# On the entropy changes and fluctuations occurring near a tensile instability

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Several liquids exhibit an apparent loss of tensile strength (tensile instability) as their temperature is lowered. Assuming that such substances exhibit a true minimum in the PT projections of their spinodal curves, the thermodynamically consistent behavior that follows from this hypothesis displays a variety of unusual phenomena, of which the PVT aspects have been recently discussed. If, along the tensile instability isochore, the reciprocal compressibility vanishes linearly with respect to temperature (as is the case for a van der Waals fluid near the spinodal) an unusual metastable phase transition with discontinuous entropy and thermal expansion coefficient but continuous volume must occur if this isochore admits a metastable solution below the tensile instability temperature. The form of the specific heat divergence, as well as the equations of phase diagram loci of constant correlation length follow from the nature of the PVT surface in the vicinity of a tensile instability.

## INTRODUCTION

In a recent paper[1] we discussed the thermodynamic implications of tensile instability, i.e., the experimentally observed[2–4] behavior whereby several liquids appear to lose tensile strength as their temperature is lowered.

Our approach has been to start from the hypothesis that the experimental observations do indeed suggest the existence of a (thermodynamic) tensile instability, and then to derive the consequences that follow. The actual (thermodynamic) or apparent loss of tensile strength in cold liquids has important practical implications. Thus, the performance of propellers, centrifugal pump rotors, and related fluid-moving equipment in which tensile stresses are induced in cold liquids is crucially dependent upon the ability of the fluid to withstand such stresses without giving rise to cavitation. Similarly, when high intensity sound waves travel within a liquid, cavitation can occur as a consequence of the alternating tensile and compressive stresses induced by the propagating wave. The problem is therefore germane to sonar and ultrasound applications. Among the latter, we cite tumor detection,[5] sonochemical catalysis,[6] liquid extraction enhancement,[7] and acoustically induced polymerization,[8] to name just a few.

The original treatment[1] was limited to PVT properties: in this paper, we explore the thermodynamics of tensile instability in terms of the entropy changes and fluctuations which occur in the vicinity of such a point. The fundamental assumption[1] is that the PT projection of the spinodal curve for a superheated liquid can, indeed, exhibit a minimum. We mention, parenthetically, a recently proposed[9] empirical equation of state for superheated water which not only gives an accurate representation of experimentally measured volumetric properties, but, in addition, predicts a tensile strength maximum.

The present analysis builds upon some features of the previous PVT treatment, which we now summarize. We assume a smooth[1] instability: loss of tensile strength, in other words, can be described by writing, for the PT spinodal projection,

$$\left(\frac{dP}{dT}\right)_{sp} = 0, \tag{1}$$

$$\left(\frac{d^2P}{dT^2}\right)_{sp} > 0, \tag{2}$$

where subscript sp denotes differentiation along a spinodal curve. Variations in pressure away from the tensile instability and into the surrounding metastable regions can then be described by the dimensionless equation

$$\pi - 1 = x(\tau - 1)^2 + y(\nu - 1)^2 + z(\tau - 1)(\nu - 1) \tag{3}$$

with

$$\pi = P/P^*, \tag{4}$$

$$\tau = T/T^*, \tag{5}$$

$$\nu = v/v^*, \tag{6}$$

$$2x = \frac{(T^*)^2}{P^*}\left(\frac{\partial^2 P}{\partial T^2}\right)_{v,*}, \tag{7}$$

$$2y = \frac{(v^*)^2}{P^*}\left(\frac{\partial^2 P}{\partial v^2}\right)_{T,*}, \tag{8}$$

$$z = \frac{T^* v^*}{P^*}\left(\frac{\partial^2 P}{\partial T\,\partial v}\right)_*, \tag{9}$$

where * denotes either the value of a property (i.e., $T^*$) or of a derivative, at the tensile instability, and $v$, the molar (or molecular) volume. The three dimensionless second order pressure derivatives, furthermore, satisfy the conditions

$$x < 0, \tag{10}$$

$$y < 0, \tag{11}$$

$$z\begin{cases} <0 & (\tau < 1), \\ >0 & (\tau > 1), \end{cases} \tag{12}$$

$$\theta \equiv 4xy/z^2 > 1, \tag{13}$$

all of which follow from assuming $\delta^2 P$ to be the lowest order, nonvanishing pressure variation ($\delta P$ must vanish identically[1]); the implications of this assumption as to the behavior of $z$ are discussed below. Equations (10)–(12), as written, are valid for $P^* < 0$ (tension).

