Coexistence and phase separation in clusters: From the small to the not-so-small regime

David J. Wales and J. P. K. Doye
University Chemical Laboratories, Lensfield Road, Cambridge, CB2 1EW, United Kingdom
(Received 27 February 1995; accepted 16 May 1995)

We generalize the necessary and sufficient conditions for finite systems to exhibit van der Waals-type loops (or “S-bends”) in thermodynamic functions. In the infinite limit, such features are forbidden by Van Hove’s theorem, and phase separation occurs instead. However, in small systems the energetic cost of the interface associated with phase separation is too great, and there is no contribution to the partition function from regions of phase space corresponding to two phases coexisting in contact. We derive a simple model that can correctly describe both limits, and investigate how the onset of phase separation will affect observable thermodynamic properties. © 1995 American Institute of Physics.

I. INTRODUCTION

When the first simulations of finite clusters began in the early 1970’s, it was the analog of the bulk first-order melting transition that immediately attracted most interest. However, the nature of this process did not prove to be clear-cut, with somewhat different interpretations being offered by different workers, some using the Monte Carlo (MC) method, some the molecular dynamics (MD), and some both. A review of this earliest work can be found by Berry et al. Of particular interest are Briant and Burton’s MD results which they interpreted in terms of a “first-order-like” melting transition, with a calorific curve ($T$ as a function of $E$) exhibiting a van der Waals-type loop. Conceptual problems continued even after technical difficulties concerning simulations that were not properly equilibrated or were not long enough had been overcome. Honeycutt and Anderson were among the first to point out that the microcanonical MD and canonical MC calculations can in fact be different for a finite system, and interpreted the solidlike and liquidlike phases in terms of “groups of inherent structures of similar energy.” The inherent structures they refer to are simply local minima on the potential energy surface, in a terminology coined by Stillinger and Weber. In fact, there were several early attempts to calculate thermodynamic properties from distributions of minima, but these were handicapped by lack of data. However, it has recently been possible to implement a harmonic superposition approximation quite accurately, and when anharmonic corrections are included the analytical results are very close to those of simulation.

Bixon and Jortner performed model calculations in which they explicitly compared calorific curves in the microcanonical and canonical ensembles, noting that a negative slope is impossible in the latter because it is proportional to the mean-squared energy fluctuation. In fact, the “negative specific heat paradox” was previously explained in terms of the different properties of the two ensembles in an astronomical context by Lynden-Bell and Lynden-Bell. This helped to rationalize the negative specific heat found by Beckenstein and Hawking to occur in the thermodynamics of black holes. Self-gravitating systems naturally have negative specific heats; when a star or star cluster loses energy its temperature must increase because of the virial theorem. Such systems are isolated, or nearly isolated, and therefore exhibit microcanonical thermodynamics. Despite the tremendous difference in size these astronomical systems are therefore analogous to isolated clusters containing only tens of atoms. Of course, the latter are bound by more complex potentials and do not obey a simple virial theorem, so negative heat capacities are not always observed. The precise conditions under which such features arise are the subject of Sec. VI. Further evidence for the presence of a loop in the microcanonical calorific curve has subsequently appeared in atomistic simulations ranging from inert gases to gold clusters.

Labastie and Whetten provided an alternative perspective by applying the histogram Monte Carlo method to calculate the energy density of states (and hence other thermodynamic properties) directly. This work has since been extended by Cheng et al. and Weerasinghe and Amar. All the most recent studies are basically in agreement with Hill’s original two-state picture where there is a range of energies in the melting region in which a particular cluster may be found either in a solidlike or liquidlike state. In some clusters, this is manifested as a van der Waals-type loop or “S-bend” in the microcanonical calorific curve, although the appearance of this feature depends upon the properties of the different regions of phase space associated with the solid and liquid.

Despite this evidence there remains a suspicion among some workers that van der Waals loops are simply a consequence of mean-field approximations. This must certainly be the case in the bulk limit according to Van Hove’s theorem, and of course we know that all ensembles must give the same result in this limit. Since the canonical calorific curve can never exhibit a negative slope, it immediately follows that the microcanonical $T(E)$ cannot either in the bulk limit. Actually, it would be more correct to say that van der Waals loops result when regions of phase space corresponding to intermediate compositions are neglected. In the bulk limit, it is wrong to neglect the phase space corresponding to solid and liquid phases in contact, but in a finite system the energetic cost of the required interface may simply be too great, and then the solidlike and liquidlike forms are the only possibilities. We shall refer to the latter situation as coexist-
ence, and the case of phases existing in contact as phase separation. Of course, phase separation involves coexistence too, but of a fundamentally different kind. Since it has become customary in the cluster literature to refer to the two-state situation as "coexistence" we shall reserve the term for this purpose.

One obvious question is how large the system needs to be before the cost of an interface ceases to be prohibitive. In the following sections, we take the first steps towards addressing this problem. The answer will certainly depend upon the nature of the interatomic potential. For (KCl)$_2$, non-wetted structures have been found in which one part of the cluster has the rock-salt structure and the other part an amorphous liquidlike structure. However, the accumulated evidence from simulations of inert gas clusters is that several hundreds of atoms, at least, will be required, since we are unaware of any reports of phase separation in such systems to date.

