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On the physical foundation and consistent formulation of atomic-level fluxes in transport processes

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ABSTRACT

Irving and Kirkwood derived the transport equations from the principles of classical statistical mechanics using the Dirac delta to define local densities. Thereby, formulas for fluxes were obtained in terms of molecular variables. The Irving and Kirkwood formalism has inspired numerous formulations. Many of the later developments, however, considered it more rigorous to replace the Dirac delta with a continuous volume-weighted averaging function and subsequently defined fluxes as a volume density. Although these volume-averaged flux formulas have dominated the literature for decades and are widely implemented in popular molecular dynamics (MD) software, they are a departure from the well-established physical concept of fluxes. In this work, we review the historical developments that led to the unified physical concept of fluxes for transport phenomena. We then use MD simulations to show that these popular flux formulas conserve neither momentum nor energy; nor do they produce fluxes that are consistent with their physical definitions. We also use two different approaches to derive fluxes for general many-body potentials. The results of the formulation show that atomistic formulas for fluxes can be fully consistent with the physical definitions of fluxes and conservation laws.

1. INTRODUCTION

Flux in transport processes is defined as the rate of flow of a physical property through a surface per unit area. This definition is applicable to all fluxes in transport phenomena, in all physical and chemical processes, and for systems at all length and time scales. Based on the physical definition, a transport flux can generally be quantified via the measurement of the physical property and the area of the surface through which the property flows without the need of a sophisticated understanding of the various theories of transport processes. By contrast, finding the mathematical representation of a flux in molecular systems must rely on the principles of mathematics and physics. This leads to different microscopic formulas for fluxes.

The formal statistical mechanics derivation of local fluxes for transport phenomena was pioneered by Irving and Kirkwood in 1950¹. The Irving-Kirkwood (IK) formalism uses the Dirac δ function to define the local densities of mass, linear momentum, and energy. Fluxes (stress and heat flux) are then obtained as ensemble-averaged point functions¹ that satisfy the differential forms of the momentum and energy conservation laws. The fluxes in the IK formulation were expressed as a power series. Closed-form expressions were obtained later, e.g., by Miller² and Kreuzer³, using an identity for the difference between two Dirac δ functions inside integrals as

$$\delta(\mathbf{r}_k - \mathbf{x}) - \delta(\mathbf{r}_l - \mathbf{x}) = -\nabla_{\mathbf{x}} \cdot \int_0^1 \mathbf{r}_{kl} \delta(\mathbf{r}_{kl} \lambda + \mathbf{r}_l - \mathbf{x}) d\lambda, \quad (1)$$

where $\mathbf{r}_{kl} = \mathbf{r}_k - \mathbf{r}_l$; \mathbf{r}_k is the position vector of particle k , and \mathbf{x} denotes a point in the three-dimensional physical space.

Using Eq. (1), stress and heat flux are then expressed as ensemble-averaged line integral of the Dirac δ ³,

$$\begin{aligned} \bar{\sigma}^{\text{IK}}(\mathbf{x}, t) = & -\left\langle \sum_k m_k \tilde{\mathbf{v}}_k \delta(\mathbf{r}_k - \mathbf{x}) \right. \\ & \left. - \frac{1}{2} \int_0^1 \sum_{k,l (\neq k)} \mathbf{F}_{kl} \mathbf{r}_{kl} \delta(\mathbf{r}_k \lambda + \mathbf{r}_l (1-\lambda) - \mathbf{x}) d\lambda \right\rangle, \end{aligned} \quad (2)$$

$$\begin{aligned} \bar{\mathbf{q}}^{\text{IK}}(\mathbf{x}, t) = & -\left\langle \sum_k \tilde{\mathbf{v}}_k \left[\frac{1}{2} m_k (\tilde{\mathbf{v}}_k)^2 + \Phi_k \right] \delta(\mathbf{r}_k - \mathbf{x}) \right. \\ & \left. - \frac{1}{2} \int_0^1 \sum_{k,l (\neq k)} (\mathbf{F}_{kl} \cdot \tilde{\mathbf{v}}_k) \mathbf{r}_{kl} \delta(\mathbf{r}_k \lambda + \mathbf{r}_l (1-\lambda) - \mathbf{x}) d\lambda \right\rangle. \end{aligned} \quad (3)$$

where m_k and \mathbf{v}_k are respectively the mass and velocity of k th particle; $\tilde{\mathbf{v}}_k = \mathbf{v}_k - \mathbf{v}$ with \mathbf{v} being the velocity field; \mathbf{F}_{kl} is the two-body interaction force between particles k and l .

The IK formulation has inspired numerous research efforts in deriving atomistic fluxes⁴⁻¹⁵. Many later developments, however, simply replace the Dirac δ in Eq. (2) and (3) with a volume-weighted average function^{4,6,16}. Noll¹⁷ is probably the first one who made it an objective to avoid the Dirac δ in his formulation, and his method is often referred to as the “Irving-Kirkwood-Noll” approach¹⁸. Hardy used a volume-weighted “*localization function*”, Δ , for local densities and another volume-averaged “*bond function*”, $B(k,l,\mathbf{x}) = \int_0^1 \Delta(\mathbf{r}_k \lambda + \mathbf{r}_l (1-\lambda) - \mathbf{x}) d\lambda$, for fluxes⁴. The resulting stress formula is thus a volume density:

$$\sigma^H(\mathbf{x}, t) = -\frac{1}{V} \left(\sum_k m_k \tilde{\mathbf{v}}_k \Delta(\mathbf{x} - \mathbf{r}_k) + \sum_{k,l} \mathbf{F}_{kl} r_{kl} B(k, l, \mathbf{x}) \right), \quad (4)$$

$$\mathbf{q}^H(\mathbf{x}, t) = -\sum_k \tilde{\mathbf{v}}_k \left[\frac{1}{2} m_k \tilde{\mathbf{v}}_k^2 + \Phi_k \right] \Delta(\mathbf{r}_k - \mathbf{x}) - \sum_{k,l} (\mathbf{F}_{kl} \cdot \tilde{\mathbf{v}}_k) r_{kl} B(k, l, \mathbf{x}). \quad (5)$$

There is also a kinetic theory for steady-state system pressure due to the collisions between gas particles and the walls of the container by Clausius¹⁹ and Maxwell²⁰⁻²¹. The theory yields the well-known formula for pressure P as

$$P = \frac{1}{3} \bar{\rho} \bar{c}^2 = \frac{k_B N T}{V}, \quad (6)$$

where \bar{c} is the root-mean square velocity, N the number of particles in the system of volume V , T the system temperature, and k_B is the Boltzmann constant.

Equation (6) was later extended by Clausius to include particle forces²², the formalism of which is called virial theorem. Further developed by Maxwell^{23,24}, the virial theorem has served as the microscopic formula for *system pressure* or *system-wide average stress* for classical or quantum systems of interacting particles. For systems with two-body interaction forces, the virial stress can be expressed as

$$\sigma^{\text{viria}} = -\frac{1}{V} \left(\sum_i m_i \mathbf{v}_i \mathbf{v}_i + \frac{1}{2} \sum_{i,j} \mathbf{F}_{ij} r_{ij} \right). \quad (7)$$

Note that Eq. (7) yields a single stress tensor for the entire system. It is thus not a formula for local stress at every point \mathbf{x} in the physical space for an inhomogeneous system. However, since it is formally written as a sum over particles, each individual term in the formula has been taken to describe the local stress at a particle and is usually referred to as the *atomic virial stress*²⁵.

A generalized virial theorem for energy flux was formulated by Eisenschitz²⁶ using Clausius' virial formalism²² in tandem with the assumption that the energy flux is constant throughout the system. This generalized virial theorem is often referred to as *heat theorem*²⁷ and is now widely used in equilibrium MD simulations with Kubo formalism to calculate thermal conductivity of materials. For system with two-body forces, the system-wide average energy flux, \mathbf{Q} , is usually written as:

$$\mathbf{Q} = \frac{1}{V} \left\langle \sum_i \left(\frac{1}{2} m_i \mathbf{v}_i^2 + \Phi_i \right) \mathbf{v}_i + \frac{1}{4} \sum_{i,j} \mathbf{F}_{ij} r_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j) \right\rangle. \quad (8)$$

The virial formalism and Hardy flux formulas, as well as most of the flux formulas developed following Noll's or Hardy's approaches, express the stress tensor or heat flux vector as a volume density.

These volume-averaged (VA) formulas constitute the majority of atomistic formulas for local stress and heat flux in the literature. They are implemented in popular MD simulators such as LAMMPS²⁸ and have been widely used in MD simulations to quantify local stress or heat flux in **homogeneous** and inhomogeneous materials.

It is worth mentioning the “*Method of Planes*” (MOP), formulated in reciprocal space for systems with flow in one direction²⁹⁻³¹, and its generalizations³²⁻³⁴. MOP may be the earliest effort that derives atomistic formulas for pressure and heat flux as a planar average. The *control volume formulation*³⁵ is another effort that describes fluxes as a planar average by linking the time derivatives of the conserved quantity in a volume element to the fluxes across the bounding surface of the volume; this work demonstrates that at the limit of zero volume the formulation returns to the IK point-function formulation. Using the integral form of conservation laws, formulas for atomic-level local stress and heat flux have recently been derived as a surface average for three dimensional inhomogeneous systems in transient transport processes^{36,37}.

Comparisons of MOP and VA using MD simulations show a good agreement for local pressure, after sufficient time averaging, in a spatially homogeneous Lennard-Jones fluid^{34,38}. By contrast, significant differences in the calculated results of local stress and heat flux between popular VA formulas and surface formulas are demonstrated for solids with defects or interfaces^{36,37,39}.

To understand the origin of the differences and see how later developments have departed from the IK flux formalism, we recall the important points noted in the IK paper about their stress and heat flux formulas:

(1) “The densities defined are point functions”; “*These point functions satisfy the hydrodynamical-like equations*”; “*to obtain the hydrodynamical equations themselves it is merely necessary to perform appropriate space and time averages*” “*determined by the resolution of one's measurements and averaging over a time interval of the order of the relaxation time of one's measuring instruments*”¹.

