

# Molecular dynamics simulation of bulk silicon under strain

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**Abstract.** In this paper, thermodynamical properties of crystalline silicon under strain are calculated using classical molecular dynamics (MD) simulations based on the Tersoff interatomic potential. The Helmholtz free energy of the silicon crystal under strain is calculated by using the ensemble method developed by Frenkel and Ladd (1984). To account for 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 using the corresponding energy deviation between the classical and quantum harmonic oscillators. We calculate the variation of thermodynamic properties with temperature and strain and compare them with results obtained by using the quasi-harmonic model in the reciprocal space.

**Keywords:** modeling of materials; silicon; finite temperature; thermodynamical properties; strain effects; Molecular Dynamics; Tersoff potential.

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## 1. Introduction

Nanoelectromechanical systems (NEMS) are sensors, actuators, devices and systems with a critical dimension ranging from a few nanometers to several tens of nanometers. They find widespread applications as nanoactuators (Chau *et al.* 2003), nanotweezers (Boggild *et al.* 2001), electrostatic switches (Li *et al.* 2007), etc. Even though NEMS can be designed using a variety of materials, silicon is one of the most popularly used materials both as a substrate and as a key device component because of its high stability under different conditions. Since NEMS can attain high frequencies, undergo large deformations and operate under high temperature conditions, it is important to clearly understand the thermodynamical and mechanical properties of silicon under various conditions including variations in temperature, strain, etc. These studies can not only lead to a better understanding of NEMS but also enable design optimization.

Various physical models and simulation techniques have been developed to understand the material properties of nanostructures. First-principles quantum-mechanical method such as *ab initio* local density functional technique (Wei *et al.* 1994) is one of the most accurate methods to predict the material properties. However, the method is restricted to small system sizes and short simulation times. Another class of methods that can be used to compute thermodynamical and mechanical

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properties are based on the theory of lattice dynamics. LeSar *et al.* (1989) proposed a local quasi-harmonic model, which is a simple and an elegant model but neglects the interactions between atoms. Based on the harmonic approximation of the Tersoff interatomic potential (Tersoff 1988), a quasi-harmonic model in the reciprocal space (QHMK model, Zhao *et al.* 2006) has been used to predict the thermodynamical properties of silicon at different temperature and strain conditions. Since the method relies on a periodic boundary condition and harmonic approximation, the method can be limited to bulk structures and moderate temperatures. Molecular dynamics (MD) method relying on interatomic potential is one of the robust techniques to understand material behavior because of its simplicity and universality. Even though MD simulations can be expensive compared to lattice dynamics theories, when interatomic potentials are sufficiently well-calibrated and accurate, MD can be a reliable method and is often used to understand fundamental issues governing material behavior and response.

In this paper, thermodynamical properties such as the Helmholtz free energy and internal energy when the silicon crystal is subjected to a compression/tension and a shear deformation are calculated using classical MD open source code LAMMPS (Plimpton 1995) with the Tersoff interatomic potential. As MD simulations obey the rules of classical statistical mechanics, they can not accurately capture quantum effects, particularly at low temperatures. As a result, quantum corrections are necessary to MD simulations in order to compare with experimental data and quantum-mechanical calculations. We investigated the extensively used temperature rescaling method (Wang *et al.* 1990) and found that although this technique can accurately predict the internal energy and Helmholtz free energy for the quantum system under zero pressure conditions, it can not directly capture all the quantum effects in the Helmholtz free energy at low temperature under general strain conditions. We suggest an approach where the quantum corrections to the internal energy and the Helmholtz free energy 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 (Frenkel and Ladd 1984).

The rest of the paper is organized as follows: in section 2, we describe MD simulations, free energy calculations using the ensemble method, calculation of quantum corrections and the MD simulations under strain. In section 3, thermodynamical properties of bulk silicon are presented. In section 4, Helmholtz free energy and internal energy calculations of bulk silicon under two types of strain are presented. The variation of pressure with temperature and strain is also shown. Finally, conclusions are presented in section 5.

