On the nature of the tensile instability in metastable liquids and its relationship to density anomalies

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Tensile instability is a hitherto unexplained phenomenon whereby a metastable liquid loses tensile strength as the temperature is reduced in the vicinity of its triple point. The thermodynamically consistent behavior which must be exhibited by any liquid in the vicinity of a tensile instability displays a variety of unusual phenomena: nonanalytic density maxima, spinodal retracing, and density anomalies (negative thermal expansion coefficient) in the vicinity of the spinodal curve. Loss of tensile strength implies (and is inseparable from) density anomalies in the vicinity of the spinodal curve. This important conclusion is derived here from first principles.

INTRODUCTION

A liquid can exist in metastable equilibrium at pressures lower than its vapor pressure (at a given temperature), or at temperatures higher than its boiling temperature (at a given pressure). This is the definition of a superheated liquid. To each subcritical temperature there corresponds a minimum pressure at which the liquid can exist: this condition constitutes a limit of stability beyond which the metastable liquid cannot exist.

A pure substance reaches a limit of stability when the inequality

$$\left(\frac{\partial \xi_2}{\partial X_2}\right)_{\xi_1, X_3} > 0 \tag{1}$$

is first violated.[1] In Eq. (1), X_i $(i = 1, 2, 3)$ denotes S, V, or N (mole number, molecule number, or mass), and ξ_i $(i = 1, 2, 3)$ denotes the corresponding conjugate property $(T, -P, \mu)$. Because 3 numbers can be ordered in 3! different ways, Eq. (1) can be expressed in six equivalent ways:

$$\left(\frac{\partial T}{\partial S}\right)_{\mu,V} > 0, \tag{2}$$

$$\left(\frac{\partial T}{\partial S}\right)_{P,N} > 0, \tag{3}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{P,S} > 0, \tag{4}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} > 0, \tag{5}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} < 0, \tag{6}$$

$$\left(\frac{\partial P}{\partial V}\right)_{\mu,S} < 0, \tag{7}$$

all of which are violated simultaneously along a spinodal curve, the latter being the locus of limits of stability. Because all of the inequalities [i.e., Eqs. (2)–(7)] are violated simultaneously, we shall henceforth restrict our attention to the particular expression [Eq. (6)] involving exclusively pressure, temperature, and volume, without loss of generality.

At sufficiently low temperatures, the condition

$$\left(\frac{\partial P}{\partial v}\right)_{T} = 0, \tag{8}$$

where v is now a molar volume, occurs at negative pressures (i.e., under conditions whereby a liquid is held under tension). We refer to the corresponding limiting tension (for a given temperature) as the liquid's tensile strength.

Tension can be produced in a liquid in many different ways, among which we cite Berthelot tube methods,[2] dynamic stressing,[3] centrifugation,[4] and acoustic stressing[5] (this enumeration is only indicative, and by no means exhaustive). In such experimental studies the objective is to approach the limit of stability in order to determine, as accurately as possible, the substance's tensile strength at the experimental temperature.

It was first reported by Briggs,[4,6] in the course of several centifugation experiments, that water, benzene, aniline, and acetic acid exhibit an apparent loss of tensile strength as the temperature is lowered near the triple point temperature.

The nature of Briggs' experiment was such that it is impossible to tell unambiguously whether the observed limit of stability (i.e., the particular tension value at which cavitation occurred within the liquid) corresponded to loss of cohesion within the liquid or loss of adhesion between the latter and the glass capillary's walls.

However, the fact that this behavior was observed with several different liquids, and, more importantly, the fact that an abrupt loss of tensile strength for water close to its triple temperature was also observed with a completely different method (dynamic stressing[3]), seems to suggest that, indeed, loss of tensile strength occurs in several liquids close to the triple point temperature.

No explanation or interpretation of this interesting phenomenon has been offered to date. The analytical treatment that follows, although originally motivated by the above experimental observations, is completely independent of the interpretation of such experiments. We will derive the thermodynamically consistent behavior that must necessarily be shown by any liquid which exhibits loss of tensile strength, a phenomenon we shall henceforth refer to as tensile instability. Thus, our conclusions are valid irrespective of whether what was observed was indeed a tensile instability. We will show that a tensile instability implies, and is inseparable from, density anomalies (negative thermal expansion coefficient) in the vicinity of the spinodal curve. Furthermore, the thermodynamic analysis of tensile instability predicts the occurrence of several unusual phenomena (nonanalytic density extrema, spinodal retracing, etc.) which have not been previously discussed.

We will now derive the thermodynamics of tensile instability in metastable liquids.

