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Calculation of elastic constants using isothermal molecular dynamics

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A new form of molecular dynamics has been developed whose trajectories generate the isothermal or canonical ensemble of classical statistical physics. We have performed molecular-dynamics calculations of the elastic constants using this new ensemble. We find that the elastic constants, as well as other thermodynamic quantities, may be calculated just as efficiently in the isothermal form of molecular dynamics as in conventional microcanonical molecular dynamics.

I. INTRODUCTION

Elastic constants, among other thermodynamic properties of solids, yield valuable dynamical and mechanical information about materials. For example, they yield information, through the Born relations, concerning the stability and strength of materials. Elastic constants are determined experimentally using various techniques including Brillouin scattering, ultrasonic wave propagation, and neutron scattering.[1-4] The comparison of experimentally measured and theoretically calculated elastic constants is an important tool for testing interaction potentials that are derived from theory. In cases where well-established potentials are available one should be able to predict the behavior of the material under various conditions of normal or extreme loading.

One traditional way of determining elastic constants in the high-temperature, anharmonic regime has been through the use of Monte Carlo calculations. The theory for these calculations was first developed by Squire *et al.*[5] Ray, Moody, and Rahman[6] presented the first calculation of elastic constants using a version of molecular dynamics which generates a microcanonical (E,h,N) ensemble, where E is the system energy, h is a matrix formed from the three vectors $\underline{\mathbf{a}}$, $\underline{\mathbf{b}}$, and $\underline{\mathbf{c}}$ which span the molecular-dynamics cell, $h=(\underline{\mathbf{a}},\underline{\mathbf{b}},\underline{\mathbf{c}})$, and N is the particle number. These calculations made use of equilibrium fluctuation formulas involving the adiabatic elastic constants derived earlier by Ray and Rahman[7] These fluctuation formulas of Ref. 7, which will be given below, were formulated in the (E,h,N) ensemble of equilibrium statistical mechanics and were used to determine the adiabatic elastic constants.

It is customary to associate molecular dynamics with the (E,V,N) ensemble of equilibrium statistical mechanics, where V is the volume of the system. The difference between (E,h,N) molecular dynamics and (E,V,N) molecular dynamics is that in the former the molecular-dynamics cell has an arbitrary shape defined by the constant matrix h. This is a significant difference since it is just this introduction of h into the theory that allows one to derive, as in Ref. 7, the fluctuation formulas containing the elastic constants.

As was also discussed in Ref. 6, the use of fluctuation formulas to calculate elastic constants in the (H,t,N) extension[7] of (E,h,N) molecular dynamics, was not successful; that is, the (H,t,N) fluctuation formulas involving elastic constants do not lead to statistically convergent results in molecular-dynamics runs of reasonable length (80 000 time steps). We recall that in the (H,t,N) ensemble the size and shape of the molecular-dynamics cell is allowed to vary; in other words, the matrix h becomes a dynamical variable. The formulas for the elastic constants in this ensemble are determined by the fluctuations in the matrix h.

Another new form of molecular dynamics is Nosé's isothermal or canonical extension of (E,h,N) molecular dynamics.[8] Nosé's method may be employed to construct a molecular dynamics which generates the (T,h,N) or the canonical ensemble, where T is the prescribed system temperature.[9] This (T,h,N) form of molecular dynamics has been discussed as well as example calculations presented by Ray and Rahman.[9] In this paper we present the relevant fluctuation formulas for elastic constants in the (T,h,N) ensemble and show by calculation that these formulas may be used in molecular dynamics to calculate elastic constants.

We note that an alternate way of determining elastic constants is to apply a given stress and to determine the resulting strain. The stress-strain relation so determined gives the elastic constants. Although it is always possible to employ this method, it is inconvenient since one must apply several different stresses to determine all the elastic constants. Sprik *et al.*[10] found this direct method of calculation of elastic constants to be computationally inefficient when compared to Monte Carlo calculations using equilibrium fluctuation formulas.

It should be mentioned that, by using the adiabatic elastic constants determined in an (E,h,N) molecular-dynamics calculation together with other thermodynamic quantities determined in the run, one can calculate the isothermal elastic constants using well-known thermodynamic relationships that we present later. Therefore, we may use the (E,h,N) form of molecular dynamics to determine the isothermal as well as the adiabatic elastic constants.

Similarly, the reverse is also true, that we may determine the adiabatic as well as the isothermal elastic constants in (T,h,N) molecular dynamics. We shall make use of this dual way of calculating elastic constants to compare the results obtained in (T,h,N) isothermal molecular dynamics with the results obtained in (E,h,N) molecular dynamics. Holt *et al.*[11] first employed this procedure to determine the adiabatic elastic constants in Monte Carlo calculations.

