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Lh. 3097

UCRL-52972

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Formulas for One-Dimensional Local Properties for Molecular-Dynamics Simulations of Shock Waves

Robert J. Hardy

January 8, 1981

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Formulas for One-Dimensional Local Properties for Molecular-Dynamics Simulations of Shock Waves

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Manuscript date: January 8, 1981

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Formulas for One-Dimensional Local Properties for Molecular-Dynamics Simulations of Shock Waves

ABSTRACT

Formulas are derived for the mass, momentum, and energy densities, the xx component of the pressure tensor P^{xx} , and the x component of the heat flux Q^x . The formulas relate these local properties to the masses, positions, and velocities of the constituent particles making up the system and are in a usable form for molecular-dynamics simulations without approximation. The formulas for P^{xx} and Q^x avoid the infinite series found in the formulas of Irving and Kirkwood.

INTRODUCTION

Recently, there has been considerable interest in using the methods of molecular dynamics to investigate the properties of shock waves.¹⁻¹⁶ One motive for such investigations is to test the validity of the continuum description of the phenomenon. Continuum theory considers local properties such as the mass density ρ , momentum density $\vec{p}$, energy density E , local velocity $\vec{u}$, pressure tensor $\vec{P}$, and heat flux $\vec{Q}$. Thus to test continuum theory, one needs formulas to relate the local properties to the masses, positions, and velocities of the particles whose motion is simulated.

Obvious choices exist for formulas for one-particle properties such as ρ , $\vec{p}$, and the kinetic contribution to E . For example, mass density is usually given by

$$\rho(\vec{R}) = \sum_i m_i \delta_3(\vec{r}_i - \vec{R}) , \quad (1)$$

where $\vec{r}_i = \vec{r}_i(t)$ is the position of particle i at time t and m_i is its mass, and $\delta(\vec{r}_i - \vec{R})$ is the three-dimension Dirac δ -function. Capital letters, $\vec{R} = (X, Y, Z)$, are used to represent the position dependence of local quantities, while lower case letters, $\vec{r}_i = (x_i, y_i, z_i)$, represent coordinates of particles. However, it is less obvious what formulas should be used for two-particle properties, such as the potential contribution to E and the force contributions to $\vec{P}$ and $\vec{Q}$.

Formulas for both the one- and two-particle properties were derived by Irving and Kirkwood¹⁷ in their classic paper on the equations of hydrodynamics. Essentially, they assumed formulas for the densities and used the equations of motion to deduce formulas for the fluxes. The resulting densities and fluxes satisfied continuity equations for mass, momentum, and energy conservation. Unfortunately, some of the formulas given by them contain Dirac δ -functions and infinite series, which must be approximated in a molecular dynamics simulation.

Here, we derive formulas for the local densities and fluxes that can be used in molecular dynamics simulations without approximation. Because our main interest is the study of shock phenomena, we assumed the local properties are functions of X but not of Y and Z . Also, we assumed the y and z components of $\vec{u}$ and $\vec{p}$ are zero. We will derive the one-dimensional conservation laws for mass, momentum, and energy as consequences of the equations of motion (Newton's laws) by considering the time rate of change of the total mass, the total momentum, and the total energy of all particles between two planes perpendicular to the x -axis. The resulting formulas for the densities and fluxes will be listed and interpreted. In the summary and discussion, the formula obtained for the pressure will be particularly compared with formulas used by others.

PRELIMINARIES

The equation of motion for the i th particle, i.e., Newton's second law, is

$$m_i \ddot{\vec{r}}_i = \sum_j \vec{F}_{ij} , \quad (2)$$

where $\vec{F}_{ij}$ is the force on particle i exerted by particle j . Double dots indicate second derivatives with respect to time, e.g., $\ddot{\vec{r}}_i$ is the acceleration of particle i . Single dots indicate first derivatives with respect to time. It is assumed that the forces can be derived from two body potentials $\phi_{ij}(|\vec{r}_i - \vec{r}_j|)$. The potentials are generally different for different pairs but are independent of the order of the subscripts. Properties of forces that are used are

$$\vec{F}_{ij} = -\nabla_i \phi_{ij} , \quad (3)$$

and

$$-\vec{F}_{ij} = \vec{F}_{ji} . \quad (4)$$

The latter equation is Newton's third law. Because a particle does not exert a force on itself, ϕ_{ij} vanishes for $i = j$ and

$$\vec{F}_{ii} = 0 . \quad (5)$$

A system with ends perpendicular to the x -axis at X_1 and X_2 , with sides parallel to the x -axis, and with cross-sectional area A will be considered (see Fig. 1). We assume the particles will be confined to the indicated cross section. One way of doing this is to use periodic boundary conditions.