RELATIONSHIP BETWEEN TENSILE INSTABILITY AND DENSITY ANOMALIES

We start by writing

$$dP = \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial v}\right)_T dv \tag{9}$$

and divide by ∂T along the spinodal, to obtain

$$\left(\frac{\partial P}{\partial T}\right)_{\text{spinodal}} = \left(\frac{\partial P}{\partial T}\right)_v. \tag{10}$$

Equation (10), first derived by Skripov,[7] is of central importance in the present context, and signifies that the spinodal curve, in (P, T) coordinates, is an envelope of extrapolated isochores. Therefore, whenever the tensile strength decreases as the temperature decreases, the extrapolated isochores, which are tangent to the spinodal, must necessarily have negative slope,

$$\left(\frac{\partial P}{\partial T}\right)_v < 0 \tag{11}$$

since

$$\left(\frac{\partial P}{\partial T}\right)_{\text{spinodal}} < 0. \tag{12}$$

We can write, in general,

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \tag{13}$$

which implies that the signs of $(\partial P/\partial T)_v$ and $(\partial v/\partial T)_P$ must necessarily coincide in the vicinity of the spinodal. Thus, we conclude that any liquid whose tensile strength decreases as the temperature is lowered must exhibit density anomalies $[(\partial v/\partial T)_P < 0]$ in the vicinity of the spinodal curve (the exact location and boundaries of this anomalous region cannot be predicted *a priori*, and depend on the specific substance being considered).

The treatment that follows is based on the assumption that a tensile instability occurs smoothly, in a mathematical sense. We assume, in other words, that at the onset of loss of tensile strength we can write for the (P, T) projection of the spinodal curve of the substance under consideration,

$$\left(\frac{\partial P}{\partial T}\right)_{\text{spinodal}} = 0, \tag{14}$$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_{\text{spinodal}} > 0. \tag{15}$$

Such a smooth variation was indeed observed by Briggs[4,6] in his centrifugation experiments on water, benzene, aniline, and acetic acid, and is shown schematically in Fig. 1.

Figure 2 shows the P–T projection of the spinodal curve (abd) corresponding to the limit of stability for a liquid exhibiting a tensile instability. Segment ab $[(\partial P/\partial T)_{sp} > 0]$ terminates at the critical point (not shown, $T_c > T_a$, $P_c > P_a$). Extrapolated isochores are tangent to the spinodal [Eq. (10)], and the corresponding volumes (densities) increase (decrease) in the direction shown by the arrow [these general features follow from Eq. (10) and the fact that, away from the spinodal, $(\partial P/\partial v)_T < 0$]. Segment bd (anomalous behavior) shows loss of tensile strength ($-P_b > -P_d$; $T_b > T_d$), and we have assumed a smooth transition between anomalous and "normal" behavior. Note that along db $[(\partial P/\partial T)_{sp} < 0]$ we must necessarily have $(\partial P/\partial T)_v < 0$. The arrow, consequently, shows volume (density) increasing (decreasing) as the temperature is lowered isobarically. This of course, is a density anomaly (and agrees

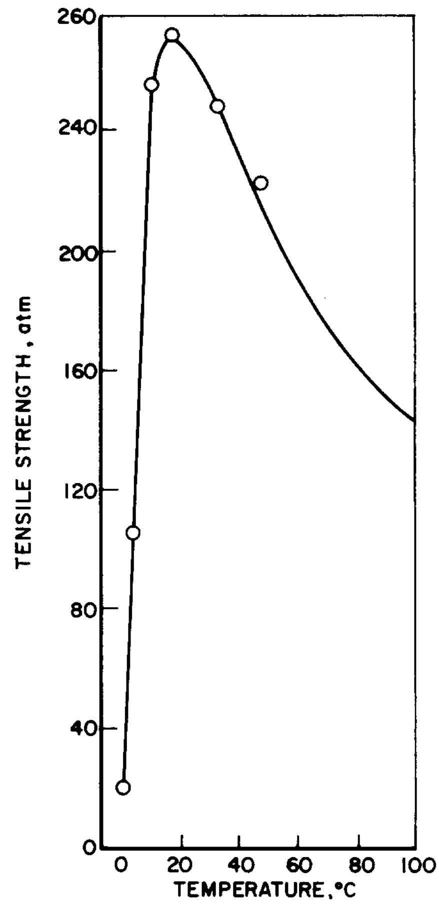

FIG. 1. Experimentally measured (Ref. 10) tensile strength of water as a function of temperature.

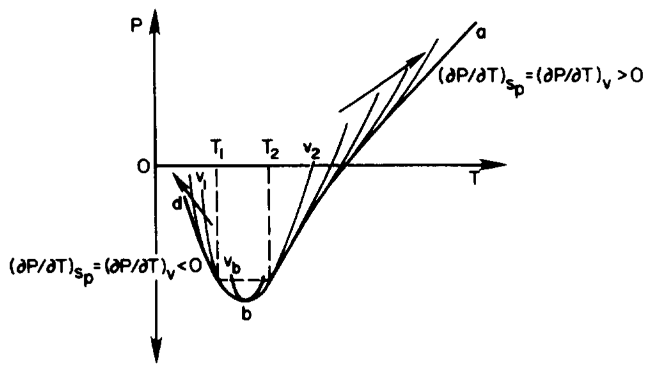

FIG. 2. Schematic (P, T) projection of the spinodal curve (dba) for a fluid exhibiting a smooth tensile instability.

with the previous derivation). Before proceeding further, we note that we have not used Eqs. (14) and (15), except for pictorial convenience in drawing Fig. 2. We will make use of these conditions below, when we develop an analytical model.

