

Statistical calculation of elastic moduli for atomistic models

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The elastic moduli of a solid can be determined from the thermal fluctuations of the stress. The so-called stress-fluctuation approach is useful in that it can provide insights into the molecular origin of a particular mechanical response, and it leads to faster convergence than methods based on fluctuations of the strain. Unfortunately the implementation of the stress-fluctuation approach is more demanding than that of the strain-fluctuation approach, particularly for atomistic models involving intramolecular interactions (e.g., bending and torsion). In this study a simple numerical method is proposed to evaluate the elastic moduli of atomistic models from knowledge of atomistic forces. It is shown that this approach leads to fast and reliable prediction of the elastic moduli for two different classes of materials. In one example the elastic moduli of crystalline silicon are compared to those reported in the literature. In the other example the elastic moduli of an atomistic polymer model for poly(methyl methacrylate) are shown to be in good agreement with experimental data.

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I. INTRODUCTION

Molecular simulations provide a powerful approach to quantify the elastic properties of solids and the molecular origins of particular constitutive behaviors. The elastic moduli can be determined directly, by applying a load to a system and observing its response, or indirectly, by computing the thermal fluctuations of the strains or stresses. The latter approach is attractive in that it provides all of the components of the elastic tensor from a single simulation, and it makes a distinction between contributions to the moduli arising from different molecular interactions.¹ Such a tensor can subsequently be used to study a system's anisotropy and mechanical stability.²

Several statistical formalisms are available for the calculation of elastic moduli.^{3–6} At constant temperature T , volume V , and number of particles N , an isothermal elastic modulus C_{ijkl} can be determined from^{3,4}

$$C_{ijkl} = C_{ijkl}^B + C_{ijkl}^K - C_{ijkl}^F, \quad (1)$$

where

$$C_{ijkl}^K = 2(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})Nk_B T/V, \quad (2)$$

$$C_{ijkl}^F = (\langle \sigma_{ij}\sigma_{kl} \rangle - \langle \sigma_{ij} \rangle \langle \sigma_{kl} \rangle) V/k_B T. \quad (3)$$

All the vectors and tensors in this study are expressed in index notation; subscripts (i, j, k, l) denote the Cartesian components (x, y, z) . The symbol δ_{ij} is the identity tensor. The brackets $\langle \rangle$ denote an ensemble average. The terms C_{ijkl}^B and C_{ijkl}^K represent the intrinsic elastic moduli of a system; superscripts B and K denote the Born term and the kinetic contribution, respectively.³ The thermal fluctuation contribution to the elastic moduli, C_{ijkl}^F , is determined from the stress tensor σ_{ij} . It should be noted that the elastic modulus tensor can also be calculated in a constant stress ensemble from the corresponding fluctuations of the strain.⁵ We prefer to work with stress fluctuations because Eq. (1) provides unique in-

sights into the intrinsic stiffness of a material and the effect of thermal motion on the elastic moduli. In addition, the stress-fluctuation approach often leads to faster convergence of the elastic moduli in molecular simulations.⁶

Ray has derived a generalized formula for the Born term of an arbitrary potential energy function U :³

$$C_{ijkl}^B = \frac{1}{V} \sum_{a<b} \sum_{c<d} \langle p(a, b, c, d) r_i^{ab} r_j^{ab} r_k^{cd} r_l^{cd} \rangle \quad (4)$$

where

$$p(a, b, c, d) = \frac{1}{r^{ab} r^{cd}} \left(\frac{\partial^2 U}{\partial r^{ab} \partial r^{cd}} - \frac{1}{r^{ab}} \frac{\partial U}{\partial r^{ab}} \delta_{ac} \delta_{bd} \right). \quad (5)$$

