4

Enhancements to the Meso Scale Model

Aim. This chapter explores the limitations of the meso scale approach discussed in the previous chapter. Using these case studies the reader should see the depth of knowledge available from molecular models and how it may be used to characterize fluid systems.

4.1 INTRODUCTION

This chapter focuses on the further development of the meso scale approach discussed in the previous chapter. The development starts by extending the method to handle flowing fluids. When a fluid flows through a pipe or channel, the interaction between the fluid and solid molecules causes the molecules close to the wall to slow down, as has been discussed in the viscous fluid discussion in Chapter 1. This, combined with the internal collisions of fluid molecules causes a boundary layer to form. Capturing this boundary layer in the form of a velocity profile can tell us a great deal about the fluid behaviour, as will be seen in Chapter 5. The section discusses the generation and capture of fluid flow behaviour in molecular systems. The first issue to be discussed is the method of driving molecules to generate a flow.

This extended method is then explored and tested in a number of case studies. The first case studies focus on the parameters of the bulk property extraction scheme, examining the sample and ensemble length, radius of sub-domain and weighting function. These studies are performed on a fluid at rest and do not employ the thermal control element of the method.
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The second section of case studies look at the collected bulk properties as distributions throughout the domain. A temperature gradient through a fluid confined between two parallel plates is considered on a fluid at rest. In this example thermal energy is propagated by the thermal motion of the molecules in the fluid. A study of a fluid flowing between parallel plates is also considered. This example employs both the thermostat and flow driving elements of the model, and is compared with results published in literature.

4.2 DRIVING FORCES

In order to generate a flow, there must be a driving force to push the molecules between one point and the next. A flow can be generated in a number of ways, varying in their complexity and computational demand. In the following section, methods for generating fluid/molecular flows will be presented and discussed, focusing on their application to meso scale systems.

The first method is the most demanding computationally, but presents the simplest concept. It relies on three components, a high-pressure reservoir, a low pressure reservoir and a test section that connects them, as shown in Figure 4.1.

The high-pressure reservoir is maintained at a constant high pressure by recycling the molecules that exit the test section into the low-pressure reservoir. This has the effect of keeping the low-pressure reservoir at a vacuum, but the high-pressure reservoir must be sufficiently large to smooth out the effect of molecules being inserted, which can lead to anomalies and discontinuities if they are inserted too close to the entrance of the test section, or overlapping another molecule.

![Figure 4.1](image_url) Schematic of molecules driven through the test section by maintaining two reservoirs at different pressures. The low-pressure reservoir is usually maintained at a vacuum.
This approach to flow generation needs a very large number of molecules, most of which are not within the test section and contribute little to the results of the simulation. This method does, however, allow pressure-driven flows to be directly modelled in a controlled and stable environment. However, in order to model the flow of fluid or molecules through a meso scale test section, the number of molecules needed would be prohibitively large.

Two similar, but reduced, approaches were developed by Liao and Yip [73] and Sun and Ebner [77]. The first, by Liao and Yip, is known as the reflecting particle method (RPM) [73]. This method removes the large reservoir and uses an extended part of the test section, with periodic boundary conditions at each end, to form a smaller reservoir in line with the flow. The high and low pressures are generated by using a selective membrane at some point along the flow, which allows molecules to pass freely across in one direction, but in the other direction a proportion of the molecules are reflected back. Figure 4.2 demonstrates the application of the membrane to model pressure-driven flow along a test section. The pressure difference can be controlled by altering the probability of reflection of the membrane.

