Loss of tensile strength in liquids without property discontinuities: A thermodynamic analysis

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The thermodynamically consistent behavior of any fluid whose tensile strength exhibits a maximum with respect to temperature (tensile instability) is derived for the case where the isochore corresponding to the fluid density at such a maximum is single branched (i.e., a metastable solution exists only for temperatures higher than the tensile instability temperature). The resulting thermal and volumetric picture is considerably simpler than for the recently derived behavior corresponding to the case where the tensile instability isochore admits metastable solutions both above and below the tensile instability temperature (double-branched limiting isochore). Density extrema are inseparable from tensile strength maxima: a tensile instability is, in fact, the low-pressure intersection of a spinodal curve and a locus of density extrema.

INTRODUCTION

In two recent publications,[1,2] we discussed the volumetric[1] and thermal[2] consequences which follow from the hypothesis whereby a superheated liquid's tensile strength can exhibit a maximum with respect to temperature, a behavior which we call tensile instability. This phenomenon has considerable practical and theoretical implications. A fluid's tensile strength can, e.g., be the controlling factor in ultrasonic applications, where cavitation can occur, among other mechanisms, through sound-induced alternating compressive and tensile stresses, if the latter exceed the liquid's tensile strength at the prevailing temperature. The most common example of fluids under tension occurs in trees, where both hydrostatic considerations and experimental observations[3] show that sap is transported under tension (although hydrostatic arguments limit the existence of tension to minimum tree heights of 10.33 m, a sufficient but not necessary condition in actual plants). This pervasive example of nature's successful implementation of a negative pressure technology is in sharp contrast with our own technological primitiveness vis-à-vis the handling of liquids under tension: potentially useful applications currently exist mostly as laboratory prototypes (tension pumping[4]) or theoretical publications (irrigation[5]).

From a theoretical point of view, a tensile instability occurs in a very interesting model,[6,7] in which the properties of metastable water are interpreted starting from the assumption of the existence of a continuous limit-of-stability locus (spinodal curve) bounding the superheated, supercooled, and subtriple (i.e., simultaneously superheated and supercooled) states. In this model, the spinodal locus is obtained from a truncated volume-explicit pressure expansion whose coefficients are fitted to an empirical equation-of-state representation of water's PVT surface.[8] It can be shown, however,[9] that a tensile instability is not a necessary condition for the existence of an uninterrupted spinodal bounding the superheated, supercooled, and subtriple states. Our recent discussion[1,2] of tensile instability is based exclusively on thermodynamic consistency arguments, and is thus valid for any fluid exhibiting such a behavior (see[10] for experimental evidence suggesting the existence of tensile instabilities in benzene, acetic acid, and aniline). In essence, the treatment involves the assumption of an analytic Helmholtz energy, whereupon variations of pressure away from the instability and into metastable regions can be expressed as a temperature and volume-explicit truncated Taylor series, the signs of the coefficients being then determined by stability considerations. No curve-fitting, substance-specific constraint is imposed upon the model's coefficients, hence its generality.

Assuming the validity of a volume and temperature-explicit pressure expansion about the tensile instability (or, equivalently,[1,2] an analytic Helmholtz energy at the instability), the thermodynamically consistent relationship between temperature, pressure, and volume[1,2] has the following mathematical property: the tensile instability isochore (i.e., the locus of states whose density equals the fluid's density at the instability) is the only isochore which admits metastable solutions both above and below the temperature at which it becomes tangent to the PT projection of the spinodal curve. The physical implication of this behavior follows from the fact that the spinodal curve, in PT coordinates,[1,11] is an envelope of isochores and, therefore, the analytic continuation of such curves past the tangency point (i.e., past the limit of stability) is, in general, unphysical, with the possible exception of the tensile instability isochore. Several unusual features follow from the assumption that, indeed, this limiting isochore admits metastable solutions above and below the tensile instability temperature. Thus, spinodal retracing,[1] nonanalytic density maxima,[1] and a metastable phase transition[2] with entropy and thermal expansion coefficient discontinuities but no associated density discontinuity are direct consequences of this double-branched limiting isochore assumption. We stress the fact that the above phenomena are possible (thermodynamically consistent) but not necessary consequences of a tensile instability. This clarification is especially important because our original treatment[1] was limited to this interesting but restricted case.

In this paper, we derive the volumetric and thermal be-

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havior that follows from a tensile instability in which the limiting isochore is metastable on one side of the instability only. Although both cases are thermodynamically consistent, the single-branched alternative analyzed in this paper gives rise to behavior which can be readily identified with the theoretically postulated volumetric properties of metastable water.[6,7]

Previously derived[1,2] relationships are not rederived here; rather, we focus upon the differences between the single- and double-branched limiting isochore cases. Such differences, as will be shown next, are minimal with respect to the governing equations, but profound as to the fluid's predicted behavior.