For convenience we employ the same notation as in earlier papers (Refs. 6, 7, and 9), and, in order to keep the equations relatively simple, we assume a pairwise additive central potential.

II. THE (T,h,N) THEORY (REFS. 8 AND 9).

The Hamiltonian in the (T,h,N) form of molecular dynamics is taken to have the form

$$\mathscr{H}_2(\underline{s},\underline{\pi},f,P)=\tfrac{1}{2}\sum_a \pi_a' G^{-1}\pi_a/(m_a f^2)+\sum_{\substack{a,b\\(a<b)}} U(r_{ab}) + \tfrac{1}{2}P^2/M+(F+1)k_B T\ln f\ , \qquad (2.1)$$

where $\underline{s}$ and $\underline{\pi}$ are the particle scaled coordinates and momenta, G^{-1} is the inverse of the metric $G=h'h$, $U(r_{ab})$ is the pair potential, $F=3N$ is the number of particle degrees of freedom, f is Nosé's scaling variable, and P is the momentum associated with f, $P=M\dot{f}$; note that the variable f is more naturally thought of as a mass-scaling dynamical variable rather than as a time-scaling one.[9] This Hamiltonian yields the equations of motion

$$m_a f^2 \ddot{s}_a=-\sum \chi_{ab} s_{ab}-2m_a \dot{f} f \dot{s}_a\ , \qquad (2.2)$$

$$M\ddot{f}=2K/f-(F+1)k_B T/f\ , \qquad (2.3)$$

where

$$\chi_{ab}=\frac{1}{r_{ab}}\frac{\partial U(r_{ab})}{\partial r_{ab}}$$

and $K=\frac{1}{2}\sum_a p_a^2/m_a$ is the kinetic energy of the particles in the system, with $p_a=f m_a h\dot{s}_a$; K is the first term on the right-hand side of Eq. (2.1).

As was discussed in Ref. 8, time averages calculated using the trajectories generated by Eqs. (2.2) and (2.3) are equal to averages in the canonical (T,h,N) ensemble of equilibrium statistical mechanics,

$$\langle A(x,p)\rangle=\frac{\int A(x,p)e^{-\mathscr{H}/k_B T}d^F x_a d^F p_a}{\int e^{-\mathscr{H}/k_B T}d^F x_a d^F p_a}\ , \qquad (2.4)$$

where

$$\mathscr{H}=\tfrac{1}{2}\sum p_a^2/m_a+\sum_{\substack{a,b\\(a<b)}} U(r_{ab})$$

is the system Hamiltonian.

III. FLUCTUATION FORMULAS IN THE (E,h,N) ENSEMBLE

Here for reference we present the (E,h,N) fluctuation formulas that were given in Ref. 7. First, we have the isostrain specific heat C_ϵ determined by fluctuations in the particle kinetic energy K;[7]

$$\delta(K^2)=\frac{3N}{2}(k_B T)^2\left[1-\frac{3Nk_B}{2C_\epsilon}\right]\ , \qquad (3.1)$$

where $\delta(AB)=\langle AB\rangle-\langle A\rangle\langle B\rangle$. Since the strain is determined by h via

$$\epsilon=\tfrac{1}{2}[(h_0')^{-1}h'hh_0^{-1}-1]\ ,$$

then if the strain is constant, so is h and vice versa; h_0 is the value of the h matrix at zero stress while h is its value at the state point under investigation.

Second, we present the fluctuation formulas involving the temperature coefficients of thermodynamic tension at constant strain (i.e., constant h),

$$\lambda_{ij}=\left[\frac{\partial t_{ij}}{\partial T}\right]_\epsilon\ ,$$

where t_{ij} is the thermodynamic tension tensor. The microscopic tension tensor is given by

$$\eta=Vh_0h^{-1}\mathscr{P}(h')^{-1}h_0'/V_0\ , \qquad (3.2)$$

where V is the volume and $\mathscr{P}_{ij}$ is the microscopic stress tensor

$$\mathscr{P}_{ij}=V^{-1}\left[\sum_a p_{ai}p_{aj}/m_a-\sum_{\substack{a,b\\(a<b)}}\chi_{ab}r_{abi}r_{abj}\right]\ . \qquad (3.3)$$

