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Observability of coexisting phases of clusters

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ABSTRACT

That two or more phases of small clusters can coexist in thermodynamic equilibrium over ranges of temperature and pressure has become well established. Moreover the explanation for this apparent violation of the Gibbs phase rule is also now well known. The origin of the phenomenon lies entirely with the difference between systems of small numbers of component atoms or molecules and those made of large numbers, e.g., tens, vs. 10^{20}. However little has been said about the maximum sizes of clusters for which such coexistence may be expected to be observable. Here we show how one can estimate that maximum size for observable coexisting phases, in which the unfavored minority phase constitutes a detectable fraction of the total sample. In addition, the role of atom thermal motion in the phase transition is analyzed.

1. Introduction

Since the mid-1970's, evidence has grown, and with it, interpretation and explanation, of how and why small clusters of atoms or molecules can exhibit bands of temperature and pressure (or of other pairs of thermodynamic variables) within which observable quantities of different phases may coexist in equilibrium [1–3]; for reviews, see [4,5]. This phenomenon is not restricted just to two phases; with small systems, more than two phases may coexist in equilibrium [6–8]. The explanation is quite simple: if one examines the equilibrium constant K_{eq} for coexisting phases α and β of a cluster of n particles,

$$K_{\mathrm{eq}} = \exp\left(-\frac{n\Delta\mu}{kT}\right),$$

where the change in chemical potential is $\Delta\mu = \mu_\alpha - \mu_\beta$, then it is easy to see that even if $\Delta\mu/kT$ is nonzero but very small, e.g., 10^{-10}, but n corresponds to a macroscopic sample, such as 10^{20}, then the unfavored phase must be present in unobservably small quantities. However if n is of order 100, then $n\Delta\mu/kT$ can be small enough, within a temperature region a little away from the point where $\Delta\mu = 0$, that observable amounts of the unfavored phase may easily exist. If, for example, $\Delta\mu/kT = \pm 0.1$ (then $n\mu/kT$ is 20), and (i), the unfavored phase comprises about 13% of the total sample. The balance between the mean energy change per particle, $\Delta\varepsilon$, and the mean contribution to the entropy per particle, $T\Delta s$, are of course what determine the value of $\Delta\mu$. Here we address the question of how large a cluster may be and exhibit observable amounts of two or more phases. The central point of this work is determining the size dependence of $\Delta\mu$ and then relating that to the sensitivity of experiments. In this analysis we will be guided by clusters with completed atom shells, specifically those of 13 and 55 atoms. These cases most clearly exhibit the role of surface melting. For other cluster sizes additional mechanisms of melting may need to be invoked to obtain more precise estimates that we establish here.

The most straightforward way to approach this question is to examine K_{eq}, and more specifically the terms $\Delta\mu/kT$ in the exponent, to determine the range in which the magnitude of the full exponent, $|n\Delta\mu/kT|$, is smaller than about 4. This corresponds to a minority concentration of about 2%, which we assume is about as small a percentage as one could detect. We must therefore estimate the energy and entropy changes for phase changes of clusters in the temperature ranges in which phase coexistence is possible. We shall do this by using as an illustrative system clusters of argon, modelled by a Lennard–Jones potential. Our target is an order-of-magnitude estimate as a guide for experimental design, not a precise computation. We intend this result to be a guide and stimulus for new experiments, and the most likely and most appropriate are probably going to involve some form of mass spectrometry.

