

Size- and Temperature-Dependent Thermal Expansion Coefficient of a Nanofilm *

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The thermal expansion coefficient (TEC) of an ideal crystal is derived by using a method of Boltzmann statistics. The Morse potential energy function is adopted to show the dependence of the TEC on the temperature. By taking the effects of the surface relaxation and the surface energy into consideration, the dimensionless TEC of a nanofilm is derived. It is shown that with decreasing thickness, the TEC can increase or decrease, depending on the surface relaxation of the nanofilm.

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At the nanoscale, many mechanical and physical properties of structures exhibit some new effects (such as surface effects, size effects and quantum effects), which are neglected at the macroscale. The new effects put forward challenges to classical theory, and simultaneously present an opportunity for a breakthrough. A nanofilm is one of the most common nanostructures, and it is a fundamental structural element of nano-electro-mechanical systems (NEMS), nano-devices and nano-oscillators, etc. Thus the mechanical and physical properties of a nanofilm have attracted a large amount of attention in recent years.

The elastic modulus and fracture toughness of a nanofilm have been extensively studied by using the experimental methods,^[1-4] theoretical models^[5-14] and molecular dynamic simulations.^[15-18] It has been shown that the elastic modulus and fracture toughness of a nanofilm are size-dependent and surface-dependent. Some researchers^[7-9] have also shown that the elastic moduli of a nanofilm are temperature-dependent. Besides the elastic modulus and fracture toughness, in engineering applications, the thermal expansion coefficient (TEC) is also an important physical property. There have been some studies concerning the size effects of the TEC.^[19-24] Similar to results for the elastic modulus, there exist some debates on the size effects of the TEC. Some experiments showed that the TEC increases with decreasing crystallite size,^[19-20] but some other experiments showed that the TEC could be smaller or larger than the TEC of bulk material.^[21] The theoretical studies give ambiguous predictions too. Some models predicted that TEC increases with decreasing crystallite size,^[22,23] but some other models showed the opposite result.^[24]

In this Letter, the TEC of an ideal crystal will be derived by using a method of Boltzmann statistics. By taking the surface relaxation and the surface en-

ergy into consideration, the dimensionless TEC of a nanofilm is obtained, and the dependence of the TEC on the size, temperature, and surface is analyzed.

The thermal expansion of a crystal is caused by the nonharmonic oscillation of the atoms according to the theory of classical solid state physics. It is assumed that the interatomic potential of an ideal crystal is $u(r)$, where r is the interatomic distance. If r_0 is the equilibrium interatomic distance, the average displacement $\langle r - r_0 \rangle$ can be derived using a method of Boltzmann statistics^[25]

$$\langle r - r_0 \rangle = \frac{\int r e^{-u(r)/k_B T} dr}{\int e^{-u(r)/k_B T} dr}, \quad (1)$$

where k_B and T are Boltzmann's constant and temperature, respectively. Thus the linear TEC of a crystal should be

$$\Omega = \frac{d\langle r - r_0 \rangle}{r_0 dT}. \quad (2)$$

The interatomic potential $u(r)$ can be expanded as Taylor series at equilibrium position

$$u(r) = u(r_0) + e(r - r_0) + f(r - r_0)^2 - g(r - r_0)^3 + h(r - r_0)^4 + \dots, \quad (3)$$

where

$$e = u'(r_0) = 0, \quad f = (1/2!)u''(r_0), \\ g = -(1/3!)u'''(r_0), \quad h = -(1/4!)u^{(4)}(r_0).$$

If the Taylor series is truncated at the fourth term, and we substitute it into Eqs. (1) and (2), then the TEC of the crystal is

$$\Omega_T = \frac{12f^2 g k_B}{r_0 (4f^2 - 3h k_B T)^2}, \quad (4)$$

where k_B is Boltzmann's constant. For a bulk crystal material, the parameters r_0 , f , g and h are invariable,

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so the TEC of a bulk crystal material only depends on the temperature, which has been proved by some experiments.^[26–28] However for a nanocrystal, due to the influence of surface effects, the TEC also depends on the characteristic dimension of the structure, as shown in the following.

