The Stability of Phase Coexistence in Atomic Clusters

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Microcanonical critical droplet theory and molecular dynamics simulations are used to examine static coexistence between solid and liquid phases in nanoscale lead clusters. It is shown that the theory predicts the existence of a metastable coexisting state above a critical cluster radius \( R_1 \), with this state becoming stable for clusters of radius \( R > R_2 \). Molecular dynamics simulations of lead clusters confirm the existence of stable coexisting states in 1427-atom and 2057-atom clusters but find no stable coexisting state in a 931-atom cluster.

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I. INTRODUCTION

The coexistence of solid and liquid phases in atomic clusters has been of experimental\(^{3,4,5}\) and theoretical\(^{6,7,8}\) interest for some time. In large clusters, as in bulk materials, static coexistence is expected theoretically\(^{9,10}\) and is readily observed in both experiments\(^{3,4,5}\) and simulations\(^{6-8}\). However, in sufficiently small clusters, simulations find that coexistence is dynamic i.e. clusters fluctuate in time between fully solid and fully liquid states.\(^{6,11}\) Small clusters avoid static coexistence because of the prohibitive cost of forming an interface. This causes an S-bend in the microcanonical caloric curve and the corresponding negative heat capacities which been observed in small sodium clusters.\(^{12}\)

However, it is currently not known at what size static coexistence gives way to dynamic coexistence. The timescale on which dynamic coexistence occurs will be governed by the height of the energy barrier separating the solid and liquid states of the cluster.\(^{6,11}\) However, if a coexisting state exists, then this coexisting state should also be dynamically accessible. This is not seen in at least some small clusters.\(^{6,11}\) Evidently, in sufficiently small clusters coexistence is unstable. At what sizes do states of static coexistence occur?

To determine when phase coexistence will be stable, one needs to know the relative cost of forming an interface between phases in a given cluster. A common approach to studying coexistence in clusters is to apply critical droplet theory in the capillarity approximation (i.e. where cluster material parameters, especially surface energies, are approximated by their bulk values). For instance Reiss et al.\(^{6,13}\) used the capillarity approximation to develop a critical droplet theory of melting in the canonical ensemble, with the (spherically-symmetric) solid fraction of a cluster acting as an order parameter.

Nielsen et al.\(^{13}\) developed a similar critical droplet theory in the microcanonical ensemble. They demonstrated that a stable static coexisting state can exist in this theory near the melting point, and validated this with constant-energy simulations of a large copper cluster. Cleveland et al.\(^{14}\) developed an aspherical model which dealt with static coexistence where the liquid only partially wets the solid. Thus, in principle, critical droplet theory can be used to discuss coexistence in a variety of circumstances.

To study coexistence we will work in the microcanonical ensemble as constant temperature ensembles tend to suppress the inherent inhomogeneity in coexisting systems.\(^{15}\) Constant energy conditions are realised in isolated systems with poor thermal coupling to their environment, such as clusters in an inert gas atmosphere. Consequently we will use microcanonical critical droplet (MCD) theory\(^{15}\) to examine the stability of static solid-liquid coexistence in small metal clusters. We will then use constant-energy molecular dynamics simulations to test the predictions of the theory.

II. MICROCANONICAL CRITICAL DROPLET THEORY

Here we use microcanonical critical droplet (MCD) theory\(^{15}\) to examine the stability of static coexistence. The spherical coexisting solid-liquid cluster of radius \( R \), is considered to consist of a solid core, of radius \( R_s \), and a liquid outer shell. The entropy (per atom), \( S_m \), of a coexisting solid-liquid cluster of solid fraction \( \eta = (R_s/R)^3 \) at energy (per atom) \( e \) is approximated by

\[
S_m(e) = \eta S_s(e_s) + (1-\eta)S_l(e_l)
\]

where \( S_s(e_s) = S^*_s + c \log \left( \frac{e_s - e_l}{e_l} + 1 \right) \) and \( S_l(e_l) = S^*_l + c \log \left( \frac{e_l - e_s}{e_s} + 1 \right) \). Here \( T_c \) is the bulk melting temperature, \( c \) is the heat capacity and quantities with a superscript \( c \) indicate values at the bulk melting point. The solid energy, \( e_s \), and liquid energy, \( e_l \), are related to the total energy, \( e \), for a cluster of radius \( R \) as follows:

