Grain boundaries exhibit the dynamics of glass-forming liquids

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Poly-crystalline materials are composites of crystalline particles or “grains” separated by thin “amorphous” grain boundaries (GBs). Although GBs have been exhaustively investigated at low temperatures, at which these regions are relatively ordered, much less is known about them at higher temperatures, where they exhibit significant mobility and structural disorder and characterization methods are limited. The time and spatial scales accessible to molecular dynamics (MD) simulation are appropriate for investigating the dynamical and structural properties of GBs at elevated temperatures, and we exploit MD to explore basic aspects of GB dynamics as a function of temperature. It has long been hypothesized that GBs have features in common with glass-forming liquids based on the processing characteristics of polycrystalline materials. We find remarkable support for this suggestion, as evidenced by string-like collective atomic motion and transient caging of atomic motion, and a non-Arrhenius GB mobility describing the average rate of large-scale GB displacement.

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Fig. 1. Illustration of string-like cooperative atomic motion within a GB. (A) Schematic microstructure of polycrystalline metal. Different colors indicate the individual grains having different orientations, and the black line segments represent GBs. (B) Equilibrium boundary structure projected onto the x-z plane for a $\theta = 40.23^\circ$ [010] general tilt boundary at $T = 900$ K ($x$, $y$, and $z$ axes are lab-fixed Cartesian coordinates, whereas [100], [010], and [001] refer to crystallographic axes). Upper and lower grains rotate relatively to each other by $40.23^\circ$ along the common tilt axis [010]. The misorientation angle $\theta = 40.23^\circ$ does not correspond to a special $\Sigma$ value ($\Sigma$ refers to the ratio of the volume of the coincidence site lattice (CSL) to the volume of crystal lattice). The atoms are colored according to their coordination numbers $q$ (orange, $q = 12$; others, $q < 12$). The simulation cell was chosen to have the GB plane normal to the $z$ axis. (C) Representative string within GB plane. Yellow and blue spheres represent the atoms at an initial time $t = 0$ and a later time, $t^\ast$. (D) Snapshot of string-like cooperative motion within the GB region at $T = 900$ K at $\Delta t = t^\ast$. The rectangular box illustrates the simulation cell in the $x$-$y$ plane. Biaxial strain $\varepsilon_{xx}$ and $\varepsilon_{yy}$ are applied to $x$-$y$ plane to induce driving force that arises from the elastic energy difference between two grains, as shown in the diagram above the box.

common superlattice can be defined if the adjacent crystal lattices are formally allowed to interpenetrate each other. This lattice is called a CSL (3), and the corresponding GB is characterized by a “coincidence number” $\Sigma$, the ratio of the volumes of the CSL and individual grain lattice cells. For most misorientation angles, there is no CSL, but there is a countable infinity of the CSL and individual grain lattice cells. For most misorientation angles, there is no CSL, but there is a countable infinity of the CSL and individual grain lattice cells. For most misorientation angles, there is no CSL, but there is a countable infinity of the CSL and individual grain lattice cells.

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For the GB region at $T = 900$ K at $\Delta t = t^\ast$, the elastic free energy of each grain (the crystals are elastically anisotropic) and a thermodynamic driving force for GB displacement. Computation details were described in our previous articles (21, 22).

Cooperative particle motion within the GB. Cooperative particle dynamics is one of the most characteristic features of the dynamics of GF fluids. In particular, both atomistic simulations and experiments on colloidal and granular fluids demonstrate that this cooperative motion takes the form of string-like motion (23–26). To examine whether a similar dynamics occurs in the GB regions of polycrystalline materials, we apply methods originally developed to identify this type of motion in GF liquids (23) to our MD simulations of GB atomic dynamics. As a first step in identifying the collective particle motion, we identify the “mobile” atoms in our system (i.e., those that move a distance in a time $\Delta t$ that is larger than the typical amplitude of an atomic vibration but smaller than the second nearest-neighbor atomic distance). Because there are no defects in either crystal, the average displacement of the atoms within the grains after any $\Delta t$ is within the scale of the mean vibrational amplitude. Therefore, the identified mobile atoms within $\Delta t$ are all located within GB region. Next, mobile atoms $i$ and $j$ are considered to be within a displacement string if they remain near one another as they move (9, 18, 23) (see Fig. 1C). We indeed find “strings” in our GB dynamics simulations as in GF liquids and provide some characterization of these structures below to determine how their geometry compares to their counterparts in GF fluids. In particular, the average “string length,”

$$
\bar{n}(\Delta t) = \sum_{n=2}^{\infty} n P(n, \Delta t).
$$

[1]
most important property of GF fluids. are correlated with the relative strength of the temperature accords with the Adams–Gibbs theory of relaxation in GF liquids effective activation energy for structural relaxation. This finding these strings in GF liquids grows after cooling, along with the probability of finding a string of length of GF liquids grows after cooling, along with the probability of finding a string of length . The nonlinearity of the Arrhenius plot indicates that this relationship does not apply to GB mobility data.

provides a natural measure of the scale of cooperative particle motion in strongly interacting liquids where is the probability of finding a string of length a time interval .

