Palmer et al. reply

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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.\textsuperscript{1} support the idea\textsuperscript{2} 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 observes\textsuperscript{3} 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\textsuperscript{4–6} and non-equilibrium amorphous ices\textsuperscript{7}.

Significant fluctuations occur in supercooled water owing to coarsening of ice and competing effects of dynamic heterogeneity. Figure 1 refers to experimental\textsuperscript{8,9} and theoretical\textsuperscript{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 lower\textsuperscript{11}, were it to exist.

The claim of Palmer et al.\textsuperscript{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.\textsuperscript{12,13} The behaviour that they report, already reproduced as the result of limiting relaxation of fluctuations\textsuperscript{12}, is transient and disappears as fluctuations are allowed to relax\textsuperscript{12}. 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 documented\textsuperscript{14}, with scripts freely available upon request, and applications taking care of reversibility\textsuperscript{12,13} establish consistent behaviour among several different models of water.

Technical problems aside, the interpretation by Palmer et al.\textsuperscript{1} is based upon system sizes too small to demonstrate interfacial scaling, and their claim of showing a stable interface contradicts some earlier work\textsuperscript{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 phases\textsuperscript{16}.

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 $\rho$ denoting temperature and pressure, respectively. Corresponding states for the simulation model used by Palmer et al.\textsuperscript{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 $10^{12}$ s or less. This region is sometimes called the ‘no man’s land’ of liquid water because observation of the liquid is difficult for $T < T_h$ (the liquid is given in ref. 8). At yet lower temperatures, $T \leq T_o$, 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\textsuperscript{7,15}, 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 experiments\textsuperscript{16}.)

The properties and transition temperatures of these glasses depend upon the timescale at which the liquid is driven out of equilibrium\textsuperscript{7}. The line between HDA and LDA domains marks the $p$ at which the $T$ to reach that timescale is minimum\textsuperscript{7}. At very low temperatures, this line relates to a first-order-like nonequilibrium transition between HDA and LDA phases\textsuperscript{18}. 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 criticality⁴, the time to equilibrate on length scale \( \xi \) is of the order of \( \tau_{\xi} = \tau_{\xi}(\xi/a)^{1/3} \), where \( a \) is a characteristic microscopic length, and \( \tau_{\xi} \) the time to relax the liquid on length scale \( a \). Clearly, \( \tau_{\xi} \ll \tau_{\MS} \), where \( \tau_{\MS} \) is the lifetime of the metastable liquid. Accordingly

\[
\xi/a < (\tau_{\MS}/\tau_{\xi})^{1/3}
\]

wherever criticality might apply. For supercooled water, that regime would be \( T \lesssim T_c \), where fluctuations are largest. There, both \( \tau_{\xi} \) and \( \tau_{\MS} \) grow with decreasing temperature \( T \), but estimates of the ratio yield \( (\tau_{\MS}/\tau_{\xi}) \lesssim 10^3 \) throughout⁶. 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 \( \xi \), not appropriate because experiments at that temperature show water ice nucleation⁹, not large fluctuations or criticality.

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**Palmer et al. reply**

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

We reported⁴ 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 Comment⁶, Chandler contends that fundamental arguments⁵ 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 argument⁵ concerns the question of whether critical fluctuations can be detected in metastable systems despite nucleation of the stable phase, it was explicitly stated⁵ 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, Chandler⁵ 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 correlations⁶ and \( \tau_{\MS} \approx 10^{-3} \) s from experiment⁸, as defined in ref. 2), we estimate that critical fluctuations at 229 K can reach \( \sim 100 \) nm—potentially large enough to characterize experimentally.

Regarding putative artefacts arising due to poor equilibration, the LDL persisted in our simulations⁴ 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 when sampling to and from the crystal, as had been predicted when incorrectly⁶ 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 computationally¹⁷,¹⁷. Each of these facts is inconsistent with poor equilibration. Moreover, the salient features of our free energy calculations have been reproduced by others⁹,¹⁰ and our code has been publicly available since 2014 (http://pablonet.princeton.edu/pgd/html/links.html). The recent demonstration⁷ of a single model parameter in ST2 (the hydrogen-bond angular flexibility) makes the LLPT thermodynamically stable with respect to ice Ih/lc 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 reported⁴, or only one liquid and one crystal⁻. Chandler argues⁹ 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 fluctuations⁷. 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 behaviour¹,²,⁸ and equilibrium dynamics¹⁰,¹⁰ of ST2. Ultimately, we are confident that continued scrutiny of codes
Brief Communications arising

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.

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