Percolation with Multiple Giant Clusters

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*

We study mean-field percolation with freezing. Specifically, we consider cluster formation via two competing processes: irreversible aggregation and freezing. We find that when the freezing rate exceeds a certain threshold, the percolation transition is suppressed. Below this threshold, the system undergoes a series of percolation transitions with multiple giant clusters ("gels") formed. Giant clusters are not self-averaging as their total number and their sizes fluctuate from realization to realization. The size distribution F_k, of frozen clusters of size k, has a universal tail, $F_k \sim k^{-3}$. We propose freezing as a practical mechanism for controlling the gel size.

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Percolation was originally discovered in the context of polymerization and gelation [1, 2] and since, it has found numerous applications in physics [3], geophysics [4], chemistry [5], and biology [6]. It plays an important role in a vast array of natural and artificial processes ranging from flow in porous media [7] and cloud formation [8, 9] to evolution of random graphs [10, 11], combinatorial optimization [12], algorithmic complexity [13], amorphous computing, and DNA computing using self-assembly [14].

We study mean-field percolation using the framework of aggregation. An aggregation process typically begins with a huge number of molecular units ("monomers") that join irreversibly to form clusters ("polymers"). At some time, a giant cluster ("gel") containing a finite fraction of the monomers in the system is born, and it grows to engulf the entire system. In this classic percolation picture only a single gel forms, but in many natural and artificial processes the system freezes into a non-trivial final state with multiple gels or even micro-gels [15, 16]. In this study, we show that aggregation with freezing naturally leads to formation of multiple gels and that freezing is a useful mechanism for controlling the gel size.

We analyze a process of aggregation with freezing where there are two types of clusters: active and frozen. Active clusters join by binary aggregation into larger active clusters. The aggregation rate is proportional to the product of the two cluster sizes [8, 17, 18]; this is equivalent to the gelation model of Flory and Stockmayer where a chemical bond between two monomers joins their respective polymers [1, 2]. In parallel, all active clusters including the gel may become frozen at a size-independent constant rate α. Frozen clusters and frozen gels are passive: they do not interact with other (active or passive) clusters.

This process is studied using the rate equation approach. The density $c_k(t)$ of active clusters of mass k at time t (that is, made up from k monomers) satisfies

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k}(ic_i)(jc_j) - m\,kc_k - \alpha\,c_k, \tag{1}$$

with $m(t)$ the mass density of active clusters. The first two terms on the right-hand side describe how the cluster size distribution changes due to aggregation, and the last term accounts for loss due to freezing. The quantity $m(t)$ equals the mass density of *all* active clusters including possibly a giant cluster. When there is no active giant cluster, $m(t) \equiv M_1(t)$ with the moments defined via $M_n(t) \equiv \langle k^n \rangle = \sum_{k\geq 1} k^n c_k(t)$.

The gelation transition. Initially, all clusters are finite in size, so $m = M_1$. The moments M_n provide a useful probe of the dynamics. From the governing equation (1), the second moment of the size distribution M_2 obeys the closed equation $dM_2/dt = M_2(M_2 - \alpha)$ and thus,

$$M_2(t) = \alpha\,\left[\left(\frac{\alpha}{\alpha_c} - 1\right)e^{\alpha t} + 1\right]^{-1}. \tag{2}$$

There is a critical freezing rate $\alpha_c = M_2(0)$. For fast freezing, $\alpha \geq \alpha_c$, the second moment is always finite indicating that clusters remain finite at all times. In this case, there is no gelation. For slow freezing, $\alpha < \alpha_c$, there is a finite time singularity indicating that an infinite cluster, the gel, emerges in a finite time [19]. This gelation time is

$$t_g = -\frac{1}{\alpha}\ln\left(1 - \frac{\alpha}{\alpha_c}\right). \tag{3}$$

The gelation point marks two phases. Prior to the gelation point, the system contains only finite clusters that undergo cluster-cluster aggregation ("coagulation phase"). Past the gelation point, the gel grows via cluster-gel aggregation ("gelation phase"). We analyze these two phases in order.

