COMMENTS

Comment on "Entropy catastrophe and configurational entropies in supercooled and superheated regimes" [J. Chem. Phys. 101, 7037 (1994)]

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Kauzmann[1] pointed out that the difference between the entropy of the crystalline and supercooled liquid phases of a substance can vanish at a temperature T_K below the melting point T_m. This condition, in which a disordered phase would attain a lower entropy at absolute zero than a perfect crystal, is known as Kauzmann's paradox. Fecht[2,3] extended Kauzmann's ideas to superheated crystals. Recently, Kishore and Shobha[4] proposed that the ultimate temperature to which a liquid can be superheated is the temperature at which its entropy equals that of the vapor. They argued, furthermore, that this temperature corresponds to the critical temperature. Cahn[5] noted, correctly, that Kishore and Shobha's analysis did not include pressure as a variable, and suggested that entropy crossing in the vapor–liquid transition deserved further investigation. We show that the entropy of a superheated liquid and a vapor at the same temperature and pressure are never equal except at the critical point, where both phases are identical. We then explain the errors involved in Kishore and Shobha's argument.

Kauzmann's paradox[1] follows from comparing the entropies of the supercooled liquid and crystal of a substance at the same temperature and pressure. Accordingly, we fix a pressure P_a (Fig. 1) and compare the entropies of the liquid and vapor phases at successively higher temperatures (e.g., 2 vs 2′, 3 vs 3′). We also compare the entropies of pairs of supercooled vapors and liquids at the same temperature and pressure (1′ vs 1). The hypothetical entropy crossing must occur before the metastable phase becomes unstable at the spinodal curve bcd. Therefore, if there is a Kauzmann condition for the superheated liquid, it must occur at $T < T_a$(liq.); likewise for the supercooled vapor, it must occur at $T > T_a$(vap.). Figure 2 shows the entropy of the Carnahan–Starling–van der Waals fluid,[6,7] at a reduced pressure P/P_c of 0.9, where P_c is the critical pressure. The vertical line is the coexistence temperature. States to the right of the coexistence temperature on the liquid curve are superheated, and those to the left of the coexistence temperature on the vapor curve are supercooled. States to the left (right) of the coexistence temperature along the liquid (vapor) branch are unsaturated. The superheated liquid branch ends at the spinodal temperature [T_a(liq.) in Fig. 1]; likewise, the supercooled vapor branch ends at the spinodal temperature [T_a(vap.) in

Fig. 1]. Thus, the superheated liquid becomes unstable before its entropy equals that of the unsaturated vapor, and the supercooled vapor becomes unstable before its entropy equals that of the unsaturated liquid. This conclusion is valid for any pressure $0 \leq P_r < 1$. At the critical point the vapor and liquid phases are identical, and the equality of entropies is trivial. At negative pressures, there is no vapor phase to which the superheated liquid's entropy can be compared. Analogous conclusions are obtained from other equations of state, such as the van der Waals equation. Identical results for the entropy difference shown in Fig. 2 are obtained by integrating the heat capacity, and using the equation of state to calculate the excess heat capacity,[8]

$$s^\alpha(T,P) - s^\alpha(T_0,P) = \int_{T_0}^{T} \frac{c_p^\alpha(T',P)}{T'} \, dT', \qquad (1)$$

$$c_p^\alpha(T,P) - c_p^\alpha(T)^{\text{ig}} = T \int_{\infty}^{v(P,T)} \left(\frac{\partial^2 P}{\partial T^2} \right)_v^\alpha dv$$
$$- \frac{T[(\partial P/\partial T)_v^2]^\alpha}{[(\partial P/\partial v)_T]^\alpha} - k, \qquad (2)$$
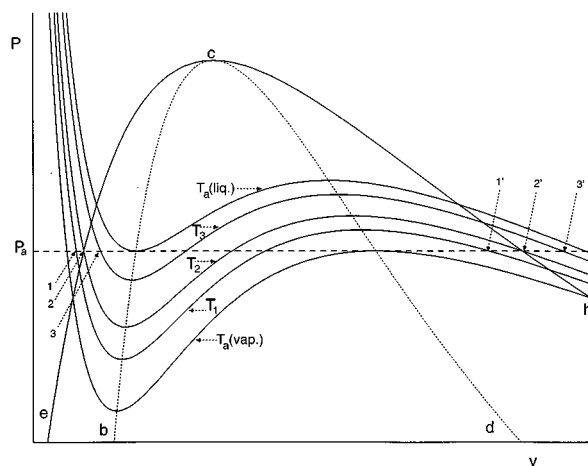

