Size dependence of thermal expansion of nanostructures

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A theory for the size dependence of the coefficient of thermal expansion (CTE) of nanostructures is developed. The theory predicts that the fractional change in the CTE from the bulk value scales inversely with the size of the nanostructure. An explicit relation for the intrinsic length scale that governs the size dependence is derived. The theory is tested against full-scale molecular dynamics simulations and excellent agreement is found. Further, it is shown that the CTE can rise or fall with size depending on the properties of the bounding surfaces of the nanostructure. The theory has the potential to be used as part of a predictive tool for the design of nanostructures.

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The effective design and use of nanoelectromechanical systems[1] (NEMS) requires the development of predictive capabilities for their properties. At macroscales, the effective device property can be thought of as arising from two distinct contributions: first, the *geometry* of the device, and second, the *property of the material* that makes up the device. For example, the resistance R of a device is $\rho\ell/A$, where ℓ, A are the geometric attributes of the device, and ρ is the resistivity of the material. There is overwhelming evidence that this simple continuum approach cannot be applied without modification at small scales. Carbon nanotubes, for instance, can be insulating or metallic depending on their radius and chirality,[2] and show strongly size-dependent elastic properties.[3] Apparently, at nanoscales, "material property" and "device geometry" cannot be separated. This is owing to the fact that one or more of its geometric dimensions is small enough for the response (usually in the longer, macro direction) to be influenced by the discrete atomistic nature of the device—both atomistic and continuum scales are important in nanostructures. An accurate predictive theory would, therefore, seem to require an explicit and expensive—sometimes even prohibitive—treatment of the discrete atomistic nature of nanosystems. Hence the development of simple theoretical models for the size dependence of properties of nanostructures remains a fertile area of research. Theoretical approaches may be broadly classified into two types:[4] (i) multiscale approaches and (ii) augmented continuum theories. Multiscale approaches[5] treat both discrete and continuum physics in the same model, and require simulations albeit of much smaller size than full-scale atomistic simulations. Augmented continuum theories,[6,7] although less general, have the advantage of simple physical insight and provide explicit expressions for size dependence of properties.

In this Brief Report, an augmented continuum theory is developed for the size dependence of coefficient of thermal expansion (CTE) of nanostructures. Starting with the idea that "nanostructure=bulk+surface,"[6,7] it is shown that the fractional change in thermal expansion coefficient (compared to the bulk), varies inversely as the size of the nanostructure. The theory is compared with full-scale molecular dynamics simulations (which serve as numerical experiments); excellent agreement is found.

The development that follows is based on theory of lattice dynamics of crystals.[8] The nanostructure considered has a slab geometry or bar geometry; in the case of a slab (bar), the thickness (cross-sectional dimensions) is (are) nanosized. The nanostructure is taken to have a crystalline arrangement of atoms (as is often the case in experiments[1,9]), allowing for a description in terms of a supercell. The supercell consists of N atoms whose equilibrium positions at zero temperature are given by $\boldsymbol{R}_i$ $(i=1,\ldots,N)$. The nanostructure is obtained by periodically repeating the supercell with periodicity vector $\boldsymbol{L}=(L_1,L_2)$ ($\boldsymbol{L}=L_1$ in the case of a nanobar). The total energy (of the supercell) of this atomistic system is described by a given energy function $\mathcal{U}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$ (several different total energy formulations of various levels of sophistication are possible[4]), where $\boldsymbol{r}_i$ are the—possibly displaced—positions of the atoms. Clearly, $\boldsymbol{R}_i$ are the positions of atoms that minimize $\mathcal{U}$.

On increase of temperature, the thermal average positions of atoms changes to $\boldsymbol{r}_i=\boldsymbol{F}\boldsymbol{R}_i+\boldsymbol{u}_i$, where $\boldsymbol{F}$ is the homogeneous deformation due to thermal expansion, and $\boldsymbol{u}_i$ are rearrangements of atoms (which is significant only at surfaces and edges). The deformation $\boldsymbol{F}$ and the rearrangements $\boldsymbol{u}_i$ are obtained by minimizing the Helmholtz (classical) free energy

$$\mathcal{A}(T,\boldsymbol{u}_1,\ldots,\boldsymbol{u}_N;\boldsymbol{F}) = \mathcal{U}(\boldsymbol{u}_1,\ldots,\boldsymbol{u}_N;\boldsymbol{F}) + k_BT\sum_{\boldsymbol{q},\mu}\ln\left(\frac{\hbar\omega(\boldsymbol{q},\mu)}{k_BT}\right) \quad (1)$$

