ELASTIC CONSTANTS AND STATISTICAL ENSEMBLES IN MOLECULAR DYNAMICS

John R. RAY

Kinard Laboratory of Physics, Clemson University, Clemson, South Carolina 29634-1911, USA

Contents

ELASTIC CONSTANTS AND STATISTICAL ENSEMBLES IN MOLECULAR DYNAMICS

John R. RAY

Kinard Laboratory of Physics, Clemson University, Clemson, South Carolina 29634-1911, USA

We review different forms of molecular dynamics and the methods of calculating elastic constants when employing these different forms. The fluctuation formulas relating the elastic constants to the fluctuation of the microscopic stress tensor are found to give accurate values of the elastic constants. These formulas are derived and illustrated with numerical results. The constant size-shape forms of molecular dynamics are employed with these formulas. The computational time involved to calculate the elastic constants is the time for the microscopic stress tensor fluctuations to converge to statistically meaningful results. We illustrate the calculation of elastic constants for a first nearest neighbor Lennard-Jones system to show that the method works. A calculation of the elastic constants of sodium using a first principles potential is presented and gives agreement with the observed elastic constants at three different temperatures with an accuracy as good as the experimental results. We also present calculations for the elastic constants of crystalline and amorphous silicon using the Stillinger–Weber potential. The comparison with experimental results is not as good as for sodium but we find the softening of the elastic constants in going from the crystalline to the amorphous phase is accurately modeled by our calculation using the Stillinger–Weber potential. We also illustrate a direct method of calculating elastic constants by applying a given tension to the system and determining the strain; the elastic constants can then be determined using the stress strain relation. This method uses the variables size-shape form of molecular dynamics. Our calculations show that the fluctuation formulas of constant size-shape molecular dynamics furnish and efficient method of calculating elastic constants and give results very close to the observed values for a good potential.

1. Introduction

The primary purpose of this paper is to discuss the determination of thermodynamic response functions by computer simulation methods. By thermodynamic response functions we mean quantities such as: heat capacities, thermal expansion coefficients, elastic constants, etc., which are regularly measured and used to characterize condensed matter systems. In this paper we shall concentrate the discussion on elastic constants.

The two computer simulation methods that are of importance for our discussion are the molecular dynamics and Monte Carlo methods. In the molecular dynamics method one solves Newton's laws of motion for the time evolution of a system of N molecules in a volume V. The molecules are taken to interact through a potential energy function U. In this paper we assume that the potential function is available and we are embarking on a calculation of thermodynamic response functions for the system described by this potential. Recently [1] density functional theory has been combined with molecular dynamics so that the potential energy function is calculated in a parallel calculation as the molecular dynamics calculation proceeds. The methods of calculating elastic constants, that we discuss later in the paper, could be used with density functional–molecular dynamics hybrid theories. Although the density functional form of molecular dynamics holds promise for the future we shall not discuss it further in this paper. In the Monte Carlo method a set of system configurations are generated by a statistical rule. Averages of a quantity over these configurations generate canonical ensembles averages of the quantity.

We could be calculating the response functions in order to compare to the experimentally observed values thereby checking the validity of the potential employed to model the system, or we could be calculating the response functions in lieu of performing experiments; that is, we could be calculating the response functions for conditions where experiments have not been performed or cannot be easily performed. We also mention that the computer simulation contains detailed microscopic information which cannot be obtained experimentally and which may be helpful in constructing theories and in understanding experimental results.

The first work on the calculation of elastic constants using computer simulation was carried out by Squire, Holt and Hoover [2]; see also Hoover, Holt and Squire [3] and Holt, Hoover, Gray and Shortle [4]. These authors used the Monte Carlo method for the calculation of elastic constants.

One advantage of the computer simulation methods over earlier harmonic theory lattice dynamics methods is that the computer simulation methods represent, in principle, an exact (classical) calculation of the elastic constants for the model potential being used. We shall not include a discussion of the harmonic theory or lattice dynamics. For an introduction one can consult Ashcroft and Mermin [5], for more details see Born and Huang [6], Venkataraman, Feldkamp and Sahni [7], and Maradudin, Montroll, Weiss and Ipatova [8].

There are several different forms of molecular dynamics which may, in principle, be used to calculate the elastic constants. In section 2 we shall present a brief review of these different forms of molecular dynamics. In section 3 we present the fluctuation formulas for the HtN ensemble and some numerical calculations using these formulas. The conclusion is that the HtN formulas do not furnish an efficient way of calculating elastic constants.

In section 4 we present fluctuation formulas that can be used in the EhN and ThN forms of molecular dynamics to evaluate elastic constants. These formulas have the same general form as

the original Monte Carlo formulas derived in refs. [2,3] and [4]. Explicit calculations are presented to show that these formulas can be employed to efficiency give accurate values for the elastic constants in either the *EhN* or *ThN* form of molecular dynamics.

In order to illustrate the agreement with experimental results, of the elastic constants calculated using the fluctuation formulas, we discuss the determination of the elastic constants of sodium using a model potential that is based on quantum mechanical perturbation theory. For a simple metal like sodium this pseudopotential method is thought to be quite good; our calculations support this belief since excellent agreement with experimental values at three different temperatures is obtained. For this application the theory developed in section 3 must be generalized slightly to deal with potentials having explicit volume dependence.

In section 6 we study the elastic constants of crystalline silicon using a model potential having both 2- and 3-body interatomic interactions. An interesting aspect of this application of the elastic constant formulas is their use to determine the elastic constants of non-primitive Bravais lattices, that is, lattices with more than one particle per unit cell. To illustrate this aspect of the fluctuation formulas we shall give results of calculations of elastic constants for crystalline silicon with two atoms per unit cell and in section 7 a model of amorphous silicon with 216 atoms per unit cell. Section 8 contains a summary and conclusions.

2. Forms of molecular dynamics

2.1. General discussion

The original form of molecular dynamics generates the microcanonical or *EVN* ensemble. Here *E* is the system energy, *V* the volume and *N* the number of particles. Andersen [9] developed a procedure for carrying out molecular dynamics at constant pressure by making the volume of the system a dynamical variable. Andersen's theory generates the isoenthalpic–isobaric or *HPN* ensemble of classical statistical mechanics; *H* is the enthalpy, and *P* the constant external pressure applied to the system.

Parrinello and Rahman [10,11] generalized Andersen's theory to allow for changes in both the size and shape of the molecular dynamics cell. If a, b, and c are the three vectors spanning the periodically repeating parallelepiped forming the molecular dynamics cell then we define a matrix h by $h = (a, b, c)$. In the Parrinello–Rahman form of molecular dynamics h becomes a dynamical variable describing the shape and size changes of the molecular dynamics cell.

Ray and Rahman [12] have shown in detail how the molecular dynamics theory developed by Parrinello and Rahman can be put into accord with the theory of finite (or nonlinear) elasticity [13]. This is important in our discussions since we can apply strains of arbitrary magnitude to the system and, therefore, the finite theory of elasticity should be used. The Parrinello–Rahman form of molecular dynamics generates the *HtN* ensemble; t is the thermodynamic tension [13] of the theory of finite elasticity and *H* is the enthalpy of that theory.

As mentioned above it is customary to associate the original form of molecular dynamics with the *EVN* ensemble of classical statistical mechanics. However, Ray and Rahman [12] pointed out that the original form of molecular dynamics actually generates the *EhN* ensemble; the latter is a generalization of the familiar *EVN* ensemble in which not only the volume ($= \det(h)$) is held

constant but also the shape of the molecular dynamics cell containing the N particles. The difference between the EVN and EhN ensembles is significant since it is just this introduction of h into the theory that allows one to give a full description of the elastic properties of the system. After formulating the EhN ensemble Ray and Rahman [12] presented the EhN ensemble fluctuation formula for the adiabatic elastic constants. We shall return to discuss this formula later in the paper.

Nosé [14] has developed a molecular dynamics method that generates canonical ensembles. Ray and Rahman [15] have presented a detailed treatment of Nosé's TtN form of molecular dynamics; here T is the preassigned temperature in the Nosé theory, that is, the temperature of the thermal reservoir in the canonical ensemble. The TtN form of molecular dynamics combines the Parrinello–Rahman variable shape-size form of molecular dynamics with the Nosé constant temperature theory. One also has available a ThN form of molecular dynamics obtained by combining Nosé's theory with the EhN form of molecular dynamics.

We have now discussed four different forms of molecular dynamics which generate the four ensembles EhN, ThN, HtN and TtN. The EhN and HtN ensembles are microcanonical ensembles whereas the ThN and TtN are canonical ensembles. We shall give a single Hamiltonian formulation which includes all of these different forms of molecular dynamics. The Hamiltonian describes the TtN form of molecular dynamics when no constraints are imposed upon the solutions of the $3N + 10$ equations of motion; the EhN, ThN and HtN forms of molecular dynamics are described by the Hamiltonian when various constraints, which we shall give later, are imposed upon the solutions. Here we are assuming there are N atoms without internal degrees of freedom whose motion is described by $3N$ equations of motion, the h matrix is described by 9 equations of motion and the Nosé mass scaling variable f has one degree of freedom. The generalization of our discussions to deal with molecules having internal degrees of freedom is not difficult to construct.

2.2. Hamiltonian for different forms of molecular dynamics

The Hamiltonian for the TtN form of molecular dynamics was presented by Ray and Rahman [15] and has the form

$$\mathcal{H}_1(s, \pi, h, \Pi, f, P) = \sum_a \tilde{\pi}_a G^{-1}\pi_a/(2m_a f^2) + U + \mathrm{Tr}(\tilde{\Pi}\Pi)/(2W) + V_0\,\mathrm{Tr}(t\epsilon)$$

$$+ P^2/(2M) + (3N+1)k_B T_0\,\ln(f), \tag{2.1}$$

where (s_a, π_a) are the scaled coordinates and conjugate momenta of particle a, U is the potential energy, (h_{ij}, Π_{ij}) are the coordinates and momenta of the molecular dynamics cell, and (f, P) are the Nosé mass scaling variable and its conjugate momenta. The constants W and, M are introduced so that h and f satisfy dynamical equations; in classical statistical mechanics equilibrium properties of the system are independent of particle masses and, therefore, do not depend upon W, M or the particle mass m_a. The tilde indicates matrix transpose, T_0 is the reservoir temperature in the canonical ensemble, ϵ is the strain matrix which is related to the metric tensor $G = \tilde{h}h$ by

$$\epsilon = (\tilde{h}_0^{-1}Gh_0^{-1} - 1)/2, \tag{2.2}$$

where h_0 is the reference value of the matrix h. We choose the reference state to be the equilibrium average value of h in a system under conditions of zero tension. Note that the strain ϵ vanishes for the system in the reference state. An efficient way of determining h_0 is to carry out a *HtN* or *TtN* calculation with the tension t set to zero. Another possible scheme would be to use a least square approach for the determination of h_0 using data collected from several *EhN* calculations; in this case one would relax the system by varying h to a state of zero stress. The value of h found for the state of zero stress is an estimate of h_0.

The first term in eq. (2.1) is the particle kinetic energy K, if we introduce the physical momenta of the particle, $p_a = m_a f h \dot{s}_a$ then $K = \Sigma_a p_a^2/(2m_a)$. Therefore, the first two terms in eq. (2.1) represent the particle Hamiltonian, which we shall denote by $\mathscr{H} = K + U$. The scaled particles variables (s_a, π_a) are related to the physical particle variables (x_a, p_a) by $x_a = hs_a$, $p_a = \tilde{h}^{-1}\pi_a/f$. As explained above the h matrix is constructed from the vectors spanning the molecular dynamics cell, therefore, the scaled coordinates s_{ai} represent a mapping of the molecular dynamics cell into the unit cube. The relationship between the physical variables and the scaled variables may be described as a canonical transformation defined by h along with a mass scaling transformation represented by f [12,15].

2.3. Thermodynamics of anisotropic media

The elastic energy in eq. (2.1) is the term $V_0\text{Tr}(t\epsilon)$, where $V_0 = \det(h_0)$ is the reference volume of the system. The enthalpy H of the theory of finite elasticity is

$$H = E + V_0 \text{ Tr}(t\epsilon), \tag{2.3}$$

where E is the average energy of the atoms, $E = \langle \mathscr{H} \rangle$. Note that the thermodynamic tension t is defined so that the work dW done in an infintesimal homogeneous distortion of the system is given by $dW = V_0 \text{ Tr}(t \, d\epsilon)$. The stress tensor σ is related to the tension by

$$\sigma = V_0 h h_0^{-1} t \tilde{h}_0^{-1} \tilde{h}/V, \tag{2.4}$$

where h is the average value of the h matrix and $V = \det(h)$ is the average volume. It is not possible to write the work of deformation dW in terms of the stress tensor σ because the strain is referred to the natural unstressed reference state h_0 whereas the stress σ is defined per unit area of the deformed body [13]; therefore, dW is not equal to the stress components times the differential of the strain components. The thermodynamic tension t is introduced so that $V_0 \text{ Tr}(t \, d\epsilon)$ equals the work done in an infintesimal deformation of the system. As we shall see later the elastic constants are related to the derivatives of the tension with respect to the strain.

