Determination of elastic constants for 3D-nanocristal

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Abstract

In this work we investigate a 3D-nanocrystal with a face-centered cubic lattice. Crystal has a finite number of layers in one of direction and an infinite number of them along the other two directions. In this model elasticity constants such as Poisson's ratio and Young modulus are defined for three directions and the dependence of their values on the size of the nanocrystal is investigated. It is shown that elasticity tensor of a smaller crystal is not symmetric. The symmetry occurs only for those directions in which the crystal is infinite. Totally, crystal has five different stiffness coefficients unlike two under isotropy.

The size of the crystal in the direction with the finite number of layers thickness is determined ambiguously, which leads to the ambiguousness in determination of its mechanical properties. The dependence of elasticity modules is determined according to the thickness of the crystal in different directions, where the way of nanocrystal thickness determination becomes essential such as Young modules of the crystal.

1 Introduction

In recent years, rapid development of nanotechnologies led to the necessity of constructing adequate physical models that make it possible to describe physical and mechanical properties of objects with a nanometer size scale. The adequateness should be especially emphasized due to some inconsistency of values of elastic module, which were obtained in microscale and macroscale experiments, was being noted by many researchers [1, 2, 3]. Probably, this inconsistency was explained as discrepancy between the evident discreteness of an object under study and a continual method of its description. This work is focus on the research on how this discreteness have effects on values of elastic modulus and sequential the works [4, 5, 6]. It is a continue of researches on this subject which were started with a study of two-dimensional strip of mono-crystal material with hexagonal close-packed lattice. This work is continue the researches for tree-dimensional case. The subject of research is a tree-dimensional mono-crystal with face-centered cubic lattice. We study the direction longwise the lattice edge (100). The interaction between atoms is assumed to be dual. To define the elastic modules we consider only the effect of scaling (stress-strain) on mono-crystal and interaction only between closest neighbors within a crystal.

2 Determination of elastic constants

We consider a three-dimensional crystal infinitely long (along the x, z axis) and $N \geq 3$ atomic layers thick (along the y axis). Crystal lattice is considered as a face-centered cubical lattice (Fig. 1).

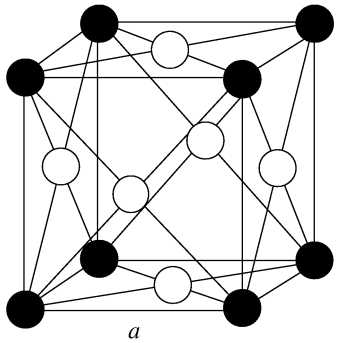

Fig. 1. 3D-nanocrystal with a FCC.

Atoms in the lattice are of one type: white and black atoms are completely identical, and the difference in colors is given only for convenience. Each atom interacts only with nearest neighbor atoms, as shown in Fig. 2. Constant tensile forces Q are applied to the atoms situated at the ends of the crystal. Consider the plane section xy. The deformed state of the crystal is fully determined

by the distance a between neighboring atoms in each layer and the distance h between adjacent layers. The distance between the nearest neighbor atoms belonging to adjacent layers is b. Obviously, we have

$$b^2 = \frac{1}{4}\,a^2 + h^2\,. \tag{1}$$

In the undeformed state, the lattice consists of isosceles triangles with edge b_0 and base a_0. Thus, in the undeformed state

$$a = a_0\,, \qquad b = b_0 \equiv \frac{a_0}{\sqrt{2}}\,, \qquad h = h_0 \equiv \frac{1}{2}\,a_0 \tag{2}$$

and the load applied to the ends is zero (Q=0).

The thickness of the crystal is defined as L_y (the length of the crystal in y direction). The thickness L_y cannot be determinated unambiguously [4, 5]. For example, if presume that the thickness of crystal equals the distance between atom layers, lying on the opposite ends, then $L_y = (N-1)h$. On the other hand, the crystal thickness can be defined as a composition of the number of layers and the thickness of one layer, which leads to the formula $L_y = Nh$. Therefore, indicate

$$L_y \stackrel{\text{def}}{=} N^*\,h\,, \qquad N-1 \le N^* \le N\,, \tag{3}$$

where N^* — is a quantity, which reflects arbitrariness in definition L_y.