FIG. 1. Region of space being considered. Cross hatched surfaces have area A .

One-dimensional conservation laws are deduced by considering the total mass $\mathcal{M}$, the x component of the total momentum $\mathcal{P}^x$, and the total energy $\mathcal{E}$ of all particles in the region described above. One has

$$\mathcal{M}(X_1, X_2) = \sum_i m_i \ell(X_1, x_i, X_2) , \quad (6)$$

$$\mathcal{P}^x(X_1, X_2) = \sum_i m_i \dot{x}_i \ell(X_1, x_i, X_2) , \quad (7)$$

and

$$\begin{aligned} \mathcal{E}(X_1, X_2) &= \sum_i \left(\frac{1}{2} m_i |\dot{\vec{r}}_i|^2 + \frac{1}{2} \sum_j \phi_{ij} \right) \ell(X_1, x_i, X_2) , \end{aligned} \quad (8)$$

where x_i and $\dot{x}_i$ are the x components of $\vec{r}_i$ and $\dot{\vec{r}}_i$, and

$$\ell(a, b, c) = \begin{cases} +1, & \text{if } a < b < c \\ -1, & \text{if } a > b > c \\ 0, & \text{otherwise} . \end{cases} \quad (9)$$

It is implicit in Eq. (8) for $\mathcal{E}$ that half the potential energy ϕ_{ij} is associated with particle i and half is associated with particle j . This assumption is certainly not the only one possible, but it is mathematically convenient and has been used by others.¹⁰ In addition, it leads to very reasonable formulas for the contributions of the two-body forces to $\vec{P}$ and $\vec{Q}$.

The location function ℓ and two other functions σ and δ are very important in this derivation. It is assumed that

$$\ell(a, b, c) = \sigma(b - a) - \sigma(b - c) . \quad (10)$$

This, not Eq. (9), is considered to be the general definition of ℓ . For Eqs. (9) and (10) to be equivalent, the function σ must be a step function, such as

$$\sigma(x) = \begin{cases} -\frac{1}{2}, & \text{if } x < 0 . \\ +\frac{1}{2}, & \text{if } x > 0 . \end{cases} \quad (11)$$

With this choice, the derivative of σ is

$$\frac{d\sigma(x)}{dx} = \delta(x) , \quad (12)$$

where $\delta(x)$ is the one-dimensional Dirac δ -function. Note that

$$\sigma(x) = -\sigma(-x) \quad (13)$$

and

$$\lim_{x \rightarrow \infty} [\sigma(x) - \sigma(-x)] = 1 . \quad (14)$$

Equations (10) and (12) define the functions of ℓ and δ in terms of the function σ , which is considered to be more basic. The formulas obtained for the densities and fluxes when σ is a step function are intuitively reasonable but are not convenient for a molecular dynamics simulation, because Dirac δ -functions are present. However, the derivation of the formulas for the densities and fluxes does not depend on σ being a step function. The crucial relations for the derivation are Eqs. (6), (7), (8), (10), (12), (13), and (14). Eqs. (9) and (11) are not crucial.

A more convenient form of σ for molecular dynamics simulations is

$$\bar{\sigma}(x) = \begin{cases} -\frac{1}{2}, & \text{if } x < -\frac{1}{2}\Delta , \\ x/\Delta, & \text{if } -\frac{1}{2}\Delta < x < \frac{1}{2}\Delta , \\ +\frac{1}{2}, & \text{if } \frac{1}{2}\Delta < x , \end{cases} \quad (15)$$

where Δ is some small but finite distance (see Fig. 2). When $\sigma = \bar{\sigma}$ is used in Eq. (10) for ℓ , Eqs. (6), (7), and (8) give the total mass, momentum, and energy of all particles between $X_1 + \Delta/2$ and $X_2 - \Delta/2$ and a fraction of the mass, momentum, and energy of the particles in the zones between $X_1 - \Delta/2$ and X_1

