

Statistical mechanics of metastable matter: Superheated and stretched liquids

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Prospects are examined for modifying the conventional statistical mechanics of condensed phases to describe stretched and/or superheated metastable liquids. The representation chosen for this task is that of “inherent structures,” i.e., multidimensional potential minima, and their basins of attraction. By examining inherent structures for the one-dimensional Lennard-Jones system, it becomes clear that in general large-void-containing inherent structures and their basins must be removed from the canonical partition function. With an appropriate choice of maximum allowable void size, this leaves the properties of the equilibrium liquid essentially unchanged, while suppressing the vaporization transition. The void-elimination constraint causes a soft-mode instability to terminate the metastable extension of the liquid at a limit of stretching or superheating.

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I. INTRODUCTION

Metastable forms of matter have always played a significant role in technology, and therefore have presented substantial challenges to the deductive and explanatory capacity of basic science. This paper is devoted to the improved understanding of metastable liquids, specifically those in the related states of superheating or of stretching (negative pressure). The objective is to construct a statistical mechanical formalism, essentially free of approximation, that describes these metastable liquid states, while coherently and naturally connecting them to states of thermodynamic equilibrium.

Owing primarily to the existence of clever experimental techniques, a substantial body of data is now available for both superheated [1–5] and stretched [5–9] liquids. In particular, limits of metastability are known for many substances: the explosive vaporization temperature point for superheating, and the disjoining pressure point for stretching. These striking phenomena and their measurements alone motivate the development of a general theory of metastable liquids, quite apart from other considerations.

The approach adopted here stems from the “inherent structure” description of the condensed phases of matter [10–13]. In fact it closely parallels a formalism created to describe supercooled liquids [14–16] with logical connections mentioned below at appropriate points. The viewpoint offered here should be beneficial both for the interpretation of experimental data, and for the design of computer simulation studies of metastable matter.

Section II provides background definitions and commentary for the general “inherent structures” approach for condensed phases [10–13]. This is followed by the examination of an elementary illustrative example in Sec. III, the one-dimensional Lennard-Jones system; its properties strongly suggest key attributes that the more general metastable-state formalism should possess. Section IV then presents that formalism. Section V contains some concluding remarks.

II. BACKGROUND

We shall deal with a volume- V closed system containing N_1 particles of species 1, ..., N_ν particles of species ν . These species may be either structureless spherically symmetric objects, or molecules with nonspherical shapes and internal degrees of freedom describing conformational flexibility. Interest ultimately lies in intensive properties evaluated in the large-system limit, that is, where V and the total number of particles

$$N = \sum_{\alpha=1}^{\nu} N_{\alpha} \quad (2.1)$$

pass to infinity at fixed number densities.

The total interaction potential Φ generally comprises three types of contributions. The first involves intramolecular distortional force fields, if any. The second encompasses all interparticle interactions. The third involves external interactions of the particles with container walls, and with the gravitational field (usually negligible). In many theoretical or simulational applications, the third category is suppressed in favor of periodic boundary conditions, especially when surface effects would be a distraction rather than the primary object of attention.

Let \mathbf{R} represent the configurational vector specifying the entire system. If species α has i_{α} internal degrees of freedom (rotation, vibration, conformation), then the number of components for \mathbf{R} will be

$$C = \sum_{\alpha=1}^{\nu} (3 + i_{\alpha}) N_{\alpha} . \quad (2.2)$$

In the following we will be concerned with the geometry of the $\Phi(\mathbf{R})$ hypersurface in the $C + 1 \equiv D$ dimensional space of (\mathbf{R}, Φ) , and how it affects both equilibrium and metastable state properties.

