

## Molecular dynamics calculation of elastic constants for a crystalline system in equilibrium

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We have performed molecular dynamics calculations for a crystalline system in equilibrium to show that by using a fluctuation formula involving the internal stress tensor it is possible to calculate the elastic constants at the ambient temperature with ease and accuracy. The method also allows one to calculate the elastic constants when the system is subjected to an arbitrary external stress.

The molecular dynamics method developed by Parrinello and Rahman<sup>1</sup> furnishes a means for studying structural phase transformations in solids; such transformations are, of course, nonequilibrium processes. However, this molecular dynamics method can also be used to calculate the equilibrium properties of a system; the trajectories generated by the equations of motion belong to an ensemble with constant enthalpy  $H$ , constant thermodynamic tension  $t$ , and constant particle number  $N$ , or briefly an  $(H, t, N)$  ensemble; the equilibrium properties may therefore be calculated by using the fluctuation formulas of the  $(H, t, N)$  ensemble. The details are given in Ref. 2 where it has also been shown how the formulation becomes relevant for the theory of finite elasticity.

It was shown by Parrinello and Rahman (see Ref. 2 for details) that the (isentropic or adiabatic) compliance tensor  $S_{ijkl}$  is given in terms of the strain fluctuations by the equation

$$\delta(\epsilon_{ij}\epsilon_{kl}) = \langle \epsilon_{ij}\epsilon_{kl} \rangle_{av} - \langle \epsilon_{ij} \rangle_{av} \langle \epsilon_{kl} \rangle_{av} = \frac{k_B T}{V} S_{ijkl}, \quad (1)$$

where  $\epsilon_{ij}$  is the strain tensor, and  $V$  the equilibrium volume of the  $N$  particle system.

However, it has been found by Sprik *et al.*<sup>3</sup> and by others<sup>4</sup> that from the point of view of convergence to statistically significant results Eq. (1) is unsatisfactory.

We present in this paper an alternative approach which shows much greater promise of producing desirable results even with molecular dynamics runs of only moderate length.

In Ref. 2 we discussed not only the  $(H, t, N)$  ensemble but also the  $(E, h, N)$  ensemble; the latter is a generalization of the familiar  $(E, V, N)$ , i.e., the microcanonical, ensemble; in the  $(E, h, N)$  ensemble the  $3 \times 3$  matrix  $h$ , to be defined below, is kept constant; this keeps not only the volume ( $=\det h$ ) constant but also holds fixed the shape of the periodically repeating molecular dynamics cell containing the  $N$  particles.

In the  $(E, h, N)$  ensemble, as shown in Ref. 2, the adiabatic elastic constants  $C_{ijkl}$  can be expressed in terms of a fluctuation formula involving fluctuations in the internal

stress tensor  $P$ . Several other average quantities also intervene and one needs to give some notational details.

The constant matrix  $h$  has as its columns the elements of the vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  which span the molecular dynamics cell;  $h = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ . For simplicity we assume the potential energy of the system to be pair-wise additive; the pair potential is denoted by  $u(r)$ . Let  $\chi$  denote  $r^{-1}u'$  and  $f$  denote  $r^{-2}(u'' - \chi)$ . The internal stress tensor is then

$$P_{ij} = \frac{1}{V} \left[ \sum_a p_{ai} p_{aj} / m_a - \sum_{b>a} \chi(r_{ab}) x_{abi} x_{abj} \right], \quad (2)$$

$p_{ai}$  being the momentum components,  $\mathbf{x}_{ab}$  the vector joining  $a$  and  $b$  of length  $r_{ab}$ , and  $V$  the volume containing the  $N$  particles.

Then the adiabatic elastic constant  $C_{ijkl}$  is given, under conditions of zero stress, by

$$C_{ijkl} = -\frac{V_0}{k_B T} \delta(P_{ij} P_{kl}) + \frac{2Nk_B T}{V_0} (\delta_{il} \delta_{jk} + \delta_{ik} \delta_{jl}) + \frac{1}{V_0} \left\langle \sum_{b>a} f(r_{ab}) x_{abi} x_{abj} x_{abk} x_{abl} \right\rangle_{av}. \quad (3)$$

Equation (3) is obtained from results in Ref. 2 by using appropriate values of the averages involving particle momenta only. The more general relation which gives the elastic constants for a system under stress will be given below [see Eq. (4)]. One further remark before we present the results of our calculations.

Under an arbitrary state of stress the molecular dynamics cell will adopt a certain shape and volume (using the Parrinello-Rahman form of molecular dynamics); in addition the particles in the cell will take on positions which can be quite varied when there is more than one atom per Bravais unit cell. To make use of Eq. (4) for determining elastic constants under an arbitrary state of stress an efficient procedure is to make an  $(H, t, N)$  calculation first at the desired stress and temperature; this will furnish an average for  $h$  and for all particle positions  $\mathbf{x}_a$ . These are then the input values in the  $(E, h, N)$  calculation of the elastic constants at the same temperature using Eq. (4).