The quantity r^{ab} represents the magnitude of the interparticle vector $r_i^{ab} (=r_i^b - r_i^a)$. The sums over $a < b$ (or $c < d$) count all possible pairs among N particles. By replacing c and d by a and b in Eqs. (4) and (5), one obtains the well-known formula for the Born term of a pairwise additive potential energy function U_2 (e.g., a Lennard-Jones (LJ) or a harmonic spring potential);^{3,4,7}

$$C_{ijkl}^{B2} = \frac{1}{V} \sum_{a<b} \left\langle \left(\frac{\partial^2 U_2}{\partial r^{ab^2}} - \frac{1}{r^{ab}} \frac{\partial U_2}{\partial r^{ab}} \right) \frac{r_i^{ab} r_j^{ab} r_k^{ab} r_l^{ab}}{r^{ab^2}} \right\rangle. \quad (6)$$

In Eqs. (4)–(6) the potential must be an explicit function of interatomic distances. While some applications of Eqs. (4)–(6) to atomistic models have been reported in the literature; e.g., the Sutton-Chen model for transition metals,⁸ the Stillinger-Weber (SW) model,³ and the Tersoff model⁹ for silicon, the use of the stress-fluctuation formula has generally been limited by the ability to evaluate the Born term in atomistic models that include non-pairwise interactions such as bending and torsion.^{1,6}

In this paper we propose a simple numerical method to estimate the Born term using expressions originally derived by Lutsko.⁴ This method does not require the transformation

of a non-pairwise potential to an explicit function of interatomic distances, and is easily implemented in molecular dynamic (MD) simulations. Results are presented for the elastic moduli of the SW silicon model³ and an atomistic model of poly(methyl methacrylate),¹⁰ referred to as PMMA. Our numerical results for the SW silicon model are in good agreement with those obtained analytically in the literature.³ For the model of PMMA, which includes bending and torsion interactions, simulated moduli are in good agreement with experimental data. The molecular origins of those elastic moduli are further discussed in Sec. III.

II. METHODOLOGY

A. Models

The SW silicon model is parametrized to yield a stable tetrahedral structure in solids whose internal energy U^S is given by¹¹

$$U^S = \sum_{a<b} u_2(r^{ab}) + \sum_{a<b<c} [u_3(r_i^{ab}, r_i^{ac}) + u_3(r_i^{ba}, r_i^{bc}) + u_3(r_i^{ca}, r_i^{cb})], \quad (7)$$

where $a < b < c$ is a summation over all possible combinations of three atoms in a system. The function u_2 is a pairwise potential

$$u_2(r^{ab}) = A[B(r^{ab})^{-4} - 1]h_{\gamma_1}(r^{ab}), \quad (8)$$

and u_3 is a three-body potential

$$u_3(r_i^{ab}, r_i^{ac}) = \lambda h_{\gamma_2}(r^{ab})h_{\gamma_2}(r^{ac})g(\theta^{bac})^2, \quad (9)$$

where

$$g(\theta^{bac}) = \cos \theta^{bac} + 1/3, \quad (10)$$

$$h_{\gamma}(r^{ab}) = \begin{cases} e^{\gamma/(r^{ab}-\zeta)}, & \text{if } r^{ab} > \zeta, \\ 0, & \text{if } r^{ab} \leq \zeta. \end{cases} \quad (11)$$

The symbol θ^{bac} denotes the angle between the vectors r_i^{ab} and r_i^{ac} .

The united-atom model adopted for the simulations of PMMA includes five contributions to the potential energy U^P :¹⁰

$$U^P = \sum_{a<b} K_r(r^{ab} - r^{eq})^2 + \sum_{a<b<c} K_{\theta}(\theta^{abc} - \theta^{eq})^2 + \sum_{a<b<c<d} \frac{V_n}{2} [1 + \cos(n\phi^{abcd} - \phi^{eq})] + \sum_{a<b} \frac{Q^a Q^b}{\epsilon r^{ab}} + \sum_{a<b} \left[A^{ab} \left(\frac{1}{r^{ab}} \right)^{12} - B^{ab} \left(\frac{1}{r^{ab}} \right)^6 \right]. \quad (12)$$

The first three terms correspond to bonding, bending, and torsional interactions, respectively. In the third term, ϕ^{abcd} is the dihedral angle between the planes $\{r_i^{ab}, r_i^{ac}\}$ and $\{r_i^{db}, r_i^{dc}\}$. The fourth and fifth terms are pairwise contributions arising from Coulombic and LJ interactions, respectively. The values of the parameters in Eqs. (8)–(12) are reported in the literature.^{10,11}

