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Waxing and waning of dynamical heterogeneity in the superionic state

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Using molecular dynamics simulations of UO_2—a type II superionic conductor—we identify a well-defined onset of dynamic disorder (T_α), which is remarkably correlated to a nontrivial advance of dynamical heterogeneity (DH). Quantified by the correlations in the dynamic propensity and van Hove self-correlation function, the DH is shown to grow with increasing temperature from T_α, peak at an intermediate temperature between T_α and T_λ—the superionic transition temperature—and then recede. Surprisingly, the DH attributes are not uniform across the temperatures—our investigation shows a low temperature (α_T) stage DH, which is characterized by weak correlations and a plateaulike period in the correlations of the propensity, and a high temperature (λ_T) stage DH with strong correlations that are analogous to those in typical supercooled liquids. Our work, which has rigorously identified the onset of superionicity, gives a different direction for interpreting scattering experiments on the basis of statistical, correlated dynamics.

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Amorphous and disordered materials are particularly challenging to characterize—neither is their structure readily amenable to geometric or topological classifications as in defected crystals, nor can their dynamics be described by hydrodynamic theories as in simple liquids. Solid state superionic or fast ion conductors, which typically fall in the class of disordered solids [1], are principally composed of two or more elements that exhibit concomitant crystalline and dynamically disordered structures with an exceptional liquidlike ionic conductivity across a range of thermodynamic states. The copious conduction pathways may be facilitated by a thermodynamic phase change (type I conductors), or may emerge gradually without an attendant phase transition (type II conductors) [2]. The remarkable increase in the ionic conductivity, often by several orders of magnitude, is the principal impetus for the recent investigations, both experimentally and theoretically, of crystalline, polymeric, glassy, and nano/heterostructured materials for a variety of applications that include fuel cells [3], batteries [4–6], sensors, switching [7], hydrogen storage [8], and thermoelectrics [9].

A key signature of the type II conductors is the sharp rise and fall of the specific heat, known as the superionic or the λ transition, at a certain thermodynamic state [2]; changes to phonon spectra, as well as to the elastic and transport properties, are also reported in the vicinity of this transition. At the microscopic level, investigations with molecular dynamics (MD) simulations show that the ions are primarily transported through correlated hopping processes, where one ion jump coerces the motion of several neighboring ions [1]. Often aided by anharmonic and asymmetric thermal vibrations, the cooperative, but peripatetic ionic motion is a distinguishing dynamic feature of type II superionic conductors [2,10–12].

Given the discrete nature of the jumps, the ionic transport, on one hand, may be cast in the framework of dynamic Frenkel clusters [2,13], which presumes precise defect types and positions that are most likely to be encountered during the hopping processes. On the other hand, ionic hopping takes place over a time scale that is $O(1\text{–}10)$ ps [13] indicating liquidlike characteristics that have been likened to those in the supercooled liquids [14,15] with the superionic transition temperature (T_λ) corresponding to the glass transition temperature (T_g). Such a comparison elicits an intriguing but unresolved question: Do type II superionic conductors portray dynamical heterogeneity—a definitive hallmark of supercooled and glassy states? Although the similarities between superionic and supercooled states have been brought out before [14–17], a concrete understanding of the evolution of dynamical heterogeneity is somewhat nebulous. A related question arises on the thermodynamic range of the superionic state, which is bounded by equilibrium crystalline and liquid phases. It is tempting to inquire whether a crossover temperature or an onset of superionicity exists, where the dynamic disorder is first manifested in type II conductors. Unlike the superionic transition temperature (T_λ), the concept of a superionic onset temperature is not well formed even though experimental evidence does attest to such an onset. And lastly, if a well-defined superionic onset exists at T_α, will the likelihood of dynamical heterogeneity occurring be more pronounced near T_α, or near T_λ as the loose correspondence to T_g suggests? The aim of this Rapid Communication is to throw more light on the extent or range of the superionic state, and elucidate the hybrid nature of the dynamically disordered species in type II superionic conductors.

First, we emphasize that several sets of experimental data on type II superionic conductors (Sec. A of [18]) reveal the existence of a definitive transition temperature (T_α) that marks the onset of disorder (primarily evaluated from neutron scattering and diffraction experiments), which is distinctly different from the superionic transition temperature (T_λ). In this work we present evidence for a clear transition at T_α using MD simulations and associate this temperature to the transition from a crystalline state to a superionic state, which is manifested by the emergence of dynamical heterogeneity (DH). We have chosen UO_2 as our model fluorite material ($T_\lambda \approx 2650$ K, $T_\alpha \approx 1950/2000$ K) as the disordered state spans a wide temperature range that allows an unambiguous examination and interpretation of superionic and disordered transitions. A rigid-ion interionic potential [19], which has

