

Two-Body Interaction and Computer Simulations for the Cohesive Energy of Metallic Nanocrystals

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A two-body interaction potential energy function is used to predict the structural stability and cohesive energy of Molybdenum (Mo) and Tungsten (W) metallic nanocrystals by size dependant potential parameter. The model proposed is a two-body part of Erkoacs potential energy function. The model applies successfully to BCC and FCC elements and predicts the size dependence of the cohesive energy of nanocrystals. This prediction agrees excellently with experimental measurements on Mo and W.

Keywords: Two-body interaction potential; Size dependence potential parameter method; cohesive energy; structural stability.

1. INTRODUCTION

Nanoscience is a widespread applied science working with nanomaterials composed of grain sizes on the order of 1-100 nm with the majority of atoms located at the surface of crystals, whereas they are the bulk in conventional materials. The behavior of such nanocrystals is different from bulk since (i) the surface to volume ratio of the number of atoms is very large, so surface atoms will be less stable than interior atoms due to their lower coordination number [1, 2], and (ii) the distance between surface atoms and the nearest interior atoms is larger than the distance between interior atoms i.e., more than half of the bonds are dangling bonds [3]. Substances with higher ratio of surface to volume number of atoms have enhanced chemical, mechanical, optical and magnetic properties [4]. Mechanical properties such as hardness, elasticity, and ductility show drastic differences in nanocrystals compared to bulk. Nanocrystals also exhibit novel super characteristics such as superheating [5], superparamagnetism [6], and superplas-

ticity [4]. Among many physical quantities, the cohesive energy is of special interest since all the thermodynamical quantities like heat capacity, surface tension, etc., may be derived from it. The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation [7]. Cohesive energy depends on the size of nanocrystals, type of atoms involved, the shape and structure. For nanocrystals, a careful measurement of the cohesive energy proved its size dependence [8], while it is constant for bulk crystals. Many theoretical models and techniques were developed to predict the size dependence of the cohesive energy [9-20]. Although all of these models successfully predict the size dependence of the cohesive energy, some of them were phenomenological [10, 17] and not computational in a sense they cannot justify some of the criteria related to the crystals such as structure transition. There are many research groups that used the semi-empirical potential energy functions and com-

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puter simulations to study the behavior of the cohesive energy of nanocrystals. W.H. Qi et al [13] tried to fit the experimental data of Mo and W by using the well known two-body Lennard-Jones potential energy function (PEF). The size dependence is included but the ratio of the cohesive energy of the nanocrystal to that of the bulk for the above mentioned elements did not match the data. Another group, T. Barakat et al [16] used two-body PEF and achieved excellent fit for Mo and W using Mie-Type potential function with (m, k) as (6, 5). The use of this model had a main problem due to two power terms of the same order. So both of them are considered to be short range terms. It was implicitly assumed in the model that long range interactions are ignored which is physically unacceptable. Another model to be discussed here is a phenomenological model by F. Aslam et al. [17], employed an empirical PEF that comprises two body terms of long range as coulomb and Van Der Waals as Lennard-Jones terms and predicts successfully the size dependence of the cohesive energy. Recently our group [18], designed a model which includes both two and three body terms in the PEF. The two body term was a Mie-Type with (m, k) as (8, 4). So one of them is for short range and the other is for long range terms. The three body term is a Teller-Axilord triple-dipole term. The only assumption made for this model was to consider the crystal as spherical, so shape factor was ignored. The model applies to all elements in the periodic table exceptionally and shows stability. In this paper the size dependant potential parameter (SDPP) method has been proposed to perform the cohesive energy and structural stability calculations. This method although simple in principle, proves to be powerful in the results it predicts.

2. MODEL AND POTENTIAL ENERGY FUNCTION

The potential energy of N interacting atoms can be expressed as a many-body expansion:

$$\phi = \phi_2 + \phi_3 + \dots \phi_n + \dots, \quad (1)$$

Where ϕ_2, ϕ_3, \dots are the two, three-body \dots , interaction energies respectively. In the present work, two-body atomic interactions are adopted to simulate and reproduce the cohesive energy and structure-related properties. The two-body PEF, uses simplified statistical mechanical formalism for calculating various thermo dynamical properties and enabled many early researchers to run simulation calculations with relatively less powerful computers [21].

