A COMPARATIVE STUDY OF ATOMISTIC-BASED STRESS EVALUATION

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ABSTRACT. This paper presents a comparative study on several issues of the microscopic stress definitions. Firstly, we derived an Irving-Kirkwood formulation for Cauchy stress evaluation in Eulerian coordinates. We showed that quantities, such as density and momentum, should to be defined properly on microscopic level in order to guarantee the conservation relations on macroscopic level. Secondly, the relation between Cauchy and first Piola-Kirchhoff stress was investigated both theoretically and numerically. At zero temperature, classical pointwise relation between these two stress is satisfied both in Virial and Hardy formulation. While at finite temperature, temporal averaging is required to guarantee this relation for Virial formulation. For Hardy formulation, an additional term need to be included in the classical relation between the Cauchy stress and the first Piola-Kirchhoff stress. Meanwhile, the linear relation between the Cauchy stress and the first Piola-Kirchhoff stress with respect to the temperature are obtained in both Virial and Hardy formulations. The thermal expansion coefficients are also studied by using quasi-harmonic approximation. Thirdly, different from that in the Lagrangian coordinates case, where the time averaging procedure can be performed in a post-processing manner when the kernel function is separable, the stress evaluation in Eulerian system must be evaluated spatially and temporally at the same time, even in separable kernel case. This can be seen from the comparison of the two procedures. Numerical examples were provided to illustrate our investigations.

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1. **Introduction.** With the advent of numerical techniques and computing power, molecular dynamics (MD) simulation is now a promising atomistic modeling tool to investigate the detailed properties and behaviors of material on microscopic level [4, 1, 28, 10]. Meanwhile, although with the lack of precision, the models based on continuum mechanics are still widely used as an efficient theoretical framework for modeling materials at macroscopic scale. Therefore, in order to study the material systems with two or more length and/or time scale, the atomistic and continuum descriptions should coexist in multiscale modeling, and the quantities in both descriptions should be consistent [1, 3]. However, since the quantities in MD simulations are in the form of positions and velocities of atoms and the quantities used in continuum theory are in the form of field variables, it is important to reinterpret the discrete data of the positions and velocities in the language of continuous field variables [3, 2, 5]. More precisely, we need the equivalent definitions of the fundamental quantities such as stress which plays a significant role in the multiscale modeling[6, 22, 21, 9] in both microscopic and macroscopic scales.

Another motivation to study the microscopic definitions of stress is to provide a realistic precise atomic-informed perspective in order to review the classical constitutive relations in continuum mechanics [1, 11]. For linear elastic solid and the Newtonian fluid, the traditional constitutive relations is based on the second thermodynamics law and the assumption that the stress tensor is a linear function of the strain or the deformation rate tensor, and the coefficients are determined by experiments. More intrinsically, with the help of MD simulations and a proper microscopic definition of the stress tensor, we could get a deeper understanding of the constitutive relation between the stress and the underlying microscopic dynamics from first principle [3, 23].

For equilibrium and homogeneous system, the most commonly adopted microscopic definition of stress is the famous Virial stress, proposed by Clausius[7] in 1870 which is similar to the definition of gas pressure and then be extended to tensorial version by Maxwell[17]. Later on Tsai[25] generalize this definition to the finite temperature case. Since this stress formulation can be derived by taking derivative of the Helmholtz free energy with respect to the deformation gradient, therefore it can be written as an ensemble average of the Virial of the system, which is the sum of multiplications of position and force. For Cauchy stress in Eulerian coordinates, the ensemble average should include the contribution of kinetic energy of the system. Thanks to the simplicity and practicality, Virial stress has been used a lot in material modeling. However, in the case of nonequilibrium and inhomogeneous system the Virial stress proved to be doubtful since it is not correct to take some ensemble average while the system has not arrived at equilibrium[22].

As an alternative approach, Irving and Kirkwood (IK)[13] proposed a pointwise defined stress tensor based on Liouvil equation, the so-called IK stress was later reformulated rigorously by Noll[20] and thus provided the explicit closed-form stress expression. Even so, the original IK formulation is not practical due to the Dirac delta functions. Hardy[12] proposed a new formulation of stress by replacing the delta weighting function used in the derivation of IK stress to a regularized spatial averaging kernel with compact support, the so-called Hardy stress was widely used in MD simulations and then be generalized to solid materials as the first Piola-Kirchhoff (PK) stress by Zimmerman et al.[30, 29]. On the other hand, in order to improve the accuracy of IK stress, Murdoch and his cooperators[18, 19] proposed a
spatial and temporal averaged stress. The time averaging procedure in their formulation, however, is a post-processing step, which cannot be derived from the original IK formalism. Later in 2012 Yang et al\cite{26} constructed a general IK (GIK) stress formulation in which a spatial and time-dependent kernel are used in the derivation similar to that in IK formalism, thus a prior time averaged stress tensor could be obtained, of which the thermal fluctuation can be reduced. In their paper they also mentioned that two different time averaging methods used in the calculation of PK stress are equivalent if the kernel function is separable. Further more in 2010 Admal and Tadmor\cite{1} gave a unified interpretation of microscopic stress tensors. In that paper, the authors reconstructed the Hardy stress, Virial stress and Tsai stress from the IK formulation with different kernel functions and did a lot numerical experiments to show the connections and difference between different atom-base stress. Although many researches had been done in this field, however, there are some important fundamental issues on the different microscopic definitions of the stress need to be clarified such as:

- The theoretical relation between PK stress and Cauchy stress in different stress formulations.
- The detailed expression of thermal effect in various microscopic stress formulations.
- Connections between different time average strategies.

Therefore the better understanding the effectiveness and correctness of these stress formulation, especially for the time averaging effect and the consistency with continuum mechanics, still ask for more theoretical and numerical work.

The rest of the paper is organized as follows. In Sec.2, we review various microscopic stress formulation in different coordinate, and derive an Irving-Kirkwood formulation for Cauchy stress evaluation in Eulerian coordinates. Then in Sec.3 the main results will be presented, including the study of the pointwise relation between PK stress and Cauchy stress, thermal expansion effect, time averaging effect. Both theoretical and numerical results will be shown. Finally we would give our main conclusions in Sec.4.

2. Microscopic descriptions of the stress in different coordinate. In continuum mechanics the stress tensor \( \sigma(x) \) can be defined as a linear function of the norm direction \( n \) to the stress vector \( T(x, n) \), namely we have

\[
T(x, n) = \sigma(x) n.
\]  

This expression could be used in the derivation of stress expressions based on conservation law.

There are two commonly used descriptions of the motion of a body. One description is based on deformed spatial coordinates or Eulerian coordinates (denoted by \( x \) in this paper). In this description, the equations for the conservation of mass \( \rho(x, t) \) and momentum \( q(x, t) = \rho(x, t)v(x, t) \) could be expressed as following

\[
\frac{\partial}{\partial t} \rho + \nabla_x \cdot q = 0, 
\]  

\[
\frac{\partial}{\partial t} q + \nabla_x \cdot (\rho v \otimes v) = \nabla_x \cdot \sigma_{\text{Cauchy}}. 
\]

The stress \( \sigma_{\text{Cauchy}}(x, t) \) in Eulerian coordinates is called Cauchy stress, which is commonly used in fluid mechanics due to large displacement and complex deformations.
Another description is referred to the undeformed reference coordinates or Lagrangian coordinates (denoted by $X$ in this paper), which is widely used in solid mechanics. In this description, the stress tensor is called the first Piola-Kirchhoff stress, and be written as $\sigma_{PK}(X, t)$. The expression of conservation of momentum $q(X, t)$ could be written as

$$\frac{\partial}{\partial t} q = \nabla_X \cdot \sigma_{PK}. \quad (2.4)$$

In this section we would respectively give the atomistic-based microscopic definition of the Cauchy stress and the first Piola-Kirchhoff stress, which could be used in molecular dynamics for practical calculations.

