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The Nature of Fluid Flow

Aim. To provide the reader with basic knowledge on the treatment of fluid at scales above and below the meso scale.

1.1 INTRODUCTION

The fundamentals of fluid flow on a wide range of scales are introduced in this chapter. The characterizing properties of a fluid and their relevance at large scales (kilometre to millimetre scale) and small scale (nanometre and angstrom scale) will be discussed. The continuum approach to describing the behaviour of a fluid will be presented along with the methods of simulation at the continuum scale. In contrast, the molecular scale is considered along with fluid structure and simulation methods used at this scale. Examples of the change in physics and fluid behaviour that occur as the scale is reduced are presented, concentrating on the effect of confinement on a fluid.

This chapter highlights the special requirements of meso scale systems. Elements from both the continuum scale and the molecular scale are needed to model and describe a meso scale fluid system fully.

1.2 BASICS OF FLUID MOTION

The basic characteristic property that defines a fluid is viscosity. Fluid, unlike solids, is unable to offer any permanent resistance to a shearing force. The fluid will continue to deform as long as the force is applied, taking the shape of any solid boundary it touches. The deformation of a fluid occurs from shearing forces.
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Figure 1.1  Internal shear between fluid layers.

acting tangentially to any solid surface. The fluid can be considered as layers parallel to a surface, which slide over each other, as shown in Figure 1.1. Each fluid layer applies a shear force to the next, and is in turn sheared by those it touches.

The ability to deform continuously under an applied force makes fluids behave differently from solids. Solid bodies are capable of maintaining an unsupported shape and structure, and can resist finite shear.

Fluids themselves fall into two categories, liquids and gases. To a fluid dynamicist, who is interested in flows at the macro scale, there are two characterizing differences between them:

- Liquids have densities an order of magnitude larger than gases.
- Liquids and gases respond very differently to changes in pressure and temperature.

Gases can also be expanded and compressed more easily than liquids due to the lower density and spacing between molecules. The motion of all fluids relies on the interaction and internal shear between fluid layers, but the actual interaction between layers occurs from collisions between many molecules on the molecular scale ($\sim 10^{-9}$ m). In fact, all fluid effects and properties occur from molecular interactions, but at the macro scale ($\sim 10^{-4}$ m) the detailed molecular physics of this behaviour can be neglected as the number of molecules within the characteristic length can be considered as sufficiently large. At these scales the fluid can be viewed as having physical properties corresponding to the statistical averages of the underlying molecules and are known as continuum or bulk properties. Molecular physics, manifested in a continuum framework, has the ability to be defined as continuous functions of time and space.
1.2.1 Continuum/Bulk Properties

Bulk or continuum properties such as velocity, density and pressure remain constant at a point and changes due to molecular motion are assumed to be negligible. These properties are also assumed to vary smoothly from point to point with no jumps or discontinuities. This assumption is correct as long as the characteristic distance of the system is of an order of magnitude greater than the distance between molecules.

This assumption of bulk physical properties allows the behaviour of fluid systems to be approximated by a set of deterministic equations that represent the underlying infinite chaotic molecular motion on a much larger scales. The definition and basis of these bulk properties will be of significant importance in later discussions, so it is necessary to explain the origin of some of these bulk properties to clarify concepts.

1.2.1.1 Density

The density of a fluid is defined as the mass contained within a unit volume. It is computed as a function of mass ($m$) and volume ($V$) of a sample as follows:

$$\rho = \frac{m}{V}. \quad (1.1)$$

This expression of density is represented in terms of mass per unit volume (kg/m$^3$). Other expressions of density used are specific weight (weight per unit volume, N/m$^3$), relative density (relative to another density, dimensionless) and specific volume (reciprocal of density, m$^3$/kg). Density can also be computed from molecular properties, in terms of sample volume, $V$, containing $N$ molecules of individual mass, $m_{\text{molecule}}$ [3]:

$$\rho = \frac{N m_{\text{molecule}}}{V}. \quad (1.2)$$

This expression also has units of kg/m$^3$ and can be defined from $N = 1$ to $N = \infty$.

1.2.1.2 Temperature

The temperature ($T$) at any point in a fluid is derived from the internal kinetic energy of the underlying $N$ molecules, each with velocity, $v_i$, and mass, $m$ [4]:

$$E_{KE} = \sum_{i=1}^{N} \frac{1}{2} m v_i^2. \quad (1.3)$$
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At continuum or bulk scales the number of molecules is assumed to be infinite, but the distribution of the velocity of this (almost) infinite number of molecules can be assumed to follow the Boltzmann distribution, which in one dimension appears as

$$ f(v) = \sqrt{\frac{m}{2\pi k_b T}} e^{-mv^2/2k_b T}, \quad (1.4) $$

where $k_b$ is the Boltzmann constant. This distribution can then be used to calculate the average squared velocity in the system to relate the velocity distribution to the kinetic energy,

$$ \langle v^2 \rangle = \sqrt{\frac{m}{2\pi k_b T}} \int_{-\infty}^{\infty} v^2 e^{-mv^2/2k_b T} dv, \quad (1.5) $$

which gives

$$ \langle v^2 \rangle = \sqrt{\frac{m}{2\pi k_b T}} \frac{\sqrt{\pi}}{2} \left( \frac{2k_b T}{m} \right)^{3/2} = k_b T \frac{m}{m}. \quad (1.6) $$

The equation for the translational kinetic energy of the molecules can now be related to the temperature of the system in one dimension:

$$ E_{KE} = \frac{1}{2} \frac{m}{m} \langle v^2 \rangle = \frac{1}{2} k_b T. \quad (1.7) $$

For three dimensions, this simply becomes

$$ \frac{1}{2} \frac{m}{m} \langle v^2 \rangle = \frac{1}{2} N k_b T, \quad (1.8) $$

which describes the temperature of a local system of $N$ molecules. In terms of bulk properties, where locally $N \to \infty$, the temperature is considered constant and varies smoothly from over the whole domain.

1.2.1.3 Pressure

The pressure is explained by kinetic theory as arising from the force exerted by colliding gas molecules on the walls of the container [5]. To explain the mechanics of pressure, consider a single molecule with velocity, $v$, along the $x$ direction contained within two walls perpendicular to its direction of travel and separated by length, $l$, as shown in Figure 1.2.
Figure 1.2  Single molecules oscillating between two walls.

By considering the collision between the molecule and one of the walls, the momentum lost by the molecule and the wall is

$$\Delta p = p_{\text{initial}} - p_{\text{final}} = m v_x - (-m v_x) = 2m v_x. \quad (1.9)$$

The time between successive collisions on this particular wall will be

$$\Delta t = \frac{2l}{v_x}. \quad (1.10)$$

Force is the rate of change of momentum, so the force on the wall from the single molecule is

$$F = \frac{\Delta p}{\Delta t} = \frac{2m v_x}{2l/v_x} = \frac{m v_x^2}{l}. \quad (1.11)$$

For a large number ($j$) of molecules and collisions with the wall, this becomes

$$F = \frac{m}{l} \sum_j v_{jx}. \quad (1.12)$$

Now, by adding in collisions with walls in all six directions this gives

$$F = 2 \frac{m}{l} \sum_j \left( v_{jx}^2 + v_{jy}^2 + v_{jz}^2 \right). \quad (1.13)$$

For equilibrium conditions and a sufficiently high collision rate with the walls, the force on all six walls can be assumed to be the same. Therefore the force on a
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single wall becomes

\[ F = \frac{1}{6} \left( \frac{m}{l} \sum_j v_j^2 \right) = \frac{m \sum_j v_j^2}{3l}, \quad (1.14) \]

where \( v_j \) is the velocity of molecule \( j \) in three dimensions. It is now possible to talk in terms of the average velocity of the molecules, \((1/N) \sum_j v_j^2\), which can be represented by \( \overline{v}^2 \):

\[ F = \frac{Nm \overline{v}^2}{3l}. \quad (1.15) \]

This can then be divided by the area, \( A \), of the wall to give the pressure

\[ P = \frac{F}{A} = \frac{Nm \overline{v}^2}{3lA}. \quad (1.16) \]

The cross-sectional area multiplied by length yields a volume, \( Al = V \), which when combined with Equation (1.2) yields

\[ P = \frac{1}{3} \rho \overline{v}^2, \quad (1.17) \]

thereby describing pressure as a function of density and kinetic energy of molecules, which, as shown in Equation (1.8), is in turn directly related to the temperature of the system. As with temperature, at continuum scales the number of molecules tends to infinity, and any fluctuations or statistical differences become approximately zero. In this case both pressure and temperature may be considered as constant at any point in the fluid domain.

1.2.1.4 Viscosity

Viscosity quantifies the resistance put up by a fluid undergoing finite shearing forces and can commonly be perceived as internal fluid friction, or resistance to pouring. This effect occurs from the drag forces occurring between adjacent fluid layers moving with different velocities. The concept of viscosity is best demonstrated by example.

