Optical and Acoustic Grüneisen Parameter of Nano-sized Particles

Abdulrahman Khaleel Suleiman[1]

[1]Department of Physics, College of Science, Salahaddin University, Erbil, Iraq
Correspondence: Abdulrahman Khaleel Suleiman, Salahaddin University, Erbil, Iraq.
Email: abdulrahman.suliman@su.edu.krd

Received: October 24, 2018 Accepted: December 20, 2018 Online Published: January 1, 2019

doi: 10.23918/eajse.v4i3sip19

Abstract: Theoretical size dependence optical and acoustic Grüneisen parameter $\gamma^{op}(r)$ and $\gamma^{ac}(r)$ at room temperature (300 K) are calculated for Si nanoparticles using modified Debye-Einstein approximation model. The obtained results are used for studying the total Grüneisen parameter $\gamma(\theta_D(r), \theta_E(r))$. All parameters forming the model including Debye's θ_D (r,T) and Einstein's θ_E (r,T) temperatures and lattice volume are calculated according to their nanoscale size dependence. These values θ_E (r,T) and θ_D (r,T) for Silicon decrease with decreasing nanoparticle size, except for lattice volume and Grüneisen parameter which increases to about 2.9 times of its bulk lattice volume and total Grüneisen parameter to about 2.45 compared with bulk value when the particle diameter reaches lower than 5 nm.

Keywords: Grüneisen Parameter, Debye's Temperature, Einstein's Temperature, Acoustic and Optical Branch, Nanoparticle

1. Introduction

The study of material properties at nanoscale continues to be an active field of research, and information of thermal properties of substance is important for nano-semiconductor industry as well as for physics and electronic engineering (Bruls *et al.*, 2001; Shobhana & Matthias, 1997). Recently, many groups have conducted theoretical and experimental studies on the relation between Grüneisen parameter and thermodynamic dimensions (T, P, V) for different materials such as (Rh, Ag, Au, Si, Ge, C, Diamond, and Ni), and compound (GaAs, $Zn(CN)_2$, $Ni(CN)_2$, $MgSiN_2$, and AlN). Wang *et al.* (2010) and Pandya (2002) showed that Grüneisen parameter increases with temperature and become constant at high temperature and pressure, for some materials this parameter can take negative or positive values.

Sanditov *et al*. (2012), studied the correlation between the Grüneisen parameter and the relation of the propagation velocities of longitudinal and transverse acoustic waves in vitreous solids using Pineda model. Pugaczowa-Michalska studied the electronic structure by using two approximations: Slater's and Dugdale-MacDonald's for Grüneisen parameter (Rycerz, 2009). Slack studied the relation between Grüneisen parameter and bond parameters (Slack, 1973). Pandya (2002) theoretically investigated the volume variation of Grüneisen parameter of ten face center cubic transition metals. According to Antonov *et al.* (1990) model, the Grüneisen parameter is pressure dependent (Pande *et al.*, 2018).

The nano-materials are very sensitive to thermodynamic parameters such as pressure and temperature. The physical and chemical properties of nanomaterials depend strongly on the crystal structure and interatomic distances due to the different asymmetries present at the surface and in the bulk. Two quantities, bulk lattice constant and interlayer distances near the surface may change quite differently upon increasing temperature. Indeed, it has long been realized that one would expect all such measures of anharmonicity (e.g. coefficients of thermal expansion, mean squared displacements (MSDs) of atoms, and the rate of change of phonon frequency with temperature) to be different at surfaces than in bulk crystals, anharmonicity means that the springs that tie atoms together in a lattice model, do not exactly and simply obey Hooke's law (Bo *et al.*, 2010). The study of size dependence of Grüneisen parameter γ is an interesting problem for researchers both theoretically and experimentally because of the lack of a proper theory and enough experimental data (Fang, 1996; Gleiter, 2000). The purpose of this work is to study the effect of nanoparticle size on the Grüneisen parameter γ(r) for both type of vibration: acoustic $\gamma^{ac}(\frac{\theta_D(r)}{T})$ and optical $\gamma^{op}(\frac{\theta_E(r)}{T})$ parameters, and total Grüneisen parameter $\gamma(\frac{\theta_D(r)}{T},\frac{\theta_E(r)}{T})$ of nanoparticle by using modified Debye-Einstein approximation model.

2. Theory of Calculations

The microscopic definition of the Grüneisen parameter (Grüneisen, 1912) volume dependence of the *i*th mode of vibration of the lattice and is given by (Vocadlo, Poirer, & Price, 2000; Sanditov *et al*., 2012). In the microscopic view such as found in lattice dynamics, there is Grüneisen parameter for each normal mode in the crystal lattice. The energy of each vibrational mode is identified by a normal mode frequency ω_i, and the mode is given by (Licea & Ioanid, 2004),

$$\gamma = -\left[\frac{\partial \ln(\omega)}{\partial \ln(V)}\right] \tag{1}$$

The vibrational amplitude of the atoms increases as expressed by Grüneisen parameter about their equilibrium positions. The effect on the frequency of a change in the temperature T, at constant pressure P (isobaric process) described by (Licea & Ioanid, 2004),

$$\left(\frac{\partial \omega}{\partial T}\right)_P = \left(\frac{\partial \omega}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial \omega}{\partial T}\right)_V \tag{2}$$

where the first term gives the “implicit" contribution accounts for the volume driven frequency changes due to the thermal expansion and the second term gives the “explicit” contribution accounts for the changes in the vibrational amplitudes (Grüneisen parameter). “The implicit anharmonicity of phonon is due to the change of the unit-cell volume and or concomitant changes of structural parameters with temperature. The explicit anharmonicity includes changes in phonon frequencies due to large thermal amplitude of atoms” (Ashcroft & Mermin, 1987) Grüneisen parameter related with Debye’s temperature and volume from the relation used by Moruzzi *et al.* (1988) is defined by,

$$\frac{\theta_D}{\theta_{D,0}} = \left(\frac{V_0}{V}\right)^{\gamma} \tag{3}$$

where $\theta_{D,0}$ is the Debye’s temperature corresponding to the equilibrium volume V_0 at 0 K (Moruzzi,

