PHYSICAL REVIEW A VOLUME 46, NUMBER 8 15 OCTOBER 1992

Monte Carlo simulations in the isoenthalpic-isotension-isobaric ensemble

Patrick J. Fay and John R. Ray
Kinard Laboratory of Physics, Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634-1911

(Received 19 May 1992)

We discuss simulations using a recently derived Monte Carlo method which generates the isoenthalpic-isotension-isobaric ensemble or *HtN* ensemble of classical statistical physics. This method is the Monte Carlo counterpart of the Andersen-Parrinello-Rahman *HtN* form of molecular dynamics. As an example of the use of *HtN* Monte Carlo calculations we discuss the calculation of the adiabatic elastic constants and other related thermodynamic properties of a crystalline solid from fluctuation formulas specific to the *HtN* ensemble and compare with the *HtN* molecular-dynamics calculation of these same quantities. The agreement of the results with earlier calculations of these quantities using other ensembles supports the inference that our probability density generates the *HtN* ensemble. For the elastic constants, the *HtN* Monte Carlo calculations have better convergence properties than the *HtN* molecular-dynamics calculations but are slower, by at least an order of magnitude, than the *ThN* and *EhN* molecular-dynamics and Monte Carlo methods.

PACS number(s): 05.20.−y, 05.70.−a, 02.50.+s

I. INTRODUCTION

The variable-cell molecular-dynamics methods presented by Andersen [1] and Parrinello and Rahman [2,3] generate the isoenthalpic (enthalpy *H*), isotension (tension *t*), isobaric or *HtN* ensemble of classical statistical mechanics for *N* particles. Further details of the relationship between the *HtN* form of molecular dynamics and the thermodynamics of elastic media were presented by Ray and Rahman [4]. If the computational cell is spanned by the vectors **a**, **b**, and **c** then one introduces the scaling matrix h_{ij}, $h=(\mathbf{a},\mathbf{b},\mathbf{c})$, and a metric tensor $G=h^Th$, where the T superscript denotes matrix transpose. The Parrinello-Rahman equation of motion for h has the form

$$W\ddot{h}=(P-P_{\rm ext})A-h\Gamma\ , \tag{1}$$

where P is the microscopic stress tensor, $P_{\rm ext}$ is the applied external pressure, $A=Vh^{T-1}$ is the area tensor, and Γ is related to the applied thermodynamic tension. In Parrinello-Rahman molecular dynamics the particles evolve via a modified Newton's law which contains coupling among h and the particle variables s_{ai},

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

where F_{aj} is the jth component of the force on particle a, and s_{ai} are the fractional coordinates of the particles within the computational cell. The enthalpy of the system is constant during the *HtN* evolution

$$H=K+U+P_{\rm ext}V+V_0\,{\rm tr}(t\epsilon)\ , \tag{3}$$

where K is the kinetic energy, U is the potential energy, and ϵ is the strain tensor. Note that the kinetic energy in Eq. (3) contains the kinetic energy of the cell variables h, however, since there are only six degrees of freedom in h and $3N$ in the particles we may safely ignore (error of order $2/N$) the kinetic energy of the cell for systems of several hundred or more particles and we shall do this in this paper.

II. *HtN* MONTE CARLO PROCEDURE

The main purpose of this paper is to introduce the *HtN* Monte Carlo procedure and we shall do this by discussing calculations for a simple system and comparing with results for these same quantities obtained by other methods. The Parrinello-Rahman form of molecular dynamics has become a standard tool in studying structural phase transformations of solids. For example, Rains, Ray, and Vashishta [5] have recently completed a detailed study of the phase diagram of AgI using this method, and we refer the reader to this paper for further references to nonequilibrium uses of the theory. Here we shall focus on equilibrium properties.

In molecular-dynamics or Monte Carlo simulations the equilibrium thermodynamic properties can be determined by calculating various average values. For the *HtN* ensemble Parrinello and Rahman [6] presented a formula showing the fluctuation of the strain tensor could be used to calculate the elastic constants of a system

$$\langle\epsilon_{ij}\epsilon_{km}\rangle-\langle\epsilon_{ij}\rangle\langle\epsilon_{km}\rangle=S_{ijkm}k_BT/V_0\ , \tag{4}$$

where $\epsilon=\frac{1}{2}(h_0^{T-1}Gh_0^{-1}-1)$, h_0 is the average value of h when the strain is zero, e.g., the reference value of h, V_0 is the reference volume, T is the temperature, and S_{ijkm} the adiabatic compliance tensor from which we can determine the adiabatic elastic constants by inversion. Further fluctuation formulas for the *HtN* ensemble allow the calculation of other response functions [7]. For example, the isobaric specific heat is related to kinetic energy fluctuations, while the volume expansivity is related to the cross fluctuation between the kinetic energy and the volume. Fluctuation formulas involving higher-order elastic constants of the system are related to higher-order strain fluctuations and some of these have been presented by Ray [8].