B. Theory

Following Lutsko, a generalized stress tensor for an arbitrary potential energy function is written as⁴

$$\sigma_{ij} = \sigma_{ij}^v + Nk_B T \delta_{ij}/V, \quad (13)$$

where σ_{ij}^v is the symmetric virial tensor

$$\sigma_{ij}^v = \frac{-1}{2V} \sum_{m=1}^N \left[r_i^m \frac{\partial U}{\partial r_j^m} + r_j^m \frac{\partial U}{\partial r_i^m} \right]. \quad (14)$$

By evaluating the derivative of σ_{ij} with respect to the Lagrangian strain tensor, a generalized Born term expression is obtained as

$$\hat{C}_{ijkl}^B = 1/4(\hat{C}_{ijkl}^B + \hat{C}_{jikl}^B + \hat{C}_{ijlk}^B + \hat{C}_{jilk}^B), \quad (15)$$

where

$$\hat{C}_{ijkl}^B = \frac{1}{V} \sum_{m=1}^N \sum_{n=1}^N \left\langle r_j^m r_l^n \frac{\partial^2 U}{\partial r_k^n \partial r_i^m} \right\rangle + \delta_{ik} \langle \sigma_{jl}^v \rangle. \quad (16)$$

Equation (16) can be transformed into other generalized formulas, namely, Eqs. (4) and (5) (see Appendix A). In this study we rewrite Eq. (16) as

$$\hat{C}_{ijkl}^B = \frac{-1}{V} \sum_{m=1}^N \sum_{n=1}^N \left\langle r_j^m r_l^n \frac{\partial f_i^m}{\partial r_k^n} \right\rangle + \delta_{ik} \langle \sigma_{jl}^v \rangle, \quad (17)$$

where f_i^m is the force acting on an atom labeled by m :¹²

$$f_i^m = - \frac{\partial U}{\partial r_i^m}. \quad (18)$$

Atomistic force calculations are an intrinsic component of any MD simulations.¹² This facilitates the numerical implementation of the Born term through Eq. (17) rather than solving Eq. (16) or Eqs. (4) and (5) analytically. As an example we consider the case of a three-body potential energy function u_3 in Eqs. (9)–(11). Using Eq. (18) the atomistic forces on the three atoms (a, b, c) are calculated from

$$f_i^b = \frac{u_3}{r^{ab}} \left[\frac{\gamma r_i^{ab}}{(r^{ab} - \zeta)^2} - \frac{2}{g} \left(\frac{r_i^{ac}}{r^{ac}} - \cos \theta^{bac} \frac{r_i^{ab}}{r^{ab}} \right) \right], \quad (19)$$

$$f_i^c = \frac{u_3}{r^{ac}} \left[\frac{\gamma r_i^{ac}}{(r^{ac} - \zeta)^2} - \frac{2}{g} \left(\frac{r_i^{ab}}{r^{ab}} - \cos \theta^{bac} \frac{r_i^{ac}}{r^{ac}} \right) \right], \quad (20)$$

$$f_i^a = - (f_i^b + f_i^c). \quad (21)$$

By substituting Eq. (21) into Eq. (17), the Born term for the three-body interaction \hat{C}_{ijkl}^{B3} is found to be

$$\hat{C}_{ijkl}^{B3} = \frac{-1}{V} \left\langle r_j^{ab} r_l^a \frac{\partial f_i^b}{\partial r_k^a} + r_j^{ac} r_l^a \frac{\partial f_i^c}{\partial r_k^a} + r_j^{ab} r_l^b \frac{\partial f_i^b}{\partial r_k^b} + r_j^{ac} r_l^b \frac{\partial f_i^c}{\partial r_k^b} + r_j^{ab} r_l^c \frac{\partial f_i^b}{\partial r_k^c} + r_j^{ac} r_l^c \frac{\partial f_i^c}{\partial r_k^c} \right\rangle + \frac{\delta_{ik}}{2V} \langle r_j^{ab} f_l^b + r_l^{ab} f_j^b + r_j^{ac} f_l^c + r_l^{ac} f_j^c \rangle. \quad (22)$$