\[
e = \eta e_s + (1-\eta)e_l + \frac{3}{\rho R} \left( \gamma_{lv} + (\gamma_{sl} + \Delta \gamma) \exp \left( -2(1-\eta^{1/3})R/\xi \right) \right) \eta^{2/3}
\]

where \( \Delta \gamma = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \) (\( \gamma_{sv} \) is the solid-vapour interfacial energy density, \( \gamma_{sl} \) is the solid-liquid interfacial energy density and \( \gamma_{lv} \) is the liquid-vapour interfacial energy density), \( \rho \) is the bulk material density and \( \xi \) is
a correlation length which characterizes the short-range interaction between the solid-liquid and liquid-vapour interface. The inclusion of this final term in equation (2) ensures that \( e \rightarrow e_s + 3\gamma_{sv}/\rho R \) as \( \eta \rightarrow 1 \).

We now show that MCD theory predicts that there is a critical cluster radius below which coexistence becomes unstable. For a given total energy per atom \( e \), we can regard \( e_1 \) as a function of \( e_s \) and \( \eta \): \( e_1 = e_1(e_s, \eta) \). We may then extremise the entropy (given by (1)) of the mixed cluster with respect to \( e_s \) and \( \eta \) at fixed \( e \). It is then straightforward show that the entropy is extremised when the following conditions hold: 1) \( T_l = T_s \), which is the normal condition for thermal equilibrium, and 2) \( \eta \) must satisfy the following equation:

\[
\eta^{4/3} - \frac{3\eta}{\rho RL} \left(\gamma_{sl} + \Delta \gamma e^{-2(1-\eta^{1/3})R/\xi}\right) + (e-e_1^{n+3\gamma_{sv}/\rho R}) + \frac{2eT_c\Delta \gamma}{\rho \xi L} e^{-2(1-\eta^{1/3})R/\xi} + \frac{2eT_c}{\rho RL^2} \left(\gamma_{sl} + \Delta \gamma e^{-2(1-\eta^{1/3})R/\xi}\right) = 0.
\]

where \( L = e_1^{n+3\gamma_{sv}/\rho R} \) is the latent heat of fusion per atom. For sufficiently negative values of \( e \), there are two positive solutions to \( \eta_1(e) > \eta_2(e) > 0 \). There is always a range of energies where \( 0 < \eta_2(e) < 1 \), as when \( e \rightarrow -\infty \), \( \eta_2(e) \rightarrow 0 \). In fact \( \eta_2(e) \) represents a local minima in the entropy, corresponding to a barrier separating the solid and liquid phases. Similarly, for values of \( e \) where \( \eta_1(e) \) exists and is less than one, \( \eta_1(e) \) is a local maxima in the entropy, corresponding to a coexisting state (note that \( \frac{d\eta}{de} \eta_1 < 0 \) and \( \frac{d\eta}{de} \eta_2 > 0 \).

A range of energies where \( 0 < \eta_1(e) < 1 \) exists only when \( R > R_1 \), where \( R_1 \) is given by:

\[
R_1 = \frac{\xi}{2} \left( -A + \sqrt{A^2 + B} \right),
\]

where \( A = \frac{3\rho L^2}{4eT_c} (\xi - 2\Delta \gamma/\rho L (1 - 2eT_c/3L)) \) and \( B = 2 \left(1 + \frac{\Delta \gamma}{eT_c} \right) (\gamma_{sv} - \gamma_{le}) \). That is if \( R > R_1 \), there is a range of energies where a locally stable coexisting state exists. At such an energy \( e \), the coexisting state, with solid fraction \( \eta_1(e) \), is separated from the liquid state by an energy barrier at \( \eta_2(e) \).

However, the coexisting state with solid fraction \( \eta_1(e) \) is not necessarily globally stable. If the coexisting state exists at an energy \( e \), then \( S_m(e) > S_s(e) \). However, there exist a range of energies where \( S_m(e) > S_s(e) \) only if \( R > R_2 \), where

\[
R_2 = \frac{\gamma_{sv} - \gamma_{le}}{\rho L} \left( \frac{3L - 2eT_c (1 - e^{-L/cT_c})}{L - cT_c (1 - e^{-L/cT_c})} \right),
\]

Thus for clusters with \( R_1 < R < R_2 \), at energies where the coexisting state exists, the state is always metastable \( (S_m(e) < S_s(e)) \). For clusters with \( R < R_1 \), no coexisting state exists at any energy.

