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The calculation of elastic constants from displacement fluctuations

M. T. Meyers and J. M. Rickman[a)]
Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

T. J. Delph
Department of Mechanical Engineering and Mechanics, Lehigh University, Bethlehem, Pennsylvania 18015

We present a methodology for the accurate and efficient extraction of elastic constants in homogeneous solids via the calculation of the atomic displacement correlation function. This approach is validated for cubic solids parametrized by both Lennard-Jones and embedded-atom method potentials. Finally, we also discuss the extension of this method to obtain the elastic properties of inhomogeneous solids. © *2005 American Institute of Physics.*
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There exist a number of methods in the literature for the numerical calculation of elastic constants of crystals for which the interatomic forces are described by an appropriate interatomic potential. These methods may be broadly classified as finite-strain techniques[1] and fluctuation techniques,[2–5] the former involving the construction of a stress-strain relation from which elastic properties may be obtained and the latter involving the calculation of correlation functions (e.g., stress-stress) and a contribution from the average of the strain derivatives of the microscopic stress. The fluctuation dissipation theorem links these two approaches in that calculated correlation functions are proportional to generalized susceptibilities, such as the elastic constants. Finally, we note that elastic constant calculations are amenable to both molecular-dynamics (MD) and Monte Carlo (MC) simulations, and have been performed in both isostress and isostrain ensembles.[6,7]

A fluctuation-based alternative that exploits thermally induced atomic displacement fluctuations to obtain elastic behavior has been advanced by Pratt.[8] This method is advantageous in that atomic displacements are relatively straightforward to determine during the course of a simulation, as opposed to, for example, more complicated local strain measures, and because this formalism can be extended to the calculation of local elastic constants. This method has only been employed indirectly,[9] possibly because of the rather complicated procedure originally proposed for the extraction of elastic constant data. Thus, we put forward a simple, numerically efficient means for accomplishing this task, and illustrate the method with numerical results of the isothermal MC and MD calculations for two different potentials. We then suggest an extension of the method to obtain local elastic behavior in inhomogeneous systems.

Consider an elastic solid consisting of N atoms contained in a simulation cell of fixed volume V that is held at a constant temperature T. The corresponding (differential) Helmholtz free energy for this system is

a)Electronic mail: jmr6@lehigh.edu

$$dF = -SdT + \int_V \sigma_{ij}(\mathbf{r})d\epsilon_{ij}(\mathbf{r})d\mathbf{r} + \mu dN, \tag{1}$$

where S is the entropy, T is the absolute temperature, μ is the chemical potential, ϵ_{ij} is the Lagrange strain tensor, and σ_{ij} the second Piola-Kirchoff stress tensor, the conjugate to the Lagrange strain. The usual summation convention for repeated subscripts is implied here. For the case of small strains, the Lagrange strain tensor may be approximated by

$$\epsilon_{ij}(\mathbf{r}) = \frac{1}{2}\left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i}\right) \tag{2}$$

where $u(\mathbf{r})$ is the displacement field at point $\mathbf{r}$.

It is convenient to introduce here the isothermal stress-strain coefficients $B_{ijk\ell} = (\partial\sigma_{ij}/\partial\epsilon_{k\ell})|_T$ that are related to the standard elastic constants $C_{ijk\ell}$ by additive terms involving the stress.[10] In the absence of stress, $B_{ijk\ell} = C_{ijk\ell}$. With this definition one finds that, in an elastically homogeneous, stress-free, isothermal system, the difference in free energy ΔF between two states having the same N is given by

$$\Delta F = \frac{C_{ijk\ell}}{2}\int_V \epsilon_{ij}(\mathbf{r})\epsilon_{k\ell}(\mathbf{r})d\mathbf{r}. \tag{3}$$