Consider the *EhN* ensemble and write the thermodynamic law in the form

$$T \, dS = dE + V_0 \text{ Tr}(t \, d\epsilon), \tag{2.5}$$

where E is the average of the particle energy, that is, the average of the first two terms in eq. (2.1), $\mathscr{H}$. Using the definition of the strain, eq. (2.2), we can write eq. (2.5) in the form

$$T \, dS = dE + V_0 \text{ Tr}\left(h_0^{-1} t \tilde{h}_0^{-1} \, dG\right)/2. \tag{2.6}$$

From this last equation we find

$$(\partial E/\partial G_{kn})_S = -(V_0 h_0^{-1} t \tilde{h}_0^{-1})_{kn}/2. \tag{2.7}$$

However, in the *EhN* ensemble we have the general relationship,

$$(\partial E/\partial G_{kn})_S = \langle \partial \mathcal{H}/\partial G_{kn} \rangle, \tag{2.8}$$

where $\mathcal{H}$ is the particle Hamiltonian and the average is an *EhN* ensemble average. Combining the last two equations we have

$$\langle \partial \mathcal{H}/\partial G_{kn} \rangle = -(V_0 h_0^{-1} t \tilde{h}_0^{-1})_{kn}/2. \tag{2.9}$$

Using the particle Hamiltonian we can obtain an explicit expression for the derivative of the particle Hamiltonian with respect to the metric tensor, namely

$$M_{kn} \equiv \partial \mathcal{H}/\partial G_{kn} = -(V h^{-1} \mathcal{S} \tilde{h}^{-1})_{kn}/2, \tag{2.10}$$

where $\mathcal{S}$ is the microscopic stress tensor of the system (see eq. (2.14)). Eqs. (2.9) and (2.10) yield the following relation connecting the thermodynamic tension and the *EhN* average of the microscopic stress tensor

$$t = V h_0 h^{-1} \langle \mathcal{S} \rangle \tilde{h}^{-1} \tilde{h}_0 / V_0. \tag{2.11}$$

Comparing eqs. (2.4) and (2.11) we find

$$\sigma = \langle \mathcal{S} \rangle, \tag{2.12}$$

that is, the stress tensor σ is equal to the average value of the microscopic stress tensor. The same relations eqs. (2.9)–(2.12) also hold in the *ThN* ensemble, however, their proof would be somewhat different since we would use the Helmholtz free energy, $F = E - TS$ instead of the energy E. In that case the relation eq. (2.8) would be replaced by $(\partial F/\partial G_{kn})_T = \langle \partial \mathcal{H}/\partial G_{kn} \rangle$ where the average is a canonical ensemble average. One point about our discussion of thermodynamics deserves comment. In the equation defining the strain in terms of the h matrix, eq. (2.2), we see that if h varies in time then ϵ also varies in time. If h is a constant matrix then it is proper to identify ϵ with the thermodynamic strain. Therefore, for the *EhN* or *ThN* forms of molecular dynamics the thermodynamic identification of ϵ with the strain is appropriate. However, when we employ variable h forms of molecular dynamics, *HtN*, *TtN*, ... we must identify the average value of ϵ with the thermodynamic strain variable. The same comment could be made for the stress tensor in eq. (2.4). Of course, the same situation occurs in the *EhN* form of molecular dynamics when one discusses the pressure which is related to the average of the virial. This same point has also been made by Sprik et al. [16].

2.4. Equations of motion for TtN molecular dynamics

The equations of motion which follow from the Hamiltonian eq. (2.1) have the form

$$m_a f^2 \ddot{s}_{ai} = - \sum_{b \neq a} \chi_{ab} s_{abi} - m_a \left(f^2 G^{-1} \dot{G} + 2 f \dot{f} \right) \dot{s}_{ai}, \tag{2.13a}$$

$$W \ddot{h} = \mathscr{S} A - h \Gamma, \tag{2.13b}$$

$$M \ddot{f} = 2K/f - (3N + 1) k_B T_0 / f, \tag{2.13c}$$

where K is the particle kinetic energy, $\mathscr{S}$ is the microscopic stress tensor, $A = V \tilde{h}^{-1}$ the area tensor, and $\chi_{ab} = (\partial U / \partial r_{ab}) / r_{ab}$, and we have assumed the potential energy is expressible in terms of the distances between the atoms only. For such a potential the microscopic stress tensor may be written

$$\mathscr{S}_{ij} = V^{-1} \left(\sum_a p_{ai} p_{aj} / m_a - \sum_{a<b} \chi_{ab} x_{abi} x_{abj} \right). \tag{2.14}$$

The general definition of the microscopic stress tensor is given by the derivative of the particle Hamiltonian with respect to h: $\mathscr{S} A = \partial \mathscr{H} / \partial h$. Note that the potential energy is not assumed to be pairwise additive in eq. (2.14). In the case of a potential which depends explicitly upon the volume, such as a metallic potential or in case the Ewald method is used to evaluate the Coulomb potential, there are extra terms added to $\mathscr{S}$ due to the volume dependence of the potential via the relation $\partial V / \partial h_{ij} = V \tilde{h}^{-1}$. Later we shall discuss a potential for sodium which contains explicit volume dependence.

The elastic energy term in $\mathscr{H}_1$ gives rise to the second term on the right hand side of eq. (2.13b) with the constant matrix $\Gamma = V_0 h_0^{-1} t \tilde{h}_0^{-1}$; this term is, therefore, related to the tension applied to the system.

If we consider a dynamical variable $B(x, p, h)$ then the time average of B along the trajectories generated by eqs. (2.13a, b, c) $\bar{B}$ is equal to the ensemble average of B in the TtN ensemble

$$\bar{B} = \langle B \rangle_{TtN}. \tag{2.15}$$

The proof of eq. (2.15) is due to Nosé [14].

2.5. Equations of motion for HtN molecular dynamics

If the Nosé variable f satisfies $\dot{f} = 0$, $f = 1$ then eqs. (2.13a) and (2.13b) are the equations of motion for the HtN form of molecular dynamics. Averages of dynamical variables along the trajectories generated by eq. (2.13a) and (2.13b) yield HtN ensemble averages

$$\bar{B} = \langle B \rangle_{HtN}. \tag{2.16}$$

Eq. (2.16) is due to Andersen [9] in the case of an isotropic pressure applied to the system,

however, the same method of proof can be used to prove eq. (2.16) for arbitrary tension applied to the system. We shall discuss Andersen's case of isotropic pressure in detail later in this paper. The Hamiltonian for the *HtN* form of molecular dynamics is given by eq. (2.1) with the last two terms omitted and the value $f = 1$ used in this equation.

2.6. Equations of motion for ThN molecular dynamics

If the h matrix satisfies $\dot{h} = 0$, $h = $ constant then eqs. (2.13a) and (2.13c) are the equations of motion for the canonical ensemble, *ThN*, form of molecular dynamics. The time averages of dynamical variables along the trajectories generated by these equations of motion are equal to *ThN* ensemble averages

$$\overline{B} = \langle B \rangle_{ThN}. \tag{2.17}$$

Thus, these equations of motion generate the same ensemble averages as the conventional Monte Carlo method. The Hamiltonian for this case is eq. (2.1) with the third and fourth terms omitted and $h = $ constant used in the remaining terms.

2.7. Equations of motion for EhN molecular dynamics

If the Nosé variable satisfies $\dot{f} = 0$, $f = 1$ and h satisfies $h = $ constant, then eq. (2.13a) generates the *EhN* form of molecular dynamics; eqs. (2.13a) is just Newton's law of motion written in terms of the scaled coordinates. The time averages of a dynamical variable is just the *EhN* ensemble average in this case

$$\overline{B} = \langle B \rangle_{EhN}. \tag{2.18}$$

The Hamiltonian for this case is just the particle Hamiltonian, the first two terms of eq. (2.1).

2.8. Molecular dynamics with hydrostatic pressure

We may consider a hydrostatic pressure P applied to the system in the presence of a tension t. The Hamiltonian eq. (2.1) then involves the sum $PV + V_0 \, \text{Tr}(t\epsilon)$. This modifies the equation of motion eq. (2.13b) to the form

$$W\ddot{h} = (\mathcal{S} - PI)A - h\Gamma, \tag{2.19}$$

where I is the unit matrix. In this case we are dealing with forms of molecular dynamics that generate the $T(t$ and $P)N$ and $H(t$ and $P)N$ ensembles of statistical physics. These "combination" ensembles with both t and P applied to the system cannot be considered to be special cases of the *TtN* and *HtN* ensembles because of way the enthalpy is defined in the theory of finite elasticity [13]. To understand this latter point in detail one may look at the expression for the work done in an infintesimal strain $dW = V_0 \, \text{Tr}(t \, d\epsilon)$ and the expression for the enthalpy $H = E + V_0 \, \text{Tr}(t\epsilon)$. In the case when the stress is a hydrostatic pressure $\sigma_{ij} = P\delta_{ij}$; we find $dW = PdV$ but $H \neq E + PV$. Thus, in order to have the conventional expression for the enthalpy

for the case of hydrostatic pressure we treat t and P separately in the theory and the enthalpy is given by $H = E + PV + V_0 \, \text{Tr}(t\epsilon)$. For simplicity of discussion in most of the rest of this paper we shall not mention these "combination" ensembles further but leave it understood that one may always make use of them. In fact most of our calculations for elastic constants are for the system in a strain free state with zero tension and pressure.

3. Elastic constants in *HtN* and *TtN* molecular dynamics

3.1. Fluctuation formulas

In the *HtN* and *TtN* forms of molecular dynamics the elastic constants are related to the fluctuation of the strain matrix ϵ given in eq. (2.2). If A and B are two dynamical variables then we define the fluctuation of A and B by $\delta(AB) = \langle AB \rangle - \langle A \rangle \langle B \rangle$ where the bracket $\langle \; \rangle$ represents the *HtN* average value. The *HtN* fluctuation formula for the adiabatic elastic constants $^S C_{ijkl}$ is

$$\delta(\epsilon_{ij}\epsilon_{kl}) = k_{\text{B}} T^{S}(C)^{-1}_{ijkl}/V_0, \tag{3.1}$$

where the adiabatic compliance tensor, $^S(C)^{-1}$, which is the inverse of the elastic constant tensor, is given by

$$^S(C)^{-1}_{ijkl} = -\left(\partial \epsilon_{ij} / \partial t_{kl} \right)_S, \tag{3.2}$$

where S is the entropy. The adiabatic elastic constants are defined by

$$^S C_{ijkl} = -\left(\partial t_{ij} / \partial \epsilon_{kl} \right)_S. \tag{3.3}$$

Note the minus sign in eqs. (3.2) and (3.3); these signs correspond to the choices made by Parrinello and Rahman [11]. In this convention the tension and stress are positive for compressive loading as can be seen from eq. (2.13b). The usual sign convention [13] gives the opposite sign to t and the minus signs do not appear in eqs. (3.2) and (3.3). We shall retain the Parrinello–Rahman sign convention in this paper since other workers have adopted this convention. As mentioned in the previous section the *HtN* form of molecular dynamics is consistent with the finite theory of elasticity [13]. In the literature dealing with the finite theory of elasticity the elastic constants defined in eq. (3.3) are often called stiffness coefficients or the elastic moduli. In this paper we shall refer to these quantities as elastic constants.

The fluctuation formula, eq. (3.1), for the elastic constants in the *HtN* ensemble was first presented by Parrinello and Rahman [17]. The same formula along with fluctuation formulas for the specific heat at constant tension, the thermal expansion tensor at constant tension and the higher order elastic constants were derived in a systematic way by Ray [18].

We shall present two proofs of eq. (3.1). These proofs will illustrate two ways of deriving the fluctuation formulas that play an important role in this paper. Later in the paper we shall present various fluctuation formulas which can be derived using one of the two methods that we illustrate now to derive eq. (3.1).

The first method of derivation uses the techniques of refs. [18,19]. The probability density for the *HtN* ensemble is given by

$$W(q, p, h) = \delta(H - V_0 \, \text{Tr}(t\epsilon) - \mathcal{H})/\omega, \tag{3.4}$$

where H is the enthalpy of the theory of finite elasticity and $\mathcal{H}$ is the particle Hamiltonian. The phase volume can be written in terms of the unit step function $\Theta(x)$ as

$$\Phi(H, t, N) = \int \Theta(H - V_0 \, \text{Tr}(t\epsilon) - \mathcal{H}) \, d\tau, \tag{3.5}$$

where $d\tau = d^{3N}x \, d^{3N}p \, dh_{11} \, dh_{21} \cdots dh_{33}$ is the $6N + 9$ volume element of the *HtN* ensemble phase space. The density of states $\omega = (\partial \Phi / \partial H)_t$ is given by

$$\omega(H, t, N) = \int \delta(H - V_0 \, \text{Tr}(t\epsilon) - \mathcal{H}) \, d\tau, \tag{3.6}$$

and the average value of any dynamical variable $A(x, p, h)$ is given by

$$\langle A \rangle = \int A(x, p, h) W(q, p, h) \, d\tau. \tag{3.7}$$

The entropy $S(H, t, N)$ is obtained by taking the logarithm of the phase volume Φ

$$S(H, t, N) = k_B \ln \Phi. \tag{3.8}$$

Since Φ is an exact adiabatic invariant S will also be an adiabatic invariant. Another simple way of seeing that eq. (3.8) is the correct definition of entropy is to calculate dS and make use of eq. (3.5) for Φ. This calculation leads to the correct thermodynamic relation [13]

$$T \, dS = dH - V_0 \, \text{Tr}(\langle \epsilon \rangle \, dt), \tag{3.9}$$

where $(\partial S / \partial H)_t^{-1} = \Phi / (k_B \omega) = T$.

In the thermodynamic limit ($N, V \to \infty$, $N/V \to$ finite) $k_B \ln \omega$ can also be used to calculate the entropy [20,21]. To see that it is better to use the adiabatic invariant phase volume to define the entropy for finite N we present the following example. If $k_B \ln \omega$ is used to define the entropy then the thermodynamic relation $\langle \epsilon_{ij} \rangle_{\text{Th}} = -T(\partial S / \partial t_{ij})_H / V_0$, derived from eq. (3.9) (the Th subscript means thermodynamic, that is, this relation comes from eq. (3.9)) leads to

$$\langle \epsilon_{ij} \rangle_{\text{Th}} = \langle \epsilon_{ij} K^{-1} \rangle / \langle K^{-1} \rangle, \tag{3.10}$$

where $\langle \ \rangle$ means the *HtN* ensemble average and K is the particle kinetic energy. If we use Φ to define the entropy as in eq. (3.8) them we obtain the accepted result

$$\langle \epsilon_{ij} \rangle_{\text{Th}} = \langle \epsilon_{ij} \rangle. \tag{3.11}$$

Although eqs. (3.10) leads to the correct relation, eq. (3.11), in the thermodynamic limit it is clear that eq. (3.8) is the correct definition of the entropy in the *HtN* ensemble. Pearson et al. [22]

reached a similar conclusion for the *EVN* ensemble. The method of deriving eqs. (3.10) and (3.11) will be discussed presently. The density of states $\omega(H, t, N)$ is the derivative of Φ with respect to the enthalpy H, therefore, the probability density $W(x, p, h)$ in eq. (3.4) is normalized to one.

