Criteria of amorphous solidification

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A different perspective on the long-standing problem of amorphous solidification is offered, based on an alternative definition of a solid as a porous medium. General, model-free results are obtained concerning the growing dynamic length accompanying solidification and its relation to the growing relaxation time. Criteria are derived for the dynamic length to diverge and for its divergence to entail the arrest of particle motion.

I. INTRODUCTION

Despite the ubiquity of amorphous solids around us, the nature of the transition from a liquid state to an amorphous solid (the glass transition) remains one of the outstanding problems in condensed-matter and chemical physics. After decades of research [1–11], the situation is still confusing, especially in the theoretical respect [10, 12]. It is unclear whether the transition is caused by thermodynamic (entropic) effects or by kinetic constraints, whether or not it is accompanied by a divergent length scale, and what symmetry, if any, is broken when the material solidifies. We shall not attempt to give here a balanced summary of all existing theories; the reader is referred to a host of recently published books and review articles on the subject [1–11]. We note only that the various theories span a broad conceptual range—from attempts to unravel purely structural regularities in the disordered solid [13, 14], all the way to describing the transition as a symmetry breaking along purely temporal trajectories [6], and other approaches in-between these two extremes.

In this state of affairs it seems constructive to pose a few modest but essential questions and try to answer them as definitely as possible on a general, model-free level. This is the goal of the current contribution. The following analysis is based on the assumption, which is in consensus, that amorphous solidification, unlike crystallization, is a continuous transition, lacking any sharp changes in the material’s state variables. In particular, the solidifying material is assumed to have a structural correlation length, \( \xi \), which does not appreciably change through the transition. Based on this minimal premise, we shall obtain several general criteria that are required for an amorphous solid to form.

II. GROWING DYNAMIC LENGTH

Approaching amorphous solidification involves an enormous increase, and possibly divergence, of the liquid’s relaxation time, \( \tau_c \). (Some have argued that an amorphous solid is nothing but a tremendously slow liq-

1 “The so-called amorphous solids are either not really amorphous or not really solid.” (E. Schrödinger) [12].

2 It has recently been argued that the divergence of the viscosity, rather than the nonvanishing of the shear modulus, is the more accurate criterion of solidity [24].
to be much smaller than the material’s steady global viscosity, \( \eta \ll \eta(k = 0) \). (The discussion focuses hereafter on the zero-frequency limit; therefore, we omit it and keep reference to the wavevector \( k \) alone.) We include momentum exchange between the two components via friction (e.g., applying stick boundary conditions) at the surfaces of the particles. To examine the state of a material, consider the following thought experiment. Go to a volume element of the pervading fluid, apply to it a steady point force \( F \) (assumed sufficiently weak to cause a strictly linear response), and measure the resulting steady fluid velocity \( v \) at a very large distance \( r \gg \xi_s \). If the composite moves coherently there, the fluid flowing together with the particulate matrix, the material is a liquid; if the fluid moves relative to the matrix, the material is a solid. This definition may seem awkward, but it will serve our purpose well. In addition, (a) the alternative definition and the mechanical one are equivalent, as shown below; and (b) the alternative definition readily reveals a broken symmetry associated with amorphous solidification—the Galilean invariance of the pervading fluid.

In more detail, up to the two leading terms in large \( r/\xi_s \), the fluid velocity at \( r \) reads

\[
v = v_1 + v_2
\]

\[
v_1 = \frac{1}{4\pi \eta(0)r} F, \quad v_2 = \frac{\xi^2}{2\pi \eta_r v_3} F,
\]