The second approach is by Sun and Ebner [77] where the high- and low-pressure regions are created by replacing the periodic boundary conditions with a source region and a sink region. The sink is maintained at a vacuum by removing all molecules from the system that enter this region. The source region, at the opposite end of the cell, is a small volume with a movable boundary at the end. This boundary acts as a piston, reducing the volume of the source region and pushing the molecules into the volume considered by the simulation. Once the boundary has travelled a short distance, the density of the system is measured and the boundary resets to its original position; the void created fills with enough molecules of the same density. Molecules are added with velocities as described by the Maxwell velocity distribution at the temperature of the wall. This approach maintains a pressure gradient between the source and sink regions, causing a flow of molecules. The number of molecules injected and the volume

![Diagram of the reflecting particle method](https://via.placeholder.com/150)

**Figure 4.2** Left: the reflecting particle method, where molecules may pass freely in one direction, but are reflected with probability $p$ when exiting the ‘high-pressure’ region. Right: the RPM membrane used to investigate channel flow. The test section must be clear of the membrane.
swept by the boundary is very small to minimize oscillations occurring as the new particles break out of the regular lattice used initially to position the particles. Sun and Ebner applied this successfully in two dimensions to study compressible flow [77] and has the potential to be applied in three dimensions.

By using these methods of applying a pressure gradient to drive the flow of molecules, force is transmitted in a very natural way, through the interactions of the particles. This is useful in modelling the reaction of a fluid to pressure gradients, as the pressure and density vary continuously along the length of the test section between the source and sink regions. However, this is not useful for considering steady, fully developed flows, which model the flow in channels with no density variation along their length (an infinitely long test section). These systems require a different approach.

To model fully developed flows, Sokhan et al. [60] modelled a driven flow between parallel plates by applying a uniform acceleration, in the required direction of flow, uniformly to all molecules in the system. The application of an acceleration is similar in a way to a gravitational effect pulling the molecules along the test section, although the acceleration is typically much larger. This, however, creates the problem that by applying an external force to the molecules energy is added to the closed system. As this external work is being done on the system in order to approximate the effect of a constant pressure gradient (effectively applied over an infinitely long section), the energy added to the molecules must be removed. The energy is removed by the application of a thermostat.

The simplest form of thermostat, velocity scaling, has been described in Section 3.4, but is far too crude for this application as temperature must be controlled throughout the duration of the simulation, even during the production phase.

4.3 THERMOSTATS

The aim of a thermostat is to maintain a control on the temperature, and hence kinetic energy, globally within the system. However, the way in which this is done is critical as controlling/altering the energy of molecules within the system affects the dynamic behaviour of the whole system. Control must be maintained without having an effect on the system behaviour. If energy is being added to the system in the form of an acceleration to model the effect of a pressure gradient acting in one direction, it should have the effect of influencing the proportions of energy within the system, but not change its global value.

4.3.1 Gaussian Thermostat

The Gaussian thermostat aims to control the temperature of the system by using Gauss’s principle of least constraint [83]. The principle of least constraint states
that the constrained trajectories actually followed should deviate as little as possible from the trajectories of the unconstrained equations of motion.

In the motion of the molecules in the system, the equation of motion is simply Newton’s law,

\[ F = ma, \]  

(4.1)

which we wish to constrain to a constant global temperature, leading to the formation of a constraint function that constrains the system temperature to the set temperature, as

\[ g(r, v, t) = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 - \frac{3}{2} N k_b T = 0, \]  

(4.2)

which is the difference between the system temperature and the temperature set by value \( T \). Differentiating once with respect to time gives the equation for the constraint plane

\[ \sum_{i=1}^{N} m_i v_i a_i = 0 \]  

(4.3)

Assuming that the unconstrained equations of motion lead the simulation away from the constraint surface, the equations of motion are corrected by considering the function of the square of the curvature \[ \{84\}, C: \]

\[ C = \frac{1}{2} \sum_{i=1}^{N} m_i \left( a_i - \frac{F_i}{m_i} \right)^2. \]  

(4.4)

The physical accelerations in the system correspond to the minimum value of \( C \), so for an unconstrained system, \( C = 0 \) and the system evolves under Newton’s equations. This leads to the constrained equation of motion:

\[ a_i m_i = F_i - \lambda v_i m_i, \]  

(4.5)

where \( \lambda \) is the friction factor applied to the molecules as scaling by their momentum and defined as

\[ \lambda = \frac{\sum_{i=1}^{N} F_i v_i}{\sum_{i=1}^{N} m_i v_i^2}. \]  

(4.6)
Equations (4.5) and (4.6) are known and implemented together as the *Gaussian isokinetic equations of motion*. It is important to note that the scaling/friction factor is different to that used in the velocity scaling approach, and friction/scaling is applied as a function of the individual molecule momentum.