Figure 1.3 shows a fluid trapped between two parallel plates separated by distance \( H \). The top plate moves with constant velocity \( U \) and the bottom plate is at rest. The fluid in between them adheres to both plates, so that the fluid layers at each of the plates has the same velocity at the plate. The velocity of the fluid changes linearly in this case, so the velocity at any point between the plates can
be computed as follows:

$$u(y) = \frac{y}{H}U.$$  \hfill (1.18)

It is known from experiments that, for Newtonian fluids, the frictional force per unit area, $\tau$, is proportional to the difference in velocity between the two plates and inversely proportional to the separation, $H$. Together, this is interpreted as the frictional force being proportional to the velocity gradient, $du/dy$,

$$\tau = \mu \frac{du}{dy},$$  \hfill (1.19)

with the proportionality factor being the fluid parameter $\mu$, which characterizes the drag between fluid layers and is known as the dynamic viscosity. This is known as Newton’s law of viscosity, where a linear relationship between velocity gradient and shear stress is assumed. While this is valid for most simple fluids such as water and most gases, non-Newtonian fluids such as plastics and pseudo plastics exhibit a more complex relationship and Newton’s law does not apply.

To obtain the coefficient of viscosity, $\mu$, for a Newtonian fluid, the situation shown above in Figure 1.3 is used. The coefficient is then extracted by comparing the applied $U$ and the drag force on the opposite plate, $\tau$.

The concept of kinematic viscosity is described in fluid systems where frictional and inertial forces interact. It is defined as the ratio of dynamic viscosity,
Causes of viscosity  Viscous effects occur due to internal friction between fluid layers, and it is important to consider the nature and cause of this drag. The molecules in a fluid are continuously moving and have little, if any, structure. Consequently, they are in constant molecular exchange between fluid layers. This exchange occurs via two mechanisms, the transfer of mass, by a fluid molecule physically crossing between fluid layers, and the transfer of energy via interlayer collisions/potential energy interactions.

This constant exchange occurring over a sufficiently large number of collisions causes energy and momentum to propagate smoothly throughout the fluid at a rate governed by the physical properties of the molecular interactions and the conditions of the fluid. However, the condition of the fluid in terms of pressure and temperature causes different effects in liquids and gases.

Viscosity of gases  In a gas, the molecules are widely spaced and interact relatively little, so an increase in temperature increases the kinetic energy of the molecules and viscosity increases as a result of increased mass transfer between layers. According to the kinetic theory of gases [5], the viscosity is proportional to the square root of the absolute temperature. This, however, is an exact solution to an approximate model while in reality, the rate of increase of viscosity is much higher [3]. In gases, viscosity is found to be independent over the normal range of pressures, with the exception of extremely high pressure.

Viscosity in liquids  In liquids, which have much higher densities, the distance between molecules is much shorter and the cohesive/attractive forces between them increase the viscous effect. The response to an increase in temperature, and hence kinetic energy, decreases the effect of these cohesive forces, which reduces the viscosity. However, the increased molecular interchange between fluid layers increases the viscosity [3]. The net result is that liquids show a reduction in viscosity for an increase in temperature.

Due to the close packing of the molecules in a liquid, high pressures also affect the viscosity. At high pressures, the energy required for the relative movement of a molecule is increased, causing an increase in viscosity.

1.2.2 Continuum Approximations

At distances above the micro scale, approximately \( \geq 10^{-6} \) m, the number of molecules in the system can be in the order of millions! In these cases, the number of molecular interactions occurring over length and time scales is also huge. Because of this, it can be considered acceptable to assume that the influence
of any individual molecular exchange/interaction is negligible as the number of molecules in any volume tends to infinity. The continuum assumption considers an infinite number of molecules in a domain and neglects their individual contributions. The interpretation of continuum is given as:

*Continuum.* A continuous thing, quantity, or substance; a continuous series of elements passing into each other [6].

If a fluid is considered as a continuum, then each part is considered as identical (i.e. the fluid is homogenous) to the next and infinitely divisible, and the molecular structure of the fluid is ignored. This means that the fluid is assumed to have the same properties even if the domain dimensions are 100 nm, 1 mm or 1 km.

By making the continuum assumption, molecular scale effects are neglected and the bulk properties are defined by the physical observable relationships between them. These properties can then be used to characterize fluid flows, as done in experiments by Reynolds [7] whose number, the Reynolds number, presents a criteria for dynamic similitude.

\[ Re = \frac{\rho u L}{\mu}. \]  

(1.21)

The Reynolds number is the ratio of inertial \((\mu/\rho)\) to viscous \((\mu/L)\) forces, where \(L\) is the characteristic dimension of a flow with speed \(u\). This can be used both to determine kinematic and dynamic similitude for comparing scale models to real applications and also to characterize the point of transition between laminar and turbulent flow (critical Reynolds number).

A large Reynolds number indicates that the inertial forces dominate the system, with a low viscosity causing the small scales of fluid motion to be relatively undamped. A low Reynolds number flow, however, has high viscous forces, which damp out small scale motion.

The Reynolds number represents simple characterization of the behaviour of a fluid system. To look more in depth at the measure and description of fluid behaviour, a set of continuum governing equations is used. However, before these are considered it is important to set out the rules for the fluid mechanics interpretation of a continuum, which are known as the continuum assumptions/approximations.

### 1.2.2.1 Continuum approximations

- **Infinitely Divisible.** The characteristic length of the fluid should be several orders of magnitude larger than molecular diameters, such that the number of molecules in the system is large enough to be considered as approximately infinite. By assuming an infinite number of molecules, the fluid is considered homogenous at all scales, and can be divided up/decomposed into an infinite number of identical sections. If the fluid is considered in terms of a finite
number of molecules, when it is divided up even in a finite number of sections, some will contain mass (a molecule) and energy and some will not (Figure 1.4).

- **Thermodynamic Equilibrium.** To maintain the assumption of continuum matter with an infinite number of molecules, there must also be an approximately infinite number of intermolecular interactions occurring over length and time scales in the system. This means that there is a continuous propagation of energy throughout the system. Discontinuities cannot occur as the fluid is continuous (infinitely divisible) and an infinite number of infinitely small intermolecular energy exchanges smooth out and propagate fluid properties and energy through the system.

This is also essential to maintain the linear relationship between the stress and strain rate and the heat flux and temperature gradient. The thermodynamic equilibrium condition also states that there are sufficient interactions or collisions to smooth out any statistical variations occurring from the molecular scale (Figure 1.5).
If these conditions are met, the fluid system can be considered as a continuum. This is an important classification, as it means the flow can be approximated using continuum laws.

The continuum laws can be applied in both simple analytical form, as in the Bernoulli equation (inviscid flows),
\[
\frac{P}{\rho} + \frac{v^2}{2} + gh = \text{constant},
\]
(1.22)
or for more complex situations that require numerical solution. For cases such as simple pipe flows, the Bernoulli equation can be of use where little information is required. However, in complex systems or geometries, a more detailed analysis and interrogation is required. In this case, fluid behaviour can be simulated using a set of conservative governing equations solved numerically. These simulations, based on the continuum assumptions and continuum scale observations and laws, provide a detailed and accurate model of fluid behaviour, where experiments are difficult or expensive, or a greater amount of information is needed.

1.2.3 Continuum Scale Simulation

Both simple and complex fluid systems can be investigated, within the limits of the continuum assumptions, by sets of governing differential equations that describe fluid behaviour. The mathematical solution of these equations throughout a fluid domain is known as computational fluid dynamics (CFD). The governing equations describe the mathematical representation of a physical model that is derived from experimental flow measurements and observations. These representative equations are then replaced with an equivalent numerical description, which is solved using numerical techniques for the dependent variables of velocity, density, pressure and temperature. One of the most widely used sets of governing equations are the Navier–Stokes equations.

1.2.3.1 Navier–Stokes governing equations

The Navier–Stokes equations are a set of governing equations that describe the behaviour of fluids in terms of continuous functions of space and time. They state that changes of momentum in the fluid are based on the product of the change in pressure and internal viscous dissipation forces acting internally. The scheme works by not considering instantaneous values of the dependent variables, but their flux, which in mathematical terms is interpreted as the derivative of the variables. The equation set is separated into three conservation laws for mass, energy and momentum.
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**Mass**  The conservation of mass, known as the continuity equation, is obtained by considering the mass flux into and out of any elemental control volume within the flow field. In the Cartesian coordinate system, \( x, y, z \), fluid velocities along those directions are \( u, v, w \) respectively. The continuity equation then becomes

\[
\frac{\delta \rho}{\delta t} + \frac{\delta (\rho u)}{\delta x} + \frac{\delta (\rho v)}{\delta y} + \frac{\delta (\rho w)}{\delta z} = 0. \tag{1.23}
\]

The first term accounts for any change in density over time, while the rest of the terms describe the change in density in the \( x, y \) and \( z \) directions.

**Energy**  The expression for the conservation of energy in a fluid system is

\[
\frac{\delta (\rho e)}{\delta t} + \frac{\delta (\rho eu)}{\delta x} + \frac{\delta (\rho ev)}{\delta y} + \frac{\delta (\rho ew)}{\delta z} = \rho Q + \frac{\delta}{\delta x} \left( \kappa \frac{\delta T}{\delta x} \right) + \frac{\delta}{\delta y} \left( \kappa \frac{\delta T}{\delta y} \right) + \frac{\delta}{\delta z} \left( \kappa \frac{\delta T}{\delta z} \right) - P \left( \frac{\delta u}{\delta x} + \frac{\delta v}{\delta y} + \frac{\delta w}{\delta z} \right) - \varphi \left( \frac{\delta u}{\delta x} + \frac{\delta v}{\delta y} + \frac{\delta w}{\delta z} \right)^2 + \mu \left\{ \frac{2}{3} \left[ \left( \frac{\delta u}{\delta x} \right)^2 + \left( \frac{\delta v}{\delta y} \right)^2 + \left( \frac{\delta w}{\delta z} \right)^2 \right] \right. \\
+ \left. \left( \frac{\delta v}{\delta y} + \frac{\delta w}{\delta z} \right)^2 + \left( \frac{\delta u}{\delta x} + \frac{\delta w}{\delta z} \right)^2 + \left( \frac{\delta u}{\delta x} + \frac{\delta v}{\delta y} \right)^2 \right\}, \tag{1.24}
\]

where \( \varphi \) is the bulk viscosity, \( Q \) is the heat added per unit mass, \( k \) is the thermal conductivity and \( e \) is the internal energy.

