Journal of
Mechanics of Materials and Structures

CONSERVATION LAWS AT NANO/MICRO SCALES

YOUPING CHEN AND JAMES LEE

This paper aims to find a field description of local conservation laws at nano/ micro scales. Atomistic definitions and field representations of fundamental physical quantities are presented. By decomposing atomic deformation into homogeneous lattice deformation and inhomogeneous relative atomic deformation, and also decomposing momentum flux and heat flux into homogeneous and inhomogeneous parts, the field representations of conservation laws at atomic scale have been formulated, which follow exactly the time evolution laws that exist in atomistic simulations, where the atomic motion is fully described, the inhomogeneous internal motion is not ignored, and the smallest particles considered are atoms.

1. Introduction

The atomic view of a crystal is as a periodic arrangement of local atomic bonding units. Each lattice point defines the location of the center of a unit. The space lattice is macroscopically homogeneous. Embedded in each lattice point is a group of bonded atoms, the smallest structural unit of the crystal. The structure of the unit together with the network of lattice points determines the crystal structure and hence the physical properties of the material.

For crystals that have more than one atom in the unit cell, elastic distortions give rise to wave propagation of two types: acoustic and optic. In the acoustic type, all atoms in the unit cell move essentially in the same phase, resulting in deformation of the lattice. In the optical type, atoms move within the unit cell, leave the lattice unchanged, and give rise to internal deformations. In real material response, atomic vibrations usually include simultaneous lattice deformation and internal deformation. The displacement of the α-th atom in the k-th unit cell, $\boldsymbol{u}(k, \alpha)$ is in fact a sum of the lattice displacement $\boldsymbol{u}(k)$ and the internal displacement $\boldsymbol{\xi}(k, \alpha)$, that is,

$$\boldsymbol{u}(k, \alpha) = \boldsymbol{u}(k) + \boldsymbol{\xi}(k, \alpha). \tag{1–1}$$
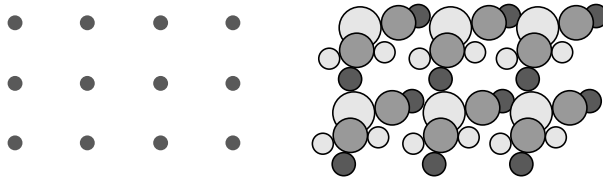
Figure 1. Atomic view of crystal structure: left, space lattice; right, crystal structure.

Analysis of phonon dispersion relations can show that, for a unit cell with ν atoms, there will be 3 acoustic and $3(\nu - 1)$ optical vibrational modes, and hence 3 lattice displacements and $3(\nu - 1)$ internal displacement patterns. There are two length/time scales associated with the atomic displacement in Equation (1–1). The lattice deformation $\boldsymbol{u}(k)$ is homogeneous up to the point of structural instability (phase transformation). It is in the low and audible frequency region, and its length scale can be from sub-nano to macroscopic. The internal displacement $\boldsymbol{\xi}(k, \alpha)$ measures the displacement of atoms relative to the lattice, and contributes to the inhomogeneous deformation. It is in the high frequency region, typically in the infrared, and its length scale is less than a nanometer.

From the viewpoint of molecular dynamics simulation, an ordered single crystal is considered to have n unit cells; each unit cell is composed of ν atoms with mass m^α, position $\boldsymbol{R}^{k\alpha}$ and velocity $\boldsymbol{V}^{k\alpha}$, where $\alpha = 1, 2, \ldots, \nu$ and $k = 1, 2, \ldots, n$. The mass m, coordinate $\boldsymbol{R}^k$ and velocity $\boldsymbol{V}^k$ at the center of the unit cell can be obtained as

$$m = \sum_{\alpha=1}^{\nu} m^\alpha, \qquad \boldsymbol{R}^k = \frac{1}{m} \sum_{\alpha=1}^{\nu} m^\alpha \boldsymbol{R}^{k\alpha}, \qquad \boldsymbol{V}^k = \frac{1}{m} \sum_{\alpha=1}^{\nu} m^\alpha \boldsymbol{V}^{k\alpha}. \qquad (1\text{–}2)$$

The relative positions and velocities between atoms and the center of the unit cell are

$$\Delta \boldsymbol{r}^{k\alpha} = \boldsymbol{R}^{k\alpha} - \boldsymbol{R}^k, \qquad \Delta \boldsymbol{v}^{k\alpha} = \boldsymbol{V}^{k\alpha} - \boldsymbol{V}^k. \qquad (1\text{–}3)$$

It follows that

$$\boldsymbol{u}(k, \alpha) = \boldsymbol{u}(k) + \boldsymbol{\xi}(k, \alpha). \qquad (1\text{–}4)$$

This again shows that the total atomic displacement $\boldsymbol{u}(k, \alpha)$ is a sum of a homogeneous lattice deformation $\boldsymbol{u}(k)$ and an inhomogeneous internal deformation $\boldsymbol{\xi}(k, \alpha)$, as is obtained in Equation (1–1) from a crystal dynamics viewpoint. Note that the inhomogeneous internal deformations will be averaged out upon cell-averages, and are ignored in classical macroscopic theories.

This paper aims to formulate a field representation of the conservation laws for multielement systems. Unlike the approach in statistical mechanics, here the

atomic motion and deformation are decomposed into homogeneous and inhomogeneous parts and the conservation equations are to be valid at atomic scale. Atomistic definitions of physical quantities are derived in Section 2; general dynamic equations (time evolution) of instantaneous and averaged physical quantities are introduced in Section 3; and the balance laws at atomic scale are formulated in Section 4. A summary and discussions are presented in Section 5. Standard dyadic notations are adopted in this paper.

2. Atomistic definitions of physical quantities

2.1. *Instantaneous physical quantities.* Macroscopic quantities are generally described by continuous (or piecewise-continuous) functions of physical space coordinates x and of time t. They are fields in physical space-time. Microscopic dynamic quantities, on the other hand, are functions of phase-space coordinates (r, p), that is, the positions and momenta of atoms (see Equations (1–2) and (1–3)):

$$r = \left\{ R^{k\alpha} = R^k + \Delta r^{k\alpha} \mid k = 1, 2, \ldots, n; \alpha = 1, 2, \ldots, \nu \right\},$$
$$p = \left\{ m^\alpha V^{k\alpha} = m^\alpha V^k + m^\alpha \Delta v^{k\alpha} \mid k = 1, 2, \ldots, n; \alpha = 1, 2, \ldots, \nu \right\},$$

where the superscript $k\alpha$ refers to the α-th atom in the k-th unit cell. Consider a one-particle dynamic function $a(R^{k\alpha}, V^{k\alpha})$. The corresponding local density at a given point x in physical space can be represented by

$$A(R^{k\alpha}, V^{k\alpha}; x) = a(R^{k\alpha}, V^{k\alpha}) \delta(R^{k\alpha} - x).$$

Here the δ-function, $\delta(R^{k\alpha} - x)$, is a localization function and provides the link between phase space and physical space descriptions. It can be a Dirac δ-function or a distribution function. For a Dirac δ-function [Irving and Kirkwood 1950], one has

$$\delta(x - R^{k\alpha}) = \begin{cases} \infty, & x = R^{k\alpha}, \\ 0, & x \neq R^{k\alpha}. \end{cases}$$

This means that, in a discontinuous atomic description, there can be a contribution to this function only if an atom happens to be located at x, that is, if $R^{k\alpha} = x$.

In the distribution or weighting function approach, the localization function is a nonnegative function that has a finite size and finite value [Hardy 1963; 1982; Ranninger 1965], peaks at $x = R^{k\alpha}$ and tends to zero as $|x - R^{k\alpha}|$ becomes large. For example, one can use the Gaussian distribution function

$$\delta(x - R^{k\alpha}) = \frac{1}{\pi^{3/2} l^3} \exp\left(-|x - R^{k\alpha}|^2 / l^2\right),$$

where l characterizes the length of the region of a lattice point or of an atom. Both the Dirac δ-function and the distribution function shall satisfy

$$\int_V \delta(\boldsymbol{x} - \boldsymbol{R}^{k\alpha})\, d^3 x = 1.$$

This is a standard treatment in statistical mechanics for defining a *mapping of phase space into physical space*.

We intend here to employ a different field description that specifies the positions of the unit cell and of the atom relative to the unit cell, similar to the MD model representation in Figure 2 of a multielement crystal. Unlike the standard treatment in statistical mechanics, we employ $\boldsymbol{x}$ throughout the rest of this paper to represent continuous collections of lattice points, corresponding to the phase space coordinates, $\boldsymbol{R}^k$ and $\boldsymbol{y}^\alpha$ to represent the α-th atomic position relative to the lattice point $\boldsymbol{x}$, corresponding to $\Delta\boldsymbol{r}^{k\alpha}$; see Figures 2 and 3. Therefore, this localization function
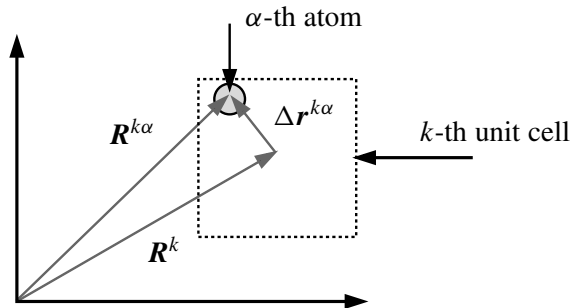

Figure 2. Atomic coordinate in terms of the positions of the unit cell and of the atom relative to the unit cell.
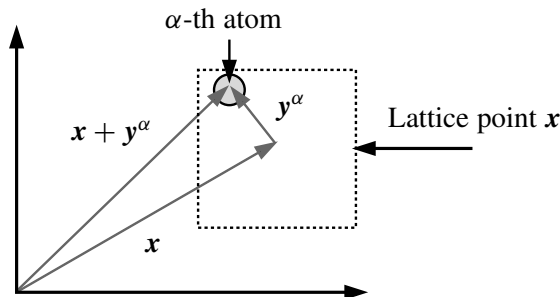

Figure 3. Field representation of the positions of the unit cell and of the atoms relative to the unit cell.

that defines the *mapping of phase space into physical space* has the form

$$\delta(\boldsymbol{R}^k + \Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{x} - \boldsymbol{y}^\alpha) = \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha),$$

with which the correspondence between a lattice point $\boldsymbol{x}$ in physical space to the position of the center of the k-th unit cell in phase space, $\boldsymbol{R}^k$, is then established, and the position of the α-th atom associated with lattice point $\boldsymbol{x}$, $\boldsymbol{y}^\alpha$, shall be in one-to-one correspondence with $\Delta \boldsymbol{r}^{k\alpha}$, the relative position of the α-th atom in the unit cell k. That is, for any given physical point $\boldsymbol{x}$ at an instantaneous time, a unit cell can be found whose center $\boldsymbol{R}^k$ is located at this point, and a physical space description of the relative position of the α-th atom, $\boldsymbol{y}^\alpha$, can be determined.

