Least square method for the calculation of elastic constants

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In this paper, a feasible formula is derived and simplified from least square method to calculate the elastic constants of materials. The simplified equation is identical to the stress and strain fluctuation formula obtained from statistical thermodynamics when the expression of the stress is redefined. It endues the formula with the theoretical validity. On the other hand, the convergence of the formula could be investigated via the theory of numerical analysis. Compared to the traditional fluctuation formula, the new technique shows better universality in the elastic bath method. Results obtained with a nearest-neighbor Lennard-Jones fcc crystal indicate that at low temperature the convergence of the formula is the same as the previous stress and strain fluctuation formula but the symmetry of the elastic constants is improved.

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1. Introduction

Elastic constants are essential properties of materials. They describe the behavior of materials to the external loadings during the elastic stage. In molecular dynamics (MD) simulations, the common ways to achieve the elastic constants depend on the fluctuation techniques in isothermal-isobaric (NPT) ensemble. The widely used strain fluctuation formula is proposed by Parrinello and Rahman (PR) [1,2].

\[ C_{ijkl} = \frac{k_B T}{\langle V \rangle} (\varepsilon_{ij} \varepsilon_{kl})^{-1} \]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \langle V \rangle \) is the average volume of the system and the brackets indicate the ensemble average. \( \varepsilon_{ij} \) are the components of the strain tensor,

\[ \varepsilon_{ij} = \frac{1}{2} \left\{ (h)_{ik}^T h_{kl} (h)_{mj}^{-1} - \delta_{ij} \right\} \]

where the scaling matrix \( h = (a, b, c) \) consists of the vectors \( a, b \) and \( c \) making up the simulation cell, \( \langle h \rangle \) is the average scaling matrix, \( h^T \) is the transpose of \( h \), and \( \delta_{ij} \) is the Kronecker tensor. In this paper, Einstein notation is used, where repeated suffixes indicate summation over the values of 1, 2 and 3.

PR method is simple but with slow convergence [3]. To overcome this issue, Gusev et al. [4] presented a modified formula, which takes advantage of the instantaneous stresses more than strains. Results from Monte Carlo simulations indicate the equation is more accurate and efficient than PR formula.

\[ C_{ijkl} = (\varepsilon_{ij} \sigma_{mn} \langle \varepsilon_{mn} \varepsilon_{kl} \rangle)^{-1} \]  (3)

where \( \sigma_{mn} \) are the components of the microscopic stress tensor,

\[ \sigma_{mn} = -\frac{1}{V} \left\{ \sum_{\alpha} (p_{\alpha m} m_{\alpha n}) - \sum_{\rho > \alpha} \frac{\partial U}{\partial r_{\rho \alpha}} (r_{\rho \alpha} m_{\alpha n}) \right\} \]  (4)

where the potential energy \( U \) is assumed as function of \( r_{\rho \alpha} \), which is the distance between the atoms \( \alpha \) and \( \rho \). \( m_{\alpha} \) and \( p_{\alpha} \) are the mass and momentum of the \( \alpha \)th atom.

Later, Cui et al. [5] applied the metric–tensor [6] method to provide the derivative of the Hamiltonian with respect to the strains. Through detailed mathematic deduction, the elastic constants could be calculated via the following expression

\[ C_{ijkl} = (\varepsilon_{ij} \tilde{\sigma}_{mn} \langle \varepsilon_{mn} \varepsilon_{kl} \rangle)^{-1} \]  (5)

where \( \tilde{\sigma} \) is the modified stress tensor,

\[ \tilde{\sigma}_{mn} = -\frac{1}{V} \left\{ \sum_{\alpha} m_{\alpha} (h_{mk} q_{\alpha k})(h_{nl} q_{\alpha l}) - \sum_{\beta > \alpha} \frac{\partial U}{\partial r_{\alpha \beta}} (h_{mk} q_{\beta k})(h_{nl} q_{\beta l}) \right\} \]  (6)

where \( q \) is the lattice coordinate and the Cartesian coordinates of the \( \alpha \)th atom is \( r_{\alpha} = h q_{\alpha} \).