**Momentum**  The conservation of momentum equations are as follows:

\[
\frac{\delta (\rho u)}{\delta t} + \frac{\delta (\rho u^2)}{\delta x} + \frac{\delta (\rho uv)}{\delta y} + \frac{\delta (\rho uw)}{\delta z} = \rho X + \frac{\delta}{\delta x} \left\{ \mu \left[ \frac{\delta u}{\delta x} - \frac{2}{3} \left( \frac{\delta u}{\delta x} + \frac{\delta v}{\delta y} + \frac{\delta w}{\delta z} \right) \right] \right\} \\
+ \frac{\delta}{\delta y} \left\{ \mu \left( \frac{\delta u}{\delta y} \frac{\delta v}{\delta x} \right) \right\} + \frac{\delta}{\delta z} \left\{ \mu \left( \frac{\delta w}{\delta z} \frac{\delta u}{\delta x} \right) \right\}, \tag{1.25}
\]
\[
\frac{\delta(\rho v)}{\delta t} + \frac{\delta(\rho vu)}{\delta x} + \frac{\delta(\rho v^2)}{\delta y} + \frac{\delta(\rho vw)}{\delta z} = \rho Y - \frac{P}{y} + \frac{\delta}{\delta y} \left\{ \mu \left[ \frac{2}{3} \left( \frac{\delta v}{\delta y} + \frac{\delta v}{\delta x} + \frac{\delta w}{\delta z} \right) \right] \right\} \\
+ \frac{\delta}{\delta z} \left[ \mu \left( \frac{\delta v}{\delta z} \frac{\delta w}{\delta y} \right) \right] + \frac{\delta}{\delta x} \left[ \mu \left( \frac{\delta u}{\delta y} \frac{\delta v}{\delta x} \right) \right], \tag{1.26}
\]

\[
\frac{\delta(\rho w)}{\delta t} + \frac{\delta(\rho wu)}{\delta x} + \frac{\delta(\rho wv)}{\delta y} + \frac{\delta(\rho w^2)}{\delta z} = \rho Z - \frac{P}{z} + \frac{\delta}{\delta z} \left\{ \mu \left[ \frac{2}{3} \left( \frac{\delta w}{\delta z} + \frac{\delta v}{\delta x} + \frac{\delta w}{\delta y} \right) \right] \right\} \\
+ \frac{\delta}{\delta x} \left[ \mu \left( \frac{\delta w}{\delta x} \frac{\delta u}{\delta z} \right) \right] + \frac{\delta}{\delta y} \left[ \mu \left( \frac{\delta v}{\delta z} \frac{\delta w}{\delta y} \right) \right], \tag{1.27}
\]

where \(X, Y\) and \(Z\) are components of body force.

Equations (1.23) to (1.27) represent the Navier–Stokes set of conservation equations used to compute fluid properties numerically. For these properties to be used to simulate a fluid system, they need to be localized at discrete points within the flow domain before they are solved using a numerical scheme.

### 1.2.3.2 Solving continuum equations

There are a number of schemes for solving the fluid conservation equations in a simulation environment, such as the finite difference, finite volume, finite element, boundary element, etc. However, the three most developed and widely used of the bunch will be considered: the finite difference method, the finite element method and the finite volume method.

**Finite difference method (FDM)** The finite difference method is a simple and efficient method for solving the continuum governing differential equations. Instead of derivatives being computed over infinitesimal elements, increments of finite width are used as an approximation. There are three varieties of finite difference, the forward, backward and central difference, which are highlighted in Figure 1.6 and are calculated as follows for parameter \(p\) at point \(P\):

\[
\left( \frac{\partial p}{\partial y} \right)_{i,j} = \frac{p_{i,j+1} - p_{i,j}}{h} \tag{1.28}
\]
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Figure 1.6 Illustrating the finite difference method calculations at point P.

Backward difference:

\[
\left( \frac{\partial p}{\partial y} \right)_{i,j} = \frac{p_{i,j} - p_{i,j-1}}{h}
\]  

(1.29)

Central difference:

\[
\left( \frac{\partial p}{\partial y} \right)_{i,j} = \frac{p_{i,j+1} - p_{i,j-1}}{2h}
\]  

(1.30)

Using this method the partial differential equations can be replaced with simple algebraic equations that can be solved either iteratively or by matrix inversion. This can be implemented for fluid flow simulations to yield the values of the flow variables at discrete points in the flow field. Due to the structures of the FDM, problems are limited to ones with simple boundaries where a structured mesh can be used. For more complex problems, the finite element method allows for more versatility but is much more complex.

Finite element method (FEM) The aim of the finite element method is to determine the values of the dependent variables of the conservative flow equations. The FEM achieves this by dividing the flow domain into a finite number of cells or elements, each containing a small portion of the continuous fluid. At points placed at the corners or sides of these elements, points that are known as nodes, the governing equations are evaluated (see Figure 1.7). Instead of working with the differential equations directly, the FEM uses these nodes to discretize and evaluate the governing equations in an integral form using weighting functions.
Finite volume method (FVM)  Similar to the finite element method, the FVM discretizes the flow domain into elemental control volumes surrounding a node. Flow parameters are then treated as fluxes between control volumes, and conservation is maintained in each element. This allows for better treatment of flows with discontinuities such as shock waves.

1.2.3.3 Advantages

Continuum simulations are able to provide an accurate model for fluid behaviour in a wide range of applications and systems. The division of the flow field into discrete elements allows complex geometries to be simulated, and smaller elements can be used to refine the solution in areas of high gradients or where a greater accuracy is needed.

By approximating the fluid as a continuum and ignoring the underlying molecular behaviour, a great deal of computational effort is saved and accuracy has been proved to be sufficient in many applications. The molecular information can be approximated at these scales, as the molecular motion cancels out, yielding only bulk properties at this scale.

Continuum simulations also have the flexibility to prescribe a wide variety of boundary conditions capable of replicating almost any system, while still maintaining global conservation laws.

1.2.3.4 Limitations

Continuum mechanics, however, has its drawbacks. It is dependent on the generation of the mesh of elements and nodes it uses in the approximation. The generation of these meshes can be almost as time consuming and challenging as the actual simulation. These meshes can also have a significant effect on the solution,
either through resolution or the distribution of nodes, and must be generated with consideration for the system of interest.

The scale of the system is also limited by the continuum approximations. Because of the continuum approximations, the matter of interest must be uniform throughout and infinitely divisible. This removes the ability to deal with discrete objects, such as, at the top of the scale, extreme planetary systems and, at the lower end, molecules. As the continuum governing equations are approximate relationships which are approximated in their solution, careful validation and testing must also be performed, which is true of any simulation method. Particular care must also be taken close to the continuum limit.

The breakdown of these approximations in the meso scale region between the continuum and molecular scales was studied in detail and the transition from continuum to molecular scale effects is explained in depth in later sections.

1.3 MOLECULAR MECHANICS

At very small scales ($\leq 10^{-8}$), the mechanics of fluid take on an entirely different form. The continuum approximations and laws are not valid as the number of molecules in the system is of the order of tens to thousands. At this scale the molecular interactions dominate the physics of the fluid, and it is debatable whether fluid is an accurate description as it is better described as a molecular flow.

1.3.1 Molecular Properties

The properties at a molecular scale ($\sim 10^{-9}$) are very different from those considered at the bulk/continuum scale. At this scale, the characteristic length of the flow is comparable to the diameters of individual molecules. There is no concept of bulk properties, and fluid-like motion is in the form of the motion of individual molecules. The fluid is now not continuous, as the molecular centres represent discontinuities in both density and energy.

The molecular chemistry of the making or breaking of bonds or changes to the internal structure of molecules is not considered in this research, although it is important to understand the mechanisms by which molecules interact in a chemically stable fluid.

A molecule is formed of an aggregate of two or more atoms bonded together by special bonding forces. The examination of interactions between bonded molecules was first undertaken by a Dutch chemist, Johannes Diderik van der Waals, whose studies into noble gases led to the characterization of the forces between molecules [8]. The van der Waals force was originally considered to
Figure 1.8  Van der Waals potential, as the sum of attractive, London, and repulsive, Pauli, forces.

describe the force between all molecules,

\[ U(r) = \frac{Ae^{br}}{r} - \frac{C_6}{r^6}, \]  \hspace{1cm} (1.31)

where \( A, b \) and \( C_6 \) are characterizing parameters for the molecules and \( r \) is the distance from the molecule centre. However, it is now mainly used to describe the polarization of molecules into dipoles.

The interaction forces are characterized in two parts, a long-range attractive force, \( \frac{C_6}{r^6} \), and a short-range but strongly repulsive force, \( \frac{Ae^{br}}{r} \), as shown in Figure 1.8.