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2. Evaluating the free energy difference: "surface melting"

Before we address the observable coexistence range for true melting of clusters, let us examine the process called "surface melting," which is really a combination of promotion of a few atoms from the surface layer to become "floaters" attached to the cluster but free to move on the otherwise empty shell outside of the cluster, while the remaining outer-shell atoms are simply vibrating more loosely [6–8]. This phenomenon seems to occur in clusters of about 45 atoms or more. By choosing argon clusters as our illustrative model, we fix the relevant range of T as that around about 35 K. The coexistence ranges for argon clusters are around this value. The energy contribution to the change of chemical potential is determined primarily by the change in the mean number of nearest-neighbor contacts. This is easy to estimate in terms of the change in the number of pair dissociations, whose energies D we can estimate as those of simple diatomic pairs, D_0, whose value we take as 12.3 meV or 143 K for argon. Estimating the entropy change is a little more subtle. We break that change into two parts, one associated with the change in configuration or available volume for whatever relocation of atoms takes place in the transition, and the other, associated with the change in the vibrational contribution to the entropy, which can be expressed in terms of the change in the anharmonicity of the vibrational motion.

For a specific, simple example, we review the Ar_{13} cluster, which we used in a recent analysis of how to evaluate the entropy change of the phase transition in clusters. In that system, the phase change is simply due to promotion of one atom from the icosahedral shell of 12 atoms to a site on the surface. The energy change from the low-temperature phase to that at higher temperatures is that of the loss of three of the nearest-neighbor contacts, because the promoted atom moves from having six contacts in its surface site to a site "sitting on top" where it contacts only three neighbors. This is just $3D$. The configurational part of the entropy change is simply that associated with the promotion of any of the 12 surface atoms from a single location to any of the 15 sites that do not border the hole left by the promotion. Hence the configurational contribution to the entropy change (in dimensionless units) is $\ln(15 \times 12) \approx 5$. The one remaining contribution is the entropy bit due to the change in anharmonic vibrations.

Now let us generalize the calculation of the configurational entropy change. Simulation studies have shown that in the first stage of melting of multilayer clusters, roughly one particle in about 15 moves out of the outermost shell and becomes a "floater", moving essentially freely on the surface of the cluster. Hence each of these moves from a volume V_0 corresponding to its own site in the solid to a volume equal to that of the next larger shell. Suppose that the radius of the unexcited cluster is R_0, and the radius of the individual (presumably atomic) particles is r and the internuclear distance is d. We make the distinction between $2r$ and d in order to allow for vibrational motion to expand the cluster. Then the volume of the shell in which the promoted particles move is $4\pi/3[(R_0+2r)^3 - R_0^3]$. The initial volume available to each atom is $v_0 = 4\pi/3(d/2)^3$. If there are n_s particles in the completed filled shell, then we can assume that $n_s/15$ of them are promoted when "surface melting" occurs. The total increased available volume for the cluster as a whole is therefore

$$\Delta V_{sm,cs} = \frac{n_s}{15}\frac{4\pi}{3}\left[(R_0+2r)^3 - R_0^3 - \left(\frac{n_s}{15}-1\right)r^3\right]$$

Therefore the configurational entropy change for surface melting of a closed-shell or "magic number" cluster is

$$\Delta S_{sm,cs} = \ln\left(\frac{\Delta V_{sm,cs}}{v_0}\right) \tag{2.1}$$

For clusters with partly filled outer shells, we should do a somewhat more elaborate but equally elementary estimate: when surface melting occurs in a cluster with a shell roughly only 2/3 filled or less, we can assume that the surface melting allows all the surface-layer atoms to move freely on that original surface, but we must of course take into account the volume excluded by the presence of the other particles in the shell. In other words the newly available volume is the fraction of the original shell that had unoccupied sites. For clusters with more than about 2/3 of the surface sites filled, we can assume that the volume available on surface melting is that of the full-shell case, plus the volume of any additional empty sites in the initial, solid-like state.

The energy change for surface melting of a closed-shell cluster $E_{sm,cs}$ is easy to approximate as the number of promoted particles, times the change of the number of closest contacts, in units of the binding energy per pair, D:

$$\Delta E_{sm,cs} = 3\frac{n_s}{15} \tag{2.2}$$

for an icosahedral closed shell, since the number of contacts drops from 6 to 3.

