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Statistical mechanics of fluids under internal constraints: Rigorous results for the one-dimensional hard rod fluid

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The rigorous statistical mechanics of metastability requires the imposition of internal constraints that prevent access to regions of phase space corresponding to inhomogeneous states. We derive exactly the Helmholtz energy and equation of state of the one-dimensional hard rod fluid under the influence of an internal constraint that places an upper bound on the distance between nearest-neighbor rods. This type of constraint is relevant to the suppression of boiling in a superheated liquid. We determine the effects of this constraint upon the thermophysical properties and internal structure of the hard rod fluid. By adding an infinitely weak and infinitely long-ranged attractive potential to the hard core, the fluid exhibits a first-order vapor-liquid transition. We determine exactly the equation of state of the one-dimensional superheated liquid and show that it exhibits metastable phase equilibrium. We also derive statistical mechanical relations for the equation of state of a fluid under the action of arbitrary constraints, and show the connection between the statistical mechanics of constrained and unconstrained ensembles. [S1063-651X(98)06804-4]

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I. INTRODUCTION

If a liquid is heated above its boiling temperature at a given pressure, while remaining homogeneous, it is said to be superheated. Likewise, a liquid is said to be supercooled if, for example, it is cooled isobarically below its freezing point without crystallizing. These are examples of metastable liquids, which play an important role in both nature and technology. Examples include sap ascent in trees under tension [1], supercooled water in clouds [2], mineral inclusions [3], phase separation in polymer mixtures [4], explosive boiling [5], cavitation in turbulent flow [5,6], and the initial stage of sonoluminescence experiments involving cavitation, owing to ultrasonic excitation [7]. In many of these cases, knowledge of the thermophysical properties of a metastable system is important. For example, the prevention of vapor explosions [8–10] requires an accurate knowledge of the equation of state of superheated liquids and their mixtures.

Despite the importance and ubiquity of metastability, fundamental questions remain concerning the development of a rigorous, microscopically based understanding of this phenomenon [3]. The application of conventional statistical mechanics to the prediction of the properties of metastable systems has an important limitation: a metastable state is never a condition of maximum entropy for an isolated system, and hence it is never the dominant (and, in the thermodynamic limit, sole) contribution to the partition function. In the thermodynamic limit, a rigorous evaluation of the partition function within the coexistence region would yield no information on metastable states [11]. In fact, the partition function, if evaluated inside the coexistence region, would produce an inhomogeneous state (e.g., equilibrium mixture of liquid and vapor phases). An exception to this statement is given by the idealized system of Refs. [12,13], which has an infinitely long-ranged attractive potential.

In commonly used approximate theories, metastable states appear exclusively as a result of the mathematical approximations used to ‘‘solve’’ the partition function. For example, in applying the maximum term method [11], one generally seeks the homogeneous (single) density that maximizes the generic term in the partition function. If the artificial constraint of strict uniformity were removed, the maximum term method, which is exact in the thermodynamic limit, would yield only an equilibrium, inhomogeneous mixture of two or more phases. Metastable and unstable states are thus obtained in mean-field treatments, such as the Bragg-Williams or van der Waals theories [11], by forcing the density to be strictly uniform even inside the coexistence region.

Are there, therefore, rigorous ways of calculating the properties of a metastable system? To answer this question, we seek guidance from experiments. In the laboratory, the way to study a metastable system is to constrain it so as to make its lifetime much longer than the observation time. One technique for accomplishing this consists of creating an emulsion of small droplets of a liquid in a second, immiscible host liquid. This technique is commonly applied to study both supercooled and superheated liquids [14,15]. The sample liquid is carefully purified to remove suspended or dissolved impurities that can trigger a phase transition. Subdivision and purification will thus cause the number of droplets to be large compared to the number of residual impurities. Therefore, a large fraction of the droplets can be maintained in metastable equilibrium. Furthermore, the homogeneous nucleation rate is proportional to the sample's volume. Hence subdivision again facilitates extensive penetration into the coexistence region. From this example we conclude that a metastable system can be studied so long as embryos of a new phase do not have enough time to form in the course of an experiment. Therefore, in order to calculate the properties of such a system rigorously, we must constrain

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the evaluation of the partition function so as to limit the exploration of phase space to regions in which configurations containing large enough nuclei of stable phases are absent. Generalizing, we say that the rigorous statistical mechanics of metastability is the statistical mechanics of constrained systems [16]. Note that this rigorous, microscopic constraint allows for density fluctuations, and is very different from the assumption of strict uniformity inside the coexistence region.

Experimental constraints are kinetic, and they are aimed at avoiding nucleation. In statistical mechanics, the constraints are time independent, and they consist of blocking access permanently to certain regions of phase space. In so doing, the system is contained within the appropriate one-phase region of its phase space, despite being inside the coexistence region of its phase diagram. However, the rigorous evaluation of the partition function over limited regions of phase space (i.e., the rigorous imposition of a constraint) is impossible except for highly idealized systems (e.g., Refs. [12,17]). Computer simulations, therefore, can play a very useful role in the rigorous study of metastability. This is because constraints are easily imposed in simulations. This application of molecular simulations has only started to receive the attention it merits (e.g., Refs. [18–21]). In these references, the analytical constraints investigated in this work are studied computationally, by imposing limits on the size of voids that are allowed to form in a superheated liquid. In particular, Ref. [20] discussed a one-dimensional system, albeit one in which attractions have a finite range.

The analytical study of simple systems, however, is not without benefits. This is especially true when exact solutions are possible, which allow one to investigate, without approximations, the effects of constraints on the thermodynamics and structure of a model system. In this paper, we analyze one such simple system, the one-dimensional hard rod fluid (see, e.g., Ref. [22]). In particular, we determine exactly the effect of a particular constraint on its equilibrium properties. The one-dimensional hard rod fluid, however, does not exhibit a first-order phase transition. Therefore, its usefulness in understanding the properties of metastable liquids is limited. We are interested in analyzing the properties of a system that is inside the coexistence region and is prevented from phase separating (remains homogeneous) by application of a suitable microscopic constraint. Upon addition of an infinitely weak and infinitely long-ranged attractive tail, the one-dimensional hard rod fluid exhibits a first-order phase transition between a liquid phase and a vapor phase [23]. Therefore, we also derive the equation of state of a hard rod fluid with an infinitely weak and infinitely long-ranged attractive potential, and determine exactly the ways in which the constraint influences the equilibrium properties of the one-dimensional superheated liquid.

The paper is organized as follows: in Sec. II we derive rigorous statistical mechanical relations for the equation of state and chemical potential of a fluid under the action of a constraint. We find that the conventional, unconstrained statistical mechanical formalism is in fact a subset of the statistical mechanics of constrained ensembles. In Sec. III we obtain the Helmholtz energy and equation of state of the one-dimensional constrained hard rod fluid in which a strict upper bound is placed on the distance between nearest neighbors. We discuss the effect of the constraint on the equilibrium properties and internal structure of the hard rod fluid. In Sec. IV, we determine the equation of state of the one-dimensional hard rod fluid with an infinitely weak and infinitely long-ranged attractive potential. We discuss the resulting phase equilibrium properties and metastable states predicted by the model. In Sec. V we summarize and suggest directions for future work.

II. RIGOROUS RELATIONS FOR INTERNALLY CONSTRAINED ENSEMBLES

In this section we derive rigorous statistical mechanical expressions for the equilibrium properties of constrained systems, some of which were previously discussed in Ref. [21]. These results are applicable not only to metastable systems (which are prevented from phase separating) but to any system under the action of a constraint. In so doing, we derive equations that are in fact more general than the results of conventional, unconstrained statistical mechanics, to which they reduce in the limit of arbitrarily weak constraints.

In order to reformulate the canonical ensemble to obtain metastable states, one must employ a mathematical device to trap the system in the appropriate region of phase space. The activation barrier that must be surmounted before a metastable state can phase separate corresponds to a bimodality of the canonical probability distribution. Within the coexistence region, this distribution is composed of two virtually distinct and nonoverlapping regions of phase space. The ‘‘bottleneck’’ region between them, corresponding to the appearance of a critical embryo within the metastable fluid, has a low probability of occupation, at least for small degrees of metastability. Thus the reformulation of the canonical ensemble requires the closing of the bottleneck via the imposition of a configurational constraint, trapping the system within the desired region of phase space. This constraint can be attained in principle by imposing an additional intermolecular or external potential [24] on the system. This potential W_N should vanish in the appropriate one-phase region of phase space, but becomes arbitrarily large in that part of phase space that corresponds to the existence of two or more phases in equilibrium.

The choice of W_N will be determined by the metastable phase of interest. In a supercooled vapor, W_N must become large if clusters beyond a given size develop. Likewise, W_N should serve to frustrate the formation of large voids or cavities within a superheated liquid [19,21]. Supercooled liquids must be free of large crystallites, so W_N must prevent their formation.

Irrespective of the form of W_N, one can write the partition function of a constrained system of N particles, in a volume V (or its d-dimensional generalization), and at a temperature T as follows [25]:

$$Q(N,V,T)=\frac{Z(N,V,T)}{N!\Lambda^{dN}}, \tag{1}$$

where Λ is the de Broglie wavelength and $Z(N,V,T)$ is the configurational integral given by

$$Z(N,V,T)=\int\cdots\int d\mathbf{r}_1\ldots d\mathbf{r}_N e^{-\beta\Phi_N}e^{-\beta W_N} \tag{2}$$

in which $\beta = 1/kT$, k is Boltzmann's constant, and the integral over $d\mathbf{r}_i$ spans the system volume. Φ_N is the instantaneous configurational energy and is a function of all the N particle coordinates. Although the discussion is limited to atomic systems for simplicity, the generalization to molecular systems is straightforward.

