Stability and Tensile Strength of Liquids Exhibiting Density Maxima

If a given liquid exhibits a density maximum anywhere in its phase diagram, thermodynamic consistency dictates that such a point cannot be isolated: a density maxima locus must necessarily exist. For a fluid that does not also exhibit density minima, the pressure-temperature projection of such a locus is negatively sloped, and can only end at a stability limit. There exist two thermodynamically consistent ways in which such an intersection can occur, and they correspond, respectively, to the highest and lowest possible temperatures at which a liquid can exhibit a negative coefficient of thermal expansion. These theoretical predictions are confirmed by experimental observations. The existence of density anomalies anywhere in a liquid's phase diagram is shown to have a profound influence in determining the shape of such a fluid's stability boundary.

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Introduction

It is a well-known fact that water exhibits a density maximum at 4°C and atmospheric pressure. This phenomenon plays a central role in the shaping of life on earth as we know it. Specifically, the existence of water layers at or close to 4°C in the bottom of frozen lakes and ponds is essential for maintaining life in water bodies exposed to subfreezing temperatures. Additional liquids that exhibit density maxima include SiO_2 and D_2O (Angell and Kanno, 1976), and Ga (Mon et al., 1979).

It is the purpose of this paper to derive general thermodynamic features that characterize any fluid exhibiting density maxima. Some of the most important consequences of the existence of density extrema in a given liquid are to be found in the metastable region where such a fluid can exist under tension. As an example, we mention tensile instability, the experimentally observed behavior whereby several liquids appear to lose tensile strength upon being cooled (Briggs, 1950, 1951; Sedgewick and Trevena, 1976). The relationship between tensile instability and density anomalies was first established by Speedy (1982a, b) for the specific case of water, and generalized by Debenedetti and D'Antonio (1986a, b) and D'Antonio and Debenedetti (1987) for any fluid.

Materials that lose tensile strength upon being cooled exhibit behavior which, being contrary to intuition, elicits scientific curiosity. Although it has hitherto received comparatively little attention from chemical engineers, the whole subject of liquids under tension has interesting technical implications and suggests numerous novel applications.

Liquids under tension surround us everywhere, this being the prevalent mode of fluid transport in trees and most plants (Scholander et al., 1965; Scholander, 1972). Nature's accomplishments in this area are in sharp contrast with our own primitive attempt towards the implementation of a negative pressure technology. At the heart of this situation lies a profound lack of knowledge of the mechanism(s) and kinetics of loss of cohesion via bubble formation.

Possible applications of a liquid's ability to withstand tension include the negative pressure pump, novel irrigation methods, and a new approach to the nondestructive testing and measurement of adhesion on flat surfaces. A prototype tension pump, which could be used to extract liquids from deep wells or in enhanced oil recovery applications, was actually built and tested. Not surprisingly, loss of cohesion due to bubble formation was the most important technical problem encountered by the original proponents of this interesting concept (Hayward, 1971), which still awaits widespread practical implementation. The idea of an irrigation system in which water is supplied at a controlled negative pressure through subterranean porous pipes (Bulman, 1969; Hayward, 1971) is potentially revolutionary, since it would virtually eliminate evaporation losses. Here again, our inability to handle liquids under tension on a large scale has kept this interesting concept from progressing beyond the realm of ideas.

If a carefully deaerated liquid with a positive thermal expansion coefficient is cooled within a rigid container that it fills

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completely, a substantial pressure decrease will occur (typically 10 bar/K for a liquid near its triple point). This technique was among the first experimental approaches used to study liquids under tension, and is known as the Berthelot tube method, after Marcellin Berthelot, who did pioneering work on the subject in the mid-19th century. Since the tension so developed is controllable, reversible, and measurable, it could be used to measure and test adhesion on flat surfaces nondestructively. A possible application of this concept is the measurement and testing of photoresist adhesion on microchips.

While all of the above are examples of technologies yet to be implemented, there are a number of current applications in which liquids are subjected to high-intensity alternating tensile and compressive stresses. In such cases, loss of cohesion and bubble formation can occur, among other mechanisms, if the local stress exceeds the liquid's tensile strength. The subsequent collapse of the bubbles (cavitation) conspires, for example, against the efficient propagation of sonar waves. In addition, cavitation is an important factor in several applications of ultrasound technology, such as liquid extraction enhancement (Flisak and Perna, 1977), or acoustically induced polymerization (Kruus, 1983); many medical uses of ultrasound, such as tumor detection, are, on the other hand, adversely affected by bubble formation and collapse. Cavitation can also cause severe mechanical damage to hydraulic turbines, ship propellers, and other fluid-moving machinery where tensile stresses are induced in liquids.

It is clear that a sound engineering design involving any of the previous applications requires an understanding of the ability of liquids to withstand tension, and, therefore, of tensile instabilities. This phenomenon, it will be shown, is a necessary consequence of the existence of density maxima. Significant progress toward the formulation of a molecular-based picture of density extrema has been made in the specific case of water (Eizenberg and Kauzmann, 1969; Stillinger, 1980). In this paper, our goal is to investigate not the molecular (and hence substance-specific) but the general (substance-independent) features that characterize the macroscopic, thermodynamic behavior of any fluid exhibiting density maxima.