The question of what happens in-between the small and infinite limits has received far less attention. However, since new experimental techniques have been developed to produce and characterize clusters containing a precise number of atoms up to sizes as large as 20,000, it seems that this regime may now be accessible. Hence, in the first part of this paper we will analyze a simple model which has the correct limit behavior, and use it to see how the change occurs.

There is also considerable support for the two-state model in small systems from other theoretical analyses. Berry and co-workers developed a quantum statistical model in which the form of the Helmholtz free energy was calculated between the rigid and nonrigid limits. This revealed a free energy barrier between the solidlike and liquidlike forms, a result also obtained from a quite different classical model by Reiss et al. using the capillarity approximation. More recently Lynden-Bell and Wales showed that the potential energy can be employed as an order parameter to reveal Landau energy barriers in magic number Lennard-Jones clusters. The order parameter approach can be generalized to pick out different regions of phase space in some detail. This helps to reconcile the interpretation of coexistence in terms of loops in the microcanonical caloric curve with an alternative analysis in terms of the short-time-averaged kinetic energy. Bimodality of this distribution indicates that the kinetic or potential energy can usefully discriminate between the solidlike and liquidlike regions of phase space. If the characteristic properties of these regions are sufficiently different then the microcanonical caloric curve can exhibit a loop, otherwise there may only be an inflection. Such studies have therefore produced various sufficient conditions for thermodynamic loops to be observed. The necessary conditions have recently been expressed in terms of probability distributions; for example, two inflections are required in the logarithm of the canonical energy distribution for a loop to appear in the microcanonical caloric curve. In Sec. VI of this paper, we will show that these necessary conditions can be generalized, and that they can be stated in a number of equivalent forms.

There is one assumption that is inherent in all of these results, namely that the phase space of the cluster is restricted to bound geometries, i.e., we do not allow atoms to evaporate. This is most often achieved by placing the cluster in a container, and the effect of the container size has been investigated systematically by Tsai and Jordan. Alternatively, one can impose a distance cutoff, and take appropriate action in a simulation if an atom attempts to violate this threshold. Although a cluster in vacuo may be inherently unstable with respect to evaporation, bound species can exist for long enough to develop well-defined thermodynamic properties. Furthermore, this appears to be generally true for temperatures in the region of the melting transition. Hence, all the analytical results that follow are implicitly restricted to the bound phase space.

II. FROM COEXISTENCE TO PHASE SEPARATION

The two-state model, previously considered by many authors, basically assumes that the density of states, $\Omega(E)$, can be written in terms of contributions from solidlike and liquidlike regions only:

$$\Omega(E) = \Omega_s(E) + \Omega_l(E).$$

Here we wish to add a term $\Omega_{mix}(E)$ corresponding to the solid and liquid in contact. It then follows that the microcanonical temperature, defined by $1/T = (\partial \ln \Omega(E)/\partial E)_{N,V}$, may be written

$$\frac{1}{T} = \frac{p_s}{T_s} + \frac{p_l}{T_l} + \frac{p_{mix}}{T_{mix}},$$

where, e.g., $p_s = \Omega_s(E)/\Omega(E)$ is the probability of finding a cluster in the solidlike region of phase space, and $1/T_s = (\partial \ln \Omega_s(E)/\partial E)_{N,V}$. We have set Boltzmann’s constant to unity for convenience. For $\Omega_s$ and $\Omega_l$, we employ a simple form that is known to be sufficient to produce a microcanonical $T(E)$ loop for suitable values of the parameters. As mentioned above, various sufficient conditions are known in terms of the distribution of local minima and the variation of the normal mode frequencies between minima from the solidlike and liquidlike regions. To render the calculations for systems containing thousands of atoms tractable we will simply take

$$\Omega_s(E) = \frac{E^{k-1}}{(k-1)!} \nu_s^k$$

and

$$\Omega_l(E) = \frac{(E - \Delta(N))^{k-1}}{(k-1)!} \nu_l^k,$$

where $\nu_s$ and $\nu_l$ are the mean vibrational frequencies associated with minima in the solid and liquid regions and $\nu = 3N - 6$ where $N$ is the total number of atoms. Hence we are not explicitly considering the distributions of minima, but subsuming all the differences between the regions into the mean potential energy difference, $\Delta$, and the mean vibrational frequencies. Our formulas are basically simplifications of the harmonic superposition approximation. Although it is necessary to account for well anharmonicity to obtain quantitative agreement between analytic partition functions and simulations the harmonic superposition approximation gives a qualitatively correct account of thermodynamic functions and therefore seems a reasonable starting point for this analysis.
The form we will take for $\Omega_{\text{mix}}$ at a given composition with $N_s$ and $N_l=N-N_s$ atoms in the solidlike and liquidlike parts, respectively, allows for the energy of the interface and employs forms for the densities of states of the two regions that are analogous to those we have assumed for $\Omega_l$ and $\Omega_s$. To obtain the total $\Omega_{\text{mix}}$ we need to sum over contributions from all compositions consistent with the total energy and the cost of the interface. If we also needed to convolute the densities of states of the solidlike and liquidlike parts over different partitionings of the energy between the two regions the result would be difficult to evaluate numerically. However, there is probably no need to do this, since it is reasonable to assume that the solidlike and liquidlike parts have the same microcanonical temperature, because they are in contact and can exchange energy. If we continue to assume a harmonic approximation for the separate regions then

