Abstract. In this paper, we present the procedure of generalization and implementation of the Cauchy-Born approximation to the calculation of stress at finite temperature for alloy system in which the effects of inner displacement should be incorporated. With the help of quasi-harmonic approximation, a closed form of the first Piola-Kirchhoff stress is derived as a summation of pure deformation contribution and linear term due to thermal effects. For alloy system with periodic boundary condition, a further simplified formulation of stress based on some invariance constraints is derived in reciprocal space by using Fourier transformation, in which the temperature effect can be efficiently taking account. Several numerical examples are performed for various crystalline systems to validate our generalization procedure of finite temperature Cauchy-Born (FTCB) method for alloy.

1. Introduction. It is widely accepted that crystalline materials are one of the most important material both in our daily life and in modern advanced technology, it had been extensively studied many years by various research communities including mechanical engineering, material science and physics from both experimental and theoretical aspect. However, due to the complexity of structure in real crystalline materials, the development of accurate and proper models for describing the properties and behavior of crystalline materials are still a primary interest in many research works.
To model the behavior of crystalline solids, various models have been developed at different scales. At macroscopic scale, classical continuum mechanics gives an efficient theoretical framework for the modeling of materials and is widely used in mechanical engineering applications. However the main disadvantage is that the discrete nature of crystalline materials can not be accurately captured in continuum mechanics, and therefore it is hard to describe the effects of microstructure characters. At microscopic scale, with the advent of numerical techniques and computing power, the models based directly on atomic information such as molecular dynamics (MD) simulation could provide accurate descriptions of crystalline materials with billions of atoms [7, 1, 55, 26]. But the limitations on both length and time scales are still always be found due to its expensive computation cost.

In order to overcome the deficiencies of these individual frameworks such as full atomistic models or full continuum models and also consider the phenomena occurring on different length and time scales, effective multiscale methods which offer the balance between accuracy and computation cost should be developed. Some multiscale models had been developed for describing various properties and behaviors in crystals such as quasicontinuum model [35], generalized Peierls-Nabarro model [50, 17], concurrent multiscale model [6] as well as other methods [16]. In all these multiscale models, the most important question is what is the coupling strategy which can develop general coupling models and construct effective linkage between the discrete phenomena taking place in atomistic level and the continuum description in macroscopic level [2, 3, 13]. One of the most well known and widely used coupling strategy is the so-called Cauchy-Born rule and its extensions [11, 51, 52].

The Cauchy-Born rule is a broadly used homogenization theory. Its original idea was first proposed by Cauchy, who claims that those atoms constitute the continuum will deform uniformly according to the deformation gradient. Born et.al. then extended this idea to complex lattice and take the shift and temperature into consideration [11], thus only the mean atom position experience a uniform deformation with an inner displacement, and for canonical ensemble the atoms shall vibrate around the mean position according to Gibbs measure. The significance of Cauchy-Born rule is that it links the microscopic structure with macroscopic deformation, which provides us with an atomistic constitutive relation. Due to the central importance of Cauchy-Born rule in atomistic-continuum modeling, numbers of groups have studied it extensively, including the theoretical study such as theoretical asymptotic analysis for two-body potential [8], stability analysis in both static and dynamic cases [21, 22], and validity in 2D mass-spring lattice [25] as well as applications in different models, such as quasicontinuum model for defects [42, 29], concurrent coupling methods [6, 49], simulations in brittle cracks [31]. Recently, more work had been done based on Cauchy-Born rule. Xiao et.al. studied the temperature effect in [51] for one and two dimensional simple lattice with a Lennard-Jones potential. Later, Yang et.al. [52] developed a FTCB method to compute the PK stress for metals with simple lattice in 3D at finite temperature.

In the present work, we focus on developing an alternative approach to compute the PK stress for alloy system by using the finite temperature Cauchy-Born approximation. In this new approach, the procedure of ensemble averaging, which is widely used in previous methods and the most time consuming step due to tens of thousands MD or MC simulation steps, is no more needed. Traditionally for homogeneous and equilibrium solid system, the PK stress is calculated based upon
Virial formulation \cite{15, 33}, which can be obtained by taking derivative of the free energy with respect to deformation gradient. The PK stress can be equivalently expressed as an ensemble average of the Virial term (i.e., the sum of multiplication of force and position vector) \cite{12}. However, the basic idea in FTCB method is the use of quasi-harmonic approximation which reduce the Gibbs measure to a Gaussian distribution, and therefore the ensemble average can be analytically integrated out. This has been done in previous work \cite{51, 20, 30, 37} to simplify the calculation for free energy and ensemble average, and in Ref. \cite{52} we further take the asymptotic expansion of the Virial term to achieve a closed form for PK stress. Besides, by taking Fourier transformation we can convert the calculation into reciprocal space, which greatly reduce the computation cost.

But it should be pointed out that previous FTCB method can not be directly generalized to complex lattice cases such as alloy system, a critical difference comes from the influence of the inner displacement in primitive cell. As argued in \cite{41, 43} that the inner relaxation procedure must be taken to correctly minimize the potential energy, thus in order to extend the FTCB approximation to alloy system, we need to take the shift vector into consideration. Other differences of the FTCB method for alloy system appears in the Fourier transformation into reciprocal space. All of these details will be discussed carefully when we reconstruct the method for alloy system.

The rest of the paper is organized as follows. In Section 2, we first derive the formulation of finite temperature Cauchy-Born approximation in complex lattice, including the reformulation of Cauchy-Born rule for alloys, the review of Virial formulation of PK stress, the derivation of closed form of stress based on quasi-harmonic approximation and a fast algorithm for computing the linear coefficients in stress expression based on periodic boundary condition in reciprocal space. In Section 3, some numerical results are shown to illustrate the effectiveness of generalized FTCB method. Finally the main conclusions and discussion would be presented in Section 4.

2. The finite temperature Cauchy-Born approximation for alloys. In this section we generalize the FTCB method \cite{53} to alloy systems, and focus on the derivation of the formulas for the calculation of averaged stress. In the derivation, we consider an alloy systems under an uniformly applied deformation gradient $\mathbf{F}$ and temperature $T$. It should be pointed out that although the derivation presented here is based on the alloy system with B2 structure (such as CsCl crystal), however, it could be easily applied to other alloy structures by following the same procedure.