+ $\Delta/2$ and between $X_2 - \Delta/2$ and $X_2 + \Delta/2$. That is, the ends of the region become indistinct. In the zones at the ends, the properties of particles towards the interior of the region are given greater weight than the properties of particles towards the exterior. When the choice for σ is $\sigma = \bar{\sigma}$, its derivative is

$$\bar{\delta}(x) = \begin{cases} 0, & \text{if } x < -\frac{1}{2}\Delta , \\ 1/\Delta, & \text{if } -\frac{1}{2}\Delta < x < \frac{1}{2}\Delta , \\ 0, & \text{if } \frac{1}{2}\Delta < x . \end{cases} \quad (16)$$

As shown in Fig. 2, $\bar{\delta}$ has a constant value over an interval of width Δ and is zero elsewhere. It follows from Eq. (10) that the functional form of $\ell(a, b, c)$ when $\sigma = \bar{\sigma}$ is that in Table 1, where the case when $a = x_j$, $b = X$, and $c = x_i$ is considered.

The results obtained in the following section are valid when σ is the step function (Eq. 12), when σ is chosen to be $\bar{\sigma}$, or when σ is any function that satisfies the crucial relations mentioned above.

FIG. 2. Functions $\sigma(x)$ and $\delta(x)$ defined by Eqs. (15) and (16).

TABLE 1. Values of the location function $\ell(x_j, X, x_i)$ when $\sigma = \bar{\sigma}$ in Eq. (15). The entries in the three columns at the right indicate the range of values of x_i and x_j for which ℓ has the value given in the left column.

Value of $\ell(x_j, X, x_i)$	Values of x_i and x_j		
	$>(-\infty)$ and $<(X - \Delta/2)$	$>(X - \Delta/2)$ and $<(X + \Delta/2)$	$>(X + \Delta/2)$ and $<(+\infty)$
$(x_i - X_j)/\Delta$		x_j, x_i	
0	x_j, x_i		
0			x_j, x_i
$+ [x_i - (X - \Delta/2)]/\Delta$	x_j	x_i	
$- [x_j - (X - \Delta/2)]/\Delta$	x_i	x_j	
$+ [(X + 1/2) - x_j]/\Delta$		x_j	x_i
$- [(X + 1/2) - x_i]/\Delta$		x_i	x_j
+ 1	x_j		x_i
- 1	x_i		x_j

TIME DEPENDENCE OF $\mathcal{M}$, $\mathcal{P}^x$, AND $\mathcal{E}$

The mass $\mathcal{M}$, momentum $\mathcal{P}^x$, and energy $\mathcal{E}$ change with time. This time dependence is entirely based on the time dependence of the position variables $\vec{r}_i = \vec{r}_i(t)$ and the velocities $\dot{\vec{r}} = \dot{\vec{r}}(t)$. In this section the time derivatives $\dot{\mathcal{M}}$, $\dot{\mathcal{P}}^x$, and $\dot{\mathcal{E}}$ are expressed as differences between properties associated with the plane at X_1 and corresponding properties associated with the plane at X_2 .

Consider the energy $\mathcal{E}$. By differentiating Eq. (8) with respect to t and using Eqs. (10), (12), and (3), one obtains

$$\dot{\mathcal{E}}(X_1, X_2)/A = [B(X_1) + C(X_1)] - [B(X_2) + C(X_2)], \quad (17)$$

where

$$B(X) = A^{-1} \sum_i \left(\frac{1}{2} m_i |\dot{\vec{r}}_i|^2 + \frac{1}{2} \phi_{ij} \right) \dot{x}_i \delta(x_i - X) \quad (18)$$

and

$$C(X) = A^{-1} \sum_i \left[m_i \dot{\vec{r}}_i \cdot \ddot{\vec{r}}_i - \frac{1}{2} \sum_j \vec{F}_{ij} \cdot (\dot{\vec{r}}_i - \dot{\vec{r}}_j) \right] \delta(x_i - X). \quad (19)$$

By using Newton's Second Law to eliminate $\ddot{\vec{r}}_i$, changing summation indices, and using Newton's Third Law, Eq. (19) can be written as

$$\begin{aligned} C(X) &= \frac{1}{2} A \sum_{ij} \vec{F}_{ij} \cdot \dot{\vec{r}}_i [\sigma(x_i - X) - \sigma(x_j - X)] \\ &= \frac{1}{2} A \sum_{ij} \vec{F}_{ij} \cdot \dot{\vec{r}}_i \ell(x_j, X, x_i), \end{aligned} \quad (20)$$

where the second equality follows from Eqs. (10) and (13).