  

The spinodal curve, in $(P,T)$ coordinates, can be written as

$$\pi - 1 = x\left(\frac{\theta - 1}{\theta}\right)(\tau_{sp} - 1)^2 \qquad (14)$$

which is symmetric about $\tau = 1$ if $z$ conserves its magnitude (though not its sign) in going from $\tau > 1$ to $\tau < 1$. In addition, the entropy and fluctuation analysis is dependent upon the behavior of the thermal expansion coefficient, which is negative for $T < T^*$, and positive otherwise, but is not zero at $T = T^*$ (isobars exhibit a cusp at $T = T^*$ when plotted in $\tau$, $v$ coordinates).

We now derive the entropy changes that follow from the above-mentioned features of the PVT behavior.

## Entropy and tensile instability

It follows from Eq. (14) that, for any given $\pi$ (pressure), there are two limits of stability, corresponding to the temperatures

$$\tau_{sp} = 1 \pm \left[\frac{\theta(\pi - 1)}{x(\theta - 1)}\right]^{1/2}. \qquad (15)$$

These limits are symmetric about the tensile instability if $\theta$ is constant (throughout this paper, we restrict our attention to this symmetric case, extensions to the unsymmetric cases being straightforward). We note that $1 \geqslant \pi > 0$ in the vicinity of the tensile instability, since both $P$ and $P^*$ are negative, and $|P| \leqslant |P^*|$.

The objective is therefore to describe the changes in entropy which occur as the temperature is varied, at constant pressure (or tension), between the two limits given by Eq. (15). From the relationship

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_p}{T}, \qquad (16)$$

where $s$ and $C_p$ are specific quantities, we conclude that isobars, when plotted in $s$ vs $T$ coordinates, must have a positive slope which diverges at the two stability limits corresponding to the given tension, where all of the stability coefficients, and, in particular $(\partial T/\partial s)_p$, become zero.

From the above-mentioned behavior of the thermal expansion coefficient, $\alpha_p\,[=(\partial \ln v/\partial T)_p]$ (i.e., $\alpha_p > 0$ for $T > T^*$, $\alpha_p < 0$ for $T < T^*$), and the identity

$$v\alpha_p = -\left(\frac{\partial s}{\partial P}\right)_T, \qquad (17)$$

where $v$ is a specific volume, we conclude that

$$\left(\frac{\partial s}{\partial P}\right)_T > 0 \quad (T < T^*), \qquad (18)$$

$$\left(\frac{\partial s}{\partial P}\right)_T < 0 \quad (T > T^*). \qquad (19)$$

Furthermore, the sign change is discontinuous, as can be seen from Eq. (17) and the previously derived[1] discontinuity in the thermal expansion coefficient. The thermodynamically consistent isobars which follow from the above discussion are shown in Fig. 1, where arrows indicate the direction of increasing pressure (decreasing tension). The lower part of Fig. 1 is the spinodal curve in the vicinity of the tensile instability, as described by Eq. (15). We note, in particular, the following features:

