Disordering and Dynamic Self-Organization in Stoichiometric UO_2 at High Temperatures

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Abstract

Using atomistic simulations and metrics from statistical mechanics we show that the oxygen anions in UO_2 predominantly hop from one native (tetrahedral) lattice site to another, above a characteristic temperature T_a (~ 2000 K). Interestingly, we discover two types of disorder – the first one, which is a measure of the fraction of anions that are displaced from their native sites, portrays a monotonic increase with temperature and shows excellent conformity to neutron scattering data. The second metric demonstrates a dynamic clustering or self-organization behavior wherein the anions are spatially correlated to those with similar mobility. The dynamic self-organization, however, experiences a non-monotonic variation with temperature depicting a maximum near the Bredig or λ -transition. We further establish that the thermodynamic metric c_p/T , which is equal to the rate of change of entropy with temperature, is a key thermodynamic indicator of the dynamic disorder among the oxygen anions.

1.0 Introduction

Uranium dioxide (UO_2) is the fuel material of choice in most nuclear reactors operating around the world. It has a fluorite structure ($Fm\bar{3}m$) with uranium ions placed in a face-centered cubic (fcc) lattice and oxygen ions occupying the corners of a simple cube. UO_2 does not amorphize easily under intense nuclear radiation. It is generally recognized that oxides with an innate proclivity to accommodate disorder without structural collapse portray high tolerance to radiation. Anion Frenkel pairs and cation antisites provide the defect reaction mechanisms to natural disordering in fluorite-related structures [1]. Intrinsic disordering among the oxygen ions also endows superionic properties to UO_2 although the current understanding of fast ion conduction is limited. Members of the fluorite family such as CaF_2 , PbF_2 , SrCl_2 and UO_2 that fall in the Type II superionic class portray high ionic conductivity within the solid state through a gradual anion disordering process [2]. Atomistic disorder can have strong structural signatures such as from stable defects, or can exhibit dynamic features that change with time with or without attendant structural motifs [3]; the characteristics of UO_2 disorder, however, are not well-elucidated at high temperatures. Much of the current understanding on high temperature disorder comes from thermal and x-ray/neutron scattering/diffraction experiments. For temperatures between 300–1200 K, investigations by Ruello *et al.* [4] confirm a classical Debye behavior for the thermal expansion. At temperatures above 1200 K, anharmonic effects become dominant, which leads to a departure from the Debye regime. Coherent diffuse quasielastic scattering experiments reveal that anions leave their native sites leading to a transient disordered anion lattice in stoichiometric UO_2 above 2000 K, with typical lifetimes ranging from 1 to 10 ps [5-6]. UO_2 also experience a Bredig or λ -transition at 2610 K (T_λ) [7], where the thermodynamic response functions such as specific heat and thermal expansivity portray a divergent-like behavior.

The anion disorder above a characteristic temperature (which we denote as T_a) is rationalized principally using quasi-static defect models that have a latitude to accommodate dynamic evolution over short periods of time. In these models, ions appear at relaxed positions, namely locations that are shifted away from geometrical vertices [5-6]. In a different approach, Gillan [8-9] has proposed that the mobile anions hop between native sites above T_a without forming any discernible defect clusters. While the dynamic structure function calculated from the hopping model shows excellent agreement to the data from neutron scattering [8-9], most experimental work in the past have relied on the underpinning provided by the dynamic cluster models [2]. The objective of the current work is to examine the nature of ionic displacements in UO_2 at temperatures above T_a (~ 2000 K) using atomistic simulations and make an assessment on the fidelity of the aforementioned competing models.

2.0 Dynamic Defect Cluster Models and Evidence for Ion Hopping at High Temperatures

The anions in UO_2 , as shown in Fig. 1 (a), arrange themselves in a simple cubic lattice (tetrahedral sites of fcc lattice) with the cations occupying the alternate cube centers (octahedral sites of fcc lattice). It is inferred from experiments that at temperatures well below T_λ , the dominant fluorite defects are anion Frenkel pairs with the interstitial ions residing at the unoccupied cube centers [2]. At higher temperatures, the enhanced anharmonic vibrations along the $\langle 111 \rangle$ directions and the presence of vacancies at closer distances destabilize the octahedral interstitials resulting in a fundamental change to the nature of defects [2, 10]. Neutron scattering/diffraction studies of fluorites at temperatures approaching T_λ imply that the anions, rather than occupying the empty cube centers, are displaced along $\langle 110 \rangle$ directions with simultaneous