The method of derivation of fluctuation formulas given in refs. [18,19] is to define, with foresight, a new potential X_{ij}

$$X_{ij} = \int \epsilon_{ij} \Theta(H - V_0 \, \text{Tr}(t\epsilon) - \mathcal{H}) \, \mathrm{d}\tau. \tag{3.12}$$

Differentiation of X_{ij} with respect to t_{kn} at constant entropy and using the thermodynamic relation $\mathrm{d}H = T \, \mathrm{d}S + V_0 \, \text{Tr}(\langle \epsilon \rangle \, \mathrm{d}t)$ we obtain

$$\delta(\epsilon_{ij}\epsilon_{kn}) = -\left(\partial X_{ij}/\partial t_{kn}\right)_S/(\omega V_0). \tag{3.13}$$

For a macroscopic system we can approximate X_{ij} by

$$X_{ij} = \langle \epsilon_{ij} \rangle \Phi. \tag{3.14}$$

Using eq. (3.14) in eq. (3.13) together with the relation $k_B T = \Phi/\omega$ leads to the new form of eq. (3.13)

$$\delta(\epsilon_{ij}\epsilon_{kn}) = -k_B T(\partial \langle \epsilon_{ij} \rangle/\partial t_{kn})/V_0, \tag{3.15}$$

or using eq. (3.2) this latter equation becomes exactly the fluctuation formula, eq. (3.1).

Our second proof of eq. (3.1) first obtains an exact result and then eq. (3.1) is obtained in the thermodynamic limit. This method uses the theory first discussed by Pearson, et al. [22] and then applied to the *HPN* ensemble by Ray and Graben [23]. This method has also been used by Çaǧin and Ray [24] to discuss the molecular dynamics, or *EhNM* ensemble where M is the total linear momentum of the system. First we use use thermodynamic relations to write the compliance tensor as

$$\begin{aligned} {}^S(C^{-1})_{ijkn} &= -\left(\partial \langle \epsilon_{ij} \rangle/\partial t_{kn}\right)_S \\ &= -\left(\partial \langle \epsilon_{ij} \rangle/\partial t_{kn}\right)_H - V_0 \langle \epsilon_{kn} \rangle \left(\partial \langle \epsilon_{ij} \rangle/\partial H\right)_t. \end{aligned} \tag{3.16}$$

For any dynamical variable A which depends only upon x and h, $A(x, h)$, the average value in eq. (3.7) becomes

$$\langle A \rangle = \int A(x, h)(H - V_0 \, \text{Tr}(t\epsilon) - U)^{(3N/2-1)} \Theta(H - V_0 \, \text{Tr}(t\epsilon) - U) \, \mathrm{d}\tau'/(C_0 \omega \Gamma(3N/2)), \tag{3.17}$$

where $\mathrm{d}\tau' = \mathrm{d}^{3N}x \, \mathrm{d}h_{11} \, \mathrm{d}h_{12} \cdots \mathrm{d}h_{33}$, Γ stands for the gamma function and $C_0 = 1/(2\pi m)^{3N/2}$. For $A = \epsilon_{ij}$ eq. (3.17) can be used to derive expressions for the strain derivatives in eq. (3.16);

when the resulting expressions for the strain derivatives are substituted into eq. (3.16) we obtain the exact expression for the compliance tensor

$$
{}^S\!\left(C_{ijkn}^{-1}\right) = (3N/2 - 1)V_0\big(\langle \epsilon_{ij}\epsilon_{kn}K^{-1}\rangle - \langle \epsilon_{ij}\rangle\langle \epsilon_{kn}K^{-1}\rangle - \langle \epsilon_{kn}\rangle\langle \epsilon_{ij}K^{-1}\rangle
$$

$$
+ \langle \epsilon_{ij}\rangle\langle \epsilon_{kn}\rangle\langle K^{-1}\rangle\big). \tag{3.19}
$$

Eq. (3.19) generalizes eq. (17) of Ray and Graben [23] which is the fluctuation formula for the adiabatic bulk modulus. To derive an asymptotic expression for the foregoing equation in the limit as $N \to \infty$ we use the following expansion in eq. (3.19)

$$
\langle K^{-1}\rangle = \langle K\rangle^{-1}\langle(1 - \delta K + (\delta K)^2 \cdots)\rangle, \tag{3.20}
$$

where $\cdots \delta K = (K - \langle K\rangle)/\langle K\rangle \ll 1$. The leading term of the expansion of eq. (3.19) is the fluctuation expression eq. (3.1).

The two derivations of eq. (3.1) serve to illustrate how formulas involving equilibrium thermodynamic response functions are obtained. Later we shall give the formulas that are used to calculate various response functions in different ensembles, the reader may construct derivations of these formulas following one of the methods used to obtain eq. (3.1). We shall also present data later that compares the results obtained using exact and thermodynamic limit formulas, such as eq. (3.1) and (3.19), to calculate elastic constants; as would be expected there is no significant difference in the results obtained for simulations using a few hundred particles together with periodic boundary conditions.

3.2. Numerical results

The only published extensive study of the use of eq. (3.1) to calculate elastic constants is the paper by Sprik, Impey and Klein [16]. The results of this paper imply that eq. (3.1) furnishes a slowly convergent way of calculating elastic constants. In another study using the same potential as in ref. [16] I obtained, using eq. (3.1), the elastic constant data shown in table 1. The calculation was for a 500 particle system at a reduced temperature of 0.3. In this calculation the particles interact via the nearest neighbor Lennard-Jones potential and are arranged in a fcc lattice. In table 1 are given, in arbitrary units the three symmetry equivalent elastic constants C_{12}, C_{23} and C_{13}, as determined using eq. (3.1), and which by cubic symmetry of the system should be equal to one another. Here and elsewhere in this paper we use the Voigt compressed notation to denote fourth rank tensors ($11 = 1$, $22 = 2$, $33 = 3$, $23 = 4$, $13 = 5$, and $12 = 6$). The large differences between the three elastic constants determined in this rather long run calls into question the usefulness of eq. (3.1) for elastic constant calculations. In order to compare the convergence of the fluctuation formula eq. (3.1) with another quantity in this same molecular dynamics calculation we show in table 2 the same components (12, 23 and 13) of the fluctuation of the microscopic stress tensor $\Delta(\mathscr{S}_{ij}\mathscr{S}_{kn})$, where $\mathscr{S}_{ij}$ is defined in eq. (2.14). This fluctuation quantity is not related to the elastic constants in the HtN ensemble but it is instructive to study its rate of convergence. It is clear from table 2 that the convergence of the microscopic stress tensor fluctuations is much better than the elastic constants in table 1. The very slow convergence of the elastic constants using eq. (3.1) had been found earlier by Parrinello and Rahman [25].

Table 1

Symmetry equivalent elastic constants as calculated using eq. (3.1) and the *HtN* form of molecular dynamics. The elastic constants are given in arbitrary units. The results in the table illustrate the slow convergence of the values of the elastic constants obtained using the strain–strain fluctuation formula eq. (3.1). This molecular dynamics calculation is for a Lennard-Jones nearest neighbor system at a reduced temperature of 0.3 and at zero pressure. The iteration time step is $0.005\sigma(m/\epsilon)^{1/2}$ where σ and ϵ are the usual Lennard-Jones parameters and m is the atoms mass

| | *HtN* Molecular Dynamics | | |
Time	C_{12}	C_{13}	C_{23}
5000	0.106	0.166	0.079
10000	0.100	0.131	0.099
15000	0.852	0.122	0.103
20000	0.729	0.104	0.097
25000	0.704	0.814	0.769
30000	0.526	0.785	0.611
35000	0.457	0.692	0.483
40000	0.367	0.454	0.389
45000	0.239	0.311	0.233
50000	0.108	0.252	0.146
55000	0.020	0.183	0.067
60000	0.183	0.022	0.107
65000	0.434	0.236	0.423
70000	0.751	0.433	0.753

Table 2

The fluctuation in symmetry equal components of the microscopic stress tensor. These are the same tensor components as in table 1. The results show that the microscopic stress tensor fluctuations converge much faster than the strain–strain fluctuations given in table 1. This data was collected from the same molecular dynamics run as the data in table 1. The numbers are in arbitrary units

| | *HtN* Molecular Dynamics | | |
Time	$\delta(\mathcal{I}_{11}\mathcal{I}_{22})$	$\delta(\mathcal{I}_{11}\mathcal{I}_{33})$	$\delta(\mathcal{I}_{22}\mathcal{I}_{33})$
5000	0.164	0.122	0.168
10000	0.176	0.148	0.170
15000	0.171	0.152	0.164
20000	0.167	0.150	0.161
25000	0.171	0.160	0.165
30000	0.178	0.166	0.177
35000	0.182	0.175	0.180
40000	0.177	0.174	0.176
45000	0.184	0.184	0.185
50000	0.184	0.180	0.180
55000	0.181	0.179	0.176
60000	0.179	0.180	0.176
65000	0.182	0.181	0.178
70000	0.182	0.181	0.178

The fact that eq. (3.1) does not furnish a satisfactory way of calculating elastic constants is a disappointment since eq. (3.1) is very simple to use and does not depend explicitly on the potential being employed. As we shall see the *EhN* fluctuation formulas involve the second derivatives of the interaction potential which can be somewhat time consuming to calculate; however, it happens that these second derivative terms converge very rapidly and, therefore, do not consume much computer time to accurately calculate. In the *EhN* fluctuations formula calculation of elastic constants the time consuming part is the calculation of the microscopic stress tensor fluctuations which as we have seen in table 2 converge much more rapidly than the strain fluctuations in eq. (3.1). This implies that from the point of view of using fluctuation formulas to calculate elastic constants the *EhN* or *ThN* forms of molecular dynamics should be employed.

In attempts to improve the convergence of the *HtN* fluctuation formula method of calculating elastic constants we modified the calculation in various ways. As an example, of modifications we attempted, we changed the h equation of motion, eq. (2.13b) to see if this would improve the convergence. One of these changes was to symmetrize the h equation of motion as has been discussed by Nosé and Klein [26]. Another modification was to replace the *h* equation in the theory by an equation of motion for *G*, namely

$$W\ddot{G} = (h^{-1}\mathscr{S}A - \Gamma)/2. \tag{3.21}$$

This equation of motion can be derived from the Hamiltonian eq. (2.1) by defining the momentum of the molecular dynamics cell in eq. (2.1) as $\Pi = W\dot{G}$ and by varying *G* instead of *h* when deriving the equations of motion for the cell. In order to define *h* in the case eq. (3.21) is employed instead of eq. (2.13b) we assumed *h* symmetric and inverted the matrix equation $G = h^2$ for *h*. We also used other potentials, introduced interactions with a thermal bath in the sense of Andersen [9], varied the cell "mass" parameter *W*, changed the numerical algorithm used to solve the equations of motion, and ran the simulation for longer times in attempts to improve the convergence of eq. (3.1). None of these modifications led to significant improvements in the results shown in table 1.

The *TtN* fluctuation formulas have the same form as eq. (3.1) except the isothermal elastic constants $^T C_{ijkl}$ enter on the left hand side instead of the adiabatic elastic constants. One would expect the same poor convergence using this *TtN* formula to determine the elastic constant although we have not actually checked on this point. As another point we mention that scalar thermodynamic quantities such as specific heat, bulk modulus etc. seem to converge about as well in *HtN* molecular dynamics as in other forms. The poor convergence appears to be limited to tensor properties.

4. Elastic constants in *EhN* and *ThN* molecular dynamics

4.1. Fluctuation formulas

The *EhN* fluctuation formula involving the adiabatic elastic constants was first presented by Ray and Rahman [12] and, for a potential that depends only on interparticle distances, has the

form

$$V_0 h_{0ip}^{-1} h_{0jq}^{-1} h_{0kr}^{-1} h_{0ns}^{-1} C_{pqrs} = -4\delta(M_{ij}M_{kn})/k_BT + 2Nk_B(G_{in}^{-1}G_{jk}^{-1} + G_{ik}^{-1}G_{jn}^{-1})$$

$$+ \sum_{\substack{a<b\\c<d}} \langle k(a, b, c, d)s_{abi}s_{abj}s_{cdk}s_{cdn}\rangle, \qquad (4.1)$$

where $M_{ij} = -Vh^{-1}\mathscr{S}\tilde{h}^{-1}/2$ is the derivative of the particle Hamiltonian with respect to the metric tensor, s_{abi} is the scaled coordinate difference between particle a and b, h_0 is the value of the h matrix in the reference state, which we choose to be the state of zero strain, and $k(a, b, c, d)$ is related to the potential energy by

$$k(a, b, c, d) = (\partial^2 U/\partial r_{ab}\partial r_{cd} - (\partial U/\partial r_{ab})\delta_{ac}\delta_{bd}/r_{ab})/(r_{ab}r_{cd}). \qquad (4.2)$$

Eq. (4.1) is valid for any potential which depends only upon the distance between the particles. If the potential is pairwise additive then the last term reduces to a simpler form, namely,

$$\sum_{a<b} \langle g(a, b)s_{abi}s_{abj}s_{abk}s_{abn}\rangle,$$

with

$$g(a, b) = (U'' - 2U')/r_{ab}^4, \qquad (4.3)$$

where the prime on $U(r_{ab})$ stands for $r\partial/\partial r$. The proof of eq. (4.1) can be given using either of the two methods discussed in the previous section. If we use the adiabatic differentiation of potential method then we can start from the potential X_{ij} given by

$$X_{ij} = \int M_{ij}\Theta(E - \mathscr{H}) \, d\tau, \qquad (4.4)$$

where $\mathscr{H}$ is the particle Hamiltonian for the *EhN* form of molecular dynamics, the first two terms of eq. (2.1). The tensor M_{ij} is the derivative of the particle Hamiltonian with respect to the metric tensor $M_{ij} = \partial\mathscr{H}/\partial G_{ij}$. Differentiating eq. (4.4) with respect to G_{kn} at constant entropy, leads to the following fluctuation formula containing the the adiabatic elastic constants

$$V_0 h_{0ip}^{-1} h_{0jq}^{-1} h_{0kr}^{-1} h_{0ns}^{-1} C_{pqrs} = -4\delta(M_{ij}M_{kn})/k_BT + 4\langle\partial^2\mathscr{H}/\partial G_{ij}\partial G_{kn}\rangle. \qquad (4.5)$$

Evaluation of the last term in eq. (4.5) leads to eq. (4.1).

Eq. (4.1) is the *EhN* fluctuation formula for the second order adiabatic elastic constants, however, it happens that the *ThN* formula has the same form except the elastic constants are the isothermal elastic constants and the average $\langle \cdots \rangle$ stand for *ThN* molecular dynamics averages. Note that this latter result is not valid for third and higher order elastic constants.