An empirical potential energy function PEF to describe the three-to-thirteen-atom microclusters was suggested in 1989 [22,23] and modified in 1990 [24] by S. Erkoç. This PEF works well for the microclusters of elements at different structures [22,23]. There are different empirical PEF's to describe the interatomic interaction of bulk and small clusters, like those suggested by Person et al, Stillinger and Weber and Tersoff. Although their predictions of the structural stability and cohesive energies are fairly good, they require an evaluation of three, nine, and eleven parameters respectively. However, the PEF proposed by Erkoç (EPEF) need the evaluation of only two parameters. The explicit form of EPEF for N interacting atoms is:

$$\phi = C_2\phi_2 + C_3\phi_3, \quad (2)$$

where

$$\phi_2 = \sum_{\substack{i,j=1 \\ i \neq j}}^N U(r_i, r_j) \quad (3)$$

and

$$\phi_3 = \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^N W(r_i, r_j, r_k) \quad (4)$$

In this project, three assumptions are made:

- (1) The structure of the nanocrystal is the same as that of a bulk.
- (2) The nanocrystals are in FCC or BCC cubic form.
- (3) All atoms are in equilibrium and interacting via two-body Erkoç potential energy function (EPEF):

More explicitly $U(r_i, r_j)$ is expressed as:

$$U(r_i, r_j) = A \left[\left(\frac{r_o}{r_{ij}} \right)^{2\beta} e^{-2\alpha(r_{ij}/r_o)^2} - \left(\frac{r_o}{r_{ij}} \right)^\beta e^{-\alpha(r_{ij}/r_o)^2} \right] \quad (5)$$

where r_o is the equilibrium distance between dimmers, r_{ij} is the interaction distance between atom i and atom j and β is a positive number. The parameters A , and α are found through the two stability conditions:

$$U_{ij}]_{r_{ij}=r_o} = \epsilon_o, \quad (6)$$

and

$$\frac{\partial U_{ij}}{\partial r_{ij}}]_{r_{ij}=r_o} = 0 \quad (7)$$

Simple calculations give the values of the two parameters as:

$$A = -4\epsilon_o, \quad (8)$$

$$\alpha = \ln(2) \quad (9)$$

The total interaction energy of a nanocrystal is found by summing all the energies of all atoms in the crystal and is expressed as:

$$\phi = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \cup(r_i, r_j) \quad (10)$$

The structure of any crystal is determined by primitive lattice cell and primitive basis. A monoatomic crystal having cubic structure is determined by the nearest neighbor distance d . Another characteristic of all elements is the equilibrium distance between dimmers r_o . The ratio r_o/d has a definite value at the bulk of all elements, but have a different value at nanoscale. So the energy ϕ may be written in a different form as a function of the parameter r^* as:

$$\phi_\beta = \frac{1}{2} A \left[\sum \left(\frac{d}{r_{ij}} \right)^{2\beta} e^{-2\alpha(r_{ij}/d)^2 r^{*\beta-2}} r^{*2\beta} \right] \quad (11)$$

The equation (12) is in continuation of equation no (11).

$$\left[\dots - \sum \left(\frac{d}{r_{ij}} \right)^\beta e^{-\alpha(r_{ij}/d)^2 r^{*\beta-2}} r^{*\beta} \right], \quad (12)$$

$$\phi_\beta^* = 2 \left(A_{2\beta} r^{*2\beta} - A_\beta r^{*\beta} \right), \quad (13)$$

where

$$\phi_\beta^* = \phi_\beta / \epsilon_0, \quad (14)$$

$$r^* = r_o/d, \quad (15)$$

$$A_{2\beta} = \sum \left(\frac{d}{r_{ij}} \right)^{2\beta} e^{-2\alpha(r_{ij}/d)^2 r^{*\beta-2}} \quad (16)$$

and

$$A_\beta = \sum \left(\frac{d}{r_{ij}} \right)^\beta e^{-\alpha(r_{ij}/d)^2 r^{*\beta-2}} \quad (17)$$

The stability condition of the nanocrystal is

$$\partial\phi/\partial V = 0 \text{ or } \partial\phi/\partial d = 0 \quad (18)$$