Janak, & Schwarz, 1988). The Grüneisen parameter, γ as well as $\theta_{D,0}$ and V_0 can be derived from the calculated total-energy binding curve. However, Equation (3) implies that,

$$\gamma = -\frac{\partial \ln \theta_D}{\partial \ln V} \quad \rightarrow \quad \gamma = -\frac{\ln \theta_D - \ln \theta_0}{\ln V - \ln V_0}$$

This is only an approximation of the definition of the Grüneisen parameter (Selleby & Sundman, 2005). Both experimentally (macroscopically) and theoretically (microscopically) determination of the value of Grüneisen parameter (γ) is extremely difficult and requires a detailed knowledge of the phonon dispersion spectrum of material (Selleby & Sundman, 2005). Using the quasi-harmonic approximation for lattice vibrations, the total Grüneisen parameter (γ) can be related to the description of how the vibration frequencies (phonons) within a crystal are altered with changing volume (i.e. γ_i). If one defines γ as the weighted average,

$$\gamma = \frac{\sum_i \gamma_i^{ac} C_{v,i}^{ac} + \sum_i \gamma_i^{op} C_{v,i}^{op}}{\sum_i C_{v,i}^{ac} + \sum_i C_{v,i}^{op}} \tag{4}$$

where $C_{v,i}$ are the contributions of the partial vibrational mode to heat capacity, and

$$C_{v,i}^{ac,op} = k_\beta \left(\frac{\hbar\omega_{v,i}}{k_\beta T}\right)^2 \exp\left(\frac{\hbar\omega_{v,i}}{k_\beta T}\right)\left[\exp\left(\frac{\hbar\omega_{v,i}}{k_\beta T}\right) - 1\right]^{-2}$$

represents to the isobaric specific heat capacity for the normal mode (*i*) (acoustic and optical branch respectively), for evaluation, both acoustic vibrational and optical vibrational frequencies expressed by some Debye's $\theta_D(T)$ and Einstein's $\theta_E(T)$ temperatures.

Corresponding to the modified Debye-Einstein approximation model and by considering temperature dependence, Grüneisen parameter for both acoustic vibrations $h\omega_{max} = k_\beta\theta_D$, and optical vibrations, $h\omega_{max} = k_\beta\theta_E$, where k_β and $h = 2\pi\hbar$ are Boltzmann and Planck constants respectively, and can be written as,

$$\gamma^{ac}\left(\frac{\theta_D}{T}\right) = -\frac{\partial \ln \theta_D(T)}{\partial \ln V}, \quad \gamma^{op}\left(\frac{\theta_E}{T}\right) = -\frac{\partial \ln \theta_E(T)}{\partial \ln V} \tag{5}$$

Equation (5) showed that acoustic and optical parameters are depending themselves on the temperature *T* from the Debye's and Einstein's temperature dependence. Corresponding the principle of Debye-Einstein approximation, the total Grüneisen parameter derived and calculated by the Licea and Ioanid, as a function of temperature using the following equation (Licea & Ioanid, 2004),

$$\gamma\left(\frac{\theta_D}{T}, \frac{\theta_E}{T}\right) = -\frac{\left[\gamma^{ac}\left(\frac{\theta_D}{T}\right).F_D\left(\frac{\theta_D}{T}\right) + (S-1)\gamma^{op}\left(\frac{\theta_E}{T}\right).F_E\left(\frac{\theta_E}{T}\right)\right]}{F_D\left(\frac{\theta_D}{T}\right) + (S-1)F_E\left(\frac{\theta_E}{T}\right)} \tag{6}$$

where S which is the number of atoms in an elementary cell, the parameters $F_D\left(\frac{\theta_D}{T}\right)$ and $F_E\left(\frac{\theta_E}{T}\right)$ are Debye's and Einstein's functions, they are equal to,

$$F_D(\frac{\theta_D}{T}) = 3\left[\frac{T}{\theta_D}\right]^3 \int_0^{\frac{\theta_D}{T}} \frac{X^4[e^{(x)}]}{[e^{(x)}-1]^2} dx \; ; \qquad F_E\left(\frac{\theta_E}{T}\right) = \left[\frac{\theta_E}{T}\right]^2 \frac{e^{\left(\frac{\theta E}{T}\right)}}{\left[e^{\left(\frac{\theta E}{T}\right)}-1\right]^2} \tag{7}$$