2.1. Cauchy-Born rule for alloy systems. In this subsection, we generalize the Cauchy-Born rule to a finite alloy system with fixed boundary condition. We suppose that there are $N_B$ atoms in the primitive cell of the alloy system (for instance, $N_B = 2$ for B2 alloy structure), and the positions of atoms in the reference (undeformed) structure and the deformed structure are denoted by $\mathbf{X} = (\mathbf{X}_I, \mathbf{X}_B)$ and $\mathbf{x} = (\mathbf{x}_I, \mathbf{x}_B)$ respectively, where the subscript $I$ and $B$ are used to distinguish the inner atoms and the boundary atoms. Then the position of $\lambda$-th atom in $l$-th primitive cell at zero temperature can be defined as

\begin{equation}
\mathbf{X}^{l,\lambda} = \sum_{i=1}^{3} d_i(l) \mathbf{A}_i + B^\lambda, \quad d_i(l) \in \mathbb{Z}, \quad \lambda = 1, ..., N_B,
\end{equation}

(2.1)
where $d_i(l)$ is the $i$-th coordinate of $l$-th primitive cell, $A_i$ is the $i$-th primitive lattice vector and $B^\lambda$ stands for the relative position of $\lambda$-th basis vector in the primitive cell. When a uniform deformation $F$ is applied to the alloy system under temperature $T$, then Cauchy-Born rule claims that each inner atom would vibrate around its average position (as shown in Figure 1), i.e.,

$$\bar{x}_I = F \circ X_I + \hat{s}_I,$$  \hspace{1cm} (2.2)

where $F \circ X_I$ is the vector which indicates the positions of all inner atoms undergo a rigid deformation $F$ without any other inner relaxation, $\hat{s}$ denotes the shift vector, which describes the shuffling or inner displacement in lattices at zero temperature. Then the exact positions of atoms can be written as

$$x_I = \bar{x}_I + u_I,$$  \hspace{1cm} (2.3)

where $u_I$ is a vector which indicates the vibration displacements of all inner atoms away from their equilibrium positions. Since the vibration of atom at temperature $T$ follows Boltzmann distribution, we can write

$$u_I \sim \rho_{eq} = \frac{1}{Z} \exp\{-\beta V(x_I, x_B)\},$$  \hspace{1cm} (2.4)

where $V(x)$ is the potential energy function, $\beta = 1/(k_B T)$ and $k_B$ is the Boltzmann constant. The positions of the boundary atoms in alloy system are written as $x_B = F \circ X_B + \hat{s}_B$ due to the fixed boundary condition, and the partition function of the system is

$$Z = \int \exp\{-\beta V(\bar{x}_I + u_I, x_B)\} \, du_I$$  \hspace{1cm} (2.5)

Since we would calculate the first Piola-Kirchhoff stress (PK stress) in reference coordinates $X$, the shift vector for both the inner atoms and the boundary atoms should be determined by the potential minimization at zero temperature as follows:

$$\hat{s} = \arg\min_{s} V(F \circ X + s).$$  \hspace{1cm} (2.6)
2.2. The molecular expression of the stress. To deduce the expression of PK stress, we begin with the definition of Helmholtz free energy density in the canonical ensemble [40, 32, 24]

\[ \Psi(F, T) = -k_B T \Omega \ln Z. \] (2.7)

Here \( \Omega \) is the volume of system in reference coordinate. For a system consists of \( N \) unit cells and the volume of unit cell is \( V_0 \), then we have \( \Omega = NV_0 \). According to the second law of thermodynamics, the PK tress can be written as the derivative of Helmholtz free energy function with respect to the deformation gradient [44]:

\[ P_{\alpha,\beta} = \frac{\partial \Psi(F, T)}{\partial F_{\alpha,\beta}}, \] (2.8)

where \( \alpha, \beta = 1, 2, 3 \). This expression could be further simplified by inserting (2.7) and (2.5) into (2.8) that

\[ P_{\alpha,\beta} = \frac{k_B T}{\Omega Z} \frac{\partial Z}{\partial F_{\alpha,\beta}} \int \rho_{eq}(u_1) \frac{\partial V}{\partial F_{\alpha,\beta}} du_1. \] (2.9)

By following the same procedure for simple lattice [53], the virial term (the sum of multiplication of force and position vector) can be defined as

\[ \phi_{\alpha,\beta} = \frac{\partial V}{\partial F_{\alpha,\beta}} = -\sum_{l,\lambda} f_{\alpha}^{l,\lambda} X^{l,\lambda}_\beta, \] (2.10)

where \( f_{\alpha}^{l,\lambda} = -\partial V/\partial x_{\alpha}^{l,\lambda} \) and \( x_{\alpha}^{l,\lambda} \) is the \( \alpha \)-th component of the position of \( \lambda \)-th atom in the \( l \)-th primitive cell \( \mathbf{x}_{\alpha}^{l,\lambda} \).

We could obtain the Virial formulation of PK stress, which is widely used in MD simulation, by substitute (2.10) into (2.9) as

\[ P = \frac{1}{\Omega} \left( -\sum_{l,\lambda} f^{l,\lambda} \otimes X^{l,\lambda} \right) = \frac{1}{\Omega} \Phi, \] (2.11)

where \( \Phi \) is a 3 \times 3 matrix with \( \Phi_{\alpha,\beta} = \phi_{\alpha,\beta} \). As a result, the stress is expressed as an ensemble average. This expression agrees with the virial stress in the reference coordinate [57, 48, 54]. At zero temperature, there are no need to take the ensemble average and the stress can be reduced to

\[ P_{\alpha,\beta} = \frac{1}{\Omega} \phi_{\alpha,\beta}. \] (2.12)

2.3. The quasi-harmonic approximation. For the alloy systems at low to moderate temperature, the magnitude of the vibration of each atom around its equilibrium position is relatively small. Therefore, we could take the Taylor expansion of \( V(\mathbf{x}) \) around the equilibrium structure to approximate the Gibbs measure of atomic positions with Gaussian distribution, this technique is known as quasi-harmonic approximation [44].

In this paper, we derive the model for B2 alloy structure, but the derivation for other alloy structure can be done in the similar way. In B2 alloy structure, there are two different types of atom in one unit cell. For an alloy system of B2 structure in which there are \( N \) inner unit cells with \( 2N \) inner atoms in total, we define a \( 6N \) dimensional vector \( \mathbf{x}_I \) to describe the deform positions of all inner atoms in 3D space, i.e.,

\[ (\mathbf{x}_I)^T = [(\mathbf{x}_1, 1)^T, (\mathbf{x}_1, 2)^T, (\mathbf{x}_2, 1)^T, (\mathbf{x}_2, 2)^T, ..., (\mathbf{x}_N, 1)^T, (\mathbf{x}_N, 2)^T], \] (2.13)
where $x^{i,j}$ stands for the position vector of the $j$-th basis atom in $i$-th primitive cell and the super-script $T$ represents the transpose. We can also define $X_I$, $s$ and $u_I$ in the similar way. Thus the potential energy of the deformed structure can be approximated as

$$V(x) \approx V_0 + (u_I)^T \frac{\partial V_0}{\partial x_I} + \frac{1}{2} (u_I)^T D(F) u_I.$$  

(2.14)

where $V_0 = V(F \circ X + \hat{s})$ is the potential energy at zero temperature and $D(F) = \frac{\partial^2 V_0}{\partial x_i \partial x_j}$ is a $6N \times 6N$ force constant matrix.