Previous work has established that the average length of these strings in GF liquids grows after cooling, along with the effective activation energy for structural relaxation. This finding accords with the Adams–Gibbs theory of relaxation in GF liquids, in which the strings are identified with the vaguely defined “cooperatively rearranging regions” of the Adams–Gibbs theory. Strings are thus of practical interest, because they are correlated with the relative strength of the temperature dependence of transport properties (see below), perhaps the most important property of GF fluids.

**Similarity of GB mobility to transport properties of GF liquids.** The GB mobility is defined by the rate of displacement of the GB after the application of a stress to the polycrystalline material so this motion occurs in a direction orthogonal to the plane of the GB in which collective atomic motions primarily occur. Fig. 2 shows the displacement of the GB position as a function of for eight representative values. Because the structure of GBs is more disordered than that of the crystal grains, the coordination number for most atoms within GB region is normally reduced. On the basis of this observation, the mean GB position can be calculated by averaging the positions of those atoms having this reduced coordination number (see Fig. 1B legend). The boundary velocity is simply obtained from the average slope of the boundary position versus , where final displacements from 1 to 5 nm were considered, depending on .

In the classical theory of GB migration, the temperature dependence of the GB mobility (ratio of the velocity to the driving force ) obeys an Arrhenius temperature dependence (i.e., ). originates from a driving force that does not apply below . Therefore, it does not apply below (at which an Arrhenius temperature dependence of relaxation is again normally recovered). Because is generally well above the temperature at which the rate of molecular diffusion formally vanishes in the VF mobility relation (see Eq. 2), the extrapolation temperature cannot be literally identified with a condition of vanishing mobility. The same situation is true for the GB mobility, so that only serves to characterize the strength of the non-Arrhenius temperature dependence of the mobility over a restricted temperature range above .

A best fit of the data in Fig. 2 to Eq. 2 yields the characteristic temperature, , which is reasonably close to the corresponding ratio (error estimate is based on a 95% confidence interval throughout this article), and below we compare the ratio, defining property, of GF liquids, and the VF equation, for our GB dynamics to for appropriate classes of GF fluids. We conclude that the temperature dependence of the GB mobility obeys the same phenomenological relationship as relaxation in GF liquids, providing some support for the physical picture of polycrystalline materials described in our introduction.

We tested the physical sensibility of to relation to GF fluids by comparing this quantity to the melting temperature . For metallic glasses, the ratio of the melting (eutectic) temperature to has been estimated to be (see Text and Table S1), which is reasonably close to the corresponding ratio (error estimate is based on a 95% confidence interval throughout this article), and below we compare the ratio, , which is essentially the same (10), and even the magnitude of the temperature dependence of relaxation is again normally recovered. Because is generally well above the temperature at which the rate of molecular diffusion formally vanishes in the VF mobility relation (see Eq. 2), the extrapolation temperature (30) cannot be literally identified with a condition of vanishing mobility. The same situation is true for the GB mobility, so that only serves to characterize the strength of the non-Arrhenius temperature dependence of the mobility over a restricted temperature range above .

**Comparison of GB mobility to transport properties of GF liquids.** As discussed above, string-like cooperative atomic motion is prevalent in all GF liquids examined to date (including water, polymer fluids, metallic GF liquids, concentrated colloidal suspensions, and even strongly driven granular fluids). It is apparently a universal property of the dynamics of strongly interacting fluids, where a strong reduction in the particle mobility and an enormous change in the rate of structural relaxation are found in association with the growth of string-like correlated motion after approaching the glass transition. We next examine the nature of the atomic motion occurring in GB migration to determine whether it follows this general pattern of “frustrated fluid” dynamics. Fig. 1C shows a typical displacement string in our simulation appearing in the plane of the GB region. The initial atom positions are shown in yellow ( ), and their positions at a later time are shown in blue (displacements are shown by using arrows; see Fig. 2 C and D). This string-like atomic motion in the GB region occurs predominantly along a direction parallel to the tilt axis (see Fig. 1D) but in a direction orthogonal to the ultimate direction of GB displacement.

