# Combination method for the calculation of elastic constants

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In this paper, a method combining the stress and strain fluctuation formula with the elastic bath method is proposed to calculate the elastic constants. Compared to the traditional method of standard fluctuation formula, the new method shows much better convergence. The significance is based on one of the benefits of elastic bath method, where the thermal strains of materials can be amplified or attenuated by appropriate choice of elastic constants of the bath. Results obtained with a nearest-neighbor Lennard-Jones fcc crystal indicate that the combination method is considerably more efficient than using its component technique separately.

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## I. INTRODUCTION

The essence of the constitutive relation of a certain material is the determination of its elastic constants. Once determined, these constants provide a way to link the loading on the material to its response. Another use of the elastic constants in the atomic simulation research is to serve as a probing of the interatomic forces employed,[1] where the calculated values of these constants using molecular simulations are compared with the experimental data. This property has been widely used and proved to be an efficient way to test the validity of the model and atomic potential functions.

Molecular dynamics (MD) and Monte Carlo method are two widely used atomic simulation methods. Conventional MD simulations conserving the total energy and volume correspond to the microcanonical (*NVE*) ensemble. However, most experiments are conducted under constant temperature or pressure, so canonical (*NVT*) or isothermal-isobaric (*NPT*) ensemble should be adopted, correspondingly, to perform the MD simulations. On the specific problem of the calculation of elastic constants, due to the limitation of algorithms in MD simulation, so far, most efforts are confined to the Monte Carlo method.[2–5]

In a creative paper, Anderson[6] proposed the extended system method, which takes the volume as a fictitious degree of freedom to carry out MD simulations in isobaric-isoenthalpic (*NPH*) ensemble. His method was then improved by Parrinello and Rahman[7,8] to apply to anisotropic cases. Later, Nosé[9] and Hoover[10] devised a method which can adjust temperature in MD simulations. With these methods, many significant efforts[3,4,11,12] have been devoted to calculate the elastic constants of anisotropic materials rapidly and accurately. Some of the drawbacks in the aforementioned methods[13–17] that lead to improper results of the calculated elastic constants have been eliminated partly by several modified algorithms.[18–20] In this paper, we shall focus on the following two algorithms: the Nosé-Poincaré thermostat method[17] and the metric-tensor flexible-cell pressostat algorithm.[16] The former keeps the symplectic structure of the Hamiltonian and the latter has eliminated the flaws of the original Parrinello-Rahman (PR) algorithm. Recently, an algorithm[21,22] combining the advantages of these two methods was proposed to perform MD simulations in various isothermal-isobaric (*NPT*) ensembles, thus extending greatly the application domains of MD simulations. The calculation of elastic constants using MD method then becomes possible.

The common ways to calculate the elastic constants depend on the fluctuation techniques[3–5] in *NPT* ensemble. For example, the isothermal elastic constant tensor can be obtained in terms of the PR strain fluctuation formula[3]

$$C_{ijkl} = \frac{k_B T}{\langle V \rangle}[\langle \epsilon_{ij}\epsilon_{kl}\rangle - \langle \epsilon_{ij}\rangle\langle \epsilon_{kl}\rangle]^{-1}, \tag{1}$$

where $\epsilon_{ij}$ is the strain tensor, $\langle V \rangle$ 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 indices $i,j,k,l$ represent the Cartesian coordinates in three dimensions and run from 1 to 3. The strain tensor is given by

$$\epsilon_{ij} = \frac{1}{2}[\langle h\rangle_{ik}^{-T} h_{kl}^{T} h_{lm} \langle h\rangle_{mj}^{-1} - \delta_{ij}], \tag{2}$$

where the scaling matrix $h=\{\vec{a},\vec{b},\vec{c}\}$ consists of the three noncoplanar basis vectors $\vec{a},\vec{b},\vec{c}$ describing the size and shape of the simulation box, and matrix $\langle h\rangle$ denotes the average shape of the system as the reference state. $h^{-T}$ is the inverse of the transpose of $h$, and $\delta_{ij}$ is the Kronecker tensor. In this paper, the conventional suffix notation is used, where repeated suffixes indicate summation over the values of 1,2,3.

