Local bond average for the size and temperature dependence of elastic and vibronic properties of nanostructures

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Abstract: With the miniaturisation of a solid down to nanometers scale, the mechanical and optical properties of such nanomaterials are different from that of their corresponding bulk materials. A systematic understanding of the atomic origin of the unusual behaviour of mechanical and optical properties of a nanosolid is presented here towards the predictions for design and controllable growth of nanostructured materials. The Local Bond Average (LBA) approximation and Bond-Order-Length-Strength (BOLS) correlation mechanism in size, temperature and pressure domain has been developed, which enables the tunability of various measurable properties, such as elastic constants, optical phonon frequency shift. Agreement between predictions and observations reveal that the shortened and strengthened surface bonds are responsible for the observed size dependent change of material properties, while the temperature induced bond expansion and weakening are the physical origin for the temperature dependent change of measurable material properties.

Keywords: local bond average, elastic properties, vibronic properties, nanostructures.


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1 Introduction

Since the discovery of nanomaterials, studies on mesoscopic systems have evolved tremendously during the past decades. There has been great interest in the synthesis, characterisation, and simulation of the properties of these nanomaterials towards discovery of new functional material and devices. It has been well observed that the mechanical, electrical, optical, and thermal properties of these nanosized materials are quite different from their corresponding bulk materials. Many efforts in theoretical derivations have been made to find out the mechanism behind. Various models have been proposed. However, a consistent understanding between various size and temperature dependent change of mechanical and optical properties are yet lacking. In this report we will demonstrate the size and temperature dependent relative change of mechanical and optical properties based on recent developed local bond average (LBA) approximation and bond order length strength (BOLS) correlation. First of all, the principle of LBA and BOLS will be discussed in Section 2, followed by some applications on Young’s modulus and Raman frequency shift in Section 3.

2 Principle

2.1 LBA (Local-Bond-Average) approximation

A bulky solid is formed by numerous atoms with bonds connecting one to another. The involvement of interatomic bonding makes the solid to perform differently from the isolated atoms. For a given specimen no matter being crystal, non-crystal, or with defects or involving impurities, the nature and the total number of bonds do not change under the external stimulus (such as temperature and pressure) unless phase transition occurs. Instead, the length and strength of all the involved bonds will response to the applied external stimulus and reflect onto the detectable quantities. Therefore, one only needs to focus on the length and strength of the representative bonds at different sites or their average in order to predict the performance of the entire specimen under external stimulus.

The LBA approach may represent the true situation of measurements and theoretical computations that collect statistic information from large number of atoms of the given specimen and could distinguish the behaviour of local bonds at different sites. The LBA approach is substantially the same to the volume partitioning approximation implemented
by Delph et al. [1,2], who have opened a way to improve the calculation of such local quantities through volume partitioning. They have showed that volume averaging was the correct way to obtain physically meaningful stress and elastic properties of complex microstructures. Compare to the volume partition approximation, the LBA approach seeks for the relative change of a quantity with the applied external stimulus to the already known bulk value. The LBA approach focuses merely on the performance of the local representative bonds without considering the number of bonds in the given specimen. The presence of broken bonds, defects, impurities, or the non-crystallinity will affect the reference values of concern rather than the nature of observations. Contribution from long-order interaction or the high-order coordinates can be simplified by folding them into the bond between the nearest neighbours. The mathematical expression for LBA approximation is given such that any detectable quantity $Q$ can be expressed as a function of bond identities (bond length $d$, bond strength $E$, bond nature $m$, and atomic coordination number $z$) of the representative bonds, i.e.,

$$Q = f(d, E, m, z).$$

Extend the LBA Approximation to temperature domain, the bond nature and atomic coordination number (CN) remains constant, while the bond length and bond strength are temperature dependent. That is

$$d_i(T) = d_i + \int_0^T \alpha_i(t) \, dt$$
$$E_i(T) = E_i + \int_0^T \eta_1(t) \, dt + \eta_2 = E_i(0) - \int_0^T \eta_1(t) \, dt$$

The subscript refers to the $i$th atomic. $\eta_1$ is the specific heat per bond and $\eta_2$ the $1/z_b$ fold of latent heat for atomisation of the atom in molten state. The specific heat $\eta_1$ follows the universal Debye relation of temperature dependence for bulk material.

