Molecular Dynamics Study on Thermodynamical Properties of Bulk Silicon Under Strain

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ABSTRACT

With classical molecular dynamics (MD) simulation, thermodynamical properties such as Helmholtz free energy and internal energy are calculated when the silicon crystal is subjected to a compression/tension and a shear deformation. In order to account for the quantum corrections under strain in the classical MD simulations, we propose an approach where the quantum corrections to the internal energy and the Helmholtz free energy are obtained by the corresponding energy deviation between the classical and quantum harmonic oscillators from the quasi-harmonic approximations. We calculate the variation of thermodynamical properties of bulk silicon with temperature and strain and compare them with results obtained by using the quasi-harmonic approximations in the reciprocal space.

Keywords: silicon, thermodynamical properties, strain effects, Molecular Dynamics.

1   Introduction

With the increasing number of applications of nanoelectromechanical systems (NEMS), silicon is one of the most popularly used materials both as a substrate and as a key device component. To understand the role of silicon as a nanoelectromechanical material, it is important to accurately predict the thermodynamical and mechanical properties of silicon at various length scales, especially when the material is under strain and at high temperature. Although a variety of physical models and simulation techniques [1]–[3] have been developed to understand the material properties of silicon, molecular dynamics technique with empirical potential is one of the robust techniques to understand material behavior because of its simplicity and universality. It is often used to understand fundamental issues governing material behavior and response.

In this paper, thermodynamical properties of silicon crystal subjected to a compression/tension and a shear deformation are calculated using classical MD open source code LAMMPS [4] with the Tersoff interatomic potential [5]. Since MD simulations obey the rules of classical statistical mechanics, quantum corrections are necessary for MD simulations results in order to compare with experimental data and quantum-mechanical calculations. We investigate the extensively used temperature rescaling method [6] and realize that this technique can not accurately predict the quantum effects in the Helmholtz free energy at low temperature under general strain conditions. We suggest an approach where the quantum corrections are obtained by investigating the corresponding energy differences between the classical and quantum harmonic oscillators. The Helmholtz free energy is then computed by the ensemble method [7].

The rest of the paper is organized as follows: in section 2, we describe MD simulations setup, free energy calculations, and quantum correction calculations. In section 3, we present the thermodynamical properties of bulk silicon for both non-strain and strain cases. The variation of pressure with temperature and strain is also shown. Finally, conclusions are presented in section 4.

2   Methodology

2.1   MD Setup

With MD simulator LAMMPS, a silicon cubic structure of 216 atoms ($3 \times 3 \times 3$ unit cells) with periodic boundary conditions in three directions is used for both non-strain and strain cases. Tersoff interatomic potential is employed to determine the interactions between silicon atoms. Nose-Hoover thermostat is adopted for both NPT and NVT ensembles with a time step of 1.0fs. The center of mass of the system is fixed during the simulation to neglect any translational movements. For each specified temperature, we first perform NPT ensemble simulations to determine the zero pressure lattice constant. With the corresponding lattice constant, NVT ensemble simulations are performed to compute the internal energy and Helmholtz free energy. Each simulation runs for $0.5 \sim 1.0$ns to obtain an equilibrium state and an additional $4.0 \sim 6.0$ns for time averaging.

In order to study the thermodynamical properties of silicon under strain, we perform MD simulations with two types of strain: compression/tension and shear. The strain is assigned to the system through the deformation gradient $\mathbf{F}$ by modifying the initial configuration of the system with the relation $\hat{\mathbf{R}}_{\mathbf{n}} = \mathbf{F}\mathbf{R}_{\mathbf{n}}$, where $\mathbf{R}_{\mathbf{n}}$ is the coordinate of atom n under non-strain conditions, and $\hat{\mathbf{R}}_{\mathbf{n}}$ is the corresponding atom coordinate with the spec-

ified strain. Note that the deformed configuration is no longer a cubic structure, but a parallelepiped structure. LAMMPS employs the Parrinello-Rahman method [8] to maintain both the volume and the shape of the parallelepiped simulation box within the NVT ensemble simulations.

2.2 Free Energy Calculations

Thermodynamical properties of a system such as free energy, entropy, chemical potential, etc. can not be computed directly from the phase-space trajectory which is the basic output of most MD simulations, because they are formally related to the accessible phase-space volume. One alternative is to transform these properties, for example, free energy, into a function which can be evaluated using the phase-space trajectory.

