PHYSICAL REVIEW A VOLUME 46, NUMBER 2 15 JULY 1992

Complete statistical thermodynamics of the cluster solid-liquid transition

Hai-Ping Cheng, Xiuling Li, Robert L. Whetten, and R. Stephen Berry
Department of Chemistry, The University of Chicago, Chicago, Illinois 60637
and Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024

(Received 23 December 1991)

A constant (N,P,T) statistical method is developed for a finite-size system. A scaling variable $\mathbf{a}$ is introduced to describe the size of the system following the method used for the bulk system. The histograms of the Boltzmann distribution function $f(E_c,V;T,P)$ (E_c and V being the configuration energy and the volume) for a 55-atom cluster bound by Lennard-Jones pair potentials are calculated at several (T,P) values by Monte Carlo (MC) simulations. From the density of states $\Omega(E_c,V)$ constructed from the MC results, important thermodynamical quantities are then obtained. In the phase-transition region, $f(E_c,V;T,P)$ shows a bimodal distribution on the (E_c,V) plane indicated by a "twin-peak" structure. The full phase equilibrium, including volume or pressure changes, of a cluster is explored in a systematic manner, and thus a complete picture of the phase diagram of a cluster is presented.

PACS number(s): 64.60.Ak

I. INTRODUCTION

The problem of phase transitions in finite-size systems remains one of great interest, both theoretically [1–5] and experimentally [6,7]. Second-order phase transitions are in principle well described by size-scaling theory and its critical exponents [8,9]. In practice, experiments on nanometer-scale systems (10–1000 degrees of freedom) have only begun to be treated using this theory. For first-order phase transitions [10–13] the situation is much less clearly defined, so that most of the evidence has come from simulations and from specific model partition functions adapted from the bulk. Perhaps the most ubiquitous of these transitions is the solid-liquid transition, which has been the subject of numerous simulations and formed the basis of several interpretations of experimental results [4,5,14].

One step has been the realization and formalization of the idea that the freezing-melting transition in small finite systems is simply different from that of large systems, but converges with increasing N to the standard first-order transition [3]. Where the change from bulk solid to bulk liquid appears discontinuous across the curve of equal free energies, $G_{\text{solid}}(P,T)=G_{\text{liq}}(P,T)$, this change is smooth and gradual for clusters across the corresponding curve where $G_{\text{solid}}(P,T,N)=G_{\text{liq}}(P,T,N)$ [1,15]. Nonetheless the curve along which $G_{\text{solid}}(P,T,N)=G_{\text{liq}}(P,T,N)$ is a useful characterization of at least one aspect of the phase equilibrium for finite systems, certainly the most important aspect with respect to how the sharp phase equilibrium of bulk systems evolves with increasing N from the phase equilibrium of clusters. This relation will be discussed in a qualitative way in the final section, in a manner that puts into a unified picture much of the available information about the cluster-to-bulk evolution of the solid-liquid equilibrium.

In this work, we construct the curves in the spaces of various pairs of thermodynamic variables along which the chemical potentials and free energies of solidlike and liquidlike clusters (of a fixed number of particles) are equal. It must be kept in mind that these curves do not correspond to sharp changes from all liquid to all solid as the equilibrium curves for bulk freezing and melting do.

In one important sense the theoretical and conceptual description of the solid-liquid transition has been incomplete. A complete thermodynamic description of a single-component system in the absence of external applied fields requires three parameters. In the past, only two have been specified and varied explicitly—these have been N, the number of particles, and either E, the thermodynamic (internal) or total energy, or T, the temperature. The first of these choices corresponds to an isolated cluster, or to a microcanonical ensemble of mass-selected clusters; the second corresponds to the cluster in contact with a heat bath, or to a canonical ensemble of mass-selected clusters. The natural third variable is either the volume V or the pressure P.

In the past people have dealt with this problem in one of two ways [16,17]. In the first, free boundary conditions have been used. If, during the course of a simulation aimed at computing statistical thermodynamic functions, a particle evaporated from the condensed cluster, then it would be returned to the main cluster and the simulation would be started again. This may be considered as equivalent to a time-scale constraint on an experiment conducted at essentially zero pressure. Limitations of this approach included its arbitrariness (although this is usually not a serious difficulty) of the criterion of whether a particle has evaporated—and inability to match some experimental situations, such as an inert gas or fluid compressed around an embedded cluster. Also, as one will see, it fails to permit a complete specification of the statistical thermodynamic properties of the system.

The second alternative has been to specify a constant volume in which the cluster is considered to move. If the volume is chosen comparable to the physical dimensions of the condensed cluster, then one faces the problem that the shape of the cluster becomes crucial, an artificial situation far removed from that arising in most experiments other than matrix and zeolite conditions. Potentially better for simulating gas-phase systems is to choose V to be several times the cluster volume, in which case one has a gas–condensed-phase equilibrium. This procedure corresponds to heating the cluster along the gas-solid coexistence curve in the (P,T) or (P,E) phase plane until the triple point is reached, then continuing along the gas-liquid coexistence curve. The most severe problems with this are the great difficulty in achieving true equilibrium with the gas phase at the lower temperatures, near and below the triple point, where the solid-liquid transition characteristics are observed, and in finding experimental conditions to which it corresponds.

In our recent research we have used a third approach: we explicitly introduce the pressure P as a thermodynamic variable. The meaning of P on the nanoscale might be questioned. However, in experiments one can without question increase the external pressure of an inert gas acting on a cluster, and under the condition of mechanical equilibrium this corresponds to exerting that pressure on the cluster. Similarly, a strongly bound metal, semiconductor, or compound cluster embedded in an inert fluid may be subjected to large hydrostatic pressures that are similarly well defined, so long as the clusters are immiscible in the solvent. The variable conjugate to P is of course the volume V. It might seem that V does not have a precise meaning for a cluster, and this would be true if one were to cling to a strictly geometric, continuum-based definition. However, an unambiguous, operational definition for changes in V can be obtained from the variations in the free energy function $G(P,T)$ of the cluster by inverting the integral expression $dG=\int V(P')dP'$ at constant T, in effect using the thermodynamic definition $V=-(\delta G/\delta P)_T$. In practice, with inert fluid exerting the pressure, the volume defined this way corresponds closely to the volume of the cluster that excludes the fluid, so that $P\Delta V$ is the work that must be done to change the cluster's volume against the applied pressure. For example, ΔV could be the volume change accompanying a solid-liquid transition, or merely the thermal expansion of the cluster. This kind of evaluation can be implemented in various ways, considered below, through simulations used to compute the statistical thermodynamic functions.