We start our analysis by investigating the question of continuity of a density maxima locus: Given the existence of a line satisfying $\alpha_p = 0$, $(\partial^2\rho/\partial T^2)_P < 0$, is it thermodynamically consistent for the (P, T) projection of such a line to end? It will be shown that this behavior is impossible. This gives rise to three "allowed" possibilities: continuation, crossover of density extrema, and merging of density extrema. Of these, the latter two, although thermodynamically consistent, imply the existence of density minima (Kennedy and Wheeler, 1983). Although we focus our attention exclusively on density maxima, it is important to mention here the work of Bridgman (1931), whose measurements suggested a merging of density maxima and minima loci in water at approximately 2 kbar and −5°C. In spite of the fact that this particular aspect of Bridgman's pioneering work has since been disproved (Angell and Kanno, 1976; Tamman and Schwarzkopf, 1928), density extrema crossover or merging are interesting and thermodynamically consistent phenomena which any fluid showing density anomalies ($\alpha_p < 0$) could theoretically exhibit. If, on the other hand, such a fluid does not exhibit density minima—which is the case we consider here—its density maxima locus cannot terminate except at a limit of stability (spinodal curve).

From the thermodynamically consistent ways in which density maxima and limits-of-stability loci intersect, there follow several unusual features that are supported by experimental evidence. The most important conclusions are:

a. A fluid exhibiting density maxima (but not density minima) must have a negatively sloped density maxima locus (in P, T coordinates)

b. Such a density maxima locus intersects a spinodal curve at two points corresponding, respectively, to the highest pressure-lowest temperature and lowest pressure-highest temperature over which such a fluid can exhibit a negative thermal expansion coefficient

c. The low-pressure intersection corresponds to a tensile instability; hence, any fluid exhibiting density anomalies must necessarily show a maximum in its tensile strength vs. temperature relationship

d. Consequently, the boundaries within which a liquid can exist have a low-pressure limit if such a liquid exhibits density maxima anywhere in its phase diagram

The essential features—(b), (c)—of the behavior derived in this paper were first described analytically by Speedy (1982a, b) for the specific case of water. Speedy's approach involved a volume-explicit pressure expansion about a limit of stability, whose temperature-dependent coefficients were fitted to match the volumetric behavior of water, as represented by the equation of state of Chen et al. (1977). The present treatment, on the other hand, is completely general and involves no adjustable parameters. We derive the thermodynamically consistent behavior that applies to any fluid exhibiting density maxima and show the relationship between this phenomenon and stability boundaries. Given the central role played by stability considerations in what follows, it is important first to discuss our basic assumptions.

Mathematical Treatment: Assumptions and Limitations

Metastability in fluids is a common phenomenon whose existence is unequivocally demonstrated by numerous experimental observations (see Skripov, 1973, for a comprehensive review). In addition, property measurements for metastable fluids yield well-defined, reproducible values (Schufle and Venugopalan, 1967; Zheleznyi, 1969; Gillen et al., 1972; Angell et al., 1973; Rasmussen et al., 1973; Chapman et al., 1975; Speedy and Angell, 1976; Richards and Trevena, 1976; Trinh and Apfel, 1978; Henderson and Speedy, 1980). These and other experimental studies unfortunately have not been accompanied by a corresponding progress in our theoretical understanding of metastability from a fundamental (molecular) viewpoint: lattice models with short range interactions, which are otherwise more realistic than mean field approaches for the quantitative description of matter under conditions where fluctuations are important, do not exhibit analytic continuation into the metastable region. The nature of the mathematical problems associated with this lack of continuation has been discussed elsewhere (Fisher, 1966). Metastability in two-dimensional lattices with an infinitely weak attractive tail added to hard-core interactions has been discussed by Hall and Stell (1973).

In this paper we assume not only that there exists a thermodynamically defined limit of stability locus along which the fluid's isothermal compressibility K_T, as well as other thermodynamic quantities, diverges, but furthermore that an analytic description of a fluid's properties applies in the immediate proximity of the spinodal curve. While these are undoubtedly simplifications, the resulting mean field picture reproduces the essential features associated with experimental observations on tensile instabilities (Briggs, 1950, 1951; Sedgewick and Trevena, 1976), and density maxima in the vicinity of homogeneous nucleation limits of supercooled liquids (Kanno et al., 1975; Angell and Kanno, 1976).

The theoretical soundness of the mean field approach to metastability has been argued most convincingly by Compagner (1974). The key point for our present purposes is that at the substantially subcritical temperatures of interest here, well-defined states, characterized by analytically describable thermodynamic functions, exist and prevail over a metastable system's tendency to relax irreversibly toward stable equilibrium. This is equivalent to saying that the limit-of-stability locus is defined by thermodynamic, as opposed to kinetic, considerations. The interested reader is referred to Compagner's paper for a detailed discussion.

The exponents that characterize the divergence of thermodynamic quantities (K_T, C_p, etc.) as the spinodal curve is approached are called pseudocritical exponents (Compagner, 1974). The present treatment gives rise to the mean field approximations to the true pseudocritical exponents. These calculations have been presented elsewhere (Debenedetti and D'Antonio, 1986b). Except for these differences in the values of the pseudocritical exponents, our analysis uncovers all of the essential features which, from thermodynamic consistency arguments, characterize the behavior of any fluid exhibiting density maxima. It is our purpose to derive and discuss this behavior and to compare the model's predictions with available experimental evidence. In this context, the exact *PVT* functionality in the vicinity of spinodal loci is of secondary importance relative to an understanding of the general relationship between density anomalies and stability boundaries.