The densities and fluxes are usually defined relative to a frame of reference moving with the medium. To allow for this, we introduce a parameter $u(X)$, which is in general different for different values of X . It is then trivially true that

$$[\vec{r}_j - u(X)\vec{i}] = \vec{r}_j - u(X)\vec{i} \quad (21)$$

and

$$|\vec{r}_j - u(X)\vec{i}|^2 = |\vec{r}_j|^2 - 2u(X)\dot{x}_j + u(X)^2, \quad (22)$$

where $\vec{i}$ is a unit vector in the positive x direction. The quantity $\vec{r}_j - u(X)\vec{i}$ is the velocity of particle j relative to a frame of reference moving with velocity $u(X)\vec{i}$.

By solving the above identities for $\vec{r}_j$ and $|\vec{r}_j|^2$ and substituting into Eqs. (18) and (20) for $B(X)$ and $C(X)$, one obtains

$$B(X) = Q_K^x(X) + [P_K^{xx}(X) + E(X)]u(X) + \frac{3}{2}p^x(X)u(X)^2 - \rho(X)u(X)^3 \quad (23)$$

and

$$C(X) = Q_F^x(X) + P_F^{xx}(X)u(X). \quad (24)$$

The equations relating ρ , p^x , E , P_F^{xx} , P_K^{xx} , Q_F^x , and Q_K^x to the properties of the individual particles are given in the next section.

Relations analogous to Eqs. (17), (23), and (24) can be obtained for the mass and momentum by using similar methods. The results are

$$\dot{\mathcal{M}}(X_1, X_2)/A = p^x(X_1) - p^x(X_2) \quad (25)$$

and

$$\dot{\mathcal{P}}(X_1, X_2)/A = D(X_1) - D(X_2), \quad (26)$$

where

$$D(X) = P_F^{xx}(X) + P_K^{xx}(X) + 2p^x(X)u(X) - \rho(X)u(X)^2. \quad (27)$$

DENSITIES AND FLUXES

The formulas relating ρ , p^x , P_F^{xx} , P_K^{xx} , Q_F^x , and Q_K^x to the properties of the individual particles are given in this section.

The mass density, the x component of the momentum density, and the total energy density are

$$\rho(X) = A^{-1} \sum_i m_i \delta(x_i - X), \quad (28)$$

$$p^x(X) = A^{-1} \sum_i m_i \dot{x}_i \delta(x_i - X), \quad (29)$$

and

$$E(X) = A^{-1} \sum_i \left(\frac{1}{2} m_i |\vec{r}_i - u(X)\vec{i}|^2 + \frac{1}{2} \sum_j \phi_{ij} \right) \delta(x_i - X). \quad (30)$$

That $\rho(X)$ is indeed the mass density at X can be seen most easily by choosing $\sigma = \bar{\sigma}$, so that $\delta = \bar{\delta}$. The function $\bar{\delta}$ is given by Eq. (15). With this choice, it follows from Eq. (28) that $\rho(X)$ is the sum of the masses of all particles between planes at $x - \Delta/2$ and $X + \Delta/2$ divided by the volume $A\Delta$ of the region between the planes. Similarly, $p^x(X)$ is the sum of the x components of the momenta divided by $A\Delta$, and $E(X)$ is the sum of the kinetic and potential energies divided by the volume $A\Delta$.

