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An Investigation of Temperature Effect on Phonon Dispersion Spectra of Ni by Molecular Dynamics Simulation

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Abstract

Lattice vibrations have great influences on physical and mechanical properties of materials. In this study, changes of acoustic phonon frequencies of Ni model system with temperature was investigated by Molecular Dynamic (MD) simulation for [100], [110] and [111] high symmetry directions of the Brillouin zone. To model the interactions between atoms, Sutton-Chen type of Embedded Atom Method (SCEAM) based on many-body interactions were used. The obtained results show that the increase of temperature causes a decrease in longitudinal and transverse acoustic phonon frequencies because of thermal expansion.

Key Words: Molecular dynamics simulation, embedded atom method, phonon dispersion spectra, dynamical matrix.

1. Introduction

It is well know that atomic lattice vibrations of metallic materials have a very important effect on the acoustic, electric, optical, mechanical and thermal properties of materials. Theoretical and experimental determination of the lattice vibrations and thermal properties of the materials takes place in important research fields [1]. At a finite temperature the atoms that form a crystalline structure vibrate about their equilibrium positions with amplitude that depends on temperature. Because a crystalline solid has symmetries, these thermal vibrations can be analyzed in terms of collective modes of atomic motion. The frequencies of lattice vibrations are determined by inelastic neutron scattering experiments which have formed or absorbed of a phonon [2, 3]. In order to calculate phonon properties at higher temperatures, non-perturbative techniques such as Molecular Dynamic (MD) simulations are desirable [4]. The phonon frequencies can be calculated by using dynamical matrix, which comes from a Fourier transformation of force constant matrix calculated directly from MD simulations [5]. The analytic investigations are complex due to dominant of anharmonic effects at high temperature. Because of this difficulty, instead of analytic studies the computer aided studies such as MD or Monte Carlo calculations are becoming increasingly frequent [6–8].

MD technique is used extensively in the simulation studies made at atomic scale [9, 10], and is conducted by applying a numerical integration algorithm for equation of motion of a statistical ensemble of interactions between particles represented by a potential energy function (PEF). Consistency of results with respect to experimental values depends on the PEF modelling of the system. Agreement between the results of the phonon frequency values obtained from experiments and MD simulation could be a very important characteristic of PEF and it can be shown as the measuring reliability of the PEF [11]. Correct determination of the parameters of the PEF is very important to reproduce the thermodynamic and structural properties of materials with good accuracy.

PEFs used in the literature are mainly classified into two groups: two-body and many-body interactions, for the modelling of interatomic interactions [12]. The EAM [13] works successfully in the MD simulations of metallic systems [14–16].

In this study, the MD technique for NPT statistical ensemble was used to determine the change of acoustic phonon frequencies with temperature. Interactions among the atoms were represented by SCEAM. The phonon frequencies of the system studied at different temperatures were calculated from dynamical matrix for [100], [110] and [111] high symmetry directions. The frequency changes at X, K and L points of the Brillouin zone with temperature was plotted. It has been obtained that the increasing of temperature decreases the longitudinal and transverse acoustic phonon frequencies.

2. The Method of Calculations

The EAM was originally developed by Daw and Baskes [13] to model the many-body interatomic interactions. The total energy of a crystalline system of N particles in the EAM formalism is given by Sutton and Chen [17]:

$$E_T = \varepsilon \sum_{i=1}^{N} \left[\frac{1}{2} \sum_{j \neq i}^{N} \left(\frac{a}{r_{ij}} \right)^n - c\sqrt{\bar{\rho}_i} \right]. \tag{1}$$