Coagulation phase. Coagulation occurs for $\alpha \geq \alpha_c$ at all times or for $\alpha < \alpha_c$ when $t < t_g$. From (1), the mass density of active clusters satisfies $dm/dt = -\alpha\, m$, and thus, ordinary exponential decay occurs,

$$m(t) = m(0)e^{-\alpha t}\,. \tag{4}$$

For concreteness, we consider the monodisperse initial conditions $c_k(0) = \delta_{k,1}$. In this case $M_n(0) = 1$ and consequently, $\alpha_c = 1$. The cluster size distribution is obtained using the standard transformation [20–22], $c_k = e^{-\alpha t}\, C_k$, and the modified time variable $\tau = \int_0^t dt' e^{-\alpha t'}$ or explicitly

$$\tau = \frac{1-e^{-\alpha t}}{\alpha}. \tag{5}$$

This time variable increases monotonically with the physical time and reaches $\tau \to 1/\alpha$ as $t \to \infty$. With these transformations, Eq. (1) reduces to the no-freezing case $dC_k/d\tau = \frac{1}{2}\sum_{i+j=k}(iC_i)(jC_j) - kC_k$. From the well-known solution of this equation [23, 24], the cluster-size distribution is

$$c_k(t) = \frac{k^{k-2}}{k!}\;\tau^{k-1}\, e^{-k\tau-\alpha t}. \tag{6}$$

Generally, the size distribution decays exponentially at large sizes and the typical cluster size is finite. The gelation time (3) is simply $\tau_g = 1$. Of course, no gelation occurs when $\alpha > 1$ because $\tau < 1/\alpha < 1$. The gelation point is marked by an algebraic divergence of the size distribution $c_k \sim (1-\alpha)k^{-5/2}$ for large k. We note that the mass density decreases linearly with the modified time, $m = 1 - \alpha\tau$, and that $m(\tau_g) = 1-\alpha$.

Gelation phase. Past the gelation transition, a giant cluster containing a finite fraction of the mass in the system forms. In addition to cluster-cluster aggregation, cluster-gel aggregation takes place with the giant cluster growing at the expense of finite clusters. In parallel, all clusters including the gel may freeze.

Formally, the size distribution (6) generalizes to

$$c_k(t) = \frac{k^{k-2}}{k!}\;\tau^{k-1}\, e^{-ku-\alpha t} \tag{7}$$

with $u(t) = \int_0^t dt'\, m(t')$ yet to be determined. Statistical properties of the size distribution are derived from the generating function $c(z,t) = \sum_{k\geq 1} kc_k(t)e^{kz}$ that equals

$$c(z,t) = \tau^{-1}e^{-\alpha t}G(z+\ln\tau - u) \tag{8}$$

where $G(z) = \sum_{k\geq 1}\frac{k^{k-1}}{k!}\, e^{kz}$ is the "tree" function [25].

During the gelation phase, active clusters consist of finite clusters, the "sol", with mass s, and the gel with mass g with the total mass density, $m = s+g$, and these masses are coupled via the evolution equations

$$\frac{dm}{dt} = -\alpha s, \tag{9a}$$
$$\frac{ds}{dt} = -\frac{s(m-s)}{1-s\tau e^{\alpha t}} - \alpha\, s. \tag{9b}$$

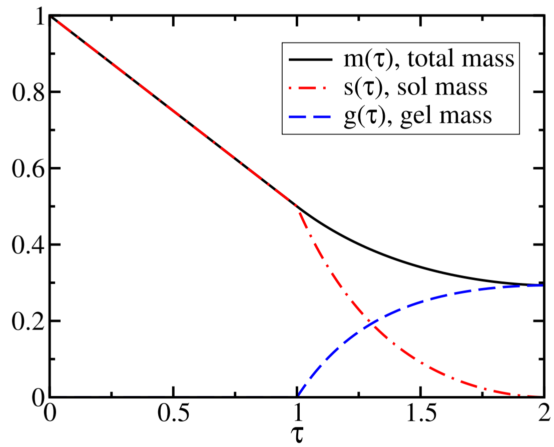

FIG. 1: The total mass, the sol mass, and the gel mass versus modified time τ for $\alpha = 1/2$. These curves hold as long as the gel remains active.

The equation governing the total mass reflects that as long as the gel is active, loss is due to freezing of finite clusters and the equation for the sol mass follows from $ds/dt = -g\, M_2 - \alpha M_1$, obtained by summing (1). To convert this equation into the explicit Eq. (9b), the first two moments are $M_1 = s$ and $M_2 = c_z(z=0) = s/(1-s\tau e^{\alpha t})$ where the identity $G'(z) = G/(1-G)$ [26] was employed.

Equations (9a) and (9b) are subject to the initial conditions $m(t_g) = s(t_g) = 1-\alpha$. Once the masses are found, the formal solution (7) becomes explicit. Results of numerical integration of Eqs. (9a) and (9b) are shown in Fig. 1.

