Hopping and the Stokes–Einstein relation breakdown in simple glass formers

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One of the most actively debated issues in the study of the glass transition is whether a mean-field description is a reasonable starting point for understanding experimental glass formers. Although the mean-field theory of the glass transition—like that of other statistical systems—is exact when the spatial dimension $d \to \infty$, the evolution of systems properties with $d$ may not be smooth. Finite-dimensional effects could dramatically change what happens in physical dimensions, $d = 3$. For standard phase transitions finite-dimensional effects are typically captured by renormalization group methods, but for glasses the corrections are much more subtle and only partially understood. Here, we investigate hopping between localized cages formed by neighboring particles in a model that allows to cleanly isolate that effect. By bringing together results from replica theory, cavity reconstruction, void percolation, and molecular dynamics, we obtain insights into how hopping induces a breakdown of the Stokes–Einstein relation and modifies the mean-field scenario in experimental systems. Although hopping is found to supersede the dynamical glass transition, it nonetheless leaves a sizable part of the critical regime untouched. By providing a constructive framework for identifying and quantifying the role of hopping, we thus take an important step toward describing dynamic facilitation in the framework of the mean-field theory of glasses.

activated processes | random first-order transition | cavity method

Glasses are amorphous materials whose rigidity emerges from the mutual caging of their constituent particles—be they atoms, molecules, colloids, grains, or cells. Although glasses are ubiquitous, the microscopic description of their formation, rheology, and other dynamical features is still far from satisfying. Developing a more complete theoretical framework would not only resolve epistemological wrinkles (1), but also improve our material control and design capabilities. However, such a research program remains fraught with challenges. Conventional paradigms based on perturbative expansions around the low-density, ideal gas limit (for moderately dense gases and liquids) or on harmonic expansions around an ideal lattice (for crystals) fail badly. Because dense amorphous materials interact strongly, low-density expansions are unreliable, whereas harmonic expansions lack reference equilibrium particle positions. These fundamental difficulties must somehow be surmounted to describe the dynamical processes at play in glass formation.

A celebrated strategy for studying phase transitions is to consider first their mean-field description, which becomes exact when the spatial dimension $d$ of the system goes to infinity (2), before including corrections to this description. In that spirit, we open the spatial dimension $d$ to infinity (“ideal”) random first-order transition (iRFOT) scenario, which, based on the analysis of simple models, brings together static- (3–5) and dynamics-based (mode-coupling) (6) results for glass formation (reviews in refs. 7 and 8) (8–11). In iRFOT, an infinitely slowly cooled simple liquid (or compressed hard sphere fluid) becomes infinitely viscous, i.e., forms a glass in which particles are completely caged, at the critical dynamical transition temperature $T_d$ (or packing fraction $\rho_d$). Upon approaching this transition, cage hopping breaks the diffusivity $D$ vanishing as a power-law $D \sim (T - T_d)^\gamma$, and the viscosity diverges as $\eta \sim (T - T_d)^{-1}$. Hence, in the critical regime one expects the Stokes–Einstein relation (SER) between transport coefficients, $D \sim \eta^{-1}$, to hold. In short, the $d \to \infty$ scenario is characterized by (i) a sharp dynamical glass transition associated with perfect caging, (ii) a power-law divergence of $\eta$, and (iii) the SER being obeyed.

As observed in ref. 12, the phenomenology of finite-dimensional systems is, however, quite different from the iRFOT scenario. In particular, it does not recapitulate elementary experimental observations, such as Vogel–Tammann–Fulcher (VTF) viscosity scaling in fragile glasses, $\eta \sim e^{B_{\text{CTF}}/(T - T_0)}$ ($B_{\text{CTF}}$ and $T_0$ are phenomenological constants), and breakdown of the SER, $D \sim \eta^{-1+\omega}$ (phenomenologically $\omega > 0$) (13–16). As a result, the relevance of the iRFOT picture for experimental systems remains the object of lively debates.

