Temperature dependent elastic, lattice vibronic and thermal properties of nanomaterials

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**Temperature dependent elastic, lattice vibronic, and
thermal properties of nanomaterials**

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To my husband Qin Jing and our beloved parents

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Summary

It is well known that the physical properties of a macroscopic system can be well described using classical approaches such as the Gibbs free energy or the continuum medium mechanics, which relates the measurable quantities directly to the external applied stimulus such as temperature, pressure, chemical composition, electric and magnetic field, etc, without considering the atomistic origin. At atomic scale, quantum effect becomes dominant and the physical properties of a small object can be reliably obtained from computations by solving the Schrödinger equations or Newton motion equations with a sum of averaged interatomic potentials as a key element. However, for a small system in nanometer scale, both classical and quantum approaches have their limitations. Therefore, an effective approach solving the difficulties encountered by both classical and quantum approximations has been a great challenge.

The recently advanced bond-order-length-strength (BOLS) correlation suggests that the size dependent material property is mainly attributed to the interaction between under-coordinated atoms in the surface skins. The coordination number imperfection in the surface skin leads spontaneous bond length contraction and bond energy strengthening. This causes densification and localization of charge, energy, mass at surface region, and hence modifies atomic coherency, Hamiltonian, etc.

By extending the BOLS correlation mechanism to temperature domain, an approach of local bond average (LBA) has been developed in this thesis, which states that: (i) the entire specimen or a specific location of a specimen can be represented by a representative bond; (ii) the detectable quantity of a specimen can be obtained once

the relationship between this detectable quantity and the bond identities (bond order, nature, length, and strength) of the representative bond and the response of these bond identities to the stimulus is established.

This thesis discusses the size and temperature dependent elastic, lattice vibronic, and thermal properties of various materials. Deeper insight into the mechanism behind the size and temperature dependence together with analytical solutions is presented. Theoretical reproductions of experimental observations reveal that the surface coordination number imperfection induced spontaneous bond contraction and bond energy strengthening dictate the size-induced mechanical strength enhancement, optical Raman frequency redshift, and thermal conductivity variation; whereas the thermally-driven bond length expansion and bond energy weakening lead to mechanical strength depression, Raman frequency redshift, as well as surface energy reduction. Reproductions of size and temperature dependent Young's modulus, Raman frequency shift, thermal expansion coefficient, thermal conductivity and surface energy for various materials, such as metals, group IV, group III-nitrides, and carbon based materials give quantitative information about the atomic cohesive energy and the dimer frequency, which is beyond the scope of currently available approaches in literature.

Current progress in BOLS correlation and LBA approximation could pave a path to bridge the gap between the classical approach in macroscopic system and the quantum confinement approach in atomic level by considering the interatomic bond formation, dissociation, relaxation, vibration and associated energetic response of corresponding atoms and electrons and the consequences on the measurable quantities.

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Nomenclatures

ω	The angular frequency
η_1	Specific heat per coordinate
η_2	Thermal energy per coordinate for evaporating a molten atom
θ_D	Debye temperature
$\alpha_i(T)$	Temperature dependent thermal expansion coefficient
γ_i	Surface to volume ratio of the i th atomic shell over the entire solid of size
τ	Dynamic dimensionality
κ	Static dimensionality
ν	Poisson ratio
λ, μ	Lamé constant
m^*	Reduced mass
AFAM	Atomic force acoustic microscope
AFM	Atomic force microscope
BOLS	Bond order-length-strength
$c_i(z_i)$	CN dependent bond contraction coefficient
$CN(z)$	Coordination number
$C_V(T)$	Debye specific heat
DFT	Density functional theory
E_B	Atomic cohesive energy
E_b	Cohesive energy per bond
EXAFS	Extended X-ray absorption fine structure spectroscopy

GB	Grain boundary
k	Thermal conductivity
k_B	Boltzmann constant
K	Dimensionless form of the radius of a sphere or the thickness of a plate
LEED	Low energy electron diffraction
LBA	Local bond average
MD	Molecular dynamics
P	Stress
$q(z_i)$	local measurable quantity in i th atomic layer
$Q(K)$	Measurable quantity of a nanosolid
R	Gas constant
SAW	Surface acoustic wave
SEM	Scanning electron microscopy
SFM	Scanning force microscope
TEM	Transmission electron microscopy
T_m	Melting point
$U(T)$	Atomic vibration/specific internal energy
Y	Young's modulus

Chapter 1 Introduction

1.1 Overview

Since the discovery of nanomaterials, there has been great interest in the synthesis and characterization of nanoscaled structures and devices because of their fascinating properties from scientific viewpoint and their great potential in technological applications [1, 2]. The increase of surface to volume ratio with decreasing size of the nanomaterials, or in another word, the percentage increase of the under-coordinated surface atoms, leads to the fact that the nanomaterials differ substantially from their elementary substances as well as their corresponding macroscopic counterparts. Compared with the corresponding bulk specimen, the surface to volume ratio of a nanoscaled specimen increases dramatically with its decreasing size. It has been reported that CdSe nanocrystals had 10%-50% of their total number of atoms exposed on the surface [3]. Taking iron particle for instance, with a diameter of 30 nm, only 5% atoms are on the surface. While for a nanoparticle with a diameter of 10 nm, the percentage of surface atoms increases to 20%, and there are more than 50% atoms sitting on the surface if the diameter of the iron nanoparticle decreases to 3 nm. The increasing surface to volume ratio leads to increasing portion of under-coordinated atoms with less atomic bonds, which provides a way to fine tune the physical properties of the nanomaterials, where the physical properties of the corresponding bulk materials are normally considered constants under given conditions. Because of the reduced mean atomic coordination number, these nanomaterials demonstrate novel mechanical,

electrical, thermal, acoustic, optical, dielectric and magnetic properties [4-7]. Substantial efforts have been made in theory [4] to uncover the mechanism behind. The unusual behaviors of a nanostructure go beyond the expectation in classical theories, such as continuum medium mechanics and statistic thermodynamics. The mechanical properties, for instance, the Young's modulus of a nanomaterial, is no longer constant but varies with the solid size, while thermal softening is often observed experimentally. It is interesting that the combination of new degrees of freedom involving both size and temperature provides us not only the opportunities to tune the physical properties, but also gain atomic information, which is beyond the scope of traditional approaches.

1.2 Challenges

Intensive experimental studies have been conducted on size and temperature dependent material properties and great amount of experimental database have been obtained in literature. However, fundamental progress in theory is still lagging far behind the experimental exploitations. Questions are still open for discussion. It is well known that the physical properties of a macroscopic system can be well described using classical approaches such as the Gibbs free energy or the continuum medium mechanics that relate the detectable quantities directly to the external stimulus such as the temperature, pressure, chemical composition, electric and magnetic field, without considering any atomistic origin. At the atomic scale, on the other hand, the quantum effect becomes the dominant factor and the physical properties of a small object can be reliably obtained from massive computations by solving Shrödinger equations or

Newton's motion equations with a sum of averaged interatomic potentials as a key element. However, for a small system in nanometer scale, both the classical approach and the quantum approach encounter some difficulties. In the continuum medium mechanics, entropy, volume, surface energy, and chemical potential of a particular element remain no longer constant but vary with material size. The quantum approach faces the boundary-condition problems, since the surface broken bonds induced surface trapping and the associated densification and localization of charge, energy, and mass in the surface skin will play significant roles in the variation of material properties. As a consequence, the averaged interatomic potential and the periodic boundary condition applied in quantum approach may be too ideal. Furthermore, the computational power increases dramatically with increasing number of atoms. Therefore, a model to bridge the gap between the classical macroscopic approach and the atomic quantum mechanics and to overcome the limitations encountered in both approaches is highly demanded. By extending the previously developed bond-order-length-strength (BOLS) mechanics [4], a set of analytical expressions from the perspective of local bond average (LBA) for the size, temperature and bond nature dependence of mechanical, lattice vibronic and thermal properties of the material under consideration are proposed and discussed in details in the following chapters.

1.3 Objectives

The main objectives of this project are:

- a) To present a survey on recent progress in both experimental observations and theoretical considerations on the size and temperature dependence of elastic, lattice vibronic, and thermal properties of various materials and structures including metals, nitrides, carbon based materials, group IV elements, nanowires, and surface skins.
- b) To develop a set of analytical solutions to predict the experimentally observed intrinsic effect of size, temperature, and bond nature on elastic, vibronic and thermal properties of systems from the perspective of bond formation, dissociation, and relaxation. To extend the previously developed bond order length strength (BOLS) correlation mechanism in size domain to local bond average (LBA) approach, which correlates the measurable quantities to the atomistic bonding identities including bond nature, bond length, bond strength, and coordination number of a representative local bond. Functional dependence of the experimental detectable quantities on the bonding identities and the response of the bonding identities to external stimulus such as coordination environment (BOLS effect), temperature (thermal expansion and vibration) will be established. A combination of the BOLS correlation and LBA approaches could provide a new way to study and predict the size and temperature dependence of various material properties.
- c) To gain atomistic insight into the physical origins of the size and temperature dependence of the mesoscopic elastic, lattice vibronic, and thermal properties in a bottom up instead of top down way. To find out dominating factors of the size and temperature dependent behaviors from the perspective of bond making and bond

breaking in order to provide guideline for device design. Furthermore, comparing the relative change of the experimental data with the standard value will allow us to distinguish the intrinsic contributions from the extrinsic artifacts involved in the experiments. More importantly, besides the theoretical consideration of its atomistic origin of various size and temperature dependent material behavior, the knowledge of general trends and the limitations of the changes are also needed prior to device design and fabrication.

- d) To extract information such as cohesive energy by matching the theoretical predictions to the experimental observations. A combination of the degrees of freedom of size and temperature may allow us to gain additional information such as the cohesive energy per bond and the dimer frequency in various systems. All these quantities are of elemental importance to surface and materials sciences.

1.4 Major achievements

The contributions to the work are as follows:

- a) Extended the previously developed BOLS correlation to temperature domain and proposed local bond average (LBA) approximation;
- b) Presented atomic understanding of the change of elastic, lattice vibronic and thermal properties upon size reduction and temperature variation;
- c) Derived analytical expressions for functional dependence of elastic, lattice vibronic and thermal properties, such as Young's modulus, Raman frequency shift, thermal expansion coefficient, surface energy density, and thermal conductivity on

bonding identities;

- d) Provided methods to obtain atomic cohesive energy and dimer frequency of various materials, which are beyond the scope of traditional approaches.

1.5 Organization of thesis

The thesis starts in Chapter 1 with a brief overview on current research interest on nanoscience and nanotechnology. A brief summary outlines existing questions and emerging problems in both classical and quantum approaches as well as the challenges faced in consistent understanding on the variation of materials properties upon size reduction into nanometer scale and temperature variation. The objects and main contributions are also discussed in this chapter. Chapter 2 presents theory considerations of the often-overlooked effect of surface broken bonds on the behaviors of the remaining bonds of the under-coordinated atoms, following recently developed bond order length strength (BOLS) correlation mechanism. The BOLS correlation has been extended to local bond average (LBA) approximation to include the temperature effect, as the thermal stimulus affects directly the length and strength of the bond through thermal expansion and thermal vibration. Principles and mathematical expressions are developed in this chapter. Chapter 3, 4, and 5 extend the analytical solutions to the functional dependence of elastic modulus, Raman frequency shift and thermal properties on the bonding identities (bond number, length, strength, and nature) and also their temperature dependence. Solutions have been applied to typical samples,

such as metals, group IV elements, carbon base materials (CBM), group III nitrides, and silicon nanowires. Good agreement between experimental observations and theoretical predictions has been obtained together with derived information on cohesive energy and dimer frequency. Improved understanding of the factors governing the intrinsic change of material properties upon size reduction and temperature variation are presented. Existing modeling considerations and understanding from various perspectives are also comparatively discussed. Chapter 6 gives a summary on the achievements and limitations of the present approaches. Prospects of recommendations on the extension of current developed approaches to atomic defects, impurities, interfaces, and systems under other stimuli such as pressure, electronic and magnetic fields are briefly addressed.

Chapter 2 Principles

2.1 The BOLS correlation

With device minimization, the dimension of solids or devices reduces into nanometer scale. The surface and interface effects become dominate factors in material property variation. The conventionally detectable physical quantities are no longer constants as in the case of bulk material, but can be adjusted by simply changing the size and the shape of the solids or devices. It is well known that a bulk solid performs differently from its elemental isolated atom because of the involvement of interatomic bonds. Comparing with the bulk solid, the nanomaterial contains a large portion of surface atoms and hence large percentage of under-coordinated atoms. As a consequence, the interaction between these under-coordinated atoms plays a significant role in the unusual behavior of nanomaterials. The general trend of size dependent material property change has attracted great research interest and led to important revolutions in material science and technology in recent decades. Numerous experiments have been carried out to study the size effect in order to fine tune the physical property prior to any device design and fabrication. However, from fundamental point of view, a consistent understanding on the physical origin and general trend of the material properties variation with size reduction is still lacking, although many models have been proposed for individual specified phenomenon. Recently developed bond order length strength (BOLS) correlation has provided us a consistent understanding on the variation of various materials properties from the perspective bond making and bond breaking.

2.1.1 Effect of lattice periodicity termination

For a perfect crystal, the unit cell repeats itself within the crystal. However, near the surface, this lattice periodicity is distorted. The termination of lattice periodicity in surface skin or at grain boundary will reduce of the coordination number (CN) of local atoms, which means the under-coordinated atoms at surface will have less number of bonds compared with those atoms in the bulk site [8]. This is called as CN imperfection in the following discussion.

Pauling [9] and Goldschmidt [10] have indicated earlier that if the CN of an atom is reduced, the ionic and metallic radius of the atom should contract spontaneously. Therefore, the under coordinated surface atoms with fewer interatomic bonds will relax and reconstruct on the quasi two dimensional surface, and hence leads to spontaneous length shrinkage of the remaining bonds of these under-coordinated atoms, disregarding the nature and the crystal structure of the specific bonds. The phenomena of bond contract have been well observed in many small systems using diffraction experiments [10, 13-18]. A coherent electron diffraction used by Huang et al. observed an out-of-plane bond length contraction of $0.2\text{\AA}$ for edge atoms, and $0.13\text{\AA}$ and $0.05\text{\AA}$ bond length contraction for $[100]$ and $[111]$ surface atoms, respectively [8]. Miller et al. observed that the interatomic bond length decreased with decreasing size for gold nanoparticles and they have reported a maximum contraction of $0.15\text{\AA}$ for gold nanoparticles with size smaller than $30\text{\AA}$ using EXAFS spectroscopy [11]. Similar results were also obtained by Comaschi et al. for gold nanoparticles ranging from 2.4 to 5.3 nm and temperature between 20K and 300K [12]. Other examples of bond length

contraction of surface layers has also been well observed in a number of simple, two-dimensional (2D), or metallic systems using experimental techniques such as low energy electron diffraction (LEED), medium-energy ion scattering, and X-ray diffraction [13, 14]. Moreover, theoretical study obtained bond length of gold dimer, trimer, and hexamers to be 2.58Å, 2.64Å, and 2.77Å, respectively from DFT calculations [15], while the bond length of bulk gold were reported to be 2.88Å. For liquid Sn, 10% contraction in spacing between first and second atomic layers comparing with that in the subsequent layers has been observed [16]. The earlier results have shown that displacements of the first three atomic layers are generally sufficient to describe the surface bond contraction [17]. Furthermore, the bond length contraction in the surface layer is expected to be stronger on a curved surface [8]. In addition to that, the CN may be slightly higher for a negative curved surface, such as the inner surface of a nanocavity [18]. The CN imperfection also happens at the following locations: facet, edge, step, corner, or grain boundary. Moreover, the bond angle deformation may also affect the CN. The driving force for the observed surface bond contraction has been attributed to surface electron charge density redistribution induced electrostatic force [19, 20] or chemical bonding strengthening with coordination reduction [9]. In addition, the relaxation of surface atoms in nanocrystals is constrained by their neighbouring atoms. Most experimental observations, if not all, have reported that surface bonds experienced bond contraction compared with those bonds in the interior (or bulk site). Some authors have experimentally observed first interlayer expansion of Rh (001), Pd (001), Be (0001). Although the aforementioned interlayer expansions have attracted a

lot of attention over the past decades, to our knowledge, despite some possible mechanisms, such as surface magnetism, finite temperature effects, as well as repulsive *d*-wave interactions for nearly filled *d*-shells, have been proposed to be possible reasons for the discrepancies, there is no theoretically model including DFT is able to predict these abnormal phenomena.

Generally, the CN of an atom in an fcc unit cell is considered to be 12, in a monatomic chain CN = 2, and in a single layer graphene, CN = 3. In this thesis, the CN of an atom is referred to the standard value of 12 in the bulk, irrespective to the bond nature or crystal structure. Comprehensive understanding in the effects of CN imperfection induced surface bond length contraction is important due to the impact they posed on surface energy, which is directly related to many size related nanoscale phenomena, including mechanical strength [4, 21, 22], thermal stability [22], magnetic modulation [23, 24], acoustic and optical phonons [25], dielectric suppression [26], and catalytic activity [8].

2.1.2 Potential well modification

Together with the bond length contraction of surface atoms, the strength of the remaining interatomic bonds will become stronger [9] spontaneously. The spontaneously strengthened surface bonds will cause localization and densification of charge, energy, and mass at these under-coordinated sites. The greater the bonding strength, the greater the localization of the electron density in the bonded region [27]. As observed in many experiments, the bond contraction is a spontaneous process.

Therefore, the binding energy of a relaxed bond must be lowered (raised in magnitude) in order to achieve a more stable state.

The surface bond contraction induced bond strengthening of under-coordinated surface atoms modifies the potential well by creating additional trapping centers in the region nearby the under-coordinated sites, as can be seen in Figure 1. The potential well confines only the nearly free electrons moving within the specimen, while the potential barrier (additional trapping centre) in the modified potential well localizes and densifies charge, energy, and mass at the trapping sites. This potential barrier perturbs the Hamiltonian, atomic coherency, and electroaffinity as well as the associated properties of a specimen. At the same time, it introduces new scattering sites. Figure 1 presents a schematic illustration of modified nanosolid potential well with multi-trapping centers introduced by CN imperfection. The conventional quantum well with a single trapping center extended from that of a single atom is also illustrated in bold line for comparison.

Figure 1 Schematic illustration of CN imperfection induced nanosolid potential

In Figure 1, V_{atom} is the intra-atomic trapping potential, which confines electrons, while V_{crystal} stands for the interatomic binding potential to bind atoms to form a solid. The

surface bond contraction together with spontaneous bonding energy enhancement of remaining bonds lowers the potential well near the surface (δ_{surf} in Figure 1), where the standard periodic potential well remains inside the bulk [28]. With increasing percentage of surface atoms upon material size reduction into nanometer scale, the modification of surface potential well becomes more and more important. Therefore, the traditional ‘quantum confinement’ theory that applies a periodic boundary condition to the whole system may be too ideal, and necessary modification to include additional surface trapping centers is required. This additional potential trapping is critical in electrical or thermal transport dynamics [29, 30].

The shortened and strengthened bonds in the surface region and the associated trappings shown in Figure 1 are believed to be the atomic origin of the various unusually tunable behaviors of a mesoscopic system whereas the degree of tunability is subject to the percentage of the under-coordinated surface atoms in the entire specimen. The pinning effect near under coordinated sites hinders atomic glide dislocations and hence enhances the mechanical strength locally. Potential well depression also contributes to the transport dynamics of phonons, electrons, and photons because of the additional trapping sites near the edges [29, 30]. Densification and localization of electrons with lowered binding energy in the traps have been observed at defect states [31], chain end states [32, 33], terrace edge states [34-36], and surface states [42-44]. Therefore, the broken bonds at the surface or defect region, or the dangling bonds, may not contribute directly to the performance of a specimen, instead, the remaining bonds of the under-coordinated atoms do take effect. Such CN imperfection induced change

of material properties can also be extended to structural defects, like voids, grain boundaries, dislocations, and so on.

2.1.3 Mathematical expressions for BOLS correlation

The core idea of BOLS correlation mechanism is that the surface under-coordinated atoms have less atomic bonds connecting with adjacent atoms, which causes the remaining bonds to contract spontaneously together with bond strength enhancement. Consequently, local strain and quantum trapping are formed immediately at the sites surrounding these surface atoms. According to Goldschmidt [10], Pauling [37], and Feibelman [38], if the coordination number (CN) of an atom is reduced from standard value 12 to 8, 6, 4, and 2, the radius of the under-coordinated atom would shrink spontaneously by 3%, 4%, 12%, and 30-40%, respectively, regardless of the nature of the specific chemical bond or the dimension or the structural phase of the substance [39]. On the premise of Goldschmidt, Pauling and Feibelman's observation, the bond contraction and the associated bond strength gain can be expressed as following:

$$\begin{cases} c_i(z_i) = d_i / d_b = 2 / \{1 + \exp[(12 - z_i) / 8z_i]\} \\ E_i = c_i^{-m} E_b \\ E_{B,i} = z_i E_i \end{cases} \quad (1)$$

where the subscripts i and b denote an atom in the i th atomic layer and in the bulk, respectively. i should be counted up to three from outmost atomic layer to the central of the sample under consideration. There is no bond order loss for $i > 3$, since the displacement of the first three atomic layers is generally sufficient to describe the

surface contraction [8]. The equation reflects 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 (with coordination number z_i) shorter and stronger with respect to their bulk counterparts. c_i is the coefficient of bond contraction, which is defined as the ratio of bond length at i th atomic layer to the bond length in bulk site, with z_i being the effective coordination of the corresponding atom of concern in the i th atomic layer. In general, $c_i < 1$. Index m is a key parameter that represents the nature of the bond. For metals $m = 1$, while for alloys and compounds m is about 4, and m value is optimized to be 4.88 for silicon [40]. In certain cases, if the remaining bonds at the surface expand, we only need to modify the value of c_i from being smaller than one to be greater than one and the m value from positive to negative to represent the spontaneous process for which the system energy is at its lowest level. E_b is the binding energy per bond, and E_B denotes the atomic cohesive energy of an atom under consideration. It is defined as the product of coordination number and single bond energy.

Figure 2(a) presents a graphical illustration of BOLS correlation. The bond contraction coefficient c_i is a function of coordination number z_i . It is presented as a solid line in Figure 2(a). The ionic radius contracts by 12%, 4%, and 3% when the CN reduces from standard value 12 to 4, 6 and 8, respectively [10]; they are presented as circles in Figure 2 (a). Squares represent the contraction of the dimer bond of Ti, Zn, and V, which is as much as 30% to 40% [38]. Furthermore, Comaschi observed 0.14%, 0.24%, 0.31%, and 1.01% of bond length contraction, which corresponds to CN = 11.8,

10.5, 11, and 9, respectively for Au nanoparticles (shown as down triangle in Figure 2(a)). Together with the literature data, we obtained an empirical expression of the bond contraction coefficient as a function of CN shown in Eq. (1), which is demonstrated as the solid line in Figure 2(a).

As a consequence of spontaneous process of bond contraction, the bond length reduces from one to c_i . Meanwhile the single bond energy at equilibrium, E_i , changes from E_b to $c_i^{-m}E_b$, which is normally greater than E_b as shown in Figure 2(b). The Lennard-Jones potential:

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

is used for illustration purpose in Figure 2(b), where ε is the depth of the potential well or the bonding energy of an atom in concern, and σ is the distance r_0 such that the inter-particle force is zero, or in another word, $\left. \frac{\partial u(r)}{\partial r} \right|_{r=\sigma} = 0$. According to Eq. (1), the binding energy increases with reduction of bond length and follows: $\varepsilon_i = c_i^{-m}\varepsilon_0$, when the bond length reduces from d_0 to d_i or the bond contraction coefficient reduces from 1 to c_i .

In Figure 2(b), the separation between $E_i(T)$ and $E_i(0)$ ($= \int_0^T \eta_{li}(t) dt$) is the thermal vibration energy or specific internal energy, which corresponds to the energy for thermal or mechanical rupture of the pairing bond. Separation between $E_i(T_{m,i})$ and $E_i(T)$ ($= \int_T^{T_{m,i}} \eta_{li}(t) dt$) corresponds the energy required for melting, which affects the extensibility and the yield strength in plastic deformation. η_1 is the specific heat per bond and η_2 is $1/z_i$ fold energy required for evaporating an atom from its molten state to

gas state or to become a completely free atom. The cohesive energy of a specified atom in i th atomic layer $E_{B,i}$, which is defined as the production of the reduced coordination number in i th atomic layer (z_i) and strengthened single bond energy (E_i), can be smaller, equal or even greater than the cohesive energy of an atom in the bulk site with different m values, as shown in Figure 2(a).

Figure 2 Illustration of the BOLS correlation. Solid line in (a) corresponds to the bond contraction coefficient with literature data from Goldschmidt (circles), Feibelman (square), and Comaschi (down triangle). The atomic cohesive energy with different m is also shown in (a). (b) Atomic CN imperfection modified pairing potential energy.

Generally, $z_1 = 1$, $z_2 = 6$, $z_3 = 8$ or 12 could be sufficient to describe the bond contract of outmost three layers. For curved surface, z_1 varies with the size and the curvature, following:

$$z_1 = \begin{cases} 4 \times (1 - 0.75 / K) & \text{for convex surface} \\ 4 \times (1 + 0.75 / K) & \text{for concave surface} \end{cases} \quad (3)$$

where K is the dimensionless form of radius of a nanowire or nanosphere that will be discussed later.

Based on BOLS consideration, the physical measurable quantities of a nanosolid containing N atoms with dimension K , can be expressed as $Q(K)$ as:

$$\begin{cases} Q(\infty) = N_j q_0 \\ Q(K_j) = Nq_0 - \sum_{i=1}^{i=3} N_i \times (q_i - q_0) \end{cases} \quad (4)$$

where q_0 and q_i correspond to the local density of measurable quantity Q inside the bulk and the region of the i th atomic layer, respectively. $Q(\infty)$ is the measurable quantity for the same sample without considering the effect of CN-imperfection or a measurable quantity for the corresponding bulk sample. Hence the relative change of size dependent quantity $Q(K)$ with respect to $Q(\infty)$ can be derived based on core-shell configuration and scaling relation, following:

$$\frac{\Delta Q(K)}{Q(\infty)} = \frac{Q(K) - Q(\infty)}{Q(\infty)} = \sum_{i=1}^{i=3} \gamma_i (q_i / q_0 - 1) = \sum_{i=1}^{i=3} \gamma_i \Delta q_i / q_0 \quad (5)$$

γ_i is the weighting factor, whose value is defined as the volume ratio between the i th atomic layer and the entire sample:

$$\gamma_i = \begin{cases} \frac{A \times d_i}{A \times H} = \frac{c_i}{K} & \text{Thin plate} \\ \frac{2\pi R \times d_i \times l}{\pi R^2 \times l} = \frac{2c_i}{K} & \text{Nanowire or nanorod} \\ \frac{4\pi R^2 \times d_i}{\frac{4}{3}\pi R^3} = \frac{3c_i}{K} & \text{Sphere} \end{cases} \quad (6)$$

$$\text{or } \gamma_i = \frac{\tau c_i}{K} \quad (7)$$

where A , L , and R are the surface area, length, and radius of thin plate, nanowire/nanorod, and sphere, respectively. K is the dimensionless form of size, which is defined as the number of atomic layers along the radius of a sphere or across the thin plate: $K = R/d_0$ or H/d_0 . τ in Eq. (7) is the dynamic dimensionality ($\tau = 1$ for thin plate or monatomic chain; $\tau = 2$ for nanowire or nanorod; $\tau = 3$ for spherical dot). In

nanostructure, when K approaches 3, only surface layers with under coordinated atoms remain. When $K = 1$, on the other hand, the nanostructure under consideration will become a thin plate, a monatomic chain, and an isolated atom when $\tau = 1, 2$, and 3, respectively. The weighting factor, γ_i , represents the geometrical contribution from dimension (K) and dynamic dimensionality (τ) of the solid, which determines the magnitude of the relative change with size reduction.

Figure 3 illustrates the derivation of the weighting factor γ_i for (a) thin plate (b) nanowire/nanorod, and (c) nanosphere.

Figure 3 Illustration of the weighting factor γ_i of a (a) thin plate (b) nanowire/nanorod, and (c) nanosphere

The quantity $\Delta q_i/q_0$ in the surface skin originates the change of various measurable quantities, 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. This is also demonstrated in deriving the size dependence of mechanical [41], electrical [29] and thermal properties [30] of nanostructures.

2.2 Local bond average (LBA) approximation

2.2.1 Limitations of classical and quantum approaches

As stated earlier, both classical and quantum approaches face difficulties in describing the variation of material properties observed in experiments.

For instances, the statistics in classical approach must be conducted over a large number of atoms N , with a standard deviation that is proportional to $N^{-1/2}$, where N is the total number of atoms in the system. In nanometer scale, the quantities such as entropy, volume, surface energy, and chemical potential of a particular element remain no longer constants but vary with solid size.

Quantum approaches are facing problems with boundary condition, which is a key component in nanoscience study. The periodic boundary condition is distorted in the surface region because of additional trapping centers created by contracted surface bonds. Furthermore, for compound materials, such as nitrides or an oxides, interactions in bonding, nonbonding (lone pair), and antibonding (dipole) are involved with rather anisotropic nature at the atomic level. During reaction, atomic positions change

collectively and the atomic valence varies dynamically associated with charge polarization and repopulation. Describing the anisotropic and dynamic bonding interactions in a small sample with the effect of skin trapping using averaged interatomic potentials and the periodic boundary conditions in quantum mechanics approach may not represent the true situation. Recent progress by extending the BOLS correlation mechanism to temperature domain shows that the difficulties could be solvable by considering the interatomic bond formation, dissociation, relaxation, and vibration, together with the associated energetic response of the corresponding atoms and electrons and their impact on the detectable quantities.