Clearly, the longer the gel remains active, the larger it grows, but its size can not exceed $g_{\max} = \lim_{t\to\infty} g(t)$ with the obvious bound $g_{\max} < 1-\alpha$ (Fig. 2). Furthermore, an involved perturbation analysis [27] of Eqs. (9a) and (9b) yields

$$g_{\max} \to \begin{cases} 1-\frac{\pi^2}{6}\alpha & \alpha\downarrow 0,\\ C(1-\alpha)^2 & \alpha\uparrow 1;\end{cases} \tag{10}$$

with $C = 1.303892$. The quadratic dependence on the freezing rate implies that the emerging gel is very small when $\alpha \uparrow \alpha_c$. Thus, micro-gels, that may be practically indistinguishable from large clusters, emerge. We conclude that freezing can be used to control the gel size, as gels of arbitrarily small size can be produced using freezing rates just below criticality.

Multiple giant clusters. At any time during the gelation phase, the gel itself may freeze. This freezing process is random: the gel lifetime T is an exponentially distributed random variable, $P(T) = \alpha e^{-\alpha T}$. Until the gel freezes, the system evolves deterministically, so the mass of the frozen gel is $g(t_g+T)$. When the gel freezes, the total active mass $m(t)$ is discontinuous: it exhibits a downward jump (Fig. 3). Given that the duration of the gelation phase is governed by a random process, the mass of the

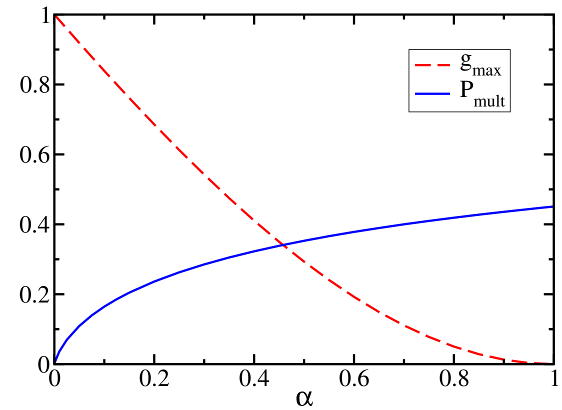

FIG. 2: The maximal gel size $g_{\max}$ and the probability of producing multiple gels $P_{\rm mult}$ versus the freezing rate α.

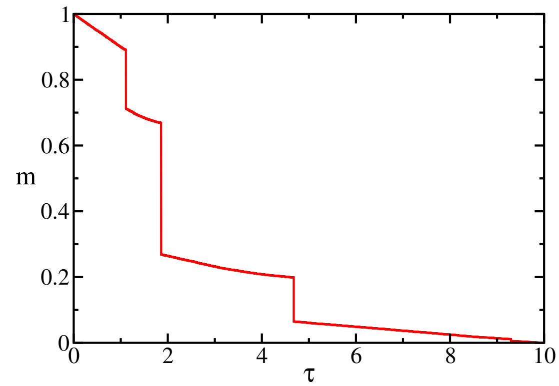

FIG. 3: The mass density m versus time τ. Shown are results of a Monte Carlo simulation with system size $N = 10^5$ and freezing rate $\alpha = 0.1$. The system alternates between the coagulation phase and the gelation phase. In the former phase the mass decreases linearly according to (4) such that depletion occurs at time $\tau = 1/\alpha$. In the latter phase, the active mass decreases slower than linear according to (9a) and (9b). The gelation phase ends when the gel freezes.

frozen gel is also random. It fluctuates from realization to realization, i.e., it is not a self-averaging quantity.

When the gel freezes, the system re-enters the coagulation phase because all remaining clusters are finite. The initial conditions are dictated by the duration of the preceding gelation phase and are therefore also stochastic. Nevertheless, once the initial state is set, the evolution in the coagulation phase is deterministic. The gel is frozen so it no longer affects the evolution and only cluster-cluster aggregation occurs. Let us assume that the gel freezes at time t_f. Reseting time to zero, the first and the second moments are simply given by Eqs. (4) and (2), respectively, with $M_n(0)$ replaced by $M_n(t_f)$. A second gelation occurs if the freezing rate is sufficiently small, $\alpha < M_2(t_f)$. Otherwise, the system remains in the coagulation phase forever.

Because M_2 diverges at the gelation point, there is a time window past the gelation time where the second moment exceeds the freezing rate. If the gel freezes during this window, another percolation transition is bound to occur. Therefore, there is no upper bound to the number of frozen gels that may possibly form. Quantitatively, the probability that a successive gelation occurs is $P_{\rm mult} = \int_0^{t_*-t_g} dT\, P(T)$ with $M_2(t_*) = \alpha$ (Fig. 2); it can be obtained using perturbation analysis [27]

$$P_{\rm mult} \to \begin{cases} \alpha \ln \frac{1}{e\alpha} & \alpha \downarrow 0, \\ 0.450851 & \alpha \uparrow 1. \end{cases} \tag{11}$$

In general, this probability is substantial and remarkably, it is discontinuous at α_c.