relaxation of the neighboring ions creating additional vacancies as shown in Fig. 1(a). These studies indicate the emergence of disorder, as shown in Fig. 1(b), among the oxygen anions at 2000 K and above [5]. Motivated by the original work of Willis [11] on the interpretation of anion clusters in hyper-stoichiometric UO_2 , Hutchings and coworkers have developed the early cluster models for UO_2 [5] and other fluorites [12]. In the Willis 2:2:2 cluster arrangement, two interstitials occupy positions that are along a line connecting the midpoint between two native anion sites and octahedral cube centers along the $[110]$ direction, while two regular anions are displaced or relaxed in the $[111]$ direction creating two additional vacancies [13-14]. In stoichiometric fluorites at high temperatures, several energetically favorable cluster configurations are attractive [14], the most prominent of these is the 3:1:2 cluster [2], which is very similar to the Willis cluster, with three vacancies (v), one interstitial (i) displaced along $[110]$ direction, and two relaxed ions (r) along $[111]$ direction. Such clusters are deemed to emerge solely from thermal fluctuations at temperatures typically above T_α .

Fig. 1. (left) Schematic of the UO_2 crystal structure. The anions (smaller spheres) form a cubic lattice arrangement while the cations occupy the alternate cube centers (bigger spheres). The distance between two neighboring anions is $a/2$, where a is the lattice parameter. At high temperatures, defect clusters with relaxed ions and interstitials are hypothesized to form. A 3:1:2 defect cluster [2] with three vacancies (v), one interstitial (i) displaced along $[110]$ direction, and two relaxed ions (r) along $[111]$ direction, is also shown. While several cluster types can be reconciled with neutron diffraction/scattering data [5], the 3:1:2 configuration is deemed most probable near Bredig or λ -transition (T_λ). (right) Neutron scattering data (X^D : integrated coherent diffuse scattering per anion) [5] showing the onset of significant anion disorder at ~ 2000 K; we identify this order-disorder transition temperature as T_α [15-16]. The superscript ($\bullet$) denotes inferred value from experiments.

In the cluster model developed by Clausen *et al.* [5] for UO_2 with a basis of uranium ion at the origin and the oxygen ions at $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, the interstitial oxygen ion can be detected at $\pm(\frac{1}{4}+y, \frac{1}{4}-y, 0)$, where $y = 0.05 \pm 0.03$. Similarly, the ions that are relaxed along the $[111]$ direction are located at $\pm(x, x, x)$ relative to the cation sites, where $x = 0.34 \pm 0.01$ [5]. At room temperature (~ 300 K), the diffraction/scattering data is best matched with the fluorite structure. As temperature increases to 1900 K, a model with uniformly distributed vacancies on the oxygen sub-lattice shows the best fit. While a model with only relaxed ions (without interstitials) provides the best agreement to the experimental data at 2403 K, both displaced

interstitials and relaxed ions ($i:r=1:2$) seem appropriate to fit the scattering/diffraction data close to the Bredig or the λ -transition temperature (T_λ). The scattering experiments also reveal that the clusters typically have a mean lifetime of the order of picoseconds [12]. It may be noted here that the scattering/ diffraction experiments give a quantitative estimate of the anions that leave their native sites.

In a recent *ab-initio* finite temperature molecular dynamics (MD) investigation of UO_{2+x} , Wang, Ewing and Becker [17] have demonstrated that the Willis 2:2:2 cluster configuration is a transition state connecting more stable split di-interstitial defect configurations [18-19]. This observation is consistent with other recent *ab-initio* MD simulations on fluorite structures; for example, Hull and coworkers [20] have shown that Br anions in SrBr_2 (a member of the fluorite family) mostly reside at their native tetrahedral sites/cavities with occasional hops to neighboring tetrahedral sites/cavities. Most importantly, the anions are observed to preferentially jump along $\langle 100 \rangle$ directions rather than along $\langle 110 \rangle$ or $\langle 111 \rangle$ directions; the mean probabilities for hops in these directions are 0.92, 0.05 and 0.02, respectively. In a separate *ab-initio* MD investigation, oxygen ions in fluorite-structured Bi_2O_3 also portray a curved path as they hop between sites along $\langle 100 \rangle$ directions [21]. Interestingly, the anions in both SrBr_2 and Bi_2O_3 are observed to avoid the 4(b) octahedral cube centers, as observed in the experiments, while passing through the 48(g) locations that correspond to the relaxed ions displaced along the $\langle 111 \rangle$ directions. Thus the picture revealed through the recent electronic structure simulations is that anions spring between native sites embracing a meandering path that passes through the periphery of octahedral cavities, perhaps, with a brief sojourn at the relaxed ion positions of the 3:1:2 cluster model.