Part of the difficulty of clarifying the situation in finite $d$, where the iRFOT description is only approximate and the dynamical transition is but a crossover, lies in the shear number of different contributions one has to take into account. From a purely field-theoretic point of view, one has to include finite-dimensional corrections to critical fluctuations. A Ginzburg criterion gives $d_g = 8$ as the upper critical dimension for the dynamical transition (17–20), and hence for $d < d_g$ critical fluctuations renormalize the power-law scaling exponents. In principle, these corrections could be captured by a perturbative $d_g - d$ expansion, and phenomenological arguments along this direction indicate that they could also induce a SER breakdown (17). A number of non-perturbative processes in $1/d$ must additionally be considered: (i) In the iRFOT picture, caging is perfect, and hence in the glass phase each particle is forever confined to a finite region of space delimited by its neighbors (6). However, it has been theoretically proved (21) and experimentally observed (22) that in low-dimensional systems the diffusivity is never strictly zero. Single particles can indeed hop between neighboring cages (23–26),

Significance

Like crystals, glasses are rigid because of the self-caging of their constituent particles. The key difference is that crystal formation is a sharp first-order phase transition at which cages form abruptly and remain stable, whereas glass formation entails the progressive emergence of cages. This loose caging complicates the description of the glass transition. In particular, an important transport mechanism in this regime, hopping, has thus far been difficult to characterize. Here we develop a completely microscopic description of hopping, which allows us to clearly assess its impact on transport anomalies, such as the breakdown of the Stokes–Einstein relation.
and the free space they leave behind can facilitate the hopping of neighboring particles. Facilitation can thus result in cooperative hopping and avalanche formation (27–29). (ii) For some glass formers, activated crystal nucleation cannot be neglected and interferes with the dynamical arrest, leading to a glass composed of microscopic geometrically frustrated crystal domains (30). (iii) In the iRFOT scenario, the dynamical arrest is related to the emergence of a huge number of distinct metastable glass states whose lifetime is infinite. In finite dimensions, however, a complex glass–glass nucleation process gives a finite lifetime to these metastable states (5, 12, 31). The dynamics of glass-forming liquids are then profoundly affected. Including glass–glass nucleation into iRFOT leads to the complete RFOT scenario (12), in which the mean-field dynamical glass transition becomes a crossover (12), and both the VTF scaling and facilitation can be recovered (32, 33).

Because the treatment of these different processes has thus far been mostly qualitative, their relative importance cannot be easily evaluated. A controlled first-principle, quantitative treatment is for the moment limited to the exact solution for $d \to \infty$ (10, 11, 34, 35). Its approximate extension to finite $d$ (6, 8, 36) completely ignores the nonperturbative effects mentioned above. This approach therefore cannot, on its own, cleanly disentangle the various corrections. Systematic studies of glass formation as a function of $d$ have encouragingly shown that these corrections are limited even down to $d = 3$ (15, 16, 37–40), provided length and timescales are not too large, as is typical of numerical simulations and experiments with colloids and grains. In particular, with increasing $d$ the distribution of particle displacements (the self-van Hove function) loses its second peak associated with hopping (16), the critical power-law regimes lengthen (41), and the SER breakdown weakens (15, 16, 40), which motivates investigating corrections to iRFOT in a controlled way.

Here we develop a way to isolate the simplest of these corrections, i.e., hopping, by studying a finite-dimensional mean-field model. Through the use of the cavity reconstruction methodology developed in the context of spin glass and information theory (42), we carefully describe caging, using self-consistent equations that can be solved numerically. We can thus compute the cage width distribution and isolate hopping processes. Our results provide an unprecedentedly clear view of the impact of hopping on the dynamical transition and on the SER breakdown in simple glass formers.

