Size, temperature, and bond nature dependence of elasticity and its derivatives on extensibility, Debye temperature, and heat capacity of nanostructures

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With the miniaturization of a solid down to nanometer scale, the elasticity, extensibility, Debye temperature, and specific heat capacity of the solid are no longer constant but change with variation of size. These quantities also change with the temperature of the measurement and the nature of the chemical bond involved. The mechanism behind the intriguing tunability and the interdependence of these quantities remain yet a high challenge. A set of analytical solutions is presented herewith showing that the observed trends could be reproduced by taking the fact of bond order deficiency into consideration. Agreement between predictions and observations clarifies that the shortened and strengthened surface bonds dictate intrinsically the observed tunability, yet atoms in the core interior remain as they are in the bulk. The thermally softening of a specimen arises from bond expansion and bond vibration due to the internal energy increases.

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I. INTRODUCTION

Young’s modulus (Y) is one of the key elemental parameters in materials science, which is related to the performance of a material such as the elasticity, extensibility, acoustic transmission velocity, Debye temperature, specific heat capacity, and thermal conductivity of the specimen. Traditionally, the Young’s modulus in a bulk material is deemed as constant at a given temperature and the value of the modulus is proportional to the melting point (T_m) of the bulk. However, upon structural miniaturization to the nanometer regime, the Young’s modulus is no longer constant but changes with the shape and size of the solid. Measurements have revealed surprisingly that the Y value changes in three different ways: elevation, depression, or retention as the solid size is reduced. For inorganic nanomaterials with higher T_m, the modulus is often measured to increase at the ambient temperature when the solid size is decreased, such as observed from Si nanospheres,2 Ag nanowires,3 quartz crystal oscillators,4 Si3N4 nanobelts,5 TiCrN and TiAlN surfaces,6 Al and Si nanobelts,7 ZnO nanowires,8 and nanobelts.9 However, an opposite trend is presented in (0001)-oriented ZnO nanobelts and wires showing lower modulus varying from 29±8 (Ref. 10) to 38–100 GPa (Refs. 11 and 12) compared with that of the bulk ZnO obtained at 140 GPa. An atomic force microscopic measurement13 has revealed that the modulus of nanocrystallined Ni films of 50–800 nm thick is lower than the bulk value. An atomic force microscopic measurement14 has revealed that the local Young’s modulus of organic thin films that can evaporate at ~450 K decreases with sizes. The moduli of Cr (Ref. 15) and Sr (Ref. 16) nanocantilevers and ZnS (Ref. 17) nanobelts are also measured to decrease sharply with decreasing diameters. In contrast, amorphous Si nanowires,18 Au (Ref. 19) and Ag (Ref. 20) nanowires show no apparent change with size despite the scattered error bars in the measurement. Therefore, it appears quite confusing that even for the same materials such as Ni, Ag, ZnO, and Si, the Y value changes in different ways, depending on the experimental techniques and operation conditions.

On the other hand, the modulus or strength, being correlated linearly, of a solid generally drops associated with enhancement of extensibility when the testing temperatures are raised,21 such as the cases of nanograined Al (Ref. 22) and diamond films.23 At higher temperatures the bending stiffness and the apparent Young’s modulus of the diamond beams are drastically reduced to one-third of the initial value before fracture. The flexural strength and modulus of hydroxylation and condensation reaction curable silicone resins also decrease when the testing temperatures are raised.24

The elastic response of nanostructures has been theoretically attributed to nonlinear effects,25 surface reconstruction,26 surface stress,27,28 and surface strain.6,8,29 However, an atomistic understanding of the size, temperature, and bond nature dependence of the modulus of a solid and its derivatives on the extensibility, Debye temperature, and heat capacity is yet lacking though a recent molecular dynamics simulation30 suggests that surface atoms play an important yet unclear role in the mechanical behaviors of nanostructures. An analytical expression for the size, temperature, and bond nature dependence of the intrinsic mechanical properties of nanomaterials is therefore highly desirable. Here we show that an extension of the recently developed bond-order-length-strength (BOLS) correlation mechanism31–33 to temperature domain could reproduce the observed trends and hence clarify for the first time the long-standing discrepancy in observations.