The repulsive forces, or London forces [9], named after the physicist Fritz London, represent the weak forces that occur between transient dipoles/ multipoles. This occurs from an uneven distribution of electrons surrounding the nucleus of the molecule, creating a temporary multipole.

The electron density in a molecule’s electron cloud varies due to the finite number of electrons orbiting the atom, but the variation of density in the cloud created hotspots of high charge, creating a temporary multipole that attracts hotspots of opposite charge on other molecules. A molecule with a temporary multipole can also attract/repel electrons from neighbouring molecules, thereby propagating the multipole effect. These short-term multipoles produce the net affect of a weak attractive force between neutral molecules such as nitrogen, methane and many others. The London forces are higher for larger molecules with more dispersed electron clouds.
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The attractive part of the potential comes from the strong short-range repulsive forces between two overlaps between negatively charged electron clouds, based on the Pauli principle [10]. The Pauli principle states that as the clouds of electrons of the two interacting particles intersect, the energy increases dramatically.

The behaviour of a molecular system is defined by the properties of a system of molecules. However, the individual properties of molecules can be combined together to describe the state, or global, properties of the system or region. An analogy can be found with the macro scale ideal gas equation of state, which relates the pressure, $P$, volume, $V$, and temperature, $T$, of an ideal gas of $n$ moles:

$$PV = nRT.$$ (1.32)

The van der Waals equation of state [11] describes a similar relationship for the molecular system,

$$P = \frac{RT}{V - b} - \frac{a}{V^2}nRT = \left(P + \frac{a}{V^2}nRT\right)(V - nb),$$ (1.33)

where $n$ is the number of moles and the gas law is corrected for the internal volume of the molecules using correction factor $b$ and adjusted with parameter $a$, which characterizes the cohesion/attraction between molecules. Parameters $a$ and $b$ can also be obtained from the critical properties of the fluid [12]:

$$a = \frac{27RT_c^2}{64P_c},$$ (1.34)

$$b = \frac{RT_c}{8P_c}.$$ (1.35)

The equation of state approaches the ideal gas law as these correction factors approach zero. This allows the description of the fluid to be made in terms of the state of the fluid, rather than as a large number of chaotic molecules. The van der Waals equation is best suited to low-temperature and pressure systems, but there are other equations of state that can be applied to other situations, e.g. Lennard–Jones equation, Clausius equation, etc.

1.3.2 Molecular Simulations

Molecular simulations play a vital role in science today by providing a framework on which to investigate theories and solutions in a relatively low-risk and low-cost environment. At the molecular scale, investigations and experiments are very costly to perform, and in some situations it is not possible with current technology. Because of this, molecular simulations are often thought of as blurring the line
between experiment and simulation, as they can be used to investigate theories that otherwise could not be tested.

Molecular simulation is the study of material/liquid by considering the individual interactions of atoms or molecules, and will be described in detail in Chapter 2. General simulation schemes involve representative molecules interacting with some sort of boundary and each other to achieve a change in position and momentum. There are many different forms of simulation methods and techniques that can be applied to many different situations, each offering different advantages. The basic mechanism behind almost all molecular simulations is relatively basic, relying on a system of particles that represent atoms or molecules that interact using Newton’s law,

\[ F = ma, \]  

(1.36)

where the force acting on a particle, \( F \), is equal to its mass, \( m \), multiplied by its acceleration, \( a \). The force acting on any one of the many particles in the system is determined by the movement of those around it. There are two branches of molecular simulation, stochastic and deterministic. The deterministic approach is in the form of a molecular dynamic (MD) simulation, where the outcome could theoretically be worked out. Stochastic methods, such as the Monte Carlo simulation method, have an element of unpredictability and chance and the result cannot be exactly calculated in advance; these will be discussed in more detail later. Despite the deterministic approach of standard molecular dynamics, it remains a statistical mechanics method, as system property values are developed from ensemble averages over the system.

Molecular simulations rely on representative molecules interacting with each other, so each molecule must possess individual properties that determine how it will move in the next time step; these are position, \( r \), and momentum, \( p \), applied in the number of dimensions present in the simulation. It is from these properties that interactions and collisions are found and evaluated, thus allowing the simulation to proceed. Given that the state of the whole system is governed by a function of the properties of all the individual particles, the concept of ‘phase space’ can be introduced. At any time in the simulation, the state of the system can be defined by a single point in a \( 6N \)-dimensional ‘phase space’, where \( N \) is the number of particles in a three-dimensional system. Each three-dimensional particle contains information about its momentum \( (p_x, p_y, p_z) \) and position \( (x, y, z) \) in each of the three dimensions, so for \( N \) particles there are \( 6N \) variables. As the simulation progresses, the phase point will move throughout phase space, sampling more of the regions accessible without violating any of the rules set at the start of the simulation, such as constant energy, pressure or temperature.

In the following sections the basics behind simulations of molecular systems will be described, before proceeding to a description of how it applies to real fluid flow problems and situations.
1.4 TYPES OF SIMULATION

The above sections have described the general form of molecular simulations used to explore the constant energy surface of a system. However, the simulation so far can describe the positions and momentum of the molecules in the system. These properties are useful within the simulation, but cannot be compared with a real situation because such information is not available. Available system properties such as temperature, entropy, pressure, etc., are the result of the motion of many particles and not properties of individual molecules. Such bulk properties are extracted from the simulation data with the use of statistical mechanics, by averaging the properties of a large number of molecules over a specified period of time.

This method of property evaluation relies on Boltzmann’s ergodic hypothesis [4]. The hypothesis assumes a quantum description of the system of particles and for any system there are \( i \) different possible energy states conforming to a constant energy \( E \) (proportional to the system volume). Over a sufficiently long period of time the hypothesis assumes that the phase space trajectory will sample almost all of these energy state configurations resulting in an average value, known as the ensemble average and considered to be representative of the system (over all state configurations, see Figure 1.9). The ergodic hypothesis therefore states that over a sufficient period of time, the ensemble average is equal to the statistical average obtained by simulation. This is a reasonable assumption for most cases, but it does not apply when considering meta-stable phases or glasses.

The ergodic hypothesis leads to the construction of many different conservation laws that can be applied to simulate different properties and situations. These groups sample different ensemble averages and conserve different properties in molecular simulations, the most common of which are listed below:

- **Microcanonical Ensemble (NVE).** A constant number of particles, volume and energy. It is also common to control the temperature of the simulation during the equilibrium stage so that the target system temperature is reached within a
suitable number of time steps. The simplest form of temperature control is to scale the velocities periodically, but this is not a truly isothermal method and must be removed before the properties are collected.

Although energy is considered to be conserved, there will be slight fluctuations and the possibility of a small drift due to truncation and rounding errors from the calculations.

This type of ensemble is useful for predicting thermodynamic response functions.

• **Canonical Ensemble (NVT)**, a constant number of particles, volume and temperature. As in the microcanonical ensemble, during the initialization stage the velocities are scaled to the desired value for the set temperature. Although useful for initialization, velocity scaling is not suitable to use as a control for a simulation as it is crude and not a truly isothermal method. Therefore, other thermostatic methods must be used to apply the temperature control, which will be explained in detail in Chapter 3. This ensemble is used to perform conformational searches of models evaluated in a vacuum without periodic boundary conditions. Even when periodic boundary conditions are used, this ensemble can be useful if pressure is not a significant factor, as the constant temperature and volume provides less perturbation due to the absence of pressure coupling.

• **Isobaric–Isothermal Ensemble (NPT and NST)**.
  – NPT: a constant number of particles, pressure and temperature. Temperature is controlled using one of the thermostatic schemes detailed in Chapter 3 and the pressure is controlled by varying the volume of the system using the Berendsen, Anderson or the Parrinello–Rahman schemes [13]. The Berendsen and Anderson schemes work by varying the size of the system, while the Parrinello-Rahman scheme is also capable of varying the shape of the system.
  – NST: a constant number of particles, stress and temperature. This is an extension to the constant pressure ensemble, which adds extra control on the stress components \( \sigma_x, \sigma_y, \sigma_z, \tau_{xy}, \tau_{yz} \) and \( \tau_{zx} \).

Both methods are mainly used in structural applications. NST can be used to evaluate stress/strain relationships and NPT is generally used when the correct pressure, volume and temperature are important.

• **NPH and NSH**.
  – NPH: a constant number of particles, pressure and enthalpy. This ensemble is similar to the NVT ensemble, only the size on the cell is allowed to vary.
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Figure 1.10 Monte Carlo integration.

- NSH: a constant number of particles, stress and enthalpy. The control of the stress of the system implies the use of one of the variable volume schemes, of which the Parrinello–Rahman scheme is used to vary the size and shape. This ensemble can only be used in fully three-dimensional periodic systems. In both ensembles, enthalpy, $h$, is conserved but it is also common, as with many of these methods, to use temperature scaling in the initialization and equilibration stages to stabilize the system. NPH and NSH are commonly used to investigate natural response functions such as specific heat (at constant temperature), thermal expansion, adiabatic compressibility and adiabatic compliance tensors.

- Grand Canonical Ensemble ($\mu VT$). Simulations with constant chemical potential $\mu$, volume and temperature are used widely to investigate capillary phenomena and other chemically driven effects.