2.1. Piola-Kirchhoff stress. In the beginning of this subsection, we review the derivations of IK formulation for the Piola-Kirchhoff stress in molecular systems. For a molecular system out of equilibrium, the positions and velocities of atoms can be used to give a pointwise definition of the density field and the momentum field in continuum mechanics. At this moment we choose the Lagrangian coordinate $X$ in the derivations. Consider a system $\Omega$ consists of $N$ atoms, of which the $i$-th atom has the mass $m_i$, reference position $X_i$, deformed position $x_i$, velocity $v_i$ and experiences a force denoted by $f_i$. For this atomic system with multi-body interactions, the force $f_i$ can be decomposed as

$$f_i = \sum_{j \neq i}^{} f_{ij}, \quad (2.5)$$

where $f_{ij}$ is the force contribution due to the $j$-th atom with $f_{ij} = -f_{ji}$. This force contribution $f_{ij}$ can be given by

$$f_{ij} = -\frac{\partial V(r_{12}, \ldots, r_{ij}, \ldots)}{\partial r_{ij}}, \quad (2.6)$$

where $V(r_{12}, \ldots, r_{ij}, \ldots)$ is the total potential energy of the system, which is a function of all relative position $r_{ij} = x_i - x_j$ for $i, j = 1, \ldots, N$. This pairwise force formula (2.6) is valid not only in pairwise inter-atomic potential models, but also in multi-body potential models such as EAM potential [26], Tersorff potential and Stillinger-Weber potential [24]. The Newton’s second law for atoms is

$$m_i \ddot{x}_i = m_i \dot{v}_i = -\nabla_{x_i} V = f_i = \sum_{j \neq i}^{} f_{ij}. \quad (2.7)$$

With the help of discrete information of each atom, the pointwise field in continuum level can be defined as follows:

$$\rho(X) = \sum_{i=1}^{N} m_i \varphi(X - X_i),$$

$$q(X, t) = \sum_{i=1}^{N} m_i v_i(t) \varphi(X - X_i). \quad (2.8)$$

Here $\varphi(X)$ could be treated as a specified weight function for spatial average, which quantize the weight of the $i$-th atom to the abstract material point $X$. Generally, $\varphi(X)$ should satisfy following restrictions:

- $X_i = \text{arg max}_X \varphi(X_i - X)$.
- $\lim_{|X_i - X| \to \infty} \varphi(X_i - X) = 0$.
- $\int_{R^3} \varphi(X_i - X)dX = 0$.
- $\varphi(X_i - X)$ is non-negative and smooth.
It should be noted that if we choose the weight function $\varphi(X)$ as the $\delta(X)$, which satisfies that $\delta(X) = 0$ everywhere except at $X = 0$, then definition (2.8) is exactly the molecular dynamics description of the system.

Now if we substitute the definition (2.8) into the equation (2.4) and introduce a bond function $b_{ij}(X) = \int_0^1 \varphi(X - (X_i + \lambda X_{ji}))d\lambda$ where $X_{ji} = X_j - X_i$, we could arrive at the following microscopic definition of the first Piola-Kirchhoff stress:

$$\sigma_{PK}^{Hardy}(X, t) = -\frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes X_{ij} b_{ij}(X). \quad (2.9)$$

Here the superscript $Hardy$ in (2.9) indicate that a regularized weight function $\varphi(X)$ proposed by Hardy [12] is used in the calculation of stress instead of the delta function used in the IK formulation, in other words, the Hardy formulation of the PK stress (Hardy-PK stress for short) could be obtained by the convolution of the IK stress with a particular regularized kernel function $\varphi(X)$. Therefore, we will not distinguish the Hardy stress from the IK stress. The bond function $b_{ij}(X)$ appeared in (2.9) can be understood as a 'bond weight' which describes the contribution of the interaction between $X_i$ and $X_j$ to the average stress defined at $X$.

For a system at thermodynamics equilibrium, another useful and convenient microscopic definition of stress is the Virial formulation. In the Lagrangian coordinates, the PK stress based on Virial formulation (Virial-PK stress for short) could be written as:

$$\sigma_{PK}^{Virial}(X, t) = -\frac{1}{2} |V_0| \sum_i \sum_{j \neq i} f_{ij} \otimes X_{ij} \quad (2.10)$$

Here $|V_0|$ is the system volume before deformation. For a homogenous system in equilibrium, the viral stress is defined as a constant, which is uniform for all $X$ in the volume. For non-equilibrium system, we can assume the system is in local thermodynamic equilibrium at every $X$ at an instant of time, in which case the $V_0$ represent the infinite volume $dX$ around $X$ and the atom appeared in the sum of Virial should be in $dX$. The Virial stress could be considered as a special case in Hardy’s formulation [24], i.e., if we choose the weight function as a step function of which the weight is set to be $(\text{Volume}(\Omega))^{-1}$ and ignore some effects of bonds $b_{ij}(X)$ when $X_{ij}$ cross the boundary, we could get the Virial stress from Hardy’s formulation.

So far we have shown two different versions of the first Piola-Kirchhoff stress which is the fundamental quantity in solid mechanics. These two types of formulation can both be considered as different realizations of the IK stress [26, 27]. It worthy to mention that the phase average is applied in (2.8) in order to reduce the thermodynamics fluctuations in original derivation of the IK stress. In our work, the phase average is replaced by the time average, which is more practical in MD simulations.

Based on the Hardy formulation introduced above, Yang et al proposed a generalized Irving-Kirkwood (GIK) formulation [26]. They argued in that paper that the Hardy stress calculated from (2.9) still fluctuates significantly, in order to solve that, they proposed a new kernel function $\Phi(X, t)$ which not only take the spatial average of the IK stress but also allows a direct temporal sampling. In that case the momentum field should be defined as

$$q(X, t) = \sum_{i=1}^N \int_\mathbb{R} m_i v_i(\tau) \Phi(X - X_{i\cdot}, t - \tau)d\tau. \quad (2.11)$$
Now once we substitute the above definition of $q(X, t)$ into (2.4) and modify the bond function $b_{ij}(X)$ by

$$B_{ij}(X, t) = \int_0^1 \Phi((X - (X_i + \lambda X_{ij}), t)d\lambda,$$

(2.12)

we could achieve a new definition of first Piola-Kirchhoff stress via the generalized Irving-Kirkwood formulation (GIK-PK stress) as

$$\sigma_{PK}^{\text{GIK}}(X, t) = -\frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes X_{ij} B_{ij}(X, t - \tau)d\tau.$$  

(2.13)

As shown in our previous work [26], the GIK-PK stress do exhibit a more temperate fluctuation. It should be mentioned that the classical procedure of the time average is operated immediately after the spatial average of Hardy stress. Namely the classical spatial-time averaged Hardy-PK stress is defined as

$$\bar{\sigma}_{PK}(X, t) = \sigma_{PK}^{\text{Hardy}}(X, t) * \tau(t)$$

$$= -\frac{1}{2} \int_R \sum_i \sum_{j \neq i} f_{ij}(s) \otimes X_{ij} b_{ij}(X) \tau(t - s) ds.$$  

(2.14)

Compared that with the GIK-PK stress defined in (2.13) we can easily find that when the weighted kernel function $\Phi(X, t)$ is separable, the obtained GIK-PK stress is identical with the spatial-time averaged Hardy-PK stress. In other words, this spatial-time averaged Hardy-PK stress can be seen as a special case of the GIK-PK stress. This conclusion can be proved only for the first Piola-Kirchhoff stress calculation in Lagrangian coordinates, but not for the Cauchy stress in Eulerian coordinates, as we will show in the Section 3.2.