GOVERNING EQUATIONS

Variations in pressure away from a tensile instability can be described, on the assumption of an analytic Helmholtz energy, by the expression[1,2]

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

where

$$\pi \equiv P/P^* \quad (P^* < 0), \tag{2}$$

$$\tau \equiv T/T^*, \tag{3}$$

$$\nu \equiv v/v^*, \tag{4}$$

$$2x \equiv \frac{(T^*)^2}{P^*}\left(\frac{\partial^2 P}{\partial T^2}\right)_{v,*} \quad (<0), \tag{5}$$

$$2y \equiv \frac{(v^*)^2}{P^*}\left(\frac{\partial^2 P}{\partial v^2}\right)_{T,*} \quad (<0), \tag{6}$$

$$z \equiv \frac{T^* v^*}{P^*}\left(\frac{\partial^2 P}{\partial T \partial v}\right)_* . \tag{7}$$

The tensile instability (denoted here by the symbol $*$) is the point at which

$$\left(\frac{dP}{dT}\right)_{\rm sp} = 0, \tag{8}$$

$$\left(\frac{d^2P}{dT^2}\right)_{\rm sp} > 0, \tag{9}$$

where the subscript sp denotes differentiation along the spinodal curve. Equation (1) is simply the second order term of the temperature and volume-explicit pressure expansion, of which the linear term (δP) is identically zero, a fact which follows from stability considerations exclusively.[1] The only difference between the present, single-branched limiting isochore case, and the previous[1,2] double-branched analysis lies in the sign of z. The two cases are illustrated in Fig. 1. Because the PT projection of the spinodal is an envelope of isochores, we must have

$$\left(\frac{dP}{dT}\right)_{\rm sp} = \left(\frac{\partial P}{\partial T}\right)_v . \tag{10}$$

For a double-branched limiting isochore[1,2] [Fig. 1(a)] we must have

$$\begin{cases} z < 0 & (\tau < 1) \\ z > 0 & (\tau > 1) \end{cases}, \tag{11}$$

whereas, for a single-branched isochore [Fig. 1(b)] we must have $z > 0$ [the single-branched case $z < 0$, $\tau < 1$, though theoretically possible, does not correspond to any experimentally observed behavior, and will not be considered here: the predicted (π,ν), (π,τ), (τ,ν), and (s,T) projections are trivial modifications of the ones to be discussed in this paper].

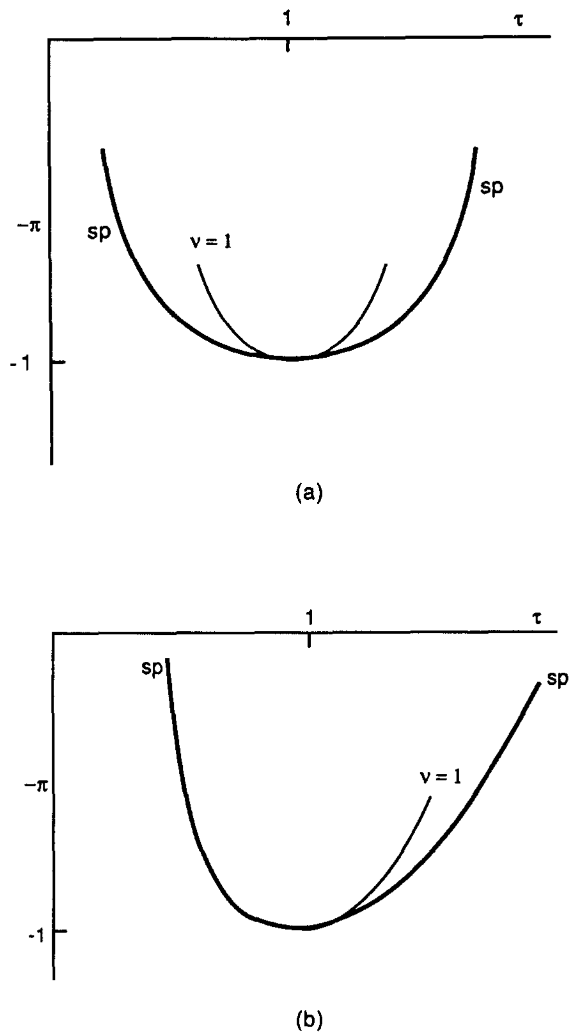

FIG. 1. (a) Double-branched limiting isochore ($\nu = 1$) showing metastable solutions for $\tau > 1$ and $\tau < 1$. (b) Single-branched limiting isochore showing metastable solutions for $\tau > 1$ only.