These ensembles are used within statistical mechanics, both for stochastic and deterministic approaches, to investigate different environments and systems. The Monte Carlo molecular simulation method represents the stochastic approach, which incorporates an element of randomness in the molecular model.

1.4.1 Monte Carlo Simulation

The Monte Carlo simulation method is a powerful tool for integrating complex equations using a relatively simple probability theory [14]. This is best illustrated by a simple example, where the value of $\pi$ is calculated using a brute force approach to Monte Carlo integration. To approach this problem, first consider an arc with radius $R$, within a square domain of side $l$, as shown in Figure 1.10. The domain is probed using a number of test points, randomly distributed over the area, as shown in Figure 1.11.
TYPES OF SIMULATION

Figure 1.11  Monte Carlo integration; domain is interrogated by random points, some of which lie within the arc.

The area inside the arc is then estimated by the ratio of the number of points inside its constraints (squares) and the total number of points (squares + circles):

$$\frac{\text{Squares}}{\text{Circles} + \text{squares}} = \frac{\text{area of arc}}{\text{area of square}},$$

(1.37)

which becomes

$$\text{Area of arc} = \frac{\text{Number of squares}}{\text{Number of circles} + \text{number of squares}} \times \text{area of square}. \quad (1.38)$$

The equation for the area of an arc is known as $\pi R^2$, so this becomes

$$\frac{\pi R^2}{4} = \frac{\text{squares}}{\text{circles} + \text{squares}} \times l^2. \quad (1.39)$$

Rearranging for $\pi$ gives

$$\pi = \frac{\text{squares}}{\text{circles} + \text{squares}} \times \frac{4l^2}{R^2}. \quad (1.40)$$

Equation (1.40) relates the ratio of particles within the arc to the value of $\pi$.

The accuracy of the estimation is mainly dependent on the number of points used to probe the domain. This approach is known as the brute force approach, and is the less sophisticated form of Monte Carlo integration, where there is an equal probability for a sample point to be taken from anywhere within the domain.

Monte Carlo simulation uses elements from this technique to move the molecules in the system in the following way:

1. A molecule is selected at random from the system.
2. The molecule is then moved a random distance in a random direction.
The distance a particle is moved is often scaled to alter the acceptance ratio of moves making the simulation more efficient.

When applied to molecular simulation there is a need to improve computational efficiency by making certain approximations for solving equations on relatively inactive regions. It is at this point that importance sampling techniques are introduced into the Monte Carlo method, as described by Metropolis et al. [15].

The Metropolis Monte Carlo method biases the contribution of each move to the statistical average based on the Boltzmann factor. The probability of a particle being selected is also influenced by the Boltzmann factor as follows:

1. The overall system energy is calculated, $E_i$.
2. From the system, one molecule is picked out. The probability of selection for each particle is determined by the probability parameter $A$.
3. The molecule is assigned a small perturbation, such as a small displacement in position, and the new system energy is calculated, $E_f$.
4. If the new system energy is smaller than the old system energy, accept the addition of the perturbation.
5. If the new system energy is greater than the old system energy, accept the perturbation with probability
   \[ B = e^{-\frac{E_f - E_i}{k_b T}} \]
   (note that $\beta = e^{-\frac{E}{k_b T}}$ is the Boltzmann factor).
6. Repeat steps 1 to 5.

This gives the probability value that an added perturbation will be accepted as $A$ multiplied by $B$. Allowing a small proportion of moves that increase the system energy to be accepted provides a limited amount of protection against settling in meta-stable configurations on quasi-equilibrium states. By doing this, the system is pushed towards the configuration that is most likely to occur, thus speeding up the simulation run time.

Another modified form of the Monte Carlo technique is the force biased method [16]. This adds some extra calculation overheads into each molecule evaluation to determine the resultant force acting on the particle by its neighbours, biasing the random move performed within the simulation. This also improves the computational efficiency as statistical averages need to sample fewer configurations.
Additional information on the Monte Carlo simulation method and its different ensembles can be found in the book by Gould et al. [17]. Gould provides examples of Monte Carlo methods, focusing on its advantages at simulating phase changes, which has been used to good effect by Levesque et al. [18] applied to hydrogen storage in carbon nanotubes.

1.4.2 Molecular Dynamics

Molecular dynamic (MD) simulations model fluid in two ways, with molecules being represented as hard or soft spheres. Modelling with hard sphere models provides a relatively simple approach to approximating a system of molecules but still has valid applications, such as looking into the liquid–gas phase transition and diffusion, and hard sphere fluids have a well-defined critical point. The drawbacks are mainly to do with the discontinuous nature of the model. The collisions are performed instantaneously and spheres only interact repulsively, whereas real systems have some form of attraction between particles. Because of this, it is also used for gas simulations where the distances between molecules are far greater than their diameter, and intermolecular interactions occur rarely. Despite these disadvantages, the model is still widely and successfully used, but care must be taken to ensure that it is appropriate to the situation being simulated.

A more realistic, but more complex and computationally demanding approach, is the soft sphere model. In this model, the long-range attractive and repulsive forces are modelled as a continuous function of the separation between pairs of molecules. The use of a continuous interaction function improves the accuracy of the simulation at the cost of increasing the computational load.

1.4.3 Introduction to the Physics of MD Simulations

Molecular dynamic simulations work on the same basic principles regardless of the actual interaction laws (hard or soft spheres) and rely on the following three steps: initialization, equilibrium and production. These stages are detailed below following the example of a molecular scale cubic cell suspended in a fluid away from any physical boundaries, as shown in Figure 1.12.

1.4.3.1 Initialization

When the simulation is run, the first task performed is to define the problem; this is known as initialization. This stage of the simulation accounts for only one time step and is used to create the system of spheres based on a set of user-defined parameters. In the example used, a control volume suspended in a fluid of set volume and density is simulated (Figure 1.12). The initialization stage is where
the dimensions of the considered volume of the system are defined and representative molecules are placed within. Therefore a method is needed to position $N$ spheres within the system. If the spheres were to be randomly assigned positions, there is a quite high probability that some of them may overlap, creating extremely high interaction forces, disrupting the system with unnatural forces. It is therefore more practical to assign positions based on a lattice or crystal structure.

However, this creates a problem, as fluid molecules do not conform to a static lattice, but move constantly within the domain. This means that the fluid molecules need to break out of the initial lattice structure and find a natural, randomized, equilibrium position. A degree of randomization is added to the molecules to allow them to break out of this structure. This can either be done by adding a degree of randomization to the initial molecular positions or to assign random initial velocities. Randomized positions, however, are generally used for very large systems to reduce the simulation time taken to settle into a random ‘cloud’. By assigning random initial velocities to the molecules it is also possible to control the initial temperature of the system by assigning velocities based on the Boltzmann velocity distribution (Equation (1.4)).

Once all of the initial positions and velocities for all of the spheres have been defined, the forces on each of the atoms must be evaluated, giving the overall force on the particle. The force calculations are used to perform changes to the dynamics of the particles in the system, but these changes are performed within the time loops of the simulation. There are two time loops within the simulation, one in the equilibrium stage and one in the production stage.

1.4.3.2 Equilibration

The simulation time allotted to the equilibrium period immediately follows the initialization stage. This provides a buffering/settling time for the particles to mix
types themselves up and reach a maintainable equilibrium state that is sufficiently randomized. Once a stable, but randomized, situation is reached, the production stage can proceed, which provides all the useful information about the run.

While the simulation is proceeding, there needs to be some way to measure how well randomized the simulation has become and whether or not an equilibrium state has been reached.

**Monitoring** Initially, the positions and velocities of all the molecules in the system are defined, both of which need to be relaxed before the production phase can take place. To ensure this has been completed, there needs to be ways of detecting the state of the simulation. The state of the dynamics of the particles are measured against the Maxwell–Boltzmann velocity distribution, while the breakdown of the positions is evaluated using the order parameter (see below).

The Maxwell–Boltzmann velocity distribution is strongly linked to the Boltzmann factor, derived from the kinetic theory of gases. By looking at a small change in height of the atmosphere, and relating the pressure to kinetic theory, the Boltzmann factor is derived from the change in pressure and can be found as shown in Figure 1.13.

**Boltzmann distribution** The force exerted on the boundary of a fluid is described as \( n \), the number density (number of molecules divided by volume) multiplied by the volume and the weight of each molecule (force due to momentum exchange at collision at the boundary)

\[
F = mgAn\Delta h. \tag{1.41}
\]
Therefore pressure becomes

\[
\Delta P = -\frac{F}{A} = -\frac{mgAn\Delta h}{A},
\]

\[
\Delta P = -mgn\Delta h.
\]

The ideal gas law can be rearranged for \( n \):

\[
Pv = Nk_bT, \quad n = \frac{N}{V} = \frac{P}{k_bT},
\]

which when substituted into the expression for \( \Delta P \) gives

\[
\Delta P = -\frac{mg\Delta h}{k_bT}P.
\]

Thus, for \( h \to 0 \),

\[
\int \frac{1}{P} \, dP = -\frac{mg}{k_bT} \int dh
\]

gives

\[
P = P_0e^{-mgk_bT},
\]

where \( e^{-mgk_bT} \) is known as the Boltzmann factor. This form of the Boltzmann factor has been derived from potential energy, and as potential energy, can be written as \( mgh \), the factor can be rewritten as

\[
\beta = e^{-E_{\text{PE}}/k_bT},
\]

where \( E \) is the energy. A similar derivation can be performed using kinetic energy, resulting in a Boltzmann factor of

\[
\beta = e^{-E_{\text{KE}}/k_bT}.
\]

This describes the probability that a molecule is at a certain energy level for a prescribed temperature, \( T \). By normalizing probability values so they add to a unit value, the Boltzmann factor can be evaluated over a range of speeds to obtain the Maxwell–Boltzmann distribution for speeds. Where speed \( v = \sqrt{v_x^2 + v_y^2 + v_z^2} \),

\[
f(v) = 4\pi \left( \frac{m}{2\pi RT} \right)^{2/3} v^2 e^{-mv^2/(2RT)}.
\]
This velocity–probability distribution (Figure 1.14) can therefore be used to assess the dynamics of a simulation, by comparing the distribution of the resultant velocity of molecules with this distribution. This is an important test, as even for systems at steady state, as the velocity of individual particles does not remain constant, they are constantly interacting and colliding with each other. It is sensible to consider the overall distribution of velocities within the system to get a view of how the system is behaving and how it is approaching equilibrium.

