Liquid-vapor coexistence and the PVT surface of a lattice fluid

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The lattice fluid model in the grand canonical ensemble is presented as a useful system for teaching liquid-vapor coexistence and the PVT surface of a fluid. The state of the fluid in the grand canonical ensemble is specified by the temperature T, the volume V, and the chemical potential μ. The $\hat{p}(T,V,\mu)$ and $v(T,V,\mu)$ equations of state of the lattice fluid, where v is the volume per particle, are derived from the grand canonical partition function in the mean-field approximation. We distinguish between the integral pressure $\hat{p}\equiv-\Omega/V$ and the differential pressure $p\equiv-(\partial\Omega/\partial V)_{T,\mu}$, where Ω is the Landau potential so that we can discuss finite size effects near first-order phase transitions. The nonequivalence of the canonical and grand canonical ensembles for describing the liquid-vapor phase transition is also discussed. © *2011 American Association of Physics Teachers.*
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I. INTRODUCTION

The continuity between the vapor and the liquid states has fascinated scientists since Andrews' first Bakerian lecture.[1] The van der Waals equation of state was the first to incorporate the liquid-vapor transition and fluid criticality.[2] This equation is easy to manipulate and its predictions are reasonable,[3] but it requires the use of either the Maxwell equal-area rule or the Gibbs equal-depth minima approach to describe liquid-vapor coexistence.[4] The van der Waals equation is based on a mean-field approximation that approximates the interaction energy between a given particle and the other particles in the fluid by assuming that the local density can be replaced by the average particle density.[5] Although the mean-field approximation occasionally leads to wrong results, it is popular because it is simple and yields equations of state that describe satisfactorily first-order phase transitions for temperatures not too close to the critical temperature.[6]

The lattice fluid model with nearest-neighbor interactions successfully describes liquid-vapor coexistence and the observed properties of a fluid at its critical point.[7,8] Because it is formally identical to the Ising model of ferromagnetism,[9] the lattice fluid model is often studied in the canonical ensemble.[10] Unlike the Ising model, the lattice fluid model was originally formulated in the grand canonical ensemble, where the number of particles is free to fluctuate.[9]

In this paper, we show that the lattice fluid model in the grand canonical ensemble is an interesting pedagogical tool. First, the concept of the chemical potential is not well understood by beginning students.[11] As evidenced by the Maxwell rule, μ is an important variable for describing liquid-vapor coexistence, and the use of the grand canonical ensemble enhances its understanding. Second, the equations of state derived in the grand canonical ensemble (in the mean-field approximation) can be used directly to make three-dimensional (3D) plots of the PVT surface of the lattice fluid, including the liquid-vapor coexistence surface, without the need to use the Maxwell rule. Third, the probability distribution of the number of particles in the two phases provides interesting insights on the liquid-vapor coexistence. Fourth, finite system size effects at first-order phase transitions,[12] a topic of interest in nanoscience,[13] can be discussed by considering lattice fluids which are not in the thermodynamic limit. Finally, because in the liquid-vapor coexistence region the grand canonical ensemble describes the stable states while the canonical ensemble describes metastable and instable states, the nonequivalence of these ensembles for describing phase transitions can be discussed.[14]

II. FUNDAMENTAL RELATIONS OF A LATTICE FLUID

A. The lattice fluid and the mean-field approximation

In the lattice fluid,[9] the volume V available to the fluid is composed of a regular space-filling array of cells of volume b (see Fig. 1). The number of cells (or lattice sites) $N_s\equiv V/b$ is an integer state variable, which is equivalent to V. Each cell can contain one particle at most. This constraint accounts for the short-range strong repulsion between particles at small separations. The model also includes an attractive interaction at larger separations. We consider attractive interactions restricted to particles occupying the nearest-neighbor positions in the lattice. The total interaction energy is $E(N_{\rm nn})=N_{\rm nn}w$, where $w<0$ is the (attractive) interaction energy and $N_{\rm nn}$ is the number of pairs of particles that are nearest neighbors.

The values of $N_{\rm nn}$ and $E(N_{\rm nn})$ depend on the distribution of particles in the lattice. Because no exact solution is known in three dimensions, the thermodynamic properties of the lattice fluid must be determined from computer simulations or approximations, such as the mean-field approximation. The latter assumes that all possible distributions of the N particles in N_s cells have the same energy $E\approx cwN^2/2N_s$, where c is the coordination number of the lattice. This energy E is deduced by assuming that all lattice sites have the same neighborhood so that the probability that one of the neighboring sites is occupied is N/N_s and the number of interacting pairs is $N_{\rm nn}\approx(1/2)N(N/N_s)c$, where the factor 1/2 avoids double counting of the interactions. If N and N_s are fixed, the mean-field approximation implicitly assumes that the fluid is homogeneous, and there is only one phase.

B. The canonical ensemble

In the canonical ensemble the fluid is a closed system characterized by (T,V,N), which are the natural variables of the Helmholtz potential F. The equation $\mathrm{d}F=-S\mathrm{d}T-p\mathrm{d}V+\mu\mathrm{d}N$ implies that the entropy S, the pressure p, and the

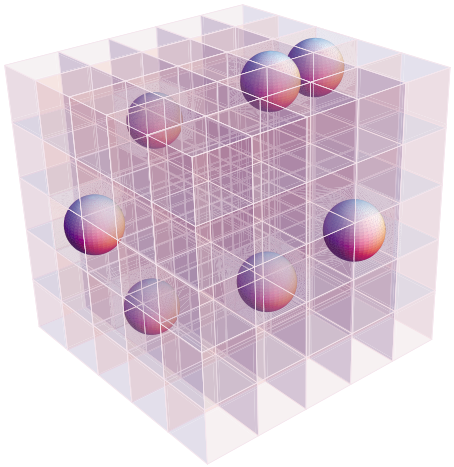

Fig. 1. In a lattice fluid model, the volume is composed of a regular space-filling array of cells of volume b. Each cell can contain at most one particle.

chemical potential μ can be obtained from $F(T,V,N)$ as partial derivatives of F with respect to its natural variables. The canonical partition function $Z(T,N_s$ or $V,N)$ is the sum of the Boltzmann factors $e^{-\beta E}$ of the different microstates, where $\beta \equiv 1/k_B T$ and k_B is Boltzmann's constant. The free energy is related to Z by $F=-k_B T \ln Z$.

