

# The Elastic Modulus of Nanometer-sized Tungsten Layers and Wires

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**Abstract.** The size-dependent elastic modulus of tungsten layers and wires is predicted according to size-dependent melting temperature model. The elastic modulus decreases with decreasing of size and the drop becomes dramatically once the size decreases below 3 and 6 nm for layers and wires, respectively. Moreover, the softening of elastic modulus for wires is nearly twice as large as that for layers when size remains the same. The accuracy of the model is verified by experimental and atomistic simulations results.

## Introduction

Materials surfaces are different from the bulk in atomic configurations and therefore behave differently under elastic deformation. When the characteristic scale of the systems is large enough, e.g. 140 nm, the surface-to-volume ratio is small and surface contribution is thus negligible [1]. However, with decreasing of the characteristic scale to several nanometers, surface contribution becomes important and may even be dominant. In this case, the mechanical properties will deviate from the macroscopic ones, which mean that the macroscopic properties cannot be applied to the nanoscale systems anymore. As result, it is necessary to study the size dependences of the mechanical properties at the nanoscale.

A great deal of research has been done on the elastic characteristics of nanoscale materials including experiments, theoretical analysis, and atomistic or molecular dynamics simulations. On the basis of measurements of thin films, some experiments shows that surfaces are softer [2-4] while others show that they are stiffer than the bulk [5-8]. Similarly, recent theoretical and simulations investigations have also reached these two opposite conclusions [9-19]. Among them, Zhou and Huang proposed that whether a metal surface is softer or stiffer depends on the competition of bond loss and bond saturation [15,17]. For close-packed metals, the bond loss can be compensated by the bond saturation, resulting in stiffer surface. It is also possible that the bond saturation does not fully compensate the bond loss, leading to softer surfaces. While for metals with open-structure (e.g. body-centered cubic structure or bcc), the bond loss of each bond is likely too much to be compensated by the bond saturation, leading to the softer surfaces. Although all these models developed from various perspectives can attribute significantly to the understanding of the size effects of elastic properties of nanocrystals, most of these methods are rather complicated to perform [18].

In this paper, an analytic method is developed to model the size-dependent elastic modulus of W layers and wires. The choice of W originates from the considerations that W is elastically isotropic and thus it is the simplest condition. The accuracy of the developed method is verified with the available experimental and atomistic simulations results.

## Methodology

It is known that the elastic modulus is fundamentally related to the interatomic bonding and is thus influenced by modifications of the atomic environment [14]. Semi-empirical methods to correlate the elastic modulus  $Y(\infty)$  and the surface thermodynamic properties are always possible with  $\infty$  being the bulk value. For example,  $Y$  has been linked to the surface energy  $\gamma$  with the following expression [20]:

$$Y(\infty) = \frac{\gamma(\infty)d_0}{2} \left[ \frac{\pi}{h(\infty)} \right]^2 \quad (1a)$$

where  $d_0$  denotes the equilibrium interplanar spacing normal to a surface of the solid, and  $h$  is a parameter, which can take the mean atomic or ionic radius of atoms or ions on the surface.

Under the assumption that the W nanocrystal remains the bcc structure and isotropic, which are the same as the corresponding bulk, Eq. 1a may thus be extended to nanometer size,

$$Y(D) = \frac{\gamma(D)d_0}{2} \left[ \frac{\pi}{h(D)} \right]^2 \quad (1b)$$

with  $D$  denoting the size, i.e. the thickness of layers or the diameter of wires.

Combining Eqs. 1a and 1b, there is,

$$\frac{Y(D)}{Y(\infty)} = \frac{\gamma(D)}{\gamma(\infty)} \left[ \frac{h(D)}{h(\infty)} \right]^{-2} \quad (2a)$$

To evaluate the size dependence of  $Y$ , the size effects of  $h$  and  $\gamma$  should be determined firstly.

It is well-known that nanocrystals have lattice contraction induced by the large surface-to-volume ratio [21]. However, the observed experimental data and theoretical predictions of  $h(D)$  for metals are usually in the range of about 0.1~2.5% when  $D$  is only several nanometers [21]. Moreover, the atomistic simulation shows that the change of lattice parameter of W is not larger than 3% even though the layer number reduces to two, while the softening of elastic modulus approaches 70% in this case [14]. As a result, the contribution of  $h(D)$  on  $Y(D)$  is negligible as a first order approximation and Eq. 2a can thus be simplified as:

$$\frac{Y(D)}{Y(\infty)} \approx \frac{\gamma(D)}{\gamma(\infty)} \quad (2b)$$

Eq. 2b is understandable since both  $Y$  and  $\gamma$  of metals are related to the bond loss of surface atoms [15,17,22,23].