A large number of classical atomistic simulations with empirical potentials are also consistent with the recent *ab-initio* simulations. Several investigations show the preponderance of ionic hopping in both UO_2 [15-16, 22] and CaF_2 [23] – two materials that have excellent interatomic potentials. Thus the prevailing and historical evidence testifies to the ion-hopping mechanism proposed in the seminal work of Gillan [8-9] even though the defect cluster hypothesis serve as the bedrock for scattering/diffraction analysis. In this work, we will confirm the hopping mechanism, as well as the absence of definitive signatures of defect clusters at high temperatures using time-resolved correlation functions extracted from molecular dynamics simulations.

3.0 Molecular Dynamics (MD) Simulations

We have employed classical MD simulations to evaluate the disorder in UO_2 at high temperatures. A rigid two-body interionic potential developed by Yakub *et al.* [24] that has been benchmarked to a wide range of high temperature properties [22] is used in the simulations; it is given by

$$V_{\alpha\beta}(r_{\alpha\beta}) = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{z_\alpha z_\beta}{r_{\alpha\beta}} + A_{\alpha\beta} e^{(-r_{\alpha\beta}/\rho_{\alpha\beta})} - \frac{C_{\alpha\beta}}{r_{\alpha\beta}^6} + D_{\alpha\beta} \left[e^{-2B_{\alpha\beta}(r_{\alpha\beta}-r_{\alpha\beta}^*)} - 2e^{-B_{\alpha\beta}(r_{\alpha\beta}-r_{\alpha\beta}^*)} \right] \quad (1)$$

where the indices α and β label the ionic species, z is the charge, $r_{\alpha\beta}$ denotes the separation distance between the ions, and A , B , C , D , ρ and r^* are six parameters. The first term in Eq. (1) represents the Coulombic interaction, while the second and third terms represent the repulsive potential due to the overlap of electron clouds and the attractive van der Waals potential, respectively. The fourth term describes the partial covalent character of the bonding. While polarization is not explicitly modeled, its effect is accommodated through the dispersion term [25]. The numerical values of the interionic parameters are listed in Table 1.

Table 1. Parameters of the Yakub *et al.* potential [24].

$z_+ (e)$	$z_- (e)$	$A_{++} (eV)$	$A_{--} (eV)$	$A_{+-} (eV)$	$\rho(\text{\AA})$	$C_{--}(eV \cdot \text{\AA}^6)$	$D_{+-} (eV)$	$B_{+-} (\text{\AA}^{-1})$	$r_{+-}^*(\text{\AA})$
2.2208	-1.1104	187.03	883.12	432.18	0.3422	3.996	0.5055	1.864	2.378
$\rho = \rho_{++} = \rho_{--} = \rho_{+-}$ $C_{++} = C_{+-} = 0$ $D_{++} = D_{--} = 0$									

The simulations are performed with periodic boundary conditions in a cubic system with 6144 ions. The Newton equations of motion are integrated using the Velocity-Verlet algorithm with a time step of 1 *fs*. The system is initially equilibrated in an NPT ensemble for 25 *ps* at zero pressure; the properties are then evaluated in an NVE ensemble and averaged over 10 independent runs with different initial conditions. The Coulombic interactions are simulated using the Wolf summation method [26], which we have benchmarked to the standard Ewald sum method. We have verified that the potential reproduces the characteristic transition temperatures as listed in Table 2 in addition to rendering reliable thermodynamic/transport properties such as specific heat and self-diffusivity [15-16]. We have further confirmed that our key results agree with those using the interionic potential developed by Basak *et al.* [27] (see Appendix 2). While several potentials have been reported for simulating UO₂ properties [28-44], our choice has been largely dictated by the ability of the potential to predict high temperature properties and transitions.

Table 2. Comparison of transition temperatures – simulation and experiments. T_λ and T_m correspond to the λ -transition temperature and the melting point, respectively. T_a represents the characteristic temperature at which anions are thermally displaced from the lattice sites.

	MD	Experiments
$T_m (K)$	3125 ^{a)}	3120 [5]
$T_\lambda (K)$	2560 ^{b)}	2610 [7]
$T_a (K)$	1900-2000 ^{c)}	~2000 [5]

^{a)} Evaluated through the two-phase method [45]. ^{b)} Evaluated from the derivative of the enthalpy with respect to temperature at constant pressure. ^{c)} Evaluated from the mean square displacement of the oxygen anions and lattice parameter (Appendix 1), long-range order (Section 4.1), and minimum of c_p/T , which is equal to the rate of change of entropy with temperature (Section 4.6).