**MK Model**

We consider the infinite-range variant of the hard sphere(s) (HS)-based model proposed by Mari and Kurchan (MK) for simple structural glass formers (43–45) (details in SI Text, section I.A). The key feature of the MK model is that, even though each sphere has the same diameter $\sigma$, pairs of spheres interact via an additional constant shift that is randomly selected over the full system volume. This explicit quenched disorder eliminates the possibility of a constant shift that is randomly selected over the full system volume. Because the treatment of these different processes has thus far been mostly qualitative, their relative importance cannot be easily evaluated. A controlled first-principle, quantitative treatment is for the moment limited to the exact solution for $d \to \infty$ (10, 11, 34, 35). Its approximate extension to finite $d$ (6, 8, 36) completely ignores the nonperturbative effects mentioned above. This approach therefore cannot, on its own, cleanly disentangle the various corrections. Systematic studies of glass formation as a function of $d$ have encouragingly shown that these corrections are limited even down to $d = 3$ (15, 16, 37–40), provided length and timescales are not too large, as is typical of numerical simulations and experiments with colloids and grains. In particular, with increasing $d$ the distribution of particle displacements (the self-van Hove function) loses its second peak associated with hopping (16), the critical power-law regimes lengthen (41), and the SER breakdown weakens (15, 16, 40), which motivates investigating corrections to iRFOT in a controlled way.

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the cavity reconstruction formalism to relax both assumptions (42). Above $\phi_d$, we can build the equilibrated neighborhood of particle $i$ to self-consistently determine the overall cage size and/or shape distribution $P_j(\Delta)$ (details in SI Text, section II.A). The process involves placing Poisson-distributed neighbors $j$ that are randomly assigned a cage size $\Delta_i$ from a prior guess of $P_j(\Delta)$, with a fixed function shape $f_{hi}(r)$ (a Gaussian or a ball function, for instance). Averaging over the vibrational relaxation of each neighboring particle gives the cavity field $\psi (r)$ felt by particle $i$, which is the probability density of the particle being at position $r$ (Fig. 2A). The existence of a cage centered around $i$ is guaranteed by the cavity reconstruction procedure. The variance $\langle \Delta^2 r \rangle = \langle r^2 \rangle - \langle r \rangle^2$ associated with the evolution of particle $i$ within this cage, which can be computed through simple Monte Carlo sampling, provides the posterior caging radius $\Delta_i$. Sufficient repeats of this determination provide a new estimate of $\hat{P}_j(\Delta)$, and iterating the overall procedure eventually converges to a fixed-point distribution $P_j(\Delta)$. We find that both Gaussian and ballistic caging functions give the same size distribution $P_j(\Delta)$ (Fig. 2B) and that $P_j(\Delta)$ is reasonably well approximated by a gamma distribution for all $\phi > \phi_d$ (Fig. 2C). The average cage size $\Delta$ also quantitatively agrees with the analytical prediction of refs. 8 and 45 (Fig. 2D), including its characteristic square-root singularity upon approaching $\phi_d$, i.e., $\Delta(\phi_d) \sim \sqrt{\phi - \phi_d}$. We thus conclude that the theoretical prediction of $\Delta$ and $\phi_d$ is fairly insensitive to both the caging form and the second (or higher) moments of the cage size distribution, as well as to the theoretical method chosen (SI Text, section II.A).

It follows that deviations from the $d \to \infty$ scenario ought to be ascribed to an imperfect caging above $\phi_d$ in finite-dimensional systems. Microscopically, these imperfections correspond toparticle trapped for a finite time before escaping to another cage through a narrow passage (Fig. 3A). Because the above calculations solely consider single-cage forms, a fixed-point distribution $P_j(\Delta)$ can only be reached by removing these “hopping” segments of the particle trajectories (details in SI Text, section II.A).