On the other hand, if we define a 6 dimensional vector $x^p_0$ by $(x^p_0)^T = [(x^{i,1})^T, (x^{i,2})^T, \ldots, (x^{i,p})^T]$. Therefore the $6N \times 6N$ force constant matrix can be regarded as an $N \times N$ block matrix $(D(F) = (D_{i,j})_{N \times N})$ with each block

$$D_{i,j} = \frac{\partial^2 V_0}{\partial x^i_0 \partial x^j_0} = \begin{pmatrix} D^{11}_{i,j} & D^{12}_{i,j} \\ D^{21}_{i,j} & D^{22}_{i,j} \end{pmatrix}$$  

(2.15)

where $D^{mn}_{ij} = \frac{\partial^2 V_0}{\partial x^m_i \partial x^n_j}$ is a $3 \times 3$ matrix which describes the interaction between the $m$-th and $n$-th basis atom in the $i$-th and $j$-th unit cell respectively. The linear term in (2.14) vanishes due to the fact that the shift vector $\hat{s}$ is determined in minimization (2.6), i.e., the deformed structure in zero temperature $F \circ X + \hat{s}$ is in equilibrium.

$$V(x) \approx V_0 + \frac{1}{2} (u_I)^T D(F) u_I.$$  

(2.16)

Since the vibration of atoms around the equilibrium position $u_I$ follows Boltzmann distribution (2.4), we could write the following normal distribution expression of $u_I$:

$$u_I \sim \mathcal{N}(0, k_BT M(F)),$$  

(2.17)

where $M(F) = \langle u_I u_I^T \rangle$ is the covariance matrix which is closely related to the lattice Green function [46, 47, 27], and can be derived from (2.16) that $M(F) = D(F)^{-1}$.

Then Virial term can be approximated in the same way that

$$\phi_{\alpha,\beta}(x) \approx \phi_{\alpha,\beta}^0 + (u_I)^T \frac{\partial \phi_{\alpha,\beta}^0}{\partial x_I} + \frac{1}{2} (u_I)^T H^{\alpha,\beta} u_I,$$  

(2.18)

where $\phi_{\alpha,\beta}^0 = \phi_{\alpha,\beta}(F \circ X + \hat{s})$ and $H^{\alpha,\beta}$ is defined as

$$H^{\alpha,\beta} = \frac{\partial^2 \phi_{\alpha,\beta}^0}{\partial x_i^2} = \frac{\partial^3 V_0}{\partial x_i \partial x_j \partial F_{\alpha,\beta}} = \frac{\partial D(F)}{\partial F_{\alpha,\beta}}$$  

(2.19)

and we can also define that

$$H_{i,j}^{\alpha,\beta} = \frac{\partial^3 V_0}{\partial x_i \partial x_j \partial F_{\alpha,\beta}} = \frac{\partial D_{i,j}(F)}{\partial F_{\alpha,\beta}},$$  

(2.20)

where $H_{i,j}^{\alpha,\beta}$ is the $ij$-th sub-block of matrix $H$. This expression (2.19) could be used to calculate $H^{\alpha,\beta}$ analytically or by finite difference method. By using the same Boltzmann distribution assumption (2.4) that the Virial term can be simplified as

$$\phi_{\alpha,\beta}(x) \approx \phi_{\alpha,\beta}^0 + \frac{1}{2} (u_I)^T H^{\alpha,\beta} u_I.$$  

(2.21)
We then obtain a closed form for stress by substitute (2.18) and (2.17) into (2.11) as

\[ P_{\alpha,\beta} = \frac{1}{\Omega} \langle \phi_{\alpha,\beta}(\bar{x}_I + u_I, x_B) \rangle \]  

\[ \approx \frac{1}{\Omega} \left( \phi^0_{\alpha,\beta} + \frac{1}{2} \langle u_I u_I^T \rangle : H^{\alpha,\beta}(F) \right) \]  

\[ = \frac{1}{\Omega} \phi^0_{\alpha,\beta} + \frac{1}{2\Omega} M(F) : H^{\alpha,\beta}(F) \]  

(2.22) (2.23) (2.24)

It is worthy to note that the first term in (2.24) is independent of the temperature and is a function of deformation matrix \( F \), the second term is a linear function of temperature \( T \), therefore this formula is consistent with the classical Duhame-Neumann’s law in the thermo-elasticity theory:

\[ \sigma_{ij} = C_{ijkl} e_{lk} + \beta_{ij} T, \]  

(2.25)

where \( C_{ijkl} \) is the fourth order elastic coefficient tensor and \( \beta_{ij} \) is a constant matrix related to the temperature effect of particular material. Namely the stress calculated by (2.24) is contributed by the elastic deformation part and the thermal expansion part.

It can be found that an obvious advantage of formula (2.24) over (2.11) is that no ensemble average needs to be taken, thus once the linear coefficient \( M(F) : H^{\alpha,\beta}(F) \) are obtained, then the stress at any temperature can be calculated by adding a linear correction proportional to the temperature to the zero temperature Virial stress, instead of running long time MD simulation and calculating the stress for different temperature by ensemble average. However the difficulty in direct using of (2.24) is that the calculation of \( M(F) : H^{\alpha,\beta}(F) \) is too expensive, since the size of force constant matrix \( D(F) \) is too large \((6N \times 6N)\) and consequently the computation of \( M(F) = D(F)^{-1} \) and \( H(F) = \partial D(F)/\partial F_{\alpha,\beta} \) becomes unfeasible.

2.4. Simplification of thermal effect in alloy system. In this subsection, we would like to overcome the problem due to the complexity in the calculation of \( M(F) : H^{\alpha,\beta}(F) \) by using the periodic boundary condition (PBCs, also known as Born-Von Karman boundary condition [4]) as well as the Fourier transform to implement the above computation in reciprocal space, which replaces the calculation of inverse of a \( 6N \times 6N \) matrix by \( N \) times inverse matrix of \( 6 \times 6 \) block matrix.

Due to the periodic boundary condition, there are two constraint should be satisfied in the derivation. The first is the conservation of total linear momentum, which ensures the central of mass be unchanged and consequently the integrability of (2.11), i.e.,

\[ \sum_i (m_1 u^{i,1} + m_2 u^{i,2}) = 0, \]  

(2.26)

where \( m_1 \) and \( m_2 \) are the mass of two types of atom, respectively. It should be noticed that the constraint (2.26) in alloy system is different with the corresponding constraint in simple lattice case (\( \sum_i u_i = 0 \) since each primitive cell only contains one atom).