The outline of this work, and its significance, is the following. We describe how to compute a complete statistical thermodynamic description of an ensemble of clusters, specifically a microcanonical or canonical distribution. To do this efficiently, we expanded the one-dimensional histogramming Monte Carlo method recently developed [14,18] into two-dimensional histogramming and applied it to a real-space system here. It will allow us to compute the fundamental function, the microcanonical density of states $\Omega(E_c,V)$ over the range of interest in the solid-liquid transition. Second, we adopt the simplest of several possible methods of incorporating the pressure-volume term into this Monte Carlo method in order to complete the N,P,T ensemble. (This and more sophisticated methods, all based on size scaling, are discussed briefly in the final section.) Third, we carry out a computation on a 55-atom cluster, represented by 6-12 pair potentials giving rise to an icosahedral ground state, to illustrate this method in detail. Fourth, we analyze the results of this calculation, a complete description of the transition, to obtain relevant quantities. Finally, we discuss future improvements to the method, particularly in the volume calculation, and implications for the mechanism of the solid-liquid transition in clusters.

A full description of the traditional thermodynamic machinery for the equilibrium properties of the first-order phase transition in finite systems was given by Hill [15]. Our concern here is largely with the statistical thermodynamics, including fluctuations and thermodynamic properties.

II. MODELS OF *NPT* STATISTICS OF FINITE-SIZE SYSTEM

The difficulty of simulating a cluster under conditions of constant number of particles, pressure, and temperature (N,P,T) arises largely because the concept of volume valid for the bulk system loses it precise meaning for a small system. The surface of a cluster is rough, fluctuating, and ill defined on a scale comparable with its dimensions; the bulk material obviously may have a fixed, smooth surface whose details and fluctuations can be neglected in measurement. In experiments, the definition of the volume of a finite cluster is much clearer than in a simulation; e.g., it may be taken as the excluded gas volume. The volume of a cluster is the space occupied by the cluster that external particles cannot reach. Rigorously, at the microscopic level, the volume should be defined in a way that (i) makes physical, operational sense, (ii) has an uncertainty within acceptable range, and (iii) leads to the precise value of the density in the bulk material as N approaches infinity.

In a direct simulation of a system consisting of a cluster plus its surrounding gas atoms the shape of the system should be predetermined. The easiest approach in Monte Carlo (MC) simulation would be to assume the whole system is in a cubic box with periodic boundary conditions. The size of the clusters should be small enough to ensure that clusters in adjacent boxes do not interact with each other at all. We found that this direct method of simulation is too time consuming even if we model the gas atoms to be hard spheres; far too large a portion of computer time is spent on the gas atoms whose details of motion are of no interest to us. Also, the simulation becomes extremely inefficient at low pressures.

We present here a more efficient approach which enables us to concentrate only on the cluster itself; the role of chemically inert gas atoms in creating a constant (mean) pressure is accounted for through the control of a scaling parameter **a**. This algorithm was introduced first in the infinite-size MC simulation for the constant (N,P,T) ensemble. The method could also be used for clusters in a gas chamber. In the following discussion, we start with the general constant (N,P,T) MC simulation method and then look at the difference between a simulation with periodic boundary conditions and our extension of Andersen's method.

In the conventional N,P,T Metropolis Monte Carlo simulation, the Gibbsian free energy of a system with N particles is

$$G=H+PV \tag{1a}$$

with

$$H=-k_B T \ln Q(N,V,T) , \tag{1b}$$

$$Q(N,V,T)=(N!h^{3N})^{-1}\{[2\pi m k_B T]^{3N/2}\}\Delta(N,V,T) , \tag{1c}$$

and

$$\Delta(N,V,T)=\int \exp[-\beta U(\mathbf{r})]d\mathbf{r} , \tag{1d}$$

where $\mathbf{r}=\mathbf{a}\rho$, and the value of ρ is constrained between 0.0 and 1.0, and k_B is Boltzmann's constant. Such a dimensionless unit box can be replicated endlessly in the two-dimensional (2D) or 3D space for an infinite system. The value of the volume is reflected in the measure of a; a^3 is proportional to the volume of the system with N particles. Details of this method have been described many times elsewhere, e.g., in Abraham's review article [19]. The configuration part of the partition function of a constant (N,P,T) system is derived as

$$Z_c=\int \int dV\, d\rho \exp\{-\beta[U(\mathbf{a}\rho)+PV-Nk_B T \ln V]\} . \tag{2}$$

The simulation of such a system is easy now. The idea here is to treat $\mathbf{a}$ as an additional independent variable, so the volume $V=\mathbf{a}^3$. The total enthapy $H=U+PV$ can be varied by random moves of both ρ and $\mathbf{a}$. The quantity which determines whether or not a move is accepted now becomes

$$\delta W=\exp\{-\beta[\delta U+P\delta V-3Nk_B T \ln(1-\delta V/V)]\} ; \tag{3}$$

that is, all moves with δW less than (3) are accepted and moves with δW greater than (3) are accepted or rejected by a random-number choice.

In applying this algorithm we took two approaches. We will concentrate on one and present only a brief description and comments on the other, a method which leads to a direct simulation.

In our first method, we rewrite Eq. (2) in real coordination space $\mathbf{r}$; the partition function Z_c then becomes

$$Z_c=\int \int dV\, dr \exp\{-\beta[U(\mathbf{a}\rho)+PV]\} . \tag{4}$$

From this expression we understand now that random moves can be made on $\mathbf{r}$ and $\mathbf{a}$ (or, say, V) with the criterion

$$\delta W=\exp[-\beta(\delta U+P\delta V)] \tag{5}$$

instead of (3).

The switch from ρ space to $\mathbf{r}$ space is necessary. Sampling according to Eq. (3) in ρ space is associated with large fluctuations in V and so that handling the statistics becomes very inefficient. Recently, other applications have been made of the change from ρ to $\mathbf{r}$ in constant-P simulations for the bulk systems [20,21]. The remaining question is how to relate the operationally or experimentally defined quantity V to the parameter $\mathbf{a}$ of the simulation for a finite-size system.

As we mentioned in the preceding section, we intend to provide a definition and a way to measure the volume for a microscopic system, even though this definition may not match precisely the conventional concept of the volume we might use for that of an infinite system. However, as N increases, this microscopic quantity merges into the value of bulk volume, and its uncertainty decreases with N, becoming infinitesimally small for macroscopic systems. A limitation of this concept is that we must have some prior knowledge about the nature of the cluster, such as the radii of atoms in the cluster and in the environment.