In both the single- and double-branched limiting isochore cases the compressibility diverges as $|T - T^*|^{-1}$ along the $\nu = 1$ isochore,

$$K_T |P^*| = \{\nu[2y(\nu - 1) + z(\tau - 1)]\}^{-1}.$$

Spinodal and density extrema loci are readily obtained from Eq. (1). For the former, we have

$$\nu - 1 = -\frac{z}{2y}(\tau - 1), \tag{12}$$

$$\pi - 1 = y\left(\frac{4xy}{z^2} - 1\right)(\nu - 1)^2, \tag{13}$$

$$\pi - 1 = x\left(1 - \frac{z^2}{4xy}\right)(\tau - 1)^2, \tag{14}$$

and for the latter,

$$\nu - 1 = -\frac{2x}{z}(\tau - 1), \tag{15}$$

$$\pi - 1 = y\left(1 - \frac{z^2}{4xy}\right)(\nu - 1)^2, \tag{16}$$

$$\pi - 1 = x\left(\frac{4xy}{z^2} - 1\right)(\tau - 1)^2. \tag{17}$$

Because $\pi \leqslant 1$, it follows that

$$\frac{4xy}{z^2} > 1 \ \left(1 > \frac{z^2}{4xy}\right). \tag{18}$$

VOLUMETRIC BEHAVIOR

The predicted behavior for the PT projection is shown in Fig. 2, in $(\tau, -\pi)$ coordinates [note that, since $P^* < 0$, the signs of $d(-\pi)$ and $d(P)$ are the same: tension decreases vertically upward in this diagram]. The metastable branch of the density maxima locus terminates at the instability $(1, -1)$, and extends towards the high density, low temperature, high pressure region. It can be seen from the continuous nature of the isochores in the vicinity of the density maxima locus that the latter is indeed the solution to the condition $\alpha_p = 0$ (α_p is the thermal expansion coefficient). In the double-branched limiting isochore case,[1,2] on the other hand, the $\tau = 1$ isotherm is the locus of density maxima, but there is a discontinuous transition, along each isochore, from $\alpha_p < 0$ $(\tau < 1)$ to $\alpha_p > 0 (\tau > 1)$. Thus, a single-branched limiting isochore gives rise to behavior which we can readily associate with the familiar occurrence of density extrema in stable regions of the phase diagram, as is the case with water at 4 °C and 1 bar.

The stability of the density maxima locus follows from substituting Eq. (15) into the expression for the stability coefficient $(\partial\pi/\partial\nu)_\tau$, whereupon we conclude that the condition $\alpha_p = 0$ admits a stable solution for $\tau < 1$ (recall that, for $P^* < 0$, we require $\partial\pi/\partial\nu > 0$ for stability). It is also easy to show that, for any $\tau \neq 1$, $-\pi$ (ρmax) $> -\pi$(spinodal). This follows from Eqs. (14) and (17), which yield the inequality

$$\frac{4xy}{z^2} - 1 > 1 - \frac{z^2}{4xy}, \tag{19}$$

and we conclude that, indeed, the density maxima locus lies above the spinodal branch in $(\tau, -\pi)$ coordinates. The region bounded by the $\tau < 1$ spinodal branch and the density maxima locus corresponds to the condition $\alpha_p < 0$ (in the double-branched limiting isochore case this corresponded to the whole $\tau < 1$ metastable region).

It can be seen from Fig. 2 that, if isochorically cooled, a metastable liquid reaches a limit of stability through a pressure decrease if $\nu > 1$; if, on the other hand, $\nu < 1$, a pressure increase accompanies the fluid's loss of stability upon isochoric cooling. In the double-branched limiting isochore case,[1,2] on the other hand, there is no limit of stability for $\nu < 1$, but points on the spinodal for which $\tau < 1$ are reached upon isochoric heating, with an accompanying pressure decrease.

The (τ,ν) projection is shown in Fig. 3. Both the spinodal and the density maxima locus are locally linear [see Eqs. (12) and (15)], the latter extending from the instability (1,1) into the low temperature, high pressure, high density region. Also shown in the figure are three isobars, the arrow indicating the direction of increasing pressure (decreasing tension). Note that, contrary to the double-branched limiting isochore case,[1,2] the spinodal curve is well defined for $\nu < 1$. Both the condition $\nu(\mathrm{sp}) > \nu(\rho_{\max})$ for any given $\tau < 1$, and the instability of the density extrema locus for $\tau > 1$ follow from Eqs. (1), (12), and (15).

