

## The Melting of Cluster Systems and Nanoparticles Models Pair Potential with an Effective Potential Well

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A quasicrystal model of cluster systems and nanoparticles, which allows using a pair potential of interaction with the effective depth of the potential well to trace the dependence of the melting temperature of clusters and nanoparticles by their.

**Keywords:** Quasicrystal model, Interaction potential, Melting point, Lindemann criterion.

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### 1. INTRODUCTION

Global conformation cluster will assume the geometric configuration of the spatial arrangement of atoms (or centers of mass of molecules) of a cluster corresponding to the global minimum of the total energy of the interaction between all the particles and will correspond to the conformation of the solid (crystalline or quasi-crystalline) cluster. In the approximation of pair interactions between particles that make up the cluster, when the energy of interaction between two particles can be set pairwise interaction potential as a function of one argument - the distance between the particles, the interaction energy of a cluster of particles is defined as the sum of the energy of the pair interactions of N particles contained in it:

$$E(r_{ij}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N V(r_{ij}) \quad (1)$$

To find the minimum of the function (1) apply various mathematical methods and using different interaction potentials. The model [2-5] Mie potentials and Lennard-Jones most clusters are icosahedral structure. The study of clusters using Morse potential [6] showed that the minima may correspond to different types of arrays, however, geometrical structures tend to be symmetrical spherical shape. Often, more sophisticated modeling applied potentials Dzyugutov [2, 3] Kratzer [7, 8] and others. Currently, the most accurate empirical interaction potentials of rare gas atoms is considered to be the potential of Aziz and his various options [9-11] with a sufficiently large set of adjustable parameters to be determined by a wide range of experimental thermodynamic properties of gaseous and liquid inert gas.

To describe the interaction between the molecules in the disordered condensed media is not enough to choose the parameter values of  $m$  and  $n$ , in the interaction potentials, we must assume that the depth of the potential well in the potentials depends on the number of particles in the cluster system and the parameters of state of the environment. In this case, the potential well depth is called the effective depth and is a function of the number of particles in the system, the density and temperature. In [12] used a modified Lennard-

Jones potential with an effective potential well, which depends on the density of the depth

$$\varepsilon_m = 4\varepsilon_0 \left[ 1 - \left( \frac{\rho_c}{\rho_m} \right)^2 \right] \left[ \left( \frac{d_w}{d_m} \right)^6 - \left( \frac{d_w}{d_m} \right)^{12} \right] \quad (2)$$

where  $\rho_m, \rho_c$  - the density of the liquid at the melting temperature and the critical point,  $d_m$  - the average distance between the molecules,  $\varepsilon_0$  - constant dispersion forces.

The effective depth of the potential well  $\varepsilon_{eff}$  in this work is determined by the formula

$$\varepsilon_{eff} = \varepsilon_0 \left[ 1 - \left( \frac{\rho_c}{\rho_m} \right)^2 \right] \quad (3)$$

it is a function of characteristics of the reference fluid, but does not depend on the state parameters substance.

In [13] it is assumed dependence of the effective depth of the potential well  $\varepsilon_{eff}$  and the effective diameter  $\sigma_{eff}$  of particles interacting by the law of temperature:

$$\frac{\varepsilon_{eff}}{k} = 117.7 + \frac{778.0}{T}, \quad K; \quad \sigma_{eff} = 3.672 - \frac{22.3}{T}, \quad \text{\AA} \quad (4)$$

Liquid argon at near the melting point  $T = 86K$  of the formula (4) gives the following values of:  $\varepsilon_{eff} = 126.7 K$ ;  $\sigma_{eff} = 3.413 \text{\AA}$ .

### 2. THE EFFECTIVE DEPTH OF THE POTENTIAL WELL IN THE PAIR INTERACTION POTENTIAL

The effective depth of the potential well in the pair interaction potential, in general, we have defined the formula [14]

$$\varepsilon_{eff} = \varepsilon_0 + \Delta\varepsilon \quad (5)$$

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where  $\varepsilon_0$  – the depth of the potential well of the pair interaction potential,  $\Delta\varepsilon$  – effective supplement to it, due to the interaction with nearest neighbors. The calculation of the value  $\Delta\varepsilon$  is the main objective when describing the intermolecular interaction of the particles within the effective field.