Since the volume V is related to d via the relation $V = N_o g d^3$, where N_o is Avogadro's number and g is a geometrical factor. This relation leads to the stability equation:

$$-2\beta A_{2\beta} r^{*2\beta} + \beta A_\beta r^{*\beta} - 4\alpha B_{2\beta-2} r^{*2\beta-2} + 2\alpha B_{\beta-2} r^{*\beta-2} = 0 \quad (19)$$

where

$$B_{2\beta-2} = \sum \left(\frac{d}{r_{ij}} \right)^{2\beta-2} e^{-2\alpha(r_{ij}/d)^2 r^{*\beta-2}} \quad (20)$$

and

$$B_{\beta-2} = \sum \left(\frac{d}{r_{ij}} \right)^{\beta-2} e^{-\alpha(r_{ij}/d)^2 r^{*\beta-2}} \quad (21)$$

The values of r^* may be found from equation (19) numerically for a specific β . These values are then plugged into equation (13) to find the equilibrium energy at any structure for the specified β . The parameters A_β , $A_{2\beta}$, $B_{2\beta-2}$ and $B_{\beta-2}$ depend on the value of r^* as well as on the size of the nanoparticle N .

The variations of these parameters are shown in figures (1-8) for FCC and BCC structures for different values of β . It is clear from the figures that the values of A 's and B 's increase rapidly for small N and converge to their bulk values slowly. The bulk sums of A 's and B 's at some values of β are given in Table 1.

β	Face-Centered cubic				Body-centered cubic			
	A_β	$A_{2\beta}$	$B_{\beta-2}$	$B_{2\beta-2}$	A_β	$A_{2\beta}$	$B_{\beta-2}$	$B_{2\beta-2}$
1.3	33.80	11.98	160.03	22.05	32.55	11.12	162.89	21.64
1.35	28.84	10.60	118.65	17.72	27.77	9.82	17.38	120.97
2	12.02	5.11	23.48	5.76	11.32	4.56	23.36	5.42
3	8.29	3.7	9.49	3.82	7.58	3.15	11.29	3.41

Table 1: The lattice sums A_β , $A_{2\beta}$, $B_{2\beta-2}$ and $B_{\beta-2}$ of the FCC and BCC structures for different values of β .

The value of the relative cohesive energy $\phi_{nanocrystal} / \phi_{bulk}$ as a function of size is of special interest since it describes the same behavior for any element.

3. NUMERICAL RESULTS AND DISCUSSIONS

Figures (9, 10) show the relative cohesive energy of metallic nanocrystals for BCC and FCC structures and for different potential ranges. The figures show clearly that the potential used predicts successfully the size dependence of the cohesive energy which increases rapidly as size increases toward the values at $N=2000$, then it gradually increases toward the bulk values. The arrows indicate the experimental values for Mo and W. The variation of β controls the range of the potential where the best fit to the experimental values of the relative cohesive energies of Mo and W were systematically found by varying β . The value of β that gives the best fit for Mo and W is 1.35 where the relative cohesive energy is given in Figure 11 for both FCC and BCC structures. The values of the relative cohesive energy are very close to 1 and this indicates clearly the possibility of structure transition between FCC and BCC. Both Mo and W

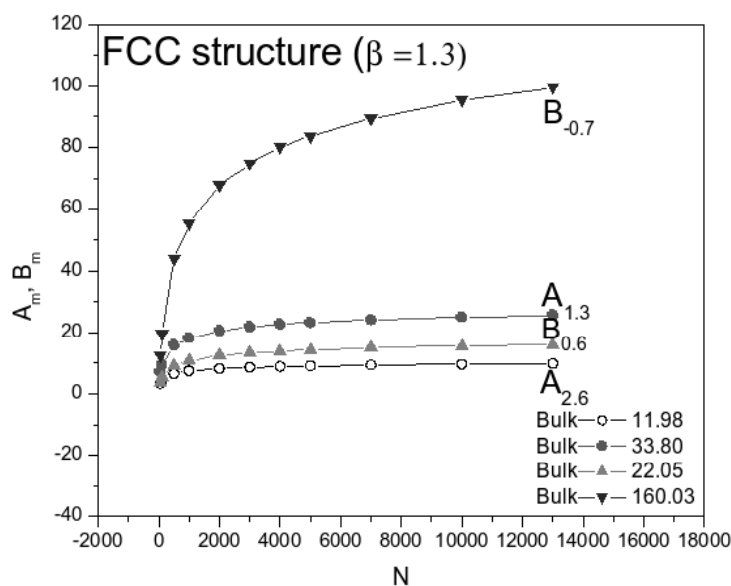


Fig. 1: Size dependence potential parameter $A_{1.3}$, $A_{2.6}$, $B_{0.6}$ and $B_{-0.7}$ of face-centered cubic structure as a function of nanocrystal size N

