Effective coordination number model for the size dependency of physical properties of nanocrystals

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Abstract
Based on the effective coordination number (ECN) viewpoint a model for the size dependency of cohesive energy of nanocrystals has been developed. In order to calculate ECN both un-relaxed and relaxed surfaces have been considered. It has been shown that bond order–length–strength (BOLS) correlation mechanism can be described successfully by adopting an average ECN approach. Based on ECN and the fundamental effect of cohesive energy on physical quantities, the size dependency of the following parameters has been established: melting temperature, evaporation temperature, Debye temperature, vacancy formation energy of nanocrystals and surface tension of nanodroplets. Predictions for the size dependency of the aforementioned properties are in good agreement with the BOLS model and available results from experimental and simulation studies.

1. Introduction

Nanocrystals have unique properties which result from their high fraction of surface atoms. They represent an intermediate state of matter which falls between the molecular and bulk solid states. Within this size regime many new phenomena have been observed which can lead to new applications. The prominent difference between a nanocrystal and its bulk state is the significant portion of the lower-coordinated surface atoms [1]. In fact a large fraction of surface atoms leads to a decrease in the average coordination number (ACN) of nanocrystals. The size dependency of many physical properties of nanocrystals can be explained by the low coordination number (CN) of surface atoms [1–7]. The activity of supported catalysts increases with decreasing particle size and that can be related to the number of low-coordinated atoms present in the particles [8, 9]. It has been found that ACN determines the effective hybridization and therefore the magnetic moment of the clusters [10]. A decrease in ACN causes a transition from bulk to atomic or molecular properties [11], e.g. as atomic CN reduces to much lower values the bond nature evolution cause a conductor–insulator transition [12]. Based on the effective coordination number (ECN) concept, the size dependency of ionization potentials [13] and core level shift of transition metal clusters have been successfully described [14]. The CN viewpoint can be useful to describe many other physical phenomena, for example the grain boundary in solids can be considered as low-coordinated atoms [15]. Also the CN distribution can explain the difference between the ordered solid and amorphous state [1]. In fact the amorphous state is the randomly distributed CN of atoms and this leads to the broad temperature range for glass transition of an amorphous state [16]. From these arguments, it is easy to conclude that measuring ACN will be a significant method to determine many physical and chemical properties. Extended x-ray absorption fine structure (EXAFS) spectroscopy is a practical way to measure the average CN of small particles, from which a size estimate can be deduced [17]. The estimate of particle size by EXAFS relies on an accurate determination of ACN for the different neighboring atomic shells [18]. It should be noted that the measured CN can be affected by temperature, so in order to reduce the errors caused by temperature the EXAFS experiments are carried out at low temperatures [19].

ECN and ACN are different quantities and the distinction between them should be considered. ECN is defined for each atom but ACN is the average CN of all the atoms of a nanocrystal. The ECN of each atom in a nanocrystal can be different and is affected by the position and the CN of other

atoms, but the ACN is identical for nanocrystals of same size. The ACN can either be expressed by the ECN or without it, for example the ACN can be obtained by geometric characteristics of clusters without considering the real (effective) CN of atoms [17]. If the average ECN of all atoms is calculated the average effective coordination number (AECN), which is a kind of ACN, will be obtained.

One of the most important properties of a solid, which depends directly on the CN, is its cohesive energy. The cohesive energy is responsible for the atomic structure, thermal stability, atomic diffusion, crystal growth and many other properties [1, 2]. In fact the cohesive energy quantity provides a natural link among the various models which have been developed to account for different physical properties. The cohesive energy of a nanocrystal is dependent upon its size, and several models discuss this size dependency [1–7, 20]. Hence from the above statements it is clear that a model which correlates ECN and cohesive energy of nanocrystals will be significant.

In this work a relation between the average ECN and the cohesive energy of nanocrystals is established. Also, attempts have been made to explain the BOLS correlation mechanism in light of the ECN of relaxed surfaces. Finally based on the size dependency of cohesive energy, some important physical properties are investigated.

2. The model

2.1. Effective coordination number (ECN) and cohesive energy

The atomic cohesive energy can be different due to the variation of atomic CN environment at various locations of the solid. Here a general equation is suggested for the atomic cohesive energy of small particles. The atomic cohesive energy of an atom i (E_i) can be generally expressed by the bulk cohesive energy (E_b) as follows

$$E_i = E_b \frac{Z_{e,i}(Z_i)}{Z_b} \tag{1}$$

where $Z_{e,i}$ and Z_b are the ECN of the atom i and the bulk atom, respectively. In this equation it has been assumed that $Z_{e,i}$ is a function of the CN of atom i (Z_i), i.e. $Z_{e,i} = f(Z_i)$. In the simplest case, ignoring surface relaxation $Z_{e,i}$ is equal to its corresponding CN, i.e. $Z_{e,i} = Z_i$. Here equation (1) can be compared to the relation presented by Tomanek *et al* [3] for the cohesive energy of an atom (E_i) for small clusters; $E_i = E_b(Z_i/Z_b)^{1/2}$. In their relation surface and bond contraction have not been considered. But in equation (1) $Z_{e,i}$ is the general quantity for the ECN of atoms which can be affected by size, bond order, bond length, surface relaxation and other parameters. The suitability of the equation suggested to predict the cohesive energy of nanocrystals will be discussed in sections 2.2 and 2.3 for un-relaxed and relaxed surfaces, respectively. Applying the summation to equation (1) and summing over the total number of atoms (n_t), we get:

$$\sum_{i=1}^{n_t} \frac{E_i}{E_b} = \sum_{i=1}^{n_t} \frac{Z_{e,i}(Z_i)}{Z_b}. \tag{2}$$

