Cluster melting in effective potential model

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Abstract. The paper shows that the melting temperature of clusters and nanoparticles is determined by the depth of potential well of pair interaction potential, the number of particles in a cluster, and the particle packing pattern. A cluster is in solid (crystalline or quasicrystalline) state, if the potential energy of interaction between cluster particles corresponds to global minimum, in this case the geometric configuration of particle spatial arrangement is considered to be the structure of a solid cluster. A formula is proposed to calculate cluster melting temperature depending on the number of particles in a cluster.

1. Introduction

Since recently phase transitions in cluster systems have been a matter of focal theoretical scientific interest and experiments. Some examples of such studies are the papers by B.M. Smirnov, [1–4]; R.S. Berry et. al. [5–10]; D.J. Wales [11, 12] and others. A comprehensive bibliography on melting processes running in cluster systems and nanoparticles can be found in G. Makarov’s review [13]. Research results have revealed main features of phase transitions in cluster systems. One of them is the phenomenon of two co-existing phases: a cluster system has a certain temperature region that ranges from the temperature of transition into solid state $T_{sol}$ to the temperature of transition into liquid state $T_{liq}$. The region of two phase coexistence is determined by the difference between these two temperatures, with this difference tending to approach zero as the number of the particles in the cluster tends to infinity. Within this co-existence region there is such temperature at which free energies of solid and liquid states get equal. In the condition of thermodynamic equilibrium this temperature is called cluster melting temperature.

Solid-liquid state phase transition in clusters is understood as configuration excitation in the cluster structure. The complexity of its description can be explained by the difficulty to find the global minimum of cluster energy and an optimal configuration of cluster atoms spatial arrangements that will agree therewith. Potential energy surface (PES) of a cluster has multiple local minimums and saddle nodes. For a Lennard-Jones cluster with particle number 13 there are 988 PES local minimums, and these local minimums are exponentially increasing in number as the quantity of atoms in the cluster increases [13].

In lattice models the melting of a cluster is described as first order “order-disorder” phase transition which is accompanied by spasmodic internal energy change and entropy of the system at a melting temperature when free energies are equal sufficiently to distribute atoms in the cluster system. Here the function of elementary configuration excitation belongs to void as an exited vacancy. For example, in cluster $X_{13}$, that is structured as a icosahedron, phase transition into liquid state takes place when only one atom moves out of the occupied shell onto its surface. Lattice models utilize...
traditional Lindemann criterion of melting and more accurate criteria for Etters-Kaelberer clusters [14,15] that can jump in the melting point.

Phase transitions in cluster systems are accompanied by an abnormal heat capacity behavior close to the melting point. Negative heat capacity of a cluster, which was predicted in [16, 17], was experimentally found for sodium ion cluster [18]. Size effect for melting temperature, that was tentatively described in [19], today has been verified by many experiments, including diffraction methods (by means of transmission electron microscopy it has been found that diffraction pattern changes in the melting point, which is explained by cluster structure disordering under melting effect [20]); reflection methods, that are based on the changes in the reflectivity of the clusters implanted into a transparent template when they transit through the melting range [21]); calorimetric methods (when the cluster, that has been deposited onto the surface of a thin-film calorimeter, is melting there is a sharp increase in the heater’s power consumption rate [22]); optical techniques (used to identify spectral changes in the clusters that consist of a giant molecule and clusters of inert gases [7, 23]). Cluster melting temperature determines the disintegration threshold of nanostructure elements and thin films.

Let’s assume that global conformation of a cluster is a geometric configuration in the spatial arrangement of atoms (or centers of masses of molecules) in a cluster and this configuration corresponds to the global minimum of the total energy of interaction between the cluster particles. In the approximation of the first-order interaction of two particles in the cluster when their interaction energy can be described through pair interaction potential as the function of one argument, which is the distance between the particles, the energy of the interaction of all cluster particles can be defined as the sum-total of the energies of first-order interactions N of the particles in its structure:

\[
E(r_0) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V(r_{ij})
\]

(1)

To find the global minimum of function (1) is a serious problem in the physics of cluster systems. There are numerous theoretical works devoted to its solution and informative databases that contain the values of cluster minimal energy with relative conformations for different numbers of atoms and different interaction potentials [24]. In order to find the minimum of function (1) different mathematical methods can be applied and different interaction potentials can be used [25, 26].

In this paper we refer to the power potential of interaction of particles with potential well effective depth that depends on the number of particles in a cluster system as it helps us to determine the dependence of cluster melting temperature on the number of particles in the cluster structure.