Not only does $\phi_d$ then appear at higher densities, but as long as the network of connected cages percolates, dynamical arrest is also formally impossible. In that context, it is interesting to note that for a prior $P_j(\Delta) = \delta(\Delta)$, the first iteration of the cavity reconstruction formalism is analogous to the void (Swiss-cheese) percolation setup for a Poisson process (49). In addition, for a nontrivial distribution of cage sizes, thresholding volume exclusion maps cavity reconstruction onto void percolation for polydisperse spheres (50) (SI Text, section II.C). This equivalence between cavity reconstruction and void percolation sheds light on the single-cage assumption. In the iRFOT description, the MSD of each particle should remain finite when $\phi > \phi_p$, but by construction the MSD can be truly bounded only if (minimally) $\phi > \phi_p$, the void percolation transition.

From MD simulations of the MK model, we detect the first hopping event of each particle (details in SI Text, section III.A). Around $\phi_d$, mode-coupling and hopping processes mix, but hopping quickly dominates the dynamics upon increasing $\phi$. Although the hopping of a particle does not leave an empty void in the MK model, it can nonetheless unblock a channel for a neighboring particle to leave its cage and hence facilitate its hopping. Facilitation is thus present, but weaker than in standard finite-dimensional HS, especially at high densities.
facilitation is notably signaled by the fact that the distribution of hopping times computed from a regular MD simulation largely coincides with the distribution obtained in the cavity procedure, where a single particle hops in an environment where neighboring particles are forbidden to do so (Fig. 3B, Inset). We find the cumulative distribution of hopping times over the accessible dynamical range to be well described by a power law $G_h(t) = (t/\tau_h)^{-\mu}$ (Fig. 3B), with the characteristic hopping time $\tau_h$ increasing roughly exponentially with $\phi > \phi_d$ and markedly increasing with $d$ (Fig. 3D). This Arrhenius-like scaling form is consistent with a gradual and uncorrelated narrowing of the hopping channels with $\phi$. Note that similar phenomenological power-law distributions have recently been reported for other glass-forming systems, such as the bead-spring model for polymer chains (51). We get back to this point in Conclusions.

Finite-Dimensional Phase Diagram

A clear scenario for hopping in the MK model follows from this analysis (Fig. 4). Dynamically, the system becomes increasingly sluggish upon increasing $\phi$ above $\phi_{\text{d,net}}$. Initially, cages are not well formed and the slowdown exhibits a power-law scaling, according to the iRFOT critical predictions. Hopping cannot be defined because cages are too loose. Upon approaching $\phi_0$, however, cages become much longer lived. In this regime, iRFOT predictions give a rapidly growing $\tau_D$, but hopping processes allow particles to escape their cages and diffuse, hence providing a cutoff to the critical divergence of $\tau_D$. The critical-like behavior of the diffusivity is also pushed to denser cages. The critical density $\phi_d$ of iRFOT corresponds to the emergence of a connected network of cages. Typical networks for $\phi_0 > \phi > \phi_d$ span the system volume. When $\phi > \phi_d$, they become finite and the mean network volume $V_{\text{net}}$ (sum of cage volumes in the network) follows a critical scaling from standard percolation (Fig. 4B). Based on this analysis, in the absence of facilitation the dynamical arrest should take place at $\phi_d$ (53). Note that although above $\phi_d$, the single-particle MSD is bounded, a particle can still explore a finite number of cages. Perfect single-cage trapping can be found at $\phi \to \infty$ only in finite $d$. Hopping is then infinitely suppressed because both the width and the number of hopping channels between cages vanish. However, even if hopping interferes with caging, well above $\phi_d$, vibrational relaxation within the cage is sufficiently quick to numerically distinguish it from hopping. This large separation of timescales enables the facile detection of hopping in MD simulations and cavity reconstruction. However, upon approaching $\phi_d$, the task becomes acutely sensitive to the arbitrary thresholding inherent to any hopping detection algorithm (22, 54) (details in SI Text, section III.A).