This concept of LBA approximation can also be extended to various other states, such as end states, defects states, impurity states, or interface states once the representative bonds can be specified.

### 2.2 BOLS (Bond-Order-Length-Strength) correlation

For a perfect crystal, the unit cell repeats itself within the crystal. However, near the surface the lattice periodicity is distorted. The termination of lattice periodicity in the surface normal direction has two effects: one is the creation of surface potential barrier, which leads to electron confinement within this region. The other effect is the reduction of coordination numbers (CN) of the surface atoms. Such CN imperfection induced material property change can also be extended to structural defects, like voids, grain boundaries, dislocations. The numerical expression of BOLS is shown in equation (2),

$$c_i(z_i) = d_i / d_b = 2 / \{1 + \exp[(12 - z_i)/8z_i]\}$$
$$E_i = c_i^{\alpha} E_b$$
$$E_{B,S} = z_i E_i$$
where \( i \) and \( b \) denote an atom in the \( i \)th atomic layer and in the bulk, respectively. \( i \) counts from outer most surface to the central of the solid up to three, as there is no bond order loss occurs for \( i > 3 \). The core idea of the BOLS correlations \([3]\) is that broken bonds of the surface atoms make the remaining bonds (with length \( d_i \) and bond energy \( E_i \)) between the under coordinated atoms shorter and stronger with respect to the bulk counterparts. \( c_i \) is the coefficient of bond contraction, which is defined as the percentage of bond length at \( i \)th atomic layer to that at bulk site, with \( z_i \) being the effective coordination of the corresponding \( i \)th atom of concern. \( m \) is a key parameter, which represents the nature of the bond. As a result of bond reduction, charge, mass, and energy localisation and densification occurs, which perturbs the Hamiltonian, atomic coherency, and electroa ffinity as well as associated properties of a specimen. \( E_b \) is the binding energy per bond.

From of BOLS consideration, the mean relative change of a measurable quantity of a nanosolid containing \( N_j \) atoms, can be expressed as \( Q(K_j)/Q(\infty) \), where \( Q(\infty) \) is the measurable quantity for the same solid without the effect of CN-imperfection involved. \( Q(K_j) \) relates to \( Q(\infty) \) through a core-shell configuration and a scaling relation:

\[
\frac{\Delta Q(K_j)}{Q(\infty)} = \sum_{i} \gamma_{ij} \left( \frac{q_i}{q_0} - 1 \right) = \sum_{i} \gamma_{ij} \Delta q_i / q_0
\]

\[
\gamma_{ij} = \frac{N_j}{K_j} = \frac{\tau_i \gamma_i}{K_j} \leq 1
\]

where \( q_i \) and \( q_b \) correspond to the local density of \( Q \) in the region of the \( i \)th atomic layer and inside the bulk, respectively. \( K_j = R_j/d_0 \) being the dimensionless form of size is the number of atoms lined along the radius of a sphere or across the thickness of a thin plate. \( \tau \) refers to the dynamic dimensionality (\( \tau = 1 \) thin plate or monatomic chain; \( \tau = 2 \) for nanowire or nanorod; \( \tau = 3 \) for spherical dot). The weighting factor, \( \gamma_{ij} \), represents the geometrical contributions from dimension (\( K_j \)) and dimensionality (\( \tau \)) of the solid, which determines the magnitude of change. The quantity \( \Delta q_i / q_0 \) in the surface skin originates the change, which depends functionally on temperature, pressure, and bond nature. As the size of the structure reduces, the volume ratio of surface atoms increases and these surface atoms will have great influence on the overall material properties, as demonstrated in deriving solutions to the size dependence of mechanical \([4]\), electrical \([5]\) and thermal properties \([6]\) of nanostructures.

