On the thermodynamics of the liquid–solid transition in a small cluster

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Abstract

Physics of phase transformations in finite systems has a long history, but there are many unresolved issues. Although there is a satisfactory qualitative picture of the phase transformations within an isolated small cluster, the experimentally observed dependence of the melting temperature on the cluster size contradicts the prediction of classical results. No clear physical picture of such a transformation exists for a condensed cluster in contact with gaseous environment. We propose a thermodynamic theory, which generalize previous results to the case of cluster with fluctuating number of constituent particles (open cluster). In this case, phase transition occurs because of size change during the nucleation/evaporation process. This allows us to explain the underlying physics of recent simulations and experiments. Although we used the grand canonical approach, our main results can be applied to isolated clusters. Particularly, we give simple arguments to explain the deviations of the cluster melting temperature dependence on cluster size from classical results.
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1. Introduction

Classical theory assumes that the nucleation process begins with small solid clusters, which eventually reach some critical size and subsequently grow into a bulk solid state [1,2]. In the simple version it is supposed to be a process of direct homogeneous solidification from a gas-like or liquid-like surrounding phase [3]. On the other hand, some systems with specific types of interaction have a liquid–liquid transition before solidification. This is particularly relevant to the system of colloids with short-range attraction [4–8].

Naturally we can imagine two scenarios for this two-step phase transition: (i) the bulk liquid$_1$–liquid$_2$ transition leads to a homogeneous state, and then a liquid$_2$–solid transition described by classical nucleation theory occurs; (ii) the nucleation process in the bulk liquid$_1$ leads to the creation of solid clusters,

but the evolution of each cluster contains two steps, creation of liquid$_2$ nuclei, and then an order-disorder transition to become a solid cluster.

The second type of solid phase growth is exotic, but can be realized in systems with specific types of inter-particle interactions. One example was recently reported for protein crystal growth [6]. Lomakin et al. carried out the numerical simulation of hard spheres with attractive square-well interaction to study the growth of small clusters in a system with a fixed number of particles N and a volume V. Their study showed that only liquid-like structures are stable for small clusters. To form the crystalline structure, cluster must reach some critical size. A two-stage nucleation process was also seen in simulations by the Frenkel group [9,10].

To the best of our knowledge, there is no general thermodynamic criterion to predict the appropriate nucleation scenario. The aim of the present Letter is to study the thermodynamics of a single cluster, assuming the second two-stage nucleation scenario to occur. A theoretical investigation of order–disorder transitions in finite systems has a long history [11]. The main

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concern in such systems is the character of the liquid–solid phase change. We call it "phase change" or "phase transformation" because it's not a phase transition in standard understanding for the bulk matter with a divergence in the heat capacity. In a finite system it would have some sharp but finite maximum. Nevertheless the difference between liquid and solid states can be well defined mechanistically. Previous theoretical investigations dealt mainly with a concept of dynamically coexisting phases in equilibrium isolated clusters [11–16]. To enrich our understanding, it is also interesting to study the open system, where the number of particles within a cluster can change. We address this problem in the present Letter.

2. Structure of the cluster

While the phase state in a bulk matter can be well defined by a phase transition, determination of liquid or solid state within a small cluster is more ambiguous. The heat capacity of a cluster has a maximum at the transition point, but it's not easily measurable for small aggregates and we need some simple mechanistic criterion before formulating it more strictly from thermodynamic arguments.

Additional difficulty of describing phase change in small aggregate consists in the inhomogeneity of the process. To explain that, it is more convenient to consider melting instead of solidification. During melting, the volume of the system (with fixed number of particles) increases, which leads to creation of vacancies, while interaction between particles does not change (i.e. pair interaction), or changes not much. Surface atoms have less nearest neighbors, so the melting process begins from the "outer shell" [11]. Such clusters have a shell structure, so that atoms in outer and inner shells are in different conditions. In this sense melting of small clusters with pair interaction is related to a problem of 2D melting [7,17]. Due to such a shell-by-shell mechanism the phase change in small aggregate is a continuous process, that cannot be treated by the conventional theory of phase transitions microscopically. To understand the phase change within a cluster during the nucleation process we need to build its thermodynamics and analyze the behavior of heat capacity to define liquid and solid state of small cluster more consistently.

Let us first describe a phase change within an open cluster during nucleation/evaporation process first by analyzing naively its microscopic characteristics. For definiteness, we consider a system of colloids with short range attraction, which is particularly relevant to a systems of globular proteins [6]. In the equilibrium closed packed structure the potential of interaction between two neighboring atom is $u(a) = -\epsilon$, where a is the equilibrium inter-atomic distance for crystalline structure, ϵ is the square-well potential depth. The total bond energy of atoms within a cluster is then given by

$$E = -\frac{1}{2} \sum_{i,j} u(r_{ij}). \tag{1}$$

For a closed packed structure, when $r_{ij} = a$, each atom has 12 nearest neighbors, and it is easy to obtain the bond energy per one atom being $\epsilon_b = 6\epsilon$.