### 4.3.2 Nosé–Hoover

The Nosé–Hoover thermostat [85, 86] is a method of temperature control that is based on the inclusion of an extra parameter in Nosé–Hoover dynamics coordinate space [87]. This means the inclusion of the thermostat parameter, $\xi$, the second derivative of which is simply a function of the kinetic energy of the system and the temperature:

$$\ddot{\xi} = \frac{1}{Q} \left[ \sum_{i=1}^{N} m_i v_i^2 - N_f k_b T \right],$$

(4.7)

where $N_f$ is the number of degrees of freedom of the system. This equation for $\ddot{\xi}$ is the difference between the actual and set temperature of the system, which is multiplied by the reciprocal of a weighting function, $Q$, and can be defined as

$$Q = N_f k_b T \tau^2,$$

(4.8)

where $\tau^2$ is the characteristic time scale of the motions of real particles [88]. This weighting function controls the application of the thermostat and can be adjusted for particular applications. A low weighting function can cause high-frequency oscillations in $\dot{\xi}$, whereas a high value can overconstrain the system.

The Nosé–Hoover thermostat is used in this method because its level of control can be tuned to the specific system of interest using the mass parameter, allowing the thermostat to work effectively while applying the minimum of constraint on the system. It is, however, more complex to implement it in the equation of motion; the implementation will be considered next.

#### 4.3.2.1 Implementation in the proposed meso scale model

The thermostat parameter therefore has its own equation of motion and can be included in the velocity Verlet equations of motion of the molecules. The equations
of motion for the complete system proceed through the simulation time as follows:

1. Thermostat parameters and mass $Q$ are computed:

$$\ddot{\xi}(t) = \frac{1}{Q} \left[ \sum_{i=1}^{N} m_i v_i(t)^2 - N_f k_b T \right],$$

$$\ddot{\xi}(t + \delta t/2) = \ddot{\xi}(t) + \ddot{\xi}(t) \delta t/2,$$

$$\ddot{\xi}(t + \delta t) = \ddot{\xi}(t) + \dddot{\xi}(t + \delta t/2) \delta t.$$

2. Molecular velocities and positions are updated, including the corrections from the thermostat parameter, using the velocity Verlet algorithm:

$$v_i(t + \delta t/2) = v_i(t) + [a_i(t) - v_i(t) \ddot{\xi}(t + \delta t/2)] \delta t/2,$$

$$r_i(t + \delta t) = r_i(t) + v_i(t + \delta t/2) \delta t.$$

3. Molecular forces are updated using interaction and boundary forces, $F = ma$.

4. Complete the time step for the velocity of molecules and the thermostat parameter:

$$v_i(t + \delta t) = v_i(t + \delta t/2) + [a_i(t + \delta t) - v_i(t + \delta t) \ddot{\xi}(t + \delta t)] \delta t/2,$$

$$\ddot{\xi}(t + \delta t) = \ddot{\xi}(t + \delta t/2) + \left[ \sum_{i=1}^{N} m_i v_i(t + \delta t)^2 - N_f k_b T \right] \frac{\delta t}{2Q}.$$

This coupled equation is then solved using the iterative Newton–Raphson method.

