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A semi-local quasi-harmonic model to compute the thermodynamic and mechanical properties of silicon nanostructures

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Abstract

This paper presents a semi-local quasi-harmonic model with local phonon density of states (LPDOS) to compute the thermodynamic and mechanical properties of silicon nanostructures at finite temperature. In contrast to an earlier approach (Tang and Aluru 2006 *Phys. Rev. B* **74** 235441), where a quasi-harmonic model with LPDOS computed by a Green's function technique (QHMG) was developed considering many layers of atoms, the semi-local approach considers only two layers of atoms to compute the LPDOS. We show that the semi-local approach combines the accuracy of the QHMG approach and the computational efficiency of the local quasi-harmonic model. We present results for several silicon nanostructures to address the accuracy and efficiency of the semi-local approach.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The calculation of thermodynamic and mechanical properties of nanostructures is important for developing physical theories and computational design tools for applications in nanoelectromechanical systems (NEMS) [1]. Generally, the most accurate approach for predicting the material properties is the first-principles quantum-mechanical method, where *ab initio* local density functional techniques have been used to determine the thermodynamic properties of silicon [2] and other materials [3]. However, due to the complexity of these methods and the need for large computational resources, these techniques are limited to very small systems. Empirical and semi-empirical interatomic potentials [4–6] have been developed to provide a simple and a reasonably accurate description of materials. The various parameters in these potentials are determined from experiments or from *ab initio* calculations. Molecular dynamics (MD) and Monte Carlo (MC) simulations are two popular methods based

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on interatomic potentials [7, 8]. Despite their popularity, their computational cost is still an inherent drawback.

Another class of methods relies on the theory of quantum-mechanical lattice dynamics, where the key step is the quasi-harmonic approximation (QHM method) of the interatomic potential [9, 10]. For a system of N atoms with a given interatomic potential, the Helmholtz free energy and other thermodynamic properties can be computed by diagonalizing the $3N \times 3N$ force constant matrix [10]. When the system contains thousands of atoms, directly solving the $3N \times 3N$ eigenvalue problem can be quite expensive. Several other methods have been proposed based on the QHM method. For a perfect crystal lattice, due to the periodicity of the atomic structure, it is more efficient to compute the relevant quantities in the reciprocal space (QHMK method) [10], e.g., we only need to solve several 6×6 eigenvalue problems for crystalline silicon. The QHMK method can accurately predict the bulk properties of silicon, but due to the assumption of periodicity this method cannot directly be used to compute properties of confined nanostructures (nanostructures with a finite number of unit cells in one or more directions). LeSar *et al* [11] proposed a local quasi-harmonic approximation (LQHM method) to reduce the $3N \times 3N$ eigenvalue problem for a system of N atoms to $N \times 3 \times 3$ eigenvalue problems, by assuming that the vibration of each atom in the system is independent of other atoms. The LQHM model is fast and simple, but the accuracy of the approach can be questionable [7, 12, 13]. By using the local phonon density of states (LPDOS) technique with on-site phonon Green's function [14] (QHMG method [15]), the thermodynamic and mechanical properties can be calculated without directly solving eigenvalue problems. The QHMG method is an accurate approach to compute the thermodynamic and mechanical properties of bulk and confined silicon structures. However, the computational cost of the QHMG approach can still be a drawback for practical NEMS applications. In this paper, we propose a semi-local QHMG method which computes the local phonon density of states, and subsequently the thermodynamic and mechanical properties, by considering only two layers of atoms around the atom of interest. We will show that the semi-local QHMG approach—to a large extent—combines the accuracy of the QHMG approach and the computational efficiency of the LQHM approach.

The rest of the paper is organized as follows: section 2 summarizes the basic concepts in the theory of lattice dynamics and the QHMG method before discussing the theoretical and implementation aspects of the semi-local QHMG method. Section 3 presents results on the calculation of thermodynamic and mechanical properties of silicon nanostructures using the semi-local QHMG method. A comparison of the semi-local QHMG method with other methods in terms of accuracy and computational efficiency is also presented. Finally, conclusions are given in section 4.

2. Theory

2.1. Lattice dynamics

The lattice dynamics theory [10] is commonly used to compute the thermodynamic properties of crystals with a quasi-harmonic approximation. For an N -atom system, the total potential energy is first expanded in the atomic displacements by using the Taylor's series expansion. In the quasi-harmonic approximation, the higher-order (>2) terms are neglected and the total potential energy can thus be rewritten as

$$U(\mathbf{x}_1, \dots, \mathbf{x}_N) = U(\mathbf{x}_1^0, \dots, \mathbf{x}_N^0) + \frac{1}{2} \sum_{\alpha, \beta=1}^N \sum_{j, k=1}^3 \frac{\partial^2 U(\mathbf{x}_1, \dots, \mathbf{x}_N)}{\partial \mathbf{x}_{\alpha j} \partial \mathbf{x}_{\beta k}} \Big|_{\mathbf{x}_1, \dots, \mathbf{x}_N = \mathbf{x}_1^0, \dots, \mathbf{x}_N^0} \mathbf{v}_{\alpha j} \mathbf{v}_{\beta k}, \quad (1)$$