The average of η gives the tension tensor in the (E,h,N) ensemble:

$$t=\langle\eta\rangle\ . \qquad (3.4)$$

The thermodynamic quantities λ_{ij} may be determined by knowing C_ϵ and using the fluctuation formulas[7]

$$\delta(K\eta_{ij})=N(k_B T)^2\left[[h_0h^{-1}(h')^{-1}h_0']_{ij}/V_0-\frac{3\lambda_{ij}}{2C_\epsilon}\right]\ . \qquad (3.5)$$

Lastly, the fluctuation formulas for the adiabatic elastic constants C_{pqrs}^S are

$$V_0h_{0ip}^{-1}h_{0jq}^{-1}h_{0lr}^{-1}h_{0ms}^{-1}C_{pqrs}^S=\frac{-4}{k_B T}\delta(M_{ij}M_{lm})+2Nk_B T(G_{mi}^{-1}G_{jl}^{-1}+G_{li}^{-1}G_{jm}^{-1})+\left\langle\sum_{\substack{a,b\\(a<b)}} g(r_{ab})s_{abi}s_{abj}s_{abl}s_{abm}\right\rangle\ , \qquad (3.6)$$

where $M=-\frac{1}{2}Vh^{-1}\mathscr{P}(h')^{-1}$ and $g(r)=(\partial^2U/\partial r^2-\chi)/r^2$.

IV. FLUCTUATION FORMULAS IN THE (T,h,N) ENSEMBLE

As we have discussed in Sec. II, Nosé's (T,h,N) molecular dynamics generates the canonical ensemble. Therefore, in the (T,h,N) ensemble the fluctuation formulas determining C_ϵ and λ_{ij} have the form

$$\delta(\mathscr{H}^2)=k_B T^2 C_\epsilon \tag{4.1}$$

and

$$\delta(\eta_{ij}\mathscr{H})=k_B T^2 \lambda_{ij} \ , \tag{4.2}$$

where $\mathscr{H}$ is specified in Eq. (2.4). The isothermal elastic constants C^T_{pqrs} are determined by the fluctuation formulas

$$V_0 h^{-1}_{0ip} h^{-1}_{0jq} h^{-1}_{0lr} h^{-1}_{0ms} C^T_{pqrs}=\frac{-4}{k_B T}\delta(M_{ij}M_{lm})+2Nk_B T(G^{-1}_{mi}G^{-1}_{jl}+G^{-1}_{li}G^{-1}_{jm})+\left\langle \sum_{\substack{a,b\\(a<b)}} g(r_{ab}) s_{abi}s_{abj}s_{abl}s_{abm}\right\rangle . \tag{4.3}$$

V. CONNECTION BETWEEN (E,h,N) AND (T,h,N) FLUCTUATION FORMULAS

From the formulas given in Sec. III we can, in an (E,h,N) molecular-dynamics calculation, determine the thermodynamic quantities C_ϵ, λ_{ij}, and C^S_{ijkl}. From Thurston[12] we find the following relationship between the isothermal and adiabatic elastic constants:

$$C^T_{ijkl}=C^S_{ijkl}-\frac{TV_0}{C_\epsilon}\lambda_{ij}\lambda_{kl} \ . \tag{5.1}$$

Therefore, from the quantities C_ϵ, λ_{ij}, and C^S_{ijkl}, which are calculated in an equilibrium (E,h,N) molecular-dynamics calculation using the formulas of Sec. III, we may calculate the isothermal elastic constants using Eq. (5.1).

In a similar manner, if we rewrite Eq. (5.1) in the form

$$C^S_{ijkl}=C^T_{ijkl}+\frac{TV_0}{C_\epsilon}\lambda_{ij}\lambda_{kl} \ , \tag{5.2}$$

we see that the quantities C_ϵ, λ_{ij}, and C^T_{ijkl}, as determined from an equilibrium (T,h,N) molecular-dynamics calculation using the formulas of Sec. IV, may be used to calculate the adiabatic elastic constants.

We now have two methods, one using (E,h,N) molecular dynamics and another using (T,h,N) molecular dynamics, for calculating the elastic constants C^S_{ijkl} and C^T_{ijkl} as well as the other thermodynamic quantities C_ϵ and λ_{ij}. The comparison of the values of these thermodynamic quantities as calculated in (T,h,N) and (E,h,N) molecular dynamics gives an indication of the practical usefulness of Nosés, (T,h,N) molecular dynamics to generate the canonical ensemble.

