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Elastic and Caloric Properties of Cluster Systems and Nanoparticles

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The mathematical relations to calculate the isobaric coefficient of thermal expansion, the coefficient of isobaric compressibility and difference of heats for cluster systems having got within the modified cluster model developed earlier by the authors on the assumption that in disordered condensed matters there is a cluster distribution by the particle number are conducted.

Keywords: Cluster, Packing factor, Cluster model, Nanoparticles, Elastic coefficients, Caloric properties.

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1. INTRODUCTION

The experimental and theoretical researches of cluster model and nanoparticles have allowed to establish that their heat capacity is more than the one of macroscopic samples of the same chemical set. The increase of heat capacity and elastic parameters at size reduction transiting to nanosystems is a general physical property regardless the chemical matter of nanosize items [1]. For example, heat capacity of Cu clusters of 50 nm size exceeds the one of Cu volume at 1.2-2.0 times at temperature 200 K-450 K [2]. The heat cpacity of nickel the diameter of which is 22 nm was at two times higher than the heat capacity of volume Ni at temperature 300 K-800 K [3]. In paper works [4, 5] heat capacity of metal Ni and Cu nanoclusters was studied by the computer molecular-dynamic method and the increase of their heat capacity versus thermal expansion of volume phase was found.

In the paper work of Ogunsola Oluwatosin A. with the help of computer modeling the samples of Ti nanoparticles are studied on the base of Monte-Carlo method. The module of elastic sample consisting of titan nanoparticles increases at the reduction of particle size. The Japanese scientists Qing-Qing Ni, Yaqin Fu, Masaharu Iwamoto got the same results. It was found out that the elastic module of nanocomposite was unchangeable within 8 % of volume fraction of quartz particles and it increased when the particle sizes were becoming nano order. The theoretical basis of elastic module increasing at nanoparticle size reduction are given at the paper work of Morozov N.F., Krivtsov A.M., Russian scientists [6].

The temperature reduction of melting at crystal size reduction was determined in 1909 [7], the increase of size effect at one and a half times in cluster and nanosystems happens [8, 9]. For example, the melting temperature of the particle Au abruptly differed from the melting point of the macroscopic body. The reduction of melting temperature of nanocluster with its diameter reduction allows to suggest the presence of dependence of heat melting and entropy ΔSm from Au cluster size [10]. The shown effect is usually studied on metal nanostructures [8-11]. Nanoscape effects can be observed for cluster formulations and particles at the melting process of inert crystals and organic liquid crystals. In the following works [12, 13] there are the results of temperature calculations of Ar nanoparticles melting depending on the particle number in their set. For Ar cluster when $Z = 13$ the calculations show the melting temperature $T_m = 28$ K (macroscopic melting temperature 84 K order).

2. ELASTIC PROPERTIES OF CLUSTER SYSTEMS

At the result of density fluctuation in condensed matters the clusters are randomly performed and at the equilibrium matter state the cluster distribution by number is installed. The distribution function for the random variable the density probability of which is determined by the formulae (Erlang distribution) is used by the authors [14–16] for the cluster distribution by their sizes.

$$f(Z) = \frac{\lambda^m}{(m-1)!} \cdot Z^{m-1} \cdot e^{-\lambda Z} \qquad (1)$$

where λ – scale parameter ($\lambda > 0$), m – shape parameter, or distribution order, Z – number of the particles in cluster.

The formulae usage (2) for the description of real cluster systems in disordered condensed matters it is necessary to find out the selection criteria of scale parameter λ and shape parameter $\alpha = m$ which are generally the functions of the liquid state parameters.

The ration (1) has made it possible find the average particle number in cluster according to the ration [14-16]

$$\bar{Z} = \pi^2 \eta \exp(\eta) \qquad (2)$$

In the formulae (2) the value η is atomic packing coefficient in the cluster system which is determined as the relation of all atom volume in cluster set $\bar{Z}\upsilon_{at.}$ to the whole cluster volume $\upsilon_{Clust.}$ in firm sphere model

$$\eta_{Clust.} = \frac{\bar{Z}\pi\sigma_0^3}{6\upsilon_{Clust.}} \qquad (3)$$

where σ_0 – diameter of atom or effective molecular diameter of firm spheres.