A bulky solid is formed by numerous atoms with bonds connecting one with another. The involvement of interatomic bonding makes the solid perform differently from its individual isolated atoms. For a given specimen no matter whether it is crystal, non-crystal, with or without defects or involving impurities, the nature and the total number of the atomic bonds do not change with external stimulus (such as temperature and pressure) unless there is a phase transition. Nevertheless, the length and strength of all involved bonds will response to the applied stimulus and react on the measurable quantities. Moreover, the changes in length and strength of all involved bonds with application of the external stimulus will directly relate to the changes of measurable quantities. Therefore, one only needs to focus on the effect of external stimulus on the length and strength of the corresponding representative bonds or their average in order to predict the performance of the entire specimen or difference sites of the specimen with the applied external stimulus. In another word, once the relation between the

measurable quantities under consideration and the bonding identity (bond length, strength, nature) of the representative bonds is established, we can predict the change of measurable quantities under external stimulus. This is the core idea of local bond average (LBA) approximation.

This LBA approach may represent the true situations of a specimen. Compared with the measurements and numerical computations, the LBA approach could distinguish the behavior of local bonds at different sites. The LBA approach is substantially similar to the volume partitioning approximation implemented by Delph and his co-workers [42, 43] who have opened a way in improving the calculation of such local quantities through volume partitioning and showed that volume averaging has been the correct way to obtain physically meaningful stress and elastic properties of complex microstructures. They examined the problem of deriving the absolute values of local stress and associated elastic constants for a region containing a fixed number of atoms that is part of a large body. By means of an expansion of the local interatomic potential energy, they derived expressions for the local second Piola-Kirchoff stress. With this approach, they have obtained good agreement with the suitably averaged continuum solutions in the far-field regime.

Unlike the volume partition approximation, the LBA approach seeks for the ratio of a quantity with the applied external stimulus against the already known standard value. It focuses merely on the performance of the local representative bonds disregarding the number of bonds in the given specimen or in the specified location. The presence of broken bonds, defects, impurities, or the non-crystallinity will affect the reference

values of concern rather the nature of observations. Contribution from long-order interaction or the high-order coordinates can be simplified by folding them into the bonds between the nearest neighbors.

2.2.2 Mathematical expressions for LBA approximation

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 bond, i.e.

$$Q = f(d_i, E_i, m, z_i) \quad (8)$$

In temperature domain, the bond nature and atomic coordination number (CN) remains constant unless phase transition happens; however, the bond length and bond strength are temperature dependent and follows:

$$E_{bi}(T) = E_{bi}(0) - \int_0^T \eta_{li}(t) dt \\ = \begin{cases} \eta_{2i} + \int_T^{T_{mi}} \eta_{li}(t) dt, & (T \leq \theta_D) \\ \eta_{2i} + \eta_{li}(T_{mi} - T) & (else) \end{cases} \quad (9)$$

$$d_i(T) = d_0 \left[1 + \int_0^T \alpha_i(t) dt \right]$$

The subscript i is the same as in Eq. (1), which refers to the i th atomic counting from outmost layer to the center of the bulk. η_1 is the specific heat per bond, which follows the universal relationship for the temperature dependence of the specific heat for most bulk materials C_V . Here C_V is the specific heat per atom, which is assumed to follow

$$\text{Debye model, } C_V(T) = \frac{9R}{N_A} (T/\theta_D)^3 \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx \quad (10)$$

or Einstein model, $C_V(T) = \frac{3R}{N_A} (\theta_E / T)^2 \cdot \exp(\theta_E / T) / [\exp(\theta_E / T) - 1]^2$ (11)

where θ_D and θ_E are the Debye and Einstein temperature, respectively. N_A is the Avogadro's constant, R is the gas constant, and $x = \hbar\omega/k_B T$. There is no substantial difference between the Debye's and Einstein's approximation of the specific heat numerically [44]. Both Debye's model and Einstein's model match each other very well at high temperature. It is therefore acceptable to assume the Debye approximation as Debye's approximation gives better fitting to experimental observation at very low temperature and there exists no better alternatives. The Debye approximation will be used in subsequent discussions. The integration of the specific heat gives the specific internal energy, which rises with the temperature due to the thermally excited lattice vibration in all possible phonon modes and is expressed as:

$$U(T/\theta_D) = \frac{\int_0^T C_V(t) dt}{N_A} = \frac{9RT}{N_A} \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \quad (12)$$

Figure 4 illustrates the temperature dependence of the specific heat C_V per atom (in unit of gas constant R) and the specific internal energy (the integration of specific heat with respect to temperature T , also in unit of R). It can be seen from Figure 4 that there are two sections in the U vs T curve. In high temperature range, especially when $T > \theta_D$, the integration of the specific internal energy increases almost linearly with temperature. This is due to the fact that the specific heat is almost a constant value in this temperature range; meanwhile in low temperature region, the specific internal energy is nonlinearly dependent on temperature and is observed to be proportional to T^4 . The non-linearity and value at high temperature range highly depends on the Debye temperature θ_D ,

which dictates the transition range from nonlinear portion to linear portion.

Figure 4 Illustration of the temperature dependence of the reduced specific heat (inset) and specific internal energy

To obtain the specific heat per bond, η_l , and the specific internal energy per bond, one only needs to divide Eqs. (10) and (12) by the number of bonds connecting the atom in concern or we have Eq. (13) following Debye's model:

$$\begin{aligned}\eta_l(T/\theta_D) &= \frac{C_V(T/\theta_D)}{zN_A} = \frac{9R}{zN_A} \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(e^x - 1)^2} dx \\ u(T/\theta_D) &= \frac{U(T/\theta_D)}{zN_A} = \frac{\int_0^T C_V(t) dt}{zN_A} = \frac{9RT}{z} \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1}\end{aligned}\quad (13)$$

In the concept of LBA approximation, one only needs to establish the relationship between the material quantities and the bonding identities of the repetitive bond in order to predict the material properties under external stimulus. Furthermore, this concept can also be extended to various other states, such as end states, defects states, impurity states, or interface states once the representative bonds is specified.

2.3 Summary

We have discussed the effect of atomic CN imperfection and its consequence on the bond length contraction and bond strength gain. Additional depressed surface potential well trapping near under coordinated sites has also been discussed following BOLS correlation. An extension of BOLS correlation to LBA approach allows us to study the entire specimen and a special location of a specimen by simply considering a representative bond and the response of this representative bond to the external stimulus. The mathematical expression for BOLS correlation and LBA approximation are presented, which will be applied in the following sections to study the size and temperature effects on various material properties towards consistent understanding of the physical insight of the size and temperature dependence of material properties as well as predictable design in current material science and technology.

Chapter 3 Elastic modulus

3.1 Definition and measurement methods

In solid mechanics, Young's modulus (Y) is defined as a measure of the stiffness of a given material, which indicates the rate of change of stress with respect to strain in elastic region. It is also known as modulus of elasticity or elastic modulus. The Young's modulus provides a way to predict the behavior of a material under external loads. For instance, it can be used to predict the amount that the specimen will extend under external tensile load, or to predict how much deformation will happen to the specimen under compression. Its SI unit is pascal ($1\text{Pa} \equiv 1\text{N/m}^2$), while the practical units are MPa or GPa. Young's modulus is one of the key elementary parameters in material science and engineering design. It is of fundamental significance not only to the mechanical behaviors, but also to the processes such as electron-phonon coupling, phonon-photon interaction, and phonon transport. Recently, many nanoscaled mechanical devices, such as nanoelectro mechanical systems (NEMS) including high-frequency oscillators and filters [45, 46], nanosensors [47] have been proposed.

According to the definition of Young's modulus, it can be calculated by dividing the tensile stress by the tensile strain, or in mathematical expression:

$$Y = \frac{\text{tensile stress}}{\text{tensile strain}} \quad (14)$$

Traditionally, for bulk solid, the Young's modulus measurement is conducted by applying an already known load to a well-characterized test instrument. Then from the deformation profile, the Young's modulus is calculated by putting stress and strain data

into Eq. (14). Some testing methods are codified by American Society for Testing and Materials (ASTM).

However, in micrometer/nanometer scale, the direct measurement of load vs deformation profile is not that straightforward and requires many sophisticated measurement techniques. The efforts to characterize small-scale mechanical properties of a material are driven by the need of reliably predicting the performance of such small scaled devices and also to develop detailed and accurate hierarchical models of the elastic behavior of complex, multi-component structural materials when the dimension and internal microstructural features are greatly reduced [48]. Similar to the measurement of Young's modulus for bulk material, the precise measurement in micro and nano scale is highly dependent on the accuracy in monitoring the applied force, stress and strain. The measurement of elastic properties requires sophisticated techniques and has been intensively studied recently. There has already been many good review works on various testing techniques of mechanical behavior of microscaled materials with the purpose of providing certain design and selection guideline for the measurement [48-53]. Han et al [53] provided a comprehensive review on the methodological development and technical applications of *in situ* microscopy, in investigating the elastic property of nanomaterial. These *in situ* microscopy include transmission electron microscopy (TEM) based tensile tester [54, 55], atomic force microscopy (AFM) based cantilever [56], nanoindenter [57-59], three-point bending tester [60] and scanning electron microscopy (SEM). Comparatively, the methods of surface acoustic waves (SAWs) [61, 62], ultrasonic

waves, field-induced oscillations, and atomic force acoustic microscopy (AFAM) [63, 64] could minimize the artifacts because of their nondestructive nature. Srikar and Spearing [50] detailed studied and compared various microscale and nanoscale mechanical test techniques, including microtension test, axisymmetric plate bend test, microbeam bend test, M-test, fabrication of passive strain sensors, and Raman spectroscopy. Besides nanoindentation methods [65, 66], scanning force microscope (SFM) [67], and bulge testing [68-72] are also well applied in small scale.

The mechanical measuring techniques in micro and nano scale have been intensively studied and greatly developed in the past few decades. Meanwhile, the operation environment of the device or structure under concern, such as the internal temperature, may vary from time to time, which also requires special attention in device design and fabrication.

3.2 Temperature dependent Young's modulus

The structures or devices are usually operated at different temperatures from their fabrication condition, and the operation temperature may also change from time to time. Hence, understanding of the thermally-induced mechanical behavior is also of fundamental importance to the material science and device design. Generally, it has been observed that the temperature dependent Young's modulus or the Y vs T curve follows [71-78]: (i) it decreases with increasing temperature monotonically; (ii) it approaches a constant value when T approaches absolute zero with near zero slope; (iii) it has a negative slope at high temperature; and (iv) it has almost linear behavior at high

temperature.

The temperature-induced softening of substances has been widely seen for both organic and inorganic specimens regardless of the sample size. Various experiments and simulations in temperature domain have been conducted and confirmed the observations. For instance, when testing temperature was raised, the mechanical strength was reduced, such as in the cases of nanograined Al films [73] and nanograined diamond films [74]. At higher temperatures, the bending stiffness and the apparent Young's modulus of the diamond beams were drastically reduced to one third of the initial value before fracture. The flexural strength and the modulus of the hydrosilylated and condensed curable silicone resins were also decreased when the testing temperature was increased [75]. The yield stress of Mg nanosolid [76] of a given size dropped when the temperature was increased. An atomic-scale simulation [77] suggested that the material became softer in both the elastic and the plastic regimes as the operating temperature was raised. When measured at 200 °C, the strength of the 300-nm-sized Cu nanograins was lowered by 15% compared with that in room temperature and the ductility increased substantially [78]. The biaxial Young's modulus of Si(111) and Si(100) dropped linearly when T was increased [79]. The Young's modulus of the TiN/Mo_xC multilayer films increased with the decrease of the modulation period and dropped when the temperature raised from 100 to 400 °C [80]. The Young's modulus of α -Pu at 0 K was 1.303 times the value of α -Pu at room temperature [81]. An MD investigation suggested that the longitudinal Young's modulus and the shear modulus for both armchair and zigzag nanotubes changed in

different trends over the temperature range of 300 - 1200 K. Y value dropped while the shear modulus increased as temperature increased [82]. Also, detailed examinations have shown that the measured Y values dropped nonlinearly at very low temperatures and then followed a linear relation at higher temperatures [83]. When the operation temperature increased from room temperature to 400 °C, the ductility of the ultrafine-grained FeCo₂V samples of 100-290 nm size increased from 3 - 13% to 22% [84].

As discussed above, the thermally induced softening of the elastic strength has been well observed in many experiments; however, the mechanism behind is still not clear enough. In the following session, theoretical consideration and reproduction of temperature dependent Young's modulus will be discussed.

3.2.1 Modeling consideration

The temperature induced change of Young's modulus has been studied in early decades. It is believed to be caused by the anharmonic effect of the lattice vibration. Born and Huang [85] showed that at sufficient low temperature, the elastic constant was proportional to T^4 that satisfied the third law of thermodynamics, and that the derivative of the elastic constant with respect to temperature must approach zero as T approaching absolute zero degree. Wachtman et al., firstly, proposed a semiempirical formula with Boltzmann factor $\exp(-T_0/T)$, to demonstrate the temperature dependent Young's modulus [86]:

$$Y(T) = Y_0 - bT \exp(-T_0 / T) \quad (15)$$

where $Y(T)$ is the Young's modulus at temperature T , and Y_0 is the Young's modulus at absolute 0 K. b and T_0 are arbitrary constants. At high temperature, that is when $T \gg T_0$, the Boltzmann factor $\exp(-T_0/T)$ tends to a unit. Then Eq. (15) can be simplified as $Y(T) \approx Y_0 - bT$, which demonstrates a linear dependence of Y on T . At absolute 0 K, the Young's modulus in Eq. (15) approaches a constant value Y_0 , which is consistent with experimental observations. Wachtman et al. have obtained well fitting to experimental data of several oxides, such as Al_2O_3 , MgO , and ThO_2 [86] and some nitrides, such as AlN , MgSiN_2 , and Si_3N_4 [87].

Later on, Anderson [88] and Nandanpawar [89] tried to justify Wachtman's equation and to relate the arbitrary constants to Grüneisen constant and Debye temperature. Anderson attempted to interpret Wachtman's exponential from Grüneisen parameter, such that:

$$b = 3R\gamma\delta / V_0 \quad (16)$$

In which, R is the gas constant, V_0 is the specific volume per “average” atom at 0 K, γ is the Grüneisen parameter, which is defined in terms of the thermal properties, following:

$$\gamma = -\frac{V(\partial V / \partial T)_p}{C_p(\partial V / \partial P)_s} = \alpha_V V B_S / C_p \quad (17)$$

and δ is another important physical constant defined as:

$$\delta = -(1/\alpha_V)(\partial \ln B_S / \partial T)_p \quad (18)$$

Both γ and δ are assumed to be temperature independent by Anderson. α_V is the volume thermal expansion coefficient and B_S is adiabatic bulk modulus. The detailed derivation of Wachtman's equation starting from Mie-Grüneisen equation of state, can be found from Ref [88] and [89]. The temperature dependent bulk modulus from Anderson [88]

and Nandanpawar [89] can be expressed as:

$$B_S(T) = B_{S_0} - \gamma\delta / V_0 \times E \quad (19)$$

where E is the internal thermal energy. Using the Debye approximation for the E , the thermal energy for one mole atoms is given as:

$$E(\theta/T) = 3RT \times H(T/\theta_D) \quad (20)$$

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

which actually is specific internal energy in Eq. (12). Eq. (19) is derived for adiabatic bulk modulus B_S in Anderson's approach. However, the bulk modulus and Young's modulus satisfy $Y/B_S = 3(1-2\nu)$, where ν denotes the Poisson constant. For small and nearly constant ν , $d\nu/dT \ll 1$, and the bulk modulus can be replaced by the Young's modulus where $B_S = 1/3Y$. Thus Eq. (19) is also valid for Young's modulus. Compared with Wachtman's model, it is easy to get that:

$$b = R\gamma\delta / V_0 \text{ and } T_0 \cong \theta_D / 2 \quad (21)$$

Lakkad obtained similar form of temperature dependent Young's modulus as Anderson [90]. He assumed that the vibrating mass points formed linear chains and the oscillation was anharmonic. By solving the Hamiltonian of 1D anharmonic oscillation subjected to stress field, the mean position of the mass points and hence the averaged effective strain over the entire frequency spectrum could be obtain. Following the definition of Young's modulus, he confirmed Anderson's expression.

3.2.2 LBA approximation

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 functional relationship between Young's modulus and the bonding identities (z_i, d_i, m_i, E_i) of the representative bond.

The surface stress P and the Young's modulus Y can be derived from the Lennard-Jones potential in Eq. (2), such that:

$$\begin{cases} P = \left. \frac{\partial u(r)}{\partial V} \right|_{r=d} \propto \frac{E_b}{d^3} \\ Y = V \frac{\partial P}{\partial V} = V \left. \frac{\partial^2 u(r)}{\partial V^2} \right|_{r=d} \propto \frac{E_b}{d^3} \end{cases} \quad (22)$$

where $u(r)$ is the pairing potential and V is the volume. Eq. (22) indicates that: the surface stress (P) corresponds to the first order differential of the binding energy with respect to volume. It reflects the internal energy response to volume change. Meanwhile, Young's modulus (Y) is the second order differential of the binding energy with respect to volume and is also proportional to binding energy per unit volume from the perspective of dimension. Hence, Young's modulus and the surface stress share the same dimension and the same functional dependence on bonding identities.

Extending Eq. (22) to temperature domain, by considering the temperature dependent bond length and bond energy in Eq. (9), it is easy to get the following relationship for the temperature dependence of Young's modulus:

$$\frac{Y(T)}{Y_0} = \left(1 + \int_0^T \alpha(t) dt \right)^{-3} \left(1 - \frac{\int_0^T C_V(t) dt}{E_B(0)} \right) \quad (23)$$

where Y_0 is the reference Young's modulus at 0 K, $\alpha(t)$ is the temperature dependent thermal expansion coefficient; $E_B(0)$ is the atomic bonding energy at 0 K; $C_V(T)$ is the

specific heat which follows Debye's model of specific heat indicated in Eq. (10). Its integration from 0 K to T gives the specific internal energy following Eq. (11). Eq. (23) is the same as the expression given in Anderson's model, Eq. (20), except the involvement of temperature induced lattice expansion in Eq. (23). Therefore, we have reconfirmed Anderson's expression from the atomistic bonding perspective, while the thermal expansion upon temperature rise must also be included in the calculation.

In high temperature range (general refers to $T \gg \theta_D$), the specific heat C_V can be considered as a constant, approaching $3R$ according to Dulong-Petit law. The thermal expansion coefficient α is normally in a range of 10^{-6} , and hence $\int_0^T \alpha(t)dt \sim 10^{-3}$ and varies very little with temperature. Therefore, Eq. (23) can be approximated as:

$$Y(T) = AY_0(1 - 3RT/E_B(0)) = AY_0 - B_1 \times T \quad (24)$$

where $A = (1 + \int_0^T \alpha(t)dt)^{-3}$ is almost a constant, and $B_1 = 3ARY_0/E_B(0)$ is also a constant; therefore, the temperature dependent Young's modulus can be simplified as:

$$Y(T) = \text{Const1} + \text{Const2} \times T,$$

It shows that the Young's modulus is having a linear relationship with temperature at very high temperature. When the temperature of consideration approaches absolute

zero, the specific heat follows: $C_V \cong \frac{12R\pi^4}{5}(T/\theta_D)^3$, and the thermal expansion effect

approaches zero ($\int_0^T \alpha(t)dt \sim 0$). Therefore Eq. (23) can be rewritten as:

$$Y(T) = Y_0 \left(1 - \frac{3R\pi^4}{E_B(0)\theta_D^3} \times T^4 \right) = Y_0 - B_2 \times T^4 \quad (25)$$

When T approaches 0 K, $Y(T)$ approaches a constant Y_0 , and the slope of Y - T curve is also zero, which are consistent with experimental observations. Furthermore, the

relative change of elastic constant is proportional to T^4 satisfies the discussion in Ref [85]. As a conclusion, Eq. (23) satisfies the characteristics (i) to (iv) of Y vs T curve discussed in earlier paragraph.

In Eq. (23), $E_B(0)$ is the only fitting parameter, which is defined as the atomic cohesive energy, the energy required to completely free an atom from the bulk site as earlier discussed. To calculate the temperature dependent Young's modulus, first of all, the Y vs T relation in high temperature range is considered. In this temperature range, the slope B_1 (in Eq. (24)) of Y - T curve can be easily obtained from experimental data, and therefore the atomic cohesive energy $E_B(0) = 3RY_0/B_1$ can be roughly estimated. This estimated $E_B(0)$ is used then as an initial guess in the iteration of refinement and it can be further refined by carefully fitting the experimental data at the whole temperature range together with the consideration of the T -dependent thermal expansion coefficient. The Debye temperature, θ_D , and temperature dependent thermal expansion coefficient, $\alpha(T)$, are taken as the known data from literature.

Figure 5 shows agreement between LBA predictions and the measured temperature dependence of Young's modulus for various materials. The solid lines correspond to LBA predictions, and the scattered symbols represent experimental data in literature, for example (a) group IV elements, (Si, Ge, and diamond), (b) metals (Ag, Au, and Pu), and (c) nitrides (AlN, GaN, and Si₃N₄) and oxides Al₂O₃. The experimental source data and derived atomic cohesive energy at 0 K, $E_B(0)$, from Figure 5 are listed in Table I. Besides, the cohesive energy of some elementary samples from Kittel [91] are also listed in Table I for comparison.

Figure 5 Agreement between predictions and the measured temperature dependence of the relative change Young's modulus of (a) Group IV elements (b) metals and (c)

nitrides and Al_2O_3 .

Table I List of experimental data source, cohesive energy derived from Figure 5, and cohesive energy of some elementary samples from Kittel.

Materials	Exp Data Source	$E_B(0)$ (eV)	Kittel (eV)
Si	[92]	4.33	4.63
Ge	[93]	2.65	3.85
Diamond	[94]	5.71	7.37
Pu	[81]	0.314	6.74
Ag	[95]	1.137	2.95
Au	[95]	1.633	3.81
AlN	[96]	5.327	-
GaN	[97]	6.348	-
Si_3N_4	[87]	12.36	-
Al_2O_3	[86]	3.90	-

3.3 Size dependent Young's modulus

Traditionally, the Young's modulus of a bulk material is deemed as a constant and is independent of the size and the shape of the structure at a given temperature [83].

However, upon structural miniaturization into nanometer regime, the Young's modulus is no longer a constant but changes with the size and shape of the solid. Experimental

observations have revealed surprisingly that the Y -value changes in three different trends: elevation, depression, or retention as the solid size is reduced. For inorganic nanomaterials with higher T_m , the modulus was often observed to increase at ambient temperature when the solid size is decreased, such as observed from Si nanospheres [98], Ag nanowires [99], quartz crystal oscillators [100], Si_3N_4 nanobelts [101], TiCrN and TiAlN surfaces [102], Al and Si nanobelts [103], ZnO nanowires [104], and nanobelts [105]. However, an opposite trend in the (0001) oriented ZnO nanobelts/wires showed lowered modulus varying from 29 ± 8 [106] to 38–100 GPa [107, 108], comparing with that of the bulk ZnO at 140 GPa. The Young's modulus of Ag and Pb nanowires with diameter of 30 nm was observed to be approximately twice the Young's modulus of bulk materials using resonant-contact atomic force microscopy (AFM) measurement [109], while for large diameters (> 70 nm for Ag, and > 100 nm for Pb), the measured Young's modulus were almost independent of size and were close to the bulk values reported in the literature. Same results were observed for polypyrrole nanotubes [110, 111]. A study using atomistic combined microscopy of high-resolution TEM/scanning probe microscopy reported that the value of Young's modulus increased to 18 ± 2 GPa for a 10-nm Si $\langle 100 \rangle$ nanowire [112]; however, the value of Y of Si [85] wires were found to be bulk like [113]. An atomic force acoustic microscopy (AFAM) measurement [114] has revealed that the modulus of nanocrystalline Ni films of 50 - 800 nm thick was lower than the bulk value. An AFM measurement in room temperature [115] has revealed that the local Young's modulus of organic thin films that can evaporate at ~ 450 K decreased with sizes. The moduli of Cr [116] and Si [117]

nanocantilevers and ZnS [118] nanobelts were also measured to decrease sharply with decreasing diameters. The Young's modulus Y of α quartz was calculated to be decreasing with decreasing size at 10 and 300K [119]. Furthermore, Haque and Saif [120] reported a 30% decrease of the elastic modulus for thin Au films with grain size of 15 nm, while films with 75 nm grain size yielded approximately the same elastic modulus as bulk Au. In contrast, amorphous Si [121], Au [122] and Ag [122] nanowires show no apparent change with size if we count out the scattered error bars in measurement. Therefore, it can be concluded that in most cases, the measured Young's modulus increases with decreasing size, but in certain cases, even for the same material such as Ni, Ag, ZnO, and Si, the value of Y may decrease or remain unchanged with decreasing size, depending on the experimental techniques and operation conditions.

In consideration of the high demand on nanoscaled materials, the process of design and fabrication of these devices and structures is extremely challenging. New techniques for synthesis, characterization, integration, as well as theoretical modeling are urgently needed.

3.3.1 Modeling consideration

Besides various new measurement means [52-55, 58, 70, 135-138], some theoretical models have been proposed to predict the shape and size effect on Young's modulus [119, 123, 124]. The elastic property of nanosized structures is expected to be size dependent because of the increase of surface to volume ratio [103, 125, 126]. This argument was emphasized through computer simulations using atomistic techniques on

α quartz [119] with empirical three body potential used by Nakano et al. [127]. In their model, the authors assumed a core-shell structure with bulk modulus Y_B for core region and a difference value of Young's modulus Y_S for surface skin:

$$Y = Y_B \left(\frac{A_B}{A_{Tot}} \right) + Y_S \left(\frac{A_S}{A_{Tot}} \right) \quad (26)$$

where A refers to cross-sectional area, and subscripts B , S , and Tot refer to bulk, surface, and total, respectively. The sum of A_B and A_S , of course, must equal to A_{Tot} . Besides the effect of surface to volume ratio, the edge to volume ratio was also considered as one of contributor to size dependent change of Young's modulus [119]. Therefore, Broughton et al. modified Eq. (26) by adding one additional term as shown in Eq. (27), where the subscript C corresponds to corner, or edge.

$$Y = Y_B \left(\frac{A_B}{A_{Tot}} \right) + Y_S \left(\frac{A_S}{A_{Tot}} \right) + Y_C \left(\frac{A_C}{A_{Tot}} \right) \quad (27)$$

In both equations, a surface skin depth $10 \text{ \AA}$ is chosen in the simulation. This core-shell structure is frequently applied in describing size dependent Young's modulus. For instance, in studying the size effect on Young's modulus for ZnO nanowires, Chen et al. defined that the effective flexural rigidity of ZnO nanowires follows [104]:

$$YI = Y_B I_B + Y_S I_S \quad (28)$$

The subscripts B , and S have the same meaning as in Eq. (26). I_B and I_S are the moment of inertia of the core and shell region, respectively. Hence for nanowires, the size dependent Young's modulus follows:

$$Y = Y_B \left[1 + 8 \left(\frac{E_S}{E_0} - 1 \right) \left(\frac{r_s}{D} - 3 \frac{r_s^2}{D^2} + 4 \frac{r_s^3}{D^3} - 2 \frac{r_s^4}{D^4} \right) \right] \quad (29)$$

where D is the nanowire diameter, and r_s is the shell or skin depth, which is estimated to

be 4.4 nm in their model, which is 4.4 times larger than that in Broughton's simulation.

Another study suggested that the size dependency of Young's modulus was contributed by the nonlinear response of the nanowire core and the surface elasticity modification resulting from surface stress [123]. The authors performed molecular static simulations for square cross-sectional copper nanowires with side length ranging from 1.2 to 14.0 nm. The core-shell structure was applied in the simulation, for which the shell layer includes surfaces as well as edges whose elastic properties deviated significantly from that of the corresponding bulk. This calculation provided an atomic insight into the surface and edge effects. However, the empirical potential applied is still a debatable point, since in multicomponent systems the empirical potential is either not available or not trustable.

With this in concern, Lee and Rudd [124] applied first principle quantum elastics to study the size dependent Young's modulus of hydrogen-passivated Si <001> nanowires based on density function theory (DFT) to predict the mechanical behavior of nanoscaled structures. This first principle calculation does not rely on any empirical potential as required in continuum model and classical atomic calculations. Instead, it is done by solving the quantum mechanical Kohn-Sham equation. In their approach, the Young's modulus was defined as the second derivative of the DFT total energy with respect to the applied longitudinal strain divided by the volume. They have concluded that the Young's modulus became softer monotonically from the bulk value with decreasing size and roughly proportional to the surface area to volume ratio. However, this method is very time consuming and requires a lot of CPU time.

3.3.2 BOLS consideration

With the LBA and the BOLS in mind, and taking the core-shell configuration of a nanosolid into consideration, we are able to reproduce the observed trends and hence clarify the long-standing discrepancy in observations. From Eq. (22), the Young's modulus is related to bond identities such as $Y \propto \frac{E_b}{d^3}$. In the core-shell configuration, the bond nature (m), shape and size (τ, K_j) dependence of the relative change of the Y can be obtained by summing the contribution over the outmost three atomic layers. According to Eq (5), the local quantity q equals E_b/d^3 . If only size effect is considered, the relative change of Young's modulus at extreme low temperature with respect to the bulk modulus can be expressed as:

$$\frac{\Delta Y(K_j)}{Y(\infty)} = \sum_{i=1}^{i=3} \gamma_i \left(\frac{E_i}{E_b} \times \frac{d_0^3}{d_i^3} - 1 \right) = \sum_{i=1}^{i=3} \frac{\tau_i}{K_j} (c_i^{-(m+3)} - 1) \quad (30)$$

Note that Eq. (30) is valid at low temperature where the temperature effect is very small.