It is now generally recognized that Eq. (4) furnishes a marginally satisfactory way of calculating elastic constants in *HtN* molecular dynamics because of its slow convergence properties. Even though Eq. (4) was given in Ref. [6] no results were presented there using this equation since satisfactory convergence could not be obtained in molecular-dynamics runs of the length employed. A later study by Sprik, Impey, and Klein [9] and Ray [10] reached essentially the same conclusion. However, this method is still used on occasion [11] for the calculation of the adiabatic elastic constants because of the simplicity of Eq. (4) compared to the corresponding formulas in the *EhN* (*E* is the energy) and *ThN* (*T* is the temperature) ensembles [4,10]. Since Eq. (4) involves only the fluctuations in the *h* matrix it furnishes a method of calculating the elastic constants which does not depend explicitly on the potential. In the *EhN* ensemble the fluctuation formula for the adiabatic elastic constants has the form [4,10]

$$
\begin{aligned}
C_{ijkm} = & -\frac{V_0}{k_B T}(\langle P_{ij}P_{km}\rangle - \langle P_{ij}\rangle\langle P_{km}\rangle) \\
& + \frac{2Nk_B T}{V_0}(\delta_{ij}\delta_{jm} + \delta_{im}\delta_{jk}) \\
& + \frac{1}{V_0}\sum_{\substack{a,b=1\\ a<b}}^{N}(U''_{ab} - U'_{ab}/r_{ab}) \\
& \times x_{abi}x_{abj}x_{abk}x_{abm}/r_{ab}^2 \,, \qquad (5)
\end{aligned}
$$

where $U_{ab} = U(r_{ab})$ is the potential and the primes indicate differentiation with respect to the distance between particles. For simplicity we have given Eq. (5) assuming a pair potential. The *ThN*-ensemble fluctuation formula for the elastic constants has the same form as Eq. (5). The first term in Eq. (5) is called the fluctuation term, the second term is called the temperature correction term, and the third term is called the Born term. Thus the fluctuation formula for the elastic constants in the *EhN* (and *ThN*) ensemble depends explicitly upon potential derivatives as is shown in Eq. (5).

Recently [12] we developed a method of carrying out Monte Carlo simulations in all of the adiabatic (shell) ensembles of classical statistical mechanics [13]. For *HtN*-ensemble Monte Carlo simulations the probability density has the form [12]

$$
\begin{aligned}
W_{HtN}(s,h) = & CV^N[H - U(q) - P_{\text{ext}}V \\
& - V_0 \operatorname{tr}(t\epsilon)]^{(3N/2-1)} \,, \qquad (6)
\end{aligned}
$$

where C is the normalization constant. Note that we have included the external pressure as well as the tension in the probability density. Thus this probability density generates the isoenthalpic-isotension-isobaric ensemble. This is in accord with the finite theory of elasticity where the enthalpy terms for isotropic pressure and tension are treated separately [10]. Therefore we can also carry out Monte Carlo simulations in the *HPN* ensemble using this same importance function. This is the Monte Carlo counterpart of Andersen's [1] *HPN* molecular dynamics and would be a more appropriate ensemble for simulating liquids. For simplicity we shall refer to simulations using Eq. (6) as the importance function as *HtN* Monte Carlo simulations.

In *HtN* Monte Carlo one moves the particles, s_{ai}, and the h matrix using the importance function W_{HtN}; the resulting configurations generate the *HtN* ensemble and can be used to calculate average values in the *HtN* ensemble and in particular the elastic constants using Eq. (4).

III. *HtN*-ENSEMBLE SIMULATION RESULTS

We have carried out *HtN* Monte Carlo calculations on a 500-particle first-nearest-neighbor Lennard-Jones fcc crystal employed in previous studies of elastic constants by Sprik, Impey, and Klein [9], Ray, Moody, and Rahman [14,15], and Cowley [16]. The main reason for using this system is that accurate values of the thermodynamic parameters are known from simulations in several ensembles using both molecular-dynamics and Monte Carlo methods. Periodic boundary conditions are employed and the usual reduced, dimensionless units of the Lennard-Jones potential are employed, the dimensionless elastic constants are reported in units of Nk_BT/V. We shall present results for a temperature of $T = 0.301$, and zero pressure. We define an *HtN* Monte Carlo move to consist of an attempt to move each particle, s_{ai}, and then an attempt to change h_{ij}. Before the simulation that we discuss, we equilibrated the system at an enthalpy of $H = -2516.105$ and zero pressure and tension in Eq. (6) for several hundred thousand moves.