For $X = \frac{\theta_D}{T}$ the ratio between Debye's and Einstein's functions are introduced by new factors (Licea & Ioanid 2004),

$$\beta\left(\left(\frac{\theta_D}{T}\right),(\frac{\theta_E}{T})\right) = \left[\frac{C_V^{op}(\frac{\theta_E}{T})}{C_V^{ac}(\frac{\theta_D}{T})}\right] = (S-1)\frac{F_E(\frac{\theta_E}{T})}{F_D(\frac{\theta_D}{T})} \tag{8}$$

where C_v is isochoric specific heat capacity for both mode (optical and acoustic, respectively), and is equal to, $C_v = C_v^{op} + C_v^{ac}$. Total Grüneisen parameters for polyatomic basis element becomes (Vocadlo, Poirer, & Price, 2000; Licea & Ioanid, 2004),

$$\gamma\left(\frac{\theta_D}{T},\frac{\theta_E}{T}\right) = -\frac{\left[\gamma^{ac}\left(\frac{\theta_D}{T}\right)+\beta\left(\frac{\theta_D}{T},\frac{\theta_E}{T}\right).\gamma^{op}(\frac{\theta_E}{T})\right]}{1+\beta\left(\frac{\theta_D}{T},\frac{\theta_E}{T}\right)} \tag{9}$$

To calculate total Grüneisen parameter $\gamma\left(\frac{\theta_D}{T},\frac{\theta_E}{T}\right)$ according to the equation (9), the room temperature value of $\gamma\left(\frac{\theta_D}{T},\frac{\theta_E}{T}\right)$ for Si bulk values are in the range; 0.685 (Botan, Omar, & Jiang, 2016). Grüneisen parameter γ determined by the change of the lattice vibration frequency in the dependence of the change of the system volume. That is,

$$\gamma\left(\frac{\theta_D}{T},\frac{\theta_E}{T}\right) = \gamma^{ac}\left(\frac{\theta_D}{T}\right) + \gamma^{op}(\frac{\theta_E}{T}) \tag{10}$$

Variation in the frequency of lattice vibration due to anharmonicity is proportional to the variation in the volume of lattice V for isotropic material. Grüneisen parameter γ represents how the Debye's temperature θ_D, which dominates the lattice vibration, depends on volume, (Licea & Ioanid, 2004; Hashimoto & WB, 2009).

To determine the nanoscale Grüneisen parameter $\gamma(r)$ as a function of the size, where (r) refers to a nanoscale size range. Therefore, all of the above equations can be written as a function of the size of nanoparticle and it is required to the following steps.

2.1 Mean Bonding Length for Nanoscale Particle

Omar (2012), derived a relation for mean bond length and size of nanoparticle $d_{mean}(r)$ in terms of bulk mean bond length, $d_{mean}(\infty)$ which is equal to 0.235 nm for bulk silicon. Nanoscale mean bond length calculated from the following relation,

$$d_{mean}(r) = h - \Delta d_{mean}(r), \tag{11}$$

where h is the surface first layer height atomic of a nanoparticle and for silicon it is equal to 0.3353 nm. Change in mean bonding length $\Delta d_{mean}(r)$ depends on the size of nanoparticle and can be calculated by the following equation (Omar, 2012),

$$\Delta d_{mean}(r) = \Delta dmean(r_c)\left[e^{\left(-\frac{2(S_m(\infty)-R}{3R(\frac{r}{r_c})-1}\right)}\right]^{\frac{1}{2}} \quad (12)$$

where $\Delta d_{mean}(r_c)$ as the maximum variation in the mean bond length (for silicon it is 0.0988 nm), and R is the ideal gas constant (8.314 J.K.mol^{-1}), $S_m(\infty)$ is bulk overall melting entropy (for silicon it is 29.48 J.K^{-1}.mole^{-1}) (Omar, 2016). Critical radius r_c means that all atoms of the particle are located on the bulk surface and it is calculated from,

$$r_c = (3-d)h,$$

and d is zero for nanoparticles (Zhang, Zhao, & Jiang, 2001; Jiang *et al.*, 1998). The nanoparticles' mean bond length $d_{mean}(r)$ depends on the lattice constant, and can be determined according to the following relation,

$$d_{mean}(r) = \frac{\sqrt{3}}{4}a(r) \quad (13)$$

where $a(r)$ is a nanoparticle's lattice constant, $a^3(r)$ is the unit cell volume and $V(\infty)$ is the Bulk lattice volume, it is calculated from the unit cell volume $a^3(\infty)$ for cubic structure and is equal to (20 $\AA^3$) for silicon. $V(r)$ is lattice volume of nanoparticle, can be determined from the size dependence lattice parameter $a(r)$ which is calculated from the following relation (Omar, 2016),

$$a(r) = \frac{4}{\sqrt{3}}d_{mean}(r) \quad (14)$$

To calculate the nanoscale size dependent Debye's $\theta_D(r)$ and Einstein's $\theta_E(r)$ temperature, the following relation is used,

$$\theta_D = c\left[\frac{T_{(\infty)}}{MV_{(\infty)}^{2/3}}\right]^{1/2} \quad (15)$$

In this equation, θ_D is the size dependent Debye's temperature, c a constant value, M the mass of the atom, $T_{(\infty)}$ bulk melting temperature and $V_{(\infty)}$ bulk lattice volume.

