PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 54, NUMBER 1 1 JULY 1996-I

BRIEF REPORTS

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review B** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Fluctuation formula for elastic constants

Andrei A. Gusev, Marcel M. Zehnder, and Ulrich W. Suter
Institut für Polymere, Departement Werkstoffe, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland

(Received 1 September 1995)

In thermal motion, the instantaneous stresses and strains are correlated throughout phase space—a fluctuation equation for the elastic constants is presented here that takes advantage of this fact. Results obtained with a nearest-neighbor Lennard-Jones fcc crystal indicate that the equation is considerably more efficient than the Parrinello-Rahman fluctuation formula. [S0163-1829(96)06726-4]

INTRODUCTION

Elastic constants are important technological properties: they determine the behavior of materials under arbitrary (sufficiently small) deformations and it is tempting to hazard calculation using microscopic simulation, i.e., based on a proposed atomistic arrangement and given interactions between the atoms. Such calculations are highly interesting, for example, for understanding the elastic properties of ultraoriented polymer fibers,[1] the stiffness of which, per unit mass, exceeds that of the best steels in some cases. These polymer fibers are highly crystalline and the stiffness of single crystals in the chain direction gives an upper bound for that of the fibers. It is practically impossible to measure the elastic constants of single polymer crystals but the quality of currently available force fields[2] seems to be already adequate for calculating the elastic constants.

Comparison of calculated elastic constants with experimental data can provide a test of the adequacy of the model used in the calculation. Accurate and rapid calculation of the elastic constants is essential for such a test.

The elastic constants can be calculated from the thermal strain fluctuations via the Parrinello-Rahman (PR) fluctuation formula[3]

$$C_{iklm}=\frac{k_BT}{\langle V\rangle}\langle \varepsilon_{ik}\varepsilon_{lm}\rangle^{-1}, \tag{1}$$

where ε_{ik} are the components of the strain tensor (the indices run from 1 to 3), $\langle V\rangle$ is the average volume of the system, k_B is the Boltzmann constant, T is the temperature, and the brackets denote the ensemble average. The average shape of the system is used as reference state for introducing the strain tensor

$$\varepsilon_{ik}=\tfrac{1}{2}\,(h_{nl}\langle h\rangle^{-1}_{lk}h_{np}\langle h\rangle^{-1}_{pi}-\delta_{ik}), \tag{2}$$

where h_{ik} are the components of the scaling matrix $h=(\mathbf{a},\mathbf{b},\mathbf{c})$ made up of the vectors **a**, **b**, and **c** forming the computational cell, $\langle h\rangle_{ik}$ stand for the components of the average scaling matrix, and δ_{ik} is the Kronecker tensor. In this paper the summation convention always applies to suffixes occurring twice in a product. Equation (1) has the same form for isothermal and adiabatic elastic constants and can be derived from the theory of finite elasticity.[4]

The elastic constants can also be calculated[4–6] in the ThN (N is the number of particles) and EhN (E is the energy) ensembles in which the scaling matrix h is fixed. For a potential depending only on the distances between the particles, the fluctuation formula can be written as follows:

$$C_{iklm}=-\frac{\langle V\rangle}{k_BT}\langle \Delta\sigma_{ik}\Delta\sigma_{lm}\rangle+\frac{2Nk_BT}{\langle V\rangle}(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl}) + \sum_{a>b,c>d}\langle B(\mathbf{r}_{ab},\mathbf{r}_{cd})\rangle, \tag{3}$$

where σ_{ik} are the components of the microscopic stress tensor, B is the so-called Born term that depends explicitly on the first and second derivatives of the potential energy, $\mathbf{r}_{ab}$ denotes the vector from particle a to particle b, and the

0163-1829/96/54(1)/1(4)/$10.00

brackets denote the ensemble average. The Born term is rather cumbersome and is written symbolically in Eq. (3). We refer the reader to the literature[4] for details.