The local density of any measurable phase-space function $A(\boldsymbol{r}, \boldsymbol{p})$ can then be defined as

$$A(\boldsymbol{x}, \boldsymbol{y}^\alpha) = \sum_{k=1}^{n} A(\boldsymbol{r}, \boldsymbol{p})\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \equiv A^\alpha(\boldsymbol{x}),$$

with normalization conditions

$$\int_V \delta(\boldsymbol{R}^k - \boldsymbol{x})\, d^3x = 1 \quad \text{for all } k, \tag{2–1}$$

where V is the volume of the whole system. Equation (2–1) implies that over the entire physical space all the unit cells ($k = 1, 2, \ldots, n$) can be found. Then, for each unit cell k, the second δ-function, $\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)$, identifies $\boldsymbol{y}^\alpha$ to be $\Delta \boldsymbol{r}^{k\alpha}$:

$$\delta(\Delta \boldsymbol{r}^{k\xi} - \boldsymbol{y}^\alpha) = \begin{cases} 1 & \text{if } \xi = \alpha \quad \text{and} \quad \Delta \boldsymbol{r}^{k\xi} = \boldsymbol{y}^\alpha, \\ 0 & \text{if } \xi \neq \alpha \quad \text{or} \quad \Delta \boldsymbol{r}^{k\xi} \neq \boldsymbol{y}^\alpha. \end{cases}$$

It follows that

$$\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) = \sum_{\xi=1}^{\nu} \delta(\Delta \boldsymbol{r}^{k\xi} - \boldsymbol{y}^\alpha),$$

and

$$\int_V \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\, d^3x = 1 \quad \text{for all } k, \alpha.$$

2.2. *Averaged field variables.*

To obtain an observable quantity in a MD simulation, one must first be able to express this observable as a function of the positions and momenta of the particles in the system. However, a measured value of A, called A_m, is not obtained from an experiment performed at an instant; rather the experiment requires a finite duration. During that measuring period individual atoms evolve through many values of positions and momenta. Therefore, the measured

value A_m is generally the phase function $A(\mathbf{r}, \mathbf{p})$ averaged over a time interval Δt:

$$A_m(t) = \frac{1}{\Delta t} \int_0^{\Delta t} A\big(\mathbf{r}(t+\tau), \mathbf{p}(t+\tau)\big) d\tau.$$

In equilibrium MD it is assumed that this time-interval average reliably approximates the time average $\langle A \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t A(\mathbf{r}(\tau), \mathbf{p}(\tau)) d\tau$, which would be obtained from a measurement performed over an essentially infinite duration:

$$A_m = \langle A \rangle. \tag{2-2}$$

In statistical mechanics a macroscopic quantity is defined as the ensemble average of an instantaneous dynamical function:

$$\langle A \rangle \equiv \int_{\mathbf{p}} \int_{\mathbf{r}} A(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}, t) \, d\mathbf{r} \, d\mathbf{p},$$

where f is the normalized probability density function $\big(\int f(\mathbf{r}, \mathbf{p}, t) \, d\mathbf{r} \, d\mathbf{p} = 1 \big)$. Equation (2–2) distinguishes molecular dynamics from statistical mechanics. Statistical mechanics replaces the time average with an ensemble average by invoking the ergodic hypothesis, which is motivated by the inability to compute the phase-space trajectory of a real system containing huge numbers of molecules. When one departs from equilibrium, very little theoretical guidance is available from statistical mechanics, and MD begins to play the role of an experimental tool.

Most current MD applications involve systems that are either in equilibrium or in some time-independent stationary state; where individual results are subject to fluctuation, it is the well-defined averages over sufficiently long time intervals that are of interest. Extending MD to open systems, where coupling to the external world is of a more general kind, introduces many new problems. Not only are open systems out of thermodynamic equilibrium, but also in many cases they are spatially inhomogeneous and time-dependent. To smooth out the results and to obtain results close to experiments, measurements of physical quantities are need to be collected and averaged over a finite time duration. *Therefore, in deriving the field descriptions of atomic quantities and balance equations, it is the time-interval averaged quantities that will be used*, and the local density function, averaged over an interval Δt around time t, reads

$$\bar{A}^\alpha(\mathbf{x}, t) = \langle A^\alpha \rangle \equiv A_m^\alpha$$

$$= \frac{1}{\Delta t} \int_0^{\Delta t} \sum_{k=1}^n A\big(\mathbf{r}(t+\tau), \mathbf{p}(t+\tau)\big) \delta(\mathbf{R}^k - \mathbf{x}) \delta(\Delta r^{k\alpha} - y^\alpha) \, d\tau.$$

The fundamental physical quantities considered in this paper are mass, momentum, atomic force, momentum flux, total and internal energy, heat flux and temperature.

2.3. *Mass density.* Define the local mass density of the α-th atom as a time-interval averaged quantity

$$\bar{\rho}^\alpha(\boldsymbol{x}, t) = \bar{\rho}(\boldsymbol{x}, \boldsymbol{y}^\alpha, t) = \left\langle \sum_{k=1}^n m^\alpha \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta\boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle.$$

The total mass of the system is then given by

$$M = \int_V \left(\sum_{\alpha=1}^v \bar{\rho}^\alpha(\boldsymbol{x}, t) \right) d^3x$$

$$= \left\langle \int_V \left(\sum_{k=1}^n \sum_{\alpha=1}^v m^\alpha \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta\boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right) d^3x \right\rangle = n \sum_{\alpha=1}^v m^\alpha = nm.$$

Here, the definition of mass densities is similar to that of Kreuzer [1981], who defined the total mass density of a system involving v different components, each with mass density ρ^α, as

$$\bar{\rho} = \sum_{\alpha=1}^v \bar{\rho}^\alpha.$$

2.4. *Linear momentum density.* The linear momentum measures the flow of mass. The link between the atomic measure of the flow of mass and the field description of momentum density is achieved through the localization function and time interval averaging:

$$\bar{\rho}^\alpha(\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^\alpha) = \left\langle \sum_{k=1}^n m^\alpha(\boldsymbol{V}^k + \Delta\boldsymbol{v}^{k\alpha}) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta\boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle,$$

where $\bar{\boldsymbol{v}} = \dot{\boldsymbol{x}}$ and $\Delta\bar{\boldsymbol{v}}^\alpha = \dot{\boldsymbol{y}}^\alpha$ are the time-interval averaged velocity of the mass center of a unit cell and the velocity of the α-th atom relative to the center of the unit cell, respectively.

2.5. *Atomic forces.* It is assumed that the interatomic force can be derived from interatomic potential. Whether the interaction is through two or three-body potential, one always has the force acting on the atom i as

$$\boldsymbol{f}^i = -\frac{\partial U}{\partial \boldsymbol{R}^i}, \tag{2–3}$$

and the mutual interaction force between atom i and atom j can be obtained as

$$\boldsymbol{f}^{ij} = -\frac{\partial U}{\partial(\boldsymbol{R}^i - \boldsymbol{R}^j)} = \frac{\partial U}{\partial(\boldsymbol{R}^j - \boldsymbol{R}^i)} = -\boldsymbol{f}^{ji}, \tag{2–4}$$

where U is the total potential energy of the system, $\boldsymbol{f}^{ij}$ the interatomic force, and $\boldsymbol{R}^i - \boldsymbol{R}^j$ the relative separation vector between the two atoms i and j.

For multielement systems, forces acting on an atom can be divided into three kinds:

(1) $\boldsymbol{f}_1^{\overset{k\alpha}{l\beta}}$: interatomic force between (k, α) and (l, β) atoms in two different unit cells, and $\boldsymbol{f}_1^{\overset{k\alpha}{l\beta}} = -\boldsymbol{f}_1^{\overset{l\beta}{k\alpha}}$;

(2) $\boldsymbol{f}_2^{\overset{k\alpha}{k\beta}}$: interatomic force between (k, α) and (k, β) atoms in the same unit cell, and $\boldsymbol{f}_2^{\overset{k\alpha}{k\beta}} = -\boldsymbol{f}_2^{\overset{k\beta}{k\alpha}}$;

(3) $f_3^{k\alpha}$: body force on atom (k, α) due to the external fields.

The total force acting on an atom (k, α) can be written as

$$\boldsymbol{F}^{k\alpha} = \sum_{l=1}^{n}\sum_{\beta=1}^{\nu} \boldsymbol{f}_1^{\overset{k\alpha}{l\beta}} + \sum_{\beta=1}^{\nu} \boldsymbol{f}_2^{\overset{k\alpha}{k\beta}} + \boldsymbol{f}_3^{k\alpha}. \tag{2-5}$$

The body force density due to an external field is

$$\bar{f}^\alpha \equiv \left\langle \sum_{k=1}^{n} \boldsymbol{f}_3^{k\alpha}\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle,$$

and body couple density is

$$\boldsymbol{L}^\alpha = \left\langle \sum_{k=1}^{n} \boldsymbol{f}_3^{k\alpha} \otimes (\boldsymbol{R}^k + \Delta r^{k\alpha})\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle = \bar{f}^\alpha \otimes \boldsymbol{x} + \bar{l}^\alpha,$$

where $\bar{l}^\alpha = \langle \sum_{k=1}^{n} \boldsymbol{f}_3^{k\alpha} \otimes \Delta r^{k\alpha}\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\alpha} - \boldsymbol{y}^\alpha) \rangle$.