Along any isobar, the isothermal compressibility and

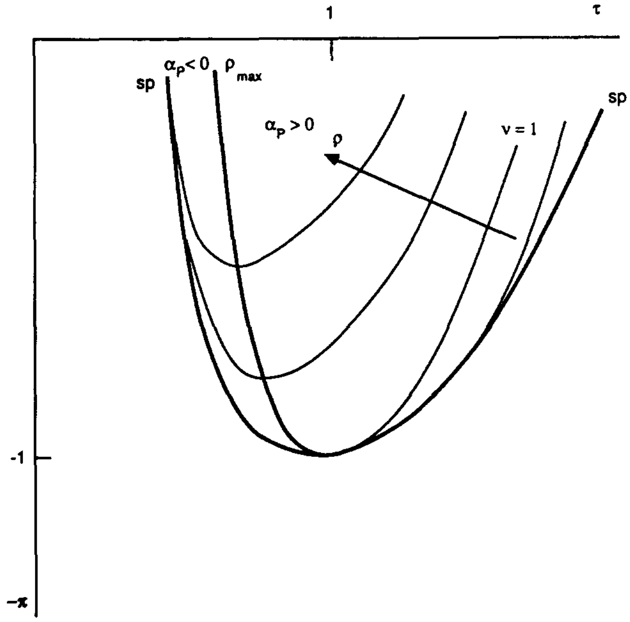

FIG. 2. Pressure-temperature projection in the vicinity of a tensile instability, showing spinodal curve (sp), density maxima locus ($\rho_{\max}$), and limiting isochore ($\nu = 1$). The arrow indicates the direction of increasing density.

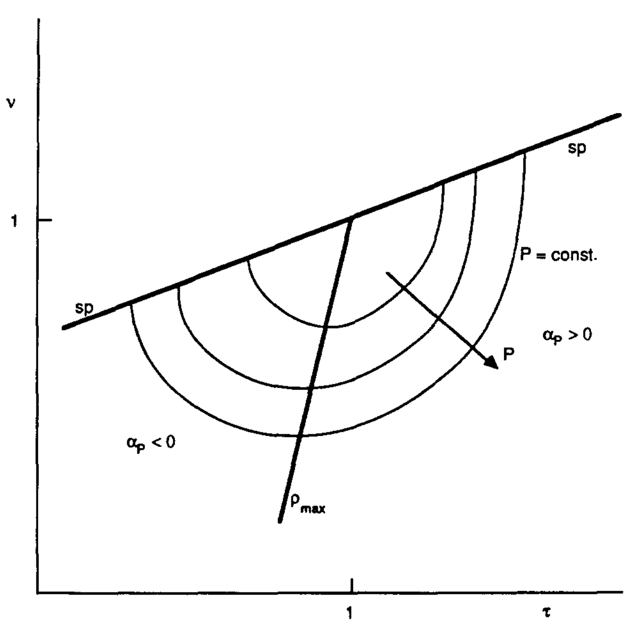

FIG. 3. Temperature-volume projection in the vicinity of a tensile instability showing spinodal curve (sp), density maxima locus ($\rho_{\max}$), and isobars. The arrow indicates the direction of increasing pressure (decreasing tension).

thermal expansion coefficient diverge as $|T - T_{\rm sp}(P)|^{-1/2}$. This follows from writing

$$\left(\frac{\partial v}{\partial \tau}\right)_\pi = vT^*\alpha_p = -\frac{2x(\tau-1)+z(v-1)}{2y(v-1)+z(\tau-1)} \tag{20}$$

and noting that, along an isobar,

$$\begin{aligned} 2y(v-1) &+ z(\tau-1) \\ &= -1/(P^*vK_T) \\ &= z\left[\left(\frac{4xy}{z^2}-1\right)\{[\tau_{\rm sp}(\pi)-1]^2-(\tau-1)^2\}\right]^{1/2}, \end{aligned} \tag{21}$$

$$\begin{aligned} z(v-1) &+ 2x(\tau-1) \\ &= T^*\alpha_P/P^*K_T = 2x\left(1-\frac{z^2}{4xy}\right)(\tau-1)+\frac{z^2}{2y} \\ &\times\left[\left(\frac{4xy}{z^2}-1\right)\{[\tau_{\rm sp}(\pi)-1]^2-(\tau-1)^2\}\right]^{1/2}, \end{aligned} \tag{22}$$

whereupon we obtain

$$\begin{aligned} vT^*\alpha_p = -\frac{z}{2y}\Bigg\{1 &+ \frac{(\tau-1)(4xy/z^2-1)^{1/2}}{|2-[\tau+\tau_{\rm sp}(\pi)]|^{1/2}} \\ &\cdot|\tau-\tau_{\rm sp}(\pi)|^{-1/2}\Bigg\}, \end{aligned} \tag{23}$$

$$\begin{aligned} vP^*K_T = &\frac{-1}{z(4xy/z^2-1)|2-[\tau+\tau_{\rm sp}(\pi)]|^{1/2}} \\ &\cdot|\tau-\tau_{\rm sp}(\pi)|^{-1/2}, \end{aligned} \tag{24}$$

or in other words, as $T(v,P) \to T_{\rm sp}(P)$,

$$\alpha_p \sim K_T \sim |T - T_{\rm sp}(P)|^{-1/2}. \tag{25}$$

This behavior applies to the single- and double-branched limiting isochore cases.