In the mean-field approximation, the $\binom{N_s}{N}$ microstates that result from redistributing the N identical particles among the N_s cells have the same energy, $E \approx cwN^2/2N_s$. Thus, Z in the mean-field approximation is (see Appendix A)

$$Z(T,N_s,N) = \binom{N_s}{N} \sigma^{N^2/N_s}, \tag{1}$$

where $\sigma \equiv e^{-\beta cw/2}$. The thermodynamic relation $p=-(\partial F/\partial V)_{T,N}$ can be written as $p=(k_B T/b)(\partial \ln Z/\partial N_s)_{T,N}$. The canonical partition function in Eq. (1) and Stirling's approximation, $\ln x! \approx x \ln x - x$ for $x \gg 1$, leads to the thermal equation of state of a lattice fluid,[10]

$$p + \frac{a}{v^2} = \frac{k_B T}{b} \ln \frac{v}{v-b}, \tag{2}$$

where $v \equiv V/N$ is the volume per particle. The parameter $a \equiv -bcw/2 > 0$ is related to the attractive molecular interactions. Equation (2) resembles the van der Waals equation because $\ln[1+b/(v-b)] \approx b/(v-b)$ when $v \gg b$.

From Eq. (2) and the conditions $(\partial p/\partial v)_{T_c}=0$ and $(\partial^2 p/\partial v^2)_{T_c}=0$, the critical point parameters are $v_c=2b$, $T_c=a/2bk_B$, and $p_c=(\ln 4-1)a/4b^2$; note that $k_B T_c = a/2b$ is equivalent to the Bragg–Williams equation,[15] $k_B T_c = -cw/4$. The compressibility factor of the lattice fluid is $z_c \equiv p_c v_c/k_B T_c = \ln 4 - 1 = 0.386$, which is close to the van der Waals value, $z_c^{\mathrm{vdW}}=0.375$.[5] Because $0.23 < z_c < 0.31$ for the vast majority of substances,[16] Eq. (2) is not likely to compare very well with the experimental data. Moreover, Eq. (2) predicts that the limiting high pressure value of the reduced volume $v_r \equiv v/v_c$ is $b/v_c=0.5$, in contrast to the experimental value of 0.26. To describe liquid states, the lattice fluid model is worse than the van der Waals equation, which predicts 0.33 for this limit. Nevertheless, many other characteristics make the lattice fluid model interesting for teaching about liquid-vapor coexistence.

C. The liquid-vapor coexistence curve

The relation $\mu=(\partial F/\partial N)_{T,V}=-k_B T(\partial \ln Z/\partial N)_{T,N_s}$ leads to

$$\mu = -\frac{2a}{v} + k_B T \ln \frac{b}{v-b}, \tag{3}$$

which is equivalent to the Frumkin–Fowler–Guggenheim adsorption isotherm,[17] $\theta/(1-\theta)=\lambda\sigma^{2\theta}$, where $\lambda \equiv e^{\mu/k_B T}$ is the absolute activity of the particles and $\theta \equiv N/N_s = b/v$ is the fraction of the occupied cells. The volume per particle evaluated from Eq. (3) is not a single-valued function of (T,μ). For subcritical temperatures and chemical potentials, Eq. (3) may yield three values of v corresponding to the same values of (T,μ). If one of these values is $v=v_c=2b$, the other two correspond to the liquid and vapor phases, which can coexist in equilibrium at that temperature. This statement follows from the condition of mechanical equilibrium $p^{\mathrm{L}}=p^{\mathrm{V}}$ for these phases and the equation $dp=(1/v)d\mu$ at constant T. We use the value $v=v_c$ to find $\mu_c=-a/b$ (or, equivalently, $\lambda_c\sigma_c=1$) from Eq. (3), and substitute this value of μ back into Eq. (3) to derive the liquid-vapor coexistence curve

$$\frac{a}{bk_B T} = \frac{v}{2b-v} \ln \frac{b}{v-b}, \tag{4}$$

Inspection of Eq. (4) for $T < T_c = a/2bk_B$ shows that if $v^{\mathrm{L}}=b/\theta^{\mathrm{L}}$ is the volume per particle of the liquid, then the volume per particle of the vapor is $v^{\mathrm{V}}=b/\theta^{\mathrm{V}}$ with $\theta^{\mathrm{L}}+\theta^{\mathrm{V}}=1$ (or $1/v^{\mathrm{L}}+1/v^{\mathrm{V}}=2/v_c$), and v^{L} and v^{V} are the two solutions of Eq. (4) that lie on the coexistence curve. The meaning of the relation $\mu_c=-a/b$, valid inside the coexistence region, is that every particle that enters the system under these conditions makes the same contribution to the decrease of the Gibbs free energy, which is determined by the interaction energy among neighboring particles independent of temperature.

In terms of the reduced variables $v_r \equiv v/v_c$, $p_r \equiv p/p_c$, and $T_r \equiv T/T_c$, the liquid-vapor coexistence curve obtained from Eqs. (2) and (4) is

$$T_r = \frac{2(v_r-1)}{v_r \ln(2v_r-1)}, \tag{5}$$

$$z_c p_r = -\frac{1}{v_r^2} + 2T_r \ln \frac{2v_r}{2v_r-1}. \tag{6}$$

Equation (6) is the law of corresponding states.

