2 Hydrodynamic Theory

In this chapter the basic theoretical framework of this thesis is introduced, in particular the microscopic expressions for the continuity equations. We then proceed to derive the pressure tensor and heat flux vector for fluids under the influence of three-body forces. Our derivation is validated against nonequilibrium molecular dynamics simulations of a confined fluid acted upon by a two-body Barker-Fisher-Watts force coupled with the Axilrod-Teller three-body force in Chapter 5. This chapter is partly based on work published in [44].

2.1 Macroscopic hydrodynamics

A central problem in the study of hydrodynamics is the computation of transport coefficients. Therefore, we are interested in the macroscopic process of mass, energy and momentum transfer. Because of conservation of these quantities, they can only change by a process of redistribution. If the process occurs on a molecular time scale, it would be unobservable at a macroscopic level. But if it is slow, it is observable and plays a macroscopic role. The macroscopic equations of motion for the densities of conserved quantities are called the Navier-Stokes equations [1]. We will now give a brief description of how these equations are derived. It is important to understand this derivation because based on these equations the microscopic expressions for the mass, momentum and energy densities are defined and the pressure tensor and heat flux vector are derived.

If $M(t)$ is the total mass contained in an arbitrary volume V, then

$$M = \int_V d\mathbf{r}\rho(\mathbf{r}, t) \tag{2.1}$$

where $\rho(\mathbf{r}, t)$ is the mass density at position $\mathbf{r}$ and time t. Because of conservation of mass, mass in the volume V changes by flowing through an enclosing surface, S.

$$\frac{dM}{dt} = -\int_S d\mathbf{S}.\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) = -\int_V d\mathbf{r}\nabla.[\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)] \tag{2.2}$$

where $\mathbf{u}(\mathbf{r}, t)$ is the fluid streaming velocity at position $\mathbf{r}$ and time t, and $d\mathbf{S}$ denotes an area element of the surface S. The rate of change of the enclosed mass can also be expressed in terms of the change in mass density $\rho(\mathbf{r}, t)$, as

$$\frac{dM}{dt} = \int_V d\mathbf{r}\frac{\partial\rho(\mathbf{r}, t)}{\partial t} \tag{2.3}$$

Equating (2.2) and (2.3) gives

$$\frac{\partial\rho(\mathbf{r}, t)}{\partial t} = -\nabla.[\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)] \tag{2.4}$$

which is the mass continuity equation governing the conservation of mass.

Similarly we can derive a momentum continuity equation. If $\mathbf{G}(t)$ is the total momentum of an arbitrary volume V, then

$$\mathbf{G} = \int_V d\mathbf{r}\mathbf{J}(\mathbf{r}, t) \tag{2.5}$$

where $\mathbf{J}(\mathbf{r}, t) = \rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)$ is the momentum density at position $\mathbf{r}$ and time t. The rate of change of momentum is given by

$$\frac{d\mathbf{G}}{dt} = \int_V d\mathbf{r}\frac{\partial\mathbf{J}(\mathbf{r}, t)}{\partial t} = \int_V d\mathbf{r}\frac{\partial[\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)]}{\partial t} \tag{2.6}$$

The total momentum of volume V can change firstly by convection, that is, by flowing through a closed surface S enclosing the volume V. This convective term is

$$\frac{d\mathbf{G}_c}{dt} = -\int_S d\mathbf{S}.[\mathbf{J}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] = -\int_S d\mathbf{S}.[\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] \tag{2.7}$$

Momentum can also change by the pressure exerted on the fluid on volume V by the surrounding fluid. The force $d\mathbf{F}$, exerted on an elementary area $d\mathbf{S}$ is,

$$d\mathbf{F} = d\mathbf{S}.\mathbf{P} \tag{2.8}$$

where $\mathbf{P}$ is the pressure tensor. We note here that $\mathbf{P} = -\boldsymbol{\sigma}$, where $\boldsymbol{\sigma}$ is the stress tensor. Thus the stress contribution to the change in momentum can be written as,

$$\frac{d\mathbf{G}_s}{dt} = -\int_S d\mathbf{S}.\mathbf{P} \tag{2.9}$$

Combining (2.7) and (2.9), we have,

$$\begin{aligned}\frac{d\mathbf{G}}{dt} = \frac{dG_c}{dt} + \frac{dG_s}{dt} &= -\int_S d\mathbf{S}.[\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) + \mathbf{P}] \\ &= -\int_V d\mathbf{r}\nabla.[\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t))\mathbf{u}(\mathbf{r},t) + \mathbf{P}] \end{aligned} \tag{2.10}$$

Equating the two expressions (2.6) and (2.10) gives,

$$\frac{\partial \mathbf{J}(\mathbf{r},t)}{\partial t} = \frac{\partial[\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)]}{\partial t} = -\nabla.[\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) + \mathbf{P}] \tag{2.11}$$

which is known as the momentum continuity equation.

