PHYSICAL REVIEW B VOLUME 38, NUMBER 12 15 OCTOBER 1988-II

Third-order elastic constants from molecular dynamics: Theory and an example calculation

Tahir Çağin* and John R. Ray
Kinard Laboratory of Physics, Clemson University, Clemson, South Carolina 29634-1911
(Received 6 May 1988)

In earlier work, fluctuation formulas have been derived which allow the calculation of the second-order elastic constants of solids with use of molecular-dynamics computer simulations; explicit calculations have shown that these fluctuation formulas furnish an efficient method of obtaining the second-order elastic constants of crystalline and amorphous solids. In this paper, we present the statistical fluctuation formulas containing the isothermal and adiabatic third-order elastic constants. As we show, these formulas also enable one to efficiently calculate the third-order elastic constants of solids, using molecular-dynamics computer simulation. We illustrate the usefulness of these new fluctuation formulas by an explicit calculation of the adiabatic second- and third-order elastic constants of argon at 20.5 K. We also give the pressure derivatives of second-order elastic constants at $T=20.5$ K.

I. INTRODUCTION

Higher-order elastic constants, especially third-order elastic (TOE) constants, play an important role in solid-state physics. The knowledge of higher-order elastic constants can be used in determining the pressure dependence of second-order elastic (SOE) constants, the equation of state, and thermal properties of a solid. Also, they can be used to assess the importance of the anharmonic contributions to the given elastic properties.

The statistical fluctuation formulas relating the SOE constants to the fluctuations of the microscopic stress tensor have been found to furnish an efficient and accurate way to obtain SOE constants from computer simulations.[1-6] In Ref. 1 the Monte Carlo method was employed to determine the SOE constants, whereas in Refs. 2-6 the molecular-dynamics method was employed. The molecular-dynamics and Monte Carlo methods have an advantage over harmonic lattice dynamics, in obtaining elastic constants, since these methods represent an exact (classical) calculation of elastic constants which contains the full anharmonic contribution.

Motivated by the efficiency of the method and accurate results obtained for the SOE constants of different systems in Refs. 2-6, we have derived the statistical fluctuation formulas containing adiabatic and isothermal TOE constants to be used in molecular dynamics. One may use these formulas to calculate the elastic constants in order to compare with experimentally observed values, thereby checking the validity of potential employed to model the system, or, instead of performing experiments, that is, for conditions where experiments have not been performed or cannot easily be performed. In the latter case we assume that an accurate interaction potential is known for the system.

The paper is organized as follows. In the next section we introduce the microcanonical, *EhN*, and canonical, *ThN*, forms of molecular dynamics and establish our notation. In Sec. III we present the fluctuation formulas for the adiabatic and isothermal TOE constants. In Sec. IV we present a sample molecular-dynamics calculation of TOE constants of a model of argon by using a nearest-neighbor Lennard-Jones potential to model the interactions between argon atoms. Finally, in Sec. V we discuss the implications and results of the calculation.

II. FINITE ELASTICITY AND FORMS OF MOLECULAR DYNAMICS

The molecular-dynamics method developed by Parrinello and Rahman[7,8] is extensively used for studying structural phase transformations in solids. However, this method can also be used to calculate the equilibrium properties of a system; the trajectories of this form of molecular dynamics generate an ensemble with constant enthalpy *H*, constant thermodynamic tension *t*, of finite elasticity theory, and constant particle number *N*, or, in short, the *HtN* ensemble. More details of this ensemble were given by Ray and Rahman,[9] where they have shown how the theory can be made consistent with the theory of finite elasticity.[10]

It was shown by Parrinello and Rahman,[11] and later by Ray[12] that the adiabatic elastic constants can be obtained from the strain fluctuations in *HtN* molecular dynamics through the equation

$$(C^{s}{}_{ijkl})^{-1}=V_0(\langle \varepsilon_{ij}\varepsilon_{kl}\rangle-\langle \varepsilon_{ij}\rangle\langle \varepsilon_{kl}\rangle)/k_BT\ , \qquad (2.1)$$

where ε_{ij} is the strain tensor, and V_0 is the reference volume of the N particle system. In Ref. 12, Ray gave the statistical fluctuation formula for adiabatic TOE constants in terms of strain fluctuations. However, it has been found by Sprik *et al.*[13] and by others[14] that from the point of convergence to statistically significant results Eq. (2.1) does not furnish a satisfactory method of calculating elastic constants because of the slow convergence of the strain fluctuations.

