Supplementary Information for

Structural changes across thermodynamic maxima in supercooled liquid tellurium: a water-like scenario

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**Supporting Information Text**

**Experimental setup**

Figure S2 shows a schematics of the experimental setup used at beamline 1-ID at the Advanced Photon Source. The sample is placed in a hollow cylindrical oven wrapped in resistive heater wires. At the center of the tube, a through path is created for both the entrance and the exit of X-rays. A control thermocouple (TC) is inserted into a fixed location in the oven. Downstream from the sample is placed, in sequence, a WAXS detector (GE 41RT (1)), a helium flight tube, a beamstop (with a diode at the center to measure the transmitted beam intensity, $I_0$), and a SAXS detector (Pixirad2). Another diode (not shown), $I_0$, is placed before the sample and measures the incoming beam intensity. The planes of the WAXS and SAXS detectors are 2.003 m and 6.420 m from the sample, respectively. The Q-positions of the WAXS detector pixels are calibrated using a CeO2 powder sample.

**Temperature calibration**

Due to the opening in the center of the oven for the passage of the X-rays, some temperature gradient is expected within the oven. In order to calibrate the sample temperature, we measure the melting of three materials, Bi, Te, and Sb, with the WAXS pattern. The temperature of the control TC is increased in small steps, and WAXS patterns are collected after equilibration at each step. Melting can be observed unambiguously as the disappearance of sharp Bragg peaks and the appearance of a halo pattern. The corresponding control TC temperature can be determined within 5 K. In Fig. S3 we plot the temperature of the control TC thus determined against the melting temperature of each sample. The data are well described by the linear fit shown in the plot, and we use the fit result for the analysis. We note that the calibrated temperature range well covers the range used in our Te measurements, from above 580 K to below 750 K.

Another way to cross-check the temperature calibration and ensure consistency between different scans is through the position of the first peak of the liquid, $Q_{m1}$. This quantity depends sensitively on the sample temperature and can be determined with a high accuracy because of the relatively strong WAXS signal. In addition, it is independent of normalization and insensitive to possible smooth changes in the background.

In Fig. S4, we plot $Q_{m1}$ against the calibrated sample temperature. We can see that data from different scans align well with each other. From these data, the temperature derivative of $Q_{m1}$ is calculated and plotted in Fig. 3c in the main text.

**Density measurements**

The density of the sample is determined via X-ray transmission measurements. Experimentally, we measure the incoming X-ray intensity $I_0$ and transmitted beam intensity $I_1$ at each sample temperature. The same measurements are also done with an empty capillary, giving the background values $I_{0bg}$ and $I_{1bg}$. We then have:

$$\frac{I_1}{I_{1bg}} = \frac{I_0}{I_{0bg}} \exp\left[\frac{-(\mu/\rho)t}{\rho}\right], \quad [1]$$

where $\mu/\rho$ is the mass attenuation coefficient of the sample, $\rho$ its density, and $t$ its thickness. For tellurium and an X-ray energy of 76.112 keV, $\mu/\rho = 3.68 \text{ cm}^2/\text{g}$ (2).

With measured values of $I_0$, $I_1$, $I_{0bg}$, and $I_{1bg}$, Eq. [1] describes a relation between $\rho$ and $t$. Since $t$ depends on both the sample and the beam position, it may change between scans. Thus, for each cycle, $t$ is determined using the literature value of $\rho$ at the highest temperature (3). The density $\rho$ at the other temperatures in the cycle can then be determined given this value of $t$. As can be seen in Fig. S5c below and Fig. 2 in the main text, the results from different cycles and different scans are consistent with each other, and all agree well with the values reported by Tsuchiya (3). This also indicates that sample movement is minimal during each cycle.

**Consistency between cycles**

As mentioned in the main text, each one of the three scans in our dataset consists of several cycles. In each cycle, the sample is first heated above its melting point and then cooled down in steps (usually 10 K) to the lowest temperature. We take scan 1 as an example to demonstrate the consistency between data from different cycles, and the results are shown in Fig. S5. Because of a high signal-to-noise ratio, the WAXS data from different cycles overlap well with each other, as shown in Fig. S5a-b. The density measurements based on X-ray transmission are also well reproduced between cycles, as shown in Fig. S5c.