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been benchmarked to a spectrum of properties [12,19,20] with reasonable accuracy, is used in the MD simulations (Sec. B of [18]). Polarization effects are important in the simulation of superionic materials; however, rigid-ion potentials can be made to reproduce the properties and dynamics reasonably well by tuning the dispersion term in the interionic potential [21]. MD simulations are performed with 1728 oxygen ions using periodic boundary conditions at zero pressure for different temperatures ranging from 1500 to 3100 K. At a temperature of ∼1900 K, we observe the onset of disorder by detecting subdiffusive dynamics from the mean square displacements and discernible changes in the properties such as lattice parameter (Sec. B of [18]).

Detecting DH in a superionic state is challenging for two reasons: First, the superionic states are completely in equilibrium enveloped by two well-defined thermodynamic states—liquid and crystal (solid). A supercooled state, in stark contrast, is in a frustrated, nonequilibrium condition, and is bounded by an equilibrium liquid and a nonequilibrium glassy state. Typically, DH is quantified by the generalized four point susceptibility function (χ_4) or through similar metrics [22–26]. The theoretical study by Toninelli *et al.* [23] shows that $\chi_4(t)$ can be divided into several time regimes such as ballistic, elastic, early beta relaxation, and so forth. For supercooled liquids, $\chi_4(t)$ shows a maximum at a time that is $O(\tau_\alpha)$, where τ_α is the alpha relaxation time. Further, the magnitude of $\chi_4(t)$-max shows a monotonic increase with decreasing temperature [27], illustrating the growing spatial correlations. Conspicuously, $\chi_4(t)$ has an elastic contribution from phonons that increases with time. For perfect crystals, $\chi_4(t)$ grows unbounded without decay, which indicates a general difficulty in differentiating deeply supercooled states from the crystalline states, especially with MD simulations that have limited time windows. In our study, we have used the correlation in the propensity—a metric defined as the mean square displacement of an ion in an isoconfigurational ensemble [28,29]—and van Hove self-correlation function [30] to uncover the onset of DH. The spatial correlation of the propensity in a system of N oxygen ions is defined as [31]

$$C_d\,(r,t) = \frac{\langle \delta w\,(i,t)\,\delta w\,(j,t)\rangle}{\langle [\delta w\,(t)]^2\rangle}, \qquad (1)$$

where $w(i,t)$ is the propensity $\langle r^2\rangle_{ic}$ of the ith ion at time t and $\delta w\,(t) \equiv w\,(i,t) - \langle w\,(i,t)\rangle$. The normalization is given by $\langle[\delta w\,(t)]^2\rangle = \frac{1}{N}\sum_{i=1}^{N}[\delta w\,(t)]^2$.

In Eq. (1), i and j are two oxygen ions such that the magnitude of the distance between them falls within an interval of 0.25 Å, centered at r. Analysis by Razul *et al.* [31] shows that C_d is a reliable metric for detecting DH in the supercooled liquids: It depicts a peak amplitude, which (i) manifests at times that scale with τ_α, and (ii) increases monotonically with decreasing temperature (Sec. C of [18]). Most importantly, the mean value of C_d is nearly zero at all times for perfectly crystalline states, especially at low temperatures. We have verified this with MD simulations for several materials at temperatures close to 0 K. While thermal vibrations enhance the magnitude of C_d, it remains nearly constant with time, unlike χ_4, which increases unbounded for perfectly crystalline states. The difference between χ_4 and C_d comes from the pair (two-ion) correlation in the latter that decays very quickly in the crystalline state.

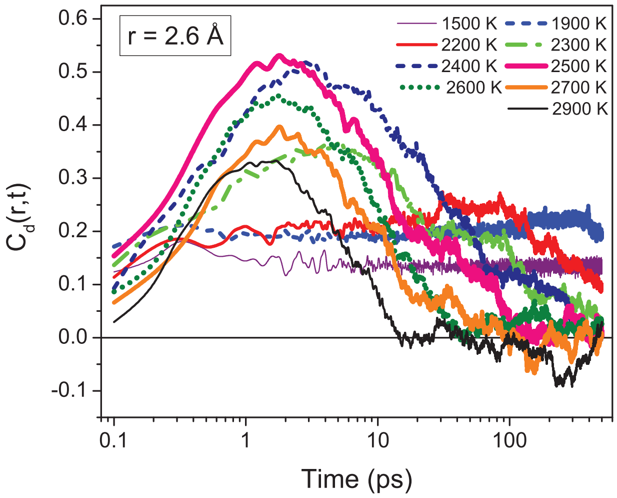

FIG. 1. (Color online) Spatial correlation (C_d) of the dynamic propensity of oxygen ions evaluated in a restricted, isoconfigurational ensemble for different temperatures.