$$\frac{E_s}{3N_s-7} = \frac{E-I-\Delta-E_s}{3N_l-7},$$

which is easily solved for $E_s$ and hence we obtain $E_f$ from $E_f=E-I-\Delta-E_s$ for given total energy and composition. If we take $N_s$ as the dependent variable and write the solution of the above equation as $E_s^{*}$ then the resulting expression for $\Omega_{\text{mix}}$ is

$$\Omega_{\text{mix}}(E) = \sum_{N_s,\min}^{N_s,\max} \left(\frac{E_E^{*}}{3N_s-7} - \left(\frac{E-I(3N_s-7)}{3N_l-7!}\right)^{\frac{1}{2}}\right)^{3N_l-7},$$

where $I$ and $\Delta$ must now be written as functions of $N_s$ and we exclude terms with $E_s^{*}$ or $E_l^{*}$ negative.

We now parametrize the frequency ratio in terms of $\Delta$ and $E_{1/2}$ where $\Omega_{\text{mix}}(E_{1/2}) = \Omega_{\text{mix}}(E_{1/2})$ so that:

$$\tilde{\nu}_l = \frac{E_{1/2}}{E_{1/2}^{*}} = \left(\frac{3N_l-7}{3N_s-6}\right)^{1/2}.$$

If we neglect the variation of $\tilde{\nu}_l$ with $N_s$ then this factor can be set to unity without affecting the calculated caloric curves. We also take $\tilde{\nu}_l=(1-\Delta/E_{1/2})<1$, with $\Delta(N_s) = a(N_N-N_s)$ and $E_{1/2} = b(N-N_s)$ where $a$ and $b$ are the assumed constants of proportionality. Hence $\tilde{\nu}_l$ is independent of the size of the liquidlike phase in this approximation, and it is convenient to take $b=1$ to fix the position of $E_{1/2}/N$ to unity when comparing $T(E)$ for different $N$. Hence the simplified expressions for the densities of states are

$$\Omega_s(E) = \frac{E_{1/2}^{*}}{(K-1)!}, \quad \Omega_l(E) = \frac{(E-E_{1/2}^{*})^{K-1}}{(K-1)!},$$

$$\Omega_{\text{mix}}(E) = \sum_{N_s,\min}^{N_s,\max} \left(\frac{E_E^{*}}{3N_s-7} - \left(\frac{E-I(3N_s-7)}{3N_l-7!}\right)^{\frac{1}{2}}\right)^{3N_l-7},$$

with 0 < $a < 1$. It is the terms in $1-a$ that make the liquidlike phase space dominate at high energy. We would expect to obtain a similar result by taking into account the distribution of minima for the liquid and solid, and we can think of these terms as generic factors which allow for the larger number of minima and the “softer” normal mode frequencies in the liquidlike regions.

The dependence of the interfacial energy upon $N_s$ can be used to determine the way in which phase separation occurs, e.g., whether a surface layer melts first or whether the boundary is essentially planar with one side of the cluster solid and the other liquid. For simplicity, we first considered a cube of atoms of side length $n$ so that $N=n^3$. The microcanonical caloric curve was calculated assuming that melting could occur only in layers of $n^2$ atoms. The interfacial area is then constant, and we took $l=\pi n^2$ for each term in the sum over $N_s=n^3, 2n^2, ..., (n-1)n^2$. The variable parameters are then the interfacial energy per unit area, $\epsilon$, the mean difference in potential energy per atom between solidlike and liquidlike clusters $a$ and the total number of atoms $N$. In the bulk limit, $\epsilon$ and $a$ can be identified with the difference in surface tensions between solid and liquid and the latent heat of fusion per atom, respectively.

We first need to know the effect of varying $N$ and $a$ on the microcanonical $T(E)$ when phase separation is excluded (or $\epsilon=\infty$). We define the melting temperature, $T_m$, as the temperature above which there is only one liquidlike branch of $T(E)$, and the freezing temperature, $T_f$, as the temperature below which there is only one solidlike branch of $T(E)$. Hence $T_m>T_f$ and the associated energies satisfy $E_m<E_f$. Figure 1(a) shows that $T_m^*-T_f$ increases with $N$, while $E_f/N-E_m/N$ decreases. For $N$ fixed $T_m^*-T_f$ increases with $a$ while $E_f/N-E_m/N$ decreases slightly [Fig. 1(b)]. The liquidlike branch of $T(E)$ is systematically shifted with $a$ as expected from our simple model where $T_m^* = (E-E_{1/2}^{*})(3N_s-7)$. The fixed values used in Fig. 1 give typical results from the range of parameter values where a loop occurs.

