

Size-Dependent Elastic Moduli of Nanofilms

I-Ling Chang* and Jen-Chin Huang

* National Chung Cheng University, Chia-Yi, Taiwan, imeilc@ccu.edu.tw

ABSTRACT

A semi-continuum model is constructed for the analysis of fcc crystal nanofilms to study the size dependence of the elastic properties. Unlike the classical continuum theory, the current model directly takes the discrete nature in the thickness direction into consideration. In-plane Young's modulus, and in-plane and out-plane Poisson's ratios are investigated with this model and it is found that the values of the elastic moduli (Young's modulus and Poisson's ratios) depend on the film thickness and approach the bulk value asymptotically.

Keywords: semi-continuum model, nanofilm, elastic moduli, face-cubic-center crystal

1. INTRODUCTION

Nanostructures have found unique features and benefits in various areas due to their small dimension. Some applications involving different nanostructured materials have already begun to emerge, especially with nanofilms as high capacity information storage device or wear resistance coating. These applications have brought new challenges to the research community whether the physical properties of materials at nanoscale differ from their bulk counterparts. It is learned that most knowledge of bulk material behavior fails to describe material response in the nanometer range¹⁻³. In order to predict deformation, stress, and other mechanical response of nanomaterials at the application, it is required to have an in-depth understanding of how the mechanical properties of nanomaterials depend on their characteristic size. Both theoretical work and experimental measurement have been conducted in the intension to answer those questions. Early theoretical predictions^{4,5} and experiments^{6,7} showed increases in elastic modulus as the constituent size decreased while

recent experiments showed either no dependence on thickness⁸⁻¹⁰ or decrease in modulus¹¹. In view of the foregoing, it is essential to study the dependence/independence of mechanical properties of the nanomaterials on their characteristic lengths. In this research, the attention is directed to nanofilms.

For nanofilms, the continuum approach can be applied to the in-plane dimensions in order to achieve simplicity. However, the dimension in the thickness direction is in the order of the atomic scale which does not allow the use of the averaging process to derive the effective continuum properties. Some researchers¹² proposed a semi-continuum model for simple cubic crystal structure, which is sodium chloride (NaCl) type materials. However, not so many materials possess simple cubic structure, and thus, in this paper, a semi-continuum model is constructed for the analysis of face-cubic-center (fcc) crystal structure nanofilms and the size dependence of the elastic moduli will be studied with this model.

2. SEMI-CONTINUUM MODEL

In semi-continuum model, the dimensions of the in-plane direction are assumed to be much larger compared to the out-plane dimension. Fig. 1 shows the geometry of a nanofilm with uniform thickness h . Along the thickness direction, there are $2N+1$ ($N=1, 2, \dots$) atomic layers. The atoms on k and $k+1/2$ layers are denoted as the same atomic layer, i.e. k^{th} atomic layer.

Each atom interacts with its nearest and second-nearest atom neighbors and the interactions are represented by linearly elastic springs with spring constants α_1 and α_2 ¹³, respectively. It is assumed that the interactions other than the nearest and second-nearest atom pairs are not significant and negligible. Choose an arbitrary atom as the origin of the Cartesian coordinate system and denote unit vectors along the

x , y , and z axes by \bar{e}_1 , \bar{e}_2 , and \bar{e}_3 , respectively. The position of any atom can be denoted as $(x_{i,i+1/2}, y_{j,j+1/2}, z^{(k,k+1/2)})$, whose position vector is $\vec{r} = (i, i+1/2)a\bar{e}_1 + (j, j+1/2)a\bar{e}_2 + (k, k+1/2)a\bar{e}_3$. $1/2$ is used to represent atoms which are sitting at the middle of the cubic face.

Due to the periodicity of the material, at a representative atom point $(x_i, y_j, z^{(k)})$, a representative unit cell of fcc crystal may be chosen as shown in Fig. 2. Except for the top layer, right most face layer, and the back most face layer, the nanofilm can be obtained by marching the representative unit cell with step size of lattice constant, a , from left bottom atom in the front surface along x , y , z directions.