## 2. Methodology

### 2.1 MD setup

In this paper, all the MD simulations are carried out using the open source molecular dynamics simulator LAMMPS. Tersoff interatomic potential is employed to determine the interactions between silicon atoms. For both non-strain and strain cases, a silicon cubic structure of 216 atoms ( $3 \times 3 \times 3$  unit cells) with periodic boundary conditions is used. No significant size effects are found when the results are compared with those from a silicon cubic structure of 512 or 1024 atoms. Nose-Hoover thermostat (Hoover 1985) is employed to maintain the prescribed system temperature for both NPT and NVT ensembles. The velocity-Verlet time stepping scheme is used with an

integration time step of 1.0 fs. 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. The simulations are run for 0.5 ~ 1.0 ns to obtain an equilibrium state and an additional 4.0 ~ 6.0 ns of simulations are performed for time averaging. Next, NVT ensemble simulations are also performed using the lattice constant obtained from NPT simulations for validation as the average pressure is approximately zero within the statistical error. As a final step, NVT ensemble simulations are performed to compute the Helmholtz free energy. The simulation time is around 5.0 ns with the starting 1.0 ns used for equilibration of the system.

## 2.2 Free energy calculations

The basic output of most MD simulations is the phase-space trajectory  $\{\mathbf{r}^N(t), \mathbf{p}^N(t)\}$ , where  $\mathbf{r}^N(t)$  and  $\mathbf{p}^N(t)$  are the time-dependent position and momentum vectors of each atom, respectively. The physical properties of the system which are functions of  $\mathbf{r}^N(t)$  and  $\mathbf{p}^N(t)$ , i.e.,  $f(\mathbf{r}^N(t), \mathbf{p}^N(t))$ , can be computed directly by evaluating their time averages. However, not all the properties of the system can be measured directly from the phase-space trajectory e.g., free energy, entropy, chemical potential, etc. can not be computed directly as these quantities are formally related to the accessible phase-space volume and not the phase-space trajectory. 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  $G$  and the enthalpy  $H$  is equal to the internal energy  $E$ . Since the Gibbs free energy can be obtained by directly integrating the thermodynamic relation

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

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 ensemble method proposed by Frenkel and Ladd (1984) has been shown to be an accurate and a robust method for free energy calculations (Lutsko *et al.* 1988). It is restricted to homogeneous solid systems but does yield absolute free energies. The basic idea in the ensemble method is to construct a reversible path from a state of known free energy to the solid phase under consideration. The reference state adopted here is a collection of identical independent harmonic oscillators (Einstein crystal) with the same structure as the solid under consideration. In this paper, we consider the diamond structure crystalline silicon. In the ensemble method, the potential energy of the system is modified by adding a parameter  $\lambda$  with the potential energy  $U_E$  for the Einstein crystal, i.e.,

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

where  $U = \sum_{\alpha=1}^N U_\alpha$  is the Tersoff potential energy computed by using the current atom positions of the  $N$  atom system,  $\alpha$  denotes the atom number, and  $U_\alpha$  is the Tersoff potential energy for atom  $\alpha$ .  $U_E =$

$\sum_{n=1}^N \frac{1}{2} \kappa \|\mathbf{r}_n - \mathbf{R}_n\|^2$ , where  $\mathbf{r}_n$  is the current atom position,  $\mathbf{R}_n$  is the initial atom position and  $\kappa$  is the

oscillator strength. By slowly varying the parameter  $\lambda$  from 0 to 1, the modified potential energy  $U_\lambda$  is switched from the Tersoff potential energy to the Einstein potential energy. The  $\lambda$ -dependent Hamiltonian is then defined as

$$H(\lambda) = \sum_{n=1}^N \frac{\mathbf{p}_n^2}{m} + (1 - \lambda)U + \lambda U_E \quad (3)$$

where  $\mathbf{p}_n$  is the momentum of the  $n$ -th atom and  $m$  is the atom mass. The derivative of the free energy of the system with respect to the coupling constant  $\lambda$  is given by