The size-dependent Debye's temperature θ_D is calculated from the relation (Abdulrahman & Omar, 2017),

$$\frac{\theta_{D(r)}}{\theta_{D(\infty)}} = \left[\frac{T_{(r)}}{T_{(\infty)}}\right]^{1/2} \quad (16)$$

According to Lindemann's criterion (Chernyshev, 2008) for melting and Motts equation (Regel & Glazov, 1995) root mean square *rms* σ(r) as a function of size has been formed to have the following form (Lai, 1996);

$$\frac{\sigma(r)}{\sigma(\infty)} = \sqrt{\exp\left(\frac{2(S_{vib(\infty)} - R)}{3R(\frac{r}{r_c} - 1)}\right)} \tag{17}$$

From the Debye model, the θ_D function is related to the root mean square *rms* **σ** by,

$$\sigma^2 \alpha \frac{T}{\theta_D^2} \tag{18}$$

where **σ** is root mean square displacement of the atoms in the crystal (average amplitude of atomic thermal vibration (Jiang *et al.*, 1998). Based on the equation (18), it is assumed that $\theta_D(r)$ has the same size dependence of $1/\sigma(r)$ as a first-order approximation, since the nature of any phase transition is related to the potential of the two-related phase of the crystals, thus,

$$\frac{\theta_{D\,(r)}}{\theta_{D\,(\infty)}} = \frac{\sigma(\infty)}{\sigma(r)} \tag{19}$$

Substituting equation (17) in the equation (19), this reads,

$$\frac{\theta_{D\,(r)}}{\theta_{D\,(\infty)}} = \sqrt{\exp\left(\frac{2(S_{vib(\infty)} - R)}{3R(\frac{r}{r_c} - 1)}\right)} \tag{20}$$

The nanoscale melting temperature $T_{(r)}$ changes according to the relation,

$$T_{(r)} = T_{(\infty)}\left[\frac{V_{(r)}}{V_{(\infty)}}\right]^{2/3} \exp\left[\frac{2(S_{vib(\infty)} - R)}{3R(\frac{r}{r_c} - 1)}\right] \tag{21}$$

Since, Einstein's temperature $\theta_E(\infty)$ proportional to $\theta_D(\infty)$ (Yang *et al.*, 2006), then the equation (20) can be extended for $\theta_E(r)$ function as,

$$\frac{\theta_{D\,(r)}}{\theta_{D\,(\infty)}} = \frac{\theta_{E\,(r)}}{\theta_{E\,(\infty)}} = \sqrt{\exp\left(\frac{2(S_{m(\infty)} - R)}{3R(\frac{r}{r_c} - 1)}\right)} \tag{22}$$

2.2 Size dependence Debye's Temperature

Consider dispersion curve, which consists of two branches: acoustic and optical vibrational frequencies, expressed by size dependence Debye's $\theta_D(r)$ and Einstein's $\theta_E(r)$ temperatures. Corresponding to equations (16), (20) and (22) the Debye's and Einstein's temperatures are determined as a function of radius of nanoparticle as follows,

$$\theta_D(r) = \theta_D(\infty)\left[e^{\frac{-2(S_m-R)}{3R\left[\left(\frac{r}{3h}\right)-1\right]}}.\left(\frac{V(r)}{V_\circ}\right)^{\frac{2}{3}}\right]^{\frac{1}{2}} \quad (23)$$

$$\theta_E(r) = \theta_E(\infty).\left[e^{\frac{-2(S_m-R)}{3R\left[\left(\frac{r}{3h}\right)-1\right]}}.\left(\frac{V(r)}{V_\circ}\right)^{\frac{2}{3}}\right]^{\frac{1}{2}} \quad (24)$$

Then applying the equations (23) and (24) in the equations from (4) to (9) will give calculations for the nanoscale size dependence of $\gamma(r)$.

Acoustic and optical Grüneisen parameters γ^{ac}(r) and γ^{op}(r) at room temperature (300 K) by using Debye's and Einstein's temperatures depend on the radius of the particle and lattice volume as a function of size as shown in the following equations (Licea & Ioanid, 2004),

$$\gamma^{ac}\left(\frac{\theta_D(r)}{T}\right) = -\frac{\partial \ln\left(\frac{\theta_D(r)}{T}\right)}{\partial \ln V(r)} \quad (25)$$

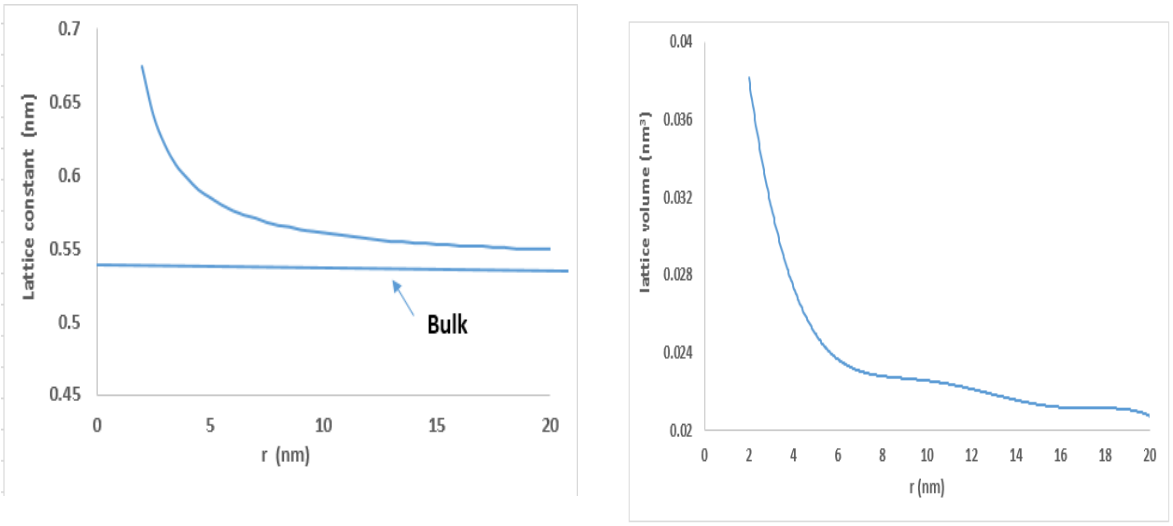
$$\gamma^{op}\left(\frac{\theta_{E(r)}}{T}\right) = -\frac{\partial \ln\left(\frac{\theta_{E(r)}}{T}\right)}{\partial \ln V(r)} \quad (26)$$