At zero pressure conditions, the Helmholtz free energy A is equal to the Gibbs free energy G while the enthalpy H is equal to the internal energy E. Since the Gibbs free energy can be obtained by directly integrating the thermodynamic relation

$$\frac{d}{dT}\left(\frac{G}{T}\right) = -\frac{H}{T^2}, \qquad (1)$$

the Helmholtz free energy can be easily computed. But this method is no longer valid under finite pressure condition, e.g. when the system is under strain.

The usual procedure to compute the Helmholtz free energy of a homogeneous crystalline solid is called the ensemble method proposed by Frenkel and Ladd[7]. The basic idea is to construct a reversible path from a state of the known free energy (Einstein crystal with the analytical expression of the Helmholtz free energy) to the system of interest by modifying the potential energy as

$$U_\lambda = (1-\lambda)U + \lambda U_E, \qquad (2)$$

where U is the Tersoff potential energy of the silicon structure, U_E is the potential energy of the Einstein crystal, which is a collection of identical independent harmonic oscillators with the same silicon structure. Thus as the parameter λ switches slowly from 0 to 1, the Helmholtz free energy of the system of interest $A = A_{\lambda=0}$ can be calculated by the thermodynamic integration

$$A = A_{\lambda=0} = A_{\lambda=1} + \int_0^1 d\lambda \langle U - U_E \rangle_\lambda, \qquad (3)$$

where $A_{\lambda=1}$ is the analytical free energy of the reference Einstein crystal [9], $\hbar$ is the Planck's constant, and $\langle \cdots \rangle_\lambda$ is the canonical ensemble average.

In this paper, we use Eq. (3) to calculate the Helmholtz free energy of bulk silicon for both non-strain and strain cases.

Table 1: Formulation of 1-D quantum harmonic oscillator and classical harmonic oscillator

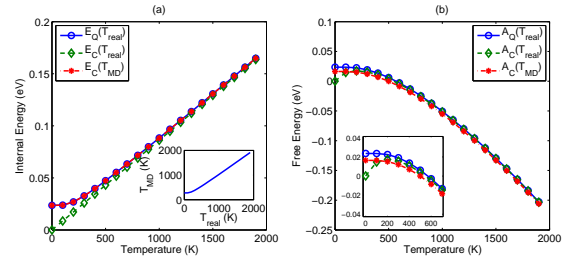| Quantum System	$A_Q(\omega) = \dfrac{\hbar\omega}{2} + k_B T \ln\left(1 - e^{-\hbar\omega/k_B T}\right)$ $E_Q(\omega) = \dfrac{\hbar\omega}{2} + \hbar\omega \dfrac{1}{e^{\hbar\omega/k_B T} - 1}$
Classical System	$A_C(\omega) = k_B T \ln\left(\dfrac{\hbar\omega}{k_B T}\right)$ $E_C(\omega) = k_B T$

Figure 1: (a): Internal energy of a 1-D Einstein oscillator obtained with the quantum model $E_Q(T_{real})$, the classical model $E_C(T_{real})$ and the classical model with temperature rescaling $E_C(T_{MD})$. (inset) Temperature rescaling relation. (b): Helmholtz free energy of a 1-D Einstein oscillator obtained with the quantum model $A_Q(T_{real})$, the classical model $A_C(T_{real})$ and the classical model with temperature rescaling $A_C(T_{MD})$. (inset) Enlarged view of free energy at low temperatures.

2.3 Quantum Corrections for the Classical MD Simulations

Classical MD simulations obey the rules of classical statistical mechanics. Considering a simple 1-D Einstein oscillator as an example, Table 1 lists the expressions for both the internal energy and Helmholtz free energy when the oscillator is treated as a quantum or as a classical model, where k_B is Boltzmann's constant, T is temperature, ω is oscillator frequency. At $T = 0K$ both the Helmholtz free energy A_C and the internal energy E_C of the classical model are zero. However, the corresponding quantum energies A_Q and E_Q are not zero because of the quantum effects at zero temperature. As a result, quantum corrections are required in order to compare the thermodynamical properties predicted by classical MD simulations with quantum simulations, especially for low temperatures.

The basic idea of the temperature rescaling method [6] is to find a one to one mapping of temperature T between the classical system and the quantum system based on the internal energy. Considering a 1-D Einstein oscillator as an example, with the scaling relation between T_{MD} and T_{real} as shown the inset of the left figure in

Fig. 1, the internal energy of the classical model with temperature rescaling matches with the quantum result. However, for Helmholtz free energy, a small deviation between the quantum result and the classical result with temperature rescaling is observed at low temperatures. It is because that the one-to-one mapping of temperature T does not exist for the Helmholtz free energy between the two systems. Even though the above discussion is based on a 1-D Einstein oscillator, we can expect similar behavior when the temperature rescaling method is used to account for quantum corrections in MD simulations of silicon structures based on the Tersoff interatomic potential.