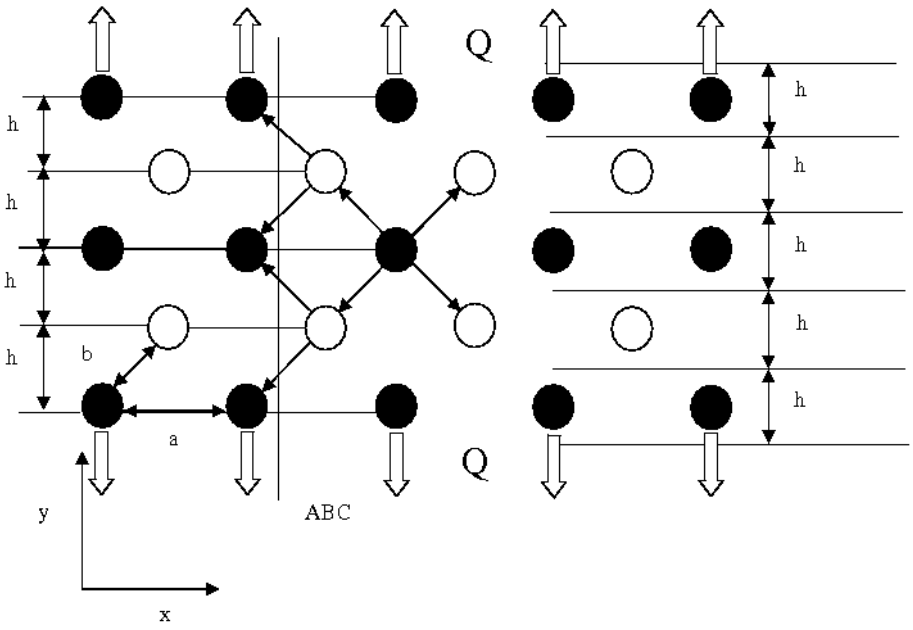

Fig. 2. The section 3D-nanocrystal with a FCC by plane xy.

Let $F(r)$ be the interaction force between two atoms separated by a distance r (the attractive force is considered to be positive). Then, the equilibrium condition (along the x axis) for an atom situated at the crystal surface has the form

$$Q = \frac{\sqrt{2}}{2}F(b_{xy}) + \frac{\sqrt{2}}{2}F(b_{yz}) \quad \Rightarrow \quad \sigma_2 \stackrel{\text{def}}{=} \frac{4Q}{a^2} = \frac{2\sqrt{2}}{a^2}F(b_{xy}) + \frac{2\sqrt{2}}{a^2}F(b_{yz})\,. \tag{4}$$

Here σ_2 — is a normal stress on the crystal ends (normal stress is in the direction y); b_{xy}, b_{xz} and b_{yz} — is the distance between the nearest atoms in the neighboring layers on the planes xy, xz and zy accordingly.

Let's cut in mind a crystal with ABC plane, which is perpendicular to the x direction. The total normal force acting from on side of the crystal to its other side, is equal

$$S\sigma_1 = (N-1)\frac{\sqrt{2}}{2}F(b_{xy}) + N\frac{\sqrt{2}}{2}F(b_{xz})\,, \tag{5}$$

similarly for z direction we get

$$S\sigma_3 = N\frac{\sqrt{2}}{2}F(b_{xz}) + (N-1)\frac{\sqrt{2}}{2}F(b_{yz})\,, \tag{6}$$

where σ_1 — is a normal stress in x direction, and σ_3 is a normal stress in the z direction, S — area elements, on which the normal stress are distributed:

$$S = N^*\left(\frac{a}{2}\right)^2. \tag{7}$$

Designate the right sides of equation for stress through the crystal deformation. For that indicate

$$a = a_0 + \delta a\,, \qquad b = b_0 + \delta b\,, \qquad h = h_0 + \delta h\,. \tag{8}$$

The quantities δa, δb, δh we will consider as small according to a_0. On account of a little deformation, the forces involved in the crystal can be written approximately in the form

$$F(a) = C\delta a\,, \qquad F(b) = C\delta b\,; \qquad C \stackrel{\text{def}}{=} F'(a_0) > 0\,, \tag{9}$$

where C is the atomic-bond stiffness. The quantities δa, δb, δh are connected to crystal deformations through equations:

$$\delta a = a_0\varepsilon_1\,, \qquad \delta h_{xy} = h_0\varepsilon_2 = \frac{1}{2}a_0\varepsilon_2\,, \qquad \delta h_{yz} = h_0\varepsilon_3 = \frac{1}{2}a_0\varepsilon_3\,, \tag{10}$$

