Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Apparent Power-Law Behavior of Water's Isothermal Compressibility and Correlation Length upon Supercooling

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I. Temperature validation

i) Comparison to homogeneous nucleation rates: Assuming that the isothermal compressibility (κ_T) would follow the apparent power law that is given by Speedy and Angell[1] which is shown as black dashed line in Figure 2(a) of the main script, we would expect the lowest temperature that was measured in the experiment to be ≈234 K instead of the reported 227.7 K. We estimate the probability of a homogeneous nucleation event to occur inside a droplet before it is hit by an x-ray pulse by

$$\frac{n_{\mathrm{hom}}}{n} = 1 - \exp\left[-\int_0^{t_{\max}} \mathrm{V}\ J_{\mathrm{hom}}(T(t))\, dt\right], \tag{S1}$$

where n_{hom} is the number of droplets which froze homogeneously, n is the total number of solid and liquid droplets, V is the volume of a water droplet, $J_{\mathrm{hom}}\big(T(t)\big) = \exp(-2.92T(t) + 706.5)\mathrm{cm}^{-3}\mathrm{s}^{-1}$ is the temperature-dependent homogenous nucleation rate reported by Murray et al.[2], $T(t)$ is the time-dependent droplet temperature and $t_{\max}$ is the lifetime of the droplet before it is hit by an x-ray pulse. The integral in the exponent is due to the droplet temperature changing during evaporation. We note that the change in droplet volume due to evaporation is much smaller than the experimentally observed uncertainty in the droplet diameter and its effect on the nucleation probability is neglected.

For the calculation, we assumed the droplet temperature to follow the temperature profile that is obtained by Knudsen theory of evaporation but rescaled to the hypothetically lowest temperature of 234 K. For the experimental condition of a 14 μm droplet with a lifetime of 4 ms, we obtain a nucleation probability of ≈0.15%. This means that we would expect Bragg peaks from ice in only 1 out of ≈650 recorded scattering patterns in case the lowest temperature would be 234 K. This is in conflict with the experimental observations where almost all droplets were frozen at the lowest temperature.[3]

ii) Comparison to droplet sizes measured by Raman resonance peaks: A recent study by Goy et al.[4] has validated the applicability of Knudsen theory of evaporative cooling to supercooled water microdroplets, although claiming that the temperatures in a previous study using x-ray laser in a similar fashion as in the current study may be underestimated.[5] This is surprising since both the studies use the same experimental set-up and the same theory of Knudsen evaporation. Their procedure involves the extraction of the droplet diameter from measurements of the Raman resonance peaks and fitting them by an iterative application of the Knudsen theory of evaporative cooling as a function of distance, using the droplet velocity and initial droplet diameter as fit parameters. Their best-fit is shown in Figure S1 with an estimated droplet velocity of 22.2±1.5 m/s. The 68% confidence interval (corresponding to ± standard deviation from the mean value) of their fit corresponds to the shaded region as shown in Figure S1. Our proposed fit would have a lower velocity of 15.4 m/s, which would be consistent with the temperature estimation of the current study. This low value of velocity also fits the data much better at measured diameter values during the start of the evaporative cooling. This region corresponds to rapid evaporative cooling and sharp changes in droplet diameters and is thus the most sensitive part for the fitting procedure as compared to later stages of evaporative cooling. At longer times, there can be expansion of the droplets due to the presence of nanometer ice crystals that may not be detectable in the Raman measurements when the droplet is not yet fully frozen.

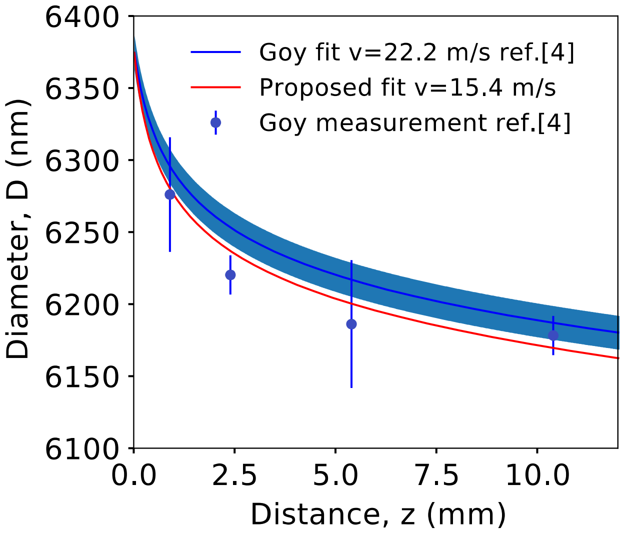

Figure S1. Figure adapted from Goy et al.[4] showing their measurement, fit to their measurement with the shaded region corresponding to ± standard deviation from the mean of the fitting parameters. The red line corresponds to our proposed value for the velocity.