At zero pressure condition, internal energy for the quantum system can be accurately obtained with temperature rescaling method. The Helmholtz free energy can then be calculated by Eq. (1). However, Eq. (1) is not valid when the system is subjected to a strain condition. As pointed out above, the Helmholtz free energy can not be accurately predicted directly with temperature rescaling technique. In this paper, we suggest to extract the quantum correction terms for both the internal energy and the Helmholtz free energy from the energy deviation between the classical model and the quantum model of the harmonic oscillators as

$$E_{qc} = \sum_{n=1}^{3N} \left\{ \frac{\hbar\omega_n}{2} + \hbar\omega_n \frac{1}{e^{\hbar\omega_n/k_BT} - 1} k_BT \right\}, \quad (4)$$

$$A_{qc} = \sum_{n=1}^{3N} \left\{ \frac{\hbar\omega_n}{2} + k_BT \ln\left(1 - e^{-\hbar\omega_n/k_BT}\right) \right.$$
$$\left. k_BT \ln\left(\frac{\hbar\omega_n}{k_BT}\right) \right\}, \quad (5)$$

where for a N atom system, all the $3N$ required normal modes ω_n are obtained from the quasi-harmonic approximation by diagonalizing the $3N \times 3N$ matrix [3]

$$\Phi_{\alpha i\beta j} = \frac{\partial^2 U}{\partial \mathbf{r}_{\alpha i} \partial \mathbf{r}_{\beta j}}, \quad (6)$$

where U is the Tersoff potential energy for the whole system, $\mathbf{r}$ is current atom position, α and β denote atom numbers, and i and j denote Cartesian components.

In this paper, we use the temperature rescaling method in classical MD simulations to obtain the lattice constants. After the lattice constants are determined, we run the classical MD simulations for each specified temperature. The Helmholtz free energy is computed by adding the quantum correction obtained from Eq. (5) to the energy obtained from Eq. (3), which does not include quantum effects. The internal energy is obtained from the time average of the total energy of the system with the quantum correction given by Eq. (4).

Table 2: Thermodynamical properties of bulk silicon

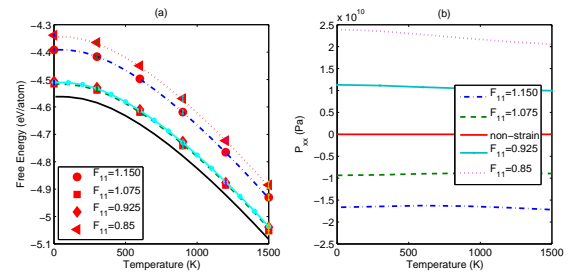| temperature (K)		Internal Energy (eV/atom)	Free Energy (eV/atom)
0	This work	-4.564	-4.563
	QHMK[10]	-4.563	-4.563
	Ref[11]	-4.562	-4.552
300	This work	-4.530	-4.580
	QHMK	-4.531	-4.584
	Ref	-4.535	-4.590
1500	This work	-4.228	-5.102
	QHMK	-4.232	-5.083
	Ref	-4.221	-5.112

Figure 2: (a): Variances of the Helmholtz free energy with temperature under different compression/tension conditions. (b): Variations of normal pressure with temperature under different compression/tension conditions. The thick solid line is the Helmholtz free energy of bulk silicon under non-strain condition. All the lines are from QHMK calculations. All the symbols are from MD calculations in this work. The error-bar is within the symbol size.

3   Results and Discussion

After the lattice constants are obtained, the internal energy and Helmholtz free energy of bulk silicon are calculated using techniques described in the previous section. Table 2 summarizes the results obtained from MD simulations at 0K, 300K, and 1500K. Two sets of comparison data are also presented in the table. Accounting for quantum corrections via Eqs. (4) and (5), we observe that at low temperatures, the internal energy and the free energy match with the QHMK results quite well. At high temperature, the anharmonicity becomes important. Since QHMK method can not capture any anharmonicity, but MD can, we see a small deviation between the MD results with QHMK results at $T = 1500K$.

