

Elastic constants of silicon using Monte Carlo simulations

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Elastic constants of a bulk silicon crystal are calculated using the Monte Carlo (MC) technique in conjunction with an isoenthalpic-isotension-isobaric ensemble (HtN ensemble) and the Stillinger-Weber (SW) potential or one of the Tersoff potentials. This MC method is the counterpart of the Parrinello-Rahman HtN molecular dynamics. We present HtN MC calculations of the adiabatic elastic constants of a crystalline silicon at three different temperatures, using an HtN ensemble fluctuation formula, and compare with the corresponding results from EhN ensemble molecular dynamics (MD) simulation. Calculation of the elastic constants of SW silicon using HtN MC simulation is a superior technique when compared to a corresponding HtN MD simulation that failed to produce accurate results. The calculation of the elastic constants using the HtN ensemble is, in general, slower in convergence than the corresponding calculation using the EhN ensemble. It is still a useful technique for the calculation of elastic constants, because it does not require any knowledge of the derivatives of the potential, which could be nontrivial for potentials with terms beyond two body. In order to investigate the convergence of another potential, elastic constants of the latest silicon Tersoff potential were calculated at a nonzero temperature. The zero-temperature elastic constants of Si SW and Si Tersoff potentials were also calculated using a direct method and extrapolation of HtN MC results to zero temperature. [S0163-1829(98)01334-4]

I. INTRODUCTION

An efficient way of calculating elastic constants is important, because these constants are directly employed in practical uses of materials. Calculation of the elastic constants at given temperatures can also serve as a measure of the reliability of the interatomic potential at those temperatures. This is generally true, since often potentials are fit to the extrapolation of experimental data at zero temperature.

There are several ways of calculating elastic constants. The direct or traditional method is to apply a tension on the sample and calculate the corresponding strain and elastic constants from the tension-strain relationship.^{1,2} The traditional method is inconvenient, because for the calculations of all elastic constants several tensions need to be applied at several times. Elastic constants can also be calculated using EhN molecular dynamics (MD) or Monte Carlo (MC) simulations.^{1,3} In the EhN MD or MC method, elastic constants are directly related to the microscopic stress tensor and first and second derivatives of the potential.^{1,3} Although EhN MD or MC calculations of the elastic constants are very accurate and converge rather quickly, they are often not used because they require derivatives of the potential. The derivatives of a potential can be nontrivial for potentials that have terms beyond pair interactions. Formulas for the elastic constants in the EhN ensemble have been developed for the Stillinger-Weber¹ and the embedded atom method (EAM) (Ref. 3) potentials. The zero-temperature limit of the EhN elastic constants was also calculated and applied to the

Stillinger-Weber silicon (SW Si) potential.^{1,4} Finally, elastic constants can be calculated using HtN MD or MC simulation.^{1,2} There are several fluctuation formulas for the calculations of elastic constants and other thermodynamics quantities in the HtN ensemble.^{1,2,5,6} The elastic constants of Lennard-Jones (LJ) solids were calculated using the fluctuation formulas in the HtN ensemble. The elastic constant values calculated from the HtN MD method are, in general, less accurate and converge much slower than the corresponding values from the EhN MD method.¹ For some potentials, one may obtain reasonable results using the HtN MD method,^{7,8} but it would be expected that the results would be more accurate and efficient using the HtN MC method.⁹ However, there is evidence to believe that the relative convergence of the elastic constants using EhN or HtN depends on the interatomic potential, as well as the simulation technique used in the calculation.^{1,2,9} In fact, convergence of the elastic constants of a LJ solid using the HtN MD method was only marginally satisfactory² and was unsatisfactory when applied to the SW solid.¹⁰ On the other hand, it was shown by Fay and Ray⁹ that the HtN MC calculation of the elastic constants of a LJ solid converges much faster than the corresponding HtN MD results. In the HtN ensemble, the elastic constants are related to the strain-strain fluctuation, while in the EhN ensemble they are directly related to the first and second derivatives of the potential. For complicated many-body potentials,^{11,12} calculation of the derivatives could be nontrivial¹ and the Parrinello-Rahman fluctuation formula for the calculation of elastic constants could be very useful

for such cases. Note that the fluctuation calculation of elastic constants presented here includes all the anharmonic effects. Other approximate methods such as quasiharmonic lattice dynamics¹³ can sometimes provide similar results.

Comparison of the results of zero-temperature elastic constants using various methods to be described in this paper, as well as analytical values of the SW silicon elastic constants, can serve as a measure of the accuracy of the models.

The main objective of doing this work is to extend the application of the elastic constants using the HtN MC method to more complicated systems. To follow this objective, we have studied the convergence of the elastic constants of the SW Si potential,¹¹ as well as one of the Tersoff silicon potentials¹² (T2 Si) using the HtN MC simulations, and we compare the corresponding results for the SW Si case with the ones from the EhN MD case and experiment. Furthermore, the elastic constants of the SW Si and T2 Si potentials at zero temperature are calculated using various methods. In Sec. II, we describe highlights of the theory. In Sec. III, we present the simulation results. In Sec. IV, we summarize and present conclusions.