For the systems studied, the PR formula was found[4,6–9] to be much more slowly converging than Eq. (3). For example, for a nearest-neighbor Lennard-Jones fcc crystal, the PR formula is about two orders of magnitude less efficient. On the other hand, the PR formula contains only terms depending on the fluctuations of the h matrix and does not depend explicitly on the potential energy derivatives. This makes the PR formula particularly attractive in situations where complicated many-body, tabulated or *ab initio* potentials are employed[2,4,10] and manipulation with the second potential energy derivatives is impractical.

In this paper we present a fluctuation formula for the elastic constants, allowing for accurate calculation from simulations in which the second moments $\langle \varepsilon_{ik}\varepsilon_{lm}\rangle$ of the strain fluctuations are not fully converged and the PR formula gives accordingly only poor estimates for the elastic constants.

ELASTIC CONSTANTS FROM FLUCTUATIONS IN STRESS AND STRAIN

Consider a system of N particles in the absence of external stresses and let H be its Hamiltonian

$$H=\sum_a \frac{p_a^2}{2m_a}+U(r_{ab}), \tag{4}$$

where $\mathbf{p}_a$ and m_a are the momentum and the mass of particle a, $U(r_{ab})$ is the potential energy (not necessarily pair-wise additive) depending only on the distances r_{ab} between the particles. If we consider six independent components (say, those with $i\geqslant k$) of the symmetric strain tensor ε_{ik} of Eq. (2) as ‘‘generalized coordinates’’ (degrees of freedom), the following identity holds:

$$\left\langle \varepsilon_{ik}\frac{\partial H}{\partial \varepsilon_{lm}}\right\rangle = k_B T\,\delta_{il}\delta_{km}\,. \tag{5}$$

Equation (5) is an example of the general form $\langle A\partial H/\partial q\rangle = k_B T\langle \partial A/\partial q\rangle$ that holds[11] for any generalized coordinate q and function A in the canonical ensemble and is valid to $O(N^{-1})$ in any ensemble.

To calculate the derivatives of the Hamiltonian with respect to the strain components, we consider two arbitrary points in the reference state specified by the average scaling matrix $\langle h\rangle$. Let these points be connected by vector $\mathbf{r}'=(x_1',x_2',x_3')$. In an instantaneous frame with scaling matrix h, the same two points are connected by a different vector $\mathbf{r}=(x_1,x_2,x_3)$ and, for homogeneous deformations, the following equation holds:[12]

$$r^2=r'^2+2\varepsilon_{ik}x_i'x_k'\,. \tag{6}$$

Equation (6) is actually the definition of the strain tensor ε_{ik} for the homogeneous deformations.[12] Differentiating both sides of Eq. (6) with respect to ε_{ik} and noting that $x_i'=\langle h\rangle_{ik}h_{kl}^{-1}x_l$ we obtain from Eqs. (4)–(6)

$$\left\langle \varepsilon_{ik}\sum_{a>b}\frac{\partial U}{\partial r_{ab}}\frac{\langle h\rangle_{lp}h_{ps}^{-1}x_s\langle h\rangle_{mt}h_{tw}^{-1}x_w}{r_{ab}}\right\rangle
=\frac{1}{2}k_B T(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl}). \tag{7}$$

We have left out in Eq. (7) the ‘‘kinetic’’ contributions because they do not contribute, since $\langle \varepsilon_{ik}\rangle=0$. From Eqs. (1) and (7) a fluctuation formula for elastic constants follows:

$$C_{iklm}=\frac{1}{\langle V\rangle}\left\langle \varepsilon_{ik}\sum_{a>b}\frac{\partial U}{\partial r_{ab}}\frac{\langle h\rangle_{np}h_{pq}^{-1}(x_{ab})_q\langle h\rangle_{jt}h_{ts}^{-1}(x_{ab})_s}{r_{ab}}\right\rangle
\times\langle \varepsilon_{nj}\varepsilon_{lm}\rangle^{-1}. \tag{8}$$