### 3 Applications

With LBA approximation and BOLS consideration, we are able to predict size, temperature, and pressure dependent measurable material properties, once the relationship between those measurable material properties and bonding identities are established. In the following part, some mechanical and optical properties are taken for example to testify the validity of our approach.

#### 3.1 Mechanical properties

Young’s modulus \( (Y) \) is one of the key elemental parameters in materials science. Generally it decreases with increasing temperature and are considered to be attributed by
the anharmonic effects of the lattice vibrations [7]. Some semi-empirical models are proposed in equations (5) [8–11]

\[
\frac{\Delta Y(T)}{Y_0} = \begin{cases} 
-A_0 T \exp(-\theta_0/T) & \text{(Wachtman et al.)} \\
-3R\gamma\theta T / Y_0 V_0 & \text{(Anderson)} 
\end{cases}
\]

with \(H(T/\theta_0) = 3(T/\theta_0)\int_0^{\theta_0/T} \frac{x^3}{e^x - 1} \, dx\)

where \(Y_0\) is the Young’s modulus measured at 0 K. The constants \(A_0\) and \(\theta_0\) are temperature independent parameters for data fitting. In Anderson’s model, \(R\) is the ideal gas constant, \(V_0\) is the specific volume per average atom at 0 K, \(\gamma\) is the Grüneisen parameter, and \(\delta\) is a parameter analogous to \(\gamma\). The product \(\gamma\delta\) is assumed to be temperature independent. Anderson’s model in equation (5) satisfies Nernst’s theorem that the temperature derivatives of the elastic constants must vanish at 0 K. Watchman’s model describes well the elastic behaviour at high temperature, whereas Anderson’s model could reproduce the measured \(Y-T\) curves reasonably well at the whole temperature range by taking \(\gamma\delta\) as an adjusting parameter.

From LBA approximation, on the other hand, in order to predict the general trend of temperature dependent Young’s modulus, we only need to establish the relationship between Young’s modulus and the bond related parameters of the representative bonds. Previously, we have derived that the Young’s modulus and surface stress share the similar formula and were derived to be proportional to the bond energy density, \(P\) (see equation (6)).

\[
P(T) = -\frac{\partial u(r)}{\partial V} \bigg|_{\rho=\tilde{\rho}} \propto Y, \quad \frac{\partial^2 u(r)}{\partial V^2} \bigg|_{\rho=\tilde{\rho}} \propto \frac{E_i(T)}{d_i^3}
\]

where \(u(r)\) is the pairing potential and \(V\) is the volume. Combining equation (1), we have

\[
\frac{Y(T)}{Y_0} = \left[\frac{1}{1 + \int_0^T \alpha(t) \, dt} \right]^{\frac{3}{2}} \left[1 - \int_0^T \frac{C_i(t) \, dt}{E_i(0)} \right]
\]

where \(\alpha(t)\) is the temperature dependent thermal expansion coefficient. \(E_i(0)\) is atomic bond energy at 0 K. \(C_i(T)\) is the specific heat which follows Debye model for specific heat

\[
C_i \left(T/\theta_0\right) = 9R \left(T/\theta_0\right) \int_0^{\theta_0/T} \frac{x^3 \exp(x)}{(e^x - 1)^2} \, dx.
\]

The integration of specific heat \(C_i\) from 0 K to \(T\) gives the specific internal energy

\[
U(T) = 9T \left(\frac{T}{\theta_0}\right)^3 \int_0^{\theta_0/T} \frac{x^3 \, dx}{e^x - 1} = 3T \times H(T/\theta_0).
\]
Comparing equation (7) with Anderson’s model, we have reconfirmed Anderson’s expression from atomistic bond point of view, while the thermal expansion upon temperature rise must also be included in the calculation.