(2) “*Since only the divergence of σ (stress) enters into the hydrodynamical equation of motion, σ itself is undetermined up to an arbitrary tensor of vanishing divergence*”; “*the only choice*” is the one “*that is in accord with the physical definition of the stress tensor as the force transmitted per unit area*”¹. Also, since the differential energy equation “*merely specifies the divergence of the heat current, and leaves \mathbf{q} (heat current) itself undetermined up to the curl of an arbitrary vector field*”, one needs to find the particular solution that “*agrees with the physical definition of the heat current density*”.

In view of the importance of “*appropriate space and time averages*”, “*hydrodynamical equations*”, and the “*physical definitions*” of stress tensor and heat flux to the IK formalism, this work compares popular volume-averaged (VA) flux formulas with the physical definitions as well as with the hydrodynamics conservation equations. This will be achieved through mathematical analysis and MD simulations. We aim to answer the following questions:

- (1) Why is volume averaging inappropriate for the formulation of fluxes in transport processes?
- (2) Can atomistic descriptions of fluxes be fully consistent with the physical definitions of fluxes?
- (3) What are the fundamental reasons that lead to the failure of VA flux formulas?

The paper is organized as follows. Following the Introduction, in Sec II, we review the physical concepts of fluxes that have been established for centuries; in Sec. III, we use two different approaches to derive stress and heat flux for general many-body potentials and show that atomistic formulas for fluxes can be fully consistent with their physical definitions; in Sec VI, we present two sets of MD simulation results to quantify the failure of VA formulas in reproducing fluxes that satisfy the momentum and energy conservation laws; in Sec V, we discuss the fundamental reasons that lead to the failure of the VA flux formulas; a summary is presented in Sec. VI.

II. A REVIEW OF THE PHYSICAL CONCEPTS OF STRESS AND HEAT FLUX

A. Stress vector and stress tensor

The physical concept of pressure or stress as force per unit area is simple and unambiguous. It is established before the classical continuum mechanics was formulated. According to Truesdell, Galileo (1564-1642) was the first to state a property of a material in terms of “*force per unit area rather than force*”⁴⁰. In 1705 James Bernoulli linked the “*resultant force divided by the area to which it is applied*” to the “*change in length per unit initial length*” in his paper on elasticity⁴¹. In 1750 Euler applied Newton’s second law to infinitesimal volume elements of bodies with “*internal pressure*” or the “*connection forces acting on the boundary of the elements*” and derived the equation of motion⁴². In 1823, Cauchy divided the resultant applied force on any part of a body into “*body force*” and “*surface contact force f_c* ”, and then defined the surface traction, i.e., the stress vector, $\mathbf{t}(\mathbf{x}, \mathbf{n})$ as the “*contact force per unit area on a very small surface element at point \mathbf{x} with normal \mathbf{n}* ” as^{43,44}

$$\mathbf{f}_c = \iint_{\partial V} \mathbf{t}_{\partial p}(\mathbf{x}, \mathbf{n}) dA^n \quad \text{or} \quad \lim_{\Delta A_n \rightarrow 0} \frac{\Delta \mathbf{f}_c}{\Delta A_n} = \mathbf{t}(\mathbf{x}, \mathbf{n}), \quad (9)$$

where ΔA_n is the area of the surface element with normal \mathbf{n} , and $\Delta \mathbf{f}_c$ is the resultant force acting on the surface element. Eq. (9) is referred to as the *Euler-Cauchy stress principle*. Cauchy first proved his fundamental lemma:

$$\mathbf{t}(\mathbf{x}, \mathbf{n}) = -\mathbf{t}(\mathbf{x}, -\mathbf{n}). \quad (10)$$

He then showed that the stress vector on any plane can be deduced from “*the stress vectors on three given rectangular planes*”⁴⁴; the latter is the stress tensor⁴³. This is the *Cauchy stress theorem*. It states that there exists a second-order tensor field $\boldsymbol{\sigma}(\mathbf{x})$ at point \mathbf{x} that determines the stress vector on any surface element passing through this point \mathbf{x} , i.e.

$$\mathbf{t}(\mathbf{x}, \mathbf{n}) = \boldsymbol{\sigma}(\mathbf{x}) \cdot \mathbf{n} \quad \text{or} \quad t^\alpha(\mathbf{x}, \mathbf{e}^\beta) = \sigma^{\alpha\beta}(\mathbf{x}), \quad (11)$$

where \mathbf{e}^β ($\beta = 1, 2, 3$) are the unit normal vectors to the coordinate planes, and $\sigma^{\alpha\beta}$ is the α -th component of the force vector per unit area acting on the β -th coordinate plane⁴⁵. Eq.(11) is the *Cauchy fundamental stress theorem*, and “*is what makes continuum mechanics possible*” according to Truesdell⁴³.

Equations (9)-(11) are the defining properties of the Cauchy stress vector and stress tensor. They form the foundation of continuum mechanics, and are called, respectively, the *Euler-Cauchy stress principle*, the *Cauchy fundamental lemma*, and the *Cauchy stress theorem*. Based on Eqs. (9)-(11), Cauchy derived the differential form of the momentum conservation law in terms of the stress tensor, in exact correspondence with the hydrodynamics equation of motion derived by Euler in terms of pressure.

B. Heat flux

The concept of heat flux as a measure of “the rate of flow of heat energy per unit area through a surface” was a key contribution of Joseph Fourier⁴⁶, when he used a partial differential equation to describe heat conduction in his paper “*Analytical theory of heat*” submitted in 1807 for publication and rejected until 1822. Fourier adopted in modified form the first rate equation in the history of physics known as Newton’s law of cooling⁴⁷ and related the rate of heat crossing a surface per unit area to the gradient of temperature perpendicular to the surface. Essentially, Fourier’s rate equation is the conservation equation of heat energy in an infinitesimally small volume element, centered at a point of a solid, with heat continuously moving across the surfaces bounding the volume element. The

model is similar to that used by Euler in 1750 in deriving the moment conservation equation for small volume elements in a deformable body⁴². The concept of heat, however, was avoided by Fourier, which was not established at the time.

The modern definition of heat can be traced back to Benjamin Thompson who introduced the mechanical theory of heat in 1798⁴⁸. William Thomson, also known as Lord Kelvin, concluded in 1851 that “*heat is not a substance, but a dynamical form of mechanical effect*”⁴⁹. In 1871 Maxwell defined heat as “*a measurable quantity, one of the forms of energy, that may be transferred from one body to another*” in his “Theory of Heat”⁵⁰. Building on these pioneering works, heat is now defined in thermodynamics as the energy transferred from one system to another due to thermal interactions, and in kinetic theory as the energy transferred between particles through particle collisions.

Heat flux can be measured using its physical concept via a heat flux sensor through directly measuring the amount of heat being transferred to/from the surface that the heat flux sensor is mounted to. It is a vector quantity with a direction and a magnitude describing the flow of heat through the surface.

Similar to that of stress and heat flux, electric flux is defined as the total number of electric lines of force passing through a surface per unit area. The similarities between the definitions of momentum flux, heat flux, electric flux, etc., as well as the mathematical descriptions and solutions, lead to a unified physical concept of fluxes in all transport phenomena.

III. STRESS AND HEAT FLUX FOR GENERAL MANY-BODY POTENTIALS

The objective of this section is to demonstrate that atomistic fluxes in transport processes can be formulated to be fully consistent with their physical concepts and conservation laws. The detailed derivations are presented in the Appendix. A different equation, rather than Eq.(1), is used to express the difference between two Dirac δ as³⁷

$$\delta(\mathbf{r}_k - \mathbf{x}) - \delta(\mathbf{r}_l - \mathbf{x}) = \nabla_x \cdot \int_{L_{kl}} \delta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi}, \quad (12)$$

where L_{kl} represents a line segment from \mathbf{r}_k to \mathbf{r}_l , and Eq. (12) holds in the distributional sense.

A. Using the IK formalism with differential conservation equations

The stress tensor $\boldsymbol{\sigma}$ and heat flux vector \mathbf{q} derived in the IK paper based on the differential form of conservation laws can be expressed as a sum of a kinetic and potential parts, with

$$\bar{\boldsymbol{\sigma}}_{\text{kin}}^{\text{IK}}(\mathbf{x}, t) = - \left\langle \sum_k m_k \tilde{\mathbf{v}}_k \tilde{\mathbf{v}}_k \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle, \quad (13)$$

$$\nabla \cdot \bar{\boldsymbol{\sigma}}_{\text{pot}}^{\text{IK}}(\mathbf{x}, t) = \left\langle \sum_k \mathbf{F}_k \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle = - \left\langle \sum_k \frac{\partial \Phi}{\partial \mathbf{r}_k} \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle, \quad (14)$$

$$\bar{\mathbf{q}}_{\text{kin}}^{\text{IK}} + \bar{\boldsymbol{\sigma}}_{\text{kin}}^{\text{IK}} \cdot \mathbf{v} = - \left\langle \sum_k E_k \tilde{\mathbf{v}}_k \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle, \quad (15)$$

$$\nabla_x \cdot (\bar{\mathbf{q}}_{\text{pot}}^{\text{IK}} + \bar{\boldsymbol{\sigma}}_{\text{pot}}^{\text{IK}} \cdot \mathbf{v}) = \left\langle \sum_k \dot{E}_k \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle, \quad (16)$$

where E_k and \mathbf{F}_k are the total energy and the atomic force of k th particle, respectively; the subscript “kin” and “pot” denote the kinetic and potential parts of the fluxes, respectively; $\tilde{\mathbf{v}}_k = \mathbf{v}_k - \mathbf{v}$; and Φ is the total potential energy of the system.

