A generalized Irving-Kirkwood formula for the calculation of stress in molecular
dynamics models

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In non-equilibrium molecular dynamics (MD) simulations, continuum mechanics quantities can be computed from the position and momentum of the particles based on the classical Irving-Kirkwood formalism. For practical purposes, the implementations of Irving-Kirkwood formulas often involve a spatial averaging using a smooth kernel function. The resulting formula for the stress has been known as Hardy stress. Usually results obtained this way still need to be further processed to reduce the fluctuation, e.g., by ensemble or time averaging. In this paper we extend Hardy’s formulas by systematically incorporating both spatial and temporal averaging into the expression of continuum quantities. The derivation follows the Irving-Kirkwood formalism, and the average quantities still satisfy conservation laws in continuum mechanics. We will discuss the selection of kernel functions and present several numerical tests.

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I. MOTIVATION AND INTRODUCTION

In molecular dynamics (MD) simulations, one generates particle position and momentum by solving the Newton’s equations of motion. However, what is often of interest is not the trajectories themselves, but rather some average quantities. For example, in many molecular simulations, one needs to compute quantities such as the strain, stress and energy fluxes, which are part of continuum mechanics models. For many problems, this is a very important procedure to interpret and understand mechanical properties and dynamics behavior of the system. Examples include molecular models of solids\textsuperscript{55,63,64,74,75,77,78,84,102}, fluids\textsuperscript{54,67,69,73,91}, and glass systems\textsuperscript{72,96}.

For homogeneous systems, one commonly used formula in MD is the virial stress, derived by Clausius in 1870\textsuperscript{59} and later by Tsai\textsuperscript{95} for the case of finite temperature. In this case the expressions for most continuum quantities can be derived either from the second law of thermodynamics or from linear response theory, and many techniques are available for the implementation of such formulas\textsuperscript{53,68}.

Such problem becomes much more difficult for non-homogeneous systems, or systems out-of-equilibrium. For example, the applicability of the virial stress is in doubt, and the limitation has been discussed in\textsuperscript{60,99}. For general non-equilibrium particle systems, Irving and Kirkwood\textsuperscript{76} (IK) were the earliest to derive correct expressions of local stress tensor and heat current density in terms of molecular degrees of freedom. The IK formalism starts with the Liouville equation for a many-particle system and considers point mass, momentum and energy distributions. The divergence of the stress was obtained as an ensemble average\textsuperscript{76}. Noll\textsuperscript{89} (English translation\textsuperscript{79}) provided a rigorous mathematical foundation for the IK formalism. In particular, they provided an explicit form of the local stress.

Due to the Dirac delta functions and ensemble averages involved in the IK expressions, direct numerical implementation is not straightforward. Hardy\textsuperscript{70} modified the Irving-Kirkwood’s formula by employing regular functions, called kernel functions, to replace the Dirac delta function. The kernel function also plays the role of spatial averaging. A few criteria were established for the selection of regularized functions\textsuperscript{71,93}. Independently, Murdoch and coworkers\textsuperscript{85,86} have considered spatial and temporal averaging to avoid the use of delta functions and ensemble averages in the original IK formalism. More recently, Zimmerman et al studied the accuracy of the Hardy’s expression of stress with numerical experiments\textsuperscript{101}. 

\[2\]
They also derived expressions for the first Piola-Kirchhoff stress\textsuperscript{100}, which is often used in solid mechanics.

In the calculation procedure of Hardy stress, the kernel functions play the role of sampling in space. In most cases, the stress obtained this way still exhibits fluctuations. Therefore, time averaging is often needed to compute the desired average, especially when only one MD realization is available. Murdoch and Bedeaux\textsuperscript{86} discussed how the time averaging can be done after the spatial average is obtained. However, this step was taken as a postprocessing step, and it is not part of the derivation that originates from the IK formalism. Motivated by this observation, we propose to generalize the IK formalism to systematically incorporate time average into the definition of continuum quantities.

In our formulation of the stress, we still follow the conservation of momentum to derive the expression of stress as in\textsuperscript{70,85}. However, we allow the kernel function to be time-dependent so that time averaging is built into the formulation. In the case when the kernel function is a Dirac delta function in time, our formula is reduced to Hardy stress. On the other hand, when the kernel function is a separable function, our expressions coincide with those of Murdoch and Bedeaux\textsuperscript{86}. For non-separable kernels, however, our expressions are completely new.

The IK formalism is an important tool in coarse-graining molecular dynamics models. In its original form, where field variables are expressed in terms of point distributions, the IK equations are equivalent to the Newton’s equations of motion, \textit{i.e.}, the MD model. This is the case when the support of the kernel function reduces to one point. On the other hand, when the support of the kernel function goes to infinity, it is generally expected that the average quantities will correspond to those in continuum mechanics. One of the appealing features of the IK formalism is that conservation laws in continuum mechanics is maintained. This is important to guarantee that in the limit of infinite sample sizes, continuum mechanics models are recovered. This limiting procedure has been analyzed mathematically in\textsuperscript{90,94}. It is also possible to vary the support of the kernel functions and consider models at intermediate scales. For example, based on the IK formalism, the connection to micromorphic models has been investigated in\textsuperscript{57,58}.

From a computational viewpoint, the IK type of formalism provides a general framework for developing multiscale methods that couple molecular dynamics and continuum mechanics to capture processes that occur over multiple physical scales, which has recently been a very active area of research\textsuperscript{80-82,87,88,92}. The challenges in developing a consistent coupling scheme
are mainly due to the fact that

1. MD is a discrete model while macroscale mechanics models are often continuum description,

2. particle position and momentum usually do not correspond directly to continuum quantities;

3. there are very few known models at intermediate scales.