It is quite obvious from Eq. (30) that the local Young's modulus in the first three layers is higher than that in the bulk region. In another word, in the core-shell model, the surface Young's modulus is greater than its corresponding bulk modulus. Figure 6 gives the predicted size and shape dependent relative change of Young's modulus. It can be seen that the Young's modulus increases with decreasing size at low temperature, and the percentage of increase is more obvious for nanosphere because of its higher surface to volume ratio compared with thin plate and nanowire. In case of thin plate, the relative change of Young's modulus is only about 1.5% when K increases to 65. Figure 7 gives one example of relative change of Young's modulus for ZnO nanowires. The scatters are from experimental measurement [104].

Figure 6 Predictions of size and shape dependent relative change of Young's modulus.

Figure 7 Size dependent Young's modulus for ZnO nanowire

As previously stated, the Young's modulus may increase, decrease or even remain unchanged depending on the measuring techniques and measurement conditions. From previous sessions, it can be seen that the Young's modulus decreases with increasing temperature of measurement, whereas it increases with decreasing size in nanometer regime when the temperature approaches absolute zero degree in nanometer regime. The individual effect of temperature or size on Young's modulus has been well discussed in previous sessions; however, there are very few experimental or simulation

results available in literature to discuss combined effects of temperature and size on

Young's modulus. Here, by combining Eqs. (23) and (30), we have:

$$\begin{aligned}
 \frac{q(i, T)}{q(b, 0)} &= \frac{Y(i, T)}{Y(\infty, 0)} = \frac{E(i, T)}{E(\infty, T)} \times \left[\frac{d(i, T)}{d_0} \right]^3 \\
 &= \left(\frac{\int_T^{T_{mi}} \eta_{1i}(t) dt + \eta_{2i}}{\int_T^{T_m} \eta_1(t) dt + \eta_2} \right) \times c_i^{-3} \times (1 + \alpha T)^{-3} \\
 &\stackrel{T \gg \theta_D}{\approx} \left(\frac{\eta_{1i}(T_{mi} - T) + \eta_{2i}}{\eta_1(T_m - T) + \eta_2} \right) \times c_i^{-3} \times (1 + \alpha T)^{-3} \\
 &\approx \left(1 - \frac{T / z_{ib} c_i^{-m}}{T_m + \eta_{21}} \right) \times c_i^{-(3+m)} \times (1 + \alpha T)^{-3} \\
 \frac{\Delta Y(K, T)}{Y(\infty, 0)} &= \sum_{i=1}^{i=3} \frac{\pi c_i}{K} \left(\frac{\Delta q_i}{q} \right) = \sum_{i=1}^{i=3} \frac{\pi c_i}{K} \left[\left(1 - \frac{T / (z_{ib} c_i^{-m})}{T_m + \eta_{21}} \right) \times c_i^{-(3+m)} \times (1 + \alpha T)^{-3} - 1 \right] \quad (31)
 \end{aligned}$$

Figure 8 shows one example of the predicted relative change of Young's modulus in high temperature range, which includes both contribution from size and temperature. In this figure, a unit T_m , $\theta_D = 0.3 T_m$ are assumed for illustration purpose. It can be seen that the Young's modulus may increase, decrease, or remain unchanged depending the combination of contradictory factors (size and temperature).

Figure 8 Predictions of size and temperature dependent relative change of Y .

3.4 Summary

The experimental observed size and temperature dependence of elastic modulus has been discussed with the theoretical models proposed. A set of analytical expressions for the size, temperature, and bond nature dependence of the elastic modulus has been established in terms of bonding identities and their thermal dependency following BOLS correlation in size domain and LBA approximation in temperature domain. Consistency between the predictions and the experimental data has evidenced the validity of BOLS correlation and LBA approximation. Furthermore, the prediction to the experimental data shows that:

- (a) The temperature dependent Young's modulus decreases monotonically with increasing temperature. The Young's modulus linearly depends on T in high temperature range, while changes nonlinearly in low temperature range.
- (b) The Young's modulus increases with decreasing size when the temperature of measurement is in low temperature range.
- (c) The Young's modulus of a nanosolid may increase, decrease, or remain unchanged depending on the size, temperature of operation, and the nature of the bond involved. Therefore, it is not surprising to observe that the Young's modulus change in different trends for different materials under different measurement conditions. It is suggested that one could not consider an individual parameter at a time without addressing the rest when discussing the mechanical and thermal properties of a material, especially for a small object.
- (d) Agreement between observations and predictions of the T -dependent Young's

modulus has allowed us to derive information about the atomic cohesive energy of an atom in the bulk, which goes beyond conventional theoretical and experimental approaches.

Chapter 4 Raman frequency shift

4.1 Definition and measurement methods

Studies of the vibronic properties of nanostructured materials are aimed at a better understanding of the fundamental physical properties of strongly confined electrons and phonons. Raman spectroscopy is one of the very efficient measuring techniques for the investigation of electron-phonon coupling (EPC) that is important for better understanding of the optical and electrical properties of nanostructures with confined electrons and phonons.

The vibronic behavior of nanoscaled materials has also been subject to intensive studies in the past few years. Raman Spectroscopy, first discovered in 1928 by Sir C.V. Raman, who won the Nobel Prize in Physics in 1930 [128, 129], is widely used to probe a material by visible light, near infrared or near ultraviolet source to obtain material vibronic information. Raman measurement was originally used as a method to identify organic solvents and compounds, which was accomplished by recognizing characteristic vibrations that correspond to different bonds in the material. The Raman scattering occurs when the incident monochromatic light (photons) impinges on a molecule and interacts with the electron cloud of the bonds of that material. The scattering process then forms a kind of electronic or vibronic spectrum: intensity vs wavelength, or so called Raman spectrum. In classic view, the Raman scattering can be seen as a perturbation of the molecule electronic field by the incident photons, while in quantum mechanics, the Raman scattering process can be described as: an incident photon

excites one atom from its lower energy state into a virtual higher energy state, and then this atom relaxes from its virtual higher energy state to a vibrational excited state. There are two kinds of Raman scattering, one is called as Stokes Raman scattering and the other is called as anti-Stokes Raman scattering, which is shown in Figure 9. The difference between these two is whether the initially excited molecule is in ground state or in an elevated vibrational energy state. Normally, the Raman shift is described in unit of frequency (cm^{-1})

Figure 9 Energy level diagram for Raman scattering, (Left) Stokes Raman scattering (Right) Anti-Stokes Raman scattering.

According to its definition, a typical Raman spectrometer is made up of three main parts: (i) A laser that generates coherent monochromatic light beam (visible, near infrared, or near ultraviolet); (ii) A collection device that collects the scattered photons and filters out unnecessary signals; (iii) A detector that detects the transmitted photos from the collection device and to record the intensity of the Raman signal at each wavelength in Raman spectrum. With these three main components in mind, several

Raman systems, such as Reinshaw Raman spectroscopy, have been well developed for Raman measurement. Meanwhile the combination with scanning probe microscopy, (e.g. AFM) and Raman spectroscopy provides a new tool in nanotechnology. Integration with additional equipments such as Linkham heating stage or diamond (or sapphire) anvils is commonly used to obtain temperature and pressure dependent Raman frequency shift. Alternatively, the temperature effect on Raman frequency shift can also be observed by modifying the incident laser power density, which creates local heating on the sample. However, this method is not used as often as the one using heating stage because the relationship between incident laser power density and local temperature cannot be that easily to be monitored.

Different frequency peaks can be observed in a Raman spectrum with different notations, such as G peak, E peak, and D peak, which correspond to different frequency modes that relate to the lattice vibration direction and manner according to group theory. Detailed discussions on the crystal structure (group theory) and Raman frequency will be presented later.

Today, as a sensitive, non-destructive, and fast measuring technique, Raman scattering has been widely used in optical characterization of solids such as lattice dynamics and electronic properties. Furthermore, Raman spectroscopy offers one major advantage for microscopic analysis: since it is a scattering technique, it is a non-destructive process and the specimens do not need to be fixed or sectioned.

4.2 Temperature dependent Raman frequency shift

The vibronic behavior of atoms with changing temperatures in a specimen is not only of fundamental significance to the processes such as electron-phonon coupling, phonon-photon interaction, and phonon transport, but also important to practical applications in the fields such as short wavelength light emitter, high temperature, high frequency, high power electronic and thermal devices [29, 146-148]. Generally, the Raman peaks shift to lower frequencies when the measurement temperature is increased. Typical samples who exhibit above mentioned behavior include group III-nitrides, like GaN [149-154], AlN [149, 155, 156], and InN [24, 130]; group IV elements, Si [158-162], Ge [160, 163-166], some carbon-based-materials (CBMs), like diamond [84, 167-172], graphite [131, 132], CNTs [175-182], and graphene [133, 134], as well as some other compounds, such as CdSe [135], ZnSe [143-145], ZnO [136]. The curve of Raman frequency shift vs T is quite similar to Y vs T curve, such that: the thermally driven Raman frequency shift of the all frequency modes decreases monotonically with increasing temperature in the entire temperature range, and it decreases nonlinearly in low temperature range and approaches a constant value when temperature approaches absolute zero degree, and almost decreases linearly with increasing temperature in high temperature range.

4.2.1 Modeling consideration

Klemens [137] assumed that the Raman redshift is arisen from the decay of one optical phonon into two acoustic phonons of the same frequency but opposite momentum.

Later, Balkanski et al. [138] modified Klemens's model by further including the phonon-phonon interaction up to the fourth order. With this model, they have calculated Raman frequency shift and line width of the first-order Raman active longitudinal optic (LO) mode.

Figure 10 Illustration of three- and four-phonon anharmonic processes that contribute to the decay of the Raman active LO mode in silicon from Ref [138].

Figure 10 schematically demonstrates three- and four-phonon anharmonic processes contributed to the decay of the Raman active LO mode for silicon [138]. The scattering process can be viewed such that an incident light with energy $\hbar\omega_I$ is absorbed followed by an emission of a photo with energy $\hbar\omega_S$ and creation of an optical phonon $0j$. This phonon is then decayed via anharmonicity into two phonons, three phonons as shown in Figure 10 (a) and (c). If the process happens at nonzero temperatures, this scattering

process may also involve absorption of another phonon and emission of one or more phonons as shown in Figure 10 (b) and (d). However, this process is seldom considered in theoretical calculations.

The observed Raman frequency redshift is believed to be attributed not only from the lattice anharmonicity [149, 169], but also from the presence of the thermal expansion of lattice constants with temperature variation. Various mechanisms for the thermally driven redshift of the Raman optic mode are still under debate with the following possible models:

$$\frac{\Delta\omega(T)}{\omega_0} = \begin{cases} \Delta_1(T) & \text{(Balkanski et al)} \\ \Delta_1(T) + \Delta_2(T) & \text{(Menendez et al)} \\ \Delta_1(T) + \Delta_2(T) + \Delta_3(T) & \text{(Qian et al)} \\ \Delta_4(T) & \text{(Liu et al)} \end{cases} \quad (32)$$

in which,

$$\begin{cases} \Delta_1(T) = A_1 \left\{ 1 + \frac{1}{e^x - 1} \right\} + A_2 \left\{ 1 + \frac{1}{e^y - 1} + \frac{1}{(e^y - 1)^2} \right\} & \text{(Anharmonic - phonon - decay)} \\ \Delta_2(T) = \exp \left[-3\gamma_i \int_0^T \alpha(t) dt \right] - 1 & \text{(Thermal - expansion)} \\ \Delta_3(T) = 2 \left(a - b \frac{C_{13}}{C_{33}} \right) \left[(1 + \varepsilon_g) \frac{1 + \int_{T_g}^T \alpha_s(t) dt}{1 + \int_{T_g}^T \alpha(t) dt} - 1 \right] & \text{(Interface - contribution)} \\ \Delta_4(T) = \frac{B_1}{e^{B_2 \hbar \omega(T_0)/k_B T} - 1} & \text{(Simplified - phonon - decay)} \end{cases} \quad (33)$$

where ω_0 is the specific Raman phonon frequency measured at reference temperature (0 K). T is the temperature of the measurement, and t is the integrand; $x = \hbar\omega_0/2k_B T$ and $y = 2x/3$, (k_B is the Boltzman'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 feely adjustable

parameters needing clear physical indications. Other parameters in Eq. (33) are physically meaningful and experimentally obtainable. For example, γ_i is the mode Grüneisen parameter and the value of γ_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 interface interaction is involved. ε_g 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 Δ_3 are phonon deformation potentials [130, 139].

The models given in Eq. (32) represent that the redshift of phonon frequency may arise from anharmonic phonon decay, thermal expansion, interface interaction or the combination of these factors. In Eq. (33), except for phonon decay, other terms originate from the change of the macroscopic properties with temperature.

Agreement between theory and measurement has been realized when phonon decay shown as Δ_1 in Eq. (33) [140-144] was considered alone. Menéndez et al [145], further revised Balkanski's [138] model by adding the contribution from lattice thermal expansion (Δ_2 in Eq. (33)) to the redshift of Raman frequency, and approved that the thermal expansion also played an important role in the temperature dependence of the Raman shift [146-151]. The lattice and thermal mismatch between the specimen and the substrate induced strain also contributed to the temperature dependent Raman shift, indicated as Δ_3 [24, 130, 152]. From quantum mechanical point of view, the T -induced Raman redshift could also be fitted to a negative Bose-Einstein population as indicated by Δ_4 in Eq. (33) [142, 153]. On the other hand, first principle *ab initio* calculations

have been conducted to calculate some of the individual terms in Eq. (33) to examine the dominating factor in the temperature dependent Raman frequency shift [196-198].

All models in Eq. (32) could fit the experimental observations quite well although numbers of fitting parameters have been applied. However, the physical meanings of these parameters are yet to be clear. One apparent question is that the Bose-Einstein population describes the density population in energy domain rather than the frequency distribution of the phonons in energy space although coincidence exists. The Grüneisen parameter represents solid with ionic nature where Coulomb interactions dominate. Therefore, atomistic understanding and analytical expressions for the temperature dependent Raman frequency shift is highly desirable [25].

4.2.2 LBA approximation and BOLS consideration

From LBA approximation, in order to understand and predict the temperature effect on Raman frequency shift, it is necessary to establish the relationship between the Raman frequency and the bond identities of the corresponding representative bond. Starting from the energy of a single bond, E_{total} , it can be expanded in Taylor's series as:

$$\begin{aligned}
 E_{total}(r, T) &= \sum_{n=0}^{\infty} \left(\frac{d^n u(r)}{n! dr^n} \right)_{r=d} (r-d)^n \\
 &= u(d) + 0 + \frac{d^2 u(r)}{2! dr^2} \Big|_d (r-d)^2 + \frac{d^3 u(r)}{3! dr^3} \Big|_d (r-d)^3 \dots \\
 &= E_b(d) + \left[\frac{k}{2} + \frac{k'}{6} (r-d) \right] (r-d)^2 + O[(r-d)^{n>3}] \dots \\
 &= E_b(d) + E_v(T)
 \end{aligned} \tag{34}$$

Here $(r-d)$ is the magnitude of lattice vibration, which is normally smaller than 3% of the equivalent bond length d even at melting temperature [154]. d is the bond length at

absolute 0 K, and r is the nonequilibrium bond length under thermal vibration. When index $n = 0$, the term corresponds to the minimal binding energy at $T = 0$ K, $E_b(d) < 0$. The $n = 1$ term corresponds to the force $[\partial u(r)/\partial r]_d = 0$ at equilibrium and terms with $n \geq 2$ correspond to the thermal vibration energy of a single bond, $E_V(T) > 0$, where

$$\begin{aligned} E_{Vj}(T) &= \left[\frac{k_j}{2} + \frac{k'_j}{6}(r-d) \right] (r-d)^2 + O[(r-d)^{n>3}] \\ &\cong m^* \omega^2 (r-d)^2 / 2 + O[(r-d)^{n>3}] \\ &\approx k_{Vj} (r-d)^2 / 2 = \int_0^T \eta_{1j}(t) dt \end{aligned} \quad (35)$$

where m^* is the reduced mass, $\eta_1(T)$ being the temperature dependent specific heat per bond following Debye's formulation as shown in Chapter 2 and ω is the angular frequency of vibration. The force constant for lattice vibration with anharmonic term contribution is:

$$k_{Vj} = m^* \omega^2 = k_j + \frac{k'_j(r_j - d)}{3} = \left. \frac{d^2 u(r)}{dr^2} \right|_d + \frac{d^3 u(r)}{3dr^3} (r-d) \Big|_d \propto E_b / d^2 \quad (36)$$

where the subscript j in Eqs. (34) and (35) refers to the j th atomic bond of an atom, counted from 1 to z . Actually, the high-order anharmonic terms O in Eq. (35) corresponding to the nonlinear contribution can be negligible in the first-order approximation because $r = d$ at equilibrium. Therefore the force constant k_V for a single bond is in the similar dimension as stress shown in Eq. (35). According to the BOLS correlation, the force constant k_{Vj} of a single bond of an under-coordinated surface atom is strengthened. Since the short-range interaction on each atom results from its neighboring coordinated atoms, the atomic vibration dislocation is the contribution from all the surrounding coordinates, z . Considering that the vibration amplitude $x \ll d$, it is convenient and reasonable to take the averaged contribution from each coordinate

for the force constants and the magnitude of dislocations in first order approximation, i.e.,

$$k_1 = k_2 = \dots = k_z = m_j^* \omega^2$$

and,

$$x_1 = x_2 = \dots = x_z = (r - d)/z.$$

Therefore, the resultant force constant of the atom under consideration could be lower or higher depending on the production of the reduced coordination number (CN) and the average force constant of the single atom that is strengthened due to surface bond contraction. The total energy of a certain atom with z coordination number is the sum of all CNs [155], such that:

$$\begin{aligned} E_{total} &= \sum_z \left[-E_b + \frac{m_j^* \omega^2}{2} \left(\frac{r-d}{z} \right)^2 + \dots \right] \\ &= -zE_b + \frac{zd^2 u(r)}{2! dr^2} \Big|_d (r-d)^2 + \dots \end{aligned} \quad (37)$$

This relation leads to an immediate expression for the phonon frequency as a function of atomic CN, bond length, d , and the cohesive energy per bond, E_b , as

$$\omega = z \left[\frac{d^2 u(r)}{m^* dr^2} \Big|_d \right]^{\frac{1}{2}} \propto \frac{z(E_b / m^*)^{1/2}}{d} \quad (38)$$

Extending the Eq. (38) to the temperature domain and by considering the change of bond length and bonding energy with temperature in Eq. (9), we have

$$\omega(T) \propto \frac{z \left[\eta_2 + \int_T^{T_m} \eta_1(t) dt \right]^{1/2}}{d \left(1 + \int_0^T \alpha(t) dt \right)} \quad (39)$$

For a bulk material, the Raman frequency shift at temperature T , relative to that

measured at the reference T_0 can be expressed as:

$$\frac{\omega(T)}{\omega(T_0)} = \frac{1 + \int_0^{T_0} \alpha(t) dt}{1 + \int_0^T \alpha(t) dt} \left(1 - \frac{\int_{T_0}^T \eta_1(t) dt}{E_b(T_0)} \right)^{1/2}, \quad (T_0 \neq 0; T < \theta_D) \quad (40)$$

where $\eta_1(t)$ and the integration of $\eta_1(t)$ with respect to T , or the conventionally termed specific internal energy per bond, $u(T)$, for a single bond can be found in Eqs. (10) and (12).

Normally, the reference temperature is chosen to be absolute zero degree. Hence Eq. (40) becomes:

$$\frac{\omega(T)}{\omega_0} = \left(1 + \int_0^T \alpha(t) dt \right)^{-1} \left(1 - \frac{\int_0^T \eta_1(t) dt}{E_b(0)} \right)^{1/2} \quad (41)$$

where $E_b(0) = \eta_2 + \int_0^{T_m} \eta_1(t) dt$ represents the Raman mode related cohesive energy per bond at $T = 0$. $E_b(0)$ is the only adjustable parameter in Eq. (41) with the given physical meaning.

When the measuring temperature T is higher than the Debye temperature ($T \gg \theta_D$), the specific heat η_1 approaches a constant value according to Debye's premise. Furthermore, since the thermal expansion coefficient α is normally in a range of 10^{-6} K^{-1} , the contribution from thermal expansion can be neglected in rough calculation. Hence, Eq. (40) can be simplified as,

$$\begin{aligned} \frac{\omega(T)}{\omega_0} &\stackrel{T \gg \theta_D}{=} \left(1 + \int_0^T \alpha(t) dt \right)^{-1} \left(1 - \frac{\eta_1 T}{E_b(0)} \right)^{1/2} \approx \left(1 - \frac{1}{2} \frac{\eta_1 T}{E_b(0)} \right) \approx A + B \times T \\ \omega(T) &\approx A \omega_0 + B \omega_0 \times T = A' + B' \times T \end{aligned} \quad (42)$$

which shows linear decrease of Raman frequency with increasing temperature when $T \gg \theta_D$. This approximation agrees quite well with experimental observation. To

compare the theory with experimental data, again, first of all, this linear relationship between the Raman frequency shift and the temperature of the measurement in high temperature range is used for rough estimation of the mode cohesive energy. From the experimental data, the slope B' of the ω vs T curve in high temperature range ($T \gg \theta_D$) can be easily determined. Hence, according to Eq. (42), $B' = B \times \omega_0 \approx \frac{1}{2} \times \eta_1 / E_b(0)$, the mode cohesive energy of a single bond can be estimated. A further refinement of the mode cohesive energy can be conducted by carefully fitting the experimental data in low temperature range and also by including the contribution from lattice thermal expansion.

With Eq. (42), we are able to reproduce the temperature dependent Raman frequency redshift with increasing temperature, with derived information about the mode related atomic cohesive energy at absolute 0 K. Figure 11 compares our predictions (solid lines) with the measured T -dependent Raman shift of the A_1 (LO) and the E_2 modes of some nitrides and the E_2 mode of group IV elements (Si, Ge, diamond), and carbon base materials (CBMs) like diamond, graphite, grapheme, and SWNTs, with derived mode cohesive energy tabulated in Table II. Exceedingly well agreement has been obtained for the temperature dependent Raman frequency redshift with T , especially in low temperature range ($T < 1/3\theta_D$). It is seen that the slow decrease of the Raman shift at very low temperatures arises from the smaller $\int_0^T \eta_1(t) dt$ values as the specific heat $\eta_1(t)$ follows Debye T^3 law at very low temperature (see the inset in Figure 4 and Eq. (9)). The fitting results, ω_0 (the intrinsic Raman frequency at 0K), and the mode related atomic cohesive energy $E_B(0)$ at 0K for each mode are tabulated in Table

II. Inputting parameters, like the Debye temperature and the T -dependent thermal expansion coefficient are obtained from literature data. The thermal expansion coefficients for AlN, GaN and InN are obtained from Ref [156], [157], and [158], respectively and are calculated as $\alpha = 1/3 \times (2 \times \alpha_a + \alpha_c)$, whereas the thermal expansion coefficient of Si, Ge, Diamond, graphite, graphene, and SWNTs are from Ref [159], [160], [161], [162], and [163], respectively. The Debye temperature θ_D determines the shoulder width in ω vs T curve. For instance, the Debye temperature of AlN is higher than that of GaN and InN. Then the linearity of the Raman shift for AlN appears at higher temperature.

Figure 11 Comparison of the predictions with the measured T-dependent Raman frequency shift of some nitrides, group IV elements, and carbon base materials.

Table II List of intrinsic Raman frequency ω_0 , and mode related atomic cohesive energy $E_B(0)$ at 0 K of various Raman active modes for group III-nitrides, group IV elements, and carbon based materials

Materials	Raman mode	Exp source data	ω_0 (cm ⁻¹)	$E_B(0)$ (eV)
AlN	E ₂ (high)	[152]	658.6	4.48
	A ₁ (LO)		892.6	4.82
	A ₁ (TO)		613	2.82
	E ₁ (LO)		914.7	5.26
	E ₁ (TO)		671.6	4.74

GaN	E ₂ (high)	[130]	570.2	5.82
	A ₁ (LO)		738	3.90
	A ₁ (TO)		534	4.89
	E ₁ (LO)		745	3.70
	E ₁ (TO)		561.2	6.28
InN	E ₂ (high)	[147]	495.1	2.10
	A ₁ (LO)		595.8	2.95
Si	E ₂ (high)	[149, 154, 168]	520	2.83
Ge	E ₂ (high)	[145]	305	2.52
Diamond	E ₂ (high)	[167-169, 171, 203]	1333	7.38
SWNT	G band	[169-172]	1593.6	3.69
Graphite	G band	Our work	1584	5.45
Graphene	G band	[164]	1583.8	4.70

As earlier stated, the mode cohesive energy in Eq. (41) is different for different Raman modes that relates to the direction and the manner of lattice vibration. In the following part, the group theory, taking the structure of group III-nitrides as an example, is applied to discuss the concept of mode cohesive energy.

For group III-nitrides, there are two kinds of crystal structures. They are hexagonal (wurtzite, space group C_{6v}^4 and two III-N atom pairs per unit cell) and cubic (zinc blend, space group T_d^2 and only one III-N atom pair per unit cell). The only difference

between these two kinds of structures is the stacking order. The first-order phonon Raman scattering is caused by phonons with wave vector $k \sim 0$ at Γ point in the reciprocal space. In the hexagonal structure, the group theory predicts that there are eight sets or phonon normal modes at the Γ point, which are $2A_1+2E_1+2B_1+2E_2$, among which one A_1 and one E_1 modes are acoustic, while the remaining six modes are optical. However, only A_1 , E_1 , and E_2 modes are Raman active [24, 165]. Here, A_1 and E_1 symmetry are the modes corresponding to the axial and planar vibrations, respectively, and they are further split into LO and TO modes, in which E_2 is non-planar mode and only TO mode can be observed. Therefore, the Raman active modes in hexagonal III-nitrides are $A_1(\text{LO})$, $A_1(\text{TO})$, $E_1(\text{LO})$, $E_1(\text{TO})$, $E_2(\text{high})$, and $E_2(\text{low})$.

Figure 12 illustrates the possible atomistic displacement schemes of these six different optical modes. The superscripts H and L refer to high and low frequencies, respectively. These six active Raman modes can be observed by different scattering geometries. Typically $A_1(\text{LO})$ and E_2 (high) modes are commonly observed in backscattering configuration, because in most cases the III-nitrides grow on the substrate with c -axis normal to the substrate. In current discussion, the focus is mainly on the Raman active modes in the hexagonal III-nitrides, especially $A_1(\text{LO})$ and $E_2(\text{high})$ modes, which correspond to two very strong peaks in Raman spectrum in backscattering configuration measurement.

Figure 12 Six optical phonon modes in hexagonal group III-nitride structure, (O) represents group III atoms, like Al, Ga or In; (•) represents N atoms. The superscript L and H indicates high and low frequencies respectively.

As shown in Figure 12, A_1 and B_1 correspond to the atomic displacement along c -axis, while E_1 and E_2 give atomic displacement perpendicular to c -axis or in planar direction. Consequently, the atomic bonding energy obtained from A_1 , B_1 and E_1 , E_2 relating to the displacement in axial and planar direction, respectively, may be different from each other. We denoted them as mode cohesive energy, and they contribute to the atomic cohesive energy. Thus, it is not surprising that the obtained mode cohesive energy in Table II is smaller than the atomic cohesive energy obtained from fitting to temperature dependent Young's modulus listed in Table I. Furthermore, for transverse optical phonon and longitudinal optical phonon, different relative vibration directions relate to different bonding strength. For instance, the $A_1(\text{LO})$ mode, which corresponds to atomic displacement along c -axis is related to the atomic bonding strength between the

group III atom (Al, Ga or In) and N atom. From Table II, the mode cohesive energy for $A_1(\text{LO})$ is obtained as 4.82eV, 3.90eV, 2.10eV for AlN, GaN, and InN, respectively, which indicates that the Al atom has stronger bond energy with N atom compared with Ga-N and In-N bonds.

4.3 Size dependent Raman frequency shift

Similar to Young's modulus, the Raman frequency also varies with sample size when the solid size is reduced down to nanometer scale. It has been well observed that the optical Raman modes shift towards lower frequencies [206-208] with reducing sample size and it is expected that the magnitude of vibration for a surface atom is always greater than that in the bulk [166, 167].

4.3.1 Modeling consideration

The size-induced redshift of Raman optical frequency has usually been suggested to be triggered by surface disorder [168], surface stress [169-171], quantum confinement [172-174], or surface chemical passivation. Choi et al. stated that the redshift of Raman frequency of TiO_2 particles were attributed to the effects of decreasing in particle size on the force constant and the amplitudes of vibration of the nearest atomic neighbors [175]. The phonon quantum confinement argument [176] attributes the redshift of the asymmetric Raman line to the relaxation of the q -vector selection rule for the excitation of the Raman active phonons. When the size of the nanostructure decreased, the

momentum conservation rule would be relaxed and the Raman active modes would not be limited to the center of the Brillouin zone [169], like the case of bulk Raman shift. A Gaussian-type phonon confinement model [177] indicated that strong phonon damping presented upon size reduction, whereas calculations by Ohtani and Kawamura [178] using the correlation functions of the local dielectric constant ignored the role of phonon damping upon size reduction for nanosolid. The large surface-to-volume ratio of a nanosolid strongly affected the optical properties mainly due to the surface polarization and surface states introduced [179]. Using a phenomenological Gaussian envelope function of phonon amplitudes, Tanaka et al. [135] showed that the size dependent redshift of Raman optical modes originated from the relaxation of the $q = 0$ selection rule based on the confinement argument with negative phonon dispersion.