Eqs. (3) and (5) combine the stresses with the strains to calculate the elastic constants. However, there is no specified evidence

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to prove its convergence. Hence in the current work, we first propose a new formula to calculate the elastic constants by means of least square method. Its convergence could be investigated by the theory of numerical analysis. A similar equation is then derived with the aid of statistical thermodynamics. After that, we find the two expressions are identical if the stress in Eq. (6) is adopted, which reveals that the formula obtained from least square method has a theoretical background of statistical thermodynamics. In addition, this formula shows some universality in other auxiliary methods, such as elastic bath. Finally, MD simulations are carried out to inspect the performance of the algorithm.

2. Elastic constants from least square method

According to the linear elasticity, stresses and strains could be connected via Hooke’s law, i.e.

\[ \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \]  

(7)

However, such formula is not satisfied exactly in each MD step. After the simulations, \( n \) pairs of stresses and strains are obtained. The difference between the stresses and the theoretical stresses is

\[ f = \sum_{i,j=1}^{n} \left( \sigma_{ij} - C_{ijkl} \varepsilon_{kl} \right)^2 \]  

(8)

Our objective is to find the elastic constants \( C_{ijkl} \) that make \( f \) reach to the minimum value. Follow the steps of least square method, the function \( f \) reaches minimum when

\[ \frac{\partial f}{\partial C_{ijkl}} = 0 \]  

(9)

Due to the symmetry of \( C_{ijkl} \), we have

\[ C_{ijmn} = \sum_{s=1}^{n} \left( \varepsilon_{mn}^s \varepsilon_{kl}^s \right) + C_{mnkl} \sum_{s=1}^{n} \left( \varepsilon_{mn}^s \varepsilon_{kl}^s \right) \]

\[ = \sum_{s=1}^{n} \left( \sigma_{ij}^s \varepsilon_{kl}^s \right) + \sum_{s=1}^{n} \left( \varepsilon_{mn}^s \sigma_{kl}^s \right) \]  

(10)

With such equation, the elastic constants could be calculated straightforwardly. If we ignore the symmetry during the derivation, then Eq. (9) leads to

\[ C_{ijmn} = \sum_{s=1}^{n} \left( \sigma_{ij}^s \varepsilon_{kl}^s \right) \]  

(11)

When \( n \) is big enough, the numerical average, i.e. the time average, could be regarded as the ensemble average, then

\[ C_{ijkl} = \langle \sigma_{ij} \varepsilon_{mn} \rangle \langle \varepsilon_{mn} \varepsilon_{kl} \rangle^{-1} \]  

(12)

Since Eq. (12) is similar to Eqs. (3) and (5) in structure, some deeper researches are needed.

Consider a system of \( N \) particles in the absence of external stresses and the Hamiltonian could be written as

\[ H = \sum_{\alpha} \frac{\pi_{\alpha} \cdot G^{-1} \cdot \pi_{\alpha}}{2m_{\alpha}} + U(q, G) \]  

(13)

where \( G = h^T h \) is the metric tensor, \( q \) is the lattice coordinates and \( \pi_{\alpha} \) is the momentum canonically conjugate to \( q_{\alpha} \).

The derivative of the Hamiltonian to the strain is [5]

\[ \frac{\partial H}{\partial \varepsilon_{ij}} = \langle V \rangle \sigma_{ij} \]  

(14)

Based on the theory of statistical thermodynamics, the following identity holds [4]:

\[ \left( \frac{\partial H}{\partial \varepsilon_{ij}} \right)_{\varepsilon_{mn}} = \frac{k_B T}{2} (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}) \]  

(15)

Then,

\[ C_{ijkl} = \frac{k_B T}{\langle V \rangle} \langle \varepsilon_{ij} \varepsilon_{kl} \rangle^{-1} = \left( \frac{\partial H}{\partial \varepsilon_{ij}} \right)_{\varepsilon_{mn}} \left( \varepsilon_{mn} \varepsilon_{kl} \right)^{-1} \]

\[ = \langle \sigma_{ij} \varepsilon_{mn} \rangle \langle \varepsilon_{mn} \varepsilon_{kl} \rangle^{-1} \]  

(16)

Comparing Eq. (16) to Eq. (12), we find out that the two formulae are identical if the stress in Eq. (16) is adopted in least square method. Thus the new method combines the preponderances of both theoretical and numerical techniques. For one thing, it takes the statistical thermodynamics as the physical background. For another, its performance could be quantified by the numerical analysis method. Although some certain samples are needed to achieve the convergence, it is no longer necessary that the \( \langle \varepsilon_{mn} \varepsilon_{kl} \rangle \) is fully converged, as explicitly required by PR formula.