The IK type of formalism can overcome many of these major difficulties. It maps discrete particles to a continuous distributions of continuum quantities. In addition it provides a smooth transition from molecular to continuum scales when the support of the kernel varies from zero to infinity.

In this paper, the new formulas will be tested in several numerical experiments. In addition to the expressions of stress, the IK formalism also allows us to define deformation gradient and the strain tensor. We will study the sampling error for the strain tensor in the numerical experiments as well.

The rest of the paper is organized as follows: In section II we review the derivation of Hardy stress that followed from the IK formalism. Then in section II D, we present the generalized Irving-Kirkwood formulation and the expression of stress. Finally in section III, we show the results of the numerical tests.

II. THE IRVING-KIRKWOOD FORMULATION FOR THE STRESS CALCULATION

A. Conservation Laws in Continuum Mechanics

A strong motivation in the IK formalism has been the form of continuum mechanics models. Continuum mechanics models can be formulated as conservation laws, in the form of mass, momentum and energy conservation. In continuum mechanics, these conservation laws can be formulated in both Lagrangian (reference) coordinate or Eulerian (current) coordinate. Here we choose to work with the reference coordinate, which is typical in solid mechanics, and all the following numerical tests are done using MD models for solid materials. We discuss the formulation in Eulerian coordinate in the appendix IV.
To begin with, we let $X \in \mathbb{R}$ represent a point in the reference frame, and after deformation, the point is displaced to $x$. We let $u = x - X$ be the displacement and $F = \frac{\partial x}{\partial X}$ be the deformation gradient. The continuum mechanics models are often written as follows\textsuperscript{61},

$$\frac{\partial}{\partial t} F = \nabla_x \cdot \mathbf{v},$$
$$\frac{\partial}{\partial t} q = \nabla_x \cdot \sigma,$$
$$\rho_0 \frac{\partial}{\partial t} e = \nabla_x \cdot J.$$  \hspace{1cm} (1)

Here $\rho_0$ is the initial density, $q$ is the momentum, $e$ is the specific energy, and $J$ is energy flux. The first equation (1) describes the time evolution of the deformation; the second and third equations are conservation of momentum and energy. Meanwhile, $\sigma$ is the first Piola-Kirchhorff stress tensor. In this paper, we primarily discuss the calculation of this stress. The calculation of energy flux is similar.

In molecular dynamics (MD) models, we may also associate the $i$-th atom in the system with a reference position, denoted by $X_i$. Similar to the formulation of continuum mechanics models, we let $x_i$ be the current position, and its displacement be $u_i = x_i - X_i$. The motion of the atoms obey the Newton’s second law:

$$m_i \ddot{x}_i = -\nabla_{x_i} V,$$  \hspace{1cm} (2)

where $m_i$ is the mass of the $i$-th atom and $V = V(x_1, x_2, \cdots, x_N)$ is the interatomic potential.

For most empirical potentials for solids, the energy can be written as the sum of the energy at each atom,

$$V = \sum_i V_i.$$  \hspace{1cm} (3)

In addition, the force can be decomposed as follows,

$$f_i = \sum_{j \neq i} f_{ij}, \quad f_{ij} = -f_{ji}.$$  \hspace{1cm} (4)

Notice that such decomposition does not imply that the interaction is pairwise. This decomposition exists even for multi-body interactions. For instance for the embedded-atom model, the expression of $f_{ij}$ is given by (29). For three-body interactions, see\textsuperscript{56,80} for details on how to obtain such force decomposition.

In deriving the atomic expression of stress, equation (4) has been an essential assumption in the IK formalism, and most of the subsequent work mentioned above. The recent work of
Admal and Tadmor\textsuperscript{52} discussed how this can be done in general. Another interesting issue raised in\textsuperscript{52} is that the decomposition (4) is not unique in general. As a result, the definition of stress the follows from this decomposition may be ambiguous. But it is expected that as the sample size increases, different choices will lead to the same stress value\textsuperscript{52}.

**B. Virial stress**

For a molecular system at equilibrium, the virial stress is the most commonly used definitions of stress in MD system. This stress is developed based on a generalization of the virial theorem\textsuperscript{95} for gas pressure. It is an average over the chosen volume (see more discussions in\textsuperscript{99}):

\[
\sigma^v = \frac{1}{2 \Omega} \sum_{j \neq i} X_{ij} \otimes f_{ij}
\]

with \(\Omega\) being the volume of the system, and \(X_{ij} = X_i - X_j\). Notice that the stress defined by this formula may not be symmetric, and it is different from that of the Cauchy stress. More importantly, there is no kinetic contribution to the stress, in contrast to the expression of Cauchy stress.

**C. The Irving-Kirkwood formulation and the Hardy stress**

For systems out of equilibrium, one is often interested in a local stress at certain point in space and time, and clearly, the virial stress is not adequate. In this case, the stress can be defined base on the Irving-Kirkwood formalism\textsuperscript{76}. This type of formulation begins with the definition of the following quantities,

\[
\begin{align*}
\tilde{\rho}(X) &= \sum_i m_i \varphi(X - X_i), \\
\tilde{q}(X, t) &= \sum_i m_i v_i(t) \varphi(X - X_i), \\
\tilde{e}(X, t) &= \frac{1}{2} \sum_i (m_i v_i^2 + V_i) \varphi(X - X_i).
\end{align*}
\]

Here \(\varphi\) can be considered as a weight function. We require that its integral be 1. In the original Irving-Kirkwood’s work, the Dirac delta function was used, and the formula for the stress was derived following the \(N\)-particle Liouville equation. Equivalently, one can follow
the conservation laws in the continuum model to obtain the expressions of the stress and energy flux. This will be the approach taken in this paper.