These thermostats allow for the control of molecular systems, while presenting the minimum effect on the dynamics of the system. This allows for molecules to be driven by a pressure gradient, modelled by an acceleration applied to the molecules. However, with such a complex system operating, there needs to be careful benchmark tests made to make sure of the accuracy of the simulated molecules.
4.4 CASE STUDIES

To explore the capabilities of the developed approach, a number of case studies are presented. These are split into two sections, a study of the parameters of the bulk property collection scheme and an examination of temperature- and flow-driven systems. The initial simulations are performed with the thermostat disabled, and thus a temperature control is not necessary, but the simulation of a driven flow has the thermostat feature enabled.

4.4.1 Sampling

To study the parameters for the extraction of the ensemble averages, a molecular scale system is used to provide the most challenging bulk method. The reason for this is twofold: to reduce the computational load of the simulations to allow many simulations to be performed in a reasonable amount of time and, second, with only a few molecules, the least squared approximating nodes are starved for data, providing an excellent test for the performance of this approach at its weakest point, systems with low numbers of molecules.

To test the operation and sensitivity of these parameters, a simple molecular dynamics simulation is used as a demonstration, and is set up in a similar way to the simulation presented in Section 3.4. For this application, the limits of the system are set to a 15 nm × 15 nm × 8.3 nm box, containing 5104 methane molecules interacting with a Lennard–Jones 12-6 potential. Periodic boundary conditions are applied in all three dimensions. The fluid is permanently at rest, with motion occurring only from internal thermal diffusion for the system temperature of 300 K. Within the molecular flow field a one-dimensional line of nodes was inserted along the y direction, at 0.5 nm intervals (shown in Figure 4.3).

As mentioned, the simulated fluid is at rest, so by recording the bulk velocity of the fluid in the x direction, the molecular velocities occurring by thermal diffusion should cancel out to yield an ensemble average of zero velocity at each of the nodes. With this knowledge, this system can be used to explore the effect of the parameters used to gather the least square approximations of the molecular behaviour. Investigations into the optimal number of time steps between samples, number of samples used in each ensemble average and the radius of the weighting function for each node are presented below. A study of the effect of the different weighting functions is also presented.

### 4.4.1.1 Case Study 1: length of time between samples

This investigation looks into the effect of coherence between samples and will identify when the molecules local to each node have had sufficient time to change
Figure 4.3 Simulation of a periodic molecular system, modelling fluid at rest; molecular properties are averaged by an array of one-dimensional nodes placed across the field.

The fluid is at rest, so the bulk velocity of the fluid is zero. However, the molecules of the fluid are constantly moving throughout the fluid, diffusing with thermal motion. Poor phase space sampling will yield a nonzero value of velocity at the nodes and lead to larger variations in the ensemble values at the nodes. A more complete sample, of a wider portion of phase space, will lead to the thermal...
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Figure 4.4 A graph demonstrating the relationship between the interval between samples and the standard deviation of the resulting one-dimensional velocity distribution. The equation of the best fit line is also shown.

motion of the molecules to cancel out, giving consistent values of velocity at the nodes. In this case, where there is no driving force applied to the fluid, the velocity at any point should be zero.

Figure 4.4 shows a plot of the average standard deviation (averaged over all nodes) of the values of velocity plotted against the number of time steps between each sample. It is necessary at this point to remember that the same number of samples are taken for each case so that every ensemble taken contains the same amount of data. The results show an exponential decrease in the standard deviation of the nodal values as the time between samples increases. This leads to the conclusion that samples taken at more than 200 time step intervals (400 ps) gives a good result, but the larger the time between samples the less variation there will be in the results. Increasing the sample interval to 400 time steps reduces the variation 18% but the ensemble time increases by 200%. The line of best fit is asymptotic to zero variation, indicating that the sample length could be extended indefinitely while still reducing the variation in the results. However, in practice a reasonable variation must therefore be accepted to allow for an acceptable resolution in time. For these cases, the variation is considered acceptable at 200 time steps or greater.