The contributions of two-body forces to the xx component of the pressure tensor and to the x component of the heat flux in a frame of reference moving with velocity $u(X)\vec{i}$ is

$$P_F^{xx}(X) = \left(\frac{1}{2} A \right) \sum_{ij} F_{ij}^x \ell(x_j, X, x_i), \quad (31)$$

where F_{ij}^x is the x -component of $\vec{F}_{ij}$, and

$$Q_F^x(X) = \left(\frac{1}{2} A\right) \sum_{ij} \vec{F}_{ij} \cdot (\vec{r}_i - u(X)\vec{i}) \ell(x_j, X, x_i) . \quad (32)$$

These are most easily interpreted by choosing δ to be the step function (11), so that ℓ is given by Eq. (9). The quantity being summed over in P_F^{xx} is then the x component of the force on particle i exerted by particle j when particle i is on the positive side of the plane at X and j is on the negative side. When particles i and j are reversed relative to the plane at X , the negative of the x component of the force on i exerted by j is given, which by Newton's Third Law is force on j exerted by i . No contribution to the sum results when both particles i and j are on the same side of the plane. Because all values of i and of j are summed over, Eq. (31) gives twice the force on all particles on one side of the plane due to all particles on the other side. The factor $1/2$ corrects for this double counting. The factor $1/A$ causes P_F^{xx} to be a force per unit area, i.e., a pressure. Similarly, it follows that the sum in Eq. (32) gives, in the moving frame of reference, the rate at which work is done on particles on one side of the plane at X by all particles on the other side. The factor $1/2$ again corrects for double counting, and the factor $1/A$ causes Q_F^x to be the rate of doing work (or rate of energy transfer) per unit area so that Q_F^x is an energy flux. It is referred to as a *heat flux*, because it is the energy flux in a frame of reference moving with the medium.

The force on a particle determines the rate of change of the momentum of the particle. Thus, a force per unit area (pressure) can be considered a contribution to the momentum flux, i.e., the rate at which momentum is transferred per unit area.

In the reference frame moving with velocity $u(X)\vec{i}$, the kinetic contributions to the xx component of the pressure (momentum flux) tensor and to the x component of the energy flux are

$$P_K^{xx}(X) = A^{-1} \sum_i [m_i(\dot{x}_i - u(X))](x_i - u(X)) \delta(x_i - X) \quad (33)$$

and

$$Q_K^x(X) = A^{-1} \sum_i \left[\frac{1}{2} m_i |\vec{r}_i - u(X)\vec{i}|^2 + \frac{1}{2} \sum_j \phi_{ij} \right] (\dot{x}_i - u(X)) \delta(x_i - X) . \quad (34)$$

The factors in square brackets in Eqs. (33) and (34) give, respectively, the x component of the momentum associated with particle i and the kinetic and potential energies associated with particle i . The factor $[\dot{x}_i - u(X)]$ gives the x component of the velocity of particle i in the moving reference frame. Thus, P_K^{xx} and Q_K^x are the contributions to the flux of momentum and to the flux of energy that result from the momentum and energy carried by the particles.

In a gas, the major contribution to the pressure is the kinetic contribution P_K^{xx} . The total xx component of the pressure tensor and the total x component of the heat flux are given by

$$P^{xx}(X) = P_F^{xx}(X) + P_K^{xx}(X) \quad (35)$$

and

$$Q^x(X) = Q_F^x(X) + Q_K^x(X) . \quad (36)$$

The formulas for ρ , p^x , P_K^{xx} , and Q_K^x are equivalent to the corresponding formulas of Irving and Kirkwood,¹⁷ and $E + p^x u - \frac{1}{2} \rho u^2$ is equivalent to their internal energy density. The formulas for P_F^{xx} and Q_F^x avoid the infinite series existing in the corresponding formulas of Irving and Kirkwood, who use a stress tensor $\vec{\sigma}$ that is the negative of the pressure tensor $\vec{P}$.

LOCAL VELOCITY AND CONSERVATION EQUATIONS

In continuum theory, momentum density is associated with the product $\rho \vec{u}$, so that the obvious definition for the x component of the local velocity is¹⁸

$$u(X) = p^x(X)/\rho(X) , \quad (37)$$

and $u(X)$ is identified with the parameter introduced in Eqs. (21) and (22). An assumption equivalent to Eq. (37) is used also by Irving and Kirkwood.¹⁷ Different material frames of reference are associated with different values of X . It follows from Eqs. (28) and (29), for $\rho(X)$ and $p^x(X)$, that $u(X)$ is a weighted average of the velocities of the individual particles. The weighting factor is the mass of the particles.