We have yet to estimate the contribution to the entropy from the vibrational motion. We make the assumption that the vibrational entropy change upon "surface melting" is approximately the same, per unpromoted atom, as that found for the 13-atom cluster. That vibrational entropy is a very linear function of the temperature, approximately $\Delta S_{13} = 25T + 1.5$, or, in terms of remaining surface atoms, the vibrational entropy per remaining unpromoted is atom $\Delta s_{13} = 2.2T + 0.13$. Note that a more accurate representation of the temperature dependence of the entropy jump for a 13-atom cluster in the coexistence range is very steep and sharp, closer to a stepwise function than to the linear dependence that we use here. Nevertheless, the linear dependence is a simple and rough approximation adequate for this estimation purpose. We shall make the assumption now that the vibrational entropy change of any closed-shell cluster, in the surface-melting process, is given by this expression, so that 14/15 of the atoms in the outer shell undergo this entropy change while the other 1/15 of the outer-shell atoms go free to roam on the surface as floaters. Hence the free energy change of the closed-shell cluster on "surface melting" is

$$\Delta F_{sm,cs} = \Delta E_{sm,cs} - T\Delta S_{sm,cs} = D\frac{n_s}{5} - \frac{T}{D}\ln\left(\frac{\Delta V_{sm,cs}}{v_0}\right) - \frac{14}{15}n_s(2.2T + 0.13). \tag{2.3}$$

For open-shell clusters, we can estimate the average number of contacts of the surface-melted state for systems with 2/3 or less of the outer shell filled just by assuming that, in the surface-melted state, each atom has three contacts with the lower layer and whatever fraction of contacts in the surface layer were occupied in the solid form, e.g., 2/3 of 5, for the cluster with 2/3 of the surface sites occupied. Thus for such a case, if fs is the fraction of the surface-layer sites that are occupied, then $\Delta E_{sm,f} = 3 + f_s n_s$, again in units of the binding energy D.

The entropy of surface melting for an open-shell cluster contains a vibrational contribution that we have still to estimate. For clusters with no more than 2/3 of the surface sites occupied, we have assumed that all the surface atoms are set free as floaters in their own original layer in surface melting. Hence it is the next layer below these that can gain larger amplitude, more anharmonic motion by the surface melting process, and therefore the vibrational contribution to the surface-melting entropy change for such a cluster should be simply the number of atoms in the next-inner shell, no-1, times that expression for the vibrational entropy increase per atom, $2.2T + 0.13$. For clusters with more than 2/3 of the outer shell filled but still with some empty sites, we can suppose that the promotion of atoms to be floaters is the appropriate description, and we can use the same model as for closed-shell clusters.

3. Evaluating the free energy difference: true melting

As the appropriate illustrative model for constructing the methods for estimating energy and entropy changes on melting of clusters, we take the 55-atom argon cluster. This has been analyzed from computer simulation results and from the viewpoint of melting as the introduction of voids into the system [9–11,13]. The energy change on melting of this system is 15 ± 1 in units of the Ar–Ar bond dissociation energy D. This emerges very straightforwardly from the computer simulations of isothermal conditions with both phases present [7,8].

Estimating the entropy change from simulations can be done, but the uncertainties are large and the alternative, using a void-formation model, yields a very similar value with a much smaller uncertainty. The void calculation is based on finding that the most probable number of atoms to be promoted from the initial sites in the 55-atom icosahedron is about 5–7. The vacancies left by these promotions then relax to undetermined and changeable shapes, the voids. We find the entropy of the phase change in two steps. First, we can estimate what that entropy change would be if 5–7 voids were to form at 0 K, and then we can add the contribution from the nonzero temperature. The first of these, S_0, can be estimated from simulations showing the maximum in the heat capacity or from simple numerics also addressing the heat capacity. From the simulations, we can infer that the entropy at the melting point, ΔS_m, is

$$\Delta S_m = \frac{\Delta E_m}{T_m} = 48 \pm 5$$

where we use the peak in the heat capacity to be approximately Gaussian, that gives [9–11]