III. STEPWISE MELTING BY PLANES OF ATOMS

We now consider the effects of including $\Omega_{\text{mix}}$ when $\epsilon$ is not infinite. Figure 2 shows results for $N=125$ and $N=1000$ with various values of $a$ and $\epsilon$. A factor of 6 was also included in $\Omega_{\text{mix}}$ to allow for the six different orientations that a separated system might adopt; this makes no qualitative difference to the results. Figure 2(a) shows that for $N=125$ and $a=0.25$ the effect of phase separation is to flatten the loop, decreasing $T_m^*-T_f$ and increasing $E_f-E_m$. The loop does not disappear completely, even for $\epsilon=0$.

Figure 2(b), we see that the extent to which the loop is flattened out depends significantly upon $a$. For $a=0.15$ the effect is quite similar to that in Fig. 2(a), while for $a=0.25$ $T(E)$ has an almost horizontal branch centered on $E_{1/2}/N$. The probability of a cluster being found in a phase-separated state, $p_{\text{mix}}(E)$, becomes almost rectangular, with a maximum value of 1, for $a=0.25$. However, the signature of the loop is not completely lost, even for $a=0.25$, where there are still “overshoots” at both ends of the flat region. All the calculations were performed with Mathematica.31

Figure 2(c) shows the results for $N=1000$, $a=0.6$ and various values of $\epsilon$. For $\epsilon=\infty$ $T(E)$ is essentially Z shaped, with a step at $E_{1/2}$, as predicted previously.19 However, for the smallest values of $\epsilon$ the “overshoots” have essentially
disappeared, although the flat region now exhibits ten ripples, or miniature loops. These result from the restriction that the cluster must melt in $n$ discrete planes of $n^2$ atoms, where $n=10$ in this case. This figure gives a clear visualization of the fact that loops result when intermediate regions of phase space are not accessible or excluded.

IV. STEPWISE MELTING BY SURFACE LAYERS

Instead of forcing the cluster to melt stepwise in discrete planes of atoms we can easily perform analogous calculations when melting occurs from the outside in or from the inside out in terms of discrete layers of atoms. Since surface melting is expected to be by far the most common phenomenon, we restrict ourselves to this case. Of course, there have been numerous previous studies of surface melting including simulations of liquid drops and, implicitly, the work of Reiss et al. involving the capillarity approximation. Nauchitel and Pertsin reported phase separation in their Monte Carlo studies of 55-atom Lennard-Jones clusters ($\text{LJ}_{55}$), where they characterized a solid 13-atom core surrounded by a fluidlike shell. They adjusted the effective pressure acting on the cluster, or that the pressure exerted by the container may have significant effects. Since Nauchitel and Pertsin report that cuboctahedral configurations are found in their simulations, which we would never expect from our results near the zero pressure limit, it seems likely that the higher pressure causes the difference. This aspect deserves further investigation, since it would rather interesting if the cuboctahedron, which is a transition state on the potential energy surface, becomes preferentially stabilized by finite pressure. We also note that the definition of pressure in such simulations is nontrivial.

In a previous model, Cheng and Berry concluded that only a single minimum in the Helmholtz free energy existed for model copper clusters as a function of the number of surface defects, defined by the number of atoms migrating over the surface of a cluster. However, Kunz and Berry revised this opinion in the context of their simulations of $\text{LJ}_{55}$ and $\text{LJ}_{147}$ and extension of the defect model of melting due to Wales and Berry. In the latter model, the microcanonical and canonical partition functions are a sum over contributions from regions of phase space with different numbers of defects. If the potential energy increases monotonically with the number of defects in the physically meaningful range, but the rate of increase is negative, then a loop can exist in the canonical temperature as a function of the defect density. This means that the probability distribution for the defect density is bimodal, with two maxima, for a specific range of the canonical temperature, and so, therefore, is the canonical probability distribution function of the potential energy. This follows because of the relation between the number of defects and the potential energy described above. In this case, as discussed in Sec. VI, the isopotential caloric curve has a loop, and this is a necessary, but not a sufficient, condition for there to be a loop in the microcanonical caloric curve. The most important conclusion of this mean field model is therefore that the net defect–defect interaction must be attractive for a loop to be possible in the microcanonical caloric curve.

Kunz and Berry have extended this approach to consider core and surface defects separately, and show that loops can be obtained in the canonical temperature as a function of either defect density for certain parameter ranges. Once again, the loops are only possible if the defect–defect interaction lowers the energy. This approach amounts to a two-
state model for the surface and a two-state model for the core. However, they further suggest that the lack of any feature due to surface melting in Labastie and Whetten’s results might be due to the sampling algorithm those authors employed. In fact, the surface defect states do not contribute a feature to the microcanonical caloric curve for LJ, primarily because their properties are not sufficiently different from the icosahedron. This is clear from Figs. 6 and 7 of Ref. 8, where the separate contributions of the surface defect structures in question are evaluated for various properties.

We emphasize that neither the loop in canonical temperature as a function of defect density, nor the existence of an order parameter for which the short-time-averaged temperature is bimodal, necessitate a loop in the microcanonical caloric curve. Lynden-Bell and Wales have shown that double minima do exist in the Landau free energy for LJ and LJ if the potential energy is employed as an order parameter. However, these minima were identified with the liquid- and solidlike states of the cluster, with no separate feature existing for the surface defect states.