From what has been said so far, we can conclude that the region surrounding point b corresponds to the highest densities, with v increasing away from point b in both directions (i.e., high T, low T). For tension values lower than $-P_b$ (the tensile strength maximum), two isochores (v_1, v_2) are tangent to the spinodal curve at the given pressure but different temperatures ($T_1 < T_b$; $T_2 > T_b$). The three different types of behavior which are thermodynamically consistent with loss of tensile strength follow from the three possible cases: $v_1 = v_2$, $v_1 > v_2$, and $v_2 > v_1$, respectively.

A quantitative treatment will be developed below: the three thermodynamcially consistent cases, as well as numerous additional features of tensile instability will be rigorously derived. It is important to note that we have arrived at Fig. 2 from purely thermodynamic considerations; given the hypothesis of (smooth) loss of tensile strength, in other words, Fig. 2 is demanded by thermodynamics, and is therefore not restricted to any specific substance.

TENSILE INSTABILITY: ANALYTICAL TREATMENT

An analytical treatment of loss of tensile strength in liquids requires the assumption of smoothness for the tensile instability [Eq. (14)]. Then, at point b (Fig. 2), we have

$$\left(\frac{\partial P}{\partial T}\right)_{\text{spinodal}} = 0, \tag{14}$$

$$\left(\frac{\partial P}{\partial v}\right)_T = 0, \tag{16}$$

the latter equation being satisfied everywhere along curve *dba*.

We want to study the relationship between pressure, temperature, and density, in the vicinity of a tensile instability. The point at which such a phenomenon occurs is an unstable limit of stability (as are all points along a spinodal curve except for critical points). The following treatment, however, is possible because the signs of all the second derivatives of pressure with respect to temperature and density are not only defined, but demanded by thermodynamic consistency, when we consider variations away from the tensile instability and into the metastable region (the first derivatives vanish identically, as will be shown below). This is equivalent to the assumption of an analytic Helmholtz energy, and we can therefore write, with $P_b = P^*$,

$$\Delta P \equiv P - P^* = \delta P + \frac{1}{2!}\delta^2 P + \frac{1}{3!}\delta^3 P + \cdots, \tag{17}$$

or, explicitly,

$$P = P^* + \left(\frac{\partial P}{\partial T}\right)_v (T - T^*) + \left(\frac{\partial P}{\partial v}\right)_T (v - v^*) + \frac{1}{2}\left(\frac{\partial^2 P}{\partial T^2}\right)_v (T - T^*)^2 + \frac{1}{2}\left(\frac{\partial^2 P}{\partial v^2}\right)_T (v - v^*)^2 + \left(\frac{\partial^2 P}{\partial T \partial v}\right)(T - T^*)(v - v^*) + \cdots, \tag{18}$$

where * denotes point b (P^*, T^*, v^*), and all derivatives are evaluated at b. Because, at point b, the fluid's compressibility diverges (and hence so do density fluctuations), the assumption of analyticity in the Helmholtz energy is not absolutely rigorous. As will become evident below, it is only the signs of the relevant derivatives that matter, and these follow from thermodynamic consistency: we therefore expect the results to be derived to describe physical reality with qualitative (though not necessarily quantitative) accuracy. We cite the classical van der Waals treatment of the critical point,[8] and Rozen's[9] analysis of dilute mixtures in the vicinity of a solvent's critical point as examples in which all of the qualitative features (though not the actual values of the critical exponents, for which these approaches predict mean field values) of the behavior being analyzed are derived from the assumption of an analytic Helmholtz energy in the vicinity of a point characterized by diverging density fluctuations.

We now return to Eq. (18) and note that the linear terms vanish identically [because of Eqs. (10), (14), and (16)], so that the leading terms of the expansion are quadratic,

$$p = at^2 + b(v')^2 + ct(v') + \cdots \tag{19}$$

with

$$p \equiv P = P^*, \tag{20}$$

$$t \equiv T - T^*, \tag{21}$$

$$v' \equiv v - v^*, \tag{22}$$

$$2a \equiv \left(\frac{\partial^2 P}{\partial T^2}\right)_v (>0), \tag{23}$$

$$2b \equiv \left(\frac{\partial^2 P}{\partial v^2}\right)_T (>0), \tag{24}$$

$$c \equiv \left(\frac{\partial^2 P}{\partial T \partial v}\right) = \frac{\partial}{\partial T}\left[\left(\frac{\partial P}{\partial v}\right)_T\right]_v. \tag{25}$$