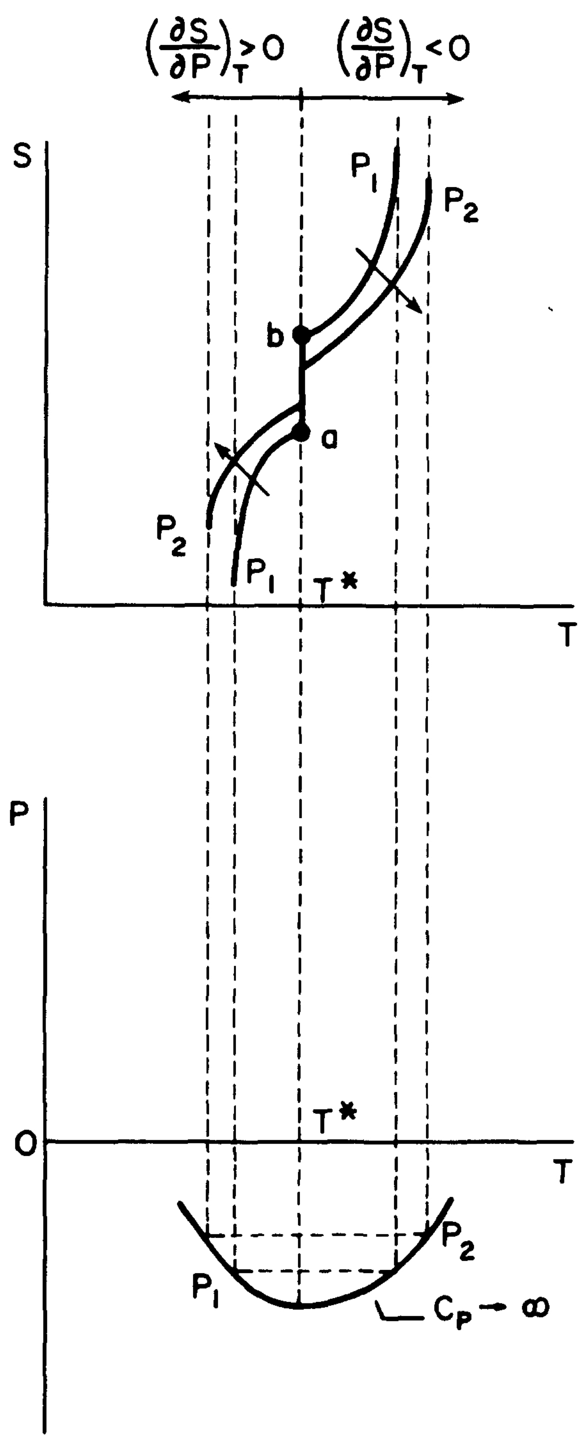


FIG. 1. Isobars in the $sT$ plane in the vicinity of a tensile instability.

At any given pressure ($\pi$), the $s$ vs $T$ curve has diverging (and positive) slope at the two temperatures given by Eq. (15).

An entropy discontinuity results, the sign of which is pressure dependent: at sufficiently low values of tension, the behavior shown in Fig. 1 will give rise to an inversion in $\Delta s$. This implies that the transition from "anomalous" ($\alpha_p < 0$; $T < T^*$) to "normal" ($\alpha_p > 0$; $T > T^*$) behavior becomes eventually exothermic, a conclusion that is valid to within the accuracy with which Eq. (3) describes a tensile instability (see below). Entropy changes along the spinodal curve, as well as the nature of the specific heat divergence, will be discussed below. Before doing this, however, we address the nature, origin, and implications of the entropy discontinuity.

Mathematically, this discontinuity arises from the implicit assumption that $(\partial P/\partial v)_T$ vanishes linearly with respect to temperature along the tensile instability isochore, and that the $T < T^*$ branch of this isochore is not unstable. This behavior is found, for example, in a van der Waals fluid, for which, along an isochore,

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{k(T-T_{sp})}{(v-b)^2} = -\frac{k\delta T}{(v-b)^2} \tag{20}$$

with $T_{sp}$ denoting the temperature at the spinodal curve corresponding to the given volume. It is obvious, however, that a van der Waals fluid does not have a $\delta T < 0$ region corresponding to the left-hand side of Fig. 2(a). Work is currently in progress on the development of a tensile instability analysis in which only the $T > T^*$ branch of the $\nu = 1$ isochore is metastable. We note, furthermore, that any power law behavior of $(\partial P/\partial v)_T$ in terms of $\delta T$ along the tensile instability isochore that contains a leading linear term will also give rise to a discontinuous $z$. If, on the other hand, the linear term vanishes identically, $z$ is zero [Fig. 2(b)] at $\delta T = 0$ ($T = T^*$), and higher order terms must then be incorporated into the expansion [Eq. (3)] in order to account for the $\tau v$-type contributions.

Both alternatives shown in Fig. 2 are thermodynamically consistent, and it is not possible to predict which one is actually exhibited by a given fluid in the vicinity of a tensile instability (in fact, the very question is thermodynamically meaningless, once the consistency of both alternatives is established). It is clear, however, that the entropic implications are different, insofar as the heat effect shown in Fig. 1 is a direct consequence of the discontinuity in $z$. We focus here on the entropic implications of the original model[1] [i.e., Eq. (12)]. The phase transition illustrated in Fig. 1 is unusual in several ways:

The transition from point $a$ to point $b$ involves a discontinuity in entropy and the thermal expansion coefficient, coupled with a continuous density change. Thus, this situation fits none of the traditional (Ehrenfest-type) classifications of phase transitions. Entropy, energy, and enthalpy are discontinuous; Gibbs and Helmholtz energies, continuous.