$$\frac{\partial A}{\partial \lambda} = -k_B T \frac{\partial}{\partial \lambda} \left\{ \ln \int \cdots \int e^{-\frac{H(\lambda)}{k_B T}} d\mathbf{q}^n \right\} = \langle U_E - U \rangle_\lambda \quad (4)$$

where  $k_B$  is Boltzmann's constant,  $T$  is temperature,  $\langle \cdots \rangle_\lambda$  is an average over the ensemble generated by  $H(\lambda)$ . By integrating Eq. (4), we obtain

$$A = A_{\lambda=0} = A_{\lambda=1} + \int_0^1 d\lambda \langle U_E - U \rangle_\lambda = A_1 + \int_0^1 d\lambda \langle U - U_E \rangle_\lambda \quad (5)$$

where  $A_1 \equiv A_{\lambda=1}$  is the analytical free energy of the reference Einstein crystal given by

$$A_1 = \frac{3}{2} N k_B T \ln \left( \frac{\hbar \sqrt{\frac{\kappa}{m}}}{k_B T} \right) \quad (6)$$

and  $\hbar$  is the Planck's constant.

In this paper, we use Eq. (5) to calculate the Helmholtz free energy. The integration in Eq. (5) is carried out using the 3-point Gaussian quadrature rule i.e., by numerically evaluating the ensemble average via MD simulation at 3 different Gaussian points. We have verified that 3-point Gaussian quadrature rule for this problem can provide reasonable accuracy. The oscillator strength  $\kappa$  can be chosen as any constant value. However, a proper value of  $\kappa$  can ensure a small variance in free energy and can also lead the system to reach its equilibrium state quickly (Lutsko *et al.* 1988). In this paper, the oscillator strength  $\kappa$  is chosen such that the oscillation of the atoms from their equilibrium lattice positions is approximately constant (Almarza 2007). Specifically, we use  $\kappa = m \bar{\omega}^2$ , where  $\bar{\omega}$  is the mean frequency obtained from the local quasi-harmonic model (LeSar *et al.* 1989).

### 2.3 Quantum corrections for the classical MD simulations

Classical MD simulations obey the rules of classical statistical mechanics. Quantum corrections are necessary when results from MD simulations are compared with results from experiments and quantum simulations, especially for low temperature conditions. Considering a simple 1-D Einstein oscillator as an example, Table 1 lists the expressions for various thermodynamical properties when the oscillator is treated both as a quantum and as a classical model. It is clear from Table 1 that at  $T = 0$  K 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, in order to compare the thermodynamical properties predicted by classical MD simulations with quantum simulations, quantum corrections are required.

Table 1 Expression for various quantities when the 1-D harmonic oscillator is treated as a quantum system and as a classical system

Quantity	Quantum Oscillator	Classical Oscillator
Hamiltonian	$H_Q = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$	$H_C = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$
Canonical partition function	$Q_Q = \frac{1}{2} \operatorname{csch}\left(\frac{\hbar\omega}{2k_B T}\right)$	$Q_C = \frac{k_B T}{\hbar\omega}$
Helmholtz free energy	$A_Q = \frac{\hbar\omega}{2} + k_B T \ln(1 - e^{-\hbar\omega/k_B T})$	$A_C = k_B T \ln\left(\frac{\hbar\omega}{k_B T}\right)$
Internal Energy	$E_Q = \frac{\hbar\omega}{2} + \hbar\omega \frac{1}{e^{\hbar\omega/k_B T} - 1}$	$E_C = k_B T$

