# Percolation Model for Slow Dynamics in Glass-Forming Materials

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We identify a link between the glass transition and percolation of regions of mobility in configuration space. We find that many hallmarks of glassy dynamics, for example, stretched-exponential response functions and a diverging structural relaxation time, are consequences of the critical properties of mean-field percolation. Specific predictions of the percolation model include the range of possible stretching exponents $1/3 \leq \beta \leq 1$ and the functional dependence of the structural relaxation time $\tau_\alpha$ and exponent $\beta$ on temperature, density, and wave number.

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As temperature is decreased near the glass transition, the structural relaxation time in glassy materials increases by many orders of magnitude with only subtle changes in static correlations [1]. In addition, structural correlations display an anomalous stretched-exponential time decay $\exp(-t/\tau_\alpha)^\beta$, where $\beta$ is the stretching exponent and $\tau_\alpha$ the $\alpha$-relaxation time. Understanding the origin of this behavior is one of the most important outstanding problems in statistical physics.

Although stretched-exponential relaxation is common to many glass-forming materials, the dependence of $\tau_\alpha$ and $\beta$ on temperature and density is not universal. For molecular, colloidal and polymer glasses, where structural relaxation is measured using density autocorrelation functions, the temperature dependence of $\tau_\alpha$ is affected by the fragility [2]. In magnetic glasses, where structural relaxation is measured using spin autocorrelation functions, $\tau_\alpha$ depends on details of the microscopic interactions [3]. In all glassy systems, the stretching exponent $\beta$ varies between $1/3$ and 1 depending on the scattering wave vector, density and temperature, and its dependence on these variables is not universal [4].

How do we understand structural relaxation in glass-forming materials where correlation functions display stretched-exponential relaxation, but the temperature and density dependence of $\tau_\alpha$ and $\beta$ vary from one material to the next? Contrary to approaches that focus on heterogeneous dynamics [5] and percolation [6] in real space, we study how properties of energy landscapes [7] affect dynamics in *configuration space*. In this picture, activation from energy minima is rare at low temperatures, and only infrequent hopping between minima allows structural correlations to decay [8].

We focus on the connection between anomalously slow dynamics in glass-forming materials and percolation of regions of mobility in configuration space. The decay of structural correlations over a time $t$ is related to the average distance that the system moves in configuration space during that time. Thus complete relaxation—decay of structural correlations to zero—only occurs after the system can diffuse over a path that percolates configuration space. We demonstrate that a percolation transition in configuration space is responsible for several hallmarks of glassy dynamics: (i) stretched-exponential relaxation of structural correlations and the experimentally observed range of values and wave-number dependence of the stretching exponent $\beta$; (ii) the form of the divergence of $\tau_\alpha$, and (iii) a diverging length scale near the glass-jamming transition for hard spheres.

*Hard spheres.*—We first consider collections of hard spheres that interact at contact with an infinite repulsion. At moderate density, hard spheres behave as simple fluids. As density increases structural relaxation becomes anomalously slow. Upon further compression, if crystallization is avoided, the system becomes confined to an amorphous *collectively jammed* [9] (CJ) state at packing fraction $\phi_J$. In CJ states any single or collective particle displacement causes particle overlap; thus, because of the hard-sphere contraints, no motion is possible at $\phi_J$. For large systems, CJ states occur at a single $\phi_J$, with $\phi_J \approx 0.64$ for monodisperse systems in $d = 3$ dimensions and $\phi_J \approx 0.84$ for bidisperse mixtures with $d = 2$ [10,11].

The transition from glass to liquid in disordered hard-sphere systems can be understood as the percolation of "allowed" regions in configuration space that do not violate hard-sphere constraints: at $\phi = \phi_J$ only CJ states (points in configuration space) are allowed; for $\phi \lesssim \phi_J$ allowed regions do not percolate and relaxation is limited; for $\phi < \phi_P$ a percolating network of allowed regions spans configuration space and the system can fully relax. Critical properties of the percolation transition do not depend on how allowed regions of configuration space are partitioned. However, to use the predictions of continuum percolation, it is useful to partition allowed regions into *mobility domains*, each of which is associated with a single CJ state. For any $\phi$, the mobility domains can be identified by compressing each allowable configuration, specified by its particle positions $\{r_i\}$, to $\phi_J$ using the Lubachevsky-Stillinger algorithm [12] in the large compression rate limit. The point in configuration space $\{r_i\}$ belongs to the mobility domain of the resulting CJ state.