Another constraint should be satisfied is that each row in the block matrix \( D(F) = (D_{i,j})_{N \times N} \) (there \( N \) sub-blocks in each row) should be equivalent, since the fact that each primitive cell is identical in periodic lattice. Namely, each block element in the \( i \)-th row can be found in the \( j \)-th row, but the same two blocks might
be in different column. This constraint can also be written as

$$\{D_{i,1}, D_{i,2}, \ldots, D_{i,N-1}, D_{i,N}\} = \{D_{j,1}, D_{j,2}, \ldots, D_{j,N-1}, D_{j,N}\}$$  \tag{2.27}$$

for any $i, j = 1, 2, 3, \ldots, N$, which means the finite set formed by $N$ block matrix in the $i$-th row is equivalent to the finite set formed by block matrix in the $j$-th row.

We could further find the fact due to the translational invariance of the periodic system that

$$\sum_{j=1}^{N}(D_{i,j}^{11} + D_{j,i}^{21}) = 0, \quad \sum_{j=1}^{N}(D_{i,j}^{21} + D_{j,i}^{22}) = 0, \quad i = 1, 2, 3, \ldots, N,$$  \tag{2.28}$$

which comes from that the force $f = \partial V(x)/\partial x_I \approx D(F)u_I$ should be zero when any rigid translation is applied to the periodic system in equilibrium state (i.e., $u_I = [u_1, u_2, u_3, u_1, u_2, u_3, \ldots, u_1, u_2, u_3]^T$ for arbitrary constants $u_1, u_2, u_3$). It is worthy to note that $H^{\alpha,\beta}$ should satisfies the same relations.

The constraints (2.27) and (2.28) imply that $D(F)$ is a singular matrix, the covariance matrix $M$ can not be calculated by $M = D^{-1}$. However, we could still use the definition of covariance matrix that $M(F) = \langle u_i u_j^T \rangle$, the periodicity of the system also implies that each block element in the $i$-th row in the covariance matrix can be found in the $j$-th row.

Based on above conclusions due to the translational invariance, we have

$$P_{\alpha,\beta} = \frac{1}{\Omega} \frac{1}{2} \langle \phi_{\alpha,\beta}^0 + M(F) \cdot H^{\alpha,\beta}(F) \rangle$$  \tag{2.29}$$

$$= \frac{1}{\Omega} \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} M_{i,j} : H_{i,j}^{\alpha,\beta}$$  \tag{2.30}$$

$$= \frac{1}{\Omega} \frac{1}{2} \sum_{i=1}^{N} M_{i,1} : H_{i,1}^{\alpha,\beta}.$$  \tag{2.31}$$

Then we derive the expressions of all quantities in reciprocal space. First, we define the following Fourier transforms:

$$\hat{u}^p(\xi) = \frac{1}{\sqrt{N}} \sum_{m=1}^{N} u_m^p e^{-i\xi \cdot x_m},$$  \tag{2.32}$$

$$\hat{M}(\xi) = \frac{1}{\sqrt{N}} \sum_{m=1}^{N} M_{m,1} e^{-i\xi \cdot x_m},$$  \tag{2.33}$$

$$\hat{H}^{\alpha,\beta}(\xi) = \frac{1}{\sqrt{N}} \sum_{m=1}^{N} H_{m,1}^{\alpha,\beta} e^{-i\xi \cdot x_m},$$  \tag{2.34}$$

$$\hat{D}(\xi) = \sum_{m=1}^{N} D_{m,1} e^{-i\xi \cdot x_m},$$  \tag{2.35}$$

where $\xi$ is the reciprocal vector in first Brillouin zone $B$ [4, 28, 10]. Then we could obtain the following orthogonal transformation from $u^p$ to independent variables $\hat{u}^p(\xi)$ as

$$\frac{1}{2} u^T D u = \frac{1}{2} \sum_{\xi \in B} \hat{u}(\xi)^T \hat{D}(\xi) \hat{u}(\xi)$$  \tag{2.36}$$
Furthermore, the centrosymmetry of the crystal implies \([4]\) the fact that covariance should be computed according to \((2.32)\):

\[
\left\langle \hat{u}^p(\xi)\hat{u}^p(\xi)^T \right\rangle = \frac{1}{N} \left\langle \sum_{n=1}^{N} \sum_{m=1}^{N} e^{-i\xi(x_n-x_m)} u_n^p(u_m^p)^T \right\rangle
\]

\[
= \frac{1}{N} \sum_{n=1}^{N} \left( \sum_{m=1}^{N} e^{-i\xi(x_n-x_m)} M_{n,m} \right) \tag{2.37}
\]

\[
= \sqrt{N} \hat{M}(\xi). \tag{2.38}
\]

Before using these transformation to simplify the calculation of our stress in \((2.31)\), we first consider how to represent the two constraints \((2.26), (2.28)\) in the reciprocal space. In fact, using the decomposition \((x_i^p)^T = [(x_i^{i,1})^T, (x_i^{i,2})^T] \text{ and } (2.15)\), the Fourier transformation for \(u\) and \(D\) can be split as

\[
\hat{u}^p(\xi)^T = [\hat{u}^1(\xi)^T, \hat{u}^2(\xi)^T], \quad \hat{D}(\xi) = \begin{pmatrix} \hat{D}^{11}(\xi) & \hat{D}^{12}(\xi) \\ \hat{D}^{21}(\xi) & \hat{D}^{22}(\xi) \end{pmatrix}. \tag{2.40}
\]

where

\[
\hat{u}^k(\xi) = \frac{1}{\sqrt{N}} \sum_{m=1}^{N} u^{m,k} e^{-i\xi \cdot x_m}, \quad \hat{D}^{mn}(\xi) = \sum_{j=1}^{N} D_{j,j}^{mn} e^{-i\xi \cdot x_j}. \tag{2.41}
\]

thus constraints \((2.26)\) and \((2.28)\) are equivalent to

\[
m_1 \hat{u}^1(\xi) + m_2 \hat{u}^2(\xi) = 0, \quad \hat{D}^{11}(\xi) + \hat{D}^{12}(\xi) = 0, \quad \hat{D}^{21}(\xi) + \hat{D}^{22}(\xi) = 0. \tag{2.42}
\]

Furthermore, the centrosymmetry of the crystal implies \([4]\) the fact that \(\hat{D}^{12}(\xi) = \hat{D}^{21}(\xi)\) and consequently \((2.42)\) may also be written as

\[
\hat{u}(\xi)^T = [\hat{u}^1(\xi)^T, -\frac{m_1}{m_2}\hat{u}^1(\xi)^T], \tag{2.43}
\]

\[
\hat{D}(\xi) = \begin{pmatrix} \hat{D}^{11}(\xi) & -\hat{D}^{11}(\xi) \\ -\hat{D}^{11}(\xi) & \hat{D}^{11}(\xi) \end{pmatrix}. \tag{2.44}
\]