$$\delta b_{xy} = \frac{a_0}{2\sqrt{2}}(\varepsilon_1 + \varepsilon_2)\,, \qquad \delta b_{xz} = \frac{a_0}{2\sqrt{2}}(\varepsilon_1 + \varepsilon_3)\,, \qquad \delta b_{yz} = \frac{a_0}{2\sqrt{2}}(\varepsilon_2 + \varepsilon_3)\,, \tag{11}$$

where ε_1, ε_2 ε_3 — is a crystal deformation in x, y and z directions accordingly. Substitution of (9) and (11) into (4), (5) and (6) gives the equation of elasticity:

$$\sigma_1 = \frac{N-1}{N^*}\frac{C}{a_0}(\varepsilon_1 + \varepsilon_2) + \frac{N}{N^*}\frac{C}{a_0}(\varepsilon_1 + \varepsilon_3); \tag{12}$$

$$\sigma_2 = \frac{C}{a_0}(\varepsilon_1 + \varepsilon_2) + \frac{C}{a_0}(\varepsilon_2 + \varepsilon_3); \tag{13}$$

$$\sigma_3 = \frac{N}{N^*}\frac{C}{a_0}(\varepsilon_1 + \varepsilon_3) + \frac{N-1}{N^*}\frac{C}{a_0}(\varepsilon_2 + \varepsilon_3). \tag{14}$$

In a common view equation of elasticity can be written in the form:

$$\begin{aligned}
\sigma_1 &= C_{11}\varepsilon_1 + C_{12}\varepsilon_2 + C_{13}\varepsilon_3\,,\\
\sigma_2 &= C_{21}\varepsilon_1 + C_{22}\varepsilon_2 + C_{23}\varepsilon_3\,,\\
\sigma_3 &= C_{31}\varepsilon_1 + C_{32}\varepsilon_2 + C_{33}\varepsilon_3\,,
\end{aligned} \tag{15}$$

where the stiffness coefficients C_{kn} are given by:

$$\begin{aligned}
&C_{11} = \frac{(2N-1)}{N^*}\frac{C}{a_0}\,, && C_{12} = \frac{(N-1)}{N^*}\frac{C}{a_0}\,, && C_{13} = \frac{N}{N^*}\frac{C}{a_0}\,;\\
&C_{21} = \frac{C}{a_0}\,, && C_{22} = \frac{2C}{a_0}\,, && C_{23} = \frac{C}{a_0}\,;\\
&C_{31} = \frac{N}{N^*}\frac{C}{a_0}\,, && C_{32} = \frac{(N-1)}{N^*}\frac{C}{a_0}\,, && C_{33} = \frac{(2N-1)}{N^*}\frac{C}{a_0}.
\end{aligned} \tag{16}$$

According to (16) we can see, that anisotropy conditional by scale effect is added to the concerned anisotropic crystal. The tensor of elasticity is unsymmetrical, the index regrouping symmetry is applied only for those directions, on which the crystal is infinite, i. e. relatively for index 1 and 3. As a result we have 5 different elasticity coefficients in contrast to 2 at infinite crystal. Same coefficients depends on the quantity N^*, i. e., on a method for determining the thickness of the nanocrystal strip. If we assume that $N^* = N$ (N is the maximal value of N^*) we obtain $C_{13} = C_{21} = C_{23} = C_{31}$, if we assume that $N^* = N - 1$ analogously $C_{12} = C_{21} = C_{23} = C_{32}$, i. e. 4 different coefficients. It will be recalled that tensor of elasticity corresponding to the infinite crystal with a FCC look as:

$$\begin{aligned}
&C_{11} = \frac{2C}{a_0}\,, && C_{12} = \frac{C}{a_0}\,, && C_{13} = \frac{C}{a_0}\,;\\
&C_{21} = \frac{C}{a_0}\,, && C_{22} = \frac{2C}{a_0}\,, && C_{23} = \frac{C}{a_0}\,;\\
&C_{31} = \frac{C}{a_0}\,, && C_{32} = \frac{C}{a_0}\,, && C_{33} = \frac{2C}{a_0}.
\end{aligned} \tag{17}$$