Naive phenomenological method of distinguishing liquid and solid states consists in estimation of number of nearest neighbors. It can be done as follows. Considering a closed packed system, let us choose the volume V containing $n_s V$ atoms, where n_s is the number density. As each atom has 12 nearest neighbors, the total number of bonds in the volume is $6n_s V$. Let n be the *average* density of cluster at some intermediate state (not close packed). Then the number of vacancies within a volume V is approximately $(n_s - n)V$. To remove one vacancy we need to create 12 bonds, or, in other words, we need to break 12 bonds to create a vacancy. This means the number of bonds within volume V in some intermediate state is $6(2n - n_s)V$ and the average number of nearest neighbors is $q = 12(2 - n_s/n)$. This last quantity can be used to distinguish the liquid and solid state phenomenologically. This approach however is obviously ambiguous. It does not provide us with the well-defined phase change point.

There are also some more precise methods based on examination of radial distribution functions (see e.g. [18]), which were successfully used in studies of various aspects of cluster physics [19–22]. Also these methods are very useful in molecular simulations, all of them do not connect directly microscopic characteristics with macroscopic measurable quantities.

To understand the physics of phase change in open clusters we need to define a phase change point. For this purpose let us first analyze thermodynamics of the cluster in vicinity of the transition curve.

3. Thermodynamics of L–S transition within an open cluster

We consider the thermodynamics of L–S transition within an open cluster using the concept of two-state approximation proposed by Berry and Smirnov for a melting of isolated cluster [16,23]. The main idea comes from the equilibrium state of the cluster as the coexistence of two locally stable and thermally equilibrated aggregate states, solid and liquid. This model can be generalized to include more cluster states, associated with the melting of different cluster shells [11,24].

To justify the two-state model we assume that there is large enough free energy barrier to ensure the relation

$$\tau_{\mathrm{eq}} \ll \tau_{LS},$$

where τ_{eq} is the characteristic time of kinetic thermal equilibration within a cluster (no matter liquid or solid), and τ_{LS} is the characteristic time for the cluster to occupy particular (liquid or solid) state. Under this strong inequality we are able to introduce two different temperatures, T_S for the solid state, and T_L for the liquid state. In general they are not equal. Say, in the simple Dulong–Petit limit we have

$$\Delta T = \frac{\Delta E}{3N - 6},$$

where ΔE is the free energy difference and N is the number of particles within a cluster.

In contrast with previous theories [16,23], we allow clusters to grow and evaporate due to a gaseous environment, so that
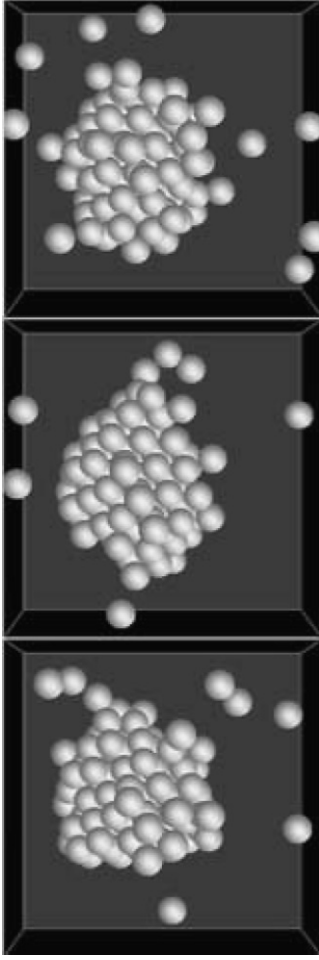
Fig. 1. Three subsequent MC steps close to the melting point.

the system must be represented through the grand canonical ensemble instead of the canonical one. To illustrate this point we refer to the simulation [6]. The authors of Ref. [6] used a canonical ensemble of particles closed in the box. However the target of our investigation is not the whole system they consider, but the cluster itself. In Fig. 1 we show three subsequent MC steps when the cluster is close to the melting point. It can be seen that the number of particles in the cluster fluctuates. This means that the system of interest (the cluster) is open to the environment, so we have to apply the grand canonical approach. However, our results can be applied to isolated clusters either, when we fix the number of particles. We will show that our approach is consistent with the canonical in this case.