TABLE I. Elastic constants in units of  $Nk_B T/V_0$  for our molecular dynamics run and Cowley's Monte Carlo run. Cowley's results are for a reduced temperature of 0.3 while the temperature of the molecular dynamics run was 0.298. For the  $C_{12}$  and  $C_{44}$  elastic constants we give only the symmetry-averaged quantity. For argon ( $\epsilon_0=120$  K,  $\sigma=3.4$  Å),  $Nk_B T/V=11.7$  MPa. The value of  $PV/Nk_B T$  was  $-0.03\pm 0.03$  for the molecular dynamics run while Cowley gives  $0.02\pm 0.02$  for his Monte Carlo run. The time step  $\Delta t$  was equal to 0.005 which for argon corresponds to about  $10^{-14}$  sec. The reduced density of the system was 0.934.

Time	$C_{11}$	$C_{22}$	$C_{33}$	$\frac{(C_{11}+C_{22}+C_{33})}{3}$	$\frac{(C_{12}+C_{13}+C_{23})}{3}$	$\frac{(C_{44}+C_{55}+C_{66})}{3}$
Molecular dynamics data						
5 000 $\Delta t$	187.6	179.8	185.9	184.4 $\pm$ 4.1	93.7 $\pm$ 2.8	84.4 $\pm$ 2.3
10 000 $\Delta t$	185.3	180.9	184.1	183.4 $\pm$ 2.3	93.7 $\pm$ 1.6	82.4 $\pm$ 1.1
15 000 $\Delta t$	185.9	181.5	182.6	183.3 $\pm$ 2.3	94.2 $\pm$ 1.7	82.4 $\pm$ 1.9
20 000 $\Delta t$	185.4	181.5	182.6	183.2 $\pm$ 2.0	94.5 $\pm$ 1.1	82.8 $\pm$ 2.2
25 000 $\Delta t$	185.8	181.6	181.9	183.1 $\pm$ 2.3	94.2 $\pm$ 0.9	83.0 $\pm$ 1.6
30 000 $\Delta t$	185.4	181.8	182.2	183.1 $\pm$ 2.0	94.7 $\pm$ 0.9	82.7 $\pm$ 1.4
35 000 $\Delta t$	185.0	181.6	182.1	182.9 $\pm$ 1.8	94.9 $\pm$ 0.9	83.0 $\pm$ 1.5
40 000 $\Delta t$	185.1	182.3	182.6	183.3 $\pm$ 1.5	94.8 $\pm$ 1.0	82.9 $\pm$ 1.4
Monte Carlo data <sup>a</sup>						
$\cong 25 000\Delta t$				182.0 $\pm$ 0.5	94.1 $\pm$ 0.5	82.2 $\pm$ 0.2

<sup>a</sup>Reference 5.

We have employed Eq. (3) in various  $(E, h, N)$  molecular dynamics runs and find that the elastic constants are determined accurately and efficiently. In Table I we show, along with other quantities, the three elastic constants  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$  calculated using Eq. (3) for a molecular dynamics system consisting of 500 particles forming a fcc lattice and interacting via the nearest-neighbor Lennard-Jones (12,6) potential. The calculation is for zero pressure and a reduced temperature of about 0.3. Various other thermodynamic quantities were also calculated during this run and are displayed in Table II.

Cowley<sup>5</sup> has calculated various quantities in a Monte Carlo calculation using 108 particles interacting with the nearest-neighbor Lennard-Jones potential at a temperature

TABLE II. Specific heats at constant volume and pressure in units of  $Nk_B$  and adiabatic and isothermal bulk moduli in units of  $Nk_B T/V_0$  for our molecular dynamics run and Cowley's Monte Carlo run. These data correspond to the same conditions as the data in Table I.

Time	$C_v$	$C_p$	$B_s$	$B_T$
Molecular dynamics data				
5 000 $\Delta t$	2.82	3.53	123.9	99.0
10 000 $\Delta t$	2.86	3.63	123.6	97.5
15 000 $\Delta t$	2.83	3.55	123.9	98.7
20 000 $\Delta t$	2.81	3.51	124.0	99.3
25 000 $\Delta t$	2.85	3.59	123.8	98.2
30 000 $\Delta t$	2.78	3.45	124.3	100.2
35 000 $\Delta t$	2.80	3.49	124.1	99.6
40 000 $\Delta t$	2.77	3.43	124.3	100.4
Monte Carlo data <sup>a</sup>				
$\cong 25 000\Delta t$	2.82	3.53	123.4	98.6

<sup>a</sup>Reference 5.

of 0.3. Cowley does not give  $C_{11}$ ,  $C_{22}$ , and  $C_{33}$  separately but only their average which he identifies as  $C_{11}=(C_{11}+C_{22}+C_{33})/3$ . Cowley's calculations correspond to roughly 25 000 molecular dynamics time steps according to the estimates made in Ref. 3.