Assuming that the total internal potential energy is U_{int} and using the force-potential function relationship (2–3)–(2–4), the internal force density due to atomic interaction can be expressed as

$$\bar{f}_{\text{int}}^\alpha(\boldsymbol{x}) \equiv \left\langle \sum_{k=1}^{n} \left(\sum_{l=1}^{n}\sum_{\beta=1}^{\nu} \boldsymbol{f}_1^{\overset{k\alpha}{l\beta}} + \sum_{\beta=1}^{\nu} \boldsymbol{f}_2^{\overset{k\alpha}{k\beta}} \right) \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$

$$= -\left\langle \sum_{k,l=1}^{n}\sum_{\xi,\eta=1}^{\nu} \frac{\partial U_{\text{int}}}{\partial(\boldsymbol{R}^{k\xi} - \boldsymbol{R}^{l\eta})}\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\xi} - \boldsymbol{y}^\alpha) \right\rangle$$

$$- \left\langle \sum_{k=1}^{n}\sum_{\xi,\eta=1}^{\nu} \frac{\partial U_{\text{int}}}{\partial(\boldsymbol{R}^{k\xi} - \boldsymbol{R}^{k\eta})}\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\xi} - \boldsymbol{y}^\alpha) \right\rangle.$$

From Equation (2–4) we have $\boldsymbol{f}_1^{\overset{l\eta}{k\xi}} = -\boldsymbol{f}_1^{\overset{k\xi}{l\eta}}$ and $\boldsymbol{f}_2^{\overset{k\eta}{k\xi}} = -\boldsymbol{f}_2^{\overset{k\xi}{k\eta}}$. Interchanging the

indices $k\xi$ and $l\eta$, we see that

$$\bar{f}_{\text{int}}^{\alpha}(\boldsymbol{x}) = \frac{1}{2}\left\langle \sum_{k,l=1}^{n} \sum_{\xi,\eta=1}^{\nu} \overset{k\xi}{f_1^{l\eta}}\left(\delta(\boldsymbol{R}^k-\boldsymbol{x})\delta(\Delta\boldsymbol{r}^{k\xi}-\boldsymbol{y}^{\alpha})-\delta(\boldsymbol{R}^l-\boldsymbol{x})\delta(\Delta\boldsymbol{r}^{l\eta}-\boldsymbol{y}^{\alpha})\right)\right\rangle$$

$$+ \frac{1}{2}\left\langle \sum_{k=1}^{n} \sum_{\xi,\eta=1}^{\nu} f_{2\eta}^{k\xi}\delta(\boldsymbol{R}^k-\boldsymbol{x})\left(\delta(\Delta\boldsymbol{r}^{k\xi}-\boldsymbol{y}^{\alpha})-\delta(\Delta\boldsymbol{r}^{k\eta}-\boldsymbol{y}^{\alpha})\right)\right\rangle, \quad (2\text{--}6)$$

Since the formulation involves many-body interactions, it is understood that the summation over k and l does not include the case $k = l$ and similarly the summation over α and β does not include the case $\alpha = \beta$. In this article, velocity-dependent interactions such as interaction with magnetic fields are not considered, and hence the forces depend only on atomic positions. However, the results can be generalized to include such cases.

2.6. *Momentum flux density.* It is well accepted that the momentum flux in an N-body dynamics system can be divided into two parts: kinetic and potential parts [Hoover 1986; 1991; Chen and Lee 2003a; 2003b; Chen et al. 2003]. The kinetic part of the momentum flux is the flow of momentum due to atomic motion, which, in the co-moving coordinate system, is

$$\boldsymbol{s}_{\text{kin}} = -\boldsymbol{p} \otimes \boldsymbol{p}/m.$$

By virtue of the possible macroscopic motion of the material body, the velocity that contributes to momentum flux is the difference between the instantaneous velocity and the stream velocity (the ensemble or time average of the velocity):

$$\tilde{\boldsymbol{V}}^{k\alpha} = \boldsymbol{V}^{k\alpha} - \langle \boldsymbol{V}^{k\alpha}\rangle = \boldsymbol{V}^{k\alpha} - (\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^{\alpha}).$$

This velocity difference $\tilde{\boldsymbol{V}}^{k\alpha}$ measures the fluctuations of atoms relative to the local equilibrium and is related to the thermal motion of atoms. In the field representation, the kinetic part of local density of momentum flux at the α-th atomic position embedded in lattice point $\boldsymbol{x}$ is

$$\bar{\boldsymbol{s}}_{\text{kin}}^{\alpha} = -\left\langle \sum_{k=1}^{n} m^{\alpha} \tilde{\boldsymbol{V}}^{k\alpha} \otimes \tilde{\boldsymbol{V}}^{k\alpha}\delta(\boldsymbol{R}^k-\boldsymbol{x})\delta(\Delta\boldsymbol{r}^{k\alpha}-\boldsymbol{y}^{\alpha})\right\rangle.$$

The potential flow of momentum occurs through the mechanism of the interparticle forces (Figure 4). For a pair of particles α and β that lie on different sides of a surface that intersects the line connecting the two particles at $\boldsymbol{x} + \boldsymbol{y}^{\alpha}$, the pair force

$$\overset{k\xi}{\boldsymbol{f}^{l\eta}} = -\overset{l\eta}{\boldsymbol{f}^{k\xi}}$$

gives the rate at which momentum is transported from particle $k\xi$ to particle $l\eta$. For each such pair the direction of this transport is along the direction of $\mathbf{R}^{k\xi} - \mathbf{R}^{l\eta}$. So, the potential contribution to the momentum flux is

$$\mathbf{s}_{\text{pot}} = -(\mathbf{R}^{k\xi} - \mathbf{R}^{l\eta}) \otimes \overset{k\xi}{f^{l\eta}},$$

which is continuous along the line connecting the two particles. Notice that

$$\delta(\mathbf{R}^k - \mathbf{x})\delta(\Delta\mathbf{r}^{k\xi} - \mathbf{y}^\alpha) - \delta(\mathbf{R}^l - \mathbf{x})\delta(\Delta\mathbf{r}^{l\eta} - \mathbf{y}^\alpha)$$
$$= \int_0^1 \frac{d}{d\lambda}\big(\delta(\mathbf{R}^k\lambda + \mathbf{R}^l(1-\lambda) - \mathbf{x})\delta(\Delta\mathbf{r}^{k\xi}\lambda + \Delta\mathbf{r}^{l\eta}(1-\lambda) - \mathbf{y}^\alpha)\big)\,d\lambda.$$

With the consideration of all interatomic forces that pass through the atomic site $(\mathbf{x}, \mathbf{y}^\alpha)$, the local density of the momentum transport at $(\mathbf{x}, \mathbf{y}^\alpha)$ due to atomic interaction is thus expressed as

$$\bar{s}_{\text{pot}}^\alpha = -\left\langle \frac{1}{2}\int_0^1 d\lambda \sum_{k,l=1}^n \sum_{\xi,\eta=1}^\nu (\mathbf{R}^{k\xi} - \mathbf{R}^{l\eta}) \otimes \overset{k\xi}{f_1^{l\eta}}\delta\big(\mathbf{R}^k\lambda + \mathbf{R}^l(1-\lambda) - \mathbf{x}\big)\right.$$
$$\left. \delta\big(\Delta\mathbf{r}^{k\xi}\lambda + \Delta\mathbf{r}^{l\eta}(1-\lambda) - \mathbf{y}^\alpha\big)\right\rangle$$
$$- \left\langle \frac{1}{2}\int_0^1 d\lambda \sum_{k=1}^n \sum_{\xi,\eta=1}^\nu (\mathbf{R}^{k\xi} - \mathbf{R}^{k\eta}) \otimes \overset{k\xi}{f_2^{k\eta}}\delta(\mathbf{R}^k - \mathbf{x})\right.$$
$$\left. \delta\big(\Delta\mathbf{r}^{k\xi}\lambda + \Delta\mathbf{r}^{k\eta}(1-\lambda) - \mathbf{y}^\alpha\big)\right\rangle.$$

The continuum counterpart of momentum flux density is the stress tensor. However, the mathematical infinitesimal volume that does not violate the continuum assumption is the volume ΔV defining the density of lattice points, which is the volume of a unit cell. The vector sum of all the atomic forces within this volume may not pass through the mass center of the ΔV. The continuum definition of stress is, therefore, not the momentum flux density; for a crystal with more than one atom in the unit cell, the continuum stress is only the homogeneous part of the momentum flux summing over a volume of at least one unit cell, and it may not be symmetric.
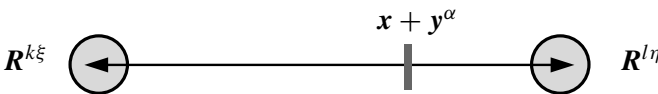

Figure 4. Flow of momentum due to interatomic force.

The total momentum flux is, therefore, better represented upon decomposition of a homogeneous part, caused by lattice motion and deformation and related to continuum stress, and an inhomogeneous part, caused by internal (relative) atomic motion and deformation. The homogeneous kinetic, inhomogeneous kinetic, homogeneous potential and inhomogeneous potential parts are given by, respectively,

$$\bar{t}_{\text{kin}}^{\alpha} = -\left\langle \sum_{k=1}^{n} m^{\alpha} \tilde{V}^{k} \otimes \tilde{V}^{k\alpha} \delta(R^{k} - x) \delta(\Delta r^{k\alpha} - y^{\alpha}) \right\rangle, \tag{2-7}$$

$$\bar{\tau}_{\text{kin}}^{\alpha} = -\left\langle \sum_{k=1}^{n} m^{\alpha} \Delta \tilde{v}^{k\alpha} \otimes \tilde{V}^{k\alpha} \delta(R^{k} - x) \delta(\Delta r^{k\alpha} - y^{\alpha}) \right\rangle,$$

$$\bar{t}_{\text{pot}}^{\alpha} = -\left\langle \frac{1}{2} \int_{0}^{1} d\lambda \sum_{k,l=1}^{n} \sum_{\xi,\eta=1}^{\nu} (R^{k} - R^{l}) \otimes f_{1}^{\overset{k\xi}{l\eta}} \delta(R^{k}\lambda + R^{l}(1-\lambda) - x) \right.$$
$$\left. \times \delta(\Delta r^{k\xi}\lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \right\rangle,$$