$$\Delta S_0 = 2\Delta S_m - 4\frac{C_{max}}{\Delta S_m} \qquad (3.1)$$

This yields

$$\Delta S_0 = 36 \pm 15,$$

a rather uncertain quantity. The uncertainty results from the different methods used in different simulations. Numerical estimates from models do better in the sense of having lower uncertainties. There are 42 atoms in the outer shell of the cluster, and 80 surface sites to which a promoted atom can move. A vacancy on the surface has l nearest-neighbor atoms, where $l = 6$ for a vacancy on an edge or a surface, and $l = 5$ for a vertex vacancy. Hence promotion of v atoms to the surface, leaving l vacancies, $v \cdot l$ bonds are lost in the process. We then estimate the configurational entropy change at 0 K from the configurational heat capacity contributions of the promoted atoms and the remaining shell:

$$\Delta S_0 = \ln C_m^v C_{42}^v,$$

where $m = 80 - v \cdot l$, the number of positions available for promotion on the cluster's surface. From this expression, we find that if v is 5, $\Delta S_0 = 28.5 \pm 0.3$; if v is 6, then $\Delta S_0 = 31.6 \pm 0.4$, and if v is 7, $\Delta S_0 = 32.3 \pm 0.7$. These numbers are similar enough that we can simply take $\Delta S_0 = 31 \pm 2$. This is significantly less uncertain than the value from simulations, but is entirely consistent with it. Now we find the entropy change at the point of equal free energies of solid and liquid. Then we use formula (3.1), that connects that connects the entropy jumps at zero temperature ΔS_0 and at the melting point ΔS_m, and also the maximum value C_{max} of the heat capacity that is taken on the basis of a sum of the results of computer simulation [14], which is $C_{max} = 650 \pm 50$. We find from these that the entropy change at melting is $\Delta S_m = 45 \pm 2$.

With these two numbers for our representative system, $\Delta E_m = 15 \pm 1$ and $\Delta S_m = 45 \pm 2$, we can begin to estimate the range of observability of coexisting solid and liquid phases. The dissociation energy of the argon dimer, D, is 143 K or 12.3 meV. The melting point, i.e., the maximum of the heat capacity and presumably the point at which $\Delta E_m = T\Delta S_m$, is, according to the simulations, approximately 0.31 in units of D, i.e., ≈ 44 K. This is not precisely the value we estimate for $\Delta E_m/\Delta S_m$, of 1/3, corresponding to ≈ 47 K, but is certainly close. Note that although we use interaction parameters corresponding to argon clusters, because of the similarities of the rare gases, our general conclusions are valid for the other inert gas clusters as well, apart from helium. Even neon, in the range of its solid–liquid transition, is moderately well described by a classical model of the kind used here [12].

Now we can estimate the range of temperature over which the solid and liquid phases might both be observable. We consider just the case of isothermal conditions. Let us take as the upper and lower values of the equilibrium constant to be 100 and 0.01, certainly somewhat optimistic, between which both phases could perhaps be detected. Then

$$0.01 < K_{eq} \equiv \exp(-F) < 100$$

with F in units of kT. Alternatively,

$$-4.6 < -F < 4.6$$

Hence T must lie between 0.4 and 0.6 in units of D, or between 33 and 57 K for the two phases to be observable. If we re-set the criterion at 10% of the minority phase, or

$$0.1 < K_{eq} \equiv \exp(-F) < 10,$$

then the temperature range is between 40 and 54 K, still a wide enough range to span easily in experiments.