By monitoring the distribution of velocities and its resemblance to the Maxwell–Boltzmann distribution, a measure of the approach to equilibrium is developed. It is then used to identify stability in the simulation. If the simulation is not stable, the temperature would fluctuate and the system would not be in equilibrium. It is therefore necessary to observe the development of the distribution over a period of time, ensuring that it converges with minimal oscillations. The graphs in Figure 1.14 show examples of the distribution at different temperatures.

The variations arise from statistical noise that occurs due to the finite number of molecules in the simulation. The greater the number of molecules, the lower is the noise in the extracted distribution. For an infinite number of molecules, the distribution would be followed perfectly, going the possibility of a continuum description.

Other measured thermodynamic properties, such as pressure and density, are also sensitive to the state of the system. By looking at these properties and seeing how they behave is another tool in the identification of equilibrium and smooth running of the simulation. Properties are averaged over a period of time and need
time to adjust themselves to the correct, stable value. If some instabilities are present and the properties are not converging, the system cannot be in a steady state.

The stability of a property does not just imply that the value remains approximately constant, but it should also be able to recover its value after a small amount of perturbation, such as a temperature adjustment.

The order parameter

The order parameter gives an indication of the randomization of the positions of the particles within the system. There are many formulations of this parameter relating to different initial structures, but only an example of a face centred cubic (f.c.c.) lattice is considered here.

First, the system of particles is broken down and the three Cartesian coordinates are considered independently. The form of the order parameter must be such that it is possible to detect when a particle is on or near an original lattice site.

The form of such a function is described for a single particle as

\[ \lambda_i = \cos \left( \frac{4\pi x_i}{a} \right), \]

where \( a \) is the spacing between lattice sites and \( x_i \) is the position of molecule \( i \). By summing this over all particles the average value can be calculated for all molecules, for each of the three directions:

\[ \lambda_x = \frac{1}{N} \sum_{i=1}^{N} \cos \left( \frac{4\pi x_i}{a} \right), \]
\[ \lambda_y = \frac{1}{N} \sum_{i=1}^{N} \cos \left( \frac{4\pi y_i}{a} \right), \]
\[ \lambda_z = \frac{1}{N} \sum_{i=1}^{N} \cos \left( \frac{4\pi z_i}{a} \right). \]

The overall value can then be calculated from the three directional components:

\[ \lambda = \frac{1}{3} \left( \lambda_x + \lambda_y + \lambda_z \right). \]

This is the order parameter for the system. After the initialization of the simulation, the order parameter can be used to confirm that the lattice has been constructed correctly; if \( \lambda = 1 \), all lattice sites are occupied. During the run the particles move from their initial position, which alters their individual order parameter to a value between \(-1\) and \(1\) (Figure 1.15). For a fully randomized simulation, the parameter should be approximately zero, indicating an even distribution of
particles between the bounds of the simulation. The order parameter can also be used to determine the point of solidification and the quality of the lattice, as used by Radhakrishnan and Gubbins [19].

A successfully equilibrated system should be sufficiently randomized and have reached a stable equilibrium point from which the production phase can begin. The stable point should have the same global properties regardless of the initial positions of the molecules, and can be tested by applying random noise to the positions of the molecular lattice and examining several equilibration phases. A fully equilibrated system will have the following properties:

- Stable levels of kinetic, potential and total energy. Variations in energy levels are to be expected, but there should be no drift in average values of energy.
- The order parameter should be zero, indicating that the molecules are sufficiently randomized.
- Velocities of all molecules should conform to velocity distributions for the set temperature for the system.
- Stable state which is independent of initial positions of molecules.

Although the above criteria help identify equilibrium, there is still a chance for undetected instabilities to be present, so care must be taken to be certain that a steady state has been reached. After sufficient randomization, the production phase of the simulation can begin.

### 1.4.3.3 Production

After the successful randomization of the system of molecules, the production phase can take place. This is basically an extension of the equilibrium phase to calculate the properties of the stable system over a set period of time. As the system is assumed to be sufficiently equilibrated, some of the controlling factors and adjustments are removed to allow the simulation to progress freely. Although the
controls are removed, the parameters such as the order parameter and velocity distribution are still monitored to check for anomalies. At the end of the equilibration phase, all property averages are reset to zero so that when the production phase starts, the properties are not affected by the approach to equilibrium and are the result of the production phase only.

This is the stage of the simulation where the interrogation and investigation of the system may start. There are two main types of dynamic models used in simulation to describe molecular dynamics, hard sphere and soft sphere. They differ in the way they handle interactions between particles. The hard sphere model considers interactions as binary collisions, whereas the soft sphere approach considers the molecules to be continually interacting via long-range potential functions with their neighbours.

1.4.4 Hard sphere model

Hard sphere simulations only interact by colliding with one another and exchanging linear momentum in a perfectly elastic way. The forces present in the hard sphere model are relatively simple and easy to calculate. As there are no long-range interactions, spheres only interact when they are colliding. The hard sphere models are generally event driven, where the simulation time only steps forward to the next event, or collision. This is based on the assumption that all spheres have an initial position and velocity, and that sphere travels along the same direction at a constant speed (as there is no acceleration), such that the position at any time can be calculated as follows [4]:

\[
\mathbf{r}_i(t) = \mathbf{r}_i(t_0) + (t - t_0)\mathbf{v}_i(t_0)
\]

where \( \mathbf{r}_i \) and \( \mathbf{v}_i \) are the position (of the centre of the sphere) and velocity of particle \( i \), \( t_0 \) is the start time and \( t \) is the new time. As all molecules move in this way the time until two spheres overlap, i.e. when a collision occurs, can be predicted, highlighting the deterministic nature of the molecular dynamics approach.

At any collision between two spheres, each with diameter \( \sigma \), the distance between the centres will be \( \sigma \). Therefore a collision occurs between two molecules with position at time \( t \), of \( \mathbf{r}_1(t) \) and \( \mathbf{r}_2(t) \), when

\[
|\mathbf{r}_1(t) - \mathbf{r}_2(t)| = \sigma,
\]

which can be calculated as

\[
(\mathbf{r}_1(t) - \mathbf{r}_2(t))^2 = \sigma^2.
\]
At this time, $t$, a collision is occurring and in a simulation of $N$ molecules the molecules that are colliding next need to be determined. By substituting Equation 1.54 for $r_1$ and $r_2$ in Equation (1.56) and rearranging for $t$, the time at which the two spheres will collide is given as

$$t_c = t_0 + \frac{(-v_{12}r_{12}) \pm \sqrt{(v_{12}r_{12})^2 - v_{12}(r_{12}^2 - \sigma^2)}}{v_{12}^2}, \quad (1.57)$$

where

$$v_{12} = (t_c - t_0)v_1 - (t_c - t_0)v_2, \quad (1.58)$$

and

$$r_{12} = r_1(t) - r_2(t). \quad (1.59)$$

This gives the collision time, $t_c$, for two spheres providing they are moving towards each other. Therefore, before $t_c$ is calculated, the state of the collision for the colliding pair must be determined.

For example, take molecule 1 from the simulation and consider the possibility that it may collide with molecule 37. There are two basic possibilities, either they are moving towards each other or away. Mathematically, this is described by the projection of the velocity difference along the line of the centres of the spheres by finding the product of $v_{12}$ and $r_{12}$. If the result is less than zero, the spheres are moving together:

$$v_{12}r_{12} < 0. \quad (1.60)$$

If the spheres satisfy this condition, they are said to be moving towards each other, but this does not guarantee a collision. To determine if they will collide we need to consider the limiting case where they come in contact as they pass each other.

By considering the one sphere to be fixed and the other to have velocity equal to the velocity difference, Figure 1.16 shows the limiting case for collision. It can be seen that, there must be a limiting value of $\theta$ that, if exceeded, ensure no collisions occur and the spheres pass each other [4].

![Figure 1.16 Hard sphere collision detection.](image)
This collision test is evaluated for every possible colliding pair within the system by looping over all molecules and calculating the next collision time for each. From these times, a table of collision times is created containing predictions for when each sphere will have its next collision. The calculation of this table is the last step in the initialization stage.

The table can then be used and updated in the equilibrium and production stages to advance the simulation and evaluate the next collision.