II. PRINCIPLES

A. Broken bond and BOLS correlation

The core idea of the BOLS correlation31,32 is that broken bonds of surface atoms make the remaining bonds (with
length $d_i$ and bond energy $E_i$ between the undercoordinated atoms shorter, $d_i = e_i d$, and stronger, $E_i = c_i E_b$, with respect to the bulk counterparts, where $c_i(z_i) = 2[1 + \exp(12 - z_i)/((8z_i))]^{-1}$ is the coefficient of bond contraction with $z_i$ being the effective coordination of the specific layer of concern (where $i = 1$ for outermost layer). The superscript $m$ is a bond nature indicator. The binding energy per atom and bond energy $E_b$ of a specific atom, in particular. The competition between the atomic co-
ervation, we may define a cutoff temperature at which the temperature-dependent thermal expansion coefficient $Y(\Delta T) = 0$ and the modulus disappears when a solid is at melting. Measurements also revealed that the tensile strength of alloys drops from the bulk values to approximately zero when the temperature approaches $T_m$. If Born’s criterion holds in effect, the latent heat of atomization makes no contribution to the mechanical strength. However, an elastic modulus should present in liquid and gas phases as the nonzero sound velocity in these phases. Therefore, Born’s criterion may be taken as a crude approximation in modeling consideration. For modeling convenience, we may define a cutoff temperature at which the mechanical strength approaches zero. Precisely, the $Y$ and $P$ are the derivatives of interatomic potential $u(r, m, T)$. However, there exists uncertainty in choosing the exact form of the $u(r, m, T)$ and what we are concerned with is the relative change of $Y$ and $P$ to the bulk values. On the other hand, from the analysis of dimension, the $P$ and $Y$ are both proportional to the energy per unit volume. Therefore, it is reasonable to take the above approximation in the analytical modeling. It is unnecessary and impractical to consider the differentiations at a point of distance away from the equilibrium atomic distance. An exact solution may be obtained in the first-principles calculations but the outcome will also be subject to the $u(r, m, T)$ selected.

An analytical solution for thermal depression of the Young’s modulus has long been a challenge in particular in terms of atomic bonding. Wachtman et al. proposed an empirical expression for $T$-dependent Young’s modulus and later Anderson proposed an expression for the $T$ dependence from the perspective of anharmonic lattice vibration, which are compared with the current proposal for large chunks ($c_i = 1$) as follows:

$$E_i(z_i, T) = E_b c_i^{-m} - \int_0^T \eta_i(t) dt \equiv c_i^{-m} E_b - \eta_i T = \eta_{2i} + \eta_i(T_m - T),$$

with $\alpha_i(t)$ being the temperature-dependent thermal expansion coefficient. $T_m$ is the local melting point. The $\eta_i$ remains constant at temperatures that are higher than the Debye temperature. Therefore, Eq. (1) can be expressed as

$$P_i(z_i, m, T) \left\{ \begin{align*}
\frac{f^{\text{Dr}}_{T} \eta_i(t) dt}{d_i (1 + \alpha_i T)^3} &= \frac{\eta_i(T_m - T)}{d_i (1 + \alpha_i T)^3} \\
\frac{\eta_{2i} + \frac{f^{\text{Dr}}_{T} \eta_i(t) dt}{d_i (1 + \alpha_i T)^3}}{d_i (1 + \alpha_i T)^3} &= \frac{\eta_{2i} + \eta_i(T_m - T)}{d_i (1 + \alpha_i T)^3} \quad \text{(BOLS)}.
\end{align*} \right.$$
where $A$, $B$, and $T_0$ are adjustable. $\eta(t)$ is the Debye specific heat, and

$$U(T) = TF(T/\theta_D) = 3\theta_D\left(\frac{T}{\theta_D}\right)^4 \int_0^{\theta_D/T} x^3 \frac{dx}{e^x - 1}$$

is the internal energy, being the integration of $\eta(t)$.