By using the values of two types of vibration (acoustic and optical) parameters as a function of size, the total Grüneisen parameter size dependence has the form,

$$\gamma\left(\frac{\theta_D(r)}{T}, \frac{\theta_E(r)}{T}\right) = -\frac{\left[\gamma^{ac}\left(\frac{\theta_D(r)}{T}\right).F_D\left(\frac{\theta_D(r)}{T}\right)+(S-1)\gamma^{op}\left(\frac{\theta_E(r)}{T}\right).F_E\left(\frac{\theta_E(r)}{T}\right)\right]}{F_D\left(\frac{\theta_D(r)}{T}\right)+(S-1)F_E\left(\frac{\theta_E(r)}{T}\right)} \quad (27)$$

3. Results and Discussion

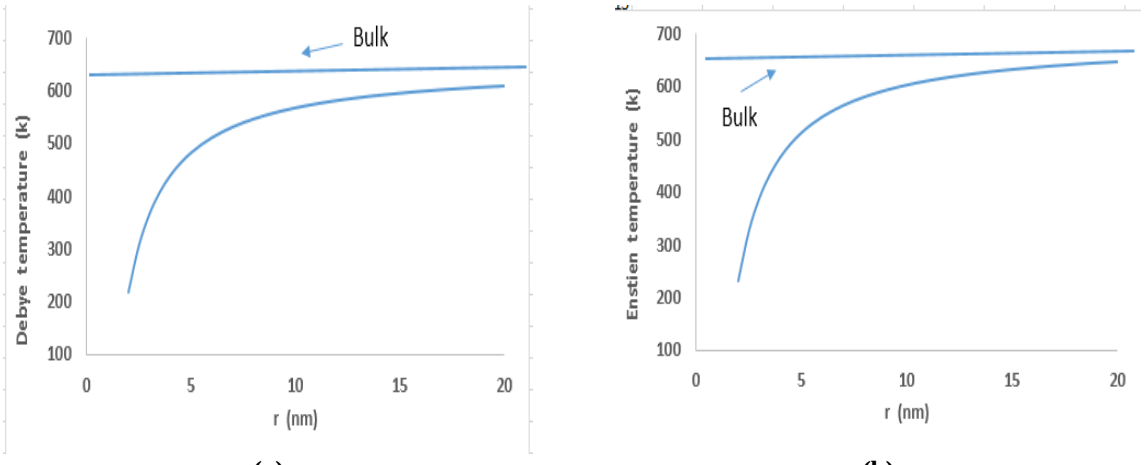
According to equation (14), lattice constant is calculated as a function of nanoparticle size at a given temperature (room temperature). Values of lattice constants are used to determine the lattice volume of nanoparticle by using the relation, $V(r)=a(r)^3/8$ and plotted as a function of nanoparticle size as shown in the figures (1a) and (1b). As the size of the particle reduces to 5 nm, the lattice constant and the lattice volume increase as much as 12% compared with the silicon bulk value, and this is due to the decrease in size followed by decrease in the density of Si nanoparticle from 2.329 g.cm^3 to 1.472 g.cm^3, due to the variation of surface to the volume ratio, atoms which leads to the increases of bond length between atoms, and it is similar to the atoms with less electron cloud (i.e. high flexibility produce due to the effect of external pressure) (Botan, Omar, & Jiang 2016, Omar, 2012). Lai *et al.* (1996) showed the effect of nanoparticle size on the lattice volume. Other researchers proved that as the size of nanoscale materials approached to 10 nm, the lattice volume increased markedly, and the result has been reported for silicon and selenium (Edmonds *et al.*, 2006; Zhao & Lu, 1997; Hailstone *et al.*, 2009).



(a) (b)

Figure 1: (a) lattice constant, and (b) lattice volume of Si-nanoparticle (curved line) as a function of size and compared with lattice constant (linear line) and lattice volume of bulk and their value is, a = 0.543 nm and V = 0.02 nm

Grüneisen parameter is a function of anharmonicity part of lattice vibration. In order to analyse the size dependence of Grüneisen parameter we shall refer to the Debye's and Einstein's temperature taking the value θ_D (300 K) = 645 K, and θ_E (300 K) = 685 K for bulk silicon. Both temperature variations as the size of nanoparticle changed as shown in the figures (2a) and (2b). At the size of the nanoparticle near 20 nm showed that $\theta_E(r) > \theta_D(r)$, because the repulsion force at short distances is greater than the corresponding attraction, but as the size of nanoparticle reduced to 2.5 nm, the inequality becomes $\theta_E(r) < \theta_D(r)$ due to the change in phase of the substance at this size.