where U is the total potential energy of the system, \mathbf{x}_α and \mathbf{x}_α^0 , $\alpha = 1, 2, \dots, N$, are the instantaneous position vector and the equilibrium position vector of atom α , respectively, $\mathbf{x}_{\alpha j}$ and $\mathbf{x}_{\beta k}$ are the components of the position vectors \mathbf{x}_α and \mathbf{x}_β along the j th and k th directions, respectively, $\mathbf{v}_\alpha = \mathbf{x}_\alpha - \mathbf{x}_\alpha^0$ is the displacement vector of atom α due to the thermal vibration, and $\mathbf{v}_{\alpha j}$ and $\mathbf{v}_{\beta k}$ are the components of the displacement vectors \mathbf{v}_α and \mathbf{v}_β along the j th and k th directions, respectively. By denoting $\mathbf{x} = (\mathbf{x}_1, \dots, \mathbf{x}_N)$, $\mathbf{x}^0 = (\mathbf{x}_1^0, \dots, \mathbf{x}_N^0)$, and $\mathbf{v} = [\mathbf{v}_1, \dots, \mathbf{v}_N]^T$, equation (1) can be rewritten in a matrix form as

$$U(\mathbf{x}) = U(\mathbf{x}^0) + \frac{1}{2} \mathbf{v}^T \Phi \mathbf{v}, \quad (2)$$

where Φ is the $3N \times 3N$ force constant matrix given by

$$\Phi_{3\alpha+j-3, 3\beta+k-3} = \left. \frac{\partial^2 U(\mathbf{x})}{\partial \mathbf{x}_{\alpha j} \partial \mathbf{x}_{\beta k}} \right|_{\mathbf{x}=\mathbf{x}^0}, \quad \alpha, \beta = 1, \dots, N, \quad j, k = 1, 2, 3. \quad (3)$$

Note that in the quasi-harmonic approximation the force constant matrix is a function of temperature T , i.e. the equilibrium position \mathbf{x}^0 in equation (3) depends on the temperature ($\mathbf{x}^0 = \mathbf{x}^0(T)$) [12].

In the theory of lattice dynamics, the phonon frequencies can be calculated from the eigenvalues of the force constant matrix, i.e. $\omega_i = \sqrt{\lambda_i/m}$, $i = 1, \dots, 3N$, where ω_i is the i th phonon frequency, λ_i is the i th eigenvalue of Φ , and m is the atom mass. Once the phonon frequencies are known, the Helmholtz free energy A can be computed as [16]

$$A = U(\mathbf{x}^0) + k_B T \sum_{j=1}^{3N} \ln \left[2 \sinh \left(\frac{\hbar \omega_j}{2k_B T} \right) \right], \quad (4)$$

where k_B is the Boltzmann constant and \hbar is the reduced Planck's constant.

2.2. QHMG- n method

The Helmholtz free energy defined by equation (4) requires the calculation of all the eigenvalues of the force constant matrix, which can be very expensive. The Helmholtz free energy can also be calculated from the local thermodynamic properties of the system, which are defined by LPDOS [10, 17]. The Helmholtz free energy for an atom at position \mathbf{x}_α , defined by A_α , can be written as [18–20]

$$A_\alpha = U_\alpha + k_B T \int_0^{\omega_{\max}} \ln \left(2 \sinh \frac{\hbar \omega}{2k_B T} \right) n(\omega, \mathbf{x}_\alpha) d\omega, \quad (5)$$

where U_α is the static potential energy of atom α , ω_{\max} is the maximum phonon frequency, and $n(\omega, \mathbf{x}_\alpha)$ is the LPDOS at position \mathbf{x}_α . $n(\omega, \mathbf{x}_\alpha)$ can be calculated from the on-site phonon Green's function [21], i.e.

$$n(\omega, \mathbf{x}_\alpha) = 2m\omega \left(-\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} \sum_{j=1}^3 G_{\alpha j, \alpha j}(m\omega^2 + i\epsilon) \right), \quad (6)$$

where $\text{Im} \sum_{j=1}^3 G_{\alpha j, \alpha j}$ represents the imaginary part of the summation of the on-site phonon Green's functions for atom α . For a given atom α and direction index j , $G_{\alpha j, \alpha j}$ can be represented by a continued fraction expression [22],

$$G_{\alpha j, \alpha j}(Z) = \frac{1}{Z - a_1 - \frac{b_2^2}{Z - a_2 - \frac{b_3^2}{\ddots \frac{b_{3N}^2}{Z - a_{3N}}}}}, \quad (7)$$

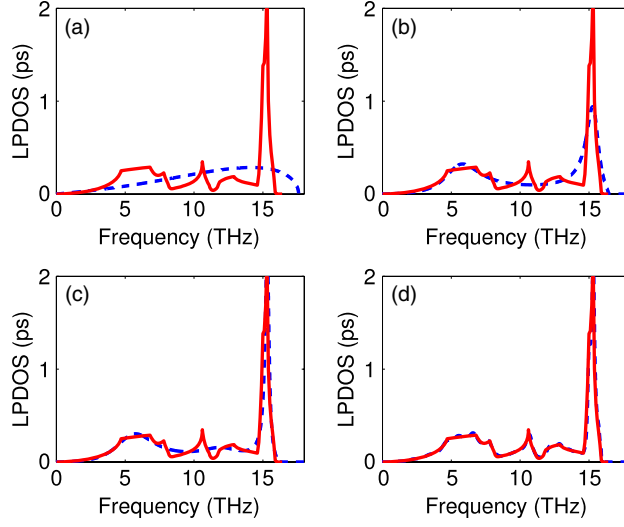


Figure 1. Comparison of LPDOS obtained with QHMG- n and QHMK methods: (a) QHMG-1, (b) QHMG-2, (c) QHMG-5, and (d) QHMG-20. The dashed lines are the LPDOS computed by QHMG- n method. The solid lines are the LPDOS obtained with the QHMK method. $T = 300$ K.

