Supplementary Materials for

Molten uranium dioxide structure and dynamics


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Other Supplementary Material for this manuscript includes the following:
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Table S1
Materials and Methods:

X-ray experiments were performed at sector 11-ID-C of the Advanced Photon Source (Argonne, IL, USA). Scattered x-rays were detected using a Perkin Elmer XRD1621 amorphous silicon area detector. High energy x-rays (111.158 keV) were used to minimize absorption and multiple scattering in the sample. The sample-detector distance was calibrated using a NIST standard CeO$_2$ powder sample. X-ray transmission through the UO$_2$ sample ~50% was achieved by using a thin incident beam (0.2 mm vertical width) and scanning the sample stage such that diffraction was measured from the top 0.2 mm of the molten drop. The aerodynamic levitation method involves floating of the sample on a 99.999% purity Ar gas stream inside an Ar filled chamber. The sample is then heated from above using a 400W CO$_2$ laser (Synrad Firestar i401). Temperature was measured at the top of the sample using a Chino IR-CAS pyrometer (0.7-0.9 μm waveband). The liquid UO$_2$ emissivity value of 0.84±0.03 was used in the temperature correction and the error in temperature is estimated to be ~2-3% due to a combination of temperature gradients in the upper part of the sample and chamber window transparency corrections. A brass sheet was placed in front of the area detector to absorb any uranium fluorescence (L-edge ~20keV), while passing >80% of the elastically scattered x-rays (standard corrections were used for attenuation). The 2D scattering patterns were integrated using Fit2D. The Q-resolution of the setup was found to be approximately constant at ~0.05 Å$^{-1}$ from the FWHM of calibration peaks for Q < 10 Å$^{-1}$. For full comparison to the x-ray measurement the MD simulated U-U, U-O and O-O partial structure factors were weighted using the Q-dependent x-ray form factors, including dispersion terms for U, and by combining formal charge and neutral form factors in a 50:50 ratio to approximate for partial covalence. The x-ray weighted pattern was then Fourier transformed using the same transform parameters as the measured x-ray data. Specifically $g_X(r)$ is related to the measured structure factor $S_X(Q)$ by

$$g_X(r) = 1 + \frac{1}{2\pi^2 r^2} \int_0^{\max Q} Q(S_X(Q) - 1) M(Q,\Delta) \sin(Qr) dQ$$

(1)

Where $\rho$ is the number density in atoms per Å$^3$ (0.0593 Å$^{-3}$ for liquid UO$_2$), and the modification function $M(Q,\Delta)$ is used to discriminate against unphysical high frequency noise in the liquid $g(r)$ patterns (Fig. 3), while avoiding broadening of real features in $g(r)$ ($\Delta$ is an $r$-space averaging width which may vary with $r$ (13, 19)). For the hot solid patterns in Figures 1 and 2 $M(Q,\Delta) = 1$ is used to avoid broadening. The $D(r)$ and $T(r)$ functions (Fig. 1, 2) emphasize higher-$r$ correlations and are related to $g(r)$ by $D(r) = 4\pi \rho r (g(r)-1)$ and $T(r) = 4\pi \rho rg(r)$ (for further detail see (10, 13, 19)). Bond lengths reported are determined from the relevant peak maximum positions in $T_X(r)$ or $T_{ij}(r)$ functions.

The $n_{UO}(r)$ and $n_{UU}(r)$ are obtained from the integral of the MD $rT_{UO}(r)$ and $rT_{UU}(r)$ pair distribution functions (10, 19). Measured $n_{UO}(r)$ curves are also obtained by reweighting
and integrating the x-ray patterns (Fig. 2A circles, see (13) for detail). Above 3Å, however, U-U correlations start to contribute to the x-ray pattern, limiting the range of applicability of the measured $n_{UO}(r)$. The cut-off for the coordination number calculations was taken as the minimum in $rT(r)$ functions, which is the inflection point in the corresponding $n(r)$ functions.

During heating there was visible vaporization from the sample surface. To minimize the effect of this, each sample was melted and measured for just 2-5 seconds. To check for stoichiometry change, the change in lattice parameter between pre-heating and recovered (post melting) samples was measured to be ~0.1%. This change is consistent with a stoichiometry change UO$_{2+x}$ where x is less than ±0.005 (27) between the initial UO$_2$ and final UO$_{2-x}$ samples.