Here, $\bar{\rho}_i$ is the electron density at the location of atom i due to all other atoms and it is given by

$$\bar{\rho}_i = \sum_{j \neq i}^{N} \left(\frac{a}{r_{ij}} \right)^m, \tag{2}$$

where, εgs a parameter units of energysg is a dimensionless parameter representing the type of crystal structure, and m and n are positive integers [17].ghe cohesive energy changes with variation of lattice constant for any metallic crystal are defined by Rose et. al. [18] using experimental data. They suggested the following equation for the cohesive energy changes of the crystalline materials (bcc or fcc structures):

$$E\left(a*\right) = -E_0 \left(1 + a*\right) e^{-a*} \tag{3}$$

$$a* = (a/a_0 - 1)/(E_c/9B_m\Omega)^{1/2}. \tag{4}$$

Here, E_0 is a constant taken as cohesive energy of solid, a_0 is the lattice constant and Ω is atomic volume, and all of these parameters are in equilibrium condition. The variation of crystal energy with lattice constant, which we have obtained from equation (3) and SCEAM approach, has been shown in Figure 1. These potential parameters are determined by fitting to the experimental properties of material such as lattice constant, cohesive energy E_c, and Bulk modulus B_m. The SCEAM parameters for Ni metal are given in Table 1 [17].

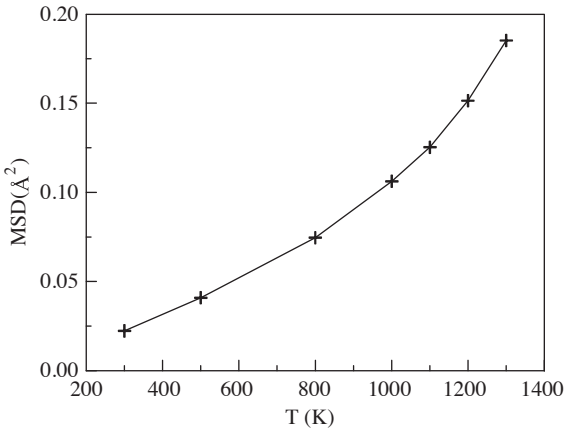

Figure 1. Variation of the mean square displacement with temperature for Ni model system.

Table 1. SCEAM PEF parameters of Ni element [16].

εgx10^{-2}eV)	a(Å)	c	m	N
1.5707	3.52	39.432	6	9

In this study, the MD method developed by Parrinello and Rahman [19], which allows anisotropic volume change, has been used and its details are given in another study [5, 20]. More detailed expositions of MD simulation method can be found from literature [20–21]. The simulations have been performed on three dimensional arrays of 7×7×7 unit cells (1372 atoms). The fcc lattice structure for the system studied has been chosen as initial structures of the systems. The interatomic interactions have been modelled with SCEAM. The initial velocities have been chosen at random values but distributed to conform a Maxwell-Boltzman distribution at a desired temperature. In order to minimize the finite size effects, periodic boundary conditions have been applied along the three axes. The potential functions have been truncated at a cut-off distance of $1.8a_0$(6.336 Å). The temperature of the system has been controlled by rescaling the atomic velocities at every two integration steps. The equations of motion have been integrated numerically by the Verlet algorithm. Time units used in the simulations were calculated by $t = a_0(m/\varepsilon)^{1/2}$. The size of the integration step was chosen as $\Delta t = 0.005t$ (1.98 fs).

The acoustic phonon frequencies at the model system was calculated along [100], [110] and [111] high symmetry directions for seven different temperature values.

At each applied temperature value, the system is equilibrated for 45,000 integration steps, and then time averages of the phonon frequencies of the systems were calculated for 5,000 integration steps (total 5×10^4MD step for each temperature value).

The phonon frequencies can be calculated by eigenvalue of the dynamical matrix which is the Fourier transform of the force constant matrix

$$\left|\mathrm{D} - mW^2\mathrm{I}\right| = 0. \tag{5}$$

Here, **D** is the dynamical matrix of the order 3×3 for mono atomic system, and **I** is the unit matrix [4, 22]. Following Daw and Hatcher [4], the dynamical matrix for the EAM can be written as

$$\mathrm{D(k)} = \sum_j \chi_{0j}(1 - \mathrm{e}^{\mathrm{ik.r}_{0j}}) + F(\rho)''\mathrm{f}^*(\mathrm{k})\mathrm{f(k)}, \tag{6}$$