4.0 Results

4.1 Long-ranged Order

The long range order (LRO), measured through the Fourier transform of the local density given by $\rho(\mathbf{q}) = \sum_{j=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_j}$ [46] where $\mathbf{q}$ is the wave vector, is a simple but powerful metric to assess quasi-static disorder at different scales. For solids characterized by spatially periodic structure, $|\rho(\mathbf{q})|$ tends to approach unity

without showing any decay in time while for liquids with disordered structure, it decays to zero indicating the absence of any long range order. Figure 2(a) depicts the temporal variation of LRO among the oxygen ions for the wave vector $\mathbf{q} = (2\pi/a) (1,0,0)$, which corresponds to the longest wavelength in the system along [100] direction. At a relatively low temperature (~ 1500 K), the magnitude of the LRO is close to unity indicating a crystalline structure with well-defined periodicity over (half) the length of the simulation box. Quite interestingly, as temperature increases, the LRO exhibits a somewhat unique characteristic – the magnitude decreases as in a liquid state but without exhibiting any temporal decay as in a solid state. This observation is consistent with the neutron scattering experiments, which signify anion disorder at higher temperatures but without the characteristics of a melt phase [5-6]. The non-decaying temporal variation of oxygen LRO reveals an intact periodic oxygen sub-lattice structure, and the decay in the magnitude strongly alludes to a form of disorder that does not significantly disturb the underlying crystalline structure of the anion sub-lattice. In Fig. 2(b) we delineate the time-averaged magnitude of the LRO with temperature. Consistent with the change in the mean square displacement (see Appendix 1), the magnitude of the long range order for oxygen ions departs from its linear (decreasing) behavior at $\sim 1900/2000$ K which is close to T_a inferred from neutron scattering experiments (see Appendix 1).

Fig. 2. (a) Time variation of the long range order (LRO) among the oxygen anions with $\mathbf{q}$ along [100] direction; the wave vector $\mathbf{q} = (2\pi/a) (1,0,0)$ corresponds to the longest wavelength in the system along [100] direction. The temperature varies from 1500 K to 3000 K in steps of 100 K. (b) Temperature variation of the time-averaged long range order for oxygen and uranium ions indicating a discernible onset for disorder at ~ 2000 K (T_a). The superscript (•) denotes inferred values from molecular dynamics simulations. The inset compares neutron scattering data with the disorder evaluated from oxygen LRO (both scaled to their respective magnitudes at T_λ).

We have computed a measure of disorder from LRO by subtracting the magnitude of time-averaged LRO from unity. In the inset of Fig. 2(b), we have compared the relative measure of disorder from LRO and the fraction of anions leaving the sub-lattice from neutron scattering, both scaled to their respective magnitudes at T_λ . The tight correlation between the simulation and the experimental data is quite striking. The cluster models necessitate the presence of interstitials and/or relaxed ions that create additional random vacancies at the native sites, and they do not appear to be compatible with the LRO behavior shown in Fig. 2(a). However, the anion hopping model proposed by Gillan [8-9], which preserves the native lattice positions of the oxygen ions while allowing dynamic disordering, is non-conflicting with the LRO behavior. Expectedly, the long range order of uranium ions depicts only a minor change even past the Bredig transition; significant loss of crystalline order for uranium ions takes place only at melting. The LRO metric from MD simulations thus establishes an onset of disorder near T_a that

appears to have a strong dynamic origin. In the next sub-sections we will probe other measures, both structural and dynamic, to draw out the characteristics of the anion disorder above T_a .

4.2 Occupation of Octahedral Sites

Fig. 3. (*left*) The crystal structure of UO_2 , with bigger and smaller ions representing uranium and oxygen, respectively. (*right*) The (110) plane of the unit cell, which has 4 oxygen ions shown in black, contains octahedral sites at the mid-point of the plane as well as at the centers of left and right edges, shown by hatched circles.

Fig. 4. Density contours of oxygen ions along the (110) plane at different temperatures.

In Fig. 3, we assess the importance of octahedral sites in promoting disorder by estimating the presence of oxygen ions at these sites at different temperatures. The unit cell shown in Fig. 3 (*a*) is partitioned into 51 equisized segments along each of the three directions, and each oxygen ion can be located in any one of the $51^3 (=132,561)$ volume elements. Contours representing the ion population of the volume elements can now be determined for any plane in the unit cell. Since each volume element is simply associated with only a scalar (number of ions), the directional motion of the ions in the volume elements is not explicitly accounted. Figure 3 (*right*) depicts a (110) plane containing octahedral sites at the mid-point of the plane as well as at the centers of left and right edges. In Fig. 4 we show the contours of the (time-averaged) distribution of oxygen ions along the (110) plane at different temperatures. As expected, the greatest probability of finding an oxygen ion is at its native tetrahedral site. At a temperature close to T_a (~ 2000 K), the octahedral sites show a higher proclivity to accommodate oxygen ions relative to their neighborhood. We estimate the fraction of time spent at the octahedral sites relative to that at the native anion sites to be $O(10^{-3})$ near T_a . As temperature increases, the ion density at other vacant regions increases significantly; near T_i (2610 K), the elevated status of the octahedral sites in accommodating the disordered anions completely disappears. It is instructive to note that there are no interstitial or relaxed sites that are preferred by the displaced anions, especially at temperatures close to T_a , which is at variance with the defect cluster hypothesis. Even the occupation probability of the octahedral sites is significantly smaller than that of regions in and around the native tetrahedral sites.

