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Specific heat of nanocrystals

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Abstract

The present study extends the Einstein model for heat capacity of solids to nanoclusters. In the case of small phases the contribution of surface energy to overall thermodynamic properties of the system is essential. On that physical background, the heat capacity depends on the size of cluster through its interface energy. Employing the same relation between Einstein temperature and the cluster melting point as that for the infinitely large phase, we derive a simple expression for the heat capacity, $C_V(n)$, dependence on the number of atoms in the cluster, n . We explain the experimentally observed increase of $C_V(n)$ compared to $C_V(\infty)$ of an infinitely large homogeneous phase, with lowering of the Einstein temperature due to the contribution of the cluster interface energy. The heat capacity in the model presented scales at high T with the classical Dulong and Petit $3R$ limit and tends to zero for $T \rightarrow 0$ as required by the third law of thermodynamics. The model reported could be applied to various systems with nanoparticles, where the knowledge of specific heat is important; for example formation of nanocomposite materials, the initial stages of formation of fogs, smog and clouds, etc.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Size effects substantially influence the thermodynamic behavior of small clusters as reviewed, e.g. by Baletto and Ferrando [1]. Usually, they are accounted for by considering the contribution of the surface free energy to the total energy of the system [1–4]. This contribution could be crucial for nanocrystals with a comparable number of bulk and surface atoms. For example, the melting point of nanoclusters is considerably lowered compared to that of the infinitely large phase [1–3]. This relates to the specific heat behavior, too. Therefore, nanosize effects, not taken into account in the Einstein–Debye model, are expected to be of great importance for thermodynamic properties of systems composed of nanoclusters. Experimental evidence of the size-dependent heat capacity of nanoparticles was recently reported for metallic nanoclusters and nanostructured dielectrics [5–7]. Despite its clear physical background this phenomenon is still subject to a limited number of theoretical models [1, 8]. Here, we discuss, in the thermodynamic approach, the contribution of surface free energy to the heat capacity of nanocrystals.

The Einstein–Debye phonon model associates the heat capacity of solids with the bulk atomic vibrations in terms of phonon modes of quantum oscillators. The model does not account for the different energies of atoms inside the crystal and on its surface. The significant reduction of the local forces as a result of broken symmetry strongly affects the atomic vibrations of surface atoms. Extensive experimental studies reveal a larger mean-square displacement of surface atoms compared to the bulk [9, 10]. Therefore, the heat capacity of clusters with a comparable number of surface and bulk atoms should deviate from that of the large systems. In the model presented here, we evaluate the contribution of surface atoms to the heat capacity of an n -atomic cluster.

The description of heat capacity is based on the Einstein–Debye model and accounts for the Lindemann theory of melting. It expresses the size dependence of $C_V(n)$ through the change of melting point of small crystals. Since the melting point $T_m(n)$ depends on the number of atoms in the cluster, the heat capacity $C_V(n)$ will also depend on it. An alternative approach assuming that the heat capacity $C_V(n)$ of an n -atomic cluster is a sum of independent bulk and surface contributions will be discussed elsewhere [11]. Although our study is concentrated on the Einstein model it is valid as well for Debye function through the well known (see for instance [12])

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approximation

$$T_D \approx T_E \sqrt[3]{\frac{6}{\pi}} \quad (1)$$

therefore the heat capacity could be expressed either by the Debye temperatures T_D (and the corresponding Debye function F_D) or through the Einstein temperature T_E (and the corresponding Einstein function F_E).

2. Results and discussion

The essential difference between bulk materials and nanoclusters originates from the role of surface. The change in thermodynamic potential $\Delta G(n)$ of n -atomic crystal as compared to the gas phase is determined by the change in chemical potential $\Delta\mu$ and the surface energy σ as follows:

$$\Delta G(n) = n_B \Delta\mu + n_S d_0^2 \sigma. \quad (2)$$

where the total number of atoms $n = n_B + n_S$, n_B and n_S being the corresponding bulk and surface atoms, d_0 is the atomic diameter.