The cohesive energy ($E_{c,t}$) or coherency of the nanocrystal is the sum of bond energies over all the coordinates, i.e. $E_{c,t} = \sum_{i=1}^{n_t} E_i$. Two average quantities can be defined for the nanocrystals, the average cohesive energy as $E_{c,n} = E_{c,t}/n_t$ ($E_{c,b} = E_b$) and the average ECN as $\bar{Z}_{e,n} = (\sum_{i=1}^{n_t} Z_{e,i})/n_t Z_b$ can be considered as the average ECN of bulk atoms ($\bar{Z}_{e,b}$) i.e. $\bar{Z}_{e,b} = \lim_{n_t \to \infty} \bar{Z}_{e,n} = Z_b$. So equation (2) can be written as $n_t E_{c,n}/E_{c,b} = n_t \bar{Z}_{e,n}/Z_b$ and finally we have:

$$\frac{E_{c,n}}{E_{c,b}} = \frac{\bar{Z}_{e,n}}{\bar{Z}_{e,b}}. \tag{3}$$

$E_{c,n}$ and $E_{c,b}$ are the cohesive energy per atom for the nanocrystal and the bulk atoms, respectively. $\bar{Z}_{e,b}$ can be considered as the CN of atoms in the lattice for the bulk, for example 12 and 8 for face-centered cubic (FCC) and body-centered cubic (BCC) lattices, respectively. When the size of nanocrystal increases, $\bar{Z}_{e,n}$ tends towards the bulk average ECN ($\bar{Z}_{e,b}$), i.e. $\bar{Z}_{e,n}(\infty)/\bar{Z}_{e,b} = 1$ and so $E_{c,n}/E_{c,b} = 1$. In equation (3) the effect of all the atoms in different positions such as edge and corner can be considered. Hence it can be applied to cluster structures such as icosahedral and cuboctahedral.

2.2. Cohesive energy for un-relaxed surfaces by $Z_{e,i} = Z_i$

In the simplest approach, it can be assumed that the ECN of each atom ($Z_{e,i}$) is equal to its corresponding CN (Z_i), without any influence from bond length, order and relaxation. However, it should be noticed that Z_i decreases with decreasing size [7]. The average ECN ($\bar{Z}_{e,n}$) of a nanocrystal is defined as the average ECN of surface and interior atoms. Considering $Z_{e,i} = Z_i$ we have: $\bar{Z}_{e,n} = (n_S \cdot Z_S + n_I \cdot Z_I)/(n_S + n_I)$, where n_S and n_I are the surface and interior number of atoms, respectively. The surface CN (Z_S) may include edge and corner as well as atoms located in faces of crystalline planes. Note that Z_S is the number of surface bonds, without considering bonds to interior atoms. Simplifying, we have:

$$\bar{Z}_{e,n} = Z_I \left(1 - \left(1 - \frac{Z_S}{Z_I} \right) \frac{n_S}{n_t} \right). \tag{4}$$

Since Z_I equals the CN of interior atoms, and surface atoms do not affect that, a good approximation is to assume that it is equal to the bulk CN and hence $Z_I \cong (Z_b = \bar{Z}_{e,b})$. This is a reasonable assumption, because theoretically, nanoparticles have an interior structure comparable to that of bulk structure [21]. n_S/n_t has been calculated by considering the effect of crystal structure in previous works [4, 5] as follows:

$$\frac{n_S}{n_t} = \frac{4P_S(3 - \lambda)/3}{P_L(D/d) + 2P_S(3 - \lambda)/3} \tag{5}$$

where D is the size of nanocrystal. D can be the diameter of spherical nanoparticles, nanowires and the thickness of nanofilms. λ is a parameter representing the dimension of the nanocrystal: $\lambda = 0$ for nanoparticles, $\lambda = 1$ for nanowires, and $\lambda = 2$ for nanofilms. P_S is the packing fraction of the surface crystalline plane (the ratio of the area of the surface plane occupied by atoms to the total area of the plane). P_L

is the lattice packing fraction (the ratio of the volume in the unit cell of lattice occupied by atoms to the total volume of the unit cell) and also $d(=2r)$ is the atomic diameter of the atoms building the nanocrystal. r is the atomic radius deduced from atomic volume $V_a = 4\pi r^3/3$. Using the term of 'sphere' or 'rounded' for nanocrystals needs more explanation. When the details of surface morphology of different isomers do not significantly affect nanocrystal surface energy, a simple 'sphere' and 'rounded shape' becomes an efficient model [17].