where, for the sake of concreteness, we have taken \( v \) as the fluid’s velocity component parallel to \( F \). These expressions are of general validity, holding for any viscous fluid embedded in a more rigid, but still fluid, isotropic structure. They stem from the conservation laws of momentum (of the entire composite) and mass (of the pervading fluid) \[25\, 27\]. The first term, \( v_1 \), dominates at very large distances. It describes the global response of the composite as a whole to \( F \). Its spatial \( 1/\eta(0)r \) decay follows from conservation of the momentum emanating from the momentum source \( F \). The second term, \( v_2 \), is the leading correction to \( v_1 \). It describes the flow of the fluid through the embedding structure at smaller (but larger than \( \xi_s \)) distances. Its \( \xi^2/\eta_r v_3 \) dependence arises from the displacement of fluid mass (effective mass dipole), caused by \( F \) within the “pore” size \( \xi_s \). If the structure becomes a stationary porous matrix for the embedded fluid, only \( v_2 \) survives \[23\, 26\, 28\], reflecting the loss of translation invariance (equivalently, momentum conservation) of the embedded fluid. Under the condition that \( \xi_s \) remain finite, this occurs if and only if \( \eta(0) \to \infty \), as demanded by the mechanical definition of a solid\[4\]

The two terms in Eq. (1) become equal at the distance \( \xi_c = \xi_s [\eta(0)/\eta_1]^{1/2} \). This distance separates two different dynamic regions. In the “porous region”, \( \xi_c \ll r \ll \xi_s \), the fluid flows relative to the matrix and imparts momentum to it through friction. In the “coherent region”, \( r \gg \xi_c \), there is bidirectional momentum exchange between the two components, and they flow together as a momentum-conserving composite. The existence of these two regions, together with the associated crossover distance, has been demonstrated experimentally and theoretically for entangled polymer networks in solution \[27\]. (There is also a small-scale, “intra-pore” region, \( r \ll \xi_s \), where the fictitious fluid flows without interacting with the matrix.)

To just determine whether the material is solid or liquid, according to the symmetry breaking introduced above, we need not specify the properties of the fictitious fluid. However, to get more details about \( \xi_c \), we must relate the hitherto unspecified \( \eta_1 \) to the material properties. The dynamics of the actual material has an upper wavevector cutoff, \( k_{\text{max}} \sim \xi_s^{-1} \). Since the pervading fluid is a continuum, the dynamics of the composite does not have this cutoff, and in the “intra-pore” region \( \eta(k > k_{\text{max}}) = \eta_s \). We thus set \( \eta = \eta(k = k_{\text{max}}) \) to get the simplest continuous extrapolation of the material’s viscosity to large wavevectors. (The requirement \( \eta_s \ll \eta(0) \) is consequently translated to the requirement that the small-scale viscosity of the material be much smaller than the large-scale one, \( \eta(k_{\text{max}}) \ll \eta(0) \) — a condition that is met by glass-forming liquids; see, e.g., Fig. \[4\].) This implies the following relation for the dynamic length in terms of the actual material properties\[4\]

\[
\xi_c = \xi_s \left[ 2 \frac{\eta(0)}{\eta(k_{\text{max}})} \right]^{1/2} = \xi_s \left[ 2 \frac{\tau_c}{\tau(k_{\text{max}})} \right]^{1/2},
\]

where \( \tau_c \) is the global relaxation time, \( \tau(k_{\text{max}}) \) is the relaxation time of structures of order \( \xi_c \), and we have used the proportionality between viscosity and relaxation time. We propose to identify the length defined in Eq. (2) with the growing length of solidification. Since we have assumed that \( \xi_s \) does not change discontinuously through the transition, \( \xi_c \) increases continuously with increasing \( \eta(0)/\eta(k_{\text{max}}) = \tau_c/\tau(k_{\text{max}}) \). Physically, the length \( \xi_c \) thus defined corresponds to the size of cooperative particle structures, submerged in a background of noncooperative particles, such that the two move relative to one another. In other words, \( \xi_c \) is the characteristic size of a dynamic heterogeneity.