Cyclic dynamics. The general picture is now clear: the process starts and ends in coagulation and throughout the evolution, the system alternates between coagulation and gelation. Once the initial conditions are set, the behavior throughout the coagulation phase and throughout the gelation phase are both deterministic. Each gelation phase ends with freezing of the active gel. Since the duration of the gelation phase is random, the size of the giant clusters, and the number of giant clusters are both random variables. Generically, the system exhibits a series of percolation transitions, each producing a frozen gel, so that overall, multiple gels are produced. The random freezing process governs the number of percolation transitions as well as the size of the frozen gels.

Monte Carlo simulation of the stochastic process of aggregation with freezing confirms this picture (Fig. 3). In the simulations, we keep track the total aggregation rate $R_a = N(M_1^2 - M_2)/2$ and the total freezing rate $R_f = \alpha N M_0$, where N is the number of particles. 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 size. Time is augmented by $\Delta t = 1/(R_a + R_f)$ after each aggregation or freezing event.

Frozen clusters. The density of frozen clusters F_k is found from $dF_k/dt = \alpha c_k$. By integrating Eq. (6), we find the density $F_k(t_g)$ of clusters produced during the first coagulation phase ($t_g \equiv \infty$ for $\alpha > 1$)

$$F_k(t_g) = \begin{cases} \frac{\alpha}{k^2 \cdot k!}\, \gamma(k, k) & \alpha \leq 1, \\ \frac{\alpha}{k^2 \cdot k!}\, \gamma(k, k/\alpha) & \alpha \geq 1; \end{cases} \tag{12}$$

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 density of frozen clusters, $F_k(\infty) = F_k(t_g)$, and at large sizes, the behavior is as follows

$$F_k(\infty) \simeq \begin{cases} \frac{1}{2} \cdot k^{-3} & \alpha = 1, \\ A(\alpha)\, k^{-7/2} \exp\left[-B(\alpha) k\right] & \alpha > 1; \end{cases} \tag{13}$$

where $A = (2\pi)^{-1/2} \alpha^2/(\alpha - 1)$ and $B = \alpha^{-1} + \ln \alpha - 1$.

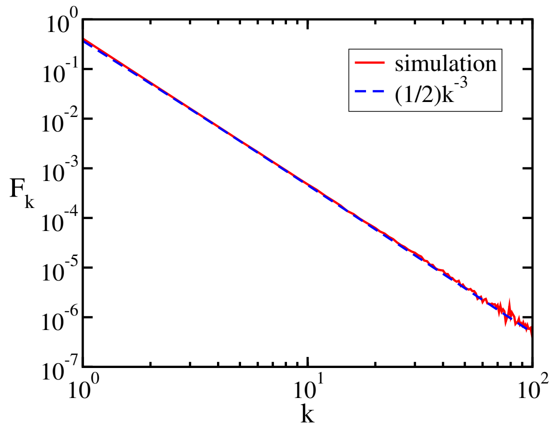

FIG. 4: The size distribution of the frozen clusters for $\alpha = 1/2$. The simulation results represent an average over 10^2 independent realizations in a system of size $N = 10^6$.

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

$$F_k(\infty) \sim k^{-3}, \qquad \alpha < 1 \tag{14}$$

is universal (Fig. 4). Indeed, Eq. (12) shows that the first coagulation phase contributes $F_k(t_g) \simeq \frac{\alpha}{2}k^{-3}$ to $F_k(\infty)$ and similarly, each successive coagulation phase should contribute the very same k^{-3} to the tail. Because large clusters quickly merge into the gel, the gelation phase yields a negligible contribution, and we conclude that freezing leads to an additional non-trivial critical exponent $\gamma = 3$.

In summary, freezing results in a rich and interesting phenomenology that includes multiple percolation transitions and multiple gels, microgels that may be indistinguishable from finite clusters, cyclic evolution with the system constantly alternating between coagulation and gelation, lack of self-averaging, and an additional non-trivial critical exponent.

Freezing also provides a practical mechanism for controlling gelation. It may be used to engineer micro-gels of desired size by implementing variable freezing rates. Slow freezing followed by rapid freezing can be used to produce gels of prescribed size, while near-critical freezing produces micro-gels of arbitrarily small size.

There are a number of interesting potential generalizations of the present work. One may consider situations with different freezing mechanisms [22], particularly for finite and infinite clusters. We also solved the Stockmayer version [2, 28] where $m = M_1$ always; in this case, there is no breakdown of self-averaging and the final density of frozen clusters mimics the critical behavior of active clusters, $F_k \sim k^{-5/2}$. Another natural generalization is percolation in finite dimensions where the final distribution of frozen clusters should be an interesting probe of the dynamics.

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* Electronic address: ebn@lanl.gov
† Electronic address: paulk@bu.edu

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