The elastic constants can also be calculated in *NhE* or *NhT* ensembles,[11,19,23] where the scaling matrix $h$ is fixed. However, the formulas are rather cumbersome because of the Born term. According to the stress and strain fluctuation formula, isothermal elastic constants can be calculated via[4]

$$C_{ijkl} = \langle \epsilon_{ij}\sigma_{mn}\rangle\langle \epsilon_{mn}\epsilon_{kl}\rangle^{-1}, \tag{3}$$

where $\sigma_{ij}$ are the components of the microscopic stress tensor

$$\sigma_{ij} = -\frac{1}{V}\left[\sum_{\alpha}\frac{(p_\alpha)_i(p_\alpha)_j}{m_\alpha} - \sum_{\beta>\alpha}\frac{\partial U}{\partial r_{\alpha\beta}}\frac{(r_{\alpha\beta})_i(r_{\alpha\beta})_j}{r_{\alpha\beta}}\right]. \tag{4}$$

In Eq. (4), the potential energy $U$ is assumed as a pair function, i.e., $U(r_{\alpha\beta})$, and $r_{\alpha\beta}$ is the distance between the atom indexed as $\alpha$ and $\beta$, and $p_\alpha$ and $m_\alpha$ are the momentum and mass of the $\alpha$th atom, respectively. Equation (3) has been proven to be more efficient than Eq. (1) for the improved convergence property.

However, as mentioned in Ref. 5, Eqs. (1)–(3) assume the validity of linear elasticity, where strains and strain fluctuations are sufficiently small, hence the elastic constants of stiff or soft materials may be inappropriately calculated with those formulas. In order to extend the application fields of Eqs. (1) and (3), the elastic bath method can be used to facilitate fast and accurate calculation of elastic constants. This idea has been implemented in Ref. 5, but only in PR strain fluctuation formula. In this paper, we extend this idea further with stress and strain fluctuation formulas to improve convergence over standard techniques.

## II. MD SIMULATIONS

Some spurious effects using the original PR method, such as the absence of virial theorem,[13] unphysical symmetry breaking effects,[14,15] spurious cell rotations,[16] have been eliminated by metric-tensor algorithm.[16] The cause for the spuriousness is the fictitious cell kinetic-energy term and the transformation matrix $h$ between spatial Cartesian reference frame and lattice coordinates, where the latter has generally nine independent components. A fix for this in the metric-tensor algorithm then is to propose a symmetrical metric tensor $G = h^T h$. Now, $G$ serves as the new dynamical variable for the system and has only six independent components, with three diagonal elements representing the lengths of the lattice vectors and three off-diagonal elements for the angles between those vectors. Hence, the matrix $G$ itself is enough to describe the shape and size of the simulation box. The volume of the box is given by $V = \det h = \sqrt{\det G}$. The position $\vec{r}_\alpha$ of the $\alpha$th atom in the system can be defined by its lattice coordinates $\vec{q}_\alpha$, i.e., $\vec{r}_\alpha = h\vec{q}_\alpha$, and the interatomic distance between the $\alpha$th atom and the $\beta$th atom can be obtained through $r_{\alpha\beta}^2 = (\vec{q}_{\alpha\beta}^{\,T} G \vec{q}_{\alpha\beta})$.

On the other hand, Nosé-Poincaré thermostat algorithm[17] can sample the *NVT* ensemble and keep symplectic structure of Hamiltonian, which is achieved by performing Poincaré transformation to the original Nosé Hamiltonian. Therefore, the combined dynamics of Nosé-Poincaré thermostat algorithm and metric-tensor flexible-cell pressostat algorithm can describe the conservation of the Gibbs free energy. For simplicity, we take the $\vec{q}_\alpha$ as the lattice coordinates of the $\alpha$th atom, $s$, extended position variable,[17] as the additional degree of freedom in Nosé-Poincaré method, and $g$ as the number of degrees of freedom of the system. Due to the Hamiltonian of Nosé-Poincaré, the Hamiltonian of the extended system is the same as Ref. 21. Hence the equations of motion in *NPT* ensemble are[21]