We note that some of these parameters may be ill-defined for small clusters. Nonetheless the values of \( R_1 \) and \( R_2 \) may be calculated using the capillarity approximation i.e. using bulk values (if available) for the material parameters. For lead we find that \( R_1 = 0.2 \) nm (or approximately 1 atom) and \( R_2 = 0.6 \) nm (or approximately 100 atoms). This suggests that coexistence ought to be stable down to quite small cluster sizes, although it is well-known that the melting behaviour of sub-100 atom clusters is quite erratic due to electron-shell effects that are certainly not captured in the MCD model.

III. SIMULATED CALORIC CURVES

Using molecular dynamics simulations of Pb clusters we have found that coexistence becomes unstable at approximately 1000-atoms. We simulated the caloric curves for three clusters: a 2073-atom icosahedron, a 1427-atom icosahedron and a 931-atom icosahedron. Here we use surface-reconstructed icosahedra which are thought to be stable in Pb clusters at these sizes using a glue potential. At each energy the cluster was equilibrated for 0.6 ns, then the kinetic energy was averaged over a further 0.6 ns. The energy increment used was 0.2 meV/atom with energies adjusted between constant energy simulations by a uniform scaling of the kinetic energy. Figure 1 shows the caloric curves for the 2073 and 1427-atom clusters moving from the solid state (on left) to the liquid state (on right). Both clusters exhibit a coexisting solid-liquid state separating the solid and liquid phases. The curves in figure 1 resemble those constructed in Ref. with their layer-by-layer model of cluster melting.

Note the change in temperature at the transition from fully solid to coexistence and in the transition from coexistence to fully liquid. In MCD theory, while the transition from coexistence to liquid is first-order, the transition from solid to coexistence is continuous. To check whether the 1427 and 2057-atom clusters are superheated when they undergo the transition from solid to the coexisting state, we cooled a 1427-atom cluster from the coexistence region down until the cluster froze. Figure 2 shows the reverse caloric curve (constructed using equilibration times of 4 ns with an energy increment of -0.2 meV/atom). The freezing transition takes place to well within 5 meV/atom of the transition from solid to coexis-
FIG. 1: Caloric curves for (a) a 1427-atom Pb cluster and (b) a 2073-atom cluster. The 1427 and 2073-atom clusters exhibit coexistence for a range of energies.

tence, suggesting that the simulated caloric curve is close to the equilibrium caloric curve and that the transition at -1.715 eV/atom is a first-order transition which exhibits little rounding due to finite-size effects. The origin of this discontinuity at this transition may correspond to the creation of a “minimum” volume of liquid and as such the discontinuity is likely to disappear as $R \to \infty$.

To characterise the coexisting state, we follow Cleveland et al.\textsuperscript{7} in using the bimodality of the distribution of diffusion coefficients to distinguish solid and liquid atoms. A sequence of snapshots at different total energies of the 1427-atom cluster is shown in figure 3. The total energy of the atoms in each snapshot decreases from top left to top right to bottom left to bottom right. Each atom in the snapshot has been coloured either white or grey depending on whether the diffusion coefficient of that atom (calculated over a carefully chosen timescale) is low mobility (solid) or high mobility (liquid). The snapshots reveal that the molten lead does not fully wet the solid. They also reveal that the liquid fraction of the coexisting cluster increases as the total energy increases. Note that the melt does not wet the solid as assumed in equation 2 whereas in bulk lead, the melt wets the solid (since in bulk lead $\Delta \gamma > 0$). This is a clear indication that the capillarity approximation has broken down at these cluster sizes.

Figure 4 shows the caloric curve for a 931-atom cluster constructed in the same way as those for the larger clusters in figure 1. Note that the curve does not show a stable solid-liquid coexisting state but that large fluctuations in temperature occur near the melting transition in the 931-atom caloric curve. Using the same method for identifying solid and liquid regions as was used in figure 3, one can verify that the fluctuations in temperature are correlated with the appearance of a liquid region in the otherwise solid cluster. This is due to the dynamic coexistence between the solid state and a coexisting state.