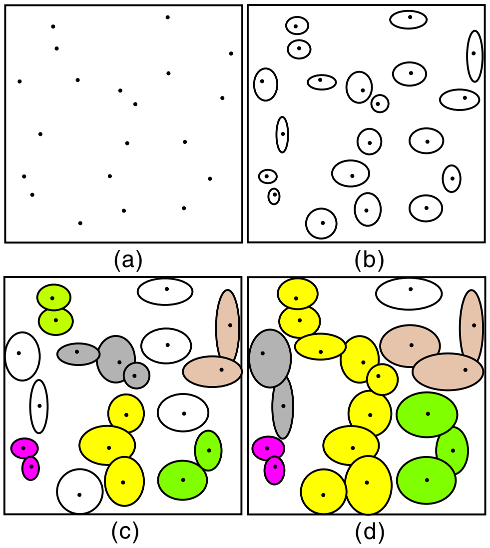

FIG. 1 (color online). Schematic of allowed regions in configuration space for hard spheres. (a) At $\phi_J$ only CJ states (points) are allowed; (b) At $\phi_1 < \phi_J$ motion occurs in closed mobility domains surrounding CJ states; (c) At $\phi_2 < \phi_1$ transitions between contacting mobility domains (shaded) occur; (d) At $\phi_P < \phi_2$ at least one network of mobility domains percolates (shaded yellow) and the system transitions from glass to metastable liquid.

The glass transition can now be described in terms of percolation of mobility domains. At $\phi_J$ the system is confined to one of many possible CJ states and no motion occurs [Fig. 1(a)]. For $\phi \lesssim \phi_J$, a closed mobility domain of allowed hard-sphere configurations surrounds each CJ state [9] [Fig. 1(b)]. For smaller $\phi$ mobility domains of different CJ states can contact, which enables the system to transition from one mobility domain to another [Fig. 1(c)]. The system will diffuse on a network of mobility domains if many are in contact. At lower $\phi$, a percolating cluster of mobility domains forms [Fig. 1(d)].

Structural relaxation in dense hard-sphere systems occurs via dynamical heterogeneities [13], and thus shapes of mobility domains are complex. Near CJ states mobility domains are roughly hyperspherical and quickly explored. Further from CJ states mobility domains become filamentary, and the time needed to explore these regions via cooperative motion is large. However, in our calculations, we assume there exists an upper critical dimension $D^*$ of configuration space, above which mean-field theory accurately describes critical exponents of the percolation transition. In this limit, the complex geometry and correlations of mobility domains can be ignored. We focus on large system sizes $N$, where the dimension of configuration space $dN > D^*$, and construct a mean-field theory in terms of the packing fraction of mobility domains $\Pi$ in configuration space. Percolation occurs at a critical value $\Pi_P$ and is controlled by mean-field exponents [14]. To derive stretched-exponential relaxation, our mean-field approach does not require detailed information about the filamentary features of mobility domains.

We quantify structural relaxation using the incoherent part of the intermediate scattering function (ISF) $\Phi_{\vec{q}}(t) = N^{-1}\sum_{j=1}^{N}\exp[i\vec{q}\cdot\Delta\vec{r}_j(t)]$, where $\Delta\vec{r}_j(t)$ is the displacement of particle $j$ over time $t$ and $\vec{q}$ is the scattering wave vector [15]. The ISF is well characterized by its Gaussian approximation [16],

$$\Phi_{\vec{q}}(t) = \exp(-q^2\Delta r^2(t)/2d), \tag{1}$$

where $\Delta r^2(t) = N^{-1}\sum_{j=1}^{N}|\vec{r}_j(t) - \vec{r}_j(0)|^2$ is the mean-square displacement. Note that $N\Delta r^2(t)$ is identical to the mean-square distance traveled in configuration space after time $t$. The infinite-time value of the ISF $f_{\vec{q}} \equiv \Phi_{\vec{q}}(\infty)$ is an order parameter for the glass transition that is zero for a liquid and positive for a glass.