The probability density of \(\hat{u}\) can be expressed explicitly as

\[
\rho_{\text{new}} = \frac{1}{Z_{\text{new}}} \exp \left\{ -\frac{\beta}{2} \sum_{\xi \in \mathcal{B}} \hat{u}^T(\xi) \hat{D}(\xi) \hat{u}^T(\xi) \right\} \delta \left( m_1 \hat{u}^1(\xi) + m_2 \hat{u}^2(\xi) \right) \tag{2.45}
\]

\[
= \frac{1}{Z_{\text{new}}} \exp \left\{ -\frac{\beta}{2} \left[ \sum_{\xi \neq 0} \hat{u}^T(\xi) \hat{D}(\xi) \hat{u}(\xi) + \eta \hat{u}^T(\xi) \hat{D}^{11}(\xi) \hat{u}^T(\xi) \right] \right\}, \tag{2.46}
\]

here we define \(\eta = \frac{2(\rho_0/\kappa + m_2)}{m_2} \). Now using relation \((2.39)\), the Fourier transform of covariance should be

\[
\hat{M}(\xi) = \frac{k_B T}{\sqrt{N}} \hat{D}(\xi)^{-1} \quad \xi \in \mathcal{B}, \xi \neq 0. \tag{2.47}
\]

In the case when \(\xi = 0\), we could also derive \(\hat{M}(0)\) by inserting \((2.43)\) and \((2.44)\) into \((2.39)\) that

\[
\hat{M}(0) = \frac{k_B T}{\eta \sqrt{N}} \begin{pmatrix} \hat{D}^{11}(0)^{-1} & -\frac{m_1}{m_2} \hat{D}^{11}(0)^{-1} \\ -\frac{m_1}{m_2} \hat{D}^{11}(0)^{-1} & \left(\frac{m_1}{m_2}\right)^2 \hat{D}^{11}(0)^{-1} \end{pmatrix}. \tag{2.48}
\]
Similarly, we could deal with $\widehat{H}^{\alpha,\beta}(0)$ in the same way that ($H$ is the derivative of $D$)

$$\widehat{H}^{\alpha,\beta}(0) = \begin{pmatrix} H_0 & -H_0 \\ -H_0 & H_0 \end{pmatrix},$$

then the zero phonon mode (terms with $\xi = 0$) could be obtained by combining this equation with (2.48) that

$$N\widehat{M}(0) : \widehat{H}^{\alpha,\beta}(0) = \frac{\eta}{4}\sqrt{Nk_BT}D^{0}_{11}(0)^{-1} : H_0. \tag{2.49}$$

On the other hand, we can rewrite $M : H^{\alpha,\beta}$ in the reciprocal space as

$$M : H^{\alpha,\beta} = N\sum_\xi \widehat{M}(\xi) : \widehat{H}^{\alpha,\beta}(\xi) \tag{2.50}$$

$$= N\sum_{\xi \neq 0} \widehat{M}(\xi) : \widehat{H}^{\alpha,\beta}(\xi) + N\widehat{M}(0) : \widehat{H}^{\alpha,\beta}(0) \tag{2.51}$$

by applying the Parseval’s equality to (2.31). Therefore we achieve the final expression of our PK stress based on the generalized FTCB method:

$$P_{\alpha,\beta} = \frac{1}{\Omega} \sum_{\xi \neq 0} \frac{\sqrt{Nk_BT}}{2\Omega} \left[ N\sum_{\xi \neq 0} \widehat{D}(\xi)^{-1} : \widehat{H}^{\alpha,\beta}(\xi) + \frac{\eta}{4} \widehat{D}^{11}(0)^{-1} : H_0 \right]. \tag{2.52}$$

Here we drop some comments on the above stress formula (2.52). First, by using (2.52) to compute the stress, we need only find the inverse of $6 \times 6$ matrix, instead of computing the inverse matrix $M$ which is a $6N \times 6N$ matrix. Secondly, (2.52) do have some differences with the FTCB method in simple lattice: the inner shift vector $\hat{s}$ and the zero phonon mode ($\xi = 0$ terms) should be considered in the calculation, which results from the complexity of alloy system. Thirdly, all the above derivations can be extended to general alloys systems, in that case we can still use the Fourier transformation to compute the stress with $3N_B \times 3N_B$ blocks instead of a $3N_B N \times 3N_B N$ force constant matrix, the derivation for general alloy system are shown in Appendix to demonstrate the procedure of generalization for more complex system.

3. Numerical verification. In this section, we compare the PK stress in Virial formulation for various temperature in several alloy systems obtained from MD simulation with volume and temporal average [14] as well as our FTCB method (2.52). The comparisons show the effectiveness of our FTCB method.

Five different crystalline systems are chosen in our numerical experiment, including $\alpha$-Fe, NiAl, FeAl, Si, (melting temperature are 1812K, 1955K, 1150K and 1683.5K respectively) and Co$_2$FeAl (phase transition temperature is 473K). The first $\alpha$-Fe system is a simple substance with BCC structure which has been calculated in our previous work, this time we treat it as a B2 type alloy with two identical basis atoms in each unit cell and recompute its PK stress. The following two systems are common B2 alloys (CsCl type), which has a simple cubic lattice structure and each unit cell contains two different atoms. The Si system is a typical example used to illustrate the importance of inner relaxation for complex lattice under uniform deformation. It is treated as a complex lattice system with each unit cell is a parallelepiped with three primitive lattice vectors along $(3\sqrt{2}, 4\sqrt{3}, \sqrt{6})a_0/12, (1, 0, \sqrt{3})a_0/2\sqrt{2}, (1, 0, 0)a_0/\sqrt{2}$, which contains two silicon atoms located at $(0, 0, 0)$ and $(3\sqrt{2}, \sqrt{3}, \sqrt{6})a_0/12$. The last Co$_2$FeAl as a kind
of Heusler compounds which possesses a $L_2$ structure, is aimed at showing FTCB can be applied to more complex alloys.

In MD simulations, we generate a simulation box consists of $12 \times 12 \times 12$ unit cells with periodic boundary conditions. For the canonical ensemble (NVT) we use the Noé-Hoover chain as heating bath [38]. After discarding the first 8000 MD steps with time step of 0.005ps for the system to reaching the thermal equilibrium, the PK stress is calculated by averaging the value obtained every 20 steps.