II. OUTLINE OF THE THEORY

In this section, we describe briefly the interatomic potentials employed in this study and summarize highlights of the HtN molecular dynamics and Monte Carlo simulations.

In this study, we employed Stillinger-Weber¹¹ and Tersoff¹² potentials of silicon. The SW potential is a sum of two- and three-body terms. The two-body term is a spherically symmetric function, while the three-body term is angle dependent. Parameters of the SW potential were determined by fitting to the zero-temperature experimental values of the lattice constant and cohesive energy, with the constraint that the melting point and liquid structure of silicon be calculated correctly. The Tersoff potentials are the sum of repulsive and attractive interactions. The repulsive part of the potential is a decreasing exponential pair term, and the attractive part of the potential depends on the local environment through a many-body angle-dependent term. Two different parametrizations of the silicon potential were developed by Tersoff. These potentials are referred to in this publication as Tersoff silicon potential 1 (T1 Si) and silicon Tersoff potential 2 (T2 Si). The T2 Si potential, which is an improvement over the T1 Si potential, was used in this study. The T1 Si potential of silicon suffered from two problems. First, it predicted the bcc structure to be the lowest-energy structure, rather than diamond. The second problem was that the elastic constants predicted by the potential were, in general, too different than those of the experimental values. In fact, the C_{44} value predicted by the potential was about a factor of 8 smaller than the corresponding experimental value. The parameters of the T1 Si potential were obtained by fitting to a database including the lattice constant, cohesive energy, and bulk modulus. The parameters of the T2 Si potential were obtained by fitting to a database similar to the one used for the T1 Si potential, except that a constraint was imposed to produce the three independent elastic constants to within 20%.¹²

In the Parrinello-Rahman form of molecular dynamics,^{14,15} the computational box is described by a 3×3 matrix h whose three columns are three vectors repre-

senting the edges of the box. The equation of motion describing the box has the following form:

$$W\ddot{h} = (P - P_{\text{ex}})A - h\Gamma, \quad (1)$$

where W is the mass associated with the box coordinates, P is the microscopic stress tensor, P_{ex} is the external pressure, $A = V\tilde{h}^{-1}$ is the area tensor, \tilde{h}^{-1} is the inverse of the transpose of matrix h , and Γ is related to the tension applied to the system. W in Eq. (1) couples the box variables h and the particle variables in the extended variable method of Andersen.¹⁶ The equations of motion describing the particles have the form

$$m_a\ddot{s}_{ai} = h_{ij}^{-1}F_{aj} - m_a(G^{-1}\dot{G}\dot{s}_a)_i, \quad (2)$$

where m_a is the mass of particle a , s_{ai} is the i th component of the scaled coordinate of particle a , one overdot represents the first time derivative of that quantity, and two overdots represent the second time derivative of that quantity, h_{ij}^{-1} is the ij component of the inverse h matrix, F_{aj} is the j th component of force on atom a , $G = h\tilde{h}$ is the metric tensor where the tilde means matrix transpose, and the real coordinate of an atom is related to its scaled coordinate by $r = hs$ or $s = h^{-1}r$. In the HtN ensemble, the enthalpy of the system is defined as

$$H = K + U + P_{\text{ex}}V + V_0\text{tr}(t\varepsilon), \quad (3)$$

where K is the kinetic energy, U is the potential energy, V_0 is the reference volume, t is the tension tensor, ε is the strain tensor, and ‘‘tr’’ denotes trace of a matrix. The enthalpy is conserved during an HtN simulation. It should be mentioned that in Eq. (3), K is the total kinetic energy of the box and particles inside the box. There are $3N$ degrees of freedom in the formula for the kinetic energy of the particles and nine degrees of freedom in the formula for the kinetic energy of the box. However, for a system of several hundred particles, one may neglect the kinetic energy of the box with a negligible error of the order $3/N$. Solutions of Eqs. (1) and (2) provide instantaneous values of h and s_{ai} , $a = 1, N$ and $i = 1, 3$, at successive time steps. The phase space configurations generated by the HtN MD simulation govern the deterministic evolution of system.