(k_B is the Boltzmann constant and T is the temperature). The quantities $\omega(\boldsymbol{q},\mu)$ are the frequencies of phonon modes labeled by wave vector $\boldsymbol{q}$ (in the Brillouin zone defined by the supercell repeat vector $\boldsymbol{L}$) and mode index μ. This formulation has been used extensively to study surface phonons[10,11] and surface thermal rearrangements.[12–14]

While Eq. (1) contains the detailed physics of thermal expansion, an approximate free energy suggested by LeSar *et al.*[15] is more useful to construct a theory for size dependence of thermal expansion. In this local harmonic approximation,[15] the free energy is written as

$$\mathcal{A}_{LH} = \mathcal{U}(\boldsymbol{u}_1, \ldots, \boldsymbol{u}_N; \boldsymbol{F}) + k_B T \sum_i \sum_{\mu=1,3} \ln\left(\frac{\hbar\omega(i,\mu)}{k_B T}\right), \quad (2)$$

where $\omega(i,\mu)$ are the vibrational frequencies of the atom i obtained by fixing all other atoms. LeSar *et al.*[15] showed that this is a good approximation for temperature ranges up to 75% of the melting temperature. This model has been used to study interfaces such as grain boundaries;[16] it can therefore serve as a simple approximation for the treatment of the thermodynamics of surfaces. Further, if the energy function is based on a pair potential or embedded atom method[17] (as is assumed here), Eq. (2) has the advantage that an approximate free energy is defined for every atom.

Roughly, the nanostructure has two types of atoms; those influenced by the surface and those in the bulk. The free energies of all the "bulk atoms" are equal [in the sense of Eq. (2)], while those of the like surface atoms are also equal. This observation motivates a continuum approximation for the free energy, invoking the ansatz "nanostructure=bulk +surface," that allows for an explicit calculation of the size dependence of the CTE. The idea is illustrated for a nanoslab (simple cubic crystal structure) of thickness h consisting of N layers ($h=Na$, a is lattice parameter). The thickness of the slab is defined using the idea of the Gibbs' dividing surface;[18] this is the thickness that would give the correct mass of the slab when used in conjunction with the bulk value of the mass density. The (augmented continuum) free energy density $\mathcal{A}_{AC}$ (per unit area of the slab in terms of the bulk and surface free energy densities), as a function of the homogeneous strain ϵ is

$$\mathcal{A}_{AC} = h\underbrace{\left[\frac{1}{2}E\epsilon^2 + 3\frac{k_B T}{a^3}\ln\left(\frac{\hbar\omega_b}{k_B T}\right)\right]}_{\text{bulk}} + 2\underbrace{\left[\frac{1}{2}S\epsilon^2 + 3\frac{k_B T}{a^2}\ln\left(\frac{\hbar\omega_s}{k_B T}\right)\right]}_{\text{surface}} \quad (3)$$

where ω_b and ω_s are geometric average vibrational frequencies [in the sense of Eq. (2)] of bulk and surface atoms respectively, E is the bulk biaxial modulus, and S is the surface biaxial modulus.[19] All rearrangements of surface atoms are accounted in the surface modulus S.[19] The factor 2 in front of the surface term is to account for upper and lower surfaces of the slab. The thermal strain $\epsilon(T)$ is found by solving $\partial A_{AC}/\partial\epsilon = 0$. A straightforward calculation gives the CTE $\alpha(=\partial[\epsilon(T)]/\partial T)$ of the nanoslab as

$$\alpha = \left(\frac{2S\alpha_s + Eh\alpha_b}{2S + Eh}\right), \quad (4)$$

where $\alpha_s = -3k_B(1/Sa^2)(\partial \ln \omega_s/\partial\epsilon)$ is the surface CTE, and $\alpha_b = -3k_B(1/Ea^3)(\partial \ln \omega_b/\partial\epsilon)$ is the bulk CTE.