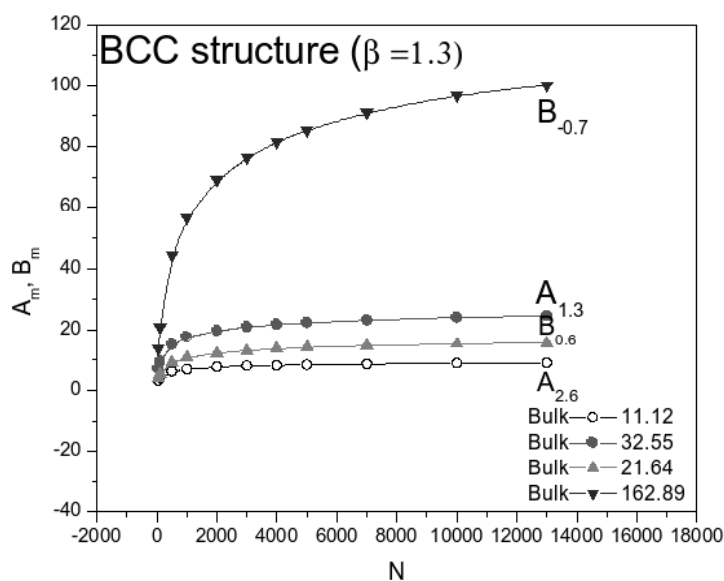


Fig. 2: Size dependence potential parameter $A_{1.3}$, $A_{2.6}$, $B_{0.6}$ and $B_{-0.7}$ of body-centered cubic structure as a function of nanocrystal size N

have BCC structure at bulk, while they have FCC structure at nanoscale [8].

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5. CONCLUSION

In conclusion, the present calculation are consistent with experimental values for Mo and W (Figure 11), where it

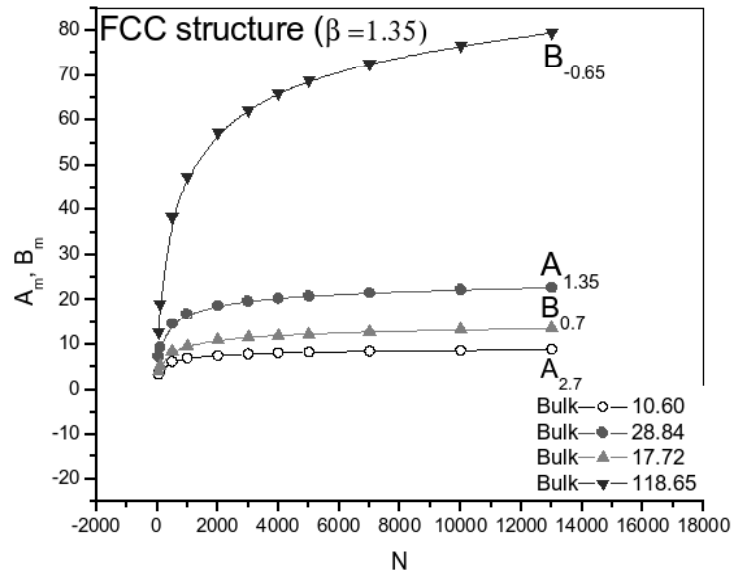


Fig. 3: Size dependence potential parameter $A_{1.35}$, $A_{2.7}$, $B_{0.7}$ and $B_{-0.65}$ of face-centered cubic structure as a function of nanocrystal size N