On the other hand, configurations generated by the HtN MC simulation are probabilistic in nature and are generated by the Metropolis Monte Carlo procedure.¹⁷ The h matrix and particle variables are disturbed by the following transformations:

$$h'_{ij} = h_{ij} + \Delta h(2R - 1), \quad (4a)$$

$$s'_{ai} = s_{ai} + \Delta s(2R - 1), \quad (4b)$$

where the primes represent the disturbed coordinates (new), h_{ij} is the ij th element of the h matrix, s_{ai} is the i th component of the a th particle scaled coordinate, Δh is the amplitude of the disturbance of the h matrix, Δs is the amplitude of the disturbance of particles, and R is a random number between 0 and 1. It is important to mention that Δh and Δs control the acceptance of h and s moves. In particular, if Δh is zero, all the h moves are accepted. On the other hand, all the h moves are rejected when Δh is very large. In the simu-

lations we have done here, we have adjusted Δh and Δs so that there is an approximately 50% acceptance in h and s . The HtN transition probability functions developed by Ray¹⁸ have the following forms for the s and h moves:

$$\frac{P(r'_N, h)}{P(r_N, h)} = \frac{[H - P_{\text{ex}}V' - U(r'_N)]^{(3N/2-1)}}{[H - P_{\text{ex}}V - U(r_N)]^{(3N/2-1)}}, \quad (5a)$$

$$\frac{P(r'_N, h')}{P(r_N, h)} = \left(\frac{V'}{V}\right)^N \frac{[H - P_{\text{ex}}V' - U(r'_N)]^{(3N/2-1)}}{[H - P_{\text{ex}}V - U(r_N)]^{(3N/2-1)}}, \quad (5b)$$

where H is the constant enthalpy of the system, P_{ex} is the external pressure, N is the total number of particles, and $U(r_N)$ and $U(r'_N)$ are the total potential energies of the system in the old and new configurations. It is important to notice that the h move not only changes h , but also the real coordinates of the atoms r through $r=hs$. The other point that is worth mentioning is that moving all particles at one time can be implemented by the same transition probability as in Eq. (5a), except that all the scaled coordinates of the atoms are disturbed at the same time that h is disturbed. Configurational moves $r_N \rightarrow r'_N$ and box moves $h \rightarrow h'$ are accepted based on the Metropolis algorithm. In the Metropolis algorithm, a move is accepted if the transition probability of that move is greater than or equal to 1. If the transition probability is less than 1, then a random number is generated between 0 and 1. If the transition probability is greater than that random number, the move is accepted. Otherwise, it is rejected and the old configuration is retained again. From Eqs. (5a) and (5b), one can also note that moves that lower the potential energy are accepted and the system, in principle, should evolve into equilibrium after a long time. One obvious advantage of the HtN MC over the HtN MD method is that the fictitious mass W is no longer involved.

In MC or MD simulations, various thermodynamics quantities are related to the average values of other quantities when the system has reached equilibrium. Several fluctuation formulas have been developed in the HtN ensemble. In particular, Parrinello and Rahman (PR) developed a formula (5) in the HtN ensemble that relates the average of the strain-strain fluctuations to the elastic constants of the system:

$$\langle \varepsilon_{ij} \varepsilon_{km} \rangle - \langle \varepsilon_{ij} \rangle \langle \varepsilon_{km} \rangle = S_{ijkl} k_B T / V_0, \quad (6)$$

where $\varepsilon = \frac{1}{2}(\tilde{h}_0^{-1} G h_0^{-1} - 1)$ is the strain, h_0 is the reference state for zero strain, \tilde{h}_0^{-1} is the inverse of the transpose of matrix h_0 , S_{ijkl} is the adiabatic compliance matrix, T is the temperature, and V_0 is the reference volume, $V_0 = \det(h_0)$. The adiabatic elastic constant matrix C is the inverse of the compliance matrix S . Using the Voigt notation, $11 \rightarrow 1$, $22 \rightarrow 2$, $33 \rightarrow 3$, $23 \rightarrow 4$, $13 \rightarrow 5$, and $12 \rightarrow 6$, and the prescription described in Ref. 19, S_{ijkl} , can be converted into an equivalent 6×6 S_{mn} matrix:

$$\begin{aligned} S_{ijkl} &= \frac{1}{3} S_{mn} \quad \text{when } m \leq 3 \text{ and } n \leq 3, \\ S_{ijkl} &= \frac{1}{2} S_{mn} \\ &\quad \text{when } m > 3 \text{ and } n \leq 3 \text{ or } m \leq 3 \text{ and } n > 3, \\ S_{ijkl} &= \frac{1}{4} S_{mn} \quad \text{when } m > 3 \text{ and } n > 3. \end{aligned} \quad (7)$$

The reason for multiplying S_{ijkl} by 1/2 and 1/4 is to keep the tension-strain relationship in a compact form $\varepsilon_i = S_{ij} t_j$ without the presence of factors of 1/2 and 1/4. Other fluctuation formulas have been developed in the HtN ensemble for the calculation of adiabatic compressibility, constant tension specific heat, constant strain specific heat, and constant tension linear coefficient of thermal expansion.^{5,6}