Noting that the Helmholtz energy A is equal to [25]

$$A(N,V,T) = -kT \ln Q(N,V,T) \tag{3}$$

and

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ln Z(N,V,T)}{\partial V}\right)_{T,N}, \tag{4}$$

then the pressure P is given by [21]

$$\frac{P}{kT} = \rho - \frac{\rho^2}{2dkT}\int_0^\infty r\phi'(r)g(r)d\mathbf{r} + \beta\rho^2\left\langle\left(\frac{\partial W_N/N}{\partial\rho}\right)_{T,N}\right\rangle, \tag{5}$$

where $\rho = N/V$, $g(r)$ is the radial distribution function of the constrained system, and $\langle\cdots\rangle$ denotes ensemble averaging *in the constrained system*. Equation (5) is exact for pairwise additive interactions,

$$\Phi_N = \sum_{1\leq i<j\leq N} \phi(r_{ij}), \tag{6}$$

where $\phi(r_{ij})$ is the pair potential energy between atoms i and j. Equation (5) is obtained in the usual way [25] by rescaling the particle coordinates

$$\mathbf{s} = V^{-1/d}\mathbf{r}. \tag{7}$$

The integrations in Eq. (2) then span a unit cube in $\mathbf{s}$ space, thereby allowing the volume derivatives required by Eq. (4) to be carried out by the chain rule. The result is given by Eq. (5), in which [21]

$$\left\langle\left(\frac{\partial W_N/N}{\partial\rho}\right)_{T,N}\right\rangle = \frac{\int_0^1 d\mathbf{s}_1\cdots\int_0^1 d\mathbf{s}_N e^{-\beta(\Phi_N+W_N)}\frac{\partial}{\partial V}W_N(V^{1/d}\mathbf{s}_1\ldots V^{1/d}\mathbf{s}_N)}{\int_0^1 d\mathbf{s}_1\cdots\int_0^1 d\mathbf{s}_N e^{-\beta(\Phi_N+W_N)}}. \tag{8}$$

The pressure of an unconstrained system would include only the first two terms in Eq. (5), but $g(r)$ would be evaluated with $W_N = 0$.

Equation (5) shows that the configurational constraint makes an additional contribution to the system pressure that is not present in unconstrained systems. Interestingly, the second, virial term in Eq. (5) is not sufficient to determine the pressure of the constrained system. This is so even if the virial is dependent upon the structure of the constrained system through the radial distribution function $g(r)$, which is altered by the addition of W_N. Consequently, there is an additional microscopic contribution to the system pressure, solely from the addition of a constraint, which is not completely accounted for by the virial.

Let us rewrite Eq. (5) as follows:

$$P = P_{\text{ideal}} + P_{\text{virial}} + P_{\text{constraint}}, \tag{9}$$

in which $P_{\text{ideal}} = \rho kT$,

$$P_{\text{virial}} = -\frac{\rho^2}{2d}\int_0^\infty r\phi'(r)g(r)d\mathbf{r}, \tag{10}$$

and

$$P_{\text{constraint}} = \rho^2\left\langle\left(\frac{\partial W_N/N}{\partial\rho}\right)_{T,N}\right\rangle. \tag{11}$$

The magnitude and sign of $P_{\text{constraint}}$ is dependent upon the form of W_N. We will see in the following sections that when the distance between nearest neighbors in a one-dimensional hard rod fluid is prevented from exceeding some specified value, $P_{\text{constraint}} \leq 0$, and its magnitude can become quite large for certain densities. Even though the internal structure of this constrained hard rod fluid is dramatically altered, P_{virial} is unable to account properly for the system pressure. At certain densities, $P_{\text{constraint}}$ is the dominant contribution to the pressure and, in fact, the total pressure becomes negative. Within a system composed of purely repulsive interactions, the constraint manifests itself as an additional long-ranged attraction, allowing the hard rod fluid to exist under tension.

The pressure is not the only thermodynamic variable which contains a term that is solely dependent upon the constraint. Due to the additional Boltzmann factor associated with W_N in the partition function, one realizes that other statistical mechanical expressions must be modified to account for contributions from the constraint. For example, the chemical potential μ of an unconstrained system is given by [11]

$$\mu = kT \ln \rho\Lambda^d + \rho\int_0^1\int_0^\infty \phi(r)g(r;\zeta)d\mathbf{r}\, d\zeta, \tag{12}$$

where $\phi(r)$ is the intermolecular potential between two particles separated by a distance r, and $\zeta(0\leq\zeta\leq 1)$ is a coupling parameter. This parameter ζ simply scales the strength of interaction between a given particle and all other particles in the fluid by a factor ζ. In terms of this coupling parameter, then,

$$\Phi_N=\sum_{j=2}^{N}\zeta\phi(r_{1j})+\sum_{2\leqslant i<j\leqslant N}\phi(r_{ij}) \tag{13}$$

where ζ alters the magnitude of the interaction between particle 1 and the remaining $N-1$ particles. Note that particle 1 is completely removed from the system when $\zeta=0$, and is completely coupled to the remaining $N-1$ particles when $\zeta=1$. For a constrained system, the corresponding expression for the chemical potential becomes

$$\mu=kT\ \ln\rho\Lambda^d+\rho\int_0^1\int_0^\infty\phi(r)g(r;\zeta)d\mathbf{r}\ d\zeta+\int_0^1\left\langle\frac{\partial W_N}{\partial\zeta}\right\rangle d\zeta. \tag{14}$$

Thus, as was the case with the pressure, constraints introduce new terms, in addition to imposing the need to evaluate existing terms in the constrained ensemble.

Carrying out the usual manipulations [25], but now in the presence of a constraint, it follows that the isothermal compressibility κ_T, and the configurational energy U, are formally identical to the corresponding unconstrained expressions, except that $g(r)$ is to be evaluated in the constrained system:

$$\rho kT\kappa_T=1+\rho\int_0^\infty[g(r)-1]d\mathbf{r}, \tag{15}$$

$$\frac{U}{N}=\frac{\rho}{2}\int_0^\infty\phi(r)g(r)d\mathbf{r}. \tag{16}$$

Equation (16) is valid for pairwise additive interactions.

III. ONE-DIMENSIONAL CONSTRAINED HARD ROD FLUID

A. Nature of the constraint

The motivation behind studying the one-dimensional hard rod fluid is the possibility of solving the equation of state of a constrained system exactly. Since we are ultimately interested in studying the properties of a metastable system, in particular a superheated liquid, we require a constraint that will prevent the liquid from boiling. This can be implemented by preventing the liquid from sampling configurations that contain large voids. For a one-dimensional fluid, this is realized by placing a strict upper bound on the distance allowed between nearest neighbors.

Elkoshi, Reiss, and Hammerich [17] studied the effect of a constraint on the properties of the one-dimensional hard rod fluid. These authors analyzed the properties of the hard rod fluid in which the concentration of holes was held fixed, where the size of a ‘‘hole’’ was defined as the number of additional hard rods which could be placed between nearest neighbors without overlap and without disturbing the original configuration. By limiting the total size of all holes allowed to form, their ‘‘internally constrained’’ ensemble exhibited dramatic structural changes and was able to exist under tension (i.e., negative pressure). In contrast, the constraint used in this work is better suited to study systems which are metastable with respect to the formation of a new phase. Our constraint is more restrictive than that of Ref. [17] since we are limiting the range of distances between nearest neighbors, and should prevent the one-dimensional liquid from boiling. The constraint used in Ref. [17] fixes the mean distance between neighbors, or the concentration of holes, and hence is not severe enough to prevent cavitation.

The study of the effect of constraints on the properties of the hard rod fluid is not limited to the work of Ref. [17]. Davis and co-workers studied the statistical mechanics of the one-dimensional hard rod fluid under the influence of external fields [22], and used this as a model system to investigate the properties of fluids confined within narrow pores. The application of an external field is equivalent to the imposition of a constraint, but the nature of this constraint is quite different from that used in the present work (and in Ref. [17]). We impose an internal constraint (i.e., one that depends on the relative positions of the particles), as required by the physical situation we are interested in, metastability. The constraint studied by Davis and co-workers is external (e.g., confining walls), as befits the study of confined and inhomogeneous fluids.

For a one-dimensional hard rod fluid in which the ‘‘diameter’’ (i.e., length) of a particle is a, placing a limit on the distance between nearest neighbors corresponds to a constraint W_N that can be written as follows:

$$W_N=kT\sum_{i=1}^{N}h(x_{i+1}-x_i), \tag{17}$$

where x_i is particle i's distance from the origin and $x_{N+1}=x_1$ (i.e., periodic boundary conditions). The position of a particle, x_i, is that of its center of mass. For each configuration of hard rods, the particles are labeled from 1 to N according to their distance from the origin ($x_{i+1}\geqslant x_i$ for all i). The step function $h(x_{i+1}-x_i)$ is equal to

$$h(x_{i+1}-x_i)=\begin{cases}0, & x_{i+1}-x_i\leqslant la\\ \infty, & x_{i+1}-x_i>la,\end{cases} \tag{18}$$

where $l\geqslant 1$. Thus, the length between adjacent hard rods is limited to distances smaller or equal to la. In the limit $l\to\infty$, W_N vanishes, and the system becomes unconstrained.

B. Derivation of the Helmholtz energy

If we have N hard rods of length a in a ‘‘box’’ of length L, held at a temperature T, the Helmholtz energy A can be written as

$$A(N,L,T)=-kT\ \ln\frac{Z_N}{N!\Lambda^N}, \tag{19}$$

where Z_N is again the configurational integral [Eq. (2)] given by

$$Z_N=\int_0^L\cdots\int_0^L dx_1\ldots dx_N e^{-\beta\Phi_N}e^{-\beta W_N}, \tag{20}$$

in which Φ_N is the total potential energy and W_N is the constraint. Φ_N is given by the sum of two-body interactions,

$$\Phi_N=\sum_{1\leqslant i<j\leqslant N}\phi(x_i-x_j), \tag{21}$$

where the summation runs over all $N(N-1)/2$ pairs, and ϕ is the intermolecular potential between hard rods i and j,

$$\phi(x_i-x_j)=\begin{cases}\infty, & x_i-x_j<a\\ 0, & x_i-x_j\geqslant a.\end{cases} \tag{22}$$

The specific form of W_N and Φ_N suggests that we evaluate Z_N such that the particle labels are arranged in increasing order from the origin. Therefore, the configurational integral Z_N is simply $N!Z_N'$, where Z_N' is the configurational integral in which the particle coordinates are constrained to satisfy $0\leqslant x_1\leqslant x_2\leqslant\cdots\leqslant x_N$ [26]. This transformation is not possible in higher dimensions. Following the method outlined in Ref. [17], Z_N' can be evaluated if we discretize all the distances between adjacent particles in terms of a quantum u which will become zero as we pass to the continuum limit. u is chosen such that the number of quanta in the length a of a rod is simply an integer ω. Therefore, $a=\omega u$, and so the number of quanta in the length L is given by $\Gamma=L/u$.