A schematic $(v, -\pi)$ projection is shown in Fig. 4. The instability $(1, -1)$ is no longer a point where spinodal retracing occurs[1,2] (i.e., the spinodal does not curve back into the low density region): instead, it is a minimum along the spinodal, as in the (P,T) projection. This, of course, is consistent with the fact that the spinodal is well defined for $v < 1$.

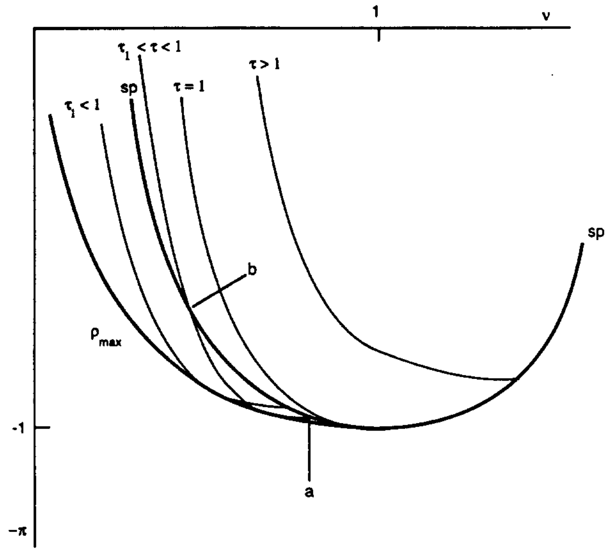

FIG. 4. Pressure-volume projection in the vicinity of a tensile instability, showing spinodal curve (sp), density maxima locus ($\rho_{\rm max}$), and isotherms. Along any given isotherm, (a) is a limit of stability, but (b) is not.

The locus of density maxima, in (P,v) coordinates, is an envelope of isotherms. This is a general property of density extrema, and follows from writing

$$dP = (1/K_T)[\alpha_p\, dT - (1/v)dv] \tag{26}$$

and therefore,

$$\left(\frac{\partial P}{\partial v}\right)_{\rho{\rm ext}} = \left(\frac{\partial P}{\partial v}\right)_T = -\frac{1}{vK_T}, \tag{27}$$

where $\rho_{\rm ext}$ denotes differentiation along a line satisfying the condition $\alpha_p = 0$. Equation (27) is simply the mathematical statement of the abovementioned property.

Note the pressure increase which accompanies isochoric cooling for $v < 1$ as the fluid approaches the spinodal curve. Intersections of $\tau < 1$ isotherms with the $v < 1$ spinodal branch at points such as a are limits of stability; at points such as b, on the other hand, the isotherm and the spinodal have different temperatures, and this point is not, therefore, a limit of stability for the given isotherm.

ENTROPY AND TENSILE INSTABILITY

A schematic (T,s) projection is shown in Fig. 5. At any given pressure, there are two different limit-of-stability temperatures (see lower part of Fig. 5) to which the corresponding isobar is asymptotic on an entropy vs temperature projection ($c_p \to \infty$). As already shown in the double-branched limiting isochore case,[2] along any isobar

$$c_p \sim |T - T_{\rm sp}(P)|^{-1/2}. \tag{28}$$

The proof of this asymptotic behavior of c_p will not be repeated here, since it is identical to the one already used in our previous analysis[2] of tensile instability.

The density maxima locus, in (s,T) coordinates, is an envelope of isobars, as shown Fig. 5. To prove this, we write

$$ds = -v\alpha_p\, dP + \frac{c_p}{T} dT \tag{29}$$

and, therefore,

$$\left(\frac{\partial s}{\partial T}\right)_{\rho_{\rm ext}} = \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}. \tag{30}$$

Equations (27) and (30), implying that the density maxima locus is an envelope of isotherms (P,v coordinates) and isobars (s,T coordinates) are generalized in the Appendix. Thus, the curve labeled $\rho_{\rm max}$ is an envelope of constant entropy, enthalpy, and chemical potential curves in P,v coordinates, and of constant volume, enthalpy, and chemical potential curves in T,s coordinates. It follows from the Maxwell relationship

$$v\alpha_p = -\left(\frac{\partial s}{\partial P}\right)_T \tag{31}$$

that, along any isobar, $(\partial s/\partial P)_T < 0$ if $\tau > \tau(\rho_{\rm max})$, and $(\partial s/\partial P)_T > 0$ if $\tau < \tau(\rho_{\rm max})$, where $\tau(\rho_{\rm max})$ denotes the temperature of maximum density, at the given pressure. This is indeed the behavior shown in Fig. 5.