The canonical partition function Z provides the usual connection to equilibrium properties for a system equilibrated at temperature T . To the extent that classical sta-

tistical mechanics applies, we can write ($\beta=1/k_B T$) [17]:

$$Z \equiv \exp(-\beta F),$$

$$= \left[K \prod_{\alpha=1}^v N_{\alpha}! \right]^{-1} \int d\mathbf{R} \exp[-\beta\Phi(\mathbf{R})]. \quad (2.3)$$

Here F is the Helmholtz free energy. The normalizing quantity K is independent of V and has the same dimensions as \mathbf{R} ; it would be a product of mean thermal deBroglie wavelengths if the system contained only structureless spherical particles, but in any case is unaffected by interparticle interactions and plays no role in the present context. The equilibrium-state pressure derived from (2.3),

$$p = -(\partial F / \partial V)_{\beta}, \quad (2.4)$$

must, in the thermodynamic large-system limit, be non-negative.

Without significant loss of generality one can assume that Φ is continuous and differentiable with respect to all components of \mathbf{R} . Furthermore it is bounded from below. But given these common features, the detailed form of Φ varies drastically from substance to substance in ways that reflect their chemical distinctions. The superheating and stretching phenomena owe their existence to attractions between particles, and these exert a profound influence on the presence and distribution of Φ extrema (minima, saddle points, and maxima) in the C -dimensional \mathbf{R} space.

The differential geometry of the Φ hypersurface can be used to transform canonical partition function Z Eq. (2.3) in a fundamental and useful way. This transformation is based upon an exhaustive division of the configuration space into nonoverlapping "basins of attraction" B_a each one of which contains a single Φ minimum a within its interior. Basin B_a is defined to be the set of all points \mathbf{R} that map onto the interior minimum a by means of the following gradient descent equation ($s \geq 0$):

$$\mathbf{w} \cdot (\partial \mathbf{R} / \partial s) = -\nabla \Phi(\mathbf{R}). \quad (2.5)$$

Here \mathbf{w} is a $C \times C$ matrix of non-negative weights. For the simplest version of (2.5), the steepest descent mapping, \mathbf{w} is just the unit matrix; an alternative motivated by chemical reaction theory also uses a diagonal \mathbf{w} , but with atom masses arrayed along that diagonal [18]. Alternative choices for \mathbf{w} produce different basin shapes, but their number remains unchanged, each includes a single minimum, and saddle points (transition states) remain segregated on basin boundaries. Starting from essentially any system configuration \mathbf{R} at $s=0$, the solution to Eq. (2.5) converges to the relevant minimum as s approaches plus infinity.

The Φ minima, and hence the corresponding basins, may be classified by their depths. For this purpose we denote the potential energy per particle by

$$\phi = \Phi / N. \quad (2.6)$$

In the large-system limit for two- and three-dimensional

systems, the density of substantially distinct minima whose depths (on a per-particle basis) equal ϕ can be asymptotically represented in the following way:

$$\exp[N\sigma(\phi)], \quad (2.7)$$

where the non-negative function σ is independent of N . Strictly speaking, $\sigma(\phi)$ can only be defined over the interval

$$\phi_l \leq \phi \leq \phi_u, \quad (2.8)$$

where ϕ_l corresponds to the absolute Φ minimum (normally a crystalline state), and ϕ_u corresponds to the "worst" particle packing (the highest-lying relative minimum).

In a general but quite precise sense, dynamical motion of the configuration point \mathbf{R} within a single basin can be viewed as vibration about that basin's minimum. Such vibrations can of course be interrupted by transitions between neighboring basins, though the lower the temperature the less frequent will such transitions be. For those basins whose minima have depths within a narrow range around ϕ , it is natural to define a mean vibrational free energy per particle $f(\beta, \phi)$ by means of the expression

$$\exp[-N\beta f(\beta, \phi)] = \langle \int_{B_a} d\mathbf{R} \exp[-\beta\Delta_a\Phi(\mathbf{R})] \rangle_{\phi}. \quad (2.9)$$