In order to describe a configuration, it suffices to know the distance between each nearest-neighbor pair. In what follows we find it convenient to describe a configuration in less detail, by focusing on the frequency of occurrence of nearest-neighbor separations of a given magnitude but not on their location. We are interested, in other words, in the number of nearest-neighbor distances having a particular length, but not on the identities of the pairs that are so connected. In this spirit, let us denote by $g_\lambda u$ the number of intervals of length λ between adjacent particles in a given configuration, where λ is the number of quanta u between two particles. Thus g_λ is a linear density and u becomes a differential length. Due to the nature of the hard rod potential and the imposed constraint, λ is constrained to lie in the range $\omega\leqslant\lambda\leqslant l\omega$, where la is the maximum allowed distance between nearest neighbors [Eq. (17)]. Each configuration which contributes to Z_N' can be characterized by a unique set of numbers $g_\lambda u$. The number of distinct arrangements corresponding to a particular distribution of $g_\lambda u$ is given by

$$\Omega=\frac{N!}{\Pi_\lambda(g_\lambda u)!}, \tag{23}$$

where N in the numerator is simply the total number of spaces between the rods. However, any arbitrary choice of the numbers $g_\lambda u$ is not permissible. Since the total number of spaces between the rods is fixed, we must have

$$\sum_{\lambda=\omega}^{l\omega} g_\lambda u=N. \tag{24}$$

Likewise, since the total length must be conserved, we require

$$\sum_{\lambda=\omega}^{l\omega} \lambda(g_\lambda u)=\Gamma. \tag{25}$$

The Helmholtz energy now becomes

$$A(N,L,T;l)=-kT\ \ln\frac{u^N\Sigma'\Omega}{\Lambda^N}, \tag{26}$$

where A is now explicitly a function of l, and Σ' runs over all possible choices of the set of numbers $g_\lambda u$ satisfying Eqs. (24) and (25). The quantity u^N is a result of the evaluation of Z_N' in terms of the quantum u, where the integral is evaluated over the scaled coordinates, $x_i'=x_i/u$, in which

$$dx^N=u^N d(x')^N, \tag{27}$$

and $0\leqslant x'\leqslant\Gamma$.

Since we are in the thermodynamic limit, we can replace $\Sigma'\Omega$ by its maximum term Ω^*. A clarification is needed at this point. The maximum term method, in which the partition function is set equal to its largest contribution, is an approximation that becomes exact in the thermodynamic limit ($N\rightarrow\infty$; $L\rightarrow\infty$; $N/L=\text{const}$). The appearance of metastable states in approximate theories, such as the van der Waals equation, is not due to the use of the maximum term method for the evaluation of a partition function. Rather, it is the artificial imposition of a uniform density inside the coexistence region that causes the appearance of these metastable states. The unconstrained evaluation of the partition function inside the coexistence region would of course yield an inhomogeneous equilibrium state even when the maximum term method is used.

The equilibrium distribution of $g_\lambda u$, that gives us Ω^*, is therefore determined by maximizing Ω, with respect to $g_\lambda u$, subject to the constraints in Eqs. (24) and (25). Using the method of undetermined multipliers, we find that the set of numbers $g_\lambda u$ is given by

$$g_\lambda u=K\alpha^\lambda. \tag{28}$$

We notice from Eq. (28) that if $K\neq 0$, then $\alpha\leqslant 1$, otherwise $g_\lambda u$ would diverge as $\lambda\rightarrow\infty$ (i.e., $l\rightarrow\infty$). The parameters K and α are determined by substituting Eq. (28) into Eqs. (24) and (25). The sums are simple geometric series and are easily evaluated [27]. The results are as follows:

$$K=\frac{N(\alpha-1)}{\alpha^\omega(\alpha^{\omega(l-1)+1}-1)}, \tag{29}$$

$$\frac{\Gamma}{N\omega}=\frac{L}{Na}=\frac{1}{1-\alpha^{\omega(l-1)+1}}-\frac{l\alpha^{\omega(l-1)+1}}{1-\alpha^{\omega(l-1)+1}}+\frac{\alpha(1-\alpha^{\omega(l-1)})}{\omega(1-\alpha)(1-\alpha^{\omega(l-1)+1})}. \tag{30}$$

At this point, we pass to the continuum limit, allowing u to approach zero and ω to approach infinity. From Eq. (30) it can be shown that if α does not differ from unity by an infinitesimal amount, then L/Na will always be unity. Since we know that a system of hard rods can be constructed for $L/Na<1$, then, in the continuum limit, α must be of the following form:

$$\alpha=1-\epsilon\rightarrow 1, \tag{31}$$

where ϵ is an infinitesimal. Thus

$$\alpha^\omega=(1-\epsilon)^\omega=e^{-\xi}, \tag{32}$$

in which $\xi=\epsilon\omega$, and $e^{-\xi}$ is the limiting expression of α^{ω} when ω goes to infinity while ϵ is infinitesimal. It will be shown later [see Eq. (44)] that ξ is a dimensionless pressure.

Substituting the above relations into Eqs. (29) and (30), and letting $\omega\to\infty$ ($\xi=$const) yields the final results

$$K=\frac{N\epsilon e^{\xi}}{1-e^{-\xi(l-1)}}, \tag{33}$$

$$\rho a=\frac{Na}{L}=\frac{\xi(1-e^{-\xi(l-1)})}{1+\xi-(l\xi+1)e^{-\xi(l-1)}}, \tag{34}$$

where ρ is the number density and ξ is completely determined once ρ and l are specified ($\xi=\xi[\rho,l]$). For an unconstrained system ($l\to\infty$),

$$\xi=\frac{\rho a}{1-\rho a}. \tag{35}$$

Since the distance between hard rods must lie within a and la ($l\geqslant1$), the density is constrained to lie in the following range:

$$\frac{1}{l}\leqslant\rho a\leqslant1. \tag{36}$$

Equation (34) indicates that as $\xi\to\infty$, $\rho a\to1$; and as $\xi\to-\infty$, $\rho a\to1/l$. In the limit as $\xi\to0$, $\rho a\to2/(l+1)$.

If we define a variable x such that $x=\lambda u$, then Eq. (28) can be rewritten as

$$\frac{g(x)}{N}=\frac{\xi e^{-\xi(x-a)/a}}{a[1-e^{-\xi(l-1)}]}, \tag{37}$$

where x has units of length and is the distance between hard rods. Consequently, Eq. (37) is simply the probability density distribution function that nearest neighbors are separated by a distance x, since $g(x)/N$ has units of inverse length and

$$\int_a^{la}\frac{g(x)}{N}\,dx=\int_a^{la}\frac{\xi e^{-\xi(x-a)/a}}{a[1-e^{-\xi(l-1)}]}\,dx=1. \tag{38}$$

Finally, by substituting Eq. (28) into Eq. (26), we obtain the Helmholtz energy per particle $\tilde{a}$

$$\frac{A(N,L,T;l)}{NkT}=\frac{\tilde{a}(\rho,T;l)}{kT}=-\ln\frac{a[1-e^{-\xi(l-1)}]}{\xi\Lambda}-\frac{\xi(1-\rho a)}{\rho a}, \tag{39}$$

where $\tilde{a}$ is now explicitly a function of ρ, T and l. If $l\to\infty$, then the Helmholtz energy per particle becomes

$$\frac{\tilde{a}(\rho,T)}{kT}=-\ln\frac{1-\rho a}{\rho\Lambda}-1, \tag{40}$$

which equals the known result for an unconstrained hard rod fluid in one dimension [26]. Therefore, the difference in Helmholtz energy between a constrained system and an unconstrained system is

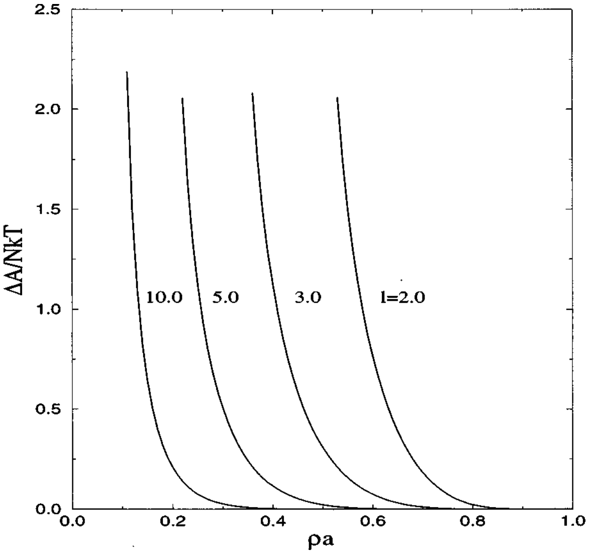

FIG. 1. Density dependence of the difference in the Helmholtz energy per particle between a constrained and unconstrained one-dimensional hard rod system, for various values of the severity of the constraint, l. ρ is the number of rods per unit length, a is the length of a rod, and the maximum allowed distance between centers of neighbor rods is la.

$$\frac{\Delta\tilde{a}}{kT}=\frac{\tilde{a}(\rho,T,l)}{kT}-\frac{\tilde{a}(\rho,T,l\to\infty)}{kT}=-\ln\frac{\rho a[1-e^{-\xi(l-1)}]}{(1-\rho a)\xi}-\frac{\xi(1-\rho a)}{\rho a}+1. \tag{41}$$

The imposition of the constraint causes an increase in the Helmholtz energy, since $\Delta\tilde{a}/kT\geqslant0$. Note that $\Delta\tilde{a}/kT\to0$ for $l\to\infty$ as expected. Typical plots of $\Delta\tilde{a}/kT$ for various values of l are shown in Fig. 1. We see that $\Delta\tilde{a}/kT\to0$ for $\rho\to1$, indicating that at the limit of close packing, where voids cannot form, the system is insensitive to the imposed constraint and behaves as if it were unconstrained. On the other hand, for $\rho a\to1/l$, $\Delta\tilde{a}/kT\to\infty$. At this limiting density, the system is stretched to the maximum limit allowed by the constraint.