One-dimensional conservation laws can be obtained by combining Eq. (37) with Eqs. (17), (23) through (27), and Eqs. (35) and (36). One obtains

$$\dot{\mathcal{M}}(X_1, X_2)/A = \rho(X_1)u(X_1) - \rho(X_2)u(X_2) , \quad (38)$$

$$\begin{aligned} \dot{\mathcal{P}}(X_1, X_2)/A &= [p^{xx}(X_1) + \rho(X_1)u(X_1)^2] \\ &- [p^{xx}(X_2) + \rho(X_2)u(X_2)^2] , \end{aligned} \quad (39)$$

and

$$\dot{\mathcal{E}}(X_1, X_2)/A = F(X_1) - F(X_2) , \quad (40)$$

where

$$\begin{aligned} F(X) &= Q^x(X) + [p^{xx}(X) \\ &+ E(X) + \frac{1}{2}\rho(X)u(X)^2]u(X) . \end{aligned} \quad (41)$$

It follows from Eqs. (10) and (12) that

$$\ell(X_1, x_i, X_2) = \int_{X_1}^{X_2} dX \delta(x_i - X) . \quad (42)$$

With this it follows from Eqs. (6), (7), (28), and (29) that

$$\mathcal{M}(X_1, X_2)/A = \int_{X_1}^{X_2} dX \rho(X) \quad (43)$$

and

$$\begin{aligned} \mathcal{P}(X_1, X_2)/A &= \int_{X_1}^{X_2} dX p^x(X) \\ &= \int_{X_1}^{X_2} dX \rho(X)u(X) , \end{aligned} \quad (44)$$

where the second equality follows from Eq. (37). It follows from Eqs. (8), (22), (28), (29), (30), (37), and (42) that

$$\begin{aligned} \dot{\mathcal{E}}(X_1, X_2)/A &= \int_{X_1}^{X_2} dX [E(X) + p^x(X)u(X) \\ &- \frac{1}{2}\rho(X)u(X)^2] = \int_{X_1}^{X_2} dX [E(X) \\ &+ \frac{1}{2}\rho(X)u(X)^2] \end{aligned} \quad (45)$$

From Eqs. (38) and (39) it follows that

$$\int_{X_1}^{X_2} dX \left\{ \dot{\rho}(X) + \frac{\partial}{\partial X} [\rho(X)u(X)] \right\} = 0 \quad (46)$$

Because this is true for all values of X_1 and X_2 , the integrand must vanish so that

$$\dot{\rho}(X) + \frac{\partial}{\partial X} [\rho(X)u(X)] = 0 . \quad (47)$$

In continuum theory, the densities and fluxes are functions of position X and of time t , and not functions of the particle trajectories $\vec{r}_i(t)$. From the

continuum point of view, the reasons for the formulas for ρ , p^x , P^{xx} , and Q_K^x and the functions $\vec{r}_i(t)$ and $\vec{v}_i(t)$ is to specify the t -dependence of $\rho(X, t)$, $P^x(X, t)$, $E(X, t)$, etc. With respect to functions of t defined in this way, the time derivative $\dot{\rho}(X)$ is equivalent to $\partial\rho(X, t)/\partial t$. When this change of notation is made, Eq. (47) takes on the continuum theory form for the continuity equation for mass conservation; i.e.,

$$\frac{\partial\rho(X, t)}{\partial t} + \frac{\partial}{\partial X} [\rho(X, t)u(X, t)] = 0 . \quad (48)$$

If similar arguments are made, one can also show that

$$\frac{\partial}{\partial t} (\rho u) + \frac{\partial}{\partial X} [P^{xx} + \rho u^2] = 0 \quad (49)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \left[E + \frac{1}{2} \rho u^2 \right] + \frac{\partial}{\partial X} \left[Q^x \right. \\ \left. + \left(P^{xx} + E + \frac{1}{2} \rho u^2 \right) u \right] = 0 \end{aligned} \quad (50)$$

where, for brevity, the dependence of ρ , u , E , P^{xx} , and Q^x on X and t have not been made explicit. Equations (49) and (50) are the continuity equations for momentum and energy conservation.