Subsequently regular functions, denoted here by \( \varphi \), have been used\(^{70,86,101} \) to replace the Dirac delta function, for the purpose of easier implementation. In particular, Hardy has established a few criteria\(^9^3 \) as guidelines for selecting \( \varphi \):

- \( \varphi(X_i - X) \) has its maximum at \( X_i = X \).

- \( \varphi(X_i - X) \to 0 \) as \( |X_i - X| \to \infty \).

- \( \varphi(X_i - X) \) is smooth and non-negative.

- \( \int_{\mathbb{R}^3} \varphi(X_i - X) dX = 1 \).

We remark that the expressions due to Hardy can be viewed as a realization of those in the original Irving-Kirkwood. In fact, for each formula in the IK formalism, instead of taking the ensemble average, one can multiply the expression by the smooth function \( \varphi \), and integrate over \( X \), which will yield the Hardy’s formulas. This is also the case for the stress formulas that follow from these definitions of field variables. It is for these reason that we do not distinguish the IK and Hardy’s formulation.

Starting with the second equation in (6), we can derive the expression of stress following the conservation laws (1). Taking the time derivative, we find that,

\[
\frac{\partial}{\partial t} \tilde{q} = \frac{\partial}{\partial t} \sum_{i=1}^{N} m_i v_i \varphi(X - X_i),
\]

\[
= \sum_{i=1}^{N} f_i \varphi(X - X_i). \tag{7}
\]
Using (4), we can proceed as follows,

\[
\frac{\partial}{\partial t} \tilde{q} = \sum_{i=1}^{N} \sum_{j \neq i} \frac{1}{2} f_{ij} \left[ \varphi(X - X_i) + \varphi(X - X_i) \right]
\]

\[
= \sum_{i=1}^{N} \sum_{j \neq i} \frac{1}{2} f_{ij} \varphi(X - X_i) + \sum_{i=1}^{N} \sum_{j \neq i} \frac{1}{2} f_{ij} \varphi(X - X_i)
\]

\[
= \sum_{i=1}^{N} \sum_{j \neq i} \frac{1}{2} f_{ij} \varphi(X - X_i) + \sum_{i=1}^{N} \sum_{j \neq i} \frac{1}{2} f_{ji} \varphi(X - X_j)
\]

\[
= \sum_{i=1}^{N} \sum_{j \neq i} \frac{1}{2} f_{ij} \left[ \varphi(X - X_i) - \varphi(X - X_j) \right]
\]

(8)

At this point, we define

\[
b_{ij}(X) = \int_{0}^{1} \varphi(X - (X_i + \lambda X_{ji})) d\lambda,
\]

(9)

with \( X_{ji} = X_i - X_j \). Then we have,

\[
\frac{\partial}{\partial t} \tilde{q} = \sum_{i=1}^{N} \frac{1}{2} \sum_{j \neq i} -f_{ij} X_{ij} \cdot \nabla b_{ij}(X)
\]

\[
= \nabla \cdot \left( -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} f_{ij} \otimes X_{ij} b_{ij}(X) \right).
\]

(10)

Now we compare this balance equation with the moment conservation in the continuum mechanics model (1), and we define the stress, called the Hardy stress \( \sigma^{\text{Hardy}} \). It is given by,

\[
\sigma^{\text{Hardy}}(X, t) = -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} f_{ij} \otimes X_{ij} b_{ij}(X).
\]

(11)

With the stress defined this way, the conservation of momentum is retained,

\[
\frac{\partial}{\partial t} \tilde{q} = \nabla \cdot \sigma^{\text{Hardy}}.
\]

(12)

**Remark II.1** If the function \( \varphi(X) = \delta(X) \), then equation (7) or (12) implies that \( m\ddot{x}_i = f_i \). Namely it is consistent with the MD model. It is generally expected that when the support of the kernel function goes to infinity, equation (7) will lead to a continuum mechanics model.
Similarly we have the energy flux,

\[ J_{\text{Hardy}}(X, t) = -\frac{1}{2} \sum_i \sum_{j \neq i} f_{ij}(v_i + v_j) \otimes X_{ij} b_{ij}(X). \]  

(13)

This procedure for deriving the atomic expression of stress can be found in\textsuperscript{70,86} for the Cauchy stress and\textsuperscript{80} for the first Piola-Kirchhoff stress. Our derivation will follow the same procedure. The function \( \varphi \) will be referred to as a kernel function. Several possible choices will be considered. It is often convenient to start with a non-dimensional, compactly supported function \( \varphi_0 \), and then let,

\[ \varphi(X) = \frac{1}{r_c} \varphi_0 \left( \frac{X}{r_c} \right). \]  

(14)

Here \( r_c \) is a scaling factor that determines the sample size.

In addition to the stress, one may also define the displacement field and the deformation gradient from the atomic positions. For example, one may define,

\[ \tilde{u}(X, t) = \sum_{i=1}^{N} u_i(t) \varphi(X - X_i), \]  

\[ \tilde{v}(X, t) = \sum_{i=1}^{N} v_i(t) \varphi(X - X_i). \]  

(15)

From this expression of the displacement, we can obtain the deformation gradient,

\[ F = I + E, \quad E \stackrel{\text{def}}{=} \nabla_X \tilde{u} = \sum_i u_i \otimes \nabla_X \varphi(X - X_i). \]  

(16)

The IK formalism, however, suggests a different formula. Following (6). We should define a continuous displacement field as follows,

\[ \tilde{u}(X, t) = \frac{1}{\tilde{\rho}} \sum_{i=1}^{N} m_i u_i(t) \varphi(X - X_i). \]  

(17)

One can easily check that this formula is consistent with the third formula in (6). In particular we have \( \tilde{q} = \tilde{\rho} \frac{\partial}{\partial t} \tilde{u} \).