As expected from the exactness of the iRFOT description in $d \to \infty$, $\phi_d/\phi_0 \to 1$ with increasing $d$. Both $\tau$ and $\gamma$ also appear to converge to the $d = \infty$ value (Fig. 1B) (34). Because $\phi_0 < \phi_d$ for all $d$, the suppression of hopping with increasing $d$ (Fig. 1D, Inset) ought to be ascribed either to the narrowing of the hopping channels or to topological changes to the cage network. Because the pressure at the dynamical transition increases only slowly with a fitting parameter associated to an effective power-law divergence of $\tau_D$. In fact, the MK dynamical data are better fitted by a VTF form than by the critical power law (Fig. 4A), although the fitting parameter $\phi_0$ has no direct static interpretation because it is intermediate between $\phi_d$ and $\phi_c$.

The dynamics can also be understood from the organization of cages. The critical density $\phi_d$ of iRFOT corresponds to the emergence of a connected network of cages. Typical networks for $\phi_0 < \phi < \phi_d$ span the system volume. When $\phi > \phi_d$, they become finite and the mean network volume $V_{\text{net}}$ (sum of cage volumes in the network) follows a critical scaling from standard percolation (Fig. 4B). Based on this analysis, in the absence of facilitation the dynamical arrest should take place at $\phi_d$ (53).
their cross section remains constant) cover a vanishingly small therefore such that the hopping channels (even assuming that the cage network fractality takes place through the single-point consistent with the distance from terestingly, for HS, distant, as is observed in many other glass formers (55, 56). In- regime, we obtain a power-law scaling that is consistent with the pure critical iRFOT (or mode-coupling) regime. Within this a larger dimensional dependence. The cage network at percola-}

Fig. 5. (A) Dimensional rescaling of the SER (black) and SER breakdown regimes for standard finite-dimensional HS. The early deviation exponent \( \omega \) is consistent with hopping in the MK model with \( \omega = 0.22 \) (red line, Fig. 10), but a growing devi- ation is observed as \( \phi \) increases. (B) The dimensional scaling of HS results for \( \Phi_\text{SER} \), \( \Phi_\text{iRFOT} \), and \( \Phi_\text{SER} \) converges as \( d \) increases, whereas \( \Phi_\text{var} \) remains distinctly smaller (compare with Fig. 1C). Note that in \( d = 8 \), \( \Phi_\text{iRFOT} \), \( \Phi_\text{SER} \), and \( \Phi_\text{var} \) are numerically indistinguishable. (Inset) Dimensional evolution of \( \gamma \) and \( \beta \), both of which are consistent with the \( d = \infty \) result (dashed line). Solid lines are guides for the eye.

dimension \( (p_\mathrm{d} \sim d) \), the typical channel width is expected to stay roughly constant. The topology of the cage network, however, has a larger dimensional dependence. The cage network at percola- for instance, has a fractal dimension \( d_1 \ll d \) (52); e.g., \( d_1 = 4 \) for \( d \geq 6 \). Although this result is valid only at \( q_\text{var} \) proper, the local network structure persists at smaller \( q_\text{var} \) because the loss of the cage network fractality takes place through the single-point inclusion of nonpercolating clusters (52). The network topology is therefore such that the hopping channels (even assuming that their cross section remains constant) cover a vanishingly small fraction of the cage surface as \( d \) increases. The limited number of ways out of a local cage thus entropically suppresses hopping.

**SER Breakdown**

With hopping events clearly identified, it becomes possible to isolate the pure critical iRFOT (or mode-coupling) regime. Within this regime, we obtain a power-law scaling that is consistent with \( \phi_\mathrm{d} \) (details in SI Text, section II.B), and the SER is followed. Devi- iations from the extrapolated critical scaling coincide with the SER breakdown in all \( d \). Although \( \phi_\text{var} \) occurs at a roughly constant distance from \( q_\text{var} \), the SER breakdown occurs in systems that are increasingly sluggish with \( d \), \( \Phi_\text{SER} \rightarrow \Phi_\text{var} \), and thus properly converges to the idealized mean-field behavior as \( d \rightarrow \infty \). In the MK model, the SER breakdown is thus clearly due to hopping.