C. Equation of state

The Helmholtz energy per particle, $\tilde{a}$, is an explicit function of T, ρ, and l. Noting that $\tilde{a}$ [Eq. (39)] is also expressed in terms of ξ, then its differential change can be written as

$$d\tilde{a}=\left(\frac{\partial\tilde{a}}{\partial T}\right)_{\rho,l,\xi}dT+\left[\left(\frac{\partial\tilde{a}}{\partial\rho}\right)_{T,l,\xi}+\left(\frac{\partial\tilde{a}}{\partial\xi}\right)_{T,l,\rho}\left(\frac{\partial\xi}{\partial\rho}\right)_{l}\right]d\rho+\left[\left(\frac{\partial\tilde{a}}{\partial l}\right)_{T,\rho,\xi}+\left(\frac{\partial\tilde{a}}{\partial\xi}\right)_{T,\rho,l}\left(\frac{\partial\xi}{\partial l}\right)_{\rho}\right]dl. \tag{42}$$

Using Eq. (39), it can be shown that $(\partial\tilde{a}/\partial\xi)_{T,\rho,l}=0$. Therefore, the system pressure P is equal to

$$\frac{P}{kT}=\rho^2\left(\frac{\partial\tilde{a}/kT}{\partial\rho}\right)_{T,l}=\rho^2\left(\frac{\partial\tilde{a}/kT}{\partial\rho}\right)_{T,l,\xi}, \tag{43}$$

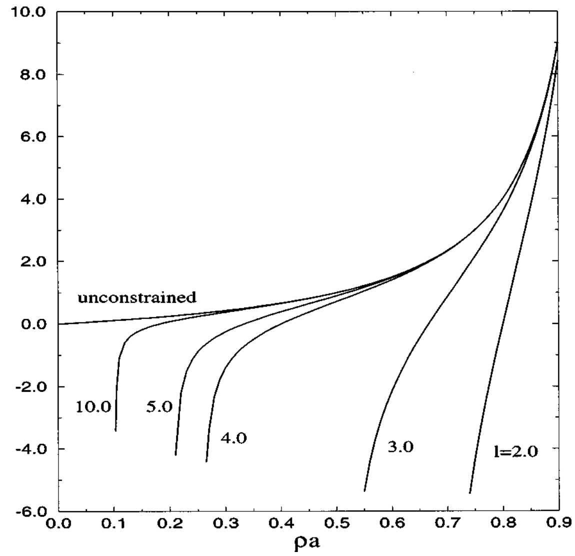

FIG. 2. Equation of state of the one-dimensional hard rod fluid for several choices of the severity of the constraint, l. Notation as per Fig. 1.

which, together with Eq. (39), yields

$$\frac{Pa}{kT}=\xi. \tag{44}$$

Thus we immediately see that the pressure of the constrained hard rod fluid can have values in the following range:

$$-\infty\leqslant\frac{Pa}{kT}\leqslant\infty. \tag{45}$$

The pressure is zero when $\xi=0$, corresponding to a density of $\rho a=2/(l+1)$ [see Eq. (34)]. For comparison, the pressure of the unconstrained system is

$$\frac{aP_{\text{unc}}}{kT}=\frac{\rho a}{1-\rho a}, \tag{46}$$

which is always greater than or equal to zero. As long as l is finite, there is a range of densities

$$\frac{1}{l}\leqslant\rho a<\frac{2}{l+1}, \tag{47}$$

in which the constrained hard rod fluid is under tension. Figure 2 shows some typical plots of the pressure versus density for several choices of the constraint. The unconstrained system, in which only repulsive interactions exist, can never exist at a negative pressure. As the constraint is weakened (l becomes larger), the properties of the constrained fluid approach those of the corresponding unconstrained system.

It was shown in Sec. II that the pressure of the constrained system is the sum of three contributions

$$P=P_{\text{ideal}}+P_{\text{virial}}+P_{\text{constraint}}, \tag{48}$$

in which

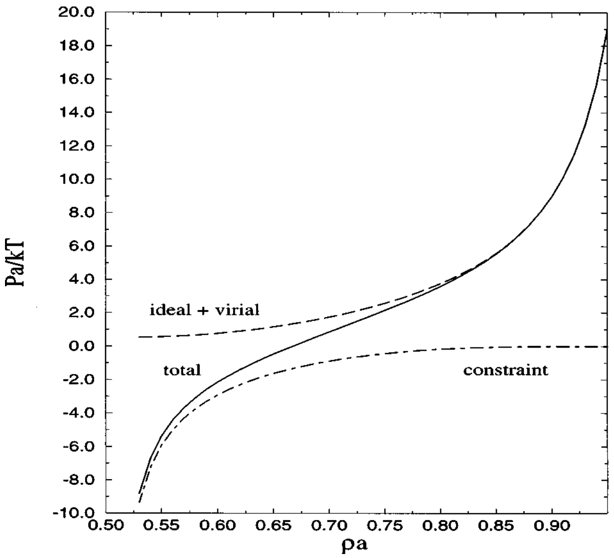

FIG. 3. Density dependence of the various contributions to the pressure for $l=2$.

$$P_{\text{constraint}}=\rho^2\left\langle\left(\frac{\partial W_N/N}{\partial\rho}\right)_{T,N}\right\rangle. \tag{49}$$

Now, P is known exactly [Eq. (44)], and $P_{\text{ideal}}=\rho kT$. Furthermore, it will be shown in Sec. III E that the radial distribution function can be calculated exactly, and hence, through Eq. (10), so can P_{virial}. Therefore, $P_{\text{constraint}}$ can be obtained exactly. We find that

$$\frac{P_{\text{constraint}}}{kT}=-\frac{\rho l\xi e^{-\xi(l-1)}}{1-e^{-\xi(l-1)}}, \tag{50}$$

which, from comparison with Eq. (37), is equivalent to

$$\frac{P_{\text{constraint}}}{kT}=-\rho laP_1(la^-). \tag{51}$$

$P_1(x)$ is the probability density that nearest neighbors are separated by a distance x, which we saw in Sec. III B was equal to $g(x)/N$ [Eq. (37)]. $P_1(la^-)$ signifies the limit of $P_1(x)$ as $x\to la$ from the left. Since by definition of probabilities $P_1(la^-)\geqslant 0$, we conclude that $P_{\text{constraint}}\leqslant 0$ at all densities. Figure 3 shows a plot of $P_{\text{constraint}}$ versus ρa for $l=2$. Included in the plot is the total pressure P, and the remaining contribution to the pressure, $P_{\text{ideal}}+P_{\text{virial}}$. We see that for high densities, when the average intermolecular distance is much less than l, $P_{\text{constraint}}\approx 0$. However, as the density approaches $1/l$, the magnitude of $P_{\text{constraint}}$ increases and becomes the dominant contribution to the pressure. Since $P_{\text{ideal}}+P_{\text{virial}}\geqslant 0$, it is $P_{\text{constraint}}$ which is responsible for allowing the hard rod fluid to exist under tension (i.e., negative pressure).

D. Other thermodynamic variables

Since the Helmholtz energy is now a function of T, L, N, and l, its differential change can be expressed as

$$dA=-SdT-PdL+\mu dN+\chi dl, \tag{52}$$

where S is the entropy, μ the chemical potential, and χ is defined by

$$\chi \equiv \left(\frac{\partial A}{\partial l} \right)_{T,N,L}. \tag{53}$$

Using Eq. (39), we find that

$$\frac{\chi}{NkT} = \frac{-\xi e^{-\xi(l-1)}}{1-e^{-\xi(l-1)}} \leqslant 0. \tag{54}$$

A decrease in l, or an increase in the severity of the constraint, will always cause an increase in the value of the Helmholtz energy. We see that $\chi/NkT \rightarrow -\infty$ as the density approaches its minimum value $1/l$.

Noting that the entropy S is related to A by

$$S = -\left(\frac{\partial A}{\partial T} \right)_{N,L,l}, \tag{55}$$

one finds that

$$\frac{S}{Nk} = \frac{1}{2} + \ln \frac{a[1-e^{-\xi(l-1)}]}{\xi \Lambda} + \frac{\xi(1-\rho a)}{\rho a}. \tag{56}$$

Therefore,

$$\left(\frac{\partial S/Nk}{\partial l} \right)_{T,\rho} = \left(\frac{\partial S/Nk}{\partial l} \right)_{T,\rho,\xi} + \left(\frac{\partial S/Nk}{\partial \xi} \right)_{T,\rho,l} \left(\frac{\partial \xi}{\partial l} \right)_{\rho}$$
$$= -\frac{\chi}{NkT} \geqslant 0, \tag{57}$$

where it can be shown that $[\partial(S/Nk)/\partial \xi]_{T,\rho,l} = 0$. As expected, an increase in the severity of the constraint (a decrease in l) yields a decrease in the entropy.

Invoking a Maxwell relation

$$\left(\frac{\partial S}{\partial L} \right)_{T,N,l} = \left(\frac{\partial P}{\partial T} \right)_{L,N,l} = \frac{\alpha_P}{K_T}, \tag{58}$$

where α_P and K_T are the thermal expansion coefficient and isothermal compressibility, respectively, defined by

$$\alpha_P \equiv \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{P,N,l}, \tag{59}$$

$$K_T \equiv -\frac{1}{L} \left(\frac{\partial L}{\partial P} \right)_{T,N,l}, \tag{60}$$

then we find, using Eq. (56), that

$$\left(\frac{\partial S/Nk}{\partial \rho} \right)_{T,l} = \frac{-\xi}{a\rho^2}, \tag{61}$$

and, therefore,

$$\frac{T\alpha_P}{kTK_T/a} = \xi. \tag{62}$$

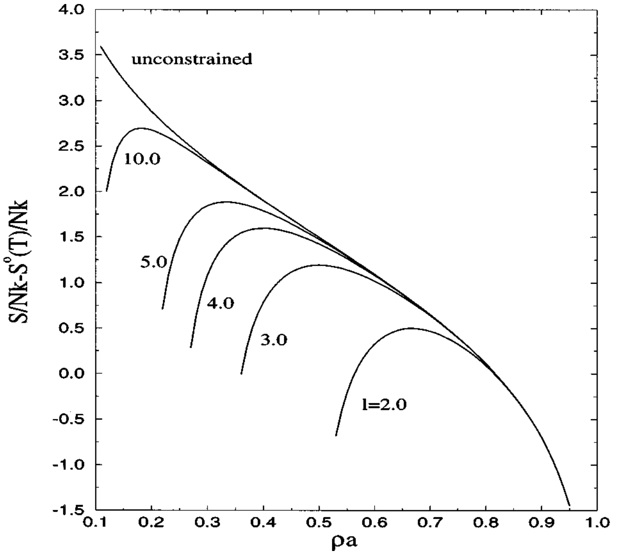

FIG. 4. Density dependence of the entropy of the one-dimensional hard rod fluid for various values of the severity of the constraint, l. For each choice of l, the entropy maximum occurs for $\rho a = 2/(l+1)$. $S^0(T)/Nk = \ln \Lambda/a$, which is a function of temperature only. Notation as per Fig. 1.

Since $K_T \geqslant 0$, one obtains the interesting result that $\alpha_P \leqslant 0$ for $\xi < 0$, or for $1/l \leqslant \rho a \leqslant 2/(l+1)$. In other words, the constrained hard rod fluid will expand when cooled isobarically within this density range. In contrast, the thermal-expansion coefficient of the unconstrained system is

$$T\alpha_P = 1 - \rho a \geqslant 0, \tag{63}$$

indicating that the unconstrained system always contracts when cooled isobarically.