D. The grand canonical ensemble

The mean-field approximation is known to fail in describing some fluid properties. However, some of these failures are the result of combining the mean-field approximation with the constraint that N is fixed. The use of the mean-field approximation in an open system leads to significantly different results.

In the grand canonical ensemble, N is variable and the state of the fluid is characterized by (T,V,μ), which are the natural variables of the Landau or grand potential $\Omega \equiv U - TS - \mu N$, with U being the internal energy. From $\Omega(T,V,\mu)$ and the relation $-d\Omega = S dT + p dV + \langle N \rangle d\mu$, the quantities S, p, and the mean number of particles $\langle N \rangle$ can be obtained as derivatives of Ω with respect to its natural variables. The potential $\Omega(T,V,\mu)$ can be obtained from

$\Omega = -k_B T \ln \Xi$, where $\Xi(T, N_s, \mu)$ is the grand canonical partition function. The corresponding microstates differ not only in the energy and the distribution of the particles among the cells but also in the number of particles N because the fluid, when described in terms of (T, N_s, μ), is an open system that can exchange energy and particles with its surroundings. The fluid can have any N ranging from 0 to N_s. For fixed V and temperature $T < T_c$, the mean number of particles $\langle N \rangle$ inside the volume V increases with increasing μ. For low values of μ, the particle density $\langle N \rangle / V$ and pressure are so small that the fluid is in a vapor state. Increasing μ will eventually lead to the formation of liquid drops, which coexist with the vapor. For larger values of μ, the fluid is in a liquid state.

In the mean-field approximation with nearest-neighbor interactions, the $\binom{N_s}{N}$ microstates that result from distributing the particles among the cells have the same energy, $E \approx cwN^2/2N_s$ (and the same statistical weight). Thus, the grand canonical partition sum Ξ is

$$\Xi(T, N_s, \mu) = \sum_{N=0}^{N_s} \lambda^N Z(T, N_s, N) = \sum_{N=0}^{N_s} \binom{N_s}{N} \lambda^N \sigma^{N^2/N_s}. \quad (7)$$

The distribution

$$P_{GC}(N) \equiv P(N; T, N_s, \mu) = \frac{1}{\Xi(T, N_s, \mu)} \binom{N_s}{N} \lambda^N \sigma^{N^2/N_s} \quad (8)$$

is the probability that the system in the state (T, N_s, μ) has N particles. Because the mean number of particles is $\langle N \rangle \equiv \Sigma_{N=0}^{N_s} N P_{GC}(N)$, the volume per particle $v = V/\langle N \rangle$ of the lattice fluid in the grand canonical ensemble is

$$\frac{1}{v} = \frac{\langle N \rangle}{bN_s} = \frac{1}{bN_s} \frac{\sum_{N=0}^{N_s} \binom{N_s}{N} N \lambda^N \sigma^{N^2/N_s}}{\sum_{N=0}^{N_s} \binom{N_s}{N} \lambda^N \sigma^{N^2/N_s}}. \quad (9)$$

In terms of the integral pressure[12,13,18] $\hat{p} \equiv -\Omega/V = (k_B T/V) \ln \Xi$, the grand canonical equation of state of the lattice fluid in the mean-field approximation is

$$\hat{p}(T, N_s, \mu) = \frac{k_B T}{N_s b} \ln \sum_{N=0}^{N_s} \binom{N_s}{N} \lambda^N \sigma^{N^2/N_s}$$

$$= \frac{k_B T}{N_s b} \ln \sum_{N=0}^{N_s} \binom{N_s}{N} \exp\left(\frac{N\mu}{k_B T} + \frac{a}{b k_B T} \frac{N^2}{N_s} \right). \quad (10)$$

Like many other simple equations of state that include liquid, vapor, and supercritical fluid states, Eq. (10) involves only two parameters characteristic of the fluid: $a \equiv -bcw/2$ and b. In contrast to Eq. (2), Eq. (10) is a fundamental thermodynamic relation[19] and contains all the information about the equilibrium states of the fluid.

The term proportional to N^2 in the exponent of σ makes it impossible to evaluate the sums in Eqs. (9) and (10) exactly in analytical form. When the pressure is calculated numerically from Eq. (10), a finite value of N_s must be used. For fluids of finite volume V, the Landau potential $\Omega \equiv U - TS - \mu N$ is not a first-order homogeneous function of V. Consequently, the Euler equation, $\Omega = -pV$, and the Gibbs–Duhem equation, $N d\mu = -S dT + V dp$, are not satisfied. Moreover, the integral pressure $\hat{p} \equiv -\Omega/V$ is not equal to the differential pressure $p \equiv -(\partial \Omega / \partial V)_{T,\mu}$ and neither is intensive. A system with these properties is not in the thermodynamic limit and is a finite system.[12,13]

In the grand canonical ensemble, the thermodynamic limit is expressed as[9]

$$\ln \xi(T, \mu) \equiv \lim_{N_s \to \infty} \frac{1}{N_s} \ln \Xi(T, N_s, \mu), \quad (11)$$

where ξ is the single-cell partition sum. After taking this limit, the Landau potential $\Omega^\infty(T, N_s, \mu) \equiv -k_B T \ln \Xi^\infty = -p^\infty V$ becomes a first-order homogeneous function of V,[12,18] where $\Xi^\infty(T, N_s, \mu) \equiv \xi^{N_s}$ and $p^\infty(T, \mu) \equiv (k_B T/b) \ln \xi$. The superscript ∞ denotes that the thermodynamic limit has been taken and makes it explicit that Ξ^∞ differs from Ξ in Eq. (7) for N_s finite.