Using this formula, we can define the deformation gradient,

\[ \nabla_X \tilde{u} = \frac{\nabla_X \tilde{q}}{\tilde{\rho}} - \frac{\tilde{q}}{\tilde{\rho}^2} \nabla_X \tilde{\rho}. \]  

(18)

Here the gradient of \( \tilde{\rho} \) and \( \tilde{q} \) can be computed directly from (6) by taking the spatial derivatives. This formula will be useful when elastic strain tensor, e.g. Cauchy strains, needs to be computed.
D. A generalized Irving-Kirkwood formulation

In practice, the Hardy stress computed from (11) still exhibits a lot of fluctuations. Therefore, it needs to be further processed to obtain the average value, e.g. by time or ensemble average. In the original IK formalism, the ensemble average was used. Here we propose to extend the IK formulism to naturally incorporate time averaging. This is particularly useful when only one copy (i.e. one realization) is generated from the molecular dynamics simulation. For this purpose, we use a kernel function $\Phi$ that also depends on time $t$, which allows a direct temporal sampling. More specifically, we re-define the field variables,

$$\tilde{q}(X, t) = \sum_i \int_{\mathbb{R}} \Phi(X - X_i, t - \tau) m_i v_i(\tau) d\tau. \quad (19)$$

To proceed, we still follow the momentum conservation and take the time derivative,

$$\frac{\partial}{\partial t} \tilde{q}(X, t) = \frac{\partial}{\partial t} \sum_{i=1}^{N} \int \Phi(X - X_i, t - \tau) m_i v_i(\tau) d\tau$$

$$= \sum_{i=1}^{N} m_i \int f_i(\tau) \Phi(X - X_i, t - \tau) d\tau$$

$$= -\sum_{i=1}^{N} \int \frac{1}{2} \sum_{j \neq i} f_{ij}(\tau) \cdot X_{ij} \nabla \cdot B_{ij}(X, t - \tau) d\tau \quad (20)$$

$$= \nabla \cdot \left( -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} B_{ij}(X, t - \tau) f_{ij}(\tau) d\tau \otimes X_{ij} \right)$$

$$= \nabla \cdot \sigma(X, t).$$

In the third step, we have defined

$$B_{ij}(X, t) = \int_{0}^{1} \Phi \left( X - (X_i + \lambda X_{ji}), t \right) d\lambda. \quad (21)$$

Here $B_{ij}(X, t)$ is a generalization of $b_{ij}(X)$ in (9). In addition, we identify the new stress formula,

$$\sigma(X, t) = -\frac{1}{2} \sum_{i} \sum_{j \neq i} \int B_{ij}(X, t - \tau) f_{ij}(\tau) d\tau \otimes X_{ij}. \quad (22)$$

This formulation incorporates time averaging in addition to spatial averaging, and it is still consistent with the momentum conservation.

We require that the function $\Phi$ be continuously differentiable with finite support, and the
integral of $\Phi$ over space and time be one,

$$\int_{\mathbb{R}^3 \times \mathbb{R}} \Phi(X, t) dX dt = 1.$$  \hspace{1cm} (23)

In practice, it is often convenient to define a dimensionless function, $\Phi_0(X, t)$, which has finite support within the unit cube. We then introduce a cut-off distance $r_c$, and a cut-off interval $t_c$, and let

$$\Phi(X, t) = \frac{1}{r_c^3 t_c^3} \Phi_0\left(\frac{X}{r_c}, \frac{t}{t_c}\right).$$  \hspace{1cm} (24)

The cut-off parameters can be adjusted to change the sample size.

When $\Phi$ is separable in the space and time variables, the current formulation can be simplified. In fact, in the case when

$$\Phi(X, t) = \varphi(X) \kappa(t),$$  \hspace{1cm} (25)

where $\varphi$ is spatial kernel and $\kappa$ only depends on time, the bond function $B_{ij}$ can be written as:

$$B_{ij}(X, t) = \int_0^1 \varphi\left(X - (X_i + \lambda X_{ji})\right) d\lambda \kappa(t) = b_{ij}(X) \kappa(t)$$  \hspace{1cm} (26)

where $b_{ij}$ is the same as that in (9). As a result, $\sigma(X, t)$ can be simplified as:

$$\sigma(X, t) = -\frac{1}{2} \sum_i \sum_{j \neq i} \int \kappa(t - \tau)f_{ij}(\tau) d\tau b_{ij}(X) \otimes X_{ij},$$  \hspace{1cm} (27)

$$= \int \kappa(t - \tau)\sigma^\text{Hardy}(X, \tau) d\tau.$$

Namely the stress calculation corresponds to the calculation of the Hardy stress, followed by a time averaging using the kernel function $\kappa$. In this case, our formulation coincides with that of Murdoch and Bedeaux$^86$.