where $Z = m\omega^2 + i\epsilon$ and the coefficients a_l , $l = 1, 2, \dots, 3N$, and b_l , $l = 2, 3, \dots, 3N$, are obtained from the force constant matrix by the tridiagonalization technique [23]. In practice, only the first n levels of coefficients are calculated and the rest of the coefficients are approximated by their asymptotic values, a_∞ and b_∞ . A square root terminator function [14] is then defined to represent the remaining part of the continued fraction, which is given by

$$t(Z) = \frac{1}{b_\infty} \left[\frac{Z - a_\infty}{2b_\infty} - i \sqrt{1 - \left(\frac{Z - a_\infty}{2b_\infty} \right)^2} \right]. \quad (8)$$

Using the square root terminator, the on-site phonon Green's function for the j th direction of atom α can be rewritten as

$$G_{\alpha j, \alpha j}(Z) = \frac{1}{Z - a_1 - \frac{b_2^2}{Z - a_2 - \frac{b_3^2}{\ddots \frac{b_n^2}{Z - a_n - b_{n+1}^2 t(Z)}}}}. \quad (9)$$

In the QHMG- n method, as outlined above, for a given atom position \mathbf{x}_α and direction j , the first n levels of recursion coefficients are calculated. Then the on-site phonon Green's function is calculated by using equation (9). Finally, the Helmholtz free energy at position \mathbf{x}_α can be calculated by using equations (5) and (6). The accuracy of the Helmholtz free energy computed by the above approach depends on the number of recursion coefficients employed. The inclusion of more levels of recursion coefficients in the calculation of the on-site phonon Green's function leads to a more accurate calculation of the Helmholtz free energy. In an earlier paper [15], it was shown that $n = 20$ (i.e. QHMG-20) can typically provide accurate results for thermodynamic and mechanical properties of silicon nanostructures.

To understand the significance of the number of recursion levels on the calculation of LPDOS, consider the results shown in figure 1, where the QHMG- n method with $n = 1, 2, 5$

and 20 is compared with the QHMK method for bulk silicon. The QHMK method, which has been discussed in detail in [12, 13], has been shown to accurately capture the LPDOS of bulk silicon. When $n = 1$, the LPDOS obtained from QHMG-1 (see figure 1(a)) is very different from that computed by the QHMK method. As shown in figure 1(b), QHMG-2 performs better than QHMG-1, as it can capture the acoustic and the optical phonon peaks. The accuracy further increases with QHMG-5, as shown in figure 1(c). Even though QHMG-5 captures the lower and the higher frequency spectrum, it does not accurately capture the middle frequencies in the range of around 10 THz. When the number of levels is increased to 20, as shown in figure 1(d), the LPDOS obtained from QHMG-20 is very similar to the LPDOS computed by using the QHMK method.

The results presented above indicate that typically a value of at least $n = 20$ is needed to accurately compute the thermal and mechanical properties of silicon nanostructures. The implementation of QHMG-20 can, however, be quite expensive. For example, when $n = 1$, in order to compute the recursion coefficients a_1 and b_2 accurately for bulk silicon, we need to consider the nearest two layers of atoms around an atom. When $n = 2$, the nearest four layers of atoms need to be taken into account. Similarly, for $n = 20$, the nearest 40 layers of atoms need to be considered to accurately compute the first 20 levels of recursion coefficients. As the number of layers increases, the number of atoms that need to be considered increases rapidly and the size of the force constant matrix becomes very large and computationally intractable. As a result, for large n , QHMG- n can be expensive for the calculation of the thermal and mechanical properties of nanostructures.

2.3. Semi-local QHMG method

As discussed in section 2, QHMG- n with a large n (typically at least a value of $n = 20$) can be an accurate method to compute the spatial variation of thermal and mechanical properties of silicon nanostructures. However, QHMG- n with a large n can be quite expensive. As pointed out in section 1, other alternative methods also have limitations. For example, LQHM [11], which considers only the vibration of the atom of interest, is a local approach which is fast but the accuracy can be questionable [12, 13]. QHM, a global approach, considers the vibrations of all the atoms. This approach can accurately predict the spatial variation of thermal and mechanical properties but can be an expensive approach for a large number of atoms in the system. QHMK is a fast and an accurate approach for bulk systems but the extension of the approach to compute spatial variation of thermal and mechanical properties, especially under deformation, is not trivial. In this paper, we develop a semi-local QHMG method, which combines—to a large extent—the accuracy of the QHMG- n approach and the efficiency of the LQHM approach. The key features of the semi-local QHMG approach are that (i) it considers two layers of atoms around an atom (it includes more atoms compared to the LQHM method, but many fewer compared to the QHMG-20 approach—hence the name semi-local) and (ii) it computes the asymptotic recursion coefficients, a_∞ and b_∞ , from the force constant matrix obtained by the LQHM method instead of the average value of the first n levels of the recursion coefficients as was done in the QHMG- n approach.