(a) **(b)**

Figure 2: Size dependence of calculated; (a) Debye's temperature and (b) Einstein's temperature of silicon nanoparticle (curved line). Value of Debye's temperature and Einstein's temperature of bulk Si (linear line) at room temperature is θ_D = 645 K, and θ_E = 685 K

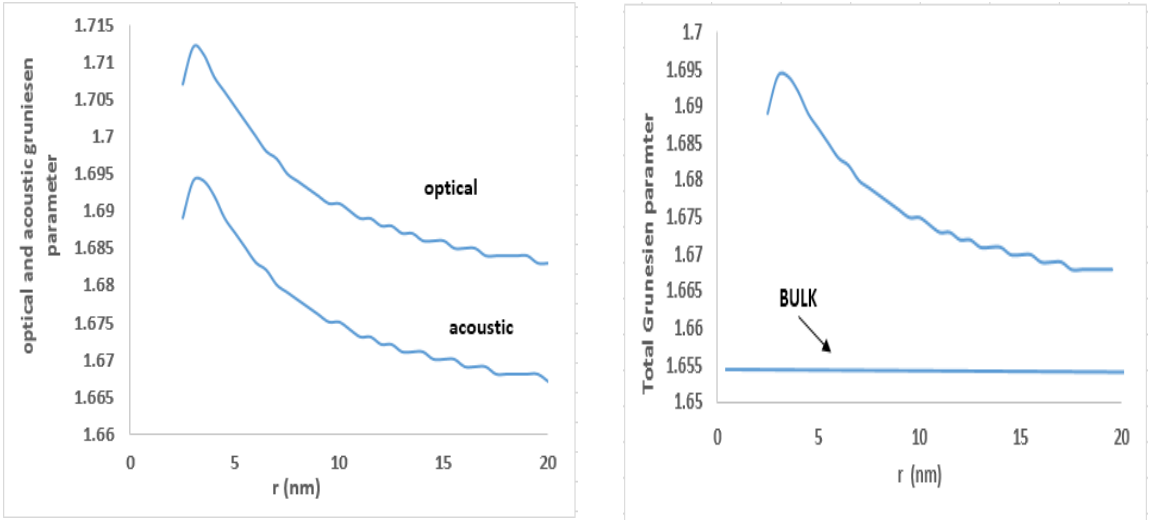
The rate of Einstein's temperature $\theta_E(r)$ reduced larger than Debye's temperature $\theta_D(r)$ as shown in the figures (2a) and (2b), and this indicates the main role played by the optical branch (optical vibrations). An increase of mean bond length corresponds to a decrease in lattice vibration, (i.e,

decrease the Debye's and Einstein's temperature) at about 35% and 30% respectively compared with the silicon bulk value of $\theta_E(r)$ and $\theta_D(r)$ (Abdulrahman & Omar, 2017).

According to earlier explanation, Omar (2016) showed the depression of nanoparticle size followed by increase in lattice volume and weaken the bond between atoms. However, an increase in bond length corresponds to a decrease in lattice vibration for acoustic and optical branch (i.e. lowering Debye's and Einstein's temperature) (Omar, 2016; Goldstein, 1996).

Due to the decreases of nanoparticles size the repulsive force increase in the small distance between two atoms (where repulsive force seen: between two adjacent atom and attractive force between all atoms). Interatomic potential is the most unsymmetrical along that direction, on the one side, atoms are strongly bonded with another atom, on the other side of surface, there is no atom at all (Hashimoto & WB, 2009; Koga, Ekeshoji, & Sugawara, 2004).

Using the value of two parameters: Debye's $\theta_D(r)$ and Einstein's $\theta_E(r)$ temperatures, and lattice volume as a function of size to determine both parameters $\gamma^{op}(r)$ and $\gamma^{ac}(r)$ at room temperature (300 K). To calculate total Grüneisen parameter size dependence $\gamma\left(\frac{\theta_D(r)}{T}, \frac{\theta_E(r)}{T}\right)$, the value of (optical and acoustic) Grüneisen parameter used from the equations (25) and (26), in the equation (27) and plotted as a function of size shown in the Figure 3.



(a) **(b)**

Figure 3: Size dependence of; **(a)** Optical and Acoustic Grüneisen parameter, **(b)** total Grüneisen parameter for silicon nanoparticles. Grüneisen parameter for Si bulk values are in the range; 0.685 (Botan, Omar, & Jiang 2016)

These parameters $\gamma\left(\frac{\theta_D(r)}{T}, \frac{\theta_E(r)}{T}\right)$ increase nonlinearly with decreases the size of the nanoparticle at about 40%, compared with the silicon bulk value (0.685), and this is due to the variation the lattice volume of crystal and lattice anharmonicity effects with a reduction in nanosize, the lattice periodicity deforms and the lattice vibration thus increases in the case of anharmonicity (Omar, 2012; Omar & Hawkar, 2009).

At lower dimensions the value of γ is largely controlled by the lower frequency transverse waves. For harmonic crystal, neighboring atoms attract one another with forces proportional to the distance between them, but such a crystal would collapse (Bruls *et al.*, 2001).