The elastic constants of silicon can also be calculated at 0 K using the HtN ensemble and molecular statics. We referred to this approach as the direct method in the Introduction. In this method, one applies a constant tension and the corresponding strain is obtained using molecular statics. The elastic constants can then be calculated from the compliance matrix elements and the tension-strain relationship. In particular, a constant tension is applied along the $11 \rightarrow 1$ direction, and the resulting strains ε_1 and ε_2 are determined from the molecular statics calculations. Similarly, all the off-diagonal elements of the external tension matrix are made equal and all the main diagonal elements are made equal to zero. From the strain-tension relationships $\varepsilon_1 = S_{11} t_1$, $\varepsilon_2 = S_{12} t_1$, and $\varepsilon_6 = S_{44} t_6$, one can calculate S_{11} , S_{12} , and S_{44} . The elastic constants are then calculated from the following relationships:¹

$$C_{11} = (S_{11} + S_{12}) / [(S_{11} - S_{12})(S_{11} + 2S_{12})], \quad (8a)$$

$$C_{12} = -S_{12} / [(S_{11} - S_{12})(S_{11} + 2S_{12})], \quad (8b)$$

$$C_{44} = 1/S_{44}. \quad (8c)$$

The 0 K elastic constants can also be calculated in the EhN ensemble using either the direct method or a relationship between the elastic constants and the first and second derivatives of the potential.³ In the direct method, one simply applies two different strains ε_1 and ε_2 at two different times, and the resulting tensions are determined from molecular statics calculations. The elastic constants are then calculated directly from the tension-strain relationships $t_1 = C_{11} \varepsilon_1$, $t_2 = C_{12} \varepsilon_1$, and $t_6 = C_{44} \varepsilon_6$. The elastic constants can also be calculated in the EhN ensemble using the energy method. Here we summarize the energy method: (a) The unstrained lattice is relaxed using the EhN molecular statics to calculate E_0 , (b) the strained lattice is relaxed using the EhN molecular statics to calculate E_{0s} , and (c) the elastic constants are then calculated using the relationships²⁰

$$\begin{aligned} U &= \frac{1}{2} C_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + \frac{1}{2} C_{44} (\varepsilon_{12} + \varepsilon_{13} + \varepsilon_{23}) \\ &\quad + C_{12} (\varepsilon_{11} \varepsilon_{22} + \varepsilon_{11} \varepsilon_{33} + \varepsilon_{22} \varepsilon_{33}), \end{aligned} \quad (9a)$$

$$C_{11} = 2U / \varepsilon_{11}, \quad C_{12} = U / (\varepsilon_{11} \varepsilon_{22}), \quad C_{44} = 2U / \varepsilon_{12}, \quad (9b)$$

$$U = (E_{0s} - E_0) / V, \quad (9c)$$

where U is the elastic energy density and V is the conserved volume of the computational box. Finally, the elastic constants of silicon at zero temperature can be determined either by a direct relationship to the first and second derivatives of the potential³ (in the EhN ensemble) or by extrapolation of nonzero-temperature HtN or EhN results.¹ It should be noted that the calculation of elastic constants using the direct

method requires that the tension-strain relationship be linear. Therefore, caution must be taken in applying an appropriate level of strain or tension on the sample. Too large of a tension or strain can make the relationship between the two nonlinear. On the other hand, too small of a tension or strain may not be enough to differentiate from their reference values.

III. HTN ENSEMBLE SIMULATION RESULTS

We employed the Stillinger-Weber silicon potential. The main reasons for adopting this potential are that the HtN MD calculation of the elastic constants of this potential failed to produce satisfactory convergence and that some EhN MD results for the elastic constants are available.¹

We have performed HtN MC simulations of the elastic constants of crystalline Stillinger-Weber silicon using a lattice of 216 silicon atoms in the diamond structure. The simulations were carried out at the same three temperatures that EhN MD results are available. Periodic boundary conditions are employed in all three directions, and units of energy, length, and elastic constants are eV, Å, and eV/Å³. We present our results of the elastic constants at the three temperatures 888, 1164, and 1477 K with zero pressure. In the HtN MC results presented here, two kinds of trial moves are considered, particles and cell. During each MC step, all particles are moved sequentially one particle at a time, and the h matrix representing the box is moved once. We also tried moving all particles at one time and obtained a similar convergence for the SW Si. The particle move is tried $3N$ times on all particles degrees of freedom of the N -particle system. The cell move is tried on nine elements of the 3×3 h matrix, and only the symmetric part of this move is considered. The antisymmetric part is related to the rotation of the cell and produces no energy change, and the move is always accepted. An alternate way to eliminate the rotation of the box is to make the h matrix symmetric. Both methods of eliminating the box rotations produced results with nonconspicuous differences. The temperature of the system is controlled by the enthalpy H . We first performed several HPN MC runs to equilibrate the system at the three temperatures 888, 1164, and 1477 K. The corresponding total enthalpies for these temperatures are -885.6 , -870.0 , and -851.0 eV, respectively. Using the three enthalpies obtained from the HPN MC runs, we performed several HtN MC runs with zero external pressure and tension to calculate the reference value of h , i.e., h_0 , for the three temperatures. In particular, at each enthalpy, we ran the simulation for about 100 000 MC steps, which also serves to equilibrate the system. In the next run of 100 000 MC steps, we determined the average value of h (h_0). The h_0 for each temperature is then used in conjunction with Eq. (6) and a subsequent HtN MC run of 100 000 MC steps to calculate the elastic constants at that temperature. Our results for the elastic constants using HtN MC along with the EhN MD results of Ref. 1 and the experimental data²¹ are reported in Table I. We estimated the error following a prescription employed by Fay and Ray.⁹ For a cubic crystal, there are three independent elastic constants C_{11} , C_{12} , and C_{44} . By symmetry, C_{11} , C_{22} , and C_{33} are all equivalent and independent. Their average and standard deviation are measures of average value and error in C_{11} .