In Ref. 9, Ray and Rahman discussed not only the *HtN* form of molecular dynamics, but also *EhN* molecular dynamics; the latter is a generalization of the familiar *EVN* or microcanonical ensemble. In the *EhN* form of molecular dynamics the 3×3 matrix, h, which has as its columns the elements of the vectors **a**, **b**, and **c** that span the molecular dynamics cell, $h=(\mathbf{a},\mathbf{b},\mathbf{c})$, is kept constant; this keeps not only the volume $[=\det(h)]$ constant, but also holds fixed the shape of periodically repeating 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[9] presented the *EhN* ensemble fluctuation formula for the adiabatic SOE constants, which were later employed in Refs. 2–6. In a later paper, Ray and Rahman[15] combined these ideas with Nosé's isothermal molecular dynamics[16,17] and discussed the *ThN* form of molecular dynamics.

Next, we shall briefly discuss the *EhN* and *ThN* forms of molecular dynamics, introduce our notation, and give the thermodynamic definitions of the isothermal and adiabatic elastic constants.

Consider a system described by the Hamiltonian $\mathcal{H}$,

$$\mathcal{H}(\mathbf{x},\mathbf{p})=\sum_{a=1}^{N}\frac{p_a^2}{2m_a}+\sum_{a<b}U(r_{ab}) , \tag{2.2}$$

We first carry out the canonical transformations

$$s_{ai}=h^{-1}{}_{ij}x_{aj} , \tag{2.3}$$

$$\pi_{ai}=h_{ij}p_{aj} , \tag{2.4}$$

where h_{ij} are the elements of the h tensor introduced above. The metric tensor G is defined by $G=\tilde{h}h$, where the tilde indicates matrix transposition. With these new canonical variables s_{ai},π_{ai},the Hamiltonian has the form

$$\mathcal{H}(s,\pi,h)=\sum_{a}\frac{\pi_{ai}G_{ij}^{-1}\pi_{aj}}{2m_a}+\sum_{a<b}U(r_{ab}) . \tag{2.5}$$

The distances r_{ab} are related to the scaled coordinate differences s_{abi} by

$$r_{ab}^2=s_{abi}G_{ij}s_{abj} . \tag{2.6}$$

The strain tensor ε, in terms of the metric G, and h_0, the reference value of h, is given by

$$\varepsilon=\tfrac{1}{2}(\tilde{h}_0^{-1}Gh_0^{-1}-1) . \tag{2.7}$$

Although the reference value of h, h_0, is arbitrary in the theory, we shall usually take it to be the value of h when the system is in a strain-free state. The microscopic stress tensor P_{ij} is defined as

$$VP_{ij}=\sum_{a}\frac{p_{ai}p_{aj}}{m_a}-\sum_{a<b}\frac{1}{r_{ab}}\frac{\partial U}{\partial r_{ab}}x_{abi}x_{abj} . \tag{2.8}$$

To establish the connection with the theory of finite elasticity, we start from the thermodynamic law

$$T\,dS=dE+V_0\mathrm{Tr}(t\,d\varepsilon) . \tag{2.9}$$

Note that we have used the Parrinello-Rahman choice for the sign of the thermodynamic tension; t_{ij} is positive for compressive loading. From Eq. (2.7) we can connect the change in strain to the change in metric,

$$d\varepsilon=\tfrac{1}{2}\tilde{h}_0^{-1}\,dG\,h_0^{-1} . \tag{2.10}$$

When we use Eq. (2.10) in Eq. (2.9), we obtain

$$T\,dS=dE+\tfrac{1}{2}V_0\mathrm{Tr}(h_0^{-1}t\tilde{h}_0^{-1}\,dG) , \tag{2.11}$$

where $V_0=\det(h_0)$. From the last equation we can write

$$\left[\frac{\partial E}{\partial G_{ij}}\right]_S=-\tfrac{1}{2}V_0(h_0^{-1}t\tilde{h}_0^{-1})_{ij} . \tag{2.12}$$

The adiabatic theorem in the *EhN* ensemble has the form

$$\left[\frac{\partial E}{\partial G_{ij}}\right]_S=\left\langle\frac{\partial \mathcal{H}}{\partial G_{ij}}\right\rangle , \tag{2.13}$$

where $\mathcal{H}$ is given by Eq. (2.5). Combining these last two equations, we can relate the derivative of the Hamiltonian to the thermodynamic tension tensor

$$\left\langle\frac{\partial \mathcal{H}}{\partial G_{ij}}\right\rangle=-\tfrac{1}{2}V_0(h_0^{-1}t\tilde{h}_0^{-1})_{ij} . \tag{2.14}$$