Although the IK fluxes were derived for two-body potentials, the IK formalism for the potential part of fluxes, represented by Eqs. (14) and (16), can be extended to systems with many-body potentials. It is noted in the IK paper that a definition of site energies is required for the local energy density in the energy transport equation to be definable. This requirement is met, e.g., for the Tersoff potential⁵¹ and the bond-order potentials⁵²⁻⁵⁵, in which the total potential is expressed in terms of site energies, i.e., $\Phi = \sum_i \Phi_i$. For such potentials, Eqs. (14) and (16) can be expressed in terms of site energies as

$$\begin{aligned} \nabla \cdot \bar{\boldsymbol{\sigma}}_{\text{pot}}^{\text{point}}(\mathbf{x}, t) &= \left\langle \sum_k \mathbf{F}_k \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle \\ &= - \sum_{k, l (l \neq k)} \left(\frac{\partial \Phi_l}{\partial \mathbf{r}_k} - \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \right) \delta(\mathbf{r}_k - \mathbf{x}), \end{aligned} \quad (17)$$

$$= \nabla_x \cdot \left\langle \sum_{k, l (l \neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int_{L_{kl}} \delta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} \right\rangle$$

$$\begin{aligned} \nabla_x \cdot (\bar{\mathbf{q}}_{\text{pot}}^{\text{point}} + \bar{\boldsymbol{\sigma}}_{\text{pot}}^{\text{point}} \cdot \mathbf{v}) &= \left\langle \sum_k \dot{E}_k \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle \\ &= \left\langle \sum_k [m_k \mathbf{v}_k \cdot \dot{\mathbf{v}}_k + \dot{\Phi}_k] \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle. \end{aligned} \quad (18)$$

$$= \nabla_x \cdot \left\langle \sum_{k, l (l \neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l \int_{L_{kl}} \delta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} \right\rangle$$

As previously mentioned, stress and heat flux obtained in the IK formulation are **ensemble-averaged** point functions, and Irving and Kirkwood noted that these point-function densities need to be averaged in space and time in order to obtain observable or **measurable** quantities. It is noticed that the Dirac δ is a singular generalized function. According to the theory of generalized functions, the average density of such functions in a sufficiently small **neighborhood** of this point exists. This means the instantaneous fluxes can be rigorously defined without the need of ensemble average. Averaging the

instantaneous potential fluxes in Eq.(17) and Eq. (18) as well as the kinetic fluxes in Eq. (13) and Eq.(15) over the path of a particle during time-interval T and a surface element β that is centered at point \mathbf{x} with area A^β and surface normal \mathbf{e}^β , we obtain the formulas for stress in terms of site energies and in terms of interaction force using $\mathbf{F}_k = \sum_i \mathbf{F}_k$, respectively, as

$$\sigma^{\alpha\beta}(\mathbf{x}, t) = \sum_{kl(\neq k)} \frac{\partial \Phi_k}{\partial r_l} \int_{L_{kl}} \bar{\delta}_{AT}^\beta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} - \sum_k m_k \tilde{v}_k^\alpha \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}), \quad (19)$$

$$\sigma^{\alpha\beta}(\mathbf{x}, t) = \frac{1}{2} \sum_{kl(\neq k)} F_{kl} \int_{L_{kl}} \bar{\delta}_{AT}^\beta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} - \sum_k m_k \tilde{v}_k^\alpha \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}), \quad (20)$$

and for heat flux as

$$q^\beta(\mathbf{x}, t) = \sum_{kl(\neq k)} \frac{\partial \Phi_k}{\partial r_l} \cdot \tilde{\mathbf{v}}_l \int_{L_{kl}} \bar{\delta}_{AT}^\beta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} - \sum_k \left(\frac{1}{2} m_k \tilde{v}_k^2 + \Phi_k \right) \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}), \quad (21)$$

where the averaged line integral of the Dirac δ over surface element β and time-step T in the potential fluxes is derived in the Appendix, with $\int_{L_{kl}} \bar{\delta}_{AT}^\alpha(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} = \int_0^T d\tau \int_{L_{kl}} \bar{\delta}_A^\alpha(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi}$ and

$$\int_{L_{kl}} \bar{\delta}_A^\beta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} = \frac{1}{A^\beta} \frac{n_{kl}^\beta}{|n_{kl}^\beta|} \begin{cases} 1 & \text{if } \mathbf{r}_{kl} \text{ intersects } A^\beta \\ 0 & \text{otherwise} \end{cases}; \quad (22)$$

$$\bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}) = \frac{1}{A^\beta T} \frac{\tilde{v}_k^\beta}{|\tilde{v}_k^\beta|} \begin{cases} 1 & \text{if } \mathbf{r}_k(t+\tau) \text{ intersects } A^\beta \text{ for } \tau \in T \\ 0 & \text{otherwise} \end{cases}. \quad (23)$$

B. Using the integral conservation equations

An alternative approach to derive flux formulas is to use the integral form of the conservation laws for a volume element V . The approach was developed in our precious work^[37], but in this work we slightly change the notation. Recall that the conservation laws of momentum and energy for a volume element in the absence of body force state that the time rate of change of a conserved quantity within V equals to the flux across the enclosing surface ∂V , i.e.,

$$\frac{\partial}{\partial t} \iiint_V \rho \mathbf{v} d^3x' = \iint_{\partial V} \mathbf{t} d^2x' - \iint_{\partial V} \rho \mathbf{v} \mathbf{v} \cdot \mathbf{n} d^2x', \quad (24)$$

$$\frac{\partial}{\partial t} \iiint_{V(\mathbf{x})} \rho E d^3x' = \iint_{\partial V} (\mathbf{q} + \boldsymbol{\sigma} \cdot \mathbf{v}) \cdot \mathbf{n} d^2x' - \iint_{\partial V} \rho E \mathbf{v} \cdot \mathbf{n} d^2x', \quad (25)$$

where $\rho \mathbf{v}$ and ρE are the momentum and energy density (per volume), respectively.

The time rate of change of momentum and energy within V can also be derived as a consequence of Newton's second law applying to the particles in V .

Denote the averaged Dirac δ over V and time-interval T as $\bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x})$, we have

$$\frac{\partial}{\partial t} \sum_k m_k \mathbf{v}_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) = \sum_k \frac{\partial}{\partial t} (m_k \mathbf{v}_k) \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) + \sum_k m_k \mathbf{v}_k \frac{\partial}{\partial t} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}). \quad (26)$$

$$\frac{\partial}{\partial t} \sum_k E_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) = \sum_k \dot{E}_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) + \sum_k E_k \frac{\partial}{\partial t} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}). \quad (27)$$

Equations (26) and (27) can be further derived utilizing the fact that the interactions between atoms completely inside or completely outside of V do not contribute to the potential part of fluxes across the bounding surfaces of V ; please see Appendix for the detailed derivation. By comparing the derivation results of Eq.(26) with Eq. (24), or that of Eq. (27) with Eq.(25), one can find that the resulting formulas for stress, or heat flux, are identical to Eq. (19), or Eq. (21), obtained using the differential form of conservation laws. This means that these flux formulas satisfy both the differential and integral forms of conservation laws.

C. Interpretations

The above formulation results show that the two different approaches lead to the same formulas for fluxes. Major points may be summarized as follows:

- (1) Both kinetic and potential fluxes are obtained in the form of line-plane intersection theorem. This can be seen more clearly from Eqs. (22) and (23): for the potential fluxes, it is the line segment \mathbf{r}_{kl} intersecting the surface element at \mathbf{x} in space, while for the kinetic fluxes, it is $\mathbf{r}_k(t)$ intersecting the surface element in time.
- (2) The integral form of the momentum conservation law involves the stress vector directly, while the differential form only involves the divergence of the stress tensor. Both approaches, however, lead to the same formula for the stress tensor; the α component of kinetic part of stress tensor represents the α -th component of momentum across the β -th coordinate surface element per unit area and time due to the thermal motion of atoms, while the potential part of stress represents the α -th component of the interaction forces transmitted across the β -th coordinate plane per unit area and time. These results are in exact correspondence with the physical definition of momentum flux due to the motion and interaction of particles.
- (3) The potential stress σ_{pot} can be expressed in terms of interaction force \mathbf{F}_{kl} or site energy Φ_k . The

derivation involving Φ_k does not require the definition of F_{kl} ; the energy-based stress formula, Eq.(19), is thus free of ambiguities associated with the definition of **interaction** force for systems with many-body potentials. On the other hand, the derivation in terms of F_{kl} is independent of the form of the potential energy; the force-based stress formula, Eq.(20), is thus valid for any form of additive potentials that satisfies $F_i = \sum_{j \neq i} F_{ij}$.

- (4) The stress vector and stress tensor formulas are fully consistent with the defining properties of the stress vector and stress tensor described in Eqs (9)-(11). They are: (a) the Euler-Cauchy stress principle that defines the stress vector as the surface contact force per unit area, (b) Cauchy's fundamental lemma that states the stress vector acting on the opposite sides of the same surface are equal in magnitude and opposite in sign, and (c) the Cauchy stress theorem for the **relationship** between stress tensor and the stress vector.
- (5) Unlike the stress tensor, heat flux can only be expressed in terms of site energies Φ_k , and a well-defined site energy is required for the IK formalism.
- (6) To understand the difference between energy flux and heat flux, we express the total energy density as

$$\begin{aligned} \rho E &= \sum_k \left\{ \frac{1}{2} m^k (\tilde{\mathbf{v}}_k)^2 + \Phi_k \right\} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) + \frac{1}{2} \rho \mathbf{v}^2 \\ &= \rho \varepsilon + \frac{1}{2} \rho \mathbf{v}^2 \end{aligned} \quad (28)$$

where $\rho \varepsilon$ is the internal energy density and $\frac{1}{2} \rho \mathbf{v}^2$ the kinetic energy density. While the energy flux represents the flow of energy through both conductive and convective mechanisms, the heat flux is only the conductive flow of energy, with the terms that involve the velocity field \mathbf{v} being the convective part.

- (7) The two different approaches, based on the differential form and the integral form of conservation laws, respectively, yield identical formulas for heat flux, with the kinetic part of heat flux measures the rate of the flow of internal energy across a surface element per unit area; while the potential part measures the rate of work done by the interaction forces between particles on the opposite sides of the surface element through the thermal motion of particles. Clearly, these formulation results are fully consistent with the physical concept of heat flux.