We now consider the energy continuity equation. Let the total energy per unit mass be $e(\mathbf{r},t)$, and the total energy density be $\rho(\mathbf{r},t)e(\mathbf{r},t)$. For a convecting fluid, the energy density has two components, one is the kinetic energy part, and the other is the thermodynamic internal energy density, $\rho(\mathbf{r},t)U(\mathbf{r},t)$. Let $E(t)$ be the total energy inside an arbitrary volume V, then

$$E = \int_V d\mathbf{r}\rho(\mathbf{r},t)e(\mathbf{r},t). \tag{2.12}$$

The rate of change of energy is given by

$$\frac{dE}{dt} = \int_V d\mathbf{r} \frac{\partial[\rho(\mathbf{r},t)e(\mathbf{r},t)]}{\partial t} \tag{2.13}$$

The total energy inside volume V can change via convection through the containing surface, diffusion through the surface and the work done on the volume V by the surface stresses. In order, these terms can be written,

$$\begin{aligned}\frac{dE}{dt} &= -\int_S d\mathbf{S}.[\rho(\mathbf{r},t)e(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) + \mathbf{J}_Q] - \int_S (d\mathbf{S}.\mathbf{P}(\mathbf{r},t)).\mathbf{u}(\mathbf{r},t) \\ &= -\int_V d\mathbf{r}\nabla.[\rho(\mathbf{r},t)e(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) + \mathbf{J}_Q + \mathbf{P}(\mathbf{r},t).\mathbf{u}(\mathbf{r},t)] \end{aligned} \tag{2.14}$$

where $\mathbf{J}_Q$ is the heat flux vector. Equating the two expressions (2.13) and (2.14) gives,

$$\frac{\partial[\rho(\mathbf{r},t)e(\mathbf{r},t)]}{\partial t} = -\nabla.[\rho(\mathbf{r},t)e(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) + \mathbf{J}_Q + \mathbf{P}(\mathbf{r},t).\mathbf{u}(\mathbf{r},t)] \tag{2.15}$$

This is the form of the energy continuity equation.

2.2 Microscopic expressions for the continuity equations

In section 2.1 we briefly outlined the continuity equations of macroscopic hydrodynamics. In this section we will give an introduction to the microscopic description for the local densities of mass, momentum and energy and the three continuity equations.

If the mass of the individual atoms in our system is m, then the mass density at a position $\mathbf{r}$ and time t can be calculated by sitting at a particular point in phase space and calculating the density of ensemble points as a function of time. The mass density can now be calculated by summing the values of mass at at a position $\mathbf{r}$, $\sum_i m\ \delta(\mathbf{r}-\mathbf{r}_i)$, but weighting these values by the current value of the N-particle distribution function $f(\mathbf{\Gamma},t)$ at that place in phase space. This is the Schrödinger representation of the mass density, $\rho(\mathbf{r},t)$

$$\rho(\mathbf{r},t) = \int d\mathbf{\Gamma}\ f(\mathbf{\Gamma},t)\ \sum_i m\ \delta(\mathbf{r}-\mathbf{r}_i)$$

Alternatively, we can calculate the value at time t by following the mass, $\sum_i m\,\delta(\mathbf{r}-\mathbf{r}_i(t))$, as it changes along a single trajectory in phase space. The mass density can then be calculated by summing the values of the mass, $\sum_i m\,\delta(\mathbf{r}-\mathbf{r}_i(t))$, with a weighting factor determined by the probability of starting from each initial phase $\mathbf{\Gamma}$. These probabilities are chosen from an initial distribution function $f(\mathbf{\Gamma},0)$. This is the Heisenberg representation of mass density,

$$\rho(\mathbf{r},t) = \int d\mathbf{\Gamma}\; f(\mathbf{\Gamma},0)\; \sum_i m\;\delta(\mathbf{r}-\mathbf{r}_i(t)) = <\sum_i m \mid \mathbf{r}_i(t) = \mathbf{r}> \tag{2.16}$$

The momentum density, $\rho\mathbf{u}(\mathbf{r},t)$, and total energy density, $\rho e(\mathbf{r},t)$, are defined similarly.

$$\begin{aligned}\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) &= \int d\mathbf{\Gamma}\; f(\mathbf{\Gamma},t)\; \sum_i m\mathbf{v}_i\;\delta(\mathbf{r}-\mathbf{r}_i)\\ &= \int d\mathbf{\Gamma}\; f(\mathbf{\Gamma},t)\; \sum_i \mathbf{p}_i\;\delta(\mathbf{r}-\mathbf{r}_i)\\ &= <\sum_i \mathbf{p}_i(t) \mid \mathbf{r}_i(t) = \mathbf{r}> \end{aligned} \tag{2.17}$$

$$\begin{aligned}\rho(\mathbf{r},t)e(\mathbf{r},t) &= \int d\mathbf{\Gamma}\; f(\mathbf{\Gamma},t)\; \left[\frac{1}{2}\sum_i m\mathbf{v}_i^2 \;+\; \frac{1}{2}\sum_{ij}\phi_{ij}^{(2)} \;+\; \frac{1}{3}\sum_{ijk}\phi_{ijk}^{(3)}\right]\;\delta(\mathbf{r}-\mathbf{r}_i)\\ &= <\frac{1}{2}\sum_i m\mathbf{v}_i^2 \;+\; \frac{1}{2}\sum_{ij}\phi_{ij}^{(2)} \;+\; \frac{1}{3}\sum_{ijk}\phi_{ijk}^{(3)} \mid \mathbf{r}_i(t) = \mathbf{r}> \end{aligned} \tag{2.18}$$

In these equations $\mathbf{v}_i$ is the velocity of particle i, $\mathbf{p}_i$ is its momentum. $\phi_{ij}^{(2)} = \phi^{(2)}(\mathbf{r}_i,\mathbf{r}_j)$ is the two-body potential and $\phi_{ijk}^{(3)} = \phi^{(3)}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)$ is the three-body potential.