We therefore prefer to identify surface melted states with sets of minima that exhibit a region where the atoms have characteristically higher potential energy and have soft vibrational modes primarily localized in this region. Our viewpoint is then that of the partition function constructed from superpositions of densities of states from different minima, and is consistent with our choice for the model developed in the above sections. We return to the question of the limits of the sum for \( V_{\text{mix}} \), i.e., the size of the region needed to exhibit a distinctive surface melted state in the next section. The model presented in the present work extrapolates smoothly to the bulk limit, whereas the nature of the core and surface

---

**FIG. 2.** Results for cubes of 125 atoms (a) and 1000 atoms (b), (c) where melting is allowed to occur in successive planes of atoms. In each case, the upper plot is the microcanonical \( T(E) \) and the lower plot is \( p_{\text{mix}} \), the probability of finding a cluster in a phase separated state as a function of energy. In (a), \( a=0.25 \). In (b), results for two different values of \( a \) are shown, i.e., 0.15 and 0.25. Part (c) shows results for \( a=0.6 \), with \( \epsilon \) ranging from 0 to \( \infty \). The ripples in the otherwise flat region of \( T(E) \) for small \( \epsilon \) are caused by the system only being allowed to melt in complete layers.
defects is likely to change with size. The features that we find in the microcanonical \( T(E) \) might be measurable experimentally by calorimetry in the future.\(^{14}\) Molecular clusters may be especially fruitful systems for study in this regard.\(^{41}\)

A cube with side length corresponding to \( n \) atoms has \( n/2 \) or \( (n+1)/2 \) layers of atoms for \( n \) even and odd. If \( m \) layers have melted, where \( m=1 \) corresponds to the surface layer, then it is easy to show that \( N_s = 2m(4m^2 - 6mn + 3n^2) \) and \( N_l = (n-2m)^3 \). We took the interfacial energy to be proportional to the number of surface atoms of the solid core, i.e., \( I = \varepsilon(6(n-2m)^2 - 12(n-2m) + 8) \). The sum for \( \Omega_{\text{mix}} \) then runs from \( m=1 \) to \( n/2-1 \) or \( (n-1)/2 \) for \( n \) even and odd. The results corresponding to Fig. 2(a) are then very similar, except that \( p_{\text{mix}}(E) \) has a longer tail at high energy. The analogs of Figs. 2(b) and 2(c) show much more pronounced oscillations in the region of phase separation, corresponding to the melting of successive layers. This effect can be ascribed to the smaller number of steps in which melting is allowed to occur, i.e., half as many as for the previous section.

Smoother results can be obtained using a more realistic model in which more layers are recognized. Cuboctahedra and Mackay icosahedra\(^{42}\) exhibit complete structures of \( O_h \) and \( I_h \) symmetry, respectively, for \( 13, 55, 147, 309, \ldots \) atoms, corresponding to \( n = 2, 3, 4, 5 \) in the formula \( N(n) = (2n-1)(5n^2 - 5n + 3)/3 \). In this case, we can allow the surface to melt in layers with \( 1 \leq m < n-1 \), for which \( N_s = (2(n-m)-1)(5(n-m)^2 - 5(n-m) + 3)/3, N_l = m(11 + 15m + 10m^2 + 30n(n-m-1))/3 \) and we take \( I = 10(n-m)(n-m-2) + 12 \). This provides for more steps in the melting process than for the cube, but still fewer than for melting in terms of atomic planes. The results which correspond to Figs. 2(b) and 2(c) are shown in Figs. 3(a) and 3(b). They are qualitatively similar to those obtained for surface melting of the cube, but there are more oscillations of smaller amplitude. The oscillations are again more pronounced than in the previous section, and are simply artifacts of the discrete set of compositions included in \( \Omega_{\text{mix}} \). However, the qualitative effect of incorporating phase separation is clear, namely to flatten out the loop that is obtained for the two-state model in the large system limit.

**V. A CONTINUOUS MODEL OF PHASE SEPARATION**

To remove the extra oscillations obtained in the above results we must evaluate \( \Omega_{\text{mix}} \) more accurately. We considered including only the largest contribution to the sum for each value of \( E \). However, we were unable to implement this approach efficiently enough to treat large clusters. Furthermore, calculating the contributions to \( \Omega_{\text{mix}} \) separately suggested that this approximation might not be very good, at least for clusters of 1000 atoms. Instead we consider a continuous approximation to surface melting where \( N_s \) varies from \( N_{s_{\text{min}}} \) to \( N_{s_{\text{max}}} \) in steps of one, \( I = \varepsilon N_s^{2/3} \), and \( \Delta = a N_s \) as before. In this section, we consider the effects of our choice of the minimum and maximum values for \( N_s \) and systematically investigate approximations to the complete sum.