In the following sections we analyze the slope and continuity of a density maxima locus, and its behavior in the vicinity of and intersection with spinodal curves; we also compare our predictions to available experimental evidence.

Behavior of a Locus of Density Maxima away from a Limit of Stability

Consider the (P, T) projection of a density maxima locus. By definition, each thermodynamic state along such a line satisfies the condition $\alpha_p = 0$. In formulating a thermodynamic description of density maxima, we first address the question: can such a locus end at an arbitrary point? We designate the temperature, pressure, and molar volume of the hypothetical termination point by T^*, P^*, and V^*, respectively, and define

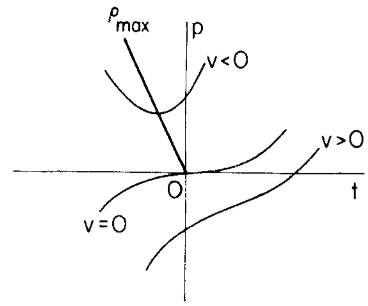
$$p \equiv P - P^* \tag{1}$$

$$t \equiv T - T^* \tag{2}$$

$$v \equiv V - V^* \tag{3}$$

The postulated situation is depicted in Figure 1a, wherein the $\alpha_p = 0$ line is negatively sloped and terminates at its lowest pressure and highest temperature. The three remaining possibilities (low-pressure termination-positive slope, high-pressure termination-negative slope, high-pressure termination-positive slope) will be analyzed below.

At the hypothetical termination point, Figure 1a, $p = 0$, $t = 0$,



(a)

Figure 1a. Postulated low-pressure termination of a negatively sloped locus of density maxima.

$v = 0$. By definition, $\alpha_p > 0$ along the $v = 0$ isochore for $p \neq 0$, $t \neq 0$, whereas $\alpha_p^* = 0$. In the vicinity of the termination point, then, the $v = 0$ isochore divides the (p, t) plane into two regions; in only one of these regions are density maxima possible. It follows that, at the termination point the pressure exhibits an odd-order dependence of at least third order with respect to temperature. Because the relationship between p, t, and v is analytic, it can be described, for small pressure changes about the hypothetical termination point, by a truncated Taylor series. Using temperature and volume as independent variables, and taking into account the vanishing of $(\partial P/\partial T)_v$ and $(\partial^2 P/\partial T^2)_v$ at the termination point (the former due to the fact that $\alpha_p^* = 0$; the latter due to the fact that $\alpha_p > 0$ for $v = 0$, $t \neq 0$, $p \neq 0$), the leading terms of such an expansion read:

$$p = \alpha v + \beta t^3 + \gamma t v \tag{4}$$

where

$$\alpha = \left(\frac{\partial P}{\partial V}\right)_{T^*} < 0 \tag{5}$$

$$6\beta = \left(\frac{\partial^3 P}{\partial T^3}\right)_{V^*} > 0 \quad \text{(for density maxima)} \tag{6}$$

$$\gamma = \left(\frac{\partial^2 P}{\partial T \partial V}\right)_* \tag{7}$$

and where * denotes differentiation at the hypothetical termination point.

For isothermal volume changes about the termination point, Figure 1a, we must have

$$\delta(\partial P/\partial T)_v > 0 \quad \text{for } v < 0 \tag{8}$$

$$\delta(\partial P/\partial T)_v > 0 \quad \text{for } v > 0 \tag{9}$$

so that

$$\gamma < 0 \quad \text{for } v < 0 \tag{10}$$

$$\gamma > 0 \quad \text{for } v > 0 \tag{11}$$

It follows from Eq. 4 that along the density maxima locus, $\gamma v = -3\beta t^2 < 0$. This implies that $v < 0$ when $\gamma > 0$ and $v > 0$

for $\gamma < 0$, in contradiction with Eqs. 10 and 11 and Figure 1a. We conclude that γ cannot be discontinuous at the termination point. Therefore, with $\gamma = 0$, the expansion now reads, taking into account the lowest order nonvanishing cross terms,

$$p = \alpha v + \beta t^3 + \delta t^2 v + \epsilon v^2 t \tag{12}$$

where

$$2\delta = \left(\frac{\partial^3 P}{\partial T^2 \partial V}\right)_* = \left(\frac{\partial \gamma}{\partial t}\right)_{v,*} < 0 \tag{13}$$

$$2\epsilon = \left(\frac{\partial^3 P}{\partial V^2 \partial T}\right)_* = \left(\frac{\partial \gamma}{\partial v}\right)_{t,*} > 0 \tag{14}$$

and where the signs follow from Eqs. 10 and 11 and the fact that isochores cannot intersect in any nonconjugate representation, such as (P, T). Such an intersection, in the case of a single-phase, single-component system, is in conflict with the second law of thermodynamics.