At low temperature, the difference between instantaneous scaling matrices \( h \) and the average scaling matrix \( \langle h \rangle \) could be neglected. Therefore, \( \langle \varepsilon_{ij} \sigma_{kl} \rangle = \langle \varepsilon_{ij} \sigma_{kl} \rangle \) is approximately satisfied. Then the results of Eq. (3) will be strongly close to those of Eq. (16). Meanwhile, Eq. (5) is absolutely identical to Eq. (16) theoretically due to Eq. (15). Hence \( \langle \sigma_{ij} \varepsilon_{kl} \rangle \) will approximately be a symmetric matrix after enough steps, which means that the results of Eq. (5) will be equal to those of Eq. (16) ultimately. When the number of the necessary steps is smaller than that of convergence, there is no significant difference between the results of Eq. (5) and Eq. (16). Otherwise there is no warranty about the accuracy of the results of Eq. (5).

Besides the advantages above, the novel equation also shows some universality in other supplementary methods, such as elastic bath [5,7], which is adopted to ensure linear elasticity assumption. In the particular case, the new Hamiltonian is

\[ H_t = H + \frac{1}{2} \langle V \rangle C_{ijkl}^b \varepsilon_{ij} \varepsilon_{kl} \]  

(17)

After the simulation with elastic bath, the elastic constants of the hybrid system are

\[ C_{ijkl} = \left( \frac{\partial H_t}{\partial \varepsilon_{ij}} \varepsilon_{mn} \right) \left( \varepsilon_{mn} \varepsilon_{kl} \right)^{-1} \]

\[ = \langle \sigma_{ij} + C_{ijkl}^b \rangle \left( \varepsilon_{mn} \varepsilon_{kl} \right)^{-1} \]

\[ = \langle \sigma_{ij} \rangle \varepsilon_{mn} \varepsilon_{kl}^{-1} + C_{ijkl}^b \]  

(18)

According to the continuum theory of linear elasticity of composites with uniform strain fields, the elastic constants could be calculated from

\[ C_{ijkl} = C_{ijkl}^l - C_{ijkl}^b = \langle \sigma_{ij} \varepsilon_{mn} \rangle \langle \varepsilon_{mn} \varepsilon_{kl} \rangle^{-1} \]  

(19)

which implies Eq. (16) could be applied universally to the calculation of the elastic constants irrespective of the elastic bath.

In practical calculations, the matrix form may be more convenient. PR formula will be

\[ E = \left( \frac{1}{\langle V \rangle} \langle \gamma^T \gamma \rangle \right)^{-1} \]

(20)

Eq. (3) will be

\[ E = g^{-1} \langle \gamma^T \gamma \rangle g \left( \gamma^T \right)^{-1} \]  

(21)
And Eq. (12) will be

$$E = \left( \gamma \gamma^T \right)^{-1}$$  \hspace{1cm} (22)

where $E$ is the stiffness matrix, $\gamma = (\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, 2\varepsilon_{23}, 2\varepsilon_{23}, 2\varepsilon_{11})^T$ is engineering strain, and $\tau = (\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23}, \sigma_{31}, \sigma_{12})^T$ is engineering stresses, and $g$ is a diagonal matrix with elements $g_{11} = g_{22} = g_{33} = 1$, $g_{44} = g_{55} = g_{66} = 2$.