The sign of a follows from the fact that the $v' = 0$ isochore must be tangent to the spinodal at point b [Eq. (10)] with $(\partial P/\partial T)_v > 0$ ($T > T^*$) and $(\partial P/\partial T)_v < 0$ ($T < T^*$) in the vicinity of the spinodal. This follows from stability, and the fact that isochores infinitesimally away from $v' = 0$ (i.e., $v' = \pm\epsilon$) must also be tangent to the spinodal, with $(\partial P/\partial T)_v > 0$ ($T > T^*$) and $(\partial P/\partial T)_v < 0$ ($T < T^*$), and implies $a > 0$, as written. The sign of b must necessarily be positive: the derivative $(\partial^2 P/\partial v^2)_T$ is positive for any point along the spinodal curve. The behavior of coefficient c is of central importance. From Fig. 2, it can be seen that c has different signs according to whether the derivative $\partial/\partial T$ is calculated in the $t > 0$ or the $t < 0$ direction; we therefore have, accordingly,

$$c < 0 (t > 0),$$
$$c > 0 (t < 0), \tag{26}$$

and, as will be shown, the three different types of behavior which are thermodynamically consistent with loss of tensile strength introduced in the previous section correspond to the cases $|c(t>0)| = |c(t<0)|$, $|c(t>0)| > |c(t<0)|$, and $|c(t>0)| < |c(t<0)|$.

We now nondimensionalize Eq. (19), by defining

$$\pi = P/P^*, \tag{27}$$

$$\tau = T/T^*, \tag{28}$$

$$\nu = v/v^*, \tag{29}$$

$$x = a(T^*)^2/P^*, \tag{30}$$

$$y = b(v^*)^2/P^*, \tag{31}$$

$$z = cT^*v^*/P^*, \tag{32}$$

to obtain

$$(\pi - 1) = x(\tau - 1)^2 + y(\nu - 1)^2 + z(\tau - 1)(\nu - 1). \tag{33}$$

The signs of coefficients x, y, z, follow from the fact that P^* is negative,

$$x < 0, \tag{34}$$

$$y < 0, \tag{35}$$

$$z\begin{cases} < 0 & (\tau < 1) \\ > 0 & (\tau > 1) \end{cases}. \tag{36}$$

From Eq. (36) we obtain the important inequality

$$z(\tau - 1) > 0 (\forall \tau). \tag{37}$$

We will now study the behavior implied by Eqs. (33)–(37). This means obtaining equations for spinodal and density maxima loci, and, of course, relating the resulting picture to physical reality (specifically, to understand, on a more quantitative basis, the relationship between density anomalies and tensile instability).

Spinodal projections follow from writing

$$\left(\frac{\partial \pi}{\partial \nu}\right)_\tau = 0, \tag{38}$$

whereupon we readily obtain

$$\nu - 1 = -\frac{z}{2y}(\tau - 1), \tag{39}$$

$$\pi - 1 = \left(\frac{4y^2x}{z^2} - y\right)(\nu - 1)^2, \tag{40}$$

$$\pi - 1 = \left(x - \frac{z^2}{4y}\right)(\tau - 1)^2, \tag{41}$$

i.e., equations for the spinodal curve in T, v; P, v; and P, T coordinates, respectively. The stability criterion is

$$\left(\frac{\partial \pi}{\partial \nu}\right)_\tau > 0. \tag{42}$$

Density extrema loci can be obtained from the relationship

$$\left(\frac{\partial \nu}{\partial \tau}\right)_\pi = -\frac{(\partial \pi/\partial \tau)_\nu}{(\partial \pi/\partial \nu)_\tau} = -\frac{2x(\tau - 1) + z(\nu - 1)}{2y(\nu - 1) + z(\tau - 1)} \tag{43}$$

and the fact that the denominator, being a stability coefficient, is necessarily finite (or zero, but only on the spinodal curve); hence, the density extrema locus, in T, v coordinates, satisfies

$$\nu - 1 = -\frac{2x}{z}(\tau - 1) \tag{44}$$

with

$$2x(\tau - 1) + z(\nu - 1) < 0 \tag{45}$$

and

$$2x(\tau - 1) + z(\nu - 1) > 0, \tag{46}$$

corresponding, respectively, to positive (i.e., "normal") and negative (i.e., "anomalous") values for the thermal expansion coefficient. The equations for the density extrema locus in P, T and P, v coordinates are readily obtained from appropriate substitutions of the numerator in Eq. (43) (equated to zero) into Eq. (33). The results are

