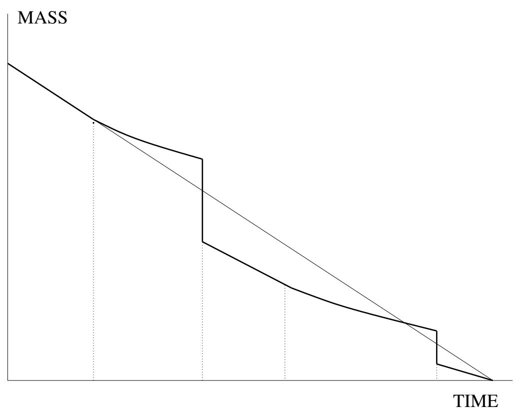

FIG. 3: The mass density m (MASS) versus time τ (TIME). The system alternates between the coagulation phase and the gelation phase. In the former phase the mass decreases linearly according to (20) such that depletion occurs at time $\tau = 1/\alpha$. In the latter phase, the active mass decreases slower than linear according to (28). The gelation phase ends when the gel freezes.

size: by using freezing rates just below the critical rate, it is possible to produce micro-gels.

The gel freezes following a random Poisson process: its lifetime T is distributed according to the exponential distribution

$$P(T) = \alpha\, e^{-\alpha T}. \tag{30}$$

As long as the gel is active the system evolves in a deterministic fashion. When the gel freezes, the total reactive mass exhibits a discontinuous downward jump (Fig. 3). Since the gel freezes according to a random process, the mass of the frozen gel is also a random variable. Moreover, this quantity is not self-averaging as it fluctuates from realization to realization.

When the gel freezes, the system consists of finite-mass clusters only and therefore, the system re-enters the coagulation phase. The system may then undergo a second gelation transition that ends when the gel freezes. Therefore, the evolution is cyclic with the system alternating between the coagulation and gelation. For the same reason that the gel mass fluctuates, so is the number of frozen gels produced a fluctuating quantity.

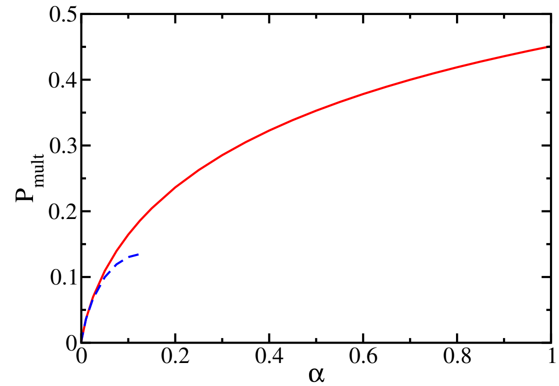

FIG. 4: The multiple gel probability $P_{\rm mult}$ versus the freezing rate α (solid line). Perturbation theory results are shown using a dashed line.

The number of gels produced is in principle unlimited, i.e., there is a finite probability $P_n > 0$ that n gels are produced. Since the second moment diverges at the gelation transition according to (21), it is necessarily larger than the freezing rate at some finite time interval following the gelation transition. If the gel freezes during this time interval then a successive gelation is bound to occur. We also note that the evolution in the coagulation phase is deterministic and for example, the first two moments follow Eqs. (20) and (21). The "initial" conditions are given by the state of the system when the gel freezes.

It is therefore natural to ask: what is the probability that multiple gels are produced? This is the probability that the gel freezes prior to time t_* given by $M_2(t_*) = \alpha$. Using the second moment $M_2 = s/(1 - s\tau e^{\alpha t})$ this condition simplifies to

$$s(t_*) = \alpha\, e^{-\alpha t_*}. \tag{31}$$

The probability that multiple gels are produced is obtained by integrating (30) up to this time, $P_{\rm mult} = \int_0^{t_*-t_g} dT\, P(T)$ with the limiting behaviors (see Appendix A)

$$P_{\rm mult} \to \begin{cases} \alpha \ln \frac{1}{e\alpha} & \alpha \downarrow 0, \\ 0.450851 & \alpha \uparrow 1. \end{cases} \tag{32}$$

This probability increases as the freezing rate increases (figure 4). It is generally substantial, and moreover, it exhibits a discontinuity at $\alpha = \alpha_c$.