When its volume V increases sufficiently, the fluid behaves like a macroscopic system and the pressures $\hat{p}(T, N_s, \mu)$ and $p(T, N_s, \mu)$ become independent of N_s and become equal to the intensive pressure p^∞ of macroscopic thermodynamics. The dependence of $v(T, N_s, \mu)$ and $\hat{p}(T, N_s, \mu)$ on N_s in Eqs. (9) and (10) disappears in the thermodynamic limit $(N_s > N \gg 1)$ and these equations become $v(T, \mu)$ and $p(T, \mu)$, which involve only intensive quantities.[20] The pressure $\hat{p} \equiv -\Omega/V$ is the quantity of choice[12,13] to study the lattice fluid because it has all the properties of the fluid pressure when N_s is large and lets us analyze the effects of finite size of the system when N_s is small.

III. RESULTS AND DISCUSSION

A. The PVT surface of a lattice fluid

The representation of the isotherms and the van der Waals liquid-gas phase diagram requires using the Maxwell construction for which several programs are available.[4,21] In contrast, the representation of an isotherm in a p-v diagram from Eqs. (9) and (10) is simple in parametric form: $[v(T, N_s, \lambda), \hat{p}(T, N_s, \lambda)]$ are evaluated for fixed (T, N_s) and varying the activity $\lambda \equiv e^{\mu/k_B T}$ in a range that includes the critical value $\lambda_c \equiv e^{\mu_c/k_B T_c} = 1/\sigma_c = e^{-2} = 0.135$.

Figure 2(a) shows a three-dimensional plot of the PVT surface of a lattice fluid. The representation of this surface is interesting and plaster or cardboard models can be constructed.[22,23] The isotherms are found by varying λ from 0.05 to 0.2. This plot also shows the liquid-vapor coexistence surface, which is given by Eqs. (5) and (6) because this surface and the critical point are the same in the canonical and grand canonical ensembles. Students can manipulate the graphics as a three-dimensional object using MATHEMATICA or similar software and observe the p-v, p-T, and v-T projections by rotating the object [see Figs. 2(b)–2(d)].

B. The continuity of the liquid and gaseous states

Students can enhance their understanding of the liquid-vapor phase transition by analyzing and modifying Fig. 2. For instance, they can consider isothermal compression to understand the difference between the discontinuous phase transition that occurs at subcritical temperatures, the continuous transition that occurs at the critical temperature, and the absence of a transition at supercritical temperatures.

If $T > T_c$, it is impossible to liquefy a gas by compression. Similarly, when $p > p_c$, it is impossible to liquefy a gas by

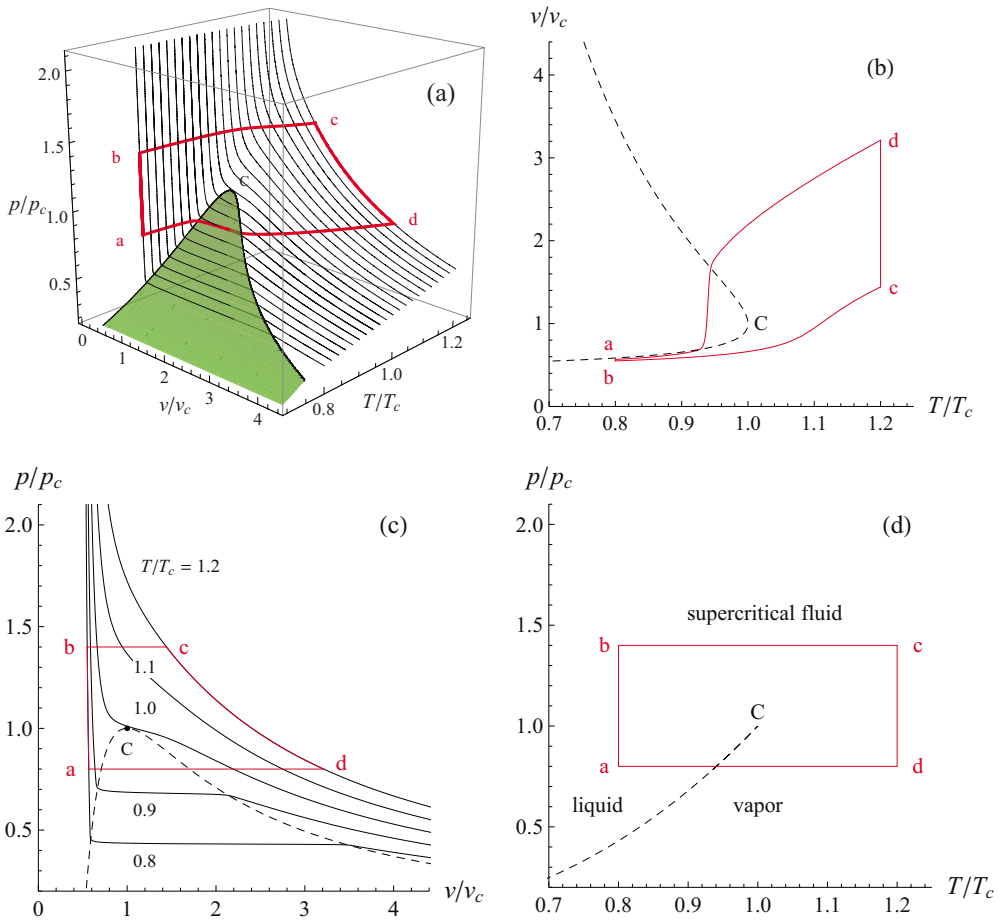

Fig. 2. (a) A three-dimensional plot of the PVT surface of a lattice fluid obtained from Eqs. (9) and (10) for $N_s=1000$. The liquid-vapor coexistence surface is given by Eqs. (5) and (6). Two paths from the liquid state a ($T/T_c=0.8$, $\hat{p}/p_c=0.8$, and $v/v_c=0.5674$) to the vapor state d ($T/T_c=1.2$, $\hat{p}/p_c=0.8$, and $v/v_c=3.2128$) are shown: The isobaric path $a\to d$ and the isothermal-isobaric-isothermal path $a\to b\to c\to d$. State b ($T/T_c=0.8$, $\hat{p}/p_c=1.4$, $v/v_c=0.5497$) is also liquid and state c ($T/T_c=1.2$, $\hat{p}/p_c=1.4$, $v/v_c=1.4424$) corresponds to a supercritical fluid. (b) The v-T projection shows the different volume changes in the isobar $a\to d$ (phase transition) and in the isobar $b\to c$ (no phase transition). (c) The p-v projection shows the absence of loops in the isotherms. (d) The p-T projection shows that the phase transition occurs when crossing the coexistence curve (dashed line), as in the process $a\to d$; no phase transition occurs along the path $a\to b\to c\to d$.