2.3 Derivation of pressure tensor and heat flux for three-body forces

In order to derive expressions for the pressure tensor and heat flux vector, we should give a brief introduction to the microscopic expressions for the mass, momentum and energy densities in **k**-space.

We define the Fourier transform pair by

$$f(\mathbf{k}) = \int d\mathbf{r}\; e^{i\mathbf{k}.\mathbf{r}}\; f(\mathbf{r})$$

$$f(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d\mathbf{k}\; e^{-i\mathbf{k}.\mathbf{r}}\; f(\mathbf{k}) \tag{2.19}$$

The instantaneous **r**-space mass density is defined as follows,

$$\rho(\mathbf{r}, t) = \sum_{i=1}^{N} m\; \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{2.20}$$

The **k**-space instantaneous mass density is then,

$$\begin{aligned} \rho(\mathbf{k}, t) &= \int d\mathbf{r}\; \sum_{i=1}^{N} m\; \delta(\mathbf{r} - \mathbf{r}_i(t))\; e^{i\mathbf{k}.\mathbf{r}} \\ &= \sum_{i=1}^{N} m\; e^{i\mathbf{k}.\mathbf{r}_i(t)} \end{aligned} \tag{2.21}$$

The instantaneous **r**-space momentum density is defined as follows,

$$\mathbf{J}(\mathbf{r}, t) = \sum_{i=1}^{N} m\mathbf{v}_i\; \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{2.22}$$

The **k**-space instantaneous momentum density is then,

$$\begin{aligned} \mathbf{J}(\mathbf{k}, t) &= \int d\mathbf{r}\; \sum_{i=1}^{N} m\mathbf{v}_i\; \delta(\mathbf{r} - \mathbf{r}_i(t))\; e^{i\mathbf{k}.\mathbf{r}} \\ &= \sum_{i=1}^{N} m\mathbf{v}_i\; e^{i\mathbf{k}.\mathbf{r}_i(t)} \end{aligned} \tag{2.23}$$

The instantaneous **r**-space energy density is

$$\rho e(\mathbf{r}, t) = \left[\frac{1}{2}\sum_i m\mathbf{v}_i^2 \;+\; \frac{1}{2}\sum_{ij} \phi_{ij}^{(2)} \;+\; \frac{1}{3}\sum_{ijk} \phi_{ijk}^{(3)}\right]\; \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{2.24}$$

The **k**-space instantaneous energy density is then,

$$\rho e(\mathbf{k}, t) = \sum_i \left[\frac{1}{2} m\mathbf{v}_i^2 \;+\; \frac{1}{2}\sum_j \phi_{ij}^{(2)} \;+\; \frac{1}{3}\sum_{jk} \phi_{ijk}^{(3)}\right]\; e^{i\mathbf{k}.\mathbf{r}_i(t)} \tag{2.25}$$

2.3.1 Pressure tensor

Since we are interested in planar interfaces with a normal parallel to the y axis, which is perpendicular to the surface of the wall, it is convenient to consider a partial Fourier transform over the y coordinate,

$$J_\alpha(k_y, x, z) \equiv \int_{-\infty}^{\infty} \sum_i mv_{\alpha i}\delta(\mathbf{r} - \mathbf{r}_i)e^{ik_y y}dy$$
$$= \sum_i mv_{\alpha i}\ \delta(x - x_i)\delta(z - z_i)e^{ik_y y_i} \quad (2.26)$$

If the fluid is assumed to be uniform in the x, z directions we can average over them and write the transformed momentum density as

$$J_\alpha(k_y) = \tfrac{1}{A}\sum_i\ mv_{\alpha i}e^{ik_y y_i} \quad (2.27)$$

where A is the magnitude of the area of the $x - z$ surface that has its normal in the y direction. m and $v_{\alpha i}$ are the mass and laboratory velocity of particle i, respectively, and $\alpha = x, y, z$.

Now we perform the Fourier transform on the momentum continuity equation,

$$\frac{\partial \mathbf{J}(\mathbf{r}, t)}{\partial t} = -\nabla.[\mathbf{P} + \rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)]\ . \quad (2.28)$$

In $\mathbf{k}$-space the momentum continuity equation is

$$\frac{\partial J_\alpha(k_y)}{\partial t} = ik_y[P_{\alpha y}(k_y) + \mathcal{F}\{\rho(y)u_\alpha(y)u_y(y)\}]\ , \quad (2.29)$$

where $\mathcal{F}\{\}$ denotes the Fourier transform of the quantity in brackets. Substituting (2.27) into (2.29) gives the potential contribution to the wave-vector-dependent pressure tensor as

$$P^U_{\alpha y}(k_y) = \frac{1}{A}\sum_i \frac{F_{\alpha i}}{ik_y}e^{ik_y y_i}\ , \quad (2.30)$$

while the kinetic contribution is

$$P^K_{\alpha y}(k_y) = \frac{1}{A}\sum_i \frac{mv_{\alpha i}}{ik_y}\frac{d}{dt}e^{ik_y y_i} - \mathcal{F}\{\rho u_\alpha u_y\}. \quad (2.31)$$