We now address the final mass distribution of frozen gels. Analytic treatment of the successive gelation phases is difficult due to the stochastic nature of the freezing process. Numerically, there are two ways to treat the problem. One may integrate the rate equations (28) up to the gel freezing time that is distributed according to (30)

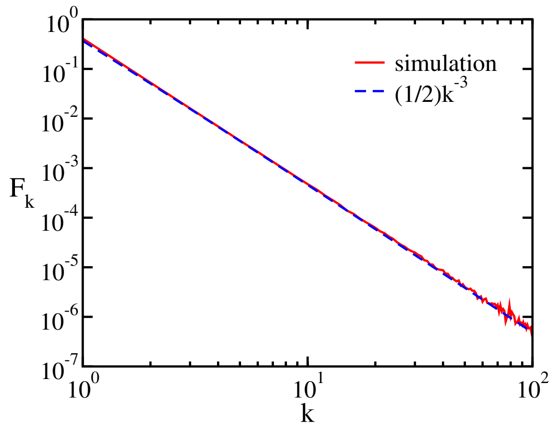

FIG. 5: The final mass distribution of the frozen clusters for $\alpha = 1/2$. The simulation results represent an average over 10^2 independent realizations in a system of mass $N = 10^6$.

and then repeat this procedure if a successive gelation occurs. We prefer Monte Carlo simulations where, since the system is finite, there is no need to distinguish the gel from the finite clusters. In the simulations, we keep track of the total aggregation rate $R_a = N(M_1^2 - M_2)/2$ and of the total freezing rate $R_f = \alpha N M_0$, where N is the number of monomers. Aggregation occurs with probability $R_a/(R_a + R_f)$, and freezing occurs with the complementary probability. A cluster is chosen for aggregation with probability proportional to its mass. Time is augmented by $\Delta t = 1/(R_a + R_f)$ after each aggregation or freezing event.

For the case $\alpha < 1$, numerical simulations provide convincing evidence that the tail behavior

$$F_k(\infty) \sim k^{-3}, \qquad \alpha < 1 \tag{33}$$

is universal (Fig. 5). This indicates that frozen clusters produced during the coagulation phase dominate at large masses as every such phase is expected to contribute k^{-3} to the tail according to Eq. (27). Intuitively, this is clear because large clusters are quickly merged into the gel and therefore, frozen clusters produced in the presence of the gel tend to be small. Interestingly, freezing leads to a new critical exponent in mean-field percolation.

V. CONCLUSIONS

In summary, we studied aggregation processes with freezing. For constant freezing rates, the problem can be formally reduced to the no freezing case. The mass distribution of frozen clusters resembles the mass distribution of reactive clusters, decaying exponentially at large masses, when the freezing is sufficiently fast. Novel behavior emerges when the freezing rate is slower than some critical value. In this case, the mass distribution of frozen clusters decays algebraically. For constant aggregation rate, the critical freezing rate is zero but for the product aggregation rate, it is finite.

For the product aggregation rate, the freezing rate controls the gelation process. If it is sufficiently high, no gelation occurs, and if it is just below the threshold, micro-gels are produced. If one gel is produced, then multiple gels are possible. In this case, the mass of the gels and their number are both controlled by a random process and as a result, they fluctuate from realization to realization. The system exhibits a series of gelation transitions and it alternates between ordinary coagulation and gelation. The random freezing process governs the number of percolation transitions as well as the mass of the frozen gels.

The behavior when freezing occurs spontaneously is quite different than that found when freezing is reaction-induced (upon merger a cluster may freeze with some fixed probability) [22, 23]. For the constant aggregation rate, the mass distribution is always algebraic and the characteristic exponent is non-universal as it depends on the freezing probability. For the product aggregation rate, the gelation transition is always suppressed, because the probability that a cluster remains reactive decays exponentially with the number of merger events.

There are many open questions raised by this study. For example, it will be interesting to investigate the behavior in low-dimensional systems where the rate equation approach no longer holds. Additionally, the exponent characterizing the mass distribution of frozen clusters represents a novel critical exponent in percolation processes and this should be a challenging problem below the critical dimension.

One can also investigate situations where there is a source of monomers. In the long-time limit, the densities of reactive clusters become stationary, and the characteristics of such steady-state solutions have been investigated in Refs. [24–26], especially in the case of mass-independent rates of aggregation and freezing. It may be interesting to study the accumulation of frozen clusters, particularly frozen gels in the model with product aggregation rate.