The size dependence of the CTE of the nanoslab is now readily obtained as

$$\frac{\alpha - \alpha_b}{\alpha_b} = 2\frac{S}{E}\frac{1}{h}\left(\frac{\alpha_s}{\alpha_b} - 1\right)\left(1 + 2\frac{S}{E}\frac{1}{h}\right)^{-1} \approx 2\frac{S}{E}\left(\frac{\alpha_s}{\alpha_b} - 1\right)\frac{1}{h}. \quad (5)$$

A similar calculation for a nanobar with a square cross section of side h (with crystallographically equivalent bounding surfaces) gives

$$\frac{\alpha - \alpha_b}{\alpha_b} \approx 4\frac{S}{E}\left(\frac{\alpha_s}{\alpha_b} - 1\right)\frac{1}{h}, \quad (6)$$

where S and E are uniaxial surface and bulk moduli respectively. The essential difference between the slab and the bar is the factor of 4 appearing in the case of the bar in place of 2. This is because there are four bounding surfaces for the bar, i.e., this factor depends on the geometrical attributes of the nanostructure.

Quite generally, the size dependence of the thermal expansion of a nanostructure is

$$\frac{\alpha - \alpha_b}{\alpha_b} \approx K\underbrace{\frac{S}{E}\left(\frac{\alpha_s}{\alpha_b} - 1\right)}_{h_0}\frac{1}{h}, \quad (7)$$

where K is a constant that depends on the geometry of the structure, S and E are the appropriate surface and bulk elastic moduli, and α_s and α_b are the surface and bulk thermal expansion coefficients. Thus the theory not only predicts that the fractional change in the CTE depends inversely on the size of the nanostructure, but also identifies the associated intrinsic length scale h_0.

The relation (7) is tested against full atomistic calculations. A simple Lennard-Jones (LJ) pair potential $V(r) = 4\varepsilon[(\sigma/r)^{18} - (\sigma/r)^6]$ is used to describe the energy function $\mathcal{U}$. The parameters chosen are $\varepsilon = 0.56$ eV, $\sigma = 2.615\,65$ Å, cutoff distance 3.923 47 Å, and atomic mass $m=27$ amu. The thermal expansion of fcc crystals (lattice parameter $a = 4.032$ Å) slabs, and bars is determined by constant-pressure molecular dynamics (MD) simulations that provide equilibrium cell lengths as a function of temperature. Thermal expansion is calculated from these data; this procedure is repeated for several different random initial seeds for velocities, and averages and deviations are calculated. To corroborate the theory further, the size dependence of the thermal expansion was also determined using the local harmonic (LH) free-energy formulation (2). The LH calculation consisted of minimizing the free energy in (2) to determine the equilibrium values of $\boldsymbol{F}$ and $\boldsymbol{u}_i$. The CTE is determined from the dependence of the equilibrium $\boldsymbol{F}$ on temperature.

The top panel of Fig. 1 shows the thickness (h) dependence of the CTE α obtained from MD simulations and LH calculations for fcc crystals slabs bounded by the (100) surface. The data are fitted to a function $\alpha(h) = \alpha_b + Kh_0/h$ (both α_b and Kh_0 are used as fitting parameters); it is evident that the predicted functional form in Eq. (7) is very closely followed by both MD and LH results, corroborating the theory. Though the values obtained of α_b and Kh_0 from the fit are different for MD and LH (owing to the approximations in the

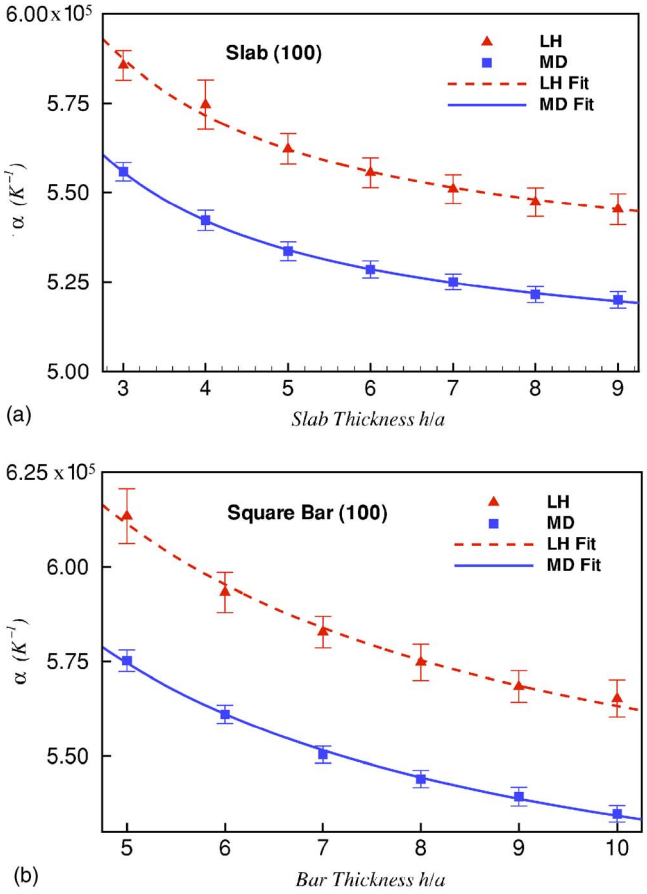

FIG. 1. (Color online) Size dependence of coefficient of thermal expansion α. Top: Results for LJ slabs bounded by (100) crystal planes of thickness h. Bottom: Results for LJ square (side h) bars bounded by (100) crystal planes. The lines indicated as "Fit" correspond to fits of simulation data to Eq. (7).