The obtained flux formulas are applicable for transient processes in inhomogeneous materials. For steady-state processes, there is also an alternative expression for the kinetic fluxes. Denote $V_k = A^\beta T |\mathbf{v}_k^\beta|$ as the volume determined by the area of the surface element and the distance that the atom k travels during time-step-interval T ; the kinetic stress tensor and heat flux vector can then be expressed as a volume average:

$$\sigma_{\text{kin}}^{\alpha\beta}(\mathbf{x}, t) = - \sum_k m_k \tilde{\mathbf{v}}_k^\alpha \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}) = - \sum_k \frac{m_k \tilde{\mathbf{v}}_k^\alpha \tilde{\mathbf{v}}_k^\beta}{V_k} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}), \quad (29)$$

$$\mathbf{q}_{\text{kin}}^\alpha(\mathbf{x}, t) = - \sum_k \frac{\tilde{\mathbf{v}}_k^\alpha \left[\frac{1}{2} m^k (\tilde{\mathbf{v}}_k)^2 + \Phi_k \right]}{V_k} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) \quad (30)$$

It is seen that the kinetic stress in Eq. (29) is identical in form to the negative gas pressure in the kinetic theory; it relates pressure to molecular kinetic energy per unit volume. However, in transient transport processes, the volume represented by V_k , as determined by the atomic velocity \mathbf{v}_k and the time-step T , is not a constant. Only in steady-state processes when the stress is averaged over long time durations, the volume-averaged formula for kinetic stress in Eq. (29) and the surface-averaged formula for kinetic stress in Eq. (19) may become identical. While the kinetic stress can be related to the kinetic temperature in steady-state systems, Eq. (19) indicates that in transient processes the kinetic stress is the rate of momentum flux across a surface element per unit area due to the thermal motion of particles. Since temperature is not well defined in transient processes, the kinetic stress is thus best represented as the kinetic part of momentum flux. Similar to that for the kinetic stress, the volume-averaged formula for \mathbf{q}_{kin} in Eq. (30) may be used in steady-state heat flow when properties are averaged over a long-time duration, but it is not appropriate for transient processes when the velocity of a particle varies rapidly in time.

Different from the kinetic fluxes, the formulas for the potential parts of stress and heat flux remain unchanged whether for transient or steady-state processes. They are the part of the fluxes resulting from the interactions between particles on the opposite sides of the surface elements. These formulas hold for both instantaneous and time-averaged measurements.

It may be worth mentioning that for systems with two-body force, we have $\partial \Phi_k / \partial \mathbf{r}_l = -\partial \Phi_l / \partial \mathbf{r}_k = \frac{1}{2} \mathbf{F}_{kl}$; the potential part of heat flux in Eq. (21) can then be expressed in terms of the interaction force as

(D) Fluxes in steady-state transport processes

$$\begin{aligned}
q_{\text{pot}}^{\alpha}(\mathbf{x}, t) &= \sum_{kl(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \tilde{\mathbf{v}}_l \int_{L_{kl}} \bar{\delta}_{AT}^{\alpha}(\boldsymbol{\varphi} - \mathbf{x}') d\boldsymbol{\varphi} \\
&= \frac{1}{2} \sum_{k,l(\neq k)} \mathbf{F}_{kl} \cdot \left(\frac{\mathbf{v}_k + \mathbf{v}_l}{2} - \mathbf{v} \right) \int_{L_{kl}} \bar{\delta}_{AT}^{\alpha}(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi}
\end{aligned} \quad (31)$$

However, if $\partial \Phi_k / \partial \mathbf{r}_l \neq -\partial \Phi_l / \partial \mathbf{r}_k$, Eq. (31) is then false. One can readily check that a force-based heat flux formula in the form of Eq. (31) does not satisfy the energy conservation equation for the Tersoff potential.

IV. MD SIMULATION RESULTS

The objective of the MD simulations is to demonstrate and quantify the failure of the VA formulas in reproducing the physical definitions of fluxes and in satisfying the momentum and energy conservation laws. We simulate two different materials systems: one with dislocations to measure local stress near defects, and one with periodic holes to measure stress and heat flux at interfaces.

4.1 Stresses near dislocation cores

The first MD computer model is a three-dimensional (3D) single crystal copper, with dimensions 54 nm \times 24 nm \times 2.2 nm, atomic mass 63.546u, and lattice constant 0.3615 nm. The crystal is modelled with the Lennard-Jones (LJ) potential using the parameters $\epsilon = 0.415$ and $\sigma = 2.277$. A full dislocation is initially built into the model, and the model is then relaxed using the NVT ensemble to 0.1 K. After the equilibration, the initially built-in full dislocation is found to have dissociated into two partials, as shown in Fig. 1.

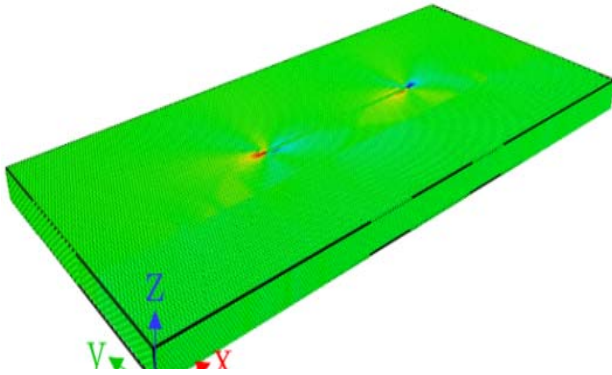


Fig. 1. A MD model containing a dissociated dislocation; atoms are color encoded with atomic shear strain.

To calculate the mechanical stress in MD simulation using its physical definition as force per unit area acting on a surface element, we employ the method described by Cheung and Yip to “set up an

element of volume surrounding an atom and calculate the force across each face of the element”²⁵. This method enables direct calculation of the mechanical stress vectors and stress tensor, with the stress tensor being the “the stress vectors on three given rectangular planes”⁴⁴. This is the stress tensor defined by Cauchy.

To use this method, we first construct a background mesh that divides the model into 3D atomic-scale rectangular elements. The elements are the rectangular primitive unit cells of crystal copper with dimensions 2.556 Å by 2.087 Å by 2.213 Å. This is the smallest element that has one atom at its center and yet is space filling to meet the continuum requirement for the stress field³⁹. A detailed study of the effects of mesh and mesh size can be found in [39]. The mechanical stresses are then measured as the resultant forces per unit area transmitted across the faces of the rectangular elements. The potential parts of stresses defined by two popular VA stress formulas: the atomic virial stress and the Hardy stress formula, are also measured, as both formulas are implemented in LAMMPS²⁸ (please see ref⁶⁶ for the implementation details). At a temperature of 0.1 K, the kinetic part of stress is negligible. It is thus not measured for this case.

In Fig. 2, we present stress distributions along the X and Y directions near the dislocation cores for the mechanical stress σ_M , atomic virial stress σ_V , and Hardy stress σ_H , respectively. In Fig. 3, we present zoomed-in stress distribution in the XY plane, i.e., a 2D view of the stress contour.

It is seen from Fig. 3 that neither the atomic virial stress nor the Hardy stress reproduces the mechanical stress measured directly using the physical definition. Both formulas yield zero stress at the dislocation cores and underestimating all stress components near the dislocations. Also, it is seen from Fig. 3 that the Hardy stress is much smaller than the virial stress. Such a result is consistent with the MD simulation results of copper using the EAM potential reported in [57,58]. In addition, the calculation results using the physical definition of mechanical stress show that the two shear stress components are not equal. This means the atomic-level stress tensor near dislocation core is not symmetric³⁹.

Stress localization near a crack tip or dislocation core is a well-known phenomenon. Failure to reproduce some of the high stress in a stress concentration region is a consequence of the failure of the VA stress formulas in reproducing the physical properties of stress. Volume averaging smooths out the stress distribution, and consequently it underestimate the high stress in a stress concentration region such as that near a dislocation core.

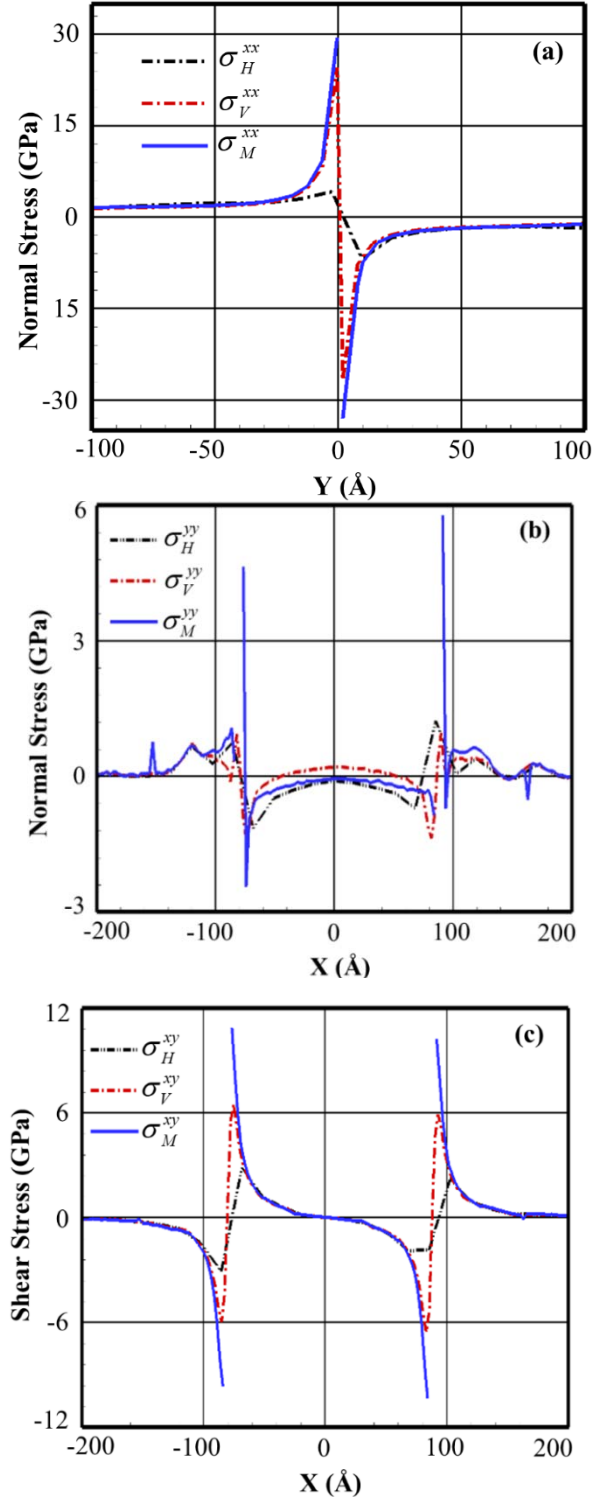


Fig.2. Stresses near dislocation cores: (a) σ^{xx} , (b) σ^{yy} and (c) σ^{xy} , where blue curves denoting mechanical stress components σ_M , red curves the virial stress σ_V , and black curves the Hardy stress σ_H .