In our FTCB method, we choose the size of $k$-points in the first Brillouin zone to be $16 \times 16 \times 16$ and adopt the Monkhorst-Pack method for the $k$-points sampling [36]:

$$k_{n_1,n_2,n_3} = \sum_i^3 \frac{2n_i - N_i - 1}{2N_i} b_i,$$

where $b_i$ are basis vectors in reciprocal space, $n_i = 1, 2, \cdots, N_i$ and $N_i$ is the number of $k$-points in each direction.

Since it is widely accepted that the quasi-harmonic approximation is reasonable below half of the melting temperature [4], therefore we calculate the PK stress at temperature varies from 0K to 500K for the first four system, and for Co$_2$FeAl, $T$ varies from 0K to 400K due to the phase transition temperature is about 473K. The following three different deformation gradients are applied to all five crystalline systems:

$$F_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad F_1 = \begin{pmatrix} 1.01 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad F_2 = \begin{pmatrix} 1 & 0.05 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$  

It is worthy to note that $F_0, F_1, F_2$ indicates no deformation, tensile deformation, and shear deformation respectively.

### 3.1. BCC Fe system

We first compute the stress for BCC $\alpha$-Fe system, while this time we treat it as a complex lattice with two identical basis atoms. We use the potential function adopted in our previous work [52], which is an analytic EAM potential possess $C^3$ smoothness. As we can see from Figure 2, the FTCB result is quite close to the stress calculated by MD simulation (The relative error is under 3%).

### 3.2. NiAl alloy system

For NiAl alloys, we adopt the EAM potential [18, 23] with the following form [19, 5]

$$E_{tot} = \sum_i F_{t_i}(p_i) + \sum_{i>j} \phi_{t_i,t_j}(r_{ij}),$$

where $t_i$ ($t_j$) indicates the type of atom $i$ ($j$), which could be either Ni or Al, $F_{t_i}$ is the embedding energy, $p_i = \sum_{j \neq i} f_{t_j}(r_{ij})$ is the host electron density due to atoms around atom $i$, and $\phi_{t_i,t_j}(r_{ij})$ is the pairwise potential function between atoms $i$ and $j$. Thus there are 7 potential functions, including $F_{Al}, F_{Ni}, f_{Al}, f_{Ni}, \phi_{AlAl}, \phi_{NiAl}$ and $\phi_{NiNi}$ need to be determined.

The general form of density function $f_{t_j}$ is parameterized as

$$f(r) = s[f_r \exp(-\chi(r - r_e))]\Psi(\frac{r - r_e}{h}),$$

where $r_e$ is the equilibrium bond length, $\chi$ is the exponential damping parameter, $s$ is the number density, and $h$ is the cutoff parameter.
Figure 2. Results for α-Fe system. The left panel shows the comparisons of the PK stress in Virial formulation ($\sigma_{11}$) calculated by (2.11) from MD simulations (red dashed lines) and (2.52) from our FTCB method (blue solid lines) under different temperatures and deformations. The right panel shows the relative error between two methods. From top to bottom the deformation gradient is $F_0, F_1, F_2$.

where $s, f_e, r_c, r_e, h$ are fitting parameters, $\Psi((r - r_c)/h)$ is a cutoff function defined by

$$\Psi(x) = \begin{cases} 
  \frac{x^4}{1 + x^4}, & x < 0 \\
  0, & x \geq 0
\end{cases}.$$  (3.4)
The pairwise potential function \( \phi_{i,j} \) between atom \( i \) and atom \( j \) is

\[
\phi_{t_i,t_j}(r) = \varphi_{t_i,t_j}(r) - \gamma \exp[-\kappa(r/r_0 - 1)] \Psi\left(\frac{r - r_c}{h}\right),
\]

where \( t_i, t_j \) could be either Ni or Al, and

\[
\varphi_{t_i,t_j}(r) = -\alpha[1 + \beta(r/r_0 - 1)] \exp[-\beta(r/r_0 - 1)] \Psi\left(\frac{r - r_c}{h}\right) + d_{t_i,t_j} f_i(r)/\rho_i + d_{t_i,t_j} f_j(r)/\rho_j.
\]

The optimized parameters are listed in Table 3.1. It can be easily found that the EAM potential function used here for NiAl system is a \( C^3 \) analytic function which guarantees the derivation order in (2.19) could be changed. Figure 3 demonstrates the numerical result of the stress computed by FTCB and MD for a NiAl system. For the tensile and shear deformation cases the relative error is rather small compared with the MD result (under 2.5% as shown in the second and the third panel in Figure 3), while for the none deformation case the relative error is slightly bigger (up to 8% as shown in the first panel in Figure 3), this error comes from the effect of higher order terms which are ignored in our quasi-harmonic approximation.

### 3.3. FeAl alloy system

The EAM potential adopted for NiAl system is a \( C^3 \) smooth function, which guarantees the effectiveness of (2.19). However, many current widely-used EAM potentials for metals and alloys are generated by cubic splines and thus only have \( C^2 \) smoothness, therefore the accuracy of changing the derivation order in (2.19) is questionable and might bring errors in our FTCB method. In this subsection, we illustrate this conclusion by comparing the results of PK stress obtained by direct MD simulations and our FTCB method in FeAl system. The

| Parameter | Ni | Al | Cross parameter | NiAl |
|-----------|----|----|-----------------|------|
| \( f_c \) | 2.81 \times 10^{-3} | 2.23 \times 10^{-3} | \( \alpha(eV) \) | 3.5442 \times 10^{-4} |
| \( r_c(\text{Å}) \) | 2.50 | 2.85 | \( \beta \) | 7.2547 |
| \( \chi(\text{Å}^{-1}) \) | 2.8411 | 2.5268 | \( \gamma(eV) \) | 1.0466 \times 10^{-3} |
| \( n \) | 3.0447 \times 10^{-1} | 4.4658 \times 10^{-1} | \( \kappa \) | -3.9796 |
| \( s \) | 1.0000 | 2.9236 | \( r_0(\text{Å}) \) | 2.5222 |
| \( \rho_c \) | 3.5085 \times 10^{-2} | 7.8227 \times 10^{-2} | \( h(\text{Å}) \) | 5.1505 \times 10^{-1} |
| \( d_{t_i,t_j}^a(eV) \) | -2.3014 \times 10^1 | 1.4317 \times 10^{-1} | \( r_c(\text{Å}) \) | 5.1786 |
| \( \alpha(eV) \) | 1.2510 \times 10^{-2} | 1.0034 \times 10^{-1} | \( d_{Ni,Al}^a(eV) \) | -2.1818 |
| \( \beta \) | 1.0000 \times 10^{-3} | 8.1857 | \( d_{Al,Al}^a(eV) \) | 1.0676 |
| \( \gamma(eV) \) | -3.5163 | 4.0514 \times 10^{-3} | \( \kappa \) | -5.2299 \times 10^{-1} |
| \( r_0(\text{Å}) \) | 2.4890 | 2.8638 |
| \( h(\text{Å}) \) | 4.9984 \times 10^{-1} | 6.4596 \times 10^{-1} |
| \( r_c(\text{Å}) \) | 5.0338 | 7.2958 |
Figure 3. Results for NiAl alloy system. The left panel shows the comparisons of the PK stress in Virial formulation ($\sigma_{11}$) calculated by (2.11) from MD simulations (red dashed lines) and (2.52) from our FTCB method (blue solid lines) under different temperatures and deformations. The right panel shows the relative error between two methods. From top to bottom the deformation gradient is $F_0, F_1, F_2$.