cooling. These states correspond to a supercritical fluid. A liquid can be vaporized by increasing the temperature at constant $p<p_c$, thus observing a first-order liquid-vapor phase transition, as shown in the isobaric path transforming the fluid from the liquid state a to the vapor state d in Fig. 2. It is also possible to transform the liquid state a to the vapor state d without observing a phase transition if the fluid does not cross the liquid-vapor coexistence curve.[24] In Fig. 2, the fluid changes continuously from liquid to vapor along the path $a\to b\to c\to d$, which traverses the region above the critical point. This behavior fascinates students when confronted with it for the first time.

C. The probability distribution for the number of particles

The probability distribution $P_{\mathrm{GC}}(N)$ in Eq. (8) provides insight into the nature of the phase transition.[25] In particular, the possibility that such a distribution has two peaks for sufficiently low temperatures can be interpreted as leading to the coexistence of two phases.[26] For $T>T_c$, $P_{\mathrm{GC}}(N)$ has a single peak, which corresponds to the mean number of particles $\langle N\rangle$ in the supercritical fluid [see Fig. 3(a)]. For $T<T_c$, there are three possible behaviors. For small values of μ, $\langle N\rangle$ is small and $P_{\mathrm{GC}}(N)$ shows a single peak corresponding to the vapor. At large values of μ, $\langle N\rangle$ is large and $P_{\mathrm{GC}}(N)$ shows a single peak corresponding to the liquid. At intermediate values of μ, $P_{\mathrm{GC}}(N)$ can have two maxima corresponding to the coexisting liquid and vapor phases [see Fig. 3(b)]. Liquid-vapor equilibrium is determined by the equal peak weight criterion,[25] which occurs when $\lambda\sigma=1$.

D. Finite-size effects on the liquid-vapor phase transition

The results we have discussed correspond to systems with N_s of the order of 1000. Figure 2(b) shows that the isobar $a\to d$ is not exactly isothermal inside the coexistence region, and Fig. 2(a) shows the slight difference between this isobar and the isotherms. Figure 2(c) shows that the isotherms are not exactly isobars inside this region. The relatively large width of the probability distributions in Fig. 3 is also a consequence of the finite size of the system. The choice $N_s=1000$ is a compromise between short computational time and sufficient accuracy to clearly show the phase transition in the p-v isotherms. Rather than considering this size de-

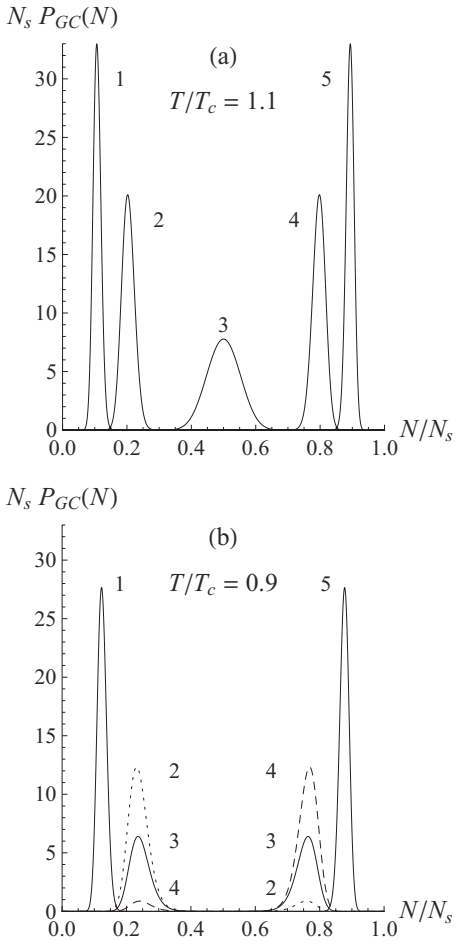

Fig. 3. The grand canonical probability distribution of a lattice fluid. (a) For $T>T_c$, the distribution is unimodal and a single (supercritical fluid) phase exists. The curves correspond to $N_s=1000$, $T/T_c=1.1$, and $\lambda\sigma=1/2$ (1), 3/4 (2), 1 (3), 4/3 (4), and 2 (5). (b) For $T<T_c$, the distribution is unimodal for equilibrium states outside the liquid-vapor coexistence region and bimodal inside it. The curves correspond to $N_s=1000$, $T/T_c=0.9$, and $\lambda\sigma=3/4$ (1), 995/1000 (2, dotted), 1 (3), 1000/995 (4, dashed), and 4/3 (5). The peaks at lower (higher) values of N/N_s correspond to the vapor (liquid) phase.