Figure 4.5 shows a plot of the average value of velocity (averaged over all nodes) plotted against the interval between samples. This shows the accuracy of the ensemble increasing as the time between samples increases, achieving an average velocity closer to the zero velocity specified. However, the data presented
Figure 4.5 Graph showing the average value of velocity plotted against the number of time steps between samples.

contains a significant level of noise making a relationship difficult to determine, but the average velocity shows a definite trend to zero as the sample time increases, giving a very close approximation for sample times greater than 250 time steps.

Both of these graphs demonstrate the same result. The more time molecules are allowed in order to change state before being re-sampled, the better the interrogation of the available phase space performed by each of the local approximations. In both cases, the improvement is exponential, although the average velocity data are noisy. However, a longer time between samples reduces the resolution of the ensembles in terms of simulation time. This must be considered when long sample times are used. A way of increasing the time between samples is to take fewer samples per ensemble, which will be discussed in detail in the next case study:

4.4.1.2 Case Study 2: number of samples per ensemble

By performing a similar study, the effect of the number of samples collected per ensemble average can be investigated. Simulations were set up as described above, with the samples taken at regular intervals of 75 time steps, but the ensembles were constructed with between 2 and 40 samples.
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Figure 4.6 Graph standard deviation of velocity plotted against the number of samples per ensemble.

Figure 4.6 shows a plot of the average standard deviation of the collected ensemble velocity over all the nodes against the number of samples collected per ensemble average. The graph shows a similar relationship to sample timing study, with a slightly lower gradient, but as the number of samples increases in each ensemble, the variation in the results of this steady state system reduces to give more stable values. As the number of sample points increases, more points throughout the available phase space are sampled, leading to a better representation of the local ensemble by the approximation.

4.4.1.3 Case Study 3: time between samples versus number of samples per ensemble

The above study suggests that increasing the time between successive samples of the molecular data should be as long as possible in order to sample the widest available area of phase space. Similarly, to obtain bulk properties with the least amount of noise, there must be the maximum number of samples taken for each ensemble average in order to sample as many different points in the phase space as possible. However, in a realistic simulation example, there is a limit to the amount of simulation time that can be allowed between the ensemble averages being taken. This could be a limit on an ensemble taken for a steady system over a long period of time or short intervals for a dynamic system, where greater resolution in terms of time is required. In these cases, there is a maximum time over
which an ensemble can be taken. This means that within one ensemble a balance must be made between the number of samples used in each ensemble and the time between each sample taken.

To test the sensitivity of this tradeoff, the same example of fluid methane at rest, as described above, was used. The total ensemble time is limited to 20000 time steps, and the sample interval is varied between 100 and 1000 time steps to correspond to 200 and 20 samples per ensemble respectively.

Figure 4.7 shows a plot of the standard deviation of the ensemble velocity, averaged over three ensembles taken for the varying time between samples. In the previous results, it has been shown that the best and most stable results are obtained by leaving long periods between taking each sample and taking a large number of samples. However, for simulations with a finite time frame, there is a limit on this behaviour. As the length between samples increases, the number of samples that can be taken in the ensemble reduces, causing the variation in the results to increase as the time between samples increases. The results shown in Figure 4.7 are dominated by the variation caused by the reduced number of samples in the ensemble, and the variation expected to be caused by the short sample times does not have an observable effect in the sampled region.

From these results, it can be concluded that the largest acceptable time between samples is approximately 400 time steps for this case. To generalize this, 400 time steps represents 2% of each ensemble time, allowing 50 samples to be taken in each ensemble. Although the variation in the solution maintains a similar value for lower times between samples, the highest available values should be used to

![Figure 4.7](image-url)  
**Figure 4.7** Plot to demonstrate the effect of trading off the length of time between samples against the number of samples per ensemble, for a fixed ensemble length of 20000 time steps.
achieve the best representation of the phase space, saving on the computational time involved with processing a higher number of samples.