**Atomistic simulations of GF liquids suggest that the distribution of string lengths** is an approximately exponential function of ,

\[
P(n) \sim \exp(-n/(n)) \tag{3}
\]

Fig. 3 shows the distribution of string lengths at , where the string length exhibits a maximum during GB migration (time dependence of not shown; see refs 22–24). Interestingly, the distributions of in GF liquids and in the GBs are essentially the same (10), and even the magnitude of is comparable to values found in GF liquids for the corresponding range (see below). Evidently, increases after cooling (see Fig. 3 Inset), where is smaller for GBs than the non-GBs,
which suggests that atoms in the Σ GBs are less frustrated than those in the more disordered non-Σ GBs.

Comparison of the characteristic temperatures of GB and GF liquids. We next consider other aspects of the phenomenology of GF liquids that have significance for understanding the transport properties of polycrystalline materials. In particular, glass formation is generally accompanied by thermodynamic changes similar to those observed in rounded thermodynamic transitions, and correspondingly, both of these transitions are characterized by multiple characteristic temperatures (31). We summarize these for GF fluids, and below we determine their analogs for GB dynamics.

The dynamics of GF liquids is characterized by a number of temperatures, which in decreasing order include $T_A$ (marking the onset of the cooperative atomic motion), a crossover temperature $T_c$ (separating high and low $T$ regimes of glass formation), the glass transition temperature $T_g$ (below which aging and other nonequilibrium behavior is overtly exhibited), and finally $T_0$ (characterizing the “end” of the glass-transformation process) (31, 33). To further our analysis, it is natural to consider the analogous characteristic temperatures for the GB MD, $T_A$ is experimentally defined as the temperature at which the Arrhenius temperature dependence of structural relaxation no longer holds. Based on the basis of the entropy theory of glass formation (33), the apparent activation energy $E_a(T)$ below $T_A$ follows a universal quadratic $T$ dependence, $E_a(T)/E_a(T \rightarrow T_A) \approx 1 + C_0(T/T_A - 1)^2$, where $C_0$ is a constant. The GB migration mobility data in Fig. 2 Inset fits this relation ($SF$) well near $T_A$ (950 K < $T$ < 1,400 K), and we estimate $T_A$ to equal 1,546 K. To determine the other characteristic temperatures (see SF), we performed a series of simulations to determine the mean-square displacement of atoms ($\langle r^2 \rangle$) within the GBs.

Following Starr et al. (30), we define the Debye–Waller factor (DWF) as the mean-square atomic displacement ($\langle r^2 \rangle$) after a fixed decorrelation time $t_0$ characterizing the crossover from ballistic to caged atom motion. Fig. 4 shows corresponding data for the GB dynamics where the same criterion is chosen for defining $t_0$ as described by Starr et al. (30). In GF liquids, $\langle r^2 \rangle$ at low $T$ exhibits a well-defined plateau after $t_0$ that persists up to the structural relaxation time of the fluid $\tau$ (a time normally many orders of magnitude larger than $t_0$ for $T \approx T_g$), and the height of this plateau defines the size of the “cage” in which particles are transiently localized by their neighbors. In Fig. 4, we observe a progressively flattening of the GB data for $\langle r^2 \rangle$ at intermediate times that illustrates the progressive caging of atomic motion after cooling in these relatively high-temperature simulations. A well-defined cage (plateau) is apparent only for the lowest temperature simulations indicated. Because $\langle r^2 \rangle$ is slowly varying with $t$ in the time interval between $t_0$ and $\tau$ in the glass state and because $\tau$ is on the order of minutes for $T \approx T_g$, any experimental estimate of $\langle r^2 \rangle$ yields a similar value in the glass state over this broad range of time scales. This observation basically explains why dynamic neutron and x-ray scattering measurements of $\langle r^2 \rangle$ with instrumental time scales on the order of $10^{-8}$ s are of direct relevance to the physics of glasses. Fig. 4 shows the DWF ($\langle r^2(T) \rangle$) for the GB atomic motion based on the same criterion (i.e., $\langle r^2(t_0) \rangle \approx \langle u^2 \rangle$) used by Starr et al. (30) for GF fluids. For reasons described below, $\langle u^2 \rangle$ is divided by $\langle r^2 \rangle$, the square of the equilibrium interatomic distance in the crystal. Fig. 4 Inset shows the original GB data from which $\langle u^2 \rangle$ was determined (the broken line denoting $t_0$).