### 2. Size dependence

Considering the fact that the $T_m$ is proportional to atomic cohesive energy, $T_m \propto z_i^+ \Delta_i$, and the relation $T_m/T = 1 + \Delta_i$ with $\Delta_i$ being the perturbation to the atomic coherency. $z_i \Delta_i$ is the normalized atomic coordination with $z_i = 12$ being the standard value in a fully coordinated system. With the relation of $E_i = c_i^+ E_i = \eta_i T_i + \eta_2i$ and $T_m = z_i c_i^+ T_i = (1 + \Delta_i) T_i$, we have $\eta_i = \zeta_i \eta_1$ and $\eta_2 = c_i^+ \eta_2$. The relative change of the local $Y$ and its inverse, or the extensibility $\beta$, of a solid measured at $T \gg \theta_D$ can be simplified,

$$\delta_Y(m, z_i, T) = \frac{Y(m, z_i, T)}{Y(m, z_i, T_0)} - 1$$

$$= c_i^{-3+m+\eta_1(T_m - T)} + \eta_2i \eta_1(T_m - T_0) + \eta_2$$

$$= c_i^{-(3+m)}\left(\frac{T_m - T}{T_m - T_0 + \eta_2i}\right)$$

$$= c_i^{-(3+m)}\left(1 + \frac{T_0 - T}{T_m - T_0 + \eta_2i}\right) - 1,$$

$$\delta_\beta(m, z_i, T) = \frac{\beta(m, z_i, T)}{\beta(m, z_i, T_0)} - 1$$

$$= c_i^{-(3+m)}\frac{T_m - T_0 + \eta_2i}{T_m - T(1 + \Delta_i) + \eta_2i} - 1$$

$$= c_i^{-(3+m)}\left(1 - \frac{T_0 - T}{T_m - T(1 + \Delta_i) + \eta_2i}\right) - 1.$$

Taking the core-shell configuration of a nanosolid into consideration, the bond nature ($m$), shape and size ($\tau, K_f$), and temperature ($T$) dependence of the relative change of the $Y$ can be obtained by summing contribution over the outermost three atomic layers:

$$\Delta Y(m, K_f, T) = \sum_i \gamma_i \delta_i(m, z_i, T)$$

The same approach applies to the extensibility. The $\gamma_i$ is the volume or number ratio between the $i$th surface atomic layer of thickness $d_i$ and the entire nanostructure of size $K_f$, with $K_f$ being the dimensionless form of size is the number of atoms lined along the radius of a spherical dot or cross the thickness of a thin slab. Equation (3) represents that the undercoordinated atoms in the surface skin dictates the relative change of mechanical properties, yet atoms in the interior remain their bulk features. Compared with the analytical expression for the inverse Hall-Petch relationship, the current form in Eq. (3) represents the intrinsic change of modulus or strength excluding the effect of dislocation accumulation and the artifacts due to indentation tip shapes, strain rates, loading scales, etc., involved in the indentation test.

### C. Debye temperature

The Debye temperature, which is defined as $\theta_D = h \omega_D/k_B$ in the Debye model of the specific heat, is a key parameter that determines the thermal transport dynamics properties. When the solid size is reduced or the temperature of measurements is varied, $\theta_D$ is no longer constant but change depending on the object size and testing temperature. Calculation results suggested that the size dependence of $\theta_D$ results from the finite cutoff of frequency and surface stresses (effectively form a size-dependent change of surface pressure), especially if the size is smaller than 20 nm. Using x-ray-absorption spectra measurements and extended x-ray-absorption fine-structure spectroscopy, Balerna and Mobilo confirmed the predicted trend. The temperature-dependent $\theta_D$ was another interesting observation. Calculations of the temperature-dependent $\theta_D$ of some fcc and bcc metals revealed that the $\theta_D$ decreases when the temperature was increased due to the temperature dependence of elastic constants and sound velocity of the solid. However, a discrepancy remains regarding the $T_m$ dependence of the $T$-independent $\theta_D$. One opinion is that the $\theta_D$ varies linearly with the $T_m$ (Ref. 49), and the other suggests a square-root dependence on $T_m$ according to Lindemann’s criterion of melting.