To understand why two layers of atoms can be a reasonable approximation for nearby interactions, consider the calculation of the Helmholtz free energy as a function of the lattice constant for bulk Tersoff silicon at 300 K. Figure 2 shows the variation of the Helmholtz free energy with lattice constant by using different levels of recursion coefficients. Results from LQHM and QHMK are also shown in the figure for comparison. The filled square symbol on each curve represents the minimum Helmholtz free energy, and the corresponding value on the x -axis is the lattice constant. As the results in the figure indicate, QHMG-1 is in significant

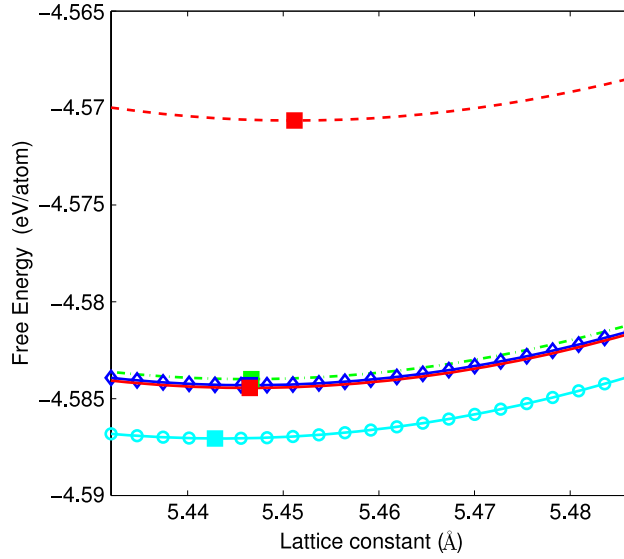


Figure 2. Variation of the Helmholtz free energy with lattice constant at 300 K. Comparison between LQHM (dashed line), QHMK (solid line) and QHMG- n (QHMG-1, solid line with circle symbol; QHMG-2, dash-dot line; QHMG-20, solid line with diamond symbol). The filled square symbol on each curve indicates the lattice constant corresponding to the minimum Helmholtz free energy.

error compared to the QHMK results, while QHMG-2 provides a good approximation to both the free energy and the lattice constant. QHMG-2, however, uses four layers of atoms around the atom of interest to accurately compute the first two levels of recursion coefficients. If we use only two layers of atoms, instead of four layers of atoms, the first two levels of recursion coefficients for various temperatures are shown in figure 3. The recursion coefficients a_1 , b_2 and a_2 obtained with two layers of atoms and four layers of atoms are identical. The recursion coefficient b_3 obtained with two layers of atoms deviates slightly when compared to its value obtained with four layers of atoms. This is due to the fact that the interactions with the atoms in the third and the fourth layers are neglected. Since the effect of the atoms in the third and the fourth layers is negligible on a_1 , b_2 and a_2 and small on b_3 , a semi-local approximation with two layers of atoms can be a reasonable approximation to determine the thermodynamic properties.

In the rest of this section, first we will present an efficient way to compute a_∞ and b_∞ using the semi-local approximation and then the moment method is introduced to calculate the first two levels of recursion coefficients by using the nearest two layers of atoms.

2.3.1. Calculation of a_∞ and b_∞ . a_∞ and b_∞ are the asymptotic values of the recursion coefficients a_n and b_n . For a large system (i.e. if N is large), a_∞ can be approximated by the trace of the tridiagonalized force constant matrix Φ^{TD} divided by $3N$ [24]. Since the transformation matrix \mathbf{L} used to compute Φ^{TD} , i.e. $\Phi^{\text{TD}} = \mathbf{L}^T \Phi \mathbf{L}$, is an orthonormal matrix [15], the trace of Φ is preserved, i.e. $\text{trace}(\Phi) = \text{trace}(\Phi^{\text{TD}})$. Thus, a_∞ can also be defined as $\text{trace}(\Phi)/3N$. Furthermore, by using the local quasi-harmonic approximation [11], without changing the trace of Φ , the force constant matrix Φ can be decomposed into N 3×3 matrices, $\Phi(\alpha)$, $\alpha = 1, 2, \dots, N$, by neglecting all the interactions between atoms. The local

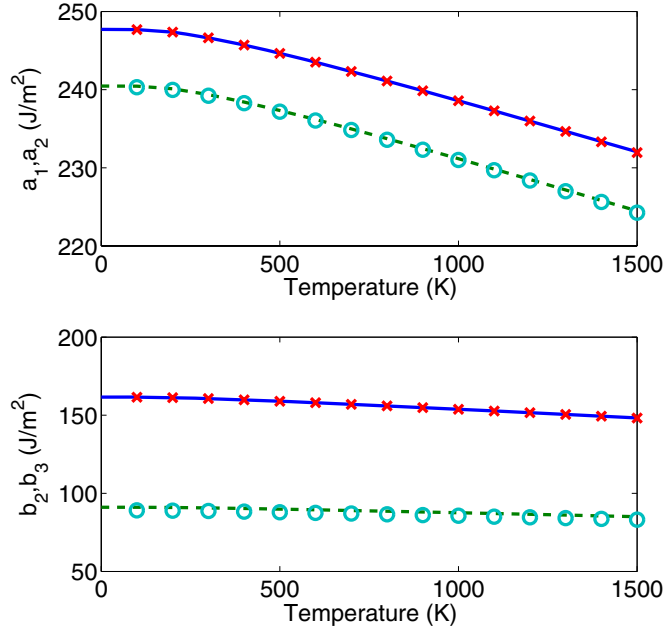


Figure 3. Comparison of the first two levels of recursion coefficients between QHMG-2 and the semi-local QHMG method. Computed by four layers of atoms, a_1 and a_2 are shown as the solid line and dashed line in the top part; b_2 and b_3 are shown as the solid line and dashed line in the bottom part. Computed by two layers of atoms, a_1 and a_2 are shown as the cross symbol and circle symbol in the top part; b_2 and b_3 are shown as the cross symbol and the circle symbol in the bottom part.