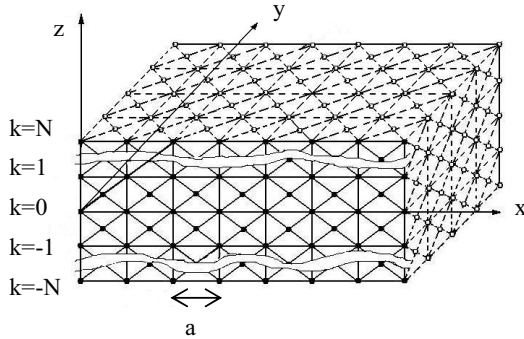


Fig. 1. A representative model of nanofilm

In view of the large in-plane dimensions of nanofilm, we attempt to employ classical continuum treatment in the x and y dimensions. This treatment is based on the long-wave assumption that displacements vary slowly from atom to atom in each layer. Therefore, the discrete displacements $u_{i,j}^{(k)}$, $v_{i,j}^{(k)}$, and $w_{i,j}^{(k)}$ of atom $(x_i, y_j, z^{(k)})$ can be expressed with continuous functions of x and y , i.e., $u_{i,j}^{(k)} = u^{(k)}(x_i, y_j)$, $v_{i,j}^{(k)} = v^{(k)}(x_i, y_j)$ and $w_{i,j}^{(k)} = w^{(k)}(x_i, y_j)$. The discrete nature along the thickness direction is still kept. The deformation energy $U_{i,j}^{(k)}$ of the representative unit cell shown in Fig. 2 can be written as

$$U_{i,j}^{(k)} = U_{1-2} + U_{1-3} + U_{1-10} + U_{1-5} + U_{3-5} + U_{1-9} + U_{9-12} + U_{1-6} + U_{6-11} + U_{2-5} + U_{4-5} + U_{2-6} + U_{6-10} + U_{3-9} + U_{9-10} + U_{6-7} + U_{7-8} + U_{8-9} + U_{6-9} + U_{5-8} + U_{8-14} + U_{6-14} + U_{5-6} + U_{5-7} + U_{7-14} + U_{9-14} + U_{5-9} + U_{6-8} + U_{5-14} + U_{7-9}$$

where U_{1-2} , U_{1-6} , ..., represent deformation energies due to the stretching/shortening of the spring between atom 1, 2, and 1, 6, ..., respectively.

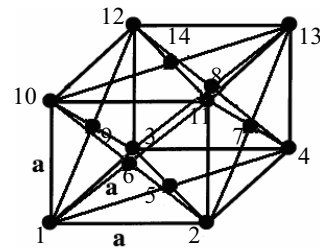


Fig. 2. Unit cell of fcc crystal model

Because displacements in each atomic layer vary slowly from atom to atom, a two-term Taylor series expansion can be used. Thus, the displacement $u_{i+1,j}^{(k)}$ at $(x_{i+1}, y_j, z^{(k)})$ can be approximately expressed in terms of the displacement $u_{i,j}^{(k)}$ at $(x_i, y_j, z^{(k)})$ and deformation energy U_{1-2} can be written as

$$U_{1-2} = \frac{1}{2} \alpha_2 (u_{i+1,j}^{(k)} - u_{i,j}^{(k)})^2 = \frac{1}{2} \alpha_2 [u^{(k)}(x_{i+1}, y_j) - u^{(k)}(x_i, y_j)]^2 \approx \frac{1}{2} \alpha_2 \left(a \frac{\partial u^{(k)}(x, y)}{\partial x} \Big|_{(x_i, y_j)} \right)^2$$