Calculating $\partial\mathcal{H}/\partial G_{ij}$ from Eq. (2.5) yields

$$\begin{aligned}M_{kl}=\frac{\partial \mathcal{H}}{\partial G_{kl}}&=-\tfrac{1}{2}\sum \pi_{ai}\pi_{aj}G^{-1}{}_{ik}G^{-1}{}_{lj}/m_a\\&\quad+\tfrac{1}{2}\sum_{a<b}\frac{1}{r_{ab}}\frac{\partial U}{\partial r_{ab}}s_{abk}s_{abl}\\&=-\tfrac{1}{2}(h^{-1}VP\tilde{h}^{-1})_{ij} ,\end{aligned} \tag{2.15}$$

where P_{ij} is the microscopic stress tensor, Eq. (2.8), and M_{kl} is a tensor which appears later in the statistical fluctuation formulas for the elastic constants. We define another tensor of fourth rank, N_{klmn}, as

$$N_{klmn}=\frac{\partial^2\mathcal{H}}{\partial G_{kl}\,\partial G_{mn}} , \tag{2.16}$$

where the explicit form of N_{klmn} is given as follows:

$$\begin{aligned}4N_{klmn}=&\sum_{a}\pi_{ai}\pi_{aj}[(G^{-1}{}_{im}G^{-1}{}_{nk}+G^{-1}{}_{in}G^{-1}{}_{mk})G^{-1}{}_{lj}+G^{-1}{}_{ik}(G^{-1}{}_{lm}G^{-1}{}_{nj}+G^{-1}{}_{ln}G^{-1}{}_{mj})]/m_a\\&+\sum_{a<b}\left[\frac{1}{r_{ab}^2}\frac{\partial^2 U}{\partial r_{ab}^2}-\frac{1}{r_{ab}^3}\frac{\partial U}{\partial r_{ab}}\right]s_{abk}s_{abl}s_{abm}s_{abn} .\end{aligned} \tag{2.17}$$

The second- and third-order elastic constants can be determined from the tension-versus-strain relations as follows:

$$C_{ijkl} = -\frac{\partial t_{ij}}{\partial \varepsilon_{kl}} \tag{2.18}$$

and

$$C_{ijklmn} = \frac{\partial C_{ijkl}}{\partial \varepsilon_{mn}} = -\frac{\partial^2 t_{ij}}{\partial \varepsilon_{kl}\,\partial \varepsilon_{mn}} \ . \tag{2.19}$$

If these derivatives are calculated at constant temperature, we obtain the isothermal elastic constants, whereas if they are calculated at constant entropy we obtain the adiabatic elastic constants.

III. THIRD-ORDER ELASTIC CONSTANTS

A. Isothermal third-order elastic constants

The partition function in the canonical ensemble has the form

$$Z = \frac{1}{C}\int e^{-\mathcal{H}/k_B T}\, d\tau \ , \tag{3.1}$$

where C is a constant and $d\tau$ the differential volume element in $6N$-dimensional phase space. The fundamental connection between thermodynamics and statistical mechanics is obtained through the equation relating the partition function to the Helmholtz free energy:

$$F = -k_B T \ln Z \ . \tag{3.2}$$

From the thermodynamic law,

$$dF = -S\, dT - V_0 \mathrm{Tr}(t\, d\varepsilon) \ , \tag{3.3}$$

we obtain the statistical expression for the tension,

$$\begin{aligned} t_{ij} &= -\frac{1}{V_0}\frac{\partial F}{\partial \varepsilon_{ij}} \\ &= -\frac{2h_{0ik}h_{0jl}}{V_0}\frac{1}{Z}\int \frac{\partial \mathcal{H}}{\partial G_{kl}} e^{-\mathcal{H}/k_B T}\, d\tau \\ &= -\frac{2h_{0ik}h_{0jl}}{V_0}\langle M_{kl}\rangle \ . \end{aligned} \tag{3.4}$$

Using the definition of elastic constants given by Eq. (2.18) and Eq. (2.17), we obtain the fluctuation formula for the isothermal SOE constants ${}^{T}C_{mnpq}$

$$V_0 (h_0^{-1})_{im}(h_0^{-1})_{jn}(h_0^{-1})_{kp}(h_0^{-1})_{lq}\, {}^{T}C_{mnpq} = 4\langle N_{ijkl}\rangle - \frac{4}{k_B T}\delta(M_{ij}M_{kl}) \ , \tag{3.5}$$

where the tensor M and its relation to the microscopic stress tensor is given by Eq. (2.15), and the explicit form of $\langle N_{ijkl}\rangle$ is given by

$$4\langle N_{ijkl}\rangle = 2Nk_B T(G^{-1}{}_{ik}G^{-1}{}_{lj} + G^{-1}{}_{il}G^{-1}{}_{kj}) + \left\langle \sum_{a<b}\left[\frac{1}{r_{ab}^2}\frac{\partial^2 U}{\partial r_{ab}^2} - \frac{1}{r_{ab}^3}\frac{\partial U}{\partial r_{ab}}\right] s_{abi}s_{abj}s_{abk}s_{abl}\right\rangle \ . \tag{3.6}$$