At low temperatures one can neglect the difference between instantaneous scaling matrices h and the average scaling matrix $\langle h\rangle$ in Eq. (8) and the following equation is obtained:

$$C_{iklm}=\langle \varepsilon_{ik}\sigma_{nj}\rangle\langle \varepsilon_{nj}\varepsilon_{lm}\rangle^{-1}, \tag{9}$$

where σ_{ik} are the components of the microscopic stress tensor

$$\sigma_{nj}=\frac{1}{V}\left\{\sum_a\frac{(p_a)_n(p_a)_j}{m_a}+\sum_{a>b}\frac{\partial U}{\partial r_{ab}}\frac{(x_{ab})_n(x_{ab})_j}{r_{ab}}\right\}. \tag{10}$$

For the sake of completeness, we retain in Eq. (10) the kinetic contributions. Formally, what one would have to do to obtain Eq. (9) is to replace the constant term $k_BT/\langle V\rangle$ in Eq. (1) by the fluctuating components of stress-strain correlation. This would in no way improve the overall convergence of the elastic constants calculation unless the instantaneous stresses and strains are correlated. However they are indeed correlated throughout phase space. This is most obvious in the limiting case of low temperatures for classical system where the entropic contributions are negligible and the instantaneous stresses are unambiguously determined by the instantaneous strains via Hooke’s law

$$\sigma_{ik}=C_{iklm}\varepsilon_{lm}\,. \tag{11}$$

Substituting Eq. (11) into Eq. (9), we immediately obtain identity, indicating that the limiting step in the convergence of Eq. (9) is the convergence of the components of the average scaling matrix, i.e., of the first moments of the strain fluctuations. Thus, in the low-temperature (harmonic) situations, Eq. (8) allows for evaluating the elastic constants without fully converged second moments $\langle \varepsilon_{ik}\varepsilon_{lm}\rangle$ of the strain fluctuations, as explicitly required by the PR equation. Metropolis Monte Carlo and molecular dynamics are designed[13] to sample the regions of the phase space in which the system size and shape are close to their averages. These regions contribute dominantly to the first moments of the fluctuations but make progressively smaller contributions to the higher moments, including the second moments of the strain fluctuations. Hence, for the classical systems considered (i.e., discarding the presence of the zero-point vibrations), Eq. (8) should, at least at low temperatures, converge better than Eq. (1).

TABLE I. Isothermal elastic constants (Voigt representation, in units of Nk_BT/V) (Ref. 15) calculated from the second half of simulation runs of 3×10^7 steps started from the minimum-energy configuration. The temperature T is measured in units of ε/k_B, where ε is the well depth of the Lennard-Jones potential energy function. C_{11}, C_{12}, and C_{44} and their standard deviations were calculated over the three sets of symmetry-equivalent elastic constants $\{C_{1111},C_{2222},C_{3333}\}$, $\{C_{1122},C_{2233},C_{1133},C_{2211},C_{3322},C_{3311}\}$, and $\{C_{4444},C_{5555},C_{6666}\}$, respectively.

T	C_{ik}	Eq. (1)	Eq. (8)	Ref. 14	Eq. (9)
0.125	C_{11}	490.6±0.8	492.1±0.3	494.0±1.1	490.9±0.6
	C_{12}	234.4±0.3	238.6±0.2	237.8±1.1	235.4±0.3
	C_{44}	248.5±0.7	250.0±0.3	250.0±0.2	250.0±0.3
	$2C_{44}/(C_{11}-C_{12})$	1.94±0.02	1.97±0.01	1.95±0.02	1.96±0.02
0.225	C_{11}	235.0±1.0	236.8±0.1	237.0±0.8	235.7±0.2
	C_{12}	108.4±0.7	111.5±0.1	108.2±0.8	108.5±0.2
	C_{44}	121.0±0.2	120.1±0.2	121.9±0.2	121.0±0.2
	$2C_{44}/(C_{11}-C_{12})$	1.91±0.03	1.92±0.01	1.89±0.03	1.90±0.01
0.3	C_{11}	155.3±0.6	156.7±0.1	157.1±1.0	155.7±0.2
	C_{12}	68.1±0.3	71.8±0.1	69.3±0.9	68.8±0.2
	C_{44}	80.6±0.4	80.2±0.1	82.2±0.2	81.1±0.1
	$2C_{44}/(C_{11}-C_{12})$	1.85±0.03	1.90±0.01	1.87±0.05	1.87±0.01