The stretching of the nearest neighbor spring between atom 1 and atom 6 can be written as

$$\sqrt{\left(\frac{a}{2} + u_{i+1/2,j}^{(k+1/2)} - u_{i,j}^{(k)}\right)^2 + \left(\frac{a}{2} + w_{i+1/2,j}^{(k+1/2)} - w_{i,j}^{(k)}\right)^2} - \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2}$$

By using the binomial expansion, deformation energy U_{1-6} due to the stretching of the nearest neighbor spring between atom 1 and atom 6 is obtained as

$$U_{1-6} = \frac{1}{2} \alpha_1 \left[\frac{\sqrt{2}}{2} (u_{i+1/2,j}^{(k+1/2)} - u_{i,j}^{(k)}) + \frac{\sqrt{2}}{2} (w_{i+1/2,j}^{(k+1/2)} - w_{i,j}^{(k)}) \right]^2$$

$$\approx \frac{1}{4} \alpha_1 a^2 \left(\frac{1}{2} \frac{\partial u^{(k+1/2)}(x,y)}{\partial x} \Big|_{x_i,y_j} + \frac{u^{(k+1/2)}(x_i,y_j) - u^{(k)}(x_i,y_j)}{a} \right. \\ \left. + \left(\frac{w^{(k+1/2)}(x_i,y_j) - w^{(k)}(x_i,y_j)}{a} + \frac{1}{2} \frac{\partial w^{(k+1/2)}(x,y)}{\partial x} \Big|_{x_i,y_j} \right) \right)^2$$

Other interaction energies can be expressed in similar way.

If the deformation energy of the representative unit cell at k^{th} atomic layer is denoted by $U_{i,j}^{(k)}$ and the deformation energy of the representative element at $(x_i, y_j, z^{(N)})$ of the top layer is denoted by $U_{i,j}^{\text{top}}$, the total deformation energy of the nanofilm U_{tot} , can then be approximated as

$$U_{\text{tot}} = \sum_i \sum_j \sum_k U_{i,j}^{(k)} + \sum_i \sum_j U_{i,j}^{\text{top}}.$$

3. ELASTIC MODULI

Define the strains in the k^{th} atomic layer as

$$\varepsilon_{xx}^{(k,k+1/2)} = \frac{\partial u^{(k,k+1/2)}}{\partial x}, \quad \varepsilon_{yy}^{(k,k+1/2)} = \frac{\partial v^{(k,k+1/2)}}{\partial y},$$

$$\varepsilon_{zz}^{\Delta(k,k-1/2)} = \frac{w^{(k+1,k+1/2)} - w^{(k)}}{(1,1/2)a},$$

$$\gamma_{xy}^{(k,k+1/2)} = \frac{\partial u^{(k,k+1/2)}}{\partial y} + \frac{\partial v^{(k,k+1/2)}}{\partial x}$$

$$\gamma_{xz}^{\Delta(k,k-1/2)} = \frac{\partial w^{(k+1,k+1/2)}}{\partial x} + \frac{u^{(k+1,k+1/2)} - u^{(k)}}{(1,1/2)a},$$

$$\gamma_{yz}^{\Delta(k,k-1/2)} = \frac{\partial w^{(k+1,k+1/2)}}{\partial x} + \frac{v^{(k+1,k+1/2)} - v^{(k)}}{(1,1/2)a}.$$

Thus, the strain energies of the springs inside the unit cell can be rewritten in terms of strains. Moreover, for a simple tension in x direction, the displacements at each atomic layer can be represented as

$$u^{(k)}(x, y) = u(x); v^{(k)}(x, y) = v(y); w^{(k)}(x, y) = ka\varepsilon_0$$

Thus, the non-zero strain terms are

$$\varepsilon_{xx}^{(k,k+1/2)} = \varepsilon_{xx} = \frac{\partial u}{\partial x}; \varepsilon_{yy}^{(k,k+1/2)} = \varepsilon_{yy} = \frac{\partial v}{\partial y}$$

$$\varepsilon_{zz}^{\Delta(k,k-1/2)} = \varepsilon_{zz} = \frac{w^{(k+1)} - w^{(k)}}{a}$$