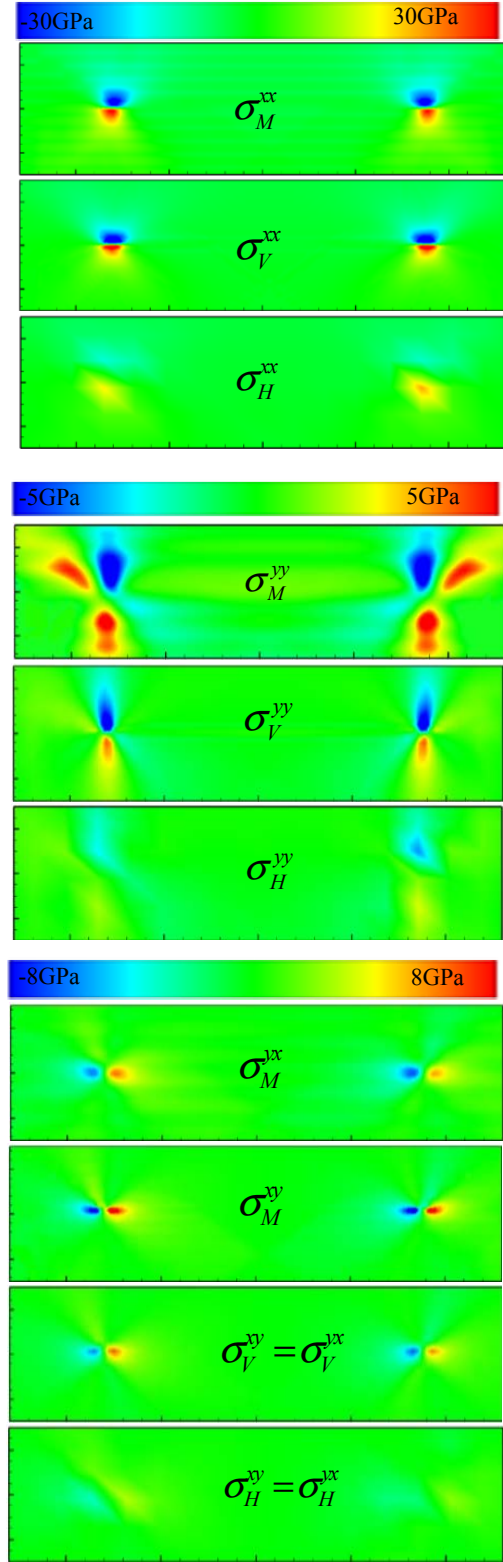


Fig. 3 Stress distribution in the XY planes showing different stress contours by different stress formulas; the size of each contour plot is 5nm by 20 nm.

4.2 Momentum and heat flux across interfaces

To quantify the failure of VA flux formulas in satisfying the momentum and energy conservation laws, we employ the method of ICM (Integral conservation law of momentum) and ICE (Integral conservation law of energy), developed in the works of the “Method of Plane”^{30,31}. In the interest of comparing the flux formulas for a many-body potential, a symmetrically structured 3D computer model is constructed to model a Si phononic crystal, as shown in Fig. 4. The simulation cell has dimension 2400 x 270 x 50 Å. Periodic boundary conditions are applied in the y and z directions of the model. The atomic interaction is described by the Stillinger-Weber potential⁵⁹.

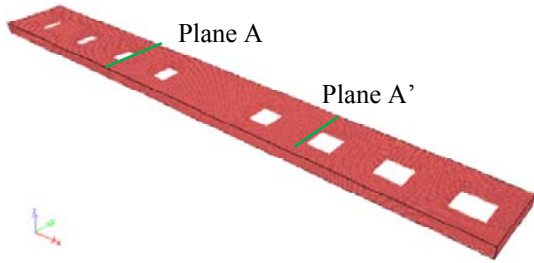


FIG.4 MD model of a holey silicon structure. The interface at which a plane intersects the model cross section to measure stress is denoted by the green line.

The fluxes are calculated using the following three formulas:

- (1) *Surface*: the surface formulas for local stress and heat flux defined in Eq.(19) and Eq. (21) with both potential and kinetic components.
- (2) *Virial*: the volume-averaged stress and heat flux formulas implemented in LAMMPS based on the virial theorem for stress and heat flux, respectively. The Hardy fluxes are not measured, since they are implemented in LAMMPS for two-body potentials only.
- (3) *ICM* or *ICE*: the momentum flux that satisfies the integral conservation law of momentum, or the energy flux that satisfies the integral conservation law of energy, for the atoms within a region that are bounded by planes A and A', or by plane A and the free surface at one end of the model, with the periodic boundary conditions in the y and z directions.

It should be noted that neither ICM nor ICE is a local flux formula. They calculate fluxes through relating the change of the total momentum or total energy in a region to the total momentum flux or energy flux across the entire surface enclosing the region. The formulas are employed in this work to calculate the

momentum and energy flux across the planes located at the interfaces A and A' because periodic boundary conditions are applied in the lateral directions.

To compare with ICM and ICE, the *Surface* fluxes are also measured at these planes, while the *virial* flux formulas are used with small volumes, several angstroms thick, encompassing the planes. If a flux formula fails to produce the ICM or ICE flux, it denotes a failure to satisfy the integral conservation law for the region enclosed by planes A and A' or by plane A and the free surface at the end of the model.

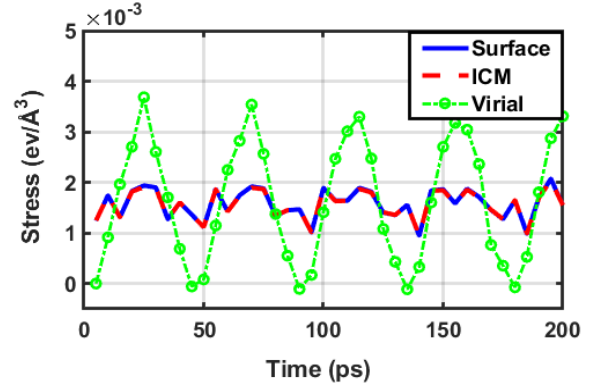


FIG.5 Stress responses calculated using three different formulas to a uniaxial tension averaged over plane A and 10^4 time steps (10 ps) per data point.

For the stress measurement, a MD simulation is performed under a uniaxial tension. The uniaxial tension is supplied as a constant source of momentum for particles near the ends of the model. The stresses, including both kinetic and potential components, are measured at the interface at plane A marked in Fig. 4. The stresses calculated using the three different formulas are plotted in Fig. 5. It is seen from Fig.5 that the *Surface* and *ICM* stress curves completely overlap. This means the *Surface* stress formula satisfies the momentum conservation law for the enclosed region. By contrast, the atomic virial stress curve is significantly different from the *ICM* stress curve. It fluctuates in time in a manner similar to the stress near a free surface reported in [58]. That the atomic virial stress fails in reproducing the *ICM* stress indicates a failure of the atomic virial stress formula to reproduce the momentum flux that satisfies the integral momentum conservation law.

For the energy flux measurement, MD simulation of the transient process of heat pulse propagation is performed. The energy fluxes measured using three different formulas are compared in FIG. 6. As can be seen from FIG. 6, the *Surface* formula and *ICE* produce identical curves that completely overlap. By contrast, the *virial* energy flux formula produces results that are drastically different from the *ICE* results.

Averaged over 20 fs, the *virial* results are still represented by spurious fluctuations. They also fail to reproduce the zero flux at the flux-free surface. Such results indicate the failure of the VA flux formulas for satisfying energy conservation as well as the flux boundary conditions.

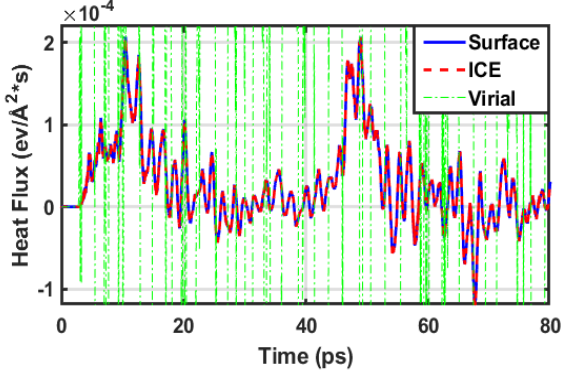


FIG.6 Energy flux during the transient simulation of the propagation of two heat pulses, input 40 ps apart, averaged over planes A and A' and 100 time steps (20 fs) per data point. Each pulse inputs a total of 32 eV over 4 fs and is then allowed to propagate.

V. WHY VA FLUX FORMULAS FAIL

The major difference between the IK point-function fluxes expressed in Eqs. (2)-(3) and the representative VA flux formulas defined in Eqs. (4)-(5) or (7)-(8) is just the difference between the Dirac δ distribution and a continuous weighting function. The consequences, as shown in above simulation results, are significant, leading to the failure of VA flux formulas in reproducing the physical definitions of fluxes and in satisfying the momentum and energy conservation laws. The fundamental reasons may be summarized as follows:

- (1) Volume averaging changes the fundamental nature of fluxes as a surface density

The VA formulas for stress tensor are no longer the “*stress vectors on three rectangular planes*”, which is the physical definition of stress tensor since Cauchy⁴³. There is in fact no description of stress vector in any VA stress formulas. Consequently, these formulas predict a stress tensor that is qualitatively and quantitatively different from Cauchy stress. For example, using the atomic virial stress formula σ_V and the Hardy stress formula σ_H with the bond function suggested by Hardy⁴, the contribution of a pair of interacting particles to the normal stress at atom k , shown in Fig. 7, yield very different values than the physical definition of mechanical stress σ_M , as shown in Eq.(32).

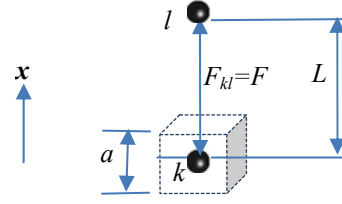


Fig.7 A pair of interaction force for calculation of its contribution to the stress tensor component σ^{xx} .

$$\begin{aligned}\sigma_V^{xx} &= \frac{F_{kl} r_{kl}}{V} = \frac{FL}{V} = \frac{FL}{a^3}, \\ \sigma_H^{xx} &= \frac{F_{kl} r_{kl} B(k, l, x)}{V} = \frac{F(a/2)}{V} = \frac{F}{2a^2}, \\ \sigma_M^{xx} &= \frac{F_{kl}}{A} = \frac{F}{a^2}\end{aligned} \quad (32)$$

While Cauchy stress only depends on the force acting on the surface element and the area of the element, both the atomic virial and the Hardy stress depend on the separation distance of the particles.