### 4.4.1.4 Case Study 4: radius of weighting function

The radius of the weighting function governs the area or volume over which the approximation is constructed at each node. This parameter is critical, as a smaller radius gives better resolution in space at the cost of fewer molecules within each sample. Simulations were performed as above for the same sample times and number of samples per ensemble, and in this case only the radius associated with the nodes was altered. To give a idea of scale, the 29 nodes are spaced at 0.5 nm intervals across the 15 nm width of the simulation. The radius at each node is changed from 0.2 nm up to 2 nm. Figure 4.8 gives an approximate idea of scale, showing the radius in two dimensions. Figure 4.9 shows a plot of the standard deviation of the velocity obtained at each of the ensembles against the ratio of the node’s radius to the diameter of the underlying molecules (for methane $\sigma = 0.381 \text{ nm}$). This shows an increasing accuracy as the radius is increased, with an abnormally large value for a standard deviation at $R/\sigma = 0.5$. This is due to the radius being so small that only a single molecule can fit in the node’s ‘zone’, making the node very sensitive to the properties of an individual molecule.

This can also be highlighted in the plot of the average velocity, shown in Figure 4.10, which reinforces the fact that one of the nodes has sampled a molecule with a speed that is on the higher side, as given by the Maxwell–Boltzmann distribution. This has had a dramatic effect on the value of one of the nodes. These results highlight that the radius of a node must be large enough to capture as many molecules as possible but be small enough to be able to capture any variations that may be present in the distribution of the property, leading to a compromise between resolution, stability and statistical error.

![Two-dimensional example of the radius of a weighting function compared to the number of molecules present, for the example simulation.](image)
**Figure 4.9** Standard deviation of velocity collected at the nodes, plotted against the ratio of the node radius to the molecular diameter.

**Figure 4.10** Average ensemble velocity plotted against the ratio of the node radius to the molecular diameter.
4.4.1.5 Case Study 5: weighting function

The weighting function plays a very important part in the property extraction, being the basis on which molecules are allowed to contribute to a node’s ensemble average. By again performing the same test simulation, the effect of the different weighting functions highlighted in Section 3.3.5 (quadratic, exponential and Gaussian weighting functions) can be tested.

Figure 4.11 shows the values of the average ensemble standard deviation for the three weighting functions tested. From this, the Gaussian weighting function comes out on top, providing the most stable result, closely followed by the exponential function. In this application, the quadratic weighting function gives the most variation.

From these studies, it can be concluded that in order to obtain good stable results for the bulk properties collected at the least squares nodes, each sample must probe the available local phase space as comprehensively as possible. To do this, the ensembles must be constructed from as many samples as possible, and the samples must be taken with long intervals between them to allow the molecules to select a new phase space position. For this reason, a sample interval between 100 and 400 time steps should be used. However, these two parameters must be selected with the resolution of the distribution of properties, with respect to time, in mind. Similarly, for the nodal radius a larger radius will provide better phase space sampling but reduces the resolution in terms of the simulation space.

Figure 4.11  Values of standard deviation for each of the weighting functions.
The parameters for the bulk property collection must therefore be carefully chosen for the system of interest, especially for systems that include gradients and properties dependent on position and time within the simulation.

### 4.4.2 Gradient Study

In the previous section, the local averages have been extracted and evaluated for stable systems with approximately uniform properties throughout. This was used to study the effect of the parameters of the bulk ensemble approximations against a known value. In this section, systems involving properties that vary in space as well as time are considered. These provide more of a challenge, as spatial and temporal resolution of the nodes must be seriously considered and traded off against the stability and accuracy of the ensemble averages collected at the nodes.

Two distributed bulk properties will be considered. First, the distribution of temperature will be studied in a fluid at rest, contained between two parallel plates at different temperatures. The nodes will then monitor the distribution of temperature throughout the field, as the thermal energy propagates through the fluid via the molecular collisions. Second, velocity distributions will be studied within a flowing fluid field. As will be shown, the study of velocity distributions requires special treatment, as extra controls on the system are needed, which will be presented and validated against existing molecular simulations.