4.2. Numerical results

The first use of eq. (4.1) to calculate the adiabatic elastic constants in *EhN* molecular dynamics was by Ray, Moody and Raman [27] where they employed the same first nearest

Table 3

ThN molecular dynamics calculation of the same three symmetry equivalent elastic constants as shown in table 1. These values were obtained using eq. (4.1) and *ThN* molecular dynamics. Note that the convergence of the values with increasing time is similar to the results shown in table 2. The system is the same Lennard-Jones system as was used to obtain the data in tables 1 and 2 but of course a different form of molecular dynamics is employed. The quantity shown is the elastic constant divided by $Nk_{B}T/V_0$ which is dimensionless

	ThN Molecular Dynamics		
Time	C_{12}	C_{13}	C_{23}
5000	78.9	83.0	81.2
10000	77.4	77.5	77.5
15000	65.0	65.0	65.5
20000	65.2	66.2	66.4
25000	70.1	71.1	71.4
30000	69.2	69.4	70.0

neighbor Lennard-Jones potential as in the calculations discussed in section 3. Later these same authors applied (eq. 4.1) to calculate the isothermal elastic constants for this same system [28] using *ThN* molecular dynamics together with eq. (4.1).

In table 3 we show the the results of using eq. (4.1) to calculate the same three, symmetry equivalent, elastic constants C_{12}, C_{13} and C_{23} as discussed in section 3. This calculation is for a 500 particle system with the atoms arranged in an fcc lattice. The reduced temperature of the system is 0.3 and the system is held at zero pressure. The *ThN* form of molecular dynamics was employed in this calculation so these are the isothermal elastic constants. This same good convergence is found using *EhN* molecular dynamics to calculate the adiabatic elastic constants from eq. (4.1). The quantity given in table 3 is the dimensionless number $C_{ijkn}V_0/(Nk_{B}T)$. The iteration time step for the calculation was $0.005\sigma(m/\epsilon)^{1/2}$ where σ and ϵ are the usual Lennard-Jones parameters $U(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^{6})$ and m is the atom mass. The interesting feature of table 3 is the rapid convergence of the elastic constants as compared to the results in table 1.

In table 4 we show the convergence of the three non-zero symmetry averaged isothermal elastic constants for this same calculation. The error estimates in the molecular dynamics results are obtained by using the three independent calculated elastic constants as three independent measurements. We also show Monte Carlo data as given by Cowley [29] for this same system. The agreement between the Monte Carlo results and *ThN* molecular dynamics results is excellent.

In order to better understand the convergence illustrated in tables 3 and 4 we study the individual terms that make up the elastic constants in eq. (4.1). The right hand side of eq. (4.1) consists of 3 separate terms; we call the first term the fluctuation term, the next term the kinetic term and the last term the Born term. For a monatomic Bravais lattice such as we are studying at present the $T = 0$ K limit of eq. (4.1) would give just the Born term evaluated at the ideal lattice positions. In general for a non-primitive lattice this is no longer the case because of internal strains. We shall explore this point in some detail later in our discussion of silicon.

In table 5 we show how the fluctuation, kinetic and Born terms converge for the same molecular dynamics calculation as used in tables 3 and 4. In table 5 we show only the results for

Table 4

The symmetry averaged elastic constants calculated for the same ThN molecular dynamics run as in table 3. Here C_{11} is calculated as $(C_{11} + C_{22} + C_{33})/3$ with similar formulas for C_{12} and C_{44}. In the molecular dynamics calculation the 9 elastic constants C_{11}, C_{23}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55} and C_{66} are independently calculated. By cubic symmetry there are only 3 independent elastic constants: $C_{11} = C_{22} = C_{33} \ldots$ The three independently calculated elastic constants can be used to obtain an error estimate; we show this error estimate at 30000 time steps. Also shown are the results of an independent Monte Carlo calculation by Cowley [29]. The last row of numbers shows the static Born values of the elastic constants. These would be the values obtained using lattice statics. The quantities shown are the dimensionless elastic constants as in table 3

Time	C_{11}	C_{12}	C_{44}
		ThN Molecular Dynamics	
5000	169.6	81.0	82.4
10000	166.1	77.5	81.8
15000	153.9	65.2	84.2
20000	155.5	65.9	83.9
25000	160.0	70.8	83.5
30000	158.7 ± 0.3	69.5 ± 0.4	83.5 ± 0.6
		Monte Carlo (Cowley)	
25000	157.1 ± 1.0	69.3 ± 0.9	82.2 ± 0.2
		Static Born Values	
	146.9	73.4	73.4

C_{11}; the data for C_{12} and C_{44} show the same behavior. As shown in table 5 the Born terms are fully converged at 5000 time steps into the run. A study of the data shows that the Born terms are converged after only 500 time steps! At 500 time steps for this run the Born term has the value 211.2. As mentioned previously, the calculation of the second derivatives of the potential enter only in the Born terms. Calculating these second derivatives is a time consuming part of the calculation. The rapid convergence of the Born terms means that one can calculate these terms in a short calculation of around 500 time steps. The calculation of the second derivatives can then

Table 5

The convergence of the three terms on the right hand side of eq. (4.1) is shown for the same Lennard-Jones system as in the previous tables. The Born terms converge after a short run of a few hundred time steps for this calculation. The fluctuation term is slower to converge and determine the computer time necessary for a given accuracy in the final value of the elastic constants. The quantities shown are the dimensionless quantities as in tables 3 and 4

Time	Fluctuation	Kinetic	Born	C_{11}
		ThN Molecular Dynamics		
5000	−45.7	4.0	211.3	169.6
10000	−49.3	4.0	211.4	166.1
15000	−61.4	4.0	211.3	153.9
20000	−59.9	4.0	211.4	155.5
25000	−55.3	4.0	211.3	160.0
30000	−56.6	4.0	211.3	158.7

be omitted and only the fluctuation terms need to be calculated. The fluctuation terms require only the first derivatives of the potential which must be calculated in the dynamics anyway. The rapid convergence of the Born terms means that the computational time involved in using eq. (4.1) is determined by the time taken for the fluctuation terms to converge to a statistically satisfactory result. Since this time is apparently much shorter than the time for the strain fluctuations in eq. (3.1) to converge, compare table 1 and 2, we see that eq. (4.1) furnishes a superior method of calculating elastic constants than eq. (3.1).

In all of our elastic constant calculations we calculate some elastic constants that should be zero based on symmetry, for example, for cubic symmetry C_{63} should vanish. In the calculations reported in tables 3, 4 and 5 C_{63} was found to be zero within the accuracy of our calculations. This calculation also serves as a check on the computer program used for the calculations.

4.3. Adiabatic from isothermal elastic constants

It should be pointed out that, by using the adiabatic elastic constants as determined in an *EhN* molecular dynamics calculation together with other thermodynamic quantities determined in the run, one can calculate the isothermal elastic constants using well-known thermodynamic relations. Therefore, we may use *EhN* molecular dynamics to determine the isothermal as well as the adiabatic elastic constants. The reverse is also true, that is, we may determine the adiabatic as well as the isothermal elastic constants in *ThN* molecular dynamics. In order to illustrate how this works we shall give results for calculating the adiabatic elastic constants from the isothermal elastic constants. The thermodynamic relation connecting the two elastic constants is

$$^{S}C_{ijkn} = {}^{T}C_{ijkn} + TV_0\lambda_{ij}\lambda_{kn}/C_\epsilon, \tag{4.6}$$

where λ_{ij} is the temperature coefficient of thermodynamic tension, $\lambda_{ij} = (\partial t_{ij}/\partial T)_\epsilon$, C_ϵ is the isostrain specific heat, $C_\epsilon = (\partial E/\partial T)_\epsilon$. The microscopic tension tensor is given by

$$\eta = Vh_0 h^{-1}\mathscr{S}\tilde{h}^{-1}\tilde{h}_0/V_0. \tag{4.7}$$

The average value of η gives the tension tensor by eq. (2.11); recall that h is constant

$$t = \langle \eta \rangle. \tag{4.8}$$

In order to use eq. (4.6) to determine the adiabatic elastic constants we must determine λ_{ij} and C_ϵ. These quantities may be determined from the *ThN* fluctuation formulas [28]

$$\delta(\eta_{ij}\mathscr{H}) = k_{\mathrm{B}}T^2\lambda_{ij}, \tag{4.9}$$

and

$$\delta(\mathscr{H}^2) = k_{\mathrm{B}}T^2C_\epsilon. \tag{4.10}$$

In table 6 we show the adiabatic elastic constants calculated using eqs. (4.6), (4.9) and (4.10) for the same Lennard-Jones system as discussed in tables 3, 4 and 5. Also shown are the values

Table 6

Comparison of adiabatic elastic constants calculated using different forms of molecular dynamics. The *ThN* results are obtained by using eq. (4.1) to calculate the isothermal elastic constants and then using eqs. (4.6) (4.9), and (4.10) to determine the adiabatic elastic constants. In *EhN* molecular dynamics eq. (4.1) is used directly, in a separate calculation, to determine the adiabatic elastic constants. Cowley's [29] Monte Carlo calculation uses the same procedure as our *ThN* calculation. The elastic constants are given in the same dimensionless form as in tables 3, 4 and 5 and the system is the same Lennard-Jones nearest neighbor model

| | ThN Molecular Dynamics | | |
Time	C_{11}	C_{12}	C_{44}
20000	185.8 ± 1.3	95.5 ± 1.1	81.3 ± 1.3
	EhN Molecular Dynamics		
20000	183.9 ± 1.6	94.8 ± 1.6	83.2 ± 1.3
	Monte Carlo (Cowley)		
25000	182.0 ± 0.5	$94.1 + 0.5$	82.2 ± 0.2

calculated using eq. (4.1) in a separate *EhN* calculation as well as the values given by Cowley [29] using the Monte Carlo method. For more details of this comparison see ref. [28].

4.4. Summary of results of elastic constants calculations

In this section we have shown how the *EhN* or *ThN* forms of molecular dynamics can be used with eq. (4.1) to accurately and efficiently calculate the elastic constants of a system given the interaction potential U. Our numerical study focused on a simple potential that has been used in previous studies of methods of calculating elastic constants in Monte Carlo [29] and molecular dynamics [21]. From our studies it appears that *ThN* and *EhN* molecular dynamics are equally efficient for the calculation of elastic constants using fluctuations formulas.

5. Elastic constants of sodium from molecular dynamics

5.1. General discussion

In the previous sections we have shown that *EHN* and *ThN* molecular dynamics fluctuations formulas furnish an efficient and accurate way of calculating elastic constants using molecular dynamics. In this section we discuss the application of these results to calculate the elastic constants of sodium using a potential derived using quantum theory. This potential contains explicit volume dependence and, therefore, requires an extension of the theory to cover this case. These extensions were carried out by Çağin and Ray [30]. Earlier theoretical studies of the elastic constants of sodium include the lattice dynamics calculation by Glyde and Taylor [31], and Monte Carlo calculations by Cohen, Klein, Duesbery and Taylor [32]. Also a more recent calculation of Schiferl and Wallace [33] made use of molecular dynamics to calculate the elastic constants of sodium using a potential developed by Wallace [34]. All of these studies differ from the present calculations; the Monte Carlo calculation of ref. [32] neglected the volume depen-

dence of the pair potential, the calculation by Schiferl and Wallace [33] used canonical ensemble fluctuation formulas and added corrections terms [35] to obtain the adiabatic elastic constants. Schiferl and Wallace take the full volume dependence of the potential into account and their method of calculation should give the same results as our method of calculation for the same system. In contrast we give and make use of the full *EhN* microcanonical fluctuation formulas to obtain the adiabatic elastic constants directly.

5.2. Model potential for sodium

The model potential used in our calculations was described in some detail in refs. [36–38] and has the following form

$$U(r, r_s) = \phi(r, r_s) + U_{eg}(r_s) + U_{bs}(r_s) + U_h(r_s), \tag{5.1}$$

where r_s is the density parameter $r_s = (3V/4\pi Z)^{1/3}$, Z is the valence, and the potential is expressed in units of $e^2/(2a_0)$ with e the elementary charge and a_0 the Bohr radius. The first term in eq. (5.1) is the interatomic pair potential, and the last three terms depend only on the volume. The electron gas term is given by

$$U_{eg} = 0.982/r_s^2 + (0.407/\xi - 0.916)/r_s - (0.115 - 0.031 \ln r_s), \tag{5.2}$$

where ξ is related to the compressibility of the electron gas. The self-energy of the band structure is given by

$$U_{bs} = \phi(r = 0, r_s), \tag{5.3}$$

and the Hartree term, which represents the average interaction between the conduction electrons and the non-electrostatic part of the bare potential, has the form

$$U_h = 3\alpha r_c^2/r_s^3. \tag{5.4}$$

Here α is a parameter which is adjusted to bring the lattice constants at 0 K into agreement with the observed value. By choosing $\alpha = 0.218$, Price [38] showed that not only the 0 K lattice constant but also the cohesive energy and bulk modulus are brought into agreement with their 0 K values. The appearance of this adjustable parameter implies that the potential, and perhaps its method of derivation needs improvement. The quantity r_c in the last equation is the core radius of the pseudopotential which has the value $1.694a_0$.

5.3. EhN fluctuation formulas

Consider a general volume-dependent potential

$$U(r_1, r_2, \ldots; V) = \Phi(r_{12}, r_{13}, \ldots; V) + \Psi(V), \tag{5.5}$$

where the first term

$$\Phi = \sum_{a<b} \phi(r_{ab}, V), \tag{5.6}$$

is the total effective pair potential and Ψ is the strictly volume-dependent part of the potential.