VI. NUMERICAL RESULTS

We have carried out several molecular-dynamics runs using the dynamical equations (2.2) and (2.3) to generate the trajectories. In order to compare with previous work we employed the same potential as in Ref. 6 and previously used by Cowley[13] in Monte Carlo calculations. Our system consists of 500 particles interacting with the Lennard-Jones (12-6) potential including only nearest-neighbor interactions. The data presented is for an fcc solid at a reduced temperature of 0.3 and at zero pressure. For this case, due to cubic symmetry, we have

$$\lambda_{11}=\lambda_{22}=\lambda_{33} \text{ and } \lambda_{12}=\lambda_{23}=\lambda_{13}=0 \ .$$

If we set

$$\Delta C=\frac{TV_0}{C_\epsilon}\lambda_{11}^2$$

then the relationship (5.1) may be summarized by[11]

$$\begin{aligned}
&C^S_{11}-C^T_{11}=C^S_{22}-C^T_{22}=C^S_{33}-C^T_{33}=\Delta C \ ,\\
&C^S_{12}-C^T_{12}=C^S_{23}-C^T_{23}=C^S_{13}-C^T_{13}=\Delta C \ ,\\
&C^S_{44}-C^T_{44}=C^S_{55}-C^T_{55}=C^S_{66}-C^T_{66}=0 \ ,
\end{aligned} \tag{6.1}$$

with all other elastic constants being zero. The equality $C_{11}=C_{22}=C_{33}$, etc. again follows from the cubic symmetry.

In Tables I, II, and III we exhibit a representative sample of the data collected in this study. In these tables the entries labeled run 1 and run 2 are independent (T,h,N) molecular-dynamics runs each of 20000 time steps; the entries labeled run 3 and run 4 are independent (E,h,N) molecular-dynamics runs each also of 20000 time steps; each time step is approximately 10^{-2} ps for argon. The four molecular-dynamics runs all had reduced temperatures within 1% of 0.3.

All rms error estimates in this paper were obtained by using the method of partitioning the molecular-dynamics run into several segments and calculating the average of the quantity of interest for each of these segments. The average values calculated in each segment were then used as independent values of the quantity to calculate the rms error estimate.

In all molecular-dynamics runs the elastic constant $C_{1233}=C_{63}$ was calculated. By cubic symmetry this elastic constant is zero. In all cases the calculated value of this elastic constant was zero within the statistical uncertainty of our calculations.

A. Isothermal elastic constants

Table I shows the symmetry-averaged isothermal elastic constants as determined in the four molecular-dynamics runs and Cowley's Monte Carlo calculation. For run 1

TABLE I. Isothermal elastic constants in units of Nk_BT/V_0 from (T,h,N) and (E,h,N) molecular dynamics and from Cowley's Monte Carlo calculations. For argon ($\epsilon_0=120$ K, $\sigma=3.4$ Å), $Nk_BT/V_0=11.8$ MPa. Δt stands for one time step of 10^{-2} pc for argon.

Run (time)	$\frac{1}{3}(C_{11}+C_{22}+C_{33})$	$\frac{1}{3}(C_{12}+C_{13}+C_{23})$	$\frac{1}{3}(C_{44}+C_{55}+C_{66})$
	(T,h,N) molecular dynamics data		
1 (20 000Δt)	166.7±3.4	76.4±3.3	81.3±1.3
2 (20 000Δt)	164.6±5.9	76.2±5.4	82.0±1.7
	(E,h,N) molecular dynamics data		
3 (20 000Δt)	160.4±3.0	71.3±3.2	83.2±1.3
4 (20 000Δt)	162.2±7.0	73.1±6.9	82.4±0.6
	Monte Carlo data, Cowley[a]		
(25 000Δt)	157.1±1.0	69.3±0.9	82.2±0.2

[a]Reference 13.

TABLE II. Adiabatic elastic constants in units of Nk_BT/V_0 from (T,h,N) and (E,h,N) molecular dynamics and from Cowley's Monte Carlo calculations.

Run (time)	$\frac{1}{3}(C_{11}+C_{22}+C_{33})$	$\frac{1}{3}(C_{12}+C_{13}+C_{23})$	$\frac{1}{3}(C_{44}+C_{55}+C_{66})$
	(T,h,N) molecular dynamics data		
1 (20 000Δt)	185.8±1.3	95.5±1.1	81.3±1.3
2 (20 000Δt)	184.4±2.1	96.0±1.6	82.0±1.7
	(E,h,N) molecular dynamics data		
3 (20 000Δt)	183.9±1.6	94.8±1.6	83.2±1.3
4 (20 000Δt)	184.2±0.6	95.1±0.8	82.4±0.6
	Monte Carlo data, Cowley[a]		
(25 000Δt)	182.0±0.5	94.1±0.5	82.2±0.2

[a]Reference 13.