The first terms in Eq. (3.6) are called the kinetic-energy terms, while the second terms that are linear in the potential are called the Born terms. These terms, when added to the fluctuation terms in Eq. (3.5), give the elastic constants. By taking a further strain derivative of Eq. (3.5), we obtain the following formula for the isothermal TOE constants ${}^{T}C_{pqrsuv}$:

$$\begin{aligned} V_0 (h_0^{-1})_{ip}(h_0^{-1})_{jq}(h_0^{-1})_{kr}(h_0^{-1})_{ls}(h_0^{-1})_{mu}(h_0^{-1})_{nv}\, {}^{T}C_{pqrsuv} &= 8\left\langle \frac{\partial^3 \mathcal{H}}{\partial G_{ij}\,\partial G_{kl}\,\partial G_{mn}}\right\rangle \\ &\quad - \frac{8}{k_B T}[\delta(N_{ijkl}M_{mn}) + \delta(N_{ijmn}M_{kl}) + \delta(N_{klmn}M_{ij})] \\ &\quad + \frac{8}{(k_B T)^2}\delta(M_{ij}M_{kl}M_{mn}) \ , \end{aligned} \tag{3.7}$$

where $\delta(N_{ijkl}M_{mn})$ and $\delta(M_{ij}M_{kl}M_{mn})$ are fluctuation terms, which are defined as follows:

$$\delta(AB) = \langle AB\rangle - \langle A\rangle\langle B\rangle \ , \tag{3.8}$$

$$\begin{aligned} \delta(ABC) &= \langle ABC\rangle - \langle AB\rangle\langle C\rangle - \langle AC\rangle\langle B\rangle \\ &\quad - \langle BC\rangle\langle A\rangle + 2\langle A\rangle\langle B\rangle\langle C\rangle \ . \end{aligned} \tag{3.9}$$

We will give the explicit form of the first term on the right-hand side of Eq. (3.7) in the next subsection.

B. Adiabatic third-order elastic constants

In deriving the adiabatic elastic-constant–fluctuation formulas, one can use either the adiabatic differentiation method[18] or the Laplace-transform method.[19–21] These two methods are equivalent in the thermodynamic, large-N limit.[5,20,21] We refer the readers to the references for the details of the calculational methods and give the results for the adiabatic TOE constants.

The statistical fluctuation formulas containing the adiabatic SOE constants have exactly the same form as Eq. (3.5), except the averages are *EhN* averages instead of *ThN* averages. As we shall see later, this same type of correspondence does not hold for the higher-order elastic constants. If we use Eq. (3.5) to calculate the adiabatic elastic constants, we refer to this as the adiabatic option. The adiabatic TOE constants are given through the following equation:

$$V_0(h_0^{-1})_{ip}(h_0^{-1})_{jq}(h_0^{-1})_{kr}(h_0^{-1})_{ls}(h_0^{-1})_{mu}(h_0^{-1})_{nv}\,{}^{S}C_{pqrsuv}$$
$$=8\left\langle \frac{\partial^3\mathcal{H}}{\partial G_{ij}\,\partial G_{kl}\,\partial G_{mn}}\right\rangle-\frac{8}{k_BT}[\delta(N_{ijkl}M_{mn})+\delta(N_{ijmn}M_{kl})+\delta(N_{klmn}M_{ij})]$$
$$+\frac{8}{(k_BT)^2}\delta(M_{ij}M_{kl}M_{mn})+\frac{8}{k_BT^2}\left[\frac{\partial T}{\partial G_{mn}}\right]_S\delta(M_{ij}M_{kl})\ . \qquad (3.10)$$

The first term on the right-hand side of Eq. (3.10) is the linear term in $\mathcal{H}$ which contains the kinetic- and potential-energy (Born terms) contributions to the TOE constants. This term has the following explicit form:

$$8\left\langle \frac{\partial^3\mathcal{H}}{\partial G_{ij}\partial G_{kl}\partial G_{mn}}\right\rangle=-3Nk_BT\ A_{ijklmn}+\left\langle \sum_{a<b}\chi s_{abi}s_{abj}s_{abk}s_{abl}s_{abm}s_{abn}\right\rangle\ , \qquad (3.11)$$

where A_{ijklmn} is given by

$$A_{ijklmn}=(G^{-1}{}_{im}G^{-1}{}_{ln}G^{-1}{}_{jk}+G^{-1}{}_{im}G^{-1}{}_{kn}G^{-1}{}_{jl}+G^{-1}{}_{in}G^{-1}{}_{km}G^{-1}{}_{jl}+G^{-1}{}_{in}G^{-1}{}_{lm}G^{-1}{}_{jk}$$
$$+G^{-1}{}_{ik}G^{-1}{}_{lm}G^{-1}{}_{jn}+G^{-1}{}_{ik}G^{-1}{}_{ln}G^{-1}{}_{jm}+G^{-1}{}_{il}G^{-1}{}_{km}G^{-1}{}_{jn}+G^{-1}{}_{il}G^{-1}{}_{kn}G^{-1}{}_{jm})\ , \qquad (3.12)$$

and χ is

$$\chi=\frac{1}{r_{ab}^3}\frac{\partial^3U}{\partial r_{ab}^3}-\frac{3}{r_{ab}^4}\frac{\partial^2U}{\partial r_{ab}^2}+\frac{3}{r_{ab}^5}\frac{\partial U}{\partial r_{ab}}\ . \qquad (3.13)$$