Using the exact method of derivation discussed in section 3 we obtain the following formula for the adiabatic elastic constants [30]

$$V_0 h_{0ip}^{-1} h_{0jq}^{-1} h_{0kr}^{-1} h_{0ns}^{-1} C_{pqrs} = \Psi_{ijkn} + \langle \Phi_{ijkn} \rangle + N k_B T \big(G_{ik}^{-1} G_{jn}^{-1}$$

$$+ G_{in}^{-1} G_{jk}^{-1} + G_{ij}^{-1} \gamma_{kn} + G_{kn}^{-1} \gamma_{ij} - G_{ij}^{-1} G_{kn}^{-1} N k_B / C_\epsilon \big)$$

$$- (3N/2 - 1) \big(\langle \Phi_{ij} \Phi_{kn} K^{-1} \rangle - \langle \Phi_{ij} K^{-1} \rangle \langle \Phi_{kn} \rangle$$

$$- \langle \Phi_{kn} K^{-1} \rangle \langle \Phi_{ij} \rangle + \langle \Phi_{ij} \rangle \langle \Phi_{kn} \rangle \langle K^{-1} \rangle \big). \tag{5.7}$$

Here Ψ_{ijkn} is a volume dependent term

$$\Psi_{ijkn} = 4\partial^2 \Psi / \partial G_{ij} \partial G_{kn}$$

$$= \Psi^{**} G_{ij}^{-1} G_{kn}^{-1} - \Psi^* \big(G_{ik}^{-1} G_{jn}^{-1} + G_{in}^{-1} G_{jk}^{-1} \big), \tag{5.8}$$

while the pair potential term Φ_{ijkn} is given by

$$\Phi_{ijkn} = 4\partial^2 \Phi / \partial G_{ij} \partial G_{kn}$$

$$= \sum_{a<b} (\phi'' - 2\phi') s_{abi} s_{abj} s_{abk} s_{abn} / r_{ab}^4 + \sum_{a<b} \phi'^* \big(s_{abi} s_{abj} G_{kn}^{-1} + s_{abk} s_{abn} G_{ij}^{-1} \big) / r_{ab}^2$$

$$+ \sum_{a<b} \big(\phi^{**} G_{ij}^{-1} G_{kn}^{-1} - \phi^* \big(G_{ik}^{-1} G_{jn}^{-1} + G_{in}^{-1} G_{jk}^{-1} \big) \big). \tag{5.9}$$

In eqs. (5.8) and (5.9) we have used the symbols * to stand for the operator $V\partial / \partial V$ and the prime ' to stand for the operator $r\partial / \partial r$ as was used earlier. Also Φ_{ij} is given by

$$\Phi_{ij} = 2\partial \Phi / \partial G_{ij} = \sum_{a<b} \big(\phi' s_{abi} s_{abj} / r_{ab}^2 + \phi^* G_{ij}^{-1} \big), \tag{5.10}$$

and C_ϵ is the constant-strain specific heat while γ_{ij} is the Grüneisen tensor $\gamma_{ij} = V(\partial t_{ij} / \partial E)_\epsilon$. These latter two thermodynamic response functions are determined by the *EhN* fluctuation formulas

$$k_B / C_\epsilon = 1 - (1 - 2/(3N)) \langle K^{-1} \rangle \langle K \rangle, \tag{5.11}$$

and

$$h_{0ki}^{-1}h_{0nj}^{-1}\gamma_{ij} = G_{kn}^{-1}Nk_B/C_\epsilon + (3N/2 - 1)\big(\langle \Phi_{kn}\rangle\langle K^{-1}\rangle - \langle \Phi_{kn}K^{-1}\rangle\big). \tag{5.12}$$

The general form of the elastic constant fluctuation formula eq. (5.7) was given and employed by Çağin and Ray [25]. In the thermodynamic limit the elastic constant formula, eq. (5.7), takes the form

$$V_0 h_{0ip}^{-1}h_{0jq}^{-1}h_{0kr}^{-1}h_{0ns}^{-1}C_{pqrs} = -4\delta(M_{in}M_{kn})/k_B T + 2Nk_B T\big(G_{ik}^{-1}G_{jn}^{-1} + G_{in}^{-1}G_{jk}^{-1}\big)$$

$$+ \langle \Phi_{ijkn}\rangle + \Psi_{ijkn}, \tag{5.13}$$

where $M_{ij} = \partial \mathcal{H}/\partial G_{ij}$ is again related to the microscopic stress tensor by $M = -Vh^{-1}\mathcal{S}\tilde{h}^{-1}/2$ and $\mathcal{S}$ is given by

$$\mathcal{S}_{ij} = \sum_a p_{ai}p_{aj}/m_a - \sum_{a<b}\big(\phi' x_{abi}x_{abj}/r_{ab}^2 + \phi^*\delta_{ij}\big) - \Psi^*\delta_{ij}. \tag{5.14}$$

This form for the microscopic stress tensor should be compared with eq. (2.14) for the case when the potential does not depend explicitly on the volume. If we set all * derivatives to zero in eqs. (5.7)–(5.14) then these equations reduce to the form appropriate for a pairwise-additive interatomic potential with no explicit volume dependence.

5.4. Numerical results

For the elastic constant calculation for sodium we performed calculations at three different temperatures: $T = 197.9$, 298.8 and 348.6 K, for a system of 432 particles arranged in a bcc lattice. The potential was truncated at a distance of $R = 23.27a_0$. With this cutoff range the average number of atoms interacting with each atom is 180, that is, the first 11 neighbor shells of the bcc lattice are included. Note that the potential we are using has a long range oscillatory behavior. In order to check if the elastic constants are sensitive to the cutoff range we present results for two different ranges. We will discuss these results later. To determine h_0, we performed simulations using *HtN* molecular dynamics with the tension and pressure equal to zero. At the end of these runs (20000 time steps of 6.85×10^{-16}s each) the average value of h, h_0, was obtained. However, the calculated value of h_0 in these runs gave rise to densities lower than the experimental densities for these temperatures. For instance, the difference between the calculated density and the zero pressure experimental density is 2.3% at 299 K. Since we wanted the elastic constants at the experimental densities we added a small external pressure to the Hamiltonian, $P_{cor}V$, to bring the system to the desired density. The experimental densities were determined from data by Aldhart et al. [39] and Seigel and Quimby [40]. We found that the pressure corrections varied with temperature having the values 1.09, 1.36, and 1.58 kbar at the three temperatures mentioned above. The pressure corrections to the elastic constants are: $C_{11} \rightarrow C_{11} - P_{cor}$, $C_{12} \rightarrow C_{12} + P_{co4}$, and $C_{44} \rightarrow C_{44} - P_{cor}$.

Table 7

Contributions to the adiabatic elastic constants for sodium from the different terms in eq. (5.13) together with experimental values for three different temperatures. The number of particles is 432, the cutoff range is $23.27a_0$, and the time for the averages is 8.22 ps or 12000 time steps. The densities at the three temperatures are 0.989, 0.970 and 0.960 g/cm^3. The elastic constants are given in kbar

| | EhN Molecular Dynamics (eq. (5.13)) | | |
	C_{11}	C_{12}	C_{44}
$T = 197.9$ K			
Pair-potential term	90.38	45.62	63.60
Only volume-dependent	−9.22	11.38	−10.30
Kinetic-energy term	2.83	0.00	1.42
Fluctuation term	−9.01	2.84	−5.79
Subtotal	74.98	59.84	−1.09
Pressure correction	−1.09	1.09	−1.09
Total theory	73.89 ± 0.66	61.93 ± 0.48	47.84 ± 0.83
Experiment	76.5 [a], 81.2 [c]	63.9 [a], 67.9 [c]	50.0 [a], 50.9 [c]
$T = 298.8$ K			
Pair-potential term	89.83	42.51	58.29
Only volume-dependent	−9.63	11.06	−10.34
Kinetic-energy term	4.19	0.00	2.09
Fluctuation term	−10.73	3.12	−8.56
Subtotal	73.66	56.69	41.48
Pressure correction	−1.36	1.36	−1.36
Total theory	72.30 ± 2.27	58.05 ± 1.52	40.12 ± 0.59
Experiment	73.8 [b], 76.9 [c]	62.1 [b], 64.7 [c]	41.9 [b], 43.4 [c]
$T = 348.6$ K			
Pair-potential term	90.83	40.70	55.50
Only volume-dependent	−9.82	11.91	−10.37
Kinetic-energy term	4.83	0.00	2.42
Fluctuation term	−13.81	3.71	−10.36
Subtotal	72.04	55.32	37.19
Pressure correction	−1.58	1.58	−1.58
Total theory	70.46 ± 1.68	56.90 ± 1.80	35.61 ± 0.57
Experiment	74.3 [d]	60.6 [d]	39.6 [d]

[a] ref. [41];
[b] ref. [42];
[c] ref. [43];
[d] ref. [44].

Table 7 presents the results of our calculations of the elastic constants of sodium using eq. (5.13) along with experimental values. In the table, contributions from the pair-potential term, the pure volume-dependent term, the kinetic term, and the fluctuation term are given separately. The results in table 7 were calculated using molecular-dynamics runs of 12000 time steps for a total time of 8.22 ps. Densities corresponding to these temperatures are $\rho = 0.989$, 0.970, and 0.960 g/cm^3. The experimental values are from measurements of Diederich and Trivosonno [41], Daniels [42], Martinson [43], and Fritsch et al. [44]. The percentage differences between the

Table 8
Calculated elastic constants of sodium at 299 K for two different cutoff ranges. The $23.27a_0$ calculation was for 432 particles run for 12000 time steps while the $27.70a_0$ calculation was for 686 particles run for 12000 time steps. The values are in kbar

| | EhN Molecular Dynamics (eq. (5.13)) | | |
	C_{11}	C_{12}	C_{44}
$R_c = 23.27a_0$			
Pair-potential term	89.83	42.51	58.29
Only volume-dependent	−9.63	11.06	−10.34
Kinetic-energy term	4.19	0.00	2.09
Fluctuation term	−10.73	3.12	−8.56
Total without pressure correction	73.66	56.69	41.48
$R_c = 27.70a_0$			
Pair-potential term	90.56	42.87	57.75
Only volume-dependent	−9.63	11.06	−10.34
Kinetic-energy term	4.18	0.00	2.09
Fluctuation term	−14.11	4.26	−8.44
Total without pressure correction	71.00	58.19	41.05

calculated elastic constants with the pressure corrections and the experimental values are 4–8% for all three moduli. Note also that the calculated values show a softening with temperature very similar to the observed values. The softening of the shear modulus is noticeably large as the temperature is increased.

The major contribution to all elastic constants in table 7 comes from the pair-potential term. The pure volume-dependent potential contributions are negative for C_{11} and C_{44} and positive for C_{12}, and all are of the order of magnitude of 10 kbar. Fluctuation contributions are large and negative for C_{11} and C_{44} and positive and small for C_{12}. The fluctuation contribution increases with temperature since the probability distribution of the microscopic stress tensor becomes broader.

5.5. Range dependence

As previously mentioned the model potential we are employing shows an oscillatory long-range behavior. In molecular-dynamics simulations using long-range potentials, a concern is the choice of the cutoff range. With this in mind we have repeated the elastic constant calculation at 299 K for a range of $27.70a_0$ for 12000 time steps. In table 8 we show the results for the two simulations; the $23.27a_0$ run is the same one as in table 7. As seen from table 8 the differences in the values of the elastic constants at these two different ranges are small. These differences are caused by the changes in the pair-potential term and the fluctuation term. Although the changes in the pair-potential term and fluctuation term are large from one range to another the sum, which makes up the elastic constant, remains the same to the accuracy of our calculation. We conclude from the results of table 8 that our calculation using a cutoff range of $23.27a_0$ gives satisfactory results.

Table 9
Comparison between the elastic constants of sodium calculated using the exact fluctuation formula eq. (5.7) and the more common thermodynamic limit formula eq. (5.13). These calculations are for a cutoff range of $17.85a_0$ and 25000 time steps. The values are in kbar

| | EhN Molecular Dynamics (eq. (5.7)) | | |
	C_{11}	C_{12}	C_{44}
Total without pressure correction	70.77	56.71	40.27
	EhN Molecular Dynamics (eq. (5.13))		
	C_{11}	C_{12}	C_{44}
Total without pressure correction	69.33	57.42	39.21

5.6. Comparison of exact and thermodynamic limit formulas

In order to compare the exact elastic constant formula, eq. (5.7) and the formula obtained from eq. (5.7) in the thermodynamic limit, eq. (5.13) we carried out a 25000 time step simulation at the shorter range of $17.85a_0$ using 432 particles at a temperature of 299 K. We calculated C_ϵ/Nk_B and γ_{ij} using eqs. (5.11) and (5.12). Due to cubic symmetry of the bcc crystal only one component of γ_{ij} is nonzero γ. We found $C_\epsilon/Nk_B = 3.278$ (experimental value 3.264, [45]) and $\gamma = 1.251$ (experimental value 1.27, [39]). The elastic constants calculated using eqs. (5.7) and (5.13) are shown in table 9. For all the elastic constants the differences are small. Thus, for the system under study the thermodynamic limit formula gives the same elastic constants to the accuracy of our calculations.

5.7. Comparison with other results

The elastic constants calculated using eq. (5.13) and the sodium potential show a good agreement with experimental values at the three temperatures, 198, 299, and 349 K. The differences between the calculated and experimental values are within 4–8% for all elastic constants. An important feature of this agreement concerns the shear modulus C_{44}. In a previous molecular dynamics calculation [33] the calculated values for C_{44} showed a similar softening with temperature but the values compared to experimental values were quite small. For example, from [33] $C_{44} = 41.7$, 35.4, and 30.2 kbar at temperatures 199, 297 and 340 K, respectively. The differences between these calculated values and the experimental values for C_{44} are considerably larger than the differences found in table 7 for our calculations. Schiferl and Wallace suggested that this large discrepancy in C_{44} is due to the use of only second-order perturbation theory in the derivation of their potential. However, the potential we have used is also derived using second order perturbation theory. We also noticed that the magnitudes of the pair-potential and pure volume-dependent potential contributions to the elastic constants in ref. [33] are much larger than in our calculations. Further study would be required to clarify the large differences between the results obtained from these two potentials.

6. Elastic constants of crystalline silicon

6.1. General discussion

Stillinger and Weber [46] have developed an effective potential-energy function to describe the crystalline and liquid phases of silicon. This potential includes both 2- and 3-body interatomic interactions. Stillinger and Weber used their potential to study the inherent structure underlying the liquid phase of silicon. Since this was one of the first potential to allow the computer simulation study of silicon, it has been used in a number of such studies [46–58]. Of particular interest to us is the work dealing with the determination of the elastic constants of crystalline silicon [48] and amorphous silicon [58].

6.2. Potential of Stillinger and Weber

In a substance where the atoms interact through strong directional bonds, as in the tetrahedral semiconductors, it is necessary to include at least two- and three-body interactions. The two- and three-body interactions arrived at by Stillinger and Weber have the form

$$U_2(r_{ab}) = A\left(Br_{ab}^{-p} - r_{ab}^{-1}\right)h_\beta(r_{ab}), \tag{6.1}$$

$$U_3(r_{ab}, r_{ac}, r_{bc}) = h_{cab} + h_{abc} + h_{bca}, \tag{6.2}$$

$$h_{cab} = \lambda h_\gamma(r_{ab})h_\gamma(r_{ac})\left(\cos\theta_{cab} + \tfrac{1}{3}\right)^2, \tag{6.3}$$

where r_{ab} is the distance between atoms a and b, $h_\delta(r) = \exp(\delta(r-a)^{-1})$ for $r < a$ and vanishes for $r > a$; Θ_{cab} is the angle between the vector r_{ab} and r_{ac}. In these equations r is expressed in units where unit distance corresponds to $\sigma = 2.0951$ Å, the energy is expressed in units where the unit of energy is $\epsilon = 3.4723 \times 10^{-12}$ erg. Stillinger and Weber indicated that they carried out a limited search over the parameters in eqs. (6.1)–(6.3) to obtain the values: $A = 7.049556$, $B = 0.602225$, $p = 4$, $q = 0$, $\beta = 1$, $a = 1.8$, $\lambda = 21$ and $\gamma = 1.2$. The unit of time is chosen as $\sigma(m/\epsilon)^{1/2} = 7.66 \times 10^{-14}$ s, where m is the mass of a silicon atom.