force constant matrix $\Phi(\alpha)$ is given by

$$\Phi_{j,k}(\alpha) = \left. \frac{\partial^2 U_{\text{local}}(\alpha)}{\partial \mathbf{x}_{\alpha j} \partial \mathbf{x}_{\alpha k}} \right|_{\mathbf{x}=\mathbf{x}^0}, \quad j, k = 1, 2, 3, \quad (10)$$

where $U_{\text{local}}(\alpha)$ is the local potential energy of atom α , which contains contributions from the first and second nearest neighbours. If the system is homogeneous, the local force constant matrix of each atom, $\Phi(\alpha)$, is identical. Thus, we have the relation

$$a_\infty \approx \frac{\text{trace}(\Phi^{\text{TD}})}{3N} = \frac{\text{trace}(\Phi)}{3N} = \frac{\sum_{\alpha=1}^N \text{trace}(\Phi(\alpha))}{3N} \approx \frac{\text{trace}(\Phi(\alpha))}{3}. \quad (11)$$

Furthermore, for a perfect silicon lattice structure, a_∞ and b_∞ are related by the expression [18, 25]

$$b_\infty = \frac{a_\infty}{2}. \quad (12)$$

Once a_∞ is obtained from equation (11), b_∞ is obtained by using equation (12).

2.3.2. Moment description and recursion coefficients. In the QHMG- n method, the force constant matrix is tridiagonalized by using the Lanczos algorithm to compute the recursion coefficients. An alternative, and a more flexible, approach to compute the recursion coefficients is by using the moments of the density of states. The moment approach has the advantage that it allows an interpretation of the recursion coefficients in terms of the atomic structure.

The r th moment of the phonon density of states $n(\omega)$, denoted as μ_r , is given by [10]

$$\mu_r = \int_{-\infty}^{\infty} (m\omega^2)^r n(\omega) d\omega = \sum_i \lambda_i^r = \text{trace}(\Phi^r) = \sum_{\alpha=1}^N \sum_{j=1}^3 \psi^T(\mathbf{x}_{\alpha j}) \Phi^r \psi(\mathbf{x}_{\alpha j}), \quad (13)$$

where λ_i is the eigenvalue of the force constant matrix Φ , $\psi(\mathbf{x}_{\alpha j}) = [\dots, 0, 1, 0, \dots]^T$ is the $3N \times 1$ orthogonal vector with the only nonzero entry being the $(3\alpha + j - 3)$ th position corresponding to atom α in the j th direction, and r is the order of the moment. The corresponding r th moment of LPDOS at atom position \mathbf{x}_{α} in the j -direction is given by

$$\mu_r(\mathbf{x}_{\alpha j}) = \psi^T(\mathbf{x}_{\alpha j}) \Phi^r \psi(\mathbf{x}_{\alpha j}) = \sum_{abc\dots k} \underbrace{\Phi_{la} \Phi_{ab} \Phi_{bc} \dots \Phi_{kl}}_r, \quad (14)$$

where $l = 3\alpha + j - 3$ and the last step follows from simple matrix multiplication. Since the matrix elements Φ_{ij} are zero except for the atoms with interactions, the only nonzero contributions to the above equation come from the ‘chains’ of atoms with interactions. These must be closed chains starting and finishing at atom α in the j -direction. Thus, $\mu_r(\mathbf{x}_{\alpha j})$ can be calculated by counting the number of such chains of length r [23]. For the force constant matrix obtained by using the Tersoff potential, the first moment represents a hop on a single atom, the second hops to the nearest two layers of neighbours and back, and so on. Based on these hopping properties, two more layers of atoms need to be considered when we increase the order of the moments by two.

The r th moment of LPDOS with an irreducible chain is a special case of equation (14). It is obtained by counting those which do not return to atom α in the j -direction at any intermediate step, i.e.

$$\bar{\mu}_r(\mathbf{x}_{\alpha j}) = \sum_{abc\dots k} \underbrace{\Phi_{la} \Phi_{ab} \Phi_{bc} \dots \Phi_{kl}}_r, \quad a, b, \dots, k \neq l. \quad (15)$$

The connection between moments and recursion coefficients can be seen by expressing the moments in terms of the recursion coefficients [14]. The relation between the moments with an irreducible chain and the recursion coefficients is as follows:

$$\begin{aligned} \bar{\mu}_0(\mathbf{x}_{\alpha j}) &= 1, \\ \bar{\mu}_1(\mathbf{x}_{\alpha j}) &= a_1, \\ \bar{\mu}_2(\mathbf{x}_{\alpha j}) &= b_2^2, \\ \bar{\mu}_3(\mathbf{x}_{\alpha j}) &= a_2 b_2^2, \\ \bar{\mu}_4(\mathbf{x}_{\alpha j}) &= a_2^2 b_2^2 + b_2^4 + b_2^2 b_3^2. \end{aligned} \quad (16)$$