Volume averaging also changes the physical meaning of heat flux. VA heat flux formulas no longer represent the rate of heat flow across a surface per unit area. Instead, “the potential heat flux is the rate at which particle i is doing work on particle j , multiplied by the distance over which this energy is transferred”, as described in [60].

- (2) Volume averaging changes the balance between fluxes and conserved quantities

Energy or momentum conservation is a local process⁶¹. The law of conservation states that “*in the absence of any sources, the rate of change of a conserved quantity in a domain V is equal to the flux coming in from the enclosing surface of V* ”. The conserved quantities in integral conservation equations are extensive quantities that depend on the volume of the element, the change of which can only be balanced by fluxes across through the boundary of V . Without a surface in the flux formulas, they cannot describe the flux across the surface boundary of a volume element. Consequently, the dynamic balance between the change of momentum or energy in a volume element and the fluxes across the surface boundary cannot be established. It is well known that most VA formulas are derived to satisfy the volume-averaged differential conservation laws by equating the time derivative of a volume-averaged conserved variable to the divergence of a VA “flux”. However, such volume-averaged “flux” is not the flux of the volume-averaged conserved quantity. This thus leads to the failure of VA formulas in conserving the

momentum or energy, as demonstrated by the MD simulation results in Sec. IV.

- (3) Volume averaging changes the description of fluxes at surface boundaries

As a result of volume averaging, the VA flux formulas cannot satisfy flux boundary conditions, including flux-free boundaries or boundaries with prescribed fluxes. For example, in the absence of an external force or temperature, the VA formulas fail to produce zero stress at free surfaces, as reported by Zimmerman et al., cf. Fig. 8²⁷. On the other hand, VA stress formulas predict zero stress at a crack tip and a dislocation core as reported by Webb et al.,⁵⁷ contradicting with well-documented experimental observations for stress in stress localization regions.

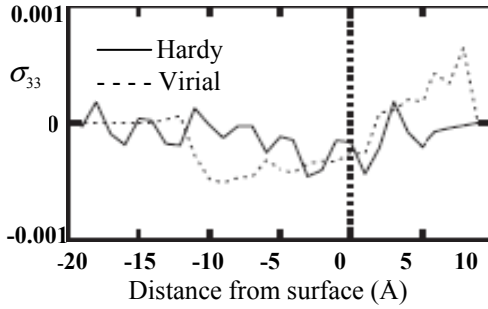


Fig. 8 Hardy and virial stress at zero temperature and pressure at and away from a stress-free surface⁵⁸;

- (4) Lack of a surface normal leads to misinterpretation of the directional properties of fluxes

The Cauchy stress tensor is a measure of the forces per unit area acting on three mutually perpendicular surface elements. A stress component, $\sigma^{\alpha\beta} = F^\alpha / A^\beta$, where A^β is the area of the surface element with normal \mathbf{e}^β , describes the α th component of the force acting per unit area on the surface element with normal \mathbf{e}^β . By contrast, the Hardy stress, as well as other VA stress formulas, calculates the dyadic product of the interaction force and interatomic distance per unit volume with $\sigma_{ij}^{\alpha\beta} = \sum_{i < j} F_{ij}^\alpha r_{ij}^\beta B(i, j, x)$. The two directions associated with the stress tensor are the interaction force vector and the inter-particle separation vector. This inconsistency is caused by the lack of a description of the normal of the surface element in the stress formula.

- (5) Volume averaging changes the applicability of the flux formulas

Volume averaging changes the properties of the stress tensor; it also make the resulting formulas inapplicable to finding the plane that has the maximum normal or shear stress, or to calculate the

stress vector acting on a given plane such as a slip plane or a cleavage plane of a crystal, in order to find yield strength or fracture stress of a material.

The VA heat flux formulas are also inapplicable for finding heat flux at a given surface such as a phase interface or a grain boundary in a material in order to calculate the thermal boundary resistance of material interfaces.

VI. SUMMARY

We have reviewed the historical developments that led to the unified physical concept of fluxes for transport phenomena. We have also demonstrated the failure of the popular VA flux formulas in producing the fluxes that are consistent with their physical definitions and the conservation laws. This work shows that replacing the Dirac δ with a volume weighting function changes the fundamental nature of fluxes as a surface density. As a result, the dynamic balance between the change of the total momentum or energy in a volume element and the fluxes across the surface boundary cannot be established. This then leads to the failure of VA flux formulas in satisfying the momentum and energy conservation laws as well as typical transport boundary conditions. In addition to being quantitatively unreliable, as demonstrated by the MD simulation results, the VA flux formulas also lose the applicability for being used to find the planes that have the largest or smallest fluxes, or to find the fluxes at a given surface or interface.

We have also used two different methods to derive formulas for instantaneous fluxes as a surface density for molecular systems with general many-body potentials. They are the IK formalism with the differential form of conservation laws¹ and a recently developed formalism based on the integral form of the conservation laws³⁷. These two approaches lead to identical flux formulas in the form of a line-plane intersection. Formulation and simulation results show that the surface flux formulas satisfy the conservation laws and transport boundary conditions, in addition to being fully consistent with the physical definitions of momentum flux and heat flux.

ACKNOWLEDGMENTS

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Appendix A: Spatial and time averages of the Dirac delta

A1. Volume average of Dirac δ

We define the averaged Dirac δ over a volume element of volume V as

$$\bar{\delta}_V(\mathbf{r}_k - \mathbf{x}) \equiv \frac{1}{V} \iiint_V \delta(\mathbf{r}_k - \mathbf{x}') d^3x' = \begin{cases} 1/V & \text{if } \mathbf{r}_k \in V \\ 0, & \text{otherwise} \end{cases} \quad (33)$$

A2. Line integral of Dirac delta

The difference between two Dirac δ -functions can be expressed, using the fundamental theorem for line integrals as,

$$\delta(\mathbf{r}_k - \mathbf{x}) - \delta(\mathbf{r}_l - \mathbf{x}) = \int_{L_{kl}} \nabla_{\phi} \delta(\phi - \mathbf{x}) d\phi = \nabla_{\mathbf{x}} \cdot \int_{L_{kl}} \delta(\phi - \mathbf{x}) d\phi \quad (34)$$

where L_{kl} represents a line segment from \mathbf{r}_k to \mathbf{r}_l , and the equation holds in distributional sense. Denote $\mathbf{n}_{kl} = (n_{kl}^x, n_{kl}^y, n_{kl}^z) = n_{kl}^{\alpha} \mathbf{e}^{\alpha}$ as the unit direction vector of L_{kl} and introduce a scalar \square such that $\phi - \mathbf{r}_k = \lambda(\mathbf{r}_l - \mathbf{r}_k) = \phi \mathbf{n}_{kl}$; the line integral can be parameterized by

$$\int_{L_{kl}} \delta(\phi - \mathbf{x}) d\phi = \mathbf{n}_{kl} \int_0^{|\mathbf{r}_{kl}|} \delta(\phi \mathbf{n}_{kl} + \mathbf{r}_k - \mathbf{x}) d\phi \quad (35)$$

A3. Surface-averaged line integral of Dirac delta

Consider a coordinate surface element A^z , centered at $\mathbf{x} = (x, y, z)$, with normal along the coordinate axis \mathbf{e}^z and area A^z . Integrating the line integral of the Dirac δ in Eq. (35) over a coordinate surface element A^z and using the sifting and the scaling properties of the Dirac δ , we obtain

$$\begin{aligned} \int_{L_{kl}} \bar{\delta}_A^z(\phi - \mathbf{x}) d\phi &= \frac{1}{A^z} \iint_{A^z} e^z dx' dy' \cdot \int_0^{|\mathbf{r}_{kl}|} \mathbf{n}_{kl} \delta(\phi \mathbf{n}_{kl} + \mathbf{r}_k - \mathbf{x}') d\phi \\ &= \frac{n_{kl}^z}{A^z} \iint_{A^z} dx' dy' \int_0^{|\mathbf{r}_{kl}|} \delta(\phi n_{kl}^x + r_k^x - x') \delta(\phi n_{kl}^y + r_k^y - y') \delta(\phi n_{kl}^z + r_k^z - z') d\phi \\ &= \frac{n_{kl}^z}{A^z} \int_0^{|\mathbf{r}_{kl}|} \delta\left(\phi + \frac{r_k^z - z'}{n_{kl}^z}\right) \iint_{A^z} \delta(\phi n_{kl}^x + r_k^x - x') \delta(\phi n_{kl}^y + r_k^y - y') dx' dy' d\phi \\ &= \frac{1}{A^z} \int_0^{|\mathbf{r}_{kl}|} \delta\left(\phi + \frac{r_k^z - z'}{n_{kl}^z}\right) d\phi \quad \text{if } r_{kl} \text{ intersects } A^z \\ &= \frac{1}{A^z} \int_0^{|\mathbf{r}_{kl}|} \delta\left(\phi + \frac{r_k^z - z'}{n_{kl}^z}\right) d\phi \quad \text{otherwise} \end{aligned} \quad (36)$$

where the solution includes the case when the line segment lies in the plane, i.e., $n_{kl}^z = 0$. For such a case, according to the theory of distributions, the distributional solution exists. This is consistent with the line-plane intersection theorem in analytic geometry; the intersection of a line and a plane can be the empty set, a point, or a line, cf. Fig. A. The value of

the integrals in Eq. (36) is zero only if there is no intersection.