The percolation model predicts a glass for $\Pi < \Pi_P$ and a metastable liquid for $\Pi > \Pi_P$. For $\Pi < \Pi_P$ no percolating cluster of mobility domains exists, $f_{\vec{q}} > 0$, and the system is a glass since the maximum distance it can diffuse in configuration space is finite, set by the percolation correlation length $\xi \propto (\Pi_P - \Pi)^{-1/2}$. In the glass state, Eq. (1) predicts $\log f_{\vec{q}} \propto -q^2\xi^2 \propto -q^2(\Pi_P - \Pi)^{-1}$. For $\Pi > \Pi_P$ at least one cluster percolates and $f_{\vec{q}} = 0$. Since percolating clusters are fractal and cover only a small fraction of configuration space, the state with $f_{\vec{q}} = 0$ is not necessarily ergodic.

The time dependence of the ISF can be determined from dynamics in configuration space using Eq. (1). The model contains two important time scales: short times where the system is confined to a single mobility domain and long times where the system diffuses on a connected cluster of mobility domains. Short-time dynamics are characterized by the average transition time $\tau_0$ between mobility domains, while longtime relaxation of the ISF is determined by diffusion on a network of mobility domains. The mean-square distance $\Delta r^2(t)$ traveled on networks near the mean-field percolation transition has been studied extensively [17,18] and obeys the scaling form

$$\Delta r^2(t) \propto (t/\tau_0)^{1/3} G[\xi^{-2}(t/\tau_0)^{1/3}], \tag{2}$$

where $\xi \propto (\Pi - \Pi_P)^{-1/2}$ and the scaling function $G[z] \propto z^2$ for $z \gg 1$ and $G[z] = 1$ for $z \ll 1$.

The structural relaxation time $\tau_\alpha$ and stretching exponent $\beta$ can be determined when a percolating network exists. If we define $\Phi_{\vec{q}}(\tau_\alpha) = e^{-1}$, Eqs. (1) and (2) give

$$\tau_\alpha \propto \begin{cases} \tau_0 q^{-2}(\Pi - \Pi_P)^{-2} & \text{for } q\xi \ll 1, \\ \tau_0 q^{-6} & \text{for } q\xi \gg 1. \end{cases} \tag{3}$$

Note that there are two contributions to $\tau_\alpha$: (1) the average transition time between mobility domains $\tau_0$ and (2) the time scale for diffusion on percolating networks that is proportional to $(\Pi - \Pi_P)^{-2}$. The $q$ dependence in Eq. (3) is consistent with experiments on dense colloidal suspensions [16] and vibrated granular materials [19]. Since $\Delta r^2(t)$ from Eq. (2) crosses over from anomalous diffusion $\propto t^{1/3}$ at small times to normal diffusion $\propto t$ at large times, Eq. (1) predicts that $\beta$ varies with time and satisfies $1/3 \leq \beta \leq 1$. In experiments, $\beta$ is typically measured by fitting the ISF to $\exp(t/\tau_\alpha)^\beta$ near $\tau_\alpha$, and thus its time dependence has not been observed. Near $\tau_\alpha$ Eqs. (1) and (2) predict that $\beta$ only depends on $q\xi$ with $\beta = 1/3$ for $q\xi \gg 1$ and $\beta = 1$ for $q\xi \ll 1$. These limiting values have been observed in experiments [19].