Here each integral spans the interior of a single basin, and the average $\langle \dots \rangle_{\phi}$ includes all basins lying within a narrow depth range around ϕ . $\Delta_a\Phi$ is the potential energy within basin B_a , measured from its value Φ_a at the minimum

$$\Delta_a\Phi(\mathbf{R}) = \Phi(\mathbf{R}) - \Phi_a. \quad (2.10)$$

The definitions given for $\sigma(\phi)$ and $f(\beta, \phi)$ permit the canonical partition function Z to be rewritten in the following way [10-13]:

$$\exp(-\beta F) = K^{-1} \int d\phi \exp\{N[\sigma(\phi) - \beta\phi - \beta f(\beta, \phi)]\}, \quad (2.11)$$

substantially without approximation in the large system limit. Moreover, that same limit asymptotically permits replacement of the ϕ integral by the maximum value of the integrand, located say at $\phi = \phi_m$. Consequently we have

$$\beta F / N \sim (\ln K) / N + \beta\phi_m + \beta f(\beta, \phi_m) - \sigma(\phi_m). \quad (2.12)$$

The temperature and density dependent quantity ϕ_m satisfies the extremum condition

$$\sigma(\phi_m) - \beta\phi_m - \beta f(\beta, \phi_m) = \text{maximum}; \quad (2.13)$$

it is the most probable basin depth to be encountered by the system under the prevailing conditions. If temperature is very low (large β), ϕ_m will be at or just above ϕ_l and will correspond to mechanically stable particle packings that exhibit virtually perfect crystallinity. Above the melting temperature, by contrast, ϕ_m will be substantially higher, and will correspond to basins that dominate the

liquid phase, and whose minima amount to amorphous particle packings [12,13]. Thermodynamic phase transitions are associated with singularities in ϕ_m as a function of temperature and density.

III. ILLUSTRATIVE EXAMPLE

In order to help clarify the general remarks of Sec. II, as well as to pave the way for the metastable-state modifications to follow, it is prudent to examine a specific simple model. The case chosen for illustration is the one-species, one-dimensional Lennard-Jones (LJ) system. Let N be the number of Lennard-Jones particles, and suppose they are confined to a "box" (line segment) of length L . Periodic boundary conditions will be imposed, so the potential energy Φ has the form (in reduced units)

$$\Phi(x_1, \dots, x_N) = \sum_{\mu=-\infty}^{+\infty} \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(x_i - x_j + \mu L), \quad (3.1)$$

$$v(y) = 4(y^{-12} - y^{-6}).$$

Here particle i is located at position x_i in the primary cell, and the summation over integer index μ accounts for all periodic images of the primary cell. For the large system limit that is of interest here, the short-range character of v implies that only $\mu = -1, 0, +1$ need to be considered, i.e., only interactions of particles in the primary cell among themselves and with the immediately flanking images are significant.

Provided that the system length is restricted to the range

$$0 < L/N \leq \ell_0 \cong 1.1193, \quad (3.2)$$

Φ in Eq. (3.1) possesses only a single type of minimum, namely, the periodic arrangement of particles that stretches across the primary cell and seamlessly connects to images. Permutations of particles along the line in this periodic array correspond to nominally different, but energetically identical, minima. On account of the free translation that is permitted by the periodic boundary conditions, the number of such equivalent minima is $(N-1)!$.

The binding energy Φ/N for periodic arrays reaches its lowest value at $L/N = \ell_0$,

$$\Phi/N = \phi_0 = -1.03473227 \dots (L/N = \ell_0). \quad (3.3)$$

Reduction of L below this point causes ϕ to rise monotonically as the repulsive cores of neighboring particles are forced together. The length per-particle ℓ_0 produces a stress-free periodic chain.