The interatomic potential for an ideal crystal can generally be described by the Morse potential energy function^[29–31]

$$u(r) = \varepsilon [e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}], \quad (5)$$

where ε is the magnitude of the minimum well depth, and the parameter α controls the shape of the potential energy curve. Thus the coefficients in Eq. (3) are $f = \alpha^2\varepsilon$, $g = \alpha^3\varepsilon$ and $h = \frac{7}{12}\alpha^4\varepsilon$, respectively. Substituting them into Eq. (4), we have

$$\Omega_T = \frac{192\varepsilon k_B}{r_0\alpha(16\varepsilon - 7k_B T)^2}, \quad (6)$$

which is obviously temperature-dependent.

In what follows, we will prove that the TEC of a nanofilm is also size- and surface-dependent. For simplification of the model, we neglect the influence of temperature, and truncate the Taylor series (Eq. (3)) at the third term. Then the thermal expansion coefficient of a crystal can be simplified to

$$\Omega = \frac{3k_B}{4r_0\alpha\varepsilon}. \quad (7)$$

In the equation, k_B and α are constants, so the value of the TEC is dependent only on ε and r_0 . Although ε and r_0 are constants for an ideal bulk crystal, they are surface-dependent for a nanostructural crystal due to the influence of the surface effects. When the surface effects are taken into consideration, we can redefine the equilibrium interatomic distance and the well depth as r_0^f and ε^f , respectively. Assume that the TEC of a nanofilm still has the form of Eq. (7). The dimensionless TEC of the nanofilm can be written as

$$\Omega^* = \frac{\Omega^f}{\Omega} = \left(\frac{r_0}{r_0^f}\right)^3 \left(\frac{\varepsilon}{\varepsilon^f}\right). \quad (8)$$

When the relaxation and the surface energy are taken into account in the model, the surface-dependent expressions of r_0^f and ε^f may be derived. Firstly, the relaxation coefficient k is introduced. On the free surface of the nanofilm, several layers of atoms will relax due to the imperfection of the coordination numbers (CNs). As a result, the equilibrium interatomic distance may be changed. The relaxation coefficient k is a parameter scaling the variation, which is the ratio of the relaxed interatomic distance and the unrelaxed interatomic distance, i.e., $r = kr_0$. It is straightforward to understand that $k < 1$ means that the interatomic distance is in contraction, while $k > 1$ means that it

is in expansion. We define an average value of the interatomic distance r_0^f of the nanofilm at which surface relaxation occurs, i.e.,

$$r_0^f = \frac{(N + 2nk)r_0}{N + 2n}, \quad (9)$$

where N is the number of unrelaxed atomic layers, and n the number of relaxed atomic layers. Thus the dimensionless form of the distance can be written as

$$\delta = \frac{r_0}{r_0^f} = \frac{N + 2n}{N + 2nk}. \quad (10)$$

The atomic number of an ideal crystal with the volume V is assumed to be N_0 , and then the cohesion energy of the crystal is in the form

$$U(r) = \frac{1}{2}N_0n_c|u(r)|, \quad (11)$$

where n_c is the atomic coordination number, and the volume V can be calculated by $V = N_0r^3$. Thus the cohesion energy of the crystal in its equilibrium state can be written as^[14]

$$U = \frac{1}{2}N_0n_c\varepsilon. \quad (12)$$

The cohesion energy of a nanofilm in its equilibrium state has the form^[14]

$$\begin{aligned} U_f &= \frac{1}{2}[(n_c - m)\eta + n_c(1 - \eta)]N_0\varepsilon^f \\ &= \frac{1}{2}N_0(n_c - m\eta)\varepsilon^f, \end{aligned} \quad (13)$$

where the parameter m denotes the decrease of the atomic coordination number on the free surface of the nanofilm, and η denotes the ratio of surface atom numbers and total atom numbers, which can be expressed as

$$\eta = \frac{2n}{N + 2n}. \quad (14)$$

If we split an ideal crystal into a nanofilm with two free surfaces, there is the following potential energy relationship, $U - U_f = \gamma A$. Thus we have

$$\frac{\varepsilon}{\varepsilon^f} = \frac{n_c - m\eta}{n_c} \cdot \left(1 - \frac{2\eta}{n_c} \cdot \frac{r_0^2\gamma}{\varepsilon}\right)^{-1}, \quad (15)$$

where γ is the surface energy, and the area A can be calculated by $A = N_0\eta r_0^2$.