As an example, for the 17-atom cluster centred at atom α , we have a 51×51 force constant matrix

$$\Phi = \begin{bmatrix} \mathbf{A} & \mathbf{B}^T \\ \mathbf{B} & \mathbf{D} \end{bmatrix}, \quad (17)$$

where $\mathbf{A} = \Phi_{1,1}$ is a scalar, \mathbf{B} is a 50×1 vector and \mathbf{D} is a 50×50 matrix. By using equation (17), for atom position \mathbf{x}_{α} in the x -direction ($j = 1$), the irreducible chain moments in equation (16) can be rewritten as

$$\begin{aligned} \bar{\mu}_0(\mathbf{x}_{\alpha 1}) &= 1, \\ \bar{\mu}_1(\mathbf{x}_{\alpha 1}) &= \mathbf{A}, \\ \bar{\mu}_2(\mathbf{x}_{\alpha 1}) &= \mathbf{B}^T \mathbf{B}, \\ \bar{\mu}_3(\mathbf{x}_{\alpha 1}) &= \mathbf{B}^T \mathbf{D} \mathbf{B}, \\ \bar{\mu}_4(\mathbf{x}_{\alpha 1}) &\simeq (\mathbf{B}^T \mathbf{B})^2 + \mathbf{B}^T \mathbf{D} \mathbf{D} \mathbf{B}. \end{aligned} \quad (18)$$

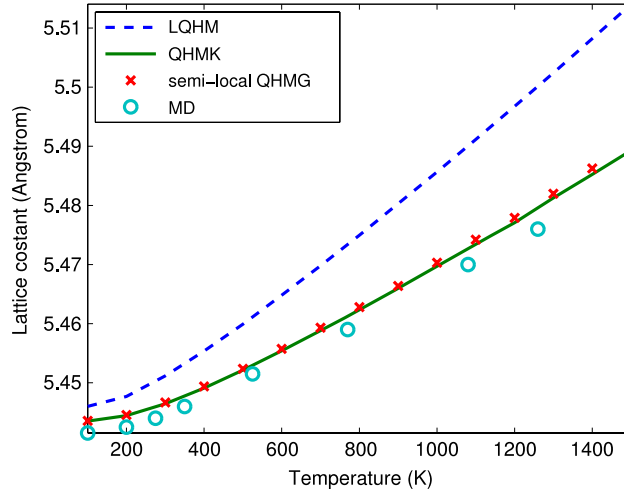


Figure 4. The lattice constant for Tersoff silicon at different temperatures. Results are from LQHM (dashed line), QHMK (solid line), semi-local QHMG (cross symbol) and MD simulations (circle symbol). The MD simulations are from [7].

By using equations (16) and (18), the first two levels of recursion coefficients can be computed. Since only the nearest two layers of neighbour atoms are considered in obtaining the force constant matrix Φ , the recursion constant b_3 has a small error as the interactions of the nearest two layers of neighbour atoms with the atoms in the third and fourth layers are neglected. But the recursion constants a_1 , b_2 and a_3 are accurate as shown in figure 3.

3. Results and discussion

3.1. Lattice constant

Lattice constant as a function of temperature is a fundamental property of materials. In the quasi-harmonic approximation, the Helmholtz free energy is a function of lattice constant $a(T)$, which is also a function of temperature T . The lattice constant $a(T)$ is obtained when the Helmholtz free energy is minimized with respect to $a(T)$, i.e.

$$\frac{\partial A}{\partial a} = 0. \quad (19)$$

We computed the zero pressure lattice constant $a(T)$ for bulk silicon at various temperatures by using the semi-local QHMG method as shown in figure 4. The results from the LQHM model, QHMK model and MD simulations are also plotted for comparison. The results from the semi-local QHMG model are in good agreement with the results obtained from the QHMK model.

Once the lattice constant a for a given temperature is computed, all the phonon structures can be easily obtained. Figure 5 shows the phonon density of states of bulk silicon at 300 K. We observe that by including the first two layers for short range interactions together with the long range interactions the results from the semi-local QHMG model capture the essential features of the LPDOS.

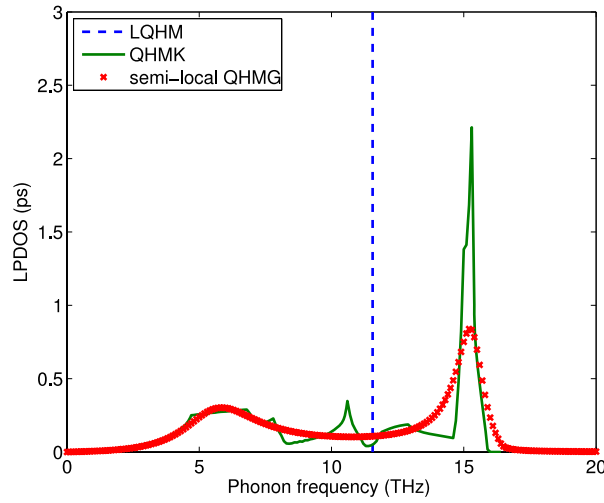


Figure 5. The LPDOS for bulk Tersoff silicon: comparison between the LQHM (dashed line), QHMK (solid line) and semi-local QHMG (cross symbol). $T = 300$ K.

Table 1. Comparison of different models at $T = 300$ K.

