Comment on 'Supercooled and glassy water'

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# Comment on 'Supercooled and glassy water'

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**Abstract**
In a review of supercooled and glassy water Debenedetti (2003 *J. Phys.: Condens. Matter* **15** R1669) proposes that the boiling line for supercooled water (a binodal) can meet a conjectured low temperature limit of stability for supercooled water (a spinodal) only at a critical point. This comment offers a counter-example to show that the meeting of a binodal and a spinodal need not be a critical point.

Debenedetti [1] proposes that the boiling line for supercooled water (a binodal) can meet a conjectured low temperature limit of stability for supercooled water [1–4] (a spinodal) only at a critical point. If correct, this proposal rules out a spinodal limit of stability for supercooled water at its equilibrium vapour pressure because it is most unlikely that the liquid and vapour become identical when cooled below the triple point. A wider implication of the same proposal is that a freezing line cannot meet a liquid spinodal when extrapolated to negative pressure [5] because the anisotropic crystal cannot become identical to the isotropic liquid [6].

This comment offers a counter-example to show that the meeting of a binodal and a spinodal need not be a critical point.

A binodal line is located where two phases, 1 and 2, are in equilibrium, with the same Gibbs free energy

$$G_1(T, P) = G_2(T, P) \tag{1}$$

at temperature $T$ and pressure $P$. Derivatives of $G$, such as the volume $V = (\partial G/\partial P)_T$ and the isothermal compressibility $\kappa = -(\partial V/\partial P)_T/V$, generally differ between the two phases at a binodal.

When a metastable phase approaches its spinodal line, $T_S(P)$, it becomes absolutely unstable [4] and $\kappa$ tends to infinity:

$$\kappa \to \infty \qquad \text{as } T \to T_S(P). \tag{2}$$

Equations (1) and (2) are both satisfied at a critical point where two phases are identical, the free energy and all its derivatives are the same in both phases, their spinodal lines meet
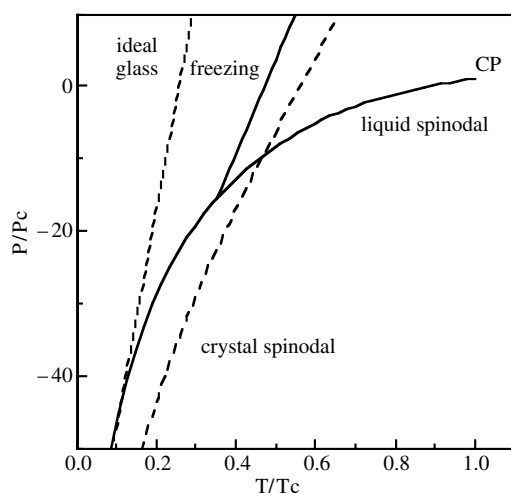
**Figure 1.** The pressure–temperature diagram for the HSvdW model (equation (3)). CP is the liquid–gas critical point. $T_c$ and $P_c$ are the critical temperature and pressure. The spinodal curves are located where $(\partial P/\partial V)_T = 0$, and the freezing line is defined by equation (1). Along the ideal glass line the liquid has the same entropy and density as a glass [8]. The curves are calculated as described in [8], using the pressure and entropy of hard spheres from equations (4) and (5) of [9] for the fluid, from equations (1) and (2) of [10] for the face centred cubic crystal and the ideal glass transition density from [11].

and the compressibility diverges. But equations (1) and (2) do not require that two phases in equilibrium become identical as one of the phases approaches its spinodal.

Longuet-Higgins and Widom [7] proposed modelling simple substances by hard spheres with van der Waals attractions (HSvdW). The HSvdW equation of state is

$$P(\rho, T) = P_{HS}(\rho, T) - a\rho^2, \tag{3}$$

where $P_{HS}$ is the pressure of hard spheres, $\rho$ is the density and $a$ measures the strength of the mean field attractions [8]. $P_{HS}$ is available from simulation studies [9–11] that also yield the entropy and free energy. The HSvdW model gives a good account of the melting of argon and its properties at the triple point [7]. Figure 1 shows that the model is also in accord with Sastry's [12] simulation results which suggest that the liquid spinodal meets the ideal glass transition line with the same slope [8, 13] when $T/T_c \approx 0.11$ and $P/P_c \approx -34$ for a Lennard-Jones mixture.

Where the freezing line meets the liquid spinodal in figures 1 and 2, the densities of the HSvdW liquid and crystal are well within the stable density ranges of the hard sphere fluid and crystal, respectively, so the hard sphere properties are not extrapolated to determine the properties of the model at the intersection. The intersection is not a critical point because (i) symmetry considerations [6] rule out a crystal–liquid critical point, (ii) the HSvdW crystal is 45% denser than the liquid there and (iii) the crystal spinodal does not meet the liquid spinodal there.

The model is thermodynamically consistent [7] so thermodynamics does not require the intersection of a binodal and a spinodal to be a critical point.

The figures are specific to the HSvdW model but the conclusion is more general. If spinodal and ideal glass lines set upper and lower temperature thermodynamic bounds on the existence of a real stretched liquid [8], then any plausible extrapolation of the freezing line to negative pressure must meet one of the lines. It is conceivable that the freezing line meets the
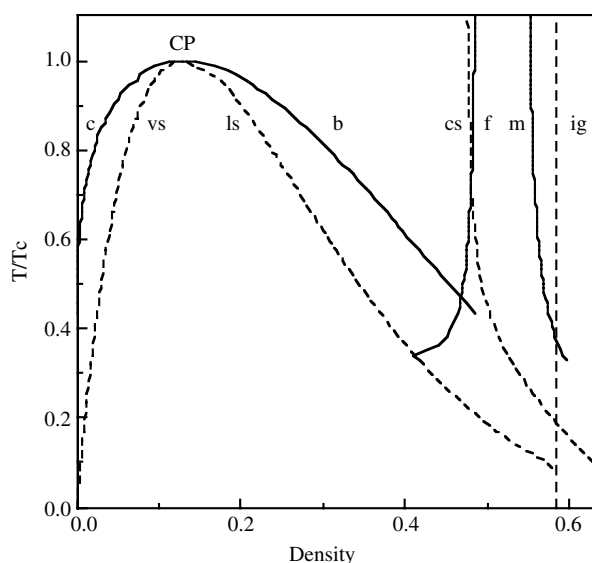
**Figure 2.** The temperature–density diagram for the HSvdW model. The density is the fraction of space occupied by the spheres. CP is the gas–liquid critical point. The solid curves are binodals where two phases coexist in equilibrium. c, b, f and m mark the vapour condensation, liquid boiling, liquid freezing and fcc crystal melting curves, respectively. Dashed spinodal curves for the vapour, liquid and fcc crystal are labelled vs, ls and cs respectively and the line labelled ig locates the ideal glass transition [11].

ideal glass line at a point where the crystal, liquid and glass have the same Gibbs free energy and that the glass is more stable than the crystal at greater tensions. (The ideal glass is the stable phase in the lower right corner of figure 2.) But the more likely scenario is that the freezing line ends at the liquid spinodal [5] as shown in the figures.

## Acknowledgment

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