#### 4.4.2.1 Case Study 6: temperature gradient

As an initial test of this method, the molecular simulation was performed on a fluid at rest. The fluid is trapped between two parallel plates of different temperatures, as shown in Figure 4.12. The plates are separated by 7.1 nm, with the left-hand wall having a temperature of 300 K and the right-hand wall having a temperature of 250 K. The fluid methane in the middle interacts with the wall via the diffuse boundary conditions. The tangential momentum accommodation coefficient was chosen to be \( f = 0.81 \), to simulate a sparse solid lattice of carbon molecules. A large value of \( f \) was used to achieve a large amount of variation of the temperature within the simulation domain to examine the ability of the bulk property extraction component to capture details of a relatively high gradient property.

The fluid molecules were equilibrated from their initial lattice and temperature of 275 K and settled to an equilibrium state. The temperature of the molecules were observed using 36 nodes placed at 0.2 nm intervals within the domain. The radius of interaction was set to 0.4 nm, and ensembles were taken over 50000 time steps (2 fs time steps).

The molecules were free to interact with each other, with the only temperature control being applied by the boundary walls. The resulting thermal profiles for
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Figure 4.12 Schematic of fluid with the temperature gradient. The wall on the left is maintained at 300 K and the wall on the right at 250 K. An array of one-dimensional least squared nodes crosses the fluid between them to collect local values for temperature.

the steady state result are shown in Figure 4.13. From this graph, the temperature gradient extracted from the molecular model can be clearly seen between the average ensemble temperature collected near the left-hand wall and the value at the right-hand wall. In the centre of the fluid section, the temperature gradient is almost linear, but the gradient becomes steeper in a relatively wide region close to the walls. This is due to the slip and jump at the boundary, where a discontinuity is allowed. Error bars are shown at 0.5 %, indicating the variation between profiles extracted.

This simple example highlights how the least squares nodes can be implemented and used to interrogate a molecular domain, providing distributions of useful engineering properties. The next step is to move this method on to a more challenging system that can aid in the validation of the molecular mechanics model.

4.4.2.2 Case Study 7: velocity

This method allows the molecular model to simulate engineering systems at meso scale dimensions with large numbers of molecules. However, the accuracy of this model with its simplifications for boundary conditions and pressure gradients needs validation with existing work to ensure that the model is still accurate. The performance of a molecular simulation can be tested in a number of ways, and in this section validation results are presented to give an idea of the accuracy
Figure 4.13  Temperature gradient for methane between two parallel plates at \( x = 0 \), maintained at 300 K, and at \( x = 7.1 \) nm, maintained at 250 K. The black line shows the average temperature profile shown with a 0.5 % variation.

of the method. There is almost no experimental data available for meso scale systems and computational restrictions limit comparisons on the continuum scales, so tests are performed at high-end molecular scales where information on simulations is readily available. This also allows the testing of the molecular model separately from the approximating (least squares) components.

The molecular dynamics model was tested against the molecular simulations performed by Sokhan et al. [60], whose simulations were performed using a model based on the DL_POLY [89] package. The system considers fully developed Poiseuille flow of methane through a graphite slit pore.

The system is simplified to methane molecules flowing between two parallel plates of graphite, which contain the molecules in the \( y \) direction and periodic boundary conditions in the \( x \) and \( z \) directions. The system dimensions are shown in Figure 4.14, with the graphite plates being separated by 7.1 nm; the lengths of the simulating cell in the \( x \) and \( z \) directions are 7.715 nm and 8.368 nm respectively. Into this volume was put 5104 methane molecules, corresponding to a reduced density of \( \rho' = 0.61 \) and interacting via a Lennard–Jones potential with a collision radius \( \sigma = 0.381 \) nm and a well depth \( \epsilon/k_B = 148.1 \) K.
The graphite plates were modelled in Sokhan’s simulation using two fully molecular solid lattices of carbon atoms ($\sigma = 0.34$ nm and $\epsilon = 28$ K). The wall used in this simulation was modelled with diffuse boundary conditions, with a tangential momentum accommodation coefficient of 0.029, which was derived for this system in the same paper by Sokhan et al. [60] and confirmed by the work of Arya et al. [61] for methane on graphite.

