A Method to Apply Piola-Kirchhoff Stress in Molecular Statics Simulation

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Abstract

A force-based optimization method is proposed to apply the first and second kind of Piola-Kirchhoff stresses in molecular statics simulation. This method is important for finite deformation problems in which the atomistic behavior can be more accurately described using Piola-Kirchhoff stresses. The performance of the method is tested and validated using Silicon as a model material.

1. Introduction

Molecular statics (MS) is widely applied in atomistic simulations for searching local minima and the minimum energy path on the potential energy landscape. In the past, the methods of applying Cauchy stress in MS simulations have been well established. However, applying Piola-Kirchhoff (PK) stresses (including the first and second kind) in MS simulations has received much less attention, and we have not seen well established algorithms so far. PK stresses have been widely used in solid mechanics for finite deformation problems [1], which however may not be familiar to nonexperts in mechanics. Briefly, the first PK stress tensor ($\mathbf{P}$) is also called engineering stress or nominal stress, because it measures the force per unit area in reference configuration. The Cauchy stress tensor ($\mathbf{\sigma}$), on the other hand, is the true stress because it measures the force per unit area in the deformed configuration, so it can be directly computed from atomistic simulations using the Viral stress formula [2, 3]. The second PK stress tensor ($\mathbf{S}$) is defined entirely in the reference configuration: using a fictitious force pulled from the deformed configuration, which is then divided by the corresponding area in the reference configuration. Although $\mathbf{S}$ has no direct physical significance, it is symmetric so can be more convenient to work with than $\mathbf{P}$.

One of the advantages of PK stresses is that they have well defined work conjugates, allowing accurate evaluation of the work done by a constant external stress under finite deformation. This has been recently exploited in nudged elastic band method for computing the barriers and minimum energy paths of solid-solid phase transitions under finite deformation [4–6]. Therefore, we believe that the method proposed in this paper is important to study atomistic behavior in the materials under finite or large deformation, where using PK stresses is more appropriate than Cauchy stress.

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Parrinello and Rahman (PR) [7] proposed a barostat to control Cauchy stress in molecular dynamics (MD) simulations, which has been adopted to apply Cauchy stress in MS simulation in the limit of zero temperature. Based on PR method, the total potential energy $\Pi$ can be expressed as $\Pi = V - V_0 \sigma^{app} : \epsilon$, where $V$ is the internal potential energy, $\sigma^{app}$ is the applied constant Cauchy stress tensor, $\epsilon$ is the Green strain tensor and $V_0$ is the volume of initial reference configuration. The second term in the equation is simply the work done by the external stress. The PR algorithm minimizes the total potential energy by adjusting the atom positions and cell vectors. It is important to note that PR algorithm is just an approximation for infinitesimal deformation. Since Cauchy stress is not the work conjugate of Green strain, the work term calculated in PR formula is not accurate for finite deformation. This problem can be overcome by periodically resetting the reference configuration to the current one, so that the PR algorithm provides good approximation in a stepwise manner. PR algorithm can be modified by rewriting the external work in terms of PK stresses [8]. In this way, one could apply PK stresses by minimizing the modified energy function. However, in this paper, we take another approach: using a force-based optimization method built upon the idea proposed by Sheppard et. al. [9]. Such method does not require an objective function so it could also be used to find the equilibrium state in systems that do not have a well-defined total energy.

2. Algorithm of Applying Piola-Kirchhoff Stress

![Computation cell and cell vectors used in the proposed algorithm.](image)

**Figure 1:** Computation cell and cell vectors used in the proposed algorithm.

In MS simulations, the atomic degrees of freedom, i.e. atom positions, can be optimized based on the atomic forces, which converge to a given tolerance force when equilibrium is achieved. Similarly, the cell degrees of freedom, i.e. the cell vectors used to describe the deformation, can be optimized based on the stress acting on the cell. At equilibrium, the externally applied stress is balanced by the internal restoring stress computed with the Viral stress formula. To apply a stress in MS simulations, the atomic and cell degrees of freedom need to be optimized simultaneously. Sheppard et. al. [9] proposed a method to treat the atomic and cell degrees of freedom in equal footing during optimization. Following their idea, the geometry
of a computation cell can be described by a cell matrix \( \mathbf{H} \) written as

\[
\mathbf{H} = \begin{bmatrix}
[h_1]_1 & [h_2]_1 & [h_3]_1 \\
0 & [h_2]_2 & [h_3]_2 \\
0 & 0 & [h_3]_3
\end{bmatrix},
\]