Hwang et al. [180] demonstrated for the first time that the effect of lattice contraction must also be considered in order to explain the observed redshift of phonon frequency for CdSe nanodots embedded in different glass matrices. The interface bond contraction has been confirmed recently by Pan et al. [181] using fluorescence x-ray absorption fine structure and x-ray diffraction. To obtain the phonon frequency as a function of the solid radius K with contribution of lattice contraction, it was assumed that [180],

$$\omega(K) - \omega_L(\infty) = \Delta\omega_D(K) + \Delta\omega_C(K) \quad (43)$$

where ω_L is the LO phonon frequency of the bulk. $\Delta\omega_D(K)$ is the peak position shift due to phonon dispersion and $\Delta\omega_C(K)$ is the peak shift due to lattice contraction, which are given as,

$$\frac{\Delta\omega_D(K_j)}{\omega_L} = \left[1 - \frac{\beta_L^2}{\omega_L} \left(\frac{\mu_{np}}{K_j d} \right)^2 \right]^{1/2} - 1 \cong - \frac{\beta_L^2}{2\omega_L} \left(\frac{\mu_{np}}{K_j d} \right)^2 \quad (44)$$

$$\frac{\Delta\omega_C(K_j)}{\omega_L} = \left(1 + \frac{3\Delta d(K_j)}{d} \right)^{-\gamma} - 1 \cong - \frac{3\gamma\Delta d(K_j)}{d}$$

where the LO phonon frequency ω_L describes the phonon dispersion and is assumed to be parabolic and μ_{np} is the nonzero n_p -th root of the equation of $\tan(\mu_{np}) = \mu_{np}$ and,

$$\begin{aligned} \frac{\Delta d(K_j)}{d} &= (\alpha' - \alpha)(T - T_g) - \frac{2\beta_c}{3} \left(\frac{\sigma_\infty}{K_j d} + \frac{b}{2(K_j d)^2} \right) \\ &\cong (\alpha' - \alpha)(T - T_g) - \frac{\beta_c b}{3(K_j d)^2} \end{aligned} \quad (45)$$

γ is the Grüneisen parameter, α' and α are the linear thermal-expansion coefficients of the host glass and the embedded nanosolid, respectively. T and T_g are the testing and the heat treatment temperature, respectively. β_c and σ_∞ are the compressibility and the surface tension of the bulk, respectively, and b is the parameter describing the size-dependent surface tension of the crystal. The surface tension for bulk crystals is assumed to be very small. The first term in Eq. (45) describes the lattice contraction by thermal mismatch between the glass matrix and the embedded nanosolid. The second term arises from the increase of surface tension with the decrease of crystal size. Substituting Eqs. (44), and (45) into (43), the phonon frequency change at a given temperature, is obtained as:

$$\begin{aligned} \frac{\Delta\omega(K)}{\omega_L(\infty)} &= -3\gamma(\alpha' - \alpha)(T - T_g) - \left[\frac{1}{2} \left(\frac{\beta_L \mu_{n_p}}{\omega_L(\infty)} \right)^2 - \gamma\beta_c b \right] (Kd)^{-2} \\ &= A(T) - BK^{-2} \end{aligned} \quad (46)$$

For the free surface, $\alpha' = \alpha$, $A(T)$ and $b = 0$. The redshift follows a K^{-2} relation. The value of coefficient B in Eq. (46) is given by the difference of the phonon negative dispersion

and the size-dependent surface tension. Thus, a positive value of B indicates that the phonon negative dispersion exceeds the size-dependent surface tension and consequently causes the redshift of phonon frequency. On the contrary, if the size-dependent surface tension is stronger than the phonon negative dispersion, blueshift of phonon frequency occurs. In case the two effects are in balance, i.e., $B = 0$, the Raman peaks will remain unchanged with size. However, in Eq. (46), the parameter b introduced by the size-dependent surface tension is hardly to be known.

4.3.2 BOLS correlation

As derived in Eq. (38), the Raman frequency is proportional to $z \times (E_b/\mu)^{1/2}/d$. According to BOLS correlation, the detectable quantity Q can be expressed as $\omega(K) - \omega_{\text{dimer}}$, that is the Raman frequency at size K reference to a dimer frequency ω_{dimer} . Therefore the size dependent Raman frequency shift can be expressed as:

$$\frac{\Delta q_i}{q} = \frac{\omega(z_i) - \omega_{\text{dimer}}}{\omega(\infty) - \omega_{\text{dimer}}} - 1 = \frac{\omega(z_i) - \omega(\infty)}{\omega(\infty) - \omega_{\text{dimer}}} = \frac{z_i / z_b \times c_i^{-(m/2+1)} - 1}{1 - \omega_{\text{dimer}} / \omega_0} \quad (47)$$

$$\begin{aligned} \frac{\Delta Q(K)}{Q} &= \frac{\omega(K) - \omega(\infty)}{\omega(\infty) - \omega_{\text{dimer}}} = \frac{1}{3} \sum_{i=1}^{i=3} \gamma_i \left[\frac{z_i / z_b \times c_i^{-(m/2+1)} - 1}{1 - \omega_{\text{dimer}} / \omega_0} \right] \\ &= \frac{1}{3} \sum_{i=1}^{i=3} \frac{\pi c_i}{K} \left[\frac{z_i / z_b \times c_i^{-(m/2+1)} - 1}{1 - \omega_{\text{dimer}} / \omega_0} \right] \end{aligned} \quad (48)$$

Note that unlike Young's modulus, which is an extensive quantity, the Raman frequency shift is an intensive quantity. Therefore, an average over the outmost three layers should be considered instead. Great success has been achieved by applying Eq. (48) to size dependence of Raman frequency blue shift as shown in Figure 13. Solid

lines correspond to our predictions while the scattered data are from literature: Si-1[144], Si-2 [182], Si-3, Si-4 [183], Si-5 [184], Si-6 [185], Si-7 [186], Si-8, Si-9 [187], Si-10, Si-11 [169], CdSe-1 [180], CdSe-2, and 8 [188], CdSe-3 [189], CdSe-4 [190], CdSe-5 [191], CdSe-6 and 7 [192], with derived dimer frequency as 505.5 cm^{-1} for Si and 191.2 cm^{-1} for CdSe, shifted by 14.5 cm^{-1} and 18.8 cm^{-1} compared with bulk Raman LO frequency, respectively.

Figure 13 Comparison of the predictions with measured or calculated size dependent Raman frequency shift of nanosolid Si and CdSe.

4.4 Summary

The experimental observed Raman frequency redshift with increasing temperature and decreasing size have been discussed with the proposed theoretical models in literature. A set of analytical expressions from the perspective of atomic bonding based on BOLS correlation and LBA approximation have been proposed. Consistency between the predictions and the experimental data has evidenced the validity of BOLS correlation and LBA approximation. Moreover, our predictions to the experimental

data show that:

- (a) The temperature dependent Raman frequency redshifts monotonically with increasing temperature, and demonstrates similar temperature dependent behaviors as Young's modulus with temperature variation.
- (b) The Raman frequency redshifts with decreasing in size, which was believed to be contributed by surface lattice contraction.
- (c) Agreement between observations and predictions of the temperature and size dependent Raman frequency redshift allows us to derive information about the mode cohesive energy of an atom in the bulk and the dimer frequency which goes beyond conventional theoretical and experimental approaches.

Chapter 5 Thermal properties

5.1 Thermal expansion coefficient

5.1.1 Definition and measurements

The thermal expansion coefficient (TEC or $\alpha(t)$) is one of the key parameters in material science, which is of great importance to the performance of a material for devices or engineering structures with temperature variation. The bond length of different samples varies with the temperature by different amounts, and it is represented in terms of TECs. Generally, most solid materials expand during heating and contract upon cooling. The absolute value and the general trend of TEC are very essential in device design and fabrication. For instance, smaller thermal expansion coefficient leads to higher thermal shock resistance, while large thermal expansion coefficient leads to lower thermal shock resistance. When a sample layer is grown on a substrate, residual stresses may be built up at the interface between the sample and the substrate because of the thermal expansion mismatch [193, 194]. Likewise, the thermal stress can also be developed in the sample during annealing [195], and hence affects the performance of the devices [196].

The thermal expansion coefficient is often defined as the increment in the lattice length per degree rise in temperature. The mathematical expression for thermal expansion coefficient depends on whether the thermal expansion is specified based a precise temperature (that is the true thermal expansion coefficient) or it is considered over a temperature range (that is the averaged or mean thermal expansion coefficient). The former one is governed by the slope of bond length vs temperature curve (shown in Eq.(49)), while the later one is only determined by the starting and ending points in bond length vs temperature curve and is defined in Eq. (50). To differentiate between

the two, α represents the true TEC, while $\bar{\alpha}$ stands for mean TEC:

$$\alpha = \frac{1}{l} \frac{dl}{dT} \text{ and } l = l_0 \exp \left[\int_0^T \alpha(t) dt \right] \quad (49)$$

$$\bar{\alpha} = \frac{l_f - l_0}{T_f - T_0} \text{ and } l_f = l_0 + \bar{\alpha}(T_f - T_0) \quad (50)$$

where l_0 , l , and l_f are the original, temperature dependent, and final bond length corresponding to temperature T_0 , T , and T_f , respectively. $\alpha(t)$ is the thermal expansion coefficient at temperature t , and $\bar{\alpha}$ is the averaged thermal expansion coefficient in temperature range from T_0 to T_f . From Eqs. (49) or (50), it can be seen that the thermal expansion coefficient has the unit of reciprocal temperature, in unit of (K^{-1}). In current discussion, we are more interested in the true thermal expansion coefficient. The temperature will affect the material in all directions. Therefore sometimes a term named volume thermal expansion coefficient α_V is used, which has similar definition as linear thermal expansion coefficient, except that the volume vs temperature curve is used. For isotropic materials, the sample expands similarly across all directions. Its volume thermal expansion coefficient relates to linear thermal expansion coefficient as $\alpha_V = 3\alpha$. For some anisotropic materials, on the other hand, they expand by different amounts in different directions depending on the crystal structure and measurement direction. For most materials, the thermal expansion coefficients are in the range of $10^{-6} K^{-1}$.

The measurement of thermal expansion coefficient is conducted based on its definition. Therefore, there are two physical quantities must be measured: bond length and temperature. The thermal expansion coefficients of different materials have been well studied experimentally during the past decades. There are three main techniques [197]: dilatometry [198, 199], interferometry [200], and thermomechanical analysis. Detailed discussions and the comparison of these three methods are available in Ref [197]. However, even for the same material, such as diamond [201-204], silicon [159,

205-207], GaN [157, 208-210], and some metals, like Ag [198, 211-213], Cu [198, 214], Ni [214, 215], etc., the experimental data scattered depending on the measurement techniques and processes.

5.1.2 Modeling consideration

Generally, the magnitude of TECs increases with rising temperature. The mechanism behind this temperature dependence of the lattice thermal expansion has long been a puzzle, in spite of various sophisticated modeling considerations [44, 161, 216, 217].

From microscopic point of view, the temperature dependent bond relaxation is usually attributed to the anharmonicity of the interatomic potential. The temperature dependent trend of TECs have been found analogous to that of specific heat [208, 216, 218], and this has been described by a number of models [95, 157, 159, 161, 201, 218-220], from the perspectives of classical thermodynamics and lattice quantum vibrations, as summarized in Eq. (51).

$$\alpha(T) = \begin{cases} \sum_0^4 A_n T^n & \text{(Bruls et al)} \\ \sum_0^3 A_n T^{n-1} & \text{(Garai)} \\ B_1 \{1 - \exp[-B_2(T - B_3)] + B_4 T\} & \text{(Okada)} \\ \sum_1^n X_i \frac{(\theta_i / T)^2 \exp(\theta_i / T)}{[\exp(\theta_i / T) - 1]^2} & \text{(Reeber)} \\ -\frac{1}{6B_0 V_0 T} \sum_{n,q} \hbar \omega_n(q) r_n(q) \frac{\xi}{1 - \cosh \xi} & \text{(Debernardi)} \\ \frac{1}{3B_0} \sum_{n,q} r_n(q) C_{v,n}(q) & \text{(Talwar)} \\ -3 \frac{1}{6B_0 V} \sum_{n,q} r_i \hbar \omega_i \frac{d}{dT} \{[\exp(\hbar \omega_i / k_B T) - 1]^{-1}\} & \text{(Xu)} \\ \frac{d}{dT} [A_0 + A_1 \theta_D f(\theta_D / T)] & \text{(Roder)} \end{cases} \quad (51)$$

where A_n , B_n , X_i , θ_i are adjustable parameters for better fitting to the measurement data;

B_0 , and V_0 are the bulk modulus and the volume, respectively; γ_n is the mode Grüneisen

parameter, $f(\theta_D/T)$ is the Debye function given by $f(x) = 3 \int_0^1 \frac{t^3}{\exp(tx) - 1} dt$ [208], and $\xi = \hbar \omega_n / k_B T$; Numerically, all the models could reproduce the general trends of the measured temperature dependent TECs. However, most of the adjustable parameters are lacking of physical justifications. Brules [218] and Garai [95] indicated that the temperature dependent bond length l could be well fitted by a polynomial $\sum_0^4 A_n T^n$. Therefore, the TECs could be represented by a polynomial empirically [95, 201, 218]. The observed TECs sometimes could also be fitted using exponential terms [207, 219]. The *ab initio* method, which computes the total energy of the equilibrium and distorted atomic configuration, was also used to calculate the temperature dependent TECs for Al and W. This method involves bulk modulus, mode Grüneisen constant, and the concave parameter as adjustable variables [220]. Phenomenological lattice dynamics theory in quasiharmonic approximation is also well applied [216]. However, deeper insight into the atomistic origin of the thermal expansion and a unified expression remains yet a great challenge.

5.1.3 LBA approximation

As earlier stated the materials expand with increasing temperature. The expansion is believed to be governed by the interatomic potential well that bonds the atoms and ions together. For instance the tightly bounded atoms reside in deeper energy wells are normally slightly less affected by the temperate than those reside in shallower energy wells. Figure 14 demonstrates the effect of interatomic potential well on the lattice thermal expansion. For the same amount of change of temperature ΔT , which corresponds to energy $k\Delta T$ (k is Boltzman constant), the bond length varies from

equivalent bond length r_0 to r_{T1} in the case of shallower interatomic potential well (Figure 14(a)), whereas the bond length varies from r_0 to r_{T2} in the case of deeper interatomic potential well (Figure 14(b)), and $r_{T1} > r_{T2}$. The illustration in Figure 14 indicates that the atomic potential energy plays an important role in temperature dependent thermal expansion coefficient.

Figure 14 Illustration of the effect of interatomic potential well on TEC

Furthermore, according to LBA approximation, if the material under consideration can be represented by a representative bond, the TEC follows:

$$\alpha(T) \cong \frac{1}{l_0} \left(\frac{dl}{dT} \right) = \frac{1}{l_0} \left(\frac{dl}{du} \right) \left(\frac{du}{dT} \right) = \frac{1}{l_0} \left(\frac{du}{dT} \right) / \left(\frac{du}{dl} \right) \quad (52)$$

where $u(l)$ is the pairing potential, taking the Leonard-Jones potential in Eq. (2) for example, the restoring force $F(l)$ at non-equilibrium position l (which is defined as the negative gradient of the potential function) is given as:

$$F(l) = -\nabla V(l) = 4\epsilon \left[12 \frac{\sigma^{12}}{l^{13}} - 6 \frac{\sigma^6}{l^7} \right] \bar{l} \quad (53)$$

The equilibrium bond length, l_0 , is the distance between two atoms when there is minimum potential or zero force. Therefore $l_0 \approx 1.122\sigma$.

since $\frac{du}{dl} = -F(l) > 0$ and $\frac{du}{dT} \cong C_v(T)$

$$\alpha(T) \cong -\frac{C_V(T)}{l_0 F(l)} \quad (54)$$

Again C_V is the specific heat per atom. By considering the fact that the product of bond length (l_0) at 0 K and the force $F(l)$ is in the dimension of atomic bonding energy, we let $-l_0 F(l) = A_1(l) E_B(0)$, where $E_B(0)$ is the intrinsic atomic bonding energy at 0 K, and $A_1(l)$ is a l -dependent coefficient similar to $F(l)$. The T -dependent TEC can then be rewritten as:

$$\alpha(T) = -\frac{C_V(T)}{l_0 F(l)} \cong \frac{C_V(T)}{A_1(l) E_B(0)} = A(l) C_V(T) \cong A C_V(T) \quad (55)$$

Hence, $A(l) = [-l_0 F(l)]^{-1} = [A_1(l) E_B(0)]^{-1}$ is related to the restoring force at non-equilibrium position l , $F(l)$. Since the thermally-induced bond expansion deviates from the equilibrium distance by a maximal amount of 3% even at the melting point [154], the force $F(l)$ is limited and deviates, due to the anharmonic contribution, slightly from the linear relation. As temperature increases, the term $-F(l)$ values from 0 to a positive finite small value. Hence the averaged $F(l)$ in the temperature under consideration can be used here. Furthermore, in real situation, the measurement is normally conducted under constant pressure. Therefore the specific heat under constant pressure C_p should be considered instead. However, in solid state, $(C_p - C_V)/C_V \approx 3\%$ or less [39]. The replacement of C_p with C_V may compensate the effect of $F(l)$ linear dependence in the range of 1% lattice expansion. Therefore, a nearly constant coefficient A can be assumed in the discussion.

On the other hand, based on Eqs (49) and (55), the bond length l can be expressed as,

$$l = l_0 \exp \left[A \times \int_0^T C_V(t) dt \right] \quad (56)$$

We have thus derived analytical expressions for the temperature dependent TEC and

thermally induced bond length expansion from the perspective of LBA approximation. The only parameter A , in unit of $(\text{eV/atom})^{-1}$, is slightly less dependent on bond length variation. It is related to the bond energy at equilibrium and determines the magnitude of the TECs at high temperature; the Debye temperature, θ_D , determines the turning point of the T -dependent TEC in the $\alpha(t)$ curve (See Figure 15).

Similar to temperature dependent Young's modulus and Raman frequency shift, the calculation was first conducted in high temperature range, where the specific heat approaches a constant value of $3R$. Hence, the value of $a(T)$ at high temperature is used to estimate the value of A in Eq. (55). The obtained A value is then further refined by careful reproducing the available experimental data in the entire temperature range. Fine tuning of A and θ_D is necessary because of the deviation of the available experimental data and errors in the measurements. The current θ_D values derived from fitting to the T -dependent lattice parameter and T -dependent the TECs are in good agreement with the findings of Redor [208]. The fitting parameter A relates to $E_B(0)$ that can be obtained from fitting to the temperature dependent Young's modulus as discussed in Chapter 3. With the given atomic bonding energy $E_B(0)$, the value of A_1 can readily be obtained. For example, the $E_B(0)$ was estimated to be 4.33, 2.65, and 5.71 eV for Si, Ge, and diamond in Table I. The corresponding A_1 values are 0.134, 0.365, and 0.142, meaning that $-Fl_0$ is A_1 portion of the atomic bond energy.

Figure 15 shows the reproduction of the measured temperature dependent TECs using Eq. (55) for some specimens. Encouragingly, the current approach covers the general trend of T -dependent $\alpha(T)$. Exceedingly good agreement with the measured data has been obtained for AlN, Si₃N₄, and GaN. However, the observed negative TECs in group IV elements at extremely low temperatures could not be reproduced in current approach. Generally, most materials expand upon heating, although rarely some

materials expand upon cooling. The unusual behaviors of materials having negative TECs have been considered to arise from the negative Grüneisen parameters of the transverse acoustic phonons near the Brillouin-zone boundary [45, 225, 231]. For certain pure metals, such as Au, Cu, and Al, the current model gives better prediction for the lattice behavior at low temperature than that at high temperature. The TECs of these pure metals still keep increasing with increasing temperature even at very high temperature ($T \gg \theta_D$). This deviation may arise from the thermal contribution from free electrons. The contribution to specific heat in Debye's model mainly comes from phonons. For metals, at high temperature, in addition to the phonon contribution to the specific heat, free electrons also play a role and their contribution increases with increasing temperature [214]. For the ferromagnetic Ni and Fe, the measured TECs exhibit an abrupt feature at the Curie temperature T_c , which corresponds to a phase transition from ferromagnetic to paramagnetic. As earlier discussed, the phase transition, which leads to the variation of the number of atomic bonds, is not covered in current LBA approximation. The abrupt feature was believed to arise from additional contribution to the specific heat from electron spin [215]. It is not surprising that these unexpected features are beyond the scope of the current model because in current LBA approximation, an ideal phonon density-of-states derived from long wavelength at the Brillouin zone center and only the phonon contribution are considered for specific heat. The contribution from electrons, or spins, or phase transition is not included. The Debye approximation of the specific heat assumes that the phonon density-of-states in an elastic medium is ideally proportional to ω^2 . In reality, one has to consider the exact form of the phonon density-of-states that is a quantity of measurement using Neutron diffraction which is way beyond the scope of our current model [44]. Nevertheless, the phonon contribution to the thermal properties is dominant and a precise prediction of

the T -dependent TECs can be obtained if the exact density-of-states $g(\omega)$ vs ω is given.

Figure 16 shows the reproduction of the T -dependent lattice parameters for various materials. The fact that much better match of the lattice constants compared with that of the TECs for the same elements indicates that experimental errors could not be ignored in practice. The agreement between the LBA approach and the available experimental data for the temperature dependent thermal expansion coefficients and lattice parameters of various materials justifies the validity of the LBA approach and reconfirms that the assumption of the slight l -dependent of $A(l)$ holds true.

The derived form is numerically consistent with the existing models in literature as summarized in Eq. (51) [208, 216, 218]. If the Einstein's model of specific heat is applied, the exponential terms in Reeber's model [157] can be obtained. Meanwhile, if the exponential term is expanded in Taylor's series the temperature dependent polynomial TECs is quite obvious [95, 218]. Therefore, with the current justification from LBA view point, the previous models discussed in Eq. (51) [201, 220] are all numerically correct.

Table III Parameters derived from fitting to the temperature dependent TECs and lattice parameters.

		Si	Ge	C	AlN	Si ₃ N ₄	GaN	Au	Cu	Al	Ni	Fe
Parameter	θ_D (K)	647	360	1860	1150	1150	600	170	315	420	375	460
$\alpha(t)$	θ_D (K)	1000	600	2500	1500	1600	850	400	500	450	600	600
	A	0.579	0.966	0.811	0.888	0.502	0.637	2.241	2.588	3.322	2.009	1.777
$l(t)$	θ_D (K)	1100	500	2150	1500	1400	800	400	500	500	600	600
	A	0.579	1.035	0.792	0.946 ^a	0.888	0.637 ^a	2.105	2.588	3.554	2.144	20.09
					0.811 ^c		0.618 ^c					
	L_0 (Å)	5.4286	5.65	3.5661	3.1095 ^a	7.7335	3.1893 ^a	4.07	3.6	4.036	3.513	2.82
					4.9774 ^c		5.1830 ^c					
Mean	θ_D (K)	1050	550	2325	1500	1500	825	400	500	475	600	600
	A	0.579	1.001	0.802	0.882	0.695	0.631	2.173	2.588	3.438	2.076	10.93

Figure 15 Reproduction of temperature dependent thermal expansion coefficient for (a) group III-Nitrides (b) group IV elements (c) metals (d) ferromagnetics.

Figure 16 Reproduction of temperature dependent lattice parameters for (a) group III-Nitrides (b) group IV elements (c) metals (d) ferromagnetics.

5.2 Surface energy and atomic cohesive energy

5.2.1 Definition and measurement

Because of CN reduction, a surface atom has fewer neighbouring atoms and hence experiences strengthened single bond energy but lower total energy compared with that of atom in bulk site. Indeed, the surface atoms must have lower energy than its corresponding bulk counterparts, otherwise the driving force will attempt to create a new surface. Surface energy quantifies the disruption of intermolecular bonds that occurs when a surface is created. The surface energetics plays the key role in the thermodynamics of solid surface, especially in nanosolid science because it links the microscopic bonding configuration at an interface with its macroscopic material properties, such as strength, elasticity, wettability, reactivity, diffusivity, stability [221-224].

During the past decades, increasing efforts have been put on processes that are strongly influenced by surface energetics such as surface reconstruction, relaxation, interfacial mixing, segregation, self-organization, and melting on solid surface. The experimental working principle to obtain surface energy is to calculate the maximum steady pulling force during measurement. Based on this, several measurement methods have been developed. For instance, traditional contact angle or the sessile drop technique is often used to measure the surface energy of liquid formed surface, but this method is greatly affected by the surface conditions of the substrate and contamination such as oxygen in the atmosphere [225]. Other measuring methods, like microgravity oscillating drop method and [226] and ring tensiometry technique [227] have overcome

the disadvantages of traditionally sessile drop method, and the later [227] has also provided a method to measure the surface tension at very high temperature.

5.2.2 Modeling consideration

The experimental determination of the absolute results on well defined surface is still very difficult and hence several theoretical attempts have been performed to calculate the surface energy using either *ab initio* [228, 229], molecular dynamics [224] or Monte Carlo simulations. Traditionally, the surface energy (γ_s), or surface free energy of a solid, or the surface tension of a liquid, is defined as the energy needed to cut the given crystal into two halves, or the energy consumed (lost) upon surface formation [83]. Usually, the un-relaxed structures at absolute zero degree are considered in the discussion of surface energy. The values obtained are then corrected to relaxation of the surface atoms, without mentioning surface reconstruction. In some cases, this correction is considered to be very small, so a simplified model can be made without including relaxations.

The temperature dependence of surface energy involves phonons and their corresponding surface modification; the vibrational effects sometimes have to be taken into account, which lead to the empirical expressions of temperature dependent surface energy. The elegantly well-accepted approaches of the surface energy are the broken-bond rules [233, 241-243], which are comparatively summarized as follows:

$$\gamma_s = \begin{cases} \frac{W_S - W_B}{20} n_d (n_d - 10) & \text{(Galanakis)} \\ (1 - z_s/z_b) E_B & \text{(Haiss)} \\ (1 - \sqrt{z_s/z_b}) E_B & \text{(Desjonqueres)} \\ \frac{[2 - z_s/z_b - (z_s/z_b)^{1/2}] + \lambda [2 - z'_s/z'_b - (z'_s/z'_b)^{1/2}]}{2 + 2\lambda} E_B & \text{(Jiang)} \end{cases} \quad (57)$$

where γ_s is the surface energy. Galanakis et al. [230] correlated the surface energy of some d -metals to the broken bonds in the tight-binding approximation. n_d is the number of d -electrons. W_S and W_B are the bandwidth of the surface and bulk density of states, for which a rectangular form is assumed. Haiss et al. [222] related the surface energy directly to the multiplication of the number of broken bonds with the cohesive energy per bond $E_B = z_b E_b$ at 0 K. The number of broken bonds in their model depended on crystallographic structure in concern. A second-moment tight-binding approximation conducted by Desjonquères et al. [231], suggested that the surface energy gain is proportional to $\sqrt{z_s}$, instead, due to the lowering of the occupied states. According to their approximation, the rearrangement of the electronic charge did not practically change the nature of the remaining bonds when one bond is broken. Thus, the energy needed to break a bond was independent of the surface orientation, so that the γ_s value is proportional to the square root of the number of the nearest-neighboring broken bonds. To obtain a more general expression, Jiang et al [232] suggested that an average of the approximations of Haiss and Desjonquères and an extension to count in the contribution from the second nearest neighbors could be more precise. λ is defined as the ratio of the total bond strength between the nearest neighboring bonds and the next-nearest neighboring bonds.

Besides the considerations in thermodynamics, the kinetic process of lattice

vibration also plays a significant role in the anisotropy of surface properties [233]. Measurements at temperature above the Debye temperature indicate that the surface energy (tension), surface stress, and the Young's modulus of a specimen vary linearly with temperature of measurement [226, 227, 234-236]:

$$\begin{aligned}\gamma_s(T) &= \gamma_s(T_m) + \alpha_t(T_m - T) \\ &= \gamma_s(0) - \alpha_t T\end{aligned}\quad (\text{J/m}^2) \quad (58)$$

where $\gamma_s(T_m)$ corresponds to the surface energy value at melting, α_t is the slope of variation, and T_m is the melting point of the bulk specimen.

5.2.3 BOLS consideration

Regardless of the various demands and measuring mechanics proposed, detailed knowledge on the processes of surface energy is still lacking [221, 222, 237, 238]. In particular, the atomistic origin, temperature dependence, and their responsibilities for surface phenomena and processes are yet far from clear. It is noted that the units of most definitions in Eq. (57) are in eV/atom, which reflects the energy loss per atom. However, the dimension of Eq. (58) is in J/m², which represents the remaining energy density per unit area. The inconsistency in the dimension has caused long confusion about the surface energy. In real situation, the performance of a surface is governed by the remaining energy in the surface skin or by the remaining bond energy of the under-coordinated surface atoms instead of the energy loss upon surface formation. Therefore, two complementary terms are necessary for a better understanding of the surface energy. The BOLS correlation and LBA approximation could allow us to clarify

the confusion by proposing the following two concepts, which are functionally dependent on the bonding identities of the representative bond. The suggested terms are:

(i) the energy-density-gain in the surface skin and (ii) the bond-energy-remain per atom upon surface formation. On the other hand, energy per unit volume in the surface skin of a certain thickness could be more appropriate than the energy per unit area without considering the thickness, as energy is always a volume-related quantity.