Considering the volume element $a \times a \times h$ of the nanofilm, the average strain energy density of this volume element at the in-plane location (x, y) is defined as

$$W(x, y) = \left(\sum_{k=-N}^{N-1} U_{ij}^{(k)} + U_{ij}^{\text{top}} \right) / a^2 h$$

where the thickness h is taken to be $(2N + \frac{1}{2})a$. For simple

tension, $\sigma_{yy} = \frac{\partial W}{\partial \varepsilon_{yy}} = 0$ and $\sigma_{zz} = \frac{\partial W}{\partial \varepsilon_{zz}} = 0$, in combined with

the conditions that the stress in y and z direction should be zero, it could be deduced that

$$v_{xy} = -\frac{\varepsilon_{yy}}{\varepsilon_{xx}} = \frac{2N\alpha_1 + \frac{1}{2}\alpha_1 - \frac{N\alpha_1^2}{\alpha_1 + \alpha_2}}{4N\alpha_1 + 4N\alpha_2 + \frac{1}{2}\alpha_1 + \alpha_2 - \frac{N\alpha_1^2}{\alpha_1 + \alpha_2}} \quad (1)$$

$$v_{xz} = -\frac{\varepsilon_{zz}}{\varepsilon_{xx}} = \frac{\alpha_1(2N\alpha_1 + 4N\alpha_2 + \alpha_2)}{(6N+1)\alpha_1^2 + (6N+3)\alpha_1\alpha_2 - (8N+2)\alpha_2^2}$$

Furthermore, Young's modulus along x direction could be obtained as

$$E = \frac{\sigma_{xx}}{\varepsilon_{xx}} = \frac{1}{(2N + \frac{1}{2})a} \left\{ \frac{4N\alpha_1 + 4N\alpha_2 + \frac{\alpha_1}{2} + \alpha_2 - \frac{N\alpha_1^2}{\alpha_1 + \alpha_2}}{\left(2N\alpha_1 + \frac{\alpha_1}{2} - \frac{N\alpha_1^2}{\alpha_1 + \alpha_2} \right)^2} - \frac{4N\alpha_1 + 4N\alpha_2 + \frac{\alpha_1}{2} + \alpha_2 - \frac{N\alpha_1^2}{\alpha_1 + \alpha_2}}{\alpha_1 + \alpha_2} \right\} \quad (2)$$

For the extreme case ($N \rightarrow \infty$),

$$E_C = \frac{1}{2a} \left\{ 4(\alpha_1 + \alpha_2) - \frac{\alpha_1^2}{\alpha_1 + \alpha_2} - \frac{(2\alpha_1 - \frac{\alpha_1^2}{\alpha_1 + \alpha_2})^2}{4(\alpha_1 + \alpha_2) - \frac{\alpha_1^2}{\alpha_1 + \alpha_2}} \right\} \quad (3)$$

$$v_C = (v_{xy})_C = (v_{xz})_C = \frac{\alpha_1^2 + 2\alpha_1\alpha_2}{3\alpha_1 + 8\alpha_1\alpha_2 + 4\alpha_2^2}$$

4. DISCUSSION AND CONCLUSION

From the semi-continuum model, it could be noticed that the elastic moduli of nanofilms depend on the film thickness, which is the total number of atomic layers. However, it is not so clear whether the elastic moduli decrease or increase as the nanofilm becomes thicker. In order to clarify the size dependence of the elastic moduli, the numeric values of spring constants representing the interaction between the nearest and second-nearest atom pairs should be obtained first. Take single crystal fcc copper as an example, lattice constant is 3.615 \AA and Young's modulus and Poisson's ratio are 67.39 GPa , 0.42^{14} , respectively. The spring constants (α_1, α_2) could be calculated from equation (3) in addition to the Young's modulus and Poisson's ratio of the bulk copper, which corresponding to the extreme case ($N \rightarrow \infty$).