### III. NUMERICAL EXPERIMENTS

We will carry out a number of numerical experiments. We consider a molecular dynamics model of FCC aluminum (Al). Atoms are assumed to be interacting through the embedded-atom model (EAM)$^62$, in which the potential energy is given by,

$$V = \frac{1}{2} \sum_{i,j} \phi(r_{ij}) + \sum_i U(\rho_i), \quad \rho_i = \sum_{j \neq i} \rho(r_{ij}).$$  \hspace{1cm} (28)
Here $\phi$ is a pairwise potential, $U$ is the glue function and $\rho$ is the electron density function of the $i$-th atom. Parameters in the expression can be found in\textsuperscript{66}. The interaction range is up to the 3-rd nearest neighbors, and the cut-off radius is 5.5 Å\textsuperscript{66}. For the EAM model, the force $f_{ij}$ is given by,

$$f_{ij} = -\left[\phi'(r_{ij}) + U' (\rho_i) + U' (\rho_j)\right] \frac{\mathbf{r}_{ij}}{r_{ij}}.$$

(29)

In the MD simulations, we use the standard neighbor list method in the force calculation\textsuperscript{53,68}. For the NVE ensemble, the standard Verlet’s time integrator is used, and for NVT ensemble, we use the No`se-Hoover chain (NHC) code with 10 atoms in the chain\textsuperscript{83}. We found that this NHC method has been very effective in bringing the system to equilibrium. The lattice constant for such a system is $a_0 = 4.032\text{Å}$. At finite temperature, however, this parameter needs to be adjusted to account for the thermal expansion. In particular, at temperature $T = 50K$ and $T = 300K$, the corresponding lattice constants are $a_0 = 4.03494$ Å and $a_0 = 4.05134$ Å, respectively. The energy unit is in eV. The time scale is 0.052880 pico-second and the unit for the stress is 160.2176 GPa. All the results will be presented in these unit. The step size for the time integration is $\Delta t = 0.5$. For averaging over time, within the support of the kernel function, we take a sample every 10 steps.

A. A system with uniform deformation

We first perform several numerical tests with uniform deformation applied to the system. This system consists of cube containing 6912 atoms. The deformation is maintained using a periodic boundary conditions with respect to the given deformation gradient. More specifically, we start with a undeformed system in a rectangular box. Then using the given deformation gradient, we deform the rectangular box and throughout the simulation, the periodic boundary condition is applied to the deformed box. In this case, the average virial stress will be considered as the exact value.
1. The calculation of the Hardy stress

We first present some results for the calculation of Hardy stress. For the spatial kernel functions, our first choice is the function suggested in\(^{101}\).

\[
\varphi^I_0(X) = \begin{cases} \frac{15}{4\pi} [1 + (2r - 3)r^2], & r \leq 1, \\ 0, & r > 1. \end{cases}
\] (30)

Here \(r = \|X\|\) is the length of the vector. Notice that this function has support inside the unit disc, and in the whole space, it is continuously differentiable.

We may also consider the step function,

\[
\varphi_0(X) = \begin{cases} \frac{3}{4\pi}, & r \leq 1, \\ 0, & r > 1. \end{cases}
\] (31)

In this case, the functions defined in (6) are discontinuous functions in \(X\). This makes it difficult to compute and interpret the gradient of these variables, e.g. the deformation gradient and the strain rate. Therefore we replace this step function by the following kernel function,

\[
\varphi^I_0(X) = \begin{cases} \frac{1}{c^{II}} \exp \frac{0.1}{r^2 - 1}, & r \leq 1, \\ 0, & r > 1. \end{cases}
\] (32)

Here \(c^{II} \approx 2.77442\) is a normalization constant. This function is infinitely differentiable, and it can be considered as an approximation of the step function. Such function is often used in functional analysis to obtain a smooth approximation with compact support for a given function.

Our third choice is a separable kernel function,

\[
\varphi^I_0(x, y, z) = \begin{cases} \frac{1}{8} \left(1 + \cos \pi x\right) \left(1 + \cos \pi y\right) \left(1 + \cos \pi z\right), & |x|, |y|, |z| \leq 1, \\ 0, & \text{otherwise}. \end{cases}
\] (33)

The cosine function, with proper scaling, is often used to approximate the Dirac delta function.

In our first set of experiments, we consider a system with uniform stretch and shear deformation. Specifically, we consider a uniform stretch with \(E_{11} = 0.5\) and uniform shear with \(E_{12} = 0.05\). We mainly compute the Hardy stress \(\sigma_{11}\) and \(\sigma_{12}\) using the three kernels previously described. We choose the point \(X\) to be at the center of the system. We vary
$r_c$ from $2a_0$ to $5a_0$ and observe the fluctuations around the average virial stress, which is obtained by a long simulation followed by sufficient averaging over time. The results are summarized in Figures 1 to 4.

![Graphs showing fluctuations in stress](image)

**FIG. 1.** The stress $\sigma_{11}$ computed from a system with uniform stretch $E_{11} = 0.05$ and temperature $T = 50K$. From top to bottom: $r_c = 2a_0$, $r_c = 3a_0$, and $r_c = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^{III}$.

We observe that in all cases, the performance of the three kernel functions is similar, with the second kernel giving slightly smaller fluctuations. We also observe that in each case, the fluctuation decreases as $r_c$ increases. Finally, we see that the fluctuation is still significant after spatial averages. Therefore, time averaging is needed to obtain a good approximation of the average stress.