Here D_o is introduced as the size of nanocrystal for which all of the atoms are located on the surface of the nanocrystal, i.e. $n_S = n_t$, hence from equation (5) D_o equals $D_o = (2/3)(3 - \lambda)(P_S/P_L)d$. So by substituting the value of D_o in equation (5) and using equations (3) and (4), the cohesive energy is obtained as follows:

$$\frac{E_{c,n}}{E_{c,b}} = \frac{\bar{Z}_{e,n}}{\bar{Z}_{e,b}} = 1 - (1 - Z_{Sb})\left(\frac{2D_o}{D + D_o}\right) \quad (6)$$

where Z_{Sb} is equal to Z_S/Z_b. Generally the system tends to minimize its total energy and this requires the surface energy be as small as possible [22]. So for an equilibrium state, changing from a higher to a lower surface energy is important. We may expect the surface energy to be less for planes having a greater density of atoms, such as the FCC (111), because generally the contribution that a surface atom makes to surface energy decreases as its CN increases [22]. So in the present model for the FCC and BCC crystal structures the most compacted crystalline planes, (111) and (110), respectively, have been considered. Hence for sufficiently large particles (close to the bulk), we have $Z_{Sb} = 1/2$ (for example, for an FCC bulk material in the bulk mode the CN of surface and lattice atoms is 6 and 12, respectively). As the particle size is reduced, the surface curvature will increase and the surface atomic CN will decrease further. In fact the CN of an atom in a highly curved surface of small sizes is lower compared with the CN of an atom on a flat surface in bulk mode [1]. Hence for very small particles we may expect that $Z_{Sb} > 1/2$ and $Z_S = Z_b/4$ is more suitable and this has been confirmed in previous works [4, 7]. In equation (6) the effects of edge and corner atoms have been ignored and this may lead to some deviation at the lower range of size. Contributions from the edges and corners are expected to be significantly smaller than that of the surfaces (faces) of nanocrystals larger than ~3 nm [23], so it is reasonable to assume that edge and corner will have limited significance for nanocrystals larger than this size.

2.3. BOLS correlation mechanism in terms of ECN ($Z_{e,i} = Z_i \cdot (c_i(Z_i))^{-m}$)

Here it will be shown that the ECN approach presented in section 2.1 is useful to describe the BOLS correlation mechanism. As a result of reduced coordination, most surfaces relax inward [24]. The finding of surface bond contraction has led to the bond order–length–strength (BOLS) correlation mechanism [1, 2, 25, 26]. In fact the BOLS correlation mechanism has been demonstrated in the shape-and-size dependence of nanocrystals [1]. In the BOLS correlation, it has been proposed that the CN imperfection of an atom at a surface

causes the remaining bonds of the lower-coordinated surface atom to relax spontaneously [2]. In the BOLS mechanism the bond length (the diameter of an atom) in the ith atomic layer d_i is a function of Z_i as $d_i = c_i(Z_i)d$, where d is the bond length of an atom without CN limitation. Contraction is greater for the lower CN of the surface atoms. The obtained relation for the $c_i(Z_i)$ based on Goldschmidt's premise and Feibelman's finding is:

$$c_i(Z_i) = \frac{d_i}{d} = 2\left(1 + \exp\left(\frac{12 - Z_i}{8Z_i}\right)\right)^{-1}. \quad (7)$$

In the BOLS model the relation between the cohesive energy of an atom and its bulk value is obtained from $E_i = c_i^{-m}E_b$ [1]. By comparing this relation with equation (1), a new value for the ECN of an atom will be obtained by:

$$Z_{e,i} = Z_i \cdot (c_i(Z_i))^{-m}. \quad (8)$$

Equation (8) suggests that the ECN of an atom depends on the energy change of the relaxed single bond with the reduced bond length $(c_i^{-m}) \cdot m$ is an adjustable parameter, which varies according to the nature of the bond. Studies [1] have revealed that for elemental solids, $m \approx 1$ and for compounds and alloys it is in the order of 4. So considering BOLS correlation the average ECN ($\bar{Z}_{e,n}$) can be defined as:

$$\bar{Z}_{e,n} = \left(\sum_{i=1}^{n_t} Z_i c_i^{-m}\right) \bigg/ n_t$$

$$= \left(n_t Z_b + \sum_{i \leqslant 3} n_{s,i}(Z_{e,i} - Z_b)\right) \bigg/ n_t \quad (9)$$

where $n_{s,i}$ is the number of atoms in the ith atomic layer. In the BOLS correlation no bond-order loss is expected up to 3 from the outermost atomic layer to the center of the solid. By simplifying, equation (9) can be written as:

$$\frac{\bar{Z}_{e,n}}{Z_b} = 1 + \sum_{i \leqslant 3} \gamma_{ij}(Z_{ib}c_i^{-m} - 1) \quad (10)$$

where $\gamma_{ij} = n_{s,i}/n_t = \tau c_i d/D$ is the portion of the atoms in the ith atomic layer from the surface compared to the total number of atoms of the entire solid and $\tau = 1, 2, 3$ correspond to plates (thin films), nanowires, and nanoparticles, respectively. Z_{ib} is equal to Z_i/Z_b and as mentioned earlier Z_b can be considered as the ECN of atoms in the bulk i.e. $\bar{Z}_{e,b}$. Now by considering the obtained relation between the cohesive energy and the average ECN (equation (3)) and using equation (10), the BOLS correlation mechanism can be expressed by this new form:

$$\frac{E_{c,n}}{E_{c,b}} = \frac{\bar{Z}_{e,n}}{\bar{Z}_{e,b}} = 1 + \sum_{i \leqslant 3} \gamma_{ij}(Z_{ib}c_i^{-m} - 1). \quad (11)$$

Equation (11) is the other interpretation of the BOLS correlation which considers the ECN model. In fact equation (11) proposes that the BOLS correlation can be deduced from the average ECN approach (equation (3)).