Expanding the system at least modestly beyond this point ℓ_0 continues to maintain the periodic array as a legitimate potential energy local minimum. However, the stretching causes the chain of particles to go into tension, and the binding energy rises. But these $(N-1)!$ minima are then joined by $N!$ others that amount to broken chains with two free ends. Since these latter are stress-free, they display internal spacing ℓ_0 and binding energy per particle ϕ_0 . Consequently the broken chains yield absolute minima, while the unbroken periodic arrays yield

higher-lying relative minima. It should be noted in passing that fragmentation into two or more shorter chains cannot produce further minima; although they are weak at large separations, particle attractions between separate "clusters" would cause reaggregation under the gradient descent mapping.

Stretched periodic chains lose their mechanical stability (i.e., cease to be relative minima) when L/N increases to

$$\ell_1 \cong 1.240945. \quad (3.4)$$

At this breaking point the chains develop a long-wavelength instability (in phonon language, a $k=0+$ soft mode develops an imaginary frequency) that could lead to separation at any one of the N nearest-neighbor contacts. The potential energy and its rate of change at this instability point are given by

$$\begin{aligned} \phi_1 &\cong -0.814315, \\ [d\phi/d(L/N)]_{\ell_1} &\cong 2.48668. \end{aligned} \quad (3.5)$$

When $L/N > \ell_1$, only the broken-chain minima exist. Figure 1 indicates how the depths of the minima vary with system length.

In this one-species case with structureless particles, it is sensible only to use the unit matrix for the weighting \mathbf{w} in Eq. (2.5). The mapping that defines basins for each minimum consequently is the strict steepest-descent connection on the Φ hypersurface. In principle, the vibrational free energies follow as specified in Sec. II, except that averaging over basins is not necessary since at most

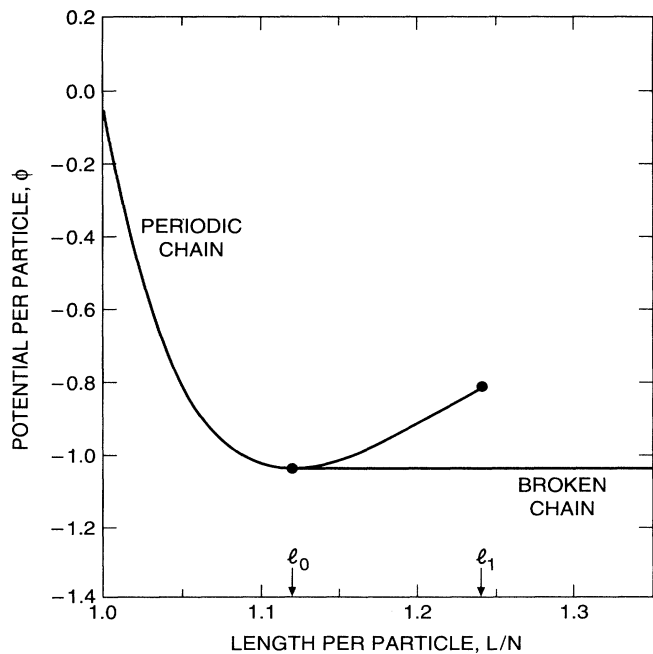


FIG. 1. Depths of potential energy minima versus system length for the one-component, one-dimensional Lennard-Jones system.

two distinct ϕ values are possible. Let f_p and f_b denote the vibrational free energies, respectively, for the periodic and the broken chains. Then the canonical partition function adopts one of three forms depending on the system length

$$Z(L < N\ell_0) \sim (KN)^{-1} \exp\{-N\beta[\phi_p(L/N) + f_p(\beta, L/N)]\}; \quad (3.6a)$$

$$Z(N\ell_0 < L < N\ell_1) \sim (KN)^{-1} \exp\{-N\beta[\phi_p(L/N) + f_p(\beta, L/N)]\} + K^{-1} \exp\{-N\beta[\phi_0 + f_b(\beta, L/N)]\}; \quad (3.6b)$$

$$Z(N\ell_1 < L) \sim K^{-1} \exp\{-N\beta[\phi_0 + f_b(\beta, L/N)]\}. \quad (3.6c)$$

In spite of the format changes at ℓ_0 and ℓ_1 , the partition function at positive temperature remains nonsingular at these points since the one-dimensional LJ system has no phase transitions. The vibrational free energies behave as functions of L in just such a way as to compensate for the changes. In particular, the $(N-1)!$ periodic-array basins vanish in size as L/N approaches the stretching limit ℓ_1 .