This difference in free energy can be written in a more useful form by first introducing the discrete Fourier transform pair

$$\widetilde{f}(\mathbf{k}) = \frac{1}{N}\sum_{\alpha=1}^{N} f^\alpha \exp(-i\mathbf{k}\cdot\langle\mathbf{r}^\alpha\rangle),$$

$$f^\alpha = \sum_{\mathbf{k}} \widetilde{f}(\mathbf{k})\exp(i\mathbf{k}\cdot\langle\mathbf{r}^\alpha\rangle), \tag{4}$$

where $\mathbf{r}^\alpha$ is the position vector of atom α and $\langle\ \rangle$ denotes a thermal average. Next, upon discretizing the integral in Eq. (3) and inserting the expression for the Fourier transform one obtains

$$\Delta F = \frac{V}{N}C_{ijk\ell}\sum_{\alpha=1}^{N} \epsilon_{ij}(\langle\mathbf{r}^\alpha\rangle)\epsilon_{k\ell}(\langle\mathbf{r}^\alpha\rangle),$$

$$= \frac{V}{N} C_{ijk\ell} \sum_{\alpha=1}^{N} \sum_{\mathbf{k}} \sum_{\mathbf{h}} \widetilde{\epsilon}_{ij}(\mathbf{h}) \widetilde{\epsilon}_{k\ell}(\mathbf{k}) \exp[i(\mathbf{k}+\mathbf{h}) \cdot \langle \mathbf{r}^{\alpha} \rangle],$$

$$= V C_{ijk\ell} \sum_{\mathbf{k}} k_j k_\ell \widetilde{u}_i(\mathbf{k}) \widetilde{u}_k(-\mathbf{k}), \tag{5}$$

where we have made use of a Kronecker delta function representation[11] to simplify the results. Now, since the probability p of a thermal fluctuation is given by $p \propto \exp[-\Delta F/k_B T]$, one obtains from Gaussian integration

$$\langle \widetilde{u}_i(\mathbf{k}) \widetilde{u}_k(-\mathbf{k}) \rangle = \frac{k_B T}{V} (C_{ijk\ell} k_j k_\ell)^{-1}. \tag{6}$$

Equation (6) was obtained by Landau and Lifshitz[12] in a discussion of the crystal structural stability and, in earlier work, by Born[13] who extended this relation to finite wave vectors via the dynamical matrix. Moreover, the $1/k^2$ behavior of the displacement correlation function can also be viewed as a consequence of the long-range order inherent in a crystalline solid.[14] Equation (6) will be employed below to obtain elastic constants from correlations in displacement fluctuations.

The elastic constants may be readily extracted from Eq. (6) by examining the dependence of the displacement correlation function on wave vector in the long-wavelength, elastic limit for which this equation is valid. Consider a system consisting of N atoms contained in a cubic simulation cell having side L and subject to periodic boundary conditions such that the corresponding allowed wave vectors $\mathbf{k} = (2\pi/L)(n,p,q)$ where n, p, and q are integers. For simplicity, take $\mathbf{k} = (2\pi/L)n\mathbf{k}'$ for two high-symmetry directions, namely, $\mathbf{k}' = (1,0,0)$ and $\mathbf{k}' = (1,1,0)$. Now, for particular choices of n and reduced wave vector $\mathbf{k}'$ the displacement correlation function should vary linearly with $1/n^2$ for small n. If η_{ik} is the slope of this linear relation, then from Eq. (6) one finds that

$$\Lambda_{ik} = \frac{k_B T}{4\pi^2 L} \eta_{ik}^{-1}, \tag{7}$$

where $V = L^3$ and $\Lambda_{ik}(\mathbf{k}') = C_{ijk\ell} k'_j k'_\ell$. η_{ik} is easily inverted numerically, and the elastic constants can be obtained from the resulting equations. (Alternatively, one can easily invert $\overline{\Lambda}$ in high-symmetry directions and obtain the desired results.) Thus, one finds for a cubic system that

$$\Lambda_{ik}[(1,0,0)] = C_{44}\delta_{ik} + (C_{11} - C_{44})\delta_{i1}\delta_{k1},$$

$$\Lambda_{ik}[(1,1,0)] = (C_{11} + C_{44})\delta_{ik} + (C_{44} - C_{11})\delta_{i3}\delta_{k3}$$
$$+ (C_{12} + C_{44})(\delta_{i1}\delta_{k2} + \delta_{i2}\delta_{k1}). \tag{8}$$

We now validate this method by application of the formalism to obtain the elastic constants of two cubic systems, one parametrized by a Lennard-Jones potential and the other by an embedded-atom method (EAM) potential. The relevant, nonzero elastic constants, in Voigt notation, are $C_{11} = C_{1111} = C_{2222} = C_{3333}$, $C_{12} = C_{1122} = C_{1133} = C_{2233}$, and $C_{44} = C_{1212} = C_{1313} = C_{2323}$.