This thermodynamically consistent expansion—Eq. 12 subject to the constraints of Eqs. 5, 6, 13, and 14—gives rise to the behavior shown in Figure 1b. We can see from this figure that the origin is not a termination point in the sense that we had originally postulated, but rather, a crossover point where a density maxima locus becomes a density minima locus and vice versa. The mathematical manipulations leading to this graphical representation are presented in the Appendix. We conclude that a negatively sloped isolated density maxima locus (i.e., one not associated with any corresponding density minima locus) cannot exhibit a low-pressure termination.

Case 2 (a low-pressure termination of a positively sloped density maxima locus) is shown in Figure 2a. Because γ is now strictly positive at the termination point [since, for isothermal changes, $\delta(\alpha_p) < 0$ for $v < 0$, and $\delta(\alpha_p) > 0$ for $v > 0$ at the termination point], Eq. 4 is valid, and the locus of density extrema satisfies

$$p(\rho \text{ ext}) = -\frac{\beta t^2}{\gamma}(3\alpha + 2\gamma t) \tag{15}$$

which, in the immediate vicinity of the hypothetical termination point, describes a parabola through $p = t = 0$, having solutions

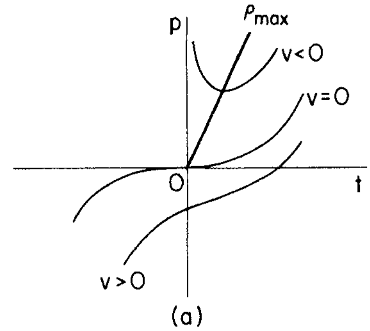


Figure 2a. Postulated low-pressure termination of a positively sloped locus of density maxima.

only for $p > 0$. Again, from Eq. 4,

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_v = \left(\frac{\partial^2 p}{\partial t^2}\right)_v = 6\beta t \quad (\beta > 0) \tag{16}$$

which means that the $t < 0$ branch is a locus of density minima, whereas the $t > 0$ branch is a locus of density maxima. This behavior is shown in Figure 2b and is, again, inconsistent with the hypothesis of a fluid exhibiting density maxima but not density minima.

Figures 3a and 3b illustrate the hypothetical high-pressure termination of an isolated density maxima locus. It can be seen that isochore intersection occurs unless the $v > 0$ curves exhibit extrema along their $\alpha_p < 0$ branch. However, since pressure and temperature are nonconjugate thermodynamic variables, isochore intersection in (p, t) coordinates is impossible. It follows that additional extrema (maxima in this case) must exist in order to make Figure 3 thermodynamically consistent. The existence of such additional maxima, however, contradicts the original hypothesis of termination of an isolated density maxima locus. This is because an isochore maximum corresponds, in (P, T) coordinates, to a density minimum.

We conclude that a locus of density maxima cannot terminate at a point away from a limit of stability. Crossover, Figure 1b, or merging, Figures 2b and 3, of density extrema are the only thermodynamically consistent possibilities, although they imply the simultaneous existence of density maxima and minima. We are not aware of any substance exhibiting such behavior.

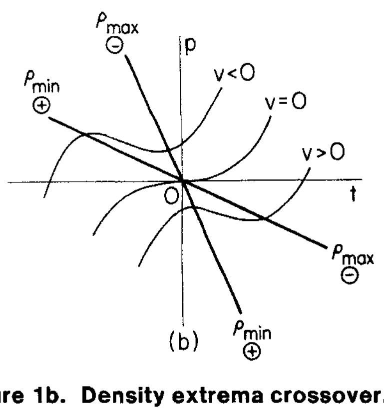


Figure 1b. Density extrema crossover.

+, − signs refer to coefficient of $|t|$, Eq. A1

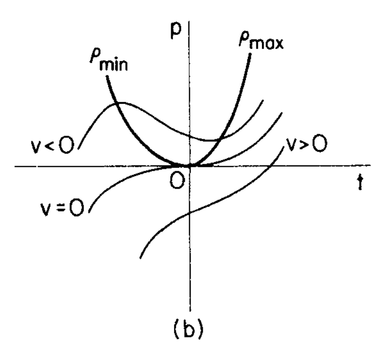


Figure 2b. Density extrema merging.

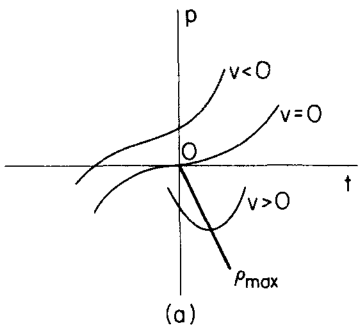


Figure 3a. Postulated high-pressure termination of a negatively sloped locus of density maxima.