To further check how the fluctuation changes as $r_c$ varies, we plot the fluctuation, measured by $\text{var}(\sigma)/\langle\sigma\rangle^2$ for several different choices of $r_c$. The error, on a log-log scale, follows
FIG. 2. The stress $\sigma_{11}$ computed from a system with uniform stretch $E_{11} = 0.05$ and temperature $T = 300K$. From top to bottom: $r_c = 2a_0$, $r_c = 3a_0$, and $r_c = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^III$.

a linear curve, with slope close to -3, shown in Fig. 5. This suggests that the error obeys the power law,

$$\frac{\text{var}(\sigma)}{\langle \sigma \rangle^2} \sim r_c^{-3}. \quad (34)$$

We now show the calculation of the deformation gradient using the formula (18) from this set of numerical tests. The results are shown in Fig. 6 to Fig. 9. Since the system is uniformed deformed, we expect the average strain to be the same as the strain that is being imposed. Interestingly, the kernel function $\varphi^II$ yields some drift in most cases, and $\varphi^III$ yields appreciable drifts when the sample size is small. Such inconsistency is also observed when the formula 16 is used. These problems can be attributed to some moment properties
FIG. 3. The stress $\sigma_{12}$ computed from a system with uniform shear $E_{12} = 0.05$ and temperature $T = 50K$. From top to bottom: $r_c = 2a_0$, $r_c = 3a_0$, and $r_c = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^{III}$.

of the kernel functions, and this issue will be investigated in a separate publication.

We now turn to the averaging in time. After $\sigma(X,t)$ is computed, we need to perform averaging in time to obtain the average. Typically, this is done as follows,

$$\langle \sigma(X,t) \rangle = \frac{1}{t_c} \int_0^{t_c} \sigma(X,t - s)ds.$$  \hspace{1cm} (35)

For the current system, we expect that the process be stationary after we bring it to equilibrium. Therefore, the result will be independent of $t$.

Another option is to use a kernel function to approximate the time average. For example, in\textsuperscript{80}, the following formula was considered,

$$\langle \sigma(X,t) \rangle = \int_0^{t_c} \kappa(s)\sigma(X,t - s)ds,$$  \hspace{1cm} (36)
FIG. 4. The stress $\sigma_{12}$ computed from a system with uniform stretch $E_{12} = 0.05$ and temperature $T = 300K$. From top to bottom: $r_c = 2a_0$, $r_c = 3a_0$, and $r_c = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^{III}$.

where

$$\kappa(\tau) = \frac{1}{t_c} \left( 1 + \cos \frac{\pi \tau}{t_c} \right).$$

This function will be referred to as a cosine kernel. Notice that (35) can also be put into the form of (36), with the kernel function being a step function.

As an example, we take the computed Hardy stress from a simulation with uniform stretch $E_{11} = 0.05$, at temperature $T = 300K$, and using the kernel function $\varphi^{II}$. The error, measured by,

$$\frac{\sigma - \langle \sigma \rangle}{\langle \sigma \rangle},$$

is plotted for various values of $t_c$. The results are plotted in Fig. 10. One can directly see that while for a large $t_c$ the error is comparable, the cosine kernel yields much better results
y = −3x − 1.1

FIG. 5. The sampling error of the stress $\sigma_{12}$ computed from a system with uniform shear $E_{12} = 0.05$ and temperature $T = 300K$. We have chosen $r_c = 2a_0$, $r_c = 3a_0$, $r_c = 4a_0$ and $r_c = 5a_0$.

FIG. 6. The strain $E_{11}$ computed from a system with uniform applied stretch $E_{11} = 0.05$ at temperature $T = 50K$. The formula (18) is used. From top to bottom: $r_0 = 2a_0$, $r_0 = 3a_0$, and $r_0 = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^{III}$.

for moderate values of $t_c$. This may be attributed to the continuity of the cosine kernel function at the end points. See$^{65}$ for some analysis of the averaging error for oscillatory solutions of some ordinary differential equations. But for long time, the MD trajectory is
FIG. 7. The instantaneous strain $E_{11}$ computed from a system with uniform applied stretch $E_{11} = 0.05$ at temperature $T = 300K$. The formula (18) is used. From top to bottom: $r_0 = 2a_0$, $r_0 = 3a_0$, and $r_0 = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^{III}$.

much less correlated and the smoothness of the kernel function does not play a role.

2. The stress from the generalized Irving-Kirkwood formulation

We now compute the stress derived from the spatial-temporal kernel functions (22). Again we need to choose the kernel functions. We will generalize the space kernel functions that were selected in the previous section. In particular, we define,

$$\Phi^I_0(x, y, z, t) = \begin{cases} \frac{7}{\pi^2} \left[1 + (2R - 3)R^2 \right] , & R \leq 1 \text{ and } t > 0, \\ 0, & \text{Otherwise}. \end{cases}$$

Here $R = \sqrt{x^2 + y^2 + z^2 + t^2}$.

Similarly we can choose the second kernel function as,

$$\Phi^{II}_0(x, y, z, t) = \begin{cases} \frac{1}{C^{II}} \exp \frac{0.1}{R^2 - 1} , & R \leq 1 \text{ and } t > 0, \\ 0, & \text{Otherwise}. \end{cases}$$

Here $C^{II} \approx 1.5113$ is a normalization constant.
FIG. 8. The instantaneous strain $E_{12}$ computed from a system with uniform applied shear $E_{12} = 0.05$ at temperature $T = 50K$. The formula (18) is used. From top to bottom: $r_0 = 2a_0$, $r_0 = 3a_0$, and $r_0 = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^{III}$.

For the third kernel function, we define it as,

$$\Phi^{III}_0 = \begin{cases} 
\frac{1}{8}(1 + \cos \pi x)(1 + \cos \pi y)(1 + \cos \pi z)(1 + \cos \pi t), & |x|, |y|, |z| \leq 1 \text{ and } 0 \leq t \leq 1, \\
0, & \text{Otherwise}. 
\end{cases}$$

Notice that this kernel is a separable function.