There are at least three ways to define the volume of a system consisting of N atoms: spherical approximation, convex hull, and α hull. The first is the simplest, is quite general, and is the one we adopt here. Especially in the solid-liquid transition region, all but the smallest clusters can be treated approximately as spheres. A radius can be measured from the center of mass to the outermost atoms and a "volume" can be estimated from this radius. To remove part of the error in this estimation, particularly when some atoms may escape temporarily from the cluster, a criterion can be established to distinguish the atoms that are part of the cluster and the atoms outside the cluster at each configuration.

To execute this, we need two parameters as input: the number of nearest-neighbor bonds and the length to which such a bond can be stretched and still be called a bond. These can be estimated by looking at the low-temperature structure. If the number of bonds to some atom is less than those of a surface atom in the cold cluster, we consider this atom outside the cluster (only in estimating the value of the volume; this criterion is not related to evaporation) and do not use its distance from the center of the mass in determining the radius of the sphere. The largest center of mass to atom distance for atom in the cluster is taken as $\mathbf{a}$. The volume of the cluster is then related to a^3 by multiplying a constant factor of $4\pi/3$. For any prismatic clusters, a different criterion must be used to identify whether an atom is attached to the cluster, but the relation between volume and the size-scaling variable $\mathbf{a}$ remains straightforward.

This simulation can be performed and the statistical mechanics for a finite system can be set up. Before we present the details of simulation in the next section we describe the basic statistical thermodynamic principles. For each MC run we obtain a distribution of number of sampling points as a function of interaction energy and "volume" of the system and enable us to construct a surface in three-dimensional space. After normalization it becomes the frequency distribution of occurrences of configurations as a function of the potential energy (or configuration energy) of the system E_c and volume V. All the thermodynamic quantities can be derived from this distribution. We first assume that a MC simulation covers the entire (E_c, V) plane.

The probability function $f(E_c, V; P, T)$ can be written as

$$f(E_c, V; T, P) = \Omega(E_c, V)\exp[-\beta(E_c + PV)] \;, \tag{6}$$

where E_c, V are the thermodynamical variables; T, P are the constant parameters and $\Omega(E_c, V)$ is the density of states of the corresponding microcanonical ensemble, the quantity whose logarithm is the microcanonical entropy of the specified ensemble. Note that $\Omega(E_c, V)$ is an intrinsic function of the system independent of T and P. Once $\Omega(E_c, V)$ is obtained for a range of values of its arguments, it can be used to extrapolate thermodynamical quantities for other values of T and P. From the knowledge of $\Omega(E_c, V)$, we derive, using conventional definitions: for the microcanonical ensemble,

$$\text{entropy:}\quad S(E_c, V) = k_B \ln\Omega(E_c, V) \;, \tag{7a}$$

$$\text{temperature:}\quad 1/T(E_c, V) = \left[\frac{\partial S}{\partial E}\right]_V \;, \tag{7b}$$

and for the canonical ensemble,

partition function:

$$Z(T, P) = \int\int \exp[S(E_c, V)/k_B - \beta(E_c + PV)]dE_c dV \;, \tag{8a}$$

internal energy:

$$U(T, P) = \langle E_c \rangle = \sum_{\text{states}} E_c \Omega(E_c, V)\exp[-\beta(E_c + pV)] \;, \tag{8b}$$

$$\text{pressure:}\quad P = k_B T \left[\frac{\partial \ln\Delta}{\partial V}\right]_T \;, \tag{8c}$$

where Δ is defined in Eq. (1),

$$\text{volume:}\quad V(T, P) = \sum_{\text{states}} V\Omega(E_c, V)\exp[-(E_c + PV)] \;, \tag{8d}$$

heat capacity:

$$C_P = \left[\frac{\partial U}{\partial T}\right]_P = (1/k_B T^2)[\langle (E_c + PV)^2 \rangle - \langle (E_c + PV) \rangle^2] \;, \tag{8e}$$

$$\text{thermal expansion:}\quad \alpha = \left[\frac{\partial V}{\partial T}\right]_P \;, \tag{8f}$$

and

$$\text{isothermal compressibility:}\quad \gamma = -(1/V)\left[\frac{\partial V}{\partial P}\right]_T \;. \tag{8g}$$

The second treatment of constant-(N, P, T) conditions, which we defined earlier as a direct simulation model, is based on Monte Carlo or molecular dynamics simulations to evaluate the properties of a cluster plus inert-gas system. It is also necessary here to introduce the scaling parameter **a** in order to imitate the external pressure; the calculation follows the same procedure as in the first method. The advantage of this method is that volume of the cluster obtained this way seems to be more acceptable intuitively and the value of the volume of such a system is equal to the cube of the scaling parameter. The price one has to pay is to deal with hundreds to thousands of gas atoms which can be modeled as hard spheres and also to separate the volume of the cluster from the whole system which includes the inert gas as well. However, in order to keep the error small enough to estimate the change in the total volume and the volume of the gas atoms accurately enough to fix the change in the cluster volume, we need a minimum of about a thousand inert-gas atoms. The simulations then become very time consuming.

III. RESULTS

We performed MC simulations for the Ar_{55} cluster over a set of (T, P) values concentrated mainly in the region where a liquid-solid phase coexistence is indicated by jumps in the configuration energy and volume. The atom-atom interaction is chosen to be the pairwise Lennard-Jones (LJ) potential,

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \;. \tag{9}$$

We use reduced units in which $\varepsilon = 1$, $\sigma = 1$, and $k_B = 1$. The scaling parameter **a** is defined as the distance from the center of mass of the cluster to the nucleus of the outermost surface atom. An atom in the cluster is distinguished from an atom detached from the cluster on the basis of the number of neighbor bonds compared with the number of nearest-neighbor bonds of a surface atom in icosahedral Ar_{55}, i.e., 8. The greatest length of that bond is a parameter which is chosen to be 1.7 in our simulations. This way of defining a size parameter for the cluster is an approximation. However, in the case of the Ar_{55} cluster, in the solid-liquid region it is not a bad approximation to treat the cluster as a sphere. Refined a bit further, the volume of the cluster is estimated by the relation

$$V = (4\pi/3)(a + a_0)^3 \;, \tag{10}$$

where a_0 is the "atomic radius" of argon. In our simulations both $a_0 = 0.0$ and 0.5 are used to test the dependence of the results on the choice of a_0. The pressure P was given the values 0.0, 0.1, 0.5, and 1.0 where $P = 1.0$ in the LJ units corresponds to about 300 atms. In each simulation we let **a** change three times during 150 random moves of a single atom in (x, y, z) space. This is infrequent enough to allow clusters to relax enough before the next overall change. On the other hand, the change in **a** should be frequent enough so that the change in **a** caused by a random move in the coordinates (x, y, z) is small comparing with the explicit move in **a**. A typical run in a one-phase region consists of $2000 \times 50 = 100\,000$ cycles and a run in the coexistence region requires $2000 \times 500\,000$ cycles.