$$\bar{\tau}_{\text{pot}}^{\alpha} = -\left\langle \frac{1}{2} \int_{0}^{1} d\lambda \sum_{k,l=1}^{n} \sum_{\xi,\eta=1}^{\nu} (\Delta r^{k\xi} - \Delta r^{l\eta}) \otimes f_{1}^{\overset{k\xi}{l\eta}} \delta(R^{k}\lambda + R^{l}(1-\lambda) - x) \right.$$
$$\left. \times \delta(\Delta r^{k\xi}\lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \right\rangle$$

$$- \left\langle \frac{1}{2} \int_{0}^{1} d\lambda \sum_{k=1}^{n} \sum_{\xi,\eta=1}^{\nu} (\Delta r^{k\xi} - \Delta r^{k\eta}) \otimes f_{2}^{\overset{k\xi}{k\eta}} \delta(R^{k} - x) \right.$$
$$\left. \times \delta(\Delta r^{k\xi}\lambda + \Delta r^{k\eta}(1-\lambda) - y^{\alpha}) \right\rangle,$$

where $\tilde{V}^{k} = V^{k} - \langle V^{k} \rangle = V^{k} - \bar{v}$, $\Delta \tilde{v}^{k\alpha} = \Delta v^{k\alpha} - \langle \Delta v^{k\alpha} \rangle = \Delta v^{k\alpha} - \Delta \bar{v}^{\alpha}$.
Using

$$\frac{d}{d\lambda} \left(\delta(R^{k}\lambda + R^{l}(1-\lambda) - x) \delta(\Delta r^{k\xi}\lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \right)$$
$$= -\nabla_{x} \cdot \left((R^{k} - R^{l}) \delta(R^{k}\lambda + R^{l}(1-\lambda) - x) \delta(\Delta r^{k\xi}\lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \right)$$
$$- \nabla_{y^{\alpha}} \cdot \left((\Delta r^{k\xi} - \Delta r^{l\eta}) \delta(R^{k}\lambda + R^{l}(1-\lambda) - x) \delta(\Delta r^{k\xi}\lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \right),$$

we see from Equation (2–6), and the last two equations of (2–7), that the divergences of the potential momentum fluxes are related to the internal forces by

$$\nabla_{x} \cdot \bar{t}_{\text{pot}}^{\alpha} + \nabla_{y^{\alpha}} \cdot \bar{\tau}_{\text{pot}}^{\alpha} = \bar{f}_{\text{int}}^{\alpha}$$
$$= \left\langle \sum_{k=1}^{n} \sum_{\eta=1}^{\nu} \left(\sum_{l=1}^{n} f_{1}^{\overset{k\alpha}{l\eta}} + f_{2}^{\overset{k\alpha}{k\eta}} \right) \delta(R^{k} - x) \delta(\Delta r^{k\alpha} - y^{\alpha}) \right\rangle. \tag{2-8}$$

2.7. *Total energy density and internal energy density.* The total energy of atom α in a microscopic N-body dynamics system is the sum of kinetic and potential energies. In continuum theory, the local energy density is usually defined as energy per unit mass. This implies

$$\bar{\rho}^{\alpha}\bar{E}^{\alpha} = \left\langle \sum_{k=1}^{n} (\tfrac{1}{2}m^{\alpha}(\boldsymbol{V}^{k\alpha})^2 + U^{k\alpha})\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle.$$

The local density of internal energy, which is the state function of thermodynamics, can be expressed as the sum of thermal energy and potential energy:

$$\bar{\rho}^{\alpha}\bar{\varepsilon}^{\alpha} = \left\langle \sum_{k=1}^{n} (\tfrac{1}{2}m^{\alpha}(\tilde{\boldsymbol{V}}^{k\alpha})^2 + U^{k\alpha})\delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle.$$

Rewriting the total energy density as

$$\bar{\rho}^{\alpha}\bar{E}^{\alpha} = \left\langle \sum_{k=1}^{n} (\tfrac{1}{2}m^{\alpha}\{(\tilde{\boldsymbol{V}}^{k\alpha})^2 + 2\tilde{\boldsymbol{V}}^{k\alpha} \cdot (\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^{\alpha}) + (\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^{\alpha})^2\} + U^{k\alpha}) \right.$$
$$\left. \times \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta r^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle,$$

there results the macroscopic relation of densities of the total energy, the internal energy and the kinetic energy as

$$\langle \rho^{\alpha} E^{\alpha} \rangle = \langle \rho^{\alpha}\varepsilon^{\alpha} \rangle + \tfrac{1}{2}\bar{\rho}^{\alpha}(\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^{\alpha})^2.$$

2.8. *Heat flux.* The flow of energy by atomic motion, for all particles in the volume ΔV, gives the kinetic contribution to the energy flux. It comes from the rate at which the local energy E^i of atom i moves with local atomic velocity $\boldsymbol{p}^i/m^i$,

$$\boldsymbol{Q}^i_{\text{kin}} = -\frac{\boldsymbol{p}^i}{m^i}E^i.$$

The potential contribution to the energy flow occurs whenever two moving particles interact in such a way that one particle transfers a part of their joint energy to the other. It comes from the rate at which energy is transported through the action of interparticle forces: atom i is doing work on atom j, multiplied by the distance $\boldsymbol{R}^i - \boldsymbol{R}^j$ over which this energy is transferred:

$$\boldsymbol{Q}_{\text{pot}} = -\frac{1}{2}(\boldsymbol{R}^i - \boldsymbol{R}^j)\left(\frac{\boldsymbol{p}^i}{2m^i} + \frac{\boldsymbol{p}^j}{2m^j}\right) \cdot \boldsymbol{f}^{ij}.$$

Noting that heat flux is the conductive flow of internal energy per unit time and area [Huang 1967; Cochran 1973], the local density functions of kinetic and

potential heat fluxes, therefore, are expressed as

$$\bar{Q}_{\text{kin}}^{\alpha} = -\left\langle \sum_{k=1}^{n} \tilde{V}^{k\alpha} \left[\tfrac{1}{2} m^{\alpha} (\tilde{V}^{k\alpha})^2 + U^{k\alpha} \right] \delta(R^k - x) \delta(\Delta r^{k\alpha} - y^{\alpha}) \right\rangle,$$

$$\begin{aligned}
\bar{Q}_{\text{pot}}^{\alpha} = &-\left\langle \frac{1}{2} \int_0^1 d\lambda \sum_{k,l=1}^{n} \sum_{\xi,\eta=1}^{\nu} (R^{k\xi} - R^{l\eta}) \tilde{V}^{k\xi} \right. \\
&\qquad \times f_1^{l\eta} \delta(R^k \lambda + R^l (1-\lambda) - x) \delta(\Delta r^{k\xi} \lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \bigg\rangle \\
&-\left\langle \frac{1}{2} \int_0^1 d\lambda \sum_{k=1}^{n} \sum_{\xi,\eta=1}^{\nu} (R^{k\xi} - R^{k\eta}) \tilde{V}^{k\xi} \right. \\
&\qquad \times f_2^{k\xi_\eta} \delta(R^k - x) \delta(\Delta r^{k\xi} \lambda + \Delta r^{k\eta}(1-\lambda) - y^{\alpha}) \bigg\rangle.
\end{aligned}$$

Clearly there are homogeneous and inhomogeneous parts. Similar to the decomposition of momentum flux density, let the heat flux density be decomposed into four parts: the homogeneous kinetic, inhomogeneous kinetic, homogeneous potential and inhomogeneous potential part of heat flux, all of which are given by, respectively,

$$\bar{q}_{\text{kin}}^{\alpha} = -\left\langle \sum_{k=1}^{n} \tilde{V}^{k} \left[\tfrac{1}{2} m^{\alpha} (\tilde{V}^{k\alpha})^2 + U^{k\alpha} \right] \delta(R^k - x) \delta(\Delta r^{k\alpha} - y^{\alpha}) \right\rangle,$$

$$\bar{j}_{\text{kin}}^{\alpha} = -\left\langle \sum_{k=1}^{n} \Delta\tilde{v}^{k\alpha} \left[\tfrac{1}{2} m^{\alpha} (\tilde{V}^{k\alpha})^2 + U^{k\alpha} \right] \delta(R^k - x) \delta(\Delta r^{k\alpha} - y^{\alpha}) \right\rangle,$$

$$\begin{aligned}
\bar{q}_{\text{pot}}^{\alpha} = &-\left\langle \frac{1}{2} \int_0^1 d\lambda \sum_{k,l=1}^{n} \sum_{\xi,\eta=1}^{\nu} (R^{k} - R^{l}) \tilde{V}^{k\xi} \right. \\
&\qquad \times f_1^{l\eta} \delta(R^k \lambda + R^l (1-\lambda) - x) \delta(\Delta r^{k\xi} \lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \bigg\rangle,
\end{aligned}$$

$$\begin{aligned}
\bar{j}_{\text{pot}}^{\alpha} = &-\left\langle \frac{1}{2} \int_0^1 d\lambda \sum_{k,l=1}^{n} \sum_{\xi,\eta=1}^{\nu} (\Delta r^{k\xi} - \Delta r^{l\eta}) \tilde{V}^{k\xi} \right. \\
&\qquad \times f_1^{l\eta} \delta(R^k \lambda + R^l (1-\lambda) - x) \delta(\Delta r^{k\xi} \lambda + \Delta r^{l\eta}(1-\lambda) - y^{\alpha}) \bigg\rangle \\
&-\left\langle \frac{1}{2} \int_0^1 d\lambda \sum_{k=1}^{n} \sum_{\xi,\eta=1}^{\nu} (\Delta r^{k\xi} - \Delta r^{k\eta}) \tilde{V}^{k\xi} \right. \\
&\qquad \qquad \times f_2^{k\xi_\eta} \delta(R^k - x) \delta(\Delta r^{k\xi} \lambda + \Delta r^{k\eta}(1-\lambda) - y^{\alpha}) \bigg\rangle.
\end{aligned}$$