We are now faced with two possibilities, depending on the increase of the large-scale relaxation time relative to the small-scale one. If \( \eta(0) \) increases more sharply than

\[3\] Another possibility to have \( v_1 \) lose ground to \( v_2 \) at large distances, is that \( \xi_s \) grows indefinitely, as in a thermodynamic second-order phase transition. This does not correspond to solidification but to the critical slowing down of relaxation in such systems \[23\, 26\].

\[4\] Essentially, the fictitious fluid has been replaced now by the material’s lower-viscosity, small-scale flow. Separating the solidifying material into two fluids is not a new idea \[23\, 41\].
\( \eta(k_{\text{max}}) \) as the transition is approached, then \( \xi_c \) will diverge; if they become proportional to one another (probably with a large proportionality factor), \( \xi_c \) will remain finite. The former possibility corresponds to indefinitely growing “porous” regions, with the small-scale dynamics remaining liquid-like; the latter describes slowing down of the entire material at all scales. As neither possibility can a priori be favored or excluded, the divergence of \( \tau_c \) is not necessarily accompanied by a divergent \( \xi_c \).

Far from the transition, we expect from Eq. (2) to have \( \xi_c \sim \tau_c^{-1/2}, \ z = 2 \). As solidification is approached, however, the relaxation at small length scales must become increasingly slow too, making the ratio \( \eta(0)/\eta(k_{\text{max}}) \), and with it \( \xi_c \), increase much more moderately. These results are in line with the observations mentioned above [18–20].

Let us examine the wavevector-dependent viscosity of the material for \( 0 < k < k_{\text{max}} \). The function \( \eta(k)/\eta(0) \) decreases from unity, its value in the limit \( k \to 0 \), to \( (2\xi_c/\xi_s)^2 \sim (k_{\text{max}}\xi_c)^{-2} \), its value at \( k = k_{\text{max}} \) as given by Eq. (2). There are two characteristic length scales, \( \xi_s \) and \( \xi_c \), of which \( \xi_c \) provides the upper wavevector cutoff, leaving us with \( \xi_s \) alone. Thus, we can write in general,

\[
\eta(k)/\eta(0) = f(k\xi_c), \quad \text{where} \quad f(x) \text{ is an unknown scaling function.}
\]

(The ability to collapse various wavevector-dependent dynamic properties, once expressed as functions of \( k\xi_c \), onto a master curve has been demonstrated in various studies.) Assuming \( \xi_c \gg \xi_s \), we obtain two physically relevant ranges of \( k \): (i) \( k \ll \xi_c^{-1} \); and (ii) \( \xi_c^{-1} \ll k \ll k_{\text{max}} \). These two ranges correspond, respectively, to the large-distance, “coherent” behavior and the smaller-distance, “porous” one, discussed above. To interpolate between the two limits, \( k = 0 \) and \( k = k_{\text{max}} \), without introducing a third regime, we must set in range (ii) \( f(k\xi_c) \sim (k\xi_c)^{-2} \). In summary, then,

\[
\eta(k)/\eta(0) \sim \begin{cases} 1, & k \ll \xi_c^{-1} \\ (k\xi_c)^{-2}, & \xi_c^{-1} \ll k \ll k_{\text{max}}. \end{cases} \tag{3}
\]

In Fig. 1 we reproduce simulation results for \( \eta(k)/\eta(0) \) in a supercooled binary Lennard-Jones liquid [32]. As the transition is approached, the curves have a broader range of \( k \) where the viscosity ratio seems to scale as \( k^{-2} \), in accord with Eq. (3).

III. MOTION ARREST

From the preceding section we conclude that, if \( \xi_c \) happens to diverge, so does \( \tau_c \), and the material must solidify, whereas the opposite direction is incorrect—if \( \tau_c \) diverges, a divergent \( \xi_c \) is not necessarily implied.