The histograms obtained for the solid region show a sharp peak; for the liquid region the peak is broader. In the coexistence region the plots of three-dimensional

$f(E_c,V)$ are bimodal distributions. They are shown in Figs. 1(a)–1(c). From Fig. 1 we see that in 3D plots the "twin peaks" identify both solid and liquid regions very well but the peaks are aligned roughly along the (E_c,V) diagonal line. Since we do see two peaks well separated it means that the system is below its critical point, if it has one. Near the critical point, one expects the two peaks to join together and form a region flat on the top (a qualitative description was given in Ref. [15]). The histogram on the (E_c,V) plane also shows that the projection of such a twin-peak structure can be viewed in 2D plots most clearly along the diagonal line while along any other direction, such as $(E_c,0)$ or $(0,V)$, the structure may be difficult to recognize. Some earlier caloric curves from simulations of Lennard-Jones clusters [22] seemed to suggest that for clusters as small as 33 atoms, the coexistence range is too narrow to be observable in experiments. This was in conflict with later results of Berry and Wales [3] and with the analysis of Ar_{55} by Labastie and Whetten [14]. The former found that the width of the coexistence region should persist, for most kinds of clusters, to arbitrarily large N. The latter demonstrated solid-liquid coexistence for the second Mackay icosahedron, the 55-atom cluster.

For each (T,P) run we construct just a piece on the density-of-states surface. The procedure for connecting these pieces together is described by Labastie and Whetten [14]. The method they invented provides an efficient tool to employ all the information from each MC run to construct a relatively complete density of states for the region of interest. We have extended the overlapping algorithm to the (E_c,V) plane (see Appendix) but have not yet implemented it in the current calculations.

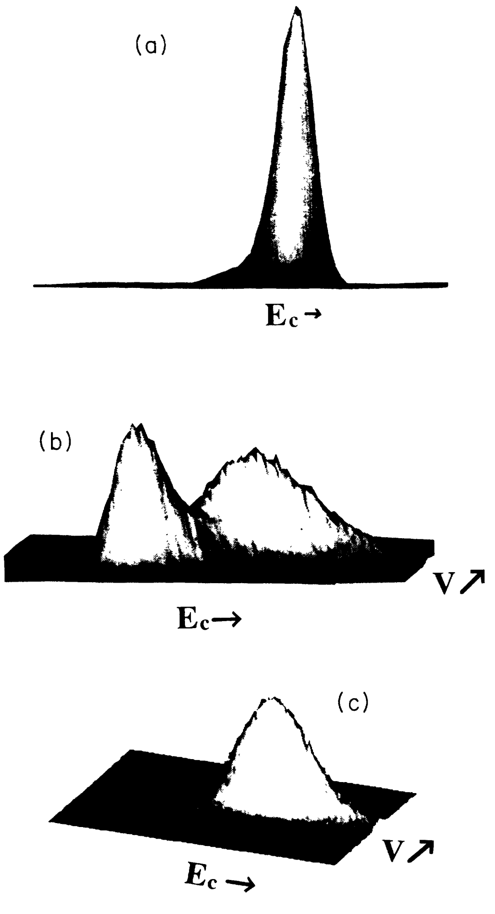


FIG. 1. Histograms of frequency as functions of E_c and V for Ar_{55}, (a) solid region, (b) coexistence region, and (c) liquid region.

Without overlapping the histograms, one is still able to obtain all the thermodynamic quantities from each window on the density-of-states surface. Through Eqs. (6)–(8) we constructed the density of states and calculated most of the important properties. The results are reliable around the center of each "window" and become less accurate away from it because in finite simulations the statistics get poorer away from the chosen (T,P) value. Figures 2–6 are, respectively, the plots of caloric curves, heat capacity, volume, thermal expansion, and pressure-volume curves around the phase coexistence region. For each MC run we calculated these curves for several (T,P) values including the set which is used in the simulations. All the calculated results portray this equilibrium in a manner consistent with the finite-system counterpart of a first-order phase transition. At zero pressure, the results agree quite well with the simulations of Labastie *et al.*, in which, below the vaporization point, the system is actually at zero pressure. The phase transition peak on the C_v curve is at $T=0.30$ of LJ reduced units, the energy changes about 22 LJ units and the volume jumps 18 LJ units which is close to a 30% expansion from the solid phase of the cluster. This number is about three times as high as in bulk argon because of the large surface of the cluster. The atoms on the surface of the liquid cluster are more mobile than those in the core region [5,23] but at the same time they still remain attached to the cluster and exclude the surrounding fluid from the cluster.

It is natural to expect that as the size of the cluster increases, the core region must play a proportionally more important role since the number of atoms in the core region increases faster than the number of atoms on the surface with the size of the cluster. As N increases the volume expansion on melting approaches that of the bulk material, and the error introduced by our simple method of measuring the volume diminishes. In fact, that error goes to zero as N approaches infinity. We should mention that earlier, the mean bond length was used as a measure of size change for Ar_{55} cluster [24] and there the value of $\langle R \rangle$ changes about only 1% from the solid region to the liquid region. In a way $\langle R \rangle$ is a measure of cluster size and it does show a sharp change at the transition. For a very small cluster, e.g., dimer or trimer, this is natural and obvious. However, as N increases the utility of this measure as a reflection of the change in the size of the system becomes much less clear and does not provide a link to the bulk phase.