Thus far we have used results from mean-field percolation to obtain stretched-exponential relaxation. To make further connections with experiment, we will determine $\tau_\alpha$ versus $\phi$. This requires that we first express $\Pi$ and $\tau_0$ in terms of $\phi$ (I and ii below), and calculate the packing fraction $\phi_P$ at which the glass transition occurs (iii). (i) $\Pi$ is equal to the number of CJ states $N_{\rm CJ}$ multiplied by the average volume $V$ of the mobility domains (normalized by the total volume $L^{Nd}$). $N_{\rm CJ} \propto N! e^{aN}$, where $a > 0$ is a constant [20,21]. $V$ is determined by the total free volume $v_f$ accessible to the system in real space and, assuming that all allowed regions (including filaments) in configuration space are explored, $V^{1/N} = v_f/L^d = (\phi_J - \phi)/\phi_J$. Thus for large $N$

$$\Pi \propto N^N (1 - \phi/\phi_J)^N. \tag{4}$$

(ii) $\tau_0 \propto N_c^{-1}$, where $N_c$ is the average number of mobility domains in contact with a single domain [22]. Assuming a random distribution of hyperspherical domains

$$\tau_0^{-1} \propto N_c = 2^{dN}\Pi. \tag{5}$$

For large $N$, $\tau_0 \propto 2^{-dN}\Pi^{-1} \propto \exp[A\phi_J/(\phi_J - \phi)]$ [23]. (iii) $\phi_P$ can be determined from Eq. (4) by solving $\Pi_P \propto N^N(1 - \phi_P/\phi_J)^N$. Using mean-field percolation results [14], percolation in configuration space occurs when $N_c = z/(z-1)$, where $z$ is the maximum number of mobility domains that can contact a single domain. Since $z$ increases with $N$, we predict $\Pi_P = 2^{-dN}$ and thus $(\phi_J - \phi_P) \propto N^{-1}$. Note that $\phi_P < \phi_J$ for finite $N$ whereas $\phi_P = \phi_J$ as $N \to \infty$. This system-size dependence suggests a diverging length scale $\ell$ in real space: since relaxation only occurs in subsystems of size $\mathcal{N} \sim \ell^d$ where $\phi_P(\mathcal{N}) > \phi$, then $\ell \propto (\phi_J - \phi)^{-1/d}$. A diverging length with the predicted exponent has been reported in experiments on granular media [24]. Using Eq. (3)–(5), the asymptotic form of $\tau_\alpha$ near $\phi_P$ is

$$q^2\tau_\alpha \propto \begin{cases} \exp[\frac{A\phi_J}{\phi_J-\phi}](\phi_P - \phi)^{-2} & \text{for } \phi_P - \phi \ll \phi_J - \phi_P \\ \exp[\frac{B\phi_J}{\phi_J-\phi}] & \text{for } \phi_P - \phi \gg \phi_J - \phi_P, \end{cases} \tag{6}$$

for $q\xi \ll 1$, where $A$ and $B$ are positive constants. For $N \to \infty$ when $\phi_P = \phi_J$ the model predicts a Vogel-Fulcher divergence at $\phi_J$. In this limit, the functional form and location of the divergence have been verified in experiments of hard spheres [19,25]. For finite $N$ when $\phi_P < \phi_J$ there is a power-law divergence near $\phi_P$ and Vogel-Fulcher behavior far from $\phi_P$.

*Finite energy barriers.*—In contrast to hard spheres, activation is important in systems with finite energy barriers. We now extend the percolation model to include activated processes in systems at constant temperature $T$ (with $k_B = 1$). We again assume that only disordered states exist, as in frustrated geometries such as the pyrochlore lattice, polydisperse colloidal suspensions, and metallic glasses above the critical quench rate.

For systems with finite energy barriers, the transition from glass to metastable liquid is described by the percolation of bonds between local energy minima. Configuration space can be decomposed into basins of attraction surrounding each local minimum, and every point in configuration space can be mapped uniquely to a single basin [26]. At short times the system is confined to a basin, whereas at long times it hops from one basin to another. Complete structural relaxation occurs once the system's trajectory percolates configuration space.