The numerical calculation of Eq. (22) can be performed as

follows. (1) Displace the x coordinate of atom a by an infinitesimal amount Δr_x^a , (2) Calculate changes of the forces associated with that displacement, Δf_i^b and Δf_i^c , (3) Ensure that the displacement is sufficiently small so that the derivatives $\Delta f_i^b/\Delta r_x^a$ and $\Delta f_i^c/\Delta r_x^a$ can be regarded as constants, (4) Displace r_x^a back to its original position, (5) Repeat steps (1) to (4) for Δr_y^a , Δr_z^a , Δr_x^b , etc. If periodic boundary conditions are applied to r_i^{ab} , r_i^b is the minimum-image position with respect to r_i^a .

One could also solve Eq. (22) by evaluating the force derivative terms analytically. For example, the analytical expression for the derivative of the force f_i^b with respect to the atom position r_k^a is given by

$$\begin{aligned} \frac{\partial f_i^b}{\partial r_k^a} = & \frac{u_3}{r^{ab}} \left\{ \frac{\gamma}{(r^{ab} - \zeta)^2} \left[\frac{r_i^{ab} q_k^a}{g} + \frac{2r_i^{ab} r_k^{ab}}{r^{ab}(r^{ab} - \zeta)} - \delta_{ik} \right] \right. \\ & + 2 \left[\frac{\delta_{ik}}{r^{ac}} - \frac{r_i^{ac} r_k^{ac}}{r^{ac^3}} + \frac{r_i^{ab} q_k^a}{r^{ab}} + \cos \theta^{ab} \left(\frac{\delta_{ik}}{r^{ab}} - \frac{r_i^{ab} r_k^{ab}}{r^{ab^3}} \right) \right] \left. \right\} \\ & + f_i^b \left\{ \gamma \left[\frac{r_k^{ab}}{r^{ab}(r^{ab} - \zeta)^2} + \frac{r_k^{ac}}{r^{ac}(r^{ac} - \zeta)^2} \right] + \frac{r_k^{ab}}{r^{ab^2}} \right. \\ & \left. - \frac{1}{g} \left[\frac{r_k^{ab} + r_k^{ac}}{r^{ab} r^{ac}} - \cos \theta^{ab} \left(\frac{r_k^{ab}}{r^{ab^2}} + \frac{r_k^{ac}}{r^{ac^2}} \right) \right] \right\}, \quad (23) \end{aligned}$$

where

$$q_k^a = \cos \theta^{ab} \left(\frac{r_k^{ab}}{r^{ab^2}} + \frac{r_k^{ac}}{r^{ac^2}} \right) - \frac{r_k^{ab} + r_k^{ac}}{r^{ab} r^{ac}}. \quad (24)$$

It is important to note that such analytical expressions can be tedious and elaborate when written for a computer program. One also needs to derive new analytical formulas and recode them for each different model. The numerical approach proposed in this study is flexible and easily extended to any potential. For instance, Eq. (22) can be used for different types of three-body interactions, such as the bending term in Eq. (12). It also has the advantage of using directly the atomistic forces, rather than requiring the transformation of non-pairwise potentials into a pairwise formula, like Eqs. (4) and (5). For three-body potentials, such a transformation could be derived with the law of cosines,^{3,9} but it becomes more demanding for other non-pairwise interactions that include more than three atoms (or molecules); e.g., the torsion term in Eq. (12). In Sec. III it is shown that the results from our numerical method are the same as those obtained from the analytical formulas, and that the computational expense for the numerical calculations can be minimized by decreasing the sampling frequency for the Born term.

For brevity, in the remainder of this study fourth-order tensors are represented in Voigt notation,¹³ e.g., $C_{11} = C_{xxxx}$, $C_{12} = C_{xyxy}$, $C_{44} = C_{xyxy}$.