The cut-offs depend on how many atoms we consider necessary for distinctive solid- and liquidlike regions to be produced, and are therefore not easy to guess. We first present results where \( T(E) \) is calculated taking only the terms spaced at intervals of \( N/20 \) in the \( \Omega_{\text{mix}} \) sum for clusters containing 500 to 40 000 atoms [Fig. 4(a)]. For 500 atoms we see the familiar loop, but at 40 000 atoms the loop region has almost completely disappeared and has been replaced by the horizontal branch expected in the infinite limit. Such behavior is present in the MD results for lead obtained by Lim et al. using a glue potential,\(^{43}\) but were not recognized as

---

**FIG. 3.** Results for icosahedra or cuboctahedra of 1415 atoms where surface melting is allowed to occur in eight steps. In each case the upper plot is the microcanonical \( T(E) \) and the lower plot is \( p_{\text{mix}} \), the probability of finding a cluster in a phase-separated state as a function of energy. In (a), results for two different values of \( a \) are shown, i.e., 0.15 and 0.25. Part (b) shows results for \( a=0.6 \), with \( \varepsilon \) ranging from 0 to \( \infty \). In contrast to Fig. 2(c) the additional oscillations decrease in separation and amplitude as \( E \) increases.
such. For 40 000 atoms the results were indistinguishable
from those obtained by including every 40th term in the sum
for \( \Omega_{\text{mix}} \).

For \( N=55 \) and \( N=56 \) we calculated \( T(E) \) for \( N_{\text{r},\text{min}} = 20 \) and \( N_{\text{r},\text{max}} = N - 20 \) using every possible step size
between 1 (every term included) and 28 (only one term
included). The results are shown for \( N=55 \) in Fig. 4(b); those
for \( N=56 \) were very similar. The loop which arises when 
\( \epsilon=\infty \) (no phase separation admitted) is clearly most flattened
(for finite \( \epsilon \)) when we take every term in the sum, and \( T(E) \)
systematically tends towards the \( \epsilon=\infty \) limit as fewer terms
are included.

Figure 4(c) shows analogous results for \( N=1000 \), with
the step size in the sum ranging from 1 to 50 and \( N_{\text{r},\text{min}} = 20, N_{\text{r},\text{max}} = N - 20 = 980 \). Again the more accurately we
evaluate \( \Omega_{\text{mix}} \), the flatter the loop region becomes. However,
taking only every 50th term, which corresponds to terms
spaced by \( N/20 \) as for Fig. 4(a), still gives a good idea of the
overall effect. We therefore consider this a reasonable
tradeoff between accuracy and efficiency, and conclude that
the gradual flattening of the loop region with increasing size
shown in Fig. 4(a) is a sensible prediction of how the finite
size effect upon the microcanonical \( T(E) \) might change from
the very small to the very large system limits. This was the
principal aim of this first part of the paper. It is also note-
worthy that the caloric curves for which phase separation is
excluded can be interpreted in terms of superheating and
supercooling. The flattened curves are appropriate for the
equilibrium situation; however, it might still be possible to
observe the solid-like or liquid-like clusters if kinetic factors
prevent equilibrium from being achieved.

VI. EQUIVALENT CONDITIONS FOR LOOPS TO OCCUR

Sufficient conditions for loops to arise in thermodynamic
functions can be found for finite systems in various forms, as
mentioned above. In this section we will show that there are
a number of equivalent necessary conditions, building on the
result of Wales and Berry.\(^{44} \) No assumptions about the nature
of the density of states will be made here, except for the
implicit restriction to bound clusters.

Let \( I \) and \( X \) represent conjugate intensive and extensive
thermodynamic variables. Wales and Berry\(^{44} \) showed that the
presence of a loop in \( I(X) \) in an ensemble with \( X \) fixed
means that \( (\dot{X}^2 \ln \dot{X}(X)/\partial X^2) \) must have two zeros, i.e.,
\( \ln \dot{X}(X) \), the probability distribution of \( X \) in the conjugate
ensemble with \( I \) fixed, has two inflections. The other two
variables that are needed to define the state of the system
must be the same in the two ensembles. We then consider the
thermodynamic function \( B \) which is a natural function of \( X \),
so that \( dB \) contains the term \( IDX \), and is related to a partition
function \( Z(X) \) by \( B=\ln Z(X) \). The thermodynamic function
\( \ddot{B}=B-IX \), a Legendre transform of \( B \), is then a natural
function of \( I \) so that \( dB \) contains the term \(-XI\dot{I}\) and is
related to partition function \( \dot{Z}(I) \) by \( B=\ln \dot{Z}(I) \). If \( B \) and \( \dot{B} \)
have dimensions of energy then \( B=-T \ln Z(X) \) and \( \ddot{B}=\)
\(-T \ln \dot{Z}(I) \) are the appropriate relations, where we continue
to take \( k=1 \).