The statistical weight of the liquid state is

$$g(N) = \exp\left\{ \frac{N\Delta\mu - \Delta E}{T} + \Delta S \right\},$$
(2)

where $\Delta\mu = \mu_S - \mu_L$, $\Delta S = S_S - S_L$, $\mu_{S,L}$ and $S_{S,L}$ are the corresponding chemical potentials of the cluster and its entropies. The corresponding probabilities for the cluster to be found in the solid or liquid state are

$$p_S = \frac{1}{1+g}, \qquad p_L = \frac{g}{1+g}.$$

Following the idea of paper [23] we introduce also the conditional probabilities, $p_i^{(j)}$ ($i, j = S, L$) which is the probability for the cluster to be in jth state, if it is first found in the ith state. The total entropy of a two-state system is given by

$$S = -p_S \sum_j p_S^{(j)} \ln\left(p_S p_S^{(j)}\right) - p_L \sum_j p_L^{(j)} \ln\left(p_L p_L^{(j)}\right)$$
$$= p_s S_S + p_L S_L + S_c,$$
(3)

where

$$S_S = \sum_j p_S^{(j)} \ln p_S^{(j)}, \qquad S_L = \sum_j p_L^{(j)} \ln p_L^{(j)},$$
(4)

are the corresponding "partial" entropies, and S_c is the configurational entropy. The latter can be expressed through the statistical weight (2) as follows

$$S_c = -p_S \ln p_S - p_L \ln p_L = \ln(1+g) - \frac{g \ln g}{1+g}.$$
(5)

Using the notation of partial entropies (4), we specify the meaning of the two temperatures T_S and T_L through the simple thermodynamic relations:

$$\frac{1}{T_S} = \left(\frac{\partial S_S}{\partial E}\right)_{V,N}, \qquad \frac{1}{T_L} = \left(\frac{\partial S_L}{\partial E}\right)_{V,N}.$$
(6)

Following Landau's arguments [25], we express the thermodynamic temperature appearing in the statistical weight (2) through the derivative $1/T = (\partial S/\partial E)_{V,N}$, which can be rewritten as a sum

$$\frac{1}{T} = \frac{p_S}{T_S} + \frac{p_L}{T_L} + \frac{dS_c}{dE}$$
$$= \frac{1}{(1+g)T_S} + \frac{g}{(1+g)T_L} - \frac{\ln g}{(1+g)^2}\frac{dg}{dE}.$$
(7)

From Eq. (2) we derive

$$\frac{dg}{dE} = \frac{g}{CT^2}\left\{ \Delta E - N\Delta\mu + CT\frac{\Delta\mu}{\mu} \right\},$$
(8)

where the specific heat C and chemical potential μ are given by

$$C = \left(\frac{\partial E}{\partial T}\right)_{V,N}, \qquad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}.$$

On the other hand, the thermodynamic chemical potential can be expressed through the "partial" chemical potentials

$$\mu = p_S \mu_S + p_L \mu_L.$$
(9)

Using the relations (3)–(9) we are able to obtain the general expression for the heat capacity of cluster. The final expression can be substantially simplified near the melting point, where we set $g \approx 1$,

$$\frac{1}{C} = \frac{1}{C_0} - \frac{\Delta T}{4T}\left\{ \frac{\Delta\mu}{\mu} + \frac{Z}{C} \right\} + \frac{1}{4}\left\{ \frac{\Delta\mu}{\mu} + \frac{Z}{C} \right\}^2,$$
(10)

where we introduce the quantity

$$Z = \frac{1}{T}(\Delta E - N\Delta\mu).$$

The physical solution to equation (10) is

$$C = 4\mu T + \mu Z \Delta T - 2TZ\Delta\mu$$
$$+ \sqrt{\mu[\mu(4T + Z\Delta T)^2 - 16T^2 Z\Delta\mu] - 16T^2\mu^2 Z^2/C_0}$$
$$\times \left[8\mu T/C_0 + 2(T\Delta\mu - \mu\Delta T)\Delta\mu/\mu\right]^{-1} \quad (11)$$

which represents the general expression of a specific heat through the well defined thermodynamic quantities within the framework of this semi-phenomenological model. In the case of bulk system, phase transition point corresponds to divergence of the heat capacity, but for the finite system C still has a maximum, which we define as the phase transformation point. In the next section we analyze its behavior in more detail.

