

Metastability and no criticality

ARISING FROM J. C. Palmer *et al.* *Nature* **510**, 385–388 (2014); <http://dx.doi.org/10.1038/nature13405>

Palmer *et al.*¹ support the idea² of two distinct liquid phases and a low temperature critical point in supercooled water. They do so claiming that molecular simulation of one particular model reveals a stable interface separating two metastable liquids. Here we note that fundamental considerations contradict the idea, and we consider that the data presented do not support the claim. There is a Reply to this Brief Communication Arising by Palmer, J. C. *et al.* *Nature* **531**, <http://dx.doi.org/10.1038/nature16540> (2016).

Binder observes³ that two-liquid criticality defined in terms of a divergent length scale is impossible at supercooled conditions: in the vicinity of a presumed critical point, growing lengths must coincide with growing equilibration times, but the time available to equilibrate can be no longer than the time it takes the metastable liquid to crystallize. Thus, metastability (or instability) implies an upper bound to the size of fluctuations that can relax in the liquid. For water, this size seems to be no larger than 2 or 3 nm, corresponding to volumes containing fewer than 1,000 molecules (see Methods).

Metastable fluctuations on smaller length scales might seem interpretable in terms of a liquid–liquid transition, but the length-scale bound implies it is impossible to know if the interpretation is correct. Further, the interpretation seems unnecessary, because reasonable molecular models known to not exhibit two-liquid behaviour account for equilibrium anomalies of water^{4–6} and non-equilibrium amorphous ices⁷.

Significant fluctuations occur in supercooled water owing to coarsening of ice and competing effects of dynamic heterogeneity. Figure 1 refers to experimental^{8,9} and theoretical^{7,10} information about these behaviours. Fluctuations are largest in the vicinity of the stability temperature, T_s , below which nanometre-scale domains of the liquid are no longer even metastable. Relaxation in that regime is slow because T_s is well below the onset temperature of glass-forming dynamics, T_o . With two (or more) irreversible glass phases of different densities, transient mesoscopic domains will appear as precursors in the reversible melt. These non-equilibrium phenomena can be confused with two-liquid criticality, as illustrated and analysed in ref. 12.

All estimated locations for a critical point in supercooled water are spread over a range of pressures below 1 kbar, and temperatures $T_s < T < T_h$ (ref. 8), arrived at through extrapolations from measurements made well outside that region. Here, T_h is the homogeneous nucleation temperature, below which ice forms rapidly. The one experiment to venture below T_h (ref. 9) finds the liquid persisting for only 10^{-3} s at 227 K, and without a hint of critical fluctuations. Thus, the putative critical temperature would need to be even lower¹¹, were it to exist.

The claim of Palmer *et al.*¹ that numerical simulation demonstrates two-liquid behaviour that is close to criticality and can be scaled to large sizes has, in our view, several technical problems^{12,13}. The behaviour that they report, already reproduced as the result of limiting relaxation of fluctuations¹², is transient and disappears as fluctuations are allowed to relax¹². The issue is not in the reliability of simulation algorithms and codes, but rather in the using of codes in ways consistent with reversibility, which can be challenging owing to slow relaxation. LAMMPS codes used in refs 5 and 12 are standard and documented¹⁴, with scripts freely available upon request, and applications taking care of reversibility^{5,12} establish consistent behaviour among several different models of water.

Technical problems aside, the interpretation by Palmer *et al.*¹ is based upon system sizes too small to demonstrate interfacial scaling,

and their claim of showing a stable interface contradicts some earlier work^{12,15}. Indeed their data are for systems containing only 200 to 600 molecules, and the data can be equally well interpreted in terms of system-size dependence of finite transient domains, not a macroscopic interface separating two phases¹⁶.