Some of the results are displayed in Fig. 11 and Fig. 12. For the first and third kernel functions, the performance is similar: The computed stress at each time is oscillating around the average value, with fluctuation decreasing as we increase $r_c$ and $t_c$. The second kernel function seems to slightly over-estimate the average, and the error still goes down as the sample size is increased.

### B. A dynamic problem

Our last test is a dynamic problem. For the molecular dynamics model, our system consists of $240 \times 12 \times 12$ cubic cells, each cell with side length $a_0$. The system position in a long box, with dimension $L_x \times L_y \times L_z$. The total number of atoms is 138240. We first bring the system to equilibrium with temperature $T = 300K$. We then add a velocity component
FIG. 9. The instantaneous strain $E_{12}$ computed from a system with uniform applied shear $E_{12} = 0.05$ at temperature $T = 300K$. The formula (18) is used. From top to bottom: $r_0 = 2a_0$, $r_0 = 3a_0$, and $r_0 = 4a_0$. From left to right, the kernel functions $\varphi^I$ to $\varphi^ III$.

FIG. 10. The sampling error of the stress $\sigma_{11}$ computed from a system with uniform stretch $E_{11} = 0.05$ and temperature $T = 300K$. The horizontal axis indicates the cut-off in time $t_c$. to each atom. The added velocity is given by,

$$\nabla(x, y, z) = \left(\frac{1}{5} \cos \frac{2\pi x}{L_x}, 0, 0\right).$$  (41)

Here $L_x = 240a_0$.  


FIG. 11. The stress $\sigma_{11}$ computed from a system with uniform stretch $E_{11} = 0.05$ and temperature $T = 50K$ using the space time kernel functions. From top to bottom: $(r_c, t_c) = (2a_0, 50)$, $(r_c, t_c) = (3a_0, 75)$, and $(r_c, t_c) = (4a_0, 100)$. From left to right, the kernel functions $\Phi^I$ to $\Phi^{III}$.

FIG. 12. The stress $\sigma_{12}$ computed from a system with uniform shear $E_{12} = 0.05$ and temperature $T = 50K$ using the space time kernel functions. From top to bottom: $(r_c, t_c) = (2a_0, 50)$, $(r_c, t_c) = (3a_0, 75)$, and $(r_c, t_c) = (4a_0, 100)$. From left to right, the kernel functions $\Phi^I$ to $\Phi^{III}$.
We then turn off the thermostat and evolve the system using the standard Verlet’s method. Fig. 13 shows the quantities that we sampled at time $t = 7000$. Experiments with different choices of the kernels function, and different sample sizes were conducted. In light of the initial condition, we expect that at least for short time, the solutions are smooth. We observe that for the sampled velocity and stress, they tend to be more smooth as the sample size increases. We also observe that for the sampled strain, the second kernel function sometimes gives very oscillatory results compared to the other two kernel functions. This may be attributed to the large gradient of the kernel function.

![Graphs of sampled quantities](image)

**FIG. 13.** The quantities sampled at time $t = 7000$ using the space time kernel functions. From left to right: the sampled strain $E_{11}$, velocity $v_1$ and stress $\sigma_{11}$. From top to bottom, $(r_c, t_c) = (2a_0, 20)$, $(r_c, t_c) = (3a_0, 30)$ and $(r_c, t_c) = (4a_0, 40)$.

**IV. SUMMARY**

The Irving-Kirkwood formalism plays critical roles in molecular modeling and simulations. It provides a rigorous approach to map particle trajectories, which are discrete in nature, to continuous distribution of mechanical properties. Compared to empirical approaches, the IK type of formalism is more systematic, and the derivation itself does not depend on the specific type of molecular structures and interatomic potentials. This formalism is also an important tool to coarse-grain molecular dynamics models. Although this has not been full investigated, some existing models based on this approach already show great
In this paper, we generalized the work of Hardy\cite{70,71}, and proposed an IK formalism that automatically incorporates time averaging into the derivation of the stress. For special cases, we recover the Hardy stress. But for general kernel functions, we have obtained expressions that are completely new. We have provided a number of specific examples for the kernel functions, and discussed how they can be implemented in practice. The numerical results shed some light on how the accuracy depends on the sample size and the selection of kernel functions.

Appendix A: Appendix: The expression for the Cauchy stress

Here we briefly discuss the generalized Irving-Kirkwood formalism in the Eulerian or current coordinate. In Eulerian coordinate, the conservation of mass ($\rho$), momentum($q$) and energy ($E$) are typically written as follows:

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

$$\frac{\partial}{\partial t} q + \nabla_x \cdot \left( \rho v \otimes v \right) = \nabla_x \cdot \sigma,$$

$$\frac{\partial}{\partial t} E + \nabla_x \cdot \left( E v \right) = \nabla_x \cdot J.$$  \hfill (A1)

Here $v = q/\rho$, and $\sigma$ is the Cauchy stress.