The Debye temperature $\theta_D$ can be derived from the mathematical expression for the normalization of phonon density states: $\int_0^{\omega_D} g(\omega) d\omega = \kappa N_A$, with $N_A$ being the total number of vibration modes, giving rise to the relation $\omega_D \propto v_s(n)^{1/\kappa} \propto v_s(d^{-\kappa})^{1/\kappa} = v_s/d$, where $v_s = \sqrt{T\rho} \sim \sqrt{T\beta}$ is the sound velocity in the medium and $\kappa$ is the fractal dimensions ($\kappa = 1$).
for nanowires, $\kappa=2$ for thin plates, and $\kappa=3$ for bulk material). Because the Debye temperature is defined as $\theta_D = \hbar \omega_D/k_B$, the normalized expression for $\theta_D$ has the following form:

$$\frac{\theta_D(z_n,m,T)}{\theta_D(z_n,m,T_0)} = \frac{\omega_D(z_n,m,T)}{\omega_D(z_n,m,T_0)} = \frac{\nu(z_n,m,T)}{\nu(z_n,m,T_0)} \cdot \frac{d_0}{d_i} = \left( \frac{Y(z_n,m,T)}{Y(z_n,m,T_0)} \right)^{1/2}.$$  

(4)

Combining Eqs (1) and (4) leads to immediate relation

$$\frac{\Delta \theta_D(K,m,T)}{\theta_D(\infty,m,T_0)} = \sum_{i=3}^{\infty} \frac{\zeta_i}{K_i} \left[ a_i \frac{T_m - T(1 + \Delta_i)}{T_m - T_0 + \eta_{21}} \right]^{1/2} - 1 \right)^{1/2}.$$  

(5)

Therefore, the current form [Eq. (5)] has a square-root dependence on $(T_m - T)^{1/2}$ for the bulk ($\Delta_i=0$, $c_i=1$, if the surface effect is ignored), being different from the linear square-root dependence on $T_m$: $\theta_D \propto T_m^{1/2}/d$ (Ref. 53).

D. Specific heat capacity

The specific heat capacity is a measurable physical quantity that characterizes the ability of a body to store the heat when the sample temperature is changed. The effect of body size on the specific heat capacity has recently attracted a lot of attention.\textsuperscript{54-57} Novotny et al.\textsuperscript{54} measured the low-temperature heat capacity of 2.2- and 3.7-nm-sized lead particles and observed the enhancement of heat capacity below 5 K. Lu\textsuperscript{58} demonstrated that the specific heat of metallic or alloying nanosolids increases with the inverse of solid size. An ac microcalorimeter measurement\textsuperscript{55} showed that the specific heat of Al thin films with film thickness varying from 13.5 to 370 nm reduces with the thickness of the Al film. The decrease of specific heat was explained by the rise of the absorption and the loss of thermal waves with specific wave vectors in the small volumes. However, Lu et al.\textsuperscript{56} calculated the size effects on the specific heat of Al thin film employing the Prasher-Phelan\textsuperscript{59} approach and derived that the reduction of phonon states was not the main reason causing the size effect on specific heat, but a thin layer of Al oxide was responsible for it. In the measurement of Yu et al.\textsuperscript{57} the heat capacity decreased with the film thickness; however, the specific heat increased as the film become thinner, in disagreement with the measured results of Song et al.\textsuperscript{55} Therefore, the discrepancies in the role of the size and temperature dependence of the heat capacity and Debye temperature for metallic nanostructures remain unsolved.

The heat capacity per unit volume is defined as the ratio of an infinitely small amount of heat $\delta E$ added to the body to the corresponding small increase in its temperature $\delta T$ when the volume is kept unchanged. In the extended Debye model the expression is given by

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = k^2 R \int_0^{\theta_D/T} \frac{x^{\kappa+1} \exp(x) [\exp(x) - 1]^{-1}}{x^{\kappa} \exp(x)} dx,$$  