At finite pressure, the volume change in the transition region decreases slightly as the pressure increases. The transition temperature band moves to higher temperatures as the pressure increases, according to the curves from each and every window. These enable us to draw a

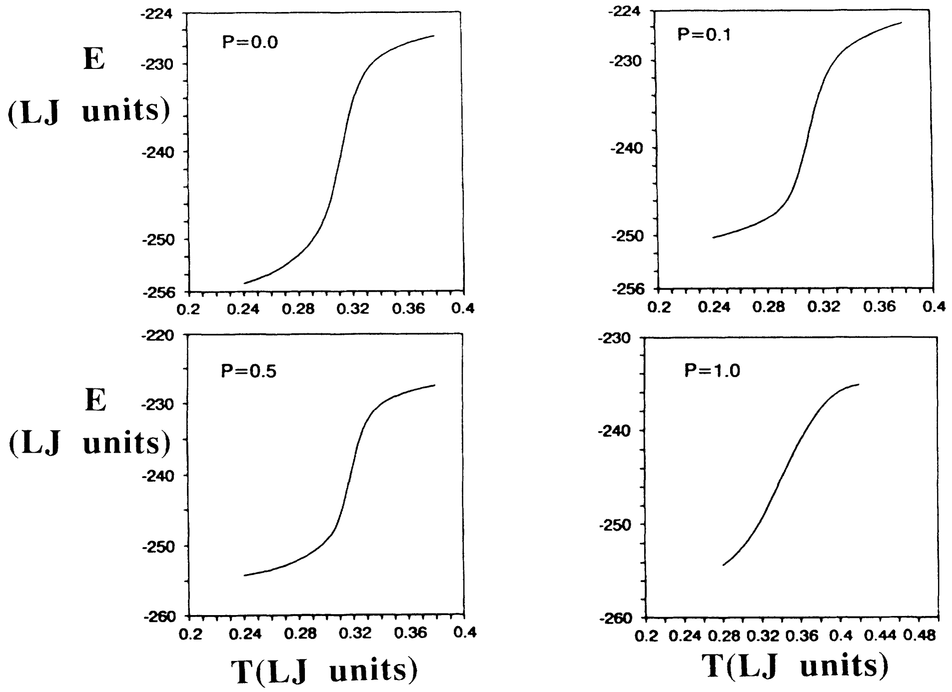


FIG. 2. Caloric curve, E vs T, for Ar_{55} at $P=0.0$, 0.1, 0.5, and 1.0. The units of energy are the Lennard-Jones well depth ε of Eq. (9); units of temperature are nominally the same, i.e., are ε/k_BT but in units in which both ε and k_B are 1. We refer to these as "Lennard-Jones units of temperature."

liquid-solid coexistence curve in the (T,P) plane, Fig. 7. At $P=1.0$, the temperature $T_c=0.34$, about 0.04 LJ units higher than the value at $P=0.0$. The transition peaks of the heat capacity and the thermal expansion become broadened as the pressure is increased. On the P-V curve the liquid-solid coexistent region is characterized by a flat region with turning points connected more smoothly to liquid and solid regions than for an infinite system. The difference in the slopes of the P-V curve corresponds to the difference in the compressibility for

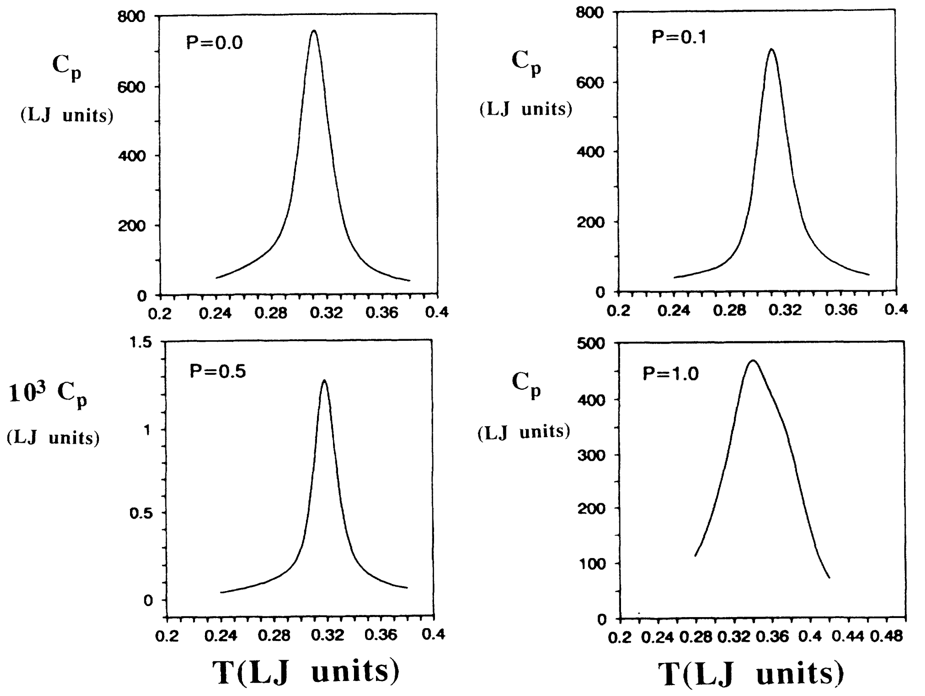


FIG. 3. Heat capacity of Ar_{55} in the transition region at $P=0.0$, 0.1, 0.5, and 1.0. Units of heat capacity are Lennard-Jones well depth per Lennard-Jones unit of temperature; these units of temperature are explained in the caption of Fig. 2.

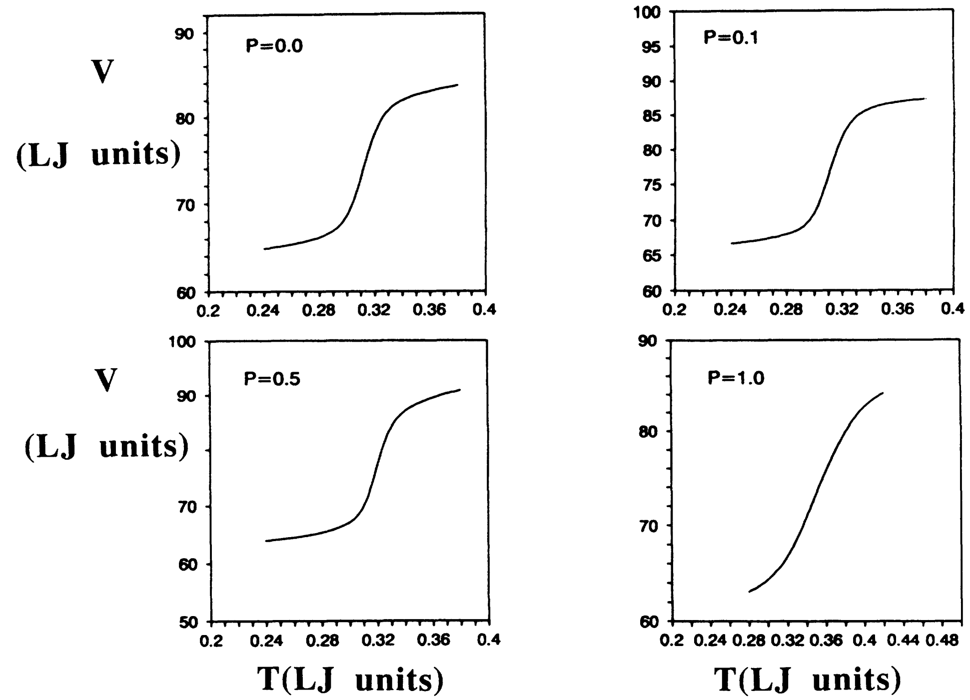


FIG. 4. Volume-temperature curve for Ar_{55} at $P=0.0$, 0.1, 0.5, and 1.0. Units of volume are the cube of the Lennard-Jones size parameter σ; units of temperature are Lennard-Jones units (see Fig. 2).