3. Cohesive energy and size dependency of physical properties

Here proportionality between cohesive energy and some important physical properties are investigated. Then the size dependency of these properties is discussed in the light of the obtained relation between the cohesive energy and the ECN (equation (3)).

3.1. Melting point of nanocrystals

The most prominent example of the deviation from thermodynamic behavior as a result of size effect is probably the depression of the melting point of small particles [27]. Hence the melting point depression can be used in order to achieve a comprehensive understanding of the thermodynamics of nanometric systems [28, 29]. Melting point is a parameter to estimate the strength of metallic bonds; hence its proportionality with cohesive energy can be expected. The scaling relation between the melting point of pure metals to their cohesive energy inferred from the universal binding theory of solids [30, 31] is $T_{m,b} = 0.032 E_{c,b}/k_B$ [32]. This expression confirms a linear relation between melting point and cohesive energy for bulk materials but the effect of crystal structure of solids has not been included. So, this is proper only for solid elements with simple crystal structure, such as FCC and BCC [33]. Hence, for those elements with a complex structure, e.g. diamond structure, orthorhombic and complex hexagonal closed packed, a noticeable deviation is predicted [33]. In many models the effect of lattice structure has not been considered and only the proportionality between cohesive energy and melting point has been used. So a model which considers the effect of lattice and surface structure seems to be necessary. By applying this proportionality to the nanoscale (i.e. $T_{m,n} = 0.032 E_{c,n}/k_B$), we have:

$$\frac{T_{m,n}}{T_{m,b}} = \frac{E_{e,n}}{E_{e,b}}. \tag{12}$$

Surface atoms of a free-standing nanocrystal experience greater vibrational amplitude than those in the bulk, as they have no neighbors above them to restrain them. However surface atoms of supported nanocrystals have lower degree of freedom. So, considering proportionality between ECN and cohesive energy, equation (12) indicates that $\bar{Z}_e$ dictates the process of overheating for supported particles when $\bar{Z}_e > Z_b$ or undercooling for free-standing particles when $\bar{Z}_e < Z_b$.

3.2. Evaporation temperature of nanocrystals

The size dependency of cohesive energy can influence the evaporation temperature (T_{vap}) of nanocrystals [34]. From the Kelvin effect, it can be expected that the evaporation of nanoparticles is size dependent and it is essential to know this for their application at higher temperature [35]. Melting and evaporation are measures of thermal stability of a material and both of them decrease with decreasing particle size [35, 36]. Nanda *et al* [36] found a linear relationship between T_{vap} and the inverse of the particle size which shows the variation of T_{vap} with particle size is similar to the variation of the melting point (T_m). All these imply that evaporation temperature is proportional to cohesive energy as is the case for melting

point. Furthermore the proportionality between T_{vap} and E_c can be found from the theory of phase transitions. Sun *et al* [26] have suggested $T_C \propto f_C^2 E_c$, where T_C is the transition temperature and f_C is a coefficient of the thermal expansion magnitude of an atom at T_C. Therefore a universal form for the relative change of critical temperatures for possible phase transitions such as evaporation and solid–liquid transition can be obtained in terms of cohesive energy. It is worth noting that the first-order phase transformation cannot happen in the nanoscale regime of size, because in small systems temperature fluctuation leads to transitions taking place over a temperature interval [37]. Therefore from the proportionality of T_{vap} and E_c we have:

$$\frac{T_{vap,n}}{T_{vap,b}} = \frac{E_{c,n}}{E_{c,b}}. \tag{13}$$

3.3. Debye temperature of nanocrystals

The Debye temperature (Θ_D) is a significant characteristic of the structural parameter of a solid, which is directly related to the binding force between atoms constituting materials [38]. Therefore, the investigation of Θ_D can play a key role in understanding many material properties of nanostructures, such as the thermal vibration of atoms, phase transitions and volume thermal expansion coefficient [38–43]. Some regard Θ_D as the most important and useful single physical property of a crystal [44]. There is a significant connection between the Debye temperature and the melting point. Lindemann [45] has suggested that at the melting point of solids, the mean square displacement of thermal vibration obtains some standard fraction of the square of the interatomic separation. Lindemann's theory of a vibrational limit can be directly described by Debye temperature as follows [46]:

$$T_{m,b} = CM \left(\Theta_{D,b}\right)^2 v^{2/3} \tag{14}$$

where M is the molecular weight, $\Theta_{D,b}$ the Debye temperature of bulk material, v the atomic volume and C a numerical constant which is identical for all solids. This relationship provides a convenient method for estimating the Debye temperature of solids from knowledge of the melting point. It has been qualitatively confirmed that the Lindemann hypothesis is valid for small particles [47]. Therefore taking into consideration the proportionality between melting point and cohesive energy and using equation (14) we have:

$$\frac{\Theta_{D,n}}{\Theta_{D,b}} = \left(\frac{E_{c,n}}{E_{c,b}}\right)^{1/2}. \tag{15}$$