2. The depth of potential well of pair interaction potential

In the most general case we have defined the depth of potential well of pair interaction potential by the formula [27]

\[
\varepsilon_{eff} = \varepsilon_0 + \Delta\varepsilon
\]

(2)

where \( \varepsilon_0 \) - the depth of potential well of pair interaction potential, \( \Delta\varepsilon \) - actual energy increment predetermined by the interaction with the nearest neighbors. The calculation of is the main objective in describing inter-molecular interaction of particles within effective field.

With When studying the interaction of a cluster with a free-moving particle having a kinetic energy that is proportional to absolute temperature \( T \) with the help of cluster model the author of this paper obtained the following relationship for \( \Delta\varepsilon \) [27 – 29]
$$\Delta \varepsilon = \left( \frac{Z-1}{Z+1} \right)^2 kT$$  \hspace{1cm} (3)

where \( Z \) - the number of particles in a cluster at a temperature \( T \).

According to formulas (2) and (3) efficient depth of the potential well of interaction potential will be defined by

$$\varepsilon_{eff} = \varepsilon_0 + \left( \frac{Z-1}{Z+1} \right)^2 kT = \varepsilon_0 \left[ 1 + \left( \frac{Z-1}{Z+1} \right)^2 \frac{kT}{\varepsilon_0} \right]$$  \hspace{1cm} (4)

The depth of the potential well of pair interaction potential \( \varepsilon_0 \) is determined by the critical temperature of a matter. For inert gases and simple fluids with Lennard-Jones potential \( \varepsilon_0 = 0.769T_c \), with Buckingham potential (6-exp) \( \varepsilon_0 = 0.82T_c \), with Morse potential \( \varepsilon_0 = 0.947T_c \).

Today more than twenty potentials are used to describe interactions between atoms in crystals and fluids. Quite often power potentials are used, for example, Mie potential [2]

$$\varphi(r_j) = \frac{\varepsilon_0}{n-m} \left( \frac{n}{m} \right)^{1/n-m} \left[ \left( \frac{\sigma}{r_j} \right)^n - \left( \frac{\sigma}{r_j} \right)^m \right]$$  \hspace{1cm} (5)

where \( \varepsilon_0 \) - the depth of potential well, \( \sigma \) - effective diameter of interacting particle, \( n \geq m \) - integer exponents, with \( m = 6 \), \( n = 9,...,24 \).

In the proposed model Mie’s power potential shall be changed by replacing the value \( \varepsilon_0 = 0.769T_c \) by the effective depth of potential well that is found by formula (4) and writing it as

$$V(r_j) = C \varepsilon_0 \left[ 1 + \frac{(Z-1)^2 kT}{\varepsilon_0} \right] \left[ \left( \frac{\sigma_0}{r_j} \right)^n - \left( \frac{\sigma_0}{r_j} \right)^m \right]$$  \hspace{1cm} (6)

$$C = \frac{n}{(n-m)} \left( \frac{n}{m} \right)^{1/n-m}, \sigma_0 = \left( \frac{m}{n} \right)^{1/n-m} R_l$$

With exponent values \( m = 6, n = 12 \) Mic potential (5) is simplified and is called Lennard-Jones (LJ) potential. Then in accordance with formula (6) the radius of the first coordination sphere will be:

\( R_{lj}(LJ) = 2^{\frac{1}{6}} \sigma = 1.1225 \sigma \), for other values of parameters \( (m,n) \) we’ll get: \( R_{lj}(6,9) = 1.1447 \sigma \), \( R_{lj}(6,18) = 1.0959 \sigma \), \( R_{lj}(6,24) = 1.08006 \sigma \) etc. It is worth noting that in Lennard-Jones potential the coefficient of proportionally 1.1225 of the first coordination sphere radius and the effective diameter of a particle correspond to fcc lattice, while with \( m = 6 \), and \( n = 18 \) it corresponds to bcc lattice.