II. Subtraction of a normal component for the isothermal compressibility

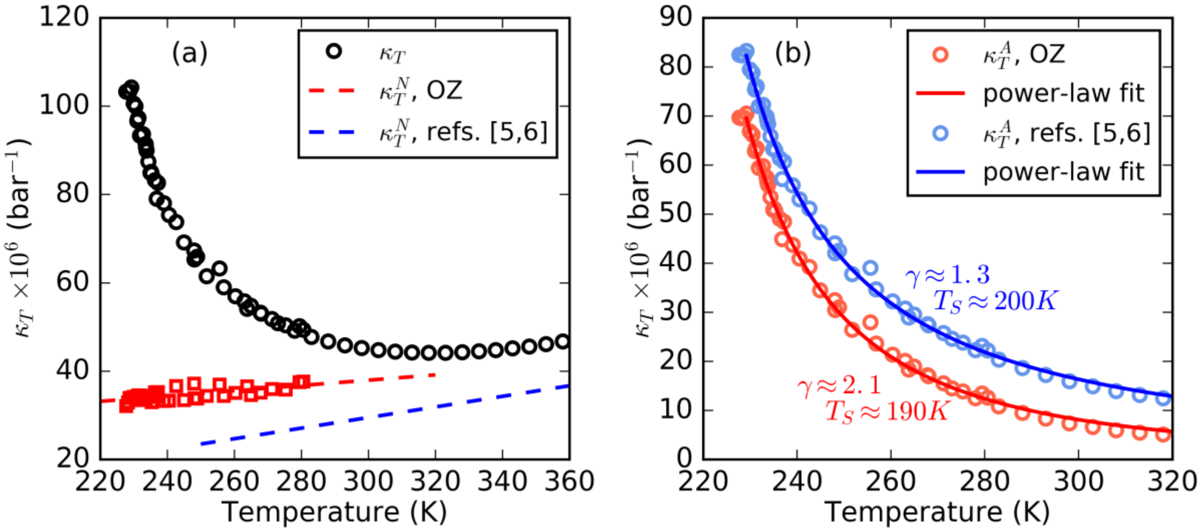

Figure S2. (a) Isothermal compressibility, κ_T, from this study and Ref. [3] (black circles). Estimates of the normal component obtained from Ornstein-Zernike analysis of the SAXS structure factor (red squares and corresponding linear fit shown as red dashed line), as well as from extrapolation of dilution experiments (blue dashed line) from Refs. [6,7]. (b) Anomalous components of κ_T (circles) obtained from the experimental κ_T after subtraction of the normal components in (a) and corresponding power-law fits according to eq. (1) in the main text (red and blue solid lines).

Microscopically, κ_T is directly related to the volume fluctuations (δV) in the liquid by $\langle(\delta V)^2\rangle = Vk_BT\kappa_T$. The influence on κ_T of these fluctuations can be divided into a normal and an anomalous contribution, even though there is no strict division based on thermodynamic grounds. The normal component is related to thermally induced fluctuations that exist in any liquid and decreases with decreasing temperature, whereas the anomalous component of κ_T is attributed to structural changes between HDL and LDL and therefore increases with decreasing temperature[8,9]. Figure S2(a) shows the experimental κ_T and its minimum around 319 K. Usually, a normal component is subtracted from κ_T in order to obtain a monotonic decrease with temperature in the remaining anomalous part of κ_T, which then can be fitted by a power law.

In other studies[6,7], the normal component for κ_T has been approximated based on the influence of small impurities in the liquid. Here we estimate the normal and anomalous components directly from the fitting of the SAXS structure factor, that is divided into a normal contribution from a hard-sphere fluid and an anomalous contribution described by

Ornstein-Zernike theory. For detailed description of the fitting of the SAXS structure factor, see Refs. [3,10].

The decomposition of κ_T into normal and anomalous contributions is an approximation and depends on the approach that is used, as shown in Figure S2. As a consequence, also the apparent power-law fits and corresponding critical exponents differ for the different approaches. We find a large variance in the critical exponent of $\gamma = 1.3$ and $\gamma = 2.1$ for the anomalous components after decomposition suggested by Refs. [6,7] and decomposition using the SAXS structure factor, respectively. Therefore, we decided not to decompose κ_T into a normal and anomalous contribution and instead use a limited temperature range for the power-law analysis, where κ_T shows a monotonous decrease with temperature. We found reliable power-law fits of κ_T for temperatures up to 300 K which supports the use of the entire experimental data set of Ref. [3], which was measured up to 281 K.

References

1 R. J. Speedy and C. A. Angell, *J. Chem. Phys.*, 1976, **65**, 851–858.

2 B. J. Murray, S. L. Broadley, T. W. Wilson, S. J. Bull, R. H. Wills, H. K. Christenson and E. J. Murray, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10380–10387.

3 K. H. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. A. Sellberg, J. H. Lee, S. Kim, J. Park, K. H. Nam, T. Katayama and A. Nilsson, *Science*, 2017, **358**, 1589–1593.

4 C. Goy, M. A. C. Potenza, S. Dedera, M. Tomut, E. Guillerm, A. Kalinin, K.-O. Voss, A. Schottelius, N. Petridis, A. Prosvetov, G. Tejeda, J. M. Fernández, C. Trautmann, F. Caupin, U. Glasmacher and R. E. Grisenti, *Phys. Rev. Lett.*, 2018, **120**, 015501.

5 J. A. Sellberg, C. Huang, T. A. McQueen, N. D. Loh, H. Laksmono, D. Schlesinger, R. G. Sierra, D. Nordlund, C. Y. Hampton, D. Starodub, D. P. DePonte, M. Beye, C. Chen, A. V. Martin, A. Barty, K. T. Wikfeldt, T. M. Weiss, C. Caronna, J. Feldkamp, L. B. Skinner, M. M. Seibert, M. Messerschmidt, G. J. Williams, S. Boutet, L. G. M. Pettersson, M. J. Bogan and A. Nilsson, *Nature*, 2014, **510**, 381–384.

6 H. Kanno and C. A. Angell, *J. Chem. Phys.*, 1979, **70**, 4008–4016.

7 O. Conde, J. Teixeira and P. Papon, *J. Chem. Phys.*, 1982, **76**, 3747–3753.

8 P. G. Debenedetti, *J. Phys. Condens. Matter*, 2003, **15**, R1669–R1726.

9 O. Mishima and H. E. Stanley, *Nature*, 1998, **396**, 329–335.

10 C. Huang, T. M. Weiss, D. Nordlund, K. T. Wikfeldt, L. G. M. Pettersson and A. Nilsson, *J. Chem. Phys.*, 2010, **133**, 134504.