where

$$\begin{aligned}\chi_{0j} = {} & (\Phi(r_{0j})'' + F(\rho)'\rho^a(r_{0j})'')\ \mathrm{r}_{0j}\mathrm{r}_{0j}/(r_{0j})^2 \\ & + (\Phi(r_{0j})' + F(\rho)'\rho^a(r_{0j})')\ \left(\mathrm{I} - \mathrm{r}_{0j}\mathrm{r}_{0j}/(r_{0j})^2\right)/r_{0j}\end{aligned} \tag{7}$$

and

$$\mathrm{f(k)} = \sum_{j\neq 0} \rho^a(r_{0j})'(\mathrm{e}^{\mathrm{ik.r}_{0j}})\,\mathrm{r}_{0j}/r_{0j}. \tag{8}$$

f^* is the complex conjugate of f expression, the sub-index zero represents the selected reference atom. Primes denote the first and second derivatives with respect to the arguments of the functions. The calculation of the dynamical matrix contains the limited volume effects and physically meaningful interaction can only be calculated by finite interatomic distances depending on the volume of the MD cell [4].

According to the Sutton-Chen version of the EAM, the functions in equations (6), (7) and (8) are defined as

$$\Phi(r) = \varepsilon \cdot \left(\frac{a}{r}\right)^n \tag{9}$$

$$\rho^a(r) = \left(\frac{a}{r}\right)^m \tag{10}$$

$$F(\bar{\rho}_i) = -\varepsilon \cdot c \cdot \sqrt{\bar{\rho}_i}. \tag{11}$$

3. Results and Discussion

To understand the physical and dynamical properties of solids at low temperatures the harmonic approach has been used. The anharmonic effects at many systems have a very important role with increase of temperature. The most common manifestation of anharmonicity are thermal expansion, changes in phonon frequencies, broadening of phonon line width due to phonon-phonon interaction and nonlinear enhancement of atomic vibrations amplitudes with increasing temperature [23].

There are several methods for determining the melting temperature of a crystalline system. In one of these methods, the MD simulations are performed on a system at various temperatures and the cohesive energy is plotted as a function of temperature. At the melting point, there is a discontinuity in the cohesive energy [24]. The melting temperature for Ni model system was calculated as 1450±20 K [21, 25]. However, the experimental melting temperature is 1728 K [3]. It is well known that this method always gives a lower melting point than experimental results. Melting temperatures of some model Ni systems with different number of particles were also calculated using EAM approximations with different potential functions [26, 27]. In these calculations, the melting temperature was found lower than experimentally observed values. In addition to melting temperature calculations, as an indicator of solid phase and anharmonic region, the changes of mean square displacement with temperature was plotted in Figure 1. As seen from Figure 1, amplitudes of atomic vibrations increase fairly at higher temperatures. From these results, it can be concluded that the SCEAM function and its parameters are suitable for our calculation up to 1450 K temperatures.

Changes of acoustic phonon frequencies with temperature were determined for 300 K, 500 K, 800 K, 1000 K, 1100 K, 1200 K and 1300 K temperature values. The variations of the phonon dispersion curves with temperature for the values of 300 K, 800 K and 1300 K at X, K and L points of the Brillouin zone are shown in Figure 2. There are three different acoustic phonon frequencies, one longitudinal (L) and the two transverse (T_1, T_2), accompany on the same value of the wave vector **k**. The data obtained from neutron scattering experiments for Ni metal are shown in Figure 2a [13]. The calculated values of the phonon frequencies are in agreement with experimentally obtained. When a wave propagate along [100], [110] and [111] directions in a crystal, the atomic plains are moved at the same phase, but the wave propagate at different velocities along these directions [3]. Then, the dispersion relations for L and T mod frequencies have been obtained as different. In Figures 2(a–c), in the model system, one can see the frequency values of the L branch are higher than values of the $T_{1,2}$ branch. Also, the difference between T_1 and T_2 mod frequencies increases at high temperatures, while it decreases at lower temperatures. As seen from Figure 2, the slopes of the dispersion curves at the boundaries of the Brillouin zone close to zero. At the same time, the group velocity of waves goes to zero and the energy condensations occur at the zone boundaries. These explanations qualitatively support the calculated dispersion curves.