(6)

where $x = \hbar \omega_D/k_BT$. It can be shown that when $\kappa=3$, Eq. (6) is reduced to the standard expression in the three-dimensional Debye model. In the case of $T \gg \theta_D$, the integration in Eq. (6) gives $(1/\kappa)(\theta_D/T)^{\kappa}$. The heat capacity $C_v$ is substituted by $\kappa R$, in agreement with the Dulong-Petit law in the case of $\kappa=3$. $C_v$ approaches a constant value at high temperatures. The low-temperature limit of the heat capacity is even more interesting. If $T \ll \theta_D$, the upper limit of the integral of Eq. (6) approaches infinity and the integration gives $\int_0^{\infty} x^{\kappa+1} \delta^2 dx \approx 3.290, 7.212$, and 25.976, for $\kappa=1, 2$, and 3. Therefore, the heat capacity in the low-temperature limit becomes

$$C_v = A \kappa^2 \left( \frac{T}{\theta_D} \right)^{\kappa} \propto \kappa^2 \theta_D^{\kappa},$$  

(7)

where $A$ is a fixed value for a given $\tau$. From Eqs. (6) and (7), we can see that the Debye temperature $\theta_D$ has a strong effect on the heat capacity. Using the same core-shell structure, we can obtain the expression for heat capacity per unit volume depending on the size, shape, and bond nature at very low temperatures ($T \rightarrow 0$):

$$\frac{\Delta C_v(m, T, K)}{C_v(m, T_0, \infty)} = \sum_{i=3}^{\infty} \frac{\zeta_i}{K_i} \left[ a_i \frac{T_m - T(1 + \Delta_i)}{T_m - T_0 + \eta_{21}} \right]^{1/2} - 1 \right)^{1/2}.$$  

(8)

Since the coefficient of bond contraction $c_i$ is always smaller than unity, the heat capacity is always lower than the bulk value at the lower temperatures and the heat capacity decreases inversely with the solid size ($K_i$). At temperature close to the Debye temperature, the heat capacity should be evaluated using Eq. (6), where the Debye temperature is size, temperature, and bond nature dependent according to Eq. (5).

III. RESULTS AND DISCUSSION

Using Eq. (3), we are able to predict the bond nature, solid shape and size, and the $x_m(T/T_m)$ dependence of the Young’s modulus and extensibility of a solid. For illustration purposes, we selected $m=1$ (for metals), 3 (carbon, 2.56), and 5 (Si, 4.88), $x_m=0.25, 0.5, 0.75$, and the dimensionality $\tau=3$ (for a sphere) to conduct the calculations. The $T_0$ was set at 0 K and $T$, respectively. For temperature dependence, we used $K_j=10$ and 50 sizes by fixing other parameters. $\eta_{21}$ was taken as zero for illustration purposes; otherwise, a small offset could hardly be identified in the predicted relative changes.

Figure 1(a) shows that elevation or depression of the Young’s modulus with decreasing sizes may happen depend-
The size, temperature, and bond nature dependence of Young’s modulus can be obtained by approaching Eq. \( T_0 = 0 \) and \( T_0 = T \) of different bond nature and \( s_m \) \( (T/T_m) \) values. Young’s modulus enhancement happens at the combinations of \( (s_m, m) = (0.25, 3) \) for \( T_0 = 0 \) and \( (s_m, m) = (0.5, 3) \) for \( T_0 = T \). The Y retention may happen at critical \( (T/T_m, m) \) combinations.

The size dependence of the Y values and \( T_0 = 0 \) elevates also occurs in the situations of \( (x_m, m) = (0.25, > 3) \). Y retention may happen at critical \( (x_m, m) \) combinations such as \( (x_m, m) = (0.25, > 3) \). The critical combination of \( (x_m, m) \) can be obtained by approaching Eq. \( (3) \) to zero. If we select \( T = T_0 \), Y elevation also occurs in the situations of \( (x_m, m) = (0.25, 2) \) and \( (0.5, > 4) \). It is not surprising therefore that the modulus may rise, drop, or remain constant upon the solid size being reduced, depending on the materials and operating conditions, and techniques as well.

Figure 2 shows the temperature-induced relative change of (a) Y values and (b) the extensibility for \( K_f = 10 \) and \( m = 1, 3, 5 \) samples. If \( T_0 = T \), the Y drops nonlinearly with T until \( T_m \). The insertion shows the case of \( T_0 = 0 \) in which the Y drops linearly with \( T \). The extensibility approaches infinity at the corresponding \( T_m(K_f) \). The inset manifests singularities because of the shell-by-shell configuration. If we treat the outermost two atomic layers as the skin with a mean \( z_s = (4 + 6)/2 \) and the singularity occurs at the melting point, the extensibility drops with the characteristic dimension. On the other hand, a smaller nanosolid with lower \( m \) value is more easily extensible at elevated temperatures than the other cases.