TABLE I. Adiabatic elastic constants of silicon SW and Tersoff potentials in units of eV/Å³. Upper values are the results of our HtN MC simulation, middle values are the results of Ray (Ref. 1) using EhN MD simulation, and lower values are the experimental (Ref. 21). The last row of values are the results of our HtN MC simulation using the Tersoff potential. The total enthalpy of the system (216 Si atoms) at the three temperatures is -885.6 , -870.0 , and -851.0 eV for the SW and -950 eV for Tersoff potentials, and the pressure is zero. Note that the SW potential is not directly fitted to the elastic constants, and so a close match is not expected between the theory and experimental values of the elastic constants.

Potential	T (K)	C_{11} (eV/Å ³)	C_{12} (eV/Å ³)	C_{44} (eV/Å ³)
Si SW	888	0.883 ± 0.007	0.470 ± 0.008	0.320 ± 0.006
Si SW	888	0.870 ± 0.000	0.470 ± 0.000	0.330 ± 0.052
	888	0.983	0.378	0.470
Si SW	1164	0.856 ± 0.018	0.466 ± 0.010	0.296 ± 0.006
Si SW	1164	0.857 ± 0.002	0.464 ± 0.000	0.285 ± 0.071
	1164	0.952	0.368	0.457
Si SW	1477	0.836 ± 0.007	0.463 ± 0.007	0.284 ± 0.005
Si SW	1477	0.831 ± 0.000	0.460 ± 0.002	0.262 ± 0.052
	1477	0.924	0.359	0.436
Si Tersoff	874	0.816 ± 0.001	0.442 ± 0.001	0.390 ± 0.006

Similarly, the average values and error in C_{12} and C_{44} were calculated and reported in Table I. In order to further study the convergence of the elastic constants of SW Si graphically, we plotted in Fig. 1 all six elastic constants C_{11} , C_{22} , C_{33} , C_{12} , C_{13} , C_{23} , C_{44} , C_{55} , and C_{66} every 1000 MC steps for the case of 1164 K. For the same average temperature, the main diagonal elements h_{11} , h_{22} , and h_{33} of the h matrix, the temperature of the system, T , and the volume of the computational box, V , are plotted in Figs. 2–4 every 1000 MC steps.

In order to further study the convergence of the elastic constants of another potential, we employed the T2 Si potential and calculated its adiabatic elastic constants using Eq. (6). We used the same conditions as we did for the SW Si potential, except that the enthalpy of the system was set to a different value and moving all particles at one time was considered. The total enthalpy of the system was adjusted to the value of -950 eV. This enthalpy equilibrated the average temperature of the system to about 874 K. The lattice was equilibrated for about 500 000 MC steps, and the average value of h_0 was calculated over a subsequent 500 000 MC steps. In order to study the convergence of the T2 Si potential graphically, we performed MC simulation with $h = h_0$ and the original unequilibrated lattice file. The results of the elastic constants from this run are plotted every 10 000 MC steps in Fig. 5. Because we replaced the instantaneous value of h with h_0 for the MC runs that were used to generate Fig. 5, the elastic constant values diverged at the first MC step, and therefore were not included in the graph.