4. Critical size of the growing cluster

To obtain the general relation between the melting temperature and the critical melting number of atoms within a cluster, i.e. the number of particles necessary for L–S transition to occur for given temperature, we need to find an extremum of Eq. (11). However, C is a function of two independent parameters, the number of particles and the temperature. To approach the problem let us first fix N. In this case cluster is described by the canonical ensemble and Eq. (11) simplifies to the following:

$$C = \frac{C_0}{2}\left\{1 + \frac{\Delta E \Delta T}{4T^2} + \sqrt{\left(1 + \frac{\Delta E \Delta T}{4T^2}\right)^2 - \frac{\Delta E \Delta T}{4T^2}}\right\}. \quad (12)$$

Maximum value of C at the melting point is therefore given by

$$C_{\max,N} = \frac{\Delta E^2}{4T_m^2}, \quad (13)$$

which is consistent with the previous results obtained by the canonical approach [11,16,23].

Now we come back to the grand canonical relation (10) to look at the dependence of the critical melting number of particles on the melting temperature (we drop the subscripts to simplify the discussion). Eq. (10) represents heat capacity as a function of two independent variables, μ and N. However, physically it is obvious that if we fix the number of particles, then the heat capacity must reach the same maximum quantity, as is determined from canonical ensemble calculations. This allows us to use Eq. (13) in the grand canonical expression (10) to obtain explicit relation between the number of particles and the temperature at the melting point. Substituting Eq. (13) to Eq. (10) and using $\Delta E = N\Delta\mu$ at the melting point, we obtain

$$\frac{\Delta\mu}{\mu}\left(\frac{\Delta\mu}{\mu} - \frac{\Delta T}{T}\right) = 4\frac{\Delta T}{N\Delta\mu}\left(\frac{4T^2}{N\Delta\mu\Delta T} - 1\right), \quad (14)$$

where N must be understood as the *average* number of particles (the actual number can fluctuate). It is the cubic algebraic equation for the number of particles N. To obtain the explicit dependence $N(T)$ we generally need a particular relation of ΔT to $\Delta\mu$ and N. For example, in the Dulong–Petit limit we

obtain

$$\frac{\Delta\mu^2}{\mu^2}\left(1 - \frac{\mu}{3T}\right)N^3 + 2\left(\frac{2}{3} - \frac{\Delta\mu^2}{\mu^2}\right)N^2$$
$$- 16\frac{T^2}{\Delta\mu^2}N + 32\frac{T^2}{\Delta\mu^2} = 0. \quad (15)$$

In general case this equation can be much more complicated and depend on the particular properties of the system.

However, in the zeroth order in $\Delta T/T$ we obtain a very simple relation

$$T_m^{(\text{cl})} = N_c \frac{\Delta\mu^2}{4\mu}. \quad (16)$$

We would emphasize that our approach deals with the chemical potential and the number of particles instead of the cluster radius, as it was done previously in phenomenological classical theory of melting in spherical finite systems [26–28]. In principle it allows the study of clusters of any shape, formed by complex particles with various interaction energies. The expression only requires the temperature and size dependence of the chemical potential.

5. Size dependence of the melting temperature

Previously we concentrated on the phase transformation in an open cluster caused by the change of particles number. However, our results also determine the melting temperature once the number of particles in the cluster is given. This allows us to relate the melting temperature to the cluster size and explain the deviation from the simple classical result.

For the bulk case, i.e. when $N_c \to \infty$, we approach the true phase transition point when $\Delta\mu \to 0$, so that

$$T_m^{(\text{b})} = \lim_{N_c \to \infty} T_m^{(\text{cl})}.$$

Although it is impossible to calculate this limit explicitly, we can use simple arguments to estimate the relation $T_m^{(\text{cl})}/T_m^{(\text{b})}$. Let us write the chemical potentials of the solid and liquid cluster as a sum $\mu_{S,L} = \mu_{S,L}^{(\text{b})} + \mu_{S,L}^{(\text{sur})}$ of the bulk part $\mu_{S,L}^{(\text{b})}$ and the surface part $\mu_{S,L}^{(\text{sur})}$. When $N \to \infty$, both surface parts tend to zero, but the bulk parts approach each other. This means that the bulk melting temperature can be represented by the same relation as Eq. (16), but without the surface contribution in the chemical potential. As a result the ratio $T_m^{(\text{cl})}/T_m^{(\text{b})}$ is given by

$$\frac{T_m^{(\text{cl})}}{T_m^{(\text{b})}} \approx \frac{\mu^{(\text{b})}}{\mu^{(\text{b})} + \mu^{(\text{sur})}}\left(1 + 2B\Delta\mu^{(\text{sur})} + B^2\Delta\mu^{(\text{sur})2}\right), \quad (17)$$

where constant B depends *only on the bulk* properties of solid and liquid systems through the chemical potentials, and $\mu^{(\text{sur})} = \mu_S^{(\text{sur})} - \mu_L^{(\text{sur})}$. Note, the expression (17) is valid for any shape of cluster. On the other hand there is well-known classical result [26–28] for a spherical droplet

$$\frac{T_m^{(\text{cl})}}{T_m^{(\text{b})}} = 1 - \frac{C}{R}, \quad (18)$$

where C is some positive constant and R is the cluster size. Even at this step it can be seen that the ratio $T_m^{(cl)}T_m^{(b)}$ approaches unity in a different way in Eqs. (17) and (18), because of the pre-factor containing surface contribution to chemical potential.

