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REPLY

Reply to Comment on 'Supercooled and glassy water'

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Abstract

In a recent review on supercooled and glassy water (Debenedetti 2003 *J. Phys.: Condens. Matter* **15** R1669) I used a thermodynamic consistency argument to rule out the possibility, proposed originally by Speedy (1982 *J. Phys. Chem.* **86** 982), that the spinodal curve for superheated liquid water can retrace to positive pressure. The argument is based on the impossibility that a thermodynamic state other than a critical point be a limit of stability (i.e., a point along a spinodal line) and simultaneously coexist with another phase. Speedy's comment offers a counter-example involving the freezing transition to argue that a thermodynamic state can in fact be a limit of stability (spinodal) and simultaneously coexist with a different phase (i.e., a non-critical point along the phase coexistence locus). Here I argue that instability to infinitesimal density fluctuations and coexistence with a different phase are mutually exclusive conditions.

The original argument against the possibility of an intersection between spinodal and binodal lines away from a critical point involved vapour–liquid coexistence [1], where both criticality and limits of stability are well defined. If the spinodal curve for the superheated liquid were to retrace towards positive pressure at low temperature, as proposed by Speedy in his stability limit conjecture on the thermodynamics of supercooled water [2], it would necessarily intersect the low temperature metastable continuation of the boiling curve. Since temperature and pressure uniquely define the equilibrium state of a pure fluid, this intersection in the pressure–temperature plane corresponds to the same state of the liquid. At this intersection the liquid would therefore be simultaneously in equilibrium with the vapour phase and unstable with respect to infinitesimal density fluctuations. The same thermodynamic state of the liquid phase would, in other words, be simultaneously on the spinodal and on the binodal. The only point where these two conditions are satisfied simultaneously is the critical point. Note, however, that in the case of a critical point the liquid and vapour phases are indistinguishable, making coexistence and diverging density fluctuations simultaneously possible. It follows that

Speedy's stability limit conjecture requires that water's boiling curve terminate at a metastable lower critical point. There is no experimental evidence of such a critical point, and this argues against the validity of the stability limit conjecture.

The very notion of a spinodal curve is a mean field approximation. In reality there is no sharp transition to instability but instead an experimentally detectable finite region where the mechanism of phase separation changes from nucleation to spinodal decomposition. Both Speedy's argument and my reply are based on a mean field description of thermodynamics. Within this approximation, the spinodal is a sharply defined line along which a fluid is infinitely compressible and unstable to infinitesimal density fluctuations. It is the postulated intersection of such a line with the phase equilibrium locus whose implications I address here.

Speedy's counter-example involves calculations on the hard sphere model supplemented by a mean field attractive term [3] (hard sphere van der Waals, HSvdW in Speedy's terminology). These calculations show a clear intersection of the superheated liquid spinodal with the freezing line (figures 1 and 2 of Speedy's comment). This state (intersection of curves ls and f in Speedy's figure 2) is at the same time unstable with respect to infinitesimal density fluctuations and able to coexist with the crystal phase. These conditions are mutually exclusive. Speedy's calculations show that it is possible for the HSvdW model to satisfy simultaneously the conditions

$$\mu_{\text{liq}}(T, P) = \mu_{\text{cryst}}(T, P) \tag{1}$$

$$\left(\frac{\partial v_{\text{liq}}}{\partial P}\right)_T = \infty \tag{2}$$

where μ denotes the chemical potential, v is the molar volume and subscripts liq and cryst denote the liquid and crystal phases, respectively. That solutions simultaneously satisfying equations (1) and (2) can be found does not render the conjectured situation physically plausible; rather, it shows that extrapolation of a realistic model can lead to predictions in which mutually exclusive conditions occur at the same thermodynamic state.

There is, however, a very interesting and fundamental question raised by Speedy in his comment, namely what is the ultimate fate of the metastable continuation, below the triple point temperature, of the freezing curve of real substances. It is clearly on a 'collision course' with the superheated liquid spinodal. A critical point is ruled out in this case, since symmetry arguments [4] disallow the possibility that a substance be simultaneously a liquid and a crystal. One possibility is that the intersection conjectured by Speedy in his comment occurs so deep inside the metastable region as to render the very notion of a thermodynamic state ambiguous at best. The rates of processes of relaxation out of the liquid state, such as crystal nucleation, would then become so large as to make the lifetime of the metastable state shorter than the characteristic time needed for the attainment of internal equilibrium [5–7]. Under these conditions, notions of thermodynamic states and of course phase coexistence become meaningless. In this case, the intersection proposed by Speedy never actually materializes but would be a limit towards which the spinodal and freezing curves tend. The validity of this and other scenarios should be tested experimentally and by computer simulation. While the solution proposed by Speedy requires matter to be simultaneously unstable with respect to density fluctuations and to coexist with a different phase, the question that he raises about the ultimate limit of the freezing line is a deep one. As regards the 'intersection' of the spinodal and binodal curves for the liquid–vapour transition, it can only occur at a critical point, where such curves become tangent to each other. The low temperature behaviour of binodals, spinodals and ideal glass transition lines, including the nature of their possible contacts, is an interesting topic that deserves attention [8].

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