In order to further study the zero-temperature behavior of the elastic constants of the SW Si and T2 Si potentials, we calculated their values using various methods outlined in Sec. II. In particular, the 0 K elastic constants of the SW Si and T2 Si potentials were calculated in the HtN and EhN ensembles and are tabulated in Table II, along with the

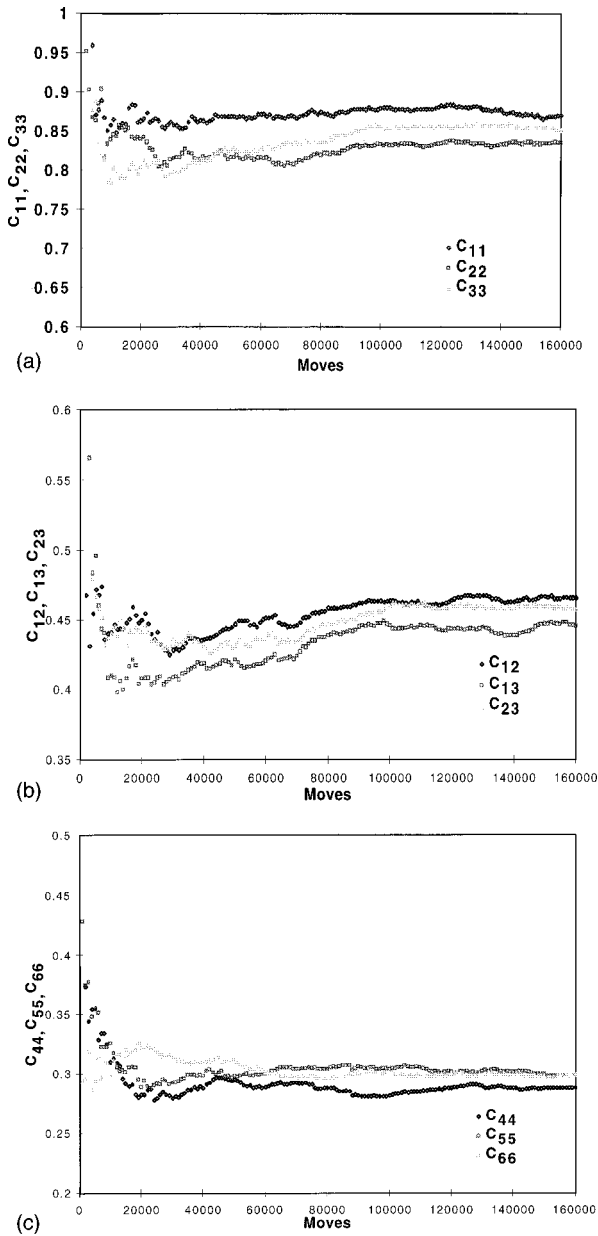


FIG. 1. Elastic constants of the Stillinger-Weber silicon potential at 1164 K and zero external pressure every 1000 MC steps. The Parrinello-Rahman fluctuation formula (PR FF) is used here. Elastic constants are in units of $\text{eV}/\text{\AA}^3$ and $1 \text{ eV}/\text{\AA}^3 = 1.60219 \text{ Mbar} = 160.219 \text{ GPa}$.

Cowley²² and Ray¹ results for comparison with the SW Si results.

IV. SUMMARY AND CONCLUSIONS

Convergence of the elastic constants using the HtN ensemble depends on the type of the simulation (MD or MC) and the potential model employed. The HtN MC calculations of the elastic constants have already been applied successfully to the Lennard-Jones and EAM potentials. We have extended the HtN MC calculation of elastic constants to two silicon potentials. We have presented the results of the Monte Carlo simulations of the elastic constants of the Stillinger-Weber and Tersoff T2 crystalline silicon using the

