PHYSICS OF WATER

Crystal-clear transition

Liquid–liquid phase separation is counted among the peculiar phenomena attributed to pure water, but rapid crystallization has rendered its existence hard to prove. Evidence of a ‘naked’ liquid–liquid transition in a system unencumbered by crystallization encourages us to keep searching.

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Everyone knows that oil and water don’t mix under normal conditions. Instead, they undergo what we call liquid–liquid phase separation. But what if only one fluid — say, water — is involved? Intuition suggests that it would never exhibit such a phase separation, because it is a pure substance. Now, writing in *Nature Physics*, Frank Smallenburg and colleagues[1] have demonstrated the possibility of a thermodynamically stable liquid–liquid transition in a pure system — with implications for the curious physics of water.

There is evidence that pure liquid water separates into distinct high- and low-density phases, a suggestion that would explain many of its anomalous properties[2]. But this unusual transition is expected to occur only in supercooled water — a liquid state that is metastable with respect to ice below the ordinary freezing temperature. Unsurprisingly, the observation of such a transition has been hindered by rapid crystallization in a ‘no-man’s land’ for the liquid state, leaving this tantalizing possibility a subject of vigorous debate for more than twenty years.

By contrast, the system studied by Smallenburg *et al.*[1] exhibits a naked liquid–liquid transition, without competition from crystallization (Fig. 1). This finding is based on an extensive set of calculations of model colloidal particles with four attractive ‘patches’ leading to local tetrahedral bonding arrangements, similar to those found in water. The key feature of the model that enables a naked liquid–liquid phase separation is that bond flexibility and core softness can be continuously varied. By tuning these parameters, the team showed that it is possible to realize phase diagrams with no liquid–liquid transition (as in most ordinary fluids), a liquid–liquid transition that is metastable with respect to the crystal (as hypothesized for water, silica and some other directionally bonded systems) or, most surprisingly, a thermodynamically stable, naked liquid–liquid transition.

What ingredients are needed to realize such a naked transition? The first step is to suppress the crystal. For highly directional links between molecules, stable, low-energy bonded states demand very specific order, and thus the crystal is favoured over the liquid at low temperature. In a previous work, Smallenburg and Sciortino[3] demonstrated that it was possible to eliminate stable crystal states, giving rise to stable liquid states all the way to zero temperature — an unusual scenario in and of itself. This can be achieved by using a large bond flexibility, which allows for fully bonded states that are disordered, and hence have larger entropy than ordered states. However, this alone is not enough to realize thermodynamically distinct liquid states.

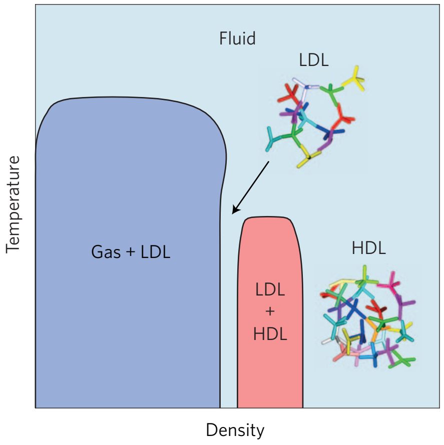

Figure 1 | The phase diagram including the ‘naked’ liquid–liquid transition. On the left is the ordinary liquid–gas coexistence. To the right, and at lower temperature, the system can phase separate into coexisting high-density liquid (HDL) and low-density liquid (LDL) states. The HDL phase has local bonding structure like that of LDL, but the softness of core interactions enables the emergence of a distinct, fully bonded HDL phase. By design, there are no stable crystal states to compete with the liquid phases. In the case of water and many other systems, the liquid–liquid transition is ‘dressed’ — it is metastable with respect to the crystal. Images courtesy of Frank Smallenburg.

Studies on model systems have revealed several possible ways of forming multiple-liquid states in a pure fluid. One is to introduce multiple scales for the isotropic intermolecular interactions, which favour distinct high- and low-density configurations[4]. Another approach uses the idea that directional bonds combined with soft-core interactions enable low-density networks that can potentially interpenetrate, yielding a distinct high-density, interconnected network state[5].