In comparison, the SAXS signal is weaker and somewhat larger variations are observed between cycles, but the data remain consistent. As mentioned in the main text, in the analysis, the SAXS data at the highest temperature of each cycle (733 K in this scan) is subtracted from the data at other temperatures, and we analyze the difference

$$\Delta S(Q) = S(Q) - S(Q; T = 733 \text{ K}). \quad [2]$$

Figure S5d shows $\Delta S(Q)$ integrated from $Q = 0.06 \text{ Å}^{-1}$ to 0.15 $\text{ Å}^{-1}$; the black crosses show the average values, with error bars representing the standard error of the mean. We then fit $\Delta S(Q)$ with a linear function:

$$\Delta S(Q) = A S(0) - kQ. \quad [3]$$
The $Q = 0$ intercept, $\Delta S(0)$, and the slope $k$ extracted from the fit are shown in Fig. S5e and f, respectively. The same trend can be observed in panels (d), (e), and (f), where a maximum around 615 K can be observed. The intercept $\Delta S(0)$ is reported in the main text and used for further analysis.

**WAXS analysis details**

This section shows details of the WAXS data analysis. To obtain $S(Q)$, we first calculate the azimuthally integrated intensity profile $I(Q)$ from the WAXS images. Next, we subtract the background measured with an empty glass ampoule without sample. The background consists of two parts: one part comes from the glass capillary and the air scattering after the sample, which is scaled by the X-ray transmission through the sample; the other part comes from air scattering before the sample which is not affected by the sample—because the sample is only about a millimeter in size while the air path is several meters long, the vast majority of the air scattering before the sample misses the sample in the WAXS geometry; only a negligible fraction, up to a few centimeters of air path immediately before the sample, adds a background affected by sample transmission. After background subtraction, we then normalize the curve, subtract the Compton scattering as well as a flat fluorescence background, and divide the data by the form factor $|f(Q)|^2$ to obtain the $S(Q)$ data. The resulting $S(Q)$ data for $T = 724$ K are shown in Fig. S6a as blue dots. Because a small amount of tellurium oxide is present, the data contain some weak powder rings which appear as sharp peaks in $S(Q)$. These outliers can be identified and excluded, resulting in the smoothed data shown as the red line, which agrees well with the X-ray data at 723 K reported by Akola et al. (4). The latter is also shown (4) to agree well with earlier neutron data by Menelle et al. (5).

For our WAXS dataset, the measured $Q$-range is from around 0.8 Å$^{-1}$ to 7 Å$^{-1}$. However, it can be seen that (4), across the wide temperature range from 623 K to 1123 K, very little change occurs in $S(Q)$ above 6 Å$^{-1}$. A similar observation can be made based on the data reported by Endo et al. (6) which included a smaller $Q$- and temperature-range. Therefore, in order to more accurately calculate the radial distribution function, $g(r)$, we append the previously reported data (4) of $S(Q)$ from 7 Å$^{-1}$ to 15 Å$^{-1}$ to our results before integration. On the low-$Q$ side, a linear interpolation is used for the reduced structure function, $Q[S(Q) − 1]$, between 0.5 Å$^{-1}$ and 0.8 Å$^{-1}$ before integration (see Fig. S6b). The result at $T = 724$ K can be compared with that at 723 K reported by Akola et al. (4), as shown in Fig. S6. A good agreement can be observed between the present data and previous results.

In Fig. S7, we show the same results at 626 K, compared with the neutron diffraction data at 623 K reported by Menelle et al. (4, 5).

**Boundaries of the intermediate region**

In the main text, we have used $R_1 = 3.14$ Å and $R_2 = 3.69$ Å as the lower and upper boundaries of the intermediate region. Here, we show that the conclusions, in particular the rapid change in $N_{int}$ around the Widom line, do not depend sensitively on the definition of the boundaries. To test this, we change the value of $R_1$ or $R_2$ by ±0.2 Å, and calculate the number of atoms for each pair of $R_1$ and $R_2$. The results are shown in Fig. S8. Although different choices lead to different $N_{int}$ values (see Fig. S8b), the derivatives all show a peak around the Widom line position (see Fig. S8c).

**SAXS and WAXS data for all scans**

In Figs. S9 and S10, we show details of the WAXS and SAXS data for scans 2 and 3, respectively. The SAXS data in these scans show larger error bars because of lower signal levels, but the results are consistent with those from scan 1 shown in the main text.