In the first study, MC simulations were carried out in the canonical ensemble for a fcc crystalline solid consisting of
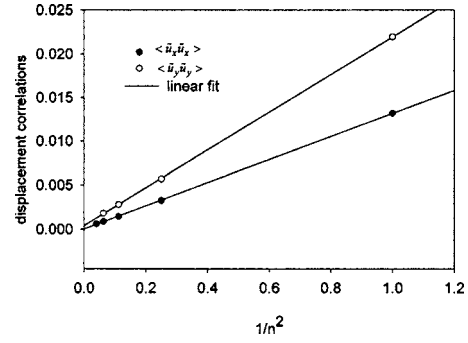

FIG. 1. The displacement correlation functions $\langle \delta \widetilde{u}_x(\mathbf{k}) \delta \widetilde{u}_x(-\mathbf{k}) \rangle$ and $\langle \delta \widetilde{u}_y(\mathbf{k}) \delta \widetilde{u}_y(-\mathbf{k}) \rangle$ vs $1/n^2$ for reduced wave vector $\mathbf{k}' = (1,0,0)$ for a Lennard-Jones solid at zero pressure and reduced temperature $T = 0.15\epsilon/k_B$. The elastic constants C_{11} and C_{44} are obtained from the slopes of these curves.

1372 atoms confined to a periodic simulation cell. A modified Lennard-Jones potential[15] with energy and length parameters ϵ and σ, respectively, was employed here and the zero-pressure lattice parameter and corresponding temperature $T = 0.15\epsilon/k_B$ (k_B is Boltzmann's constant) were fixed for the simulations. Typical runs consisted of 50×10^3 MC steps (MCS). It should be noted that, since the center of mass of the system is unconstrained, calculated atomic displacements had to be corrected for center-of-mass translation. After making this correction and allowing the system to reach equilibrium, displacement correlations were tabulated every five MC steps for a number of wave vectors in each of the three high symmetry given above. This sampling was sufficient to ensure nearly independent samples for the correlation functions.

To illustrate the procedure for extracting the elastic constants, Fig. 1 shows the expected linear behavior of two displacement correlation functions, $\langle \delta \widetilde{u}_x(\mathbf{k}) \delta \widetilde{u}_x(-\mathbf{k}) \rangle$ and $\langle \delta \widetilde{u}_y(\mathbf{k}) \delta \widetilde{u}_y(-\mathbf{k}) \rangle$ vs $1/n^2$ for the wave vector $\mathbf{k}' = (1,0,0)$. With similar plots in the other principal directions, the elastic constants were found to be $C_{11} = 76.9$, $C_{12} = 46.0$, and $C_{44} = 41.7$, respectively, in units of ϵ/σ^3. (The error estimate for these quantities is ± 3.0.[16])

In the second study, isothermal MD simulations were carried out for copper, parametrized by an EAM potential,[17] at 75 K.[18] More specifically, a periodic simulation cell containing 500 atoms was employed along with velocity rescaling to maintain a constant temperature. After equilibration, the displacement correlations were tabulated at every 40 time steps to achieve nearly independent data samples and then postprocessed using a discrete Fourier transform. Figure 2 shows the expected linear behavior of the displacement correlation function versus $1/n^2$ for the choice of wave vector $\mathbf{k}' = (1,0,0)$.

The corresponding elastic constants were extracted using least-squares minimization for wave vectors $\mathbf{k}' = (1,0,0)$ and $\mathbf{k}' = (1,1,0)$. It was found that $C_{11} = 171.9$ GPa, $C_{12} = 135.8$ GPa, and $C_{44} = 81.7$ GPa. (The approximate errors in these quantities is ± 8.0 GPa.) These values agree well with those reported in the literature.[19]