Figure 1 delineates the main result of our investigation: It shows the progression of C_d based on 100 independent isoconfigurational runs evaluated at $r = 2.6$ Å, which is close to the shortest O-O interionic separation distance. At 1500 K, C_d shows an oscillatory behavior that emanates from the vibratory motion of the oxygen ions; the mean value, however, remains constant for the whole duration of the simulation (500 ps). On increasing the temperature, C_d exhibits two discernible changes: (i) the magnitude of C_d, which represents the strength of the correlation increases, and (ii) the magnitude increases gently and then decreases after passing through a maximum. Unlike in the supercooled states, C_d, however, exhibits a plateaulike period before decay. Thus the correlation in the propensity brings out the transition from a crystalline state into a superionic state through an increased correlation strength, and a peaking and decay behavior in C_d that signifies the emergence of dynamical heterogeneity. With increasing temperature, the magnitude of C_d increases with the peaks being exhibited at shorter times—the maximum amplitude can be observed at 2500 K. And on further increase in the temperature, the amplitude of C_d decreases. Figure 2, which shows the variation of the peak magnitude of C_d, depicts the waxing and waning of DH among the oxygen ions. For temperatures 2200 and 1900 K, the peak amplitude of C_d is determined as the mean value during the "plateau" period: 30–80 ps and 200–400 ps for 2200 and 1900 K, respectively. Note that C_d averaged over 1 Å is somewhat smoother with the peak magnitude observed at approximately 2400 K; similar trend is observed at other radial locations as well. Based on the peak magnitudes of C_d, the maximum DH intensity can be regarded to fall in the temperature range of 2400–2500 K.

The temporal behavior of C_d reveals a low temperature (α_T) and a high temperature (λ_T) DH behavior with the former corresponding to the lower temperatures near T_α (1900–2300 K), while the latter corresponds to the higher temperatures near T_λ

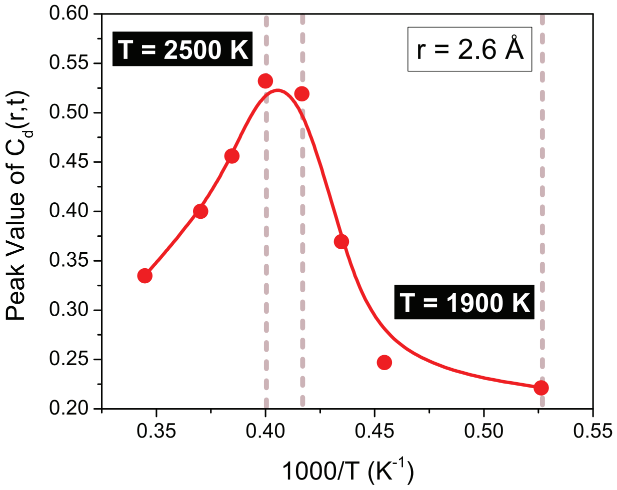

FIG. 2. (Color online) Waxing and waning of DH among the oxygen ions, illustrated by the variation of the peak amplitude of C_d with temperature.

(2400–2900 K). The α_T stage is characterized by deviations from a constant C_d, low correlation strength and a relatively long plateaulike period, signifying correlated but hindered ionic motion. The low correlation strength also indicates that only a relatively small number of ions participate in the DH process.

The α_T DH stage is distinctively different from that observed in typical supercooled liquids—given the preceding crystalline state and the weak growth, it can be characterized as solidlike. While only 500 ps have been simulated for the lower temperatures, we have verified that the system remains in a vibratory state at temperatures lower than T_α. Further, we have used the temperature accelerated dynamics (TAD) of Voter [32] to gauge the long-time dynamics—no transitions were accepted for a perfect UO_2 crystal at temperatures lower than T_α, indicating the dominant vibratory motion of the ions without crossing an energy barrier to another state (diffusive motion). In contrast, the high temperature λ_T DH stage is characterized by a significant strength in the correlations and a peaking behavior that is analogous to supercooled liquids. The crossover from the solidlike DH behavior to a more liquidlike response (at ~2300 K) has a structural origin, which is described in Sec. D of [18].