2.2. Cauchy stress. In this section we would reconstruct all the stress formulations mentioned above in the Eulerian coordinate in order to get the corresponding formulations of Cauchy stress, which is the classical description of stress in fluid mechanics. We start with the definition the local continuum field of density and momentum:

$$\begin{align*}
\rho(x, t) &= \sum_{i=1}^N m_i \phi(x - x_i(t)), \\
q(x, t) &= \sum_{i=1}^N m_i v_i(t) \phi(x - x_i(t)).
\end{align*}$$

(2.15)

The conservation law of mass can be naturally guaranteed by the above definitions:

$$\frac{\partial}{\partial t} \rho + \nabla \cdot q = -\sum_{i=1}^N m_i v_i(t) \cdot \nabla \phi(x - x_i(t)) + \nabla \cdot \left[ \sum_{i=1}^N m_i v_i(t) \phi(x - x_i(t)) \right] = 0.$$  

(2.16)

Then the velocity field can be obtained by

$$v(x, t) = \frac{q(x, t)}{\rho(x, t)} = \frac{\sum_{i=1}^N m_i v_i(t) \phi(x - x_i(t))}{\sum_{i=1}^N m_i \phi(x - x_i(t))}.$$

(2.17)

It is worthy to point out that if the velocity field are defined as

$$v(x, t) = \sum_{i=1}^N v_i(t) \phi(x - x_i(t))$$  

(2.18)
and then use $q(x, t) = v(x, t)\rho(x, t)$ to define the momentum, the conservation law (2.16) is not hold anymore. Taking derivative of $q$ with respect to time $t$ and denote $b_{ij}(x, t) = \int_0^1 \varphi(x - (x_i(t) + \lambda x_j(t)))d\lambda$, we have

\[
\frac{\partial q}{\partial t} = \sum_{i=1}^N f_i \varphi(x - x_i) - \sum_{i=1}^N m_i v_i \nabla_x \varphi(x - x_i) v_i
\]

\[
= \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} f_{ij} [\varphi(x - x_i) - \varphi(x - x_j)] + \nabla_x \cdot \left[ - \sum_{i=1}^N m_i v_i \otimes v_i \varphi(x - x_i) \right]
\]

\[
= \nabla_x \cdot \left[ - \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} f_{ij} \otimes x_{ij} b_{ij}(x, t) - \sum_{i=1}^N m_i (w_i + v) \otimes (w_i + v) \varphi(x - x_i) \right]
\]

\[
= \nabla_x \cdot \left[ - \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} f_{ij} \otimes x_{ij} b_{ij}(x, t) - \sum_{i=1}^N m_i w_i \otimes w_i \varphi(x - x_i) \right] - \nabla_x (\rho v \otimes v),
\]

where $w_i(x, t) = v_i - v(x, t)$ is the relative velocity. Substitute the above result into (2.3) we could get the corresponding Hardy formulation of Cauchy stress (Hardy-Cauchy stress) as

\[
\sigma^{Hardy}_{Cauchy}(x, t) = -\frac{1}{2} \sum_{i} \sum_{j \neq i} f_{ij}(t) \otimes x_{ij}(t) b_{ij}(x, t) - \sum_{i=1}^N m_i w_i(x, t) \otimes w_i(x, t) \varphi(x - x_i(t)).
\]

(2.19)

The weight function $\varphi(x)$ here is defined in the spatial coordinate $x$ rather than the reference coordinate $X$. Notice that there is an important equality for the relative velocities:

\[
\sum_{i=1}^N m_i w_i \varphi(x - x_i) = \sum_{i=1}^N m_i v_i \varphi(x - x_i) - v \sum_{i=1}^N m_i \varphi(x - x_i) = 0
\]

Similar to the derivation of Virial-PK stress, if we choose the weight function as the step function in the Eulerian coordinates, then we can get the Virial formulation of the Cauchy stress (Virial-Cauchy stress):

\[
\sigma^{Virial}_{Cauchy}(x, t) = -\frac{1}{|V|} \left( \frac{1}{2} \sum_{i} \sum_{j \neq i} f_{ij} \otimes x_{ij} + \sum_{i=1}^N m_i w_i \otimes w_i \right)
\]

(2.20)

where the $|V|$ is the system’s volume after the deformation. In both Hardy-Cauchy and Virial-Cauchy stress, the weight functions $\phi$ only depends on the spatial coordinate, we could also define Cauchy stress via the GIK formulation in [26] by using a more general spatial and temporal weight function $\phi(x, t)$, then the pointwise mass and momentum is defined as

\[
\begin{align*}
\tilde{\rho}(x, t) &= \sum_{i=1}^N m_i \int_R \phi(x - x_i(s), t - s)ds, \\
\tilde{q}(x, t) &= \sum_{i=1}^N m_i \int_R v_i(s) \phi(x - x_i(s), t - s)ds.
\end{align*}
\]

(2.21)
Notice that this definition also guarantees the conservation of mass. For the velocity field,

\[ \tilde{v}(x, t) = \frac{\tilde{q}}{\rho} = \sum_{i=1}^{N} m_i \int_R v_i(s) \phi(x - x_i(s), t - s) ds \]  

(2.22)

and if we denote \( \tilde{w}_i(x, s, t) = v_i(s) - \tilde{v}(x, t) \) as the relative velocity, we have

\[ \sum_{i=1}^{N} m_i \int \tilde{w}_i(x, s, t) \phi(x - x_i(s), t - s) ds = \tilde{q} - \tilde{q} \tilde{v} = 0. \]  

(2.23)

Now by changing variable \( s' = t - s \) and taking the time derivative of \( \tilde{q}(x, t) \),

\[
\frac{\partial \tilde{q}}{\partial t} = -\frac{\partial}{\partial t} \sum_{i=1}^{N} m_i \int v_i(t - s') \phi(x - x_i(t - s'), s') ds' \\
= - \sum_{i=1}^{N} \int f_i(t - s') \phi(x - x_i(t - s'), s') ds' + \sum_{i=1}^{N} m_i \int v_i(t - s') [\nabla x \phi(x - x_i(t - s'), s') \cdot v_i(t - s')] ds' \\
= \sum_{i=1}^{N} \int f_i(s) \phi(x - x_i(s), t - s) ds - \sum_{i=1}^{N} m_i \int v_i(s) [\nabla x \phi(x - x_i(s), t - s) \cdot v_i(s)] ds \\
= \nabla x \cdot \left[ -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \int f_{ij}(s) \otimes x_{ij}(s) B_{ij}(x, t - s) ds \right] \\
- \sum_{i=1}^{N} m_i \int v_i(s) \otimes v_i(s) \phi(x - x_i(s), t - s) ds \\
= \nabla x \cdot \left[ -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \int f_{ij}(s) \otimes x_{ij}(s) B_{ij}(x, t - s) ds ight] \\
- \sum_{i=1}^{N} m_i \int \tilde{w}_i(x, s, t) \otimes \tilde{w}_i(x, s, t) \phi(x - x_i(s), t - s) ds - \nabla x (\rho \tilde{v} \otimes \tilde{v}),
\]

where we have used (2.23) in the last equality and defined the bond weight function

\[ B_{ij}(x, s, t - s) = \int_0^1 \phi(x - (x_i(s) + \lambda x_{ij}(s), t - s)) d\lambda \]  

(2.24)

Compared with the conservation law (2.3), we could get the generalized IK formulation of the Cauchy stress (GIK-Cauchy stress) as follows:

\[
\sigma_{\text{Cauchy}}^{GIK}(x, t) = -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \int f_{ij}(s) \otimes x_{ij}(s) B_{ij}(x, s, t - s) ds \\
- \sum_{i=1}^{N} m_i \tilde{w}_i(x, s, t) \otimes \tilde{w}_i(x, s, t) \phi(x - x_i(s), t - s) ds
\]  

(2.25)
3. Thermodynamics property of various kinds of stress. In this section we would present a series of numerical examples with some analysis to illustrate our main results as a comparative study on different stress formulations, especially for their thermodynamics property. Our main conclusions consist of three aspects: the thermodynamics expansion effect of different stress; the relation between PK stress and Cauchy stress; the difference of two time average methods for stress calculation.