Equation (63) also reveals that the entropy of the unconstrained system never exhibits a maximum with respect to the density. However, this is not so for the constrained system [Eq. (61)]. For densities lower than $2/(l+1)$, an increase in density causes an increase in entropy. At the minimum allowed density, the hard particles are only allowed to exist in a single conformation (i.e., all particles are separated from each other by a distance equal to la). As the density increases, additional configurations become accessible and, therefore, the entropy must increase. On the other hand, at the limit of close packing ($\rho a = 1$), the hard rods again have only one allowed conformation (i.e., all particles are in contact, separated by a distance a from one another). Therefore, at some density between these two limits, the entropy must reach a maximum, which, from Eq. (61), occurs when the pressure is zero ($\xi = 0$) or at $\rho a = 2/(l+1)$. Figure 4 displays a plot of S/Nk versus ρa for various values of l.

E. Radial distribution function

Restricting the maximum allowed distance between nearest neighbors is equivalent to constraining the maximum size of voids allowed in the hard rod fluid. We have already seen how sensitive the thermophysical properties are to the size of the maximum allowed void. We now consider the effect of the constraint on the internal structure of the fluid.

When the system is unconstrained ($l \rightarrow \infty$), the nearest-neighbor distribution function [Eq. (37)] is given by

$$aP_1(x) = \frac{\rho a}{1-\rho a}\, e^{-(x-a)\rho/(1-\rho a)}, \tag{64}$$

in which $x \geqslant a$. However, when a limit is placed on the size of voids in the fluid, the nearest-neighbor distribution function becomes

$$aP_1(x) = \begin{cases} \dfrac{\xi e^{-\xi(x-a)/a}}{1-e^{-\xi(l-1)}}, & a \leqslant x \leqslant la \\ 0, & x > la. \end{cases} \tag{65}$$

The severe nature of the imposed constraint is evident by the immediate discontinuity [$aP_1(x)=0$ for $x > la$], which is imposed on the unconstrained nearest-neighbor distribution function. Subsequently, if the constraint were eliminated, then the hard rod fluid would irreversibly move toward an unconstrained state; the probability that the system would, in the future, return to its original constrained state is essentially zero. Therefore, the constrained hard rod fluid is in fact ‘‘metastable’’ [17].

Using Eq. (65), it is possible to determine the distribution function for the second-nearest neighbor, $P_2(x)$. If the system were unconstrained, then $P_2(x)$ is simply [17]

$$P_2(x) = \begin{cases} 0, & x < 2a \\ \displaystyle\int_a^{x-a} P_1(x-x')P_1(x')dx', & 2a \leqslant x \leqslant 2la \\ 0, & x > 2la. \end{cases} \tag{66}$$

However, in the constrained system, x' can no longer range from a to $x-a$ for any choice of x. For example, if $x > (l+1)a$, then x', the distance between one pair of nearest neighbors, cannot equal a since the distance between the adjacent pair of nearest neighbors, $x-x'$, would violate the constraint, exceeding the maximum allowed value of la. Thus, P_2 for the constrained system must be evaluated as follows:

$$P_2(x) = \begin{cases} 0, & x < 2a \\ \displaystyle\int_a^{x-a} P_1(x-x')H(x-x'-la)P_1(x')H(x'-la)dx', & 2a \leqslant x \leqslant 2ja \\ 0, & x > 2la, \end{cases} \tag{67}$$

where

$$H(y-la) = \begin{cases} 1, & y \leqslant la \\ 0, & y > la. \end{cases} \tag{68}$$

H ensures that the distances between nearest neighbors in Eq. (67) never exceeds la.

In general, the jth nearest-neighbor distribution function $P_j(x)$ is equal to

$$P_j(x) = \begin{cases} 0, & x < ja \\ \displaystyle\int_{(j-1)a}^{x-a} P_1(x-x')H(x-x'-la)P_{j-1}(x')H(x'-la)dx', & ja \leqslant x \leqslant jla \\ 0, & x > ja. \end{cases} \tag{69}$$

By repeated application of the convolution theorem for the Laplace transform of Eq. (69), we find, with $t = x - ja$, that

$$P_j(t+ja) = \mathcal{L}^{-1}\mathcal{L}[P_1(t+a)H(t+a-la)]^j, \tag{70}$$

in which $\mathcal{L}$ denotes the Laplace transform, $\mathcal{L}^{-1}$ the inverse transform, and

$$\mathcal{L}[P_1(t+a)H(t+a-la)] = \int_0^\infty e^{-st}P_1(t+a)H(t+a-la)dt. \tag{71}$$

In arriving at Eq. (70), the following relation was used:

$$\mathcal{L}[P_j(t+jla)] = 0, \tag{72}$$

where, by definition, $P_j(t+jla)=0$ for $t \geqslant 0$.

The radial distribution function $g(x)$ is given by [17]

$$\rho g(x) = \sum_{j=1}^{\infty} P_j(x), \tag{73}$$

which is evaluated by repeated application of Eq. (70). If we let $x^* = x/a$, then $P_j(x)$ is given by

$$aP_j(x^*) = \frac{\xi^j e^{-\xi(x^*-j)}}{[1-e^{-\xi(l-1)}]^j (j-1)!} \times \sum_{k=0}^{j-1} (-1)^k \frac{j!}{k!(j-k)!}[x^*-j-k(l-1)]^{j-1} \times f[x^*-j-k(l-1)] \tag{74}$$

for $j \leqslant x^* \leqslant jl$, in which

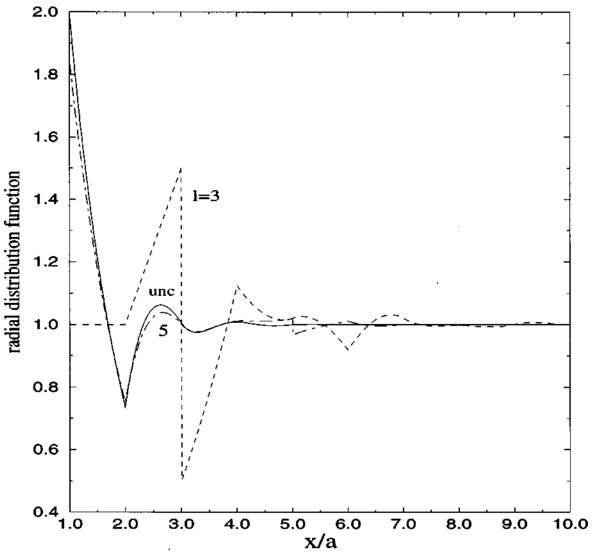

FIG. 5. Radial distribution function of the one-dimensional hard rod fluid for $\rho a = 0.5$. The pressure of the fluid with $l = 3$ is zero. Note that there is a discontinuity at $x/a = 5$ and $x/a = 3$ for $l = 5$ and 3, respectively. unc denotes the unconstrained fluid.

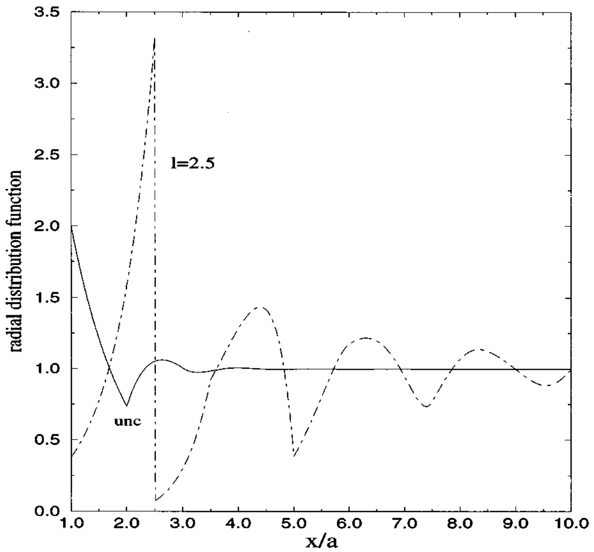

FIG. 6. Radial distribution function of the one-dimensional hard rod fluid for $\rho a = 0.5$. The hard rod fluid is under tension for $l = 2.5$. Note the initial positive slope for the curve for $l = 2.5$ and a corresponding discontinuity at $x/a = 2.5$. unc denotes the unconstrained fluid.

$$f(y) = \begin{cases} 0, & y < 0 \\ 1, & y \geqslant 0. \end{cases} \tag{75}$$

Note that as $l \to \infty$ only the $k = 0$ term survives and we recover the correct radial distribution function of the unconstrained hard rod fluid [26], where

$$aP_j(x^*) = \frac{(\rho a)^j e^{-\rho a(x^* - j)/(1-\rho a)}}{(1-\rho a)^j (j-1)!} [x^* - j]^{j-1} \tag{76}$$

for $x^* \geqslant j$.

Figures 5 and 6 show plots of $g(x^*)$ for various values of l at a density of $\rho a = \frac{1}{2}$. The drastic effects of the constraint on the fluid's internal structure are clearly shown. Let $s(x^*)$ be defined as follows ($\beta = 1/kT$):

$$g(x^*) \equiv e^{-\beta s(x^*)}. \tag{77}$$

Then $s(x^*)$ is the potential of mean force [25], whose derivative yields the force between two hard rods located a distance x^* apart, averaged over all possible configurations of the other $N-2$ hard rods. Therefore, the slope of $-kT \ln g(x^*)$ is the mean force required to hold two particles fixed at a distance x^*. Note that $s(x^*)$ is not just a function of the intermolecular forces between particles, but includes contributions of forces imparted to hard rods from the imposition of the constraint. Figure 5 shows $g(x^*)$ at $\rho a = \frac{1}{2}$ for $l = \infty$ (unconstrained), $l = 5$, and $l = 3$. Note that for $l = 3$ the pressure at this density is zero. We see that for $x^* < 2$ and $l = 3$, $g(x^*)$ has zero slope. Therefore, hard rods separated by a distance less than two particle diameters exert no net force on each other, a result not inconsistent with the system having zero pressure. This is in contrast to the unconstrained $g(x^*)$, which exhibits a negative slope in this interval, indicative of the net repulsion between nearest neighbors. Note that the radial distribution function of each constrained system exhibits a discontinuity when $x^* = l$. Figure 6 compares $g(x^*)$ for an unconstrained system with that for a fluid under tension ($l = 2.5$). For $x^* < 2.5$, the constrained system has a pair correlation function with a positive slope, indicating net attraction between nearest neighbors when the system is under tension. Figure 6 also shows the longer-ranged correlations that exist in the system under tension. This illustrates how the constraint manifests itself as an additional potential of considerable range; correlations over large distances, not seen in the unconstrained fluid, are thereby created in a system with strictly short-ranged intermolecular interactions.