In Fig. 1 we show the variation of the diagonal elements of the h matrix along with their average value during a 200 000-move *HtN* Monte Carlo simulation. In this figure we have plotted every 500th configuration along the Monte Carlo sequence. The off-diagonal elements vary about zero. Figure 1 illustrates that the cell variables vary about the fcc cube in the *HtN* simulation in a manner entirely similar to *HtN* molecular dynamics. In Fig. 2 we show the volume $V = \det(h)$ as determined every 500th move in the same 200 000-move simulation.

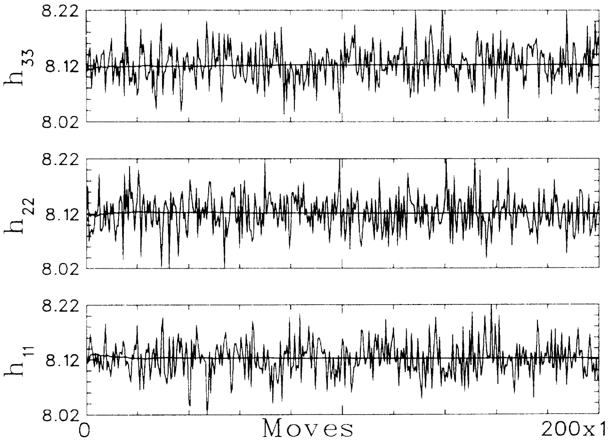

FIG. 1. The diagonal elements of the dimensionless scaling matrix plotted every 500th move along the *HtN* Monte Carlo sequence generated using the weighting function Eq. (6). The average value of h_{ii} is also shown and is 8.1216.

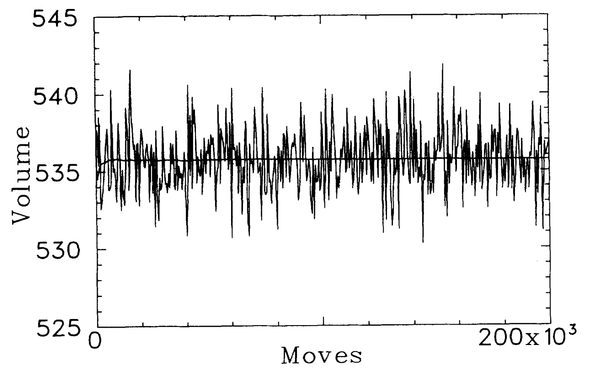

FIG. 2. The dimensionless volume plotted every 500th move along the *HtN* Monte Carlo sequence. The average of V is 535.70.

The average values of h and V determined for this simulation give the reference values h_0 and V_0 and are consistent with the results obtained in molecular-dynamics simulations [14,15] at this same temperature and pressure.

For atomic systems in *HtN* molecular dynamics the computational cell does not rotate if one starts the simulation with no cell rotation since the angular momentum of the cell is a constant of the motion for a symmetric microscopic stress tensor [17]. In *HtN* Monte Carlo simulations, on the contrary, moves of h that correspond to rotations are accepted since they do not change the energy. In order to eliminate this nuisance rotation we impose the constraint that the h matrix remains symmetric [17]. For consistency of our comparisons we imposed the same constraint on the h matrix of the *HtN* molecular-dynamics simulations.

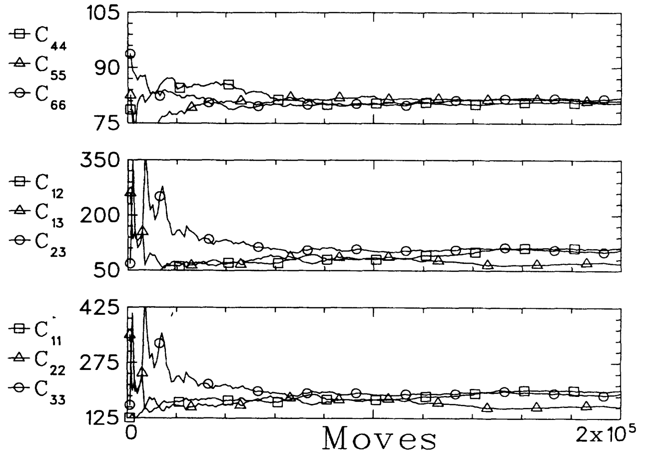

FIG. 3. The dimensionless elastic constants in units of Nk_BT/V as calculated during the 200000-move *HtN* Monte Carlo simulation using Eq. (4). Here we show the three elastic constants that should be equal by cubic symmetry for the fcc crystal. The degree of coincidence of the three lines in each graph is a measure of the convergence of the calculation.