There is yet another issue to consider. If a system exhibits cooperative motion of arbitrarily many particles, must the associated divergent length coincide with \( \xi_c \) of the preceding section and lead to solidification? That the answer to this question is negative is evident from known counter-examples, of which we mention two:

(a) single-file diffusion — the random motion of particles along a line without bypassing one another [33]; and (b) the dynamics of a long flexible polymer chain in solution [34]. In both examples the large-distance motion of a constituent particle requires cooperative motion of an arbitrarily large number of other particles. The particles in these systems are even distinguishable — a broken symmetry previously suggested as a criterion of solidity [22, 23, 31]. Yet, these systems are obviously not solid. Their cooperativity leads to subdiffusion rather than freezing. In single-file diffusion the mean-square displacement (MSD) of a particle scales with time as \( \langle \Delta r(t) \rangle \sim t^{1/2} \); the MSD of a monomer in an ideal polymer chain scales, respectively, as \( t^{1/2} \) or \( t^{3/2} \) for Rouse or Zimm dynamics (i.e., excluding or including hydrodynamic interactions). Thus, over a sufficiently long time, any particle in these systems can get arbitrarily far away from its initial position — a characteristic of a fluid, not a solid.

The natural fourth question, therefore, is what criterion an indefinitely growing dynamic heterogeneity should satisfy to ensure arrest of particle motion. To answer this last question we employ an additional assumption — that the divergent dynamic length is accompanied by dynamic scaling [24, 35] — a property found also in the two examples just mentioned.

Consider a system of particles, in which a single particle undergoes subdiffusion with MSD \( \langle (\Delta r)^2 \rangle \sim t^\alpha \), \( 0 < \alpha < 1 \). We assume that the subdiffusion is caused by cooperative dynamics — i.e., at increasingly long times the motion of a single particle is determined by the cooperative motion of an increasingly large body of particles to which it belongs. Let us first consider an isolated body of \( N \) particles and spatial extent \( \xi_N \sim N^{d/d} \), where \( d \) is the body’s Hausdorff dimension. The isolated body
is embedded in a background of noncooperative particles. Under these conditions, at sufficiently long time, $t_N$, the random motion of a single particle in the body will cross over from subdiffusion to the normal diffusion of the body’s center of mass. (Such a crossover is seen, for instance, in simulations of supercooled liquids [22].) This will occur when $t_N \sim D_N t_N$, where $D_N$ is the center-of-mass diffusion coefficient. Assuming that $D_N$ decreases with size as $D_N \sim \xi_N^{-\beta/(1-\alpha)}$.

Now, instead of being isolated, let the body be part of an indefinitely large cooperative system and interact with its surroundings over a relaxation time $\tau_N \sim \xi_N^{-\beta}$. We demand that there be no crossover time for this arbitrary size $N$, such that the single-particle subdiffusion should persist at all times. We therefore equate $t_N \sim \tau_N$, which leads to the relation,

$$\alpha = 1 - \beta/z. \tag{4}$$

Before turning to the case of solidification, let us first check the validity of this scaling scheme for the cooperative but fluid systems mentioned above. In single-file diffusion, $d = 1$, $D_N \sim N^{-1} \sim \xi_N^{-1}$, and $\tau_N \sim \xi_N^{-\beta}$. Thus, $\beta = 1$ and $z = 2$, leading, according to Eq. (4), to $\alpha = 1/2$. For an ideal polymer with Rouse dynamics, we have $d = 2$, $D_N \sim N^{-1} \sim \xi_N^{-2}$, and $\tau_N \sim \xi_N^{-\beta}/D_N \sim \xi_N^{-2-\beta}$, where $\beta = 2$ and $z = 4$. This leads again, but for different reasons, to $\alpha = 1/2$. For an ideal polymer with Zimm dynamics, $D_N \sim \xi_N^{-1}$ and $\tau_N \sim \xi_N^{-2}/D_N \sim \xi_N^{-1}$. The resulting $\beta = 1$ and $z = 3$ yield $\alpha = 2/3$. Thus, the known subdiffusion exponents are correctly reproduced. (One can verify this scheme for other examples as well, e.g., self-avoiding polymers.)