IV. ONE-DIMENSIONAL CONSTRAINED HARD ROD FLUID WITH ATTRACTIVE POTENTIAL

Although the one-dimensional hard rod fluid is helpful in understanding the equilibrium properties of constrained systems, it offers limited insight into the properties of systems that are metastable with respect to a new phase. The one-dimensional hard rod fluid, with or without constraints, does not exhibit a first-order phase transition. This system, however, can be altered to reveal a first-order transition between a liquid phase and a vapor phase. If an infinitely weak and infinitely long-ranged attractive potential [28] is added to the hard core, then the one-dimensional hard rod fluid will have a two-phase region below a given temperature [23]. One can therefore limit the maximum size of voids in the hard rod fluid, thereby preventing the superheated liquid from boiling, and determine the effect of the constraint on the equilibrium properties of the metastable liquid phase. In addition, we compare the equation of state of the superheated liquid with that predicted by mean-field theory (e.g., the van der Waals equation of state).

Lebowitz and Penrose [23] derived the equation of state of a system of identical particles interacting with a pair potential $v(r)$ of the following form:

$$v(r)=q(r)+\gamma^d\phi(\gamma r), \tag{78}$$

where $r\geqslant 0$, d is the dimensionality of the system, and $q(r)$ is a hard-core potential. $\gamma^d\phi(\gamma r)$ is the ‘‘Kac potential’’ [28], which is always attractive, and γ is inversely proportional to the range of the potential. They showed that in the limit as the attractive potential becomes infinitely long ranged and, simultaneously, infinitely weak $(\gamma^{-1}\rightarrow\infty)$, the system's Helmholtz energy per unit volume, $\hat{a}=A/V$, is given by

$$\hat{a}(\rho,T)=\mathcal{E}_C[\hat{a}_0(\rho,T)-\hat{\alpha}\rho^2], \tag{79}$$

where $\hat{a}_0(\rho,T)$ is the free energy density of the hard-core fluid and $\hat{\alpha}$ is a positive constant denoting the integrated strength of the attractive potential, defined by

$$\hat{\alpha}=-\tfrac{1}{2}\gamma^d\int\phi(\gamma r)d\mathbf{r}, \tag{80}$$

in which $d\mathbf{r}$ is a differential volume. The symbol $\mathcal{E}_C$ indicates the convex envelope operator, or the maximal convex function whose value nowhere exceeds $\hat{a}_0(\rho,T)-\hat{\alpha}\rho^2$. Since $\hat{\alpha}$ is positive $[\phi(\gamma r)\leqslant 0$ for $r>r_o]$, the function $\hat{a}_0(\rho,T)-\hat{\alpha}\rho^2$ need not be convex even though $\hat{a}_0(\rho,T)$ must be. Determining the convex envelope of the Helmholtz energy per unit volume is identical to performing Maxwell's equal-area construction.

So far we have only discussed the prescription for calculating the phase equilibrium properties of the hard-core fluid with an infinitely long-ranged attraction. In fact, Penrose and Lebowitz [12,13] showed that this system can exist for a very long time in a homogeneous state that is metastable with respect to vapor-liquid phase separation. The proof involves dividing the volume V into subcells of size ν. In order not to violate the condition of homogeneity, the system is constrained to sample only those configurations in which the density in each subcell falls within two bounds, ρ_- and ρ_+. If at a given density $(\rho_-<\rho<\rho_+)$ the conditions

$$\hat{a}_o(\rho)-\hat{\alpha}\rho^2>\mathcal{E}_C[\hat{a}_0(\rho,T)-\hat{\alpha}\rho^2], \qquad \left(\frac{\partial^2\hat{a}_o}{\partial\rho^2}\right)-4\hat{\alpha}>0 \tag{81}$$

are satisfied, then the system is metastable and will remain so for a long time (i.e., a small escape rate). Penrose and Lebowitz's proof that the system can exist in a metastable state is dependent upon the possibility of dividing the system into the following length scales

$$V^{1/d}\gg\gamma^{-1}\gg\nu^{1/d}\gg r_o\ \ln(V/r_o^d)\,. \tag{82}$$

Equation (82), in which r_o is the hard-core radius, is to be interpreted in such a way that $V^{1/d}/\gamma^{-1}\rightarrow\infty$, $\gamma^{-1}/\nu^{1/d}\rightarrow\infty$, and $\nu^{1/d}/r_o\ \ln(V/r_o^d)\rightarrow\infty$ simultaneously. As before, the separation of the intermolecular potential into short-ranged and arbitrarily long-ranged components enables one to define a length scale $\nu^{1/d}$, with characteristics that we now discuss [12,13]. Since ν is macroscopic, the inequality $\nu^{1/d}\gg r_o\ \ln(V/r_o^d)$ ensures that there are always enough molecules in a subcell to make a violation of the uniformity condition $\rho_-<\rho<\rho_+$ unlikely, guaranteeing that the rate of phase separation is small. The inequality $\gamma^{-1}\gg\nu^{1/d}$ suppresses phase transitions within a subcell, since the range of attractions is now large with respect to the size of a subcell. The last inequality, $V^{1/d}\gg\gamma^{-1}$, ensures that we are dealing with the thermodynamic limit, which satisfies the condition that if the metastable state were to phase separate, it would have a negligible probability of returning to its original state. Note that Eq. (81) is more restrictive than Maxwell's prescription [13] for obtaining metastable states,

$$\hat{a}_o(\rho)-\hat{\alpha}\rho^2>\mathcal{E}_C[\hat{a}_0(\rho,T)-\hat{\alpha}\rho^2], \qquad \left(\frac{\partial^2\hat{a}_o}{\partial\rho^2}\right)-2\hat{\alpha}>0, \tag{83}$$

which allows the system to exist arbitrarily close to a limit of thermodynamic stability where $(\partial P/\partial\rho)_T=0$ (i.e., spinodal). Due to the appearance of $4\hat{\alpha}$ in Eq. (81), Penrose and Lebowitz's requirements for metastability do not allow the system to approach the spinodal curve. In addition, there is a limited range of subcritical temperatures in which Eq. (81) is satisfied. As will be shown below, the van der Waals equation of state obeys Penrose and Lebowitz's metastability condition only for $T\leqslant 0.765T_c$ (supercooled vapor) and $T\leqslant 0.642T_c$ (superheated liquid), where T_c is the critical temperature.

A. Phase equilibrium properties

The one-dimensional hard rod fluid exhibits a first-order phase transition when a ‘‘Kac potential’’ is added to its hard core. The equation of state of the system is (we are discussing phase equilibrium properties only)

$$\hat{a}(\rho,T,l)=\mathcal{E}_C[\hat{a}_0(\rho,T,l)-\hat{\alpha}\rho^2], \tag{84}$$

where $\hat{a}_0(\rho,T,l)$ is the free energy density of the constrained hard rod fluid and is a function of the constraint, l. If we define a dimensionless temperature $T^*=akT/\hat{\alpha}$, a dimensionless density $\rho^*=\rho a$, and $\Lambda^*=\Lambda/a$, then, upon substituting Eq. (39) into Eq. (84), we find

$$\hat{a}^*=\mathcal{E}_C\left[-T^*\rho^*\ \ln\frac{1-e^{-\xi(l-1)}}{\Lambda^*\xi}-T^*\xi(1-\rho^*)-(\rho^*)^2\right], \tag{85}$$

where $\hat{a}^*=\hat{a}a^2/\hat{\alpha}$. If the system becomes unconstrained $(l\rightarrow\infty)$, then

$$\hat{a}^*=\mathcal{E}_C\left[-T^*\rho^*\ \ln\frac{1-\rho^*}{\Lambda^*\rho^*}-T^*\rho^*-(\rho^*)^2\right], \tag{86}$$

which is simply the van der Waals equation of state. The van der Waals equation has a critical point at $T^*=\frac{8}{27}$, $\rho^*=\frac{1}{3}$, and $P^*=Pa^2/\hat{\alpha}=\frac{1}{27}$. It is convenient to reference the temperature, pressure, and density of the constrained system to that of the unconstrained system. Thus let us define a re-

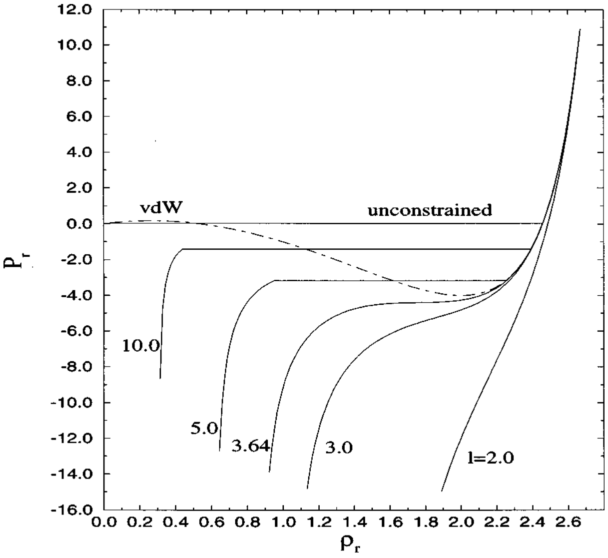

FIG. 7. Equation of state of the constrained hard rod fluid with an infinitely weak and infinitely long-ranged attractive potential for various values of the constraint, at $T_r = 0.5$. The van der Waals equation is labeled vdw. Note that for values of l lower than 3.64, the system does not exhibit a first-order phase transition. P_r, ρ_r, and T_r denote the pressure, density, and temperature of the constrained fluid divided by the corresponding value of the same property at the critical point of the unconstrained fluid.

duced variable $X_r = X/X_c$, which references the quantity X in the constrained hard rod fluid to its value at the critical point for the unconstrained system. Rewriting Eq. (85) in terms of these reduced variables yields

$$\hat{a}^* = \mathcal{E}_C\left[\frac{-8T_r\rho_r}{81}\ln\frac{1-e^{-\xi(l-1)}}{\Lambda^*\xi} - \frac{8T_r\xi(3-\rho_r)}{81} - \frac{\rho_r^2}{9}\right]. \tag{87}$$

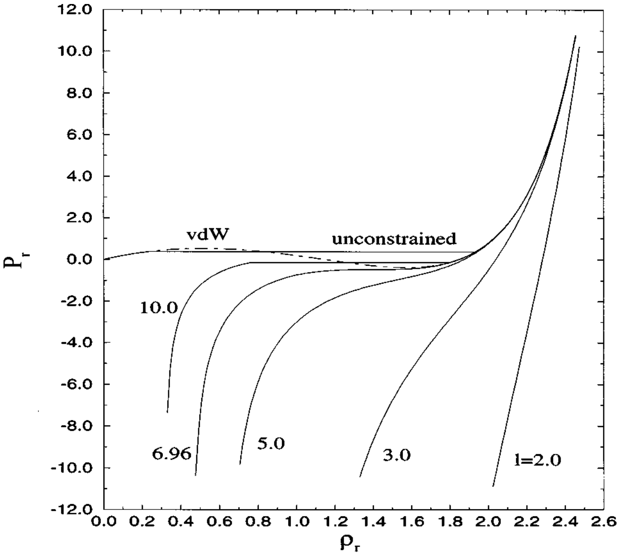

FIG. 8. Equation of state of the constrained hard rod fluid with an infinitely weak and infinitely long-ranged attractive potential for various values of the constraint, at $T_r = 0.8$. The van der Waals equation is labeled vdw. Notation as per Fig. 7.