The formula used by Cowley to calculate elastic constants may be obtained from Eq. (3) by identifying  $C_{ijkl}$  as the isothermal elastic constants and interpreting averages as canonical ensemble averages. In this way all momenta can be integrated out of the resulting equation, which is then in a form suitable for a Monte Carlo calculation. The resulting formula for the elastic constants in the canonical, or  $(T, h, N)$ , ensemble was first given by Squire *et al.*<sup>6</sup> (see also Wallace *et al.*<sup>7</sup>). A direct transformation between the  $(E, h, N)$  fluctuation formula (3) and its  $(T, h, N)$  counterpart can be obtained by using generalized ensemble theory. We shall discuss this latter point in detail in a later paper.

It is clear from the results of Table I that Eq. (3) furnishes a very efficient method for calculating elastic constants in molecular dynamics. The error quoted, for the symmetry averaged  $C_{11}$  in our calculation, is found from the mean-square deviation of the three numbers which make up the symmetry averaged  $C_{11}$ . Cowley's error was determined by breaking the Monte Carlo chain into segments and calculating the quantity  $(C_{11}+C_{22}+C_{33})/3$  for each segment. The relative efficiency of the molecular dynamics and Monte Carlo calculation of elastic constants needs to be investigated.

Looking in detail at our calculation shows that if one is only interested in 5% accuracy for the elastic constants then the molecular dynamics calculation need only be run for 2000 time steps. The other two elastic constants,  $C_{12}$  and  $C_{14}$ , as well as other thermodynamic variables like specific heats, showed this same rapid convergence and

TABLE III. Elastic constants for our system under tensile loading in units of  $Nk_B T/V_0$ . The stretch of the system is 5% along the [001] direction. The temperature of the system is 0.299. The only component of the stress that is nonzero is the 33 component where the 3 axis is parallel to the [001] direction. As the system is stretched its area perpendicular to the [001] direction decreases. The reduced density of the system is 0.909.

Time	$C_{11}$	$C_{22}$	$C_{33}$	$C_{12}$	$C_{13}$	$C_{23}$	$C_{44}$	$C_{55}$	$C_{66}$
Molecular dynamics data									
5 000 $\Delta t$	180.6	181.9	107.2	123.6	59.2	60.7	49.0	48.7	101.7
10 000 $\Delta t$	180.6	179.4	106.2	122.9	62.5	61.9	50.7	49.5	102.1
15 000 $\Delta t$	179.5	178.7	104.7	121.2	61.6	60.9	51.1	50.0	104.1

precision.

The generalization of Eq. (3) to the case of a system with nonzero stress applied to it has the form<sup>2</sup>

$$\begin{aligned}
 & V_0 h_{0ip}^{-1} h_{0jq}^{-1} h_{0lr}^{-1} h_{0ms}^{-1} C_{pqrs} \\
 &= \frac{-4}{k_B T} \delta(M_{ij} M_{lm}) + 2Nk_B T (G_{mi}^{-1} G_{jl}^{-1} + G_{li}^{-1} G_{jm}^{-1}) \\
 &+ \left\langle \sum_{b>a} \sum f(r_{ab}) s_{abi} s_{abj} s_{abm} s_{abl} \right\rangle_{av}, \quad (4)
 \end{aligned}$$

where  $M = -(V/2)h^{-1}Ph'^{-1}$ ,  $s_{abi}$  is a scaled coordinate related to the real coordinate by  $x_{abi} = h_{ij}s_{abj}$ ,  $G$  is the metric tensor  $G = h'h$ ,  $h_0$  is value of the matrix for the case of zero stress, and  $h$  is its value when the system is under the prescribed stress. The values of  $h_0$  and  $h$  to be used in Eq. (4) are obtained by carrying out appropriate  $(H, t, N)$  runs as already discussed above.

In Table III we show the calculation of the elastic constants using Eq. (4); the system was stretched by about 5% along the [001] direction by the application of a suitable tension. For argon this load would be 62 MPa for nearest-neighbor interactions. The rapid convergence and

accuracy of this calculation was the same as the previous case of zero stress, Table I. Notice that the elastic constants for this calculation show the necessary tetragonal symmetry. The differences between the elastic constants in Table I (zero stress) and Table III (finite stress) are related to the higher-order elastic constants of the material.<sup>8</sup>

The  $(T, h, N)$  ensemble fluctuation formula for elastic constants has the same form as Eq. (4) except that we must identify the elastic constants as isothermal and the averages as canonical ensemble  $(T, h, N)$  averages. On performing the momentum averages in the  $(T, h, N)$  formula corresponding to Eq. (4) one obtains a result suitable for calculating elastic constants at finite stress in a Monte Carlo calculation. The results in this paper are, apparently, the first accurate calculation of elastic constants using molecular dynamics.

We shall publish a more detailed discussion of our calculations in a later paper.

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