We will now provide more evidence for the evolution of DH as well as for the crossover from solidlike to liquidlike behavior of the oxygen ions. The van Hove self-correlation function for oxygen ions—shown in the top panels of Fig. 3 at different temperatures—delineates two striking features: At temperatures above 1900 K, $G_s(r,t)$ deviates from the Gaussian shape and develops a tail, which (i) depicts discernible peaks, particularly prominent at longer times, and (ii) varies exponentially with distance at a time when C_d exhibits a peak amplitude (τ_α). The peaks are characteristic of hopping processes wherein ions undergo discrete jumps [33] (Sec. E of [18]); we have verified that the peak locations agree closely with the nearest neighbor positions in the O-O radial distribution function. The exponential tail in $G_s(r,t)$, on the other hand, connotes the presence of faster moving ions—the characteristic signature of DH—which is also observed in supercooled liquids, colloids, and granular materials [30]. With increasing temperature, the exponential tail at τ_α strengthens, which confirms the presence of DH. The α_T and λ_T stages of DH can also be distinguished from the progression of the exponential tail. At 2200 K, the exponential tail in G_s at τ_α (80 ps), which is somewhat underdeveloped with corrugations, sustains for longer periods of time suffering only a modest change, signifying a solidlike (α_T) DH response. In contrast, at a temperature of 2400 K (and above), the G_s tail at τ_α is smoother, which is analogous to that in typical supercooled liquids, signifying a liquidlike (λ_T) DH response; for the higher temperatures, the exponential tail of G_s also deteriorates faster.

In the bottom panels of Fig. 3, we highlight the crossover from a solidlike state to a more liquidlike state by alerting one to the appearance of a hydrodynamic Rayleigh peak ($\nu \approx 0$) in the partial dynamic structure function of the oxygen ions for a wave vector, $k = 0.28$ Å^{-1}. For 1900 K $> T <$ 2200 K, a partially formed hydrodynamic peak is discernible, indicating a somewhat lethargic disordering mechanism. The Rayleigh peak, however, becomes unmistakable with increasing temperature and its magnitude relative to that of the elastic peak again confirms a liquidlike state beyond 2400 K.

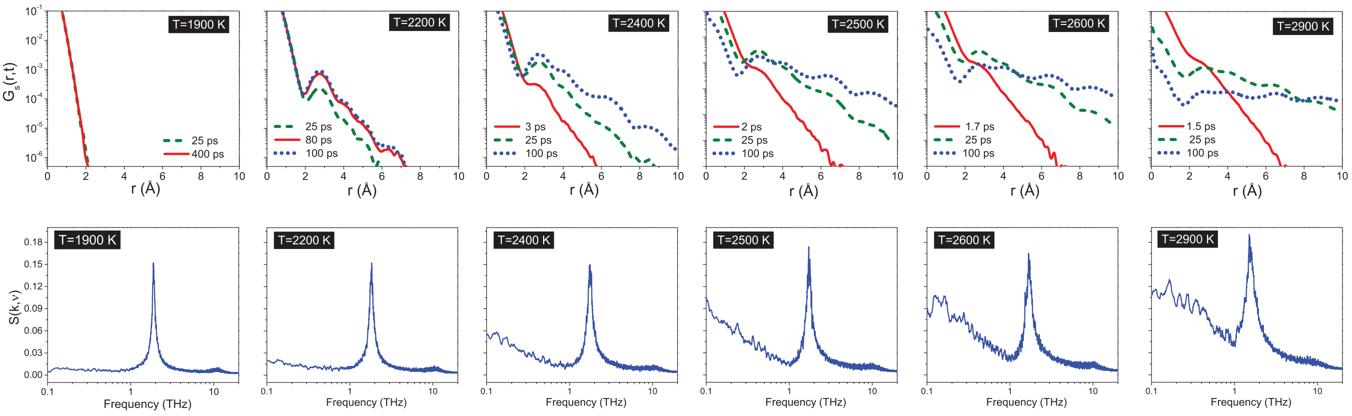

FIG. 3. (Color online) Top panels: The van Hove self-correlation function $G_s(r,t)$ for the oxygen ions at different temperatures—the solid line corresponds to the time when C_d exhibits a peak amplitude. Bottom panels: Partial dynamic structure function for oxygen ions (arb. units) for a wave vector of $k = 0.28$ Å^{-1}, which is representative of the hydrodynamic limit.

Outlook. Illustrated by the correlations in the propensity, DH is demonstrated to advance from a well-marked onset temperature (T_α)—shown unambiguously—peak at an intermediate temperature between T_α and T_λ, and then recede. Currently, the superionic state is largely analyzed from a static picture of defect positions [2]; indeed, most neutron and light scattering experiments to date have been interpreted on such a basis. Our investigations have uncovered the remarkable significance of correlated dynamics, in particular, the nontrivial manifestation of DH that grows against the destabilizing effects of entropy. Our investigations thus give a different direction for interpreting scattering experiments on the basis of statistical, correlated dynamics. Further, the nuanced attributes of the α_T and λ_T stages of DH in the superionic state, which have become transparent through our inquiry, will be of vivid interest from a theoretical point of view.

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