We see that the inhomogeneous heat flux is closely associated with the inhomogeneous stress and may represent the thermal currents that flow back and forth during vibration between stress inhomogeneities. With the definition of the potential parts of momentum fluxes and the identity of δ function, it is straightforward to prove that the divergences of potential heat fluxes have the following characteristics:

$$
\begin{aligned}
\nabla_x \cdot \left(\bar{\boldsymbol{q}}^\alpha_{\mathrm{pot}} + \bar{\boldsymbol{t}}^\alpha_{\mathrm{pot}} \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \right) + \nabla_{y^\alpha} \cdot \left(\bar{\boldsymbol{j}}^\alpha_{\mathrm{pot}} + \bar{\boldsymbol{\tau}}^\alpha_{pot} \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \right) \\
= \left\langle \frac{1}{2} \sum_{k,l=1}^n \sum_{\eta=1}^v (\boldsymbol{V}^{k\alpha} + \boldsymbol{V}^{l\eta}) \cdot \boldsymbol{f}_1^{l\eta} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle \\
+ \left\langle \frac{1}{2} \sum_{k=1}^n \sum_{\eta=1}^v (\boldsymbol{V}^{k\alpha} + \boldsymbol{V}^{k\eta}) \cdot \boldsymbol{f}_2^{k\alpha}_\eta \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle. \quad (2\text{--}9)
\end{aligned}
$$

2.9. Temperature. The temperature T for the microscopic N-body system is also an average quantity. It can be most simply expressed in terms of thermal energy by the mean-squared velocity relative to the local stream velocity [Hoover 1991], as

$$
\begin{aligned}
T^\alpha(\boldsymbol{x}) &= \left\langle \frac{\Delta V}{3k_B} \sum_{k=1}^n m^\alpha (\tilde{\boldsymbol{V}}^{k\alpha})^2 \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle \\
&= \left\langle \frac{\Delta V}{3k_B} \sum_{k=1}^n m^\alpha (\boldsymbol{V}^{k\alpha})^2 \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle - \frac{m^\alpha}{3k_B} (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha)^2,
\end{aligned}
$$

where k_B is Boltzmann constant, $\tilde{\boldsymbol{V}}^{k\alpha}$ are the velocity differences or the fluctuations of atoms, and ΔV is the volume that defines the density of lattice points, that is, the volume of a unit cell.

3. Time evolution of physical quantities

As mentioned above, an observable quantity in a MD simulation is supposed to be a function of the positions and momenta of the particles in the system:

$$
A(\boldsymbol{x}, \boldsymbol{y}^\alpha) = \sum_{k=1}^n A(\boldsymbol{r}, \boldsymbol{p}) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \equiv A^\alpha(\boldsymbol{x}).
$$

With

$$
\nabla_{\boldsymbol{R}^k} \delta(\boldsymbol{R}^k - \boldsymbol{x}) = -\nabla_x \delta(\boldsymbol{R}^k - \boldsymbol{x}),
$$
$$
\nabla_{\Delta \boldsymbol{r}^{k\alpha}} \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) = -\nabla_{y^\alpha} \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha),
$$

and in the general case that the phase space function A does not involve field quantities, the time evolution of its local density function can be expressed as

$$\frac{\partial A^\alpha}{\partial t}\bigg|_{x,y^\alpha} = \sum_{k=1}^{n} \dot{A}\delta(R^k - x)\delta(\Delta r^{k\alpha} - y^\alpha)$$

$$- \nabla_x \cdot \left(\sum_{k=1}^{n} V^k \otimes A\delta(R^k - x)\delta(\Delta r^{k\alpha} - y^\alpha) \right)$$

$$- \nabla_{y^\alpha} \cdot \left(\sum_{k=1}^{n} \Delta v^{k\alpha} \otimes A\delta(R^k - x)\delta(\Delta r^{k\alpha} - y^\alpha) \right). \quad (3\text{--}1)$$

For the time-interval averaged (at time t in the interval Δt) field quantity $\bar{A}^\alpha$,

$$\bar{A}^\alpha(x, t) = \langle A^\alpha \rangle \equiv A_m^\alpha = \frac{1}{\Delta t}\int_0^{\Delta t} A(r(t+\tau), p(t+\tau), x, y^\alpha)\,d\tau,$$

one has

$$\frac{\partial \bar{A}^\alpha}{\partial t}\bigg|_{x,y^\alpha} = \left\langle \sum_{k,l=1}^{n}\sum_{\gamma=1}^{\nu}\delta(R^k - x)\delta(\Delta r^{k\alpha} - y^\alpha)\left(V^{l\gamma}\cdot\nabla_{R^{l\gamma}} + \frac{1}{m^\gamma}F^{l\gamma}\cdot\nabla_{V^{l\gamma}}\right)A \right\rangle$$

$$- \nabla_x \cdot \left\langle \sum_{k=1}^{n} V^k \otimes A\delta(R^k - x)\delta(\Delta r^{k\alpha} - y^\alpha) \right\rangle$$

$$- \nabla_y^\alpha \cdot \left\langle \sum_{k=1}^{n} \Delta v^{k\alpha} \otimes A\delta(R^k - x)\delta(\Delta r^{k\alpha} - y^\alpha) \right\rangle. \quad (3\text{--}2)$$

Equations (3–1) and (3–2) are the time evolution laws for instantaneous quantity A^α and averaged field quantity $\bar{A}^\alpha$, respectively. When A^α is a conserved property, it results in the local conservation laws that govern the time evolution of A^α and $\bar{A}^\alpha$, respectively.

4. Formulation of the balance laws

A thermodynamic theory of irreversible processes starts with a set of general balance equations that govern the time evolution of the system. It is the objective of this paper to establish differential balance equations for a thermodynamic system on the same foundation of molecular dynamics: the classical N-body dynamics. Those balance equations will follow exactly the time evolution laws that exist in a molecular dynamics simulation, where the atomic motion is fully described, the inhomogeneous internal motion is not ignored, and the smallest particles are atoms.

4.1. *Conservation of mass.* With $\bar{\rho}^\alpha = \langle \sum_{k=1}^n m^\alpha \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \rangle$, the time evolution of mass density can be obtained as

$$\frac{\partial \bar{\rho}^\alpha}{\partial t} = -\nabla_{\boldsymbol{x}} \cdot \left\langle \sum_{k=1}^n m^\alpha \boldsymbol{V}^k \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$

$$- \nabla_{\boldsymbol{y}^\alpha} \cdot \left\langle \sum_{k=1}^n m^\alpha \Delta \boldsymbol{v}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle.$$

From the definition of linear momentum, one immediately finds

$$\frac{\partial \bar{\rho}^\alpha}{\partial t} + \nabla_{\boldsymbol{x}} \cdot (\bar{\rho}^\alpha \bar{\boldsymbol{v}}) + \nabla_{\boldsymbol{y}^\alpha} \cdot (\bar{\rho}^\alpha \Delta \bar{\boldsymbol{v}}^\alpha) = 0 \qquad \text{or} \qquad \frac{d\bar{\rho}^\alpha}{dt} + \bar{\rho}^\alpha (\nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{v}} + \nabla_{\boldsymbol{y}^\alpha} \cdot \Delta \bar{\boldsymbol{v}}^\alpha) = 0.$$

For cell-average mass density $\bar{\rho} = \langle \sum_{k=1}^n m \delta(\boldsymbol{R}^k - \boldsymbol{x}) \rangle$, we readily see that

$$\frac{\partial \bar{\rho}}{\partial t} + \nabla_{\boldsymbol{x}} \cdot (\bar{\rho} \bar{\boldsymbol{v}}) = 0 \qquad \text{or} \qquad \frac{d\bar{\rho}}{dt} + \bar{\rho} \nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{v}} = 0.$$

This is identical to the continuity equation in macroscopic physics.

4.2. *Balance of linear momentum.* Recall the field representation of local linear momentum density as

$$\bar{\rho}^\alpha (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \equiv \left\langle \sum_{k=1}^n m^\alpha \boldsymbol{V}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle.$$

Substituting it into Equation (3–2), it follows that

$$\frac{\partial \bar{\rho}^\alpha (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha)}{\partial t} = \left\langle \sum_{k,l=1}^n \sum_{\gamma=1}^\nu \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \frac{\boldsymbol{F}^{l\gamma}}{m^\gamma} \cdot \nabla_{\boldsymbol{V}^{l\gamma}} (m^\alpha \boldsymbol{V}^{k\alpha}) \right\rangle$$

$$- \nabla_{\boldsymbol{x}} \cdot \left\langle \sum_{k=1}^n m^\alpha \boldsymbol{V}^k \otimes \boldsymbol{V}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$

$$- \nabla_{\boldsymbol{y}^\alpha} \cdot \left\langle \sum_{k=1}^n m^\alpha \Delta \boldsymbol{v}^{k\alpha} \otimes \boldsymbol{V}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle.$$

With the divergence of momentum flux, Equation (2–8), one has

$$\left\langle \sum_{k=1}^n \boldsymbol{F}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle = \nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{t}}_{\text{pot}}^\alpha + \nabla_{\boldsymbol{y}^\alpha} \cdot \bar{\boldsymbol{\tau}}_{\text{pot}}^\alpha + \bar{\boldsymbol{f}}^\alpha. \qquad (4\text{–}1)$$

Since

$$\left\langle \sum_{k=1}^n m^\alpha \tilde{\boldsymbol{V}}^k \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle = \left\langle \sum_{k=1}^n m^\alpha \Delta \tilde{\boldsymbol{v}}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle = 0,$$

this gives

$$\nabla_{\boldsymbol{x}} \cdot \left\langle \sum_{k=1}^{n} m^{\alpha} \boldsymbol{V}^{k} \otimes \boldsymbol{V}^{k\alpha} \delta(\boldsymbol{R}^{k} - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle$$

$$= \nabla_{\boldsymbol{x}} \cdot \left\langle \sum_{k=1}^{n} m^{\alpha} \big(\tilde{\boldsymbol{V}}^{k} \otimes \tilde{\boldsymbol{V}}^{k\alpha} + \bar{\boldsymbol{v}} \otimes (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \big) \delta(\boldsymbol{R}^{k} - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle$$

$$= \nabla_{\boldsymbol{x}} \cdot \big(-\bar{\boldsymbol{t}}_{\text{kin}^{\alpha}} + \bar{\rho}^{\alpha} \bar{\boldsymbol{v}} \otimes (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \big), \tag{4-2}$$

$$\nabla_{\boldsymbol{y}^{\alpha}} \cdot \left\langle \sum_{k=1}^{n} m^{\alpha} \Delta \boldsymbol{v}^{k\alpha} \otimes \boldsymbol{V}^{k\alpha} \delta(\boldsymbol{R}^{k} - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle$$

$$= \nabla_{\boldsymbol{y}^{\alpha}} \cdot \left\langle \sum_{k=1}^{n} m^{\alpha} \big(\Delta \tilde{\boldsymbol{v}}^{k\alpha} \otimes \tilde{\boldsymbol{V}}^{k\alpha} + \Delta \bar{\boldsymbol{v}}^{\alpha} \otimes (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \big) \delta(\boldsymbol{R}^{k} - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle$$

$$= \nabla_{\boldsymbol{y}^{\alpha}} \cdot \big(-\bar{\boldsymbol{\tau}}_{\text{kin}}^{\alpha} + \bar{\rho}^{\alpha} \Delta \bar{\boldsymbol{v}}^{\alpha} \otimes (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \big). \tag{4-3}$$