Typically a temperature rescaling method (Wang *et al.* 1990) is employed to account for quantum corrections in classical MD simulations. The basic idea in this method is to calculate a simulation temperature  $T_{MD}$  based on the real (given) temperature  $T_{real}$  such that the internal energy of the classical system at  $T_{MD}$  is equal to the internal energy of the quantum system at  $T_{real}$ . To account for quantum corrections, classical MD simulations are then performed at  $T_{MD}$  instead of  $T_{real}$ . Considering a 1-D Einstein oscillator as an example, with the expressions for internal energy as listed in Table 1, the temperature rescaling relation between  $T_{MD}$  and  $T_{real}$  is given by

$$k_B T_{MD} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T_{real}}} - 1} \quad (7)$$

where  $\omega = \sqrt{\kappa/m}$  is the normal mode of the oscillator. The scaling relation between  $T_{MD}$  and  $T_{real}$  with  $\kappa = 15 \text{ eV}/\text{\AA}^2$  is plotted in the inset of Fig. 1. The results for the internal energy and the Helmholtz free energy obtained with the quantum model, classical model and the classical model with temperature rescaling are shown in Fig. 1 and Fig. 2. The results indicate that the internal energy of the classical model with temperature rescaling matches with the quantum result. However, in the case of Helmholtz free energy, a small deviation between the quantum result and the classical result with temperature rescaling is observed at low temperatures. The temperature rescaling method works effectively for internal energy as there exists a one to one mapping of the internal energy between the classical model and the quantum model. However, in the case of the Helmholtz free energy (see inset, Fig. 2), the maximum value predicted by the classical model is smaller than the maximum value predicted by the quantum model. This means that a one-to-one mapping for temperature rescaling does not exist for the Helmholtz free energy, especially in the low temperature region. 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

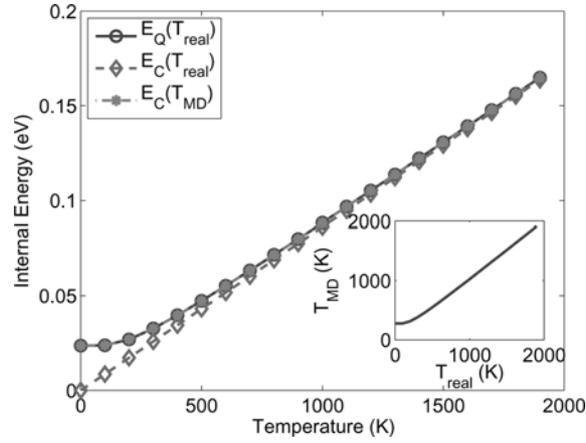


Fig. 1 Internal energy of a 1-D Einstein oscillator obtained with the quantum model  $E_Q(T_{real})$  (circle solid line), the classical model  $E_C(T_{real})$  (diamond dash line) and the classical model with temperature rescaling  $E_C(T_{MD})$  (star solid line) (inset) Temperature rescaling relation

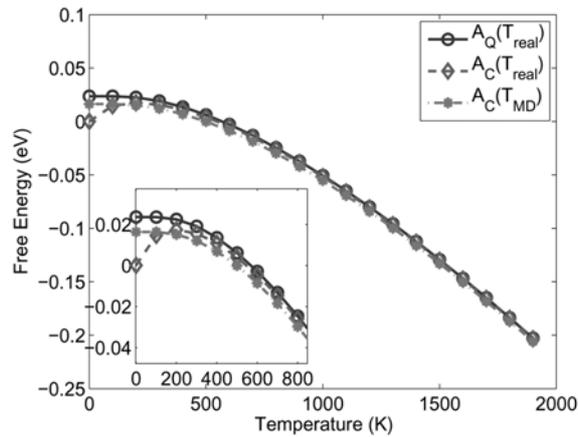


Fig. 2 Helmholtz free energy of a 1-D Einstein oscillator obtained with the quantum model  $A_Q(T_{real})$  (circle solid line), the classical model  $A_C(T_{real})$  (diamond dash line) and the classical model with temperature rescaling  $A_C(T_{MD})$  (star solid line). (inset) Enlarged view of free energy at low temperatures

from the classical MD simulation with temperature rescaling method. The Helmholtz free energy can then be calculated from the thermodynamic relation, Eq. (1). However, Eq. (1) is not suitable when the material is under strain. As pointed out above, the Helmholtz free energy can not be accurately predicted from classical MD simulation with temperature rescaling technique. In this paper, we 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 with the required normal modes obtained from the quasi-harmonic approximation of the Tersoff potential (Zhao *et al.* 2006). With a quasi-harmonic approximation,  $3N$  normal modes  $\omega_n$  of the  $N$  atom system can be obtained by diagonalizing the  $3N \times 3N$  force