We can construct a convenient, general estimate of the range of temperatures in which two phases may be observable. The free energy change in the passage between phases is

$$\Delta F = \frac{\Delta E}{T} - \Delta S,$$

which is of course zero at T_m so that there, $\Delta E/T = \Delta S$. Let us define

$$\delta F = \frac{\Delta E \delta T}{T^2},$$

where δT now allows us to define the observability range. Since $\Delta E/T_m = \Delta S$ at T_m, and the observability range is relatively narrow, we can assume, for purposes of our estimation, that ΔE and ΔS are approximately constant in this range. With $\delta F \approx 4.6$ in the coexistence range, we may thus write the approximate expression for the observable temperature range of coexistence in terms of just the one parameter ΔS and the melting temperature:

$$\frac{\delta T}{T_m} \approx \frac{5}{\Delta S_m},$$

Next, we make a leaping assumption, that we can write the free energy of clusters in this size range and up to the limit we seek by using the same value of the chemical potential, the free energy per particle, that we obtain for the 55-atom cluster. That is, we suppose we can write $\ln K_{\text{eq}}$ for a cluster of n atoms as $\exp(-n\Delta\mu)$ with the same values of energy and entropy per atom that we use for Ar_{55}, namely 15/55 or 0.27 for the energy per particle, and 45/55 or 0.82 for the entropy change per particle. With this assumption, we can now make a quick estimate that for a cluster of 100 particles, the range within which the minority phase is present in a ratio of 1:10 is only 0.1 K. For a 100-particle cluster with an allowance of a ratio of 1:100, the range only extends to that between 46.9 and 47.3. With 75 particles, the range for an allowable ratio of 1:10 is almost 4 K, from about 45 to 49 K, clearly an observable range. In short, while we could refine the means of estimating the terms of the chemical potential for clusters of sizes larger than 55 atoms, we can be fairly confident that the largest clusters for which coexisting solid and liquid phases are likely to be observable is in the range of about 75 atoms.

4. A model of aggregate states

Our analysis aims to give some position in the character of cluster phase transitions, not to obtain some numerical values. Therefore we now glance on this problem from another standpoint that allows us to see some advantages and weak points of simple models under consideration. Of course, the main advantage of simple models is the clearness that allows us to understand the peculiarities of the object or process by simple means. But simple models relate usually to specific conditions, and to understand this in the considering case, we use another approach. Let us represent the entropy of a configurational state, as well the entropy jump at the phase transition between two aggregate states, as a sum of the configuration and thermal parts

$$S = S_{con} + S_{th} \tag{4.1}$$

The configurational entropy part is $S_{con} = \ln g$, where g is the number of different atomic configurations for this state. For example, for a 13-atom cluster with icosahedral structure, $g = 1$ for the solid state because of the completed surface shell. If the lowest excited aggregate state corresponds to transition of one atom onto the cluster surface, we have $g = 12 \times 15$, where the first value is the number of possible positions of a vacancy in the cluster shell, and the second value is the number of atomic positions on the cluster surface where a promoted atom has three nearest neighbors. Correspondingly, $S_{con} \approx 5$ in this case. Note that this consideration holds true for dielectric clusters as well as for inert gas clusters, both being excited aggregate states that may be described in terms of perturbed vacancies.

Another part of the entropy relates to thermal motion of atoms. Considering atoms to be classical, let us draw a region in a space where a probe atom may be located. Of course, the boundary of this region depends on coordinates of neighboring atoms and the current energy of a test atom. For simplicity, one can fix positions of neighboring atoms and take the average kinetic energy of a test atom to be $3kT/2$, where T is the cluster temperature. In particular, we have for the thermal part of the entropy if thermal atomic motion is vibrational [15]

$$S_{th} = 3(n-2)\ln\left[\frac{T\,\exp(4/3)}{\theta_D}\right], \tag{4.2}$$

where θ_D is the average Debye temperature, and the assumption $\theta_D \ll T$ is used [15]. Of course, the Debye model is strictly valid for macroscopic systems, but this approximation allows us to get a bit of insight into properties of finite atomic systems and how they relate to bulk properties. We include in the thermal entropy of an aggregate cluster state only vibrational degrees of freedom. This formula holds true more or less for the solid aggregate state. In this case the region of location of a test atom is close to an ellipsoid, and a temperature increase leads to an increase of size of this ellipsoid. In other words, energetic barriers on the cluster's potential energy surface are high compared to the atomic thermal energy on the boundary of the region of atomic location. However the barriers for passage from one local minimum to another are obviously low enough to allow liquid-like behavior on the time scales of the appropriate observations, for systems in the liquid state.