Combining Equations (4–1)–(4–3) with $\bar{\boldsymbol{t}}^{\alpha} = \bar{\boldsymbol{t}}_{\text{kin}}^{\alpha} + \bar{\boldsymbol{t}}_{\text{pot}}^{\alpha}$ and $\bar{\boldsymbol{\tau}}^{\alpha} = \bar{\boldsymbol{\tau}}_{\text{kin}}^{\alpha} + \bar{\boldsymbol{\tau}}_{\text{pot}}^{\alpha}$, the time evolution of linear momentum is obtained as

$$\frac{\partial}{\partial t} \big(\bar{\rho}^{\alpha} (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \big)$$

$$= \nabla_{\boldsymbol{x}} \cdot \big(\bar{\boldsymbol{t}}^{\alpha} - \bar{\rho}^{\alpha} \bar{\boldsymbol{v}} \otimes (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \big) + \nabla_{\boldsymbol{y}^{\alpha}} \cdot \big(\bar{\boldsymbol{\tau}}^{\alpha} - \bar{\rho}^{\alpha} \Delta \bar{\boldsymbol{v}}^{\alpha} \otimes (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \big) + \bar{\boldsymbol{f}}^{\alpha},$$

or

$$\bar{\rho}^{\alpha} \frac{d}{dt} (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) = \nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{t}}^{\alpha} + \nabla_{\boldsymbol{y}^{\alpha}} \cdot \bar{\boldsymbol{\tau}}^{\alpha} + \bar{\boldsymbol{f}}^{\alpha}.$$

For cell-average linear momentum density, $\bar{\rho}\bar{\boldsymbol{v}} \equiv \langle \sum_{k=1}^{n} m \boldsymbol{V}^{k} \delta(\boldsymbol{R}^{k} - \boldsymbol{x}) \rangle$, the time evolution is obtained as

$$\frac{\partial}{\partial t} (\bar{\rho}\bar{\boldsymbol{v}}) = \nabla_{\boldsymbol{x}} \cdot \big[\bar{\boldsymbol{t}} - \rho \bar{\boldsymbol{v}} \otimes \bar{\boldsymbol{v}} \big] + \bar{\boldsymbol{f}} \qquad \text{or} \qquad \bar{\rho} \frac{d}{dt} \bar{\boldsymbol{v}} = \nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{t}} + \bar{\boldsymbol{f}}, \tag{4-4}$$

where $\bar{\boldsymbol{t}} = \sum_{\alpha=1}^{\nu} \bar{\boldsymbol{t}}^{\alpha}$ and $\bar{\boldsymbol{f}} = \sum_{\alpha=1}^{\nu} \bar{\boldsymbol{f}}^{\alpha}$ are the cell averages of homogeneous momentum flux density and body force density, respectively. Equation (4–4) is identical with the conservation law of linear momentum in macroscopic continuum mechanics. However, the latter no longer holds at atomic scale.

4.3. *Balance of angular momentum.* The angular momentum density can be defined as

$$\bar{\rho}^{\alpha} \bar{\boldsymbol{\psi}}^{\alpha} \equiv \left\langle \sum_{k=1}^{n} m^{\alpha} \boldsymbol{V}^{k\alpha} \times \boldsymbol{R}^{k\alpha} \delta(\boldsymbol{R}^{k} - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^{\alpha}) \right\rangle = \bar{\rho}^{\alpha} (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^{\alpha}) \times (\boldsymbol{x} + \boldsymbol{y}^{\alpha}).$$

Substituting it into Equation (3–2), there results

$$
\frac{\partial}{\partial t}(\bar\rho^\alpha \bar{\boldsymbol\psi}^\alpha) = \left\langle \sum_{k=1}^{n} m^\alpha \boldsymbol{V}^{k\alpha} \cdot \boldsymbol{V}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle
$$

$$
+ \left\langle \sum_{k=1}^{n} \boldsymbol{F}^{k\alpha} \cdot \boldsymbol{R}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle
$$

$$
- \nabla_{\boldsymbol{x}} \cdot \left\langle \sum_{k=1}^{n} (\tilde{\boldsymbol{V}}^k + \bar{\boldsymbol{v}}) \otimes m^\alpha (\tilde{\boldsymbol{V}}^{k\alpha} + \bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \times \boldsymbol{R}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle
$$

$$
- \nabla_{\boldsymbol{y}^\alpha} \cdot \left\langle \sum_{k=1}^{n} (\Delta \tilde{\boldsymbol{v}}^{k\alpha} + \Delta \bar{\boldsymbol{v}}^\alpha) \otimes m^\alpha (\tilde{\boldsymbol{V}}^{k\alpha} + \bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \times \boldsymbol{R}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle
$$

$$
\equiv A + B + C + D,
$$

where

$$
A = \left\langle \sum_{k=1}^{n} (m^\alpha \boldsymbol{V}^{ka} \times \boldsymbol{V}^{ka}) \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle = 0,
$$

$$
B = \left\langle \sum_{k=1}^{n} \left(\sum_{l=1}^{n} \sum_{\eta=1}^{\nu} \boldsymbol{f}_1^{\overset{k\alpha}{l\eta}} \times \boldsymbol{R}^{k\alpha} + \sum_{\eta=1}^{\nu} \boldsymbol{f}_2^{k_\eta^\alpha} \times \boldsymbol{R}^{k\alpha}\right) \times \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle + \bar{\boldsymbol{L}}^\alpha
$$

$$
= \left\langle \sum_{k=1}^{n} \left(\sum_{l=1}^{n} \sum_{\eta=1}^{\nu} \boldsymbol{f}_1^{\overset{k\alpha}{l\eta}} + \sum_{\eta=1}^{\nu} \boldsymbol{f}_2^{k_\eta^\alpha}\right) \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle \times (\boldsymbol{x} + \boldsymbol{y}^\alpha) + \bar{\boldsymbol{L}}^\alpha
$$

$$
= (\nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{t}}_{\text{pot}}^\alpha + \nabla_{\boldsymbol{y}^\alpha} \cdot \bar{\boldsymbol\tau}_{\text{pot}}^\alpha) \times (\boldsymbol{x} + \boldsymbol{y}^\alpha) + \bar{\boldsymbol{L}}^\alpha,
$$

$$
C = -\nabla_{\boldsymbol{x}} \cdot \left(\left\langle \sum_{k=1}^{n} m^\alpha \tilde{\boldsymbol{V}}^k (\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right) - \nabla_{\boldsymbol{x}} \cdot (\bar{\boldsymbol{v}} \otimes \bar\rho^\alpha \bar{\boldsymbol\psi}^\alpha)
$$

$$
= -\nabla_{\boldsymbol{x}} \cdot \left(\bar{\boldsymbol{v}} \otimes \bar\rho^\alpha \bar{\boldsymbol\psi}^\alpha - \bar{\boldsymbol{t}}_{\text{kin}}^\alpha \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right),
$$

$$
D = -\nabla_{\boldsymbol{y}^\alpha} \cdot \left(\Delta \bar{\boldsymbol{v}}^\alpha \otimes \bar\rho^\alpha \bar{\boldsymbol\psi}^\alpha + \left\langle \sum_{k=1}^{n} \Delta \tilde{\boldsymbol{v}}^{k\alpha} \otimes m^\alpha \boldsymbol{V}^{k\alpha} \times \boldsymbol{R}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \times \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle\right)
$$

$$
= -\nabla_{\boldsymbol{y}^\alpha} \cdot (\Delta \bar{\boldsymbol{v}}^\alpha \otimes \bar\rho^\alpha \bar{\boldsymbol\psi}^\alpha)
$$

$$
-\nabla_{\boldsymbol{y}^\alpha} \cdot \left(\left\langle \sum_{k=1}^{n} \Delta \tilde{\boldsymbol{v}}^k \alpha \otimes m^\alpha (\tilde{\boldsymbol{V}}^k \alpha + \bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \delta(\boldsymbol{R}^k - \boldsymbol{x})\delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha)\right\rangle \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right)
$$

$$
= -\nabla_{\boldsymbol{y}^\alpha} \cdot \left(\Delta \bar{\boldsymbol{v}}^\alpha \otimes \bar\rho^\alpha \bar{\boldsymbol\psi}^\alpha - \bar{\boldsymbol\tau}_{\text{kin}}^\alpha \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right).
$$

Combining A, B, C, and D gives

$$\frac{\partial}{\partial t}(\bar{\rho}^\alpha \bar{\boldsymbol{\psi}}^\alpha) = -\nabla_{\boldsymbol{x}} \cdot \left(\bar{\boldsymbol{v}} \otimes \bar{\rho}^\alpha \bar{\boldsymbol{\psi}}^\alpha - \bar{\boldsymbol{t}}_{\text{kin}}^\alpha \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right)$$
$$-\nabla_{\boldsymbol{y}^\alpha} \cdot \left(\Delta \bar{\boldsymbol{v}}^\alpha \otimes \bar{\rho}^\alpha \bar{\boldsymbol{\psi}}^\alpha - \bar{\boldsymbol{\tau}}_{\text{kin}}^\alpha \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right) + (\nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{t}}_{\text{pot}}^\alpha + \nabla_{\boldsymbol{y}^\alpha} \cdot \bar{\boldsymbol{\tau}}_{\text{pot}}^\alpha) \times (\boldsymbol{x} + \boldsymbol{y}^\alpha) + \bar{\boldsymbol{L}}^\alpha,$$

or

$$\bar{\rho}^\alpha \frac{d\bar{\boldsymbol{\psi}}^\alpha}{dt} = \nabla_{\boldsymbol{x}} \cdot \left(\bar{\boldsymbol{t}}_{\text{kin}}^\alpha \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right) + \nabla_{\boldsymbol{y}^\alpha} \cdot \left(\bar{\boldsymbol{\tau}}_{\text{kin}}^\alpha \times (\boldsymbol{x} + \boldsymbol{y}^\alpha)\right)$$
$$+ (\nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{t}}_{\text{pot}}^\alpha + \nabla_{\boldsymbol{y}^\alpha} \cdot \bar{\boldsymbol{\tau}}_{\text{pot}}^\alpha) \times (\boldsymbol{x} + \boldsymbol{y}^\alpha) + \bar{\boldsymbol{L}}^\alpha.$$