As stated earlier, the key idea of the BOLS correlation is that the termination of lattice periodicity, or bond broken, causes the remaining bonds of the under coordinated atoms to contract (from d to d_i by $d_i = c_i d$) spontaneously associated with bond strength gain (from E_b to E_i by $E_i = c_i^{-m} E_b$). Therefore, the shorter and stronger bonds between the under-coordinated surface atoms should take the full responsibility for the surface energy and the unusual properties in the surface region. We can hence establish the functional dependence of the surface energy on the bonding identities of the corresponding representative bonds and therefore to study their temperature dependency without involving other tunable parameters. The definitions, analytical expressions, and atomic origins of various surface related energy, as well as their related physical properties are summarized in

Table IV.

Table IV List of definitions of surface energy-density-gain (γ_{ds}), surface atomic coherency (γ_{fs}), surface energy (γ_s), and their origins and functionalities

Definitions	Expression	Atomistic origin	Functionality
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γ_{ds} (eV/nm ³)	$\frac{\sum_{i=1}^{i=3} E_i(T)/d_i^3(T) \times d_i(T)}{\sum_{i=1}^{i=3} d_i(T)}$	Energy gain per unit area due to broken bond induced surface strain	Surface stress; elasticity; Hamiltonian; surface optics; dielectrics; surface trapping states; electron and photon transport dynamics; work function.
γ_{fs} (eV/atom)	$\frac{\sum_{i \leq 3} z_i E_i(T)}{3}$	Binding energy remain per discrete atom upon surface formation	Thermal stability; melting and evaporating ability; wettability; diffusivity; reactivity; acoustics;
γ_s (eV/atom)	$z_b E_b - \gamma_{fs}$ or equivalent to the forms in Eq (57)	Traditional definition of energy loss per atom upon surface formation	self-assembly; reconstruction.

At a given temperature, the magnitude of the cohesive energy per bond is the difference between the binding energy at 0 K and the thermal energy of vibration,

$$E_i(T) = \eta_{2i} + \int_T^{T_{mi}} \eta_{1i}(t) dt = E_i(0) - \int_0^T \eta_{1i}(t) dt$$

When $T \gg \theta_D$ $E_i(T) \cong E_i(0) - \eta_i T$ and becomes approximately coincides with the experimentally derived form of temperature dependence described in Eq. (57).

According to BOLS correlation, where $q_i = \gamma_{di}$ or γ_{fi} , the proposed temperature dependent surface energy density gain, γ_{di} , and the surface atomic coherency, γ_{fi} , for i th atomic layer can be expressed as:

$$\begin{aligned} \gamma_{di}(T) &\propto \frac{E_i(T)}{d_i^3(T)} = \frac{E_i(0) - \int_0^T \eta_{li}(t) dt}{d_i^3(1 + \alpha_i T)^3} \\ \gamma_{fi}(T) &\propto z_i E_i(T) = z_i \left[E_i(0) - \int_0^T \eta_{li}(t) dt \right] \end{aligned} \quad (59)$$

where α_i being the coefficient of thermal expansion. Compared with Eq. (22), surface energy gain has the same dimension as the surface stress and Young's modulus:

$$P_i(T) = - \left. \frac{\partial u(r)}{\partial V} \right|_{r=d_i} \propto Y_i(T) = -V \left. \frac{\partial^2 u(r)}{\partial V^2} \right|_{r=d_i} \propto \frac{E_i(T)}{d_i^3} = \gamma_{di}(T)$$

This expression demonstrates the correlation between the surface energy density and the mechanical properties, such as stress and elasticity. Here we use the proportional form because we are more interested in the value of these qualities relative to the value of their bulk counterparts. Therefore, we have:

$$\begin{aligned} \frac{\gamma_{di}(T)}{\gamma_d(0)} &= \frac{d^3}{d_i^3(1 + \alpha_i T)^3} \times \frac{E_i(0) - \int_0^T \eta_{li}(t) dt}{E_b(0)} \\ &= \frac{c_i^{-(3+m)}}{(1 + \alpha_i T)^3} \times \begin{cases} 1 - \frac{\int_0^T \eta_{li}(t) dt}{z_i / z_b \times c_i^{-m} E_b(0)}, & (T \leq \theta_D) \\ 1 - \frac{\eta_{li} T}{z_i / z_b \times c_i^{-m} E_b(0)}, & (T > \theta_D) \end{cases} \\ \frac{\gamma_{fi}(T)}{\gamma_f(0)} &\cong z_i / z_b \times c_i^3 (1 + \alpha_i T)^3 \times \frac{\gamma_{di}(T)}{\gamma_d(0)} \end{aligned} \quad (60)$$

If the outmost three atomic layers of a nanostructure with size K is considered, the

T -independent $\langle \gamma_{ds} / \gamma_{db} \rangle$ and $\langle \gamma_{fs} / \gamma_{fb} \rangle$ can be derived by averaging the individual sum

over the outmost three atomic layers. Therefore we can obtain the mean

energy-density-gain per unit area by $\langle \gamma_{ds} \rangle = (\sum_{i=3} \gamma_{di} d_i) / (\sum_{i=3} d_i)$ and the mean

energy remain per discrete atom by $\langle \gamma_{fs} \rangle = [\sum_{i=3} \gamma_{fi}] / 3$. Then the temperature

dependence of mean γ_{ds} and γ_{fs} on the bind energy can be expressed as:

$$\begin{aligned} \left\langle \frac{\gamma_{ds}(T)}{\gamma_{db}(0)} \right\rangle &= \frac{\sum_{i \leq 3} c_i^{-2}(T) \times E_i(T) / E_b(0)}{\sum_{i \leq 3} c_i(T)} \\ \left\langle \frac{\gamma_{fs}(T)}{\gamma_{fb}(0)} \right\rangle &= \sum_{i \leq 3} z_{ib} \frac{E_i(T)}{E_b(0)} \end{aligned} \quad (61)$$

Table V gives predicted ratio of energy density gain, $\langle \gamma_d \rangle$, and atomic coherency, $\langle \gamma_f \rangle$

with respect to the bulk values at $T = 0$. The subscripts 1, 2, and 3 stand for the i th

atomic layers counted from outmost layer. Results show that at $T = 0$, the

surface-energy-density (with unit eV/nm³) is always higher and the surface atomic

coherency (with unit eV/atom). Therefore, it is not surprising that the previous

measurements are inconsistent with each other.

Table V Predicted bond nature (m) dependent ratio of energy density gain, $\langle \gamma_d \rangle$, and

atomic coherency (free energy), $\langle \gamma_f \rangle$, with respect to the bulk values

m	γ_{d1}/γ_{db}	γ_{d2}/γ_{db}	γ_{d3}/γ_{db}	$\langle \gamma_{ds}/\gamma_{db} \rangle$	γ_{f1}/γ_{fb}	γ_{f2}/γ_{fb}	γ_{f3}/γ_{fb}	$\langle \gamma_{fs}/\gamma_{fb} \rangle$
1	1.700	1.294	1.135	1.485	0.381	0.356	0.344	0.360
2	1.942	1.380	1.172	1.616	0.435	0.379	0.355	0.390
3	2.219	1.472	1.210	1.761	0.497	0.404	0.367	0.423
4	2.533	1.570	1.249	1.924	0.567	0.431	0.378	0.459
5	2.893	1.675	1.289	2.105	0.647	0.460	0.391	0.500

To be in line with the previous discussed surface energy in Eq. (58), the energy density gain γ_d relates to the surface energy γ_s following $\gamma_d = \gamma_s/D$, where D is the surface thickness. Therefore,

$$\frac{\gamma_s(T)}{\gamma_b(0)} = \frac{\gamma_s(T_m)}{\gamma_b(0)} + \frac{\alpha_t T_m}{\gamma_b(0)} \left(1 - \frac{T}{T_m}\right) = \frac{\gamma_s(0)}{\gamma_b(0)} - \frac{\alpha_t T}{\gamma_b(0)} \quad (62)$$

Therefore, by combining Eqs. (61) and (62), we have:

$$\begin{aligned} \gamma_b(0)/D &\stackrel{\alpha T \ll 1}{\cong} \frac{\gamma_s(0)/D}{c_1^{-(m+2)} + c_2^{-(m+2)} + c_3^{-(m+2)}} = A_1(m) \gamma_s(0)/D \\ E_b(0) &\stackrel{\alpha T \ll 1}{\cong} \frac{\frac{c_1 + c_2 + c_3}{z_{b1}c_1^{-2} + z_{b2}c_2^{-2} + z_{b3}c_3^{-2}} \eta_1 \gamma_b(0)}{c_1 + c_2 + c_3} = A_2 \frac{\gamma_b(0)}{\alpha_t} \end{aligned}$$

In the calculation, the thermal expansion coefficient is the input parameter and the atomic cohesive energy $E_b(0)$ is the derived output, as summarized in Table VI. In Table VI, the atomic cohesive energy $E_B(0)$ derived from fitting predictions to measured T -dependent surface tension γ_b for Ni, Hg, H₂O, and Co. The bond energy $E_b(0)$ for elementary specimen is available by dividing the atomic coherency $E_B(0)$ with coordination z_b and the energy density can be obtained by multiplying the $\gamma_s(0)$ and $\gamma_b(0)$ with surface skin thickness, D (3 atomic layers are normally recommended).

Table VII lists the derived atomic bonding energy from fitting to the measured T -dependent surface tension of some polymers. The experimental data in Table VII are from Ref [239]. In these calculations, no other parameters, except the single bond energy or atomic bonding energy are involved. The accuracy of the derived atomic cohesive energy is very sensitive to the measured data.

Table VI List of derived atomic cohesive energy and surface energy at melting temperature for Ni, Hg, H₂O, and Co

Material	Data	$\gamma_s(T_m)$ (mJ/m ²)	α_t (mJ/(m ² K))	α_i (10 ⁻⁵ K ⁻¹)	$E_B(0)$ (eV)
Ni	[235]	1823	0.46	1.6	3.645
Hg	[236]	493	0.22	6.04	1.79
Co	[240]	1930	0.33	13.0	4.80
H ₂ O	[241]	75.4	0.162	-	0.38

Table VII List of derived value of atomic bonding energy, α_t in Eq. (58) at melting temperature for some polymers

	$\gamma_s(T_m)$ (mJ/m ²)	α_t (mJ/(m ² K))	$E_B(0)$ (eV)
hexadecane (C16)	49.5	0.094	0.30
PE (C2000)	26.89	0.065	0.41
PEO	41.9	0.08	0.40
PCAP	40.32	0.068	0.43
PEKK	39.4	0.08	0.60
PBT, poly (butylene terephthalate)	41.46	0.08	0.54
Poly (trimethylene terephthalate)	38.86	0.067	0.56
PET	37.73	0.0646	0.59
Poly (amide ester) copolymer	47.6	0.08	0.52
nylon 66	34.1	0.115	0.47
Polyamide MPMD-12	39.16	0.081	0.49

Figure 17 gives the our predictions and the measured temperature dependent surface tension for (a) liquid Hg and Ni, (b) Co and H₂O, and (c) Hexadecane and Polyethylene, from which the atomic cohesive energy is estimated.

Figure 17 Predictions of the measured T dependent surface tension for (a) Hg and Ni liquid, (b) Co and H₂O liquid, and (c) Hexadecane and Polyethylene.

In current discussion, the correlation between the surface energetics and the interatomic bonding has been established for the first time from the perspective of BOLS correlation and LBA approximation, from which we conclude that:

- The concepts that energy density gain per unit volume and cohesive energy remain are suggested to be essential to classify the surface energy. The deviation of surface energy from the bulk values arises from the shortened and strengthened bonds between the under-coordinated surface atoms
- The thermally weakened surface energy is dominated by thermal expansion and the surface bond weakening with increasing temperature.
- The BOLS correlation allows us to estimate the atomic bonding energy by reproducing the temperature dependent surface tension, which is beyond the scope of existing models.

It is noted that the adatoms or atomic vacancies may present during material growth, and they will affect the surface energy in a dynamic way by introducing additional traps. As the focus in this thesis is on static surface here, the dynamic behavior of adatoms or vacancies is not discussed. However, the dynamic process of adatoms growth or defect/impurity formation and its influence on the surface energy would be a challenging topic for further studies. The accuracy of estimation is strictly subject to the measurement condition. Factors such as material purity, defect concentration, and testing techniques may lead to significant deviation of $E_B(0)$ from its intrinsic value. Nevertheless, the results obtained and the progress made so far demonstrate that the current approach represents the true situation of observations with a simple and straight forward solution.

5.3 Thermal Conductivity

5.3.1 Phonon dispersion relation

Phonons are quantized modes of vibration occurring in a rigid crystal lattice. It can be considered as quasi-particles of the energy $\hbar\omega$, and quasi-momentum $p = \hbar q$ obeying Bose-Einstein statistics [242]. Similar to electrons, one can characterize the properties of phonons by their dispersion relation $\omega(q)$, which is defined as the dependence of phonon frequency on its wave vector q . In bulk semiconductors with n atoms per unit cell, there are $3n$ phonon dispersion branches for every given q . In the limit of long waves length, three modes out of $3n$ phonon dispersion branches correspond to the motion of the unit cell (acoustic phonons, which have nearly linear dispersion written as

$\omega = v_s q$, where v_s is the sound velocity) and the rest $3(n-1)$ branches describe the relative motion of atoms in a unit cell (optical phonons, which are nearly dispersion-less and have small group velocity $v_g = d\omega/dq$ for small q). Generally, both acoustic phonons and optical phonons limit electrical conductivity. The optical phonons strongly influence optical properties of semiconductors while acoustic phonons are the dominant heat carriers in insulators and semiconductors. Spatial confinement of phonons in nanostructures can strongly affect the phonon dispersion relation and hence modify phonon properties, such as phonon group velocity, polarization, density of states, and also the interaction between phonon and phonon, electron or defects. The nanostructures, which can create such phonon confinement, offer a new way to control the phonon transport via tuning its dispersion relation, which is called as “Phonon Engineering” [243].

5.3.1.1 Modeling consideration

In last decades, there have been a great amount of theoretical works on calculating the confined phonon dispersion relations, like the work done by Bannov [244], Strosio [245, 246], Nishiguchi [247], Svizhenko [248], and Yu [249, 250], in which most paper used the elastic continuum approach. In recent years, Mingo [251] used atomistic model to calculate the complete dispersion relation. In his approach, the externally imposed cutoff frequency is not required. In the following analysis, simple isotropic elastic continuum model is applied to exam the effect of the surface bond modification

on phonon dispersion relation.

5.3.1.2 BOLS effect on phonon dispersion relation

In Chapter 3, the relation of the change of Young's modulus due to surface bond modification has been well studied. In the following discussion, it is focused on low temperature region, where the Young's modulus has the following relation according to Eq. (22)

$$Y = -V \left. \frac{\partial^2 u(r)}{\partial V^2} \right|_{r=d} \approx \frac{E_i}{d_i^3}$$

According to the BOLS correlation, at temperature far below the melting point, the local Young's modulus of the surface layer increases as:

$$\frac{Y_i}{Y_b} = c_i^{-(m+3)} \quad (i \leq 3) \quad (63)$$

The bond contraction of the outmost layers differs from layer to layer; however, to simplify the analysis, we treat the relaxed surface as a uniform shell with averaged Young's modulus Y_2 and Lamé constants λ_2, μ_2 . In this case, a core-shell nanowire structure is assumed, where the core has bulk Young's modulus Y_1 and Lamé constants λ_1, μ_1 . Figure 18 gives a schematic diagram of a core-shell structure, where a is the radius of the core and the shell has a thickness of $\delta a = 1.47$ nm, which contains outmost three layers. And the two Young's moduli of the core-shell structure satisfy the relation

$$\frac{Y_2}{Y_1} = \frac{1}{3} \sum_{i=1}^{i=3} c_i^{-(m+3)} \quad (64)$$

Figure 18 Schematic diagram of a core-shell structure for a cylindrical nanowire

Now we have discontinuity in material properties at the core-shell interface. The crucial point of this approach is to impose the physical continuity condition of the displacement field and stress (at the core-shell interface) on the system, which will lead to determinantal equations that govern the phonon spectrum in the presence of BOLS. In the presence of BOLS, the calculation of phonon spectrum in nanowires based on atomistic model is very complicated. To simplify the calculation, isotropic elastic continuum model is applied to both core and shell part of the silicon wire with infinite length in axial direction. The core radius and the shell thickness are denoted as a and δa , respectively. The transverse and longitudinal sound speeds are

$$c_{t1,2} = \sqrt{\frac{\mu_{1,2}}{\rho_{1,2}}} \quad \text{and} \quad c_{l1,2} = \sqrt{\frac{\lambda_{1,2} + 2\mu_{1,2}}{\rho_{1,2}}} \quad (65)$$

where the subscripts 1 and 2 are referred to the core and the shell region, respectively.

Here ρ is the mass density. According to isotropic elastic continuum model, the Lamé constants in each region are related to Young's modulus Y and Poisson ratio ν :

$$\begin{cases} \lambda = \frac{Y\nu}{(1+\nu)(1-2\nu)} \\ \mu = \frac{Y}{2(1+\nu)} \end{cases} \quad (66)$$

We could assume that the Poisson ratio is the same for both the core and the shell region,

then both λ and μ are simply proportional to Y , and the Lamé constants for the core and the shell region satisfy the relation

$$\frac{\mu_2}{\mu_1} = \frac{\lambda_2}{\lambda_1} = \frac{Y_2}{Y_1} = \frac{1}{3} \sum_{i=1}^{i=3} c_i^{-(m+3)} \quad (67)$$

Also, for the sound velocities, we have

$$\frac{c_{t2,l2}}{c_{t1,l1}} \propto \sqrt{\frac{E_2}{E_1} \cdot \frac{\rho_1}{\rho_2}} = \frac{1}{3} \sum_{i=1}^{i=3} c_i^{-m/2} \quad (68)$$

Atoms vibrate around their lattice sites and the lattice vibration is approximated by the continuous displacement field $\vec{u} = (u_r, u_\theta, u_z)$. The general solution of $\vec{u}$ can be expressed in terms of three scalar functions ϕ, φ , and χ [246]:

$$\vec{u} = \nabla \phi + \nabla \times (\vec{i}_3 \varphi) + a \nabla \times \nabla \times (\vec{i}_3 \chi) \quad (69)$$

where

$$\begin{cases} \nabla \times (\vec{i}_3 \varphi) = \left(\frac{1}{r} \frac{\partial \varphi}{\partial \theta} \right) \vec{r} + \left(-\frac{1}{r} \frac{\partial \varphi}{\partial r} \right) \vec{\theta} \\ \nabla \times \nabla \times (\vec{i}_3 \chi) = \frac{\partial}{\partial z} \left(\frac{\partial \chi}{\partial r} \right) \vec{r} + \frac{\partial}{\partial z} \left(\frac{1}{r} \frac{\partial \chi}{\partial \theta} \right) \vec{\theta} + \left[\frac{1}{r} \frac{\partial}{\partial r} \left(-r \frac{\partial \chi}{\partial r} \right) - \frac{1}{r} \frac{\partial}{\partial \theta} \left(\frac{1}{r} \frac{\partial \chi}{\partial \theta} \right) \right] \vec{i}_3 \\ \nabla \phi = \frac{\partial \phi}{\partial r} \vec{r} + \frac{1}{r} \frac{\partial \phi}{\partial \theta} \vec{\theta} + \frac{\partial \phi}{\partial z} \vec{i}_3 \end{cases} \quad (69a)$$

In the above equation, $\vec{i}_3$ is the unit vector in the z (wire) direction, $\vec{r}$ and $\vec{\theta}$ are standard unit vectors in r and θ direction. Consequently, the components of the displacement field $\vec{u}$ in different direction are given by:

$$\begin{cases} u_r = \frac{\partial \phi}{\partial r} + \frac{1}{r} \frac{\partial \varphi}{\partial \theta} + a \frac{\partial^2 \chi}{\partial z \partial r} \\ u_\theta = \frac{1}{r} \frac{\partial \phi}{\partial \theta} + a \frac{\partial^2 \chi}{\partial z \partial \theta} - \frac{\partial \varphi}{\partial r} \\ u_z = \frac{\partial \phi}{\partial z} - a \frac{1}{r} \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \chi}{\partial r} \right) - a \frac{1}{r^2} \frac{\partial^2 \chi}{\partial \theta^2} \end{cases} \quad (69b)$$

The scalar functions ϕ, φ , and χ satisfy certain wave equations [246]. Generally,

ϕ , φ , and χ are obtained by solving the wave equations and they are then substituted into Eq. (69b) for the determination of u_r , u_θ and u_z . Together with the boundary conditions that the stress and displacement are continuous at the core-shell interface and there is no stress at the outer most shell for free standing nanowires, the calculation of the phonon dispersion can be derived into a determinantal problem. The detailed calculation is shown in Appendix.

Figure 19 shows the first six phonon dispersion relations for torsional mode, longitudinal mode and flexural mode with $\delta a/a = 0, 0.05, 0.10$ and 0.15 . The y-axis corresponds to the normalized the phonon frequency, and x-axis is normalized wavevector. We only consider the $\delta a/a$ up to 0.15 which corresponds to a diameter of 22 nm for cylindrical nanowire. For higher $\delta a/a$ values, (i.e., diameter < 22 nm), the elastic continuum model is not suitable and a more sophisticated atomic model [251, 252] should be applied. Nevertheless some conclusions on the behavior of thermal conductivity in this region could be made based on the simple isotropic elastic continuum model.

It is seen from Figure 19 that as $\delta a/a$ increases, that is, as the diameter of the cylindrical nanowire reduces, the phonon frequencies of torsional mode decreases for all branches except the first one. For longitudinal branches, BOLS effect also causes the phonon frequency to decrease except for a small range of the wave vector q .

Figure 19 Phonon dispersion relations for torsional, longitudinal, and flexural modes

with $\delta a/a=0, 0.05, 0.10$ and 0.15 .

The increase of phonon frequency for this small range of wave vector can be understood as a resonant effect. We find a similar behavior for the flexural mode.

Another important point is that the phonon group velocity $v(\alpha, \omega) = d\omega/dq$ is increasing

in most cases in the presence of the effect BOLS. The circular nanowires could be considered as a waveguide with well defined set of eigenstates, but the question about the influence of roughness and other irregularities of the nanowire structure is still open. The current study discloses the behavior of phonon spectrum under BOLS effect. Moreover, this approach is applicable to the case of nanowires covered with different layers, where appropriate elastic constants in the shell are required.

5.3.2 Thermal conductivity (for silicon nanowires)

The ballistic transport in mesoscopic system has been an active area of research. The quantization of electron conductance has already been well studied [253, 254]; however, there are not many investigations on heat transport by phonons [252, 255]. For metals, heat is carried by both electrons and phonons though the contribution of electrons dominates. In insulators, on the other hand, thermal transmission is dominated by phonons, and in semiconductors, similarly, the main contribution to the thermal conductivity comes from phonons. As the dimension of semiconductor devices reduces to nanometer scale, self-heating and thermal stability becomes increasingly important in device design. Hence deeper insight into the nature of size dependent thermal conductivity of semiconductor nanowires is an important and necessary step before the fabrication of these nanodevices.

5.3.2.1 Definition and measurements

In physics, thermal conductivity, k , is an intensive property of a material that indicates its ability to conduct heat. For a material suspended between two heat reservoirs with different temperature T_h and T_c , the heat will be transferred from hot side (T_h) to cold side (T_c). The thermal conductance is then defined as the heat flux Δq divided by ΔT , where $\Delta T = T_h - T_c$ is the temperature difference between the two reservoirs.

Mathematically, the thermal conductance is written as:

$$\sigma(T) = \lim_{\Delta T \rightarrow 0} \frac{\Delta q}{\Delta T} \quad (70)$$

Analogous to electrical conductivity, the thermal conductivity k is defined as:

$$k(T) = (L / A) \times \sigma(T) = (L / s) \times \lim_{\Delta T \rightarrow 0} (\Delta q / \Delta T) \quad (71)$$

where L is the length of the nanowires and A is the cross sectional area of the nanowire.

Eq. (71) serves as the guideline for experimental measurement of thermal conductivity.

That is the thermal conductivity is usually determined by measuring the temperature gradient produced by a steady flow of the heat in a 1D geometry. Measurement on thermal conductivity is a quite standard procedure in the case of bulk materials; however, thermal conductivity measurement in low dimensional systems with nanoelements is rather difficult and sparse. Li et al [256] applied microfabricated suspended device to measure the thermal conductivity of Si nanowires with diameter varying from 22nm to 115nm over a temperature range of 20K to 320K. They have observed that the measured thermal conductivity was two orders of magnitude smaller than that of the bulk Si and decreased with decreasing wire diameter. Similar results have been obtained by Liu's et al [257] using Joule heating when the thermal

conductivity of a 20nm thick silicon thin film measured at room temperature was about 15% of the bulk value. However, the experimental values are still rare and no reports are available on the thermal conductivity of nanowires with diameters less than 20nm. Therefore, quantitative calculations of thermal conductivity of nanowires with tiny diameters to explain the observed results and to predict new phenomena are crucial for future applications.

5.3.2.2 Modeling consideration

Recently, Mazumder [258] and Chen [259] have applied Monte Carlo simulation to simulate the thermal conductivity of silicon thin film and nanowire by considering phonon dispersion relation as well as various scattering mechanism. They have suggested that the dispersion relation for nanowires obtained from elasticity theory should be used to evaluate thermal conductivity of nanowires in sub-100nm scale. Balandin and Wang [260] calculated the thermal conductivity based on the bulk Callaways's expression while taking into account the influence of Umklapp process, impurity and boundary scattering on the dispersion of confined acoustic-phonon modes. Later, Zou and Balandin [261] extended Balandin's previous work and took the nonequilibrium phonon distribution due to boundary scattering into consideration and calculated the thermal conductivity of Si nanowires with diameters comparable to the phonon mean free path. Mingo [251] numerically calculated the complete set of phonon dispersion curves using atomistic model of Si nanowires and his results were in good

agreement with experimental data [256] for Si nanowires with diameters greater than 35nm.

Following Mingo's approach, in diffusive regime of phonon propagation, the coefficient of thermal conductivity of semiconductor nanowires with diameter a can be written as a sum over all phonon branches:

$$k(T) = \frac{1}{\pi a^2} \sum_{\alpha} \int_{\omega_{\alpha}^l}^{\omega_{\alpha}^f} v(\alpha, \omega) \cdot \tau(\omega) \cdot \frac{\hbar \omega}{2\pi} \cdot \frac{df}{dT} d\omega \quad (72)$$

where f is Boson-Einstein function given by: $f(\omega) = \frac{1}{\exp(\hbar\omega/k_B T) - 1}$ and $\tau(\omega)$ is the life time of phonon. Mingo [251, 252] used this expression to calculate thermal conductivity of Si nanowires (in the absence of BOLS effect), with the averaged group velocity $\langle v_z(\omega) \rangle \equiv [\sum_{\alpha} v(\alpha, \omega) / N_b(\omega)]$, which was obtained from the complete set of dispersion relations based on the atomistic model of Si wires. As is discussed above, we propose to use the isotropic elastic continuum model for analytical simplicity to calculate various phonon branches and the corresponding phonon group velocity $v(\alpha, \omega) = d\omega/dq$. For convenience of numerical integration, we change the integration variable ω to $x = \hbar\omega/k_B T$. Therefore, Eq. (72) can be explicitly rewritten as:

$$k(T) = \frac{1}{\pi a^2} \frac{k_B^2}{\hbar^3} T \sum_{\alpha} \int_{x_{\alpha}^l}^{x_{\alpha}^f} \frac{d\omega_{\alpha}}{dq} \cdot \tau(x) \cdot \frac{x}{2\pi} \cdot \frac{x \cdot e^x}{(e^x - 1)^2} dx \quad (72.1)$$

The most intriguing parameter in Eq.(72.1), is the phonon life time τ , which depends on frequency, temperature and system size [303, 305, 306]. We shall assume that the interference of scattering process could be neglected, and then the phonon lifetime obeys the Matthiessen's rule similar to the case of conductivity:

$$\tau^{-1}(\omega) = \tau_B^{-1}(\omega) + \tau_i^{-1}(\omega) + \tau_U^{-1}(\omega) \quad (73)$$

where τ_B , τ_i and τ_U refer to the boundary scattering, impurity scattering and Umklapp scattering, respectively.

Table VIII lists some parameters used in the calculation.

Table VIII Shell thickness, Lamé constants, phonon velocities, and parameters related to the different scattering mechanism

shell thickness	$\delta a = 1.47\text{nm}$		
Lamé constant	$\mu_2 / \mu_1 = 1.879$		
Bond contraction coefficient	$c_i(z_i) = 2 / \{1 + \exp[(12 - z_i)/(8z_i)]\}$		
Velocity	c_t	c_l	v_0 (averaged bulk v)
	4650m/s	8410m/s	7400m/s
Scattering mechanism	Scattering rates	Fitting parameter	
Boundary scattering:	$\tau_B^{-1}(\omega) = D / v_0$ [252, 260]	$v_0^{-1} = 1 / 3(2c_t^{-1} + c_l^{-1})$	
Umklapp process	$\tau_U^{-1}(\omega) = AT\omega^2 e^{-C/T}$ [270, 271, 273, 274]	$A = 1.73 \times 10^{-19} \text{ s/KT}\omega^2$ [251] $C = 137.3\text{K}$	
Impurity scattering	$\tau_i^{-1}(\omega) = B\omega^4$ [252, 259-263]	$B = 1.32 \times 10^{-45} \text{ s}^3$ [251]	

From Figure 20, it can be seen that the difference in phonon frequencies in the core and shell (due to BOLS) modifies the phonon oscillations and increases the group velocities in the system significantly. Therefore, we then conclude from Eq. (72) that BOLS effect increases the thermal conductivity in silicon nanowires. Such behavior of nanowire conductivity probably could be explained by the presence of the relatively thin shell,

which “intermix” the eigenmodes of the ideal core and hence increase the total number of phonon channels for heat conduction.