TABLE III. Specific heats at constant volume and pressure in units of Nk_B and adiabatic and isothermal bulk modulii in units of Nk_BT/V_0 from (T,h,N) and (E,h,N) molecular dynamics and from Cowley's Monte Carlo calculations.

Run (time)	C_V	C_P	B_S	B_T
		(T,h,N) molecular dynamics data		
1 (20 000Δt)	2.78±0.22	3.49±0.54	124.8±2.0	100.7±8.2
2 (20 000Δt)	2.67±0.18	3.22±0.38	126.2±1.8	105.4±6.5
		(E,h,N) molecular dynamics data		
3 (20 000Δt)	2.78±0.10	3.43±0.21	124.5±0.7	101.0±3.1
4 (20 000Δt)	2.70±0.22	3.28±0.48	124.8±1.6	102.8±7.0
		Monte Carlo Data, Cowley[a]		
(25 000Δt)	2.82±0.03	3.53±0.04	123.4±0.5	98.6±0.9

[a]Reference 13.

and run 2 [with the (T,h,N) ensemble] the elastic constants are determined using Eq. (4.3). For run 3 and run 4 the elastic constants are determined by using Eqs. (3.1), (3.5), and (3.6) together with (5.1). Cowley's results are obtained from Eq. (4.3) after replacing the momenta averages by

$$\langle p_{ai} p_{aj} \rangle / m_a = k_B T \delta_{ij} \;,$$
$$\langle p_{ai} p_{aj} p_{ak} p_{al} \rangle / m_a^2 = (k_B T)^2 (\delta_{ij}\delta_{kl} + \delta_{li}\delta_{jk} + \delta_{ki}\delta_{jl}) \;. \tag{6.2}$$

When these momenta averages are used in Eq. (4.3), we obtain formulas that are suitable for a Monte Carlo calculation of isothermal elastic constants, as in Squire *et al.*[5] and in Wallace *et al.*[14]

As can be clearly seen from Table I the (T,h,N) and (E,h,N) forms of molecular dynamics give comparable results for molecular-dynamics runs of equal length.

B. Adiabatic elastic constants

In Table II we show the adiabatic elastic constants as calculated using (T,h,N) and (E,h,N) molecular dynamics along with Cowley's results. Here the (E,h,N) elastic constants are calculated using Eq. (3.6). The (T,h,N) adiabatic elastic constants are calculated using Eqs. (4.1), (4.2), (4.3) together with (5.1). Cowley's results in this table are determined in the same way as the (T,h,N) values. It is again clear that the two forms of molecular dynamics give comparable results.

C. Scalar thermodynamic quantities

Table III shows the specific heats at constant volume and pressure and the adiabatic and isothermal bulk modulli as determined from appropriate fluctuation formulas in the (E,h,N) and (T,h,N) ensembles, respectively.

VII. DISCUSSION

The data in Tables I and II clearly show that Nosé's isothermal form of molecular dynamics is just as efficient for calculating elastic constants as conventional microcanonical molecular dynamics. This is strong evidence in support of the ability of the trajectories defined by Eqs. (2.2) and (2.3) to generate a satisfactory canonical ensemble. As previously mentioned some of the other new forms of molecular dynamics, the (H,t,N) ensemble, for example, have not yielded convergent values for the elastic constants. An investigation into this difference in the practical utility of the two methods may turn out to be enlightening.

By comparing Tables I and II one will notice that the first two elastic constants C_{11} and C_{12} have larger variance for the isothermal elastic constants, Table I, than for adiabatic elastic constants, Table II. The more rapid convergence of C_{11}^S and C_{12}^S as compared to C_{11}^T and C_{12}^T has been noticed previously.[11,13,15]

It should be remarked that even though there is a larger error estimate in some of the isothermal elastic constants, this is *not* dependent on which of the two forms of molecular dynamics we use for the calculation; in other words, the slower convergence is associated with the basic statistical physics of the fluctuations which determine the isothermal elastic constants and not with the form of molecular dynamics employed, as Tables I and II show.

The present calculations are carried out on an unstressed fcc crystal. However, we have shown earlier[6] that one obtains the same rapid convergence for the elastic constants of this same system subjected to a 5% elongation (stretch) along the [001] direction. Also, we should point out that there is no apparent reason that the present method of calculation of elastic constants could not be employed to determine the elastic constants of noncrystalline materials.

An interesting subject for further study would be the comparison of the relative efficiency of the molecular dynamics and Monte Carlo calculations of elastic constants.

Note added in proof. Schiferl and Wallace[16] have recently used (E,h,N) molecular dynamics to calculate elastic constants for a model of sodium.

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