C. Simulations

All simulations of the SW silicon model comprise 216 atoms with periodic boundary conditions. To reproduce literature results,³ the temperature and pressure were set to

0 Pa and 1477 K, respectively. A perfect diamond structure was used for the initial configuration. First we performed $N\sigma_{ij}T$ Monte Carlo (MC) simulations to obtain the equilibrium density.^{7,12} We sampled the data at every 100 MC steps over simulations of 2×10^6 steps. The resulting averaged density was 2297 kg/m^3 . Second, we ran NVT MC simulations over 2×10^6 steps at that density, and calculated the elastic moduli from the stress-fluctuation formula, Eqs. (1)–(3). The Born term for the two-body potential, $C_{\alpha\beta}^{B2}$ ($\alpha, \beta = 1, 2, \dots, 6$), was analytically calculated from Eq. (6) since the potential energy u_2 depends solely on an interatomic distance. The Born term for the three-body potential $C_{\alpha\beta}^{B3}$ was estimated both analytically and numerically from Eq. (22). All the trial displacements Δr_i^m were set to 10^{-7} in dimensionless units.

For the case of PMMA the initial configuration was generated by placing 80 linear syndiotactic PMMA molecules uniformly in a cubic simulation box. Each molecule consists of 10 monomers. By performing NPT MD simulations, we equilibrated the system at a high temperature (500 K) and cooled it down gradually until room temperature (300 K) was attained. The pressure and time step were set at 0.1 MPa and 1 fs, respectively. The resulting density of amorphous PMMA glass was approximately 1084 kg/m^3 . After the equilibration of the system, we ran NVT MD simulations over 3×10^5 time steps, sampling the instantaneous Born terms and the stress tensor at every 100 time steps. The Born terms for LJ and bonding potentials were calculated analytically from Eq. (6), and those for bending and torsion potentials were estimated numerically from Eq. (17). In order to evaluate Coulombic interactions, the Ewald method was applied and its Born term was calculated analytically from expressions available in the literature.¹⁴

III. RESULTS AND DISCUSSION

Table I summarizes our results for the Born term, the kinetic term, the stress-fluctuation term, and the elastic moduli of the SW silicon model at $T = 1477 \text{ K}$. The three characteristic components of each term are listed; $\bar{C}_{11} = (C_{11} + C_{22} + C_{33})/3$, $\bar{C}_{12} = (C_{12} + C_{23} + C_{31})/3$, $\bar{C}_{44} = (C_{44} + C_{55} + C_{66})/3$. The error of \bar{C}_{ij} indicates the standard deviation of three indistinguishable components; e.g., C_{11} , C_{22} , and C_{33} for \bar{C}_{11} .

It is shown that all results are in good agreement with the values in the literature,³ which were obtained analytically from Eqs. (4) and (5). In addition our numerical results for $C_{\alpha\beta}^{B3}$ are found to be the same as those calculated analytically from Eqs. (22)–(24); $\bar{C}_{11} = 55.3 \text{ GPa}$, $\bar{C}_{12} = -9.4 \text{ GPa}$, $\bar{C}_{44} = 15.8 \text{ GPa}$. It should be emphasized that the analytical calculations of $C_{\alpha\beta}^{B3}$ require newly derived, elaborate formulas be coded for each different model, whereas our numerical calculations can be implemented simply by using an intrinsic component of MD simulations; i.e., the atomistic forces.

It is interesting to observe in Table I that the contribution of the thermal stress fluctuations to the elastic modulus, $C_{\alpha\beta}^F$,

TABLE I. Two-body and three-body Born terms, kinetic term, stress-fluctuation term, and elastic moduli of SW silicon at $T=1477$ K. The sum of $C_{\alpha\beta}^{B2}$ and $C_{\alpha\beta}^{B3}$ is denoted by $C_{\alpha\beta}^B$. The right column for each \bar{C}_{ij} represents the analytical values reported in the literature³ (see Appendix B for data conversion). In *NVT* MC simulations, the kinetic contributions are constant.