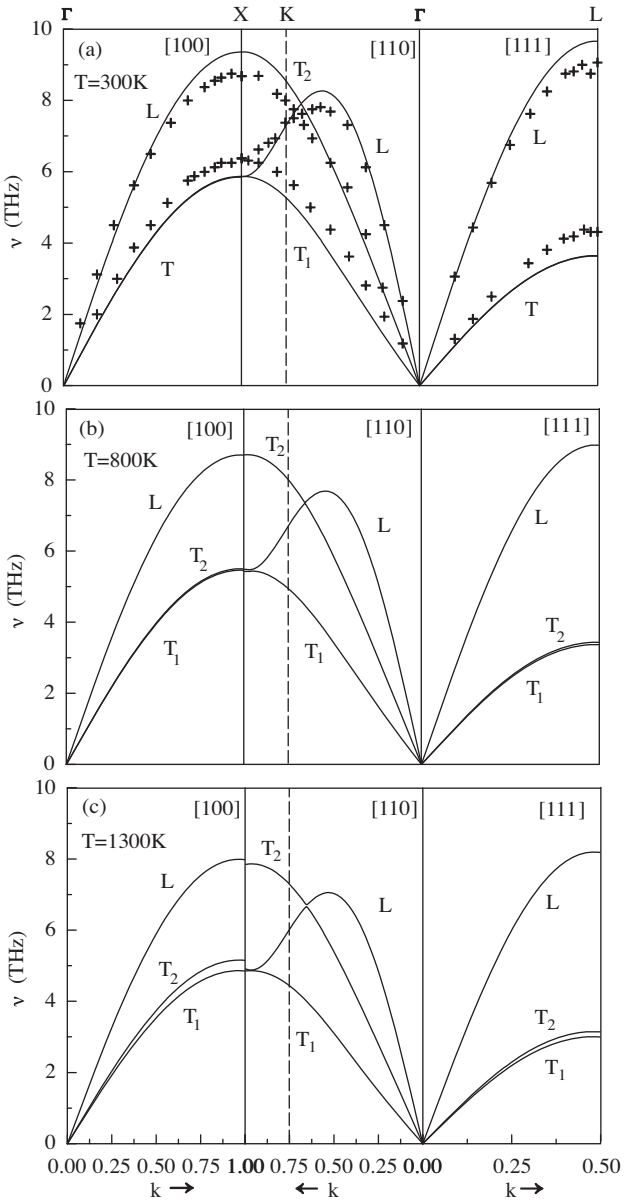

Figure 2. The acoustic phonon dispersion spectra of Ni for (a) T=300 K, (b) T=800 K and (c) T=1300 K. The "+" denotes data obtained from neutron scattering experiments [13].

Changes of acoustic phonon frequencies with temperature up to 1300 K at X, K and L points of the Brillouin zones are shown in Figure 3. From the frequency-temperature plots in Figure 3, it has been seen that the phonon frequencies for three points of the Brillouin zone decrease with increasing temperature. The temperature dependence of phonon frequencies is due to thermal expansion that comes about from force constants that are sensitive to increasing temperature; that is, with increasing temperature phonon-phonon interactions increases with the occurrence of new phonon modes. These anharmonic phenomena generally have been investigated by three-phonon or four-phonon processes including the creation or annihilation of phonons [4, 22, 28, 29]. Also, in a study on characteristic features of anharmonic effects for fcc metals carried out by Katsnelson et al. [28], they found that the anharmonic effects depend sharply on the wave vector in the directions Γ-X, X-W, and Γ-L and, in contrast to bcc metals, the magnitude of the effects is not due to the softness of the initial phonon spectrum. As a result of these effects, T_1 and T_2 branches of phonons

on the Γ-X and Γ-L directions have the same values at low temperatures while they have different values at high temperatures, as seen from Figure 3.