Let us introduce the notation:

$$E_1 \stackrel{\text{def}}{=} \frac{\sigma_1}{\varepsilon_1}\Big|_{\sigma_2=0,\ \sigma_3=0}\,, \qquad E_2 \stackrel{\text{def}}{=} \frac{\sigma_2}{\varepsilon_2}\Big|_{\sigma_1=0,\ \sigma_3=0}\,, \qquad E_3 \stackrel{\text{def}}{=} \frac{\sigma_3}{\varepsilon_3}\Big|_{\sigma_1=0,\ \sigma_2=0}\,. \tag{18}$$

$$\nu_{12} \stackrel{\text{def}}{=} -\frac{\varepsilon_2}{\varepsilon_1}\Big|_{\sigma_2=0,\ \sigma_3=0}\,, \qquad \nu_{13} \stackrel{\text{def}}{=} -\frac{\varepsilon_2}{\varepsilon_1}\Big|_{\sigma_2=0,\ \sigma_3=0}\,, \qquad \nu_1 \stackrel{\text{def}}{=} \tfrac{1}{2}(\nu_{12}\ +\nu_{13})\ ;$$

$$\nu_{21} \stackrel{\text{def}}{=} -\frac{\varepsilon_1}{\varepsilon_2}\Big|_{\sigma_1=0,\ \sigma_3=0}\,, \qquad \nu_{23} \stackrel{\text{def}}{=} -\frac{\varepsilon_3}{\varepsilon_2}\Big|_{\sigma_1=0,\ \sigma_3=0}\,, \qquad \nu_2 \stackrel{\text{def}}{=} \tfrac{1}{2}(\nu_{21}\ +\nu_{23})\ ; \tag{19}$$

$$\nu_{31} \stackrel{\text{def}}{=} -\frac{\varepsilon_1}{\varepsilon_3}\Big|_{\sigma_1=0,\ \sigma_2=0}\,, \qquad \nu_{32} \stackrel{\text{def}}{=} -\frac{\varepsilon_2}{\varepsilon_3}\Big|_{\sigma_1=0,\ \sigma_2=0}\,, \qquad \nu_3 \stackrel{\text{def}}{=} \tfrac{1}{2}(\nu_{31}\ +\nu_{32})\ .$$

Here ν_1 and E_1 — Poisson's ratio and Young modulus, respectively, characterizing the tension along the x axis, values ν_2 and E_2 are the respective quantities characterizing the tension along the y axis, ν_3 and E_3 — along the z axis. Using (15), we obtain for the Young modulus:

$$E_1 = \frac{D}{C_{22}C_{33} - C_{23}C_{32}}\,, \qquad E_2 = \frac{D}{C_{11}C_{22} - C_{12}C_{21}}\,, \qquad E_3 = \frac{D}{C_{11}C_{33} - C_{31}C_{13}}\,; \tag{20}$$

$$D \stackrel{\text{def}}{=} C_{11}C_{22}C_{33} + C_{12}C_{23}C_{31} + C_{12}C_{21}C_{32} - \\ -C_{12}C_{22}C_{31} - C_{11}C_{23}C_{32} - C_{33}C_{21}C_{12}\ . \tag{21}$$

Analogously to Poisson's ratio, taking into consideration $\varepsilon_1 = \varepsilon_3$, when $\sigma_1 = 0$, $\sigma_3 = 0$, we have:

$$\nu_{12} = \tfrac{(C_{23}C_{31}-C_{21}C_{33})}{(C_{22}C_{33}-C_{23}C_{32})}\,, \qquad \nu_{13} = \tfrac{(C_{21}C_{32}-C_{22}C_{31})}{(C_{22}C_{33}-C_{23}C_{32})}\,;$$

$$\nu_{21} = \tfrac{(C_{32}C_{13}-C_{12}C_{33})}{(C_{11}C_{33}-C_{13}C_{31})}\,, \qquad \nu_{23} = \tfrac{(C_{31}C_{12}-C_{32}C_{11})}{(C_{11}C_{33}-C_{13}C_{31})}\,; \tag{22}$$

$$\nu_{31} = \tfrac{(C_{23}C_{12}-C_{13}C_{22})}{(C_{11}C_{22}-C_{12}C_{21})}\,, \qquad \nu_{32} = \tfrac{(C_{21}C_{13}-C_{23}C_{11})}{(C_{11}C_{22}-C_{12}C_{21})}\,.$$

As $C_{12} = C_{32}$, $C_{11} = C_{33}$, $C_{21} = C_{23}$, $C_{13} = C_{31}$, obviously

$$E_1 = E_3\,, \qquad \nu_{21} = \nu_{23}\,, \qquad \nu_{12} = \nu_{32}\,, \qquad \nu_{13} = \nu_{31}\,. \tag{23}$$