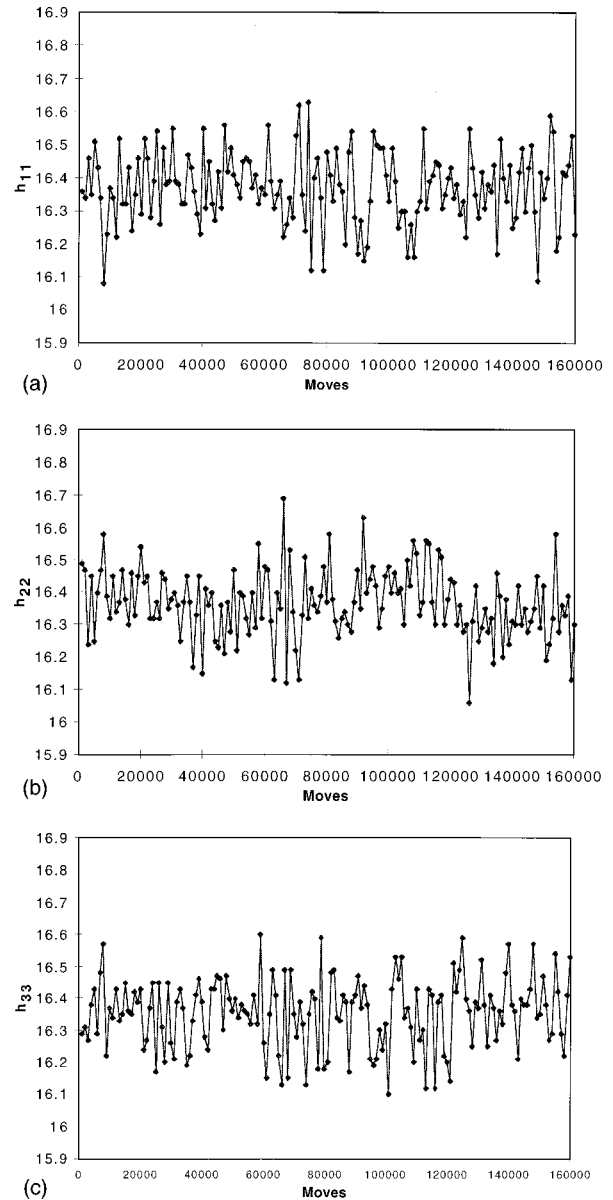


FIG. 2. Main diagonal elements of the h matrix every 1000 MC steps. Conditions are similar to Fig. 1. Average values of h_{11} , h_{22} , and h_{33} are 16.3558, 16.3552, and 16.3586, respectively. h is in units of \AA .

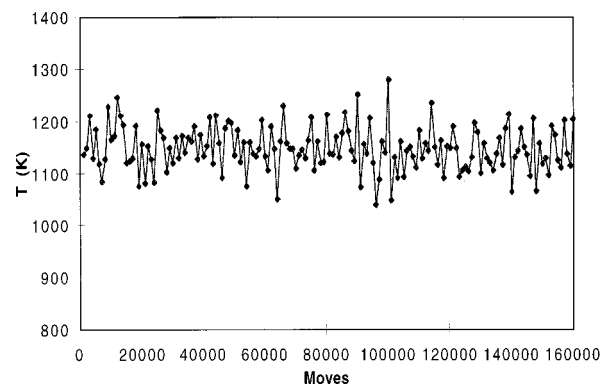


FIG. 3. Temperature of the system every 1000 MC steps. Conditions are similar to Fig. 1.

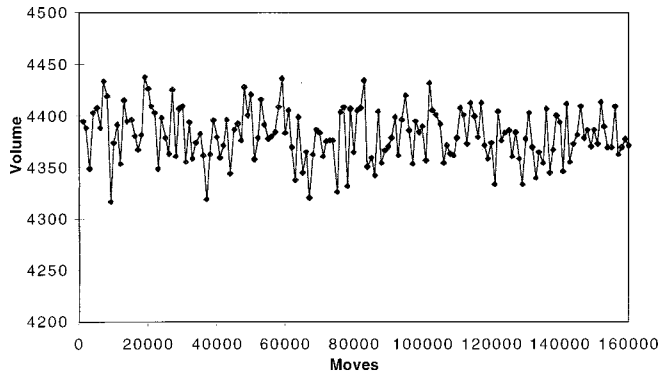


FIG. 4. Volume of the computational box every 1000 MC steps. Conditions are similar to Fig. 1. Average volume of the system is 4376 \AA^3 .

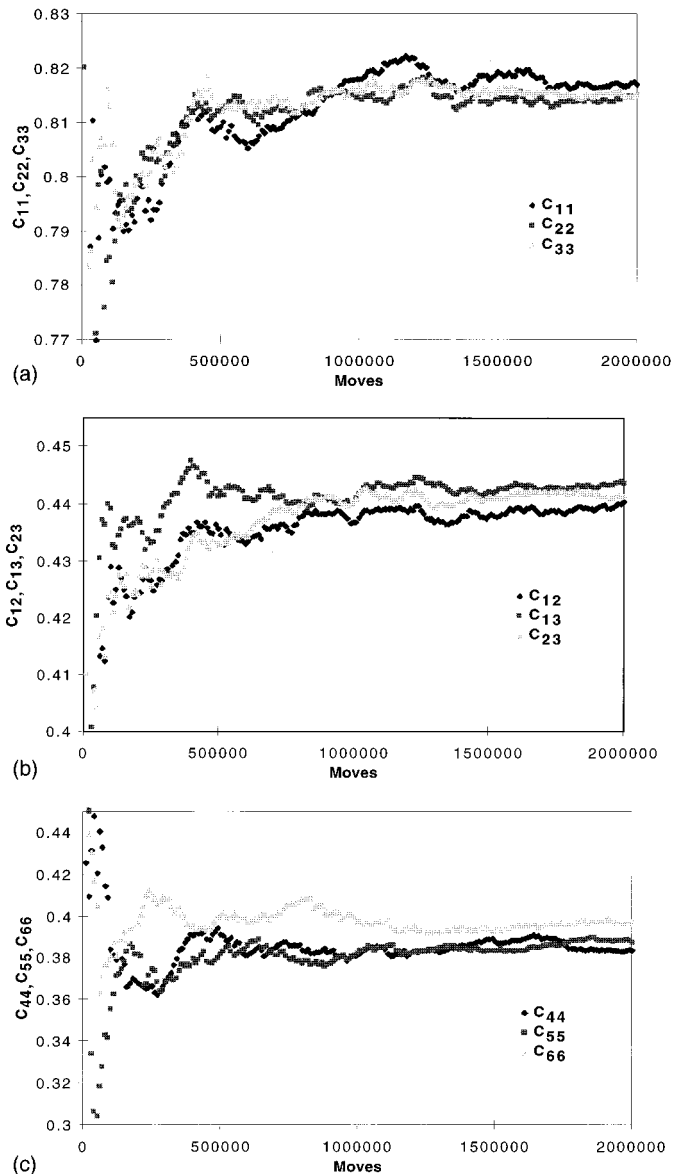


FIG. 5. Elastic constants of T2 silicon potential at 874 K and zero external pressure every 10 000 MC steps. The PR FF is used here. Elastic constants are in units of eV/\AA^3 .