$$\pi - 1 = \left(x - \frac{z^2}{4y}\right)(\tau - 1)^2, \tag{47}$$

$$\pi - 1 = \left(y - \frac{z^2}{4x}\right)(\nu - 1)^2. \tag{48}$$

We now derive inequalities which govern the behavior of the above expressions. It follows from its definition [Eq. (27)] that π is always smaller than 1. Then, because $y < 0$ [Eq. (35)], it follows from Eq. (40) that

$$\frac{4xy}{z^2} > 1 \tag{49}$$

or, equivalently [Eq. (41)],

$$\frac{z^2}{4xy} < 1.$$

A fundamental property of liquids exhibiting a tensile instability is the absence of an analytic density extrema locus in the stable or metastable region. That this is so follows from writing:

$$\left(\frac{\partial \pi}{\partial \nu}\right)_\tau = 2y(\nu - 1) + z(\tau - 1) \tag{50}$$

and substituting the density extrema locus condition [Eq. (44)], to obtain, along the density extrema locus,

$$\left(\frac{\partial \pi}{\partial \nu}\right)_\tau = z(\tau - 1)\left(1 - \frac{4xy}{z^2}\right). \tag{51}$$

The right-hand side is necessarily negative [see Eqs. (37) and (49)], and we therefore conclude that, indeed, the density extrema locus is unstable. This behavior will now be explained.

We first consider the $P, T(\pi, \tau)$ projection. Because of the way π is defined, it is more convenient to plot $-\pi$ vs τ, since, for $P^* < 0$, $d(-\pi)$ has the same sign as $d(P)$. Figure 3(a) is a schematic $(-\pi, \tau)$ projection, corresponding to the symmetric case [i.e., $|c(t>0)| = |c(t<0)|$]. Curve *abd* is the spinodal [Eq. (41)], and *a′bd′* is the density extrema locus [Eq. (47)]. It can be shown that, for any τ, $-\pi_{\rho\text{ext}} > -\pi_{\text{spinodal}}$: this follows from Eqs. (41) and (47), and the fact that $4xy/z^2 > 1$ [Eq. (49)]. The inequality, in other words, follows from the fact that

$$\frac{4xy}{z^2} - 1 > 1 - \frac{z^2}{4xy}, \tag{52}$$

which can be proved by multiplying both sides by $4xyz^2$, a positive number,

$$4xy(4xy - z^2) > z^2(4xy - z^2) \tag{53}$$

and noting that Eq. (53) is always satisfied because $4xy > z^2$.

Also shown in Fig. 3 are two isochores of equal volumes $(v_1 = v_2)$, reaching their stability limits at the same value of (negative) pressure $[\pi(q) = \pi(q')]$, which, in P, T coordinates, corresponds to tangency between isochore and spinodal. The analytical (but unphysical) extrapolation of these isochores beyond the spinodal curve, and therefore into the

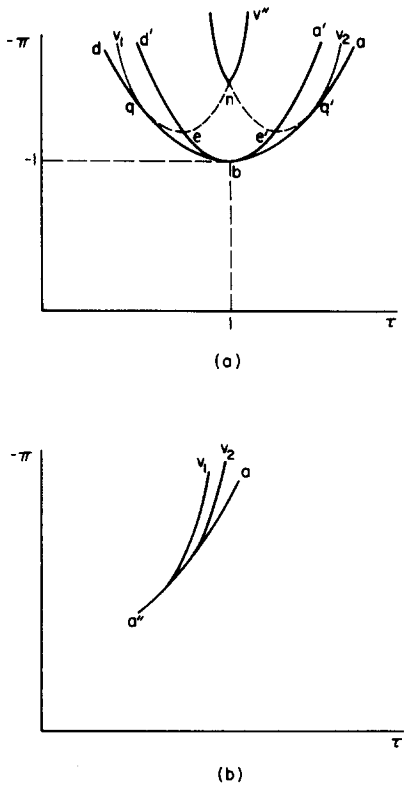

FIG. 3. (a) Model predictions for the $(-\pi, \tau)$ projection of the spinodal (dba), unphysical density extrema locus ($d'ba'$), and isochores ($v_1 = v_2$, v''), for the symmetric case $|z(\tau > 1)| = |z(\tau < 1)|$. (b) Proof that the tensile instability corresponds to an absolute density maximum along the spinodal.

unstable region, is illustrated by the dotted segments qen and $q'e'n$. The locus of the unphysical minima (e, e') is $d'ba'$, along which the mathematical criterion for the existence of density extrema is satisfied.

The isotherm $\tau = 1$ represents a singularity, the nature of which will now be explained. In the first place, further extrapolation of the isochores beyond their minima (e, e') leads to a "cusp" (n) at $\tau = 1$ which, for the symmetric case $[|c(t>0)| = |c(t<0)|]$ is symmetric about the $\tau = 1$ axis. Along any isochore for which $\nu > 1$, then, there are five points (q,e,n,e',q') at which the thermal expansion coefficient changes sign, and one of these points always lies on the $\tau = 1$ isotherm. This aspect of the $\tau = 1$ singularity is merely numerical, since the isochores are unphysical beyond their tangency points (q, q').