FIG. 4. (a) Microcanonical \( T(E) \) calculated for surface melting with the
continuous model, taking \( a=0.2, \epsilon=0 \) and including terms spaced at
intervals of \( N/20 \) in the sum for \( \Omega_{\text{mix}} \). (b) \( T(E) \) for \( N=55, a=0.2, \epsilon=0 \) with
\( N_{\text{r},\text{min}} = 20 \) and \( N_{\text{r},\text{max}} = 35 \). The sum for \( \Omega_{\text{mix}} \) is evaluated including every
term, every second term etc. up to a step of 28 for which only one term with
\( N_{\text{r}} = 28 \) is included. (c) \( T(E) \) for \( N=1000, a=0.2, \epsilon=0 \) with \( N_{\text{r},\text{min}} = 20 \)
and \( N_{\text{r},\text{max}} = 980 \). The sum for \( \Omega_{\text{mix}} \) is evaluated including every term,
every second term etc. up to a step of 50 for which 19 terms are included as
for (a).
If the conjugate variables are $E$ and $1/T$ then the appropriate ensembles are, of course, the microcanonical and canonical and the corresponding thermodynamic functions can be taken as $S$ and $-A/T=S-E/T$ with

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

and

$$-d\left(\frac{A}{T}\right) = -E d\left(\frac{1}{T}\right) + \frac{P}{T} dV - \frac{\mu}{T} dN.$$

For conjugate variables $N$ and $\mu$ the appropriate ensembles are the canonical and grand canonical where the corresponding thermodynamic functions are $A$ and $-PV=A-\mu N$ with

$$dA = -SdT - PdV + \mu dN$$

and

$$-d(PV) = -SdT - PdV - Nd\mu.$$

It is easily shown that the two partition functions are related by $\tilde{Z}(I) = \int Z(X) \exp(-IX)VX$ assuming $X$ is continuous. The probability distribution of $X$ in the ensemble with $I$ fixed is therefore

$$\mathcal{A}(X) = Z(X) e^{-XI/\tilde{Z}(I)}.$$  (1)

From this Wales and Berry derived the condition for the mean value of $I$ to exhibit a loop as a function of $X$ in the ensemble where $X$ is fixed. Differentiating we find

$$\left(\frac{\partial \ln \mathcal{A}(X)}{\partial X}\right)_I = \frac{\partial \ln Z(X)}{\partial X} - I = \langle I \rangle - I,$$

$$\left(\frac{\partial^2 \ln \mathcal{A}(X)}{\partial X^2}\right)_I = \left(\frac{\partial I}{\partial X}\right),$$

where $\langle I \rangle$ is the expectation value of $I$ in the ensemble with fixed $X$. A loop in $\langle I(X)\rangle$ necessitates two turning points in this function [see, e.g., Fig. 1(a)] and hence two inflections in $\ln \mathcal{A}(X)$. No loop is possible for $\langle X(I)\rangle$ in the other ensemble because the derivative of $\langle X \rangle$ is proportional to the mean-square fluctuation of $X$.

Simple considerations of thermodynamic stability show that the branch between the two turning points of a loop generally corresponds to instability. For example, in the microcanonical ensemble the entropy must be a maximum, and the system is stable with respect to energy fluctuations if $(\partial I/\partial E)_{N,V} > 0$, and unstable for the opposite sign. The same is true for the derivative $(\partial \mu/\partial N)_{V,E}$ for fluctuations in $N$ and $-(\partial P/\partial V)_{N,E}$ for fluctuations in $V$. In the canonical ensemble the last two conditions define a minimum in the Helmholtz free energy and a stable state, except that constant $E$ is replaced by constant $T$. The corresponding result in the generalized ensemble can be obtained by considering a system with $X$ constant undergoing local fluctuations in $X$ in two parts such that $X$ is conserved.

We now extend the above analysis and show that there are a number of conditions that are equivalent to the appearance of an $S$-bend in the microcanonical $T(E)$. The generalization of this theory to other pairs of conjugate variables should be obvious. First, since

$$\left(\frac{\partial^2 \ln \mathcal{A}(E)}{\partial E^2}\right)_{N,V} = \left(\frac{\partial^2 \ln \mathcal{A}(E)}{\partial E^2}\right)_{N,V} = \left(\frac{\partial^2 S}{\partial E^2}\right)_{N,V},$$

it is clear that the double inflection condition could be phrased equally well in terms of $\ln \mathcal{A}(E)$ or $S$. With the reasonable assumption that $T(E)$ increases monotonically with $E$ for $E<E_m$ and $E>E_f$ and decreases monotonically between these points we can derive some less trivial results by considering

$$\left(\frac{\partial \ln \mathcal{A}(E)}{\partial E}\right)_{N,V} = \frac{1}{(T_f - T^2)}.$$

If $T_f<T<T_m$ then there are three solutions to the equation $(\partial \ln \mathcal{A}(E)/\partial E)_{N,V}=0$; one for an energy $E<E_m$, one for an energy $E>E_f$ and one for an intermediate energy. For a canonical temperature $T$ outside this range there is always a single solution. Furthermore, it is clear from the sign of $(\partial^2 \ln \mathcal{A}(E)/\partial E^2)_{N,V}$ that the three stationary points of $\ln \mathcal{A}(E)$, when they exist, correspond to two maxima and an intervening minimum. Otherwise this function has a single maximum. Hence, we conclude that if the microcanonical $T(E)$ exhibits a loop with turning points at $T_m>T_f$ then the function $\ln \mathcal{A}(E)$ is bimodal for canonical temperatures in this range.