We make an inverse Fourier transform of the configurational component of the pressure tensor (2.30), to find that

$$P^U_{\alpha y}(y) = \frac{1}{2\pi A}\int\limits_{-\infty}^{\infty}\sum_i \frac{F_{\alpha i}}{ik_y}e^{ik_y y_i}e^{-ik_y y}dk_y \ . \tag{2.32}$$

Utilizing the fact that

$$\frac{1}{\pi}\int\limits_{-\infty}^{\infty}\frac{exp(iky)}{ik}dk = sgn(y) \ , \tag{2.33}$$

it is straightforward to show

$$P^U_{\alpha y}(y) = \frac{1}{2A}\sum_i F_{\alpha i} sgn(y_i - y) \ , \tag{2.34}$$

where $F_{\alpha i}$ is the α component of the total force on atom i including both two- and three-body contributions. For two-body contributions, Todd *et al* [45] have detailed the derivations. In what follows we specifically consider the case of three-body forces and use symmetry relations to generate a useful expression for the potential contribution to the three-body pressure. The kinetic contribution remains unchanged as it implicitly contains the full two- and three-body force contributions in the particle momenta.

We now separate out the two- and three-body contributions to the pressure

$$\begin{aligned} P^U_{\alpha y}(y) &= \frac{1}{2A}\sum_i F_{\alpha i} sgn(y_i - y) \\ &= \frac{1}{2A}\sum_i (F^{(2)}_{\alpha i} + F^{(3)}_{\alpha i}) sgn(y_i - y) \\ &= P^{(2)U}_{\alpha y}(y) + P^{(3)U}_{\alpha y}(y) \ , \end{aligned} \tag{2.35}$$

where $P^{(2)U}_{\alpha y}(y)$ and $P^{(3)U}_{\alpha y}(y)$ are contributions from two-body and three-body forces, respectively. In [45] it was shown that

$$\begin{aligned} P^{(2)U}_{\alpha y}(y) &= \frac{1}{2A}\sum_i F^{(2)}_{\alpha i}\, sgn(y_i - y) \\ &= \frac{1}{4A}\left[\sum_{ij} F^{(2)}_{\alpha ij}\, sgn(y_i - y) + \sum_{ij} F^{(2)}_{\alpha ji}\, sgn(y_j - y)\right] \\ &= \frac{1}{4A}\sum_{ij} F^{(2)}_{\alpha ij}[sgn(y_i - y) - sgn(y_j - y)] \\ &= \frac{1}{2A}\sum_{ij} F^{(2)}_{\alpha ij}[\Theta(y_i - y)\Theta(y - y_j) - \Theta(y_j - y)\Theta(y - y_i)]\ , \end{aligned} \tag{2.36}$$

where Θ is the Heaviside step function. $F^{(2)}_{\alpha i}$ is the α component of two-body force on atom i. $\mathbf{F}^{(2)}_{ij}$ is defined here to be the contribution to the total two-body force on atom i due to atom j. If $\phi^{(2)}_{ij} = \phi^{(2)}(\mathbf{r}_i, \mathbf{r}_j)$ is the two-body potential, then

$$\mathbf{F}^{(2)}_i \equiv \sum_j \mathbf{F}^{(2)}_{ij} = -\sum_j \frac{\partial \phi^{(2)}_{ij}}{\partial \mathbf{r}_i}$$

Making similar use of particle exchange symmetry, the three-body contribution to the pressure tensor can be expressed as

$$\begin{aligned} P^{(3)U}_{\alpha y}(y) &= \frac{1}{2A}\sum_i F^{(3)}_{\alpha i}\, sgn(y_i - y) \\ &= \frac{1}{6A}\left[\sum_i F^{(3)}_{\alpha i}\, sgn(y_i - y) + \sum_j F^{(3)}_{\alpha j}\, sgn(y_j - y) \right.\\ &\quad \left. + \sum_k F^{(3)}_{\alpha k}\, sgn(y_k - y)\right], \end{aligned} \tag{2.37}$$

where

$$\mathbf{F}^{(3)}_i \equiv \sum_{jk}(\mathbf{F}^{(3)}_{ij} + \mathbf{F}^{(3)}_{ik}) = -\sum_{jk}\left(\frac{\partial \phi^{(3)}_{ijk}}{\partial \mathbf{r}_{ij}} + \frac{\partial \phi^{(3)}_{ijk}}{\partial \mathbf{r}_{ik}}\right) \tag{2.38}$$

$$\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j\ , \qquad \mathbf{F}^{(3)}_{ij} \equiv -\frac{\partial \phi^{(3)}_{ijk}}{\partial \mathbf{r}_{ij}}$$

$\mathbf{F}^{(3)}_i$ is the three-body force on atom i. $\mathbf{F}^{(3)}_{ij}$ is defined here to be the contribution to the total three-body force on atom i due to atom j. Substitution of Eq. (2.38) into (2.37) yields

$$\begin{aligned}
P_{\alpha y}^{(3)U}(y) &= \frac{1}{6A}\Bigg[\sum_{ij} F_{\alpha ij}^{(3)} sgn(y_i - y) + \sum_{ik} F_{\alpha ik}^{(3)} sgn(y_i - y) \\
&+ \sum_{ji} F_{\alpha ji}^{(3)} sgn(y_j - y) + \sum_{jk} F_{\alpha jk}^{(3)} sgn(y_j - y) \\
&+ \sum_{ki} F_{\alpha ki}^{(3)} sgn(y_k - y) + \sum_{kj} F_{\alpha kj}^{(3)} sgn(y_k - y)\Bigg] \\
&= \frac{1}{6A}\Bigg\{\sum_{ij} F_{\alpha ij}^{(3)}[sgn(y_i - y) - sgn(y_j - y)] \\
&+ \sum_{ik} F_{\alpha ik}^{(3)}[sgn(y_i - y) - sgn(y_k - y)] \\
&+ \sum_{jk} F_{\alpha jk}^{(3)}[sgn(y_j - y) - sgn(y_k - y)]\Bigg\}
\end{aligned} \tag{2.39}$$