At temperatures above T_a , the disordered anions typically engage in large amplitude anharmonic and asymmetric vibrations – this leads to certain intrinsic difficulties in assessing the occupation probabilities at different sites. Since there are no unique ways to determine the time-averaged occupancy of ions, different metrics have been used in the past that have led at times to conflicting interpretations [2, 47]. The primary objective of the current analysis is to (i) confirm that the oxygen ions spend most of the time near the native tetrahedral sites, and (ii) draw out the diminishing role of the octahedral sites with increasing temperature as shown in Fig. 4. The maps in Fig. 4, however, do not offer any further information on the ionic dynamics. In the next sub-section, we use metrics from statistical mechanics to establish that the disordered anions mostly hop from one native site to another at temperatures above T_a in accordance with Gillan’s viewpoint [8-9] .

4.3 Ion-Hopping Signature from van Hove Self-Correlation Function

In our earlier investigation [15] we had used the single ion van Hove density correlation function to establish an arrested glass-like state for the oxygen anions in UO_2 above T_a . Typically used in the investigation of liquid states, space-time correlation functions provide information on the location of ions/atoms at different times. The van-Hove self-correlation function $G_s(\mathbf{r}, t)$, is a spatio-temporal quantity that describes the correlation of the same ion at different times – it signifies the probability of finding an ion in a small volume element $d\mathbf{r}$, centered at $\mathbf{r}$, and time t , when the *same* ion was at the origin at time $t = 0$ [48]. It is given by

$$G_s(\mathbf{r}, t) \equiv \left\langle \frac{1}{N} \sum_{i=1}^N \delta(\mathbf{r} - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \right\rangle \quad (2)$$

For isotropic systems, low order moments (typically 2) completely specify the above density correlation function. Under such conditions $G_s(\mathbf{r}, t)$ follows the diffusion equation given by [49]

$$\frac{\partial}{\partial t} [G_s(\mathbf{r}, t)] = D \nabla^2 G_s(\mathbf{r}, t) \quad (3)$$

where D is the self-diffusivity. The solution to the above equation for an initial delta spike in the density is a Gaussian function decaying in time. When higher order moments arise, for example from local defects or disorder, there will be a deviation from the Gaussian character – we will exploit this departure from the Gaussian behavior to characterize the disorder among anions and identify plausible transient defect structures.

Figure 5(a), which depicts $G_s(r, t)$ at different temperatures for the oxygen ions at 25 ps, portrays several interesting features of the anion space-time dynamics. At a temperature of 1900 K, there is no perceptible tail for the distribution indicating a predominant vibratory motion of the anions in the bulk. At 2200 K, $G_s(r, t)$ depicts a characteristic diffusive tail, however, with well-defined peaks. Strikingly, these peaks correspond exactly to the native tetrahedral locations of the oxygen ions. In Fig. 5(b) we have plotted $G_s(r, t)$ and the corresponding $g(r)$ at 2400 K – as evident, the peaks/shoulders in the $G_s(r, t)$ and $g(r)$ show remarkable congruence. The multiple peaks at the tetrahedral sites in $G_s(r, t)$ provide the key evidence for collective hops among the oxygen ions. Thus when an oxygen ion gets displaced thermally, it pushes out another anion from a neighboring site and occupies the vacant position; simultaneous peaks in $G_s(r, t)$ indicate that many ions perform multiple hopping over distinct sites as opposed to the more commonly observed back and forth hopping process.

Fig. 5. (a) van Hove density space-time correlation function $G_s(r,t)$ at different temperatures for oxygen ions at 25 ps. (b) Superimposed radial distribution function $g(r)$ and $G_s(r,t)$ at 2400 K (100 ps); the dotted lines show the locations of the nearest five oxygen neighbors. Note that the peaks/shoulders in $g(r)$ and $G_s(r,t)$ correspond to high occupancy sites. The shaded area between 0 to ~ 1.7 Å delineates the extent of typical vibrations of the oxygen ions without displacements. In the 3:1:2 cluster model [5], the relaxed ions are located ~ 0.9 Å away from the native oxygen sites while the corresponding separation distance for the interstitials is ~ 1.47 Å at temperatures near T_d .