FIG. 1. (Color online) Prediction of size \( K_f \) dependence of Young’s modulus with (a) \( T_0 = 0 \) and (b) \( T_0 = T \) of different bond nature and \( s_m \) \( (T/T_m) \) values. Young’s modulus enhancement happens at the combinations of \( (s_m, m) = (0.25, 3) \) for \( T_0 = 0 \) and \( (s_m, m) = (0.5, 3) \) for \( T_0 = T \). The Y retention may happen at critical \( (T/T_m, m) \) combinations.

FIG. 2. \( T/T_m \) dependence of (a) Young’s modulus and (b) extensibility of a spherical nanosolid with different \( m \) and \( T/T_m \) \( (x_m) \) ratios. The insertion shows the cases of \( T_0 = 0 \). The Y values of nanosolid of lower \( m \) values and smaller sizes drop faster when the test temperature is raised. The extensibility approaches infinity at the melting point. The singularities in the inset exhibit the shell-by-shell melting features.

Figure 3 compares the prediction with observations of the size dependence of the ZnO and (b) polymers measured at room temperature and temperature-dependent Y value for (c) bulk Al2O3 and (d) bulk AlN. Predictions agree exceedingly well with the measured data for ZnO nanowires \( (m = 4, \tau = 3) \). For the polymer, predictions agree with the general trend of measurement \( [m = 4, \tau = 1 \text{ (film)}] \) with accuracy subject to the precision of the size determination. Numerical agreement of the temperature dependence of the Y [Fig. 3(c)] at higher temperatures could be made by the discussed models despite the physical mechanisms. However, we found that the \( B = [E_b(0) \times (1 + \alpha T)^{-1}] \) in Anderson’s and the \( T_0 \) in Wachtman’s correspond to the turning point \( T_0 \) at which the \( T-Y \) curve transits from nonlinear to linear, which is governed by the Debye temperature. Besides, our approach covers the contribution from thermal expansion. The overall performance of the BOLS prediction may represent the true situation of thermally softened specimens.

The predicted \( m, K_f, \) and \( x_m \) dependence of the modulus and extensibility covers all the possible trends as observed. For example, the predicted Y depression in Fig. 1 agrees well with the measured trends of Al \( [m = 1, x_m = 300/650 \sim 0.5 \text{ (Ref. 22)}] \) and polymers \( [T_b = 300/450 \sim 2/3 \text{ (Ref. 24)}] \). The extensibility of nanoscaled Al-Cu alloys in the semisolid state,30 and nanoscaled Al2O3 (Ref. 60) and PbS (Ref. 61) at
room temperature increases generally with grain refinement. The $m$ values for compounds or alloys are around 4 or higher, and their $T/T_m$ ratios are relatively lower. The increase of the compressibility and extensibility of Al$_2$O$_3$ and PbS nanosolids renders Young’s modulus. The superplasticity of materials such as Cu wires [$m=1, x_m \sim 1/2$ (Ref. 62)] with grain size less than tens of nanometers in the temperature range 0.5–0.6 $T_m$ (Ref. 63) also agrees with the predictions. The $Y$ elevation of ZnO nanowire [$m=4, x_m \sim 1/4$ (Ref. 8)] and Si nanosphere [$m=4.88, x_m \sim 1/6$ (Ref. 2)] is also within the prediction because of their high $m$ values and low $x_m$ ratios. However, the discrepancy of ZnO wires$^{8,11}$ and Si spheres$^2$ and belts$^{16}$ may arise from different $x_m$ of operation or different experimental conditions or methods. It is anticipated that modulus enhancement as observed from TiCrN and GuAlN surfaces$^5$ may not be observable at room temperature for the low-$T_m$ metals such as Sn, Pb, Al, Zn, Mg, and In.