In Figure 20, the relative change of thermal conductivity (that is, the thermal conductivity in Si nanowire including BOLS effect compared to the same diameter wire without considering BOLS effect) with respect to temperature for the first three modes are applied. We separate the torsional mode, longitudinal mode and flexural mode in order to distinguish the BOLS effects on these modes separately. Here, in order to keep Eq. (63) valid, the temperature considered must be much smaller than melting temperature. The highest temperature in Figure 20 is chosen to be room temperature, which is considerably smaller than the melting temperature for silicon, and hence Eq. (63) is valid. We can see from Figure 20 that the “plateau” value of the thermal conductivity increases with $\delta a/a$. This is expected from Eq. (72). In the equation, the term $\hbar\omega/k_B T$ (phonon heat capacity) approaches a constant value k_B at sufficiently high temperature, and the temperature has smaller effect on phonon life time, given that the parameters A , B and C listed in

Table VIII are independent of temperature. Hence the thermal conductivity depends critically on the group velocity at sufficiently high temperature. Since phonon group velocity increases with $\delta a/a$, the plateau value increases with $\delta a/a$.

Figure 20 Temperature dependence of relative change of thermal conductivity contributed from torsional, longitudinal, and flexural modes, respectively with $\delta a/a=0$, 0.05, 0.10 and 0.15.

The relationship between the relative change of thermal conductivity $\delta k/k$ and the diameter of silicon cylindrical nanowires at room temperature is also shown in Figure 21. As is expected, our result shows that for Si nanowire with larger diameter, the

BOLS effect does not affect the value significantly. As the diameter reduces, $\delta k/k$ increases and the increase of $\delta k/k$ is more pronounced for torsional mode. When $D = 62\text{nm}$, $\delta k/k$ is around 5% for torsional mode, 3% for longitudinal mode and about 2.6% for flexural mode. As the diameter reduces, $\delta k/k$ increases. When $D = 22\text{nm}$, $\delta k/k$ increases to 19%, 13% and 10% for torsional, longitudinal and flexural modes, respectively. The increase of $\delta k/k$ with decreasing of D can be explained in the following way. When the wire diameter D decreases, that is when $\delta a/a$ increases, the phonon frequencies ω increase. This makes the term $\hbar\omega(df/dT)$ smaller for a fixed T and from Eq. (73) we can see that thermal conductivity decreases. However, the BOLS effect pushes down the phonon branches, resulting in slower decrease of $\hbar\omega(df/dT)$ (and hence thermal conductivity) with decreasing diameter D . The great relative change of thermal conductivity shown in Figure 21 demonstrates the significant effect of BOLS on phonon spectrum and thermal conductivity. Although the isotropic elastic model does not give a very good approximation for short wavelength, this model discloses the BOLS effect which causes the decrease of phonon frequency and the increase of phonon group velocities, and hence the increase of thermal conductivity. These facts should be true even when other more accurate models are used.

Figure 21 Size dependence of the relative change of thermal conductivity at R.T.

5.4 Summary

Simple and straightforward analytical solutions for thermal expansion coefficient and surface energy density have been developed from the perspective of LBA approximation and BOLS correlation.

Our model demonstrates that the thermal expansion coefficient follows closely the temperature dependent specific heat and there is no empirical parameter or concepts in classical thermodynamics are required. Good agreement between the experimental data and theoretical predictions of T dependent TECs and lattice parameters for nitrides, metals, and diamond structures may evidence that LBA approach may represent the true situation of the experimental observations although further refinement by using the exact phonon density-of-states for the specific heat of a particular specimen is required.

The concepts of the energy density gain per unit volume and cohesive energy remain are suggested being essential to classify the surface energetics. The variation of surface energetics from the bulk values arises from the shortened and strengthened

bonds between the under-coordinated surface atoms. The functional dependence of the surface energy on the bonding identities and their temperature dependency are derived. The thermal weakening of surface energy is dominated by thermal expansion and surface bond contraction. Furthermore, the BOLS correlation approach allows us to estimate the atomic cohesive energy by reproducing the measured temperature dependence of surface tension.

The relative change of thermal conductivity of cylindrical silicon nanowire due to the BOLS effects has been discussed with a core-shell structure. The enhanced local Young's modulus in the shell region leads to increased group velocities and modifies the phonon dispersion relation. It is found that the overall phonon frequency decrease due to BOLS effect and the relative change of the thermal conductivity (comparing the calculated thermal conductivity when the BOLS effect is considered to that when the BOLS effect is not considered) increases with decreasing diameter.

Chapter 6 Conclusions and recommendations

6.1 Achievements

A set of analytical expressions have been developed here to describe the size and temperature dependent elastic, lattice vibronic, and thermal behaviors following the BOLS correlation and LBA approximation. The core idea of BOLS correlation is that the spontaneous surface bond contraction and associated bond strengthening dictate the size dependent change of material properties. By extending BOLS correlation into temperature domain, the approach named LBA approximation has been developed. The core idea of LBA approximation is that in order to predict the change of any measurable quantities under external stimulus, one only need to establish the functional dependence of the measurable quantities on the atomic bonding identities (bond length, strength, nature) of the representative bond and the response of these bonding identities to the external stimulus. These two approaches may provide a way to overcome the obstacle encountered in both classical and quantum approaches. Consistent understanding and the good agreement between predictions and experimental data provide evidence that the current approaches may represent the true situation in the less-coordinated systems.

Following the BOLS correlation and LBA approximation, improved atomic understanding and derived information about atomic cohesive energy, and dimer frequency have been obtained from good agreement between theoretical predictions and experimental data for size and temperature dependent Young's modulus, Raman frequency shift, thermal expansion coefficient and surface energy density, which are

beyond the scope of traditional theoretical approaches. The reproduction of observations reveals that:

- (a) The Young's modulus is proportional to the atomic energy density. Therefore, the monotonic decrease of Young's modulus with increasing temperature arises from thermal softening of atomic bonding energy and the thermal lattice constant expansion. Fitting to temperature dependent Young's modulus gives atomic cohesive energy.
- (b) The surface bond contraction and associated bond strengthening are responsible for the size dependent change of Young's modulus in nanoscale.
- (c) Derivation shows that the Raman frequency is proportional to CN , the square root of bonding energy and the reciprocal of bond length. Therefore the thermally induced redshift of Raman frequency arises from both bond length expansion and bond strength weakening with increasing temperature. The mode cohesive energy that relates to the relative motion of neighboring atoms can be obtained by fitting to the temperature dependent Raman frequency shift.
- (d) The dimer frequency of a monotonic chain can be obtained by studying the size dependent Raman frequency shift.
- (e) The temperature dependent thermal expansion coefficient is derived to follow the relationship for temperature dependent specific heat.
- (f) The concepts of the energy density gain per unit volume and cohesive energy remain are suggested being essential to classify the surface energetics.
- (g) The effect of surface bond contraction (also called BOLS effect) reduces the

phonon frequency, but increases the group velocity in phonon dispersion relation.

The thermal conductivity is calculated to be greater with additional BOLS effect comparing with the case without the consideration of BOLS effect.

6.2 Limitations

The current approach starts from a perfect crystal structure, where defects, impurities, or surface oxidation that are commonly observed in measurements, are not included.

However, if both the samples under consideration and the corresponding bulk sample are prepared and measured under exactly the same condition and the relative change instead of absolute value is used, the effect from artifacts such as impurities or defects can be minimized, and the results are purely size or temperature dependent.

Furthermore, the measurement technique may also affect the experimental data. For example, in mechanical strength measurement, besides the intrinsic material response, the applied strain rate or loading mode may sometimes affect the stress-strain profile, and hence leads to data variation. However, as an approximation, one is not able to cover all the aspects of deviations that may arise from material growth or measurement technique from perfect situation in a single theoretical model, as these fluctuations are random artifacts that are difficult to be controlled. Again, these effects can be minimized in current approach by using relative change.

Moreover, the dangling bonds are not considered in current approach, as a dangling bond is not a real bond that forms between two neighboring atoms.

As the current derived analytical expressions of the functional dependence of

various detectable material properties on bonding identities are the first order approximation (also the main contribution), there is still plenty of room for improvement by involving higher orders. For illustration purpose, we are more interested in the atomic origin and general trend of size and temperature dependent material properties in order to provide some guidance for device design and application. Therefore the first order approximation, for the mentioned purpose, is sufficient. Of course, further studies to include higher orders and therefore more precise predictions may be more fascinating.

6.3 Recommendations for future work

The concept of using a representative bond to study the entire specimen in LBA approach provides a new way to study the variation of material properties with applied external stimulus. The concept of representative bonds can be extended to different locations, such as edge, defect, impurity, and interface. Moreover, the combination of BOLS mechanics in size domain and LBA approach in temperature domain provides us a guideline to tune the physical properties of nanoscaled materials for the design and fabrication of new devices. Extension of the approaches to domains such as pressure, external electric and magnetic field could be more interesting.

Furthermore, the effect of bond order loss also exists for amorphous materials and hence affects the material properties. Studies on the similarities and differences between the crystal structure and the amorphous structure would be of great interest.

Author's publications:

1. **M. X. Gu**, T. C. Au Yeung, V. Nosikb and C. M. Tan, "Change in thermal conductivity of cylindrical silicon nanowires induced by surface bonding modification" *J. Appl. Phys.* 100, 094304 (2006).
2. **M. X. Gu**, L. K. Pan, B. K. Tay, and C. Q. Sun, "Atomistic origin and temperature dependence of Raman optical redshift in nanostructures: a broken bond rule" *J. Raman Spec.* 38 (2007).
3. **M. X. Gu**, C. Q. Sun, Z. Chen, T. C. Au Yeung, S. Li, C. M. Tan, and V. Nosik, "Size, temperature, and bond nature dependence of elasticity and its derivatives on extensibility, Debye temperature, and heat capacity of nanostructures", *Phys. Rev. B* 75, 125403 (2007).
4. **M. X. Gu**, L. K. Pan, Z. Sun, Y. Zhou, S. Z. Wang and C. Q. Sun, "Temperature dependence of the elastic and vibronic behavior of Si, Ge, Diamond crystals" *J. Appl. Phys.* 102, 083524 (2007).
5. **M. X. Gu**, L. K. Pan, T. C. Au Yeung, C. Q. Sun, "Atomic origin of the thermally driven softening of Raman optical phonons in group III nitrides", *J. Phys. Chem. C* 111, 13606 (2007).
6. **M. X. Gu** and C. Q. Sun, "Local bond average for the temperature dependence of lattice expansion", *J. Phys. Chem. B* 112, 7992 (2008).
7. T. C. Au Yeung, **M. X. Gu**, C. Q. Sun, George C. K. Chen, D. W. K. Wong, and V. Nosik, "Impact of surface bond-order loss on the phonon dispersion relations and the thermal conductivity of cylindrical Si nanowires" *Phys. Rev. B* 74, 155317

- (2006).
8. G. Ouyang, **M. X. Gu**, S. Y. Fu, C. Q. Sun, and W. G. Zhu “Determination of the Si-Si bond energy from the temperature dependence of elastic modulus and surface tension”. *Europhys. Lett.* **84**, 66005 (2008).
 9. M. Zhao, W. Zhen, J. Li, Zi Wen, **M. X. Gu**, and C. Q. Sun “Atomic origin and temperature dependence of surface energetics: an extended broken rule”. *Phys. Rev. B* **75**, 085427 (2007).
 10. T. C. Au Yeung, T. C. Chiam, C. Q. Sun, **M. X. Gu**, W. Z. Shangguan, and C. H. Kam, “Effect of surface bond-order loss on the electronic thermal conductivity of metallic polycrystalline films” *J. Appl. Phys.* **98**, 113707 (2005).

References:

- [1] F. A. Buot, "Mesoscopic physics and nanoelectronics: nanoscience and nanotechnology " *Physics Report*, vol. 234, pp. 73-174, 1993.
- [2] F. Rosei, "Nanostructured surfaces: challenges and frontiers in nanotechnology," *J. Phys. : Condens. Matter*, vol. 16, pp. S1373-S1436, 2004.
- [3] J. E. Bowen-Katari, V. L. Colvin, and A. P. Alivisatos, "X-Ray photoelectron spectroscopy of CdSe nanocrystals with applications to studies of the nanocrystal surface," *Journal of Physical Chemistry*, vol. 98, pp. 4109-4117, 1994.
- [4] C. Q. Sun, "Size dependence of nanostructures: impact of bond order deficiency," *Prog Solid State Chem* vol. 35, pp. 1-1567, 2007.
- [5] B. Cappella and G. Dietler, "Force-distance curves by atomic force microscopy," *Surf. Sci. Rep.*, vol. 14, pp. 1-104, 1999.
- [6] C. Binns, "Nanoclusters deposited on surfaces," *Surf. Sci. Rep.*, vol. 44, pp. 1-49, 2001.
- [7] A. I. Rusanov, "Surface thermodynamics revisited," *Surf. Sci. Rep.*, vol. 58, pp. 111-238, 2005.
- [8] W. J. Huang, R. Sun, J. Tao, L. D. Menard, R. G. Nuzzo, and J. M. Zuo, "Coordination-dependent surface atomic contraction in nanocrystals revealed by coherent diffraction " *Nature Materials*, vol. 7, 2008.
- [9] L. Pauling, "Atomic radii and interatomic distances in metals," *J. Am. Chem. Soc.* , vol. 69, pp. 524-553, 1947.

- [10] V. M. Goldschmidt, *Ber Deut Chem Ges*, vol. 60, p. 1270, 1927.
- [11] J. E. Miller, A. J. Kropf, Y. Zha, J. R. Regalbuto, L. Delannoy, C. Louis, E. Bus, and J. A. Bokhoven van, "The effect of gold particle size on Au-Au bond length and reactivity toward oxygen in supported catalysts," *Journal of Catalysis*, vol. 240, pp. 222-234, 2006.
- [12] T. Comaschi, A. Balerna, and S. Mobilio, "Temperature dependence of the structural parameters of gold nanoparticles investigated with EXAFS," *Physical Review B*, vol. 77, p. 075432, 2008.
- [13] J. B. Pendry, "LEED and the crystallography of surfaces," *Surf. Sci. Rep.*, vol. 19, pp. 87-97, 1993.
- [14] K. P. Bohnen and K. M. Ho, "Structure and dynamics at metal surfaces," *Surf. Sci. Rep.*, vol. 19, pp. 99-120, 1993.
- [15] P. K. Jain, "A DFT based study of the low-energy electronic structures and properties of small gold clusters," *Structural Chemistry*, vol. 16, pp. 421-426, 2005.
- [16] O. G. Shpyrko, A. Y. Grigoriev, C. Steimer, P. S. Pershan, B. Lin, M. Meron, T. Graber, J. Gerbhardt, B. Ocko, and M. Deutsch, "Anomalous layering at the liquid Sn surface" *Physical Review B*, vol. 70, p. 224206, 2004.
- [17] W. J. Huang, R. Sun, J. Tao, L. D. Menard, R. G. NUZZO, and J. M. ZUO, "Coordination-dependent surface atomic contraction in nanocrystals revealed by coherent diffraction " *Nature Material*, vol 7, pp. 308-313, 2008.
- [18] Y. Ding, C. Q. Sun, and Y. C. Zhou, "Nanocavity strengthening: Impact of the

- broken bonds at the negatively curved surfaces," *Journal of Applied Physics*, vol. 103, p. 084317, 2008.
- [19] R. Smoluchowski, "Anisotropy of the electronic work function of metals," *Physical Review*, vol. 60, p. 661, 1941.
- [20] M. W. Finnis and V. Heine, "Theory of lattice contraction at aluminium surfaces," *Journal of physics F*, vol. 4, pp. L37-L41, 1974.
- [21] B. Gilbert, F. Huang, H. Zhang, Glenn A. Waychunas, and J. F. Banfield, "Nanoparticles: Strained and Stiff," *Science*, vol. 305, pp. 651-654, 2004.
- [22] J. Wang, H. L. Duan, Z. P. Huang, and B. L. Karihaloo, "A scaling law for properties of nano-structured materials," *Proceedings of the Royal Society. A-Mathematical, physical, and engineering sciences*, vol. 462, pp. 1355-1363, 2006.
- [23] V. Baltz, J. Sort, B. Rodmacq, B. Dieny, and S. Landis, "Size effects on exchange bias in sub-100 nm ferromagnetic-antiferromagnetic dots deposited on prepatterned substrates," *Applied Physics Letters*, vol. 84, pp. 4923-4925, 2004.
- [24] Z. G. Qian, W. Z. Shen, H. Ogawa, and Q. X. Guo, "Experimental studies of lattice dynamical properties in indium nitride," *J. Phys.: Condens. Matter*, vol. 16, pp. R381-R414, 2004.
- [25] X. H. Hu and J. Zi, "Reconstruction of phonon dispersion in Si nanocrystals," *Journal of Physics-Condensed Matter*, vol. 14, pp. L671-L677, Oct 21 2002.
- [26] L. K. Pan, C. Q. Sun, T. P. Chen, S. Li, C. M. Li, and B. K. Tay, "Dielectric

- suppression of nanosolid silicon," *Nanotechnology*, vol. 15, pp. 1802-1806, 2004.
- [27] G. V. Gibbs, M. B. Boisen, L. L. Beverly, and K. M. Rosso, "A computational quantum-chemical study of the bonded interactions in Earth materials and structurally and chemically related molecules. Molecular modeling theory: applications in the Geosciences.," *Mineralogical Society of America*, vol. 42, pp. 345-382, 2001.
- [28] C. Q. Sun, T. P. Chen, B. K. Tay, S. Li, H. Huang, Y. B. Zhang, L. K. Pan, S. P. Lau, and X. W. Sun, "An extended 'quantum confinement' theory: surface-coordination imperfection modifies the entire band structure of a nanosolid," *J. Phys. D: Appl. Phys.*, vol. 34, pp. 3270-3479, 2001.
- [29] T. C. Au Yeung, T. C. Chiam, C. K. Chen, C. Q. Sun, W. Z. Shangguan, and C. H. Kam, "Effect of surface bond-order loss on the electrical resistivity of metallic polycrystalline thin films," *Physical Review B*, vol. 72, p. 155417, 2005.
- [30] T. C. Au Yeung, M. X. Gu, C. Q. Sun, C. K. Chen, and V. Nosik, "Impact of surface bond-order loss on phonon dispersion relations and thermal conductivity of cylindrical Si nanowires," *Physical Review B*, vol. 74, p. 155317, 2006.
- [31] Y. Niimi, T. Matsui, H. Kambara, and H. Fukuyama, "STM/STS measurements of two-dimensional electronic states trapped around surface defects in magnetic fields," *Physica E*, vol. 34, p. 100, 2006.

- [32] V. S. Stepanyuk, A. N. Klavsyuk, L. Niebergall, and P. Bruno, "End electronic states in Cu chains on Cu(111): Ab initio calculations," *Physical Review B*, vol. 72, p. 153407, 2005.
- [33] J. N. Crain and D. T. Pierce, "End states in one-dimensional atom chains " *Science*, vol. 307, p. 703, 2005.
- [34] Y. Kobayashi, K. Kusakabe, K. Fukui, and T. Enoki, "STM/STS observation of peculiar electronic states at graphite edges," *Physica E*, vol. 34, pp. 678-1, 2006.
- [35] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, "Edge state in graphene ribbons: Nanometer size effect and edge shape dependence," *Physical Review B*, vol. 54, p. 17954, 1996.
- [36] S. Mattila, J. A. Leiro, M. Heinonen, and T. Laiho, " Core level spectroscopy of MoS₂," *Surface Science*, vol. 600, p. 5168, 2006.
- [37] L. Pauling, "Atomic radii and interatomic distancedcs in metals," *J. Am Chem Soc*, vol. 69, pp. 542-543, 1947.
- [38] P. J. Feibelman, "Relaxation of hcp (0001) surfaces: A chemical view," *Physical Review B*, vol. 53, pp. 13740-13746, 1996.
- [39] M. J. Simnot, "The solid state of engineers," *Wiley. & Sons, New York*, 1963.
- [40] C. Q. Sun, L. K. Pan, Y. Q. Fu, B. K. Tay, and S. Li, "Size dependence of the 2p-level shift of nanosolid silicon," *J Phys Chem B*, vol. 107, pp. 5113-5115, 2003.
- [41] C. Q. Sun, L. K. Pan, C. M. Li, and S. Li, "Size-induced acoustic hardening and optic softening of phonons in CdS, InP, CeO₂, SnO₂, and Si nanostructures,"

- Physical Review B*, vol. 72, p. 134301, 2005.
- [42] T. J. Delph, "Local stresses and elastic constants at the atomic scale," *Proceedings of the Royal Society. A-Mathematical, physical, and engineering sciences*, vol. 461, pp. 1869-1888, 2005.
- [43] J. Cormier, J. M. Rickman, and T. J. Delph, "Stress calculation in atomistic simulations of perfect and imperfect solids," *Journal of Applied Physics*, vol. 89, p. 99, 2001.
- [44] G. Dalba, P. Fornasini, R. Grisenti, and J. Purans, "Anharmonicity and thermal expansion in crystalline germanium," *Journal of Synchrotron Radiation*, vol. 6, pp. 253-254, May 1 1999.
- [45] A. N. Cleland and M. L. Roukes, "Fabrication of high frequency nanometer scale mechanical resonators from bulk Si crystals," *Applied Physics Letters*, vol. 69, p. 2653, 1996.
- [46] T. F. Li, Y. A. Pashkin, O. Astafiev, Y. Nakamura, and J. S. Tsai, "High-frequency metallic nanomechanical resonators," *Applied Physics Letters*, vol. 92, p. 043112, 2008.
- [47] S. P. Reilly, R. K. Leach, A. Cuenat, S. A. Awan, and M. Lowe, "Overview of MEMS sensors and the metrology requirements for their manufacture. NMS Programme for Engineering Measurement 2005-2008," *NPL report DEPC-EM 008*, 2006.
- [48] K. J. Hemker and W. N. Sharpe Jr., "Microscale characterization of mechanical properties," *Annual Review of Materials Research*, vol. 37, pp. 93-126, 2007.

- [49] O. Kraft and C. A. Volkert, "Mechanical testing of thin films and small structures," *Advanced Engineering Materials*, vol. 3, pp. 99-110, 2001.
- [50] V. T. Srikar and S. M. Spearing, "A critical review of microscale mechanical testing methods used in the design of microelectromechanical systems," *Experimental Mechanics*, vol. 43, pp. 238-247. , 2003.
- [51] M. A. Haque and M. T. A. Saif, "A review of MEMS-based microscale and nanoscale tensile and bending testing " *Experimental Mechanics*, vol. 43, p. 248, 2003.
- [52] E. P. S. Tan and C. T. Lim, "Mechanical characterization of nanofibers-A review," *Compos. Sci. Technol.*, vol. 66, pp. 1102-1111, 2006.
- [53] X. Han, Z. Zhang, and Z. L. Wang, "Experimental nanomechanics of one dimensional nanomaterials by in situ microscopy," *Nano: Brief Report and Reviews*, vol. 2, pp. 249-271, 2007.
- [54] O. Lourie and H. D. Wagner, "Transmission electron microscopy observations of fracture of single-wall carbon nanotubes under axial tension," *Applied Physics Letters*, vol. 73, p. 3527, 1998.
- [55] H. Xu and J. M. K. Wiezorek, "Transmission electron microscopy of room temperature deformed polytwinned L10-ordered FePd," *Acta Materialia*, vol. 52, pp. 395-403, 2004.
- [56] C. H. Lin, M. Chang, X. Li, and J. R. Deka, "Measurement of mechanical properties of boron nanowire using nano-manipulation system," *PROCEEDINGS OF THE 35TH INTERNATIONAL MATADOR*

- CONFERENCE - FORMERLY THE INTERNATIONAL MACHINE TOOL DESIGN AND RESEARCH CONFERENCE* pp. 275-278, 2007.
- [57] X. Li, P. Nardi, C.-W. Baek, J.-M. Kim, and Y.-K. Kim, "Direct nanomechanical machining of gold nanowires using a nanoindenter and an atomic force microscope," *J. Micromech. Microeng.*, vol. 15, pp. 551-556, 2005.
- [58] X. D. Li, H. S. Hao, C. J. Murphy, and K. K. Caswell, "Nanoindentation of silver nanowires," *Nano Letters*, vol. 3, pp. 1495-1498, 2003.
- [59] H. D. Espinosa, B. C. Prorok, and M. Fischer, "A methodology for determining mechanical properties of freestanding thin films and MEMS materials," *Journal of the Mechanics and Physics of Solids*, vol. 51, pp. 47-67, 2003.
- [60] S.-H. Lee, C. Tekmen, and W. M. Sigmund, "Three-point bending of electrospun TiO₂ nanofibers," *Materials Science and Engineering A*, vol. 398, pp. 77-81, 2005.
- [61] F. Vaz, S. Carvalho, L. Rebouta, M. Z. Silva, A. Paúl, and D. Schneider, "Young's modulus of (Ti,Si)N films by surface acoustic waves and indentation techniques," *Thin Solid Films*, vol. 408, pp. 160-168, 2002.
- [62] D. Schneider, T. Schwarz, and B. Schultrich, "Determination of elastic modulus and thickness of surface layers by ultrasonic surface waves," *Thin Solid Films*, vol. 219, pp. 92-102, 1992.
- [63] D. C. Hurley, K. Shen, N. M. Jennet, and J. A. Turner, "Atomic force acoustic microscopy methods to determine thin-film elastic properties," *Journal of Applied Physics*, vol. 94, p. 2347, 2003.