The $a \to b$ process is a phase transition between two qualitatively different metastable regions: a low temperature ($T < T^*$), anomalous ($\alpha_p < 0$), and a high temperature ($T > T^*$), normal ($\alpha_p > 0$) region.

Although the finite enthalpy change associated with the $a \to b$ transition could be rationalized in molecular terms, the predicted sign change is highly unusual, and suggests a (qualitative) criterion for establishing the outer boundaries within which the model [i.e., Eq. (3)] is an accurate representation of reality. A quantitative calculation requires independent knowledge of the behavior of the nondiverging contribution to the specific heat (see below), as well as the magnitude of the entropy discontinuity at a particular pressure ($P^*$, for example).

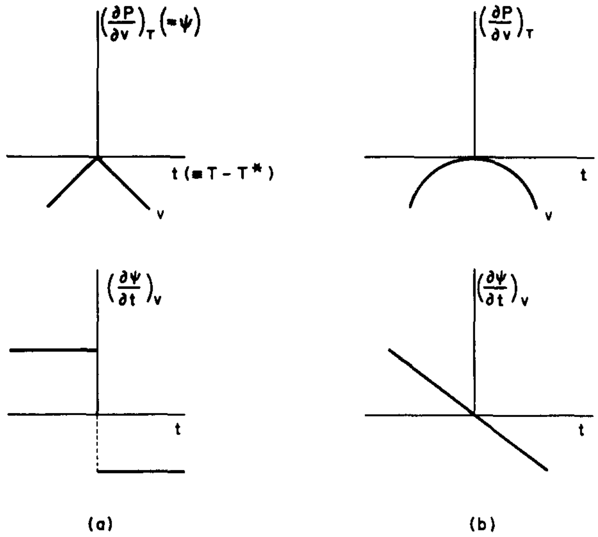


FIG. 2. Linear (a) and quadratic (b) temperature dependence of inverse isothermal compressibility along the tensile instability isochore.

### Specific heat divergence

An important feature of Fig. 1 is the diverging slope of the entropy isobars as $T \to T_{sp}$. As already mentioned above, this behavior follows from stability considerations (specifically, from the fact that stability coefficients vanish along spinodal curves). Thus, we can write, for $T < T^*$

$$C_p = C_p^o\, t^{-\beta} \quad (\beta > 0) \tag{21}$$

with

$$t \equiv \frac{T - T_{sp}(P)}{T_{sp}(P)} \tag{22}$$

and $C_p^o$, a weak function of pressure which, for our purposes, can be considered constant (the treatment for $T > T^*$ is identical, with $t$ redefined as a positive quantity). We have not included in Eq. (21) a (here unimportant) nondiverging additive contribution to $C_p$. For finite entropy changes, we require that $\beta < 1$; we will now calculate the exact value of $\beta$ that follows from Eq. (3). To this end, we first write, for $t \ll 1$

$$s(t,P) = s_{sp}(P) + f(t)\,, \tag{23}$$

$$f(t) = \frac{C_p^o\, t^{1-\beta}}{1-\beta}. \tag{24}$$

We now write (see Fig. 3)

$$\left(\frac{\Delta s}{\Delta P}\right)_{T=T_2} = \frac{s_\mu - s_\nu}{\Delta P}\,, \tag{25}$$

$$\left(\frac{\Delta s}{\Delta P}\right)_{T=T_1} = \frac{s_\delta - s_\gamma}{\Delta P}\,, \tag{26}$$

$$\frac{\Delta(\Delta s/P)}{\Delta T} = \frac{1}{\Delta T}\left[\frac{(s_\mu - s_\epsilon) - (s_\nu - s_\beta)}{\Delta P} - \frac{(s_\delta - s_\epsilon) - (s_\gamma - s_\beta)}{\Delta P}\right], \tag{27}$$

or [see Eq. (23)]

$$\frac{\Delta(\Delta s/\Delta P)}{\Delta T} = \frac{1}{\Delta T}\left[\frac{f(T_2,P_2) - f(T_2,P_1)}{P_2 - P_1} - \frac{f(T_1,P_2) - f(T_1,P_1)}{P_2 - P_1}\right]. \tag{28}$$