Note that the three-body energy eq. (6.2) vanishes for the perfect tetrahedral angle $\cos\theta = -1/3$ and, therefore, also for the static diamond lattice. An important part of the parameter search carried out by Stillinger and Weber was to ensure that the diamond lattice have the lowest energy compared to several other simple lattices sc, bcc, fcc, ... The three-body energy effectively destabilizes these other lattices.

6.3. Elastic constant formulas

Since the Stillinger–Weber potential can be written in a form where it depends only upon the distances between particles the elastic constant formulas eq. (4.1) and (4.2) are applicable. If eq. (4.1) is written for the Stillinger–Weber potential then we obtain the fluctuation formula

$$V_0 h_{0ip}^{-1} h_{0jq}^{-1} h_{0kr}^{-1} h_{0ns}^{-1} C_{pqrs} = -4\delta\left(M_{ij}M_{kn}\right)/k_{\rm B}T + 2Nk_BT\left(G_{in}^{-1}G_{jk}^{-1} + G_{ik}^{-1}G_{jn}^{-1}\right)$$

$$+ \langle(\text{two-body Born})_{ijkn}\rangle + \langle(\text{three-body Born})_{ijkn}\rangle. \tag{6.4}$$

Table 10

Adiabatic elastic constants of silicon in units of 10^{11} dyne/cm² from a 216 particle simulation. The theoretical values are calculated using the fluctuation formula eq. (6.4) and the experimental values are from the Landolt–Bornstein compilation [59]. The experimental values at $T = 1477$ K are extrapolated values from the data in ref. [59]. The theoretical values are obtained in a molecular dynamics run of 150000 time steps or 115ps. The density of the system at the three temperatures is 2.30, 2.30 and 2.29 g/cm³ and the pressure is zero

| | *EhN* Molecular Dynamics | | |
	C_{11}	C_{12}	C_{44}
$T = 888$ K			
Theory (eq. (6.4))	14.14 ± 0.01	7.52 ± 0.00	5.24 ± 0.84
Experiment	15.75	6.05	7.53
$T = 1164$ K			
Theory (eq. (6.4))	13.73 ± 0.03	7.43 ± 0.01	4.57 ± 1.14
Experiment	15.25	5.90	7.32
$T = 1477$ K			
Theory (eq. (6.4))	13.32 ± 0.01	7.39 ± 0.04	4.20 ± 0.83
Experiment	14.80	5.75	7.00

where $M_{ij} = -Vh^{-1}\mathscr{S}\tilde{h}^{-1}/2$ is the derivative of the particle Hamiltonian with respect to the metric tensor and contains both a two-body and three-body contribution. The two-body Born term has the form given in eq. (4.3) and depends only upon U_2, while the three-body Born term has a similar but somewhat more involved form and depends only on U_3. In discussing the results obtained using eq. (6.4) we shall again break down the result of the calculation into the different terms from this equation, namely the fluctuation term, the kinetic term the two-body Born term and the three-body Born term.

6.4. Numerical results of crystalline silicon

In table 10 we present the results of our calculation of the elastic constants for a 216 particle system at three different temperatures and at zero pressure [48]. At each temperature h_0 was first determined by allowing a well equilibrated system to run in *HtN* molecular dynamics at zero pressure and tension for 5000 time steps with each time step being 7.66×10^{-16}s. The relative standard deviations of h_0 were less than 3×10^{-4}. An analysis of the average of the microscopic pressure tensor in subsequent *EhN* runs with h fixed at this value, indicated that the stress in the system was on the order of tens of atmospheres, which is a negligible stress for silicon. We note than any error in the determination of h_0 has no effect on the applicability of eq. (6.4), but only means that the elastic constants are not those at zero strain but at some small strain.

The system was then equilibrated in the *EhN* form of molecular dynamics with h_0 determined as explained. A run of 150000 timesteps was made at each temperature and data for calculation the averages in eq. (6.4) kept every step. Because of the rapid convergence of the Born terms only 5000 timesteps were used in their determination and then that part of the calculation omitted in the remaining 145000 timesteps.

The results of this calculation are shown in table 10. The elastic constants are given in units of

10^{11} dyne/cm^2 and the experimental values are from the Landolt–Bornstein handbook [59]. As in the previous cases of cubic symmetry the error estimates are standard deviations of symmetry equivalent elastic constants. From the results presented in table 10 we see that the shear moduli C_{44} are 30–40% lower, C_{12} values are about 25% higher, and C_{11} values about 20% lower than the observed values. Note the accuracy of the calculated values is a few-tenths of a percent for C_{11} and C_{12} and a few percent for C_{44}; as we shall see this difference is associated with the convergence of the fluctuation term for the different components.

Although the values of the elastic constants of Stillinger–Weber silicon show significant differences with the observed values, we notice that the softening with increasing temperature of the calculated values is similar to the observed behavior. We also point out that no mechanical information was used in developing the Stillinger–Weber potential, therefore, it is not surprising that the calculated elastic constants show differences from the observed values. These results should be compared with the results of the previous section for sodium where we employed a potential which was developed from first principles and for which the calculated elastic constants show much better agreement with experimental results.

There have been other potentials developed to study silicon using computer simulation, however, no accurate calculations of elastic constants for these potentials are yet available. The embedded-atom method potential discussed by Baskes [60] is a semiempirical potential which uses elastic constant as well as other experimental data to determine its form.

6.5. Elastic constants and internal strain

In order to study the convergence of the elastic constant calculation of silicon we present, in table 11, the symmetry averaged individule terms from eq. (6.4) which when added together make up the elastic constants. This data is for the highest temperature calculation $T = 1477$ K.

The most interesting entry in table 11 is the large value of the fluctuation terms for the shear elastic constants C_{44}. These fluctuation terms are the same order of magnitude as the Born terms. It is well known that for a crystal with more than one particle per unit cell the motion of the

Table 11
The four contributions to the elastic constants of silicon from eq. 6.4 in units of 10^{11} dyne/cm^2 for the highest temperature calculation, 1477 K. Also shown are the static Born values

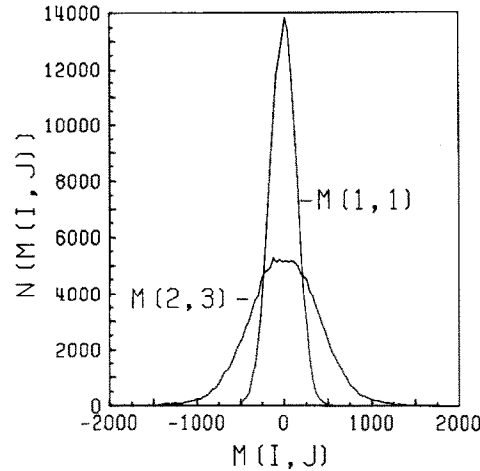| Term	C_{11}	C_{12}	C_{44}
2-body Born	8.00	8.34	8.34
3-body Born	5.65	−8.89	1.64
Kinetic	0.40	0.00	0.20
fluctuation	−0.73	−0.06	−5.98
Total	13.32	7.39	4.20
Static Born Terms			
2-body Born	9.77	9.77	9.77
3-body Born	4.79	−2.39	0.80
Total	14.56	7.38	10.57

Fig. 1. Histogram of M_{11} and M_{23} for the 1477 K, 216 particle simulation. The histogram is constructed using all the data from the 150000 time steps. M_{ij} is given in erg/cm^2. The histograms for M_{22} and M_{33} are similar to M_{11} while those for M_{12} and M_{13} are similar to M_{23}. The histogram have the same general form for the other temperatures and practice numbers studied.

particles within the unit cell may not be homogeneous under a homogeneous deformation of the crystal, that is, the system has an internal strain. This point is clearly discussed by Guttman [61] and is also illustrated by the calculations of Keating [62] for the diamond lattice. Lax [63] also has a detailed discussion of the effect of internal strain on the elastic constants. For the diamond lattice it follows by symmetry that for an applied tension t_{11} the strain within the unit cell is homogeneous. For an applied tension t_{12} the strain within the unit cell is not homogeneous and there is a relative motion of the particles within the unit cell of the same order of magnitude as that induced by the homogeneous strain [61], [62] and [63]. In the fluctuation formula calculation the internal strain shows up as a broader distribution for the M_{23} (or M_{12}, M_{13}) as compared to M_{11} (or M_{22}, M_{33}). In fig. 1 we show the histograms of M_{23} and M_{11} over the 150000 time step calculation used to calculate the elastic constants. Fig. 1 clearly shows that the distribution for M_{23} is broader than that for M_{11}. Since the variances of these distributions are just the fluctuation contribution to the elastic constants, $\delta(M_{23}M_{23})$ for C_{44} and $\delta(M_{11}M_{11})$ for C_{11}, this shows why the fluctuation term is large for C_{44}. In the earlier examples we presented the crystal structures were fcc for the nearest neighbor Lennard-Jones interaction and bcc for sodium. Both of these are primitive Bravais lattices and there is no internal strain.

Another interesting result associated with internal strain is the zero temperature limit of the fluctuation formula eq. (6.4). The kinetic term approaches zero as T goes to zero and the Born terms approach their static limit, since the atoms are located near their ideal lattice positions as the temperature approaches zero. The fluctuation term is, however, divided by T so it must go to zero at least as T so that the elastic constants remain finite at low temperature. If the fluctuation term does vary as T then the limit of this term as T goes to zero may be nonzero. While we have not evaluated eq.(6.4) analytically in the low temperature limit we can consider a static method of calculating the elastic constants of silicon where we assume that the crystal deforms homogeneously on all length scales even within the unit cell under an infinitesimal strain. Under

Table 12

The fluctuation terms, static Born terms, and the sum of these two terms compared to the elastic constants of silicon calculated using eq. (6.4); all quantities have been extrapolated to 0 K by least-squares linear regression. Although it is not claimed that this extrapolation is very accurate, it is accurate enough to illustrate the point that the fluctuation-term contribution to the elastic constant C_{44} is nonzero at 0 K, whereas the fluctuation-term contribution to C_{11} and C_{12} is zero at 0 K. These results are associated with the internal strain in the diamond crystal under homogeneous deformation. The entries are given in units of 10^{11} dyne/cm^2

	C_{11}	C_{12}	C_{44}
		Fluctuation	
$T = 0$ K	0.2	0.04	-4.6
		Static Born	
$T = 0$ K	15.1	7.6	10.9
		Sum of fluctuation and static Born	
$T = 0$ K	15.3	7.6	6.3
		Elastic constants	
$T = 0$ K	15.4	7.7	6.7

this assumption one obtains a formula which may be use to calculate the $T = 0$ K elastic constants for primitive Bravais lattices or when there is no internal strain

$$V_0 h_{0ip}^{-1} h_{0jq}^{-1} h_{0kr}^{-1} h_{0ns}^{-1} C_{pqrs} = (\text{two-body Born})_{ijkn} + (\text{three-body Born})_{ijkn}. \tag{6.5}$$

Eq. (6.5) is just eq. (6.4) without the kinetic term, the fluctuation term and with no averages on the Born terms; the Born terms are evaluated at the ideal lattice positions of the crystal. Eq. (6.5) is derived by two differentiations of the potential energy, like the formula of the bulk modulus is derived in lattice statics. In deriving eq. (6.5) we have assumed that the deformation is homogeneous on all scales, including those smaller than the unit cell. The strain associated with a t_{11} tension is homogeneous for the diamond lattice so that eq. (6.5) may be used to calculate the zero temperature elastic constants C_{11} and C_{12} of crystalline diamond. However, for a tension t_{12} the strain is not homogeneous within the unit cell and eq. (6.5) cannot be used to calculate the zero temperature elastic constants C_{44}.

In order to see how the internal strain effects our numerical results we can extrapolate the elastic constants to zero temperature using the results given in table 10 and compare with the static Born terms which are calculated using eq. (6.5). In table 12 we show the fluctuation contributions to the elastic constants, the static Born terms, and the elastic constants extrapolated to 0 K using least-square linear regression. Although this is not a highly accurate procedure since we are extrapolating over a large temperature region, it is accurate enough to illustrate the effect of the internal strain on the zero temperature limit of eq. (6.4). Table 12 shows that the fluctuation terms at 0 K are consistent with the value zero for the elastic constants C_{11} and C_{12} whereas the fluctuation-term contribution to C_{44} extrapolates to about half value of the Born term, namely -4.6. If we add the fluctuation terms and the static Born terms in table 12 we obtain the third row, which should be compared with the elastic constants constants extrapolated to 0 K shown in the last row. These results are consistent with the static Born terms giving the

entire contribution to the elastic constants at 0 K for C_{11} and C_{12} but for C_{44} the fluctuation term is an important contribution to the shear modulus at 0 K. This is another way of saying that eq. (6.5) can be used to calculate the 0 K elastic constants C_{11} and C_{12} for crystalline silicon but cannot be used to calculate the shear modulus C_{44} because of the contribution of the internal strain. If the tension applied to a system induces an internal strain, then the fluctuation term contributes more to the elastic constants determined by this tension because of the broader distribution of the microscopic stress tensor; also the zero temperature limit of the fluctuation contribution may be nonzero and contribute in an important way to the value of the elastic constants as is shown in table 12. For a crystal structure with more particles per unit cell than the diamond lattice the fluctuation term may be important for all elastic constants. We shall illustrate this in the next section for a model of amorphous silicon which has 216 particles per unit cell and in which the fluctuation term is large for both C_{11} and C_{44}.

6.6. Number dependence

In order to check on the elastic constants dependence on particle number we also carried out a simulation with 1728 particles, $1728 = 2^3 \times 216$, [48]. This calculation gave the same results for the elastic constants to the accuracy of our calculations.

6.7. Numerical convergence of fluctuations

As we have mentioned previously the molecular dynamics runs used to calculate the elastic constants of crystalline silicon were of duration 150000 time steps or 115 ps. The reason that we ran these simulation for such a long time was to study the convergence of the fluctuation terms in this system. When we made this calculation our previous experience had been for primitive Bravais lattices and the fluctuation terms gave much smaller contributions to the elastic constants than the C_{44} contribution for silicon shown in table 11.