- [64] U. Rabe, S. Amelio, E. Kester, V. Scherer, S. Hirsekorn, and W. Arnold, "Quantitative determination of contact stiffness using atomic force acoustic microscopy," *Ultrasonics*, vol. 38, pp. 430-437, 2000.
- [65] T. D. Shen, C. C. Koch, T. Y. Tsui, and G. M. Pharr, "On the elastic moduli of nanocrystalline Fe, Cu, Ni, and Cu-Ni alloys prepared by mechanical milling/alloying," *Journal of Materials Research*, vol. 10, p. 2892, 1995.
- [66] G. E. Fougere, L. Riester, M. Ferber, J. R. Weertman, and R. W. Siegel, "Young's modulus of nanocrystalline Fe measured by nanoindentation," *Materials Science and Engineering A*, vol. 204, pp. 1-6. , 1995.
- [67] B. Kracke and B. Damaschke, "Measurement of nanohardness and nanoelasticity of thin gold films with scanning force microscope," *Applied Physics Letters*, vol. 77, p. 361, 2000.
- [68] T. Tsakalakos and J. E. Hilliard, "Elastic modulus in composition-modulated copper-nickel foils," *Journal of Applied Physics*, vol. 54, p. 734, 1983.
- [69] C. K. Huang, W. M. Lou, C. J. Tsai, T. C. Wu, and H. Y. Lin, "Mechanical properties of polymer thin film measured by the bulge test " *Thin Solid Films*, vol. 515, pp. 7222-7226, 2007.
- [70] A. J. Kalkman and A. H. Verbruggen, "High-temperature bulge-test setup for mechanical testing of free-standing thin films," *Rev. Sci. Instrum.*, vol. 74, p. 1383, 2003.
- [71] J. D. Hall, N. E. Apperson, B. T. Crozier, C. Xu, R. F. Richards, and D. F. Bahr, "A facility for characterizing the dynamic mechanical behavior of thin

- membranes for microelectromechanical systems," *Rev. Sci. Instrum.*, vol. 73, p. 2067, 2002.
- [72] A. Karimi, O. R. Shojaei, T. Kruml, and J. L. Martin, "Characterisation of TiN thin films using the bulge test and the nanoindentation technique " *Thin Solid Films*, vol. 308-309, pp. 334-339, 1997.
- [73] M. A. Haque and M. T. A. Saif, "Thermo-mechanical properties of nano-scale freestanding aluminum films," *Thin Solid Films*, vol. 484, pp. 364-368, 2005.
- [74] F. Szuets, M. Werner, R. S. Sussmann, C. S. J. Pickles, and H. J. Fecht, "Temperature dependence of Young's modulus and degradation of chemical vapor deposited diamond," *Journal of Applied Physics*, vol. 86, pp. 6010-6017, 1999.
- [75] Y. H. Wu, F. J. McGarry, B. Z. Zhu, J. R. Keryk, and D. E. Katsoulis, "Temperature effect on mechanical properties of toughened silicone resins," *Polymer Eng. Sci.*, vol. 45, pp. 1522-1531, 2005.
- [76] N. Ono, R. Nowak, and S. Miura, "Effect of deformation temperature on Hall-Petch relationship registered for polycrystalline magnesium," *Mater. Lett.*, vol. 58, pp. 39-43, 2004.
- [77] J. Schiotz, T. Vegge, F. D. Di Tolla, and K. W. Jacobsen, "Atomic-scale simulations of the mechanical deformation of nanocrystalline metals," *Physical Review B*, vol. 60, p. 11971, 1999.
- [78] N. A. Krasilnikov, Z. Pakiel, W. Lojkowski, and R. Z. Valiev, "Excellent mechanical properties of nickel processed by high pressure technique," *Solid*

- State Phenomena*, vol. 94, pp. 51-54, 2003.
- [79] P. Kury and M. Horn-von, "Impact of thermal dependence of elastic constants on surface stress measurements," *Rev. Sci. Instrum.*, vol. 75, pp. 1357-1358, 2004.
- [80] Q. Liu, X. P. Wang, F. J. Liang, J. X. Wang, and Q. F. Fang, "Hardness enhancement and oxidation resistance of nanocrystalline TiN/MoxC multilayer films," *Mater. Res. Bull.*, vol. 41, pp. 1430-1436, 2006.
- [81] H. Ledbetter, A. Migliori, J. Betts, S. Harrington, and S. El-Khatib, "Zero-temperature bulk modulus of alpha-plutonium," *Physical Review B*, vol. 71, p. 172101, 2005.
- [82] C. L. Zhang and H. S. Shen, "Temperature-dependent elastic properties of single-walled carbon nanotubes: Prediction from molecular dynamics simulation," *Applied Physics Letters*, vol. 89, p. 081904, 2006.
- [83] R. Dingreville, J. M. Qu, M. Cherkaoui, and M. J., "Surface free energy and its effect on the elastic behavior of nano-sized particles, wires and films," *J. Mech. Phys. Solids*, vol. 53, pp. 1827-1854, 2005.
- [84] A. Duckham, D. Z. Zhang, D. Liang, V. Luzin, R. C. Cammarata, R. L. Leheny, C. L. Chien, and T. P. Weihs, "Temperature dependent mechanical properties of ultra-fine grained FeCo2V," *Acta Materialia*, vol. 51, pp. 4083-4093, 2003.
- [85] M. Born and K. Huang, *Dynamical theory of crystal lattices*: Clarendon Press, 1954.
- [86] J. B. Wachtman, W. E. Tefft, D. G. Lam, and C. S. Apstein, "Exponential

- temperature dependence of Young's modulus for several oxides," *Physical Review*, vol. 122, p. 1754, 1961.
- [87] R. J. Bruls, H. T. Hintzen, G. de With, and R. Metselaar, "The temperature dependence of the Young's modulus of MgSiN_2 , AlN , and Si_3N_4 ," *Journal of the European Ceramic Society*, vol. 21, pp. 263-268, 2001.
- [88] O. L. Anderson, "Derivation of Wachtman's equation for the temperature dependence of elastic moduli of oxide compounds," *Physical Review*, vol. 144, p. 553, 1966.
- [89] M. L. Nandanpawar and S. Rajagopalan, "Wachtman's equation and temperature dependence of bulk moduli in solids," *Journal of Applied Physics*, vol. 49, p. 3977, 1978.
- [90] S. C. Lakkad, "Temperature dependence of the elastic constants," *Journal of Applied Physics*, vol. 42, p. 4277, 1971.
- [91] C. Kittel, *Introduction to solid state physics*, 6th ed. New York: J. Wiley, 1986.
- [92] U. Gysin, S. Rast, P. Ruff, E. Meyer, D. W. Lee, P. Vettiger, and C. Gerber, "Temperature dependence of the force sensitivity of silicon cantilevers," *Physical Review B*, vol. 69, p. 045403, Jan 2004.
- [93] M. E. Fine, "Elasticity and thermal expansion of germanium between -195 and 275," *Journal of Applied Physics*, vol. 24, p. 338, 1953.
- [94] D. A. Czaplewski, J. P. Sullivan, T. A. Friedmann, and J. R. Wendt, "Temperature dependence of the mechanical properties of tetrahedrally coordinated amorphous carbon thin films," *Applied Physics Letters*, vol. 87, p.

- 161915', Oct 17 2005.
- [95] J. Garai and A. Laugier, "The temperature dependence of the isothermal bulk modulus at 1 bar pressure " *Journal of Applied Physics*, vol. 101, p. 023514, 2007.
- [96] S. P. Dodd, G. A. Saunders, M. Cankurtaran, and B. James, "Ultrasonic study of the elastic and nonlinear acoustic properties of ceramic aluminum nitride," *Journal of Materials Science*, vol. 36, pp. 723-729, Feb 2001.
- [97] T. Ito, T. Araki, T. Akiyama, and K. Nakamura, "A simple approach to temperature dependence of strain energy: Application to GaN-based semiconductors," *Journal of Crystal Growth*, vol. 301-302, pp. 62-66, 2007.
- [98] W. W. Gerberich, W. M. Mook, C. R. Perrey, C. B. Carter, M. I. Baskes, R. Mukherjee, A. Gidwani, J. Heberlein, P. H. McMurphy, and S. L. Girshick, "Superhard silicon nanospheres," *J. Mech. Phys. Solids* vol. 51, pp. 979-992, 2003.
- [99] G. Y. Jing, H. L. Duan, X. M. Sun, Z. S. Zhang, J. Xu, Y. D. Li, J. X. Wang, and D. P. Yu, "Surface effects on elastic properties of silver nanowires: Contact atomic-force microscopy," *Physical Review B*, vol. 73, p. 235409, 2006.
- [100] J. Q. Broughton, C. A. Meli, P. Vashishta, and R. K. Kalia, *Physical Review B*, vol. 56, p. 611, 1997.
- [101] G. Y. Jing, H. Ji, W. Y. Yang, J. Xu, and D. P. Yu, "Study of the bending modulus of individual silicon nitride nanobelts via atomic force microscopy," *Applied Physics A-Materials Science & Processing*, vol. 82, pp. 475-478, Mar 2006.

- [102] C. Q. Sun, B. K. Tay, S. P. Lau, X. W. Sun, X. T. Zeng, S. Li, H. Bai, H. Liu, Z. H. Liu, and E. Y. Jiang, "Bond contraction and lone pair interaction at nitride surfaces," *Journal of Applied Physics*, vol. 90, p. R2615, 2001.
- [103] R. E. Miller and V. B. Shenoy, "Size-dependent elastic properties of nanosized structural elements," *Nanotechnology*, vol. 11, pp. 139-147, 2000.
- [104] C. Q. Chen, Y. Shi, Y. S. Zhang, J. Zhu, and Y. J. Yan, "Size dependence of Young's modulus in ZnO nanowires," *Physical Review Letters*, vol. 96, p. 075505, 2006.
- [105] A. J. Kulkarni, M. Zhou, and F. J. Ke, "Orientation and size dependence of the elastic properties of zinc oxide nanobelts," *Nanotechnology*, vol. 16, pp. 2749-2756, 2005.
- [106] J. Song, X. Wang, E. Riedo, and Z. L. Wang, "Elastic property of vertically aligned nanowires," *Nano Letter*, vol. 5, pp. 1954-158, 2005.
- [107] X. D. Bai, P. X. Gao, Z. L. Wang, and E. G. Wang, "Dual-mode mechanical resonance of individual ZnO nanobelts," *Applied Physics Letters*, vol. 82, pp. 4806-4808, 2003.
- [108] K. Yum, Z. Wang, A. P. Suryavanshi, and M. F. Yu, "Experimental measurement and model analysis of damping effect in nanoscale mechanical beam resonators in air," *Journal of Applied Physics*, vol. 96, pp. 3933-3938, 2004.
- [109] S. Cuenot, C. Fretigny, S. Demoustier-Champagne, and B. Nysten, "Surface tension effect on the mechanical properties of nanomaterials measured by atomic force microscopy," *Physical Review B*, vol. 69, p. 165410, 2004.

- [110] S. Cuenot, S. Demoustier-Champagne, and B. Nysten, "Elastic and Shear Moduli of Single-Walled Carbon Nanotube Ropes," *Physical Review Letters*, vol. 82, p. 944, 2000.
- [111] S. Cuenot, C. Frétiigny, S. Demoustier-Champagne, and B. Nysten, "Measurement of elastic modulus of nanotubes by resonant contact atomic force microscopy," *Journal of Applied Physics*, vol. 93, pp. 5650-5655, 2003.
- [112] T. Kizuka, Y. Takatani, K. Asaka, and R. Yoshizaki, "Measurements of the atomistic mechanics of single crystalline silicon wires of nanometer width," *Physical Review B*, vol. 72, p. 035333, 2005.
- [113] A. San Paulo, J. Bokor, R. T. Howe, R. He, P. Yang, D. Gao, C. Carraro, and R. Maboudian, "Mechanical elasticity of single and double clamped silicon nanobeams fabricated by the vapor-liquid-solid method," *Applied Physics Letters*, vol. 87, p. 053111, 2005.
- [114] M. Kopycinska-Muller, R. H. Geiss, J. Muller, and D. C. Hurley, "Elastic-property measurements of ultrathin films using atomic force acoustic microscopy," *Nanotechnology*, vol. 16, pp. 703-709, 2005.
- [115] W. J. Price, S. A. Leigh, S. M. Hsu, T. E. Patten, and G. Y. Liu, "Measuring the size dependence of Young's modulus using force modulation atomic force microscopy," *Journal of Physical Chemistry A*, vol. 110, pp. 1382-1388, 2006.
- [116] S. G. Nilsson, X. Borrise, and L. Montelius, "Size effect on Young's modulus of thin chromium cantilevers," *Applied Physics Letters*, vol. 85, pp. 3555-3557, 2004.

- [117] X. Li, T. Ono, Y. Wang, and M. Esashi, "Ultrathin single-crystalline-silicon cantilever resonators: Fabrication technology and significant specimen size effect on Young's modulus," *Applied Physics Letters*, vol. 83, p. 3081, 2003.
- [118] X. Li, X. Wang, Q. Xiong, and P. C. Eklund, "Mechanical Properties of ZnS Nanobelts," *Nano Letters*, vol. 5, pp. 1982-1986, 2005.
- [119] J. Q. Broughton, C. A. Meli, P. Vashishta, and R. K. Kalia, "Direct atomistic simulation of quartz crystal oscillators: Bulk properties and nanoscale devices," *Physical Review B*, vol. 56, pp. 611-618, 1997.
- [120] M. A. Haque and M. T. A. Saif, "Deformation mechanisms in free-standing nanoscale thin films: A quantitative in situ transmission electron microscope study," *PNAS*, vol. 101, p. 6335, 2004.
- [121] C. Garie, D. X. Ye, F. Tang, R. C. Picu, G. C. Wang, and T. M. Lu, "Mechanical testing of isolated amorphous silicon slanted nanorods " *J. Nanosci. Nanotech.*, vol. 5, pp. 1893-1897, 2005.
- [122] B. Wu, A. Heidelberg, and J. J. Boland, "Mechanical properties of ultrahigh-strength gold nanowires," *Nat. Mater.*, vol. 4, p. 525, 2005.
- [123] H. Liang, M. Upmanyu, and H. Huang, "Size-dependent elasticity of nanowires: Nonlinear effects," *Physical Review B*, vol. 71, p. 241403, 2005.
- [124] B. Lee and R. E. Rudd, "First-principles calculation of mechanical properties of Si<001> nanowires and comparison to nanomechanical theory," *Physical Review B*, vol. 75, p. 195328, 2007.
- [125] J. W. Cahn, "Surface stress and the chemical equilibrium of small crystals—I.

- the case of the isotropic surface," *Acta Metallurgica*, vol. 28, pp. 1333-1347, 1980.
- [126] R. E. Rudd, "Coarse-grained molecular dynamics for computer modeling of nanomechanical systems," *Int. J. Multiscale Comp. Engin.*, vol. 2, pp. 203-220, 2004.
- [127] A. Nakano, R. K. Kalia, and P. Vashishta, "First sharp diffraction peak and intermediate-range order in amorphous silica: finite-size effects in molecular dynamics simulations," *J. Non-Cryst. Solids*, vol. 171, pp. 157-163, 2004.
- [128] http://en.wikipedia.org/wiki/Raman_spectroscopy#History.
- [129] D. A. Long, "Early history of the Raman Effect," *International Reviews in Physical Chemistry*, vol. 7, p. 317, 1988.
- [130] X. D. Pu, J. Chen, W. Z. Shen, H. Ogawa, and Q. X. Guo, "Temperature dependence of Raman scattering in hexagonal indium nitride films," *Journal of Applied Physics*, vol. 98, p. 033527, 2005.
- [131] P. H. Tan, Y. M. Deng, Q. Zhao, and W. C. Cheng, "The intrinsic temperature effect of the Raman spectra of graphite," *Applied Physics Letters*, vol. 74, pp. 1818-1820, Mar 29 1999.
- [132] S. A. Solin and N. Casewell, "Raman scattering from alkali graphite intercalation compounds," *Journal of Raman Spectroscopy*, vol. 10, pp. 129-135, 1991.
- [133] M. Haluška, D. Obergfell, J. C. Meyer, G. Scalia, G. Ulbricht, B. Krauss, D. H. Chae, T. Lohmann, M. Lebert, M. Kaempgen, M. Hulman, J. Smet, S. Roth, and

- K. von Klitzing, "Investigation of the shift of Raman modes of graphene flakes," *Phys. Stat. Sol. (b)*, vol. 244, pp. 4143-4146, 2007.
- [134] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, "Raman Spectrum of Graphene and Graphene Layers," *Physical Review Letters*, vol. 97, p. 187401, 2006.
- [135] A. Tanaka, S. Onari, and T. Arai, "Raman-Scattering from Cdse Microcrystals Embedded in a Germanate Glass Matrix," *Physical Review B*, vol. 45, pp. 6587-6592, Mar 15 1992.
- [136] V. V. Ursaki, I. M. Tiginyanu, V. V. Zalamai, E. V. Rusu, G. A. Emelchenko, V. M. Masalov, and E. N. Samarov, "Multiphonon resonant Raman scattering in ZnO crystals and nanostructured layers," *Physical Review B*, vol. 70, p. 155204, 2004.
- [137] P. G. Klemens, "Anharmonic Decay of Optical Phonons," *Physical Review*, vol. 148, p. 147, 1996.
- [138] M. Balkanski, R. F. Wallis, and E. Haro, "Anharmonic Effects in Light-Scattering Due to Optical Phonons in Silicon," *Physical Review B*, vol. 28, pp. 1928-1934, 1983.
- [139] V. Darakchieva, P. P. Paskov, E. Valcheva, T. Paskova, B. Monemar, M. Schuber, H. Lu, and W. J. Schaff, "Deformation potentials of the E1(TO) and E2 modes of InN," *Applied Physics Letters*, vol. 84, p. 3636, 2004.
- [140] S. Anand, P. Verma, K. P. Jain, and S. C. Abbi, "Temperature dependence of

- optical phonon lifetimes in ZnSe," *Physica B-Condensed Matter*, vol. 226, pp. 331-337, 1996.
- [141] M. S. Liu, L. A. Bursill, S. Prawer, and R. Beserman, "Temperature dependence of the first-order Raman phonon line of diamond," *Physical Review B*, vol. 61, pp. 3391-3395, Feb 1 2000.
- [142] J. B. Cui, K. Amtmann, J. Ristein, and L. Ley, "Noncontact temperature measurements of diamond by Raman scattering spectroscopy," *Journal of Applied Physics*, vol. 83, pp. 7929-7933, Jun 15 1998.
- [143] C. Ramkumar, K. P. Jain, and S. C. Abbi, "Raman-scattering probe of anharmonic effects due to temperature and compositional disorder in III-V binary and ternary alloy semiconductors," *Physical Review B*, vol. 53, pp. 13672-13681, 1996.
- [144] G. Viera, S. Huet, and L. Boufendi, "Crystal size and temperature measurements in nanostructured silicon using Raman spectroscopy," *Journal of Applied Physics*, vol. 90, pp. 4175-4183, 2001.
- [145] J. Menéndez and M. Cardona, "Temperature-Dependence of the 1st-Order Raman-Scattering by Phonons in Si, Ge, and α -Sn - Anharmonic Effects," *Physical Review B*, vol. 29, pp. 2051-2059, 1984.
- [146] W. S. Li, Z. X. Shen, Z. C. Feng, and S. J. Chua, "Temperature dependence of Raman scattering in hexagonal gallium nitride films," *Journal of Applied Physics*, vol. 87, pp. 3332-3337, 2000.
- [147] M. Kuball, J. M. Hayes, Y. Shi, J. H. Edgar, A. D. Prins, N. W. A. van Uden, and

- D. J. Dunstan, "Raman scattering studies on single-crystalline bulk AlN: temperature and pressure dependence of the AlN phonon modes," *Journal of Crystal Growth*, vol. 231, pp. 391-396, Oct 2001.
- [148] H. Tang and I. P. Herman, "Raman Microprobe Scattering of Solid Silicon and Germanium at the Melting Temperature," *Physical Review B*, vol. 43, pp. 2299-2304, 1991.
- [149] H. H. Burke and I. P. Herman, "Temperature-Dependence of Raman-Scattering in Ge_{1-x}Si_x Alloys," *Physical Review B*, vol. 48, pp. 15016-15024, 1993.
- [150] N. M. Gasanly and R. Pala, "Anharmonic line shift and linewidth of the Raman modes in GaS_{0.75}Se_{0.25} layered crystals," *Physica Status Solidi B-Basic Research*, vol. 234, pp. 665-673, 2002.
- [151] J. Jiménez, E. Martín, A. Torres, and J. P. Landesman, "Temperature dependence of the Raman spectrum of Al_xGa_{1-x}As ternary alloys," *Physical Review B*, vol. 58, pp. 10463-10469, Oct 15 1998.
- [152] A. Link, K. Bitzer, W. Limmer, R. Sauer, C. Kirchner, V. Schwegler, M. Kamp, D. G. Ebling, and K. W. Benz, "Temperature dependence of E₂ and A₁(LO) phonons in GaN and AlN," *Journal of Applied Physics*, vol. 88, p. 6256, 1999.
- [153] M. S. Liu, L. A. Bursill, S. Praver, K. W. Nugent, Y. Z. Tong, and G. Y. Zhang, "Temperature dependence of Raman scattering in single crystal GaN films," *Applied Physics Letters*, vol. 74, pp. 3125-3127, 1999.
- [154] M. A. Omar, *Elementary Solid State Physics: Principles and Applications*. New York: Addison-Wesley, 1975.

- [155] L. K. Pan, C. Q. Sun, and C. M. Li, *Journal of Physical Chemistry B*, vol. 108, p. L3404, 2004.
- [156] G. A. Slack and S. F. Bartram, *Journal of Applied Physics*, vol. 46, p. 89, 1975.
- [157] R. R. Reeber and K. Wang, "Lattice parameters and thermal expansion of GaN " *J. Mater. Res.*, vol. 15, pp. 40-44, 2000.
- [158] A. U. Sheleg and V. A. Savastenko, *Vestsi Akad. Navuk BSSR, Ser. Fiz-Mat. Navuk*, vol. 3, p. 126, 1976.
- [159] Y. Okada and Y. Tokumaru, "Precise Determination of Lattice-Parameter and Thermal-Expansion Coefficient of Silicon between 300-K and 1500-K," *Journal of Applied Physics*, vol. 56, pp. 314-320, 1984.
- [160] H. P. Singh, "Determination of the thermal expansion of germanium, Rhodium, and Iridium by X-rays," *Acta Cryst.*, vol. A24, pp. 469-471, 1968.
- [161] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, "Theory of the Thermal-Expansion of Si and Diamond," *Physical Review B*, vol. 43, pp. 5024-5027, Feb 15 1991.
- [162] D. K. L. Tsang, B. J. Marsden, S. L. Fok, and G. Hall, "Graphite thermal expansion relationship for different temperature ranges," *Carbon*, vol. 43, pp. 2902-2906, 2005.
- [163] C. Li and T.-W. Chou, "Axial and radial thermal expansions of single-walled carbon nanotubes," *Physical Review B*, vol. 71, p. 235414, 2005.
- [164] I. Calizo, A. A. Balandin, W. Bao, F. Miao, and C. N. Lau, "Temperature dependence of the Raman spectra of graphenene and graphene multilayers,"

- Nano Letter*, vol. 7, pp. 2645-2649, 2007.
- [165] H. Harima, "Properties of GaN and related compounds studied by means of Raman scattering," *Journal of Physics-Condensed Matter*, vol. 14, pp. R967-R993, 2002.
- [166] F. G. Shi, *J. Mater. Res.*, vol. 9, p. 1307, 1994.
- [167] Q. Jiang, Z. Zhang, and J. C. Li, *Chemical Physics Letters*, vol. 22, p. 549, 2003.
- [168] A. Diéguez, A. Romano-Rodríguez, A. Vilà, and J. R. Morante, "The complete Raman spectrum of nanometric SnO₂ particles," *Journal of Applied Physics*, vol. 90, p. 1550, 2001.
- [169] Z. Iqbal and S. Vepřek, "Raman scattering from hydrogenated microcrystalline and amorphous silicon," *Journal of Physics C*, vol. 15, pp. 377-392, 1982.
- [170] E. Anastassakis and E. Liarokapis, "Polycrystalline Si under strain: Elastic and lattice-dynamical considerations," *Journal of Applied Physics*, vol. 62, p. 3346, 1987.
- [171] A. V. Korotcov, Y. S. Huang, D. S. Tsai, and K. K. Tiong, "Raman scattering characterization of vertical aligned 1D IrO₂ nanocrystals grown on single crystal oxide substrates," *Solid State Communications*, vol. 137, pp. 310-314, 2006.
- [172] S. Piscanec, M. Cantoro, A. C. Ferrari, J. A. Zapien, Y. Lifshitz, S. T. Lee, S. Hofmann, and J. Robertson, "Raman spectroscopy of silicon nanowires," *Physical Review B*, vol. 68, p. 241312, 2003.
- [173] E. S. Zouboulis and M. Grimsditch, "Raman-Scattering in Diamond up to

- 1900-K," *Physical Review B*, vol. 43, pp. 12490-12493, May 15 1991.
- [174] K. R. Zhu, M. S. Zhang, Q. Chen, and Z. Yin, "Size and phonon-confinement effects on low-frequency Raman mode of anatase TiO₂ nanocrystal," *Phys. Lett. A*, vol. 340, pp. 220-227, 2005.
- [175] H. C. Choi, Y. M. Jung, and S. B. Kim, "Size effects in the Raman spectra of TiO₂ nanoparticles," *Vibrational Spec.*, vol. 37, pp. 33-38, 2005.
- [176] H. Richter, Z. P. Wang, and L. Ley, "The one phonon Raman spectrum in microcrystalline silicon," *Solid State Communication*, vol. 39, pp. 625-629, 1981.
- [177] I. H. Campbell and P. M. Fauchet, "The effects of microcrystal size and shape on the one phonon Raman spectra of crystalline semiconductors," *Solid State Communications*, vol. 58, pp. 739-741, 1986.
- [178] N. Ohtani and K. Kawamura, "Theoretical investigation of Raman scattering from microcrystallites," *Solid State Communication*, vol. 75, pp. 711-715, 1990.
- [179] L. Banyai and S. W. Koch, *Semiconductor Quantum Dots*, World Scientific, Singapore, 1993.
- [180] Y. N. Hwang, S. H. Shin, H. L. Park, S. H. Park, U. Kim, H. S. Jeong, E. J. Shin, and D. Kim, "Effect of lattice contraction on the Raman shifts of CdSe quantum dots in glass matrices," *Physical Review B*, vol. 54, pp. 15120-15124, Dec 1 1996.
- [181] Z. Y. Pan, Z. H. Sun, Z. Xie, J. H. Xu, I. Kojima, and S. Q. Wei, "erfacial intermixing of TiN/Si₃N₄ super-hard multilayer films studied by fluorescence

- x-ray absorption fine structure," *Journal of Physics D*, vol. 39, pp. 2796-2806, 2006.
- [182] C. Ossadnik, S. Vepek, and I. Gregora, "Applicability of Raman scattering for the characterization of nanocrystalline silicon," *Thin Solid Films*, vol. 337, pp. 148-151, 1999.
- [183] P. M. Fauchet and I. H. Campell, "Raman spectroscopy of low-dimensional semiconductors " *Critical Reviews in Solid State and Materials Sciences*, vol. 14, pp. S79-S101, 1988.
- [184] W. Cheng and S. F. Ren, "Calculations on the size effects of Raman intensities of silicon quantum dots," *Physical Review B*, vol. 65, p. 205305, 2002.
- [185] G.-X. Cheng, H. Xia, K. Chen, -J., W. Zhang, and X.-K. Zhang, "man measurement of the grain size for silicon crystallites," *Phys. Status Solidi A*, vol. 118, pp. K51-K54, 1990.
- [186] A. K. Sood, K. Jayaram, D. Victor, and S. Muthu, "Raman and high-pressure photoluminescence studies on porous silicon," *Journal of Applied Physics*, vol. 72, pp. 4963-4965, 1992.
- [187] J. Zi, H. Büscher, C. Falter, W. Ludwig, K. M. Zhang, and X. D. Xie, "Raman shifts in Si nanocrystals," *Applied Physics Letters*, vol. 69, pp. 200-202, 1996.
- [188] C. Trallero-Giner, D. A. C. M., E. Menéndez-Proupín, and A. I. Ekimov, "Optical vibrons in CdSe dots and dispersion relation of the bulk material," *Physical Review B*, vol. 57, pp. 4664-4669, 1999.
- [189] R. W. Meulenberg, T. Jennings, and G. F. Strouse, "Compressive and tensile

- stress in colloidal CdSe semiconductor quantum dots," *Physical Review B*, vol. 70, p. 235311, 2004.
- [190] L. Saviot, B. Champagnon, E. Duval, I. A. Kudriavtsev, and A. I. Ekimov, "Size dependence of acoustic and optical vibrational modes of CdSe nanocrystals in glasses " *J. Non-Cryst. Solids*, vol. 197, pp. 238-246, 1996.
- [191] J. Y. Zhang, X. Y. Wang, M. Xiao, L. Qu, and X. Peng, "Lattice contraction in free-standing CdSe nanocrystals," *Applied Physics Letters*, vol. 81, pp. 2076-2078, 2002.
- [192] V. M. Dzhagan, M. Y. Valakh, A. E. Raevskaya, A. L. Stroyuk, S. Y. Kuchmiy, and D. R. T. Zahn, "Size effects on Raman spectra of small CdSe nanoparticles in polymer films," *Nanotechnology*, vol. 19, p. 305707, 2008.
- [193] Z. h. Fang, "Thermal expansion of ionic materials at high temperature," *Journal of Applied Physics*, vol. 102, p. 013523, 2007.
- [194] M. Sreemany and S. Sen, "Effect of substrate temperature and annealing temperature on the structural, electrical and microstructural properties of thin Pt films by rf magnetron sputtering," *Appl. Surf. Sci.*, vol. 253, pp. 2739-2746, 2006.
- [195] J. M. Zhang, K. W. Xu, and V. Ji, "Competition between surface and strain energy during grain growth in free-standing and attached Ag and Cu films on Si substrates," *Appl. Surf. Sci.*, vol. 187, pp. 60-67, 2002.
- [196] J. Kim, J. A. J. Freitas, P. B. Klein, S. Jang, F. Ren, and S. J. Pearton, "The Effect of Thermally Induced Stress on Device Temperature Measurements by Raman

- Spectroscopy," *Electrochemical and solid-state letters*, vol. 8, pp. G345-G347, 2005.
- [197] S. D. Bagdade, *Chapter 2 Thermal expansion in ASM Ready Reference: Thermal Properties of Metals*: ASM International 2002.
- [198] I.-K. Suh, H. Ohta, and Y. Waseda, "High-temperature thermal expansion of six metallic elements measured by dilatation method and X-ray diffraction," *Journal of Materials Science*, vol. 23, pp. 757-760, 1998.
- [199] K. Takegawa, K. Fukao, and Y. Saruyama, "Simultaneous measurement of thermal expansion and heat capacity using temperature modulation technique," *Thermochimica Acta*, vol. 432, pp. 212-215, 2006.
- [200] E. G. Wolff, "Fundamentals of optical interferometry for thermal expansion measurements," in *Thermal Conductivity 27: Thermal Expansion 15*. vol. 27, H. Wang, W. D. Porter, and G. Worley, Eds., 2005, pp. 615-633.
- [201] T. Sato, K. Ohashi, T. Sudoh, K. Haruna, and H. Maeta, "Thermal expansion of a high purity synthetic diamond single crystal at low temperature," *Physical Review B*, vol. 65, p. 092102, 2002.
- [202] C. Giles, C. Adriano, A. F. Lubambo, C. Cusatis, I. Mazzaroc, and M. G. Ho..nnicke, "Diamond thermal expansion measurement using transmitted X-ray back-diffraction," *Journal of Synchrotron Radiation*, vol. 12, pp. 349-353, 2005.
- [203] G. A. Slack and S. F. Bartram, "Thermal expansion of some diamondlike crystals," *Journal of Applied Physics*, vol. 46, pp. 89-98, 1975.