Substituting Eqs. (10) and (15) into Eq. (8), we can derive the dimensionless TEC of the nanofilm,

$$\Omega^* = \frac{\delta\xi}{1 - \beta}, \quad (16)$$

where $\xi = \frac{n_c - m\eta}{n_c}$ and $\beta = \frac{2\eta}{n_c} \frac{r_0^2\gamma}{\varepsilon}$. It can be proved that Ω^* is size- and surface-dependent.

As an example, the TEC of an aluminum (Al) crystal will be discussed in the following. The values of the parameters in the calculation are listed as follows:

$k_B = 1.38054 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$, $\varepsilon = 4.3264 \times 10^{-20} \text{ J}$,^[31]
 $\alpha = 1.0341 \times 10^{10} \text{ m}^{-1}$,^[32] $r_0 = 3.4068 \times 10^{-10} \text{ m}$,^[32]
 $\gamma = 0.96 \text{ N}\cdot\text{m}^{-1}$,^[33] $n_c = 12$, $n = 2$, $m = 6$.

According to Eq. (6), the variation of the TEC with the temperature can be obtained as illustrated in Fig. 1. It can be found from the figure that the TEC of an ideal crystal decreases with decreasing temperature, consistent with the experimental results.^[26–28]

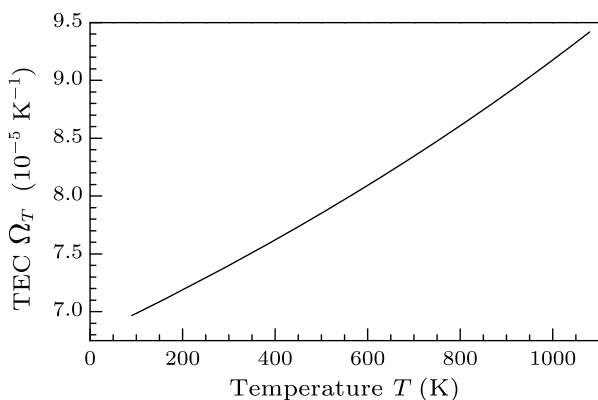


Fig. 1. TEC versus temperature.

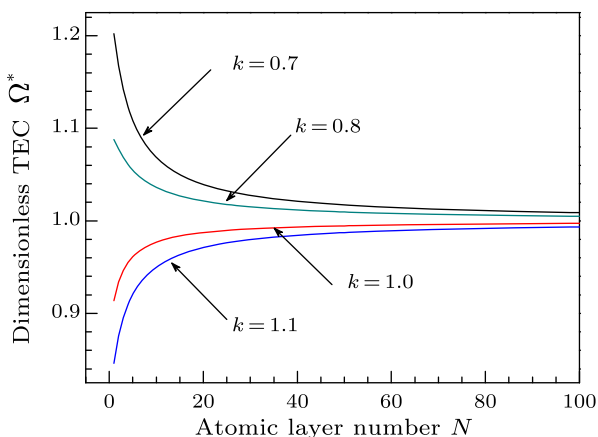


Fig. 2. Dimensionless TEC with the decrease of the atomic layer number for different values of the surface relaxation coefficient k .

The variations of the dimensionless TEC of an Al nanofilm with decreasing atomic layer number are illustrated in Fig. 2. It is seen that the TEC of the Al nanofilm is size- and surface-dependent. It can increase or decrease with decreasing thickness of the nanofilm, depending on the surface relaxation. With a decrease of the film thickness, when the relaxation is in contraction, the TEC increases, but it decreases when the relaxation is in expansion. The present theoretical prediction gives in fact a reasonable explanation for the ambiguous results in the literature. When the number of atomic layers is relatively small (less than about 50 in this case), the thickness shows a significant effect on the TEC, which agrees with the experimental results qualitatively.^[21] Even for nanofilms with the same thickness, the value of the TEC may be dif-

ferent due to the difference of the surface relaxation coefficient k .

In summary, we have presented an analytic expression of the TEC using a method of Boltzmann statistics. The TEC is temperature-dependent, and it is also size-dependent for a nanostructure. When the Morse potential energy function is adopted to describe the interatomic potential, and the effects of the surface relaxation and the surface energy are taken into consideration, the TEC of a nanofilm is shown to be size-dependent and surface-dependent. It is shown that, with decreasing thickness, the TEC can increase or decrease, depending on the surface relaxation of the nanofilm.

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