3.4. Vacancy formation energy in nanocrystals

Vacancies are significant point defects that have a considerable effect on the physical and chemical properties of materials such as electrical resistance, heat capacity and diffusion activity [48]. A vacancy is characterized by its formation energy (E_v), which is equal to the energy that can form a vacancy in a material. Tiwari and Patil [49] have shown that there is a linear relation between vacancy formation energy and the cohesive energy. This proportionality can be inferred
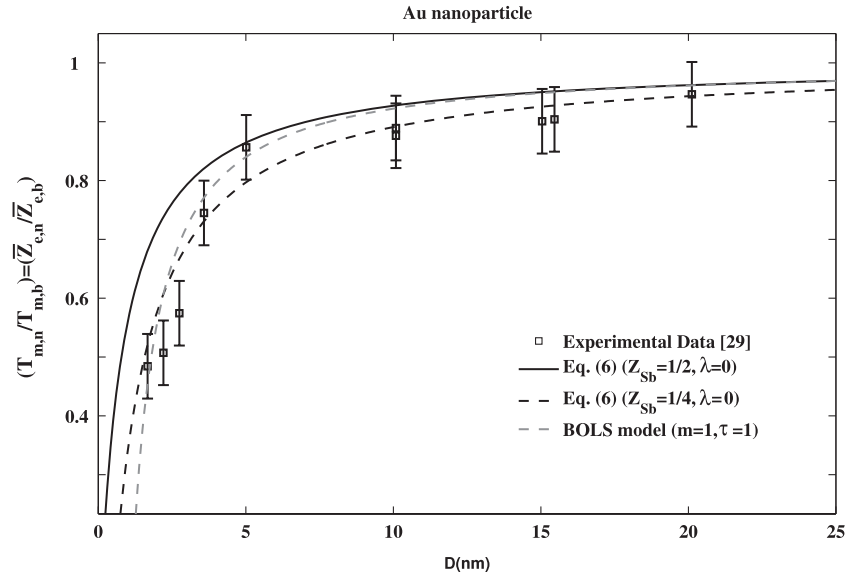
Au nanoparticle

Figure 1. Dependence of melting point on the size of Au nanoparticles in terms of equation (6) and the BOLS model. The lattice type of Au is FCC ($P_L = 0.74$, $P_S = 0.91$). For Au $r = 0.1594$ nm and $T_{m,b} = 1337$ K [29].
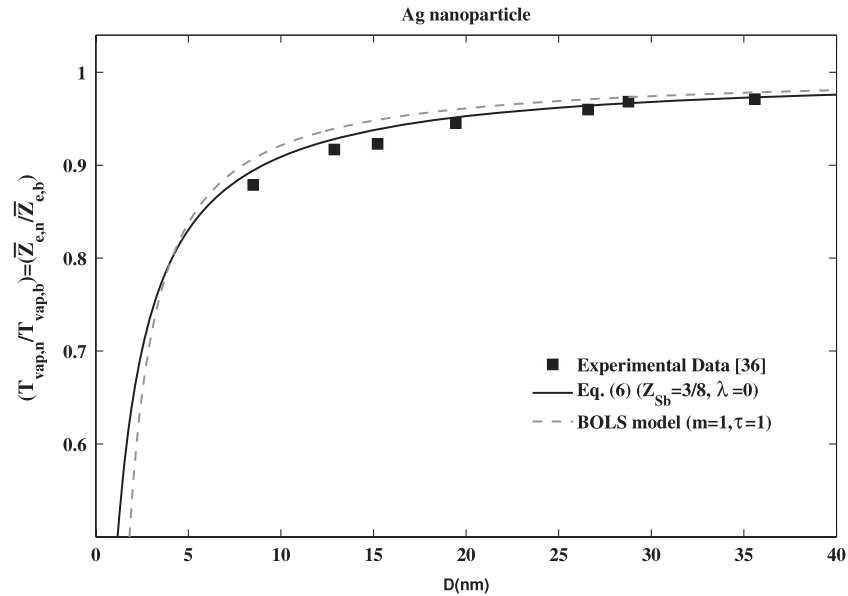
Ag nanoparticle

Figure 2. Dependence of evaporation point on the size of Ag nanoparticles in terms of equation (6) and the BOLS model. The lattice type of Ag is FCC ($P_L = 0.74$, $P_S = 0.91$). For Ag $r = 0.1597$ nm and $T_{vap,b} = 1097$ K [36].

from a thermal stability viewpoint. In fact vacancies can lead to a significant decrease of the instability point compared to an ideal lattice and hence high vacancy concentrations can be a sign of melting point [50]. Therefore the energy of vacancy formation is a function of the bond energy of the solid [51]. Furthermore, we can expect that the stronger bonds are harder to break and so to create vacancies, E_v is naturally proportional to the E_c e.g. for the metals it has been reported that $E_v \approx 1/3 E_c$ [52]. Hence by transferring the proportionality between E_v and E_c to the nanoscale, we have:

$$\frac{E_{v,n}}{E_{v,b}} = \frac{E_{c,n}}{E_{c,b}}. \tag{16}$$

3.5. Size-dependent surface energy and surface tension

The surface energy of solids (γ_{sv}) is defined as the energetic difference between the surface atoms and interior ones. It is an important physical parameter in controlling a wide range of phenomena, such as the melting, coalescence, sintering rate, phase transition and growth of nanoparticles [53, 54]. For this reason, there have been many attempts to derive values of the surface free energies. There are some models indicating there is a linear relation between γ_{sv} and E_c. The simplest approach for non-spin-polarized atoms [53] is counting the broken bond number to create a surface area and multiplying this number by the cohesive energy per bond which suggests