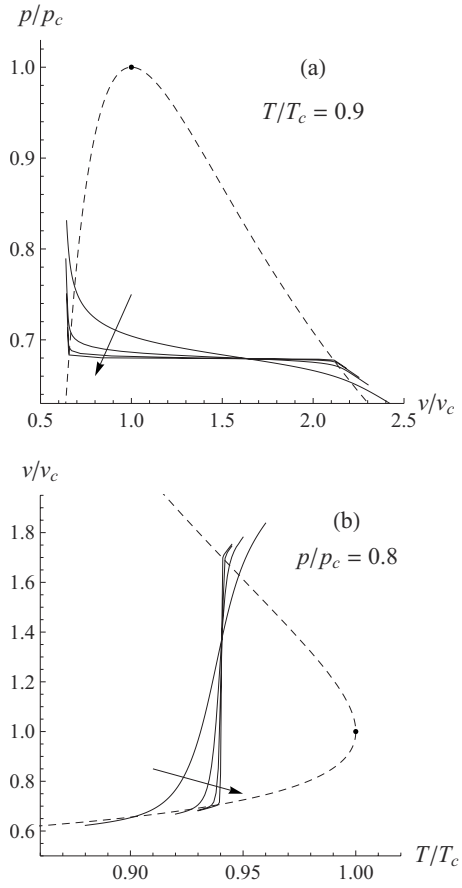

Fig. 4. (a) The subcritical $\hat{p}$-v isotherm $T/T_c=0.9$ for $N_s=300$, 1000, 3000, and 10000 (increasing in the direction of the arrow). (b) The subcritical v-T isobar $\hat{p}/p_c=0.8$ for the same values of N_s.

pendence to be a problem, we can take advantage of Eq. (10) to discuss the physics of phase transitions in small systems.[13,27]

Figure 4 shows the phase transition part of the $T/T_c=0.9$ isotherms and the $\hat{p}/p_c=0.8$ isobars for $N_s=300$, 1000, 3000, and 10000. The isotherm $T/T_c=0.9$ shows a phase transition that becomes first-order-like when the system size is increased: The portion of the isotherm inside the coexistence region becomes more horizontal (that is, isobaric) and the change in the slope when crossing the coexistence curve becomes more abrupt. We see that it is not necessary to consider systems with N_s of the order of Avodagro's number to observe a behavior similar to that of a macroscopic system, and $N_s \gtrsim 10^4$ is sufficient. Also, for increasing N_s, the isobar $\hat{p}/p_c=0.8$ shows a phase transition that becomes first-order-like: The part of the isobar inside the coexistence region becomes more vertical (isothermal), and the change in the slope when crossing the coexistence curve becomes more abrupt. A remarkable characteristic of the liquid-vapor phase transition at constant pressure $\hat{p}$ is that vaporization takes place over a temperature range that widens with decreasing system size.

E. The nonequivalence of the ensembles

The different ensembles in statistical thermodynamics are often considered equivalent for macroscopic systems. However, this equivalence requires that the fluctuations of the state variables vanish in the thermodynamic limit, and therefore it does not hold when describing phase transitions (see Appendix B).[14] Also, the ensembles are not equivalent for the description of small systems, such as a lattice fluid with N_s small.[12,13]

The canonical thermal equation of state [Eq. (2)] shows that the fluid pressure is a single-valued function of (T,v). However, if Eq. (2) is used to obtain v as a function of (T,p), there can be three values of v that satisfy Eq. (2) for subcritical temperatures and pressures. That is, the isotherms described by Eq. (2) exhibit a loop in the liquid-vapor coexistence region of the p-v diagram, just like the van der Waals isotherms. Also, for both Eq. (2) and the van der Waals equation, the critical isotherm is a cubic curve in the neighborhood of the critical point, $p_c-p \propto (v-v_c)^3$.[8]

The isothermal compressibility κ_T diverges at the critical point for macroscopic systems.[6] From Eq. (2), the compressibility in the canonical ensemble is

$$\frac{1}{\kappa_T} = -v\left(\frac{\partial p}{\partial v}\right)_T = \frac{k_B T}{v-b} - 2\frac{a}{v^2}. \tag{12}$$

The actual κ_T differs from that in Eq. (12) because the latter predicts a physically meaningless region of mechanical in-

stability (negative compressibility) between the two points of infinite compressibility, $v=2b/(1\pm\sqrt{1-T/T_c})$. These two points define the spinoidal curve[26] and converge at the critical point. When Eq. (2) yields three values of v for a given (T,p), the value inside the region of mechanical instability has no physical meaning and the other two correspond to a stable liquid and metastable supersaturated vapor, stable vapor and metastable superheated liquid, or stable liquid and vapor states on the coexistence curve. Similarly, Eq. (3) shows a nonphysical loop. These loops are a consequence of using the mean-field approximation in the canonical ensemble.[15]

In contrast, the isotherms described by Eqs. (9) and (10) show no loop in the coexistence region of the p-v region [see Fig. 2(c)], and $v(T,N_s,\mu)$ shows no loop when evaluated from Eq. (9) at constant N_s. In the grand canonical ensemble, the isothermal compressibility[18]

$$\kappa_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial \hat{p}}\right)_{T,N_s} = \frac{1}{\langle N\rangle}\left(\frac{\partial \langle N\rangle}{\partial \hat{p}}\right)_{T,N_s} = \frac{bN_s}{\langle N\rangle^2}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,N_s}$$
$$= \frac{bN_s}{k_BT\langle N\rangle^2}\lambda\left(\frac{\partial \langle N\rangle}{\partial \lambda}\right)_{T,N_s} = \frac{bN_s}{k_BT}\frac{\langle N^2\rangle-\langle N\rangle^2}{\langle N\rangle^2} \geq 0 \qquad (13)$$

is positive, as required by the condition of mechanical stability (note that $-d\Omega = Vd\hat{p} = Nd\mu$ at constant T and V). The difference between Eqs. (12) and (13) shows that results in the grand canonical and the canonical ensemble in the mean-field approximation are not equivalent. Although phenomena such as metastability and instability arise naturally in the canonical ensemble, the grand canonical ensemble is the appropriate formalism for studying the stable states in the liquid-vapor coexistence region.