3.1. The relation between PK stress and Cauchy stress and the thermodynamics expansion effect. As we have introduced before, in continuum mechanics the PK stress and Cauchy stress are two different representations of surface force acted on material, the Eulerian representation (Cauchy stress) is more often used for fluids while the Lagrangian representation (first PK stress) is more common for solids. In order to illustrate the relation between two stress, we use \( \psi(X) \) to denote the deformation function, which maps the point \( X \) in undeformed region \( \Omega_0 \) in Lagrangian coordinate to \( x \) in deformed region \( \Omega \) in Eulerian coordinate. Furthermore, the spatial and material differentials are related by

\[
\frac{d}{dx} = A \frac{d}{dX},
\]

where \( A \) is called the deformation gradient and defined as

\[
A(X) = \frac{\partial \psi(X)}{\partial X}. \tag{3.1}
\]

By computing the resultant surface force for the same region in both Eulerian coordinate and Lagrangian coordinate over the same region \( \Omega_0 \), i.e.,

\[
\int_{\partial \Omega_0} \sigma_{PK}(X, t) \cdot n_0(X, t) d\Gamma_0(X) = \int_{\partial \Omega} \sigma_{Cauchy}(\psi(X, t), t) \cdot n(x, t) d\Gamma(x),
\]

and using the Nanson’s formula [24]:

\[
n(x, t) d\Gamma(x) = |A| A^{-T} n_0(X, t) d\Gamma_0(X),
\]

we can obtain the well known Piola transform between the first Piola-Kirchhoff stress and the Cauchy stress:

\[
\sigma_{PK} = |A| \sigma_{Cauchy} \cdot A^{-T}. \tag{3.2}
\]

It is worthy to be noted that the relation (3.2) should hold in continuum level at any time \( t \) for a given reference coordinate \( X \) and the corresponding spatial coordinate \( x = \psi(X, t) \), only if we can compute the deformation gradient \( A \). It means the equation (3.2) would not be influenced by other thermodynamics factors, like the temperature \( T \). This fact, however, proves to be not the same story for microscopic stress formulations based on the atomistic model. The reason for this difference is that in the finite temperature case those atoms constitute the macroscopic material will experience thermo vibration around the uniform deformation \( A \), so we need to take some phase average to get this classical relation. In the rest of this subsection we would first give some detailed analysis for the difference (3.2) and then present some numerical results to illustrate the main effect of temperature.

3.1.1. Virial formulation. First let us deal with the Virial stress formulation. Suppose the infinitesimal volume \( dX \) we consider in the continuum model is a molecular system consists of \( N \) atoms as introduced before, of which the reference positions and deformed positions are denoted by \( X_i \) and \( x_i \) respectively. Once we apply a uniform deformation \( A \) to the systems under temperature \( T \), the atoms would vibrate around the uniform deformed positions \( AX_i \) and the vibration should satisfy the Boltzmann distribution if the system have reached the thermodynamics equilibrium. Namely we have

\[
x_i = AX_i + u_i \quad \text{and} \quad u_i \sim \rho_{eq} = \frac{1}{Z} \exp\{-\beta V(AX_i + u_i)\}. \tag{3.3}
\]
where $Z = \int \exp\{-\beta V(Ax_I + u_I)\}du_I (I = 1, 2, \ldots, N)$ is the partition function and $\beta = 1/(k_BT)$, $k_B$ is the Boltzmann constant and $T$ is the temperature.

According to the definitions of Virial-PK stress (2.10) and Virial-Cauchy stress (2.20) in last section, we can derive the relation between these two stress at finite temperature that

$$
\sigma_{\text{Cauchy}}^{\text{Virial}} = -\frac{1}{|V|} \frac{1}{2} \sum_{i} \sum_{j \neq i} f_{ij} \otimes x_{ij} + \sum_{i=1}^{N} m_i w_i \otimes w_i
$$

Therefore, we can shifted the average velocity to zero at the beginning of our simulation. As a result, we have the relation that $w_i = v_i$. This condition, actually, is exactly what we set in our numerical simulations.

Then we consider the two additional terms. Due to the fact that macroscopic physical quantities are obtained by taking phase average based on the ensemble we choose, then the relation between the averaged Virial-Cauchy stress and the averaged Virial-PK stress is

$$
\langle \sigma_{\text{Cauchy}}^{\text{Virial}} \rangle = \frac{1}{|A|} \sigma_{PK}^{\text{Virial}} \cdot A^T - \frac{1}{|V|} \sum_{i=1}^{N} f_i \otimes u_i - \frac{1}{|V|} \sum_{i=1}^{N} m_i w_i \otimes w_i. \quad (3.4)
$$

Note here we have used the relation $|V| = |A| \cdot |V_0|$ and the force decomposition (2.5). From the last equation we could find that (3.2) is well satisfied at zero temperature. For finite temperature case, the Virial-Cauchy stress own two additional terms: $-|V|^{-1} \sum_i f_i \otimes u_i$ and $-|V|^{-1} \sum_{i=1}^{N} m_i w_i \otimes w_i$. Suppose that the considered molecular system consists of a single kind of atoms whose mass are identical and be in the thermodynamic equilibrium state, since we are dealing with Virial formulation, then the average velocity $v$ defined by (2.17) can be computed as

$$
v(x, t) = \frac{\sum_{i=1}^{N} m_i v_i(t) \phi(x - x_i(t))}{\sum_{i=1}^{N} m_i \phi(x - x_i(t))} = \frac{\sum_{i=1}^{N} v_i}{N}. \quad (3.5)
$$

Therefore, we can shifted the average velocity to zero at the beginning of our simulation. As a result, we have the relation that $w_i = v_i$. This condition, actually, is exactly what we set in our numerical simulations.

The bracket stands for the phase average in canonical ensemble:

$$
\langle g(u_I, v_I) \rangle = \frac{1}{Z} \int du_I dv_I g(u_I, v_I)e^{-\beta H(u_I, v_I)}, \quad (3.7)
$$
where \( H(\mathbf{u}_I, \mathbf{v}_I) = V(\mathbf{AX}_I + \mathbf{u}_I) + \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \). Suppose we apply the well-known quasi-harmonic approximation to the potential

\[
V(x) = V(\mathbf{AX}_I) + \frac{1}{2} \mathbf{u}_I^T D(\mathbf{A}) \mathbf{u}_I
\]

and use the relation that

\[
f_i = - \frac{\partial H}{\partial \mathbf{u}_i} = - \sum_{j=1}^{N} D_{ij} \mathbf{u}_j \quad \text{and} \quad m_i \mathbf{v}_i = \frac{\partial H}{\partial \mathbf{v}_i},
\]

we could obtain that

\[
\langle f_i \otimes \mathbf{u}_i \rangle = - \sum_{j=1}^{N} D_{ij} \langle \mathbf{u}_j \otimes \mathbf{u}_i \rangle = -(\frac{\partial H}{\partial \mathbf{u}_i} \otimes \mathbf{u}_i), \quad \langle m_i \mathbf{v}_i \otimes \mathbf{v}_i \rangle = \langle \frac{\partial H}{\partial \mathbf{v}_i} \otimes \mathbf{v}_i \rangle
\]