By modifying the cavity reconstruction analysis, a self-consis- tently determined interparticle gap \( d_\text{var} \) should also be possible for standard finite-dimensional HS. We do not attempt such a computation here, but instead use the insights gained from the MK model to associate the SER breakdown in HS with hopping. We fit the dynamical data from the regime over which the SER is constant to the idealized mean-field behavior as \( d \rightarrow \infty \). Although this result is valid only at \( q_\text{var} \) proper, the local network structure persists at smaller \( q_\text{var} \) because the loss of the cage network fractality takes place through the single-point inclusion of nonpercolating clusters (52). The network topology is therefore such that the hopping channels (even assuming that their cross section remains constant) cover a vanishingly small fraction of the cage surface as \( d \) increases. The limited number of ways out of a local cage thus entropically suppresses hopping.

**Conclusions**

We have numerically and theoretically studied a model glass former in which it is possible to isolate hopping from the critical mode-coupling dynamical slowing down and in which no other dynamical effects are present besides these two. The results illuminate the key role played by hopping in suppressing the iRFOT dynamical transition in finite \( d \) and in breaking the SER scaling. The MK model gives an example where single-particle hopping is sufficient to cause the SER breakdown, but in HS facilitation likely amplifies the effect, which may explain the dependence of \( \omega \) on density (Fig. 5) (57).

For standard finite-dimensional HS and other structural glass formers, we expect the situation to be made more complex by the other dynamical processes mentioned in the Introduction. One might then conjecture the existence of at least three dynamical regimes for glass formers, upon increasing density: (i) an iRFOT/ mode-coupling regime below \( \phi_\text{SER} \); (ii) a MK-like hopping re- gime around \( \phi_\text{SER} \), where hopping is the dominant correction to the iRFOT description, the mode-coupling critical scaling holds, but the apparent mode-coupling transition shifts to higher densi- ties and the effective exponent \( \gamma \) changes, and the SER breakdown is incipient (in this regime the hopping timescale increases (exponen- tially) quickly with density (Fig. 3D)); we expect this increase to be similar for HS and MK liquids, because the probability of finding a neighboring cage is roughly \( \exp(-q) \) for both models; and (iii) at yet higher densities, hopping becomes too slow and other dynamical effects likely become important. If glass–glass nucleation barriers do not grow as quickly as the hopping barriers, then these processes may eventually become the dominant relaxation mechanism, following the RFOT prediction (5, 12, 31).

In this regime (and hence in deeply supercooled liquids much below \( T_\text{g} \)) the VTF law and the associated Adam–Gibbs relation should be reasonably well obeyed. Note that other processes such as cooperative hopping dressed by elasticity might also occur in this regime (26). Note also that these different regimes are probably not separated by sharp boundaries in realistic systems, and hence all these relaxation processes might coexist, making their identifi- cation quite challenging.

We also stress, in line with previous studies, that VTF fits of the structural relaxation time in regimes i and ii should not be used to extract the putative Kauzmann transition point. In our opinion it makes no sense to test the Adam–Gibbs relation in these dynamical regimes. In the MK model, although the VTF law can be used to fit the dynamical data, there is no associated Adam–Gibbs relation and thus \( \phi_\text{var} \) has no thermodynamic meaning. In particular, \( \phi_\text{var} \) is not associated with a Kauzmann transition [since in the MK model \( \phi_\text{var} \) only at \( \phi = \infty \) (44)]. This observation is particularly important for numerical simulations and experiments on colloids and granular systems, which are most often performed in the vicinity of \( \phi_\text{var} \) and \( \phi_\text{SER} \) and hence are found within the first two regimes.

Finally, we note that the MK model could also serve as a test bench for descriptions of hopping (24, 25, 58), as well as for re- lating percolation and glass physics more broadly (59). These studies may further clarify other finite-dimensional effects, such as the correlation observed between local structure and dynamics (30).

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