(1)

where \([h_i]_j\) is the \(j\)th component of the cell vector \(h_i\). Particularity, \(h_1\) and \(h_2\) are confined to axis-1 and plane 1-2 as illustrated in Fig. 1. In this way, the rotational degrees of freedom of the cell are eliminated so that the cell only contains 6 independent components. The change of these components can be considered as the kinematics resulting from the corresponding Cauchy stress acting on the cell. Specifically, the six components of the Cauchy stress tensor can be expressed by three stress vectors defined as:

\[
\Sigma_1 = (\sigma_{11}, 0, 0),
\]

\[
\Sigma_2 = (\sigma_{21}, \sigma_{22}, 0),
\]

\[
\Sigma_3 = (\sigma_{31}, \sigma_{32}, \sigma_{33}).
\]

(2)

The stress vector \(\Sigma_i\) can be used to drive the change of the computation cell vector \(h_i\), along with the change of the atom positions driven by the atomic forces, leading to a deformed equilibrium configuration in terms of both atomic and cell degrees of freedom.

Next, the algorithm is presented by considering a second PK stress \(\mathbf{S}^{\text{app}}\) that is applied to a computation cell described by the matrix \(\mathbf{H}\). This stress is not directly used to drive the cell deformation but converted to a Cauchy stress during each optimization step by

\[
\sigma^{(n)} = \det(\mathbf{F}^{(n)})^{-1} \mathbf{F}^{(n)} \mathbf{S}^{\text{app}}(\mathbf{F}^{(n)})^T,
\]

(3)

where \(n\) indicates \(n\)th optimization step and the deformation gradient,

\[
\mathbf{F}^{(n)} = \mathbf{H}^{(n)} (\mathbf{H}^{\text{ref}})^{-1},
\]

(4)

is defined with respect to a pre-defined reference cell \((\mathbf{H}^{\text{ref}}, \text{which could be chosen as a zero-stress configuration})\). Then, \(\sigma^{(n)}\) is used to form the stress vectors \(\Sigma_i^{(n)}\) defined in Eq. (2). In order to update the cell vectors and atom positions simultaneously, \(\Sigma_i^{(n)}\) are combined with the atomic force vectors to form a generalized force vector, defined as

\[
\hat{\mathbf{f}}^{(n)} = \left( f_1^{(n)}, f_2^{(n)}, \ldots, f_N^{(n)}, \alpha(\Sigma_1^{\text{cell}(n)} - \Sigma_1^{(n)}), \alpha(\Sigma_2^{\text{cell}(n)} - \Sigma_2^{(n)}), \alpha(\Sigma_3^{\text{cell}(n)} - \Sigma_3^{(n)}) \right),
\]

(5)

where \(f_i\) is the force vector of \(i\)th atom of a system containing total \(N\) atoms, \(\Sigma_i^{\text{cell}}\) is the \(i\)th stress vector corresponding to the internal restoring Cauchy stress \(\sigma^{\text{cell}}\), which can be calculated by interatomic potentials or Density Functional Theory (DFT). The parameter \(\alpha\) is a scaling factor to scale the stress to the order of atomic force for the convenience of convergence. A simple and intuitive choice of \(\alpha\) is illustrated in Fig. 2.

Consider a simple cubic system, the stress acting on the unit cell \(\sigma\) is related to the interatomic force \(f\) by

\[
f = \left( \frac{V}{N} \right)^{\frac{4}{3}} \sigma,
\]

(6)
so the scaling factor can be taken as

$$\alpha = \left( \frac{V}{N} \right)^{\frac{2}{3}}. \tag{7}$$

The generalized force vector $\hat{f}$ can then be used by any force-based optimization methods to drive the change of the atomic and cell degrees of freedom. Such change is described by a generalized displacement vector

$$\Delta \hat{r}^{(n)} = \left( \Delta r_1^{(n)}, \Delta r_2^{(n)}, \ldots, \Delta r_N^{(n)} \right), \tag{8}$$

where the vector $\Delta r_i$ represents the change of $i$th atom's position and $\Delta r_i^*$ represents the generalized displacement that is used to update the cell vectors by

$$\Delta h_i = \beta \Delta r_i^*. \tag{9}$$

A scaling factor, $\beta$, is introduced to scale $\Delta r_i^*$ to the order of cell vector $\Delta h_i$. $\beta$ can be chosen as

$$\beta = (N)^{\frac{1}{3}}, \tag{10}$$

if we consider the simple cubic system shown in Fig. 2. Once the cell vectors are changed, the deformation gradient $F^{(n)}$ and the Cauchy stress $\sigma^{(n)}$ can be respectively updated by Eq. (4) and Eq. (3). Subsequently, the updated generalized force vector $\hat{f}^{(n)}$ drives another change on atom positions and cell vectors, generating an iterative process, which is converged until the force vectors of all elements inside $\hat{f}^{(n)}$ are less than a given tolerance $f_{\text{max}}$, namely