Another result from our calculations is that the phonon anomaly, which appears during any phase transformation that affects the structure of material, such as solid-solid phase transformations or melting, has not been observed.

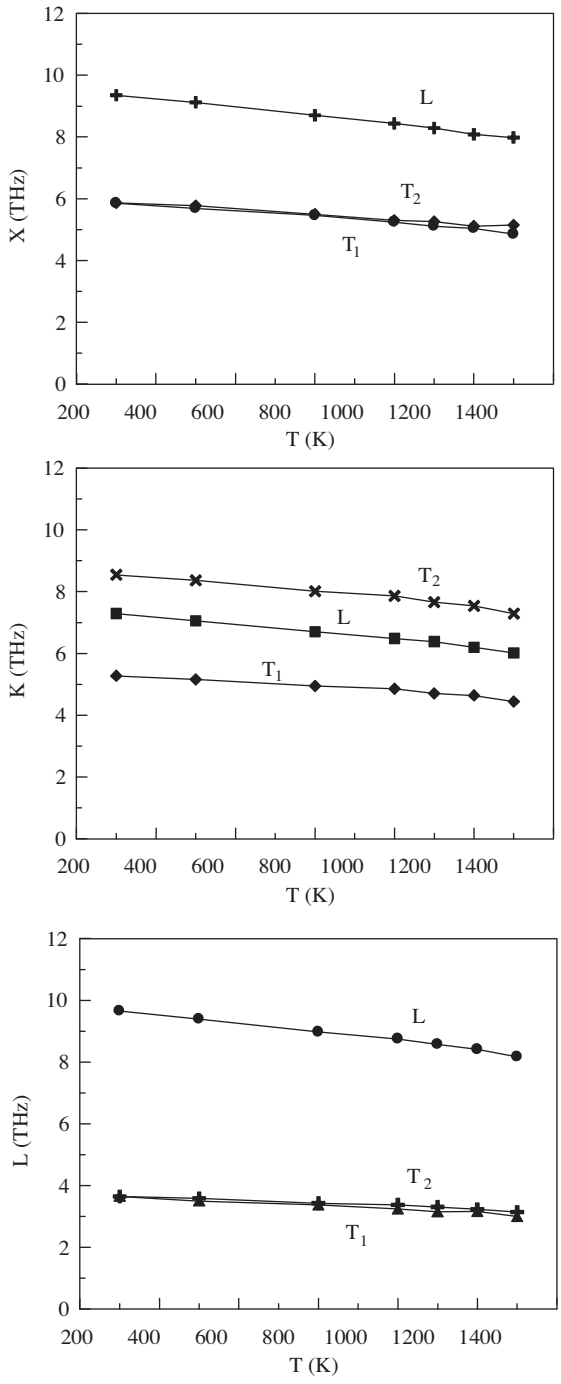

Figure 3. Variation of the acoustic phonon frequencies with temperature at X, K and L points of the Brillouin zone.

4. Conclusion

In our MD simulation study, based on many-body interactions represented by the SCEAM for Ni, temperature effects on acoustic phonon frequencies have been investigated. First, the validity of SCEAM functions and its parameters have been tested for a model system. From test calculations, we find that functions and parameters reproduce model system properties such as lattice parameter, cohesive energy, bulk modulus and phonon frequencies. Second, it is been observed that the increase in temperature decreases the phonon frequencies along three high symmetry directions, as predicted theoretically. With the increase of temperature, force constants of the material changes with thermal expansion. Therefore, a change has been observed in phonon frequencies. Another contribution comes from phonon-phonon interactions which become more important as the temperature increases up to melting point. We have also not observed any phonon anomaly produced by solid-solid phase transformations or melting for the model system at the investigated temperatures.

References

[1] Y. F. Guo, H. F. Zhang, H. B. Liu, D. L. Zhao and C. Y. Wang, *Computational Materials Science*, **20**, (2001), 228.

[2] E. Kaxiras, *Atomic and Electronic Structure of Solids*, (Cambridge University Press, U.K., 2003), p.145.