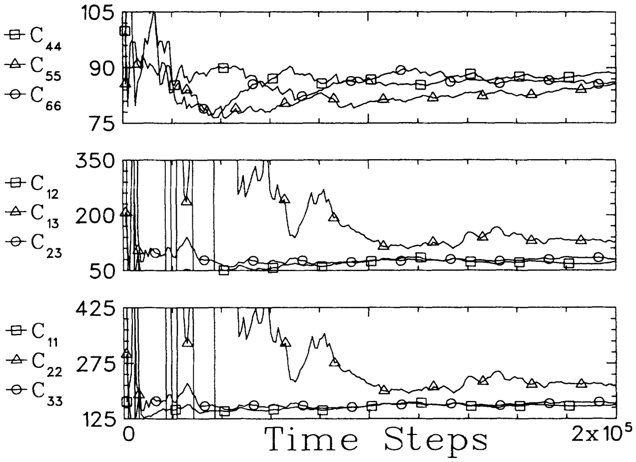

FIG. 4. The elastic constants as calculated during a 200000 time-step *HtN* molecular-dynamics simulation using Eq. (4). The same quantities are plotted as in Fig. 3.

In Fig. 3 we show the calculated values of the three sets of symmetry equivalent elastic constants C_{11}, C_{22}, C_{33}; C_{12}, C_{23}, C_{13}; and C_{44}, C_{55}, C_{66}, for the crystal at the given temperature and pressure using Eq. (4) in a 200000-move Monte Carlo simulation. In Fig. 4 we show the same quantities as calculated in *HtN* molecular dynamics using a time step of 0.0025. With this value for the time step we observed excellent energy (enthalpy) conservation in all of the molecular-dynamics simulations. These *HtN* molecular-dynamics results are similar to those given by Sprik, Impey, and Klein [9] for this same system. A comparison of Figs. 3 and 4 shows that the Monte Carlo calculation has better convergence behavior. (As a point of correction we mention that the wrong values were given in Table I by Ray [10]; the values in Table I in this reference should show convergence of the same nature as the values shown in Fig. 4.) If we use the three values of the symmetry equivalent elastic constants to introduce an error estimate we find that the Monte Carlo error estimate is generally smaller than the molecular-dynamics error estimate as is obvious from studying Figs. 3 and 4. In Table I we give these values along with the error estimates determined using the three values as three independent determinations of the elastic constants. We have also calculated other properties of the system using other *HtN* fluctuation formulas; kinetic-energy fluctuations give C_p while kinetic-

TABLE I. Elastic constants of the nearest-neighbor Lennard-Jones model at 200000 moves (time steps), with a temperature of 0.301 and zero pressure as calculated in *HtN* Monte Carlo and *HtN* molecular dynamics using Eq. (4). Under each group of three elastic constants an average value is listed together with an error estimate.

C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
MC								
196.4	162.9	187.5	109.8	75.6	99.6	81.7	83.2	81.8
$C_{11}=182.3\pm14.2$			$C_{12}=94.8\pm14.1$			$C_{44}=82.2\pm0.7$		
MD								
162.6	215.3	166.4	73.0	127.8	79.8	79.8	88.6	85.6
$C_{11}=181.4\pm24.0$			$C_{12}=93.5\pm24.4$			$C_{44}=84.7\pm3.7$		

TABLE II. Properties of the nearest-neighbor Lennard-Jones system at a temperature of 0.301 and zero pressure as calculated in different ensembles by molecular dynamics (MD) and Monte Carlo (MC). The elastic constants are the adiabatic elastic constants divided by Nk_BT/V, the specific heat at constant pressure C_p is divided by Nk_B, and the isothermal and adiabatic bulk modulii B_T and B_s are divided by Nk_BT/V. All of these thermodynamic quantities are calculated using fluctuation formulas specific to the particular ensemble denoted in the first row. The agreement of the values is within the error bars associated with each quantity. The first column gives the *HtN* Monte Carlo values at the end of the 3×10^6-move simulation while the second column gives the *HtN* molecular-dynamics values at the end of the 3×10^6-time-step simulation.

