Smoothed Particle Modelling of
Liquid-Vapour Phase Transitions

Andrew Nicholas Charles (BSci, BA, AdvDipCompSci)

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy (Applied Physics)

School of Applied Sciences
RMIT University

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**Supervisors:** Professor Peter Daivis and Professor Gary Bryant
Melbourne, Australia
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and ethics procedures and guidelines have been followed.

Melbourne, Australia, January 2014

Andrew Nicholas Charles
(BSci, BA, AdvDipCompSci)
Abstract

Liquid-vapour phase transition in a simple fluid is studied using Smoothed Particle Hydrodynamics (SPH), a Lagrangian numerical method. A continuum fluid model displaying a liquid-vapour phase transition, based on the van der Waals equation of state with a squared density gradient capillary force and linear constitutive relations for viscosity and heat flux, is solved using SPH. The liquid vapour interface is intrinsically diffuse in both the analytical model and the numerical method.

In SPH a continuous field is represented by interpolation over particles whose properties are smoothed over space and which interact with an environment dependent two-body potential. By applying SPH to the partial differential equations of continuum mechanics, a set of ordinary differential equations governing an N-body system of particles is obtained.

A two dimensional SPH code was developed and used to simulate phase transitions. Temperature quenches were used to produce an instability driven decomposition into co-existing liquid and vapour. Stable coexisting vapour and liquid phases, with densities in good agreement with theory, are produced. Condensation emerges from the solution of the model with no explicit tracking of the vapour-liquid interface. Simulated fluids phase separate with a flow that appears realistic and without gross artifacts, containing droplets and bubbles which coalesce when driven together by flow. The kinetics of the growth of liquid domains in the phase separating fluid are divided into two regimes: an initial period in which density perturbations grow with an exponent close to one third, followed by a coarsening of liquid droplets where the exponent is strongly influenced by the quench depth.

A three dimensional SPH code was developed in order to investigate the behaviour of the model when parameterised for water and used to simulate mesoscopic systems with length scales of the order of $10^{-9}$ metres. When stable liquid vapour interfaces were formed for the continuum model of water, the density gradient and associated surface tension are resolved, however the surface tensions were found to be orders of magnitude too small. At coarse spatial resolution the interface is artificially broadened, leading to spuriously low surface tension. It is found that the spatial resolution must be of the order of the liquid-vapour interfacial width in order to accurately resolve density gradients and surface energy. Ultimately, liquid-vapour phase transitions can be modelled using SPH, however the microscopic width of the interface requires either microscopic simulation resolution or parameterisation to account for unresolved spatial scales.
Science may be described as the art of systematic over-simplification.
— Karl Popper, quoted in Observer, London, 1 Aug 1982

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1 Introduction

On earth, we are surrounded by processes that depend on the transformation of matter between its vapour and liquid phases. Condensation in the atmosphere drives much of our experienced weather, with efforts to improve our understanding of clouds still a major focus of meteorological research. Improved understanding of cavitation caused by vapour bubbles induced by pressure variations in turbulent flow is sought due to the damage it can cause to surfaces.

Numerous authors have pointed out the similarities between the patterns formed as a quenched fluid phase separates and the patterns arising from phase separation in biological systems. Beysens [19] compared the pattern formation produced by embryonic chicken cells with those formed by quenched SF\(_6\). Improved understanding of liquid-vapour phase transitions will inform understanding of these more complex biological phase transitions. Potential applications exploiting the fine scale structure of quenched fluids include the simulation of phase transitions in the formation of biological structures and the manufacture of membrane structures for medical and industrial applications. Understanding of the conditions under which phase transitions occur in confined geometries will have a direct impact on the manufacture of microfluidics devices and on the use of porous rock formations for the storage of carbon dioxide in its liquid state [12]. Such microfluidics applications have motivated recent studies into condensation and evaporation on small scales [12] [11].

This thesis is a study of liquid-vapour phase transition and dynamics using numerical simulation, with a focus on condensation and equilibrium coexistence in mesoscopic systems with length scales of the order of \(10^{-9}\) metres. The objective of this work is to model the process of the liquid-vapour phase transition, the equilibrium properties of the coexisting phases and the properties of the liquid-vapour interface, using a numerical solution of the continuum description of the system. The primary question addressed in this investigation is whether the chosen numerical method, Smooth Particle Hydrodynamics (SPH) can model liquid-vapour phase transitions accurately. To this end, several aspects of the phase transition process are assessed: the thermodynamic conditions under which condensation takes place in a pure fluid; the spatial structure and rate of the transition; the densities of the coexisting phases; and the surface tension of the diffuse interface between liquid and vapour.
1.1 Modelling of liquid-vapour phenomena

Phase separating liquid-vapour systems can be simulated atomistically, however the computational demands of simulating individual atoms places an upper limit on the spatial and temporal scales that can be modelled. Several molecular dynamics studies have examined the structure and properties of liquid vapour interfaces and have computed the interfacial width and surface tension \[114, 113, 127, 5\]. Ghoufi \[42\] and Ismail \[55\] reported good agreement between molecular models and experimentally computed surface tensions for water. While molecular dynamics provides information about the structure of interfaces at an atomic resolution, it is limited in its ability to access the hydrodynamic regime because of computational demands.