For $\nu < 1$, however, the singularity of the $\tau = 1$ isotherm is physical (and not merely numerical) in nature. This is shown in Fig. 3(a) by the curve v'' $(v'' < v^*)$. That v'' must necessarily correspond to a volume lower than v^* follows from stability $[(\partial\pi/\partial\nu)_\tau > 0]$. Furthermore, the slope discontinuity at $\tau = 1$ follows from Eq. (33), from which, for $\tau = 1$, we obtain

$$\left(\frac{\partial(-\pi)}{\partial\tau}\right)_\nu = -z(\nu - 1)$$

which is positive for $\tau > 1$, negative for $\tau < 1$, and, for $\nu \neq 1$, is never zero. The $\tau = 1$ isotherm, therefore, has the property of sharply dividing the substance's behavior into an anomalous region, $\tau < 1$, where the thermal expansion coefficient is everywhere negative (for stable and metastable states), and a normal region, with a positive thermal expansion coefficient.

That the isochore v'' $(\nu < 1)$ never attains a (smooth) density maximum [i.e., one for which the derivative $(\partial v/\partial\tau)_\pi$ is zero] is a consequence of the fact that, in this model, z changes discontinuously in going from the $\tau > 1$ to the $\tau < 1$ region. The $\tau = 1$ singularity, as well as the essential features of the model, are of course independent of the way in which z does in fact change in the immediate vicinity of $\tau = 1$: this can, at most, alter the shape of curves such as v'' in the immediate vicinity of $\tau = 1$, at which temperature a minimum (whether smooth or cusped) must necessarily exist.

At any given τ, the condition $-\pi < -\pi_{\text{spinodal}}$ is completely unphysical and does not even correspond to analytical extrapolations into the unstable region: both stable and analytically extrapolated unstable states are "contained within" the parabola dba.

To complete the discussion of the P, T projection, we will show that, indeed, isochores, as predicted by the model, are tangent to the spinodal, and, secondly, that $\nu = 1$ is an absolute volume minimum along both $d'ba'$ and dba. First, from Eq. (33) we write, for the slope of an isochore in π, τ coordinates,

$$\left(\frac{\partial\pi}{\partial\tau}\right)_\nu = 2x(\tau - 1) + z(\nu - 1) \qquad (54)$$

and, for the corresponding slope along the spinodal [i.e., from Eq. (41)],

$$\left(\frac{\partial\pi}{\partial\tau}\right)_{\text{spinodal}} = 2x\left(1 - \frac{z^2}{4xy}\right)(\tau - 1). \qquad (55)$$

If we now substitute the limit of stability criterion [Eq. (38)] into Eq. (54) we readily obtain Eq. (55). This completes the isochore tangency proof [in this last derivation we have introduced an expression for the slope of an isochore in P, T coordinates: it is clear that, upon equating Eq. (54) to zero, we obtain the τ, ν equation for the density extrema locus; this will be verified when we discuss the τ, ν projection].

That ν decreases uniformly towards 1 along both spinodal branches (i.e., that $\nu = 1$ is an absolute volume minimum) follows from the (π, ν) spinodal expression [Eq. (40)], which, upon differentiation, yields

$$\left[\frac{\partial(-\pi)}{\partial\nu}\right]_{\text{spinodal}} = -2y\left(\frac{4xy}{z^2} - 1\right)(\nu - 1), \qquad (56)$$

where the coefficient $-2y(4xy/z^2 - 1)$ is necessarily positive. From Fig. 3(b) (where aa'' is a spinodal segment, and v_1, v_2 are isochores) we can at once see that, if $\partial(-\pi)/\partial\nu$ along aa'' were negative $(v_1 > v_2)$, the isochores would be unstable, since $[\partial(-\pi)/\partial\nu]_\tau$ would be positive. We conclude, therefore, that all points on dba correspond to $\nu > 1$. This will also follow from analysis of π, ν and τ, ν projections.

Although we have outlined most of the peculiar characteristics that are thermodynamically consistent with a tensile instability, it is important to analyze the behavior in other projections. This will highlight features that are not evident in $(-\pi, \tau)$ coordinates, and, in addition, the inter-