Upon taking the limit $\Delta T \to 0$, $\Delta P \to 0$, we obtain the result

$$\frac{\partial^2 s}{\partial T \partial P} = \frac{\partial^2 f}{\partial T \partial P}, \tag{29}$$

which can be rewritten, through a Maxwell relationship, as

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_P = -\frac{\partial^2 f}{\partial T \partial P}. \tag{30}$$

From Eq. (3) and the fact that the stable solution for $\nu$ corresponds to[1]

$$\nu - 1 = -\frac{z}{2y}\left\{(\tau - 1) + \left[\frac{4y}{z^2}(\pi - 1) - (\theta - 1)(\tau - 1)^2\right]^{1/2}\right\} \tag{31}$$

we obtain, after appropriate manipulations,

$$\left(\frac{\partial^2 \nu}{\partial \tau^2}\right)_\pi = \frac{z}{2y}(\theta - 1)^{1/2} \times \frac{(\tau_{sp} - 1)^2}{[(\tau_{sp} - 1)^2 - (\tau - 1)^2]^{3/2}} = -\frac{(T^*)^2}{v^*}\frac{\partial^2 s}{\partial T \partial P}. \tag{32}$$

Similarly, from the definition of $f$ and Eq. (14) we obtain

$$\frac{\partial^2 f}{\partial T \partial P} = \left[\frac{C_p^o T^* 2y}{P^* z^2(\theta - 1)}\right]\frac{t^{-\beta}(\beta - 1 + \beta/t)}{T_{sp}^2[\tau/(t+1) - 1]}. \tag{33}$$

From Eqs. (30), (32), and (33) we obtain, after rearranging and taking the limit $t \to 0$,

$$\frac{C}{\tau_{sp}^2}\cdot\frac{4y^2}{z^3}\cdot\frac{\beta}{(\theta - 1)^{3/2}}\cdot[2\tau_{sp}/(1 - \tau_{sp})]^{3/2} = t^{\beta - 1/2} \tag{34}$$

with

$$C = \frac{T^* C_p^o}{P^* v^*}, \tag{35}$$

and we therefore conclude

$$\beta = \tfrac{1}{2},$$

since the left-hand side of Eq. (34) is finite and nonvanishing as $t \to 0$. Thus, the exponent which characterizes the specific heat divergence is dictated by the expansion [i.e., Eq. (3)] and its associated consistency conditions [i.e., Eqs. (10)–(13)].

## Entropy changes along the spinodal curve

Although the specific form of the relationship $s_{sp}(P)$ was not invoked in the previous derivation, Eq. (23) implies the existence of such a functionality, the nature of which we now derive. We consider Fig. 3 and write, for $T < T^*$

$$s_\beta - s_\alpha = (s_\beta - s_\gamma) + (s_\gamma - s_\alpha), \tag{36}$$

$$s_\beta - s_\gamma = -\frac{C_p^o}{1 - \beta}t^{1/2} = -2C_p^o t^{1/2}, \tag{37}$$

$$s_\gamma - s_\alpha = -\int_P^{P + \delta P}\left(\frac{\partial v}{\partial T}\right)_P dP. \tag{38}$$

In order to integrate the thermal expansion coefficient, we write

$$\left(\frac{\partial \nu}{\partial \tau}\right)_\pi = -\frac{2x(\tau - 1) + z(\nu - 1)}{2y(\nu - 1) + z(\tau - 1)}, \tag{39}$$

which follows from Eq. (3), and

$$y[\pi - \pi_{sp}(\tau)] = \left[\frac{z(\tau - 1)}{2} + y(\nu - 1)\right]^2, \tag{40}$$

whereupon we obtain

$$s_\gamma - s_\alpha = -\frac{P^* v^*}{T^*}\left[\frac{2x}{y}\left(\frac{1 - \theta}{\theta}\right)(\tau_\alpha - 1)(y\delta\pi)^{1/2} - \frac{z}{2y}\delta\pi\right] \quad (>0), \tag{41}$$

where

$$\delta\pi = \pi_\gamma - \pi_\alpha \quad (<0) \tag{42}$$

or, in other words,

$$s_\beta - s_\alpha = -2C_p^o t^{1/2} - \left(\frac{P^* v^*}{T^*}\right) \times \left[\frac{2x}{y}\left(\frac{1 - \theta}{\theta}\right)(\tau_\alpha - 1)(y\delta\pi)^{1/2} - \frac{z}{2y}\delta\pi\right]. \tag{43}$$