different phases. These fundamental physical properties from our calculations agree very well with the qualitative description of thermodynamics of small systems. These properties are given quantitatively for a finite-size cluster. The choice of different values of a_0 does not change the transition temperature too much (this indicates that some thermodynamical properties are not very sensitive to the error in volume calculations) but makes a difference in the values used for the volume and the relative volume change. One thing we have noticed is that as the pressure becomes higher the window through which we observe an accurate picture gets narrower and thus the scale of simulations must be made finer as P increases in order to maintain the accuracy of the calculation.

IV. DISCUSSION

We implemented the histogram method and constant-pressure method, originally developed for infinite systems, in our MC simulations in order to add one dimension to the picture of phase transitions in finite systems. The histogram of the cluster system is expanded from a one-parameter (E) to a two-parameter (E,V) function. Much richer thermodynamic information can thus be obtained from the density-of-states function which depends on both the configuration energy and the volume.

The Ar_{55} cluster has been well studied by many simulations previously, but our results provide information on the change of its size as a function of temperature and

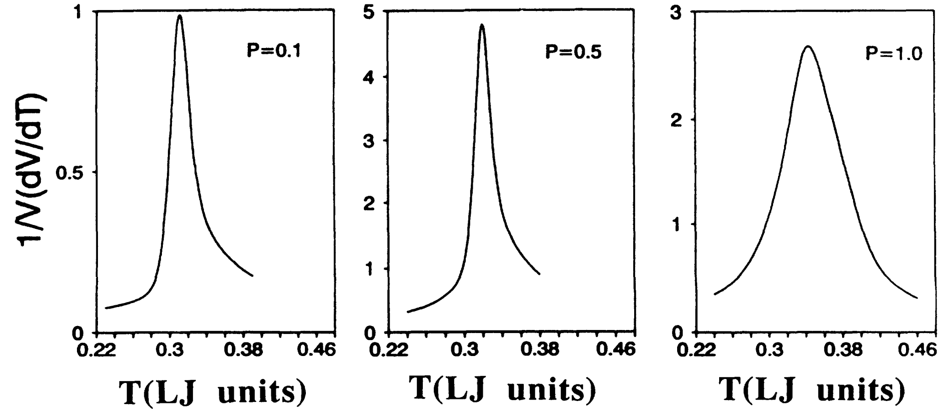


FIG. 5. Coefficient of thermal expansion for Ar_{55} at $P=0.0$, 0.1, 0.5, and 1.0. Units are K^{-1} for the coefficient and Lennard-Jones units for the temperature (see Fig. 2).

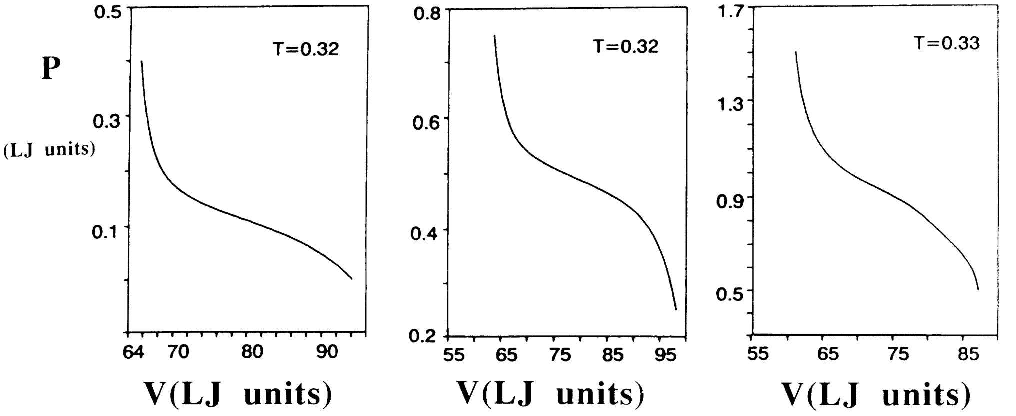


FIG. 6. Pressure-volume curve for Ar_{55} at $T=0.3$, 0.315, 0.325, and 0.337 Lennard-Jones units (see Fig. 2). Units of pressure are Lennard-Jones units, well depth ε, per unit of Lennard-Jones volume, σ^3.

pressure. This constant (N,P,T) MC simulation with histogram method can also be applied to many other cluster systems with a little careful consideration of cluster shape.

The spherical approximation used in this work thus far can be improved by use of either the convex-hull approximation or the α-hull approximation. The question is still open as to whether the thermodynamic functions and particularly the curves of equal free energies would be affected significantly by replacing the spherical approximation by a more sophisticated counterpart; in any event, it will be important to explore this issue. The convex hull is useful for moderately complicated shapes. It can be built up by a simplex method (tetrahedra in three dimensions) [25,26]; and the volume of clusters can be obtained by summing the volumes of tetrahedra, plus the products of surface area and the radii of the atoms on the surface. Mathematically, it is the intersection of many half spaces.

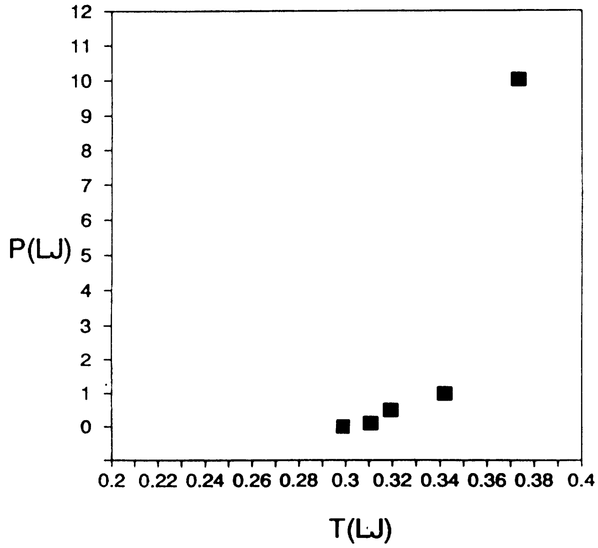


FIG. 7. Points on the curves of $G_{\text{solid}}(P,T,N)=G_{\text{liq}}(P,T,N)$ for Ar_{55} in the liquid-solid coexistence region. Energy units are the Lennard-Jones well depth *e*; temperature is in Lennard-Jones units (see Fig. 2).