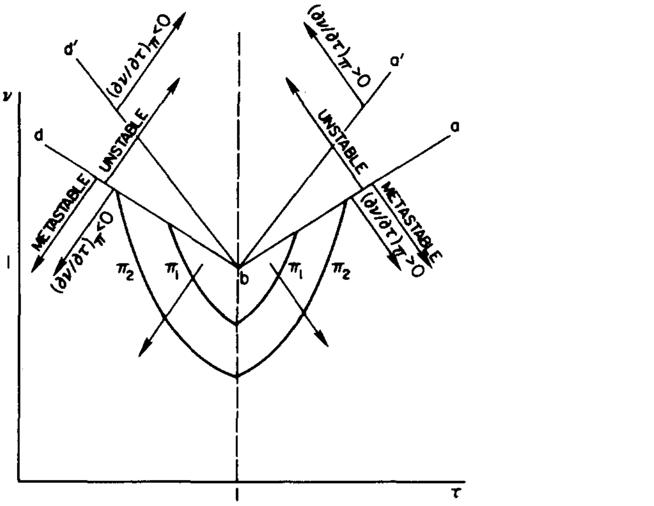

FIG. 4. Model predictions for the (ν, τ) projection of spinodal (dba), unphysical density extrema locus $(d'ba')$, and isobars (π_1, π_2). Also shown are the various regions corresponding to positive and negative thermal expansion coefficients, and to metastable and unstable states.

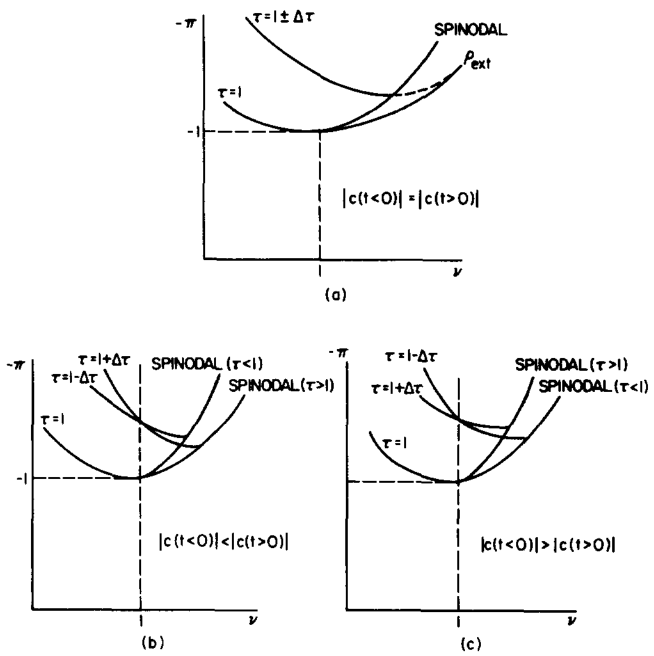

FIG. 5. Model predictions for the $(-\pi, \nu)$ projection of spinodal, unphysical density extrema locus, and isotherms, for the symmetric (a) and unsymmetric [(b) and (c)] cases.

nal consistency of the treatment will be demonstrated.

The spinodal (dba) and density extrema locus $(d'ba')$ projections in τ, ν coordinates [Eqs. (39) and (44), respectively] are shown in Fig. 4, corresponding, again, to the symmetric case whereby $|c(t>0)| = |c(t<0)|$. Again, we first show that for any τ, ν $(\rho\text{ext}) > \nu(\text{spinodal})$. For $\tau < 1$ $(z<0)$, from Eqs. (39) and (44), we must have, for the above condition to hold

$$-\frac{2x}{z}(\tau - 1) > -\frac{z}{2y}(\tau - 1), \tag{57}$$

or, equivalently,

$$\frac{2x}{z} > \frac{z}{2y}, \tag{58}$$

from which, upon multiplying by $2y$ and dividing by z, we recover Eq. (49),

$$\frac{4xy}{z^2} > 1.$$

For $\tau > 1$, on the other hand, we multiply both sides of inequality (57) by $\tau - 1$ (>0), to obtain

$$\frac{2|x|}{z} > \frac{z}{2|y|}, \tag{59}$$

from which Eq. (49) follows at once.

That the density extrema loci are unstable can be seen from the stability criterion $(\partial P/\partial v)_T < 0$: any isotherm attains its maximum volume (and minimum pressure) at the spinodal. Thus, in Fig. 4, the stable (and metastable) region lies below the spinodal lines dba. For $\tau > 1$, the coefficient of thermal expansion is everywhere positive in the stable region: this follows from Eq. (45), which can be rewritten as an explicit criterion for any point with a positive coefficient of thermal expansion,

$$\nu < 1 - \frac{2x}{z}(\tau - 1). \tag{60}$$

For $\tau < 1$, on the other hand, the above criterion reads

$$\nu > 1 - \frac{2x}{z}(\tau - 1) \tag{61}$$

and the stable (and metastable) region corresponding to $\tau < 1$ is therefore everywhere anomalous.

Also shown in Fig. 4 are two isobars $(\pi_1 > \pi_2, P_2 > P_1)$, the essential features of which can be obtained from solving Eq. (33) for ν, with π as a parameter, and using the stability criterion to indentify the stable solution. The arrows indicate increasing pressures.