$$\ddot{\vec{q}}_\alpha = -\frac{1}{m_\alpha}\frac{\partial U(r_{\alpha\beta})}{\partial r_{\alpha\beta}}\frac{\vec{q}_{\alpha\beta}}{r_{\alpha\beta}} - G^{-1}\dot{G}\dot{\vec{q}}_\alpha - \frac{\dot{s}}{s}\dot{\vec{q}}_\alpha,$$

$$\ddot{G} = \frac{s^2}{2W_G}\left[\frac{GPG}{\det G} - \frac{GP_{\text{ext}}}{\sqrt{\det G}}\right] + \frac{\dot{s}}{s}\dot{G} + \dot{G}G^{-1}\dot{G} + \frac{1}{2}\mathrm{Tr}(\dot{G}G^{-1}\dot{G}G^{-1})G - \mathrm{Tr}(G^{-1}\dot{G})\dot{G},$$

$$\ddot{s} = \frac{s}{W_s}\left(\sum_{\alpha} m_\alpha \dot{\vec{q}}_\alpha^{\,T} G \dot{\vec{q}}_\alpha - g k_B T_{\text{ext}} - \Delta H\right) + \frac{\dot{s}^2}{s}, \tag{5}$$

where

$$P = \left(\sum_{\alpha} m_\alpha \dot{\vec{q}}_\alpha \dot{\vec{q}}_\alpha^{\,T} - \sum_{\beta>\alpha}\frac{\partial U}{\partial r_{\alpha\beta}}\frac{\vec{q}_{\alpha\beta}\vec{q}_{\alpha\beta}^{\,T}}{r_{\alpha\beta}}\right). \tag{6}$$

Note that the superimposed dot denotes the time derivative in Eqs. (5) and (6), $\mathrm{Tr}(A)$ is the trace of the matrix $A$, $W_G$ is the fictitious mass of variable $G$ and $W_s$ for variable $s$, and

$$\Delta H = \frac{1}{2}\sum_{\alpha} m_\alpha \dot{\vec{q}}_\alpha^{\,T} G \dot{\vec{q}}_\alpha + U + g k_B T_{\text{ext}}\ln(s) + \frac{W_s\dot{s}^2}{2s^2} + P_{\text{ext}}\sqrt{\det G} + \frac{W_G \det G}{2s^2}\mathrm{Tr}(\dot{G}G^{-1}\dot{G}G^{-1}) - H_0, \tag{7}$$

where $H_0$ represents $H(t=0)$. Here, all the formulas have been written in a matrix form for some predictor-corrector integral algorithms.[24] If the time-reversible and symplectic numerical integrators, such as the generalized leapfrog scheme,[25,26] have been applied, the formulas should be rewritten in a covariant-contravariant form.

With the aid of the metric tensor $G$ and the kinetic term of system $\frac{W_G}{2}(\det G)\mathrm{Tr}(\dot{G}G^{-1}\dot{G}G^{-1})$, drawbacks mentioned above can be eliminated. However, since the degree of freedom of $G$ is 6, less than that of scaling matrix $h$ (being 9), $h$ could not be obtained from $G$. In other words, with the evolution of $G$ with time, $h$ cannot be obtained in every MD step. In addition, $G$, as the dynamical variable, is independent of spatial Cartesian reference frame. Hence, the positions $(r_\alpha)$, velocities $(v_\alpha)$ of atoms, and other information associated with transformation matrix $h$ cannot be obtained from the formulas above. This immediately tells that Eqs. (3) and (4) cannot be applied at all. Therefore, the original stress and strain fluctuation formula should be modified with this pressostat algorithm.

Consider a system of $N$ particles without external stresses and let $H$ be its Hamiltonian[16]

$$H = \sum_{\alpha}\frac{\vec{p}_\alpha^{\,T} G^{-1}\vec{p}_\alpha}{2m_\alpha} + U(\vec{q}, G), \tag{8}$$

where $\vec{p}_\alpha$ is the momentum canonically conjugate to $\vec{q}_\alpha$. With chain rule, we have (refer to the Appendix for more details)

$$\frac{\partial H}{\partial \epsilon_{kl}} = 2\langle h\rangle_{km}\frac{\partial H}{\partial G_{mn}}\langle h\rangle_{nl}^T = -\langle h\rangle_{km}P_{mn}\langle h\rangle_{nl}^T. \tag{9}$$