3. Cluster melting temperature

For macroscopic crystals there is empirical rule according to which the crystal melting temperature is proportional to the potential well of pair interaction potential. In the first approximation this rule applies both to cluster systems and nanoparticles [30]. The influence of the surrounding particles on the energy of first-order interaction results in the dependence of cluster melting temperature on the quantitative composition of a cluster or its geometrical dimensions. To evaluate the depth of effective potential well we shall use formula (4). For the cluster system \( T_m = c \varepsilon_{eff}, c = const \), and considering the formula (4) melting temperature will be defined by the following relationship.
\[ T_m(Z) = c \epsilon_0 \left[ 1 - c \left( \frac{Z-1}{Z+1} \right)^2 \right]^{-1} \]  
(7)

Empirical constant \( c \) will be defined through passage to the limit. For a macroscopic sample with \( Z \to \infty, T_m(Z) \to T_m(\infty) \) i.e. cluster melting temperature will tend to the melting temperature of the macroscopic sample, hence by applying approved data on inert gases and formula (7) we’ll get the empirical constant value:

\[ c = \left[ 1 + \frac{\epsilon_0}{T_m(\infty)} \right]^{-1} = \frac{2}{3}(\Phi - 1) = 0.412... \]  
(8)

Considering the obtained value of the empirical constant the relationship (7) can be written as

\[ T_m(Z) = 0.56(56)...(\Phi - 1)\epsilon_0 \left[ 1 + \left( \frac{Z-1}{Z+1} \right)^2 \right] \]  
(9)

where \( \Phi = 1.6180339... \) – golden section ratio that defines Lindemann criterion for cluster melting [31, 32].

In cluster systems with a finite number of particles the cluster melting temperature reduced to pair interaction energy will be the universal function of the number of particles in the cluster irrespective of the cluster nature.

In formula (9) the depth of potential well of pair interaction potential will depend on the potential type, thus any cluster melting temperature predictions made by means of this formula may be uncertain. So it might be proper to write formula (9) as follows

\[ T_m(Z) = \frac{1}{2} T_m(\infty) \left[ 1 + \left( \frac{Z-1}{Z+1} \right)^2 \right] \]  
(10)

where \( T_m(\infty) \) - bulk sample melting temperature that can be experimentally found with sufficient accuracy.

The obtained relationship to be used to calculated cluster melting temperature (10) does not contain any empirical constants, satisfies limiting processes and agrees with empirical data received by means of different methods.

Figure 1 shows reduced melting temperature of inert gas quasicrystal clusters - cluster qualitative composition dependences that have been found by formula (10) (b), and similar diagrams obtained for argon by molecular dynamics methods (a) [33]. According to theoretical model proposed in [34] for organic nanocrystals the dependence of cluster melting temperature from cluster size is essentially similar to our calculations and simulations made in [33].

The paper [34] was devoted to the size effect of melting temperature in organic nanocrystals that were produced by filling porous materials with appropriate organic liquids. Its authors showed that the dependence of the melting temperature of such object on its size can be described by the following formula:

\[ \frac{T_m(r)}{T_m(\infty)} = \frac{\sigma^2(\infty)}{\sigma^2(r)} = \exp \left[ \frac{-(\alpha - 1)}{\left( r / r_0 \right) - 1} \right] \]  
(11)

where \( r \) - the radius of a crystal; \( T_m(\infty) \) - bulk crystal melting temperature; \( r_0 \) - critical radius at which all atoms of a nanoparticles are located on its surface; \( \sigma^2(r) \) - mean square displacement.
(MSD) of atoms of a particle with a radius $r$; $\sigma^2(\infty)$ - is MSD of atoms of the relevant bulk crystal; $\alpha$ - the ratio of MSDs of surface and internal atoms of the crystal.

In [35–37] it was demonstrated that the dependence of a metal cluster melting temperature on the cluster radius can be described by simple relationship

$$T_m(R) = T_m(\alpha) \left[ 1 - \frac{\alpha}{R} \right]$$

where $\alpha$ - empirical constant that is approximately equal for all metals with fcc structure.

In such systems the relationships (11), (12) and our formula (10) yield such cluster melting temperature - number of particles relations that have good qualitative agreement (calculation disagreement is about 10-15%), so simultaneous solution of these equations allows us to determine the relationship between the radius of a cluster system and the number of particles in this system.

4. Conclusion
Melting temperature of clusters and nanoparticles is determined by the depth of potential well of pair interaction potential, the number of particles in a cluster and particle packing pattern. A cluster is in solid (crystalline or quasicrystalline) state, if the potential energy of interaction between cluster particles corresponds to global minimum, in this case the geometric configuration of particle spatial arrangement is considered to be the structure of a solid cluster.

A certain energy imparted to a cluster system destructs the original particle arrangement that agrees with global minimum, and a new particle configuration is formed. This particle rearrangement can be interpreted as the configuration of melting onset; this melting process ends when the initial global configuration of particles is lost completely. Cluster melting process runs with a constant number of particles in the cluster in contrast to the process of particle emission either out of cluster space or from the surface of a cluster or a nanoparticle.

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