Throughout the intermediate density range limited by ℓ_0 and ℓ_1 , the broken-chain term in Eq. (3.6b) essentially completely dominates the canonical partition function and all thermodynamic properties that would be derived therefrom. But it is clear that the recessive periodic-array term in Eq. (3.6b) offers a natural definition of a stretched metastable state applicable to this intermediate regime. In other words, we simply project out of consideration all broken-chain minima and their basins, and extend the one-term expression in Eq. (3.6a) up to ℓ_1 . At sufficiently low, but positive, temperature this will yield metastable states in tension (negative pressure). It must be emphasized that ℓ_1 amounts to an absolute endpoint of the metastable state specifically for this one-dimensional LJ system; a different choice of interaction potential would in general lead to a different absolute endpoint (but still with soft-mode, vanishing-basin character).

Although the simple form (3.6a) serves for definition of the metastable extension, it does so at a price. Free energy is strictly and inevitably singular at ℓ_0 with this protocol. The singularity is associated with the sudden change in shape of the retained basins, due to first appearance of the rejected broken-chain basins at ℓ_0 and their subsequent growth as L/N increases. This in turn confers singular behavior on f_p . However the effects of this singularity should be minor, especially at low temperature where vibrational excursions from basin minima should seldom reach the basin boundaries.

While the one-dimensional LJ system is in the intermediate density range, $\ell_0 < L/N < \ell_1$, each of the periodic-array basins will have N transition states (saddle points) in their boundaries; these correspond to the N breakage sites. The lifetime of the stretched metastable state reflects the rate at which the dynamical

configuration can reach and pass through the neighborhood of any one of those saddle points. As L/N increases toward ℓ_1 , the elevation of the saddle points above the basin minimum declines to zero, implying a shorter and shorter lifetime at any positive temperature.

IV. BASIN RESTRICTION

The potential energy minima, or inherent structures, are far more diverse for two- and three-dimensional systems than for the elementary one-dimensional LJ example of Sec. III. In particular, these more numerous kinds of minima possess depths distributed over a continuous range of the intensive parameter ϕ , permitting definition of the enumeration quantity $\sigma(\phi)$, Eq. (2.7). By contrast, at most two distinct ϕ values appear in the one-dimensional LJ system, rendering definition of $\sigma(\phi)$ via (2.7) strictly inapplicable.

The major benefit of the one-dimensional LJ example is that it legitimizes a projection procedure for stretched or superheated metastable states that only retains void-free inherent structures and their basins in the partition function. The voids to be rejected amount to cracks or cavitation sites in the stretching case, and to nascent boiling bubbles in the case of superheating. As has been pointed out before [3,5] there are really just variants of the same general metastability scenario, where the vapor pressure exceeds the ambient pressure in the liquid.

To be precise, we shall eliminate all basins for inherent structures with the property that a radius- r_0 sphere could be inserted somewhere without overlapping the position of any atomic nucleus. In any specific application it is obviously necessary to fix r_0 , but for the moment we can suppose that the test sphere has about the volume of 20 to 50 close-packed particles. Imposition of this condition should have the effect of eliminating "weak spots" in the dense liquid medium that could act as nucleation sites for cracks or bubbles. At the same time this should have virtually no influence on the stable liquid, since spontaneous appearance of empty cavities of the size considered should be a very rare occurrence.