$$\begin{aligned}
P_{\alpha y}^{(3)U}(y) &= \frac{1}{3A}\Bigg\{\sum_{ij} F_{\alpha ij}^{(3)}[\Theta(y_i - y)\Theta(y - y_j) - \Theta(y_j - y)\Theta(y - y_i)] \\
&+ \sum_{ik} F_{\alpha ik}^{(3)}[\Theta(y_i - y)\Theta(y - y_k) - \Theta(y_k - y)\Theta(y - y_i)] \\
&+ \sum_{jk} F_{\alpha jk}^{(3)}[\Theta(y_j - y)\Theta(y - y_k) - \Theta(y_k - y)\Theta(y - y_j)\Bigg\}
\end{aligned} \tag{2.40}$$

Equation (2.39) demonstrates that the potential contribution to the three-body pressure at a plane located at y occurs when components of the three-body force intersect that plane, in complete analogy with the two-body force contributions. For example, consider the situation shown in Fig. 2.1, in which a triangular configuration of three particles is shown. Only the force contributions along the vectors $\mathbf{r}_{12}$ and $\mathbf{r}_{13}$ intersect the plane at $y = y_0$ and contribute to the three-body pressure at this plane.

The kinetic part of the pressure tensor can be obtained by making an inverse Fourier transform of the kinetic component of the pressure tensor (2.31)

$$P_{\alpha y}^{K}(y) = \frac{1}{2\pi A}\int_{-\infty}^{\infty} dk_y \sum_i \frac{mv_{\alpha i}}{ik_y}\frac{d}{dt} exp[ik_y(y_i - y)] - \rho u_\alpha u_y \ . \tag{2.41}$$

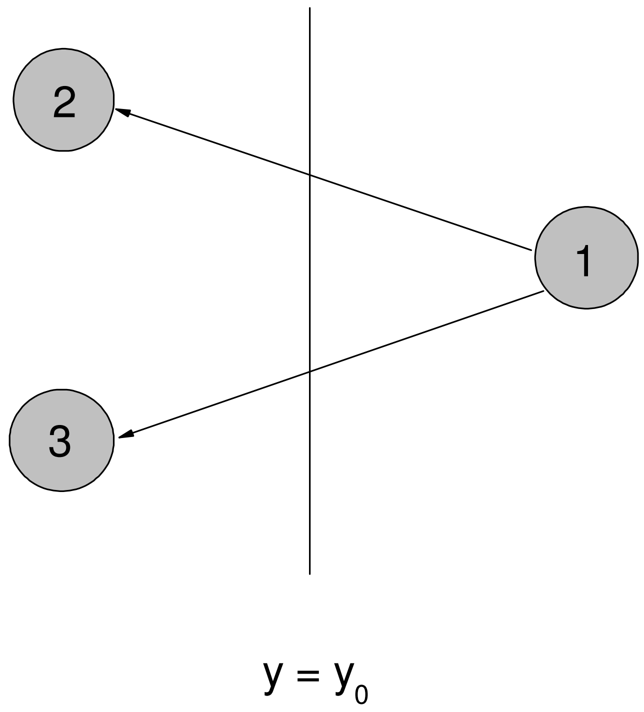

Figure 2.1: Triangular configuration of atoms and the plane located at $y = y_0$. Contributions to the pressure tensor are included from atoms 1, 2, and 3 along the vectors $\mathbf{r}_{12}$ and $\mathbf{r}_{13}$.

If we interchange the order of integrating with respect to k_y and differentiating with respect to time we find

$$\begin{aligned} \mathrm{P}^K_{\alpha y}(y) &= \frac{1}{2\pi A}\sum_i m v_{\alpha i}\frac{d}{dt}\int_{-\infty}^{\infty} dk_y \frac{exp[ik_y(y_i - y)]}{ik_y} - \rho u_\alpha u_y \\ &= \frac{1}{2A}\sum_i m v_{\alpha i}\frac{d}{dt} sgn(y_i - y) - \rho u_\alpha u_y \end{aligned} \quad (2.42)$$

In obtaining the second of these equalities, (2.33) has been used. Utilizing the fact that

$$\begin{aligned} &\frac{d[sgn(y_i - y)]}{dt} = \frac{d[sgn(y_i - y)]}{d(y_i - y)}\frac{d(y_i - y)}{dt} = \frac{d[sgn(y_i - y)]}{d(y_i - y)} \cdot v_{yi}\,,\ \ and \\ &\frac{d}{dy} sgn(y) = 2\delta(y) \end{aligned} \quad (2.43)$$

(2.42) can be written as

$$P^K_{\alpha y}(y) = \frac{1}{A}\sum_i \frac{p_{\alpha i}p_{yi}}{m}\delta(y_i - y)\ , \tag{2.44}$$

where $p_{\alpha i}$ and p_{yi} are α and y components of the peculiar momenta of particle i. Here the peculiar momentum is defined as $\mathbf{p}_i \equiv \mathbf{v}_i - \mathbf{c}(y)$, where $\mathbf{v}_i$ is the laboratory momentum of particle i and $\mathbf{c}(y)$ is the streaming velocity at y. The time averaged kinetic component of the pressure tensor can be usefully expressed as

$$< P^K_{\alpha y}(y) >= \lim_{t\to\infty}\frac{1}{At}\sum_{0<t_{i,j}<t}\sum_i p_{\alpha i}(t_{i,j})sgn[p_{yi}(t_{i,j})]\ . \tag{2.45}$$

Here it is noted that particle i crosses the plane at y at a set of times $(t_{i,j};\ i = 1,\cdots,N;\ j = 1,2,\cdots)$.