The numerical setup for FeAl alloy system is the same as previous example for NiAl system, and FeAl alloy also has the B2 structure as NiAl alloy system. The EAM potential function we use here is the extended Finnis-Sinclair potential developed in [34] and commonly implemented in LAMMPS [5] for FeAl alloy, this EAM potential has only $C^2$ smoothness (the expressions and parameters of the cubic splines used
The following form:

\[ E = \frac{1}{2} \sum_{i,j} f_C(r_{ij})[a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})], \]  

(3.8)

where \( f_R(r) \) and \( f_A(r) \) are Morse potentials with exponential form as \( f_R(r) = A \exp(-\lambda_1 r) \) and \( f_A(r) = -B \exp(-\lambda_2 r) \), the cutoff function \( f_C(r) \) is set to be

\[ f_C(r) = \begin{cases} 
  1, & r < R - D \\
  \frac{1}{2} - \frac{1}{2} \sin \left( \frac{\pi}{2} \left( r - R \right) / D \right), & R - D \leq r \leq R + D \\
  0, & r > R + D.
\end{cases} \]  

(3.9)

The coefficients \( a_{ij} \) and \( b_{ij} \) in (3.8) are defined by

\[ a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n} \quad \text{and} \quad b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n}, \]

where \( \eta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \), \( \zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \) and \( g(\theta) = 1 + c^2 / d^2 - c^2 / [d^2 + (h - \cos \theta)^2] \).

The bond angle between \( ij \) bond and \( ik \) bond.

All the parameters in our used Tersoff potential are listed in Table 3.2. It should be noticed that the Tersoff potential function has \( C^3 \) smoothness almost everywhere except two points \( r = R + D \) and \( r = R - D \), since the cutoff function \( f_C(r) \) is only \( C^1 \) at these two points. However, this fact should not lead to a very large relative error between the direct MD simulations and the FTCB method. The intrinsic reason accounts for this robustness is that the practical tabulated EAM potential functions as adopted in previous example do not have \( C^3 \) smoothness almost everywhere due to the spline interpolation, and of course leads to a unreasonable deviation between the MD method and MD simulations. But in silicon system with Tersoff potential, only two points are not smooth enough to guarantee the exchangeability.
Figure 4. Results for FeAl alloy system. The left panel shows the comparisons of the PK stress in Virial formulation ($\sigma_{11}$) calculated by (2.11) from MD simulations (red dashed lines) and (2.52) from our FTCB method (blue solid lines) under different temperatures and deformations. The right panel shows the relative error between two methods. From top to bottom the deformation gradient is $F_0, F_1, F_2$.

In our MD simulations with Tersoff potential, we do find the inner shift when the shear deformation is applied as pointed in [43] that the inner displacement of derivative in (2.19), and while most quantities are calculated inside the cutoff radius, and consequently these two nonsmooth points should not bring large relative error in FTCB method.
occurs in silicon under shear deformation. The calculation results show that when shear deformation $F_2$ is applied to our system, the second atom in the primitive cell (located at $(3\sqrt{2}, \sqrt{3}, \sqrt{6})a_0/12$ in the perfect lattice) would take an inner shift mainly in the [100] direction, that is $s = (-0.026527, 0.001353, 0.000888)$ where the length unit is angstrom.

The results of the comparisons of PK stress calculated by two different methods in silicon system with inner relaxation are shown in Figure 5. We can find that the relative error is rather small (under 6.5%) when comparing to the result of FTCB method with MD simulation. This conclusion demonstrates that our FTCB method can be applied to complex alloy system when inner shift due to the applied deformation should be considered.

3.5. Co$_2$FeAl system. In this subsection, we demonstrate that our generalized FTCB procedure can also be used in more complex alloy system such as Co$_2$FeAl. Since the structure of Co$_2$FeAl will take a phase transformation from L2$_1$ to B2 when temperature is higher than 473K [39], therefore we should compute the PK stress below the transformation temperature, i.e., form 0 to 400K. The EAM potential we adopted here is developed in [56], which could also be applied in other 16 alloy systems. A detailed derivation of expression of PK stress based on FTCB method for Co$_2$FeAl lattice can be found in the appendix, which requires carefully treatment on the constraints due to PBCs and the zero phonon mode (i.e., $\xi = 0$ term).

Figure 6 illustrates the validity of FTCB method applied to Co$_2$FeAl system, we can find that the relative errors compared with direct MD simulations are less than 5% for almost all temperatures. Besides, it can also be observed that unlike the calculation in simple lattice [52] the effect of zero phonon mode can not be ignored.

4. Summary and discussion. In this paper, we generalized the idea of finite temperature Cauchy-Born approximation from simple lattice to general alloy system, and derived the corresponding expression of the PK stress in Virial formulation for alloy system. The expression of PK stress in our generalized FTCB method is the sum of a deformation stress at zero temperature and a linear thermal expansion term proportional to the temperature. We also proposed a fast algorithm to calculate the linear thermal expansion coefficients for PK stress at various temperatures for alloy system when quasi-harmonic approximation holds. The computation complexity in the calculation of the linear thermal coefficients are reduced by using the periodic boundary condition and be implemented in reciprocal space. The numerical comparisons showed that when the potential function used in our generalized FTCB method satisfies the requirement of $C^3$ smoothness, then the PK stress calculated by our fast FTCB method agrees well with the results obtained in ensemble average in long time MD simulations.

As demonstrated in [52], the quasi-harmonic approximation can be regarded as the asymptotic expansion using the Laplace method [9] to the second order, and thus we can expect to improve the approximation accuracy by using higher order Laplace method. On the other hand, the FTCB procedure proposed here has the potential to be generalized to defect system as well as be used to compute the stress for mixtures. There are also some theoretical issues such as stability analysis related to the finite temperature Cauchy-Born approximation still need to be studied.