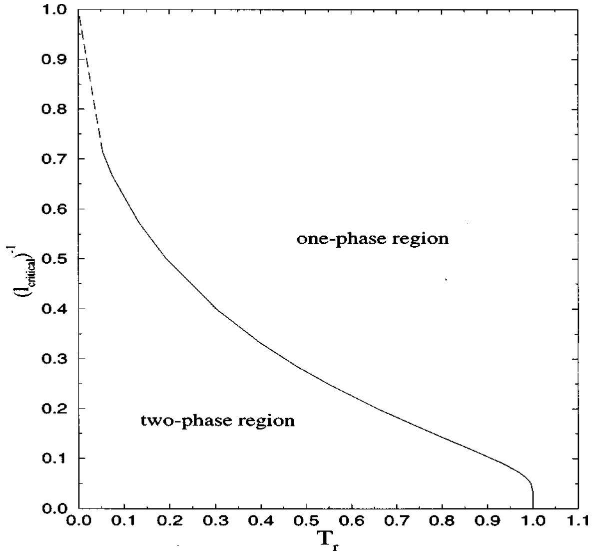

FIG. 9. Temperature dependence of the critical value of l, such that a phase transition does not occur if $l < l_{\text{critical}}$. The dashed line is a numerical extrapolation of the data to $l_{\text{critical}}^{-1} \rightarrow 1$. Notation as per Fig. 7.

The reduced pressure then is simply

$$P_r = 8\xi T_r - 3\rho_r^2, \tag{88}$$

which, in the limit $l \rightarrow \infty$, yields the familiar van der Waals equation of state

$$P_r(l \rightarrow \infty) = \frac{8T_r\rho_r}{3-\rho_r} - 3\rho_r^2. \tag{89}$$

Equation (89) is identical in form but not quite equivalent to the van der Waals equation of state. The van der Waals equation is a mean-field expression and therefore yields states that are thermodynamically unstable [i.e., $(\partial P/\partial \rho)_T < 0$]. Equation (89), in accordance with the convex envelope prescription [i.e., Eq. (87)], never yields unstable states. The convex envelope in Eq. (87) can also be determined by integrating Eq. (88) according to Maxwell's equal area construction.

Figures 7 and 8 show the reduced pressure as a function of the reduced density for various values of l for $T_r = 0.5$ and 0.8, respectively. At these temperatures, the unconstrained system exhibits a first-order phase transition. There is a temperature-dependent critical value of l, $l_{\text{critical}}(T)$, such that the system may not phase separate if it is more severely constrained (i.e., $l < l_{\text{critical}}$). Above this critical value, the system exhibits a phase transition. For $l > l_{\text{critical}}$ but near l_{critical}, the two coexisting phases are in equilibrium at negative pressures. This is a rigorously derived example of metastable phase equilibrium. Figure 9 shows a plot of the inverse of l_{critical} as a function of the reduced temperature. We see that the curve divides the diagram into two distinct regions: phase equilibrium can only occur if $l > l_{\text{critical}}$; if $l < l_{\text{critical}}$, on the other hand, the system does not exhibit a phase transition at the given temperature. The temperature-density and pressure-temperature projections of the phase diagram of the constrained hard rod fluid are shown in Figs. 10 and 11, respectively, for several values of l. Within each phase envelope (Fig. 10), the system may phase separate; outside of

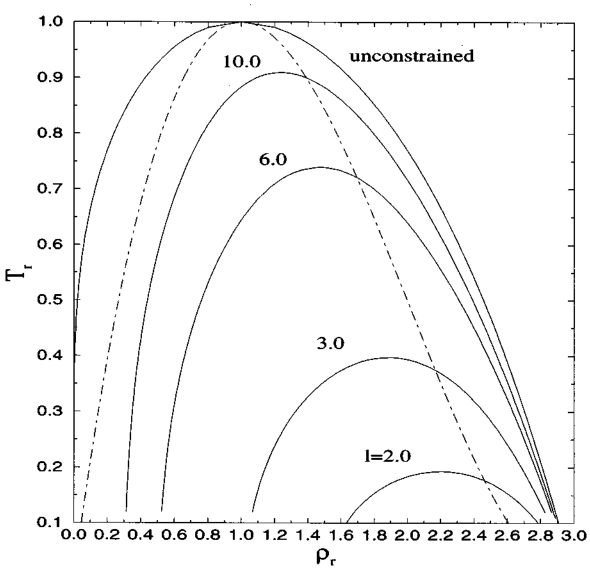

FIG. 10. Temperature-density projection of the phase diagram of the one-dimensional constrained hard rod fluid with attractive tail for various values of the constraint, l. For a particular choice of l, the system does not exhibit a first-order phase transition for values of the temperature and density outside of the corresponding phase envelope. The dot-dashed line is the predicted mean-field spinodal. Notation as per Fig. 7.

this region, the system only exists as a single phase. We see from Fig. 11 that for certain values of l the hard rod fluid can only exhibit a first-order phase transition at a negative pressure. We can determine the range of l in which coexistence occurs between two phases under tension by plotting the value of the reduced critical pressure, $P_{r,c}[=P_c(l)/P_c(l\rightarrow\infty)]$, versus the severity of the constraint, l^{-1} (see Fig. 12). For $l<8.14$, the entire vapor pressure curve of the constrained hard rod fluid is under tension.

Figures 7 and 8 also include a van der Waals loop at each temperature. This mean-field equation of state predicts the existence of a superheated liquid, which can persist below the equilibrium pressure of the unconstrained system. Regardless of the value of the constraint, the pressure of the constrained fluid equals that of the unconstrained system for sufficiently high densities. For small values of $l(l<l_{\text{critical}})$, the equation of state of the constrained hard rod fluid exhibits lower pressures, even for densities well within the stable region. For constraints close to l_{critical}, the constrained fluid accurately predicts the pressure of the mean-field superheated liquid but eventually produces higher tensions as the superheated liquid spinodal, as predicted by the van der Waals equation of state, is approached. On the other hand, for constraints less severe than the critical value, where phase separation can occur, the equation of state of the constrained system represents the pressure of the mean-field superheated liquid accurately up to the density at which the constrained fluid phase-separates.

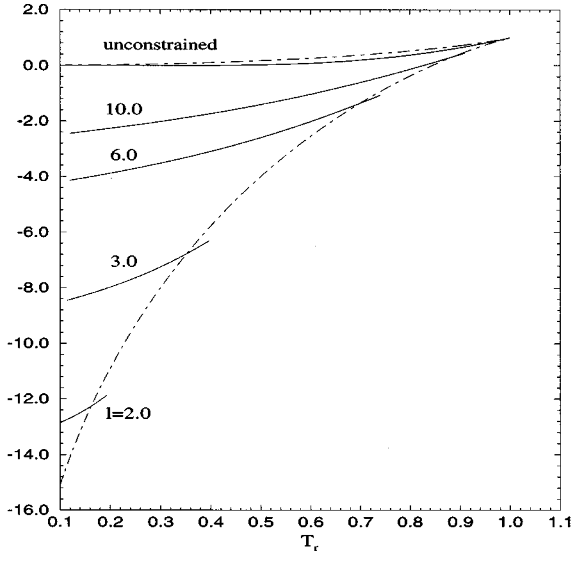

FIG. 11. Pressure-temperature projection of the vapor-liquid binodal of the one-dimensional constrained hard rod fluid with attractive tail for various values of the constraint, l. The dot-dashed line is the predicted mean-field spinodal. Notation as per Fig. 7.

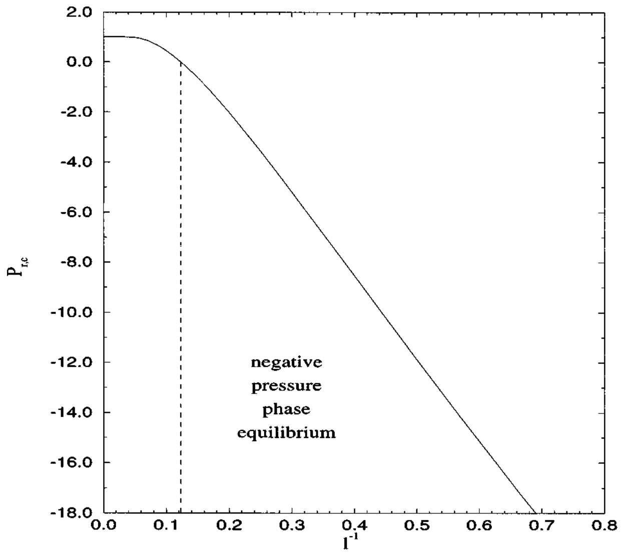

FIG. 12. Reduced critical pressure $P_{r,c}$ as a function of the constraint. The dashed line corresponds to the constraint at which the critical pressure is zero.

B. Metastable states

The constrained hard rod fluid with attractive potential can exist in a metastable state if the conditions given in Eq. (81) are satisfied. Therefore, we are interested in comparing the equation of state of various constrained systems with the equation of state of the superheated liquid in the unconstrained limit $(l\rightarrow\infty)$, and the mean-field equation of state (van der Waals equation). The difference between the van der Waals and unconstrained $(l\rightarrow\infty)$ equations is that metastability in the latter is defined by Eq. 81, and therefore it occurs only over a limited range of densities inside the coexistence region. In the van der Waals equation, on the other hand, metastability occurs up to the spinodal curve. Both equations of state are identical in the stable region and over the range of conditions when Eq. (81) is satisfied. (In what follows, when we refer to the superheated liquid without making reference to a constraint, we are talking about the unconstrained superheated liquid.)