2.3.2 Heat flux vector

As with the pressure tensor derivation, we follow the method of planes formalism developed in [46] for the heat flux vector. That approach uses the microscopic definitions of the local energy density and the Fourier transform of the energy continuity equation to obtain a **k**-space expression for the heat flux vector, which is again back transformed into **r**-space.

We start the derivation at the Fourier transformed energy density continuity equation (2.15)

$$\frac{\partial[\rho e(\mathbf{k},t)]}{\partial t} = i\mathbf{k}.[\mathbf{J}_Q(\mathbf{k},t) + \mathcal{F}\{\rho e\mathbf{u}\} + \mathcal{F}\{\mathbf{P}.\mathbf{u}\}]\ . \tag{2.46}$$

As we have shown in Eq. (2.25) the **k**-space instantaneous energy density is

$$\rho e(\mathbf{k},t) = \sum_i \left[\frac{1}{2}m\mathbf{v}_i^2 + \frac{1}{2}\sum_j \phi^{(2)}_{ij} + \frac{1}{3}\sum_{jk}\phi^{(3)}_{ijk}\right] e^{i\mathbf{k}.\mathbf{r}_i(t)}\ .$$

The total energy of atom i is

$$e_i = \frac{1}{2}m\mathbf{v}_i^2 + \frac{1}{2}\sum_j \phi^{(2)}_{ij} + \frac{1}{3}\sum_{jk}\phi^{(3)}_{ijk}.$$

We first compute the time derivative of the energy density in **k**-space, Eq. (2.25)

$$
\begin{aligned}
\frac{\partial[\rho e(\mathbf{k},t)]}{\partial t} &= i\mathbf{k}\cdot\left(\sum_i \mathbf{v}_i e_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\right) + \sum_i m\mathbf{v}_i\cdot\dot{\mathbf{v}}_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&+ \frac{1}{2}\sum_{ij}\left(\dot{\mathbf{r}}_i\cdot\frac{\partial\phi_{ij}^{(2)}}{\partial\mathbf{r}_i} + \dot{\mathbf{r}}_j\cdot\frac{\partial\phi_{ij}^{(2)}}{\partial\mathbf{r}_j}\right) e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&+ \frac{1}{3}\sum_{ijk}\left(\dot{\mathbf{r}}_i\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_i} + \dot{\mathbf{r}}_j\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_j} + \dot{\mathbf{r}}_k\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_k}\right) e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&= i\mathbf{k}\cdot\left(\sum_i \mathbf{v}_i e_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\right) + \sum_i \mathbf{v}_i\cdot(\mathbf{F}_i^{(2)} + \mathbf{F}_i^{(3)}) e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&- \frac{1}{2}\sum_{ij}(\mathbf{v}_i\cdot\mathbf{F}_{ij}^{(2)} + \mathbf{v}_j\cdot\mathbf{F}_{ji}^{(2)}) e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&+ \frac{1}{3}\sum_{ijk}\left(\dot{\mathbf{r}}_i\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_i} + \dot{\mathbf{r}}_j\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_j} + \dot{\mathbf{r}}_k\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_k}\right) e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&= i\mathbf{k}\cdot\left(\sum_i \mathbf{v}_i e_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\right) + \frac{1}{2}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}_{ij}^{(2)}(e^{i\mathbf{k}\cdot\mathbf{r}_i} - e^{i\mathbf{k}\cdot\mathbf{r}_j}) \\
&+ \sum_i \mathbf{v}_i\cdot\mathbf{F}_i^{(3)} e^{i\mathbf{k}\cdot\mathbf{r}_i} \\
&+ \frac{1}{3}\sum_{ijk}\left(\dot{\mathbf{r}}_i\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_i} + \dot{\mathbf{r}}_j\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_j} + \dot{\mathbf{r}}_k\cdot\frac{\partial\phi_{ijk}^{(3)}}{\partial\mathbf{r}_k}\right) e^{i\mathbf{k}\cdot\mathbf{r}_i}\ . \qquad (2.47)
\end{aligned}
$$