For an arbitrary function, $g(x)$, it does not follow that $g(x)$ will exhibit two inflections if $\ln g(x)$ does. However, $\mathcal{A}(E)$ certainly exhibits the same stationary points as $\ln \mathcal{A}(E)$ [so long as $\mathcal{A}(E)$ does not also vanish], and so we can say that $\mathcal{A}(E)$ must also be bimodal for $T_f<T<T_m$ under the same conditions. This is clearly true for the function plotted by Labastie and Whetten and has been observed in previous calculations using the superposition approximation.

Lynden-Bell and Wales have derived the analogous results for the isopotential ensemble, in which the configurational energy, $E_c$, is held constant. Their results are immediately obtained from the above formulas by substituting $\Omega(E)$ by $\Omega_c(E_c)$, the configurational density of states, $\mathcal{A}(E)$ by $\mathcal{A}(E_c)$ etc., where $\mathcal{A}(E_c)dE_c$ is the probability of finding the system with potential energy in the range $E_c$ to $E_c+dE_c$ in a canonical ensemble at a given temperature. The purpose of the present section is to collect the various conditions together more clearly and show how they arise in a general context. We also wish to emphasize here the equivalence of these conditions. Lynden-Bell and Wales further showed that the existence of a loop in the isopotential caloric curve is a necessary, but not sufficient, condition for the existence of a loop in the microcanonical caloric curve. Another equivalent condition for a loop to occur in the isopotential ensemble is the existence of a double minimum in the Landau free energy, $F(E_c;T)$, where the configurational energy plays the role of an order parameter and by definition

$$F(E_c;T) = E_c - T \ln \Omega_c(E_c)$$
where \( Z_c(T) \) is the configurational part of the canonical partition function. To generalize this condition we would need to define the Landau free energy as a function of the extensive variable, \( X \), to obtain

\[
F(X; I) = IX - \ln Z(X) = -\ln \tilde{Z}(I) - \ln \mathcal{A}(X),
\]

assuming that the product \( IX \) is dimensionless.

## VII. DISCUSSION

Hill previously deduced some of the results\(^{46}\) in Sec. VI for \( \mu(N) \) calculated in the canonical ensemble and the grand canonical probability distribution function \( \mathcal{A}(N) \). He compared the behavior of the Bragg–Williams canonical partition function when used to calculate \( \langle \mu(N) \rangle \) canonically and \( \langle N(\mu) \rangle \) in the grand canonical ensemble, where \( N \) in this case represented the number of solute molecules adsorbed from solution by a protein with a large number of equivalent binding sites. The mean field Bragg–Williams partition function gives a loop in \( \langle \mu(N) \rangle \) in the large \( N \) limit because it does not allow for nonuniform adsorption. When used to calculate \( \langle N(\mu) \rangle \) there is, of course, no loop, even for the approximate canonical partition function. However, the presence of the loop in \( \langle \mu(N) \rangle \) produces bimodality in \( \mathcal{A}(N) \) even for large \( N \), which cannot be correct.\(^{46}\)

Hill returned to the above problem\(^{21}\) when he explained how the results of Katsura,\(^{47}\) which showed that bimodality in \( \mathcal{A}(N) \) did indeed occur for an exact treatment of a finite system, were not in conflict with Van Hove’s theorem.\(^{20}\) In agreement with the present work, he concluded that exact theories can give a loop in \( \langle \mu(N) \rangle \) and bimodal \( \mathcal{A}(N) \) distributions for finite \( N \), but that these features must disappear as \( N \to \infty \). Hill distinguished such loops from van der Waals loops, which he defined to be those which do not vanish in this limit.\(^{21}\) We note that this usage has not been generally adhered to, as the loops found in the microcanonical \( T(E) \) for small clusters are often referred to as either S bends, van der Waals loops or van der Waals-type loops.

The present work pursues a complementary approach to Hill’s studies,\(^{18,21,46}\) in showing how a model partition function which \( \text{does} \) admit phase separation can bridge the limits between large and small systems. All our results are quite consistent with studies of simpler finite systems for which partition functions can be calculated relatively accurately, as illustrated, for example, by Hüller’s study of the eight-states Potts model.\(^{48}\) Hüller’s conclusion that the peak height of the heat capacity should vary as \( N L^2 / T_a^2 \), where \( L \) is the latent heat per particle and \( T_a \) the transition temperature, agrees with a previous analysis by Imry.\(^{49}\) The \( N \) dependence for the height and width of the heat capacity also agree with Fisher and Berker’s results.\(^{50}\)

### ACKNOWLEDGMENTS

We are grateful to the Royal Society (D.J.W.) and the EPSRC (J.P.K.D.) for financial support.

---

1. R. S. Berry, T. L. Beck, H. L. Davis, and J. Jellinek, Adv. Chem. Phys. 70, 75 (1988). Note, however, that the difference between the canonical and microcanonical caloric curves, which is of central importance in the present work, was not fully appreciated in this review. The statement “Exact superposition is what one would expect for thermodynamic variables” at the bottom of p. 129, is erroneous.
44 D. J. Wales and R. S. Berry, Phys. Rev. Lett. 73, 2875 (1994).