In addition to the mean particle-displacement scale $\langle r^2 \rangle$ in the caging regime, the distribution function $G_q(q)$, for the atomic displacement $r(t)$, also provides valuable information about how much GB atomic motion resembles the dynamics of GF liquids, and this property also allows for the determination of the characteristic temperature $T_c$ (34, 35). In particular, we calculate the GB self-intermediate scattering function $F_q(\mathbf{q})$ (35), which is the Fourier transform of $G_q(r)$, over a broad temperature range, 1,050 K ≤ $T$ ≤ 1,150 K. Specifically, $F_q(\mathbf{q})$ is defined as $F_q(\mathbf{q},t) = \langle \exp(-i\mathbf{q} \cdot r(t) - r(0)) \rangle$, where the
Fourier transform variable $q$ is termed the scattering “wavevector” because of its measurement interpretation. Because the variation of $F_{\gamma}(q,t)$ with $T$ is an apparently universal property of GF liquids, an examination of $F_{\gamma}(q,t)$ for the GB dynamics provides an opportunity to examine how much the GB atomic motion resembles the MD of GF liquids.

In Fig. 5, we see that $F_{\gamma}(q,t)$ for the GB dynamics develops a progressive tendency to flatten out at time scales after the inertial dynamics regime, as in the GB data for $T_{f}$ (defined in the text). The dashed curves are a fit of the stretched exponential relation, $F_{\gamma}(q,t) = \exp[-(t/\tau)^{\beta}]$ to the long-time data, where the short-time decay arises from the inertial atomic dynamics. (Inset) A power fit of $t^{-0.7}$ to $T_{f}$, where $T_{f}$ and $\gamma$ are adjustable parameters as in previous measurements and simulations.

To complete our comparison of the characteristic temperatures of GF liquids with those of the GBs, we must also determine the low-$T$ glass regime temperatures, $T_{g}$ and $T_{u}$. Equilibrium simulations of liquids are normally limited to $T > T_{g}$ because of the growing relaxation and equilibration times of cooled liquids. The same difficulty holds for studying GB motion. Thus, $T_{g}$ must be obtained through extrapolation of high-$T$ simulation data. With this difficulty in mind, we observe that $(\tau_{\gamma}^{2})$ in Fig. 4 exhibits a linear $T$ dependence up to $\approx 940$ K, a $T$ near $T_{g}$. Temperatures above $T_{g}$ define a different regime of behavior for $(\tau_{\gamma}^{2})$ and high-$T$ regime of glass formation more broadly (33). The $(\tau_{\gamma}^{2})$ data in Fig. 4 extrapolate to 0 at a $T$ close to the VF temperature ($T_{\theta}$) (see Eq. 2) determined from our GB mobility data in Fig. 2. This finding accords with previous simulation observations by Starr et al. [30] on GF fluids where the temperature at which $(\tau_{\gamma}^{2})$ extrapolates to zero coincides within simulation uncertainty with the VF temperature characterizing the $T$ dependence of the structural relaxation time $\tau$ at low $T$, where $\tau$ was determined, as described above, from $F_{\gamma}(q,t)$. Thus, we find another striking correspondence between GB atomic dynamics and the dynamics of GF liquids.

Physically, $T_{g}$ corresponds to a condition in which particles become localized in space at essentially random positions through their strong interaction with surrounding particles, and an (arguably nonequilibrium) amorphous solid state having a finite shear modulus emerges under this condition. A particle localization–delocalization also underlies crystallization, and the Lindemann criterion is known to provide a good rough criterion for the melting transition. Correspondingly, the same instability condition (33, 36) has been advocated generally for GF liquids, which allows a direct estimation of $T_{g}$. Following Dudowicz et al. (33), we define $T_{g}$ by the Lindemann condition, $(\mu_{T}^{2})/\sigma = 0.125$, and we estimate $T_{g} = 695$ K, which is a typical magnitude for metallic GF liquids (37). In practice, experimental estimates of $T_{g}$ depend somewhat on the rate of sample cooling and other sample history effects, which leads to some uncertainty in this characteristic temperature. The Lindemann criterion for $T_{g}$ is just a rough criterion for a roughly defined quantity. We have now defined all of the analogs of the characteristic temperatures of GF fluids for our simulations of GB dynamics; next, we compare to the relationships between these temperatures for both GB and GF liquids.