Predictions also agree with the temperature dependence of Young’s modulus of chemical vapor deposition (CVD) nanodiamond films,$^{23}$ the silicone resins,$^{24}$ and the yield stress (linearly proportional to modulus) of Mg nanosolid$^{65}$ of a given size. The ductility increases exponentially with temperature until infinity at $T_m$ that drops with solid size. An atomic-scale simulation$^6$ also suggests that the material becomes softer in both the plastic and elastic regimes as the operating temperature is raised. When measuring at 200 °C, the strength of 300-nm-sized Cu nanograins is lowered by 15% and the ductility increases substantially.$^{66}$ When the operation temperature is increased from room temperature to 400 °C the ductility of ultrafine-grained FeCo$_2$V samples of 100–290 nm sizes increases from 3–13% to 22% rendering with strength attenuation.$^{67}$ The biaxial Young’s modulus of Si (111) and Si (100) drops linearly when the $T$ is increased.$^{68,69}$ A 280% superplasticity of single-walled carbon nanotube ($m=2.56, x_m \sim 2/3$) has been realized at high temperature.$^{70}$

It is true that the Young’s modulus and tensile stress and strength are indeed different quantities despite the similarity in the trends of change with external stimulus as widely observed from specimens such as polymers$^{71}$ and Al oxide$^5$ on the size and temperature dependence. From an atomistic point of view, these quantities are intrinsically related to the bonding energy and bond length and thus we can explain why they perform with similar trends. Artifacts in the measurement, in particular in the plastic deformation regime, may dominate as extrinsic contributions to modulate the slope of measured data. The consistency between observations and predictions of the linear dependence of mechanical properties may provide evidence for the BOLS consideration.

Using Eq. (5), we are able to predict the dependence of $\theta_p$ on the size ($K_j$), temperature ($T$), and bond nature ($m$). Figure 4 shows the relative change of $\theta_p$ for nanowires ($\tau = 2, \kappa=1$) with $m=1,3,5$ and $x_m=0, 0.25,$ and 0.50. When the temperature of the measurement is much lower than the melting point ($x_m \ll 1$), $\theta_p$ increases with the decrease of material dimension $K_j$, while $\theta_p$ increases faster at larger $m$. On the other hand, $\theta_p$ decreases with increasing operation temperature.

![Graph showing relative change of $\theta_p$ for nanowires](image-url)
temperature and the relative change of $\theta_D$ is greater for smaller $m$ values. A close examination of Fig. 4(a) and Eq. (5) could lead to a conclusion that for a certain $(x_m, m)$ combination, the Debye temperature may vary insignificantly with particle size, being the same as Young’s modulus retention. Figure 4(b) shows the temperature-induced relative change of $\theta_D$ for nanowires ($\tau=2, \kappa=1$) of size $K_j=10$ and 50. If we set $T_0=T$, the $\theta_D$ decreases nonlinearly with temperature $T$ until $T$ approaches $T_m$, the local melting temperature of the $i$th atomic site. The two transition points for each of the $(m, K_j)$ combinations arise from the loss of bond that happens only to the outermost two discrete atomic layers. Moreover, the variation of $\theta_D$ with the temperature and size is more pronounced for larger $m$ and smaller $K_j$ values.

Figure 5 compares the predictions with various theoretical or experimental data (a) for Au particles and (b) Debye temperature from Debye-Waller parameter measurements for Se nanoclusters. Couchman and Karasz’s approach shows that the change of Debye temperature involves the particle size $R$ and cutoff acoustic wave vectors $K_j$: $\Delta \theta_D/\theta_D = -3 \pi/8RK_0$, without temperature being involved. By applying Eq. (5), with $T_0=0.245T_m$ and $T=0.16T_m$, agreement between the BOLS prediction and Couchman and Karasz’s estimation has been reached. If we set $T_0=0.224T_m$ and $T=0.204T_m$, our model fits Balerna and Mobilio’s measurement results quite well, which is also shown in Fig. 5(a). In Fig. 5(b), the prediction shows the general trend of the Debye temperature with respect to size; agreement is not satisfied. However, the measurement was conducted at $T=293 \text{ K}$, which is higher than the local melting temperature of the first two layers, about $0.6T_m$ for Se $T_m=494 \text{ K}$, and hence the giving feature is dominated by a core interior with less temperature dependence.