Volumetric Behavior near a Point of Intersection of a Locus of Density Maxima and a Limit of Stability

Having shown that a density maxima locus cannot terminate away from a limit of stability unless the liquid in question exhibits also density minima, we now discuss the thermodynamically consistent behavior that follows from the intersection of such a line with a spinodal curve. We assume throughout the treatment that a thermodynamically defined curve satisfying $(\partial p/\partial v)_T = 0$ exists. Furthermore, by definition, the intersection of spinodal and density extrema loci also satisfies $(\partial P/\partial T)_v = 0$, since $(\partial P/\partial T)_v = \alpha_p/K_T$. Assuming, therefore, that the Helmholtz energy is analytic at the intersection, we can expand the pressure in terms of temperature and volume changes about said point. To leading order, such an expansion reads

$$p = at^2 + bv^n + ctv \tag{17}$$

where

$$2a = \left(\frac{\partial^2 P}{\partial T^2}\right)_{v,*} > 0 \tag{18}$$

$$n!b = \left(\frac{\partial^n P}{\partial V^n}\right)_{T,*} \tag{19}$$

$$c = \left(\frac{\partial^2 P}{\partial T \partial V}\right)_* < 0 \tag{20}$$

and where * now signifies that a quantity is evaluated at the intersection point. p, t, and v are now differences in pressure, temperature, and molar volume, respectively, from the corresponding value at the point of intersection; and n is an integer greater than one (i.e., we consider the possibility that not only $\partial p/\partial v$, but also higher order terms, might vanish at the spinodal-density extrema merging point).

Once again, we limit our attention to density maxima ($a > 0$). The sign of c follows from rejecting as improbable (though not thermodynamically inconsistent) behavior in which a liquid could become unstable upon isochoric heating. This special case, and its peculiar thermodynamic implications, have already been discussed elsewhere (Debenedetti and D'Antonio, 1986a, b). Finally, since all points on a spinodal curve are unstable (except for the critical point), we require either that $b > 0$ if n is odd, or $b \neq 0$ if n is even. The possible cases are summarized in Table 1.

Cases 3, 4, and 5 are incompatible with the assumption of the existence of a spinodal locus, since they result in unbounded regions of stability for $p < 0$ (cases 3, 4) and $p > 0$ (case 5). This situation being unphysical, we focus our attention on the two remaining cases.

Case 1 (n odd, $b > 0$) is illustrated in Figure 4. From Eq. 17, the spinodal and density maxima locus are described by the equations

$$p(K_T \rightarrow \infty) = at^2 \pm (1 - n)b\left[\frac{|c|t}{nb}\right]^{n/n-1} \tag{21}$$

$$p(\alpha_P = 0) = -at^2 + b\left[\frac{2at}{|c|}\right]^n \tag{22}$$

From Eq. 21, and the fact that $b > 0$, the spinodal is not defined for $t < 0$. Since n is at least 3, the density maxima locus intersects the spinodal from the $p < 0$ region. This case, in other words, corresponds to the intersection of the high-pressure end of a density maxima locus with the supercooled liquid spinodal curve. P^* and T^* represent the highest pressure and lowest temperature, respectively, for which density anomalies can exist. The cusp along the spinodal at P^*, T^* is very similar qualitatively to the behavior exhibited by a fluid in the vicinity of its critical point. In particular, for a van der Waals fluid such similarity is not only qualitative, but also quantitative. Equation 17, with $n = 3$, $b < 0$, and a leading linear term in t, describes the PVT behavior of such a fluid near its critical point.

Case 2 is illustrated in Figure 5, and has already been discussed elsewhere in detail (D'Antonio and Debenedetti, 1987). It corresponds to the low-pressure intersection of the density maxima and spinodal loci, or tensile instability. The intersection represents the point at which the liquid's tensile strength attains its maximum value (i.e., its pressure is negative and at a minimum). Upon further cooling, the liquid loses tensile strength,

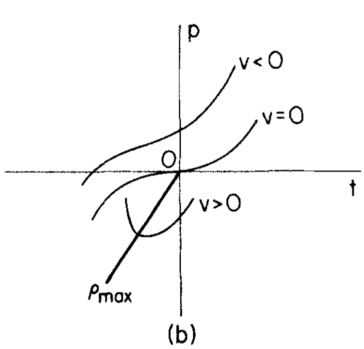


Figure 3b. Postulated high-pressure termination of a positively sloped locus of density maxima.

Table 1. Possible Intersections of Spinodal and Density Maxima Loci ($c < 0$)

Case	n	b	Comments
1	Odd	>0	High-pressure cusp
2	2	>0	Tensile instability
3	2	<0	Unphysical
4	Even (>2)	<0	Unphysical
5	Even (>2)	>0	Unphysical

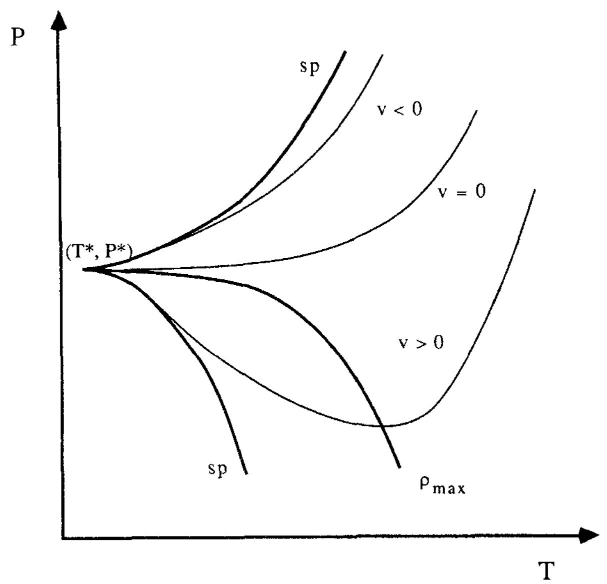


Figure 4. High-pressure termination of a density maxima locus: spinodal cusp.