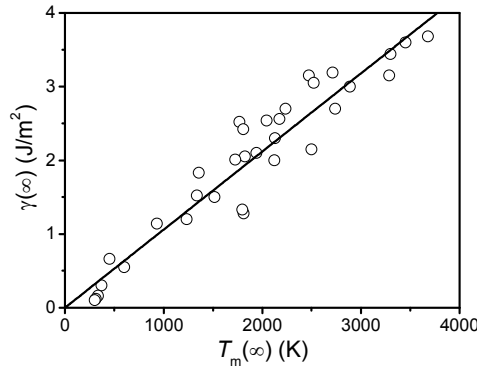


Fig. 1  $\gamma(\infty)$  as a function of  $T_m(\infty)$  for transition metals.

Although the size effects of surface energy of nanoparticles have been modeled [22], it is unknown whether the established models can be extended to nanometer-sized films and wires. However, since the surface energy denotes the bond energy difference between surface atoms and interior ones while the melting temperature  $T_m$  is directly proportional to the bond strength, an empirical relation between surface energy and melting temperature should exist. As shown in Fig. 1, the surface energy is plotted against the melting temperature of transition metals where the experimental values of  $\gamma(\infty)$  are taken from literature [23] and those of  $T_m(\infty)$  are cited from literature [24]. The linear relation between  $\gamma(\infty)$  and  $T_m(\infty)$  can be linearly regressed as,

$$\gamma(\infty) \approx kT_m(\infty) \quad (3a)$$

where the linearly regressed slope  $k$  equals  $1.06 \times 10^{-3} \text{ J/m}^2\text{-K}$  with the standard deviation of  $5.96 \times 10^{-3} \text{ J/m}^2\text{-K}$  and the correlation coefficient of the fit is 0.955.

Since it has been assumed that W nanocrystal has the same structure of the corresponding bulk,  $k$  is size-independent. Thus, Eq. 3a can also be extended to nanometer size with the same form, namely,

$$\gamma(D) \approx kT_m(D) \quad (3b)$$

Combining the above consideration for  $h(D)$ , Eq. 3, and the  $T_m(D)$  function reported in literatures [25,26], there is,

$$\frac{Y(D)}{Y(\infty)} \approx \frac{\gamma(D)}{\gamma(\infty)} \approx \frac{T_m(D)}{T_m(\infty)} = \exp\left(\frac{-2S_{vib}}{3R} \frac{1}{D/D_0 - 1}\right) \quad (4)$$

where  $R$  is the ideal gas constant and  $S_{vib}$  denotes the vibrational component of the melting entropy  $S_m$  at  $T_m(\infty)$ . For W with metallic bond, the electronic entropy is negligible since the nature of chemical bonds does not vary on melting, namely  $S_{vib} \approx S_m - S_{pos}$  with  $S_{pos}$  being the positional entropy.  $S_{pos}$  has been given by  $S_{pos} = -R(x_A \ln x_A + x_B \ln x_B)$  with  $x_A$  and  $x_B$  respectively denoting the molar fractions of the crystals and vacancies [27]. For a melting process,  $x_A = 1/(1 + \Delta V/V)$  and  $x_B = 1 - x_A$  where  $\Delta V/V$  is the normalized volume change on melting.  $D_0$  denotes a critical size where all atoms are located on its surface, which has been determined as  $D_0 = 2(3-d)h(\infty)$  with  $d$  being the dimension [26]. It is known that  $d = 0$  for nanoparticles,  $d = 1$  for nanowires, and  $d = 2$  for thin films [26].

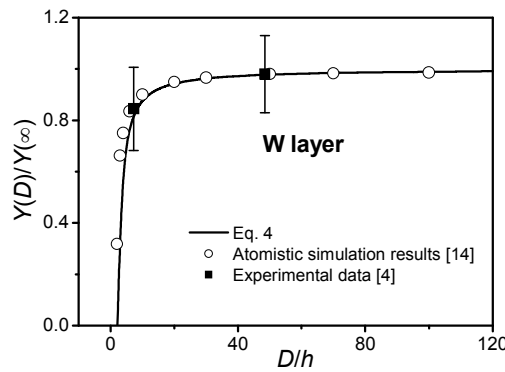


Fig. 2 Comparisons of the  $D/h$  dependence of  $Y(D)/Y(\infty)$  function of W layers among the model predictions with  $D_0 = 2h$ , experimental data [4], and atomistic simulation results [14]. For W,

$$S_m = H_m/T_m \approx 9.62 \text{ J/mol-K with } H_m \text{ being the melting enthalpy,}$$

$$\Delta V/V \approx 12\% [30], S_{vib} \approx S_m - S_{pos} \approx 6.62 \text{ J/mol-K.}$$