Two-liquid coexistence and criticality are in general possible, but not in water where this behaviour would be required to exist at deeply supercooled conditions. Given that fact and that suitable models of liquid water do not exhibit two-liquid coexistence, it seems most fruitful to treat supercooled water on its own terms, as a metastable or unstable non-equilibrium material with the largest fluctuations manifesting

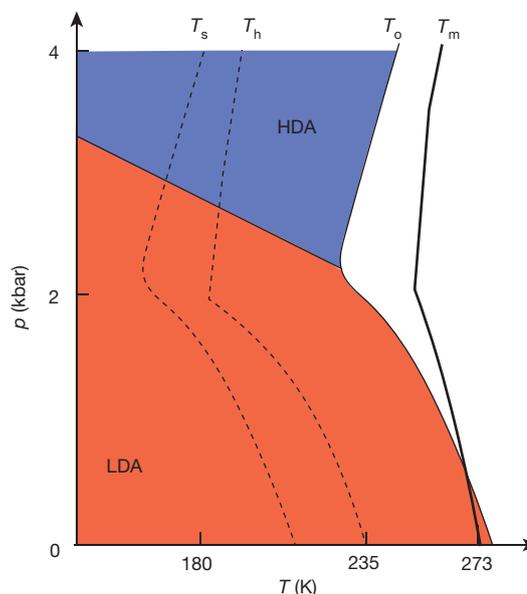


Figure 1 | Phase diagram of supercooled water, with T and p denoting temperature and pressure, respectively. Corresponding states for the simulation model used by Palmer *et al.*¹ are shifted to higher temperatures by 10%–15%. For $T > T_m$, liquid is stable; for $T < T_m$, where ices are stable, irreversible behaviours of the liquid are varied, depending upon experimental protocols. For $T < T_h$, the lifetime of the liquid is of the order of $10^{\pm 1}$ s or less. This region is sometimes called the ‘no man’s land’ of liquid water because observation of the liquid is difficult for $T < T_h$ (T_h is given in ref. 8). At yet lower temperatures, $T \lesssim T_s$, coarsening rather than simple nucleation becomes rate determining. At that stage, the liquid is dominated by fluctuations, and its lifetime increases with decreasing temperature. Below the onset temperature, T_o , dynamics in the liquid are heterogeneous and intermittent, and far enough below, water can be driven out of equilibrium into high-density and low-density amorphous ices, HDA and LDA. (In this figure, the lines showing T_o and T_s are estimated from theory^{7,10}, and equation (16) of ref. 10 is a formula for the temperature dependence of metastable lifetime. These results have been tested to a limited extent. Further tests await future experiments¹⁶.) The properties and transition temperatures of these glasses depend upon the timescale at which the liquid is driven out of equilibrium¹⁷. The line between HDA and LDA domains marks the p at which the T to reach that timescale is minimum⁷. At very low temperatures, this line relates to a first-order-like non-equilibrium transition between HDA and LDA phases¹⁸. Observations of the transition show a large range of hysteresis with the average of the forward and backward transition pressures being close to that line.

ice coarsening. These non-equilibrium phenomena are distinct from equilibrium liquid–liquid criticality.

Methods

At conditions of two-liquid criticality³, the time to equilibrate on length scale ξ is of the order of $\tau_\xi = \tau_R(\xi/a)^3$, where a is a characteristic microscopic length, and τ_R the time to relax the liquid on length scale a . Clearly, $\tau_\xi < \tau_{MS}$, where τ_{MS} is the lifetime of the metastable liquid. Accordingly

$$\xi/a < (\tau_{MS}/\tau_R)^{1/3} \quad (1)$$

wherever criticality might apply. For supercooled water, that regime would be $T \lesssim T_s$, where fluctuations are largest. There, both τ_R and τ_{MS} grow with decreasing temperature T , but estimates of the ratio yield $(\tau_{MS}/\tau_R) \lesssim 10^3$ throughout¹⁰. Thus, because $a \approx 0.2$ or 0.3 nm, $\xi < 2$ or 3 nm. Further details and discussion about uncertainties regarding these estimates are presented elsewhere¹⁶. I note that applying equation (1) at 227 K, where $\tau_{MS} \approx 10^{-3}$ s yields a much larger value for ξ , is not appropriate because experiments at that temperature show water ice nucleation⁹, not large fluctuations or criticality.