FIG. 1. Schematic pressure–volume projection of the phase diagram of a fluid. ech and bcd are the binodal (coexistence) and spinodal (limit of stability) loci, respectively. T_a(vap.) is the temperature on the vapor branch of the spinodal curve at a pressure P_a. T_a(liq.) is the temperature on the liquid branch of the spinodal at a pressure P_a. T_a(liq.)$>T_3>T_2>T_1>T_a$(vap.).
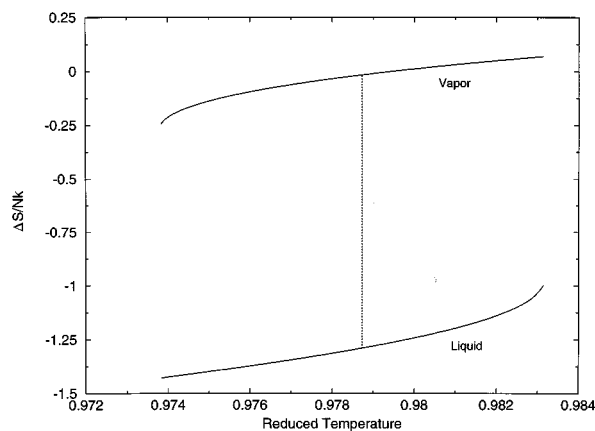
FIG. 2. Entropy of the Carnahan–Starling–van der Waals fluid (Ref. 6,7) at a reduced pressure of 0.9, showing the absence of a Kauzmann temperature. The vertical line is the coexistence temperature. The entropy and pressure of the Carnahan–Starling–van der Waals fluid (Refs. 6,7) are given by $\Delta S/Nk = S/Nk - [5/2 + \ln v_c/(\Lambda_c)^3] = 3/2 \ln T_r - \ln \rho_r + [\rho_r(3\rho_r - 30.6645)]/(7.6661 - \rho_r)^2$ and $P/\rho kT = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 - \rho a/kT$, where N is the number of molecules; k is Boltzmann's constant; $\Lambda_c = h/(2\pi m k T_c)^{1/2}$ is the deBroglie wavelength referred to the critical temperature T_c; h is Planck's constant; m is the mass of the molecule; $T_r = T/T_c, \rho_r = \rho/\rho_c$; v_c and ρ_c are the critical volume per molecule and number density, respectively; $\eta = \rho b/4$, with b, the van der Waals excluded volume per molecule; and $-\rho a$ is the configurational energy per molecule. The quantity plotted in this figure is $\Delta S/Nk$ for each phase, at fixed pressure.

where superscript α denotes the phase (vapor or liquid), superscript ig denotes ideal gas conditions at the given temperature and pressure, and T_0 is a reference temperature.

The calculations shown in Fig. 2 are model-specific. To generalize, we write $(\partial s/\partial v)_T = (\partial P/\partial T)_v$, where s and v are the specific entropy and volume. As long as $(\partial P/\partial T)_v > 0$, entropy is an increasing function of volume along an isotherm, hence the entropy of a superheated liquid is smaller than that of a less dense unsaturated vapor at the same temperature and pressure. The condition $(\partial s/\partial v)_T = (\partial P/\partial T)_v < 0$ does occur in liquids, for example in water at low temperature. There, however, the decrease in entropy upon expansion is due to icelike ordering close to the freezing point.[9] Models can be constructed in which ordering upon expansion occurs at conditions relevant to the vapor–liquid transition, but we are not aware of any physical justification. Thus, a Kauzmann condition does not arise in the vapor–liquid transition of real substances.

Another argument against entropy crossing follows from the fact that a liquid is denser and has lower energy than its vapor at any subcritical temperature and pressure. Using the notation $\Delta x = x(\text{vapor}, T, P) - x(\text{liquid}, T, P)$, we must have

$$\Delta h = \Delta u + P\Delta v \geq 0 \quad (T \leq T_c; 0 \leq P \leq P_c), \quad (3)$$

where h, u, and v are the specific enthalpy, energy, and volume. The equality in Eq. (3) holds only at the critical point. A superheated liquid is less stable than the unsaturated vapor at the same temperature and pressure. Hence

$$\Delta \mu = \Delta h - T\Delta s \leq 0 \quad [T \geq T_b(P); 0 \leq P \leq P_c], \quad (4)$$

where μ is the chemical potential and $T_b(P)$ is the equilibrium boiling temperature. An entropy crossing implies

that there is some temperature T_K, where $\Delta s = 0$. This means

$$\Delta \mu = \Delta h \leq 0 \quad [T = T_K(P); 0 \leq P \leq P_c], \quad (5)$$

which is clearly inconsistent with Eq. (3). Equation (5) requires that the enthalpy difference Δh, which is positive at T_b and negative at T_K, must vanish before Δs vanishes, but Eq. (3) only allows $\Delta h = 0$ at the critical point. Hence the entropy of a superheated liquid must be lower than that of the unsaturated vapor at the same temperature and pressure. The argument based on Eqs. (3)–(5) does not hold for the supercooled vapor because the sign of the inequality (4) is then reversed.

In extending the concept of a Kauzmann paradox to the vapor–liquid transition, Kishore and Shobha[4] made two mistakes. First, they did not use pressure as a variable in their analysis. If there is a Kauzmann temperature for a superheated liquid, it should depend on pressure. Second, they did not take into account the stability of the superheated liquid. Their starting point is the correct equation $\Delta s^v = \int_{T_b}^{T_K}(\Delta c_p/T)dT$, where Δs^v is the entropy of vaporization at the given pressure, T_b is the boiling temperature at the given pressure, T_K is the Kauzmann temperature, and Δc_p is the difference between the heat capacities of the liquid and vapor phases at the given pressure. Using a polynomial of the form $c_p = \alpha + \beta T + \gamma T^{-2}$, one obtains Kishore and Shobha's Eq. (4) for the calculation of T_K

$$\Delta s^v = \Delta \alpha \ln \frac{T_K}{T_b} + \Delta \beta(T_K - T_b) - \Delta \gamma/2(T_K^{-2} - T_b^{-2}), \quad (6)$$

where $\Delta \alpha = \alpha^{\text{liq}} - \alpha^{\text{vap}}$, and likewise for β and γ. We note, however, that the isobaric heat capacity diverges at the spinodal. A polynomial of the form $\alpha + \beta T + \gamma T^{-2}$ cannot be used to extrapolate c_p data deep into the metastable region, because it has an incorrect temperature dependence. One should instead use Eq. (2). Clearly, the second term in the right-hand side of Eq. (2) diverges at the spinodal. The calculation done by Kishore and Shobha is therefore incorrect. No such problem exists for the liquid–solid transition because there is no spinodal associated with this transition, at least for supercooled liquids with a positive thermal expansion coefficient.[10]

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