In the Irving-Kirkwood formulation, the local mass, momentum and energy is defined as,

$$\begin{aligned}
\tilde{\rho}(x, t) &= \sum_i m_i \varphi(x - x_i(t)), \\
\tilde{q}(x, t) &= \sum_i m_i v_i \varphi(x - x_i(t)), \\
\tilde{E}(x, t) &= \sum_i \left[ \frac{m_i v_i^2}{2} + V_i \right] \varphi(x - x_i(t)). 
\end{aligned} \quad \hfill (A2)$$

Notice that the current position of the atoms now appears in the kernel functions.
1. The Hardy stress

We define the relative velocity $\mathbf{w}_i(t) = \mathbf{v}_i(t) - \tilde{\mathbf{v}}(t)$. We take the time derivative of $\tilde{\mathbf{q}}$,

$$\frac{\partial \tilde{\mathbf{q}}(\mathbf{x}, t)}{\partial t} = \sum_{i=1}^{N} f_i \varphi(\mathbf{x} - \mathbf{x}_i) - \sum_{i=1}^{N} m_i \mathbf{v}_i (\mathbf{v}_i \cdot \nabla_x) \varphi(\mathbf{x} - \mathbf{x}_i)$$

$$= \nabla_x \cdot \left( -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \mathbf{x}_{ij} \otimes f_{ij} b_{ij}(\mathbf{x}, t) \right) - \nabla_x \cdot \left( \sum_{i=1}^{N} m_i \mathbf{v}_i \otimes \mathbf{v}_i \varphi(\mathbf{x} - \mathbf{x}_i) \right) \quad (A3)$$

$$= \nabla_x \cdot \left( -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \mathbf{x}_{ij} \otimes f_{ij} b_{ij}(\mathbf{x}, t) - \sum_{i=1}^{N} m_i \mathbf{w}_i \otimes \mathbf{w}_i \varphi(\mathbf{x} - \mathbf{x}_i) \right) - \nabla_x \cdot (\tilde{\rho} \tilde{\mathbf{v}} \otimes \tilde{\mathbf{v}}).$$

At this point we define Cauchy stress $\mathbf{\tau}$ as

$$\mathbf{\tau} = - \left( \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \mathbf{x}_{ij} \otimes f_{ij} b_{ij}(\mathbf{x}) + \sum_{i=1}^{N} m_i \mathbf{w}_i \otimes \mathbf{w}_i \varphi(\mathbf{x} - \mathbf{x}_i) \right) \quad (A4)$$

where

$$b_{ij} = \int_{0}^{1} \varphi(\mathbf{x} - (\mathbf{x}_i(t) + \lambda \mathbf{x}_{ji}(t))) d\lambda. \quad (A5)$$

2. The case for spatial and temporal kernel

In this case, we define the local mass and momentum as,

$$\begin{cases} 
\tilde{\rho}(\mathbf{x}, t) = \sum_{i=1}^{N} m_i \int_{\mathbb{R}} \Phi(\mathbf{x} - \mathbf{x}_i(t), t - s) ds, \\
\tilde{\mathbf{q}}(\mathbf{x}, t) = \sum_{i=1}^{N} m_i \int_{\mathbb{R}} \Phi(\mathbf{x} - \mathbf{x}_i(t), t - s) \mathbf{v}_i(s) ds.
\end{cases} \quad (A6)$$
Following the same procedure, we take the time derivative,

\[
\frac{\partial \tilde{q}(\mathbf{x}, t)}{\partial t} = \frac{\partial}{\partial t} \sum_{i=1}^{N} m_i \int \Phi(\mathbf{x} - \mathbf{x}_i, t - s) \mathbf{v}_i(s) ds
\]

\[
= - \frac{\partial}{\partial t} \sum_{i=1}^{N} m_i \int \Phi(\mathbf{x} - \mathbf{x}_i, \xi) \mathbf{v}_i(t - \xi) d\xi
\]

\[
= - \sum_{i=1}^{N} m_i \int \Phi(\mathbf{x} - \mathbf{x}_i, \xi) \mathbf{f}_i(t - \xi) d\xi
\]

\[
+ \sum_{i=1}^{N} m_i \int \mathbf{v}_i(t - \xi) \partial_\xi \Phi(\mathbf{x} - \mathbf{x}_i, \xi) \cdot \mathbf{v}_i(t - \xi) d\xi
\]

\[
= \nabla_\mathbf{x} \cdot \left( -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \int B_{ij}(\mathbf{x}, t - s) \mathbf{f}_i(s) ds \otimes \mathbf{x}_{ij} \right) \tag{A7}
\]

\[
- \nabla_\mathbf{x} \cdot \left( \sum_{i=1}^{N} \int m_i \mathbf{v}_i(s) \otimes \mathbf{v}_i(s) \Phi(\mathbf{x} - \mathbf{x}_i, t - s) ds \right)
\]

\[
= \nabla_\mathbf{x} \cdot \left( -\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \int B_{ij}(\mathbf{x}, t - s) \mathbf{f}_i(s) ds \otimes \mathbf{x}_{ij} \right)
\]

\[
- \nabla_\mathbf{x} \cdot \left( \sum_{i=1}^{N} \int m_i \mathbf{w}_i(s) \otimes \mathbf{w}_i(s) \Phi(\mathbf{x} - \mathbf{x}_i, t - s) ds \right) - \nabla_\mathbf{x} \cdot (\tilde{\rho} \tilde{\mathbf{v}} \otimes \tilde{\mathbf{v}}).
\]

This suggests that define Cauchy stress \( \tau \) in this case as,

\[
\tau(\mathbf{x}, t) = - \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \int B_{ij}(\mathbf{x}, t - s) \mathbf{f}_i(s) ds \otimes \mathbf{x}_{ij} \quad \tag{A8}
\]

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

where

\[
B_{ij}(\mathbf{x}, t) = \int_0^1 \Phi(\mathbf{x} - (\mathbf{x}_i(t) + \lambda \mathbf{x}_{ji}(t)), t) d\lambda. \quad \tag{A9}
\]

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