Notice that the time evolution of angular momentum can also be expressed from its field definition as

$$\bar{\rho}^\alpha \frac{d\bar{\boldsymbol{\psi}}^\alpha}{dt} = \bar{\rho}^\alpha \frac{d(\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha)}{dt} \times (\boldsymbol{x} + \boldsymbol{y}^\alpha) = (\nabla_{\boldsymbol{x}} \cdot \bar{\boldsymbol{t}}^\alpha + \nabla_{\boldsymbol{y}^\alpha} \cdot \bar{\boldsymbol{\tau}}^\alpha + \bar{\boldsymbol{f}}^\alpha) \times (\boldsymbol{x} + \boldsymbol{y}^\alpha).$$

Since $\bar{\boldsymbol{t}}^\alpha + \bar{\boldsymbol{\tau}}^\alpha$ is symmetric (see Equations (2–7) and $\boldsymbol{x}$ and $\boldsymbol{y}^\alpha$ are mutually independent within any unit cell, the balance law of angular momentum is shown to be identically satisfied.

4.4. *Conservation of energy.* With the definition of local total energy density

$$\bar{\rho}^\alpha \bar{E}^\alpha = \left\langle \sum_{k=1}^{n} \left(\tfrac{1}{2}m^\alpha (V^{k\alpha})^2 + U^{k\alpha}\right) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle,$$

Equation (3–2) results in

$$\frac{\partial}{\partial t}(\rho^\alpha \bar{E}^\alpha) = -\nabla_{\boldsymbol{x}} \cdot \left\langle \sum_{k=1}^{n} \boldsymbol{V}^k \left(\tfrac{1}{2}m^\alpha (V^{k\alpha})^2 + U^{k\alpha}\right) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$- \nabla_{\boldsymbol{y}^\alpha} \cdot \left\langle \sum_{k=1}^{n} \Delta \boldsymbol{v}^{k\alpha} \left(\tfrac{1}{2}m^\alpha (V^{k\alpha})^2 + U^{k\alpha}\right) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$+ \left\langle \sum_{k=1}^{n} \boldsymbol{F}^{k\alpha} \cdot \boldsymbol{V}^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$+ \left\langle \sum_{k,m=1}^{n} \sum_{\gamma=1}^{\nu} (\boldsymbol{V}^{m\gamma} \cdot \nabla_{\boldsymbol{R}^{m\gamma}}) U^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$\equiv A + B + C + D.$$

A, B, C and D can be further derived as

$$A = -\nabla_{\boldsymbol{x}} \cdot \left\langle \sum_{k=1}^{n} (\boldsymbol{V}^k - \bar{\boldsymbol{v}} + \boldsymbol{v}) \left(\tfrac{1}{2} m^\alpha (\tilde{\boldsymbol{V}}^{k\alpha})^2 + \tilde{\boldsymbol{V}}^{k\alpha} \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \right. \right.$$
$$\left. \left. + \tfrac{1}{2} m^\alpha (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha)^2 + U^{k\alpha} \right) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$= -\nabla_{\boldsymbol{x}} \cdot \left(-\bar{\boldsymbol{q}}_{\text{kin}}^\alpha - \bar{\boldsymbol{t}}_{\text{kin}}^\alpha \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) + \bar{\boldsymbol{v}} \left(\bar{\rho}^\alpha \bar{\varepsilon}^\alpha + \tfrac{1}{2} \bar{\rho}^\alpha (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha)^2 \right) \right),$$

$$B = -\nabla_{\boldsymbol{y}}^\alpha \cdot \left\langle \sum_{k=1}^{n} (\Delta \boldsymbol{v}^{k\alpha} - \Delta \bar{\boldsymbol{v}}^\alpha + \Delta \bar{\boldsymbol{v}}^\alpha) \left(\tfrac{1}{2} m^\alpha (\tilde{\boldsymbol{V}}^{ka})^2 + \tilde{\boldsymbol{V}}^{ka} \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \right. \right.$$
$$\left. \left. + \tfrac{1}{2} m^\alpha (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha)^2 + U^{k\alpha} \right) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{ka} - \boldsymbol{y}^\alpha) \right\rangle$$
$$= -\nabla_{\boldsymbol{y}^\alpha} \cdot \left(-\bar{\boldsymbol{j}}_{\text{kin}}^\alpha - \bar{\boldsymbol{\tau}}_{\text{kin}}^\alpha \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) + \Delta \bar{\boldsymbol{v}}^\alpha \left(\bar{\rho}^\alpha \bar{\varepsilon}^\alpha + \tfrac{1}{2} \bar{\rho}^\alpha (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha)^2 \right) \right),$$

$$C = \left\langle \sum_{k=1}^{n} \sum_{\beta=1}^{\nu} \boldsymbol{V}^{k\alpha} \cdot \left(\sum_{l=1}^{k\alpha} \boldsymbol{f}_1^{l\eta} + \boldsymbol{f}_2^{k_\beta^\alpha} \right) \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$+ \left\langle \sum_{k=1}^{n} \boldsymbol{V}^{k\alpha} \cdot \boldsymbol{f}_3 \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle,$$

$$D = \frac{1}{2} \left\langle \sum_{k=1}^{n} \sum_{l=1}^{n} \sum_{\gamma=1}^{\nu} (\boldsymbol{V}^{l\gamma} \cdot \nabla_{\boldsymbol{R}^{l\gamma}}) U^{k\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$= -\frac{1}{2} \left\langle \sum_{k=1}^{n} \sum_{l=1}^{n} \sum_{\gamma=1}^{\nu} (\boldsymbol{V}^{k\alpha} - \boldsymbol{V}^{l\gamma}) \cdot \boldsymbol{f}_1^{k\alpha}_{l\gamma} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$- \frac{1}{2} \left\langle \sum_{k=1}^{n} \sum_{\gamma=1}^{\nu} (\boldsymbol{V}^{k\alpha} - \boldsymbol{V}^{k\gamma}) \cdot \boldsymbol{f}_2^{k_\gamma^\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle.$$

With the divergence of heat flux (Equation (2–9)), we see that

$$C + D = \left\langle \frac{1}{2} \sum_{k,l=1}^{n} \sum_{\eta=1}^{\nu} (\boldsymbol{V}^{k\alpha} + \boldsymbol{V}^{l\eta}) \cdot \boldsymbol{f}_1^{k\alpha}_{l\eta} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$+ \left\langle \frac{1}{2} \sum_{k=1}^{n} \sum_{\eta=1}^{\nu} (\boldsymbol{V}^{k\alpha} + \boldsymbol{V}^{k\eta}) \cdot \boldsymbol{f}_2^{k_\eta^\alpha} \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) \right\rangle$$
$$= \nabla_{\boldsymbol{x}} \cdot \left(\bar{\boldsymbol{q}}_{\text{pot}}^\alpha + \bar{\boldsymbol{t}}_{\text{pot}}^\alpha \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \right) + \nabla_{\boldsymbol{y}^\alpha} \cdot \left(\bar{\boldsymbol{j}}_{\text{pot}}^\alpha + \bar{\boldsymbol{\tau}}_{\text{pot}}^\alpha \cdot (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \right)$$
$$+ \left\langle \sum_{k=1}^{n} (\boldsymbol{V}^{k\alpha} - \bar{\boldsymbol{v}} - \Delta \bar{\boldsymbol{v}}^\alpha) \cdot \boldsymbol{f}_3 \delta(\boldsymbol{R}^k - \boldsymbol{x}) \delta(\Delta \boldsymbol{r}^{k\alpha} - \boldsymbol{y}^\alpha) / \Delta V^\alpha \right\rangle$$
$$+ (\bar{\boldsymbol{v}} + \Delta \bar{\boldsymbol{v}}^\alpha) \cdot \bar{\boldsymbol{f}}^\alpha.$$

If the external field is not velocity-dependent, the sum of A, B, C, and D reads

$$\frac{\partial(\bar{\rho}^\alpha \bar{E}^\alpha)}{\partial t}$$
$$= \nabla_x \cdot \left(\bar{q}^\alpha - \bar{v}\bar{\rho}^\alpha \bar{\varepsilon}^\alpha + \bar{t}^\alpha \cdot (\bar{v} + \Delta\bar{v}^\alpha)\right) + \nabla_{y^\alpha} \cdot \left(\bar{j}^\alpha - \Delta\bar{v}^\alpha \bar{\rho}^\alpha \bar{\varepsilon}^\alpha + \bar{\tau}^\alpha \cdot (\bar{v} + \Delta\bar{v}^\alpha)\right)$$
$$- \nabla_x \cdot \left\{\tfrac{1}{2}\bar{\rho}^\alpha \bar{v}(\bar{v} + \Delta\bar{v}^\alpha)^2\right\} - \nabla_{y^\alpha} \cdot \left\{\tfrac{1}{2}\bar{\rho}^\alpha \Delta\bar{v}^\alpha(\bar{v} + \Delta\bar{v}^\alpha)^2\right\} + (\bar{v} + \Delta\bar{v}^\alpha) \cdot \bar{f}^\alpha.$$

From the conservation equation of mass and the balance equation of linear momentum, the total energy equation can be rewritten in terms of internal energy as

$$\frac{\partial}{\partial t}(\bar{\rho}^\alpha \bar{E}^\alpha) = \frac{\partial}{\partial t}\left(\bar{\rho}^\alpha \bar{\varepsilon}^\alpha + \tfrac{1}{2}\bar{\rho}^\alpha(\bar{v} + \Delta\bar{v}^\alpha)^2\right)$$
$$= \frac{\partial}{\partial t}(\bar{\rho}^\alpha \bar{\varepsilon}^\alpha) - \nabla_x \cdot \left(\tfrac{1}{2}\bar{\rho}^\alpha \bar{v}(\bar{v} + \Delta\bar{v}^\alpha)^2\right) - \nabla_{y^\alpha} \cdot \left(\tfrac{1}{2}\bar{\rho}^\alpha \Delta\bar{v}^\alpha(\bar{v} + \Delta\bar{v}^\alpha)^2\right)$$
$$+ (\bar{v} + \Delta\bar{v}^\alpha) \cdot (\nabla_x \cdot \bar{t}^\alpha + \nabla y^\alpha \cdot \bar{\tau}^\alpha + \bar{f}^\alpha).$$