Even after imposing the above no-void constraint, the surviving inherent structures should still have a depth distribution that asymptotically conforms to the earlier format (2.7), now to be expressed

$$\exp[N\sigma_s(\phi)]. \quad (4.1)$$

However the removal of void-containing inherent structures (with results denoted by subscripts) implies that

$$\sigma_s(\phi) \leq \sigma(\phi) \quad (4.2)$$

over the ϕ range for which both functions are defined. A vibrational free energy $f_s(\beta, \phi)$ can next be defined in exact analogy to the prior Eq. (2.9), but where the basin averaging involves only void-free inherent structures.

$$\exp[-N\beta f_s(\beta, \phi)] = \left\langle \int_{B_a} d\mathbf{R} \exp[-\beta\Delta_a \Phi(\mathbf{R})] \right\rangle_{s, \phi}. \quad (4.3)$$

It then follows that the system free energy can be calcu-

lated by the same procedure as before to yield

$$\beta F_s / N \sim (\ln K) / N + \beta \phi_{ms} + \beta f_s(\beta, \phi_{ms}) - \sigma_s(\phi_{ms}), \quad (4.4)$$

where in this metastable extension ϕ_{ms} satisfies the modified extremum condition analogous to Eq. (2.13):

$$\sigma_s(\phi_{ms}) - \beta \phi_{ms} - \beta f_s(\beta, \phi_{ms}) = \text{maximum}. \quad (4.5)$$

The pressure in the resulting liquid, whether in a stable or a metastable condition, follows from the thermodynamic relation (2.4), with F_s replacing F .

Figure 2 symbolically shows a portion of the p - V plane for a typical substance, indicating the liquid-vapor coexistence curve from the triple point (TP), through the critical point (CP), and into the dilute vapor regime. The figure also indicates two thermodynamic paths crossing the liquid branch of the coexistence curve at a common point (B). One of these (ABC) corresponds to isothermal expansion of the initially stable liquid to a pressure that is less than the equilibrium vapor pressure at the given temperature, and into the negative-pressure stretched-liquid regime. The other (DBE) corresponds to isobaric heating past the normal boiling temperature for the given pressure. The dotted extensions are possible because imposition of the void-free constraint on inherent structures frustrates the normal equilibrium phase change to vapor in both cases.

The theoretical strategy just described has a close parallel in the analysis of liquid supercooling [14–16]. In that case, the relevant constraint projects out of consideration all inherent structures that contain crystallites (nucleation sites) that are compact and contain roughly 20–50 particles. The resulting enumeration function σ_a and vibrational free energy per-particle f_a for the surviving amorphous inherent structures (denoted by subscript a) form the basis for study of supercooled liquids and glasses [14–16]. Both the void-free and crystallite-free constraints in principle require the use of pattern recog-

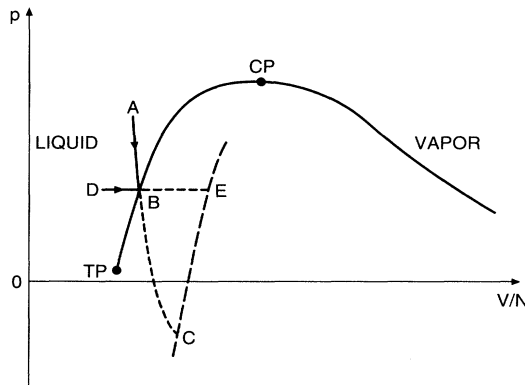


FIG. 2. Metastable extensions, into the liquid-vapor coexistence region of the pressure-volume plane, of two liquid-state curves. Trajectory ABC corresponds to isothermal expansion, and as shown may enter the negative-pressure regime; trajectory DBE corresponds to isobaric heating. Termination points C and E represent the related sudden processes of cavitation and of explosive vaporization, respectively.

nizing capacity to sift through all inherent structures and to carry out the respective rejections. It is even possible to apply both constraints (projections) at once to produce $\sigma_{as}(\phi)$, $f_{as}(\beta, \phi)$, and an equation of state for a liquid that frustrates both vaporization and crystallization, while substantially reproducing the equilibrium equation of state where the liquid is thermodynamically stable. This permits description of supercooled liquids in tension.