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Let us define the coefficient of thermal expansion of the average cluster (the cluster contacting the average particle number in its set) at the constant pressure by the formulae

$$\alpha_{Z,P} = -\frac{1}{\bar{Z}}\left(\frac{\partial \bar{Z}}{\partial T}\right)_P \tag{4}$$

Taken into account the formulae of the average number of particles in the cluster (2) for the coefficient $\alpha_{Z,P}$ the following ration is found

$$\alpha_{Z,P} = (1+\eta)\alpha_P \tag{5}$$

where α_P – the isobaric coefficient of thermal expansion of macroscopic sample, η – the packing coefficient of particles in the cluster set.

For real nuclear and molecular systems the packing coefficient takes the value from 0.16 (6) at the critical area of liquid to 0.62-0.68 near crystallization temperature hence according to the formulae thermal expansion of cluster system exceeds the one of macroscopic sample approximately at one and a half times. The metallic cluster set has almost the same features as fcc (face-centerd-cubic) or hcp (hexagonal close packed) of volume sample up to melting point, after firm cluster melting in the liquid cluster set the packing coefficient of particles in cluster becomes a temperature function, however, it should be noted that at the critical liquid point the packing coefficient differs from zero and cluster heat expansion exceeds microscope sample heat expansion at 16 %.

The isothermal compressibility coefficient of the middle cluster is defined by the formulae:

$$\beta_{Z,T} = \frac{1}{\bar{Z}}\left(\frac{\partial \bar{Z}}{\partial P}\right)_T \tag{6}$$

On the base of the formulae (2) there is a ration for the isothermal compressibility coefficient of the middle cluster

$$\beta_{Z,T} = (1+\eta)\beta_T \tag{7}$$

where β_T – the isothermal compressibility coefficient of microscope sample.

The ration (5) and (7) show that coefficients of isothermal heat expansion and isothermal compressibility of the middle cluster are defined by the packing coefficient in the cluster set which is proportional to the middle number of particles in the cluster (shown at the formulae (3)), that's why the more particles are in the cluster set, the more its isothermal compressibility is. At Table 1 the equilibrium values of elastic module and isothermal compressibility for Si particles what show that elastic module of particles quickly reduces with size particle growth are given [17].

The fluctuation free capacity at condensed matter is defined by the formulae

$$\upsilon_f = \frac{\beta_T}{\alpha_P} \tag{8}$$

virtue of justice the ratios (5) and (7) are the same as in the middle cluster

$$\upsilon_{f,cluster} = k\frac{\beta_{Z,T}}{\alpha_{Z,P}} = k\frac{\beta_T}{\alpha_P} \tag{9}$$

Table 1 – The isothermal compressibility of Si particles [17]

Nanocluster	Elastic module at equilibrium, GPa	Isothermal compressibility, GPa^{-1}
Si_5	585	0.00171
Si_{10}	342	0.00292
Si_{18}	206	0.00485
Massive Si	166	0.00602

This conclusion is important for theoretical research of cluster systems by statistic physics methods where rations of free capacity are defining for the calculations of thermodynamic and structural fluid properties [18].

3. THE CALORIC PROPERTIES OF CLUSTER SYSTEMS

The heat capacities at the constant pressure and volumes define caloric properties and are the fundamental features of material. The phenomenological thermodynamic allows to get a ratio series connecting heat capacity of C_P and C_V and elastic properties for microscope samples [15]:

$$C_p - C_V = \frac{\alpha_p^2 V T}{\beta_T} \tag{10}$$

The elastic coefficients α_P and β_T can be experimentally defined by *P-V-T* are measurements in the material and allow to trace the dependency of heat capacity differences of the material on state parameters and external disturbances.

For cluster systems the ration (10) should be with the account of the obtained formulas as

$$(C_P - C_V)_{Clust.} = (1+\eta)(C_P - C_V) \tag{11}$$

The isobaric heat capacity of the cluster system containing $\bar{Z}$ particles with the account of the packing coefficient η according to the rations (2), (3) and (11) will be defined by the formulae

$$C_{PClust.} = \left[1 + \frac{\bar{Z}}{8}\left(\frac{\sigma_0}{R_{Clust.}}\right)^3\right] C_P \tag{12}$$

where $R_{Clust.}$ – a radius of sphere cluster.