Within the framework of the cluster model when looking at the interaction of clusters with a freely moving particle with a kinetic energy that is proportional to absolute temperature  $T$ , for the value  $\Delta\varepsilon$  of the ratio obtained by the authors [15-17], which allowed us to describe features of the IR spectra of liquids and minerals:

$$\Delta\varepsilon = \left(\frac{Z-1}{Z+1}\right)^2 kT \quad (6)$$

where  $Z$  – the number of particles at a temperature  $T$  in the.

The effective depth of the potential well of the interaction potential in accordance with the formulas (5) and (6) defined by the expression

$$\varepsilon_{eff} = \varepsilon_0 \left[ 1 + \left(\frac{Z-1}{Z+1}\right)^2 \frac{kT}{\varepsilon_0} \right] \quad (7)$$

The depth of the potential well of the pair interaction potential is determined by the critical temperature of the transition liquid-vapor substance. For inert gases and liquids with a simple Lennard-Jones potential  $\varepsilon_0 = 0,769T_c$ , with the potential (6-exp) – Buckingham  $\varepsilon_0 = 0,82T_c$ , for Morse potential  $\varepsilon_0 = 0,947T_c$ . At low temperatures  $T \rightarrow 0$  according to the formula (7), the depth of the effective potential well becomes equal to the energy of pair interaction between particles  $\varepsilon_{eff} \rightarrow \varepsilon_0$ .

### 3. THE TEMPERATURE OF MELTING OF CLUSTER SYSTEMS

For macroscopic crystals set a rule of thumb, according to which the crystalline melting temperature is proportional to the depth of the potential well of the pair interaction potential. As a first approximation, this rule holds for cluster systems and nanoparticles [18]. The influence of the surrounding particles of energy pair interaction leads to a dependence of the melting temperature of the cluster system by its quantitative composition, or the geometric dimensions. The depth of the effective potential well can be estimated by the formula (7), then it is possible to put a cluster system  $T_m = c\varepsilon_{eff}$ ,  $c = const$ , taking into account the formula (7), the melting point is determined as

$$T_m = c\varepsilon_0 \left[ 1 - c \left(\frac{Z-1}{Z+1}\right)^2 \right]^{-1} \quad (8)$$

The empirical constant  $c$  in equation (8) is determined by the limiting process. For a macroscopic sample at  $Z \rightarrow \infty$ ,  $T_m \rightarrow T_m(\infty)$ , i.e. an infinite number of

particles in the cluster, the cluster system becomes equal to the melting point of the melting point of the macroscopic sample, so using well-proven data for the noble gases and the formula (8) for the empirical constant derived from the value of

$$c = \left[ 1 + \frac{\varepsilon_0}{T_m(\infty)} \right]^{-1} = \frac{2}{3}(\Phi - 1) = 0.412... \quad (9)$$

Considering the value obtained empirical constant, the ratio of (8) can be presented in a convenient form and written as

$$T_m(Z) = 0.56(56)...(\Phi - 1)\varepsilon_0 \left[ 1 + \left(\frac{Z-1}{Z+1}\right)^2 \right] \quad (10)$$

where  $\Phi = 1.6180339 \dots$  - factor "gold" section, which defines the Lindemann criterion  $\delta_L$  on melting cluster systems.

For clustered systems with a finite number of particles reduced to the pair interaction energy of the melting temperature of clusters of different nature is a universal function of the number of particles in their structure. The number of particles in the cluster system can be expressed by any and any positive integer, but according to one of the theorems E. Zeckendorf (1939): Every positive integer has a unique representation as a sum of Fibonacci numbers, in which the two adjacent Fibonacci numbers are never used. Edward Zeckendorf proved that this result is general and valid for any positive integer, the result is used to solve Hilbert's 10-th problem [19]. In the formula (10) under the value of  $Z$  should be understood the sum of Fibonacci numbers corresponding to the number of particles in the cluster.

The depth of the potential well of the pair interaction potential in the formula (10) depends on the type of the selected potential, so the prediction cluster systems melting point of this formula has some uncertainty [20]. Formula (10) is conveniently written as

$$T_m(Z) = \frac{1}{2} T_m(\infty) \left[ 1 + \left(\frac{Z-1}{Z+1}\right)^2 \right] \quad (11)$$

where  $T_m(\infty)$  – the melting temperature of the respective sample volume, which can be experimentally determined with good accuracy.