Termination points (C and E) have been indicated for the two metastable extensions in Fig. 2. The no-void constraint implies that qualifying inherent structures would develop instabilities, analogous to that of the one-dimensional LJ system, as the volume per particle increases. In fact there must be some characteristic maximum volume per-particle V_0/N which is consistent with the existence of any inherent structure free of r_0 -radius voids. The termination points for the metastable extensions could not be to the right of this location in Fig. 2. It should be emphasized that V_0 is a monotonically increasing function of r_0 , and in fact in the $r_0 \rightarrow \infty$ limit V_0/N should diverge, owing to the possibility of very tenuous “aerogel” structures (low-density networks).

An experimentally significant termination criterion should not be based on V_0/N , however. Rather, it seems most natural to base it on the lifetime of the metastable state. Just as in the case of the glass transition for supercooled liquids, the time scale of observation should at least be weakly relevant [19]. Requiring, for example, that a 1 cm^3 sample have a mean lifetime of 10^{-3} s would identify a termination point V_1/N ; increasing the mean lifetime to 10^3 s would displace the termination point to V_2/N , where

$$V_2 < V_1 < V_0. \quad (4.6)$$

However the strong dependence of nucleation rates on externally controllable parameters [20] suggests that V_2 is only slightly less than V_1 .

Locating these termination points for any given many-particle model is not a simple task. One should expect it to require detailed computer study of the participating inherent structures, and of the dynamics that controls interbasin transitions between allowed and disallowed (void-containing) basins.

V. DISCUSSION

The void-free constraint on inherent structures that is needed for superheated and stretched liquid metastable states is only one of a wider class of configurational constraints that is useful for the general study of metastability. Section IV also discusses the crystallite-free constraint that is relevant for supercooled liquids. Analogous constraints can be formulated for metastability encountered in binary liquid phase separation, in liquid crystal transitions, in solid-solid phase transitions, and in surface transitions. Each example in principle requires implementation of a pattern recognition capacity to carry out the required projections on the full inherent structure set for the system.

In connection with the metastable states of liquid wa-

ter, it has been suggested that the supercooling limits and the superheating or stretching limits together form a common smooth-curve locus in the temperature-pressure plane [21]. The present approach seems to require at least a minor revision of this stability-limit conjecture. The two relevant constraints, respectively eliminating voids and crystallites, are logically independent and separately generate their own stability-limit curves. While these curves may indeed intersect in the negative-pressure regime, they would be expected to do so at a cusp (slope discontinuity), and would not together yield a single smooth stability-limit curve.

Stability limits for superheating or stretching liquids are often identified with a spinodal line at which the isothermal compressibility diverges. Approximate equations of state of the mean field, or van der Waals, type automatically supply such spinodal lines which, in fact, pass through the liquid-vapor critical point [3]. The statistical mechanical formalism presented in this paper does not invoke a mean-field approximation, so it is natural to ask if the metastable-state isotherms it produces terminate at stability limits with infinite, or at least very large, iso-

thermal compressibilities. The one-dimensional LJ example examined in Sec. III suggests that the answer is affirmative, since a long-wavelength phonon instability is involved. Recalling that generally a diverging compressibility is associated with diverging long-wavelength density fluctuations [22], we can reasonably expect a form of soft-mode behavior to develop in three dimensions as well. It should arise in part from vibrational modes that develop vanishingly small frequencies, but also from a statistical tendency for sub- r_0 -radius cavities in the participating allowed inherent structures to be found in spatially aggregated arrangements.

A challenging research area for computer simulation becomes clear as a result of these considerations. It is the numerical study, for specific models such as the three-dimensional LJ system, water, or the alkanes, of the void distribution in inherent structures at the equilibrium phase boundary, and at least slightly into the superheated or stretched metastable regime. This could provide useful guidance on the precise choice of r_0 , and on the validity of the diverging-compressibility conjecture for the stability limit.

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