Since a peak or a shoulder will emerge at sites of significant ion population, the tail of $G_s(r,t)$ can also be used to identify interstitial locations. In the 3:1:2 cluster model at ~ 2600 K, the relaxed ions and the interstitials are located at ~ 0.9 Å, and ~ 1.47 Å, respectively, from the native oxygen sites. As noticeable from Fig. 5 (a and b), there are no identifiable peaks/shoulders at these locations, which indicate that these positions are no more probable to be occupied than the regions near them. Interestingly, there is no peak/shoulder at the octahedral site (~ 2.44 Å) as well, which is consistent with the small relative occupation probability depicted in Fig. 4. The somewhat strange lack of occupation of the octahedral sites may very well be traced to the increased proclivity of the anions to engage in cooperative hopping between the tetrahedral sites. Thus the energy barrier for collective motion appears to be lower than that of octahedral occupation at higher temperatures. The lack of discernible signature for the cluster defect locations [5] together with the simultaneous peaks in $G_s(r,t)$ support the anion-hopping mechanism in UO_2 at temperatures above T_d . As elegantly demonstrated by Gillan [8-9], ion hopping is entirely consistent with the neutron scattering/diffraction data without the need for dynamic cluster models.

4.4 Preferred Directions for Anion Hops

Having identified that the oxygen anions predominantly hop across their native locations, we will now characterize this motion in somewhat more detail. Most of the jumps take place along the $\langle 100 \rangle$ direction separated by a distance of $a/2$, but a small fraction of the oxygen ions also jumps along the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions as shown in Fig. 6. On an average, the oxygen ions have a prolonged sojourn at their native sites, vibrating back and forth, before making a jump to a neighboring site (by pushing out its occupant). At 2500 K, we have estimated that 88% of the oxygen ions hop along the $\langle 100 \rangle$ direction, while 10% and 2% of them undergo displacements along the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions, respectively. These

values are in reasonable agreement with an earlier study of CaF_2 indicating 79% of the fluorine ions hopping along the $\langle 100 \rangle$ direction, with the remaining 21% along the $\langle 110 \rangle$ direction [50] at temperatures close to T_L .

Fig. 6. (a) Three oxygen ion trajectories depicting hopping motion along $\langle 100 \rangle$ direction at 2500 K. The first and the third ion displacements (shown in red and blue) are shifted by $(a/2)$ and $(-a/2)$, respectively, for clarity. Note that hopping of one ion is also often accompanied by a simultaneous hopping of another ion; this characteristic feature manifests as simultaneous peaks in $G_s(r, t)$ in Fig. 5. (b) Hopping along $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. Similar discrete jumps among oxygen ions have also been reported in [22].

4.5 Dynamic Self-Organization among Anions

While anion hopping is established, the nature of disorder is not evident yet. In our recent work [15] we have shown that the oxygen anions exhibit dynamic heterogeneity – a hallmark of frustrated or arrested states typically exhibited by glasses and supercooled liquids. We will now show that the arrested state is synonymous with disorder and self-organization that is inherently dynamic in origin. As previously mentioned, disorder can be static or dynamic; from the discussion thus far, it is clear that oxygen ions do not show a significant static disorder that arises from stable defects. To quantify the dynamic disorder, we employ a metric known as propensity, which is defined as the mean square displacement of an atom or ion in an iso-configurational ensemble. Rather than averaging the properties over all ions in a thermodynamic ensemble, the averaging is performed for each ion in the iso-configurational ensemble with properties derived from several copies that have the same initial configuration though with different momenta. The most useful feature of the iso-configurational ensemble is in its ability to forecast the dynamic tendency of individual ions. We will take advantage of the per-ion displacement metrics to construct a three-dimensional propensity map, which has been used in the past [51] to visually identify the dynamic clustering of atoms in the supercooled states. The maps are constructed by assigning a sphere of radius (r) to every oxygen ion given by [51-52]

$$r = R_{\min} \exp \left\{ \left| \frac{(R_i - N/2)}{(1 - N/2)} \right| \log \left(\frac{R_{\max}}{R_{\min}} \right) \right\} \quad (4)$$

where R_i is a sorted integer rank of the propensity values ranging from the smallest to largest and varying between 1 to N , where N is the total number of oxygen ions in the simulation; $R_{\min}$ and $R_{\max}$ assume the values 0.01 Å and 0.5 Å, respectively [51]. The most mobile ions (top-half) are then colored green and by definition, the largest green spheres represent the *most* mobile oxygen ions in the system. For the ions with rank R_i varying from 1 to $N/2$ (least mobile), the ranks are reversed before evaluating their radii; these are then assigned the color red. Thus the largest red spheres represent *the least* mobile ions.