Finally, the time evolution of internal energy is obtained as

$$\frac{\partial}{\partial t}(\bar{\rho}^\alpha \bar{\varepsilon}^\alpha) + \nabla_x \cdot (-\bar{q}^\alpha + \bar{v}\bar{\rho}^\alpha \bar{\varepsilon}^\alpha) + \nabla_{y^\alpha} \cdot (-\bar{j}^\alpha + \Delta\bar{v}^\alpha \bar{\rho}^\alpha \bar{\varepsilon}^\alpha)$$
$$= \bar{t}^\alpha : \nabla_x(\bar{v} + \Delta\bar{v}^\alpha) + \bar{\tau}^\alpha : \nabla_{y^\alpha}(\bar{v} + \Delta\bar{v}^\alpha),$$

or

$$\bar{\rho}^\alpha \frac{d\bar{\varepsilon}^\alpha}{dt} = \nabla_x \cdot \bar{q}^\alpha + \nabla_{y^\alpha} \cdot \bar{j}^\alpha + \bar{t}^\alpha : \nabla_x(\bar{v} + \Delta\bar{v}^\alpha) + \bar{\tau}^\alpha : \nabla_{y^\alpha}(\bar{v} + \Delta\bar{v}^\alpha),$$

where

$$\bar{t}^\alpha : \nabla_x(\bar{v} + \Delta\bar{v}^\alpha) \equiv \bar{t}_{ij}^\alpha \frac{\partial(\bar{v}_j + \Delta\bar{v}_j^\alpha)}{\partial x_i},$$

$$\bar{\tau}^\alpha : \nabla_{y^\alpha}(\bar{v} + \Delta\bar{v}^\alpha) \equiv \bar{\tau}_{ij}^\alpha \frac{\partial(\bar{v}_j + \Delta\bar{v}_j^\alpha)}{\partial y_i^\alpha}.$$

One can find that the time evolution law of cell-averaged energy is different from the macroscopic equation of conservation of energy. This indicates that the macroscopic form of the conservation of energy equation no longer holds even at cell level; the energy density of a unit cell is not a homogeneous quantity; and the contribution of the internal motion and deformation of atoms to the evolution of energy density cannot be ignored.

5. Summary and discussion

By decomposing atomic displacements, momentum and heat fluxes into homogeneous and inhomogeneous parts, we have formulated a field representation of

conservation laws at an atomic scale. The mathematical representations for conservation of mass, balance of linear momentum and conservation of energy are

$$\frac{d\bar{\rho}^\alpha}{dt} + \bar{\rho}^\alpha(\nabla_x \cdot \bar{\boldsymbol{v}} + \nabla_{y^\alpha} \cdot \Delta\bar{\boldsymbol{v}}^\alpha) = 0,$$

$$\bar{\rho}^\alpha \frac{d}{dt}(\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^\alpha) = \nabla_x \cdot \bar{\boldsymbol{t}}^\alpha + \nabla_{y^\alpha} \cdot \bar{\boldsymbol{\tau}}^\alpha + \bar{\boldsymbol{f}}^\alpha,$$

$$\bar{\rho}^\alpha \frac{d\bar{\varepsilon}^\alpha}{dt} = \nabla_x \cdot \bar{\boldsymbol{q}}^\alpha + \nabla_{y^\alpha} \cdot \bar{\boldsymbol{j}}^\alpha + \bar{\boldsymbol{t}}^\alpha : \nabla_x(\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^\alpha) + \bar{\boldsymbol{\tau}}^\alpha : \nabla_{y^\alpha}(\bar{\boldsymbol{v}} + \Delta\bar{\boldsymbol{v}}^\alpha),$$

and the balance law of angular momentum at atomic scale is identically satisfied. Here are some conclusions:

(1) The field representations of conservation equations were formulated within the framework of atomic N-body dynamics. They are the exact time evolution laws of conserved quantities in MD simulations.

(2) Recall that in micromorphic theory [Eringen and Suhubi 1964; Eringen 1999], the balance laws for mass, linear momentum, generalized spin, and energy were obtained as

$$\frac{d\bar{\rho}}{dt} = -\bar{\rho}\nabla_x \cdot \bar{\boldsymbol{v}}$$

$$\bar{\rho}\frac{d\bar{\boldsymbol{v}}}{dt} = \nabla_x \cdot \bar{\boldsymbol{t}} + \bar{\boldsymbol{f}},$$

$$\bar{\rho}\frac{d\bar{\boldsymbol{\phi}}}{dt} = \nabla_x \cdot \bar{\boldsymbol{m}} + \bar{\boldsymbol{\omega}} \cdot \overline{\rho\boldsymbol{i}} \cdot \bar{\boldsymbol{\omega}}^T + (\bar{\boldsymbol{t}} - \bar{\boldsymbol{s}})^T + \bar{\boldsymbol{l}},$$

$$\bar{\rho}\frac{d\bar{\varepsilon}}{dt} = \bar{\boldsymbol{t}} : \nabla\bar{\boldsymbol{v}} + \bar{\boldsymbol{m}} \vdots \nabla\bar{\boldsymbol{\omega}} + \bar{\boldsymbol{\omega}} : (\bar{\boldsymbol{s}} - \bar{\boldsymbol{t}})^T + \nabla \cdot \bar{\boldsymbol{q}},$$

where φ is generalized spin, ω the gyration tensor and l the external couple. Assuming that the inner atomic structure is a continuum and thus $\Delta\boldsymbol{v}^{k\alpha} = \boldsymbol{\omega} \cdot \Delta\boldsymbol{r}^{k\alpha}$, one will find that the obtained balance laws in this paper can be reduced to the balance laws in micromorphic theory upon such continuum assumption and cell averaging [Chen and Lee 2003a; 2003b; Chen et al. 2003]. Note that because the atomic motion and deformation as well as momentum and heat fluxes are decomposed into homogeneous and inhomogeneous parts, the higher order moment stress is avoided in this paper. Also, if the structural unit of the crystal is considered as a point mass, ignoring the atomic structure of the primitive unit cell and relative motion and deformation within this cell, the balance equations we obtain can be reduced to those of continuum mechanics.

(3) For a single component system the obtained balance laws are identical with those obtained by Irving and Kirkwood [1950].

(4) The averaged quantities are time-interval averages. If one uses ensemble averages, it is straightforward to prove that Liouville's theorem would result in the same form as in Equation (3–2) for the time evolutions in equilibrium statistical mechanics; the Boltzmann transport equation as well as BBGKY theory would also yield the same for conserved properties in nonequilibrium statistical mechanics [Chen and Lee 2003a; 2003b; Chen et al. 2003; Kreuzer 1981].

(5) The formulation in this paper has proved that for multielement systems the local conservation equations at atomic scale differ from that at macroscopic scale, and the contribution of the internal motion and deformation of atoms cannot be ignored.

(6) While in molecular dynamics simulations, some physical phenomena may depend on the initial condition, the time-interval Δt, and the choice of the localization function δ, it is noticed that the obtained mathematical representation of the conservation laws is fully in terms of field variables, and is independent of the initial conditions, the time interval and the choice of the localization function.

References

[Chen and Lee 2003a] Y. Chen and J. D. Lee, "Connecting molecular dynamics to micromorphic theory, I: Instantaneous mechanical variables", *Physica A* **322** (2003), 359–376.

[Chen and Lee 2003b] Y. Chen and J. D. Lee, "Connecting molecular dynamics to micromorphic theory, II: Balance laws", *Physica A* **322** (2003), 377–392.

[Chen et al. 2003] Y. Chen, J. D. Lee, and A. Eskandarian, "Atomistic counterpart of micromorphic theory", *Acta Mech.* **161**:1–2 (2003), 81–102.

[Cochran 1973] W. Cochran, *The dynamics of atoms in crystals*, Edward Arnold Limited, London, 1973.

[Eringen 1999] A. C. Eringen, *Microcontinuum field theories, I: Foundations and solids*, Springer, New York, 1999. MR 2000i:74007

[Eringen and Suhubi 1964] A. C. Eringen and E. S. Suhubi, "Nonlinear theory of simple microelastic solids, I", *Int. J. Eng. Sci.* **2**:2 (1964), 189–203.

[Hardy 1963] R. J. Hardy, "Energy-flux operator for a lattice", *Phys. Rev.* **132**:1 (1963), 168–177. MR 28 #948

[Hardy 1982] R. J. Hardy, "Formulas for determining local properties in molecular-dynamics simulations: Shock waves", *J. Chem. Phys.* **76**:1 (1982), 622–628.

[Hoover 1986] W. G. Hoover, *Molecular dynamics*, Springer, Berlin, 1986.

[Hoover 1991] W. G. Hoover, *Computational statistical mechanics*, Elsevier, Amsterdam, 1991.

[Huang 1967] K. Huang, *Statistical mechanics*, Willey, New York, 1967.

[Irving and Kirkwood 1950] J. H. Irving and J. G. Kirkwood, "The statistical mechanical theory of transport processes, IV: The equations of hydrodynamics", *J. Chem. Phys.* **18**:6 (1950), 817–829. MR 12,230d

[Kreuzer 1981] H. J. Kreuzer, *Nonequilibrium thermodynamics and its statistical foundations*, Oxford University Press, London, 1981. MR 82d:82001

[Ranninger 1965] J. Ranninger, "Lattice thermal conductivity", *Phys. Rev.* **140**:6A (1965), A2031–A2046.

YOUPING CHEN: ypchen2@gwu.edu
School of Engineering and Applied Science, The George Washington University, Academic Center T739, 801 22nd Street NW, Washington, DC 20052, United States

JAMES LEE: jdlee@gwu.edu
School of Engineering and Applied Science, The George Washington University, Academic Center T739, 801 22nd Street NW, Washington, DC 20052, United States