	LQHM	QHM	QHMK	QHMG-20	Semi-local QHMG
Space	Real	Real	Reciprocal	Real	Real
Model	Local	Nonlocal	Nonlocal	Nonlocal	Local
Vibration correlations	No	Yes	Yes	Yes	Yes
Dimension of the force constant matrix	3×3	$3N \times 3N$	6×6 for silicon	$3N \times 3N$	51×51 for Tersoff silicon
Lattice parameter (Å)	1.00353	1.00267	1.00267	1.00267	1.00270
Free energy (eV/atom)	-4.571	-4.580	-4.584	-4.584	-4.583
Internal energy (eV/atom)	-4.531	-4.531	-4.531	-4.531	-4.531
Entropy (J mol ⁻¹ K ⁻¹)	12.887	15.833	17.128	17.090	16.860
Heat capacity (J mol ⁻¹ K ⁻¹)	18.903	19.142	19.2308	19.201	19.148
C_{11} (Mbar)	1.373	1.377	1.372	1.372	1.372
C_{12} (Mbar)	0.726	0.733	0.732	0.732	0.731
C_{44} (Mbar)	0.667	0.664	0.662	0.662	0.660
CPU time (s)	0.01	$0.2(N = 64)$	0.1	4.97	0.03

3.2. Thermal and mechanical properties of bulk silicon

Once the Helmholtz free energy is known, other thermodynamic properties can be easily calculated. For example, the internal energy is given by $E = A - T(\partial A/\partial T)$, the entropy is given by $S = (E - A)/T$ and the heat capacity is given by $C_v = -T(\partial^2 A/\partial T^2)$. Similarly, the elastic constants characterizing the material behaviour can be computed by the second derivatives of the Helmholtz free energy density with respect to the Green–Lagrange strain (see [13] for details).

In addition to the calculation of the lattice constant, Helmholtz free energy and LPDOS as discussed above, we have also used the semi-local QHMG method to compute the internal energy, entropy, heat capacity and elastic constants (C_{11} , C_{12} and C_{44}) of bulk silicon at 300 K. These results are summarized in table 1. The predictions from other methods such as LQHM,

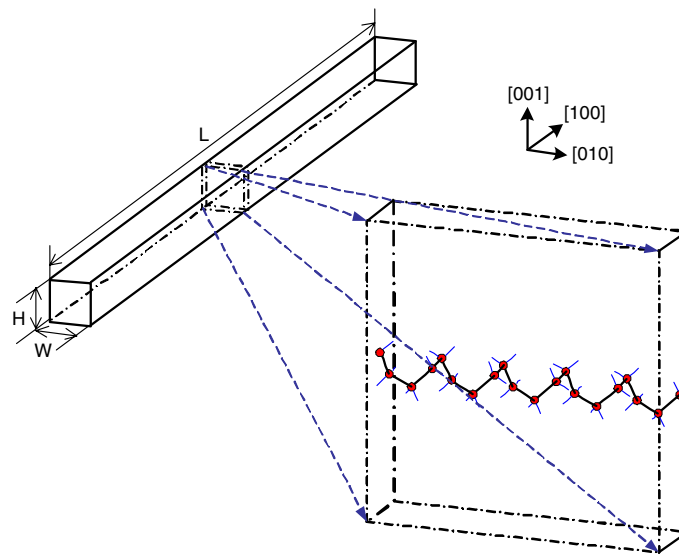


Figure 6. A silicon nanowire with $H = 2.58$ nm, $W = 2.58$ nm and $L = 54.3$ nm. The atoms of interest are shown in the figure.

QHM, QHMK and QHMG-20 are also shown in table 1 for comparison. The results from the semi-local QHMG model are in good agreement with the results obtained from QHM, QHMK and QHMG-20, while the results from LQHM can have significant error. For example, the relative error in entropy between LQHM and QHMK models is 24.7606%, but the relative error in entropy between semi-local QHMG and QHMK models is only 1.5647%. Table 1 also summarizes the computational cost of each method. The computational cost of the semi-local QHMG method is comparable to the computational cost of the LQHM method while QHM, QHMK and QHMG-20 are clearly more expensive. From the results presented here, it can be seen that the semi-local QHMG method achieves the computational efficiency of the LQHM method and the accuracy of the QHM, QHMK and QHMG-20 methods.

3.3. Surface effects of silicon nanostructures

For silicon nanostructures confined in one or more directions, the use of bulk thermal and mechanical properties is not accurate as these properties can vary spatially. In addition, surface effects can become important. For example, the silicon atoms on the surface can have a different configuration (e.g. hydrogen passivation, surface reconstruction etc) compared to bulk silicon atoms. Here we simply adopt a clean silicon surface to end the nanowire or the silicon cluster. To illustrate the spatial variation of the thermodynamic and mechanical properties, we consider the silicon nanowire presented in [15] which has a cross-section of $2.58 \text{ nm} \times 2.58 \text{ nm}$. The positions of the atoms of interest are also shown in figure 6. Note that for the nanowire with ideal surfaces the surface atoms have only two bonds.