Fig. 7. Propensity maps depicting the growth and decay of dynamic clustering of oxygen ions with temperature. The red and green spheres represent the most mobile and the least mobile ions, respectively. As evident, mobile ions are more likely to be found near other mobile ions, and *vice-versa*, in a state of *dynamic* self-organization.

The propensity maps for the oxygen ions are shown in Fig. 7 for temperatures varying from 1900 K to 2900 K. A remarkable evolution of dynamic self-organization among the oxygen ions – depicted by the growth and decay of heterogeneous clusters of slow (red) and fast (green) moving ions – can be observed in Fig. 7. Notice that the fast ions tend to be spatially correlated to the other fast ions, and *vice-versa*. From the onset at ~ 2000 K, the heterogeneous dynamic clusters spread spatially with increasing temperatures, and become most prominent at a temperature of 2500 K. Remarkably, the dynamic clusters retract with further increase in temperature, and by 2900 K they have shrunk considerably. The presence of dynamic clusters indicates that the groups of oxygen ions that collectively jump across lattice sites are spatially separated from those which do not attempt to engage in cooperative hopping. While there is a certain amount of isotropy in the structural disorder, there is a marked anisotropy in the dynamic characteristics.

More interesting is the observation that the dynamic self-organization is not sustained with increasing temperature. Thus there is a fundamental difference between the quasi-static disorder characterized by LRO in Fig. 1(b) and the dynamic self-organization predicted by propensity in Fig. 7. The disorder from LRO is an estimate of the fraction of anions that are displaced from the sub-lattice and hence, it shows a monotonic increase with temperature; the close agreement to neutron scattering data in Fig. 1(b), which also is a measure of anions leaving the lattice sites [12], provides a strong confirmation. The propensity maps in Fig. 7, however, indicate that not all anions that are displaced are eager to form dynamic clusters, and those which participate in such clusters are limited by the thermodynamic state. Any form of disorder will entail an increase in entropy, which will then tend to destabilize the elements of self-organization. Thus, the dynamic clustering will involve additional entropic cost – we will show in the next sub-section that this is indeed demonstrable from thermodynamic metrics.

4.6 Entropic Signature for Dynamic Self-Organization

A direct evaluation of the entropic changes that are associated with the dynamic disorder can be evaluated with methods such as thermodynamic integration (TI) [53]. However, TI can be limited by the optimal choice of the integration path that is not known *a priori*, and it is also constrained in having a reversible path that implicitly excludes a first order phase change [54]. In this work, we use an indirect method for calculating the change in entropy. First we note that Eq. (5) is an exact thermodynamic relationship under equilibrium conditions. Thus the rate of change of entropy (s) with temperature can be computed if the specific heat (c_p) is known.

$$\frac{ds}{dT} = \frac{c_p}{T} \quad (5)$$

Fig. 8. (a) The specific heat (at constant pressure) of UO_2 from MD simulations as a function of temperature. (b) Variation of the ratio c_p/T (left axis), which is the rate of change of entropy (ds/dT), and peak value of Θ (right axis), with temperature. The superscript ($\bullet$) denotes inferred value of T_a from the variation of c_p/T .

The variation of c_p , evaluated as the derivate of enthalpy with respect to temperature, shown in Fig 8(a) shows the Bredig or λ -transition at 2560 K, which is close to the experimental value of 2610 K. The ratio c_p/T , which is depicted in Fig. 8(b) shows several interesting features. First c_p/T shows a decrease at low temperatures, which indicates that entropy is increasing sub-linearly with temperature. Conspicuously, a

change of slope is noticeable near T_a where dynamic self-organization sets in; as can be inferred this leads to a super-linear increase in the entropy. Thus the zero slope in c_p/T is a valuable metric to identify the onset of dynamic disorder in UO_2 . Remarkably, with increasing temperature, c_p/T shows a second change of slope close to the λ -transition temperature. The entropy growth, therefore, is *greatest* at T_a and *least* near T_λ , which noticeably is consistent with the rise and fall of the dynamic self-organization shown in Fig. 7. To quantify the changes to the dynamic self-organization depicted in Fig. 7, we employ a space-time correlation of the propensity given by [52]

$$\Theta(r, t) = \frac{\langle \delta w(i, t) \delta w(j, t) \rangle}{\langle [\delta w(t)]^2 \rangle} \quad (6)$$

where i and j are two ions such that the magnitude of the distance between them falls within an interval of Δr , and $w(i, t)$ is the propensity of the i^{th} ion at time t with $\delta w(i, t) \equiv w(i, t) - \langle w(t) \rangle$ denoting the instantaneous fluctuation of the propensity. At low temperatures below T_a , Θ is nearly constant at all times without showing a peak (results not shown). Above T_a , Θ shows a peak in time depicting a dynamic correlation [15], with a magnitude that rises and falls with increasing temperature analogous to the variation portrayed in Fig. 7. It is quite remarkable to note the tight correlation between the peak value of Θ and the rate of change in entropy (c_p/T) as depicted in Fig. 8(b). Thus there is a demonstrable entropic change that accompanies the non-monotonic variation of the dynamic self-organization among oxygen anions.