D. Chandler¹

¹Department of Chemistry, University of California, Berkeley, California 94720, USA.

email: chandler@berkeley.edu

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Palmer *et al.* reply

REPLYING TO D. Chandler *Nature* **531**, <http://dx.doi.org/10.1038/nature16539> (2016)

We reported¹ for the ST2 model of water advanced free energy calculations using six sampling techniques, all of which show the existence of a low-density liquid (LDL) as well as a high-density liquid (HDL) and a liquid–liquid phase transition (LLPT) between them. In the accompanying Comment², Chandler contends that fundamental arguments³ preclude an LLPT in water and reiterates his claim⁴ that the LDL phase is an artefact associated with poor equilibration.

We point out that although the fundamental argument³ concerns the question of whether critical fluctuations can be detected in metastable systems despite nucleation of the stable phase, it was explicitly stated³ that it has firm implications only for the detection of a critical point, but does not preclude liquid–liquid phase separation. When applying this argument, Chandler² concludes that critical fluctuations larger than 2–3 nm cannot be equilibrated in deeply supercooled water. Following the same analysis but using different values for relevant timescales ($\tau_R \approx 10^{-10}$ s from experimentally derived correlations⁵ and $\tau_{MS} \approx 10^{-3}$ s from experiment⁶, as defined in ref. 2), we estimate that critical fluctuations at 229 K can reach ~ 100 nm—potentially large enough to characterize experimentally.

Regarding putative artefacts arising due to poor equilibration, the LDL persisted in our simulations^{1,7} after relaxing all accessible fluctuations by sampling reversibly between the liquid and crystal regions, and two liquid basins were obtained independently of the sampling method and duration. The LDL basin did not disappear over time

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when sampling to and from the crystal, as had been predicted when incorrectly⁴ assuming our calculations to be poorly equilibrated. The free energy exhibits scaling consistent with an LLPT over the range of system sizes that can be explored computationally^{1,7}. Each of these facts is inconsistent with poor equilibration. Moreover, the salient features of our free energy calculations have been reproduced by others^{8,9}, and our code has been publicly available since 2014 (<http://pablonet.princeton.edu/pgd/html/links.html>). The recent demonstration⁹ that adjustment of a single model parameter in ST2 (the hydrogen-bond angular flexibility) makes the LLPT thermodynamically stable with respect to ice Ih/Ic disproves the claim⁴ that crystallization was mistaken for an LLPT.

The main issue is the irreconcilable difference between seemingly identical free energy calculations for the same water model: these identified either two liquids and a crystal as we reported¹, or only one liquid and one crystal⁴. Chandler argues² that LLPT-like artefacts arise from limiting relaxation of fluctuations, but this was only observed when transforming simulation data using a theory whose key assumption is that density fluctuations in HDL decay much faster than bond-orientational fluctuations⁴. In contrast, molecular dynamics simulations show that density is the slowly relaxing variable in the HDL region¹⁰. Chandler's explanation is therefore contradicted by the reversible phase behaviour^{1,8,9} and equilibrium dynamics^{1,10} of ST2. Ultimately, we are confident that continued scrutiny of codes

and methods used in the free energy calculations will reveal the cause of the different behaviours predicted for ST2. The question of which one occurs in real water must await an answer by experiment, not by theory or simulation.

Jeremy C. Palmer^{1,†}, Fausto Martelli², Yang Liu^{1,†}, Roberto Car², Athanassios Z. Panagiotopoulos¹ & Pablo G. Debenedetti¹

¹Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, USA.

email: pdebene@princeton.edu

²Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA.

†Present addresses: Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204, USA (J.C.P.); Air Products and Chemicals, Inc., Allentown, Pennsylvania 18195, USA (Y.L.).

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