In the case of solidification, which necessitates the formation of a rigid reference frame of particle positions [22], we require (on the ensemble-average level) that the long-distance motion of particles be arrested, i.e., $\alpha \rightarrow 0$. From Eq. (4) we then get the criterion of solidification as $\beta = z$, which is equivalent to $N \tau_N \sim N^0 \sim l^2$, $l$ being the size of a particle. The physical meaning of this result is that, as the material solidifies, the center-of-mass displacement of an arbitrarily sized heterogeneity before it relaxes does not extend to more than a few particle sizes.

Utilizing once again the proportionality between relaxation time and viscosity, we have

$$\frac{\eta(k)}{\eta(0)} = \frac{\tau_N(k \sim \xi_N^{-1})}{\tau_N(k \sim \xi_N^{-1} \rightarrow 0)} \sim (\xi_N k)^{-z}. \tag{5}$$

Comparison of Eqs. (3) and (5) leads to the more precise criterion,

$$\beta = z = 2, \tag{6}$$

the fulfillment of which ensures that the divergent cooperativity length coincide with the solidification length of the preceding section and lead to arrest.

Furthermore, we claim that the center-of-mass diffusion coefficient of a heterogeneity is inversely proportional to the number of particles that it contains, $D_N \sim N^{-1}$. Such Rouse-like dynamics takes place when the friction with the environment, experienced by each particle, is independent of the other particles in the object. This happens, in turn, when the propagation of stresses in the environment across the object is not fast enough relative to the object’s motion. In ordinary circumstances, where a body moves through a fast-relaxing fluid, the opposite holds. The time scale of stress propagation is $\xi_N^{-\beta}/\nu$, $\nu$ being the fluid’s kinematic viscosity, and the one related to the object’s motion is $\xi_N^{-\beta}/D_N$. Their ratio is $D_N/\nu$, which is very small unless the object is of atomic dimensions. Consequently, in this case $D_N \sim \xi_N^{-1}$, as in the Stokes-Einstein formula or the Zimm dynamics of a polymer. In our case the stress-propagation time is the same, $\xi_N^{-\beta}/\nu$, but the object’s motion is much more restricted. According to the foregoing discussion, the latter time scale is only $\tau_N \sim l^2/D_N$. The ratio, therefore, is $(\xi_N/\nu)^2(D_N/\nu) \sim (l/\xi_N)^{2-2}$.

Some of these predictions are in line with available experimental and numerical data, while others call for

IV. CONCLUSION

The conditional arguments developed here are not to be mistaken for a theory of the glass transition. For example, they do not provide information as to how the dynamic heterogeneities form, the specific properties that lead to their fractal dimension, the dependence of the transition properties on control parameters such as temperature or density, the actual value of the ratio $\eta(0)/\eta(k_{max})$ determining the divergence of $\xi$, and whether all these and other features are universal or differ from one system to the next.

Nevertheless, these arguments have yielded several concrete predictions, which we now wish to summarize. (a) The growing length scale in amorphous solidification depends on the (square-root of) the ratio between the material’s largest- and smallest-scale relaxation times. Consequently, it may or may not diverge, depending on the asymptotic behavior of that ratio as the transition is approached. This finding implies also that different glassy systems may behave qualitatively differently. (b) For $k > \xi^{-z}$, the wavevector-dependent viscosity (and relaxation time) scales as $\eta(k)/\eta(0) \sim (k\xi)^{-z}$ with $z = 2$. (c) In case of a divergent $\xi$, the dynamic exponents, characterizing the relaxation time and center-of-mass diffusion coefficient of dynamic heterogeneities, are equal, $z = \beta = 2$, and the heterogeneities’ Hausdorff dimension is 2.

Selecting $\alpha \rightarrow 0$ includes also logarithmic creeping.
further study — in particular, those pertaining to the divergence of the dynamic length. On the one hand, the successful dynamic scaling might indicate a divergent $\xi_c$. On the other hand, if the transition is found to be a genuine dynamic criticality, a more accurate analysis (e.g., concerning the critical exponents) will be called for. Most of all, we hope that the general results obtained here are found useful when a widely accepted molecular theory of amorphous solidification emerges and its validity is checked.

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