Collisions are modelled as binary interactions, occurring instantaneously, where the molecules exchange linear momentum.

### 1.4.4.1 Time steps

The first task in the time step loop is to look at the table of predicted collision times and find which collision will occur next. The first collision to happen is the only reliable prediction as the collisions afterwards may occur in a different order. The simulation is then progressed by advancing to the time of this collision and moving all spheres using

\[
r(t + \Delta t) = r(t) + v(t)\Delta t.
\]

(1.61)

The new position for each sphere, \(r(t + \Delta t)\), is calculated from the old position, \(r(t)\), by adding the distance travelled at constant velocity, \(v(t)\), during \(\Delta t\). When all spheres have been moved, the two that are colliding will be in contact and the momentum exchange can take place. As the masses of the spheres are the same, the mass terms can be cancelled out of the momentum equation completely, leaving just an exchange of velocity. The velocities of the two spheres are projected along the line of their centres, as in the two-dimensional example in Figure 1.17. At the collision, the component of velocity along the line connecting the two spheres

![Figure 1.17](image-url)
centres is exchanged, while the component of velocity perpendicular to this line remains the same for both spheres. The velocities of both spheres are updated and can be used to update the prediction table for the next collision time for the pair. There is no need to update the table for all the molecules, as only the colliding pair experience a change in velocity. The updated tables can then be used to predict the time step to the next collision.

1.4.5 Soft sphere model

The soft sphere model of molecular interactions considers molecules to interact by exerting a force on each other relative to the distance between them. These interactions occur continually, with each molecule having a ‘zone’ in which any other molecule present is influenced. Hard spheres will only interact when contact is made.

The initialization stage starts as stated above, where the initial positions and velocities have been defined for all molecules in the system. Force calculation for soft sphere models is more complex due to the addition of long-range interactions. Particles in the system continually attract and repel their neighbours through a predefined potential function, as opposed to the instantaneous and perfectly elastic collisions of the binary collisions described above.

This is best described with the use of Figure 1.18, where the centre particle is interacting with particles within a set radius, $R_C$. The most common potential used is the Lennard–Jones 12-6 potential, which provides an approximation of the attractive and repulsive forces experienced by nonbonded molecules.

![Figure 1.18 Soft sphere interaction detection.](image-url)
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The potential functions are continuous and become weaker as the distance between molecules increases, so it is therefore convenient to set a limit to the ‘zone of influence’ (typically around 2 to 3 times the interaction radius of the molecules) of any one molecule (outside which the potential is approximately zero). This finite limit cuts off the weak, long-range interactions between far-off particles, interactions that can be approximated by ‘long-range correction factors’ [4] to increase the efficiency of the simulation. Despite this streamlining, the process of finding a particle neighbour is time consuming and there needs to be an effective method of storing the lists of neighbouring particles for each sphere.

Soft sphere molecular dynamics provides an accurate model for molecular scale fluids and is generally used for dense fluids, where the cohesive part of the intermolecular interaction plays a more important role. Travis and Gubbins [20] and Tuzun et al. [21] show good examples of general molecular simulations. Other applications include chemical gradient driven flows [22] and studies of pore roughness [23] on flow parameters.

1.5 EFFECTS AT MOLECULAR SCALE

In this section, the effect of scale on the mechanics of a fluid at molecular scale are discussed along with the different mechanisms that are present which cannot be modelled on a continuum scale. The most obvious effects are present in highly porous media, where there is a high mix of fluid and solid molecules.

1.5.1 Phase Change in Confined Systems

The process of changing phases is in some cases modelled relatively well with hard spheres, but with soft sphere models when thawing, the melting temperature is often overestimated by up to 30 % [24]. The melting temperature is the point at which solid and liquid can coexist, but for there to be liquid present, there needs to be a section within the simulation domain where the structure starts to break down (nucleation of the new phase). At any phase change a good indication is a jump in the caloric curve relating to the adsorption of latent heat.

If the system properties come close to the temperature and pressure of the phase boundary, the dynamics of the system can change quite substantially, and this needs to be taken into consideration. The change between liquid and gas is not as drastic as the change between liquid and solid, where the molecules fall into or out of a structured formation. As the temperature of the molecules is lowered, molecules possess less energy and do not interact with each other as strongly, and consequently they move less and less. The kinetic energy of the particles then reaches a point where, for a given density, they are kept in the same position by
all the other particles. At this point, the particles do not possess enough energy to break out of their position, due to the proximity of other molecules. During a phase change, energy is absorbed or discharged in the form of latent heat at constant temperature; this is the extra amount of energy needed by the molecules to break out of the lattice and start moving around the container.

Phase change is a well-understood mechanism, but the molecules behave slightly differently when the solid/liquid is confined. Simulations of hard sphere fluids confined between hard walls were found to exhibit quasi-one-dimensional motion near the wall [25], where the molecules near the walls were pushed up against the container and could only move approximately parallel to the wall. This effectively creates different phase behaviour parallel and perpendicular to the boundary. The compressibility factor parallel and perpendicular was measured using the radial free space distribution function (RFSDF) within a Monte Carlo simulation of hard spheres [26]. The study showed that as the distance between the plates was reduced from a separation to sphere diameter ratio of 21 to 3, the difference between the compressibility factors was increased between the parallel and perpendicular directions (with respect to the wall). This indicates that there is also a difference in pressure between the two components.

The RFSDF has components from both the compressibility factor and the order parameter, so by looking at the order parameter the phase of the fluid can be determined as a function of distance from the wall. Molecules away from the walls are still in the liquid phase and are free to move, but molecules closer to the wall are trapped between a nonmoving boundary and the moving particles colliding against them.

The quasi-one-dimensional motion combined with the difference in pressure results in the phenomena of anisotropic phases, where close to the wall molecules are in the solid phase perpendicular to the wall and in the liquid phase parallel to the wall. Taking this quasi-one-dimensional theory one step further, and constraining a fluid within a cylindrical pore only two molecular diameters wide (between centres of molecules within the wall), freezing of the fluid is not observed to occur. The study by Peterson et al. [27] showed that no phase transitions are observed in a single nano-pore with a diameter twice that of the molecule diameter (between the centres of wall molecules), right down to absolute zero. However, Radhakrishnan and Gubbins [28] showed that phase change was possible when the nano-tubes were arranged in a cluster, due to correlation effects. Using a grand canonical Monte Carlo (GCMC) simulation (constant chemical potential, volume and temperature) they first showed that a phase change was not observed in a single pore; however, this also highlighted the problem of fluctuations in thermodynamic properties due to the limited number of particles in the system. The investigation then turned to simulating a hexagonal cluster of pores, and the same cluster surrounded by periodic images of itself. The walls were oxygen molecules and the transported molecules were methane, and the periodic pore model showed that clusters of pores do show evidence of freezing at a temperature of about 40 K.
Figure 1.19 Confined geometry for simulation of liquid–liquid phase coexistence, $L = 10.95$, periodic boundary conditions along the $x$ and $y$ axes. Two parallel plates in the $xy$ plane are separated by length $L$ in the $z$ direction.

The simulation also replicated the hysteresis effect of regular phase change, but highlighted the importance of the correlation effect between pores.

In a Monte Carlo simulation of water, Meyer and Stanley [29] investigated the coexistence of two liquid phases of water within a strongly confined geometry, shown in Figure 1.19. The theory of this is based on the fact that amorphous solidified water displays two distinct phases, one with a lower density than the other, and by extrapolating the transition line to a higher temperature to the meta-stable liquid region, there is a possibility of two liquid phases being present. This has been shown for bulk liquids, so Meyer and Stanley [29] investigated the same theory, where the geometry is confined as above. It was found that the pressures normal and parallel to the wall were different and, furthermore, at temperatures below 230 K the pressure parallel to the wall was found to become density independent, typical of the coexistence of phases of different densities in constant volume simulations [30]. The pressure normal to the wall, however, remained density dependent right down to absolute zero. They concluded that it was possible for these high and low density phases to coexist within the simulation.

A combination of these works was looked at by Gatica et al. [31] to investigate the adsorption of fluids within carbon nanotubes. As with the work above, adsorbed fluid was expected to exhibit one-dimensional or quasi-one-dimensional behaviour. The study found the corrugation experienced by an adsorbed molecule to be much less when compared to planar graphite [31, 32], leading to fluid adsorbed on to the wall, showing what is known as a cylindrical shell phase. When the density within the nanotube is increased significantly, the cylindrical shell phase solidifies and becomes similar to the incommensurate monolayer solid film on graphite, which is well known and studied [33]. At some point there must be a transition between the solid and fluid, and at this threshold there must also be the possibility of coexistence of the two phases. The solid ‘axial phase’ is recognized when the fluid becomes confined close to the axis of the tube as the number of
molecules in the system is increased (hence increasing the density of the fluid). This axial phase transition operates in a similar way to capillary condensation and layering transition. The layering transitions are known to occur at higher temperature, but the one-dimensionality of the system limits the transition to occur at $T = 0^\circ C$. It has also been shown that a bundle of adsorbing tubes exhibits correlation effects, which raises the transition temperature above zero [30, 34].

The work of Radhakrishnan and Gubbins [19] agrees with the above discussion of confined phase change, but applied to slit shaped pores. As with the cylindrical pores, fluids confined within slit shaped pores showed strong evidence of a third phase close to the walls. They investigated the effect of the wall–fluid interaction strength on the phase change, varying it from strongly attractive to repulsive, with respect to the fluid–fluid interaction strength.