The resulting ratio calculation melting temperature cluster systems (11) does not contain any empirical constants, and corresponds to the passage to the limit is consistent with the experimental data obtained by different methods.

Fig. 1 is a plot of the reduced temperature melting quasicrystalline clusters of noble gases according to their numerical composition according to formula (11) (a) and similar graphs obtained by calculation using molecular dynamics (MD) for argon (b) [21]. For organic nanocrystals according to the theoretical model proposed in [22] cluster melting temperature dependence of their size qualitatively repeat our calculations and simulation MD results in [21].

In [22] studied the size effect the melting point for the organic nanocrystals obtained by filling the appropriate organic liquids and porous materials show that the dependence of the melting temperature of such objects by their dimensions can be described by the formula

$$\frac{T_m(r)}{T_m(\infty)} = \frac{\sigma^2(\infty)}{\sigma^2(r)} = \exp\left[\frac{-(\alpha-1)}{(r/r_0)-1}\right], \quad (12)$$

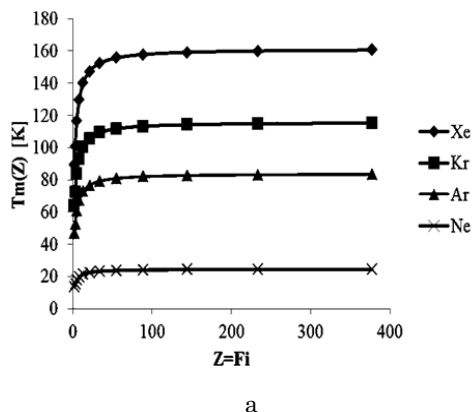
where  $r$  – the radius of the crystal,  $T_m(\infty)$  – melting temperature of the bulk crystal,  $r_0$  – the critical radius at which all the atoms are on the surface of the nanoparticles,  $\sigma^2(r)$  – the mean square displacement (MSD) of the atoms of a particle with a radius  $r$ ,  $\sigma^2(\infty)$  – is MSD atoms to the corresponding bulk crystals,  $\alpha$  – the ratio of surface MSD atoms and internal atoms of the crystal.

In a series of studies [23-25] have shown that the dependence of the melting temperature of metal clusters on their radius can be described by the simple expression

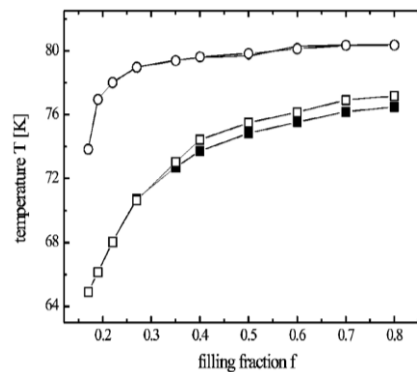
$$T_m(R) = T_m(\infty) \left[1 - \frac{\alpha}{R}\right], \quad (13)$$

where  $\alpha$  – constant, is approximately the same for the metal in the fcc structure.

The relations (13), (12) and the proposed formula (11) give the dependence of the melting temperature of



a



b

**Fig. 1** – the melting temperature of the noble gas clusters (a), the crystallization temperature and the melting temperature of the argon cluster system at the triple point  $T = 83.3$  K [21] (b)

the cluster systems the number of particles in such systems is qualitatively consistent with each other (the difference in the calculations in the range of 10-15 %) and the joint solution of these equations allows us to establish a relationship between the radius of the cluster system and the number of particles in the system.

#### 4. CONCLUSIONS

The melting temperature of clusters and nanoparticles is determined by the depth of the potential well of the pair interaction potential, the number of particles in the cluster system and the method of packing of particles in the cluster structure. The cluster is in solid (crystalline or quasi-crystalline) state, if the potential energy of the interaction of its constituent particles corresponds to the global minimum, with the geometric configuration in the spatial arrangement of the particles is considered to be a solid structure of the cluster

At a certain value of energy reported a cluster system destroys the original order in the arrangement of the particles corresponding to the global minimum, a new configuration of the particles, which can be interpreted as the configuration of the onset of melting, and the end of melting occurs at a total loss of initial global configuration of particles in the cluster. Melting cluster system process occurs at a constant number of particles in the system, unlike the particles from evaporation from the surface of the volume or cluster or nanoparticles.

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