contrary to normal behavior. The spinodal and density maxima locus are now described by the equations

$$p(K_T \to \infty) = at^2\left(1 - \frac{c^2}{4ab}\right) \tag{23}$$

$$p(\alpha_P = 0) = at^2\left(\frac{4ab}{c^2} - 1\right) \tag{24}$$

where $4ab/c^2 > 1$ and $1 > c^2/4ab$, since the instability represents a point of minimum pressure. It follows from Eq. 17, with $n = 2$, that the condition $(\partial p/\partial t)_v = 0$, $t > 0$ implies $(\partial p/\partial v)_t > 0$ along the density maxima locus. This means that the $t > 0$ solution to the $\alpha_p = 0$ condition is unstable. From Eq. 17 we readily conclude that the slope of the physically meaningful branch of the density maxima locus ($t < 0$) is negative. From this and our previous analysis of case 1 (high-pressure intersection) we conclude that, in general, the locus of density maxima must have a negative slope in (P, T) coordinates. We have not considered here the possibility that an extremum could occur along the locus of density maxima. It can easily be shown, however, that such an extremum implies the simultaneous existence of density minima.

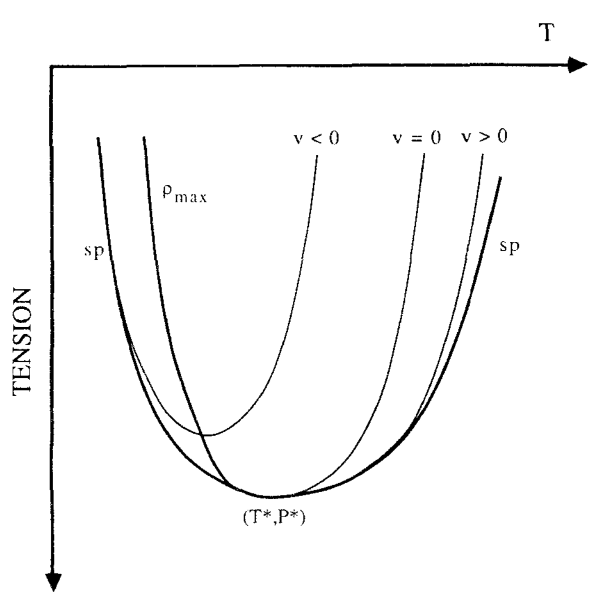


Figure 5. Low-pressure termination of a density maxima locus: tensile instability.

The density maxima locus intersects the spinodal curve at two points corresponding, respectively, to the highest pressure-lowest temperature and the lowest pressure-highest temperature for which the given fluid's thermal expansion coefficient can be negative. Each of these intersections causes a change in the sign of the slope of the spinodal curve's (P, T) projection (Speedy, 1982a, b). At high pressure, the spinodal exhibits a cusp that is mathematically related to the critical point of a van der Waals fluid. At low pressure (high tension), a tensile instability occurs (D'Antonio and Debenedetti, 1987).

This general relationship between density maxima and limits of stability is illustrated in Figure 6. A qualitatively similar behavior was derived by Speedy (1982a, b) for the specific case of water by fitting the temperature-dependent coefficients of his volume-explicit expansion to an empirical equation of state (Chen et al., 1977). Shown in Figure 6 are the melting (*di*), sublimation (*hd*), and boiling (*dc*) loci (binodal curves), as well as the triple (*d*) and critical (*c*) points. Line *aeb* is the density maxima locus, bounded by the high-pressure cusp (*a*) and the tensile instability (*b*). The spinodal curve *cgbfa* is the boundary within which the liquid can exist. If, as in Figure 6, the density maxima locus crosses the region bounded by lines *id*, *dc*, density maxima

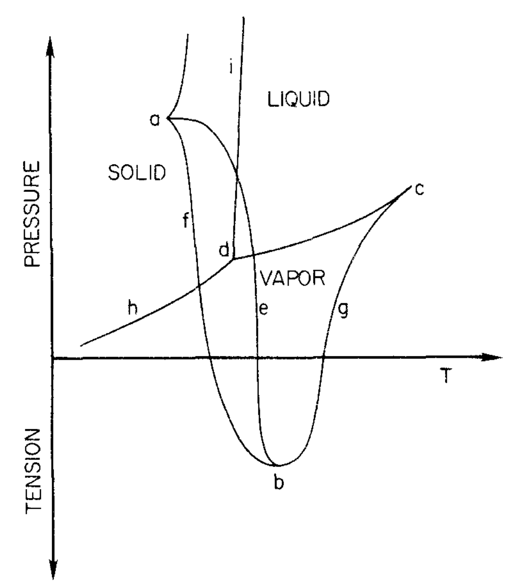


Figure 6. General relationship between density anomalies and stability boundaries of a fluid exhibiting density maxima but not density minima.

a. High-pressure termination
b. Tensile instability
c. Critical point
d. Triple point

aeb. Density maxima locus
afbgc. Liquid spinodal
hd, di, dc. Binodal lines

can be found in the stable liquid region. Otherwise, as is the case with SiO_2 (Angell and Kanno, 1976), the liquid exhibits only metastable density maxima.