If, then, the limiting isochore is single branched, there is

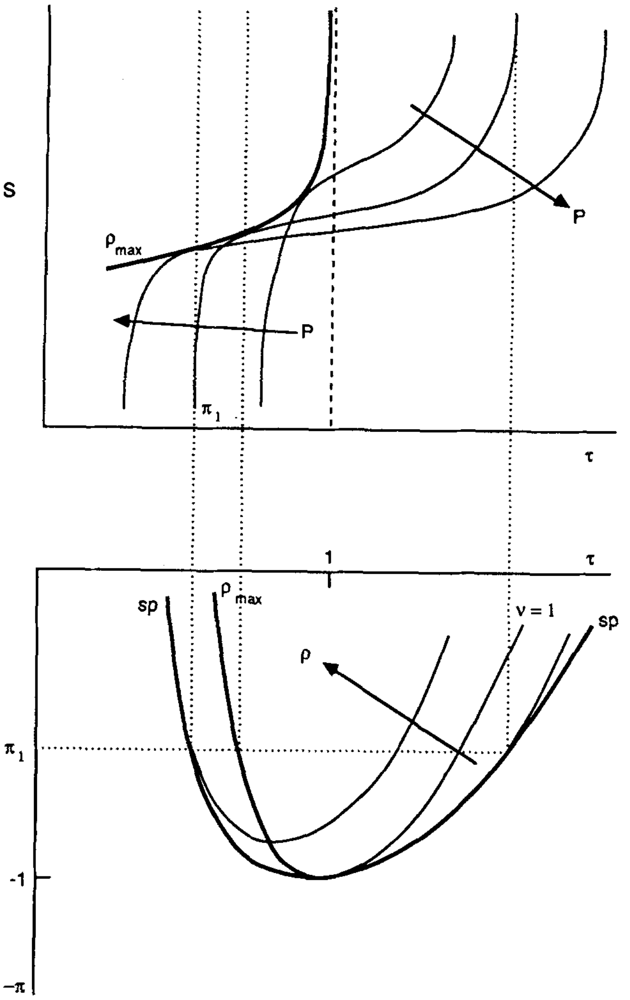

FIG. 5. Entropy-temperature projection in the vicinity of a tensile instability, showing asymptotic behavior of isobars at limits of stability. Also shown is the density maxima locus ($\rho_{\max}$), as well as the directions of increasing pressure (decreasing tension).

no entropy discontinuity at $\tau = 1$ and, consequently, no associated metastable phase transition with discontinuous thermal expansion coefficient, and continuous volume, as was the case for a double-branched limiting isochore.[1,2]

FLUCTUATIONS

We consider Helmholtz energy changes associated with number density fluctuations within a fixed volume region of fluid, in the vicinity of a tensile instability,

$$\Delta A = \int (a - \langle a \rangle) d^3\mathbf{r}, \tag{32}$$

where a and $\langle a \rangle$ are instantaneous and (metastable) equilibrium Helmholtz energy densities, respectively, and integration extends to the fluid region under consideration. The truncated free energy density expansion reads

$$a - \langle a \rangle = \mu(\rho - \langle \rho \rangle) + \frac{1}{2\langle \rho \rangle}\left(\frac{\partial P}{\partial \rho}\right)_T (\rho - \langle \rho \rangle)^2 + g\left[\frac{\partial(\rho - \langle \rho \rangle)}{\partial \mathbf{r}}\right]^2 + \cdots, \tag{33}$$

where the last term is the leading contribution to free energy changes associated with inhomogeneities caused by long wavelength density fluctuations ($g > 0$).[12] Upon Fourier analyzing the instantaneous density variation,

$$\delta \equiv \rho - \langle \rho \rangle = \sum_{\mathbf{k}} \delta(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{34}$$

we obtain[2] the following expression for the correlation function ($\beta = 1/kT$):

$$\beta G(r) = \frac{1}{8\pi g r}\exp(-r/r_c), \tag{35}$$

where the positive coefficient g is defined in Eq. (33), and

$$G = \langle \delta(\mathbf{r}_1)\delta(\mathbf{r}_2) \rangle \tag{36}$$

with fluctuations weighed according to the Boltzmann factor $\exp(-\beta \Delta A)$. The mathematical details whereby Eq. (35) is obtained from Eqs. (33), (34), and (36) have already been discussed elsewhere[2,12] and will not be repeated here. The quantity r_c in Eq. (35) is a correlation length, and is given, in dimensionless form, by the expression[2]

$$\frac{r_c v^*}{[2g/(-P^*)]^{1/2}} \equiv r_c' = \{v^3[2y(v-1) + z(\tau - 1)]\}^{-1/2}. \tag{37}$$

The locus of points with constant correlation length is thus the solution of the equation

$$z(\tau - 1) = \frac{C}{v^3} - 2y(v - 1) \equiv \Omega(v), \tag{38}$$

where

$$r_c' = C^{-1/2}, \tag{39}$$

and where the relevant solutions correspond to $v \gtrsim 1$ (i.e., the physically meaningful fluctuations under consideration are caused by the proximity of the spinodal curve and not, obviously, by the vanishing of v).