In Eq. (3.11) we have assumed that the potential U is a pairwise-additive central potential, but the extension of the theory to more general potentials[4–6] is trivial. Note that, in contrast to the fluctuation formulas for the SOE constants, the fluctuation formulas for the TOE constants do not have the same form in the *EhN* and *ThN* ensembles, as can be seen by comparing Eqs. (3.7) and (3.10). Equations (3.7) and (3.10) are very general expressions for the TOE constants in the sense that they are applicable to systems with any or no symmetry, including amorphous systems as well as systems under strain. We obtain the formulas for zero strain by taking $h=h_0$, i.e., replacing G by G_0. For example, Eq. (3.10) becomes, in this limit,

$${}^{s}C_{ijklmn}=-\frac{3Nk_BT}{V_0}D_{ijklmn}+\frac{1}{V_0}\left\langle \sum\chi x_{abi}x_{abj}x_{abk}x_{abl}x_{abm}x_{abn}\right\rangle+\frac{V_0}{k_BT}[\delta(R_{ijkl}P_{mn})+\delta(R_{ijmn}P_{kl})+\delta(R_{lkmn}P_{ij})]$$
$$-\left[\frac{V_0}{k_BT}\right]^2\delta(P_{ij}P_{kl}P_{mn})+\frac{V_0}{k_BT^2}\left[\frac{\partial T}{\partial\varepsilon_{mn}}\right]\delta(P_{ij}P_{kl})\ . \qquad (3.14)$$

We shall call the first terms on the right-hand side of Eq. (3.14) the kinetic-energy terms (D), the second term the Born term (linear in U), and the last three terms fluctuation terms, which we denote F_1 [$\delta(RP)$], F_2 [$\delta(PPP)$], and F_3 [$\delta(PP)$], respectively. The explicit forms of D_{ijklmn} and R_{ijkl} are given as follows:

$$D_{ijklmn}=(\delta_{im}\delta_{ln}\delta_{jk}+\delta_{im}\delta_{kn}\delta_{jl}+\delta_{in}\delta_{km}\delta_{jl}+\delta_{in}\delta_{lm}\delta_{jk}+\delta_{ik}\delta_{lm}\delta_{jn}+\delta_{ik}\delta_{ln}\delta_{jm}+\delta_{il}\delta_{km}\delta_{jn}+\delta_{il}\delta_{kn}\delta_{jm}) \qquad (3.15)$$

and

$$V_0R_{ijkl}=\sum_a\frac{1}{m_a}(p_{aj}p_{ak}\delta_{il}+p_{aj}p_{al}\delta_{ik}+p_{ai}p_{al}\delta_{jk}+p_{ai}p_{ak}\delta_{jl})+\sum_{a<b}\left[\frac{1}{r_{ab}^2}\frac{\partial^2U}{\partial r_{ab}^2}-\frac{1}{r_{ab}^3}\frac{\partial U}{\partial r_{ab}}\right]x_{abi}x_{abj}x_{abk}x_{abl}\ . \qquad (3.16)$$

The temperature derivative in the last term in Eq. (3.14) can be calculated by using the *EhN* statistical fluctuation formula,

$$\frac{1}{T}\left[\frac{\partial T}{\partial\varepsilon_{ij}}\right]_S=-\tfrac{2}{3}\delta_{ij}+\frac{2V_0}{3N(k_BT)^2}\delta(KP_{ij})\ , \qquad (3.17)$$

where K is the kinetic energy of the system.

IV. THIRD-ORDER ELASTIC CONSTANTS OF ARGON FROM MOLECULAR DYNAMICS

In order to test the applicability and efficiency of the statistical fluctuation formula (3.10) for the third-order elastic constants, we have calculated the adiabatic TOE constants of a model argon. The system of 500 argon atoms interact through a nearest-neighbor (12,6) Lennard-Jones potential:

$$U(r)=4\varepsilon\left[\left[\frac{\sigma}{r}\right]^{12}-\left[\frac{\sigma}{r}\right]^{6}\right]\ , \qquad (4.1)$$

where $\varepsilon=2.35\times10^{-14}$ erg, $\varepsilon/k_B=170.2$ K, and $\sigma=3.3035$ Å. Presently, no experimental values for the higher-order elastic constants are reported for the rare-gas solids. However, Mock and Rose[22] have calculated third- and fourth-order elastic constants of all inert-gas solids at 0 K using harmonic lattice dynamics. In con-

TABLE I. Symmetry-averaged adiabatic SOE constants of argon at $T=20.5$ K. The density of the system is $\rho=1.794$ g/cm^3. The calculations are over 80 000 time steps with $\Delta t=0.0004\tau$, where τ is 1.240 56 ps. All entries are in 10^9 dyn/cm^2.