Quantity \ Ensemble Simulation	*HtN* MC	*HtN* MD	*EhN*[a] MD	*ThN*[b] MC	*ThN*[a] MD
C_{11}	179.9	180.2	183.3	182.0	184.4
C_{12}	92.7	93.2	94.8	94.1	96.0
C_{44}	81.6	81.3	82.9	82.0	82.0
C_p	3.53	3.49	3.43	3.53	3.49
B_T	96.98	97.5	102.8	98.6	105.4
B_s	121.81	122.0	124.3	123.4	125.5

[a] References [10,14,15].
[b] Reference [16].

energy volume cross fluctuations together with C_p and the adiabatic bulk modulus, $B_s=(C_{11}+2C_{12})/3$, give the isothermal bulk modulus B_T; these other properties are listed in Table II, along with previous calculations of these quantities in *EhN* molecular-dynamics and *ThN* Monte Carlo simulations.

In order to further study the convergence of the elastic constants we extended the Monte Carlo simulations to 3×10^6 moves and the molecular-dynamics simulation to 3×10^6 time steps. In Fig. 5 we show the elastic constants for the extended Monte Carlo simulation and in Fig. 6 we show the same for the molecular-dynamics simulation. Note that we have changed the scale in order to show the convergence in these extended simulations. The original, first 200 000-move (time steps) simulations in Figs. 3 and 4 are often off the scale in Figs. 5 and 6. The superior convergence of the Monte Carlo calculations is again clear from a comparison of Figs. 5 and 6 as well as by detailed error estimates.

IV. CONCLUSIONS

We have discussed Monte Carlo simulations which generate the *HtN* ensemble and compared the calculation of equilibrium properties in *HtN* Monte Carlo simulations with the calculation in *HtN* molecular-dynamics simulations. At low enough temperatures molecular dynamics will not furnish accurate average values because the system becomes harmonic, however, the Monte Carlo averages are still valid at low temperatures. Hence at low enough temperatures the only reliable method of carrying out *HtN*-ensemble simulations is with the *HtN* Monte Carlo method.

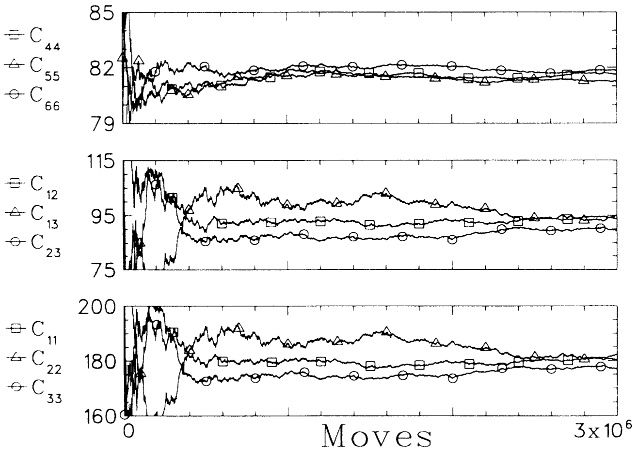

FIG. 5. The same as in Fig. 3 but extended to 3×10^6 moves to investigate convergence. The first 200 000 moves correspond to Fig. 4.

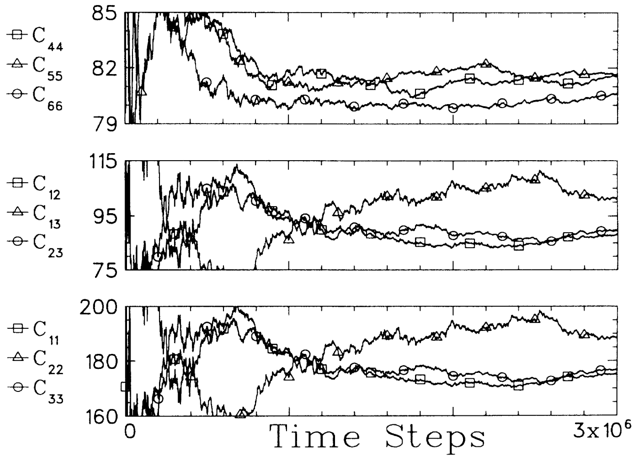

FIG. 6. The same as in Fig. 4 but extended to 3×10^6 moves to investigate convergence. The first 200 000 time steps correspond to Fig. 4.