CONCLUSIONS AND DISCUSSION

The conservation laws are exact consequences of Newton's laws, the formulas for the densities and fluxes, and the definition of the local velocity (Eq. (37)). Furthermore this is true independent of the choice made for the function σ used in the definition (see Eq. (10)) of the location function ℓ .

When σ is chosen to be the step function Eq. (11), the functions δ in the densities and fluxes are Dirac δ -functions and ℓ is given by Eq. (9). With this choice, the two-body force contribution to the pressure tensor $P_F^{xx}(X)$ is simply the x component of the total force exerted across the surface at X divided by the area of that surface.

When σ is chosen to be the function $\bar{\sigma}$ defined by Eq. (15), the functions δ in the densities and fluxes equal the function δ given by Eq. (16) and ℓ has the form seen in Table 1. This latter choice is convenient for molecular dynamics simulations, because the Dirac δ -function is absent. Of course for other applications, there may be more convenient choices for σ than the two considered here.

When $\mathcal{M}$, $\mathcal{P}^x$, and $\mathcal{E}$ are negligible, the conservation laws in the form seen in Eqs. (38), (39), and (40) reduce to

$$\rho_1 u_1 = \rho_2 u_2 , \quad (51)$$

$$P_1^{xx} + \rho_1 u_1^2 = P_2^{xx} + \rho_2 u_2^2 , \quad (52)$$

and

$$\begin{aligned} Q_1^x + \left(P_1^{xx} + E_1 + \frac{1}{2} \rho_1 u_1^2 \right) u_1 \\ = Q_2^x + \left(P_2^{xx} + E_2 + \frac{1}{2} \rho_2 u_2^2 \right) u_2 , \end{aligned} \quad (53)$$

where $\rho_1 = \rho(X_1)$, $u_1 = u(X_1)$, etc. Note that E is the energy unit per volume, not the energy per unit mass $\epsilon = E/\rho$. When the heat flux Q^x vanishes, Eqs. (51) and (52) can be combined to give

$$\begin{aligned} (P_1^{xx}/\rho_1) + \epsilon_1 + \frac{1}{2} u_1^2 \\ = (P_2^{xx}/\rho_2) + \epsilon_2 + \frac{1}{2} u_2^2 . \end{aligned} \quad (54)$$

This is the form for the law of energy conservation that is commonly used with the conservation laws for mass and momentum, Eqs. (51) and (52), to derive the Rankine-Hugoniot equation¹⁹

$$(\epsilon_2 - \epsilon_1) = \frac{1}{2} (P_1^{xx} + P_2^{xx})(V_1 - V_2) , \quad (55)$$

where $V = 1/\rho$ is the specific volume. Thus, the Rankine-Hugoniot equation is automatically satisfied in any molecular dynamics simulation provided (a) the formulas for the densities and

fluxes in section 4 are used, (b) a steady state is achieved (i.e., $\mathcal{M}, \mathcal{P}^x, \mathcal{E} = 0$), and (c) the heat flux is negligible at the ends of the region considered (i.e., $Q^x(X_1) = Q^x(X_2) = 0$). It is certainly possible that the heat flux is not negligible in the vicinity of a shock wave, particularly when the shock is driven by a chemical reaction, as in a detonation.

The conservation laws in the form of Eqs. (48) through (50) are formally equivalent to the one-dimensional continuity equations for mass, momentum, and energy in continuum theory. The continuity equations for mass, momentum, and energy which follow from Eqs. (1.2), (7.1), (15.1), (15.2), (49.1), and (49.2) of Landau and Lifshitz¹⁸ and from $W = \epsilon + P/\rho$, where W = enthalpy/mass are

$$\partial \rho / \partial t + \nabla \cdot (\rho \vec{u}) = 0,$$

$$\partial (\rho v) / \partial t + \nabla \cdot (P + \rho \vec{u} \vec{u}) = 0,$$

and

$$\partial (E + \frac{1}{2} \rho u^2) / \partial t + \nabla \cdot \left[\vec{u} (E + \frac{1}{2} \rho |u|^2) + \vec{u} \cdot \vec{P} + \vec{Q} \right] = 0.$$

This equivalence indicates that the xx component of the pressure tensor P^{xx} given in section 4¹⁸ corresponds in continuum theory to the sum of the reversible (or equilibrium) and the irreversible (or viscous) contributions to the pressure. The quantity P^{xx} defined in section 4 is not necessarily the pressure that would be measured by a gauge. However, it and the other quantities in section 4 do satisfy conservation laws. This is more important, because the conservation laws and their consequences are extensively used in the study of shock phenomena, while the direct measurement of pressure near a shock is difficult. It should also be emphasized that the energy density E in Eq. (30) is not necessarily a function only of the pressure and density, as is often assumed in the study of shock phenomena. Such assumptions are only true when the medium is in local equilibrium.