The WAXS results for all three scans, including the calculated $g(r)$, are presented in Figs. S11 to S13. The results are consistent between different scans.
Fig. S1. Schematics of a likely phase diagram of liquid water (7–9). The line of liquid-liquid transition (LLT) separates the low-density (LDL) and high-density liquid (HDL) phases. The LLT ends at a liquid-liquid critical point (LLCP), with a critical pressure expected to be on the order of one to a few kilobars (9, 10). From the LLCP emanates the line of isothermal compressibility maxima along isobars ($\kappa_T \max$), which intersects the $P \approx 0$ isobar around 229 K (9). Also shown is the line of density maxima along isobars ($\rho \max$), which is known to intersect $P = 1$ bar at $T = 277$ K. Our study suggests that a similar phase diagram may be expected for liquid Te.
Fig. S2. Experimental setup (not to scale).
Fig. S3. Temperature calibration. The red crosses show the temperature reading of the control TC at melting plotted against the actual melting temperature for each sample. The solid black line shows a linear fit.
Fig. S4. Position of the first peak, $Q_{m1}$, plotted against the calibrated sample temperature, $T$, for all three scans.
**Fig. S5.** Consistency of data from different cycles in scan 1. (a) Dots: WAXS data around the first peak; lines: fit to the data with a Gaussian function and a linear background. From dark red to dark blue the temperature decreases from 733 K to 608 K, same as Fig. 1 in the main text. Data and fits for all four cycles are shown, and the results well overlap. (b) The position of the first peak, $Q_{m1}$, extracted from the fits. The symbols representing different cycles overlap. (c) Density $\rho$ based on X-ray transmission measurements; also shown are the average (black crosses with error bars) as well as the results reported by Tsuchiya (3) (gray line). (d) SAXS data $\Delta S(Q)$ integrated from 0.06 Å$^{-1}$ to 0.15 Å$^{-1}$. (e) The intercept $\Delta S(0)$ and (f) the slope $k$ extracted from the linear fit to $\Delta S(Q)$. 
Fig. S6. WAXS analysis. (a) Structure factor $S(Q)$. Blue dots: data at $T = 724$ K. Red line: smoothed data after exclusion of sharp peaks. Gray line: X-ray diffraction data at 723 K reported by Akola et al. (4). (b) Reduced structure function, $Q[S(Q) − 1]$. The dotted part shows the low-$Q$ extension used in the calculation of the radial distribution function, $g(r)$, shown in (c).
Fig. S7. Same as Fig. S6 but for $T = 626$ K, compared with neutron diffraction data at 623 K reported by Menelle et al. (4, 5).
Fig. S8. Test of the boundaries of the intermediate region. (a) The function $r^2 g(r)$. Colored solid lines: liquid Te from scan 3, from dark red to dark blue are decreasing temperatures from 738 K to 585 K, as shown in the color bar. Also shown are trigonal Te (11) (gray solid line) and electron diffraction results on amorphous Te (12) (black dashed line). Vertical dashed lines indicate different values of $R_1$ and $R_2$; the values are shown on the upper x-axis. (b) The number of atoms between $R_1$ and $R_2$, and (c) its temperature derivative. Different colors represent different choices of $R_1$ and $R_2$, as shown in the legend. Data from all three scans are included. Blue dots ($R_1 = 3.14 \text{ Å}, R_2 = 3.69 \text{ Å}$) correspond to the choice in the main text. The derivatives show a maximum near the Widom line (dashed vertical line), independent of the choice.
Fig. S9. Same as Fig. 1 in the main text, but for scan 2. (a) Te WAXS profiles (structure factor $S(Q)$) from scan 2. From dark red to dark blue are decreasing temperatures as indicated by the color scale. (b) Te SAXS profiles from the same scan, subtracting the highest temperature profile (628 K) in the scan. The color scheme is the same as in (a). Data are shown with error bars, and the dashed lines show a linear fit to the data. Selected temperatures are marked next to the fit lines with the corresponding colors. Inset shows the intercept $\Delta S(0)$ plotted against sample temperature.
Fig. S10. Same as Fig. S9, but for scan 3.
Fig. S11. WAXS results for scan 1. (a) Structure factor $S(Q)$. The appended data (4) from 7 Å$^{-1}$ to 15 Å$^{-1}$ is shown as dashed black line. (b) Radial distribution function $g(r)$. Dotted vertical lines shows the boundary of the intermediate region, $R_1$ and $R_2$, as discussed in the main text. (c) The function $r^2 g(r)$. (d) Running coordination number $N(r)$. 
Fig. S12. WAXS results for scan 2. Same as Fig. S11.
Fig. S13. WAXS results for scan 3. Same as Fig. S11.
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