constant matrix

$$\Phi_{\alpha i \beta j} = \frac{\partial^2 U}{\partial \mathbf{r}_{\alpha i} \partial \mathbf{r}_{\beta j}} \quad (8)$$

where  $U$  is the Tersoff potential energy for the whole system,  $\alpha$  and  $\beta$  denote atom numbers, and  $i$  and  $j$  denote Cartesian components. The Hamiltonian of the system can then be expressed as the sum of the energies of  $3N$  independent harmonic oscillators. Using the notation shown in Table 1, when the silicon system is treated as the classical system, the Helmholtz free energy and the internal energy can be defined as  $\sum_{n=1}^{3N} A_C(\omega_n)$  and  $\sum_{n=1}^{3N} E_C(\omega_n)$ , respectively. When the silicon system is treated as the quantum-mechanical system, the Helmholtz free energy and the internal energy can be defined as  $\sum_{n=1}^{3N} A_Q(\omega_n)$  and  $\sum_{n=1}^{3N} E_Q(\omega_n)$ , respectively. The quantum corrections for the Helmholtz free energy  $A_{qc}$  and the internal energy  $E_{qc}$  are then obtained from the deviation between the two systems, i.e.,

$$E_{qc} = \sum_{n=1}^{3N} (E_Q(\omega_n) - E_C(\omega_n)) = \sum_{n=1}^{3N} \left\{ \frac{\hbar \omega_n}{2} + \frac{\hbar \omega_n}{e^{\frac{\hbar \omega_n}{k_B T}} - 1} - k_B T \right\} \quad (9)$$

$$A_{qc} = \sum_{n=1}^{3N} (A_Q(\omega_n) - A_C(\omega_n)) = \sum_{n=1}^{3N} \left\{ \frac{\hbar \omega_n}{2} + k_B T \ln(1 - e^{-\hbar \omega_n / k_B T}) - k_B T \ln\left(\frac{\hbar \omega_n}{k_B T}\right) \right\} \quad (10)$$

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. (10) to the energy obtained from Eq. (5), 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. (9).

#### 2.4 Molecular dynamics simulations under strain

We perform MD simulations of bulk silicon under two types of strain: compression/tension and shear. The strain is assigned to the system by modifying the initial configuration of the system with the relation  $\hat{\mathbf{R}}_n = \mathbf{F} \mathbf{R}_n$ , where  $\hat{\mathbf{R}}_n$  is the atom coordinate with the specified strain, and  $\mathbf{F}$  is the deformation gradient. For example, as shown in Fig. 3 (a), the lattice with big symbols is the configuration of the system with  $F_{11} = 1.15$ . In Fig. 3 (b), the lattice with big symbols is the configuration of the system with  $F_{12} = 0.15$ . The lattice with small symbols in both figures is the equilibrium configuration of the silicon structure without strain. Note that the deformed configuration is no longer a cubic structure, but a parallelepiped structure. LAMMPS employs the Parrinello-Rahman method (1980) to maintain both the volume and the shape of the parallelepiped simulation box within the NVT ensemble simulations. The pressure component applied to the system can be calculated as

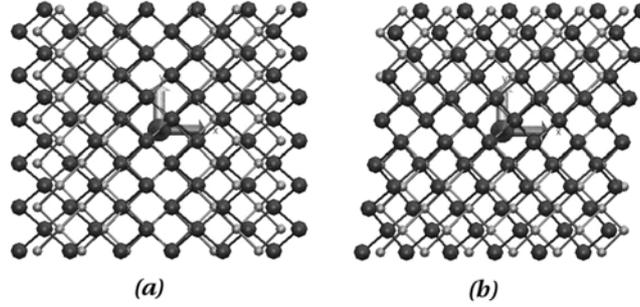


Fig. 3 (a) (001) projection of silicon structure under tensile deformation,  $F_{11} = 1.15$  (large particle lattice) (b) (001) projection of silicon structure with shear deformation,  $F_{12} = 0.15$  (large particle lattice) The lattice with smaller particles is the lattice free of deformation