A4. Line-plane intersection in time

The motion of particles across a surface is also a line-plane intersection problem. Since it takes a finite time for a particle to reach and cross a surface, and also since in atomistic simulations the equation of motion is solved step-by-step in discrete time intervals, we define the averaged Dirac δ over a coordinate surface element A^z and over the path of a particle during a simulation time-step T as

$$\begin{aligned} \bar{\delta}_{AT}^z(\mathbf{r}_k - \mathbf{x}) &\equiv \frac{1}{A^z T} \iint_{A^z} e^z dx' dy' \cdot \int_0^T \delta(\mathbf{r}_k - \mathbf{x}') \tilde{\mathbf{v}}_k d\tau \\ &= \frac{1}{A^z T} \tilde{\mathbf{v}}_k^z \int_0^T \delta(r_k^z + \tilde{\mathbf{v}}_k^z \tau - z') \iint_{A^z} \delta(r_k^x + \tilde{\mathbf{v}}_k^x \tau - x') \delta(r_k^y + \tilde{\mathbf{v}}_k^y \tau - y') dx' dy' d\tau \\ &= \frac{1}{A^z T} \tilde{\mathbf{v}}_k^z \int_0^T \delta\left(\tau - \frac{z' - r_k^z}{\tilde{\mathbf{v}}_k^z}\right) \iint_{A^z} \delta(r_k^x + \tilde{\mathbf{v}}_k^x \tau - x') \delta(r_k^y + \tilde{\mathbf{v}}_k^y \tau - y') dx' dy' d\tau \\ &= \frac{1}{A^z T} \tilde{\mathbf{v}}_k^z \int_0^T \delta\left(\tau - \frac{z' - r_k^z}{\tilde{\mathbf{v}}_k^z}\right) d\tau \quad \text{if } r_k(t + \tau) \in A^z \text{ for } \tau \in T \\ &= \frac{1}{A^z T} \tilde{\mathbf{v}}_k^z \int_0^T \delta\left(\tau - \frac{z' - r_k^z}{\tilde{\mathbf{v}}_k^z}\right) d\tau \quad \text{otherwise} \end{aligned} \quad (37)$$

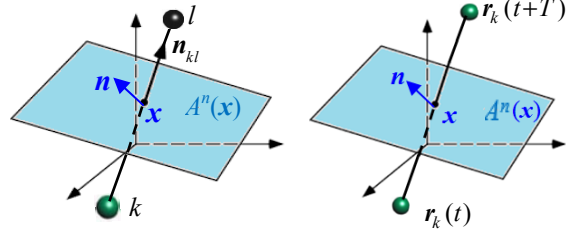


FIG.A (Left) Line L_{kl} in space and (right) \mathbf{r}_k in time intersect with the surface element A^n centered at \mathbf{x} .

Equation (36) can be extended to arbitrarily oriented surface elements. Using $dA = n^{\alpha} dA = e^{\alpha} dA^{\alpha}$ ($\alpha = 1, 2, 3$), the averaged line integral of Dirac δ over an arbitrary surface element at point \mathbf{x} can be expressed in terms of coordinate surface elements as

$$\begin{aligned} \int_{L_{kl}} \bar{\delta}_A^n(\phi - \mathbf{x}) d\phi &\equiv \frac{1}{A^n} \iint_{A^n} dA \cdot \int_{L_{kl}} \delta(\phi - \mathbf{x}') d\phi \\ &= \frac{1}{A^n} \iint_{A^n} n^{\alpha} e^{\alpha} dA \cdot \int_{L_{kl}} \delta(\phi - \mathbf{x}') d\phi \quad (38) \\ &= n^{\alpha} \int_{L_{kl}} \bar{\delta}_A^{\alpha}(\phi - \mathbf{x}) d\phi \end{aligned}$$

Also, if the time interval T is a simulation time step, we have

$$\int_{L_{kl}} \bar{\delta}_{AT}^{\alpha}(\phi - \mathbf{x}) d\phi = \int_{L_{kl}} \bar{\delta}_A^{\alpha}(\phi - \mathbf{x}) d\phi \quad (39)$$

Appendix B: Flux formulas using the differential conservation equations

B1. Particle force

For interatomic potentials that have well-defined site energies, i.e., $\Phi = \sum_i \Phi_i$, the total force on particle i can be expressed as

$$\mathbf{F}_i = -\frac{\partial \Phi}{\partial \mathbf{r}_i} = -\sum_j \frac{\partial \Phi_j}{\partial \mathbf{r}_i} = -\sum_{j(\neq i)} \frac{\partial \Phi_j}{\partial \mathbf{r}_i} \frac{\partial \Phi_i}{\partial \mathbf{r}_j} = -\sum_{j(\neq i)} \left(\frac{\partial \Phi_j}{\partial \mathbf{r}_i} \frac{\partial \Phi_i}{\partial \mathbf{r}_j} \right) \quad (40)$$

B2. Potential part of the point-function stress tensor and heat flux

The internal force density can be expressed, according to Eq.(40) and Eq.(34), as

$$\begin{aligned} \left\langle \sum_i \mathbf{F}_i \delta(\mathbf{r}_i - \mathbf{x}) \right\rangle &= \left\langle \sum_{i,j(\neq i)} \left(\frac{\partial \Phi_j}{\partial \mathbf{r}_i} \frac{\partial \Phi_i}{\partial \mathbf{r}_j} \right) \delta(\mathbf{r}_i - \mathbf{x}) \right\rangle \\ &= \left\langle \sum_{i,j(\neq i)} \frac{\partial \Phi_i}{\partial \mathbf{r}_j} (\delta(\mathbf{r}_i - \mathbf{x}) - \delta(\mathbf{r}_j - \mathbf{x})) \right\rangle, \quad (41) \\ &= \nabla_x \cdot \left\langle \sum_{i,j(\neq i)} \frac{\partial \Phi_i}{\partial \mathbf{r}_j} \int_{L_{ij}} \delta(\varphi - \mathbf{x}) d\varphi \right\rangle \end{aligned}$$

The potential part of the point-function stress can thus be expressed, using the relationship between stress and internal force, as

$$\bar{\sigma}_{\text{pot}}^{\text{point}}(\mathbf{x}, t) = \left\langle \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int_{L_{kl}} \delta(\varphi - \mathbf{x}) d\varphi \right\rangle. \quad (42)$$

Similarly, with

$$\begin{aligned} \left\langle \sum_k \dot{E}_k \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle &= \left\langle \sum_k [m_k \mathbf{v}_k \cdot \dot{\mathbf{v}}_k + \dot{\Phi}_k] \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle \\ &= \left\langle \sum_k [\mathbf{F}_k \cdot \mathbf{v}_k + \sum_l \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \mathbf{v}_l] \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle \\ &= \left\langle \sum_{k,l} \left[-\frac{\partial \Phi_l}{\partial \mathbf{r}_k} \cdot \mathbf{v}_k + \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l \right] \delta(\mathbf{r}_k - \mathbf{x}) \right\rangle, \quad (43) \\ &= \left\langle \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l [\delta(\mathbf{r}_k - \mathbf{x}) - \delta(\mathbf{r}_l - \mathbf{x})] \right\rangle \\ &= \nabla_x \cdot \left\langle \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l \int_{L_{kl}} \delta(\varphi - \mathbf{x}) d\varphi \right\rangle \end{aligned}$$

we obtain

$$\begin{aligned} \bar{q}_{\text{pot}}^{\text{point}} &= \left\langle \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l \int_{L_{kl}} \delta(\varphi - \mathbf{x}) d\varphi \right\rangle - \bar{\sigma}_{\text{pot}}^{\text{point}} \cdot \mathbf{v} \\ &= \left\langle \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \tilde{\mathbf{v}}_l \int_{L_{kl}} \delta(\varphi - \mathbf{x}) d\varphi \right\rangle. \quad (44) \end{aligned}$$

B3 Surface-averaged stress vector and heat flux

Averaging the instantaneous potential and kinetic part of fluxes over a surface element β and a time-step interval T (the path of a particle during time-interval T), we obtain the stress vector and heat flux vector on the surface element β , according to Eq. (42), Eq.(13), Eq.(44), and Eq.(15), respectively, as

$$\begin{aligned} \mathbf{t}_{\text{pot}}(\mathbf{x}, \mathbf{e}^\beta) &= \frac{1}{A^\beta} \frac{1}{T} \int_0^T \iint_{A^\beta} \mathbf{e}^\beta dA \cdot \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int_{L_{kl}} \delta(\varphi - \mathbf{x}') d\varphi d\tau \\ &= \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int_{L_{kl}} \bar{\delta}_{AT}^\beta(\varphi - \mathbf{x}) d\varphi \end{aligned} \quad (45)$$

$$\begin{aligned} \mathbf{t}_{\text{kin}}(\mathbf{x}, \mathbf{e}^\beta) &= -\frac{1}{A^\beta} \frac{1}{T} \int_0^T \iint_{A^\beta} \mathbf{e}^\beta dA \cdot \sum_k m_k \tilde{\mathbf{v}}_k \delta(\mathbf{r}_k - \mathbf{x}') d\tau \\ &= -\sum_k m_k \tilde{\mathbf{v}}_k \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}) \end{aligned} \quad (46)$$

$$\begin{aligned} \mathbf{q}_{\text{pot}} &= \frac{1}{A^\beta} \frac{1}{T} \int_0^T \iint_{A^\beta} \mathbf{e}^\beta dA \cdot \sum_{k,l(\neq k)} \frac{\partial \Phi_l}{\partial \mathbf{r}_k} \cdot \tilde{\mathbf{v}}_k \int_{L_{kl}} \delta(\varphi - \mathbf{x}') d\varphi d\tau \mathbf{e}^\beta \\ &= \sum_{k,l(\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \tilde{\mathbf{v}}_l \int_{L_{kl}} \bar{\delta}_{AT}^\beta(\varphi - \mathbf{x}) d\varphi \end{aligned} \quad (47)$$

$$\begin{aligned} \mathbf{q}_{\text{kin}} &= -\frac{1}{A^\beta} \frac{1}{T} \int_0^T \iint_{A^\beta} \mathbf{e}^\beta dA \cdot \sum_k E_k \tilde{\mathbf{v}}_k \delta(\mathbf{r}_k - \mathbf{x}) d\tau \mathbf{e}^\beta - \bar{\sigma}_{\text{kin}} \cdot \mathbf{v} \\ &= -\frac{1}{A^\beta} \int_0^T \iint_{A^\beta} \left[\left(\frac{1}{2} m_k \tilde{\mathbf{v}}_k^2 + \Phi_k + \frac{1}{2} m_k \mathbf{v}_k^2 \right) \tilde{\mathbf{v}}_k \delta(\mathbf{r}_k - \mathbf{x}') d\tau \mathbf{e}^\beta dA \right] \\ &= -\sum_k \left(\frac{1}{2} m_k \tilde{\mathbf{v}}_k^2 + \Phi_k \right) \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}) \end{aligned} \quad (48)$$

where the surface element β has area A^β and surface normal \mathbf{e}^β ; $E_k = \frac{1}{2} m_k \mathbf{v}_k^2 + \Phi_k = \frac{1}{2} m_k \tilde{\mathbf{v}}_k^2 + m_k \tilde{\mathbf{v}}_k \cdot \mathbf{v} + \frac{1}{2} m_k \mathbf{v}^2 + \Phi_k$. The stress tensor can then be obtained, using Eq. (11), as $\sigma_{\text{pot}}^{\alpha\beta}(\mathbf{x}, t) = \bar{\sigma}_{\text{pot}}^\alpha(\mathbf{x}, t, \mathbf{e}^\beta)$.