With the following identity[27]

$$\left\langle \epsilon_{ij}\frac{\partial H}{\partial \epsilon_{kl}}\right\rangle = \frac{1}{2}k_B T(\delta_{ik}\delta_{lj}+\delta_{il}\delta_{kj}), \tag{10}$$

we can obtain the following expression:

$$C_{ijkl} = \langle \epsilon_{ij}\tilde{\sigma}_{mn}\rangle\langle \epsilon_{mn}\epsilon_{kl}\rangle^{-1}, \tag{11}$$

where $\tilde{\sigma}_{ij}=-\langle h\rangle_{ik}P_{kl}\langle h\rangle^T_{lj}/\langle V\rangle$. Obviously, since Eq. (11) is based on the rigorous mathematical derivation with chain rule, it gives more reasonable results than Eq. (3). In addition, due to the correlation of stresses and strains in the phase space, Eqs. (11) and (3) have better convergent properties than Eq. (1), which has only the second moments $\langle \epsilon_{ij}\epsilon_{kl}\rangle$.

In MD simulations, the fluctuations of simulation box under equilibrium state are determined by the fictitious cell mass $W_G$ with the dimensions of mass×(length)$^{-4}$. If the value of $W_G$ is too big, it will take a long time to reach the equilibrium state, i.e., linear elasticity assumption breaks, or to oscillate very frequently for contrary situation. In other words, the value of mass $W_G$ can make the simulation system stiffer or softer, thus it determines adequate sampling of the accessible strains and stresses. In order to attenuate the dependence of $W_G$, the elastic bath method is employed.

## III. ELASTIC BATH METHOD

Strain energy density of a deformed system with small strains can generally be written as follows:[5]

$$\tilde{E}_s = \frac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl}. \tag{12}$$

The main idea of the method in Ref. 5 is to immerse the simulation system in an elastic bath with appropriately chosen elastic constants $C^b_{ijkl}$, where the strain and stress fluctuations can be amplified or attenuated. Since the elastic bath is merely a mathematical construction, the elastic constants $C^b_{ijkl}$ can be chosen freely, including nonphysical values, i.e., less than zero, which implies to amplify fluctuations. With the elastic bath method, the dependence of the fictitious cell mass $W_G$ will weaken. Meanwhile, the Hamiltonian in Eq. (8) should have the strain energy due to the elastic bath included, i.e.,

$$H_1 = H + \langle V\rangle\tilde{E}^b_s = H + \frac{1}{2}\langle V\rangle C^b_{ijkl}\epsilon_{ij}\epsilon_{kl}. \tag{13}$$

Thus, the evolution of metric tensor $G$ in Eq. (5) can be rewritten as

$$\ddot{G} = \frac{s^2}{2W_G}\left[\frac{GP_1G}{\det G} - \frac{GP_{\text{ext}}}{\sqrt{\det G}}\right] + \dot{G}G^{-1}\dot{G} + \frac{1}{2}\mathrm{Tr}(\dot{G}G^{-1}\dot{G}G^{-1})G - \mathrm{Tr}(G^{-1}\dot{G})\dot{G} + \frac{\dot{s}}{s}\dot{G}, \tag{14}$$

where

$$(P_1)_{ij} = P_{ij} - \langle V\rangle\langle h\rangle^{-T}_{ki}\langle h\rangle^{-1}_{jl}C^b_{klmn}\epsilon_{mn}. \tag{15}$$

The second part of Eq. (15) is contributed from the additional strain energy of elastic bath, i.e.,

$$\frac{\partial \frac{1}{2}\langle V\rangle C^b_{ijkl}\epsilon_{ij}\epsilon_{kl}}{\partial G_{ij}} = \langle V\rangle\langle h\rangle^{-T}_{ki}\langle h\rangle^{-1}_{jl}C^b_{klmn}\epsilon_{mn}. \tag{16}$$