II. Perspective on Nature of Applied Stress and Impurities on GB Dynamics. Our paradigm for GB dynamics emphasizes the importance of string-like cooperative motion in understanding the transport properties of both polycrystalline materials and GF liquids, and we now apply this perspective to investigate a formerly puzzling phenomenon relating to GB migration under large deformation conditions. Various types of perturbations (e.g., hydrostatic pressure, molecular and nanoparticle additives, nanoconfinement) can be expected to influence molecular packing and, thus, the extent of packing frustration in the fluid and should influence the collective string dynamics. In previous work, we found that a variation of $T$ and the GB type both influenced (18) the average string length ($n$), so a sensitivity of $\langle n \rangle$ to thermodynamic conditions is established. We can also expect that varying the type of loading conditions, such as applying compressive stress, tensile stress, or even a constant hydrostatic pressure, will influence the character of string formation, because these forms of applied stress naturally affect molecular packing differently. These resulting changes in string geometry should then be directly reflected in $M$, providing an interesting test of the formal relationship between the dynamics of GB and GF fluids.

In previous simulations, we showed that large compressive versus tensile stresses led to appreciable changes in the $T$ dependence of $M$ (21), where $M$ at 800 K differed for these modes of stress by a factor of order 10, even when driving forces...
had the same magnitude. This sensitivity of \( M \) to the mode of applied stress is difficult to explain in terms of conventional GB migration theories. This effect is readily understood from our perspective of GB dynamics. In particular, a reexamination of our former simulation results indicates that \( n \) for 2\% tensile and compressive strains at \( T = 800 \text{ K} \) equals 1.63 and 2.13, respectively (\( \chi \)). If one assumes that the apparent activation energy \( Q \) for GB migration can be scaled by \( n \) [i.e., \( Q \propto (n) E_a \), where \( E_a \) is the high temperature activation energy (near \( T_a \)), then the observed change of \( n \) (and thus \( Q \)) in tension and compression accounts for the change in magnitude of \( M \). We suggest that the main origin of this shift in the scale of collective motion \((n) \) derives from a shift of \( T_g \) with deformation, compressive deformation acting similarly to an increase in the hydrostatic pressure, which generally increases \( T_g \). The extensional deformation has an opposite effect. Temperature and pressure studies will be required to confirm this interpretation of the origin of the deformation-induced changes in \( M \) in terms of the influence of the mode of deformation on cooperative GB atomic motion.

The addition of impurities and nanoscale confinement can also be expected to affect the cooperativity of atomic motions in strained polycrystalline materials, as recently shown in simulations of GF liquids (8, 9). Specifically, if the impurities help relieve packing frustration, then \( n \) should be greatly attenuated (8) and the \( T \) dependence of \( M \) should be weakened (i.e., the glass formation becomes “stronger”), whereas if the impurities disrupt molecular packing, then the scale of collective motion should become amplified and the \( T \) dependence of \( M \) should be amplified. Large changes in \( M \), and the resulting properties of polycrystalline materials, are then expected from the application of strains and the presence of impurities through the influence of these effects on the scale of collective motion in the GB region.

**Discussion**

We conclude that the atomic dynamics within the GB region of polycrystalline materials and the GB mobility at elevated \( T \) exhibit many features in common with GF liquids. Highly cooperative string-like atom motion in the plane of the GB can generally affect the average rate of GB motion transverse to the GB plane. This understanding of GB dynamics is expected to shed significant light on the mechanical properties of polycrystals. Indeed, we expect that the correlation between highly temperature-dependent properties of the complex GB “fluid” enveloping the crystalline grains to have a large impact on the plastic deformation of these materials. This viewpoint of the polycrystalline materials is contrasted with recent work that attributes the deformational properties of polycrystalline materials to simply the presence of solid crystalline grains within the uncrytallized fluid melt (38, 39). In our view, the uncrytallized material is a “complex fluid” that imparts its own viscoelastic effects on the polycrystalline material. Moreover, the frustrated atoms within the GB region should exhibit a high sensitivity to impurities, pressure, and geometrical confinement as in the case of GF liquids so that we can anticipate significant changes in the plastic deformation properties of polycrystalline materials arising from a modulation of the collective motion in the GB regions through these perturbations. This perspective of polycrystalline materials offers the promise of an increased control of the properties of semicrystalline materials based on further quantification of this phenomenon. Although this conceptual view of polycrystalline materials was intuitively recognized by scientists and engineers involved in the fabrication of iron materials at the beginning of the last century (11), the present work puts this working model of the deformation properties of polycrystalline materials on a sound foundation through direct MD simulation.

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