Now if we use the fact that \( \mathbf{u}_I \) will experience a variance \( k_B T D(\mathbf{A})^{-1} \) \([15, 16]\), which can also be proved by the equipartition theorem under the condition (3.3) (for a periodic system or an unbounded system with atomic interaction vanishing at infinity, we can use integration by part to achieve the same result), we can find that

\[
\langle \frac{1}{|V|} \sum_{i=1}^{N} f_i \otimes \mathbf{u}_i \rangle = - \frac{N k_B T}{|V|} I_{3 \times 3} \quad \text{and} \quad \langle \frac{1}{|V|} \sum_{i=1}^{N} m_i \mathbf{v}_i \otimes \mathbf{v}_i \rangle = \frac{N k_B T}{|V|} I_{3 \times 3}.
\]

Substitute these two equations into (3.6), we could find a similar pointwise relation between the Virial-PK stress and Virial-Cauchy stress as shown in (3.2) in atomistic model in the sense of statistic mechanics, when the system is in thermodynamic equilibrium, i.e.,

\[
\langle \sigma_{\text{Virial}} \rangle = \frac{1}{|A|} \langle \sigma_{\text{PK}} \rangle \cdot A^T
\]

The numerical evaluations of the stress in Virial formulation obtained from MD simulations for pre-deformed face-centered cubic (FCC) crystal aluminum at different temperatures are shown in Figure 1. In the MD simulations, we construct a simulation box consists of 50 \( \times \) 50 \( \times \) 50 periods in x-, y-, and z-axis (\( 5 \times 10^5 \) Al atoms in total) with the periodic boundary conditions. We use the Nose-Hoover chain to simulate the canonical ensemble (NVT) at different temperature from 0K to 500K. The lattice constant for Al in our simulations is \( a_0 = 4.032\)Å and for the time integration we have \( \Delta t = 0.5 \) with time scale 0.052880ps. After discarding the first 8000 MD steps to allow for the molecular system reaching the thermodynamic equilibrium, the time-averaged quantities are calculated based on the atomic configurations obtained in simulations every 10 MD steps. The initial simulation boxes of pre-deformed aluminum are constructed based on two different deformation matrix \( A_1 \) and \( A_2 \) shown as follows

\[
A_1 = \begin{pmatrix}
1.01 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}, \quad A_2 = \begin{pmatrix}
1 & 0.05 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

The numerical results are shown in Figure 1. The top and the middle panels are shown the calculated Virial-PK stress and Virial-Cauchy stress, respectively. It can be founded that both Virial-PK and Virial-Cauchy stress exhibit a linear relation with respect to the temperature. It is worthy to note that the stress is not perfect linear at \( T = 100K \) for the shear strain case and the reason is that the EAM
The average Virial stress of the Al systems under different temperature and deformation. From top to bottom panel, the Virial-PK stress $\langle \sigma_{\text{Virial}}^{PK} \rangle$, the Virial-Cauchy stress $\langle \sigma_{\text{Virial}}^{\text{Cauchy}} \rangle$ and the term $\langle \sigma_{\text{Virial}}^{\text{Cauchy}} \rangle - 1 \langle A \sigma_{\text{PK}} \rangle A^T$ (line III) are shown respectively. For comparison we also plot the $\langle |V|^{-1} \sum_{i=1}^{N} f_i \otimes u_i \rangle$ (line I) and $\langle |V|^{-1} \sum_{i=1}^{N} m_i v_i \otimes v_i \rangle$ (line II) in the bottom panel pictures. The left and right panel show the results obtained based on different deformation matrix $A_1$ and $A_2$, respectively.

Potential is defined by cubic spline interpolation, and this could lead to a nonlinear result for stress-temperature relation at low temperature [27].

The bottom panel of Figure 1 demonstrate that the pointwise relation (3.12) for Virial formulation is indeed satisfied for almost all temperatures in our simulations,
the green dots here show that the difference between $\langle \sigma^{\text{Virial}}_{\text{Cauchy}} \rangle$ and $\langle \sigma^{\text{Virial}}_{\text{PK}} \rangle A^T / |A|$ (i.e., the summation of last two terms in the right hand side of (3.6)) are small once the system arrived at the thermodynamic equilibrium. In continuum mechanics for some linear elastic materials, this linear response is well known as Duhamel-Neumann’s law in the thermoelasticity theory:

$$\sigma_{ij} = C_{ijkl} \epsilon_{lk} + \gamma_{ij} T$$

(3.14)

where $C_{ijkl}$ is the Hooker coefficient matrix and $\gamma_{ij}$ is a constant related to the material itself.

The expression of linear coefficient $\beta_{ij}$ has been derived theoretically by using asymptotic expansion and harmonic approximation, known as the finite temperature Cauchy-Born rule (FTCB) [27], i.e., $\langle \sigma^{\text{Virial}}_{\text{PK}} \rangle = \langle \sigma^{\text{Virial}}_{\text{PK}} \rangle_{T=0} + \Gamma T$, where $\Gamma$ is a coefficient matrix related to thermal expansion effects with its $ij$-th component equals to $\gamma_{ij}$. With the help of equation (3.12), we can generalize this conclusion to the Virial-Cauchy stress as follows

$$\langle \sigma^{\text{Virial}}_{\text{Cauchy}} \rangle = \frac{1}{|A|} \langle \sigma^{\text{Virial}}_{\text{PK}} \rangle_{T=0} + \frac{1}{|A|} \Gamma A^T T.$$  

(3.15)

3.1.2. Hardy formulation. So far our theoretical analysis and the numerical example can match each other well for the Virial formulation, which give a clear illustration of the thermodynamics expansion effect and the classical linear relation between PK stress and Cauchy stress. These results, however, are not trivial for the general weight function $\varphi(x)$. As a matter of fact, since the weight function $\varphi(x)$ depends on the position of each atom, it is hard to obtain the effect of two additional terms by the same procedure as in (3.6).

Nevertheless, by taking Taylor expansion for weight function $\varphi(x)$ and using the quasi-harmonic approximation for potential function $V(x)$ (similar to the work in Virial formulation), we can generalize the previous conclusions in Hardy formulation. Recall that we have $x = AX$ to connect the corresponding points in deformed and reference configuration, atoms are vibrated around their uniform deformed positions. Then we can derived the following expressions for averaged Hardy-Cauchy stress based on the definition (2.19)

$$\sigma^{\text{Hardy}}_{\text{Cauchy}}(AX, t) = -\frac{1}{2} \sum_i \left[ \sum_{j \neq i} f_{ij}(t) \otimes x_{ij}(t) b_{ij}(AX, t) - \sum_{i=1}^N m_i w_i \otimes w_i \varphi(AX - x_i(t)) \right].$$

(3.16)

First we consider the expression of $I_f$. By using (3.3), we have $x_{ij} = AX_{ij} + u_{ij}$, where $u_{ij} = u_i - u_j$. Insert this into the first term $I_f$, we can get

$$I_f = -\frac{1}{2} \sum_i \left[ \sum_{j \neq i} f_{ij} \otimes ((AX_{ij} + u_{ij}) b_{ij}(AX, t)) \right]$$

$$= -\frac{1}{2} \sum_i \left[ \sum_{j \neq i} f_{ij} \otimes (AX_{ij}) b_{ij}(AX, t) - \frac{1}{2} \sum_{j \neq i} f_{ij} \otimes u_{ij} b_{ij}(AX, t) \right].$$

(3.17)
Taking Taylor expansion to $\varphi(x)$ at the point $AX - (AX_i + \lambda AX_{ji})$, we could get

\[
\begin{align*}
    b_{ij}(AX, t) &= \int_0^1 \varphi(AX - (AX_i + \lambda AX_{ji}) - (u_i + \lambda u_{ji})) d\lambda \\
    &= \int_0^1 \varphi(AX - (AX_i + \lambda AX_{ji})) d\lambda - \int_0^1 \nabla_y \varphi(AX - (AX_i + \lambda AX_{ji})) \cdot (u_i + \lambda u_{ji}) d\lambda + O(\| u \|^2).
\end{align*}
\]