Experimental observations of a size-dependent melting (see e.g. [29–31]) mainly concentrated on the identification of shell closing and the corresponding variation of the melting temperature. However even if we only consider the closed shells there is notable difference in behavior of the melting temperature with changing cluster size. Experiment [29] clearly indicated that the data cannot be fitted by the classical result (18), and the cluster melting cannot be extrapolated to the bulk value. To address this question we simplify Eq. (17) for the case of spherical cluster using the simple Tolman formula for the surface tension of a cluster [32–34]

$$\sigma = \sigma_0 \left(1 - \frac{2\delta}{R}\right),$$

where σ_0 is the tension of a plate surface and δ is the Tolman length. After some algebra, Eq. (17) takes the form

$$\frac{T_m^{(cl)}}{T_m^{(b)}} \approx \frac{\mu^{(b)}}{\mu^{(b)} + \mu^{(sur)}}\left(1 - 2B^*\frac{\Delta\delta}{R} + B^{*2}\frac{\Delta\delta^2}{R^2}\right), \quad (19)$$

where B^* again contains only the bulk quantities, $\Delta\delta = \delta_S - \delta_L$, and we neglected terms proportional to $\Delta\sigma_0/\sigma_0$. First notable feature as compared to the classical formula is the last term in the brackets, which can be quite essential for very small clusters. But what is more important, there is a non-unity pre-factor in Eq. (19), which is strongly dependent on the surface characteristics. On Fig. 2 we show the best fit of our result (19) to the experimental data [29], which could not be explained by the simple formula (18). The explicit expression for $\mu^{(sur)}$ essentially depends on the particular type of atoms, their interaction and experimental conditions. Of course $\mu^{(sur)} \to 0$ when $N \to \infty$, but this term governs the deviation from the classical behavior for the intermediate size of clusters observed in experiment.
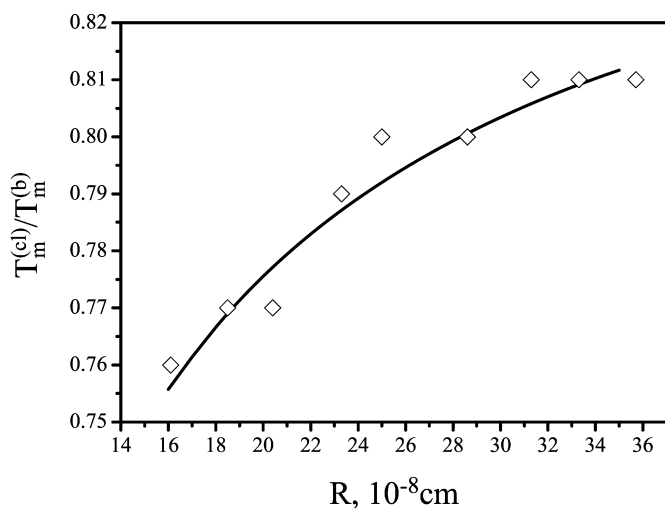

Fig. 2. The best fit of our theoretical result (19) to the experimental data from Ref. [29].

6. Conclusions

It was suggested previously [6,8], that protein crystals should nucleate to a stable disordered aggregate and crystalize when some certain critical size is reached. To understand the underlying physics of the simulation [6], we proposed a semi-phenomenological model for a phase transformation within a finite system with changing number of particles. It is particularly related to the study of nucleation processes in colloidal systems, when the phase transformation within a cluster can occur [6,9,10]. In contrast with the bulk system, the liquid–solid transition within a cluster is not a true first order phase transition, but a continuous one, characterized by maximum of its specific heat. This phase transformation can be achieved in two different ways. First, we can keep the cluster size fixed and change temperature. The semi-phenomenological theory of this kind of transition is well developed [11,16,23]. Second possibility is the isothermal growth of a cluster, which is the object of present study.

Extending the two-state cluster model [16,23], we treat cluster as a grand canonical ensemble. This allows us to obtain the general thermodynamic relation between the melting temperature of the cluster and its size, which resolves deviations from the classical prediction of melting temperature behavior. Our results agree qualitatively with available experimental data [29].

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