In equation (7), only one fitting parameter \( E_b(0) \) (the atomic cohesive energy) is required. Figure 1 shows the agreement between LBA predictions and the measured temperature dependence of Young’s modulus with derived atomic cohesive energy to be 4.33 eV for Si and 2.58 eV for Ge [12]. The solid lines correspond to our predictions, while the scattered symbols represent experimental data from (a) Gysin et al. [7] and (b) Fine [13].

Traditionally, the Young’s modulus in a bulk material is deemed as constant at a given temperature [14] and the value of the modulus is proportional to the melting point \( T_m \) of the bulk. However, upon structural miniaturisation 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: increase, decrease, or remain unchanged with decreasing solid size. 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 for Ag nanowires [15], Al and Si nanobelts [16], ZnO nanowires [17]. However, an opposite trend presents in the (0001) oriented ZnO nanobelts and nanowires [18,19]. The moduli of Cr [20] and Si [21] nanocantilevers and ZnS [22] nanobelts are also measured to decrease sharply with decreasing diameters. In contrast, amorphous Si nanowires [23], Au [24], and Ag [25] 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 Ag, ZnO, and Si, the \( Y \) value changes in different ways, depending on the experimental techniques and operation conditions.

Figure 1  Agreement between predictions and the measured temperature dependence of the relative change Young’s modulus of Si (a), and Ge (b)

Here we show that an by extending BOLS correlation [3,26,27] to temperature domain, we are able to reproduce the observed trends and hence clarify for the first time the long-standing discrepancy in observations.

Taking the core-shell configuration of a nanosolid into consideration, the bond nature \((m)\), shape and size \((\tau, K)\), and temperature \((T)\) dependence of the relative change of the \( Y \) can be obtained by summing contribution over the outermost three atomic layers.
If only size effect is considered, the relative change of Young’s modulus with respect to the bulk modulus is expressed as:

\[
\frac{\Delta Y(K_j)}{Y(\infty)} = \sum_{i=3}^{\infty} \frac{\tau_i}{K_j} (c_i^{-(n+3)} - 1). \tag{8}
\]

If the temperature is involved, the Young’s modulus can be expressed as:

\[
\frac{Y(K_j, T)}{Y(\infty, 0)} = \frac{Y(K_j, T)}{Y(\infty, T) \times Y(0)} \\
= \left[ \sum_{i=3}^{\infty} \frac{\tau_i}{K_j} (c_i^{-(n+3)} - 1) + 1 \right] \left[ 1 + \int_0^T \alpha(t) \, dt \right]^{-1} \left[ 1 - \int_0^T C_i(t) \, dt \right] \frac{E_a(0)}{E_a(T)} \tag{9}
\]

Figure 2 gives one example of relative change of Young’s modulus for ZnO nanowires. The scatters are from experimental measurement [17].

**Figure 2**  Size dependent Young’s modulus for ZnO nanowire

### 3.2 Acoustic properties

The vibronic behaviour of atoms in a specimen is not only of fundamental significance to the processes such as electron-phonon coupling, phonon-photon interaction, phonon transport and thermal conductivity, but also of technical importance to practical applications in the fields such as short wavelength light emitting, high temperature, high frequency, high power electronic and thermal devices [28,29]. Generally, a redshift of Raman optical phonons happens when the measuring temperature is raised, such as in the case of some group III nitrides [30–33]. Similar trends of the temperature dependence of Raman shift have also been observed from some other materials [34–39]. However, the mechanisms for the observations are still puzzling with the following possible models [30–39]:

\[
\frac{\Delta\omega(T)}{a_b} = \begin{cases} 
\Delta_i(T) & \text{(Balkanski et al.)} \\
\Delta_i(T) + \Delta_j(T) & \text{(Menendez et al.)} \\
\Delta_i(T) + \Delta_j(T) + \Delta_k(T) & \text{(Qian et al.)} \\
\Delta_j(T) & \text{(Liu et al.)}
\end{cases} \tag{10}
\]
Local bond average for the size and temperature dependence