If a horizontal line (isochore) is drawn from the $\tau < 1$ to the $\tau > 1$ region, we note that, if $\nu < 1$, the $\tau = 1$ line constitutes the sole point at which the thermal expansion coefficient changes from negative $(\tau < 1)$ to positive $(\tau > 1)$ values. This is consistent with isochore v'' in Fig. 3(a). For $\nu > 1$, on the other hand, there are five changes in the sign of the thermal expansion coefficient for any isochore (horizontal line), all of which occur in the unstable region: two along the analytical but unstable density extrema locus $d'ba'$, and one upon intersecting the $\tau = 1$ line. Again, this is the behavior exhibited by the $v_1qene'q'v_2$ isochore in Fig. 3(a).

We now consider the salient features of tensile instability in $-\pi, \nu$ (P, v) coordinates (Fig. 5). Figure 5(a) shows the symmetric case $|z(\tau > 1)| = |z(\tau < 1)|$. The spinodal "retraces itself" exactly in $(-\pi, \nu)$ coordinates. The $\tau = 1$ isotherm has zero slope at $\nu = 1$, and a negative slope given by

$$\left[\frac{\partial(-\pi)}{\partial \nu}\right]_{\tau=1} = 2|y|(\nu - 1) \tag{62}$$

for $\nu < 1$. This follows from the model's defining equation [i.e., Eq. (33)]. The $\tau = 1$ isotherm is unstable for $\nu > 1$. The (unphysical) density extrema locus is also shown. Both this line and the spinodal have zero slope at $\nu = 1$. It is easy to verify that, for any given ν, $(-\pi)_{\text{spinodal}} > (-\pi)_{\rho\text{ext}}$:

this follows from the spinodal [i.e., Eq. (40)] and density extrema [i.e., Eq. (48)] relationships in $(-\pi, \nu)$ coordinates.

The spinodal's positive curvature is unusual: normally $(\partial^2 P/\partial v^2)$ along the spinodal is negative (certainly, at least, near the critical point). Isotherms symmetric about $\tau = 1$ (i.e., $\tau = 1 \pm |\Delta|$) are identical. Their unphysical but mathematically defined continuation beyond the spinodal is shown in the diagram to illustrate tangency to the density extrema locus: although unphysical, this constitutes an internal consistency check, and, again, can be easily verified from the model's equations. That $\tau = 1$ is a density maxima locus can be seen by considering an isobaric temperature decrease, starting at any arbitrary temperature $\tau > 1$: density increases (ν decreases) until $\tau = 1$ is reached, whereupon a further temperature decrease causes a density decrease (volume increase) whereby, for the symmetric case, a given volume (ν) corresponds to two different temperatures, symmetric about 1, for any pressure.

Also shown in Fig. 5 are the two unsymmetric cases [the analytical density extrema loci have not been included since their behavior has already been explained; furthermore being unphysical, they would unnecessarily complicate both figures, which would now have four different branches, i.e., two spinodals (shown), and two density extrema loci (not shown) per diagram]. In each case, symmetric isotherms $(\tau = 1 \pm \Delta)$ intersect at $\nu = 1$ [this follows from the model's defining relationship, Eq. (33)]. As was the case for symmetric behavior, the $\tau = 1$ isotherm is a (nonanalytical) locus of density maxima, a property that can be verified, as we did in the symmetric case, by considering the volumes along any isobar as the temperature is decreased from $\tau > 1$ to $\tau < 1$.

It follows from the figures that $(\partial \nu/\partial \tau)_\pi < 0$ (anomalous behavior) everywhere for $\tau < 1$ and $(\partial \nu/\partial \tau)_\pi > 0$ (normal behavior) everywhere for $\tau > 1$, as we have already mentioned before. This can also be seen by following the intersections of any isochore (vertical line) with the isotherms: pressure $(-\pi)$ will decrease to a minimum (located on the $\tau = 1$ isotherm if $\nu < 1$, or on the spinodal if $\nu > 1$) upon reducing the temperature, as long as $\tau > 1$. For $\tau < 1$, on the other hand, pressure increases as τ decreases at constant volume. That this increase is unbounded (and hence unphysical) is obviously due to the fact that the model is based upon a truncated expansion, and should only be used in the vicinity of the tensile instability locus: in real cases, we expect a phase transition to occur, as τ cannot be decreased without bounds in the fluid state.

CONCLUSIONS

The thermodynamically consistent behavior corresponding to a tensile instability has been derived on the assumptions of smoothness for the instability and an analytic Helmholtz energy. There follow a variety of unusual phenomena which are demanded by thermodynamics, and which the present analysis describes and predicts with qualitative accuracy: spinodal retracing, nonanalytic density maxima, regions with positive (normal) and negative (anomalous) thermal expansion coefficients in the vicinity of the spinodal.

The molecular implications of these phenomena have not been considered here: a fluctuation analysis, as well as an entropy expression, are currently being developed, and will be addressed in future publications.

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