Previous work by Miyahara and Gubbins [35] had already found that the strength of the interaction affects the hysteresis loop of the freezing temperature relative to the bulk material. However, Maddox and Gubbins [36] also found that the reduced confinement of the fluid in slit pores, as opposed to cylindrical pores, leads to higher freezing temperatures.

The study found that for strongly attractive walls the layer of particles nearest the wall froze at a higher temperature than those in the middle of the pore, similar to many of the examples described above for cylindrical pores. However, as the interaction swings the other way, becoming repulsive, the freezing effect also switches so that the centre of the pore freezes before the layer in contact with the walls. This implies that there must be a level of attraction or repulsion where the fluid freezes at one temperature, making the intermediate shell phase metastable, or disappear completely. The attractive/repulsive interaction potentials at the walls represent the difference between graphite carbon/silica walls, as carbon walls are strongly attractive and silica walls are weakly repulsive. However, most silica-based porous materials have cylindrical pores.

Kim and Steele [37] also looked at phase change at solid boundaries, studying the effect corrugation had on the monolayer of methane on graphite. Their small scale simulations of 289 molecules showed that increased corrugation leads to pre-transitional effects that are not present in solidification against smooth walls.

### 1.5.2 Adsorption/Desorption in Pores

Adsorption is the process by which a fluid adheres in a thin film to a solid or liquid with which it has contact. As an example, the following discussion considers the effect of the conditions for filling and emptying of a silicate nanotube, as studied by Gelb [38]. The first thing to remember is that classical statistical mechanics laws do not allow a first-order phase transition to take place within short-range one-dimensional systems, even for the case of meso scale pores, despite their three-dimensional structure. Bundles of pores or tubes add to the system’s
dimensionality, which alters the behaviour due to the long-range interactions. This can result in a first-order change of phase within such a cluster due to the presence of neighbouring tubes. These interpore effects are difficult to characterize in real materials and are therefore not, at present, widely investigated by simulations [28]. The filling of a pore involves three basic components, a high density phase representing the filled part of the pore, a low density part representing the multilayer adsorption and the interface between the two, as shown in Figure 1.20.

As would be expected from continuum scale observations of surface tension, the interface between the ‘wet’ walls of the pore and the ‘filled’ region is almost hemispherical. Higher temperature adsorption results in a thicker layer at the walls through the adsorption layer, resulting in a lower surface tension and an increase in the number of interfaces within the pore. The effect of inhomogeneity of phases along the length of a pore becomes negligible when there is no hysteresis present between adsorption and desorption, and leads to a rounding-off of the phase transition, similar to the effect of periodic boundaries on bulk fluid [38]. It is therefore acceptable to think of the phase transition within nano scale pores as almost first order and apply standard transition thermodynamics, as long as the temperature does not approach the critical point and the distance between phase interfaces is comparable to the pore diameter. The term ‘critical point’ used in capillary confined fluids has a different meaning to that of a bulk fluid, and is used to describe the point at which adsorption/desorption hysteresis disappears. As a consequence of the inhomogeneity along the pore, it is not possible to observe a critical point in the bulk fluid sense, or its associated properties. At lower temperatures, the adsorption layer is thinner and the interfaces are further apart, so small periodic cells are used whereas, for very high temperatures, the adsorption layer grows to such an extent and the interfaces are so close together that only one phase is present. The hysteresis, with respect to chemical potential during filling and emptying, is present in both experiment and simulation, but its effects are more pronounced in simulation, possibly due to the short time scale accessible. Longer pores have more capacity to exhibit inhomogeneity along their length which can present differences in nucleation on new phases and hysteresis loops. Pores with closed ends can have the effect of the closed end acting as an already nucleated dense phase while filling and affect the hysteresis loop.

The simulations performed by Gelb [38] were for adsorption of xenon on silica. A simplified model for silica was used, with the surface molecules modelled by
Figure 1.21 Cylinder oxygen atoms removed from the system to create a pore.

oxygen. Silicone molecules are not present on the surface of silica and are weakly interacting and were therefore removed from the model. The pore was created by defining a box, 5.4 nm square at one end with a length varying from 8 nm to 108 nm, full of a standard configuration of oxygen atoms for silica and removing a cylindrical volume of atoms from the centre to create the desired pore geometry (Figure 1.21). A small amount of relaxation was applied to the system after the removal of the cylinder in order to remove some of the translational symmetry experienced by the use of smooth continuum walls, although this was done at the cost of increasing the computational load of the simulation. Three geometries were explored in this investigation, a finite pore with two open ends, an infinite pore with periodic boundary conditions and a single-ended pore. The geometries were also modified in diameter and length for further comparison. The simulations were based on a grand canonical Monte Carlo (GCMC) method (constant chemical potential, volume and temperature) as it samples the correct ensemble for adsorption/desorption simulations and has been found to be reliable, despite inaccuracies when dealing with transport to and from the interface.

During the filling and emptying of long pores (108 nm) it was noted that equilibration became extremely slow at the top of capillary rise and the bottom of desorption drop and required up to thirty times as many more moves than usual. During the desorption of the long open-ended pore, the interface between the two phases moves steadily away from the open end, and there was no evidence of nucleation of either phase away from the interface. Desorption within an open-ended pore often results from the nucleation of the low-density phase within the high-density region, resulting in ‘bubbles’ forming. However, in this case, the interface also moves at an almost constant velocity.
The filling of the single-ended pore shows the reverse happening; the closed end acts as an already nucleated phase and the interface moves up the pore towards the open end at a relatively steady rate. Open-ended ‘infinite’ pores do not have the ‘head start’ of the closed end and must nucleate the start of the high-density phase before the filling process can properly begin. This means that capillary rise occurs at a higher chemical potential than closed-ended pores. Because of this higher potential, the closed-ended pore has a smaller width hysteresis loop than the open-ended tube, which also reduces the temperature at which hysteresis disappears.

It was also found that the reduced hysteresis loop found with the single-ended pore occurs at a chemical potential almost exactly in the middle of the larger loop of the open-ended pore. Gelb [38] also noticed that at the ends of the pore, weaker repulsive interactions could be affecting the stability of the simulation as the interface approached the ends of the tube.

Open-ended and infinite pores were also compared using two different pore diameters of 4 nm and 3 nm (see Figure 1.22). Although the hysteresis loop for the open-ended pore was smaller than for the closed-ended pore, it is still smaller than the loop for the periodic pore. The effects of the open-ended pore are more dramatic for the 4 nm diameter as a much higher chemical potential is needed to induce nucleation of a new phase, making the presence of the open end more important. The hysteresis experienced by the open-ended pores for both diameters is mainly on the desorption drop and not on the adsorption side. However, the capillary rise occurs at a slightly higher chemical potential, indicating that the open ends may be stabilizing the low density phase at the ends.

The final investigation performed by Gelb [38] looked into the effect of changing the length of the pore cell for the periodic/infinite pore. Three lengths were tested, 8 nm, 16 nm and 108 nm, and it was found that as the length was increased, the width of the hysteresis loop was reduced. This was attributed to the fact that the longer pores contained more density fluctuations, leading to a higher probability of nucleation of a new phase. This, however, could have been due to poor sampling resolution as the difference is fairly small and is most pronounced at a reduced temperature of $\tilde{T} = 0.927$. There was a fairly close agreement between the two longest pores, of 8 nm and 108 nm, which could indicate that the

![Figure 1.22 Infinite versus open pores.](image-url)
difference in the hysteresis loops is not affected when the length becomes significantly greater than the pore diameter.

Gelb’s [38] observations have been summarized below:

- Pore length has little effect on the adsorption/desorption hysteresis despite the added probability of nucleation, but the effect is greatest when the length is close to the pore diameter.
- Open ends on pores show much less desorption hysteresis for 3 nm diameter pores than for 4 nm diameter pores.
- Single-ended pores show almost no hysteresis due to the nucleation of phases at the end of the pores. Density also fluctuates greatly at pressures near condensation.
- Interpore correlation effects could yield a ‘novel type of phase transition in two dimensions’.

The effect of the length of the tube is a fairly expected result. As long as the tube is long enough to separate the effects of the ends of the tube, the middle section shows little variation along its length. The difference in desorption hysteresis between pore sizes is mainly due to the nucleation of the ease of progression of the new phase, which is made easier by the effectively larger particles, due to the narrower pore. The lack of hysteresis shown in single-ended pores is mainly due to the closed end acting as a dense phase, giving a good start to phase nucleation.

1.6 SUMMARY

In this chapter a general overview of fluid behaviour on continuum and molecular scales was presented. The bulk, or continuum, properties have been discussed along with their origins from molecular mechanics. Several methods for solving for these continuum properties were presented in terms of the governing equations that quantify the relationships between them.

On the molecular scale, the origin of intermolecular forces and interactions has been presented and a wide variety of molecular simulation schemes have been discussed, from the deterministic molecular dynamics to the stochastic Monte Carlo method. Finally, the importance of these methods has been highlighted by considering the molecular examples in Section 1.5.

This chapter has shown the different approaches to fluid simulation that are needed as the scales of the system changes. The meso scale lies in between the continuum and molecular scales and must use elements from both to capture correctly the proper physics (from the molecular scale) and provide a description in terms of useful fluid properties (as characterized on the continuum scale).