At elevated temperatures, where the entropic contributions are significant, there is no unique correspondence between the instantaneous stresses and strains, but the stresses and strains are still somewhat correlated. To understand the situations in which accounting for the correlation between instantaneous stresses and strains improves the convergence of the elastic constant calculation, we take as a benchmark a calculation with a first-nearest-neighbor Lennard-Jones fcc crystal.[4,5]

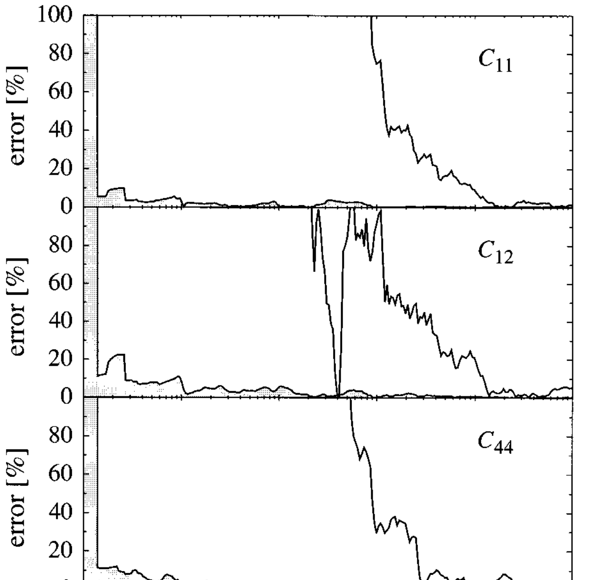

FIG. 1. Comparing the convergence of Eq. (8) (lines delimiting shaded areas) and Eq. (1) (the other solid lines) at a low temperature of $T=0.01$. The second half of a simulation run of 10^7 MC steps was used. The running accuracy of calculated C_{ik} were evaluated as $|C_{ik}-C_{ik}^0|/C_{ik}^0$, where C_{ik}^0 were the static (classical, zero-temperature) values of C_{ik} obtained from the components of the system's Hessian matrix. See also the legend of Table I.

AN ILLUSTRATION: A 108-ATOM FIRST-NEAREST-NEIGHBOR LENNARD-JONES FCC CRYSTAL

We carried out a variable-shape Monte Carlo (MC) simulation of a classical first-nearest-neighbor Lennard-Jones fcc crystal of $N=108$ atoms. A Monte Carlo move consisted of an attempt to randomly alter the scaled coordinates