In order to illustrate the convergence of the calculation with time we present in fig. 2 the fluctuation contribution to the elastic constants, C_{44}, $4\delta(M_{23}M_{23})h_0/k_BT$, C_{55}, $4\delta(M_{13}M_{13})h_0/k_BT$, and C_{66}, $4\delta(M_{12}M_{12})h_0/k_BT$ for the 1477 K calculation. We see that the averages are fairly stable after approximately 50000 time steps. Thus, values of the elastic constants as good as those obtained from the entire simulation could have been obtained after only 50000 time steps. However, we note that the values of the fluctuation terms for C_{44}, C_{55}, and C_{66} in fig. 2 are not converged to the same values even after 150000 time steps; these values are 5.08, 6.06 and 6.80, respectively. A study of the fluctuation terms for the other elastic constants show that they are more nearly converged to a common value and since they are much smaller in magnitude compared to the accurately known Born terms this explains why the error estimates for these elastic constants are much smaller in table 11. In order to reduce the error estimate of the shear elastic constant C_{44} one would have to run the simulation even further so that the quantities in fig. 2 were more nearly converged to a common value. Given the quality of the potential function being employed this would certainly not be justified in this particular case.

6.8. Direct calculation of elastic constants

As a check on the calculation of the elastic constants of silicon discussed in the previous section we also calculated these quantities in a way independent of the fluctuation formulas [64].
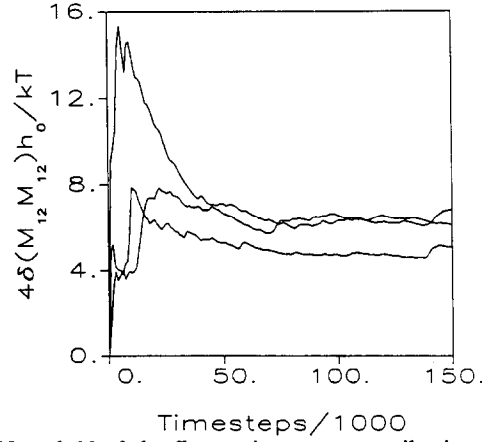
Fig. 2. The shear components 44, 55 and 66 of the fluctuation-term contribution of the elastic constants of silicon at 1477 K. This shows the convergence of these symmetry equivalent quantities which determines the accuracy of the calculation. Notice that we could stop the calculation at 50000 time steps and obtain essentially the same values for the elastic constants.

Using the *HtN* form of molecular dynamics, it is possible to apply any external tension to the system and determine the strain. From the tension–strain relation we can determine the elastic constants by extrapolation to zero tension. This method was employed by Sprik et al. [16] for the Lennard-Jones nearest neighbor potential. For small applied tensions we can write

$$t_{ij} = -C_{ijkn}\epsilon_{kn}, \tag{6.6}$$

where we have used the summation convention. Inverting eq. (6.6) we have

$$\epsilon_{ij} = -S_{ijkn}t_{kn}, \tag{6.7}$$

where S_{ijkn} is the compliance tensor. For a system with cubic symmetry the compliance and elastic constants are related by

$$C_{44} = 1/S_{44}, \tag{6.8}$$

$$C_{11} = (S_{11} + S_{12})/((S_{11} - S_{12})(S_{11} + 2S_{12})), \tag{6.9}$$

$$C_{12} = -S_{12}/((S_{11} - S_{12})(S_{11} + 2S_{12})). \tag{6.10}$$

By appropriately choosing the non-zero components of t to be applied, we can simplify eq. (6.7) and obtain values for the components of S. For, example, if all components of t except the 11 component are zero, then eq. (6.7) reduces to the three equations

$$\epsilon_{11} = -S_{11}t_{11}, \tag{6.11a}$$

$$\epsilon_{12} = -S_{12}t_{11}, \tag{6.11b}$$

$$\epsilon_{13} = -S_{13}t_{11}. \tag{6.11c}$$

Since we know the value of the applied tension and we determine the strain we may solve eqs. (6.11) for S_{11}, S_{12} and S_{13}. We then may use eqs. (6.9) and (6.10) to calculate the values of C_{11} and C_{12}. Similarly, if an external tension is applied whose diagonal elements are zero and whose off diagonal elements are all equal then we may obtain three independent values for S_{44} from which we may determine C_{44} from eq. (6.8). By cubic symmetry the values of S_{11}, S_{22} and S_{33} are equal for the unstressed crystal, however, in the stressed crystal the symmetry is tetragonal and not cubic. For small stresses (and therefore small strains) the differences between the elastic constants for cubic and tetragonal symmetry will be small. If we make a series of determinations of the elastic constants at different stresses, then the zero stress limit of the values calculated should yield the elastic constants.

In order to apply this direct method, the previously equilibrated sample of 216 silicon atoms at 1477 K was used, with various stresses applied to it. Also to check for sample size we carried out the same calculation for 1728 particles. The two particle numbers yielded equivalent results so we shall discuss only the 216 particle cases.

After the application of each stress, the system was equilibrated for 2000 time steps. The system was then allowed to run undisturbed for 6000 timesteps, during which the average strain was evaluated. Values of C for that stress were then calculated.

Although the main interest of this study was in the zero stress limit, it was found that the calculated elastic constants converged poorly with small tensions while under larger tensions they converged more rapidly. The poor convergence of the elastic constants is associated with the small strain which is difficult to evaluate accurately. Therefore, the results presented here are for

Table 13

Values of the elastic constants of silicon at 1477 K at different tensions calculated using the direct method, which corresponds to assuming Hooke's law. Also shown are the values extrapolated to zero tension by linear least-squares regression. The tension is given in arbitrary units and the elastic constants are given in units of 10^{11} dyne/cm^2

Tension	C_{11}	AVE.	C_{12}	AVE.	C_{44}	AVE.
0.1	13.9		7.79		4.47	
	12.3	13.1	5.99	6.89	4.72	
					4.54	4.58
0.3	13.3		7.25		4.52	
	13.6	13.4	7.60	7.43	4.45	
					4.47	4.48
0.5	14.4		8.87		4.39	
	15.0	14.7	8.37	8.62	4.38	
					4.42	4.39
0.7	14.5		8.45		4.16	
	15.1	14.8	9.06	8.75	4.15	
					4.18	4.16
0.0 (least squares)	12.6		6.6		4.7	

tensions sufficiently large so that the strain converged in the 6000 time steps used for its determination. The results of these calculations are shown in table 13. Performing linear regression on these data we obtain the zero tension limit elastic constants: $C_{11} = 12.6$, $C_{12} = 6.6$, and $C_{44} = 4.7$ in units of 10^{11} dyne/cm^2. The corresponding values determined from fluctuation formulas are 13.32, 7.39 and 4.2 from table 10. These values are in reasonably good agreement. Note from table 13 that the three independently calculated values of C_{44} are close together for each tension and the zero tension limit is more precise than the fluctuation formula result in table 10. The fluctuation formula gives, in principle, an exact determination of the elastic constants, although one must wait for convergence to obtain a given accuracy. The agreement obtained by the two methods, the direct and fluctuation formula, suggests that they do calculate approximately the same physical quantity.

In terms of computational efficiency, the two methods are comparable. The fluctuation method was run for 15000 time steps, although as noted previously, the same results would have been obtained had the run been ended at 50000 time steps. The direct method required 8000 total time steps for each tension, for a total of 80000 time steps at each temperature.

7. Elastic constants of amorphous silicon

7.1. General discussion

As the another example of calculating elastic constants we discuss the calculation of the elastic constants of a model of amorphous silicon [58]. In ref. [65] we formed a model of amorphous silicon by rapidly cooling ($\approx 10^{13}$ K/s) a well equilibrated liquid. Our formation procedure made use of *HPN* molecular dynamics using the Stillinger–Weber potential. As was shown in ref. [65] the geometrical structure factor gave excellent agreement with the structure factor of amorphous silicon determined using neutron scattering. Also a study of the structure factor, at the Bragg vectors for the crystal, shows that the samples contain no memory of the crystalline phase. Although we have produced several such samples and, are still studying the formation process, we shall discuss the elastic constants for only one of the samples.

In table 14 we show the experimental and calculated elastic constants of crystalline silicon at room temperature. The experimental values are from the Landolt–Bornstein compilation [59] whereas the calculated values are extrapolated to room temperature from the values in table 10. Also shown in table 14 are the average Young's modulus and the maximum and minimum shear velocities as determined from the elastic constants. All elastic constants are in units of 10^{11} dyne/cm^2 while the shear velocities are in units of 10^5 cm/s. As shown previously the values calculated using the Stillinger–Weber potential are different by $\sim 30\%$ for some of the elastic constants. In the present section we shall show that the change in the elastic properties between the crystalline and amorphous phases is very accurately modeled by our model of amorphous silicon.

7.2. Elastic constants

In table 15 we show our calculated values of the elastic constants C_{11} and C_{44} of a 216 atom model of amorphous silicon; further details of the model may be obtained by consulting [65]. In

Table 14

The calculated and observed elastic properties of crystalline silicon at room temperature. The elastic constants are given in units of 10^{11} dyne/cm^2 while the shear velocities are given in units of 10^5 cm/s. The experimental values are from ref. [59] whereas the calculated values are extrapolated from table 10. The shear velocity v_{T1} is determined from the shear modulus $(C_{11} - C_{12})/2$ and v_{T2} is determined from C_{44}.

	c-Si (exp) [a]	c-Si (theory) [b]
C_{11}	16.6	15.0
C_{12}	6.4	7.6
C_{44}	7.9	6.0
Y_{av}	16.0	12.4
B	9.8	10.1
v_{T1}	4.7	4.0
v_{T2}	5.8	5.1

[a] ref. [59];
[b] ref. [48].

table 15 we give only two symmetry averaged elastic constants C_{11} and C_{44} since for an isotropic system there are only two independent elastic constants; the isotropy condition $C_{11} - 2C_{44} = C_{12}$, may be used to determine C_{12}. Using the fluctuation formulas we can calculate C_{12} independently and check on the isotropy condition. For C_{12} for the 478 K calculation we found $C_{12} = 8.3$, whereas for $C_{12} - 2C_{44}$ we find from table 15 the value 8.0. Thus, our system satisfies the isotropy condition to the accuracy of our calculation. The same conclusion is reached for the low temperature run. Note from table 15 the significant softening of the elastic constants with increasing temperature; unfortunately there are no experimental results at the higher temperature to check on this softening.

In table 16 we show a breakdown of the 294 K calculation in terms of the individule terms that make up eq. (6.5). Notice the large value of the fluctuation terms for both C_{11} and C_{44}; the internal strain shows up in both of these elastic constants. Also the three-body Born term is much larger than for crystalline silicon shown in table 11.

Table 15

Two independent elastic constants of a 216 atom sample of amorphous silicon calculated using *EhN* fluctuation formulas. The 294 K calculation was for 50000 time steps (38.3 ps) while the 478 K calculation was for 80000 time steps (61.2 ps). The pressure of the system is zero and the density is $0.98\rho_c$ where ρ_c is the density of crystalline silicon, 2.33 g/cm^3. Note the significant softening with increasing temperature. There are no experimental results available at the higher temperature. The elastic constants are in units of 10^{11} dyne/cm^2

	C_{11}	C_{44}
$T = 294$ K eq. (6.4)	15.20 ± 0.9	3.29 ± 0.2
$T = 478$ K eq. (6.4)	13.44 ± 0.7	2.27 ± 0.2

Table 16
The contribution of the various terms of eq. (6.4) to the calculated room temperature elastic constants of amorphous silicon given in table 15. Note the large fluctuation contribution associated with the nonprimitive Bravais lattice of the amorphous sample. The 478 K calculation shows the same qualitative results.

Term	C_{11}	C_{44}
2-body Born	8.96	2.89
3-body Born	13.63	4.44
Kinetic	0.08	0.04
fluctuation	−7.48	−4.08
Total	15.19	3.29

7.3. Comparison with experiment

The bulk modulus of the sample of amorphous silicon may be found from

$$B = C_{11} - 4C_{44}/3, \tag{7.1}$$

while the shear modulus μ and Young's modulus Y are given by

$$\mu = C_{44}, \tag{7.2}$$

and

$$Y = 3B\mu/(B + \mu/3). \tag{7.3}$$

Here we have used the fact that the pressure is zero in our sample of amorphous silicon [65].

The elastic properties of amorphous silicon have been studied experimentally by Grimsditch, Senn, Winterling and Brodsky [66], Senn, Winterling and Grimsditch [67] and Tan, Berry and Crowder [68]. In table 17 we show the comparison between the calculated and observed

Table 17
The experimental Rayleigh surface wave velocity v_R and the Young's modulus Y for amorphous silicon compared to our calculated value at 294 K. Also shown are the differences between the crystalline minimum shear velocity from table 14 and the Rayleigh velocity, and the difference between the average Young's modulus in the crystal from table 14 and the Young's modulus of the amorphous material. Note the excellent agreement in these changes between the crystalline and amorphous phases. The elastic constants are in units of 10^{11} dyne/cm^2 while the velocities are in units of 10^5 cm/s

	a-Si (exp) [a,b]	a-Si (theory)
v_R	4.2	3.6
$v_{T1} - v_R$	0.5	0.4
Y	12.4	8.9
$Y_{av} - Y$	3.6	3.6

[a] ref. [67];
[b] ref. [68].

properties of amorphous silicon. The observed Rayleigh surface wave velocity is 4.2×10^5 cm/s [67] whereas we obtain 3.6×10^5 cm/s in our calculation. The observed Young's modulus is 12.4×10^{11} dyne/cm^2 whereas we obtain 8.9×10^{11} dyne/cm^2. Also shown are the differences between the crystalline shear velocity v_{T1} from table 14 and the surface wave velocity v_R in the amorphous system; the observed difference is 0.5×10^5 cm/s while our calculations give a difference of 0.4×10^5 cm/s. The difference between the average Young's modulus in the crystal and in the amorphous phase is 3.6×10^{11} dyne/cm^2 observed to 3.5×10^{11} dyne/cm^2 calculated. Thus, while the absolute values calculated for v_R and Y for the amorphous model are not so close to the observed values, the changes are very close to the observed changes. Note that this conclusion is unchanged if we use v_{T2} or the average of v_{T1} and v_{T2} for the comparison. This shows that the Stillinger–Weber potential yields the correct *softening* in the elastic properties in going from the crystalline solid to the amorphous solid. This suggests that the softening of the elastic properties depends more strongly on the structure differences than the details of the potential.