One can see that if this formula is suitable both for the solid and liquid states, the contribution to the entropy jump at melting will be small. Therefore, a notable contribution to the entropy jump results from the situation in which high barriers separating regions of atomic location are opened. In particular, for clusters with completed atomic shells, this occurs when atoms initially locked in wells surrounded by other surface atoms are promoted to become floaters that may move relatively freely over the cluster surface.

Note that the conceptual models invoked here are based on single-atom and pairwise interaction behavior and can give only limited insight into the phase transitions in clusters. These models do not incorporate simultaneous interactions of many atoms and that are not described by one-atom models. On the other hand, computer simulation by molecular dynamics is suitable for a more detailed, quantitative analysis. Therefore, our experience in this process is much influenced by our familiarity with the results of computer simulations. Based on this, we simplified the description by taking the contributions of the configurational and thermal excitation to the entropy jump at the melting point to be identical. This is satisfied with an accuracy of approximately 10 % for 13-atom and 55-atom Lennard–Jones clusters, and also for bulk inert gases [9–11]. For example, for the 13-atom Lennard–Jones cluster with one floater we obtain on the basis of this model for the entropy jump at the melting point $\Delta S \approx 2S_o \approx 10$, while a more accurate value is 9.4 [9–11]. Thus, such a model is suitable for the rough estimate needed here of the entropy jump at melting, for a given number of floaters.

We also point out that we assumed an excited aggregate state occurs as a result of formation of perturbed vacancies in a cluster as a result of transitions of atoms onto the cluster surface, where they become floaters. Hence any specific excited aggregate state corresponds to a restricted number of atomic configurations. Therefore, the models under consideration are suitable for Lennard–Jones and some dielectric clusters, but are not generally valid for metal clusters, particularly those that admit a high number of excited equilibrium atomic configurations. This estimation can be used for dielectric clusters to the extent that the assumptions, e.g., of slowly varying energies and entropies of the phase change in the coexistence range, are valid.

5. Conclusion

The above analysis exhibits that, although we apply thermodynamic parameters for clusters, notably T, S, E and F, the phase transition between two aggregate states proceeds not by a jump, as it takes in bulk thermodynamic systems; rather, coexistence of two phases in thermodynamic equilibrium occurs over some range of temperature and pressure (or other parameters that are responsible for the phase change). This is explained by a small number of atoms; roughly, the coexistence range is narrower, the larger the cluster. Next, the entropy jump at the melting point is the sum of the configurational and thermal contributions, in accordance with formula (4.1). In the case of inert gas clusters of different sizes, the contributions of these parts are comparable in the vicinity of the melting point. The first part, determined by atomic configurations, is very nearly independent of the temperature. The second part occurs because the upper aggregate state is looser than the lower one. The thermal part of the entropy jump is zero at zero temperature and grows not smoothly, but practically by jumps, when barriers in motion of transferred atoms – floaters or internal atoms – can be overcome. Nevertheless, for simple estimations over narrow temperature ranges, we use a monotonic temperature dependence for the entropy jump based on the results of cluster computer simulations. Thus, the conclusion from this analysis, that although the phase transition results from configurational excitation of an atomic system, thermal motion of atoms in the aggregate states of transition is nevertheless important for the numerical parameters of the phase transition.

The above analysis was done with the parameters for argon. What about other substances? The crucial term determining the temperature range in which the two phases are observable is the ratio of the log of the chosen concentration ratio to the entropy change of the transition. The smaller is that entropy change, the larger is the range of observability. Of course the smaller the entropy change, the higher the melting point must be, for a given energy change in the transition. This underlies the observations of coexistence of clusters of well over 100 sodium atoms; the melting of sodium clusters of order 138 atoms shows a clearly distinguishable coexistence band [16,17].

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