Correspondingly, $\Delta H$ in Eq. (7) should include the strain energy. Thus, Eq. (9) should count in a term as

$$\frac{\partial H_1}{\partial \epsilon_{ij}} = \langle V\rangle(\tilde{\sigma}_{ij}+\tau_{ij}), \tag{17}$$

where

$$\tau_{ij} = \frac{\partial \tilde{E}^b_s}{\partial \epsilon_{ij}} = \frac{\partial \frac{1}{2}C^b_{ijkl}\epsilon_{ij}\epsilon_{kl}}{\partial \epsilon_{ij}} = C^b_{ijkl}\epsilon_{kl}. \tag{18}$$

According to Eq. (12) in Ref. 5, the elastic constants can be calculated via

$$C_{ijkl} = C^t_{ijkl} - C^b_{ijkl}, \tag{19}$$

where $C^t_{ijkl}=\langle \epsilon_{ij}(\tilde{\sigma}_{mn}+\tau_{mn})\rangle\langle \epsilon_{mn}\epsilon_{kl}\rangle^{-1}$ are the elastic constants of the material including the elastic bath. Since the elastic bath and the simulation system have identical strains, their reference states can have the same form, $\epsilon^0_{ij}=0$. Therefore, the equilibrium state for the combined system will also be the reference state, $\epsilon^0_{ij}=0$. The additional strain energy of the elastic bath, Eq. (12), provides an additional stress $\tau_{ij}$ to the system, which is zero for the reference state. As mentioned in Ref. 5, the choice of $C^b_{ijkl}$ is always available, of order −10–10.

## IV. SIMULATION RESULTS

To check the validity of the aforementioned algorithms, a MD simulation code is developed to study a fcc crystal using a first-nearest-neighbor interatomic model. A classical pair potential of Lennard-Jones is used. The simulation system including 108 atoms[2–5] is employed. The *NPT* ensemble is adopted, implemented by using Nosé-Poincaré thermostat,[17] metric-tensor pressostat,[16] and Gear algorithm[24] for the time integration. The isotropic material is employed as the elastic bath, and the elastic constants are given by[28]

$$C_{11} = \lambda + 2\mu, \quad C_{12} = \lambda, \quad C_{44} = \mu, \tag{20}$$

where $\lambda$ and $\mu$ are the Lamé coefficients. Our simulation results are represented using the Voigt matrix notation[29] in reduced units. For fcc crystals, there are only three independent elements of the elastic constant matrix, $C_{11}$, $C_{12}$, $C_{44}$, and $C_{11}=C_{22}=C_{33}$, $C_{12}=C_{23}=C_{13}$, and $C_{44}=C_{55}=C_{66}$.

In Fig. 1, $\langle C_{11}\rangle$, $\langle C_{12}\rangle$, and $\langle C_{44}\rangle$ as functions of temperature are calculated by using Eq. (19). Each simulation is first equilibrated for $1.0\times10^6$ steps, then additional $2.0\times10^6$ steps are evolved before the results are collected. Three different strengths of the elastic bath ($\lambda^b=\mu^b=20$, $\lambda^b=\mu^b=0$, and $\lambda^b=\mu^b=-20$) are employed and the $C^b_{ij}$ can be obtained by Eq. (20). There is excellent agreement between all sets of data. The same results have been found in Table I, where the isothermal elastic constants in units of $Nk_BT/V$ for six temperatures are listed for comparison with literature data.[2] The