The stability of Eq. (22) could be easily evaluated by the condition number $[8]$ of matrix $\left( \gamma \gamma^T \right)$, because Eq. (22) is, in fact, the solution of a linear equation group. The smaller the condition number is, the better the stability of the algorithm has. Better stability represents a better convergence. Hence, the condition number could be considered to measure the convergence of the algorithm.

For an arbitrary $n \times n$ matrix $A$, its condition number is defined as

$$\text{Cond}(A) = \frac{\|A\| \|A^{-1}\|}{\|A\| \|A^{-1}\|}$$  \hspace{1cm} (23)

where $\|A\|$ is the norm of $A$. In this work, the $\infty$-norm is adopted.

$$\|A\|_\infty = \max_{1 \leq i \leq n} \sum_{j=1}^{n} A_{ij}$$  \hspace{1cm} (24)

### 3. Simulation results

MD simulations of an fcc crystal, the first-nearest-neighbor Ar, are carried out to verify the validity of the aforementioned formula. A classical Lennard-Jones (LJ) pair potential is employed. The simulation system includes 500 atoms. The NPT ensemble is adopted, implemented by the algorithm [9,10] using Nosé–Poincaré thermostat [11], metric–tensor pressostat [6] and Generalized leap frog integral algorithm [12]. Each simulation is first equilibrated for $1 \times 10^6$ steps, and then additional $2 \times 10^6$ steps are evolved before the results are collected.

In the simulations, the following two equations are introduced to describe the symmetric error of the stiffness matrix roughly.

$$\text{error}_{12} = \frac{|E_{12} - E_{21}| + |E_{13} - E_{31}| + |E_{23} - E_{32}|}{3(E_{12})}$$  \hspace{1cm} (25)

$$\text{error}_{\text{others}} = \sum_{i > j} |E_{ij} - E_{ji}|$$  \hspace{1cm} (26)

The first equation describes the relative error of the $\{E_{12}, E_{13}, E_{23}, E_{23}, E_{31}, E_{32}\}$, which are employed to calculate $E_{12}$. The second equation describes the error of the components which are
Fig. 2. Comparison the symmetric of the stiffness matrix of the fcc crystal at $T = 0.05$; (□) for Eq. (5) and (○) for Eq. (16).

Fig. 3. Convergence of the condition number of the matrix $\langle \gamma \gamma^T \rangle$ at $T = 0.05$.

supposed to be zero. The summation is exclusive of $E_{21}$, $E_{31}$ and $E_{32}$.

First, we tabulate the elastic constants from several equations in Table 1. All the results are in good agreement with literature data [13]. Obviously, the results of the stress and strain fluctuation formulae are much better than those of PR formula. In addition, as we discussed previously, the results of Eq. (16) are close to those of Eqs. (3) and (5). Similar situation also occurs with Eq. (10), which illustrates that the preceding simplification is reasonable.

We then compare the convergence of the three main elastic constants $E_{11}$, $E_{12}$ and $E_{44}$ via Eqs. (5) and (16) at $T = 0.05$. The computation data are depicted in Fig. 1. There are little differences between the results of Eqs. (5) and (16) after the first $2 \times 10^5$ steps. Moreover, the elastic constants could be assumed to be converged after $1 \times 10^6$ steps. In order to show the benefits of our method, we utilize Eqs. (25) and (26) to calculate the symmetric error. Clearly, the symmetry of the novel formula is better than that of Eq. (5), as shown in Fig. 2.

Finally, the condition numbers of matrix $\langle \gamma \gamma^T \rangle$ are shown in Fig. 3. It is found that the convergence of the condition number is coincident with the elastic constants tendency. Therefore this technique could be used as the convergence criterion to verify the validity of the results.

4. Conclusion

In this paper, we propose a new stress and strain fluctuation formula to calculate the elastic constants derived by both least square method and statistical thermodynamics. The validity of the formula is guaranteed by the theory of statistical thermodynamics. And its stability could be investigated by the theory of numerical analysis. The condition number of the strain fluctuation term is proposed as a criterion of convergence. Besides the high efficiency, the formula possesses good universality. In addition, the MD simulations of the classical first-nearest-neighbor LJ fcc crystal indicate
that the novel formula has better symmetry than previous version with the same convergence.

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