It is important to note that there are small deviations to the perfect configuration during the loadings and energy minimization of an atomic system, however, these
small deviations will not lead to relatively large errors if those processes are quasi-static. In a quasi-static process, a related equilibrium structure at zero temperature can be defined and the Taylor expansion can be taken around this equilibrium structure, then our model still works and will not lead to relatively large errors.
Figure 6. Results for Co$_2$FeAl system. The left panel shows the comparisons of the PK stress in Virial formulation ($\sigma_{11}$) calculated by (2.11) from MD simulations (red dashed lines) and (2.52) from our FTCB method (blue solid lines) under different temperatures and deformations. The right panel shows the relative error between two methods. From top to bottom the deformation gradient is $F_0, F_1, F_2$. Notice that the result obtained by FTCB method without $\xi = 0$ are shown by brown solid lines.

As shown in our results, there are several factors lead to the errors, for example, the smoothness of potential function, nonlinear effect of thermal vibration, imperfection of lattice, small unsatisfaction of the constraint from periodic boundary conditions. The imperfection of lattice and small unsatisfaction of the constraint
from periodic boundary conditions are not the main contributions to the errors, we can always find a proper equilibrium structure at zero temperature and take the Taylor expansion of the potential energy around this equilibrium structure, thus a similar expression for the stress calculation using quasi-harmonic approximation can be derived. The equilibrium structure may not satisfies the translational invariance and the conservation of total momentum as stated in Section 2.4, and the violation of these assumptions will leads to the failure of the simplification and fast algorithm as shown before. So if we do not use the fast algorithm, then the errors due to these two factors can be ignored. As shown in our simulations, the errors increase generally for all samples and that is because the nonlinear thermal vibration plays more and more important role in high temperature. We can also find that the errors for $\alpha$-Fe, NiAl alloy, Si and CoFeAl system, whose potential functions are $C^3$ analytical functions, is relative small (less than 8% as shown in Figure 2, 3, 5 and 6), but the errors for FeAl alloy, whose potential function is only $C^2$ function, is significantly larger ($\approx 20%$ as shown in Figure 4). Therefore, the smoothness of potential function is the most important factor for errors.

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Appendix: Derivation of FTCB method for general alloy system. For more complex alloy, the main difference in the formulation in FTCB compared with B2 alloy is that there may be more basis atoms in each primitive cell, which leads the change in the size of $u_i$ and block force constant matrix $D_{i,j}$ (This has been pointed in the comments at Section 2.4).

For an alloy system with $N_B$ atoms in one primitive cell, we have

$$u_i^T = [(x_i^{1,1})^T, (x_i^{1,2})^T, ..., (x_i^{1,N_B})^T], \quad (4.1)$$

and then the Fourier transformation can be decomposed as

$$\tilde{u}(\xi)^T = [\tilde{u}^1(\xi)^T, \tilde{u}^2(\xi)^T, ..., \tilde{u}^{N_B}(\xi)^T] = [\tilde{u}^1(\xi)^T, a(\xi)^T], \quad (4.2)$$

where we denote $a(\xi)^T = [\tilde{u}^2(\xi)^T, ..., \tilde{u}^{N_B}(\xi)^T]$. Similarly we can divide the dynamic matrix at $\xi = 0$ as

$$\tilde{D}(0) = \begin{pmatrix} \tilde{D}_{11}(0) & \gamma^T \\ \gamma & C \end{pmatrix}, \quad (4.3)$$

where $\tilde{D}_{11}(0)$ is an $3 \times 3$ matrix and $C$ is an $3(N_B - 1) \times 3(N_B - 1)$ block matrix.

The first constraint due to the PBCs can be written as

$$\sum_i (m_1 u_i^{1,1} + ... + m_{N_B} u_i^{1,N_B}) = 0, \quad (4.4)$$

and this equation can be rewritten in reciprocal space as

$$m_1 \tilde{u}^1(0) + ... + m_{N_B} \tilde{u}^{N_B}(0) = 0 \quad (4.5)$$
Then we have \(\hat{u}^1(0) = (-\frac{m_3}{m_1} I_3, \ldots, -\frac{m_{3N}}{m_1} I_3) \cdot a = E\hat{a}.\) (\(I_3\) is the \(3 \times 3\) identity matrix and \(a = a(0)\)). Using \(\hat{u}^1(0) = E\hat{a}\) and (4.3), we could derive that
\[
\hat{u}(0)^T \hat{D}(0) \hat{u}(0) = \hat{u}(0)^T \hat{D}^{11}(0) \hat{u}(0) + a^T \gamma \hat{u}^1(0) + \hat{u}(0)^T \gamma^T a + a^T Ca
\]
\[
= a^T E\hat{D}(0) E^T a + a^T \gamma E^T a + a^T E\gamma^T a + a^T Ca
\]
\[
= a^T (E\hat{D}(0) E^T + \gamma E^T + E\gamma^T + C) a
\]
\[
= a^T C a.
\]

Recall that the probability density of \(\hat{u}\) is
\[
\rho_{\text{new}} = \frac{1}{Z_{\text{new}}} \exp \left\{ -\beta \sum_{\xi \in B} \hat{u}(\xi)^T \hat{D}(\xi) \hat{u}(\xi) \right\} \delta\left( \sum_{i} m_i \hat{u}^i(0) \right), \quad (4.6)
\]
then we have \(\langle aa^T \rangle = k_B T \hat{C}^{-1}\).

On the other hand, (2.39) implies that \(\hat{M}(\xi) = \frac{1}{\sqrt{N}} k_B T \hat{D}(\xi)^{-1}\) when \(\xi \neq 0\), and
\[
\hat{M}(0) = \langle \left( \frac{1}{{\sqrt{N}}} \begin{pmatrix} \hat{u}(0) & a^T \hat{u}(0) \\ a \hat{u}(0) & a^T \end{pmatrix} \right) \rangle
\]
\[
= \frac{1}{\sqrt{N}} k_B T \begin{pmatrix} E\hat{C}^{-1} E^T & E\hat{C}^{-1} \\ E\hat{C}^{-1} & \hat{C}^{-1} \end{pmatrix} . \quad (4.7)
\]

Now we could obtain a practical FTCB formula of PK stress in Virial formulation for general alloy system by substituting (4.8) into the following equation:
\[
P_{\alpha,\beta} = \frac{1}{\Omega} \left[ \phi_{0,\alpha,\beta}^0 + \frac{1}{2} \hat{H}^{\alpha,\beta}(F) \right]
\]
\[
= \frac{1}{\Omega} \left[ \phi_{0,\alpha,\beta}^0 + \frac{N}{2} \sum_{\xi \neq 0} \hat{M}(\xi) : \hat{H}^{\alpha,\beta}(\xi) + \frac{N}{2} \hat{M}(0) : \hat{H}^{\alpha,\beta}(0) \right].
\]

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