[3] C. Kittel, *Introduction to Solid State Physics*, (John Wiley & Sons, Inc., New York, 1986), p. 72-74.

[4] H. Haas, C.Z. Wang, K.M. Ho, M. Fähnle and C. Elsässer, *J. Phys., Condens. Matter*, **11**, (1999), 5455.

[5] S. Kazanc, S. Ozgen, *Physica B*, **365**, (2005), 185.

[6] N.I. Papanicolaou, G.C. Kallinteris, G.A. Evangelakis, D.A. Papaconstantopoulos, *Computational Materials Science*, **17**, (2000), 224.

[7] S. Kazanc, Y.Ö. Çiftci, K. Çolakoğlu, S. Ozgen, *Physica B*, **381**, (2006), 96.

[8] G. Simonelli, R. Pasianot and E.J. Savino, *Phys. Rev. B*, **55(9)**, (1997), 5570.

[9] L. Qi, H.F. Zhang, Z.Q. Hu, *Intermetallics*, **12**, (2004), 1191.

[10] Q. X. Pei, C. Lu and H.P. Lee, *J. Phys.: Condens. Matter*, **17**, (2005), 1493.

[11] Y. Mishin, M.J. Mehl, D.A. Papaconstantopoulos, A.F. Voter and D.J. Kress, *Phys. Rev. B*, **63**, (2001), 1.

[12] Ş. Erkoç, *Physics Reports*, **278**, (1997), 79.

[13] M. S. Daw and R.D. Hatcher, *Solid State Comm.*, **56(8)**, (1985), 697.

[14] W. Hu, H. Xu, X. Shu, X. Yuan, B. Gao and B. Zhang, *J. Phys. D: Appl. Phys.*, **33,** (2000), 711.

[15] S.A. Ostanin and V.Y. Trubitsin, *Computational Materials Science*, **17**, (2000), 174.

[16] T. Çağın, G. Dereli, M. Uludoğan and M. Tomak, *Phys. Rev. B.*, **59(5)**, (1999), 3468.

[17] A.P. Sutton, J.B. Pethica, H. Rafaii-Tabar and J.A. Nieminen, *Mechanical properties of metals at the nanometre scale, in Electron theory in alloy design*, ed. Pettifor D. G. and Cottrell A. H., Institute of materials, (The Alden Pres Ltd., Oxford, (1992)), p.191.

[18] J.H. Rose, J.R. Smith, F. Guinea, J. Ferrante, *Phys. Rev. B*, **29(6)**, (1984), 2963.

[19] M. Parrinello, A. Rahman, *Phys. Rev. Lett.*, **45(11),** (1980), 1196.

[20] S. Kazanc, S. Ozgen, O. Adiguzel, *Physica B*, **334**, (2003), 375.

[21] Y. Gurler, S. Ozgen, *Materials Letters*, **57**, (2003), 4336.

[22] P. Brüesch, *Phonons: Theory and Experiments I*, (Springer-Verlag Berlin Heidelberg, Germany, (1982)), p.19.

[23] T.S. Rahman, J.D. Spangler and A. Al-Rawi, *Surfece Science*, **502**, (2002), 429.

[24] M. Karimi, G. Stapay, T. Kaplan, M.Mostoller, *Model. Simul. Mater.Sci. Eng.*, **5**, (1997), 337u

[25] S. Ozgen, S. Kazanc, *Firat University J. of Sci. and Eng.*, **15(4)**, (2003), 505.

[26] S.K. Nayak, S.N. Khanna, B.K. Rao, P. Jena, *J. Phys. Condens. Matter*, **10**, (1998), 10853.

[27] Y. Qi, T. Çağin, W. L. Johnson, W. A. Goddard III, *J. Chem. Phys.*, **115**, (2001), 385.

[28] M. I. Katsnelson, A. V. Trefilov and K. Yu. Khromov, *Condensed Matter*, **69**, (1999), 688.

[29] M. I. Katsnelson, A. F. Maksyutov, A. V. Trefilov, *Condensed Matter Material Science*, **0201412**, (2002).