To study the strain effect on the thermodynamical and mechanical properties of silicon, we consider two types of strain: compression/tension and shear, by varying the deformation gradient component F_{11} from 0.85
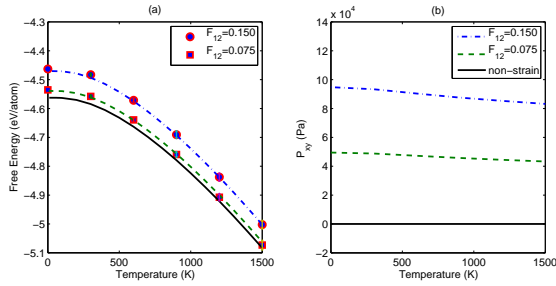
Figure 3: (a): Comparison of the Helmholtz free energy with temperature for different shear magnitude. (b): Variation of pressure p_{xy} with temperature under different shear magnitude. The thick solid line is the Helmholtz free energy of bulk silicon without deformation. All the lines are from QHMK calculations. All the symbols are from MD calculation in this work. The error-bar is within the symbol size.

(compression) to 1.15 (tension) and F_{12} from 0.0 (no deformation) to 0.075 and 0.15 (shear along the x-direction), respectively. Fig. 2(a) and Fig. 3(a) show the variation of Helmholtz free energy with temperature when the silicon crystal is under a compression/tension strain and a shear strain, respectively. The corresponding results from QHMK model are also shown for comparison. We note that the MD results match well with the QHMK results. Fig. 2(b) shows the variation of pressure with temperature under compression/tension in the x-direction. For the temperature range considered, the absolute value of pressure p_{xx} appears to be smaller under tension than under compression, implying that silicon material is softer under tension than under compression. When the material is under constant compression, the value of p_{xx} decreases mildly with temperature indicating that the stiffness of silicon decreases at high temperature under compression. Under tension, we observe that the stiffness of the material does not change very much at high temperature. Fig. 3(b) shows the variation of pressure p_{xy} with temperature when the crystal is under shear deformation. We note that pressure p_{xy} decreases with the increase in temperature, implying that shear modulus of the material decreases with the increase in temperature. These observations are consistent with the results presented in Ref [12].

4   Conclusions

In this paper, we presented results from MD simulations for Tersoff silicon at different temperature and under two types of strain – compression/tension and shear. The Helmholtz free energy is calculated by employing the ensemble method. We investigated the widely-used temperature rescaling method to account for quantum corrections in classical MD simulations and we observed that it may not be accurate for Helmholtz energy calculations at low temperatures. We propose a method where the quantum corrections of both the internal energy and the Helmholtz free energy are obtained from the deviation of the corresponding energy between the classical and quantum harmonic oscillators with the required normal modes obtained from the quasi-harmonic approximation of the Tersoff potential. We show that the computed Helmholtz free energies match with the published QHMK results. Finally, using MD we also computed the variation of pressure with temperature and strain and discussed how this can effect the mechanical properties.

5   Acknowledgments

REFERENCES

[1] S. Wei, C. Li, and M. Y. Chou, Physical Review B **50** (19), 14587, 1994.

[2] R. LeSar, R. Najafabadi, and D. J. Srolovitz, Physical Review Letters, **63** (6), 624 - 627, 1989.

[3] H. Zhao, Z. Tang, G. Li, and N. R. Aluru, Journal of Applied Physics, **99** (6), 064314, 2006.

[4] S. J. Plimpton, Journal of Computational Physics, **117** (1), 1 - 19, 1995.

[5] J. Tersoff, Physical Review B, **38** (14), 9902 - 9905, 1988.

[6] C. Z. Wang, C. T. Chan, and K. M. Ho, Physical Review B, **42** (17), 11276-11283, 1990.

[7] D. Frenkel, and A. J. C. Ladd, Journal of Chemical Physics, **81** (7), 3188 - 3193, 1984.

[8] M. Parrinello, and A. Rahman, Physical Review Letters, **45** (14) 1196-1199, 1980.

[9] J. F. Lutsko, D. Wolf, and S. Yip, Journal of Chemical Physics, **88** (10), 6525 - 6528, 1988.

[10] L. J. Porter, S. Yip, M. Yamaguchi, H. Kaburaki, and M. Tang, Journal of Applied Physics **81** (1), 96 - 105, 1997.

[11] I. Barin, and O. Knake, "Thermochemical Properties of Inorganic Substances", Springer, Berlin, 1973.

[12] Z. Tang, H. Zhao, G. Li, and N. R. Aluru, Physical Review B, **74** (6), 064110, 2006.