Applying the assumption

\[
\varphi(AX) = \frac{\bar{\varphi}(X)}{|A|},
\]

and the following definition

\[
\begin{align*}
    \alpha_{ij} &= -\int_0^1 \nabla_y \varphi(AX - (AX_i + \lambda AX_{ji})) d\lambda \\
    \beta_{ij} &= -\int_0^1 \lambda \nabla_y \varphi(AX - (AX_i + \lambda AX_{ji})) d\lambda
\end{align*}
\]

we can get

\[
\begin{align*}
    b_{ij}(AX, t) &\approx \frac{B_{ij}(X, t)}{|A|} + \alpha_{ij}^T u_i + \beta_{ij}^T u_{ji}.
\end{align*}
\]

Insert it into $I_1, I_2$,

\[
\begin{align*}
    I_1 &= -\frac{1}{2|A|} \sum_i \sum_{j \neq i} f_{ij} \otimes AX_{ij} B_{ij}(X, t) - \frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes AX_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji}) \\
    &= -\frac{1}{2|A|} \sum_i \sum_{j \neq i} f_{ij} \otimes AX_{ij} B_{ij}(X, t) + \frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes AX_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji}) \\
    &\quad - \frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes [AX_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji}) + AX_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji})].
\end{align*}
\]

\[
\begin{align*}
    I_2 &= -\frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes u_{ij} \int_0^1 \varphi(AX - (AX_i + \lambda AX_{ji})) d\lambda + c(u) \\
    &= \frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes \int_0^1 [\varphi(AX - (AX_i + \lambda AX_{ji})) \frac{d}{d\lambda} (u_i + \lambda u_{ji})] d\lambda + c(u).
\end{align*}
\]

where we have defined the following function of $u$:

\[
c(u) = -\frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes u_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji})
\]

Notice that in the derivation of $I_1$ we chose to add and subtract the following term:

\[
f_{ij} \otimes AX_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji}) = f_{ij} \otimes \int_0^1 \left[ \frac{d}{d\lambda} \varphi(AX - (AX_i + \lambda AX_{ji})) (u_i + \lambda u_{ji}) \right] d\lambda
\]

which can help us combine terms with $I_2$. Actually if we let

\[
\begin{align*}
    \sigma &= -\frac{1}{2|A|} \sum_i \sum_{j \neq i} f_{ij} \otimes AX_{ij} B_{ij}(X, t) \\
    h(u) &= -\frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes [AX_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji}) + AX_{ij} (\alpha_{ij}^T u_i + \beta_{ij}^T u_{ji})]
\end{align*}
\]
we can get

\[ I_f = \sigma + \frac{1}{2} \sum_{j \neq i} f_{ij} \otimes \int_0^1 \frac{d}{d\lambda} [\varphi(AX - (AX_i + \lambda AX_{ji}))(u_i + \lambda u_{ji})] d\lambda \\
+ h(u) + c(u) \]

\[ = \sigma + \frac{1}{2} \sum_{j \neq i} f_{ij} \otimes (u_j \varphi(AX - AX_j) - u_i \varphi(AX - AX_i)) + h(u) + c(u) \]

\[ = \sigma - \sum_i f_i \otimes u_i \varphi(AX - AX_i)) + h(u) + c(u). \]

It should be reminded that the Hardy stress in Lagragian coordinate is:

\[ \sigma_{PK}^{Hardy} = -\frac{1}{2} \sum_i \sum_{j \neq i} f_{ij} \otimes X_{ij} B_{ij}(X, t) \tag{3.22} \]

compared with \( \sigma \), we have the following form of \( I_f \):

\[ I_f = \frac{1}{|A|}\sigma_{PK}^{Hardy} A^T - \sum_i f_i \otimes u_i \varphi(AX - AX_i)) + h(u) + c(u) \tag{3.23} \]

As to \( I_k \) term:

\[ I_k = -\sum_i m_i (v_i - v) \otimes (v_i - v) \varphi(x - x_i) \]

\[ = -\sum_i m_i v_i \otimes v_i \varphi(x - x_i) + 2 \sum_i m_i v \otimes v_i \varphi(x - x_i) \]

\[ - \sum_i m_i v \otimes v \varphi(x - x_i) \]

\[ = -\sum_i m_i v_i \otimes v_i \varphi(x - x_i) + \sum_i m_i v \otimes v \varphi(x - x_i) \]

\[ = -\sum_i m_i v_i \otimes v_i \varphi(x - x_i) + q \otimes v \]

where we have used the definition of average velocity \( v \) in (2.17). By taking Taylor approximation for we have

\[ I_k = -\sum_i m_i v_i \otimes v_i \varphi(AX - AX_i - u_i) + q \otimes v \]

\[ = -\sum_i m_i v_i \otimes v_i \varphi(AX - AX_i) + \sum_i m_i v_i \otimes v_i (\nabla_y \varphi(AX - AX_i) \cdot u_i) \]

\[ + q \otimes v \]

As before, to get the true macro physical observable we need take the ensemble average, the Cauchy stress should be

\[ \langle \sigma_{Cauchy}^{Hardy} \rangle = \langle I_f \rangle + \langle I_k \rangle \]

\[ = \langle \sigma \rangle - \sum_i \langle f_i \otimes u_i + m_i v_i \otimes v_i \rangle \varphi(AX - AX_i) \]

\[ + \sum_i \langle m_i v_i \otimes v_i \nabla_y \varphi(AX - AX_i) \cdot u_i \rangle + \langle q \otimes v \rangle + \langle h(u) \rangle + \langle c(u) \rangle \]

\[ \tag{3.24} \]
Under quasi-harmonic approximation, \( u \) and \( v \) are two independent norm distributed random variables:

\[
\langle g(u,v) \rangle = \frac{1}{Z} \int du dv g(u,v) e^{-\beta (u^T D_A u + \sum_i \frac{1}{2} m_i v_i^2)},
\]

with this distribution we can further simplify above terms:

\[
T_1 = \sum_i \left[ \langle f_i \otimes u_i \rangle + \langle m_i v_i \otimes v_i \rangle \right] \varphi(AX - AX_i)
\]
\[
= \sum_i \left[ -\sum_j D_{ij} \langle u_j \otimes u_i \rangle + k_B T_3 \langle v_i \otimes v_i \rangle \right] \varphi(AX - AX_i)
\]
\[
= \sum_i \left[ -k_B T_3 + k_B T_3 \right] \varphi(AX - AX_i)
\]
\[
= 0.
\]

\[
T_2 = \sum_i \langle v_i \otimes v_i \rangle \nabla_y \varphi(AX - AX_i) \cdot \langle u_i \rangle
\]
\[
= 0.
\]

Furthermore, the harmonic approximation can also be formulated as:

\[
v(x) = V(AX) + \frac{1}{4} \sum_{i,j} u_{ij} T_{ij} u_{ij}.
\]

Here \( T \) is related with \( D \) in the following way:

\[
D_{ij} = \delta_{ij} \sum_k D_{ik} - \hat{D}_{ij}.
\]

In this case \( f_{ij} = D_{ij} u_{ij} \), substitute it into \( c(u) \) we can get

\[
\langle c(u) \rangle = \frac{1}{2} \sum_i \sum_{j \neq i} D_{ij} \langle u_{ij} u_{ij}^T (\alpha_{ij} u_i + \beta_{ij} u_{ji}) \rangle
\]
\[
= 0.
\]