The proportional coefficient between the isobaric heat capacity of the cluster system containing the particle number from 10 to 100 (small clusters) and the isobaric heat capacity of microscope sample is the function of three parameters- particle number in cluster $\bar{Z}$, radius, or cluster size $R_{Clust.}$ and particle diameter σ_0.

At the conditions of computer simulation of cluster systems the condition of constancy of the particle number in cluster $\bar{Z}$ can be imposed and change its geometrical

Table 2 – The nanosize effect of heat capacity of Cu and Ni particles

$\bar{Z}$ [19]	$R_{Clust.}A$ [19]	$\frac{C_{PClust.}-C_P}{C_P}100\%$ (12)	$\Delta H_{melt}(Ry)$ [19]	$\Delta S_{melt}(mRy/K)$ [19]	T_m, K [19]
Cu, $\sigma_0 = 2.56A$, ГЦК$(a = 3.605\text{A})$, $T_{0melt} = 1356.55\text{K}$, $T_D = 315\text{K}$					
201	16.4	9.54	0.673	0.851	791
369	20.1	9.47	0.907	1.019	890
555	23.3	9.22	1.525	1.639	930
791	26.5	8.99	2.280	2.315	985
1157	29.6	9.25	2.811	2.755	1020
1505	32.6	9.22	4.681	4.404	1063
Ni, $\sigma_0 = 2.48A$, ГЦК$(a = 3.524\text{A})$, $T_{0melt} = 1726.0\text{K}$, $T_D = 375\text{K}$					
201	15.9	9.54	0.768	0.786	977
369	19.3	9.71	1.314	1.253	1049
555	22.7	9.00	2.058	1.798	1145
791	25.4	9.27	3.239	2.671	1213
1157	29.0	9.04	5.868	4.657	1260
1505	31.7	9.00	8.028	6.175	1300

Notes. At Table the temperature values of nanoparticle crystallization at the dependence of its geometrical sizes and numerical set having got by the authors are given [19].

dimensions, i.e. cluster radius $R_{Clust.}$, then in firm sphere module ($\sigma_0 = const$)the isobaric heat capacity increases with the cluster radius decrease.

One of the most constant Ar clusters is a cluster consisting of 13 particles $\bar{Z} = 13$ with radius 8.0 A and Ar atom diameter 3.40 A, then the ration concludes to the result $C_{Clust.} = 1.13C_P$, which corresponds with the results of computer experiments by molecular dynamic and Monte-Carlo giving the value growth of heat capacity at 15 % [4].

The isochoric heat capacity of cluster system is defined by the ration similar to the formulae (12) which has the following expression

$$C_{VClust.} = \left[1 + \frac{\bar{Z}}{8}\left(\frac{\sigma_0}{R_{Clust.}}\right)^3\right]C_V \qquad (13)$$

Because of the constancy of cluster volume its radius is permanent and only the number of particles in the cluster can be changed, while the more the number of particles in cluster structure, the more the difference between cluster and macroscope isochoric heat capacities.

It should be noted that the ration of isobaric to isochoric heat capacity is the same for cluster system and microscope sample at the same chemical set

$$\gamma = \frac{C_P}{C_V} = \frac{C_{PClust.}}{C_{VClust.}} \qquad (14)$$

For metallic nanoparticles particularly Ni and Cu nanoparticles the increase of heat capacity is defined versus to the heat capacity of corresponding volume phase, but according to different values this increase is within 200 % to 10 % [4, 19].

4. CONCLUSIONS

In the given paper work the values of isobaric heat capacity of Ni and Cu nanoparticles of different sizes by the formulae (12) on base of data given in the article [19] which showed (Table 2) that the heat capacity of Ni and Cu nanoparticles exceed the heat capacity of corresponding volume sample approximately at 10 % reaching maximum possible value in 1.74 times for the densest packing atoms in particle structure ($\eta = 0.74$) are conducted. Nanoscale effect of heat capacity comprising at the increasing effect of cluster heat capacity with the reduction of geometrical sizes of nanoparticles within its numerical set from 20 to 1500 particles in the set are proved by the authors' module in the given article.

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