	C_{11}	C_{12}	C_{44}
Fluctuation	-2.28	-0.85	-2.04
Born term	43.70	21.74	21.74
Kinetic energy	0.61	0	0.30
Total (Theor.)	42.03	20.89	20.00
Experimental	46.8,[a] 51.9[b] 42.0,[c] 39.1[d]	12.2,[a] 13.6[b] 18.0,[c] 19.4[d]	12.2,[a] 15.6[b] 15.3,[c] 19.0[d]
Av. (Expt.)	44.9	15.8	15.5

[a] Reference 24.
[b] Reference 25.
[c] Reference 26.
[d] References 27 and 28.

trast to lattice dynamics, molecular-dynamics calculations using Eqs. (3.7) or (3.10) take all interactions into account exactly (within the assumption of a given force law and classical mechanics); thus, it includes anharmonic and finite-temperature effects in an exact manner.

A. Method of calculation

We calculated the TOE constants at $T=20.5$ K (0.12 in reduced units) for a system of 500 argon atoms arranged in a fcc lattice, with each particle interacting with its 12 first-nearest neighbors only.

To determine h_0, we performed a simulation with variable-size and -shape (HtN) molecular dynamics with the tension (or stress) equal to zero. At the end of this run (24 000 time steps, each being 0.0004τ, where $\tau=1.240\,56$ ps) the average value of h, i.e., h_0, was obtained, which yields the zero-pressure density of 1.794 g/cm^3 [the experimental value for the density at $T=20$ K is 1.7641 g/cm^3 (from Peterson, Batchelder, and Simmons[23])].

Due to the symmetry of the fcc crystal, only six of the 20 nonzero TOE constants are independent. In Voigt notation they are

$$\begin{aligned}
&C_{111}=C_{222}=C_{333}\ ,\\
&C_{112}=C_{113}=C_{122}=C_{133}=C_{223}=C_{233}\ ,\\
&C_{123}\ ,\\
&C_{144}=C_{255}=C_{366}\ ,\\
&C_{155}=C_{166}=C_{244}=C_{266}=C_{344}=C_{355}\ ,\\
&C_{456}\ .
\end{aligned}\tag{4.2}$$

Using Eq. (3.14) we have calculated these 20 elastic constants independently. Also, for a check of the calculation we calculated C_{114}, which should be, and was, to the accuracy of calculation, zero. Calculating these 21 elastic constants independently allowed us to follow the convergence of the calculation. At the end of the calculation we used these independently determined values to calculate the symmetry-averaged TOE constants.

B. Results

We present the result of our calculation of adiabatic SOE constants at $T=20.5$ K in Table I. These results were calculated using Eq. (3.5) and the adiabatic option. In the table the kinetic-energy terms, fluctuation terms, and potential-energy (Born) terms are tabulated separately. These quantities are calculated with a molecular-dynamics run of 80 000 time steps (39.70 ps). In the same table we also give the experimental values taken from Moeller and Squire,[24] Gsanger *et al.*,[25] Keeler and Batchelder,[26] and Meixner *et al.*[27,28] As seen from these, the experimental values for the SOE constants exhibit a wide variation from experiment to experiment.

In Ref. 2, Ray, Moody, and Rahman have calculated the adiabatic SOE constant of argon at $T^*=0.298$ (dimensionless). They give the results in terms of Nk_BT/V. Converting the calculated SOE constants in Ref. 2 to the Lennard-Jones parameters used here gives $C_{11}=33.16$ kbar, $C_{12}=17.15$ kbar, and $C_{44}=15.00$ kbar for a temperature of $T=50.7$ K and a density of $\rho=1.687$ g/cm^3. Comparison of our calculation at $T=20.5$ K with these results obtained at $T=50.7$ K shows the correct softening behavior for elastic constants as the temperature is elevated.

In Table II we present the results of our calculation of the adiabatic TOE constants for argon, which are calcu-

TABLE II. Symmetry-averaged adiabatic TOE constants of argon at $T=20.5$ K, $\rho=1.794$ g/cm^3. The calculation is performed at zero pressure. The 0 K lattice dynamics results are from Ref. 22. All entries are in 10^9 dyn/cm^2.

	C_{111}	C_{112}	C_{123}	C_{114}	C_{155}	C_{456}
F_1	57.03	25.68	3.61	-5.66	43.46	-5.34
F_2	10.52	2.97	15.11	-14.13	-15.71	-8.61
F_3	6.83	2.53	2.53	6.10	6.10	0
Kinetic energy	-3.66	0	0	0	-0.46	-0.46
Born term	-531.06	-261.05	-1.84	-1.84	-261.05	-1.84
Total (Theor.)	-460.34	-229.87	16.88	-15.53	-227.66	-15.80
0 K (static)	-447	-223	0	0	-223	0
0 K lattice dynamics	-479	-236	1.18	-13.0	-231	0

TABLE III. Time evaluation of some of the symmetry-averaged Born terms for second- and third-order elastic constants. All entries are in molecular-dynamics units, i.e., ε/σ^3.