$$\max_i \| \hat{f}_i^{(n)} \| < f_{\text{max}}. \tag{11}$$

Based on our numerical tests, a slight modification to the values of scaling factors $\alpha$ and $\beta$ (for example, multiplying them by 2) is not likely to jeopardize the convergence of the algorithm, however, it may lead to a different convergence rate. Following the same algorithm described above, a first PK stress $\mathbf{P}^{\text{app}}$ can be also applied by replacing Eq. (3) with

$$\sigma^{(n)} = \det(F^{(n)})^{-1} \mathbf{P}^{\text{app}}(F^{(n)})^T. \tag{12}$$
The algorithm described above can be integrated to many optimization methods, such as steepest descents, conjugate gradient and damped dynamics. Here, we use the MDmin optimization method, as implemented in Atomic Simulation Environment (ASE) package [10], to demonstrate a detailed implementation of the algorithm. MDmin is a damped dynamics routine where the damping parameter is replaced by a projection of the velocity along the force direction. It is simply a modification of the Velocity Verlet molecular dynamics algorithm where all masses are set to one. In addition, the conventional velocity is generalized in order to include the cell degrees of freedom,

\[
\mathbf{\hat{v}}^{(n)} = \left( v^{(n)}_1, v^{(n)}_2, \ldots, v^{(n)}_N, v^{* (n)}_1, v^{* (n)}_2, v^{* (n)}_3 \right),
\]

where \( v_i \) is the velocity of \( i \)th atom and \( v^*_i \) represents the generalized velocity induced by the generalized forces. The procedure of applying a second PK stress is summarized in Algorithm 1, where the MDmin method is applied from line 9 to line 16. At each time step, the dot product between the forces and the velocity vectors is checked. If it is zero, the velocity is set to zero, otherwise, the velocity is projected to the force direction and its magnitude is set equal to the damping parameter. The atomic and cell degrees of freedom are both updated by Velocity Verlet. The MDmin method can perform very efficiently for large systems because it takes advantage of the physics of the problem.

Algorithm 1: Apply Piola-Kirchhoff stress using MDmin optimizer

1: initialize \( \hat{f}^{(0)} \) defined in Eq. (3)
2: set the initial velocity \( \hat{v}^{(0)} \) defined in Eq. (13) to zero
3: \( n = 0 \)
4: while \( \max_i \| \hat{f}^{(n)}_i \| \geq f_{\text{max}} \) do
5: compute deformation gradient \( F^{(n)} \) with Eq. (4)
6: compute applied Cauchy stress \( \sigma^{(n)} \) with Eq. (3)
7: compute atomic forces \( f^{(n)}_i \) and Cauchy stress \( \sigma^{\text{cell}} \) from empirical potentials or DFT
8: form generalized force vector \( \hat{f}^{(n)} \) using Eq. (5)
9: \( \hat{\mathbf{g}}^{(n+\frac{1}{2})} = \hat{g}^{(n)} + \hat{f}^{(n)} \Delta t/2 \)
10: if \( \hat{f}^{(n)} \cdot \hat{\mathbf{g}}^{(n+\frac{1}{2})} < 0 \) then
11: \( \hat{\mathbf{g}}^{(n+\frac{1}{2})} = 0 \)
12: else
13: \( \hat{\mathbf{g}}^{(n+\frac{1}{2})} = \hat{f}^{(n)} \frac{\hat{f}^{(n)} \cdot \hat{g}^{(n+\frac{1}{2})}}{\hat{f}^{(n)} \cdot \hat{f}^{(n)}} \)
14: end if
15: \( \hat{g}^{(n+1)} = \hat{g}^{(n+\frac{1}{2})} + \hat{f}^{(n)} \Delta t/2 \)
16: compute \( \Delta \hat{r}^{(n)} \) defined in Eq. (8): \( \Delta \hat{r}^{(n)} = \hat{g}^{(n+1)} \Delta t \)
17: update atomic positions \( \hat{r}^{(n+1)}_i = \hat{r}^{(n)}_i + \Delta \hat{r}^{(n)} \) and cell vectors \( \hat{h}^{(n+1)}_k = \hat{h}^{(n)}_k + \beta \Delta \hat{r}^{* (n)} \)
18: \( n = n + 1 \)
19: end while
3. Numerical Example

In this section, we use diamond cubic silicon as a model material to demonstrate the performance and application of the proposed algorithm. Fig. 3a shows a computation cell containing 1000 atoms which are randomly disturbed from their equilibrium positions. In this way, both the atoms and the cell are initially set to non-equilibrium state. A zero stress equilibrium configuration is taken as the reference configuration for measuring PK stresses. Two stress states are applied in this example (units: GPa, unspecified stress components are zeros):

(i) uniaxial compression: the first PK stress $P_{33} = -13.452$; the second PK stress $S_{33} = -15.823$, which are both equivalent to a Cauchy stress $\sigma_{33} = -12$.