The graphical solution to Eq. (38) is shown in Fig. 6 for the case $2|y| > z$ (corresponding to positive v along the spinodal curve as $\tau \to 0$). Figure 6(a) is the actual solution to $z(\tau - 1) = \Omega$; the resulting r_c = constant lines in (τ, v) coordinates are shown in Fig. 6(b). The correlation radius diverges as the spinodal curve (labeled $r_c' \to \infty$) is approached, as expected from stability considerations. At the tensile instability volume ($v = 1$), the relationship between temperature and correlation radius is

$$\tau(v = 1) = 1 + \frac{C}{z} = 1 + \frac{1}{z(r_c')^{1/2}} \tag{40}$$

or, equivalently,

$$r_c'(v = 1) = \left[\frac{1}{z(\tau - 1)}\right]^2. \tag{41}$$

CONCLUSION

The thermodynamically consistent behavior that follows from the assumption that a superheated liquid can exhibit a maximum tensile strength (tensile instability) at a particular temperature has been derived on the assumption that a volume and temperature-explicit pressure expansion about the tensile instability is admissible. This is equivalent to the assumption of an analytic Helmholtz energy at the tensile instability.

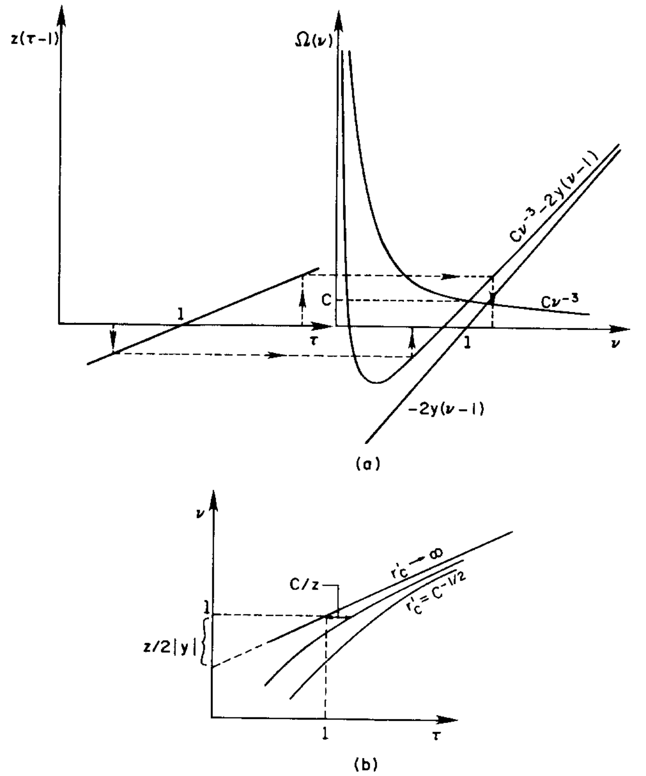

FIG. 6. (a) Graphical solution to the constant-correlation-radius condition [Eq. (38)]. (b) Spinodal line ($r_c \to \infty$) and constant correlation radius lines in the vicinity of a tensile instability, in temperature-volume coordinates.

In previous publications[1,2] we analyzed the case where the tensile instability isochore admits a metastable solution both above and below T^*: there followed a variety of highly unusual phenomena, such as spinodal retracing,[1] nonanalytic density maxima,[1] and a metastable phase transition[2] with entropy and thermal expansion coefficient discontinuities but no volume change. In this paper we address the case in which the limiting isochore, as all other isochores, has no metastable analytic continuation below the spinodal tangency temperature. The only mathematical difference between both models is the sign of the expansion coefficient z. This means that all of the purely mathematical relationships, such as the exponents characterizing the divergence of K_T, α_p, and c_p are common to both types of behavior. Also common to both cases is the necessary existence of an $\alpha_p < 0$ region in the vicinity of the spinodal branch along which the tensile strength increases with temperature.