Which state is globally stable? We have resolved this with a very long duration run near the melting transition. Figure 5 shows a history of the temperature (as determined using the method above) for a 931-atom cluster at a total energy of $E = -1.688$ eV/atom over approximately 15 ns. The final state of the cluster is liquid (achieved after approximately 8 ns), which suggests that the fluctuations (between 0 and 8 ns in figure 5) and be-
FIG. 3: A sequence of snapshots showing the coexisting solid-liquid state as the energy is increased from $E = -1.712$ eV/atom (top left) to $E = -1.706$ eV/atom (bottom right). Atoms are classified by their mobilities: the dark grey atoms are liquid (high mobility) while the light grey atoms are solid (low mobility).

between $-1.690$ and $-1.686$ eV/atom in figure 4 are non-equilibrium precursors to melting rather than true dynamic coexistence. MCD theory certainly suggests that at sizes $R < R_2$ the coexisting state is metastable with respect to the liquid rather than the solid. However, the caloric curve in figure 4 suggests that the coexisting state is metastable with respect to both the solid and liquid states, as the cluster appears to spend more time in the solid state. Nonetheless, we conclude that there is no stable coexisting state for the 931-atom cluster at any energy. In Ref 18, we constructed a less detailed caloric curve for 1130-atom lead clusters by coalescence. This curve also showed no evidence for stable coexistence.

IV. DISCUSSION

The molecular dynamics simulations and MCD theory in the capillary approximation do not agree on the size at which coexistence becomes metastable in Pb clusters. However, the snapshots in figure 3 strongly suggest that the capillarity approximation has broken down at these cluster sizes (at least when it comes to reproducing the behaviour of the simulated clusters). This should not be surprising as atomic clusters are interesting precisely because their properties depend strongly on size. However, if we are to take MCD theory beyond the capillarity approximation, we would require a detailed understanding of how surface energies, and other quantities such as latent heat, depend on surface curvature and/or size. It is not simply a matter of inserting more accurate material properties into (5).

It is also important to recognise that the spherically symmetric geometry assumed in equation (2) is inappropriate for situations involving partial wetting where $\Delta \gamma < 0$. In Ref 2, a critical droplet model was developed...
for the partial wetting case, although it was applied in the canonical ensemble. Evidently a generalisation of MCD theory to the partially wetting case would also be desirable. Similarly it would be interesting to determine by simulation and experiment the size at which $\Delta \gamma = 0$ in Pb clusters i.e. the size below which complete wetting gives way to partial wetting. Partial and complete wetting has been observed recently in isolated metal alloy clusters using transmission electron microscopy.

Finally, in the simulations the transition from solid to solid-liquid coexistence was discontinuous. In MCD theory this transition is continuous as the energy of the coexisting cluster, as given by equation (2), approaches the energy of an entirely solid cluster as $\eta \rightarrow 1$. This limit is an artificial feature of equation (2); if this constraint were to be relaxed so that the energy of the coexisting cluster approached some other value as $\eta \rightarrow 1$ (for instance, $c_s + 3(\gamma_{lv} + \gamma_{sl})/\rho R$) then the transition from solid to solid-liquid would be discontinuous. Provided the energy of the solid cluster and that of the limiting solid-liquid cluster differed only by surface energy, this discontinuity would disappear as $R \rightarrow \infty$.

V. CONCLUSION

In summary, MCD theory predicts that the static coexistence of solid and liquid phases can only occur in clusters above a certain size given by equation (3). Below this critical size coexistence is metastable or unstable. Molecular dynamics simulations of Pb clusters using a glue potential appear to corroborate this scenario, although the transition occurs at a larger size, $N_2$, (where $1100 < N_2 < 1400$) than that predicted by MCD theory using bulk material parameters in the capillarity approximation. Indeed this discrepancy between theory and simulation is probably due to the breakdown of this approximation at small cluster sizes. We note that Pb has an unusually large value of the prefactor $x = (\gamma_{sv} - \gamma_{lv})/\rho L$ that appears in equation (5) due to a relatively small latent heat of fusion. Other metals with small latent heats (which are correlated with low melting points), such as Hg or the alkali metals, will also have large values of $x$. It may be that in such metals coexistence is forbidden at quite large sizes. In most metals, however, with relatively large latent heats of fusion, we might expect static coexistence to remain stable down to rather small sizes.

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