Calculated the Poisson's ratio. Substitution of (16) into (22) gives

$$\nu_{12} = \tfrac{(N-1)}{(3N-1)}\,, \qquad \nu_{13} = \tfrac{(N+1)}{(3N-1)}\,, \qquad \nu_1 = \tfrac{N}{(3N-1)}\,;$$

$$\nu_{21} = \tfrac{(N-1)}{(3N-1)}\,, \qquad \nu_{23} = \tfrac{(N-1)}{(3N-1)}\,, \qquad \nu_2 = \tfrac{N-1}{(3N-1)}\,; \tag{24}$$

$$\nu_{31} = \tfrac{(N+1)}{(3N-1)}\,, \qquad \nu_{32} = \tfrac{(N-1)}{(3N-1)}\,, \qquad \nu_3 = \tfrac{N}{(3N-1)}\,.$$

As a result there are three different values of Poisson's ratio defined for the three directions. Note that $\nu_{13} = \nu_{31} = 1$ assuming that $N = 1$. This anomalous value of Poisson's ratio is evidently associated with that when the thickness of the plate equals one atom the crystal FCC lattice is loosing its stability and shrinks like accordion. Something like that also happens when $N = 2$. The full-value lattice we get only if $N = 3$. Note that for the infinite 3D crystal with FCC lattice for the 4-fold axis it applies $\nu = \nu_\infty = 1/3$. The diagrams of the Poisson's ratio depend on the number of atomic layers represented in the Figure 3.

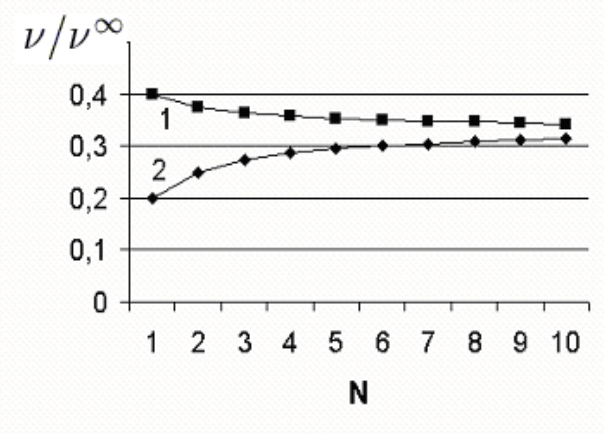

Fig. 3. Dependences of the Poisson's ratio on the number of atomic layers.
1. $\nu_1(N) = \nu_3(N)$; 2. $\nu_2(N)$

In this case when stretching both in y direction and x and z directions the Poisson's ratio are greatly depend on the number of layers N. At a big N they are close to ν_∞, but when N is decreasing they could substantially differ from a limiting value. At that for y direction when N is decreasing the Poisson's ratio is also decreasing, and for the x and z directions on the contrary it is increasing. Consider the Young modulus. From (20) using (16) and (21) we obtain:

$$E_2 = \frac{4NC}{a_0(3N-1)}\,, \qquad E_1 = E_3 = \frac{4NC(N-1)}{N_* a_0(3N-1)}\,. \tag{25}$$

This equation we can written in form:

$$E_2 = \frac{3N}{3N-1}\,E_\infty\,, \qquad E_1 = E_3 = \frac{3N(N-1)}{N_*(3N-1)}\,E_\infty\,; \qquad E_\infty \stackrel{\text{def}}{=} \frac{4C}{3a_0}\,. \tag{26}$$

Here E_∞ — is the value of the Young modulus corresponding to the infinite crystal. The diagrams of the Young modulus depend on the number of atomic layers represented in the Figure 4.

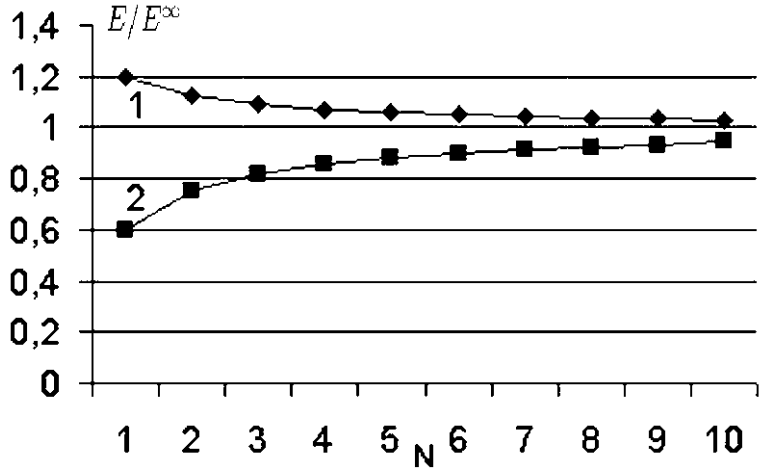

Fig. 4. Dependences of the Young modulus on the number of atomic layers.
1. $E_1^{max}(N)/E_\infty = E_3^{max}(N)/E_\infty = E_2(N)/E_\infty$; 2. $E_1^{min}(N)/E_\infty = E_3^{min}(N)/E_\infty$

When stretching in the direction, which is perpendicular to the atom layers (in the y direction), the Young modulus depends on N, but if the number of layers is decreasing it is increasing (in contrast to the Poisson's ratio for the same direction).