5.0 Concluding Remarks

Motivated by the seminal work of Gillan [8-9] on disorder in Type II superionic conductors, we show, using atomistic simulations, that oxygen anions in UO_2 predominantly hop from one native (tetrahedral) lattice site to another above a characteristic temperature T_a (~ 2000 K). The degree of disorder calculated from the long range order (LRO) among the oxygen ions portrays a noticeable change near T_a and shows a remarkable congruence to the neutron scattering data [5]. Interestingly, we uncover two forms of disorder. The first quasi-static disorder metric, which is calculated from the LRO, shows a monotonic increase with temperature without any significant change at the Bredig or λ -transition. Physically, this metric is correlated to the number of anions that are getting dynamically displaced from their native sites.

The second metric based on the mean square displacement of the anions in an isoconfigurational ensemble (propensity) depicts a dynamic clustering behavior at temperatures above T_a . The presence of dynamic clusters indicates that the oxygen ions that collectively jump across the lattice sites are spatially separated from the relatively immobile anions. Thus the anions manifest a *dynamic* self-organization in which the anions prefer to be spatially correlated to those with similar mobility. Fascinatingly, this dynamic self-organization shows a peak near the λ -transition and collapses at higher temperatures. The change in entropy evaluated through the ratio c_p/T confirms that the highest entropic growth is recorded near T_a , and the least near T_λ , which is remarkably correlated to the rise and fall of the dynamic self-organization. The thermodynamic metric c_p/T is thus a key indicator of the change in dynamic disorder in UO_2 as well as in other Type II superionic conductors.

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Appendix 1

Figure A1 depicts two key properties that help in identifying the onset of disorder at high temperatures. The first is the mean square displacement (Δr^2) of the oxygen anions, the slope of which correlates to the self-diffusivity of the anions (left panel in Figure A1). The second is the lattice parameter, which increases with increasing temperature at constant (zero) pressure (right panel in Figure A1). Note that all the states are in thermal equilibrium – the flat plateau in MSD at low temperatures indicates trapped dynamics of a crystalline state. A significant change in the slope of MSD for O ions (with liquid-like diffusivities) is detected at $\sim 1900/2000\text{ K}$ (T_α). The lattice parameter also shows a transition near the same temperature.

FIG. A1. Properties from MD simulations identifying T_α . (a) Mean square displacement (Δr^2) of the oxygen ions at different temperatures ranging from 1700 to 2900 K in steps of 100 K. (Inset) MSD with a longer time window of 1 ns. The self-diffusivity of the oxygen ions, which can be evaluated as $\lim_{t \rightarrow \infty} (\Delta r^2/6t)$, shows a sharp increase at $\sim 1900/2000\text{ K}$ (results not shown); a behavior also noted by Lunev and Tarasov [22] with the same interionic potential. (b) Lattice parameter at different temperatures showing a transition at $\sim 2000\text{ K}$. The superscript ($\bullet$) denotes inferred values from the MD simulations.

Appendix 2

The potential developed by Basak and coworkers [27] uses a Busing-Ida form, which is identical to that adopted by Yakub *et al.* (see Eq. (1) in the main text). The parameters are given in Table A1.

Table A1. Parameters for the Basak *et al.* potential [27]

$z_+ (e)$	$z_- (e)$	$A_{++} (eV)$	$A_{--} (eV)$	$A_{+-} (eV)$	$\rho (\text{\AA})$	$C_{..} (eV \cdot \text{\AA}^6)$	$D_{+-} (eV)$	$B_{+-} (\text{\AA}^{-1})$	$r_{+-}^* (\text{\AA})$
2.40	-1.20	294.75	1633.66	693.92	0.327022	3.950	0.5774	1.65	2.369

$$\rho = \rho_{++} = \rho_{--} = \rho_{+-} \quad C_{++} = C_{+-} = 0 \quad D_{++} = D_{--} = 0.$$

Figure A2 contrasts the time-averaged long range order predicted by Yakub *et al.* and Basak *et al.* potentials. The disorder transition temperatures (T_a) predicted by these potentials are in good agreement with that from neutron scattering/diffraction data [5].

Fig. A2. Comparison of long range order obtained with the potentials developed by Yakub *et al.* ([24]) and Basak *et al.* [27]. The superscript (*) denotes inferred values from MD simulations.