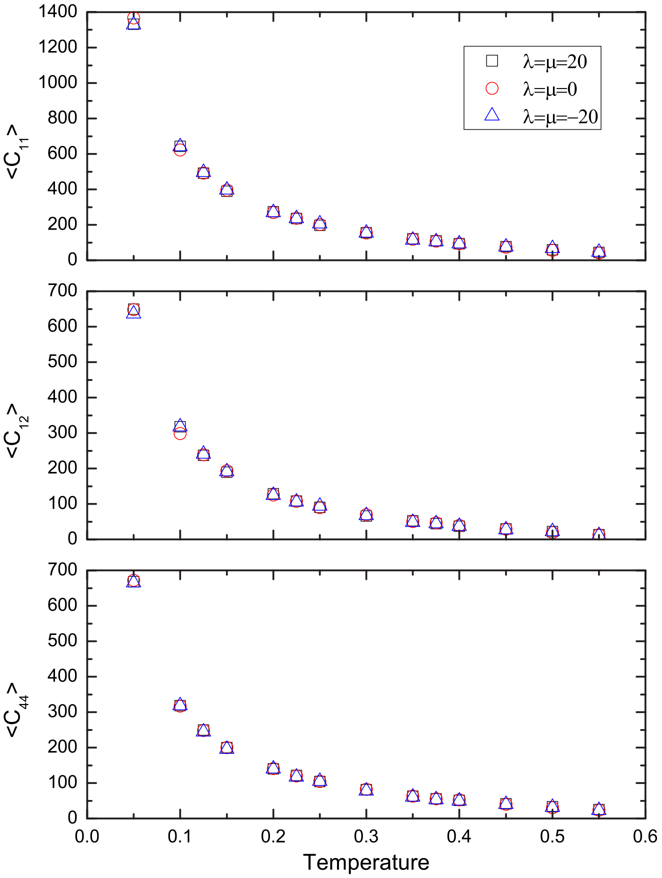

FIG. 1. (Color online) The elastic constants (in units of $Nk_BT/V$) of the fcc crystal as a function of temperature (measured in units of $\epsilon/k_B$): (□) positive elastic bath, (○) zero elastic bath, (△) negative elastic bath.

significance of the combination method is best seen by comparing the convergence of the calculation from different elastic strengths and temperatures.

When $\lambda^b=\mu^b=0$, all formulas degenerate to the usual stress and strain fluctuation techniques, i.e., without elastic bath. The convergence of $\langle C_{11}\rangle$ from Eq. (11) is slow at both low and high temperatures [see Figs. 2(a) and Fig. 3(a)].

When $\lambda^b=\mu^b=-20$, the system is immersed in a negative stiffness elastic bath, i.e., the composite material is softer than in the absence of the bath, therefore the thermal strains are enhanced. Since small strain fluctuation of stiff material at low temperature can hinder adequate sampling of accessible strain values, the elastic constants may be calculated imprecisely using Eqs. (1) or (3). Therefore, with Eq. (19), strains can be amplified to get an adequate sample for accurate calculation of elastic constants [see Fig. 2(b)].

When $\lambda^b=\mu^b=20$, the system is immersed in a positive stiffness, isotropic elastic bath. In this case, the composite system is stiffer than in the previous case, and the strains due to thermal fluctuations are attenuated. Using Eq. (19), the correct elastic constants can be obtained, as shown in Fig. 1 and Table I. Due to the first-nearest-neighbor Lennard-Jones potential used in the fcc crystal, the system is very soft at high temperature, i.e., the strain fluctuation may not satisfy the theory of linear elasticity, thus that choice of elastic bath has better convergence [see Fig. 3(b)].

TABLE I. Isothermal elastic constants (in units of $Nk_BT/V$) calculated via Eq. (19) from additional $2.0\times10^6$ steps for three different sets of Lamé coefficients of the elastic bath. The temperature is measured in units of $\epsilon/k_B$, where $\epsilon$ is the well depth of the Lennard-Jones potential-energy function. Data from the literature (Ref. 2) are shown in the last column.