The melting point, determined by the equality condition [1–3] of thermodynamic potentials of n -atomic clusters of the molten and crystalline phase,

$$\Delta G_{\text{cryst}}(n) = \Delta G_{\text{melt}}(n) \quad (3)$$

will deviate from that of the infinitely large crystal [2, 3]. On that physical background the dependence of cluster melting point $T_m(n)$ on the number of atoms can be expressed following [1–3] by:

$$T_m(n) = T_m \left(1 - \frac{C}{\sqrt[3]{n}} \right) \quad (4)$$

where T_m is the melting point of the infinitely large crystal and C is a dimensionless adjustable constant. Equation (4) shows that the temperature of phase transition of small clusters could be considerably lowered as a result of the surface energy contribution.

Apparently, the increase of thermodynamic potential presented in equation (2) will affect the heat capacity of the corresponding small phase. It should be noticed, that the Einstein approach was originally developed for bulk materials. According to it, the crystal is considered as system of single-frequency, ν_E , quantum harmonic oscillators with Bose–Einstein statistical distribution of energy in the vibrational state. Single phonon modes involve an infinitely large, homogeneous phase without interface. The broken symmetry at the interface generates surface phonons different from that assumed in the bulk. Therefore, in the case of small phases, the Einstein frequency, ν_E , has to be divided in two parts; surface and bulk. Here we demonstrate that for nanoclusters, ν_E could be replaced by an effective frequency ν_E^{eff} that accounts for surface phonon modes as well.

The Lindemann model of melting employs the vibration of atoms in the crystal to explain the melting transition. It states that on increasing the temperature at some critical point, the average amplitude of atomic vibrations becomes larger

than the nearest neighbors distance, causing melting. In the approximation of the single atom harmonic oscillator, the Lindemann model [13] gives the following relation between the Einstein frequency of atomic vibrations, ν_E and the melting point T_m :

$$\nu_E = M \sqrt{\frac{T_m}{A d_0^2}} \quad (5)$$

where A and d_0 are the atomic weight and atomic diameter respectively, and M is a constant.

The above expression could be applied to evaluate the variation of Einstein frequency $\nu_E(n)$ with system size. According to equation (4), the melting temperature $T_m(n)$ is a function of the number of atoms building the nanocluster. Therefore, the variation of Einstein frequency with cluster size can be obtained by replacing T_m with $T_m(n)$ in equation (5). In this case the Einstein frequency $\nu_E(n)$ varies with the number of atoms in the cluster as follows:

$$\nu_E^{\text{eff}}(n) = \nu_E \sqrt{1 - \frac{C}{\sqrt[3]{n}}}. \quad (6)$$

The corresponding effective Einstein temperature T_E^{eff} is proportional to the Einstein frequency ν_E^{eff} :

$$T_E^{\text{eff}} = \frac{h \nu_E^{\text{eff}}}{k_B}. \quad (7)$$

Consequently, the Einstein temperature of the small clusters relates to n as:

$$T_E^{\text{eff}}(n) = T_E \sqrt{1 - \frac{C}{\sqrt[3]{n}}}. \quad (8)$$

According to Einstein model, the basic equation for heat capacity, C_V , is expressed through the Einstein function $F_E(\frac{T_E}{T})$ as follows:

$$C_V = 3R F_E \left(\frac{T_E}{T} \right); \quad T_E = \frac{h \nu_E}{k_B} \quad (9)$$

F_E being defined as:

$$F_E(x) = \frac{x^2 e^x}{(e^x - 1)^2}; \quad x = \frac{T_E}{T}. \quad (10)$$

Hence, the resultant heat capacity $C_V(n)$ for an n -atomic cluster can be expressed by T_E^{eff} accounting for the cluster size after substitution of T_E with T_E^{eff} from equation (8).

$$C_V(n) = 3R F_E \left(\frac{T_E^{\text{eff}}}{T} \right) = 3R F_E \left(\frac{T_E \sqrt{1 - \frac{C}{\sqrt[3]{n}}}}{T} \right). \quad (11)$$

The above expression reveals the heat capacity dependence on the number of atoms in the system, i.e. on the size of nanocluster. The value of the dimensionless constant C , estimated after expressing the interface energy in the terms of Skapski–Turnbull equation, is of order of 1 [11, 14–16]. Hereafter in our calculations, C in equation (11) is set to 1.