Steps	C_{11}	C_{12}	C_{111}	C_{112}	C_{123}
500	67.12	33.39	−815.54	−400.77	−2.89
1000	67.07	33.37	−814.94	−400.44	−2.85
1500	67.07	33.36	−814.98	−400.66	−2.82
2000	67.06	33.36	−814.98	−400.65	−2.81
10 000	67.04	33.34	−814.78	−400.45	−2.83
20 000	67.03	33.34	−814.72	−400.47	−2.84
30 000	67.03	33.34	−814.70	−400.45	−2.83
40 000	67.04	33.35	−814.70	−400.45	−2.83
50 000	67.04	33.35	−814.71	−400.49	−2.83
60 000	67.04	33.35	−814.70	−400.50	−2.83
70 000	67.04	33.35	−814.71	−400.45	−2.82
80 000	67.04	33.35	−814.70	−400.44	−2.82

lated in the same run as the results in Table I. In Table II we tabulate contributions from each term appearing in Eq. (3.14) separately, along with the static calculation results at 0 K obtained by using only the Born terms evaluated with the particles at their ideal lattice positions. Also given are the lattice dynamics results from Ref. 22. By inspecting Table II for the temperature variation of the Born terms, we see a substantial change with temperature; this change is about 20% of the 0-K values for C_{111}, C_{112}, and C_{155}. In addition, the overall contribution of fluctuation terms, the sum of F_1, F_2, and F_3, is considerable, about 20% for C_{111} and 15% for C_{112}.

C. Calculational efficiency

The Born terms for the TOE constants converges as fast as the Born terms of the SOE-constant calculation, which can be seen from Table III, where we tabulated the time evolution of a few of the symmetry-averaged Born terms for both second- and third-order elastic constants. Even though we have continued calculating and averaging the Born terms for the TOE constants throughout the calculation, we could have averaged them only for the first 1000 time steps, and obtained the same values. This is important because the Born terms are calculated within the force loop for each interaction and take considerable time. Thus, removing the calculation of the Born terms for the TOE constants after 1000 steps increases the efficiency. Note that one must still calculate the second derivatives of the potential in the force loop because of the fluctuation term F_1.

The length of the calculation is determined by the convergence of the fluctuation terms, which has been found earlier for the SOE-constant calculations.[14] The fluctuation term F_1 containing the tensors R_{ijkl} and P_{mn} has converged as fast as the fluctuation term of the SOE constants, i.e., $\delta(P_{ij},P_{kl})$, that is, within 30 000 steps. Thus, after sufficient accuracy for this term is obtained, removing these terms will reduce the simulation to a standard molecular-dynamics calculation, with only the first derivatives of the potential being calculated in the force loop. As one might guess, the slowest convergence has been observed in the triple-fluctuation term F_2 containing the microscopic stress tensor, i.e., $\delta(P_{ij}P_{kl}P_{mn})$, which is also the least accurate term in the calculation and determines the estimated errors in the values.

D. Pressure dependence of elastic constants

Using the zero-pressure second- and third-order elastic constants, we can calculate the pressure derivatives of the SOE constants of our model of argon at 20.5 K.

Birch[29] and later Ghate,[30,31] extending Murnaghan's treatment of finite deformation of isotropic solids,[32,33] obtained the expressions for the SOE constants of cubic crystals under finite hydrostatic pressure in terms of zero-pressure second- and higher-order elastic constants. In these expressions, the ratio of the pressure P and the zero-pressure bulk modulus B is used as the expansion parameter. If we define the expansion parameter η as

$$\eta = -P/3B = -P/(C_{11}+2C_{12}) , \tag{4.3}$$

then the effective SOE constants of a cubic crystal under the hydrostatic pressure P are given by

$$\begin{aligned} C'_{11} &= C_{11}+\eta(2C_{11}+2C_{12}+C_{111}+2C_{112}) , \\ C'_{12} &= C_{12}+\eta(-C_{11}-C_{12}+2C_{112}+2C_{123}) , \\ C'_{44} &= C_{44}+\eta(C_{11}+2C_{12}+C_{44}+C_{144}+2C_{155}) , \end{aligned} \tag{4.4}$$

to the first order in η. The primed quantities represent the effective SOE constants, whereas the unprimed quantities represent zero-pressure elastic constants.