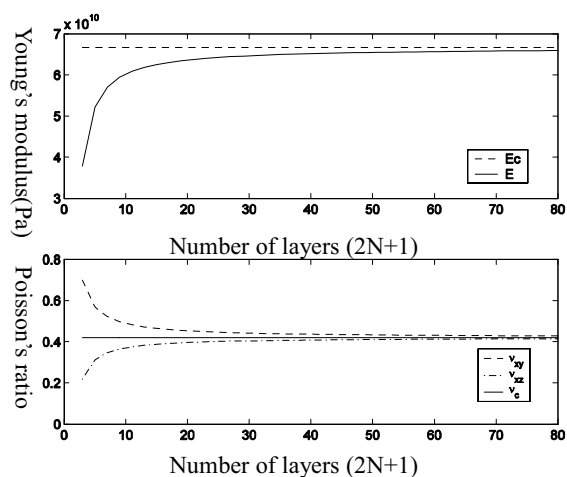


Fig. 3. The relation between the elastic moduli and numbers of atomic layers

With the attained values of spring constants, the size dependence of elastic moduli could be easily obtained from equation (2) as shown in Fig. 3. It could be observed that the elastic moduli (i.e. in-plane Young's modulus, in-plane and out-plane Poisson's ratios) approach the bulk values as the numbers of atomic layers increase. Moreover, the anisotropic behavior of in-plane and out-plane Poisson's ratios (ν_{xy}, ν_{xz}) is observed even though fcc crystal structure material should behave the same along [100] and [001] axes. The anisotropy is

induced by the finite size in the thickness direction since the anisotropic behavior becomes less significant as the total number of atomic layers increases. Moreover, both Poisson's ratios approach the same bulk value.

5. ACKNOWLEDGMENT

This research work is supported by National Science Council of Taiwan under the grant NSC94-2212-E-194-018.

6. REFERENCES

- [1] J.Q. Broughton, C.A. Meli, P. Vashishta, and R.K. Kalia, *Physical Review B*, **56**, 611, 1997.
- [2] R.E. Rudd, J.Q. Broughton, *Journal of Modeling and Simulation of Microsystems*, **1**, 29, 1999.
- [3] K. Petersen, and C. Guarnieri, *Journal of Applied Physics*, **50**, 6761, 1979.
- [4] A.F. Jankowski and T. Tsakalakos, *Journal of Physics F: Metal Physics*, **15**, 1279, 1985.
- [5] R.C. Cammarata and K. Sieradzki, *Physical Review Letters*, **62**, 2005, 1989.
- [6] W.M.C Yang, T. Tsakalakos, and J.E. Hilliard, *Journal of Applied Physics*, **48**, 876, 1977.
- [7] D. Baral, J.B. Ketterson, and J.E. Hilliard, *Journal of Applied Physics*, **57**, 1076, 1985.
- [8] H. Huang, and F. Spaepen, *Acta Materialia*, **48**, 3261, 2000.
- [9] R.C. Cammarata, T.E. Schlesinger, S.B. Qadri, and A. S. Edelstein, *Applied Physics Letters*, **56**, 1862, 1990.
- [10] A. Moreau, J.B. Ketterson, and B. Davis, *Journal of Applied Physics*, **68**, 1622, 1990.
- [11] J.A. Ruud, T.R. Jarvis, and F. Spaepen, *Journal of Applied Physics*, **75**, 4969, 1994.
- [12] H. Zhang and C. T. Sun, *AIAA*, 2002-1316, 2002.
- [13] A. K. Ghatak and L. S. Kothari, "An Introduction to Lattice Dynamics", (Addison-Wesley, Reading MA), 76-111, 1972.
- [14] S. M. Foiles, M. I. Baskes, and M. S. Daw, *Physical Review B*, **33**, 7983, 1986.