Table 2 Thermodynamical properties of bulk silicon at different temperatures

Temperature (K)		Lattice Constant (Å)	Internal Energy (eV/atom)	Free Energy (eV/atom)	Entropy (J/mol-K)
0	This work	5.441	-4.564	-4.563	0.0
	QHMK <sup>a</sup>	5.443	-4.563	-4.563	0.0
	Ref MD <sup>b</sup>	5.440	-4.562	-4.552	
300	This work	5.445	-4.530	-4.580	16.125
	QHMK	5.446	-4.531	-4.584	17.125
	Ref MD	5.449	-4.535	-4.590	19.048 <sup>c</sup>
1500	This work	5.483	-4.228	-5.102	55.657
	QHMK	5.489	-4.232	-5.083	54.732
	Ref MD	5.479	-4.221	-5.112	58.1 <sup>c</sup>

<sup>a</sup>QHMK Data from Zhao *et al.* (2006)

<sup>b</sup>MD Data from Porter *et al.* (1997)

<sup>c</sup>Experimental data from Barin and Knake (1973)

$$P_{ij} = \frac{m}{\Omega} \sum_{\alpha=1}^N v_{\alpha i} v_{\alpha j} + \frac{1}{D\Omega} \sum_{\alpha=1}^N r_{\alpha i} f_{\alpha j} \quad (11)$$

where  $m$  is the atom mass,  $\Omega$  is the system volume,  $D$  is the dimensionality of the system,  $i$  and  $j$  denote the Cartesian components, and  $\mathbf{v}_{\alpha}$ ,  $\mathbf{r}_{\alpha}$  and  $\mathbf{f}_{\alpha}$  denote the velocity, position and force vectors of atom  $\alpha$ , respectively.

### 3. Results: bulk properties

In this section, we calculate several thermodynamical properties of bulk silicon using the MD simulation technique described in the previous section. After the Helmholtz free energy is calculated, the entropy can be computed using the expression  $S = (E - A) / T$ . Table 2 summarizes

the results obtained from MD simulations at 0 K, 300 K, and 1500 K. Two sets of comparison data are also presented in the table. The lattice constants predicted in this work match with the published MD data quite well. The maximum error is about 0.2%, which is within the statistical error. Accounting for quantum corrections via Eqs. (9) and (10), 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  $T = 1500$  K.

#### 4. Results: strain effects

In this section, we discuss the effect of strain on the thermodynamical and mechanical properties of silicon by considering two types of strain. The first type of strain we consider is compression/tension. To introduce compression/tension in the material along  $x$ -direction, the deformation gradient  $F_{11}$  is varied from 0.85, which represents compression, to 1.15, which represents tension. Fig. 4 and Fig. 5 show the variation of internal energy and Helmholtz free energy with temperature when the silicon crystal is under compression/tension in the  $x$ -direction. The results from QHMK model are also shown for comparison. We note that the MD results match well with the QHMK results. Fig. 6 shows the variation of pressure component  $P_{xx}$  with temperature when the crystal is under compression/tension in the  $x$ -direction. For the temperature range considered, the absolute value of  $P_{xx}$  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. These observations are consistent with the results presented earlier by Tang *et al.* (2006).