Smallenburg *et al.*[1] followed the second approach, and adjusted the softness of the core interparticle interactions. Increasing the bonding range relative to the core interactions allowed for open, low-density bonded structures that could interpenetrate to form denser networks with the same local bond structure — not unlike the structure of some high-pressure ice polymorphs, like ice VII. Of course, in this case, the networked states were amorphous, rather than crystalline, due to bond flexibility. Intermediate densities were not able to bond completely, and as a result they were excluded by phase separation. Thus, using the right bond flexibility to eliminate crystal states, combined with the correct softness to encourage interpenetration, the authors achieved an exposed, stable liquid–liquid transition.

Water is the most prominent and ubiquitous fluid for which a liquid–liquid transition has been hypothesized, so it forms a natural focal point for the implications of this work. To be clear though, the results of Smallenburg *et al.*[1] do not prove whether or not such a transition occurs in water. Numerous simulation studies of more realistic representations of water have shown metastable liquid–liquid transitions, but at this point, only an experiment can finally resolve the question.

However, the finding of a naked transition is vital to this discussion, as it has been argued that the liquid–liquid transition observed in many water models is in fact a liquid–crystal transition, appearing only as a liquid–liquid transition due to insufficient sampling of states[6]. Following this line of reasoning, metastable liquid–liquid transitions are artefacts, which would nullify the hypothesis that liquid water's anomalies are related to such a transition. The finding of a naked transition puts this question of existence to rest: a liquid–liquid transition cannot be a failed crystallization when there is no crystal. Therefore, it must also be possible to have a liquid–liquid transition that is metastable with respect to the crystal, and very recent simulations of a water model strongly support this scenario[7]. Additionally, experiments on more exotic fluids (phosphorus[8] and cerium[9]) offer direct experimental evidence of a liquid–liquid transition. Consequently, the liquid–liquid hypothesis for water remains alive and well, if unresolved.

The model system studied by Smallenburg *et al.*[1] may offer further insight into how to experimentally resolve whether or not there is a liquid–liquid transition in water. Specifically, much of the experimental evidence for such a transition relies on studies of the glassy state of water, which is accessible by rapid cooling or pressurization[10]. Simulations of water suggest that its behaviour in the glass state can be markedly different in the presence or absence of a liquid–liquid transition[11], but such models cannot systematically tune between these conditions. As the present model allows such tuning, the difference in properties of the glass state as the transition is adjusted might indicate a 'smoking gun' that is accessible to experiments.

On a more practical note, the findings of Smallenburg *et al.*[1] may also guide the design of synthetic, customizable colloid or nanoparticle interactions. Micron-size colloidal particles with specific directionality have already been synthesized[12], and nanoparticles functionalized by DNA offer another route to highly specific interactions[13]. Consequently, a colloidal model for water where the no-man's land can be arbitrarily adjusted to expose the liquid–liquid transition may be within reach. Tetrahedral or diamond-structured systems are of further interest due to their anticipated unusual electronic and optical properties. The study by Smallenburg *et al.*[1] may offer the insights needed to realize some of these new and exciting structures in the lab. ❐

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References

1. Smallenburg, F., Filion, L. & Sciortino, F. *Nature Phys.* http://dx.doi.org/10.1038/nphys3030 (2014).
2. Poole, P. H., Sciortino, F., Essmann, U. & Stanley, H. E. *Nature* **360,** 324–328 (1992).
3. Smallenburg, F. & Sciortino, F. *Nature Phys.* **9,** 554–558 (2013).
4. Skibinsky, A., Buldyrev, S. V., Franzese, G., Malescio, G. & Stanley, H. E. *Phys. Rev. E.* **69,** 061206 (2004).
5. Hsu, C. W., Largo, J., Sciortino, F. & Starr, F. W. *Proc. Natl Acad. Sci. USA* **105,** 13711–13715 (2008).
6. Limmer, D. T. & Chandler D. *J. Chem. Phys.* **135,** 134503 (2011).
7. Palmer, J. C. *et al. Nature* **510,** 385–388 (2014).
8. Katayama, Y. *et al. Nature* **403,** 170–173 (2000).
9. Cadien, A. *et al. Phys. Rev. Lett.* **110,** 125503 (2013).
10. Loerting, T. & Giovambattista, N. *J. Phys. Condens. Matter* **18,** R919–R977 (2006).
11. Giovambattista, N., Loerting, T., Lukanov, B. R. & Starr, F. W. *Sci. Rep.* **2,** 390 (2012).
12. Wang, Y. *et al. Nature* **491,** 51–55 (2012).
13. Dai, W., Hsu, C. W., Sciortino, F. & Starr, F. W. *Langmuir* **26,** 3601–3608 (2010).