7.4. Comparison with other work

Guttman [69] determined the elastic constants of amorphous silicon by homogeneously deforming random network models and measuring the change in the energy for a series of strains. The elastic constants were determined from derivatives of the energy with respect to the strain. Guttman made use of Keating potential [62] in these calculations. The models employed by Guttman were composed of 16 and 54 atoms with periodic boundary conditions, that he had constructed earlier. Guttman's results for the Young's modulus, shear modulus and bulk modulus of amorphous silicon are: $Y = 0.74(\alpha/r_0)$, $\mu = 0.30(\alpha/r_0)$, and $B = 0.46(\alpha/r_0)$, where α is the bond-stretching force constant in the Keating potential and r_0 is the interatomic distance in the crystal. The Keating potential bond-bending force constant β was chosen to satisfy $\beta/\alpha = 0.3$ which implies that the elastic constants of the crystalline silicon may fit to about 5%. If we fit the crystalline value of C_{11} then we find $\alpha/r_0 = 20.2$. Using this value for α/r_0 we determine the values $Y = 14.9 \times 10^{11}$ dyne/cm^2, $\mu = 6.05 \times 10^{11}$ dyne/cm^2 and $B = 9.28 \times 10^{11}$ dyne/cm^2 from Guttman's work. The Rayleigh surface wave velocity determined from these elastic constants is $v_R = 4.7 \times 10^5$ cm/s. Recall that the observed Young's modulus is 12.4×10^{11} dyne/cm^2 while the observed Rayleigh velocity is 4.2×10^5 cm/s. Thus, Guttman's values are too high for both quantities. Recall that the Stillinger–Weber calculations gave values too small for both quantities. When compared to the average crystalline value Guttman's Young's modulus softens by 1.1×10^{11} dyne/cm^2 where the Rayleigh surface wave velocity is the same as the shear velocity v_{T1} in the crystal. Recall that in our calculations using the Stillinger–Weber potential one obtains excellent agreement in the changes between crystalline and amorphous values for Y and v_R.

8. Summary and conclusions

We have presented a discussion of the calculation of elastic constants using different forms of molecular dynamics. Our conclusion is that the fluctuation formulas in the *EhN* and *ThN* forms

of molecular dynamics furnish the best way of calculating elastic constants in molecular dynamics. We have illustrated two simple ways of deriving fluctuation formulas in statistical mechanics and we have calculated the elastic constants using both the *ThN* and *EhN* forms of molecular dynamics. We have also recently presented *EhN* and *ThN* fluctuation formulas giving the third order elastic constants and have shown by explicit calculation that they furnish a practical way of calculating these quantities [70]. In this calculation the time to obtain an answer of a given accuracy is determined by the convergence of the tuple fluctuation of the microscopic stress tensor.

The Lennard-Jones nearest neighbor potential was used to illustrate that the molecular dynamics fluctuation formulas furnish a practical way to calculate elastic constants. By comparing with Cowley's Monte Carlo calculations it appears that the molecular dynamics and Monte Carlo calculations require approximately the same amount of computer time for the same accuracy, however, more work should be done to compare the two methods.

By using a first principle potential to model sodium we have demonstrated that the molecular dynamics fluctuation formulas can give results that are as accurate as the experimental results, even giving the correct temperature dependence.

In order to illustrate the fluctuation formulas for a 3-body potential we presented calculations of the elastic constants of silicon using the Stillinger–Weber potential. Earlier work by Klein and Murphy [71] calculated the elastic constants of rare gas solids using 3-body potentials and the Monte Carlo method. The values of the elastic constants of silicon are not nearly as accurate as for sodium but we did find that the change in the elastic properties in going from crystalline to amorphous silicon was accurately modeled by our calculation. This seems to imply that the elastic softening in going from crystalline to amorphous silicon is associated more with the structural changes in the system than the details of the potential.

One important aspect of the silicon calculation was the appearance of the internal stain for a non primitive Bravais lattice. This aspect is automatically taken care of in the fluctuation formula calculation since under stress fluctuations the atoms will tend to "oscillate" about positions of zero net force; how the particle moves in the simulation is determined by the force law and the positions of the other particles.

A direct calculation of the elastic constants of silicon was presented using *HtN* molecular dynamics. While it is always possible to use this method we feel the fluctuation formula method is better. Since the Born terms converge very rapidly one can calculate the elastic constants in a parasitic manner, requiring very little extra computer time, if one is carrying out equilibrium molecular dynamics runs for other reasons. It is also perhaps easier to estimate the errors in the calculation using the fluctuation formulas.

As another example of molecular dynamics work using the *EhN* fluctuation formulas to calculate elastic constants we mention the work of Hsieh and Yip [72] on the study of changes in the elastic constants of a Lennard-Jones system when going from the crystalline to the amorphous state.

An aspect of the elastic constant calculation that we have omitted in the present work is the calculation of quantum corrections to the value of the elastic constants. All of the results of this paper have used classical statistical mechanics, whereas, we should use quantum mechanics. In our calculation of the elastic constants of sodium the quantum corrections are apparently small, however, one should include an estimate of their magnitude. Klein and Murphy [71] consider

quantum corrections in their calculations on rare gas solid and give references to earlier work in this area.

The fully quantum mechanical generalization of our classical calculations is probably the work by Nielsen and Martin [73–75], see also the paper by Baroni, Giannozzi and Testa [76]. Nielsen and Martin use density functional theory together with the quantum virial theorem to determine elastic properties by numerical differentiation of the energy, calculated for different strains. This is the analog of the direct method of calculating elastic constants present in section 6.8. In ref. [76] the authors present a quantum calculation that is similar to the fluctuation formula method; the elastic constants are calculated in a single calculation using formulas obtained from Nielsen's and Martin's by using perturbation theory based on the strain. This is similar to our derivation of the fluctuation formulas by differentiation with respect to the metric tensor G_{ij} which is directly related to the strain. These quantum calculations and the theory they use are formulated at zero temperature, therefore, there does not seem to be a way to use these methods, as they are now formulated, to study the temperature dependence of the elastic properties of matter. The Car–Parrinello molecular dynamics density functional hybrid theory combined with the fluctuation formulas of this paper would seem to be the best way to study the temperature dependence, at high enough temperatures, of the elastic properties of matter at the present time, however, until this method becomes practical, from the point of view of computer time, the methods we have discussed in this paper together with a good potential will be useful.

Acknowledgements

References

[1] R. Car and M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471.
[2] D.R. Squire, A.C. Holt and W.G. Hoover, Physica 42 (1969) 388.
[3] W.G. Hoover, A.C. Holt and D.R. Squire Physica 44 (1969) 437.
[4] A.C. Holt, W.G. Hoover, S.G. Gray and D.R. Shortle, Physica 49 (1970) 61.
[5] N.W. Ashcroft and N.D. Mermin, Solid State Physics (Saunders, Philadelphia, 1976).
[6] M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Clarendon Press, Oxford, 1954).
[7] G. Venkataraman, L.A. Feldkamp and V.C. Sahni, Dynamics of Perfect Crystals (M.I.T. Press, Cambridge, 1975).
[8] A.A. Maradudin, E.W. Montroll, G.H. Weiss and I.P. Ipatova, Theory of Lattice Dynamics in the Harmonic Approximation, 2nd ed. (Academic Press, New York, 1971).
[9] H.C. Andersen, J. Chem. Phys. 72 (1980) 2384.
[10] M. Parrinello and A. Rahman, Phys. Rev. Lett. 45 (1980) 1196.
[11] M. Parrinello and A. Rahman, J. Appl. Phys. 52 (1981) 7182.
[12] J.R. Ray and A. Rahman, J. Chem. Phys. 80 (1984) 4423.

[13] R.N. Thurston, in: Physical Acoustic, Vol. 1, ed. W.P. Mason (Academic Press, 1964) Part A.
[14] S. Nosé, Mol. Phys. 52 (1984) 255; J. Chem. Phys. 81 (1984) 511.
[15] J.R. Ray and A. Rahman, J. Chem. Phys. 82 (1985) 4243.
[16] M. Sprik, R.W. Impey and M.L. Klein, Phys. Rev. B 29 (1984) 4368.
[17] M. Parrinello and A. Rahman, J. Chem. Phys. 76 (1982) 2662.
[18] J.R. Ray, J. Appl. Phys. 53 (1982) 6441.
[19] J.R. Ray and H.W. Graben, Mol. Phys. 43 (1981) 1293.
[20] R. Becker, Theory of Heat, 2nd ed. (Springer, New York, 1967).
[21] A. Munster, Statistical Thermodynamics, vol. 1 (Springer, New York, 1969).
[22] E.M. Pearson, T. Halicioglu and W.A. Tiller, Phys. Rev. A 32 (1985) 3030.
[23] J.R. Ray and H.W. Graben, Phys. Rev. A 34 (1986) 2517.
[24] T. Çağin and J.R. Ray, Phys. Rev. A 37 (1988) 247.
[25] M. Parrinello and A. Rahman, unpublished.
[26] S. Nosé and M.L. Klein, Mol. Phys. 50 (1983) 1055.
[27] J.R. Ray, M.C. Moody and A. Rahman, Phys. Rev. B32 (1985) 733.
[28] J.R. Ray, M.C. Moody and A. Rahman, Phys. Rev. B33 (1986) 895.
[29] E.R. Cowley, Phys. Rev. B 28 (1983) 3160.
[30] T. Çağin and J.R. Ray, Phys. Rev. B 37 (1988) 699.
[31] H.R. Glyde and R. Taylor, Phys. Rev. B 5 (1972) 1206.
[32] S.S. Cohen, M.L. Klein, M.S. Duesbery and R. Taylor, J. Phys. F 6 (1976) 337.
[33] S.K. Schiferl and D.C. Wallace, Phys. Rev. B 31 (1985) 7662.
[34] D.C. Wallace, Phys. Rev. 176 (1968) 832.
[35] J.L. Lebowitz, J.K. Percus and L. Verlet, Phys. Rev. 153 (1967) 250.
[36] D.L. Price, K.S. Swingi and M.P. Tosi, Phys. Rev. B 2 (1970) 2983.
[37] Wei-Mei Shyu, K.S. Swingi and M.P. Tosi, Phys. Rev. B 3 (1971) 237.
[38] D.L. Price, Phys. Rev. A 4 (1971) 358.
[39] W. Aldhart, G. Frisch, A. Heidemann and E. Luscher, Phys. Lett. A 47 (1974) 91.
[40] S. Seigel and S.L. Quimby, Phys. Rev. 54 (1938) 76.
[41] M.E. Diederich and J. Trivosonno, J. Chem. Phys. Solids 27 (1966) 637.
[42] W.B. Daniels, Phys. Rev. 119 (1960) 1246.
[43] R.H. Martinson, Phys. Rev. 178 (1969) 902.
[44] G. Fritsch, F. Geipel, and A. Prasetyo, J. Chem. Phys. Solids 34 (1971) 1961.
[45] D.L. Martin, Phys. Rev. 154 (1967) 571.
[46] F.H. Stillinger and T.A. Weber, Phys. Rev. B 31 (1985) 5262.
[47] F.F. Abraham and J. Broughton, Phys. Rev. Lett. 56 (1986) 734.
[48] M.D. Kluge, J.R. Ray and A. Rahman, J. Chem. Phys. 85 (1986) 4028.
[49] K. Ding and H.C. Andersen, Phys. Rev. B 34 (1986) 6987.
[50] M. Schneider, I.K. Schuller and A. Rahman, Phys. Rev. B 36 (1987) 1340.
[51] U. Landman, W.D. Luedka, R.N. Barnett, C.L. Cleveland, M.W. Ribarsky, E. Arnold. S. Ramesh, H. Baumgart,
     A. Martinez and B. Kahn, Phys. Rev. Lett. 56 (1986) 734.
[52] B.W. Dodson, Phys. Rev. B. 33 (1986) 7361.
[53] B.W. Dodson and P.A. Taylor, Appl. Phys. Lett. 49 (1986) 642.
[54] J.Q. Broughton and F.F. Abraham, J. Crys. Growth 75 (1986) 613.
[55] M.D. Kluge, J.R. Ray and A. Rahman, J. Chem. Phys. 87 (1987) 2336.
[56] B.P. Feuston, R.K. Kalia and P. Vashishta, Phys. Rev. B 35 (1987) 6222.
[57] J.Q. Broughton and X.P. Li, Phys. Rev. B 35 (1987) 9120.
[58] M.D. Kluge and J.R. Ray, Phys. Rev. B 37 (1988) 4132.
[59] Landolt–Bornstein: Crystal and Solid State Physics, vol. 11, ed. K.-Hellwege (Springer, Berlin, 1979) p. 116.
[60] M.I. Baskes, Phys. Rev. Lett. 59 (1987) 2666.
[61] L. Guttman, Phys. Rev. 19 (1979) 6062.
[62] P.N. Keating, Phys. Rev. 145 (1966) 637.
[63] M. Lax, Symmetry Principles in Solid State and Molecular Physics, (John Wiley, New York, 1974).

[64] M.D. Kluge, PhD dissertation, Clemson University 1987, available from University Microfilms, Ann Arbor, Michigan.
[65] M.D. Kluge, J.R. Ray and A. Rahman, Phys. Rev. B 36 (1987) 4234.
[66] M. Grimsditch, W. Senn, G. Winterling, and M. Brodsky, Solid State Commun. 26 (1978) 229.
[67] W. Senn, G. Winterling, M. Grimsditch and M. Brodsky, Inst. Phys. Conf. Ser. No. 43, 1979, chap. 21.
[68] S.I. Tan, B.S. Berry and B.L. Crowder, Appl. Phys. Lett. 20 (1972) 88.
[69] L. Guttman, Solid State Commun. 24 (1977) 211.
[70] T. Çağin and J.R. Ray, preprint.
[71] M.L. Klein and R.D. Murphy. Phys. Rev. B 6 (1972) 2433.
[72] H. Hsieh and S. Yip, Phys. Rev. Lett. 59 (1987) 2760.
[73] O.H. Nielsen and R.M. Martin, Phys. Rev. Lett. 50 (1983) 697.
[74] O.H. Nielsen and R.M. Martin, Phys. Rev. B 32 (1985) 3780.
[75] O.H. Nielsen and R.M. Martin, Phys. Rev. B 32 (1985) 3792.
[76] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. 59 (1987) 2662.