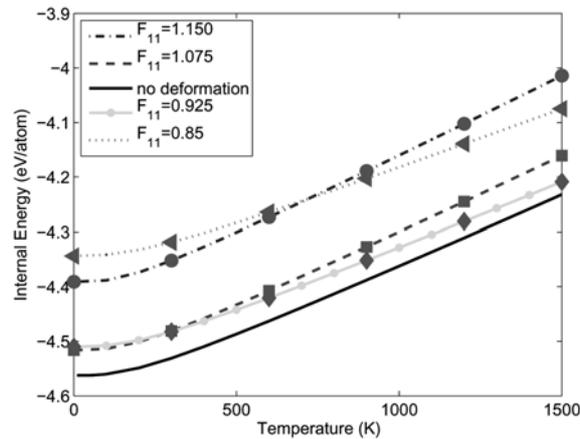


Fig. 4 Comparison of the internal energy with temperature for tension  $F_{11} = 1.15$  (dash dot line, filled circle),  $F_{11} = 1.075$  (dash line, square) and compression  $F_{11} = 0.925$  (solid line with a small filled circle, diamond),  $F_{11} = 0.85$  (dot line, triangle) of a bulk silicon crystal. The thick solid line is the internal energy of bulk silicon without deformation. All the lines are from QHMK calculations All the symbols are from MD calculations in this work. The error-bar from MD is within the symbol size

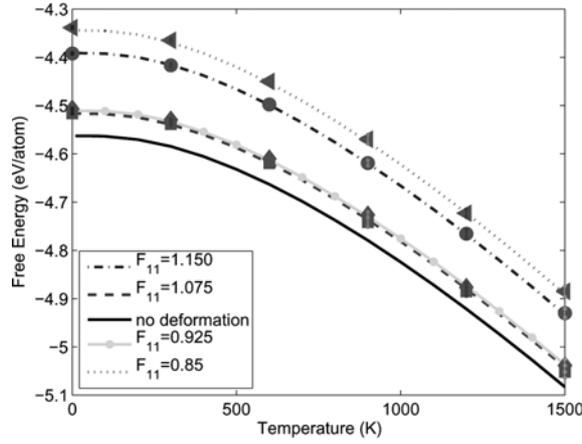


Fig. 5 Comparison of the Helmholtz free energy with temperature for tension  $F_{11} = 1.15$  (dash dot line, filled circle),  $F_{11} = 1.075$  (dash line, square) and compression  $F_{11} = 0.925$  (solid line with a small filled circle, diamond),  $F_{11} = 0.85$  (dot line, triangle) of a bulk silicon crystal. 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 calculations in this work. The error-bar from MD is within the symbol size

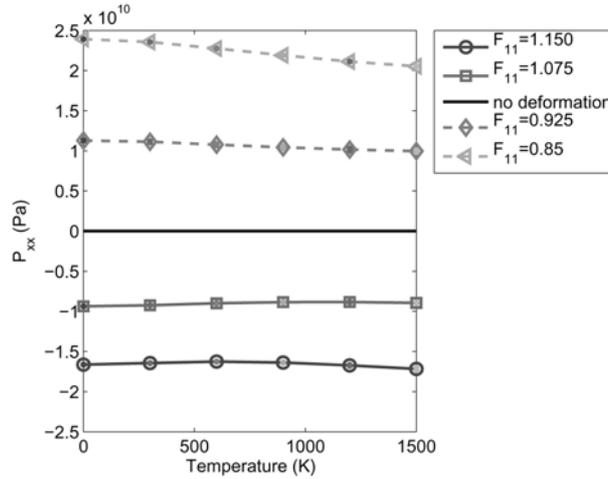


Fig. 6 Variation of pressure component  $P_{xx}$  with temperature for tension  $F_{11} = 1.15$  (circle solid line),  $F_{11} = 1.075$  (square solid line) and compression  $F_{11} = 0.925$  (diamond dash line),  $F_{11} = 0.85$  (triangle dash line). The error-bar is within the symbol size

The second type of strain we consider is shear. To subject the material under shear, the deformation gradient  $F_{12}$  is varied from 0.0, implying no shear deformation, to 0.075 and 0.15, which represent shear along the  $x$ -direction. Fig. 7 and Fig. 8 show the variation of the internal energy and Helmholtz free energy with temperature when the crystal is under shear deformation. The results from QHMK method are also shown for comparison. We again note that the results from MD match quite well with the results from QHMK method. Fig. 9 shows the variation of pressure component  $P_{xy}$  with temperature when the crystal is under shear deformation. We note that  $P_{xy}$  decreases with the increase in temperature, implying that shear modulus of the material