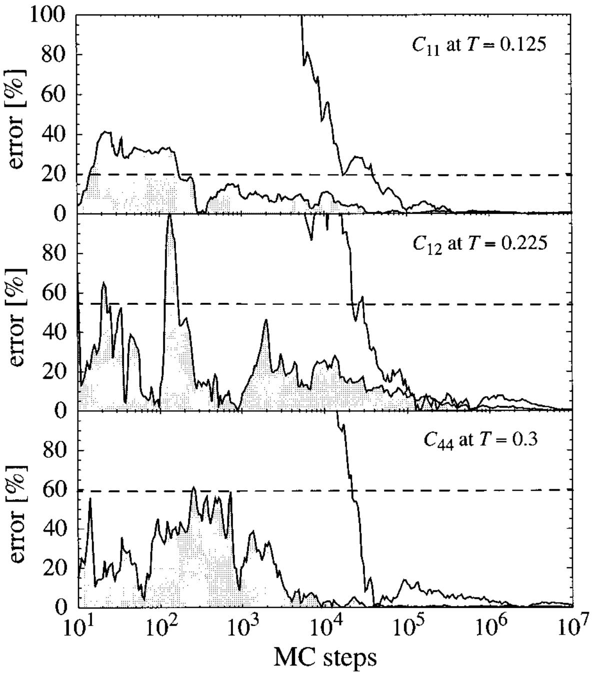

FIG. 2. Comparing the convergence of Eq. (8) (lines delimiting shaded areas) and Eq. (1) (the other solid lines) for the second half of simulation runs of 3×10^7 steps. The running accuracy of calculated C_{ik} were evaluated as $|C_{ik}-C_{ik}^\infty|/C_{ik}^\infty$, where the values given in Table I [obtained with Eqs. (8) and (1), respectively] were used as estimates for C_{ik}^∞. The dashed lines show the static (classical, zero-temperature) values of C_{ik} obtained from the components of the system's Hessian matrix. See also the legend of Table I.

$h_{ik}^{-1}(x_a)_k$ of each atom a accompanied by small random changes in the components h_{ik} of the scaling matrix. The Metropolis scheme was implemented to generate states with a limiting distribution proportional to $V^N \exp\{-U/k_BT\}$, where U is the system's potential energy, depending only on the separations between the nearest neighbors.

Table I shows that the calculated elastic constants are in good agreement with literature data.[14] In the classical statistics at low temperature, the harmonic approximation is adequate for describing the atomic thermal motion, and the conditions $2C_{44}/(C_{11}-C_{12})=2$ and $C_{12}=C_{44}$ (the so-called Cauchy condition) should hold for the Lennard-Jones crystal studied.[16] One can see from Table I that indeed, the lower the temperature, the smaller the deviations from these conditions.

As we discussed above, at low temperatures the fluctuation formula of Eq. (8) should generally have better convergence properties than Eq. (1). Figure 1 illustrates the situation at a reduced temperature of $T=0.01$ where the elastic constants differ from their static values by less than a tenth of a percent. With the fluctuation formula it takes only a hundred MC steps to calculate the elastic constants to within a few percent. A few hundred thousand steps are needed to reach the same level of accuracy with the PR formula.

Figure 2 shows that the fluctuation formula also has superior convergence properties in situations where the anharmonicity is significant and the elastic constants are considerably smaller than their static values. In particular, Eq. (8) is at least two orders of magnitude more efficient than Eq. (1) in obtaining better than the static estimates of the elastic constants (dashed lines in Fig. 2); estimates of the elastic constants within 5–10 %—most often adequate in practice—are also obtained much more rapidly with Eq. (8).

CONCLUSIONS

We have presented a fluctuation equation for the elastic constants. The formula has the same validity as the Parrinello-Rahman fluctuation formula and benefits from the fact that in thermal fluctuations the instantaneous stresses and strains are correlated. For the classical first-nearest-neighbor Lennard-Jones fcc crystal, the presented fluctuation formula had superior convergence properties. The use of this fluctuation formula may be rewarding in various applications, especially where the simulation technique employed (for example, molecular dynamics) already requires the evaluation of the first potential derivatives.

---

[1] R. J. Meier, Macromolecules **26**, 4376 (1993); D. J. Lacks and G. C. Rutledge, J. Phys. Chem. **98**, 1222 (1994); and references cited therein.

[2] For example, see J. R. Maple, M.-J. Hwang, T. P. Stockfisch, U. Dinur, M. Waldman, C. S. Ewig, and A. T. Hagler, J. Comput. Chem. **15**, 162 (1994).

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

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

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

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

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

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

[9] P. J. Fay and J. R. Ray, Phys. Rev. A **46**, 4645 (1992).

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

[11] A. Münster, *Statistical Thermodynamics* (Springer, Berlin, 1969), Sec. 17.

[12] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 7 (Pergamon, London, 1986), Sec. 1.

[13] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987), Sec. 7.2.

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

[15] One reduced pressure unit is ≈3.67 MPa at the reduced temperature $T=0.125$, 6.46 MPa at $T=0.225$, and 8.44 MPa at $T=0.3$.

[16] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954), Sec. 11.