## Results and Discussion

Fig. 2 shows the comparison of  $Y(D)/Y(\infty)$  function of W layers among the model predictions in terms of Eq. 4 with  $D_0 = 2h$ , the experimental data [4], and available atomistic simulation results [14]. It is found that the model predictions correspond well to the experimental and atomistic simulation results and  $Y(D)$  function decreases with decreasing of size  $D$ . Moreover, the decrease becomes dramatically once the size decreases below about 3 nm.

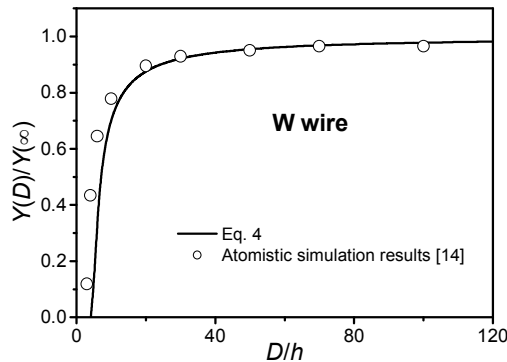


Fig. 3 Comparisons of the  $D/h$  dependence of  $Y(D)/Y(\infty)$  function of W wires between the model predictions with  $D_0 = 4h$  and atomistic simulation results [14].

The  $Y(D)/Y(\infty)$  function of W nanowires determined by Eq. 4 with  $D_0 = 4h$  is shown in Fig. 3. As comparison, available atomistic simulation results [14] are also indicated in this figure. Good agreement can be found between the model predictions and atomistic simulation results. Similar to W layers,  $Y(D)$  function of W nanowire also decreases with decreasing of size  $D$ , while the sharp decrease starts at about 6 nm rather than 3 nm.

Considering the mathematical relation of  $\exp(-x) \approx 1-x$  when  $x$  is small enough (e.g.  $x < 0.1$ , or  $D/D_0 > 6$  since  $2S_{\text{vib}}/3R \approx 1/2$  for W), Eq. (4) can be rewritten as

$$Y(D)/Y(\infty) \approx 1 - 2S_{\text{vib}}D_0/(3RD) \quad (5)$$

Since  $D_0 = 2h$  for layers while  $D_0 = 4h$  for wires, the softening of  $Y(D)$  of wires is twice as large as that of layers in terms of Eq. 5 when  $D$  remains the same and is large enough ( $D/D_0 > 6$ ). It is also the reason why the dramatic decrease of  $Y(D)$  of wires starts at about 6 nm while that of layers does at about 3 nm.

Eq. 5 obeys the general thermodynamic consideration that the decrease of the any size-dependent physical quantity is proportional to  $1/D$ . Eq. 5, or  $1/D$  correlation mechanism implies that the physical properties of interior atoms are the same with those of the corresponding bulk crystal and the size dependence may solely originate from the increase of the surface/volume ratio as size drops [11]. In fact, similar to surface atoms, the vibrational amplitude of interior atoms also increases with decreasing size, and the ratio of the vibrational amplitude between surface atoms and interior ones keeps constant at all sizes [28,29]. Thus, not only surface atoms but also interior atoms should have contributions to the softening of elastic modulus.

In addition,  $Y(D)$  increases with the surface energy in terms of Eq. 2. In fact, similar conclusion has been proposed for elastic composite materials where effective shear modulus and bulk modulus are also considered to be proportional to the surface energy [13]. This similarity and the agreements shown in Figs. 2 and 3 may in turn confirm the validity of the assumptions made in Eq. 1b.

In comparison with existing methods, the method developed here provides us with a new insight and way to understand and estimate the size dependence of the elastic modulus of layers and wires because of the analytical and explicit nature of the method. However, it is noted that only the bond loss is considered in our model while the bond saturation induced by the electron redistribution is not included. This is the reason that our model can only predict the softening of elastic modulus.

## Summary

The size-dependent elastic modulus of W layers and wires has been modeled where the elastic modulus decreases with decreasing of  $D$  and the drop becomes dramatically once the size decreases below about 3 and 6 nm for the layers and wires, respectively. Moreover, the softening of elastic modulus for the wire is nearly twice as large as that for the layer when  $D$  remains the same and is large enough. The model predictions correspond well to the corresponding experimental and atomistic simulations results for W layers and wires.

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