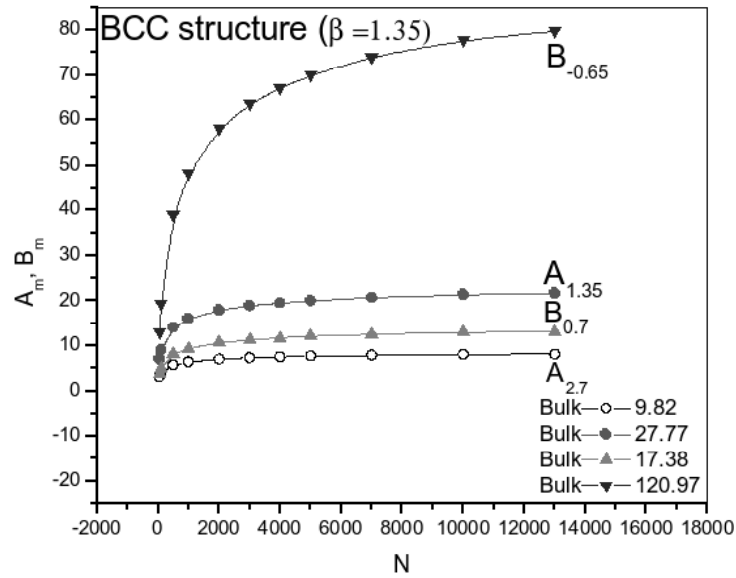


Fig. 4: Size dependence potential parameter $A_{1.35}$, $A_{2.7}$, $B_{0.7}$ and $B_{-0.65}$ of body-centered cubic structure as a function of nanocrystal size N .

was reported that the cohesive energy of Mo nanocrystal of the size $N = 2000$ is -4.25 eV/atom, whereas the cohesive energy of the bulk Mo is -6.2 eV/atom. For a W nanocrystal of size $N = 7000$, its cohesive energy is -6.42 eV/atom and that of the corresponding bulk W is -8.55 eV/atom. In addition, the size dependence

and the relative cohesive energy is shown for both FCC and BCC structures. The two-body ErkoC PEF which comprises both long-range and short-range terms can be possible candidate to study different thermo-dynamical properties of nanocrystals.

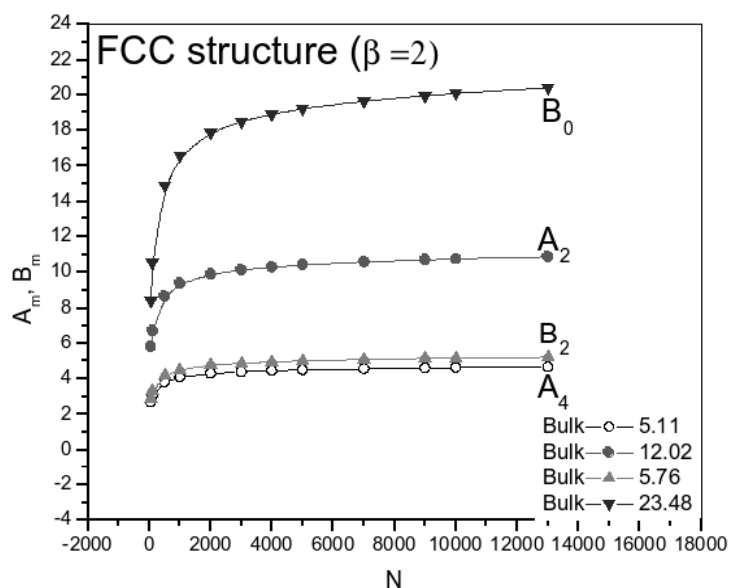


Fig. 5: Size dependence potential parameter A_2, A_4, B_2 and B_0 of face-centered cubic structure as a function of nanocrystal size N .