LH scheme), the functional form (7) is very closely followed in both cases, illustrating the robustness of (7). Similar results are shown for the case of a square bar (bottom panel of Fig. 1), where, again, the agreement with Eq. (7) is excellent.

Calculations were also performed with fcc crystal slabs bounded by (110) and (111) surfaces where, again, excellent fit to Eq. (7) is found (results not shown). Since the crystal is cubic, the bulk thermal expansion is isotropic. Thus the values of α_b obtained from fits in the three cases of (100), (110), and (111) slabs must be equal within error bars—the values fitted to MD data are, respectively, 4.93×10^{-5}, 5.02×10^{-5}, 5.00×10^{-5} (the bulk CTE value determined separately is 5.01×10^{-5}). Similar agreement is found for the LH data as well, further demonstrating the correctness of Eq. (7). Since α_s is not determined separately in this work, the close agreement of fit values of α_b with the bulk CTE values provides further corroboration of the correctness of Eq. (7).

In all the cases discussed thus far, the magnitude of the thermal expansion increased with decreasing size. This is *not* a general result. In fact, the rise or fall of the CTE with size is determined by the sign of $h_0=(S/E)(\alpha_s/\alpha_b-1)$. It is known that the surface elastic constant S can be of either sign.[19] Thus for a surface with $S<0$ and $\alpha_s>\alpha_b$, the CTE will fall with decreasing size. It is known[19] that the biaxial

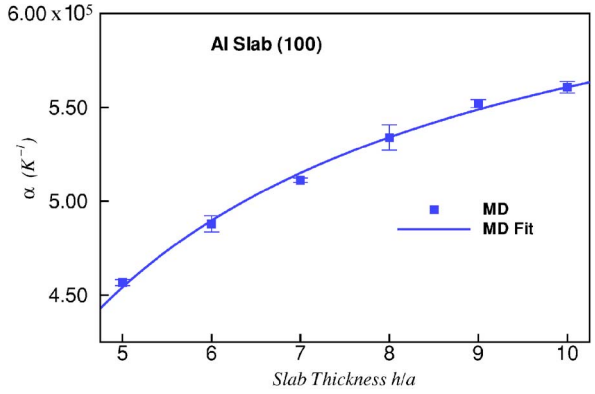

FIG. 2. (Color online) Variation of CTE with thickness of Al[20] slabs bounded by (100) crystal surface. This surface is known to have a negative biaxial modulus. The line indicated as "Fit" correspond to fits of simulation data to Eq. (7).

modulus (100) surface of fcc Al modeled with the embedded atom potentials of Ercolessi and Adams[20] is negative. Figure 2 shows the variation of CTE with the slab thickness for Al, where it is seen that the CTE falls with decreasing thickness. Again, the functional form of Eq. (7) is closely followed in this case (Al described by embedded atom potentials as opposed to Lennard-Jones pair potentials discussed before), clearly demonstrating the correctness of Eq. (7) in describing very different systems.

The relation (5) for the size dependence of the CTE was derived from a classical formulation for the free energy (3). The classical formulation was chosen to develop the theory so that theory can be tested against classical simulations. It is easily seen that the relation (5) also follows from a quantum version of the free energy

$$\mathcal{A}_{AC}^{Quantum} = h\underbrace{\left[\frac{1}{2}E\epsilon^2 - \frac{k_BT}{a^3}\sum_i f\left(\frac{\hbar\omega_{bi}}{k_BT}\right)\right]}_{\text{bulk}} + 2\underbrace{\left[\frac{1}{2}S\epsilon^2 - \frac{k_BT}{a^2}\sum_i f\left(\frac{\hbar\omega_{si}}{k_BT}\right)\right]}_{\text{surface}}, \tag{8}$$