Experimental Evidence

The pressure dependence of the density maxima locus of water (Tamman and Schwarzkopf, 1928), and D_2O and SiO_2 (Angell and Kanno, 1976) has been studied experimentally. In all cases, $dP/dT < 0$ along such a locus, confirming our theoretical prediction that a pressure increase causes a lowering of the maximum density temperature. This conclusion can also be reached by noting that if $dP/dT > 0$ along the $\alpha_p = 0$ locus, the region of the phase diagram where a fluid exhibits density anomalies extends toward the ideal gas regime, and this is inherently contradictory. Thus, if a fluid exhibits a positively sloped density maxima locus, it must necessarily show density minima also (except, of course, in the hypothetical case where the positively sloped locus intersects a superheated liquid spinodal).

The homogeneous nucleation limits of supercooled water and D_2O (Kanno et al., 1975; Angell and Kanno, 1976) were both studied by means of an emulsion technique, the reliability of which can be inferred from the fact that the measured homogeneous nucleation temperatures were independent of the emulsion carrier fluid. In these experiments—which include measurements at temperatures as low as $-92°C$ (H_2O) and $-85°C$ (D_2O), and pressures as high as 3,000 bar (H_2O) and 2,800 bar (D_2O)—the (P, T) projection of the homogeneous nucleation limit exhibited a sharp low-temperature cusp where its slope changed sign in the vicinity of the density maxima locus. The sharp change in the slope of this experimentally measured limit of stability (whether kinetically or thermodynamically defined) and the relationship of this phenomenon to density maxima is in agreement with the theoretically predicted behavior shown in Figures 4 and 6 for thermodynamically defined limits of stability.

Briggs (1950, 1951) measured the tensile strength of several liquids using a centrifugation method. In this approach, both ends of an open capillary were bent so that the tube became slightly Z-shaped; after filling with the liquid under study, the tube was rotated about a vertical symmetry axis perpendicular to the capillary's horizontal plane, and passing through its center. The experimentally measured tensile strength was then obtained from knowledge of the angular velocity at which the liquid cavitated. The most interesting aspect of these experiments (Briggs, 1950) was the dramatic drop in the measured tensile strength of water, from ~273 bar at $\sim 10°C$ to <10 bar at 0°C. Tensile strength maxima (although not as pronounced) were also observed for benzene, acetic acid, and aniline (Briggs, 1951). Although the presence of a solid-liquid interface in Briggs' experiments probably means that cavitation occurred at least partly as a result of loss of adhesion, and therefore was not the manifestation of a thermodynamic, as opposed to kinetic, limit of stability [theoretical estimates of water's tensile strength (Speedy, 1982a, b) far exceed Briggs' measured values], additional experiments performed a quarter of a century later (Sedgewick and Trevena, 1976) have made it all but impossible not to associate Briggs' observation with the phenomenon we call tensile instability (Debenedetti and D'Antonio, 1986a, b; D'Antonio and Debenedetti, 1987).

In these more recent experiments, Sedgewick and Trevena again observed a sharp maximum in the measured tensile strength of water, but this time using a technique (dynamic stressing) the most important characteristic of which is, for the present purposes, the absence of a solid-liquid interface at the point where cavitation occurred. This clearly rules out the loss-of-adhesion hypothesis, and one can only conclude that the observations of Briggs and of Sedgewick and Trevena are different, kinetically controlled manifestations of the same underlying phenomenon: loss of tensile strength, a necessary property of any liquid exhibiting density maxima. Thus, what is important is not the actual measured tensile strength (for which Briggs and Sedgewick and Trevena report very different figures) but the fact that water, when stressed in two completely different ways (centrifugation, dynamic stressing) exhibited the same sharp decrease in its apparent tensile strength, indicating kinetic limits of stability whose (P, T) projection show a clear extremum. This is of course exactly the behavior that one would predict for a fluid exhibiting density maxima and, therefore, a tensile instability, Figures 5, 6.

As for Briggs' observations on liquids other than water which also appear to show loss of tensile strength, if true they would indicate the existence of density anomalies in the metastable region of benzene's, aniline's, and acetic acid's phase diagrams (we are not aware of reported density maxima for any of these fluids).

The main features of the volumetric behavior that must necessarily characterize a fluid exhibiting density maxima can thus be derived, assuming the existence of a continuous, thermodynamically defined limit of stability locus bounding the superheated, supercooled, and subtriple (i.e., simultaneously superheated and supercooled) states, and analyticity up to and including the spinodal curve. While some of these assumptions are undoubtedly simplifications, the resulting behavior is in agreement with a variety of experimental observations. The water-specific behavior first derived by Speedy (1982a, b) is thus shown to be a particular case of the more general, substance-independent case addressed here.

Conclusions

A variety of liquids exhibit negative thermal expansion coefficients in some region of their phase diagram. This simple experimental observation can be used as the starting point for the derivation of the general features that characterize the behavior of any such fluid. A density anomaly is not an isolated phenomenon: a locus of density maxima must exist, the (P, T) projection of which is negatively sloped. If the particular fluid under study does not exhibit density minima, the line along which its thermal expansion coefficient vanishes can only terminate at a limit of stability. The temperature range within which a fluid can exhibit density anomalies is bound by the two points where the spinodal and density maxima loci intersect.