Here we have used the fact that the integral of an odd function is zero. As to \( h(u) \),

\[
h(u) = -\frac{1}{2} \sum_{j \neq i} [D_{ij} \langle (AX_{ij})^T \alpha_{ij} \rangle u_{ij} u_i^T + D_{ij} \langle (AX_{ij})^T \beta_{ij} \rangle u_{ij} u_{ji}^T] \quad (3.28)
\]
\[
-\frac{1}{2} \sum_{j \neq i} [D_{ij} u_{ij} (u_{ij}^T \alpha_{ij})(AX_{ij})^T + D_{ij} u_{ij} (u_{ij}^T \beta_{ij})(AX_{ij})^T]
\]
\[
= O(\|u\|^2). \quad (3.29)
\]

Insert the ensemble average result of \( T_1, T_2, c(u) \) and \( h(u) \) into (3.24) we have obtained that

\[
\langle \sigma^{Hardy}_{Cauchy} \rangle = \frac{1}{|A|} \langle \sigma^{Hardy}_{PK} \rangle \cdot A^T + \langle q \otimes v \rangle + O(\|u\|^2). \quad (3.31)
\]

We can find that the pointwise relation (3.2) between PK and Cauchy stress is not valid in Hardy formulation anymore. However under the relation (3.17) the two stress still possess the above general relation, which contains two additional terms \( \langle q \otimes v \rangle \) and \( O(\|u\|^2) \). Here we make a remark on the condition (3.17):
Remark 1. Assumption \( \varphi(AX) = \frac{\varphi(X)}{|A|} \) means the weight of any infinitesimal volume element \( dX \) does not change after the deformation \( A \). Further more, in the Virial case this assumption is exactly satisfied since at that time \( \varphi(AX) = \frac{F_0(X)}{|AX|} = \frac{F_0(X)}{|A||X|} = \frac{\varphi(X)}{|AX|} \). In the more general case, we may use this assumption to induce the definition of \( \varphi \) from \( \tilde{\varphi} \), which could guarantee (3.31).

Figure (2) shows numerical results of the stress in Hardy formulation for pre-deformed body-centered cubic (BCC) crystal iron at different temperatures. The simulation box consists of 50 \( \times \) 50 \( \times \) 50 periods in x-, y-, and z-axis (2.5 \( \times \) 10\(^5\) Fe atoms in total). The setup of MD simulations are the same as previous simulations for Virial formulation. We chose the weight function used previously in [26]:

\[
\tilde{\varphi}(X) = \frac{1}{r_c^3} \Phi_0(\frac{X}{r_c})
\]

where \( r_c \) is the cut-off parameter and \( \Phi_0 \) is defined as

\[
\Phi_0(x, y, z) = \frac{1}{8} (1 + \cos \pi x)(1 + \cos \pi y)(1 + \cos \pi z) I_{K_0},
\]

\( K_0 = \{(x, y, z)||x| \leq 1, |y| \leq 1, |z| \leq 1\} \) is the influenced region of weight function. Then \( \varphi \) can be defined by (3.17). The bottom panel in Figure 2 clearly show that the linear relation between PK stress and the Cauchy stress is not hold anymore. The term \( \langle \sigma^{Hardy}_c \rangle - \frac{1}{|A|} \langle \sigma^{PK}_c \rangle A^T \) is not zero at finite temperature and it would increase linearly as the temperature become larger.

The contributions in \( \langle \sigma^{Hardy}_c \rangle - \frac{1}{|A|} \langle \sigma^{PK}_c \rangle A^T \) are shown more clearly in Figure 3. The left picture shows the value of \( \langle q \otimes v \rangle \) versus temperature. It can be found that \( \langle q \otimes v \rangle \) is relatively small (\( O(10^{-5}) \)), and is negligible compared with \( \langle \sigma^{Hardy}_c \rangle - \frac{1}{|A|} \langle \sigma^{PK}_c \rangle A^T \). The right picture in Figure 3 numerically demonstrate the equipartition theorem \( T_1 = 0 \) (as shown by line III in that picture), which means quasi-harmonic approximation does not bring too much error here. These two pictures show that the main difference comes from the rest higher order terms \( O(||u||^2) \) of the Taylor expansion of \( \varphi \). Furthermore, in an NVT ensemble, we have \( \langle O(||u||^2) \rangle \sim C_0 \times T \) which implicates that the difference between Cauchy stress and Virial stress will depends linear on temperature.

It is worthy to note that the linear thermodynamics expansion effect for both Hardy-PK and Hardy-Cauchy stress can be found in Figure 2. The linear coefficients can also be revealed by using quasi-harmonic approximation as what we have done in Virial formulation.

\[
\langle \sigma^{Hardy}_PK(X, t) \rangle = \langle \frac{1}{2} \sum_{\ell, j \neq i} f_{ij}(AX + u) \otimes X_{ij}b_{ij}(X) \rangle
\]

\[
= \langle \frac{1}{2} \sum_{\ell, j \neq i} [ f_{ij}(AX) + \frac{\partial f_{ij}(AX)}{\partial y} u + u^T \frac{\partial^2 f_{ij}(AX)}{2\partial y^2} u ] \otimes X_{ij}b_{ij}(X) \rangle
\]

\[
= \sigma^{Hardy}_{PK}|_{T=0} - \frac{1}{2} \sum_{\ell, j \neq i} (D(A)^{-1} : F^{ij}) \otimes X_{ij}b_{ij}(X)]_{k_B T},
\]

where we have used the fact that \( u \) will experience a variance \( k_B T D(A)^{-1} \) under the quasi-harmonic approximation. Notice here the force constant \( D(A) \) is a \( N \times N \) block matrix with each element being a \( 3 \times 3 \) matrix and \( F^{ij} = \frac{\partial^2 f_{ij}(AX)}{2\partial y^2} \) is a
Figure 2. The averaged Hardy stress of the α-Fe systems under different temperature and deformation. From top to bottom panel, the Hardy-PK stress \( \langle \sigma_{\text{HardyPK}} \rangle \), the Hardy-Cauchy stress \( \langle \sigma_{\text{HardyCauchy}} \rangle \) and the difference term \( \langle \sigma_{\text{HardyCauchy}} \rangle - \frac{1}{\langle \sigma_{\text{PK}} \rangle A^T} \) are shown respectively. The left and right panel show the results obtained based on different deformation matrix \( A_1 \) and \( A_2 \), respectively.

\( N \times N \times 3 \) tensor, thus the term \( D(A)^{-1} : F^{ij} = \sum_{k,m=1}^{N} D_{km} F_{km}^{ij} \) should be a three-dimensional vector.

For Hardy-Cauchy stress, if we use the above result together with the relation (3.31), we can also find that under quasi-harmonic approximation, the \( \langle \sigma_{\text{HardyCauchy}} \rangle \) will increase linearly as the temperature become higher.
3.2. The difference of two time average methods for stress calculation.

In order to obtain the macroscopic physical quantities from MD simulations, it is more convenient to take time average instead of phase average \( \langle \sigma \rangle \), once the MD simulation has reached thermodynamics equilibrium. For the first PK stress, we know from (2.14) that the spatial-time averaged Hardy-PK stress can be seen as a special case of the GIK-PK stress, when the kernel function in GIK formulation is separable:

\[
\phi(X, t) = \varphi(X) \tau(t),
\]

and then we have

\[
B_{ij}(X, t - s) = \int_0^1 \phi((X - (X_i + \lambda X_{ij}), t - s) d\lambda
\]

\[
= \int_0^1 \varphi((X - (X_i + \lambda X_{ij}) d\lambda \cdot \tau(t - s)
\]

\[
= b_{ij}(X) \tau(t - s).
\]

Substitute it into (2.14) we could get

\[
\bar{\sigma}_{PK}(X, t) = \sigma^{Hardy}_{PK}(X, t) * \tau(t) = \sigma^{GIK}_{PK}(X, t)
\]

This means that for the PK stress we may obtain the same result regardless the time-average procedure are done before or after the calculation of point-wise stress. The posterior time average method can be treated as a special case in the generalized IK stress, when the kernel is separable.