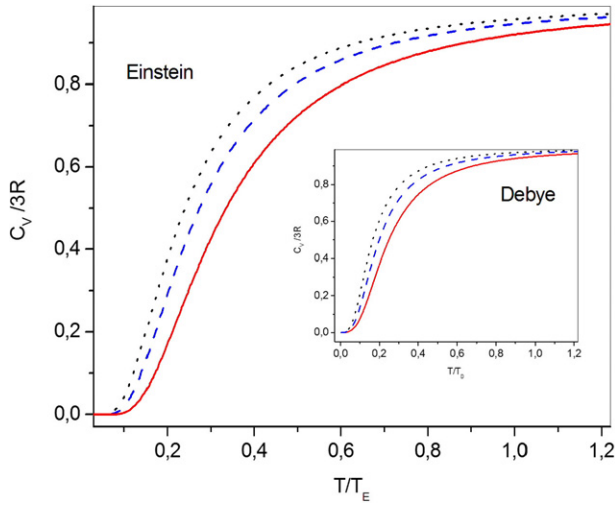


Figure 1. The heat capacity of an infinitely large homogeneous phase (solid curve) compared to that of phases consisting of n -atomic clusters. The upper dotted curve reflects the heat capacity behavior of a 27-atomic nanocluster; the dashed line in between is respectively for a 125-atomic complex. The Einstein temperature is $T_E = 450$ K. The increase of $C_V(n)$ is a result of the contribution of the clusters interfacial energy to the overall heat capacity of the system. The inset shows the same result in the framework of the Debye approach with Debye temperature $T_D = 558$ K (see equation (1)).

Figure 1 shows the heat capacity of an infinitely large homogeneous phase (solid line) compared to that of a phase consisting of n -atomic clusters (dotted line is for $n = 27$ and dashed line is for $n = 125$). The Einstein temperature is $T_E = 450$ K. The inset shows the same result in the framework of the Debye approach with Debye temperature $T_D = 558$ K according equation (1). The increase of $C_V(n)$ is clearly pronounced in both models. The enhancement of $C_V(n)$ is a result of the contribution of the interfacial energy to the overall heat capacity of the system.

The increase of heat capacity of a phase consisting of n -atomic clusters as compared to an infinitely large phase $\frac{C_V(n) - C_V^{inf}}{3R}$ also depends on temperature. This is demonstrated in figure 2 where the above variation is normalized to the Dulong and Petit $3R$ limit.

The observed enhancement of heat capacity is in agreement with experimental findings, [5, 17, 18]. According to the present model, this is the result of the lowering of the effective Einstein temperature T_E^{eff} accounted for by equations (8), (11). As expected, at high temperatures both the infinitely large phase and the phase consisting of n -atomic nanoclusters satisfy the Dulong and Petit $3R$ limit.

The dependence of the relative increase of heat capacity, $\frac{C_V(n) - C_V^{inf}}{C_V^{inf}}$ on the number of atoms n is presented in figure 3.

The variation of $C_V(n)$ is shown at $T = 0.25T_E$ where the deviation of heat capacity is clearly pronounced, as demonstrated in figure 1. It is seen that the relative increase remains significant even for $n = 10^5$ atoms. At $T = 0.25T_E$, the variation of the heat capacity of the n -atomic cluster phase with respect to the infinitely large phase remains larger than 1%. The difference $C_V(n) - C_V^{inf} \geq 0.01$ holds for $n \leq 10^4$ atoms, or nanocrystals with cubic shape and 46 atoms on a side.