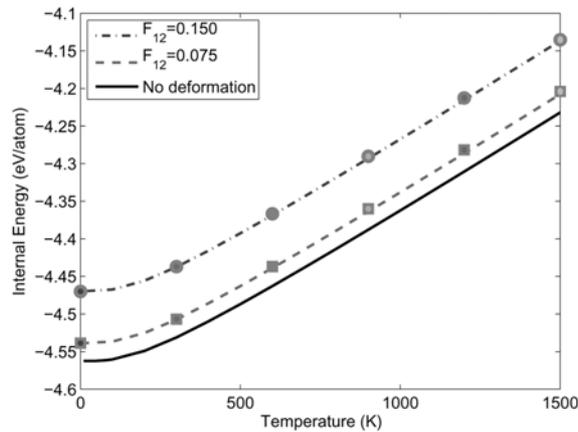


Fig. 7 Comparison of the internal energy with temperature for shear  $F_{12} = 0.15$  (dash dot line, circle) and  $F_{12} = 0.075$  (dash line, square). The thick solid line is the internal energy of bulk silicon without deformation. All the lines are from QHMK calculations. All the symbols are from MD calculations in this work. The error-bar from MD is within the symbol size

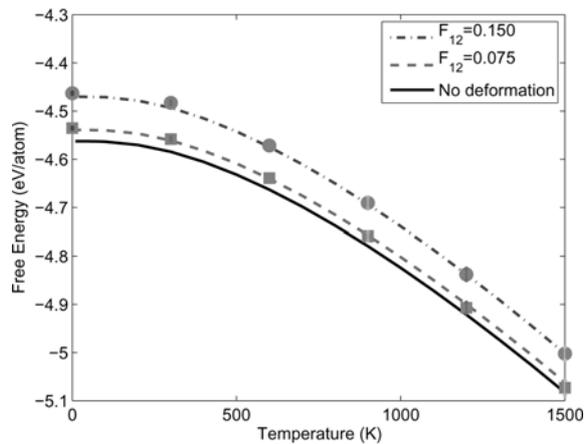


Fig. 8 Comparison of the Helmholtz free energy with temperature for shear  $F_{12} = 0.15$  (dash dot line, circle) and  $F_{12} = 0.075$  (dash line, square). The thick solid line is the Helmholtz free energy of bulk silicon without deformation. All the lines are from QHMK calculations. All the symbols are from MD calculations in this work. The error-bar from MD is within the symbol size

decreases with the increase in temperature. These observations are again consistent with those reported in Tang *et al.* (2006).

## 5. 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

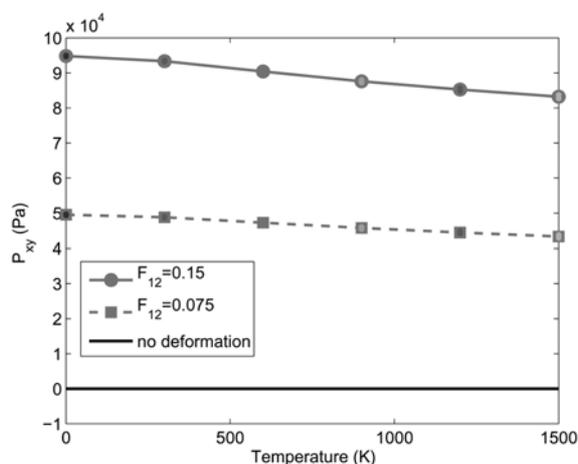


Fig. 9 Variation of pressure component  $P_{xy}$  with temperature under different shear  $F_{12} = 0.15$  (solid line with filled circle) and  $F_{12} = 0.075$  (dash line with square). The error-bar is within the symbol size

temperature rescaling method to account for quantum corrections in classical MD simulations and we observed that it may not be accurate for Helmholtz free 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 and the anharmonicity contribution is not significant on the thermodynamical properties of bulk silicon at high temperature. Finally, using MD we also computed the variation of different pressure components with temperature and strain and discussed how this can effect the mechanical properties.

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