As the radius of a nanoparticle decreases lower than 5 nm as shown in the Figure 3 the total Grüneisen parameter increases to 1.695 nm than inflexion of curve caused due to the deformation of structure. Omar (2012), showed that this scale is 1.68 nm and represents the limit of crystallinity of substance. Others showed increase of Grüneisen parameter of Si nanoparticle with size and become zero at 5 nm (Botan, Omar, & Jiang 2016), While the Grüneisen parameter is a function of anharmonic term of potential energy in this case the anharmonic term depressed. The Grüneisen parameter possess a positive value for all phonon modes in many materials, and γ is an important physical quantity in solving many research problems of condensed matter physics and geophysics (Fang, 1996). Slawomir and Matthias showed the optical phonon bonds become softer and acoustic bands become harder in some part of the Brillion zone (Jiang *et al.*, 1998; Scheffler & Biernacki, 1989).

Grüneisen parameter for some materials are negative especially for transverse acoustic phonon near Brillion zone boundary, and this means that the speed of longitudinal waves become less than the specified value of transvers waves, i.e. Grüneisen parameter becomes a negative value ($\gamma < 0$), also if the value between the speeds of longitudinal and transvers waves $\nu_L = 1.15\ \nu_T$ and crystal becomes harmonized (i.e. $\gamma = 0$) for some materials, and this is similar to that in a certain temperature ranges the anharmonicity of a single optical branch dominated to the thermal expansion. And this occurs near the phase change of the material, where the optical branch is soft, or geometrically called "rigid unit modes" anomalously soft and anharmonic optical phonons (i.e. phonon frequency increases as lattice volume of crystal increases) (Zhao & Lu, 1997; Omar, 2013; Scheffler & Biernacki, 1989; Tang *et al.*, 2006; Xu, 1991).

4. Conclusions

In this work, modified Debye-Einstein approximation model for calculating Grünesin parameter well applicable for nanoscale size solids without any adjustable parameters. When the material sizes reduces to a nanoscale range, the Grüneisen parameter no longer remains constant but accordingly changes and plays an important role as size effect dominates the change of crystal parameter such as lattice constant and lattice volume (increase) for naonscale particle lead to the change of Debye's and Einstien's temperature (decrease) and these effect to rise of the Grüneisen parameter for both acoustic and optical mode vibration. Total Grüneisen parameter increases to about 2.45 at small size of nanoparticle compared with bulk value, and at very small size Grüneisen parameter decreased, because the nanoparticle exposed to the inflexion due to the change of phase of substance and break bonding.

Acknowledgement

This study is partially supported by Ishik University Research Center.

References

Abdullah, B.J., Omar, M.S., & Jiang, Q. J. (2016). Grüneisen Parameter and Its Related Thermodynamic Parameters Dependence on Size of Si Nanoparticles. *ZANCO Journal of Pure and Applied Sciences*, 28(4), 126-132.

Abdulrahman, K., & Omar, M, (2017), Debye–Einstein approximation approach to calculate the lattice specific heat and related parameters for a Si nanowire. *J. Taibah.Univ. for Sci,* 11 1226–1231.

Antonov, V M., Milman, V Yu, Nemoshkalenko, V., & Zhalko, V. (1990). Lattice dynamics of FCC transition metals: A pseudopotential approach. *Z. Phys. B. Condens Matter*, 79, 223.

Ashcroft, N.W.& Mermin N. D. (1987). Solid State Physics (HRW Internat. ed.), W. B. Saunders College Chap. 23.

Bo, L., Mu, G., Xiao-Lin, L., Shi-Ming, H., Chen, N., Ze-Ren, L., & Rong-Bo, W. (2010). First-principles study of lattice dynamics and thermodynamics of osmium under pressure. *Chinese Physics B*, 19 (2), 026301.

Brulsa, R. J., Hintzena, H.T., de Witha, G., Metselaara, R., & van Miltenburgb J.C. (2001). The temperature dependence of the Grüneisen parameters of MgSiN2, AlN and β-Si3N4. *J. Phys and Chem of Solids*, 62, 783-792.

Chernyshev, A. P. (2008). Melting of surface layers of nanoparticles: Landau model. *Materials Chemistry and Physics*, 112 (1), 226-229.

Childress, J.R., Chien, C.L., Zhou, M.Y., & Sheng, P. (1991). Lattice softening in nanometer-size iron particles. *Physical Review B*, 44 (21), 11689.

Edmonds, D.V., He, K., Rizzo, F.C., De Cooman, B.C., Matlock, D.K. & Speer, J.G. (2006). Quenching and partitioning martensite—A novel steel heat treatment. *Materials Science and Engineering: A*, 438, 25-34.

Fang, Z. H. (1996). Pressure dependence of the melting temperature of rare-gas solids. *Journal of Physics: Condensed Matter*, 8 (38), 7067.

Gleiter, H., (2000). Nanostructured materials: basic concepts and microstructure. *Acta Materialia*, 48 (1), 1-29.

Goldstein, A.N., (1996). The melting of silicon nanocrystals: Submicron thin-film structures derived from nanocrystal precursors. *Applied Physics A*, 62 (1), 33-37.

Hailstone, R.K., DiFrancesco, A.G., Leong, J.G., Allston, T. D., & Reed, K. J. (2009). A study of lattice expansion in CeO2 nanoparticles by transmission electron microscopy. *The Journal of Physical Chemistry C*, 113(34), 15155-15159.

Hashimoto, H., & WB, T. (2009). First-principles study on thermodynamic properties of Ti2AlC and Ti2SC. *Materials Transactions*, 50(9), 2173-2176.