Finally, we must express $t$ in terms of $\delta\pi$. This is easily done by invoking Eq. (14); for $t \ll 1$, we obtain

$$\delta\pi \approx -\frac{2x(\theta - 1)\tau_\alpha(\tau_\alpha - 1)}{\theta}t \tag{44}$$

or, finally, after rearranging,

$$s_\beta - s_\alpha = \Lambda(-\delta\pi) + \phi(-\delta\pi)^{1/2} \tag{45}$$

with

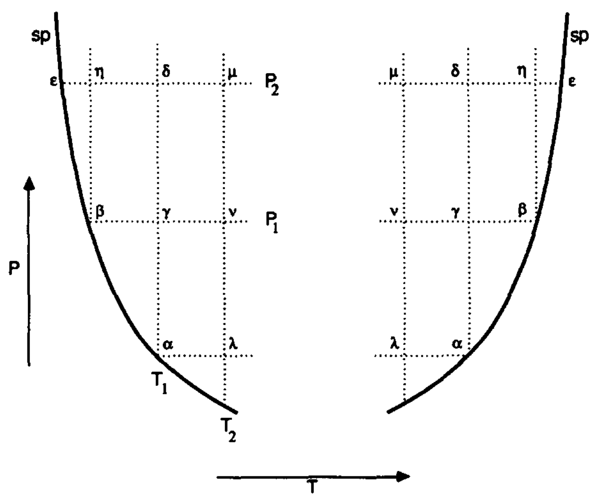


FIG. 3. Calculation of entropy variations in the vicinity of the spinodal curve.

$$\Lambda = -\frac{zP^*v^*}{2yT^*} \quad (>0), \tag{46}$$

$$\phi = -\frac{2C_p^o}{\tau_\alpha^{1/2}}\left[\left(\frac{\partial\tau}{\partial\pi}\right)_{sp}\right]^{1/2} + \frac{(-P^*)v^*}{T^*|y|^{1/2}}\left(\frac{\partial\pi}{\partial\tau}\right)_{sp}, \tag{47}$$

and where $\phi$ is the difference of two positive contributions. For the $\tau > 1$ branch of the spinodal [Fig. 3], and with

$$t(T>T^*) \equiv \frac{T_{sp} - T}{T_{sp}}, \tag{48}$$

we have ($\tau_\alpha > 1$)

$$s_\beta - s_\gamma = 2C_p^o t^{1/2}, \tag{49}$$

$$s_\gamma - s_\alpha = -\frac{P^*v^*}{T^*}\left[\frac{2x}{y}\left(\frac{1-\theta}{\theta}\right)(\tau_\alpha - 1)(y\delta\pi)^{1/2} - \frac{z}{2y}\delta\pi\right] \quad (<0), \tag{50}$$

$$\delta\pi \approx \frac{2x(\theta-1)\tau_\alpha(\tau_\alpha-1)}{\theta}t \quad (<0), \tag{51}$$

$$s_\beta - s_\alpha = \Lambda'(-\delta\pi) + \phi'(-\delta\pi)^{1/2}, \tag{52}$$

$$\Lambda' = -\frac{zP^*v^*}{2yT^*} \quad (<0), \tag{53}$$

$$\phi' = \frac{2C_p^o}{\tau_\alpha^{1/2}}\left[\left(-\frac{\partial\tau}{\partial\pi}\right)_{sp}\right]^{1/2} - \frac{(-P^*)v^*}{T^*|y|^{1/2}}\left(-\frac{\partial\pi}{\partial\tau}\right)_{sp}, \tag{54}$$

which, again, is the difference of two positive contributions. From this treatment we conclude:

Entropy changes along the spinodal curve are well defined: the $(-\delta\pi)^{1/2}$ dependence is indicative of a diverging $(\delta s/\delta P)_{sp}$. This $(-\delta\pi)^{-1/2}$ singularity is, however, integrable, and results in finite entropy changes, as was the case for the $C_p$ divergence.

As $\tau \to 1$, the first term in $\phi$ (and $\phi'$) dominates the behavior of entropy changes. Note that, in this region (i.e., for $\tau \to 1$), $s$ increases along the spinodal for $\tau > 1$ and decreases for $\tau < 1$, as implied by the thermodynamically consistent behavior shown in Fig. 1.