Consider now the two terms containing the three-body forces. The first term may be symmetrized as

$$
\begin{aligned}
\sum_i \mathbf{v}_i\cdot\mathbf{F}_i^{(3)} e^{i\mathbf{k}\cdot\mathbf{r}_i} &= \frac{1}{3}\left[\sum_i \mathbf{v}_i\cdot\mathbf{F}_i^{(3)} e^{i\mathbf{k}\cdot\mathbf{r}_i} + \sum_j \mathbf{v}_j\cdot\mathbf{F}_j^{(3)} e^{i\mathbf{k}\cdot\mathbf{r}_j} + \sum_k \mathbf{v}_k\cdot\mathbf{F}_k^{(3)} e^{i\mathbf{k}\cdot\mathbf{r}_k}\right] \\
&= \frac{1}{3}\left[\sum_{ijk} \mathbf{v}_i\cdot(\mathbf{F}_{ij}^{(3)} + \mathbf{F}_{ik}^{(3)}) e^{i\mathbf{k}\cdot\mathbf{r}_i} + \sum_{ijk} \mathbf{v}_j\cdot(\mathbf{F}_{ji}^{(3)} + \mathbf{F}_{jk}^{(3)}) e^{i\mathbf{k}\cdot\mathbf{r}_j}\right. \\
&\left.+ \sum_{ijk} \mathbf{v}_k\cdot(\mathbf{F}_{ki}^{(3)} + \mathbf{F}_{kj}^{(3)}) e^{i\mathbf{k}\cdot\mathbf{r}_k}\right]\ . \qquad (2.48)
\end{aligned}
$$

The second term containing three-body forces in Eq. (2.47) may be similarly expanded:

$$
\begin{aligned}
&\frac{1}{3}\sum_{ijk}\left(\dot{\mathbf{r}}_i\cdot\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_i}+\dot{\mathbf{r}}_j\cdot\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_j}+\dot{\mathbf{r}}_k\cdot\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_k}\right)e^{i\mathbf{k}\cdot\mathbf{r}_i}\\
&=\frac{1}{3}\sum_{ijk}\left[\mathbf{v}_i\cdot\left(\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_{ij}}+\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_{ik}}\right)+\mathbf{v}_j\cdot\left(\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_{ji}}+\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_{jk}}\right)+\mathbf{v}_k\cdot\left(\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_{ki}}+\frac{\partial\phi^{(3)}_{ijk}}{\partial\mathbf{r}_{kj}}\right)\right]e^{i\mathbf{k}\cdot\mathbf{r}_i}\\
&=-\frac{1}{3}\sum_{ijk}(\mathbf{v}_i\cdot\mathbf{F}^{(3)}_{ij}+\mathbf{v}_i\cdot\mathbf{F}^{(3)}_{ik}-\mathbf{v}_j\cdot\mathbf{F}^{(3)}_{ij}+\mathbf{v}_j\cdot\mathbf{F}^{(3)}_{jk}-\mathbf{v}_k\cdot\mathbf{F}^{(3)}_{ik}-\mathbf{v}_k\cdot\mathbf{F}^{(3)}_{jk})e^{i\mathbf{k}\cdot\mathbf{r}_i}\ . \qquad (2.49)
\end{aligned}
$$

Defining $S^{(3)}$ as the sum of Eqs. (2.48) and (2.49) gives

$$
\begin{aligned}
S^{(3)}=-\frac{1}{3}\sum_{ijk}&[\mathbf{v}_j\cdot\mathbf{F}^{(3)}_{ij}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j})\\
&-\mathbf{v}_j\cdot\mathbf{F}^{(3)}_{jk}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j})\\
&+\mathbf{v}_k\cdot\mathbf{F}^{(3)}_{ik}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_k})\\
&+\mathbf{v}_k\cdot\mathbf{F}^{(3)}_{jk}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_k})]\ . \qquad (2.50)
\end{aligned}
$$

We now permute the triplet indices in Eq. (2.50) such that all velocities are in term of the index i to obtain

$$
\begin{aligned}
S^{(3)}&=\frac{1}{3}\sum_{ijk}\mathbf{v}_i\cdot[\mathbf{F}^{(3)}_{ik}+\mathbf{F}^{(3)}_{ij}](e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_k})\\
&+\frac{1}{3}\sum_{ijk}\mathbf{v}_i\cdot[\mathbf{F}^{(3)}_{ij}+\mathbf{F}^{(3)}_{ik}](e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j})\\
&=\frac{1}{3}\sum_{ik}\mathbf{v}_i\cdot\mathbf{F}^{(3)}_{i}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_k})\\
&+\frac{1}{3}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}^{(3)}_{i}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j})\ . \qquad (2.51)
\end{aligned}
$$

Substituting Eq. (2.51) back into Eq. (2.47) gives

$$\begin{aligned}\frac{\partial[\rho e(\mathbf{k},t)]}{\partial t} &= i\mathbf{k}\cdot\left(\sum_i \mathbf{v}_i e_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\right)\\ &+ \frac{1}{2}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}_{ij}^{(2)}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j})\\ &+ \frac{1}{3}\sum_{ik}\mathbf{v}_i\cdot\mathbf{F}_{i}^{(3)}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_k})\\ &+ \frac{1}{3}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}_{i}^{(3)}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j})\ . \end{aligned} \tag{2.52}$$

Substitution of Eq. (2.52) into the Fourier transformed energy continuity equation (2.46) yields

$$\begin{aligned} i\mathbf{k}\cdot\mathbf{J}_Q(\mathbf{k},t) &= i\mathbf{k}\cdot\left(\sum_i[\mathbf{v}_i-\mathbf{u}(\mathbf{r}_i,t)]e_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\right)\\ &+ \frac{1}{2}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}_{ij}^{(2)}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j})\\ &+ \frac{1}{3}\sum_{ik}\mathbf{v}_i\cdot\mathbf{F}_{i}^{(3)}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_k})\\ &+ \frac{1}{3}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}_{i}^{(3)}(e^{i\mathbf{k}\cdot\mathbf{r}_i}-e^{i\mathbf{k}\cdot\mathbf{r}_j}) - i\mathbf{k}\cdot\mathcal{F}\{\mathbf{P}.\mathbf{u}\}\ . \end{aligned} \tag{2.53}$$