(ii) compression plus shear: the first PK stress $P_{11} = -0.620$, $P_{12} = 5.653$, $P_{21} = 5.703$ and $P_{33} = -7.401$; the second PK stress $S_{11} = -1.211$, $S_{12} = S_{21} = 5.522$ and $S_{33} = -8.042$, which are both equivalent to Cauchy stress $\sigma_{12} = \sigma_{21} = 6$ and $\sigma_{33} = -7$.

All calculations are performed with Stillinger-Weber (SW) [11] interatomic potential as implemented in LAMMPS [12]. The convergence of both the atomic forces and stresses are monitored during the optimizations, as shown in Fig. 4 and Fig. 5 respectively for stress states (i) and (ii). It can be seen that the atomic forces and stresses converge at very similar rates, meaning that the atomic and cell degrees of freedom are treated equivalently during optimization. In addition, a similar convergence behavior is shown for the first and second PK stress, because they are both converted to the Cauchy stress before being passed to the

![Figure 3](image_url)

**Figure 3:** The computation cell of diamond cubic Si containing 1000 atoms. (a) Initially, all atoms are randomly perturbed from their equilibrium positions. (b) When PK stress is applied on [001] direction as in stress state (i), both atoms and cell are optimized to the equilibrium configuration.
optimizer. It is also confirmed that the optimizations under the first and second PK stress prescribed in (i) and (ii) yield the correct configurations where both the atoms and the computation cell are brought to the equilibrium states, as shown in Fig. 3b.

Figure 4: Convergence of the atomic forces and stress under uniaxial compressive stress specified by (i) in the text, (a) for first PK stress and (b) for second PK stress.

Figure 5: Convergence of the atomic forces and stress under compressive and shear stresses specified by (ii) in the text, (a) for first PK stress and (b) for second PK stress.

The numerical examples and the proposed algorithm are implemented based on the Atomic Simulation Environment (ASE) [10], an open source Python package. The advantage of ASE is that it provides an interface to various external atomistic computational codes, such as VASP and LAMMPS, which can be used as the calculators to compute atomic forces and stresses. The code and the example scripts reported in this paper are available at: https://github.com/Gao-Group/stressbox.

Finally, we use the phase transition of Silicon, from a diamond cubic (Si-I) phase to a metallic β-tin structure (Si-II) [13], as an example to explain the importance of applying PK stresses in MS simulations. The transition from Si-I to Si-II is accompanied with finite lattice deformation, and the work done by the external stress contribute significantly to the transition barriers and the minimum energy path (MEP). As
mentioned in the introduction, using Cauchy stress yields inaccurate evaluation of the work done by the stress, and hence lead to inaccurate barriers and deviated MEP. Because of this, PK stresses are better suited for phase transition problems when material is subjected to finite deformation. Recently, we proposed a finite deformation nudged elastic band (FD-NEB) method to compute the transition barrier and MEP under a constant PK stress. In order to compute the barrier and MEP of Si-I to Si-II phase transition, one important step is to apply the PK stress to both the initial state Si-I and the final state Si-II using the algorithm described above. After that, a number of intermediate states generated between the initial and final states are optimized simultaneously under the applied PK stress until a converged MEP is established. A typical MEP calculated under 8 GPa compressive first PK stress is shown in Fig. 6. SW interatomic potential is used in this calculation, which overestimates the phase transition barriers comparing to DFT results, as noted by previous studies [14]. It is noted that although the MS algorithm presented in this paper has been used in FD-NEB calculations in [4], this is the first time we present the detailed implementation and discussion of the algorithm.

Figure 6: The minimum energy path of Si-I to Si-II phase transition under 8 GPa compressive first PK stress applied along [001] direction.

4. Summary

A new method is formulated to apply the first and second kind of PK stresses in MS simulation. The proposed force-based algorithm can be integrated to a variety of optimization methods. A damped dynamics optimizer, MDmin, is used to demonstrate the implementation of the proposed algorithm. The performance of the method is tested on diamond cubic silicon material, showing that the atomic and cell degrees of freedom can be optimized equivalently under constant PK stresses. The method is useful for finite deformation problems in which PK stresses are more appropriate to describe the atomic behavior, such as the phase transitions in the materials subjected to finite deformation.
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