## Tensile instability and fluctuations

We consider number density fluctuations within an open, constant volume subsystem in the vicinity of a tensile instability. To this end, write, for the Helmholtz energy change associated with an instantaneous fluctuation away from (metastable) equilibrium[10]

$$\Delta A = \int (a - \langle a \rangle) d\mathbf{r}, \tag{55}$$

where $a$ is a free energy density, integration is over the fixed region under consideration, and $\langle\ \rangle$ denotes (metastable) equilibrium values. The free energy density can be expanded in powers of density deviations (fluctuations) away from the metastable equilibrium value,

$$a - \langle a \rangle = \mu(\rho - \langle\rho\rangle) + \frac{1}{2\langle\rho\rangle}\left(\frac{\partial P}{\partial\rho}\right)_T(\rho - \langle\rho\rangle)^2 + \cdots. \tag{56}$$

In addition, we must take into account contributions due to inhomogeneities within the subsystem itself caused by long-wavelength fluctuations. To leading order, these can be accounted for by a quadratic term of the form,[10]

$$a - \langle a \rangle = \mu(\rho - \langle\rho\rangle) + \frac{1}{2\langle\rho\rangle}\left(\frac{\partial P}{\partial\rho}\right)_T(\rho - \langle\rho\rangle)^2 + g\left[\frac{\partial(\rho - \langle\rho\rangle)}{\partial\mathbf{r}}\right]^2 + \cdots, \tag{57}$$

where $g$ is a positive coefficient of dimensions mass $\times$ length$^7$ $\times$ time$^{-2}$. The linear term must necessarily vanish upon integration. We now write

$$\delta \equiv \rho - \langle\rho\rangle = \sum_{\mathbf{k}} \delta(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{58}$$

whereupon we obtain

$$\Delta A = \frac{V}{2}\sum_{\mathbf{k}}(\langle\lambda\rangle + 2gk^2)|\delta(\mathbf{k})|^2 \tag{59}$$

with

$$\langle\lambda\rangle = \langle v\rangle^3\left(\frac{-P^*}{v^*}\right)[2y(\nu-1) + z(\tau-1)] = -P^*v^{*2}\nu^3[2y(\nu-1) + z(\tau-1)]. \tag{60}$$

This implies

$$\langle|\delta(\mathbf{k})|^2\rangle = \frac{kT}{2V(\langle\lambda\rangle/2 + gk^2)}, \tag{61}$$

where we have weighed fluctuations according to

$$w \sim \exp(-\beta\Delta A); \quad \beta = 1/kT. \tag{62}$$

In order to calculate a correlation length ($r_c$) we define a correlation function,

$$G \equiv \langle\delta(\mathbf{r}_1)\delta(\mathbf{r}_2)\rangle = \sum_{\mathbf{k}}\langle|\delta(\mathbf{k})|^2\rangle e^{i\mathbf{k}\cdot\mathbf{r}} \tag{63}$$

from which, taking into account Eq. (61), and the Fourier inversion relationship[10]

$$\int \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\alpha^2 + k^2}\frac{d\mathbf{k}}{(2\pi)^3} = \frac{e^{-\alpha r}}{4\pi r},$$

we obtain

$$\beta G(r) = \frac{1}{8\pi g r}\exp(-r/r_c), \tag{64}$$

$$r_c = \left(\frac{2g}{\langle\lambda\rangle}\right)^{1/2} \tag{65}$$

or, in dimensionless form,

$$\frac{r_c v^*}{[2g/(-P^*)]^{1/2}} = \frac{1}{\{\nu^3[2y(\nu-1) + z(\tau-1)]\}^{1/2}} \equiv r_c'. \tag{66}$$

We now seek solutions to the condition $r_c' =$ constant. This will give rise to curves along which the fluctuations have the same characteristic wavelength. We therefore write

$$\nu^3[2y(\nu-1) + z(\tau-1)] = C \quad (>0), \tag{67}$$

$$r_c' = C^{-1/2}, \tag{68}$$

where the fact that $C > 0$ follows from stability [see Eq. (3)], and from the sign of $P^*$. Thus, we seek to solve for $\nu$

such that, at any given temperature,

$$z(\tau - 1) = \frac{C}{\nu^3} - 2y(\nu - 1) = \Omega(\nu) . \qquad (69)$$

The physically meaningful long-wavelength fluctuations which we are analyzing are caused by the proximity of the spinodal curve, and not by the vanishing of $\nu$ [see Eq. (66)]: we thus require that $C$ be small (long range fluctuations), and, in addition, $C/\nu^3$ be comparable to $C$. A graphical solution to Eq. (69) is shown in Fig. 4, where we have used $|z(\tau<1)| = |z(\tau>1)|$, and the fact that $z(\tau - 1) > 0$ for $\tau \neq 1$.