Term	\bar{C}_{11} (GPa)		\bar{C}_{12} (GPa)		\bar{C}_{44} (GPa)	
		Ref. 3		Ref. 3		Ref. 3
$C_{\alpha\beta}^{B2}$	81.2±0.0	80.0	84.0±0.0	83.4	84.0±0.0	83.4
$C_{\alpha\beta}^{B3}$	55.3±0.0	56.5	-9.4±0.0	-8.9	15.8±0.0	16.4
$C_{\alpha\beta}^B$	136.5±0.0	136.5	74.6±0.0	74.5	99.8±0.0	99.8
$C_{\alpha\beta}^K$	4.0	4.0	0.0	0.0	2.0	2.0
$C_{\alpha\beta}^F$	5.5±0.0	7.3	0.8±0.1	0.6	55.3±1.4	59.8
$C_{\alpha\beta}$	135.1±0.0	133.2±0.1	73.8±0.1	73.9±0.4	46.5±1.4	42.0±8.3

is negligible for \bar{C}_{11} and \bar{C}_{12} , but significant for \bar{C}_{44} . This is mainly due to large shear displacements of atoms that arise after a homogeneous deformation of diamond structures.^{2,3,9,15} Such microscopic motions decrease the system's free energy and are driven by the thermal fluctuations at finite temperature,³ or by minimization of the energy at zero temperature.^{2,9,15} The stress-fluctuation term $C_{\alpha\beta}^F$ implicitly describes the effects of internal strains on a system's elastic modulus.^{3,9}

The results for PMMA are shown in Table II. At room temperature (300 K), simulated PMMA forms an amorphous glass. It is found that the bonding interactions ($C_{\alpha\beta}^{Br}$) contribute most to the overall Born term $C_{\alpha\beta}^B$; 68%, 102%, and 58% for \bar{C}_{11} , \bar{C}_{12} , and \bar{C}_{44} , respectively. The spring constant of the bonding potential in Eq. (12) is therefore an important parameter that characterizes the instantaneous mechanical response of this PMMA model. It is also observed that the stress-fluctuation term $C_{\alpha\beta}^F$ has a magnitude comparable to the corresponding Born term $C_{\alpha\beta}^B$ for all three components. This finding suggests that the free energy of amorphous polymer glasses exhibits a large decrease after a system's homogeneous deformation due to large rearrangements of

TABLE II. Born terms, kinetic term, stress-fluctuation term, and elastic moduli of an atomistic PMMA model at $T=300$ K. $C_{\alpha\beta}^{BQ}$, $C_{\alpha\beta}^{BLJ}$, $C_{\alpha\beta}^{Br}$, $C_{\alpha\beta}^{B\theta}$, and $C_{\alpha\beta}^{B\phi}$ denote the Born term arising from Coulombic, LJ, bonding, bending, and torsion potential energy contributions in Eq. (12), respectively.

Term	\bar{C}_{11} (GPa)	\bar{C}_{12} (GPa)	\bar{C}_{44} (GPa)
$C_{\alpha\beta}^{BQ}$	-0.2±0.0	-0.1±0.0	-0.1±0.0
$C_{\alpha\beta}^{BLJ}$	11.1±0.7	3.8±0.2	3.8±0.2
$C_{\alpha\beta}^{Br}$	41.6±0.7	14.0±0.3	14.0±0.3
$C_{\alpha\beta}^{B\theta}$	7.7±0.6	-3.8±0.4	5.8±0.4
$C_{\alpha\beta}^{B\phi}$	0.5±0.1	-0.3±0.1	0.4±0.1
$C_{\alpha\beta}^B$	60.8±0.8	13.7±0.2	23.9±0.3
$C_{\alpha\beta}^K$	0.7±0.1	0.0±0.0	0.3±0.1
$C_{\alpha\beta}^F$	55.5±0.5	10.5±0.7	23.0±0.4
$C_{\alpha\beta}$	6.0±1.2	3.2±0.8	1.2±0.1

polymer molecules. The remaining values of elastic moduli $C_{\alpha\beta}$ for the PMMA are considerably smaller than those of the SW crystalline silicon.