The reported melting slope ($dT_m / dP$) of UO$_2$ (16) is greater than that predicted from the Calusius-Clapeyron relation ($T \Delta V / L$, where L is the latent heat and $\Delta V$ is the volume change on melting), by roughly a factor 1.5-2. The MD simulations support a steep melting slope by predicting high O-disorder in the hot-solid and a relatively low L. An alternative explanation for this high melting slope is also given in (16) as a slight non-stoichiometry (<0.005%) of the high vapor pressure melt, affecting the melting slope measurement.

MD simulations were performed using the DL_POLY classic package (28). Liquid simulations were initiated from random configurations where all atoms had been moved to have a minimum separation of 1.5Å. Simulations were then run under NPT conditions at 6000K for 50ps, and 4000K for 50ps before running at experimental temperatures each for 100ps, configurations were collected and analyzed from the last 50ps of each 100 ps run. Crystalline configurations were initiated from the crystal structure of (29) using a box size of $8\times8\times8$ unit cells. This crystal was run at 300K for 200ps before temperatures were increased to the experimental values. Again each temperature step was run under NPT conditions for 100ps with only the last 50ps used in the analysis. The $r_{UO}$ of the Yakub model is 2.24±0.01 (compared to 2.22±1 measured).

The potential refinement involved adjusting the U-O and O-O potentials to improve agreement with the measured liquid structure. The Morse potentials used for the refined model are given by

$$U_{ij}(r) = \frac{e^2}{4\pi\varepsilon_0} \frac{z_i z_j}{r} + D_{ij} \exp\left(-2W_{ij}(r - R_{ij})\right) - 2D_{ij} \exp\left(-W_{ij}(r - R_{ij})\right)$$

(2)

Where $i, j$ are U or O, $z_U = 2.2$, $z_O = -1.1$, were chosen to be close to the Yakub model, and the refined constants $D_{ij}$, $W_{ij}$, and $R_{ij}$ were 0.21 eV, 1.5 Å$^{-1}$, and 2.880 Å for U-O and 0.02 eV, 1.48 Å$^{-1}$, and 3.76 Å for U-U respectively. The effect of the sharp simulated $S_X(Q)$ peak on the simulated $g_X(r)$ is visible in the $r > 5$ Å oscillations which have slightly different damping and amplitude in the MD models compared to the x-ray measurement (Fig. 3).
By defining two U sub-species $U_6 (U_{uo} \leq 6)$ and $U_7 (n_{uo} \geq 7)$, the distribution of $U_6$ and $U_7$ subspecies is investigated through the Bhatia-Thornton concentration-concentration pair distribution function ($g_{cc}(r)$) \(^{(20)}\). Positive values of $g_{cc}(r)$ indicate a preference for neighbors of like subspecies, whereas negative values indicate a preference for unlike subspecies. Here, the small peak in $g_{cc}(r)$ (Fig. S1) indicates a slight preference for $U_6$-$U_6$ and $U_7$-$U_7$ connections over $U_6$-$U_7$ and $U_7$-$U_6$ connections, implying only very slight clustering of these polyhedral types.
In the analysis the probability of bond breaking (neighbor swapping), was found to have roughly stretched exponential decay \((\exp(-at^b), b < 1)\). For simplicity, just the time for half the initially neighboring pairs is reported. The cut-offs taken for the U-O and U-U neighbor pairs were \(r_{\text{cut}} = 3.1\,\text{Å} \text{ U-O and } r_{\text{cut}} = 5.1 \,\text{Å} \text{ U-U}\). Equal temperatures of 3000K were chosen for the liquid vs. crystal analysis, even though the liquid is only stable above 3270K the short times scales of the MD model meant that no crystallization is observed at 3000K. The U-O and U-U \(\tau_{50}\) values in the liquid at 3270K were 0.42 ps and 1.3 ps, which are slightly faster than the supercooled liquid at 3000K.

**Author Contributions:**

LBS original idea, wrote proposal, wrote paper, data analysis, MD simulations.
CJB safety exp. planning, manuscript prep., data analysis.
JKRW original idea, exp. planning, equipment prep.
MW safety, exp. planning, sample prep.
AT equipment design & prep.
AH TW chamber design, sample prep.
OLGA experiment, contributions to manuscript.
MG, LL, JD, JBP, contributions to manuscript.
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11. Materials and methods are available as supporting material on Science Online.

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