As indicated in Eq. (6), the specific heat capacity depends unambiguously on the $\theta_D$ and hence on the size, temperature, and bond nature. Figure 6(a) shows the reduced $C_v$ (in units of $R$, where $R$ is a gas constant) versus temperature ($T/\theta_D$) for Si nanowires ($m=4, 8$) and Al nanowires ($m=1$) of different diameters ($K_j=5, 10, 20$). The shape of the $C_v$ curve is similar to that of the bulk $C_v$ curve of the Debye model, but with the size-induced depression over the whole temperature range. For the same $K_j$ at the given $T/\theta_D$, the reduction of heat capacity is larger for larger $m$. Figure 6(b) plots $C_v/C_v0$ (where $C_v0$ is the bulk heat capacity at a given temperature) vs $K_j$ at $T=100$ and $300 \text{ K}$ for Al nanowires and Si nanowires. The heat capacity decreases with the size at fixed temperature (except for Al nanowires measured at room temperature, such that the heat capacity is very close to the bulk $C_v$ value obtained when $K_j>15$ and increases slightly with decreasing size). For a given size, the reduction of the heat capacity is more significant at lower temperatures or larger $m$ value. In this analysis, we set $T_0=T$. If $T_0$ is assumed to be 0, the general trend of the heat capacity is preserved, but the reduction of the heat capacity is greater.
specific heat of nanostructures has been established in terms of bonding identities and their coordination and temperature dependence, which covers the essential parameters and their interdependence. Understanding clarifies why the $Y$ values for some materials are elevated and why those of others are not upon size reduction and how the mechanical strength drops when the measuring temperature is increased. Conclusions can be drawn as follows.

(a) The Young’s modulus of a nanosolid may depress, increase, or remain unchanged, depending on the size, temperature of operation, and the nature of bond involved, as well as experimental conditions. It is therefore not surprising to observe the elastic modulus change in different trends of different materials measured under different conditions. It is suggested that one could not consider a certain parameter at a time without addressing the rest when discussing the mechanical and thermal properties of a material, especially a small object.

(b) The similarity of the size and temperature dependence of the mechanical properties such as Young’s modulus, tensile stress and strength, and surface energy arises intrinsically from the same origin of bonding energy and bond length. Artifacts in measurements, in particular in the plastic regime, may dominate as extrinsic contributions to modulate the observations extrinsically.

(c) Agreement between observations and predictions of the $T$-dependent Young’s modulus has allowed us to derive information about the bonding energy of an atom in the bulk, which goes beyond conventional theoretical and experimental approaches.

(d) The $\theta_D$ has a square-root dependence on $(T_m-T)$, rather than a linear or square-root dependence on the $T_m$. The currently derived solution may provide complementary information for the $T$-independent form of $\theta_D$ given by Lindemann.

(e) The specific heat capacity generally decreases when the solid size is reduced. The reduction of the specific heat capacity is more pronounced for larger $m$ values at lower temperatures.

(f) Further exploration of the temperature dependence of $Y$, $\beta$, $\theta_D$, and $C_v$ at extremely low temperature would be even more interesting and an investigation is in progress.

IV. CONCLUSION

A set of analytical expressions for the size, temperature, and bond nature dependence of the elastic modulus and its derivatives on the extensibility, Debye temperature, and specific heat of nanostructures has been established in terms of bonding identities and their coordination and temperature dependence, which covers the essential parameters and their interdependence. Understanding clarifies why the $Y$ values for some materials are elevated and why those of others are not upon size reduction and how the mechanical strength drops when the measuring temperature is increased. Conclusions can be drawn as follows.

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SIZE, TEMPERATURE, AND BOND NATURE DEPENDENCE


42 The $z_i$ for the outermost atomic layer changes with the surface curvature or the dimensionality of the nanostructure (for spheri-

cal dot, $\tau=3$, for a cylindrical rod, $\tau=2$) in the form of $z_i = 4 \times (1 - 0.75/K_i)$. For a flat surface ($\tau=1$), $z_i = 4$. Generally, $z_i = 6$ and $z_i = 3$.

43 The relative specific heat heats that inverse Hall-Petch relation $\eta_i / H_i = 1 + AK_j^{0.5}$, which includes the effect of dislocation accumulation.