The nonequivalence is also evident when determining the energy of the lattice fluid. The mean-field approximation in the canonical ensemble for the interaction energy is $E\approx cwN^2/2N_s=-aN^2/V$. Hence, the contribution of the attractive interactions to the internal energy per particle is

$$u = \frac{E}{N} = -\frac{a}{v}, \qquad (14)$$

which is the same as for a van der Waals gas. In the grand canonical ensemble, the thermodynamic quantities $U\equiv\langle E\rangle$ and $\langle N\rangle$ are evaluated as average values. The contribution of the attractive interactions to the internal energy per particle is

$$u = \frac{\langle E\rangle}{\langle N\rangle} = -\frac{a}{bN_s}\frac{\langle N^2\rangle}{\langle N\rangle} = -\frac{a}{bN_s}\frac{\sum_{N=0}^{N_s}\binom{N_s}{N}N^2\lambda^N\sigma^{N^2/N_s}}{\sum_{N=0}^{N_s}\binom{N_s}{N}N\lambda^N\sigma^{N^2/N_s}}$$
$$= -\frac{a}{v}\frac{\langle N^2\rangle}{\langle N\rangle^2}. \qquad (15)$$

Because $\langle N^2\rangle/\langle N\rangle^2\geq 1$, Eq. (15) implies that $u\leq -a/v<0$, which means that the internal energy can be decreased by forming two coexisting phases of different densities when $T<T_c$. The canonical ensemble estimate $u=-a/v$ is incorrect when the liquid and vapor coexist.

IV. CONCLUSIONS

We have shown that the equation of state $\hat{p}(T,V,\mu)$ has a number of advantages when used to describe liquid-vapor coexistence. It allows for a straightforward representation of the PVT surface of a fluid by using software, such as MATHEMATICA, to visualize and manipulate the surface as a 3D object. Because the isotherms on this surface are parametric in the chemical potential, this representation enhances the understanding of this important thermodynamic quantity. The $\hat{p}(T,V,\mu)$ equation also helps us to understand the effects of finite system size and the nonequivalence of the canonical and grand canonical ensembles in the mean-field approximation of first-order first transitions.

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APPENDIX A: THE AVERAGE KINETIC ENERGY OF THE PARTICLES IN THE LATTICE FLUID MODEL

The pressure can be split into a contribution k_BT/v related to the translational motion of the particles and a contribution that accounts for the interactions.[28] We show here that although the lattice model does not incorporate an integration over particle momenta, the pressure calculated from the canonical partition function in Eq. (1) and from the grand canonical partition function in Eq. (7) is the total pressure of the fluid and contains both contributions. This conclusion is supported by the fact that in the absence of attractive interactions ($a=0$), Eqs. (2) and (10) reduce to the ideal gas equation of state $pv=k_BT$ when $v\gg b$.

The integration over particle momenta is often considered when a continuous fluid model is employed. The canonical partition function is then

$$\bar{Z}(T,V,N) = \frac{1}{N!h^{3N}}\int e^{-\beta K(\vec{p}_1,\ldots,\vec{p}_N)}d^3\vec{p}_1,\ldots,d^3\vec{p}_N$$
$$\times\int_V e^{-\beta\Phi(\vec{r}_1,\ldots,\vec{r}_N)}d^3\vec{r}_1,\ldots,d^3\vec{r}_N = \frac{Q}{N!\Lambda^{3N}}, \qquad (A1)$$

where $K(\vec{p}_1,\ldots,\vec{p}_N)$ and $\Phi(\vec{r}_1,\ldots,\vec{r}_N)$ are the total kinetic and potential energy of the fluid particles, respectively, $Q(T,V,N)\equiv\int_V e^{-\beta\Phi(\vec{r}_1,\ldots,\vec{r}_N)}d^3\vec{r}_1,\ldots,d^3\vec{r}_N$ is the configuration integral, and $\Lambda(T)\equiv h/(2\pi mk_BT)^{1/2}$ is the thermal de Broglie wavelength of the particles. The overbar on Z denotes that the integration over particle momenta is included. Because the integral $\int e^{-\beta K(\vec{p}_1,\ldots,\vec{p}_N)}d^3\vec{p}_1,\ldots,d^3\vec{p}_N$ is independent of V, we conclude that this integral is irrelevant for the statistical thermodynamics determination of the fluid pressure, $p=k_BT(\partial \ln \bar{Z}/\partial V)_{T,N}=k_BT(\partial \ln Q/\partial V)_{T,N}$. (This irrelevance justifies that the usual lattice fluid model yields a correct thermal equation of state in spite of the absence of an integration over momenta.) For instance, in the absence of interactions ($\Phi=0$), the configuration integral is $Q=V^N$ and the expression $p=k_BT(\partial \ln Q/\partial V)_{T,N}$ yields the ideal gas pres-

sure, $p=Nk_BT/V$. Hence, the relation $p=Nk_BT/V$ stems from the configurational entropy. This fact is also known in macroscopic thermodynamics where it is often said that the ideal gas pressure has a purely entropic origin[29] in the sense that $p=T(\partial S/\partial V)_{T,N}$. Similarly, in the ideal lattice gas, the ideal gas pressure stems from the number of distributions $\binom{N_s}{N}$, which accounts correctly for the configurational entropy of the gas. These comments do not mean that $p=Nk_BT/V$ is not related to the translational motion of the particles, but is evidence of the different possible interpretations of the ideal gas pressure.[28]