If the system has important concave regions or a highly convoluted shape, the convex-hull method is not accurate enough to evaluate the volume reliably. For such cases, we probably need a still more sophisticated way to define and calculate the volume. The α-shape method [27,28] does provide a more powerful tool to study systems with arbitrary shape and topology. Instead of constructing the body by the intersection of half spaces (convex hull), this method constructs the body from the intersections of the regions excluded by predetermined spheres, or by the intersection of many spheres of negative radius. Since the radius of the sphere is an adjustable parameter, one can choose different values for the problem at hand according to the type of cluster and the surrounding gas.

In both of these methods, the volume is no longer an explicit function of **a**. The significance of **a** still remains for these systems because the overall stretching and compressing of the whole system in its environment allows us to imitate the external pressure. When **a** changes, all the interatomic distances change at once, causing the volume to change, independent of the method used to estimate the volume. A further refinement is to allow anisotropic changes in volumes. This requires that we use three scaling parameters we call **a**, **b**, and **c**. Numerically, anisotropic size scaling does not consume substantially more computer time than isotropic, one-parameter scaling and in certain types of problems it can be important to do, e.g., shear stress on matrices. However, in the trials to approach simulations of constant-*P* conditions for clusters, we adopt the very simplest way, and consider an isotropic system with only one scaling constant.

Within the temperature and pressure range of these simulations, we observed no atoms evaporating from the surface. In general, evaporation can be seen in simulations at higher temperatures or, if one waits long enough, it can be observed even in the solid region. In our past work, when we encountered such evaporation, we have stopped the simulation and started again with a different initial condition and then averaged the results from each initial condition. In this way, we preserved constant mass in our systems.

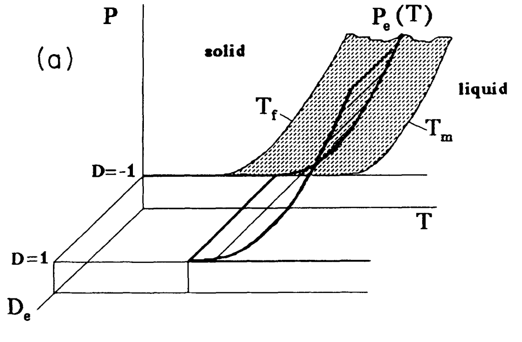
Finally, we ask what the relation is between the phase diagrams presented here for a finite cluster and those of bulk matter. Specifically we examine the traditional phase coexistence curve in a (P,T) space and sketch in a qualitative manner the corresponding picture for a cluster. To do this, instead of simply drawing a curve in the (P,T) plane along which the bulk chemical potentials μ_{liq} and μ_{solid} are equal, we add a third variable related to the equilibrium constant,

$$K_{\text{eq}}(T)=[\text{liquid}]/[\text{solid}] .$$

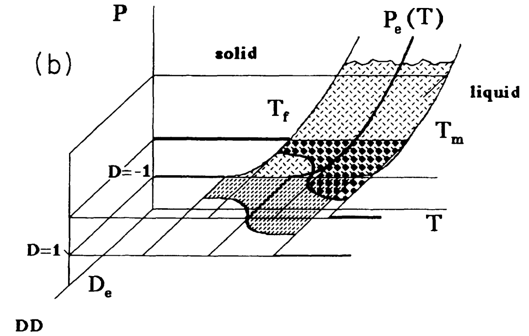
We define the equilibrium distribution $D_{\text{eq}}(T)$ [1],

$$D_{\text{eq}}(T)=[K_{\text{eq}}(T)-1]/[K_{\text{eq}}(T)+1] = \frac{[\text{liquid}]-[\text{solid}]}{[\text{liquid}]+[\text{solid}]} .$$

For a bulk system, D_{eq} is -1 in the solid region and $+1$ in the liquid region, appearing to change by a discontinuous step function but is in actuality an extremely steep but strictly continuous function around $\mu_{\text{liq}}=\mu_{\text{solid}}$ [29]. For a finite cluster of N particles, at constant P, however, $D_{\text{eq}}(T,P,N)$ is a smoothly rising, presumably monotonic, S-shaped function between $T_f(P)$, the lower temperature limit of the local stability of the liquidlike cluster, and $T_m(P)$, the upper temperature limit of the local stability of the solidlike cluster. At $T_f(P)$, $D_{\text{eq}}(T,P,N)$ is discontinuous, rising from -1 to its value $\tanh[N\Delta\mu(T_f)/k_B T_f]$. At T_m, $D_{\text{eq}}(T,P,N)$ again rises discontinuously from $\tanh[N\Delta\mu(T_m)/k_B T_m]$ to $+1$. It has been argued that for most substances, T_f and T_m can be expected to persist and remain roughly as separated when $N\rightarrow\infty$ as they are in clusters just large enough to be treated by the continuum approximation [1,3]. Figure 8 contains (a) schematic representations of $D_{\text{eq}}(T,P,\infty)$ as a function of P and T, and (b) $D_{\text{eq}}(T,P,N)$ for a relatively small N.



VERY LARGE SYSTEM



MEDIUM-SIZE CLUSTER

FIG. 8. Schematic displays of the surface $D(P,T,N)$, $\{[\text{liquid}]-[\text{solid}]\}/[\text{total}]$, for (a) $N\rightarrow\infty$ and (b) some relatively small N, e.g., 55.

At this time, we do not yet venture to speculate how $T_f(P)$ and $T_m(P)$ behave as P grows very large. The behavior at the triple point is unknown. If there were a critical point on the liquid-solid coexistence curve, then T_f and T_m could be expected to meet at that point, just as the two branches of the liquid-vapor spinodal meet at the liquid-vapor critical point. We merely present the qualitative picture, the geometric representation shown in Fig. 8, saving for future discussion the transcription of E,V distributions such as those in Fig. 1 into (P,T) distributions to the kind sketched in Fig. 8, and addressing the other open questions.