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$\gamma_{sv,b} = 1 - (1 - Z_S/Z_b)E_{c,b}$. In another approach (second-moment tight bonding approximation) [55] the total energy of a system can be expressed as a sum of the energetic contributions of each atom which are proportional to the square root of the related CNs, hence $\gamma_{sv,b} = 1 - (1 - \sqrt{Z_S/Z_b})E_{c,b}$. All these approaches demonstrate that the bulk material surface energy is directly proportional to cohesive energy i.e. $\gamma_{sv,b} = \alpha E_{c,b}$, where α is a constant and a function of the CN. If the nanocrystal has the same structure as the corresponding bulk [56], the proportionality between surface energy and cohesive energy can be extended to the nanoscale as follows:

$$\frac{\gamma_{sv,n}}{\gamma_{sv,b}} = \frac{E_{c,n}}{E_{c,b}}. \tag{17}$$

For droplets the liquid–vapor interfacial energy or surface tension (γ_{lv}) is an important quantity just like the surface free energy for solids. Tolman [57] predicted that γ_{lv} should decrease with decreasing particle size. It is known that for metallic elements at melting point the ratio $\gamma_{sv,b}/\gamma_{lv,b} = \alpha'$ exists [53]. Here α' is a constant and $\gamma_{lv,b}$ is the surface tension of a droplet when its curvature is approximately equal to a flat surface. Since the structure and energy differences between solid and liquid are small in comparison with that between solid and gas or between liquid and gas, the above expression for the bulk solids is assumed to be applicable to nanometer size with the same form, namely, $\gamma_{sv,n}/\gamma_{lv,n} = \alpha'$ [58]. Hence the size-dependent surface energy ($\gamma_{sv,n}$) can be used to determine the $\gamma_{lv,n}$ of nanodroplets and we have:

$$\frac{\gamma_{lv,n}}{\gamma_{lv,b}} = \frac{E_{c,n}}{E_{c,b}}. \tag{18}$$

4. Results and discussion

Since cohesive energy is a fundamental physical quantity it is expected that its variation will affect other physical properties. If cohesive energy (E_c) at the bulk state is proportional to a physical property, f, then we have $E_c(\infty) = kf(\infty)$. Here k is the proportionality constant and its value depends on the nature of the physical property. For example, k is 0.032 in the case of melting point [32]. This confirms that at the bulk state in order to establish a relation between cohesive energy and any other properties, the physical nature of properties should be considered. If we assume that the proportionalities between cohesive energy and other physical quantities are valid at the nanoscale, we have $E_c(D) = kf(D)$. By merging the last two proportionality equations, we obtain a new relation which is independent of k: $E_c(D)/E_c(\infty) = f(D)/f(\infty)$, similar to the equations obtained in section 3. This equation indicates that the size dependency of physical properties which are proportional to cohesive energy get the same form. However to obtain this result, the following assumptions have been made. The proportionality between cohesive energy and a physical property is valid for the bulk state and nanoscale alike and that they share the same proportionality constant. The obtained proportionality relation provides a useful means by which we can estimate the size dependency of physical properties and
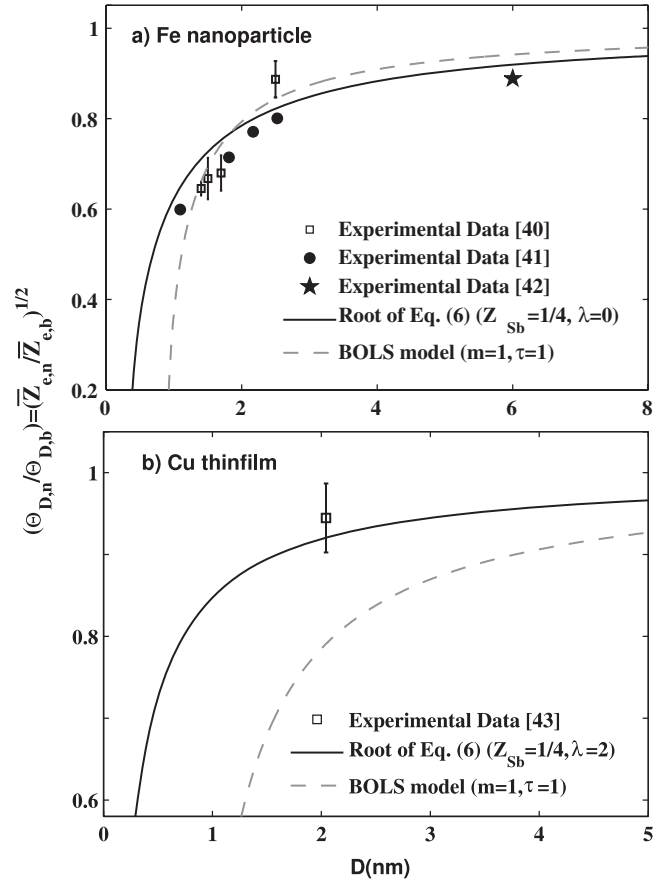

Figure 3. Dependence of Debye temperature on the size for Fe nanoparticles and Cu thin films in terms of equation (6) and the BOLS model. The lattice type of Fe and Cu is BCC ($P_L = 0.68$, $P_S = 0.83$). For Fe $r = 0.1411$ nm and $\Theta_{D,b} = 388$ K [39] and for Cu $r = 0.1413$ nm and $\Theta_{D,b} = 343$ K [39].

ideally to determine their exact quantities, provided that the nature of them is considered.