| $T$ | $\langle C_{ij}\rangle$ | $\lambda^b=\mu^b=20$ | $\lambda^b=\mu^b=0$ | $\lambda^b=\mu^b=-20$ | Ref. 2 |
|---|---|---|---|---|---|
| 0.125 | $\langle C_{11}\rangle$ | 491.6±1.5 | 492.2±1.5 | 496.7±2.5 | 494.0±1.1 |
| | $\langle C_{12}\rangle$ | 236.7±1.1 | 238.3±0.8 | 241.1±2.0 | 237.8±1.1 |
| | $\langle C_{44}\rangle$ | 250.0±1.1 | 248.5±2.2 | 244.7±1.5 | 250.0±0.2 |
| 0.225 | $\langle C_{11}\rangle$ | 235.0±1.7 | 236.3±1.5 | 234.9±1.3 | 237.0±0.8 |
| | $\langle C_{12}\rangle$ | 108.3±0.9 | 107.6±1.8 | 106.1±1.1 | 108.2±0.8 |
| | $\langle C_{44}\rangle$ | 121.5±1.0 | 120.2±2.0 | 116.7±2.0 | 121.9±0.2 |
| 0.3 | $\langle C_{11}\rangle$ | 155.4±1.5 | 154.8±1.9 | 154.2±2.2 | 157.1±1.0 |
| | $\langle C_{12}\rangle$ | 66.0±1.3 | 69.3±0.8 | 67.7±1.8 | 69.3±0.9 |
| | $\langle C_{44}\rangle$ | 81.5±1.1 | 82.2±1.2 | 78.0±2.1 | 82.2±0.2 |
| 0.375 | $\langle C_{11}\rangle$ | 109.7±0.9 | 108.2±1.5 | 105.2±2.2 | 111.0±0.7 |
| | $\langle C_{12}\rangle$ | 44.3±1.1 | 46.5±1.4 | 44.4±1.8 | 46.8±0.7 |
| | $\langle C_{44}\rangle$ | 55.3±1.2 | 55.6±0.9 | 53.5±1.1 | 58.1±0.2 |
| 0.45 | $\langle C_{11}\rangle$ | 76.9±1.1 | 73.5±2.0 | 75.5±2.2 | 78.4±0.9 |
| | $\langle C_{12}\rangle$ | 29.4±1.1 | 28.7±1.2 | 27.1±1.8 | 31.0±1.0 |
| | $\langle C_{44}\rangle$ | 41.2±0.8 | 39.7±1.5 | 40.1±0.5 | 42.0±0.3 |
| 0.5 | $\langle C_{11}\rangle$ | 60.0±1.1 | 56.7±0.9 | 66.5±1.3 | 61.7±0.7 |
| | $\langle C_{12}\rangle$ | 22.0±1.5 | 19.6±1.3 | 21.9±0.5 | 22.8±0.8 |
| | $\langle C_{44}\rangle$ | 33.7±0.8 | 30.4±1.8 | 32.0±2.2 | 33.8±0.2 |

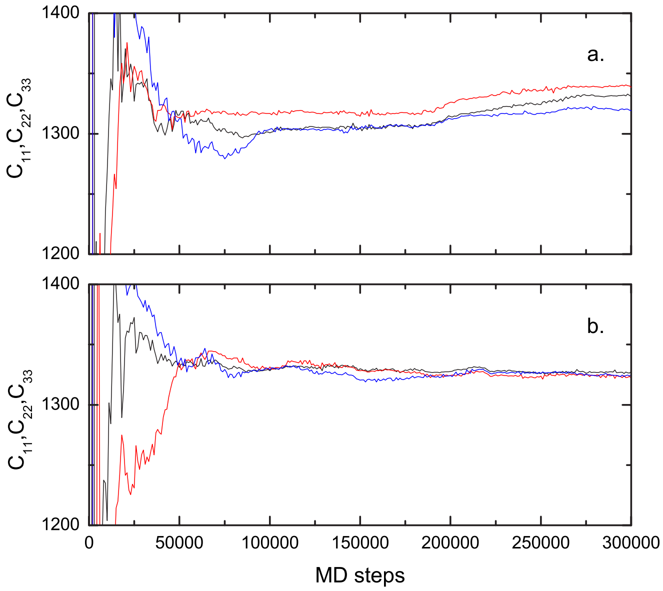

FIG. 2. (Color online) Convergence of $\langle C_{11}\rangle$ for the fcc crystal at $T=0.05$. (a) Using Eq. (11) without elastic bath. (b) Using Eq. (19) with negative bath.