The equation for the pressure when $\sigma = \bar{\sigma}$ is simplified by neglecting the contribution to P_F^{xx} from all pairs of particles not both between the planes at $X - \Delta/2$ and $X + \Delta/2$, i.e., by setting $\ell = 0$ in all rows in Table 1 except the top one. When this is done, it follows from Eqs. (33) and (34) that the

xx component of the total pressure at the plane at X is given approximately by

$$P(X) = (A\Delta)^{-1} \sum_i' m_i (\dot{x}_i - u)^2 + (2A\Delta)^{-1} \sum_i' \sum_j' F_{ij}^x (x_i - x_j), \quad (56)$$

where the sums include only particles i or j in the interval between $X - \Delta/2$ and $X + \Delta/2$.

If the y and z components of $\vec{r}_i$, $\vec{r}_j$, and $\vec{F}_{ij}$ were included in Eq. (56) and the result divided by 3, one would have the *virial formula for the pressure*, which is the formula used by Klimenko and Dremis¹⁵ in their molecular dynamics simulations. The contribution of two body forces to the virial formula involves the dot product of $\vec{F}_{ij}$ times $\vec{r}_i - \vec{r}_j$, while formula (32) for P_F^{xx} involves the product of F_{ij}^x times the x component of the part of the line connecting particles i and j within the interval from $X - \Delta/2$ to $X + \Delta/2$ (see Fig. 3). The virial formula includes only those pairs of particles with connecting lines entirely within the interval (or region) being considered, while formula (32) includes all pairs of particles with a connection line at least partially within the interval being considered. Effectively, the validity of the virial formula requires (a) the system be isotropic (i.e., pressure is the trace of the pressure tensor when the one-dimensional conservation laws require the xx component) and (b) the range of the

FIG. 3. Values of $\ell(x_j, X, x_i)$ times Δ when $\sigma = \bar{\sigma}$ (see Table 1). The products ℓF_{ij}^x with (ℓ, i, j) equal to (ℓ_1, i_1, j_1) , (ℓ_2, i_2, j_2) and (ℓ_3, i_3, j_3) occur in Eq. (31) for P_F^{xx} , while only ℓF_{ij}^x with $(\ell, i, j) = (\ell_1, i_1, j_1)$ occurs in the virial formula for pressure.

interparticle forces is small compared to the size of the region considered. In the usual derivation of the virial formula, these requirements enter when the product of pressure times volume is identified with the part of the virial resulting from external forces.²⁰

When we consider an isotropic system and use intervals that are large compared to the range of the interparticle forces, the difference between the pressure calculated with the virial formula and with the formulas in section 4 is negligible; then the x , y , and z directions are equivalent, and the number of strongly interacting pairs of particles with connecting lines partially within the interval is small compared to the number with connecting lines entirely within the interval. However, in an investigation of the behavior of a system near a shock front, anisotropy may be important, and it may be desirable to use intervals that are not large compared to the range of the interparticle forces. Thus

at least near a shock front, the corrections to the virial formula obtained here could be of importance.

The formula for pressure used by Paskin and Dienes⁸ appears to be quite similar to Eq. (32) for P_F^{xx} with the choice of ℓ following from σ as a step function (although all forces acting across the considered plane may not have been included).¹ The neglect of the kinetic contribution may be justified by arguing that the pressure was evaluated at planes where there were no particles. However, it is not apparent how their pressure is related to the conservation laws. They defined σ to be a step function, and this led to Dirac δ -functions in the densities ρ , P^x , and E . In a molecular dynamics simulation, Dirac δ -functions must be approximated; and in systems with rapidly changing properties, the values obtained for the densities depend on the approximation used.

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