where $f(\xi)=e^{\xi/2}/(e^{\xi}-1)$, and the index i runs over the three modes (in the LH sense) of bulk and surface atoms. The thermal expansion of the nanostructure is given by Eq. (5), with $\alpha_s=-(1/Sa^2k_BT^2)\Sigma_i f''(\hbar\omega_{si}/k_BT)\hbar\omega_{si}\partial\omega_{si}/\partial\epsilon$ and $\alpha_b=-(1/Ea^3k_BT^2)\Sigma_i f''(\hbar\omega_{bi}/k_BT)\hbar\omega_{bi}\partial\omega_{bi}/\partial\epsilon$. Thus, in the temperature regime $k_BT\leqslant\hbar\omega$ (ω is a typical mode frequency), quantum effects manifest strongly, and both α_s and α_b can depend strongly (exponentially) on temperature. Consequently the length scale h_0 defined in Eq. (7) can also depend strongly on temperature. This is in contrast to the high-temperature limit where h_0 will be, comparatively, a weak function of temperature. The important point to be noted is that the dependence of the CTE at a fixed temperature on the size of the nanostructure does not depend

on the type of formulation (classical or quantum). In particular, the theory is therefore expected to be applicable to room-temperature nanostructures made of metals (low Debye frequency, classical limit), and to covalent (e.g., carbon) nanostructures (high Debye frequency, quantum effects included).

In addition to providing basic physical insight into the size dependence of the CTE, the theory developed here has the strong potential to be a predictive tool for the design of nanostructures. To this end, the bulk properties (E, α_b), and surface properties (S, α_s) of various crystal faces are to be calculated from—preferably first principles—atomistic calculations. A fertile research direction is the calculation of the surface CTE for various crystal faces for materials used in NEMS applications along lines similar to the calculation of surface elastic properties.[19]

In summary, a theory for the size dependence of the CTE in nanostructures is developed and tested with full-scale atomistic simulations. It is predicted that the fractional change in the CTE from the bulk value scales inversely with the size of the nanostructure. The intrinsic length scale that the governs the size dependence is identified. It is shown that the CTE can rise or fall depending on the properties of the bounding surfaces of the nanostructure.

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[1] M. L. Roukes, in *Technical Digest of the 2000 Solid State Sensor and Actuator Workshop* (Transducers Research Foundation, Cleveland, OH, 2000).
[2] R. Saito, G. Dresselhaus, and M. Dresselhaus, *Physical Properties of Carbon Nanotubes* (World Scientific, Singapore, 1998).
[3] R. Gao, Z. L. Wang, Z. Bai, W. A. de Heer, L. Dai, and M. Gao, Phys. Rev. Lett. **85**, 622 (2000).
[4] V. B. Shenoy, *Nanomechanics* (SPIE Press, Bellingham, WA, 2004), Chap. 7, pp. 255–318.
[5] R. Phillips, *Crystals, Defects and Microstructures—Modeling Across Scales* (Cambridge University Press, Cambridge, UK, 2001).
[6] R. E. Miller and V. B. Shenoy, Nanotechnology **11**, 139 (2000).
[7] V. B. Shenoy, Int. J. Solids Struct. **39**, 4039 (2002).
[8] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).
[9] J. Yang, T. Ono, and M. Esashi, J. Vac. Sci. Technol. B **19**, 551 (2001).
[10] R. F. Wallis, *Effects of Surfaces in Lattice Dynamics* (North-Holland, Amsterdam, 1975), Chap. 7, pp. 491–495.
[11] R. F. Wallis, Surf. Sci. **299/300**, 612 (1994).
[12] L. Dobrzynski and A. A. Mardaudin, Phys. Rev. B **7**, 1207 (1973).
[13] R. E. Allen, J. Vac. Sci. Technol. **9**, 934 (1972).
[14] A. N. Al-Rawi, A. Kara, P. Staikov, C. Ghosh, and T. S. Rahman, Phys. Rev. Lett. **86**, 2074 (2001).
[15] R. LeSar, R. Najafabadi, and D. J. Srolovitz, Phys. Rev. Lett. **63**, 624 (1989).
[16] R. Najafabadi, D. J. Srolovitz, and R. LeSar, J. Mater. Res. **5**, 2663 (1990).
[17] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[18] P. Nozières and D. E. Wolf, Z. Phys. B: Condens. Matter **70**, 399 (1987).
[19] V. B. Shenoy, Phys. Rev. B **71**, 094104 (2005).
[20] F. Ercolessi and J. Adams, Europhys. Lett. **26**, 583 (1993).