Using the results of $C_{\alpha\beta}$ in Table II, the Young's modulus E , shear modulus G , and Poisson's ratio ν of PMMA can be obtained as follows:¹³

$$E = \frac{(3\bar{C}_{12} + 2\bar{C}_{44})\bar{C}_{44}}{\bar{C}_{12} + \bar{C}_{44}} = 3.3 \text{ GPa}, \quad (25)$$

$$G = \bar{C}_{44} = 1.2 \text{ GPa}, \quad (26)$$

$$\nu = \frac{\bar{C}_{12}}{2(\bar{C}_{12} + \bar{C}_{44})} = 0.36. \quad (27)$$

These values are consistent with available bulk experimental data at room temperature: $E \approx 3.0$ GPa, $G \approx 1.0$ GPa, and $\nu \approx 0.35$.^{16,17} Although the elastic properties of PMMA are time or frequency dependent, they remain nearly constant below the glass transition temperature (≈ 400 K).¹⁷

The Born terms, \bar{C}_{12}^{B3} in Table I and $\bar{C}_{12}^{B\theta}$ in Table II, are largely negative; both terms are associated with an angle potential including three atoms. Based on Eq. (27) a negative value of \bar{C}_{12} could correspond to a negative Poisson's ratio if $\bar{C}_{12} + \bar{C}_{44} > 0$. In such a case the material would exhibit a transverse expansion under longitudinal extension.¹⁸ For a three-body potential the middle atom would vertically move up to maintain an angle when two edge atoms are laterally pulled out. Due to other internal constraints of the molecular configurations (e.g., bond lengths), however, the overall \bar{C}_{12} becomes strongly positive; the negative Poisson's effect does not show up in the deformation of our systems.

Figure 1 shows the convergence of the Born term and the stress-fluctuation term for the SW silicon and the PMMA models. In both cases the running average of C_{11}^B attains a stable value shortly after the simulation begins, whereas C_{11}^F fluctuates around the equilibrium value with a relatively long period. These results are expected since the Born term is an averaged quantity, but the

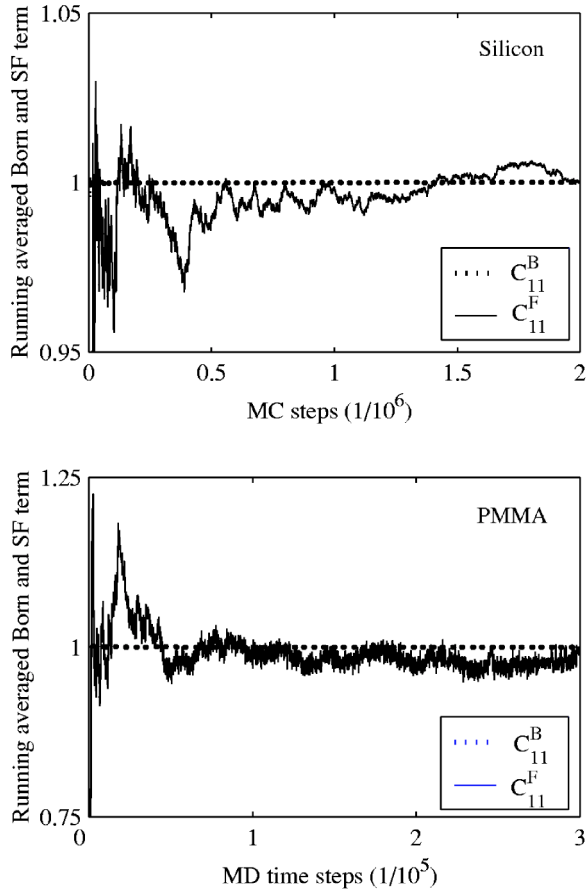


FIG. 1. Running average of the Born term (dotted line) and stress-fluctuation (SF) term (solid line) normalized by their values at the end of the simulation. The top and the bottom figure show results for silicon and PMMA, respectively. Although only one tensorial component is shown here, a similar behavior was observed for all other components.

stress-fluctuation term is a correlation function.³ It is therefore not necessary to calculate the Born term as frequently as the stress-fluctuation term, which helps reduce the computational demands of numerical calculations.