Note also that in *HtN* Monte Carlo simulations we do not have to worry about the influence of the arbitrary "wall" mass parameter or the form of the kinetic energy of the "walls" (e.g., the form of the equation for the *h* matrix) on the results of simulations. Of course, in order to study properties of the system as a function of time, such as diffusion and time correlation functions, molecular-dynamics simulations must be employed.

We presented detailed calculations for a nearest-neighbor Lennard-Jones crystal at a temperature of 0.301 and zero pressure. Other simulations at higher and lower temperatures for this system lead to the same conclusions. Other preliminary simulations using embedded-atom-method potentials have also given consistent results among *HtN* Monte Carlo, *HtN* molecular-dynamics, and *EhN* molecular-dynamics simulations. A study of Figs. 3–6 and Table I shows that the *HtN* Monte Carlo method is a better method of calculating elastic constants than the *HtN* molecular-dynamics method, but both methods are inefficient. Recall that *EhN* or *ThN* molecular-dynamics calculation of the elastic constants gives an error $\approx 1\%$ in 20 000 time steps [10,14,15]. The reason the *EhN* and *ThN* calculations are more efficient is that the fluctuation formula for the elastic constants in the *EhN* ensemble involves the Born terms as the major contributor, Eq. (5), and this term is not a fluctuation expression and, therefore, converges to an accurate value in a few thousand time steps. Fluctuation expressions, which involve the difference between quantities which are close in value, are inherently slower to converge. The same advantage would be present in *EhN* Monte Carlo [12] calculation of the elastic constants which would use the same fluctuation formulas as the *EhN* molecular-dynamics method. Comparing the convergence of *EhN* molecular-dynamics formulas for the elastic constants to the *HtN* results in this paper we see that one must run the *HtN* Monte Carlo simulations at least ten times as long to reduce the error to the approximate values obtained in the *EhN* or *ThN* simulations [10,14,15]. Somewhat longer simulations would be required in *HtN* molecular-dynamics simulations as is clear from our previous discussion.

Although we have concentrated on equilibrium simulations using the *HtN* Monte Carlo method it is clear that this method can be used to study solid-solid phase transformations or other nonequilibrium processes in a manner similar to *HtN* Andersen-Parrinello-Rahman molecular dynamics and we are presently studying such processes using *HtN* Monte Carlo methods. Monte Carlo simulations in the isothermal *TtN* ensemble have been used by Toukan, Carrion, and Yip [18] to study solid-solid phase transformations.

The results of the present study show that *HtN* Monte Carlo, using the importance function given in Eq. (6), is a viable method for carrying out Monte Carlo simulations. Figures 1–6 and Tables I and II show that the probability density W_{HtN}, Eq. (6), gives equivalent values for thermodynamic properties as *EhN* molecular-dynamics or conventional *ThN* Monte Carlo simulations. The accurate calculation of the elastic constants using the *HtN* fluctuation formulas given in Eq. (4) is a superior method compared to the more slowly converging results obtained in *HtN* molecular dynamics using this same formula but neither method is competitive with *EhN* or *ThN* molecular dynamics or Monte Carlo simulations. Obtaining accurate first and second derivatives of the potential can often be a nontrivial problem in the case of complicated many-body, tabulated, or *ab initio* potentials and therefore *HtN* Monte Carlo calculations of the elastic constants will remain useful for such cases.

ACKNOWLEDGMENT

We thank SCUREF for support of this project.

---

[1] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).

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

[3] M. Parrinello and A. Rahman, J. Appl. Phys. **52**, 7182 (1981).

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

[5] C. A. Rains, J. R. Ray, and P. Vashishta, Phys. Rev. B **44**, 9228 (1991).

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

[7] J. R. Ray, H. W. Graben, and J. M. Haile, Nuovo Cimento B **64**, 191 (1981).

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

[9] M. Sprik, R. W. Impey, and M. L. Klein, Phys. Rev. B **29**, 4368 (1983).

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

[11] J. S. Tse and D. D. Klug, Phys. Rev. Lett. **67**, 3559 (1991).

[12] J. R. Ray, Phys. Rev. A **44**, 4061 (1991).

[13] H. W. Graben and J. R. Ray, Phys. Rev. A **43**, 4100 (1991).

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

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

[16] E. R. Cowley, Phys. Rev. B **28**, 3160 (1983).

[17] S. Nosé and M. Klein, Mol. Phys. **50**, 1055 (1983).

[18] K. Toukan, F. Carrion, and S. Yip, J. Appl. Phys. **56**, 1455 (1984).