Now consider the Young modulus when stretching in the directions x and z. According to (26) they are determined ambiguously as their definition contains N_* quantity, which depends on how the crystal thickness is determined. If consider that crystal thickness equals to the composition of the number of layers and the thickness of one layer, then $N_* = N$ and we got a formula

$$E_1 = E_3 = \frac{3(N-1)}{(3N-1)}\,E_\infty\,, \tag{27}$$

according to which Young modulus E_2 and E_3 are decreasing with N amplification. If determine the crystal thickness as a distance between the atom layers, which are on the opposite sides, then $N_* = N-1$, and we got the following formula for the Young modulus

$$E_1 = E_3 = \frac{3N}{(3N-1)}\,E_\infty\,, \tag{28}$$

according to which Young modulus E_1=E_2=E_3 coincide in all three directions. So, E_2 doesn't depend on N_*, and when decreasing the number of layers grows up. On the contrary E_1 and E_3 are decreasing with the increase of the number of layers, i.e. behave itself oppositely to E_2, and when $N_* = N-1$ they increasing with the increase of the number of layers, i.e. similarly to E_2. So, when $N_* = N-1$ Young modulus coincide in all three directions even in the case of small values of N.

The values of elastic modulus for different are N assembled to table 1.

3 Conclusion

1. The results of the work show that the shape and sizes of nanocrystal bring additional anisotropy to its elastic properties. We can see that additional anisotropy caused by the crystal size and shape is imposed upon anisotropy coupled with the type of crystal lattice. The tensor of elasticity for the considered model is unsymmetrical, we have 5 different elasticity coefficients in contrast to 2 for infinite crystal.
2. The elasticity properties of $3D$ nanocrystal substantially depend on the number of atom layers N in all 3 directions. When the number of layers grows up the elastic moduli are tending to their values, corresponding to the infinite crystal. Note that when $N = 10$ then the maximum deviation is 7 percents, and when $N = 100$ it is only 1 percents.

N	E_1/E_∞	E_1^{min}/E_∞	ν_1	ν_2
3	1.125	0.750	0.375	0.250
4	1.091	0.818	0.364	0.273
6	1.059	0.882	0.353	0.294
10	1.034	0.931	0.345	0.310
20	1.017	0.966	0.339	0.322
50	1.007	0.987	0.336	0.329
100	1.003	0.993	0.334	0.331

Table 1: Dependence of the elastic modulus of a nanocrystal on the number of atomic layers.

3. For the Young modulus of nanocrystal only a possible interval of values is determined, which is connected with the impossibility of a unique definition of nanoobject size. At the direction upon which the crystal is limited the Young modulus doesn't depend on N_*, and it rises at the decrease of the number of layers, which is similar to the two-dimensional model. On the contrary, the Young modulus for the directions upon which the crystal is infinite behave themselves ambiguously, depending on the choice of N_*. When $N_* = N$ then they decrease with the rise of the number of layers, and when $N_* = N - 1$ then they increase with the rise of the number of layers. Thus, when $N_* = N-1$ then the Young modulus coincide with each other in all the three directions even at small N. Note that for the two-dimensional model the Young modulus for the lengthwise direction (upon which the crystal is infinite) is also ambiguous depending on the choice of N_*. When $N_* = N - 1$ then it doesn't depend on the number of layers and equals to its own infinite value, and when $N_* = N - 1$ then it increases at the decrease of the number of atom layers, achieving at $N = 2$ the value, which two times exceeds E_∞.
4. Poisson's ratio also considerably depend on the number of layers N. For the big values of N they are close to ν_∞, but for small N they could substantially vary from their continuum value. The Poisson's ratio in the direction upon which the crystal is limited, decreases at the decrease of N, and at the directions upon which the crystal is infinite, it increases on the contrarily.

Resuming the above we can conclude that concepts of continuum theory of elasticity requires very careful application to nanoscale, where the scale effects should be taken into account.

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