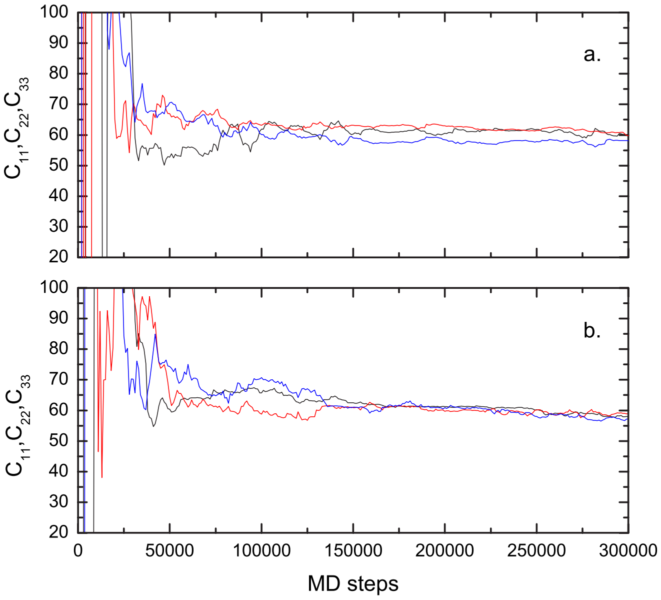

FIG. 3. (Color online) Convergence of $\langle C_{11}\rangle$ for the fcc crystal at $T=0.5$. (a) Using Eq. (11) without elastic bath. (b) Using Eq. (19) with positive bath.

## V. CONCLUDING REMARKS

In this paper, the elastic bath method is applied in stress and strain fluctuation formulas to improve the convergence and to extend the application areas of the MD method. Since the strains and stresses may be enhanced or attenuated with bath, the proposed combination method can keep the linear elasticity assumption of fluctuation formula in various materials. In addition, for the classical first-nearest-neighbor Lennard-Jones fcc crystal, the results show a better convergence than the standard technique.

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## APPENDIX

In this appendix, we show the derivation of Eq. (9). From the Hamiltonian defined in Eq. (8),

$$H=E_K+E_U=\sum_{\alpha}\frac{\vec{p}_{\alpha}^{T}G^{-1}\vec{p}_{\alpha}}{2m_{\alpha}}+U(\vec{q},G), \tag{A1}$$

we can obtain

$$\frac{\partial H}{\partial \epsilon_{kl}}=\frac{\partial H}{\partial G_{ij}}\frac{\partial G_{ij}}{\partial \epsilon_{kl}}=\left(\frac{\partial E_K}{\partial G_{ij}}+\frac{\partial E_U}{\partial G_{ij}}\right)\frac{\partial G_{ij}}{\partial \epsilon_{kl}}. \tag{A2}$$

For $G_{ij}$, according to Eq. (2), we have

$$G_{ij}=(h^T)_{ik}h_{kj}=2\langle h\rangle_{ik}^{T}\epsilon_{kl}\langle h\rangle_{lj}+\langle G\rangle_{ij}. \tag{A3}$$

This leads to

$$\frac{\partial G_{ij}}{\partial \epsilon_{kl}}=2\langle h\rangle_{ki}\langle h\rangle_{jl}^{T}. \tag{A4}$$

We now evaluate the two terms inside the parentheses of Eq. (A2). From Eq. (A1), we have

$$\frac{\partial E_U}{\partial G_{ij}}=\frac{1}{2}\sum_{\alpha>\beta}\frac{\partial U}{\partial r_{\alpha\beta}}\frac{(\vec{q}_{\alpha\beta})_i(\vec{q}_{\alpha\beta})_j}{r_{\alpha\beta}}, \tag{A5}$$

$$\frac{\partial E_K}{\partial G_{ij}}=\frac{\partial E_K}{\partial G_{kl}^{-1}}\frac{\partial G_{kl}^{-1}}{\partial G_{ij}}=\left[\sum_{\alpha}\frac{(p_{\alpha})_k(p_{\alpha})_l}{2m_{\alpha}}\right](-G_{ki}^{-1}G_{jl}^{-1}). \tag{A6}$$

According to Eq. (5) in Ref. 21, Eq. (A6) can be written as follows:

$$\frac{\partial E_K}{\partial G_{ij}}=-\frac{1}{2}\sum_{\alpha}m_{\alpha}(\dot{\vec{q}}_{\alpha})_i(\dot{\vec{q}}_{\alpha})_j. \tag{A7}$$

Therefore, with Eqs. (A2), (A5), and (A7), we can get the following expression:

$$\frac{\partial H}{\partial \epsilon_{kl}}=2\langle h\rangle_{ki}\frac{\partial H}{\partial G_{ij}}\langle h\rangle_{jl}^{T}=-\langle h\rangle_{ki}P_{ij}\langle h\rangle_{jl}^{T}. \tag{A8}$$

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