This analysis can be straightforwardly extended to other projections (Pv, PT) by applying Eq. (3) to the constant-correlation-length condition [Eq. (67)], and solving for the appropriate variables.

We note, finally, that the assumed discontinuity in $z$ gives rise to another interesting effect. We first write the identities

$$\langle \delta S \delta V \rangle_N = NkT \left(\frac{\partial v}{\partial T}\right)_P , \qquad (70)$$

$$\langle \delta T \delta P \rangle_N = \frac{kT^2}{NC_v}\left(-\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P , \qquad (71)$$

which quantify correlations between fluctuations in entropy and volume, and between the corresponding conjugate pair (temperature and pressure), within a closed subsystem ($N$). Both covariances are proportional to the isothermal compressibility, and must therefore be negative for $T < T^*$, and positive otherwise (note that the proportionality "constants" between the fluctuation covariances and the thermal expansion coefficient are necessarily positive except along the spinodal). If, on the other hand, $z$ behaves as in Fig. 2(b), we expect a smooth transition between positively and negatively correlated regions, with the density maxima line as a locus of points where fluctuations in entropy and volume (or in temperature and pressure) within closed subsystems are uncorrelated.

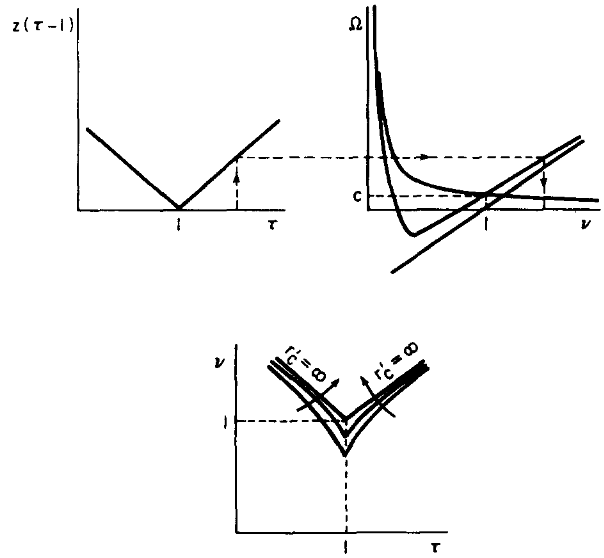


FIG. 4. Calculation of constant correlation radius lines in the $\tau\nu$ plane.

## CONCLUSION

A tensile instability in which the reciprocal isothermal compressibility exhibits a linear temperature dependence along the maximum tensile strength isochore gives rise to a metastable phase transition between a low temperature state with a negative thermal expansion coefficient and a high temperature state with a positive thermal expansion coefficient, if this isochore is also metastable for $T < T^*$. The transition is endothermic, and the associated heat effect decreases away from the tensile instability. Such a phase transition is peculiar in that it involves discontinuities in entropy and the thermal expansion coefficient, with no volume discontinuity. A $t^{-1/2}$ specific heat divergence follows from the nature of the PVT surface in the vicinity of a tensile instability.

The experimentally observed behavior whereby several liquids appear to lose tensile strength slightly above their triple point has thus been analyzed both in PVT[1] and entropic implications on the assumption that such observations are indeed related to a thermodynamic limit of stability. There follow a variety of unusual phenomena, of which the univocal relationship between tensile instability and density anomalies in the vicinity of the anomalous spinodal branch, as well as the existence of metastable density maxima are independent of the assumed behavior of the tensile strength maximum isochore. The entropy discontinuity and associated metastable phase transition, as well as the nonanalytic (cusped) nature of the previously reported density maxima are direct consequences of the assumptions concerning the way in which the compressibility diverges along such an isochore: work is currently in progress on the development of a pressure expansion in which the $\nu = 1$ isochore is only metastable for $T > T^*$.

A hitherto unexplained experimental observation (apparent loss of tensile strength) with obvious practical implications in areas as diverse as ultrasonics and pump performance has thus been analyzed from a thermodynamic perspective, and a variety of new phenomena have been derived.

## ACKNOWLEDGMENT

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