We have presented here a technique, originally described by Pratt,[8] for the calculation of elastic constants that makes
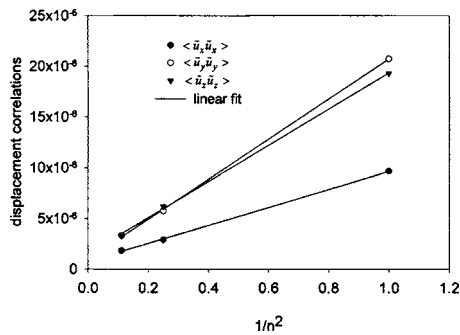
FIG. 2. The same as in Fig. 1, except for EAM copper at 75 K. Also shown is the correlation function $\langle \delta \tilde{u}_z(\mathbf{k}) \delta \tilde{u}_z(-\mathbf{k}) \rangle$ which, by symmetry, should equal $\langle \delta \tilde{u}_y(\mathbf{k}) \delta \tilde{u}_y(-\mathbf{k}) \rangle$.

use of the atomic displacement fluctuation data obtained from standard MD or MC simulations. We have likewise presented an easily implemented method for extracting the elastic constants from the computed displacement fluctuation data. This technique is attractive from several standpoints, most notably its simplicity with respect to competing techniques. As this method is not based on atomic level stress and strain measures, it has the advantage of not requiring the calculation of derivatives of either the interatomic potential or the displacement field.

It is also worth noting that the methodology outlined here can be extended to the case of spatially inhomogeneous systems for which one can define local elastic constants $C_{ijk\ell}(\mathbf{r})$. For example, in some geophysical applications,[21] it is convenient to define such local constants at position $\mathbf{r}$ via a local stress-strain relationship $\sigma_{ij}(\mathbf{r}) = C_{ijk\ell}(\mathbf{r})\epsilon_{k\ell}(\mathbf{r})$, where $\sigma_{ij}(\mathbf{r})$ is the local stress. This definition enables one to describe elastic bodies with inclusions using the formalism of scattering theory. Following an analysis similar to that presented above, one can construct a displacement correlation function that embodies local elastic behavior. Given the loss of translational invariance, however, this function will depend, in general, on two wave vectors. The extension of this technique to inhomogeneous systems is the subject of ongoing work.

[1] M. D. Kluge, D. Wolf, J. F. Lutsko, and S. R. Phillpot, J. Appl. Phys. **67**, 2370 (1990).

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

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

[4] J. F. Lutsko, J. Appl. Phys. **65**, 2991 (1989).

[5] J. M. Rickman and J. A. Jaszczak, Phys. Rev. B **43**, 13285 (1991).

[6] T. Cagin and J. R. Ray, Phys. Rev. B **38**, 7940 (1988).

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

[8] L. R. Pratt, J. Chem. Phys. **87**, 1245 (1987).

[9] J. M. Rickman, J. Viñals, R. F. Sekerka, and W. W. Mullins, Phys. Rev. B **45**, 7750 (1992).

[10] D. C. Wallace, *Thermodynamics of Crystals* (Dover, New York, 1998).

[11] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge, Cambridge, 1995).

[12] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1980).

[13] M. Born, Rep. Prog. Phys. **9**, 294 (1942).

[14] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin, Reading, MA, 1975).

[15] J. Q. Broughton and G. H. Gilmer, J. Chem. Phys. **79**, 5095 (1983).

[16] By comparison, the use of fluctuation formulas based on derivatives of the potential (Ref. 2) yield $C_{11}=72.8$, $C_{12}=44.4$, and $C_{44}=45.8$, respectively, in units of ϵ/σ^3. It should be noted that $C_{12} \approx C_{44}$ due to the fact that a pair potential was employed here at relatively low temperature. Finally, rough error estimates, as indicated in the text, associated with the linear fit in the figures can be obtained by calculating the elastic constants corresponding to each wave vector and then averaging.

[17] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[18] For this purpose we employed the parallel PARADYN code developed at Sandia National Laboratory.

[19] By comparison, reported values (Refs. 17 and 20) for the low-temperature elastic constants of copper using the EAM potential are $C_{11}=167-176$ GPa, $C_{12}=124-129$ GPa, and $C_{44}=76.0-81.8$ GPa.

[20] S. Chantasiriwan and F. Milstein, Phys. Rev. B **58**, 5996 (1998).

[21] M. Jakobsen, J. A. Hudson, and T. A. Johansen, Geophys. J. Int. **154**, 533 (2003).