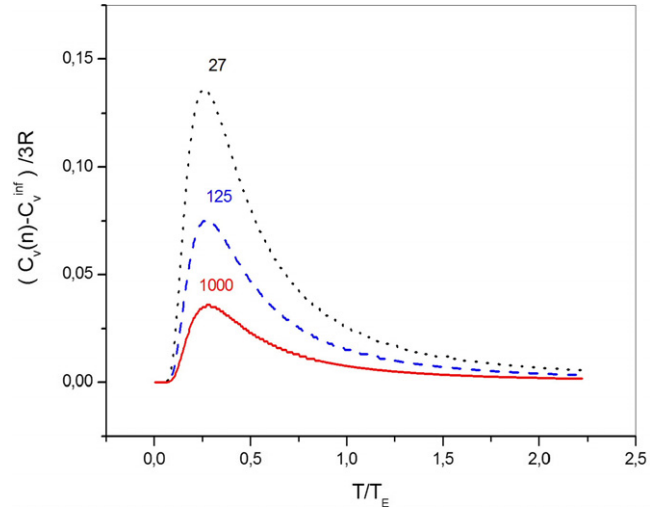


Figure 2. The increase of the heat capacity $C_V(n)$ of a phase consisting of n -atomic clusters ($n = 27, 125$ and 1000) with respect to C_V^{inf} for an infinitely large homogeneous phase as a function of T . As expected, at high T both the infinitely large homogeneous phase and the phase consisting of nanoclusters satisfy the Dulong and Petit $3R$ limit.

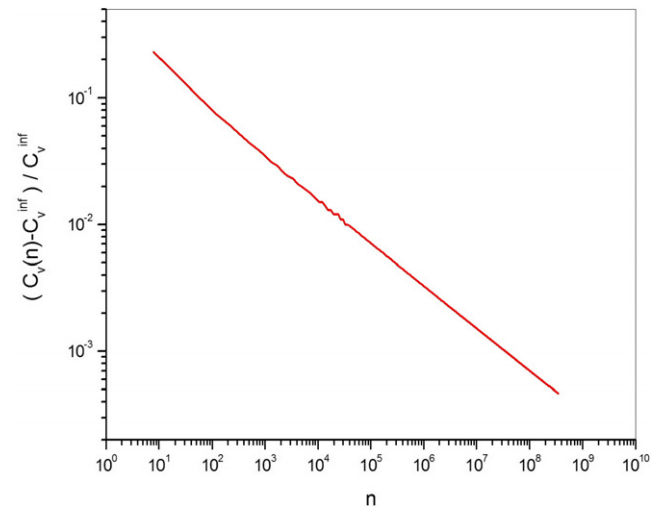


Figure 3. The dependence of the relative increase of heat capacity on the number of atoms n at $T = 0.25T_E$. The deviation of $C_V(n)$ from C_V^{inf} is about 1% for clusters up to 10^5 atoms (as example: nanocrystal with cubic shape with 46 atoms on a side).

The heat capacity of nanoclusters in the present model was compared with experimental data for Fe published in [19, 20]. We found a good agreement with experimental findings for cubic nanoclusters of 40 nm size. The only fitting parameter in equation (4) was set to $C = 2.3$ which provides a sufficiently adequate evaluation. It is important to notice that the comparison with experiment is not straightforward, since the nanocrystalline materials are not perfectly mono-disperse. Therefore, in the presence of nanoparticles with different sizes, the contribution of smaller nanocrystals could dominate over the total heat capacity of the system, (see equation (11)). Our results are also in line with [21, 22] who reports a relationship between the melting point, Debye temperature, size and structure of Lennard-Jones rare-gas clusters.

The heat capacity of nanocrystals could be also expressed through the Debye temperatures T_D and the corresponding Debye function F_D . However, the direct application of the Debye model to small atomic complexes is still problematic, since in a small cluster an additional restriction has to be accounted for. The wavelength of standing waves could not exceed the nanocluster size.

3. Conclusions

The present study reveals in a thermodynamic approach the contribution of surface energy to the heat capacity of nanoclusters. In the framework of the Lindemann model of melting, the dependence of specific heat on the cluster size is shown. At constant temperature (all over the interval $0.05 < T/T_E < 1.5$) the heat capacity, $C_V(n)$, of a cluster with a comparable number of surface and bulk atoms deviates significantly from that of the large system. Outside this large temperature gap, the heat capacity of the phase consisting of n -atomic nanoclusters and the infinitely large homogeneous phase are equal. The observed increase of $C_V(n)$ reflects the variation of the effective Einstein temperature T_E^{eff} due to the interface energy contribution. At fixed nanocrystal size, the temperature dependence of $C_V(n)$ deviates from heat capacity C_V^{inf} of the respective infinitely large system. Being in good agreement with recent experimental findings, the specific heat in the model presented scales at high T with the classical Dulong and Petit $3R$ limit and goes to zero for $T \rightarrow 0$ as required by the third law of thermodynamics.

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