\[ \Delta_1(T) = A_1 \left( 1 + \frac{1}{e^{\eta}} - 1 \right)^{1/2} + A_2 \left( 1 + \frac{1}{e^{\eta}} - 1 \right)^{1/2} \]
\[ \Delta_2(T) = \exp\left[ -3\gamma \int_0^T \alpha(t) \, dt \right] - 1 \]
\[ \Delta_3(T) = 2 \left( a - b \frac{C_{33}}{C_{13}} \right) \left( 1 + \int_0^T \alpha(t) \, dt \right) \]
\[ \Delta_4(T) = \frac{B_1}{e^{\frac{2\hbar\omega_0}{k_BT}} - 1} \]

where \( \omega_0 \) is the specific Raman phonon frequency measured at reference temperature 0 K. \( T \) is the temperature of measurement, and \( t \) is the integrand. \( x = \frac{\hbar \omega_0}{2k_BT} \) and \( y = \frac{2x}{3} \) (\( k_B \) is the Boltzmann’s constant) correspond to the third and the forth order of phonon decay, respectively. The constants \( A_1, A_2, B_1, \) and \( B_2 \) are freely adjustable parameters needing clear physical indications. The other parameters in equation (2) are physically meaningful and experimentally obtainable. For example, \( \gamma_i \) is the mode Grüneisen parameter and the value of \( \gamma_i \) varies from mode to mode. \( \alpha(T) \) is the coefficient of thermal expansion of the specimen and \( \alpha_s(T) \) is the coefficient of thermal expansion of the substrate when the interface interaction is involved. \( \varepsilon_{33} \) is the residual strain in the sample at the growth temperature \( T_g \). \( C_{13}/C_{33} \) is the elastic constant ratio of the 13 and 33 elements in the elastic tensor. The parameters \( a \) and \( b \) in \( \Delta_1 \) are phonon deformation potentials [33,40].

The models in equation (10) show that the phonon redshift may arise from anharmonic phonon decay, thermal expansion, or the interface interaction or the combination of these factors. Except for the terms of phonon decay, the additional terms originate from the change of macroscopic properties with temperature. The redshift of the optical modes represented by the \( A_1 \)-related term in \( \Delta_1 \) was firstly assumed arising from the decay of one optical phonon into two acoustic phonons of the same frequency but opposite momentum upon the sample being excited by the incident photons [41]. The phonon decay has been extended to the higher fourth order represented by the \( A_2 \)-related term in \( \Delta_2 \) [42]. Later, the effect of thermal expansion in \( \Delta_2 \) was considered [43]. Some work have shown that well reproduction of the measured \( T \) dependence of the redshift of Raman optical phonon could be reached without considering the effect of thermal expansion [38,39,41,44]. However, some calculations indicated that thermal expansion also played a certain non-negligible role in the \( T \) induced redshift of Raman frequency [31,32,36,45]. Sometimes the temperature dependent strain induced by lattice and thermal mismatch between the specimen and the substrate became essential when the interface effect was considered, and this is represented by \( \Delta_3 \) [30,33]. From quantum mechanical point of view, the \( T \)-induced Raman redshift can be fitted to a Bose-Einstein population as indicated by \( \Delta_4 \) [39]. On the other hand, the first principle \( ab \) initio calculations have also been conducted to calculate some of the individual terms in equation (2) and then add them up to examine the factors dominating the temperature dependence [46,47] on the Raman modes.
In fact, the T-induced Raman redshift can be numerically reproduced using all the models in equation (2). Unfortunately, no relation has been established between the T-induced Raman shift and the atomistic parameters. According to LBA approximation, the Raman frequency is found to be related to bonding identities in the following expression [3]

\[ \omega \propto \frac{1}{d} \left[ \frac{zE_a}{m^*} \right]^{\frac{1}{2}}. \]

And hence in the temperature domain the Raman frequency can be expressed as

\[ \frac{\omega(T)}{\omega_0} = \left(1 + \int_0^T \alpha(t) \, dt \right)^{-1} \left(1 - \frac{\int_0^T C_v(t) \, dt}{E_a(0)} \right)^{\frac{1}{2}} \] (12)

which could lead to an immediate solution with one fitting parameter termed as mode cohesive energy \( E_a(0) \) in current expression by fitting to experimental data.