Figure 7 shows the local thermodynamic properties (Helmholtz free energy, internal energy, entropy, heat capacity, vibrational energy and kinetic energy) as a function of atom positions obtained with LQHM, QHMG-20 and semi-local QHMG methods. We do not show results from the QHMK model as it cannot capture the spatial variation (see [15] for results obtained from the QHMK method). Both LQHM and semi-local QHMG models can capture the variation of the thermodynamic properties near the surface, but the results from the semi-

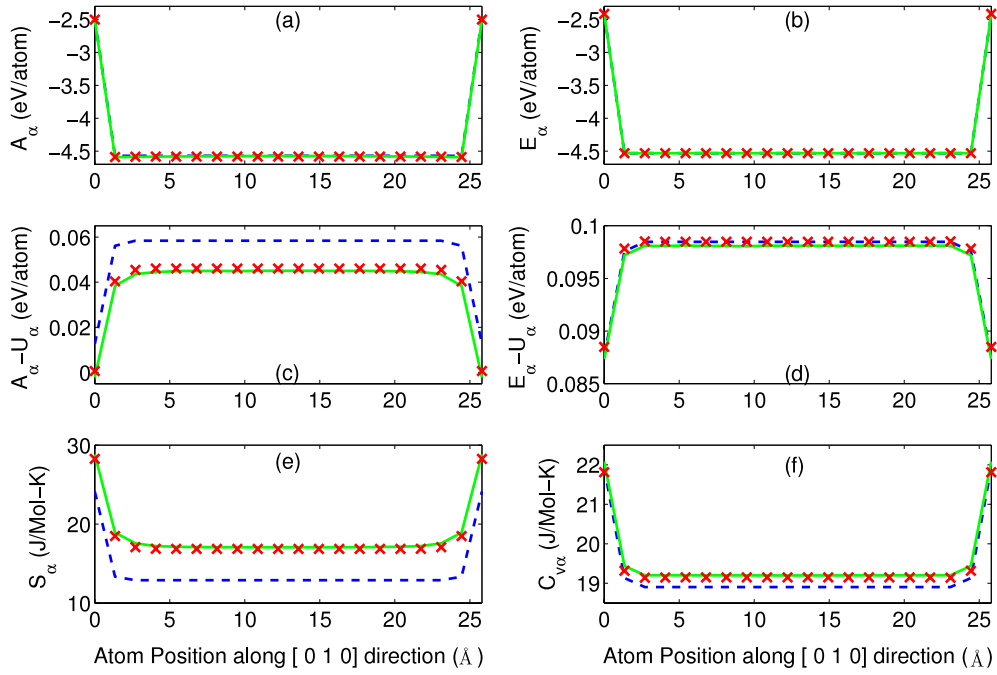


Figure 7. Variation of thermodynamic properties ((a) Helmholtz free energy, (b) internal energy, (c) vibrational energy, (d) kinetic energy, (e) entropy, (f) heat capacity) with different atom positions shown in figure 6. Results are from LQHM (dashed line), QHMG-20 (solid line) and semi-local QHMG (cross symbol). $T = 300$ K.

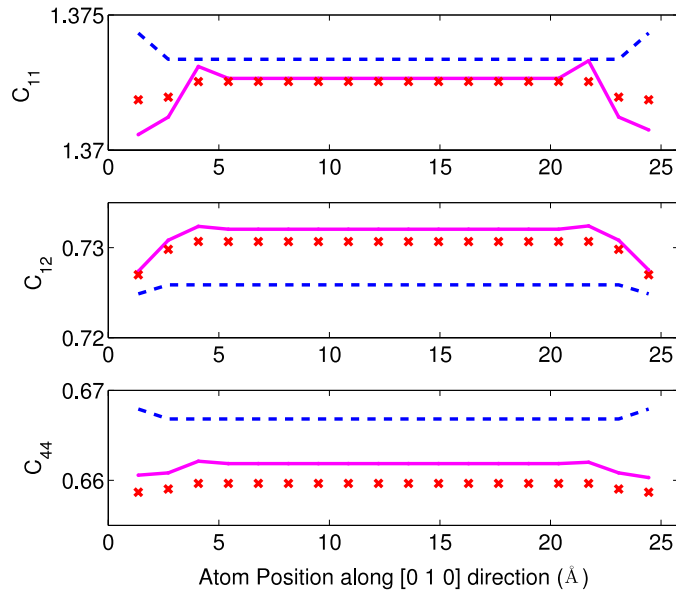


Figure 8. Variation of elastic constants (in Mbar) with different atom positions shown in figure 6. Results are from LQHM (dashed line), QHMG-20 (solid line) and semi-local QHMG (cross symbol). $T = 300$ K.

local QHMG model are closer to the QHMG-20 compared to the LQHM results. Figure 8 shows the spatial variation of the elastic constants computed using LQHM, semi-local QHMG and QHMG-20 methods. We again observe that the results obtained with the semi-local QHMG are closer to the QHMG-20 results while the results obtained with LQHM can have significant errors.

4. Conclusions

In this paper, we presented a semi-local QHMG method to compute the thermodynamic and mechanical properties of both bulk crystalline silicon and silicon nanostructures described by the Tersoff interatomic potential. In contrast to the QHMG- n method, which considers many layer of atoms, the semi-local QHMG method considers only two layers of atoms. We note that the LPDOS computed by the semi-local QHMG method captures the essential features of the LPDOS computed by the QHMG- n method even though the semi-local QHMG method uses only two layers of atoms. We have also shown that the semi-local QHMG method can approach the efficiency and simplicity of the local quasi-harmonic method, and at the same time predict the thermodynamic and mechanical properties of both bulk silicon and silicon nanostructures more accurately compared to the local quasi-harmonic method.

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