A single-branched limiting isochore, however, does not give rise to discontinuities in entropy or thermal expansion coefficient. Instead, a mathematically defined metastable solution to the condition $\alpha_p = 0$ exists: the density maximum extends from the instability into the low temperature, high pressure, high density region. The simplicity of the PVT features associated with the single-branched limiting isochore case is in sharp contrast with the variety of unusual phenomena which necessarily accompany double-branched limiting isochore behavior. Perhaps more significantly, the single-branched limiting isochore case reproduces all of the essential features of the water-specific model of Speedy,[6,7] obtained by curve-fitting experimental PVT properties to a volume-explicit pressure expansion about a generic spinodal point.

Now that the connection between density extrema and loss of tensile strength has been firmly established[1,2,6,7] a number of interesting questions arise naturally:

(1) Assuming the existence of density extrema in a given fluid, can this locus of points satisfying $\alpha_p = 0$ end in any way(s) other than by intersecting a spinodal curve?

(2) In how many ways can a spinodal and a density extrema locus intersect? What thermodynamic consequences follow in each case?

(3) Can a spinodal locus bounding the superheated, supercooled, and simultaneously superheated and supercooled states[6,7] exist independently of density anomalies?

In the present paper, as well as in our previous[1,2] analysis of the double-branched limiting isochore case, we have used an essentially classical thermodynamic analysis to derive general conclusions and to pose equally general and fundamental questions on the behavior of metastable liquids. The insights gained from this approach will, it is hoped, contribute to dispel the widespread attitude according to which concepts such as metastable states and thermodynamically defined limits of stability are relegated to the unglamorous status of "mean field approximations" and hence ignored altogether. We recognize that a thermodynamically defined spinodal curve may indeed be an idealization: it is certainly a useful one. Is it, after all, possible (indeed, desirable) to postulate a scientific theory dealing with the macroscopic world of everyday experience that is free of idealizations?

ACKNOWLEDGMENT

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APPENDIX: DENSITY EXTREMA IN *T,s* AND *P,v* PROJECTIONS

We first write

$$dP = \left(\frac{\partial P}{\partial v}\right)_s dv + \frac{T}{c_v}\cdot\frac{\alpha_p}{K_T} ds \tag{A1}$$

which implies, along a density extrema locus,

$$\left(\frac{\partial P}{\partial v}\right)_{\rho_{\rm ext}} = \left(\frac{\partial P}{\partial v}\right)_s. \tag{A2}$$

Similarly, with h denoting specific enthalpy,

$$dP = \left(\frac{\partial P}{\partial v}\right)_h dv + \left[\frac{\alpha_p/K_T}{c_v + v\alpha_p/K_T}\right] dh \tag{A3}$$

and, therefore,

$$\left(\frac{\partial P}{\partial v}\right)_{\rho_{\rm ext}} = \left(\frac{\partial P}{\partial v}\right)_h. \tag{A4}$$

Finally, in terms of the chemical potential, we have

$$dP = \left(\frac{\partial P}{\partial v}\right)_\mu dv + \left[\frac{\alpha_p/K_T}{v\alpha_p/K_t - s}\right] d\mu \tag{A5}$$

or, along a density extrema locus,

$$\left(\frac{\partial P}{\partial v}\right)_{p_{\text{ext}}} = \left(\frac{\partial P}{\partial v}\right)_{\mu}. \qquad (A6)$$

Equations (27), (A2), (A4), and (A6) imply, therefore, that a density extrema locus is an envelope of isotherms, isentropes, isenthalpics, and constant chemical potential curves, in (P,v) coordinates. In order to derive the corresponding (T,s) properties, we write

$$ds = \left(\frac{\partial s}{\partial T}\right)_{v} dT + \frac{\alpha_p}{K_T} dv \qquad (A7)$$

or, along a density extrema locus

$$\left(\frac{\partial s}{\partial T}\right)_{p_{\text{ext}}} = \left(\frac{\partial s}{\partial T}\right)_{v}. \qquad (A8)$$

In terms of h, we have the expansion

$$ds = \left(\frac{\partial s}{\partial T}\right)_{h} dT - \left[\frac{\alpha_p}{1 - T\alpha_p}\right] dh \qquad (A9)$$

and, therefore,

$$\left(\frac{\partial s}{\partial T}\right)_{p_{\text{ext}}} = \left(\frac{\partial s}{\partial T}\right)_{h}. \qquad (A10)$$

Finally, in terms of μ,

$$ds = \left(\frac{\partial s}{\partial T}\right)_{\mu} dT - \alpha_p d\mu \qquad (A11)$$

which implies

$$\left(\frac{\partial s}{\partial T}\right)_{p_{\text{ext}}} = \left(\frac{\partial s}{\partial T}\right)_{\mu}. \qquad (A12)$$

Equations (30), (A8), (A10), and (A12) imply, therefore, that a density extrema locus is an envelope of isobars, isochores, isenthalpics, and constant chemical potential curves, in (T,s) coordinates.

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