Thus the pressure derivatives of the SOE constants could be obtained from Eq. (4.4),

$$\begin{aligned} \frac{dC'_{11}}{dP} &= -\frac{2C_{11}+2C_{12}+C_{111}+2C_{112}}{C_{11}+2C_{12}} , \\ \frac{dC'_{12}}{dP} &= -\frac{-C_{11}-C_{12}+2C_{112}+2C_{123}}{C_{11}+2C_{12}} , \\ \frac{dC'_{44}}{dP} &= -\frac{C_{11}+2C_{12}+C_{44}+C_{144}+2C_{155}}{C_{11}+2C_{12}} . \end{aligned} \tag{4.5}$$

Using the calculated values for the zero-pressure second-and third-order elastic constants of argon in Eq. (4.5), we have obtained the pressure derivatives of the SOE constants. They are

$$\frac{dC'_{11}}{dP}=9.41,\quad \frac{dC'_{12}}{dP}=6.03,\quad \frac{dC'_{44}}{dP}=4.01\ . \qquad (4.6)$$

V. CONCLUDING REMARKS

We have given statistical fluctuation formulas for the adiabatic and isothermal TOE constants and written these equations out explicitly for a pairwise-additive central potential. The extension to more general potentials is straightforward. In order to test whether these formulas furnish a practical method for calculating higher-order elastic constants, we performed a simulation using a nearest-neighbor Lennard-Jones model of argon. The results show that the method gives an efficient way of calculating higher-order elastic properties of solids. The length of the calculation is determined by the time required for the convergence of triple fluctuations of the microscopic stress tensor.

The extension of these results to higher than third-order elastic constants is also straightforward, although perhaps not of much practical interest at the present time.

ACKNOWLEDGMENTS

One of us (T.C.) would like to thank Dr. M. J. Skove for helpful discussions. The computations were carried out on the Clemson University Computer System. We thank Dr. C. J. Duckenfield and his staff for making these facilities available for this project.

---

*Present address: Department of Chemistry, University of Houston, Houston, TX 77204-5641.

[1] D. R. Squire, A. C. Holt, and W. G. Hoover, Physica **42**, 388 (1969).

[2] J. R. Ray, M. C. Moody, and A. Rahman, Phys. Rev. B **32**, 733 (1985).

[3] J. R. Ray, M. C. Moody, and A. Rahman, Phys. Rev. B **33**, 895 (1986).

[4] M. D. Kluge, J. R. Ray, and A. Rahman, J. Chem. Phys. **85**, 4028 (1986).

[5] T. Çağin and J. R. Ray, Phys. Rev. B **37**, 699 (1988).

[6] M. D. Kluge and J. R. Ray, Phys. Rev. B **37**, 4132 (1988).

[7] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980).

[8] M. Parrinello and A. Rahman, J. Appl. Phys. **80**, 7182 (1981).

[9] J. R. Ray and A. Rahman, J. Chem. Phys. **80**, 4423 (1984).

[10] R. N. Thurston, in *Physical Acoustics,* edited by W. P. Mason (Academic, New York, 1964), Vol. 1, Pt. A.

[11] M. Parrinello and A. Rahman, J. Chem. Phys. **76**, 2662 (1982).

[12] J. R. Ray, J. Appl. Phys. **53**, 6441 (1982).

[13] M. Sprik, R. W. Impey, and M. L. Klein, Phys. Rev. B **24**, 4368 (1984).

[14] J. R. Ray, Comput. Phys. Rep. **8**, 109 (1988).

[15] J. R. Ray and A. Rahman, J. Chem. Phys. **82**, 4243 (1985).

[16] S. Nosé, Mol. Phys. **52**, 255 (1984).

[17] S. Nosé, J. Chem. Phys. **81**, 511 (1985).

[18] J. R. Ray and H. W. Graben, Mol. Phys. **43**, 1293 (1981).

[19] E. M. Pearson, T. Halicioglu, and H. A. Tiller, Phys. Rev. A **32**, 3030 (1985).

[20] J. R. Ray and H. W. Graben, Phys. Rev. A **34**, 2517 (1986).

[21] T. Çağin and J. R. Ray, Phys. Rev. A **37**, 247 (1988).

[22] W. Mock, Jr. and M. F. Rose, Phys. Status Solidi **38**, 317 (1976).

[23] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).

[24] H. R. Moeller and C. F. Squire, Phys. Rev. **151**, 689 (1966).

[25] M. Gsanger, H. Egger, and E. Lüscher, Phys. Lett. **27A**, 695 (1968).

[26] G. J. Keeler and D. N. Batchelder, J. Phys. C **3**, 510 (1970).

[27] H. Meixner, P. Leiderer, and E. Lüscher, Phys. Lett. **37A**, 39 (1971).

[28] H. Meixner, P. Leiderer, P. Berberich, and E. Lüscher, Phys. Lett. **40A**, 257 (1972).

[29] F. Birch, Phys. Rev. **71**, 809 (1947).

[30] P. B. Ghate, Phys. Rev. **139**, A1666 (1965).

[31] P. B. Ghate, Phys. Status Solidi **14**, 325 (1966).

[32] F. D. Murnaghan, Am. J. Math. **49**, 235 (1937).

[33] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (Dover, New York, 1967).