The reproduction of the observations for some group III-nitrides (Figure 3) revealed that the redshift arises simply from thermally-induced bond vibration and bond expansion. In Figure 4, the experimental data for AlN, GaN, and InN are from Link et al. [30], Kuball et al. [32] and Pu et al. [33] respectively.

**Figure 3** Temperature dependent Raman frequency redshift

**Figure 4** Size dependent Raman redshift of Si nanoparticle
Furthermore, it has also been observed that the Raman frequency redshift with decreasing size, which has been suggested to be originated from surface disorder [48], surface stress [49,50], quantum confinement [51,52], local heating effects [53–55], or surface chemical passivation. Hwang et al. [56] and Kim and Jang [57] demonstrated for the first time that the effect of lattice contraction must also be considered to explain the observed redshift of phonon energies.

When the size dependent Raman frequency shift is considered, according to equations (1) and (2), the measurable quantity \( Q(\infty, T_0) = \alpha(\infty, T_0) - \alpha(2, T_0) \), with \( \alpha(2, T_0) \) being the vibration frequency of a monatomic chain measured at temperature \( T_0 \), which is the reference point for the optical redshift upon nanosolid and bulk formation (normally 0 K). The scaling relation becomes:

\[
\frac{\alpha(K, T) - \alpha(2, 0)}{\alpha(\infty, 0) - \alpha(2, 0)} - 1 = \frac{\alpha(K, T) - \alpha(\infty, 0)}{\alpha(\infty, 0) - \alpha(2, 0)}
\]

\[= \Delta_i(K, T) = \sum_{\gamma_i} Y_i \delta_i(z_i, T) \quad (13)\]

\[
\delta_i(z_i, T) = \frac{\alpha(z_i, T) - \alpha(z, 0)}{\alpha(z, 0) - \alpha(2, 0)}
\]

\[= \frac{z_i c_i^{1+(1/m/2)} [1 - \int_0^T \eta_i(t) dt]}{E_i(0)(1 + \Delta_i) z_i c_i^{1-(1/m/2)}} \quad (14)\]

where \( \Delta_i = z_i c_i^{1-(1/m/2)} - 1 \) with \( \Delta_i \) being the perturbation to the atomic coherency. \( T_{\text{m}} = (1 + \Delta_i) T_m \) and the subscript (2) corresponds to monatomic chain. The frequency shift \( \omega(\infty, T_0) - \omega(2, T_0) \), and chain vibration frequency \( \omega(2, 0) \) can be obtained by simultaneously matching the measured size- and temperature-dependent data to the theoretical predicted lines.

In Figure 4, we compared the prediction to the measured \( T \)-dependent Raman frequency shifts for silicon nanoparticles, the experimental data are from Mishra and Jain [58].

4 Conclusion

A systematic understanding of the atomic origin of the unusual behaviour of mechanical and optical properties of a nanosolid from the Local Bond Average (LBA) and the bond-order-length-strength (BOLS) correlation mechanism have been proposed with application in size and temperature domain. The Local Bond Average (LBA) states that once the relationship between the measurable material property and bonding identities (bond length, strength, nature, and coordination number) of the representative bonds is established, the relative change of this measurable material property under external stimulus can be predicted. Consistency between the BOLS prediction and measurements evidences not only the validity of BOLS correlation mechanism, but also the significance of the surface coordination number imperfection to the low dimensional system.
References