Typically, the solid–fluid interaction parameters are computed using the Lorentz–Berthelot combining rule, which between the carbon and methane molecules leads to parameters $\sigma = 0.3605$ nm and $\epsilon/\k_B = 64.39$ K. However, the work presented by Sokhan et al. shows results for different strengths of interaction between the wall and fluid molecules, so a stronger potential of $\epsilon/\k_B = 148.1$ K was used to simulate a higher degree of wetting.

The fluid molecules are driven down the channel by applying a uniform acceleration to all molecules of $4 \times 10^{-11}$ m/s$^2$. In Sokhan’s simulations with flexible walls, the energy added via this acceleration could be removed and adsorbed by the wall molecules. However, in the case of the rigid molecular walls and the diffuse boundaries used in the present model, a Gaussian thermostat was used to perform the same task.
Figure 4.15  Comparison between the presented model and results published by Sokhan et al. [60]. Error bars are shown at ±3 m/s.

The resulting velocity profiles are shown for comparison in Figure 4.15. The results from Sokhan were taken over a 1 ns period, whereas the results obtained by the presented method were constructed within a 0.1 ns long ensemble. The variation displayed by successive profiles extracted by the presented method is less than ±3 m/s or 5% of the average velocity; the variation of Sokhan’s comparison is not known. The two velocity profiles show very similar curvature, but the results of Sokhan et al. [60] display a slightly lower average velocity than the results of the presented method. The similarity between the profile shapes means that the fluid molecules propagate the fluid energy in the same way, although the differences in the average velocity appear to be caused by differences in the boundary conditions applied. As an additional check extra validation tests were performed to test the system conformity to the thermal distributions.

The molecular dynamics of the fluid molecules was checked against the Maxwell–Boltzmann velocity distribution in each of the three dimensions, as well as the total speed distribution. Figure 4.16 shows the distributions from a short snapshot of the steady state simulation above, along with the exact versions of the distributions. All distributions show good agreement with the profile of the exact versions within 15%, demonstrating that the molecules of the fluid conform to the correct thermodynamic state and that the thermostat is not having adverse effects on the velocity distributions.
Figure 4.16  Distribution of $X$, $Y$ and $Z$ components of velocity, and the distribution of resultant speeds compared to distributions for temperature of 300 K with 15 % error bars.

The velocity distribution for the velocities assigned to the thermalized molecules at the boundary were also tested, to ensure that the thermalization was being performed correctly. Figure 4.17 shows the same level of variation as the bulk temperature distributions within the fluid.

Figure 4.17  Velocity distribution of molecules thermalized by the boundary, shown against the velocity distribution for 300 K with 15 % variation
These results provide confidence in the developed meso scale molecular model. The simplifications applied to allow larger molecular systems to be accessed have not had an adverse effect on the mechanics, as shown by this molecular scale example compared to existing molecular simulation data from a well-established and developed code.

4.5 SUMMARY

In this chapter the method developed in the previous chapter has been extended to enable the simulation of flowing fluid systems. The generations of a flow have been implemented in the form of applying a representative acceleration to all molecules in the system. This addition of energy is balanced by a thermostetting system designed to remove thermal energy from the simulation without affecting the dynamics of the molecules.

A number of case studies have been presented to look at the behaviour of the bulk property extraction scheme. These highlighted the importance of sample length and the size of the ensemble as well as their effect on the stability and resolution of the solution. Also highlighted was the tradeoff between sample and ensemble times for simulations within a restricted time frame.

Case studies involving property gradients were also considered. The temperature gradient simulation example highlights the thermal control that can be imparted on the fluid by the boundaries. This also highlighted the method’s ability to capture bulk property distributions with high accuracy and resolution. The velocity profile case study results demonstrated good agreement with both published results and thermal distributions.