The modeling results from equation (6) have been used to predict several properties of nanocrystals. These predictions, along with results from experimental studies and computer simulations, are plotted in figures 1–5. In all the figures, predictions of equation (6) for un-relaxed surfaces have been compared with the results produced by the BOLS model. To obtain numerical results for the BOLS correlation the CN of the outermost three atomic layers are taken as 4, 6, and 8, respectively [25]. Furthermore, all atomic radii used in equation (6) are calculated from atomic volumes found in [59].

Figure 1 illustrates the size dependency of melting point depression of Au nanoparticles. Predictions made by equation (6) are in good agreement with the experimental data. Also good agreement with the BOLS model is achieved by using $Z_{Sb} = 1/2$ and $Z_{Sb} = 1/4$ in equation (6) for large and small particles, approximately $D > 10$ nm and $D < 10$ nm, respectively. This illustrates that Z_{Sb} will decrease as the fraction of surface atoms in nanocrystals increases upon decreasing the size.

The size dependency of evaporation temperature, T_{vap}, of Ag nanoparticles is shown in figure 2. Results plotted in
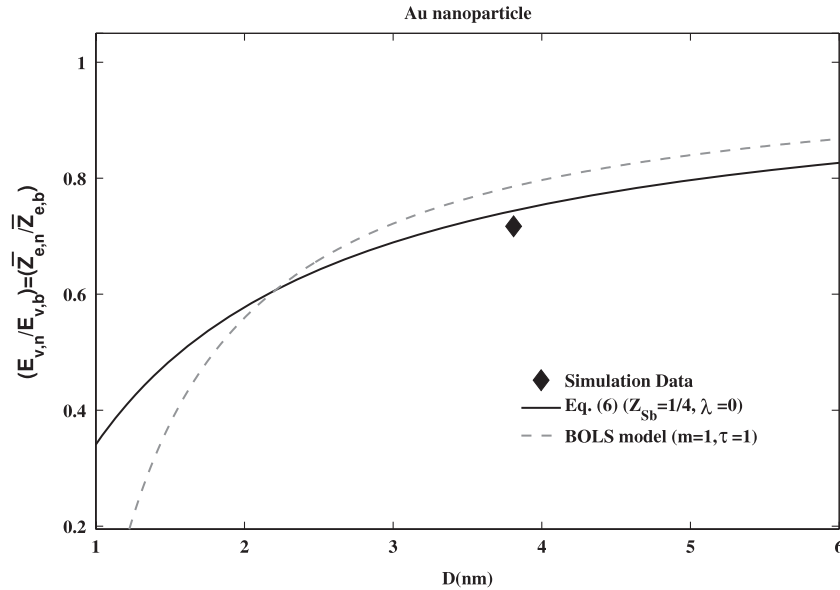
Figure 4. Dependence of vacancy formation energy on the size of Au nanoparticles in terms of equation (6) and the BOLS model. The lattice type of Au is FCC. For Au $r = 0.1594$ nm and $E_{v,b} = 1.27$ eV [20]. The computer simulation result is according to the data in [20].

this figure illustrate the good agreement between predictions made by equations (6) and (11) (the BOLS correlation) as well as experimental data [36]. In order to plot equation (6), $Z_{Sb} = 3/8$ has been used (which is the average of $Z_{Sb} = 1/2$ and $Z_{Sb} = 1/4$). This value was selected because the size range of experimental data is moderately between the large and small particles. The experimental data considered has been measured by monitoring the temperature at which the particle size decreases due to partial evaporation [36]. Decreasing evaporation temperature with decreasing size has a significant physical meaning and it leads to a higher surface energy for nanocrystals than the bulk.

Model predictions in terms of equation (6) and the available experimental data on the size dependency of Debye temperature, Θ_D, of Fe nanoparticles and Cu thin films are shown in figure 3. The model results for different kinds of free-standing nanocrystals correspond well to the experimental data. This indicates that equation (6) is capable of making reasonable predictions of the size dependency of Θ_D. Also the model predictions for Fe nanoparticles are in good agreement with those obtained from the BOLS correlation.

The size dependency of the vacancy formation energy of Au nanoparticles has been shown in figure 4. Due to a lack of experimental data on E_v the only available molecular dynamic results according to the data in [20] has been used for comparison with the developed model as shown in figure 4. From the figure it can be seen that E_v decreases with decreasing size and the model's results are in good agreement with the simulated results and BOLS predictions.

Comparisons of $\gamma_{lv,n}/\gamma_{lv,b}$ between the model predictions and the computer simulation results [60] are shown in figure 5. The model predictions demonstrate good agreement with the results of computer simulations and are close to the predictions made by the BOLS correlation. The decreasing surface tension of the nanodroplet predicted by equation (6) is in agreement

with the Tolman prediction [57] for the size dependency of surface tension.