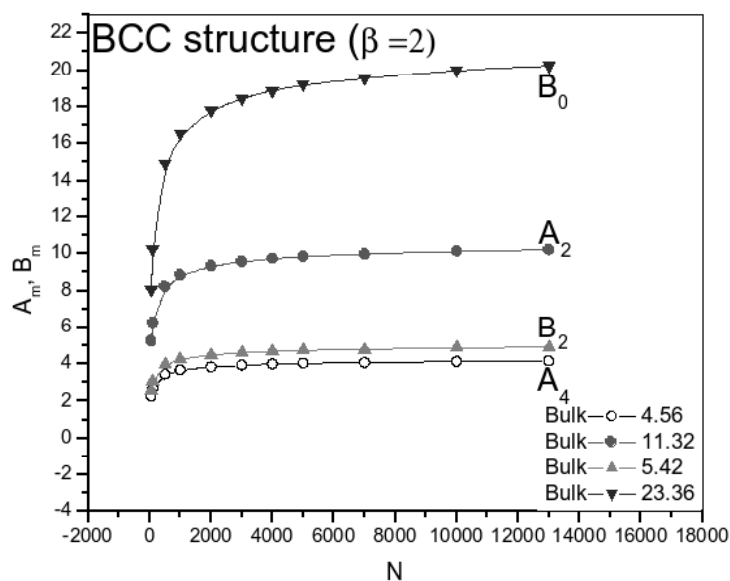


Fig. 6: Size dependence potential parameter A_2, A_4, B_0 and B_2 of body-centered cubic structure as a function of nanocrystal size N .

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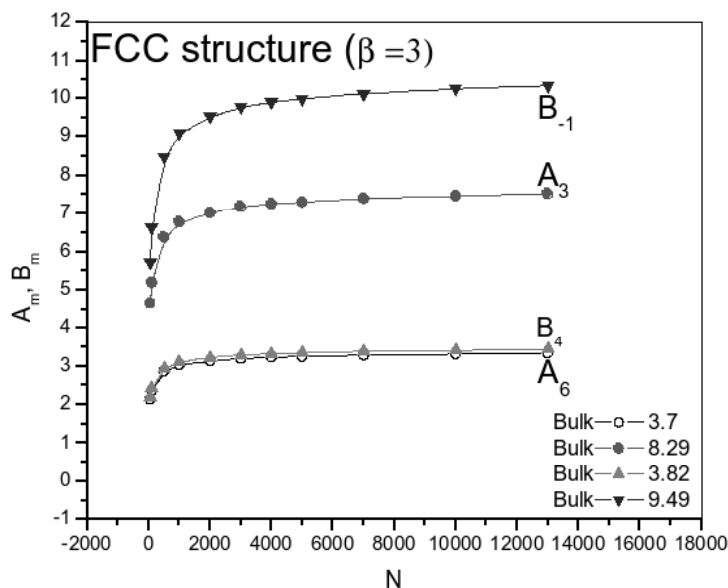


Fig. 7: Size dependence potential parameter A_3 , A_6 , B_4 and B_{-1} of face-centered cubic structure as a function of nanocrystal size N .

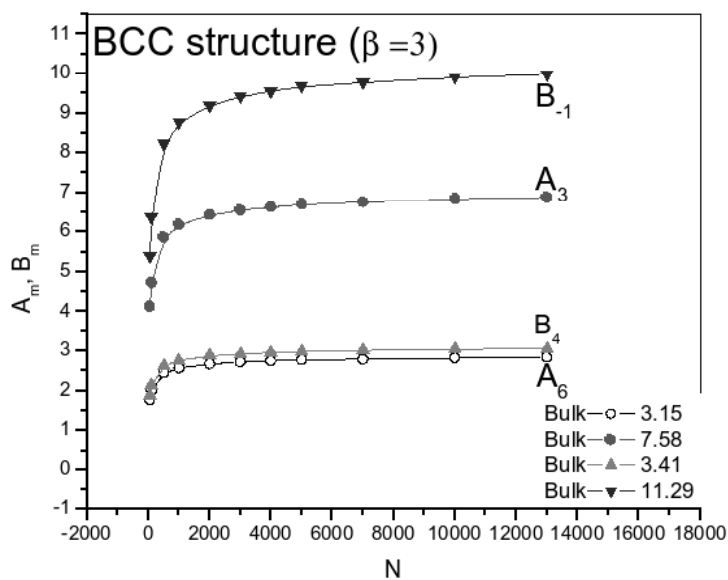


Fig. 8: Size dependence potential parameter A_3 , A_6 , B_4 and B_{-1} of body-centered cubic structure as a function of nanocrystal size N .

