International Journal of Mass Spectrometry 280 (2009) 204–208

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

# Observability of coexisting phases of clusters

R. Stephen Berry [a,*], Boris M. Smirnov [b]

[a] Department of Chemistry and the James Franck Institute, The University of Chicago, 929 East 57th Street,
Chicago, IL 60637, United States
[b] Joint Institute for High Temperatures, Moscow 127412, Russian Federation

ARTICLE INFO

*Article history:*
Received 15 July 2008
Received in revised form
19 September 2008
Accepted 23 September 2008
Available online 4 October 2008

*Keywords:*
Atomic cluster
Phase transition
Coexistence
Melting
Freezing

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 $K_{\rm eq}$ for coexisting phases $\alpha$ and $\beta$ of a cluster of $n$ particles,

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

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 $K_{\rm eq}$, 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.

---

* Corresponding author. Tel.: +1 773 702 7021.
*E-mail address:* berry@uchicago.edu (B.M. Smirnov).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.09.012

## 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 $\mathrm{Ar}_{13}$ 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