The proportionality between the average ECN and cohesive energy can be considered as an important relation to use in obtaining the size dependency of physical properties. For free-standing nanocrystals the average ECN decreases with decreasing size and this leads to a fall off in the cohesive energy. Hence in all the figures a decrease of the obtained physical properties with decreasing size can be expected. In figures 3–5 only $Z_{Sb} = 1/4$ has been used to plot the graphs, because all the experimental and simulation results are in the lower range of size and are smaller than 10 nm. It should be noted that by increasing the size of a nanocrystal, the value of a physical property may become closer to the assumption of $Z_{Sb} = 1/2$; however, there are not enough experimental and simulation results to show this.

In all the figures, using $\tau = 1$ which is for the flat shape in the BOLS model gave good consistency with experimental and simulation results. Using $\tau = 1$ to provide best correspondence with experimental and simulation results has been corroborated in the work of Sun and his co-workers [1, 2]. From figures 1–5 it is found that the un-relaxed ECN approach (equation (6)) and the BOLS correlation mechanisms are generally consistent with each other. Only in figure 3(b) does the un-relaxed ECN predict different results as compared with the BOLS model, because $\lambda = 2$ has been used to plot equation (6). A decrease of the ECN of surface atoms (using $Z_{Sb} = 1/4$) may explain the consistency between the results of equation (6) (for un-relaxed surfaces) and the BOLS model. In fact decreasing the CN of surface atoms and their relaxation can be compared with each other. From the viewpoint of numerical calculations, one could hardly judge which model is preferred to the other though the physical indications of the compared models are different.

The BOLS correlation model is applicable for many nanomaterials [1, 2] such as Si, Ge, and carbon nanotubes
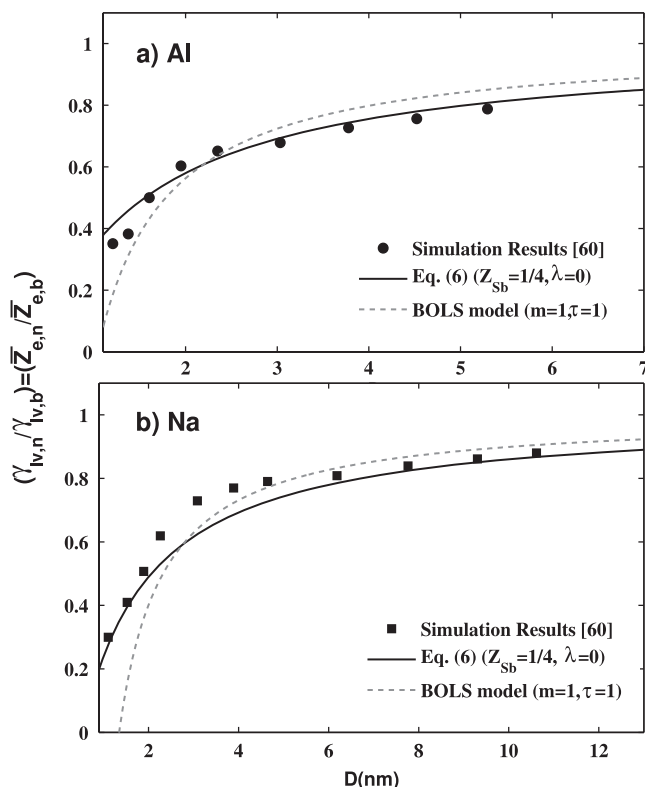
Figure 5. Dependence of surface tension of Al and Na nanodroplets on the size in terms of equation (6) and the BOLS model. The lattice type of Al and Na is FCC ($P_L = 0.74$, $P_S = 0.91$). For Al $r = 0.1582$ nm and for Na $r = 0.2112$ nm.

as well as many metals like Ag, Au, Sn, Pb. Also, the BOLS model has been used successfully for different size ranges, e.g. for nanocrystals larger or smaller than 5 nm and even for clusters smaller than 1 nm [1]. The reason for the BOLS model's success is its dependence on the nature of bonds and the difference of m (in equation (11)) for metals, semiconductors, alloys and compounds. From the above discussion it can be inferred that the ECN approach (equation (3)) in terms of the BOLS model can be applicable to various materials and the whole range of size.

Equation (3) has been derived for nanocrystals having the same kind of atoms as well as no segregated atoms at their surfaces. The applicability of the model for the alloys and segregated surfaces needs more investigation and hence it cannot be claimed that equation (3) has the same form for them. Also, the results presented in this paper (figures 1–5) are generally for the metallic elements. Hence, the applicability of equation (6) (un-relaxed surfaces) for nonmetallic and other elements needs more investigation. Furthermore, for very small sizes, quantum effects and the fluctuation of values of physical properties in that range cannot be ignored and hence equation (6) is not applicable at this size range.

5. Conclusion

Based on the concept of the ECN, the size dependency of the cohesive energy of nanocrystals, for both un-relaxed and relaxed surfaces, has been modeled. It has been shown that the ECN viewpoint can be useful in order to explain the BOLS correlation mechanism. Furthermore, the ECN approach has been used to investigate the size dependency of melting point, evaporation temperature, Debye temperature, vacancy formation energy, surface energy of nanocrystals and surface tension of nanodroplets. All model predictions show good agreement with the available experimental data and computer simulations and also results obtained from the BOLS model.

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