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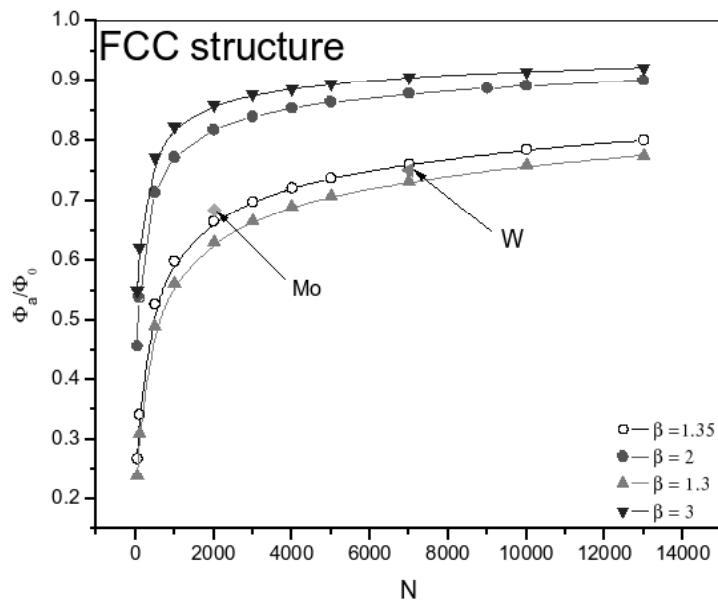


Fig. 9: Size dependence of the relative cohesive energy of face-centered cubic structure with different potential ranges as a function of nanocrystal size N.

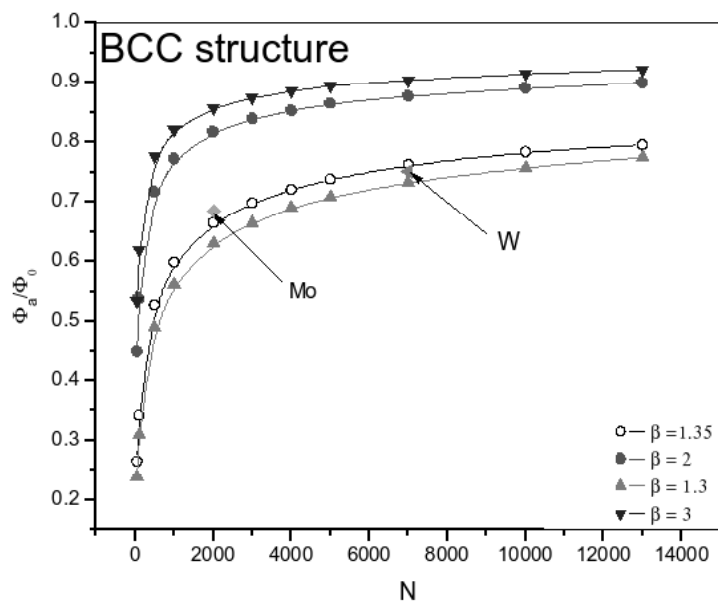


Fig. 10: Size dependence of the relative cohesive energy of body-centered cubic structure with different potential ranges as a function of nanocrystal size N.

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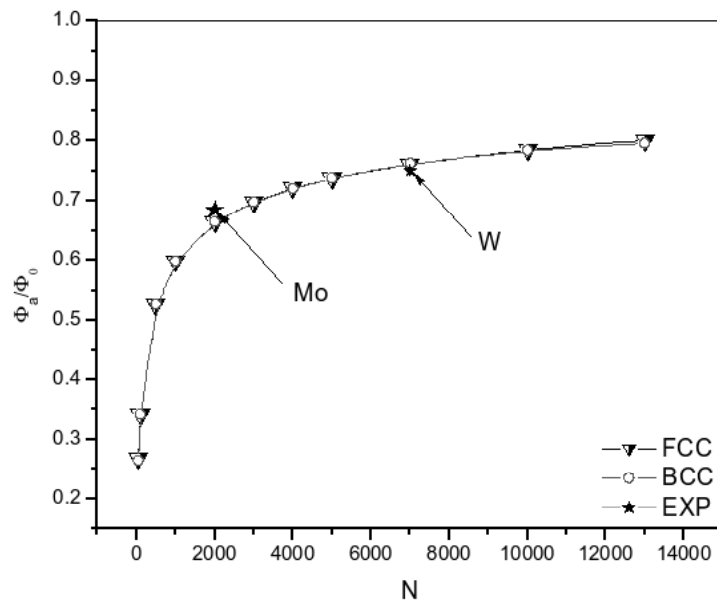


Fig. 11: Size dependence of the relative cohesive energy of face-centered cubic and body-centered cubic structures with $\beta = 1.35$ as a function of nanocrystal size N .

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