Some authors included the integration over particle momenta in the lattice fluid[26,30] and evaluated the canonical partition sum as[31]

$$\bar{Z}=\binom{N_s}{N}\sigma^{N^2/N_s}\left(\frac{V_s}{\Lambda^3}\right)^N=Zz^N, \tag{A2}$$

where Z is given by Eq. (1) and $z(T)\equiv V_s/\Lambda^3$ is the canonical partition sum of one particle in a cell. Both the usual lattice fluid model[5,9,10,12,15] and the one including the integration over particle momenta[31] predict the same pressure because $(\partial \ln \bar{Z}/\partial N_s)_{T,N}=(\partial \ln Z/\partial N_s)_{T,N}$, and hence we have employed the former in this paper. Nevertheless, Eq. (A2) has several interesting characteristics: For a dilute fluid with no interactions, it predicts the canonical partition function of an ideal gas, $\bar{Z}=(V/\Lambda^3)^N/N!$, as in Eq. (A1), because $\ln[N_s!/(N_s-N)!]\approx N\ln N_s$ for $N\ll N_s$. Also, using the relation $\bar{\mu}=k_BT(\partial \ln \bar{Z}/\partial N)_{T,N_s}$, it includes a temperature-dependent contribution from particle translations in the chemical potential, $\bar{\mu}=\mu+k_BT\ln(\Lambda^3/V_s)$, while $\mu=k_BT(\partial \ln Z/\partial N)_{T,N_s}$ in Eq. (3) does not. Moreover, using the Gibbs–Hemholtz equation $\bar{U}=[\partial(\bar{F}/T)/\partial(1/T)]_{V,N}=k_BT^2(\partial \ln \bar{Z}/\partial T)_{V,N}$, it includes the contribution from particle translations in the internal energy per particle, $\bar{u}=(3/2)k_BT-a/v$, because Eq. (A2) incorporates the kinetic energy of the particles through the integral over the particle momenta.

APPENDIX B: NEGLECTING FLUCTUATIONS OF THE NUMBER OF PARTICLES

The grand canonical ensemble for the study of the lattice fluid requires the evaluation of the sums in Eqs. (9) and (10). These sums cannot be evaluated analytically due to the term σ^{N^2/N_s}. We next discuss the consequences of introducing the approximation $N^2\approx 2N\langle N\rangle-\langle N\rangle^2$ in the exponent of σ. The quantities evaluated using this approximation are identified with a subscript NF (for negligible fluctuations).

When the approximation $N^2\approx 2N\langle N\rangle-\langle N\rangle^2$ is used, the grand canonical partition sum can be evaluated using the binomial formula, and Eq. (7) becomes $\Xi_{NF}=(\xi_{NF})^{N_s}$, where $\xi_{NF}(T,\mu)=(1+\lambda\sigma^{2\langle N\rangle/N_s})\sigma^{-\langle N\rangle^2/N_s^2}$ is the single-cell partition function. The probability distribution of N [Eq. (8)] is then transformed to the binomial distribution

$$P_{NF}(N)=\binom{N_s}{N}\frac{(\lambda\sigma^{2\langle N\rangle/N_s})^N}{(1+\lambda\sigma^{2\langle N\rangle/N_s})^{N_s}}=\binom{N_s}{N}\left(\frac{N_s-\langle N\rangle}{N_s}\right)^{N_s}\left(\frac{\langle N\rangle}{N_s-\langle N\rangle}\right)^N, \tag{B1}$$

where $\langle N\rangle$ is evaluated as a function of (T,N_s,μ) using Eq. (3), $\langle N\rangle/(N_s-\langle N\rangle)=\lambda\sigma^{2\langle N\rangle/N_s}$. This approximation transforms the equations of state, Eqs. (9) and (10), derived in the grand canonical ensemble to the corresponding ones, Eqs. (3) and (2), obtained in the canonical ensemble. The factorization $\Xi_{NF}=(\xi_{NF})^{N_s}$ implies that the cells behave independently and that $-\Omega_{NF}=k_BT\ln\Xi_{NF}=pV$ is extensive. The pressure $p=(k_BT/b)\ln\xi_{NF}$ is intensive and coincides with Eq. (2).

The fluctuation in the number of particles

$$\frac{\langle N^2\rangle_{NF}-\langle N\rangle^2}{\langle N\rangle^2}=\frac{1}{N_s\lambda\sigma^{2\langle N\rangle/N_s}}=\frac{1}{\langle N\rangle}-\frac{1}{N_s}, \tag{B2}$$

where $\langle N^2\rangle_{NF}\equiv\Sigma_{N=0}^{N_s}N^2P_{NF}(N)$, decreases with increasing $\langle N\rangle$ and becomes negligible for macroscopic systems. This trend is related to the fact that the probability distribution $P_{NF}(N)$ is unimodal and implies that Eq. (B1) cannot describe two-phase coexistence.[26] The same conclusion applies to any equation that neglects fluctuations.

Equation (2) has been derived in the mean-field approximation and the canonical ensemble. The mean-field approximation combined with the canonical ensemble implies that all cells behave similarly and have the same probability $\theta=b/v$ of being occupied so that the fluid has only one phase, consistent with the unimodal character of $P_{NF}(N)$ in Eq. (B1).

In contrast, the grand canonical ensemble describes the fact that a fluid may be found in a two-phase equilibrium state because the mean-field approximation does not imply then that the fluid must be homogeneous. Although all cells have the same (T,μ), the bimodal probability distributions in Fig. 3 indicate that different parts of the fluid may be found in (liquid and vapor) states with different particle densities.

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Apparatus Stands by CV Boys. Charles Vernon Boys (1855-1944) is known to us today mainly as the author of Soap Bubbles and the Forces That Mould Them (1890). He was a versatile experimentalist who invented the quartz fiber suspension and the Radio-Micrometer for delicate measurements of thermal radiation. On a humbler level he designed these sets of geometric tripods that were sold by W.G. Pye & Co. of Cambridge, England in 1911 for 12 shillings. The self-centering segments use grooves in two of the legs and a flat spot on the other to provide repeatable and stable positioning. These stands are still in use at Kenyon College in Ohio. (Notes and photograph by Thomas B. Greenslade, Jr., Kenyon College.)