Jiang, Q., Tong, H.Y., Hsu, D.T., Okuyama, K., & Shi, F.G. (1998). Thermal stability of crystalline thin films. *Thin Solid Films*, 312(1-2), 357-361.

Koga, K., Ikeshoji, T., & Sugawara, K.I. (2004). Size-and temperature-dependent structural transitions in gold nanoparticles. *Physical Review Letters*, 92(11), 115507.

Lai, S.L., Guo, J.Y., Petrova, V., Ramanath, G., & Allen, L. H. (1996). Size-dependent melting properties of small tin particles: nanocalorimetric measurements. *Physical Review Letters*, 77 (1), 99.

Licea, I., & Ioanid, A. (2004). Temperature dependence of Grüneisen's parameters in a solid with polyatomic basis. *Journal of Optoelectronics and Advanced Materials*, 6, 857-864.

Lu, X.G., Selleby, M., & Sundman, B. (2005). Assessments of molar volume and thermal expansion for selected bcc, fcc and hcp metallic elements. *Calphad*, 29 (1), 68-89.

Moruzzi, V. L., Janak, J.F., & Schwarz, K. (1988). Calculated thermal properties of metals. *Physical Review B*, 37(2), 790.

Müllejans, H., & Bruley, J. (1995). Electron energy-loss near-edge structure of internal interfaces by spatial difference spectroscopy. *Journal of Microscopy*, 180 (1), 12-21.

Omar, M. S. (2016), Structural and Thermal Properties of Elementary and Binary Tetrahedral Semiconductor Nanoparticles. *Int J Thermophys*, 37,11.

Omar, M.S. (2012). Models for mean bonding length, melting point and lattice thermal expansion of nanoparticle materials. *Materials Research Bulletin*, 47 (11), 3518-3522.

Omar, M.S., & Hawkar, T. (2009). Lattice dislocation in Si nanowires. *Physica B*, 404 5203–5206.

Omar, M. S. (2013), Critical Size Structure Parameters for Au Nanoparticles. *Advanced Material Research*, 626, 976-679.

Pande, B.K., Pandey, A. K., & Singh, C.K. (2018). Pressure dependent Grüneisen parameter for semiconductors. In AIP Conference Proceedings, 1942(1), 120004.

Pandya, C.V., Vyas, P.R., Pandya, T.C., & Gohel, V.B. (2002). Volume variation of Grüneisen parameters offcc transition metals. *Bulletin of Materials Science*, 25 (1), 63-67.

Regel, A. R., & Glazov, V.M. (1995). Entropy of melting of semiconductors. *Semiconductors*, 29, 405-417.

Rycerz, A. (2009). Aharonov-Bohm effect and valley polarization in nanoscopic graphene rings. *Acta Phys. Polon.*, 115, 322-325.

Sadaiyandi, K. (2009). Size dependent Debye temperature and mean square displacements of nanocrystalline Au, Ag and Al. *Materials Chemistry and Physics*, 115(2-3), 703-706.

Sanditov, D. S., Munkueva, S. B., Batlaev, D. Z., & Sangadiev, S. S. (2012). Grüneisen parameter and propogation velocities of acoustic waves in vitreous solids. *Physics of the Solid State*, 54 (8), 1647-1643

Scheffler, M., & Biernacki, S. (1989). Negative thermal expansion of diamond and zinc-blende semiconductors. *Physical Review Letters*, 63(3), 290.

Shobhana, N., & Scheffler, M. (1997). A model for the thermal expansion of Ag (111) and other metal surfaces. *Zeitschrift für Physikalische Chemie*, 202 (1-2), 253-262.

Slack, G. A. (1973). Nonmetallic crystals with high thermal conductivity. *Journal of Physics and Chemistry of Solids*, *34*(2), 321-335.

Tang, X., Dong, J., Hutchins, P., Shebanova, O., Gryko, J., Barnes, P., Cockcroft, J.K., Vickers, M. & McMillan, P.F., (2006). Thermal properties of Si 136: theoretical and experimental study of the type-II clathrate polymorph of Si. *Physical Review B*, 74 (1), 014109.

Vocadlo, L., Poirer, J. P., & Price, G. D. (2000). Grüneisen parameters and isothermal equations of state. *American Mineralogist*, 85(2), 390-395.

Wang, F., Han, Y., Lim, C.S., Lu, Y., Wang, J., Xu, J., Chen, H., Zhang, C., Hong, M., & Liu, X., (2010). Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping. *Nature*, 463 (7284), 1061.

Xu, C. H., Wang, C. Z. Chan, C. T., & Ho, K. M. (1991). Theory of the thermal expansion of Si and n. *Diamondphys Rev, B.* 43, 6.

Yang, C. C., Xiao, M.X., Li, W., & Jiang, Q. (2006). Size effects on Debye temperature, Einstein temperature, and volume thermal expansion coefficient of nanocrystals. *Solid-state Communications*, 139 (4), 148-152.

Zhang, Z., Zhao, M., & Jiang, Q. (2001). Melting temperatures of semiconductor nanocrystals in the mesoscopic size range. *Semiconductor Science and Technology*, 16(6), L33.

Zhao, Y. H., & Lu, K. (1997). Grain-size dependence of thermal properties of nanocrystalline elemental selenium studied by x-ray diffraction. *Physical Review B*, 56 (22), 14330.