IV. CONCLUSIONS

In this study a simple numerical approach has been proposed for calculation of elastic moduli from stress-fluctuation formulae. By using the atomistic forces calculated routinely in MD simulations, it has been shown that our numerical results for the elastic moduli of the SW silicon model agree with analytical values reported in the literature. Unlike past analytical calculations, our numerical method does not require the derivation or coding of tedious and elaborate expressions for the Born terms. We have also shown that the computational expense of numerical calculations can be minimized by sampling the Born term less frequently. Our numerical approach is particularly useful for atomistic models that comprise various types of non-pairwise interactions. As an example, we have applied this numerical method to an atomistic PMMA model that includes bending

and torsion interactions. The resulting elastic moduli are shown to be in good agreement with experimental results. We have observed that the magnitude of the stress-fluctuation terms is relatively large for amorphous PMMA, causing the elastic moduli of PMMA to be much smaller than those of crystalline silicon.

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APPENDIX A: CONNECTION BETWEEN EQUATIONS (4) and (16)

Using chain rules the virial stress tensor in Eq. (14) can be written in pairwise form.⁴

$$\sigma_{kl}^v = \frac{-1}{V} \sum_{n<s} \frac{r_k^{ns} r_l^{ns}}{r^{ns}} \frac{\partial U}{\partial r^{ns}}. \quad (\text{A1})$$

From Eq. (A1) and the following identity,

$$\frac{\partial^2 U}{\partial r_k^n \partial r_i^m} = \frac{\partial}{\partial r_i^m} \left(r_l^n \frac{\partial U}{\partial r_k^n} \right) - \delta_{mn} \delta_{il} \frac{\partial U}{\partial r_k^n}, \quad (\text{A2})$$

Eq. (16) is transformed into

$$\hat{C}_{ijkl}^B = \langle D_{ijkl} \rangle + \delta_{il} \langle \sigma_{jk}^v \rangle + \delta_{ik} \langle \sigma_{jl}^v \rangle, \quad (\text{A3})$$

where

$$D_{ijkl} = \frac{1}{V} \sum_{m=1}^N r_j^m \frac{\partial}{\partial r_i^m} \left(\sum_{n<s} \frac{r_k^{ns} r_l^{ns}}{r^{ns}} \frac{\partial U}{\partial r^{ns}} \right). \quad (\text{A4})$$

Equation (A4) can be further expanded to

$$\begin{aligned} VD_{ijkl} &= \sum_{n<s} (\delta_{il} r_j^{ns} r_k^{ns} + \delta_{ik} r_j^{ns} r_l^{ns}) \frac{1}{r^{ns}} \frac{\partial U}{\partial r^{ns}} \\ &+ \sum_{m<t} \sum_{n<s} p(m,t,n,s) r_i^{mt} r_j^{mt} r_l^{ns} r_k^{ns} \\ &= -(\delta_{il} \sigma_{jk}^v + \delta_{ik} \sigma_{jl}^v) + \sum_{m<t} \sum_{n<s} p(m,t,n,s) r_i^{mt} r_j^{mt} r_l^{ns} r_k^{ns}. \end{aligned} \quad (\text{A5})$$

After substituting Eq. (A5) into Eq. (A3) the pairwise formula in Eq. (4) can be derived.

APPENDIX B: RELATION BETWEEN ISOTHERMAL AND ADIABATIC ELASTIC MODULUS

Literature values³ reported for the SW silicon model correspond to the adiabatic elastic moduli (calculated at constant enthalpy, as opposed to constant temperature). The thermodynamic relation between the adiabatic Young's modulus E^A and the isothermal Young's modulus E is given by,¹³

$$E^A/E = 1 + \lambda^2 TE^A / \rho C_p \quad (\text{B1})$$

where ρ , λ , and C_p are the density, thermal expansion coefficient, and specific heat at constant pressure, respectively. For bulk silicon diamond, $\lambda \approx 4 \times 10^{-6} (1/\text{K})$ and

$C_p \approx 700 \text{ J}/(\text{kg K})$ at $T = 1477 \text{ K}$.¹⁹ After substituting these values in Eq. (B1), the last term is found to be negligibly small. The isothermal elastic moduli are therefore assumed the same as the adiabatic moduli for the conditions relevant to this study.

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