Appendix C: Flux formulas using the integral conservation equations

The total force acting on an atom can be expressed in terms of site energy, Φ_k , using Eq.(40), or in terms of interaction force using $\mathbf{F}_k = \sum_l \mathbf{F}_{kl}$. Utilizing the fact that the total internal force in a volume element is equal to the total interaction forces crossing the bounding surface, we have the following two different expressions for the total internal force in the volume element V ,

$$\begin{aligned} \frac{1}{T_0} \int_0^T d\tau \iiint_V d^3x' \sum_k F_k \delta(\mathbf{r}_k - \mathbf{x}') &= \frac{1}{T_0} \int_0^T d\tau \iiint_V \sum_{k \in V, l \in V} \left(\frac{\partial \Phi_k}{\partial \mathbf{r}_l} - \frac{\partial \Phi_l}{\partial \mathbf{r}_k} \right) \delta(\mathbf{r}_k - \mathbf{x}') d^3x' \\ &= \iiint_{\partial V} \sum_{k, l (\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int d\varphi \bar{\delta}_{AT}^n(\varphi - \mathbf{x}') dA^n \end{aligned} \quad (49)$$

$$\begin{aligned} \frac{1}{T_0} \int_0^T d\tau \iiint_V d^3x' \sum_k F_k \delta(\mathbf{r}_k - \mathbf{x}') &= \frac{1}{T_0} \int_0^T d\tau \iiint_V \sum_{k \in V, l \in V} F_{kl} \delta(\mathbf{r}_k - \mathbf{x}') d^3x' \\ &= \iiint_{\partial V} \sum_{k < l} F_{kl} \int d\varphi \bar{\delta}_{AT}^n(\varphi - \mathbf{x}') dA^n \end{aligned} \quad (50)$$

where the area-averaged path integral of Dirac δ is used to describe the interaction force across the surface element dA^n whose normal is \mathbf{n} .

The conservation law of linear momentum for a volume element in the absence of body force states that the time rate of change of the linear momentum within V equals to the momentum flux across the enclosing surface ∂V , i.e.,

$$\frac{\partial}{\partial t} \iiint_V \rho \mathbf{v} d^3x' = \iiint_{\partial V} t d^2x' - \iiint_{\partial V} \rho \mathbf{v} \mathbf{v} \cdot d\mathbf{A} \quad (51)$$

The time rate of change of the linear momentum within V can also be derived by applying Newton's second law to the particles in V . It follows

$$\begin{aligned} \frac{\partial}{\partial t} \sum_k m_k \mathbf{v}_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) &= \sum_k \frac{\partial}{\partial t} (m_k \mathbf{v}_k) \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) \\ &+ \sum_k m_k \mathbf{v}_k \frac{\partial}{\partial t} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) \end{aligned} \quad (52)$$

The first term can be derived using Newton's second law as

$$\begin{aligned} \sum_k \frac{\partial}{\partial t} (m_k \mathbf{v}_k) \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) &= \sum_k \mathbf{F}_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) \\ &= \frac{1}{VT_0} \int_0^T d\tau \iiint_V \left\{ \sum_{k, l (\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int d\varphi \delta(\varphi - \mathbf{x}') d^2x' d\tau \right\} \\ &= \frac{1}{VT_0} \iiint_V \sum_{k, l (\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int d\varphi \bar{\delta}_{AT}^n(\varphi - \mathbf{x}') dA^n \end{aligned} \quad (53)$$

The second term is a distributional derivative, which can be obtained, according to the theory of distributions⁶², as

$$\begin{aligned} \sum_k m_k \mathbf{v}_k \frac{\partial}{\partial t} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) &= \frac{1}{T_0} \int_0^T d\tau \iiint_V \left\{ \sum_k m_k \mathbf{v}_k \delta(\mathbf{r}_k - \mathbf{x}') \cdot \mathbf{n} d^2x' \right\} \\ &= \frac{1}{VT_0} \int_0^T d\tau \iiint_V \left\{ \sum_k m_k \mathbf{v}_k \delta(\mathbf{r}_k - \mathbf{x}') + \rho \mathbf{v} \mathbf{v} \cdot \mathbf{n} d^2x' \right\} \end{aligned} \quad (54)$$

Comparing Eqs. (52)-(54) with Eq.(51) allows one to arrive at the following operator equivalence

$$\mathbf{t}(\mathbf{x}, \mathbf{n}) = \sum_{k, l (\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \int \bar{\delta}_{AT}^n(\varphi - \mathbf{x}) d\varphi - \sum_k m_k \tilde{\mathbf{v}}_k \bar{\delta}_{AT}^n(\mathbf{r}_k - \mathbf{x}). \quad (55)$$

The stress tensor can thus be obtained, according Eq.(38), in terms of site energies as

$$\sigma^{\alpha\beta}(\mathbf{x}, \mathbf{t}) = - \sum_k m_k \tilde{\mathbf{v}}_k^\alpha \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}) + \sum_{k, l (\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l^\alpha} \int \bar{\delta}_{AT}^\beta(\varphi - \mathbf{x}) d\varphi, \quad (56)$$

or in terms of the interaction force as

$$\sigma^{\alpha\beta}(\mathbf{x}, \mathbf{t}) = - \sum_k m_k \tilde{\mathbf{v}}_k^\alpha \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}) + \sum_{k < l} F_{kl}^\alpha \int \bar{\delta}_{AT}^\beta(\varphi - \mathbf{x}) d\varphi. \quad (57)$$

Similarly, surface-averaged heat flux can be derived based on the integral form of the energy conservation for the volume element centered at \mathbf{x} ³⁷

$$\begin{aligned} \frac{\partial}{\partial t} \iiint_V \rho E d^3x' &= \iiint_{\partial V} (\mathbf{q}_{\text{pot}} + \sigma_{\text{pot}} \cdot \mathbf{v}) \cdot d\mathbf{A} \\ &+ \iiint_{\partial V} (\mathbf{q}_{\text{kin}} + \sigma_{\text{kin}} \cdot \mathbf{v} - \rho E \mathbf{v}) \cdot d\mathbf{A} \end{aligned} \quad (58)$$

The time rate of change of the energy density can also be expressed in terms of molecular variables as

$$\frac{\partial}{\partial t} \sum_k E_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) = \sum_k \dot{E}_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) + \sum_k E_k \frac{\partial}{\partial t} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}), \quad (59)$$

in which the first term in the right hand side is a classical derivative while the second term is a distributional derivative, with

$$\begin{aligned} \sum_k \dot{E}_k \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) &= \sum_k (m_k \mathbf{v}_k \cdot \dot{\mathbf{v}}_k + \dot{\Phi}_k) \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) \\ &= \sum_k \left(\mathbf{F}_k \cdot \mathbf{v}_k + \sum_l \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \dot{\mathbf{r}}_l \right) \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) \\ &= \sum_{k, l} \left(- \frac{\partial \Phi_l}{\partial \mathbf{r}_k} \cdot \mathbf{v}_k + \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l \right) \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) \\ &= \frac{1}{TV} \iiint_V \left\{ \sum_{k, l (\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l \int \delta(\varphi - \mathbf{x}') d\varphi \right\} \cdot \mathbf{n} d^2x' \\ &= \frac{1}{TV} \iiint_V \left(\sum_{k, l (\neq k)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \mathbf{v}_l \int d\varphi \delta(\varphi - \mathbf{x}') \right) \cdot \mathbf{n} d^2x' \end{aligned} \quad (60)$$

and

$$\begin{aligned} \sum_k E_k \frac{\partial}{\partial t} \bar{\delta}_{VT}(\mathbf{r}_k - \mathbf{x}) &= \frac{1}{T_0} \int_0^T d\tau \int \sum_{k \in V} \frac{1}{V} E_k \delta(\mathbf{r}_k - \mathbf{x}') \cdot \mathbf{n} d^2x' \\ &= \frac{1}{T_0} \int_0^T d\tau \int \sum_k \left(\frac{1}{2} m_k \tilde{\mathbf{v}}_k^2 + m_k \tilde{\mathbf{v}}_k \cdot \mathbf{v} + \Phi_k \right) (\tilde{\mathbf{v}}_k + \mathbf{v}) \delta(\mathbf{r}_k - \mathbf{x}') \cdot \mathbf{n} d^2x' \\ &= \frac{1}{TV_0} \int_0^T d\tau \iiint_V \left(\sum_k \left(\frac{1}{2} m_k \tilde{\mathbf{v}}_k^2 + \Phi_k \right) \tilde{\mathbf{v}}_k \delta(\mathbf{r}_k - \mathbf{x}') - \sigma_{\text{kin}} \cdot \mathbf{v} + \rho E \mathbf{v} \right) \cdot \mathbf{n} d^2x' \end{aligned} \quad (61)$$

Comparing Eqs.(60)-(61) with Eq. (58), the heat flux vector can be obtained as a surface density as

$$q^\beta(\mathbf{x}, t) = -\sum_k \left(\frac{1}{2} m_k \tilde{\mathbf{v}}_k^2 + \Phi_k \right) \bar{\delta}_{AT}^\beta(\mathbf{r}_k - \mathbf{x}) \\ + \sum_{k, l (k \neq l)} \frac{\partial \Phi_k}{\partial \mathbf{r}_l} \cdot \tilde{\mathbf{v}}_l \int_{L_{kl}} \bar{\delta}_{AT}^\beta(\boldsymbol{\varphi} - \mathbf{x}) d\boldsymbol{\varphi} \quad (62)$$

It is seen that the stress tensor in Eq. (56) and the heat flux in Eq. (62) are respectively identical to the stress tensor and heat flux obtained in appendix B.

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