Any fluid that contracts upon being heated isobarically will have a maximum tensile strength at a particular temperature, corresponding to the low-pressure intersection of its spinodal and density maxima loci. Below this temperature, the liquid exhibits counterintuitive behavior, its tensile strength decreasing upon cooling.

A thermodynamic exploration of the density extremum phenomenon uncovers those features that are general (i.e., substance-independent) and in so doing brings forth relationships between apparently unconnected phenomena, such as tensile strength and thermal expansion coefficients. This generality, as is always the case with strictly macroscopic arguments, is attained at the expense of ignoring the molecular origins of the phenomena under investigation. It is hoped that a synthesis of molecular and thermodynamic insights will shed light on this important phenomenon. We believe that chemical engineers can contribute significantly toward the transformation of negative pressure in liquids from a scientific curiosity to a useful technology. We live, after all, surrounded by the ultimate example of the successful implementation of such a technology: trees.

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Notation

a = $(1/2)(\partial^2P/\partial T^2)_v$ evaluated at density maxima and spinodal loci intersection
b = $(1/n!)(\partial^nP/\partial V^n)_T$ evaluated at density maxima and spinodal loci intersection
c = $(\partial^2P/\partial T\partial V)$ evaluated at density maxima and spinodal loci intersection
K_T = isothermal compressibility, $Lt^2 \cdot M^{-1}$
n = exponent in v, t-explicit pressure expansion, Eq. 17
P = pressure, $ML^{-1} \cdot t^{-2}$
p = difference between actual and termination or intersection point pressure, $ML^{-1} \cdot t^{-2}$
T = temperature, θ
t = difference between actual and termination or intersection point temperature, θ
V = molar volume, $L^3 \cdot mol^{-1}$
v = difference between actual and termination or intersection point molar volume, $L^3 \cdot mol^{-1}$

Greek letters

α = $(\partial P/\partial V)_T$ evaluated at hypothetical density maxima termination
α_p = thermal expansion coefficient, θ^{-1}
β = $(1/6)(\partial^3P/\partial T^3)_v$ evaluated at hypothetical density maxima termination
γ = $(\partial^2P/\partial T\partial V)$ evaluated at hypothetical density maxima termination
δ = $(1/2)(\partial^3P/\partial T^2\partial V)$ evaluated at hypothetical density maxima termination
ϵ = $(1/2)(\partial^3P/\partial V^2\partial T)$ evaluated at hypothetical density maxima termination

Subscripts

$*$ = value of a property evaluated at termination or intersection points
ext = density extrema
max = density maxima
min = density minima

Appendix: Construction of Figure 1b

From Eqs. 5, 6, 12, 13, and 14, the density extrema locus can be written as

$$p_{\rho ext} = -\frac{\alpha\delta}{\epsilon}t \pm \frac{\alpha(\delta^2 - 3\beta\epsilon)^{1/2}}{\epsilon}|t| + t^3\left[\frac{\delta^2}{\epsilon} - 2\beta \mp \frac{|t|}{t}\frac{\delta}{\epsilon}(\delta^2 - 3\beta\epsilon)^{1/2}\right] \quad (A1)$$

or, equivalently, for small t,

$$p_{\rho ext} \approx -\frac{\alpha\delta}{\epsilon}t \pm \frac{\alpha(\delta^2 - 3\beta\epsilon)^{1/2}}{\epsilon}|t| \quad (A2)$$

where (see Eqs. 5, 6, 13, 14)

$$\frac{\alpha\delta}{\epsilon} > 0 \quad (A3)$$

$$\frac{\alpha(\delta^2 - 3\beta\epsilon)^{1/2}}{\epsilon} < 0 \quad (A4)$$

Thus, in the vicinity of the hypothetical termination point ($\beta\epsilon > 0$),

$$\left(\frac{dp}{dt}\right)_{\rho ext} < 0 \quad (A5)$$

In order to find whether the extrema locus corresponding to Eq. A1 is a maximum or a minimum, we write (see Eq. 12)

$$\left(\frac{\partial p}{\partial t}\right)_v = 3\beta t^2 + 2\delta tv + \epsilon v^2 = 0 \quad (A6)$$

and substitute this into the relationship

$$\left(\frac{\partial^2 p}{\partial t^2}\right)_v = 6\beta t + 2\delta v \quad (A7)$$

to obtain,

$$\left(\frac{\partial^2 p}{\partial t^2}\right)_{\rho ext} = \pm\frac{2\delta}{\epsilon}(\delta^2 - 3\beta\epsilon)^{1/2}|t| - \frac{2}{\epsilon}(\delta^2 - 3\beta\epsilon)t \quad (A8)$$

from which we conclude that

$$p_{\rho max} = -\frac{\alpha\delta}{\epsilon}t - \frac{\alpha(\delta^2 - 3\beta\epsilon)^{1/2}}{\epsilon}|t| + O(t^3) \quad (A9)$$

$$p_{\rho min} = -\frac{\alpha\delta}{\epsilon}t + \frac{\alpha(\delta^2 - 3\beta\epsilon)^{1/2}}{\epsilon}|t| + O(t^3) \quad (A10)$$

This is the behavior shown in Figure 1b.

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