However, in Eulerian coordinates, we find that the order of time average do influences the result in the stress calculation. Under the separable assumption \( \Phi(x, t) = \varphi(x) \tau(t) \), we could obtain that \( B_{ij}(x, s, t - s) = b_{ij}(x, s) \tau(t - s) \) as before. Substitute this relation into the definition (2.19) and (2.25), we could have
\[ \mathbf{\hat{\sigma}}_{\text{Cauchy}}(\mathbf{x}, t) - \sigma^{\text{GIK}}_{\text{Cauchy}}(\mathbf{x}, t) = \sigma^{\text{Hardy}}_{\text{Cauchy}}(\mathbf{x}, t) \ast \tau(t) - \sigma^{\text{GIK}}_{\text{Cauchy}}(\mathbf{X}, t) \]

\[ = \sum_{i=1}^{N} \int m_i \bar{w}_i(\mathbf{x}, s, t) \otimes \bar{w}_i(\mathbf{x}, s, t) \phi(\mathbf{x} - \mathbf{x}_i, t - s) ds \]

\[ - \sum_{i=1}^{N} [m_i w_i(\mathbf{x}, t) \otimes w_i(\mathbf{x}, t) \varphi(\mathbf{x} - \mathbf{x}_i(t))] \ast \tau(t). \] 

By using the definitions (2.15) and (2.21) and the relation \( \mathbf{\hat{v}}(\mathbf{x}, t) = \frac{\hat{q}(\mathbf{x}, t)}{\rho(\mathbf{x}, t)} \), we have

\[ \sum_{i=1}^{N} \int m_i \bar{w}_i(\mathbf{x}, s, t) \otimes \bar{w}_i(\mathbf{x}, s, t) \phi(\mathbf{x} - \mathbf{x}_i, t - s) ds \]

\[ = \int \tau(t - s) ds \sum_{i=1}^{N} m_i \varphi(\mathbf{x} - \mathbf{x}_i(s))(\mathbf{v}_i(s) - \mathbf{\hat{v}}(\mathbf{x}, t)) \otimes (\mathbf{v}_i(s) - \mathbf{\hat{v}}(\mathbf{x}, t)) \]

\[ = \int \tau(t - s) ds \sum_{i=1}^{N} m_i \varphi(\mathbf{x} - \mathbf{x}_i(s)) \mathbf{v}_i(s) \otimes \mathbf{v}_i(s) - 2\mathbf{v}_i(s) \otimes \mathbf{\hat{v}}(\mathbf{x}, t) + \mathbf{\hat{v}}(\mathbf{x}, t) \otimes \mathbf{\hat{v}}(\mathbf{x}, t)) \]

\[ = \int \tau(t - s) ds \sum_{i=1}^{N} m_i \varphi(\mathbf{x} - \mathbf{x}_i(s)) \mathbf{v}_i(s) \otimes \mathbf{v}_i(s) - \hat{q}(\mathbf{x}, t) \otimes \frac{\hat{q}(\mathbf{x}, t)}{\rho(\mathbf{x}, t)}. \] 

Similarly, we could prove that

\[ \sum_{i=1}^{N} [m_i w_i(\mathbf{x}, t) \otimes w_i(\mathbf{x}, t) \varphi(\mathbf{x} - \mathbf{x}_i(t))] \ast \tau(t) \]

\[ = \int \tau(t - s) ds \sum_{i=1}^{N} m_i \varphi(\mathbf{x} - \mathbf{x}_i(s)) \mathbf{v}_i(s) \otimes \mathbf{v}_i(s) - [q(\mathbf{x}, t) \otimes \frac{q(\mathbf{x}, t)}{\rho(\mathbf{x}, t)}] \ast \tau(t). \] 

Apply this two results into equation (3.36) and notice the fact that \( \hat{q}(\mathbf{x}, t) = q(\mathbf{x}, t) \ast \tau(t) = \hat{\rho} \) resulted from the separability of \( \phi(\mathbf{x}, t) \), we can get that

\[ \mathbf{\hat{\sigma}}_{\text{Cauchy}}(\mathbf{x}, t) - \sigma^{\text{GIK}}_{\text{Cauchy}}(\mathbf{x}, t) = q(\mathbf{x}, t) \otimes \frac{q(\mathbf{x}, t)}{\rho(\mathbf{x}, t)} - \hat{\rho}(\mathbf{x}, t) \otimes \frac{\hat{q}(\mathbf{x}, t)}{\rho(\mathbf{x}, t)} \]

\[ (3.39) \]

The right hand side of the above equation is not zero generally. In fact, if we consider the norm stress \( \sigma_{11} \), we could find that

\[ \mathbf{\hat{\sigma}}_{\text{Cauchy}}(\mathbf{x}, t)_{11} - \sigma^{\text{GIK}}_{\text{Cauchy}}(\mathbf{x}, t)_{11} = \hat{\rho} \frac{q_{1} \times \hat{q}_{1}}{\rho} - \hat{\rho} \frac{q_{1} \times \hat{q}_{1}}{\rho} = \frac{\hat{\rho}}{\rho} \cdot \hat{\rho} - \hat{q}_{1} \times \hat{q}_{1} \]

\[ \geq 0. \] 

where we have used the Cauchy-inequality in the last step.

Figure 4 presents the numerical results of the term \( \mathbf{\hat{\sigma}}_{\text{Cauchy},11}(\mathbf{x}, \frac{t_{\text{cut}}}{2}) - \sigma^{\text{GIK}}_{\text{Cauchy},11}(\mathbf{x}, \frac{t_{\text{cut}}}{2}) \) under different temperature and deformation, where \( t_{\text{cut}} \) is the total steps we have chosen to compute the time average. All the numerical set up are the same as previous calculation in Virial formulation. Two different temporal kernel function : \( \tau_{1}(t) = 1/t_{\text{cut}} \), \( \tau_{2}(t) = \frac{1}{2\pi t_{\text{cut}}} \cos(\frac{\pi t}{t_{\text{cut}}}) \) are used in calculations.
According to the results, the differences between the two stress is always positive as proved in (3.40), and it would increase as the temperature rise up. This means that different from the PK-stress’s case, the generalized Irving-Kirkwood formulation dose give a different time-average result from the posterior time average method, even if the kernel function is separable. The higher the temperature, the lager the difference will become and this growth will also be affected by the type of temporal kernel and the deformation gradient. This difference indicates that the stress evaluation in Eulerian system must be evaluated spatially and temporally at the same time.

4. Conclusions. We have presented a comparative study on various microscopic stress formulation based upon atomistic information for the first Piola-Kirchhoff stress and Cauchy stress. There are three fundamental issues about the microscopic definition of stress are discussed in this paper from both theoretical and numerical points of view. The first one is the issue about the theoretical relation between PK stress and Cauchy stress in different stress formulations. We prove that the pointwise relation shown in (3.2) between these two stress in continuum mechanics will still hold in Virial formulation in the sense of ensemble average, once the system has arrived at thermodynamic equilibrium. However, in Hardy formulation, the pointwise relation is more complicated as shown in (3.31). The second issue is about
how to incorporate the thermal effect in various microscopic stress formulations, we first generalize the FTCB method from the PK stress to the Cauchy stress in Virial formulation with the help of PK-Cauchy stress relation obtained previously. For Hardy stress we also showed the linear dependence of both PK and Cauchy stress with respect to temperature theoretically and numerically, however, we also found that the expression of linear coefficient is different from the traditional PK-Cauchy stress relation. The third issue is about the connection between different time average strategies, we numerically demonstrate that there are indeed differences between two different time average methods utilized in the calculation of microscopic formulation of stress. Therefore, we give the conclusion that in the process of stress calculation in Eulerian coordinate, the spatial and temporal average should be evaluated simultaneously.

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