ACKNOWLEDGMENTS

R.S.B. and H.-P.C. wish to acknowledge the support of a grant from the Office of Naval Research.

APPENDIX

In parallel to the overlapping method in one parameter we write down the error function for least-squares fitting as

$$y_n(E_c,V)=N_n(E_c,V)+\beta(E_c,V) , \tag{A1}$$

$$\Delta^2=\sum_n\sum \frac{N_n(E_c,V)^2}{g_n} \times\{y_n(E_c,V)-\ln\Omega(E_c,V)+f_n+\ln n_n\}^2 . \tag{A2}$$

Minimizing Δ^2 with respect to $\ln\Omega(E_c,V)$ and f_n we obtain the equations

$$\ln\Omega(E_c,V)=\frac{\sum_n \frac{N_n(E_c,V)^2}{g_n}\{y_n(E_c,V)+f_n+\ln n_n\}}{\frac{\sum_n N_n(E_c,V)^2}{g_n}} \tag{A3a}$$

and

$$f_n=\frac{\sum_n \frac{N_n(E_c,V)^2}{g_n}\{y_n(E_c,V)-\ln\Omega(E_c,V)+\ln n_n\}}{\frac{\sum_n N_n(E_c,V)^2}{g_n}} . \tag{A3b}$$

[1] R. S. Berry, J. Jellinek, and G. Natanson, Phys. Rev. A **30**, 919 (1984).

[2] H. Reiss, P. Mirabel, and R. L. Whetten, J. Chem. Phys. **29**, 7214 (1988).

[3] R. S. Berry and D. J. Wales, Phys. Rev. Lett. **63**, 1156 (1989); D. J. Wales and R. S. Berry, J. Chem. Phys. **92**, 4473 (1990).

[4] R. S. Berry, T. L. Beck, H. L. Davis, and J. Jellinek, Adv. Chem. Phys. **90**, 75 (1988).

[5] H.-P. Cheng and R. S. Berry, in *Clusters and Cluster-Assembled Materials,* edited by R. S. Averback, J. Bernholc and D. L. Nelson, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991); p. 241; Phys. Rev. A **45**, 7969 (1992).

[6] M. Y. Hahn and R. L. Whetten, Phys. Rev. Lett. **61**, 1190 (1988).

[7] J. Bösiger and S. Leutwyler, Phys. Rev. Lett. **59**, 1985 (1987).

[8] M. E. Fisher and A. N. Berker, Phys. Rev. B **26**, 2607 (1982).

[9] Y. Imry, Phys. Rev. B **21**, 2042 (1980).

[10] J. L. Cardy and P. Nightingale, Phys. Rev. B **27**, 4256 (1982).

[11] V. Privman and M. E. Fisher, J. Stat. Phys. **33**, 385 (1983).

[12] M. E. Fisher and V. Privman, Phys. Rev. B **32**, 447 (1985).

[13] K. Binder, Rep. Prog. Phys. **50**, 783 (1987).

[14] P. Labastie and R. L. Whetten, Phys. Rev. Lett. **65**, 1567 (1990).

[15] T. L. Hill, *Thermodynamics of Small Systems* (Benjamin, New York, 1963), Chap. 5.

[16] J. K. Lee, J. A. Barker, and F. F. Abraham, J. Chem. Phys. **58**, 3166 (1973).

[17] H. Muller-Krumbhaar, in *Monte Carlo Method in Statistical Physics,* edited by K. Binder (Springer-Verlag, New York, 1986), pp. 195–223.

[18] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. **63**, 1195 (1989).

[19] F. F. Abraham, Adv. Phys. **35**, 1 (1986).

[20] Z.-G. Wang, U. Landman, R. L. B. Selinger, and W. M. Gelbart, Phys. Rev. B **44**, 378 (1991).

[21] R. L. B. Seliberg, Z.-G. Wang, and W. M. Gelbart (unpublished).

[22] T. L. Beck and R. S. Berry, J. Chem. Phys. **88**, 3910 (1988).

[23] V. V. Nauchitel and A. J. Pertsin, Mol. Phys. **40**, 1341 (1980).

[24] H. Matsuoka, T. Hirokawa, M. Matsui, and M. Doyama (private communication).

[25] R. J. Zauhar and R. S. Morgan, J. Comput. Chem. **11**, 603 (1990).

[26] S. Saxena, P. C. P. Bhatt, and V. C. Prasad, IEEE Trans. Comput. **39**, 400 (1990).

[27] H. Edelsbrunner, in *Algorithms in Combinatorial Geometry,* edited by W. Brauer, G. Rozenberg, and A. Saloma (Springer-Verlag, New York, 1987), Chap. 13.

[28] E. Mucke and H. Edelsbrunner (private communication).

[29] L. Van Hove, Physica **15**, 951 (1949).

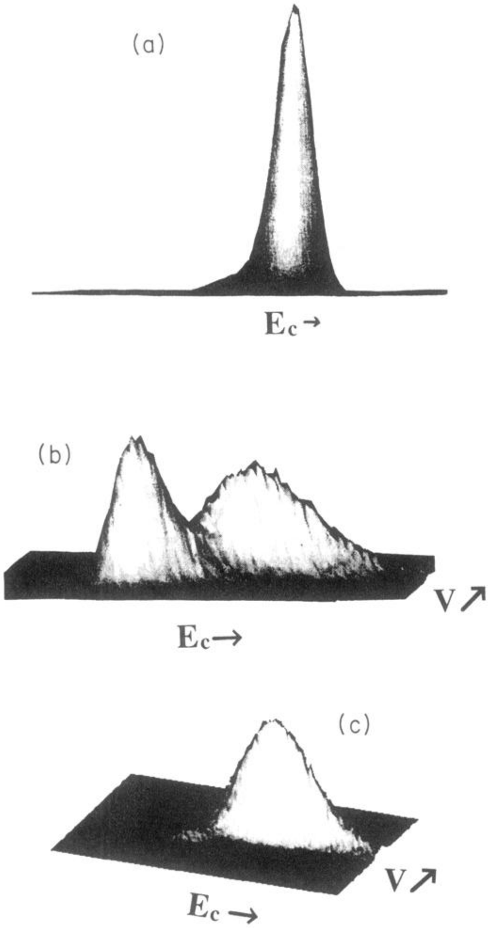


FIG. 1. Histograms of frequency as functions of E_c and V for Ar_{55}, (a) solid region, (b) coexistence region, and (c) liquid region.