TABLE II. Adiabatic elastic constants of Stillinger-Weber and Tersoff T2 silicon at zero temperature. Elastic constants are in units of eV/\AA^3 . The experimental values are at $T=77 \text{ K}$ from Ref. 23. The EhN(extrapolation)/SW are from Ref. 1.

Method/potential	C_{11} (eV/\AA^3)	C_{12} (eV/\AA^3)	C_{44} (eV/\AA^3)
EhN(direct) ^a /SW	0.945	0.477	0.352
HtN(direct)/SW	1.126	0.491	0.349
EhN(analytical)/SW ^b	0.946	0.477	0.352
HtN(extrapolation)/SW	0.961	0.480	0.418
EhN(extrapolation)/SW	0.962	0.481	0.419
EhN(direct) ^a /T2	0.889	0.470	0.431
HtN(direct)/T2	1.103	0.477	0.433
Experiment ^c	1.048	0.406	0.501

^aDirect methods of calculating elastic constants using the EhN ensemble produced the same values either using the tension-strain or energy method.

^bCowley results (Ref. 22).

^cReference 23.

HtN ensemble and compared the Stillinger-Weber results with the corresponding EhN results from molecular dynamics simulations. The HtN Monte Carlo calculations of the elastic constants of SW silicon are in close agreement with the corresponding results from the EhN molecular dynamics simulations. Averages of physical quantities are calculated more accurately using the HtN Monte Carlo method rather than the corresponding molecular dynamics for cases where harmonic modes are involved and the molecular dynamics does not sample phase space effectively. Based on our results, vibrations of the computational box may be approximately harmonic in HtN molecular dynamics. This along with the fact that HtN MC accuracy is not affected by the harmonic motion of the dynamics may explain the superior convergence of elastic constants in HtN MC simulations. Calculations of the elastic constants of SW silicon, using HtN molecular dynamics, did not converge satisfactorily. The only reliable calculation of the elastic constants for these potentials, using the HtN ensemble, is using the HtN Monte Carlo method. Although the EhN molecular dynamics and Monte Carlo simulations of the elastic constants are, in general, more efficient than the corresponding HtN calculations, they are often not used due to their requirement for the first and second derivatives of the potential. The derivatives of some of the potentials that have terms beyond pairs can be nontrivial, and therefore, the HtN Monte Carlo calculations of the elastic constants could be an alternative method for such cases. The reason for the higher accuracy and more rapid convergence of the elastic constants using the EhN ensemble as compared to the HtN ensemble is that the elastic constants using the EhN ensemble are directly related to the Born terms that are nonfluctuating. On the other hand, the elastic constants obtained from the HtN ensemble are related to the strain fluctuations which will converge more slowly in general. For cases where we do not wish to calculate derivatives of the potential, the HtN MC method is a useful method.

The fictitious mass W , which is an arbitrary parameter in HtN molecular dynamics, is not present in HtN Monte Carlo

simulations. This in itself removes some of the arbitrariness in the form of the kinetic energy of the computational box and its equation of motion.

Furthermore, we have studied the convergence of the elastic constants of SW Si and T2 Si graphically by plotting them versus MC steps and checking the degree of overlap between the symmetry-equivalent elastic constants. Based on our simulations, the errors in the C_{11} and C_{12} elastic constants using HtN MC simulations are larger than the corresponding error from the EhN MD results. On the other hand, the C_{44} error from the HtN MC simulation is much smaller than the corresponding error from the EhN MD result. This is consistent with the previous result using the Lennard-Jones potential.

Although an accurate way of calculating elastic constants at zero temperature is through an analytical expression in the EhN ensemble, it has not received considerable attention because in this approach the elastic constants are related to the first and second derivatives of the potential, which could be

nontrivial with potentials that have terms beyond pairs. The zero-temperature elastic constants of SW Si and T2 Si have been calculated using direct HtN or EhN molecular statics. The results of SW Si are in very good agreement with the analytical results. Finally, as an alternative method for the calculation of elastic constants at zero temperature, we extrapolated (linearly) our HtN results to zero temperature. The results are in reasonable agreement with the analytical results at 0 K.

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