To calculate $\tau_\alpha$, we specify the ensemble of bond-percolating networks on which the system can relax and select the subset that minimizes $\tau_\alpha$. To build the ensemble, we prescribe a maximum energy barrier height $nT$ and draw bonds between minima with barriers below $nT$. If one of the networks formed in this manner percolates, it is included in the ensemble. For a given value of $n$, the fraction of bonds $b(n)$ and the average time $\tau_0(n)$ to make transitions between two basins are given by

$$b(n) = \int_0^{nT} P_b(E)dE, \tag{7}$$

$$\tau_0(n) \propto b(n)^{-1}\int_0^{nT} P_b(E)\exp(E/T)dE, \tag{8}$$

where $P_b(E)$ is the distribution of energy barriers. For sufficiently large $N$, we can describe the properties of the percolating networks using a mean-field description. For any $n$, a percolating network exists if $b(n)$ is larger than a critical value $b_P$, and the $\alpha$-relaxation time is

$$\tau_\alpha(n) \propto \begin{cases} \tau_0(n)q^{-2}[b(n) - b_P]^{-2} & \text{for } q\xi \ll 1, \\ \tau_0(n)q^{-6} & \text{for } q\xi \gg 1, \end{cases} \tag{9}$$

using arguments similar to those given for Eq. (3). Note that there are a range of relaxation times $\tau_\alpha(n)$, depending on $n$. For large $N$ a saddle-point approximation holds and the system selects the $n^*$ that minimizes $\tau_\alpha(n)$. Minimizing Eq. (9) for $q\xi \ll 1$ gives

$$\frac{b(n^*) - b_P}{b(n^*)} = \frac{2}{Ce^{n^*}/\tau_0(n^*) - 1}, \tag{10}$$

where $C$ is the proportionality constant from Eq. (8) with units of time. Equation (10) can be solved to determine $n^*$ [27]. Since $Ce^{n^*} > \tau_0(n^*)$ for all $T > 0$, Eq. (10) predicts that $b(n^*) > b_P$, and thus no glass transition occurs for $T > 0$. The $T$ dependence of $\tau_\alpha(n^*)$ depends sensitively on $P_b(E)$. If we assume a Gaussian-shaped $P_b(E)$, we recover experimentally observed glassy behavior, including fragile (strong) behavior for large (small) standard deviation relative to the average energy barrier height.

As for hard spheres, the percolation model for finite barriers predicts that structural correlations such as the

ISF or spin correlations exhibit stretched-exponential relaxation with $1/3 \leq \beta \leq 1$. These limits for $\beta$ agree with experimental values for many glass-forming materials [4]. We predict that $\beta$ increases slowly with time, but if it is measured near $\tau_\alpha$ we expect $\beta = 1/3$ for $q\xi \gg 1$ and $\beta = 1$ for $q\xi \ll 1$, where $\xi \propto [b(n^*) - b_P]^{-1/2}$. Our results for the limiting values of $\beta$ are consistent with measurements at different $\xi$ values in Lennard-Jones [28] and magnetic [29,30] glasses and different $q$ values in magnetic [31] and molecular [32] glasses.

Equations (7)–(10) can be applied to hard-sphere systems to determine $\tau_\alpha(\phi)$ even far from $\phi_P$, where details of filamentary regions of mobility domains are important, if we generalize the assumption used to derive Eq. (4). Instead of energy barriers, hard spheres overcome entropic barriers to explore filamentary regions. If a fraction $f$ of the mobility domain hypervolume $V$ is explored before making a transition to a new mobility domain, there is an average transition time $\tau_0(f)$ and a corresponding percolating network with bond fraction $b(f) \propto f\Pi$. For $N \rightarrow \infty$, the system will choose the $f^*$ that minimizes $\tau_\alpha$. Equation (4) was derived assuming $f^* = 1$, which holds near $\phi_P$. For $\phi \ll \phi_P$, $f^* \ll 1$ and only the hyperspherical regions of mobility domains are explored. Glassy behavior begins when $f^*$ becomes sufficiently large that filamentary regions of mobility domains are explored.

We introduced a percolation model that predicts stretched-exponential relaxation in glassy materials, which is commonly explained by invoking underlying heterogeneity [5]. Percolating networks organize into densely connected blobs below $\xi$ and homogeneous nodes above $\xi$ [33], and thus have a built-in heterogeneity that leads to $\beta < 1$. Further studies of the geometry of percolating networks and dynamics on these networks, will lead to new predictions for slow dynamics and cooperative motion in glassy materials.

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