- [204] K. Haruna, H. Maeta, K. Ohashi, and T. Koike, "Thermal Expansion Coefficient of Synthetic Diamond Single Crystal at Low Temperatures," *Jpn. J. Appl. Phys.*, vol. 31, pp. 2527-2529, 1992.
- [205] H. Ibach, "Thermal expansion of silicon and zinc oxide. I " *Phys. Status Solidi A*, vol. 31, pp. 625-634, 1969.
- [206] K. G. Lyon, G. L. Salinger, and C. A. Swenson, "Linear thermal expansion measurements on silicon from 6 to 340 K," *Journal of Applied Physics*, vol. 48, pp. 865-868, 1977.
- [207] R. B. Roberts, "Thermal-Expansion Reference Data - Silicon 300-850-K," *Journal of Physics D-Applied Physics*, vol. 14, pp. L163-L166, 1981.
- [208] C. Roder, S. Einfeldt, S. Figge, and D. Hommel, "Temperature dependence of the thermal expansion of GaN," *Physical Review B*, vol. 72, p. 085218, Aug 2005.
- [209] M. Leszczynski, T. Suski, H. Teisseyre, P. Perlin, I. Grzegory, J. Jun, S. Porowski, and T. D. Moustakas, "Thermal expansion of gallium nitride," *Journal of Applied Physics*, vol. 76, pp. 4909-4911, 1994.
- [210] H. P. Maruska and J. J. Tietjen, "The preparation and properties of vapor-deposited single crystal line GaN," *Applied Physics Letters*, vol. 15, pp. 327-329, 1969.
- [211] Y. Zoo, D. Adams, J. W. Mayer, and T. L. Alford, "Investigation of coefficient of thermal expansion of silver thin film on different substrates using X-ray diffraction," *Thin Solid Films*, vol. 513, p. 170, 2006.

- [212] J. Hu, W. Cai, C. Li, Y. Gan, and L. Chen, "In situ x-ray diffraction study of the thermal expansion of silver nanoparticles in ambient air and vacuum," *Applied Physics Letters*, vol. 86, p. 151915, 2005.
- [213] X. J. Xu, G. T. Fei, W. H. Yu, L. D. Zhang, X. Ju, X. P. Hao, D. N. Wang, and B. Y. Wang, "In situ x-ray diffraction study of the size dependent thermal expansion of silver nanowires," *Applied Physics Letters*, vol. 89, p. 181914, 2006.
- [214] G. D. Mukhkerjee, C. Bansal, and A. Chatterjee, "Electron-magnetic, lattice and magnon Gruneisen parameters of iron and nickel: Results from thermal expansion measurements and model calculations," *International Journal of Modern Physics B*, vol. 12, pp. 449-470, Feb 10 1998.
- [215] T. G. Kollie, "Measurement for the thermal-expansion coefficient of nickel from 300 to 1000 K and determination of the power-law constants near the Curie temperature," *Physical Review B*, vol. 16, p. 4872, 1977.
- [216] D. N. Talwar and J. C. Sherbondy, "Thermal-Expansion Coefficient of 3c-Sic," *Applied Physics Letters*, vol. 67, pp. 3301-3303, Nov 27 1995.
- [217] J. Xie, d. S. Gironcoli, S. Baroni, and M. Scheffler, "First-principle calculation of the thermal properties of siliver," *Physical Review B*, vol. 59, pp. 965-969, 1999.
- [218] R. J. Bruls, H. T. Hintzen, G. d. With, R. Metselaar, and J. C. v. Miltenburg, "The temperature dependence of the Grüeisen parameters of MgSiN₂, AlN and beta-Si₃N₄," *Journal of Physics and Chemistry of Solids*, vol. 62, pp. 783-792,

- 2001.
- [219] R. R. Reeber, "Thermal expansion of some group IV elements and ZnS," *Phys. Solidi. A*, vol. 32, pp. 321-331, 1975.
- [220] A. Debernardi, M. Alouani, and H. Dreysse', "ab initio thermodynamics of metals: Al and W," *Physical Review B*, vol. 63, p. 064305, 2001.
- [221] H. Ibach, "The role of surface stress in reconstruction, epitaxial growth and stabilization of mesoscopic structures," *Surf. Sci. Rep.*, vol. 29, pp. 195-263, 1997.
- [222] W. Haiss, "Surface stress of clean and adsorbate-covered solids," *Rep. Prog. Phys.*, vol. 64, pp. 591-648, 2001.
- [223] K. K. Nanda, A. Maisels, F. E. Kruis, H. Fissan, and S. Stappert, "Higher Surface Energy of Free Nanoparticles," *Phys Rev Lett*, vol. 91, p. 106102, 2003.
- [224] A. Rytkönen, S. Valkealahti, and M. Manninen, "Melting and evaporation of argon clusters," *J. Chem. Phys.*, vol. 106, pp. 1888-1892, 1997.
- [225] Z. Yuan, J. Li, Y. Pan, J. Fan, and J. Ke, "Comparison of Surface Tension Measured Values for Molten Tin at Different Oxygen Potentials," *Process Metallurgy-Non-Ferrous Metals*, vol. 77, pp. 495-499, 2006.
- [226] H. Fujii, T. Matsumoto, S. Izutani, S. Kiguchi, and K. Nogi, "Surface tension of molten silicon measured by microgravity oscillating drop method and improved sessile drop method," *Acta Materialia*, vol. 54, pp. 1221-1225, 2006.
- [227] H. Nakanishi, K. Nakazato, and K. A. Terashima, 6487 (2000), "surface tension variation of molten silicon measured by ring tensiometry technique and related

- temperature and impurity dependence," *Jpn J Appl Phys: Part I*, vol. 39, pp. 6487-6492, 2000.
- [228] J. Kollár, L. Vitos, and H. L. Skriver, "Surface energy and work function of the light actinides," *Physical Review B*, vol. 49, pp. 11288-11292, 1994.
- [229] H. L. Skriver and N. M. Rosengaard, "Surface energy and work function of elemental metals," *Physical Review B*, vol. 46, pp. 7157-7168, 1992.
- [230] I. Galanakis, N. Papanikolaou, and P. H. Dederichs, "Applicability of the broken-bond rule to the surface energy of the fcc metals," *Surface Science* vol. 511, pp. 1-12, 2002.
- [231] M. C. Desjonquères and D. Spanjaard, *Concepts in Surface Physics. Springer Series in Surface: Berlin, Heidelberg: Springer-Verlag*, , vol. 30, 1993.
- [232] Q. Jiang, H. M. Lu, and M. Zhao, "Modelling of surface energies of elemental crystals," *J Phys Condens Matter*, vol. 16, pp. 521-530, 2004.
- [233] O. L. Alerhand, J. D. Joannopoulos, and E. J. Mele, "Thermal amplitudes of surface atoms on Si(111) 2×1 and Si(001) 2×1 ," *Phys. Rev. B*, vol. 39, pp. 12622-12629, 1989.
- [234] Q. Zhao, Y. Lim, and E. W. Abel, 174 (2004), "Effect of temperature on the surface free energy of amorphous carbon films," *J. Colloid Interf. Sci.*, vol. 280, pp. 174-183, 2004.
- [235] F. Xiao, R. Yang, and C. Zhang, 183 (2006), "Surface tension of molten Ni-W and Ni-Cr alloys," *Mater. Sci. Eng. B*, vol. 132, pp. 183-186, 2006.
- [236] S. Halas and T. Durakiewicz, "Temperature dependence of the surface energy of

- mercury from 0 to 250 degree," *J. Phys.: Condens. Matter*, vol. 14, pp. L735-L737, 2002.
- [237] M. N. Magomedov, *Rus J Phys Chem*, vol. 79, p. 711, 2005.
- [238] S. B. Zhang and S.-H. Wei, "Surface Energy and the Common Dangling Bond Rule for Semiconductors," *Phys. Rev. Lett.*, vol. 92, p. 086102, 2004.
- [239] B. B. Sauer and G. T. Dee, "Surface tension and melt cohesive energy density of polymer melts including high melting and high glass transition polymers," *Macromolecules*, vol. 35, pp. 7024-7030, 2002.
- [240] W. J. Yao, X. J. Han, M. Chen, B. Wei, and Z. Y. Guo, "Surface tension of undercooled liquid cobalt," *J. Phys.: Condens. Matter*, vol. 14, pp. 7479-7485, 2002.
- [241] <http://hyperphysics.phy-astr.gsu.edu/hbase/surten.html#c3>.
- [242] J. M. Ziman, *Electrons and phonons: the theory of transport phenomena in solids*: Clarendon Press, Oxford, 2001.
- [243] A. A. Balandin, "Nanophononics: phonon engineering in nanostructures and nanodevices " *J. Nanosci. Nanotech.*, vol. 5, pp. 1015-1022, 2005.
- [244] N. Bannov, V. Mitin, and M. A. Strosio, "Confined acoustic phonons in a free-standing quantum well and their interaction with electrons," *Phys. Stat. Sol. (b)*, vol. 183, p. 131, 1994.
- [245] M. A. Strosio, K. W. Kim, S. Yu, and A. Ballato, "Quantized acoustic phonon modes in quantum wires and quantum dots," *J. Appl. Phys.* , vol. 76, pp. 4670-4675, 1994.

- [246] M. A. Stroschio, Y. M. Sirenko, S. Yu, and K. W. Kim, "Acoustic phonon quantization in buried waveguides and resonators " *J. Phys.: Condens. Matter*, vol. 8, pp. 2143-2151, 1996.
- [247] N. Nishiguchi, Y. Ando, and M. Mybourn, "Acoustic phonon modes of rectangular quantum wires," *J. Phys.: Condens. Matter*, vol. 9, p. 5751, 1997.
- [248] A. Svizhenko, A. Banlandin, S. Bandyopadhyay, and M. A. Stroschio, "Electron interaction with confined acoustic phonons in quantum wires subjected to a magnetic field," *Phys. Rev. B*, vol. 57, pp. 4687-4693, 1998.
- [249] S. Yu, K. W. Kim, M. A. Stroschio, and G. J. Iafrate, "Electron-acoustic-phonon scattering rates in rectangular quantum wires," *Physical Review B*, vol. 50, pp. 1733-1738, 1994.
- [250] S. Yu, K. W. Kim, M. A. Stroschio, and G. J. Iafrate, "Electron-acoustic-phonon scattering rates in cylindrical quantum wires," *Physical Review B*, vol. 51, pp. 4695-4698, 1995.
- [251] N. Mingo, "Calculation of Si nanowire thermal conductivity using complete phonon dispersion relations," *Physical Review B* vol. 68, p. 113308, 2003.
- [252] N. Mingo and D. A. Broido, "Lattice Thermal Conductivity Crossovers in Semiconductor Nanowires," *Phys. Rev. Lett.* , vol. 93, p. 246106, 2004.
- [253] J. Kim, O. Benson, H. Kan, and Y. Yamamoto, "A single-photon turnstile device " *Nature*, vol. 397, pp. 500-503, 1999.
- [254] F. Elhoussine, S. Mátéfi-Tempfli, A. Encinas, and L. Piraux, "Conductance quantization in magnetic nanowires electrodeposited in nanopores," *Applied*

- Physics Letters*, vol. 81, pp. 1681-1683, 2002.
- [255] K. Schwab, E. A. Henriksen, J. M. Worlock, and M. L. Roukes, "Measurement of the quantum of thermal conductance," *Nature* vol. 404, pp. 974 - 977 2000.
- [256] D. Li, Y. Y. Wu, P. Kim, L. Shi, P. D. Yang, and A. Majumdar, "Thermal conductivity of individual silicon nanowires," *Appl. Phys. Lett.*, vol. 83, pp. 2934-2936, 2003.
- [257] W. J. Liu and M. Asheghi, "Thermal Conductivity Measurements of Ultra-Thin Single Crystal Silicon Layers," *Journal of Heat Transfer*, vol. 128, pp. 75-83, 2006.
- [258] S. Mazumder and A. Majumdar, "Monte Carlo study of phonon transport in solid thin films including dispersion and polarization," *J. Heat Transfer*, vol. 123, pp. 749-759, 2001.
- [259] Y. F. Chen, D. Y. Li, J. R. Lukes, and A. Majumdar, "Monte Carlo Simulation of Silicon Nanowire Thermal Conductivity," *J. Heat Transfer* vol. 127, pp. 1129-1137, 2005.
- [260] A. Balandin and K. L. Wang, "Significant decrease of the lattice thermal conductivity due to phonon confinement in a free-standing semiconductor quantum well," *Phys. Rev. B*, vol. 58, pp. 1544-1549, 1998.
- [261] J. Zou and A. Balandin, "Phonon heat conduction in a semiconductor nanowire," *J. Appl. Phys.*, vol. 89, pp. 2932-2938, 2001.
- [262] J. D. Chung, A. J. H. McGaughey, and M. Kaviani, "Role of Phonon Dispersion in Lattice Thermal Conductivity Modeling," *Transaction of the ASME*, vol. 126,

pp. 376-380, 2004.

- [263] P. Chantrenne, J. L. Barrat, X. Blase, and J. D. Gale, "An analytical model for the thermal conductivity of silicon nanostructures," *J. Appl. Phys.*, vol. 97, p. 104318, 2005.

Appendix

In case where phonon wave propagates in the z direction with wave vector q , the components of the displacement field in the inner core ($r < a$) are given by:

$$\begin{cases} u_r = [iC_l k_{l1} J'_m(k_{l1}r) + iC_t \frac{m}{r} J_m(k_{l1}r) + i\bar{C}_l q a k_{l1} J'_m(k_{l1}r)] \cdot \exp(im\theta + iqz - i\omega t) \\ u_\theta = [-C_l \frac{m}{r} J_m(k_{l1}r) - C_t k_{l1} J'_m(k_{l1}r) - \bar{C}_l \frac{mqa}{r} J_m(k_{l1}r)] \cdot \exp(im\theta + iqz - i\omega t) \\ u_z = [-C_l q J_m(k_{l1}r) + a\bar{C}_l (k_{l1})^2 J_m(k_{l1}r)] \cdot \exp(im\theta + iqz - i\omega t) \end{cases} \quad (A-1)$$

where m here denotes the order of harmonics. While the components of the displacement field in the outer shell ($a < r < a + \delta a$) is:

$$\begin{cases} u_r = [iD_l k_{l2} J'_m(k_{l2}r) + iE_l k_{l2} N'_m(k_{l2}r) + iD_t \frac{m}{r} J_m(k_{l2}r) + iE_t \frac{m}{r} N_m(k_{l2}r) \\ \quad + i\bar{D}_l q a k_{l2} J'_m(k_{l2}r) + i\bar{E}_l q a k_{l2} N'_m(k_{l2}r)] \cdot \exp(im\theta + iqz - i\omega t) \\ u_\theta = [-D_l \frac{m}{r} J_m(k_{l2}r) - E_l \frac{m}{r} N_m(k_{l2}r) - D_t k_{l2} J'_m(k_{l2}r) - E_t k_{l2} N'_m(k_{l2}r) \\ \quad - \bar{D}_l \frac{mqa}{r} J_m(k_{l2}r) - \bar{E}_l \frac{mqa}{r} N_m(k_{l2}r)] \cdot \exp(im\theta + iqz - i\omega t) \\ u_z = [-D_l q J_m(k_{l2}r) - E_l q N_m(k_{l2}r) \\ \quad + a\bar{D}_l (k_{l2})^2 J_m(k_{l2}r) + a\bar{E}_l (k_{l2})^2 N_m(k_{l2}r)] \cdot \exp(im\theta + iqz - i\omega t) \end{cases} \quad (A-2)$$

In the above expressions, J_m and N_m are the ordinary Bessel and Neumann functions.

$C_l, C_t, \bar{C}_l, D_l, D_t, \bar{D}_l, E_l, E_t$ and $\bar{E}_l$ are coefficients to be determined, ω is the phonon frequency, the transversal and longitudinal wave vectors $k_{l,t1}$ and $k_{l,t2}$ in the above expression are connected to the wave vector q in such a way that:

$$k_{l,t1} = \frac{\omega^2}{c_{l,t1}^2} - q^2 \text{ and } k_{l,t2} = \frac{\omega^2}{c_{l,t2}^2} - q^2 \quad (A-3)$$

where $c_{l,t1}$ ($c_{l,t2}$) are the velocities of the longitudinal and transverse phonons, respectively, in the core region (shell region). The stress in polar coordinate has the

following relation

$$\begin{cases} \tau_{rr} = \lambda \cdot \left[\frac{u_r}{r} + \frac{\partial u_r}{\partial r} + \frac{1}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{\partial u_z}{\partial z} \right] + 2\mu \cdot \frac{\partial u_r}{\partial r} \\ \tau_{r\theta} = \mu \cdot \left[\frac{\partial u_\theta}{\partial r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta} - \frac{1}{r} u_\theta \right] \\ \tau_{rz} = \mu \cdot \left[\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \right] \end{cases} \quad (\text{A-4})$$

For free standing quantum wire, the stress at the surface of the wire (i.e. $r = a + \delta a$) is zero. This condition, together with boundary condition that the displacement field and stress are continuous at the core-shell interface gives the following eigenvalue equation:

$$\begin{bmatrix} U_1 & -U_2 & -U_3 \\ \mu_1 F_1 & -\mu_2 F_2 & -\mu_2 \bar{F}_2 \\ 0 & -\mu_2 F_2(a + \delta a) & -\mu_2 \bar{F}_2(a + \delta a) \end{bmatrix} \begin{bmatrix} C \\ D \\ E \end{bmatrix} = 0 \quad (\text{A-5})$$

where

$$C = \begin{pmatrix} C_l \\ C_t \\ \bar{C}_l \end{pmatrix}, D = \begin{pmatrix} D_l \\ D_t \\ \bar{D}_l \end{pmatrix}, E = \begin{pmatrix} E_l \\ E_t \\ \bar{E}_l \end{pmatrix}, \quad (\text{A-5a})$$

$$U_1 = \begin{bmatrix} L_1 & mt_1 & (qa)T_1 \\ -ml_1 & -T_1 & -m(qa)t_1 \\ -(qa)l_1 & 0 & (k_{t1}a)^2 t_1 \end{bmatrix}, \quad (\text{A-5b})$$

$$U_2 = \begin{bmatrix} L_2 & mt_2 & (qa)T_2 \\ -ml_2 & -T_2 & -m(qa)t_2 \\ -(qa)l_2 & 0 & (k_{t2}a)^2 t_2 \end{bmatrix}, \quad (\text{A-5c})$$

$$\bar{U}_2 = \begin{bmatrix} \bar{L}_2 & m\bar{t}_2 & (qa)\bar{T}_2 \\ -m\bar{l}_2 & -\bar{T}_2 & -m(qa)\bar{t}_2 \\ -(qa)\bar{l}_2 & 0 & (k_{t2}a)^2 \bar{t}_2 \end{bmatrix}, \quad (\text{A-5d})$$

$$F_1 = \begin{bmatrix} -2(qa)L_1 & -m(qa)t_1 & (k_{t1}^2 a^2 - q^2 a^2)T_1 \\ 2m(l_1 - L_1) & (k_{t1}^2 a^2 - 2m^2)t_1 + 2T_1 & 2mqa(t_1 - T_1) \\ (2m^2 + q^2 a^2 - k_{t1}^2 a^2)l_1 - 2L_1 & 2m(T_1 - t_1) & 2qa[m^2 - k_{t1}^2 a^2)t_1 - T_1] \end{bmatrix}, \quad (\text{A-5e})$$

$$F_2 = \begin{bmatrix} -2(qa)L_2 & -m(qa)t_2 & (k_{i2}^2 a^2 - q^2 a^2)T_2 \\ 2m(l_2 - L_2) & (k_{i2}^2 a^2 - 2m^2)t_2 + 2T_2 & 2mqa(t_2 - T_2) \\ (2m^2 + q^2 a^2 - k_{i2}^2 a^2)l_2 - 2L_2 & 2m(T_2 - t_2) & 2qa[m^2 - k_{i2}^2 a^2]t_2 - T_2 \end{bmatrix}, \text{(A-5f)}$$

$$\bar{F}_2 = \begin{bmatrix} -2(qa)\bar{L}_2 & -m(qa)\bar{t}_2 & (k_{i2}^2 a^2 - q^2 a^2)\bar{T}_2 \\ 2m(\bar{l}_2 - \bar{L}_2) & (k_{i2}^2 a^2 - 2m^2)\bar{t}_2 + 2\bar{T}_2 & 2mqa(\bar{t}_2 - \bar{T}_2) \\ (2m^2 + q^2 a^2 - k_{i2}^2 a^2)\bar{l}_2 - 2\bar{L}_2 & 2m(\bar{T}_2 - \bar{t}_2) & 2qa[m^2 - k_{i2}^2 a^2]\bar{t}_2 - \bar{T}_2 \end{bmatrix}, \text{(A-5g)}$$

$$F_2(a + \delta a) = \begin{bmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \end{bmatrix}$$

$$\begin{cases} Q_{11} = -2(qa)L_2(a + \delta a) \\ Q_{12} = 2m[l_2(a + \delta a) - L_2(a + \delta a)] \\ Q_{31} = [2m^2 + q^2(a + \delta a)^2 - k_{i2}^2(a + \delta a)^2]l_2(a + \delta a) - 2L_2(a + \delta a) \\ Q_{12} = -m(qa)t_2(a + \delta a) \\ Q_{22} = (k_{i2}^2(a + \delta a)^2 - 2m^2)t_2(a + \delta a) + 2T_2(a + \delta a) \\ Q_{32} = 2m[T_2(a + \delta a) - t_2(a + \delta a)] \\ Q_{13} = (k_{i2}^2 a^2 - q^2 a^2)T_2(a + \delta a) \\ Q_{23} = 2mqa[t_2(a + \delta a) - T_2(a + \delta a)] \\ Q_{33} = 2qa[m^2 - k_{i2}^2(a + \delta a)^2]t_2(a + \delta a) - T_2(a + \delta a) \end{cases}, \quad \text{(A-5h)}$$

$$\bar{F}_2(a + \delta a) = \begin{bmatrix} \bar{Q}_{11} & \bar{Q}_{12} & \bar{Q}_{13} \\ \bar{Q}_{21} & \bar{Q}_{22} & \bar{Q}_{23} \\ \bar{Q}_{31} & \bar{Q}_{32} & \bar{Q}_{33} \end{bmatrix}$$

$$\begin{cases} \bar{Q}_{11} = -2(qa)\bar{L}_2(a + \delta a) \\ \bar{Q}_{12} = 2m[\bar{L}_2(a + \delta a) - \bar{L}_2(a + \delta a)] \\ \bar{Q}_{13} = [2m^2 + q^2(a + \delta a)^2 - k_{t2}^2(a + \delta a)^2]\bar{L}_2(a + \delta a) - 2\bar{L}_2(a + \delta a) \\ \bar{Q}_{21} = -m(qa)\bar{t}_2(a + \delta a) \\ \bar{Q}_{22} = (k_{t2}^2(a + \delta a)^2 - 2m^2)\bar{t}_2(a + \delta a) + 2\bar{T}_2(a + \delta a) \\ \bar{Q}_{23} = 2m[\bar{T}_2(a + \delta a) - \bar{t}_2(a + \delta a)] \\ \bar{Q}_{31} = (k_{t2}^2a^2 - q^2a^2)\bar{T}_2(a + \delta a) \\ \bar{Q}_{32} = 2mq a[\bar{t}_2(a + \delta a) - \bar{T}_2(a + \delta a)] \\ \bar{Q}_{33} = 2qa[m^2 - k_{t2}^2(a + \delta a)^2]\bar{t}_2(a + \delta a) - \bar{T}_2(a + \delta a) \end{cases}, \quad (A-5i)$$

In the above tedious formulae, we have defined:

$$\begin{aligned} l_1 &= J_m(k_{t1}a) & l_1(a + \delta a/a) &= J_m(k_{t1}a(a + \delta a/a)) \\ L_1 &= (k_{t1}a)J'_m(k_{t1}a) & L_1(a + \delta a) &= (k_{t1}a)(1 + \delta a/a)J'_m(k_{t1}a(1 + \delta a/a)) \\ t_1 &= J_m(k_{t1}a) & t_1(a + \delta a/a) &= J_m(k_{t1}a(a + \delta a/a)) \\ T_1 &= (k_{t1}a)J'_m(k_{t1}a) & T_1(a + \delta a) &= (k_{t1}a)(1 + \delta a/a)J'_m(k_{t1}a(1 + \delta a/a)) \\ l_2 &= J_m(k_{t2}a) & l_2(a + \delta a/a) &= J_m(k_{t2}a(a + \delta a/a)) \\ L_2 &= (k_{t2}a)J'_m(k_{t2}a) & L_2(a + \delta a) &= (k_{t2}a)(1 + \delta a/a)J'_m(k_{t2}a(1 + \delta a/a)) \\ t_2 &= J_m(k_{t2}a) & t_2(a + \delta a/a) &= J_m(k_{t2}a(a + \delta a/a)) \\ T_2 &= (k_{t2}a)J'_m(k_{t2}a) & T_2(a + \delta a) &= (k_{t2}a)(1 + \delta a/a)J'_m(k_{t2}a(1 + \delta a/a)) \\ \bar{l}_2 &= N_m(k_{t2}a) & \bar{l}_2(a + \delta a/a) &= N_m(k_{t2}a(a + \delta a/a)) \\ \bar{L}_2 &= (k_{t2}a)N'_m(k_{t2}a) & \bar{L}_2(a + \delta a) &= (k_{t2}a)(1 + \delta a/a)N'_m(k_{t2}a(1 + \delta a/a)) \\ \bar{t}_2 &= N_m(k_{t2}a) & \bar{t}_2(a + \delta a/a) &= N_m(k_{t2}a(a + \delta a/a)) \\ \bar{T}_2 &= (k_{t2}a)N'_m(k_{t2}a) & \bar{T}_2(a + \delta a) &= (k_{t2}a)(1 + \delta a/a)N'_m(k_{t2}a(1 + \delta a/a)) \end{aligned} \quad (A-5j)$$

The torsional and logitudinal modes can be obtained by setting $m = 0$ in Eq. (A-5). The

torsional mode, where the stresses in the r and z directions equal zero, they are governed by the equation:

$$\begin{bmatrix} -T_1 & T_2 & \bar{T}_2 \\ -\mu_1(k_{t1}^2 a^2 t_1 + 2T_1) & -\mu_2(k_{t2}^2 a^2 t_2 + 2T_2) & -\mu_2(k_{t2}^2 a^2 \bar{t}_2 + 2\bar{T}_2) \\ 0 & A_{32} & A_{33} \end{bmatrix}$$

$$A_{32} = -\mu_2[k_{t2}^2(a + \delta a)^2 t_2 + 2T_2(a + \delta a)] \quad (\text{A-6a})$$

$$A_{33} = -\mu_2[k_{t2}^2(a + \delta a)^2 \bar{t}_2 + 2\bar{T}_2(a + \delta a)]$$

Similarly, the longitudinal mode, where the stress in θ direction equals zero is governed

by the equation:

$$\begin{bmatrix} L_1 & qaT_1 & -L_2 & -qaT_2 & -\bar{L}_2 & -qa\bar{T}_2 \\ -qal_1 & (k_{t1}a)^2 t_1 & qal_2 & -(k_{t2}a)^2 t_2 & qal_2 & -(k_{t2}a)^2 \bar{t}_2 \\ -\mu_1 2qaL_1 & B_{32} & \mu_2 2qaL_2 & B_{34} & \mu_2 2qa\bar{L}_2 & B_{36} \\ B_{41} & B_{42} & B_{43} & B_{44} & B_{45} & B_{46} \\ 0 & 0 & B_{53} & B_{54} & B_{55} & B_{56} \\ 0 & 0 & B_{63} & B_{64} & B_{65} & B_{66} \end{bmatrix} \begin{bmatrix} C_l \\ \bar{C}_l \\ D_l \\ \bar{D}_l \\ E_l \\ \bar{E}_l \end{bmatrix} = 0 \quad (\text{A-6b})$$

where

$$\begin{aligned} B_{32} &= \mu_1(k_{t1}^2 a^2 - q^2 a^2)T_1 & B_{34} &= -\mu_2(k_{t2}^2 a^2 - q^2 a^2)T_2 \\ B_{36} &= -\mu_2(k_{t2}^2 a^2 - q^2 a^2)\bar{T}_2 \\ B_{41} &= \mu_1[(q^2 a^2 - k_{t1}^2 a^2)l_1 - 2L_1] & B_{42} &= \mu_1(2qa)(-k_{t1}^2 a^2 t_1 - T_1) \\ B_{43} &= -\mu_2[(q^2 a^2 - k_{t2}^2 a^2)l_2 - 2L_2] & B_{44} &= -\mu_2(2qa)(-k_{t2}^2 a^2 t_2 - T_2) \\ B_{45} &= -\mu_2[(q^2 a^2 - k_{t2}^2 a^2)\bar{l}_2 - 2\bar{L}_2] & B_{46} &= -\mu_2(2qa)(-k_{t2}^2 a^2 \bar{t}_2 - \bar{T}_2) \\ B_{53} &= \mu_2 2qaL_2(a + \delta a) & B_{54} &= -\mu_2(k_{t2}^2 a^2 - q^2 a^2)T_2(a + \delta a) \\ B_{55} &= \mu_2 2qa\bar{L}_2(a + \delta a) & B_{56} &= -\mu_2(k_{t2}^2 a^2 - q^2 a^2)\bar{T}_2(a + \delta a) \\ B_{63} &= -\mu_2[(q^2(a + \delta a)^2 - k_{t2}^2(a + \delta a)^2)l_2(a + \delta a) - 2L_2(a + \delta a)] \\ B_{64} &= -\mu_2(2qa)[-k_{t2}^2(a + \delta a)^2 t_2(a + \delta a) - T_2(a + \delta a)] \\ B_{65} &= -\mu_2[(q^2(a + \delta a)^2 - k_{t2}^2(a + \delta a)^2)\bar{l}_2(a + \delta a) - 2\bar{L}_2(a + \delta a)] \\ B_{66} &= -\mu_2(2qa)[-k_{t2}^2(a + \delta a)^2 \bar{t}_2(a + \delta a) - \bar{T}_2(a + \delta a)] \end{aligned} \quad (\text{A-6c})$$