Integrating over x and z, dividing by ik_y and taking the inverse Fourier transform yields

$$\begin{aligned} AJ_{Qy}(y,t) &= \sum_i(v_{yi}-u_y)e_i\delta(y-y_i)\\ &- \frac{1}{4}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}_{ij}^{(2)}[sgn(y-y_i)-sgn(y-y_j)]\\ &- \frac{1}{6}\sum_{ij}\mathbf{v}_i\cdot\mathbf{F}_{i}^{(3)}[sgn(y-y_i)-sgn(y-y_j)]\\ &- \frac{1}{6}\sum_{ik}\mathbf{v}_i\cdot\mathbf{F}_{i}^{(3)}[sgn(y-y_i)-sgn(y-y_k)] - A\{\mathbf{P}.\mathbf{u}\}_y\ . \end{aligned} \tag{2.54}$$

We substitute the expression for the pressure tensor, Eq. (2.39), into Eq. (2.54) to give the kinetic and potential contributions to the heat flux vector

$$J_{Qy}(y,t) = J_{Qy}^K(y,t) + J_{Qy}^U(y,t)\ . \tag{2.55}$$

The kinetic contribution is, as with the pressure tensor, identical in form to the original derivation in [46]:

$$J^K_{Qy}(y,t) = \frac{1}{A}\sum_i [v_{yi} - u(y)] U_i \delta(y - y_i) \tag{2.56}$$

except that here U_i is the internal energy of a particle defined as

$$U_i = \frac{1}{2} m[\mathbf{v}_i - \mathbf{u}(y_i)]^2 \ + \frac{1}{2}\sum_j \phi^{(2)}_{ij} \ + \frac{1}{3}\sum_{jk} \phi^{(3)}_{ijk} \ . \tag{2.57}$$

The potential contribution to the heat flux vector is

$$\begin{aligned} J^U_{Qy}(y,t) = &- \frac{1}{4A}\sum_{ij} [\mathbf{v}_i - \mathbf{u}(y)]\cdot\mathbf{F}^{(2)}_{ij}[sgn(y - y_i) - sgn(y - y_j)] \\ &- \frac{1}{6A}\sum_{ij} [\mathbf{v}_i - \mathbf{u}(y)]\cdot\mathbf{F}^{(3)}_{ij}[sgn(y - y_i) - sgn(y - y_j)] \\ &- \frac{1}{6A}\sum_{ik} [\mathbf{v}_i - \mathbf{u}(y)]\cdot\mathbf{F}^{(3)}_{ik}[sgn(y - y_i) - sgn(y - y_k)] \\ &- \frac{1}{6A}\sum_{ijk} \mathbf{v}_i\cdot\mathbf{F}^{(3)}_{ij}[sgn(y - y_i) - sgn(y - y_k)] \\ &- \frac{1}{6A}\sum_{ijk} \mathbf{v}_i\cdot\mathbf{F}^{(3)}_{ik}[sgn(y - y_i) - sgn(y - y_j)] \\ &+ \frac{1}{6A}\sum_{jk} \mathbf{u}(y)\cdot\mathbf{F}^{(3)}_{jk}[sgn(y - y_j) - sgn(y - y_k)] \ . \end{aligned} \tag{2.58}$$

An alternative, more concise form of Eq. (2.58) is [44]

$$\begin{aligned} J^U_{Qy}(y,t) = &- \frac{1}{2A}\sum_i [\mathbf{v}_i - \mathbf{u}(y)]\cdot\mathbf{F}^{(2)}_i sgn(y - y_i) \\ &- \frac{1}{2A}\sum_i [\mathbf{v}_i - \mathbf{u}(y)]\cdot\mathbf{F}^{(3)}_i sgn(y - y_i) \\ &+ \frac{1}{6A}\sum_{ijk} \mathbf{v}_i\cdot\mathbf{F}^{(3)}_i [sgn(y - y_i) + sgn(y - y_j) + sgn(y - y_k)] \ . \end{aligned} \tag{2.59}$$

The last three terms in Eq. (2.58) and the last term in Eq. (2.59) are not direct analogies of the two-body heat flux, unlike the case in the pressure tensor three-body expressions, which are direct analogies. They are a result of particle velocities coupling to three-body forces, which does not occur in the pressure tensor calculation. However, it will be shown in Chapter 5 that these additional terms are negligible, if not zero. As was the case for the kinetic term for the pressure tensor, the kinetic term for the heat flux vector in (2.56) can be written in a more useful way for computer simulation as [46]

$$J_{Qy}^{K}(y) = \lim_{t\to\infty} \frac{1}{At} \sum_{0<t_{i,j}<t} \sum_{i} U_i sgn[c_{yi}(t_{i,j})] \ , \tag{2.60}$$

where $\mathbf{c}_i \equiv \mathbf{v}_i - \mathbf{u}(y)$ is the plane peculiar velocity of atom i.

Eqs. (2.36), (2.39), (2.59) and (2.60) will be used for computing the pressure tensor and heat flux vector in Chapter 5.