To illustrate the consequences of Penrose and Lebowitz's condition for the existence of metastability [Eq. (81)], the

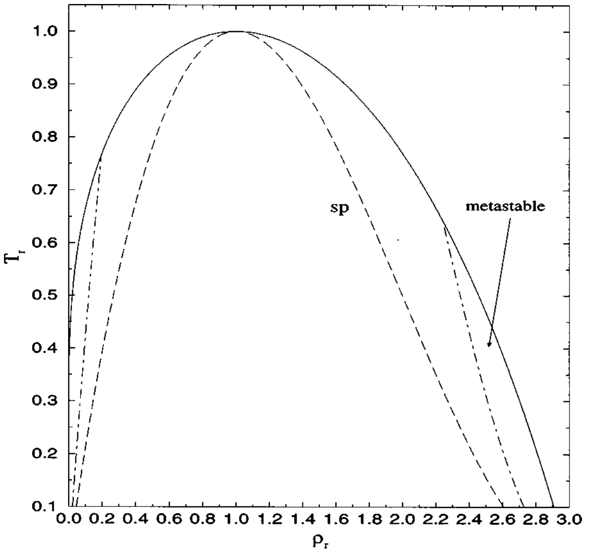

FIG. 13. Temperature-density projection of the phase diagram of the unconstrained hard rod fluid with attractive tail showing the regions of metastability for the supercooled vapor and superheated liquid. The regions of metastability are bounded by the binodal (solid line) and the limit of metastability (dot-dashed line). Equation (81) is satisfied in this region. The vapor and liquid cannot become metastable for $T_r > 0.765$ and $T_r > 0.642$, respectively. For reference, the spinodal curve (sp) of the van der Waals equation of state is included.

phase diagram of the unconstrained hard rod fluid with attractive potential is shown in Fig. 13. The limit of metastability is defined by the condition in which Eq. (81) is first violated, or, equivalently,

$$\left(\frac{\partial P_r}{\partial \rho_r}\right)_{T_r,l} = 6\rho_r, \qquad (90)$$

and

$$P_r < P_r^{\mathrm{eq}}(T_r) \quad \text{superheated liquid}$$

$$P_r > P_r^{\mathrm{eq}}(T_r) \quad \text{supercooled vapor.} \qquad (91)$$

Beyond this limit it is no longer possible to define single-phase states with macroscopic lifetimes [12]. Note that this limit is not the same as the spinodal, where the system reaches an absolute limit of stability. For the unconstrained system, Eq. (90) becomes

$$T_r = \tfrac{1}{2}\rho_r(3-\rho_r)^2. \qquad (92)$$

There is a maximum temperature for which Eq. (92) is satisfied. Only for $T_r < 0.765$ can the vapor become supercooled; the liquid can only be superheated for $T_r < 0.642$. Above these temperatures, the vapor and liquid cannot remain metastable and must phase separate. The metastable regions are therefore bounded by the binodal and the corresponding vapor and liquid limits of metastability. In Fig. 13, the limit of metastability is shown as a dot-dashed line. Note the contrast between the mean-field prediction, according to

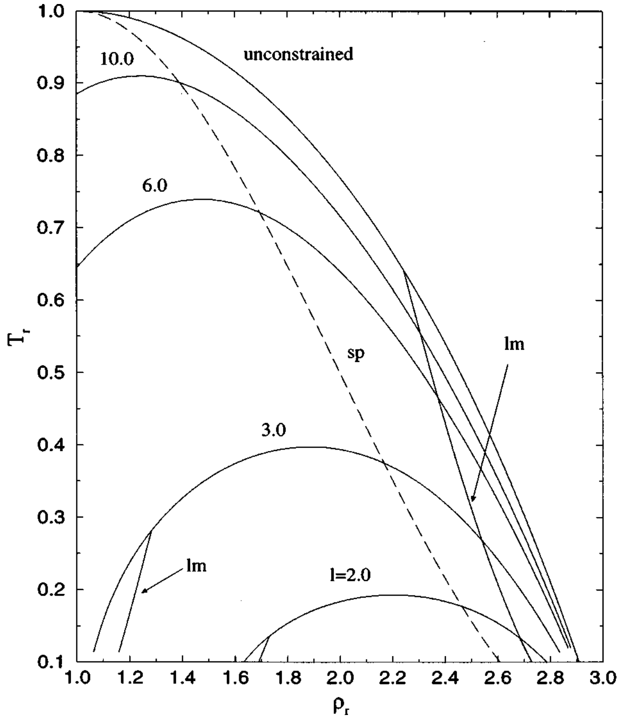

FIG. 14. Temperature-density projection of the phase diagram of the constrained hard rod fluid with attractive tail for various values of the constraint, l. Within each phase envelope, the solid line indicates the limit of metastability, lm, defined by Eq. (81). The dot-dashed line is the limit of stability of the unconstrained hard rod fluid. Also shown is the mean-field superheated liquid spinodal (sp).

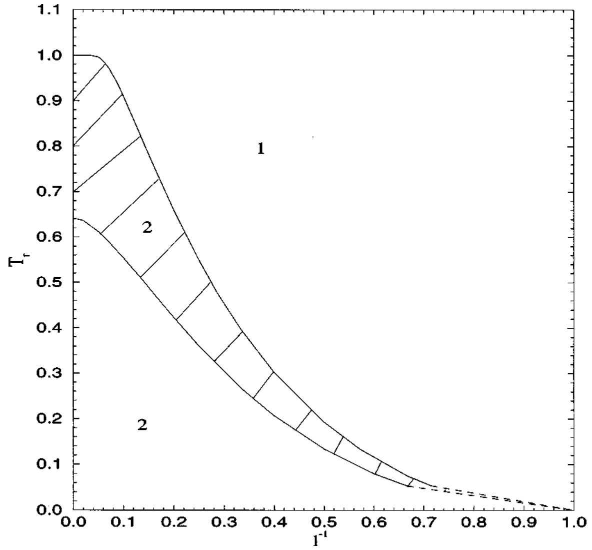

FIG. 15. The dependence of the critical temperature (top curve) and the maximum temperature at which the liquid reaches a limit of metastability (bottom curve) upon the severity of the constraint, for the constrained hard rod fluid with attractive tail. The dashed lines are extrapolations to $l^{-1} \rightarrow 1$. There is no phase transition in the region labeled 1. For any value of l, phase separation without metastability for the superheated liquid [as defined by Eq. (81)] occurs in the dashed region; metastability is possible in the nondashed region labeled 2.

which metastable states can exist arbitrarily close to the critical point, and Eq. (81), which predicts a subcritical upper limit to metastability.

In the presence of a constraint, the limit of metastability is determined by the condition

$$T_r = \frac{3}{2}\, \rho_r \left(\frac{\partial \rho_r}{\partial \xi} \right)_l , \tag{93}$$

which, is of course, a function of l. Figure 14 again displays the temperature-density projection of the phase diagram of the constrained hard rod fluid with attractive potential for various values of the constraint, l (as in Fig. 10), but also includes the predicted regions of metastability for various values of l. The locus of limits of metastability of the superheated liquid coincides with that of the unconstrained fluid for all choices of l. The same is not true for the supercooled vapor. Within each superheated liquid region, the pressures of each constrained fluid, if the corresponding value of the temperature and density fall inside a phase envelope, are essentially identical. This conclusion cannot be drawn, in general, for values of l in which the fluid is stable (i.e., the chosen temperature and density lie outside the phase envelope for the particular value of l), since small values of l show significant deviations from the equation of state of the unconstrained system (e.g., Fig. 7).

Figure 15 shows the dependence of the size of the phase coexistence and liquid metastable regions on the severity of the constraint. In the figure, the top curve shows how the critical temperature varies with the inverse of l. The lower curve displays the highest temperature at which metastability is possible for the liquid [i.e., Eq. (81) is satisfied] as a function of l^{-1}. These two curves divide the figure into three distinct regions: a region in which only one phase is present (labeled 1), a region in which phase coexistence must occur (dashed region labeled 2), and a region in which the liquid may become superheated (nondashed region labeled 2). Clearly, both the superheated liquid and coexistence regions decrease in size as the constraint becomes more severe. In addition, the highest temperature at which the liquid can exist in the superheated state (bottom curve in Fig. 15) increases with l. Therefore, the limiting temperature of superheating for the unconstrained system ($l \to \infty$) defines a strict upper bound for all constrained systems. Regardless of the choice of l, constrained liquids can never be superheated if $T_r > 0.642$; they either fall within the stable one-phase region or must separate into two coexisting phases.

V. CONCLUSIONS

We have applied the rigorous statistical mechanics of internally constrained ensembles to derive the equilibrium properties of a one-dimensional constrained hard rod fluid with and without an additional infinitely weak and infinitely long-range attractive potential. We find that there are additional contributions to the properties of constrained systems that are not properly accounted for if the relations of unconstrained statistical mechanics are used.

We analyzed the effect of the severity of an internal constraint, in which a limit is placed on the maximum allowed distance between nearest-neighbor hard rods, on the equilibrium properties of the constrained hard rod fluid. The equation of state of the hard rod fluid is extremely sensitive to the severity of the constraint. This type of system, which always exists at a positive pressure when unconstrained, is able to exist under tension when a severe enough constraint is applied. Within this negative pressure region, the hard rod fluid is anomalous, having a negative thermal expansion coefficient. In contrast, the unconstrained hard rod fluid always has a thermal expansion coefficient that is non-negative. The internal structure of the hard rod fluid is also significantly affected by the imposition of the constraint, which gives rise to discontinuities and long-range correlations in the radial distribution function. If an infinitely weak and infinitely long-ranged attractive potential is added, then the hard rod fluid exhibits a first-order vapor-liquid phase transition. For certain temperatures and severities of the constraint, the hard rod fluid is able to exist as an equilibrium mixture between two phases that are under tension, an example of metastable phase equilibrium.

While the present work sheds light on the effect of constraints on the behavior of the hard rod fluid, additional studies of this idealized system should be pursued. For the superheated liquid, one such study would be to constrain not the formation of voids, but of finite-density ‘‘bubbles.’’ Also, it would be instructive to constrain the formation of clusters in the supercooled vapor. Such analytical studies of idealized systems, coupled with computational investigations of more realistic fluids [18,19,21] will be beneficial for an improved understanding of the behavior of fluids outside of their normal range of thermodynamic stability.

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