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APPENDIX A: PERTURBATION ANALYSIS

1. $\alpha \uparrow 1$

To investigate the behavior in the time domain $1 < \tau < \alpha^{-1}$, we make the transformation $\tau = 1 + (\alpha^{-1} - 1)\,x$ with $0 \le x \le 1$. The governing equations (28) become

$$\frac{dm}{dx} = -\frac{s}{1-x} \tag{A1a}$$

$$\frac{ds}{dx} = -\frac{s}{1-x} - \frac{s(m-s)}{\alpha\left(1 - x - \frac{s}{1-\alpha}\right) - sx}. \tag{A1b}$$

The initial conditions are now $m(0) = s(0) = 1 - \alpha$. When $\alpha \uparrow 1$, we perform perturbation analysis using the small parameter $\epsilon = 1 - \alpha$. Given the initial conditions $m(0) = s(0) = \epsilon$, we write

$$m = \epsilon F_1 + \epsilon^2 F_2 + \cdots \qquad s = \epsilon G_1 + \epsilon^2 G_2 + \cdots\,. \tag{A2}$$

Substituting these expansions into the governing equations (A1a)–(A1b) and keeping only dominant, linear in ϵ, terms we obtain

$$\frac{dF_1}{dx} = -\frac{G_1}{1-x}\,, \tag{A3a}$$

$$\frac{dG_1}{dx} = -\frac{G_1}{1-x}. \tag{A3b}$$

The initial conditions are $F_1(0) = G_1(0) = 1$. Solving these equations, we find

$$F_1 = G_1 = 1 - x. \tag{A4}$$

Thus, the gel mass vanishes to first order in ϵ, and we should consider the second order terms. The second order terms are coupled according to

$$\frac{dF_2}{dx} = -\frac{G_2}{1-x} \tag{A5a}$$

$$\frac{dG_2}{dx} = -\frac{G_2}{1-x} + (1-x)\,\frac{F_2 - G_2}{G_2 + x(1-x)}. \tag{A5b}$$

The boundary conditions are $F_2(0) = G_2(0) = 0$. We seek the non-trivial solution with the following derivatives at the origin: $F_2'(0) = 0$, and $G_2'(0) = -2$.

To find the probability that multiple gels are produced, we notice that the Poisson distribution (30) is uniform in terms of the transformed time, $P(x) = 1$ and therefore, the probability of forming multiple gels is simply $P_{\rm mult} = \int_0^{x_*} dx\, P(x) = x_*$. Also, the condition (31) becomes $s(x_*) = \alpha(1-\alpha)(1-x_*)$. Substituting the perturbative expansion $\epsilon(1-x_*) + \epsilon^2 G_2(x_*) = \epsilon(1-\epsilon)(1-x_*)$, this condition becomes $G_2(x_*) = x_* - 1$. It also implies $G_2(1) = 0$. Numerical integration yields $P_{\rm mult} = x_* = 0.45081$.

To find the maximal gel mass, we write $g = m - s = \epsilon^2(F_2 - G_2)$ and use $G_2(1) = 0$. Thus, the maximal gel mass $g_{\max} = g(x = 1)$ is

$$g_{\max} = (1-\alpha)^2 F_2(1). \tag{A6}$$

Integrating these equations numerically, we determine $F_2(1) = 1.303892$. Moreover, the perturbation analysis shows that in general, the gel mass vanishes quadratically close to the critical freezing rate, $g \propto (1-\alpha)^2$.

2. $\alpha \downarrow 0$

When freezing is slow, we may drop the freezing loss term $-\alpha R_k$ from the master equation (19) as done in section III. The problem therefore reduces to the no-freezing case where $u = \tau = t$ and thus, the generating function (24) is $\mathcal{R}(z,t) = t^{-1} G(z + \ln t - t)$. Invoking the identity $Ge^{-G} = e^z$, the sol mass $s = \mathcal{R}(z = 0)$ satisfies $s = e^{-(1-s)t}$. In the long time limit,

$$s(t) = e^{-t} + t\,e^{-2t} + \ldots \tag{A7}$$

From the one-gel criterion (31) and (A7) we obtain $t_* = \frac{1}{1-\alpha}\ln\frac{1}{\alpha}$. Finally, using $P_{\rm mult} = 1 - \exp[-\alpha(t_* - 1)]$, we find the multiple-gel probability: $P_{\rm mult} \simeq -\alpha\ln(e\,\alpha)$.

To leading order, the total mass m remains constant. Using the exact governing equation $dm/dt = -\alpha s$, we derive the first order correction:

$$m(t) = 1 - \alpha - \alpha \int_1^t dt'\, s(t'). \tag{A8}$$

The maximal mass of the gel is therefore

$$g_{\max} = 1 - B\alpha, \quad B = 1 + \int_1^\infty dt\, s(t). \tag{A9}$$

Using $t = -(1-s)^{-1} \ln s$ we change the integration variable and then transform the integral:

$$B = 1 + \int_0^1 ds\, s \left[\frac{1}{s(1-s)} + \frac{\ln s}{(1-s)^2} \right]. \tag{A10}$$

Performing the integration, we find $B = \pi^2/6$.