A number of impressive experiments have produced data about the phase transition kinetics of real substances, for both two component solutions and pure fluids \[19\]. Despite these successes, the very early time kinetics are experimentally inaccessible due to the short timescales involved.

Analysis of the continuum equations has gleaned much useful information, indeed the insights of van der Waals were obtained without any numerical modelling whatsoever, as described in his 1893 paper \[116\], translated by Rowlinson \[100\]. Analytical methods are limited in their ability to solve for the time dependent behaviour of unstable systems. When these limits are reached, numerical solutions are required.

Coarse grained computer simulation techniques are used to go beyond the very short time and length scales accessible to molecular dynamics. In coarse-grained modelling, the system is modelled in the continuum limit by a set of macroscopic field variables which are short time and small scale temporal and spatial averages of functions of the molecular positions and momenta. Such coarse grained mesoscopic models are of interest for their potential to resolve the transient fine scale structure associated with rapid phase transitions, to run for long enough to obtain equilibrium properties and for resolving sufficient quantities of fluid to be relevant to engineering problems in microfluidics.

The key decisions made in developing coarse grained methods are the selection of an appropriate set of continuum equations to describe the system, the selection of an equation of state and constitutive relations to relate the pressure tensor and heat flux to the state variables and the selection of a numerical method to solve the continuum equations.

1.2 The continuum description of liquid-vapour coexistence

Guggenheim \[44\] showed that the coexisting densities of vapour and liquid in many pure fluids can be scaled such that they collapse onto a universal curve, confirming the prediction of such universal behaviour by the van der Waals equation of state. The van der Waals equation of state \[116, 117\] has a sound although simplified microscopic basis, being based on the assumption of a long range mean field attraction between molecules and a hard core excluded volume.
Despite its simplicity, when inhomogeneous density is allowed by an appeal to free energy minimisation, the van der Waals equation of state predicts a two phase vapour-liquid equilibrium. It is not considered accurate enough to model real materials quantitatively, because the critical exponent characterising the relationship between coexisting densities and temperature is found to systematically differ from that found in real materials [46].

Early theories of gas-liquid interfaces, for example those of Young and Gauss [7], treated the dividing surface as infinitesimal, with properties such as surface tension inherent in the interface and physical quantities discontinuous across it. The first detailed theories in which the interface was considered a continuous region were developed by van der Waals [116] and Rayleigh [99], as outlined in an historical review by Widom and Rowlinson [101]. In their model, inhomogeneities contribute to the free energy with a term proportional to the square of the density gradient. This squared gradient theory of van der Waals remains important [14] and has been discussed extensively [123]. The numerical simulation of the van der Waals square gradient model has attracted significant interest [66] [90].

1.3 The process of phase separation

The process of spontaneous phase separation that takes place when a system is quenched into a thermodynamically unstable state is called ‘spinodal decomposition’. Spinodal decomposition has received much interest in the context of two component systems because of the relative ease of performing numerical and actual experiments to study it: the phase separation of solutions is much easier to observe in the laboratory than phase separation into liquid and vapour.

In a thermal quench of a one-component system, the separation of phases involves up-hill wave growth against density gradients. This wave growth, superimposed on thermal noise and modified by hydrodynamic flow, is responsible for the kinetics and morphology of the phase separating system. At longer time-scales hydrodynamic terms become important in the description of domain coalescence [67].

Experimental studies of liquid-vapour phase separation using real, rather than simulated systems are rare, due to the very short time and length scales involved with the liquid-vapour transition. Several studies do exist, including Klein et al.’s light scattering studies of the spinodal decomposition of sulfur hexaflouride [60] and Beysens microgravity studies. It is difficult for molecular dynamics to access the longer timescales and for experiment to access the early timescale. Consequently there is a need for simulation methodologies that bridge the gap.

1.4 Numerical methods for solving the continuum equations

Several families of candidate numerical methods exist for solving the problem and some have been used in recent studies to model liquid vapour coexistence [88] [122]. As shown by Lamorgese [66] and Onuki [91], Eulerian grid schemes can be used to solve continuum
equations tailored to the mesoscale but can suffer from grid tangling and artifacts related to the growth of spurious unstable modes \cite{49, 50}. Despite the limitations, Onuki \cite{91} used grid based integration of a continuum model of a van der Waals fluid to produce two dimensional simulations of droplet formation and boiling.

One family of coarse grained methods consists of the mesh-free Lagrangian particle techniques, the foremost of which is SPH. Such methods represent the fluid as a collection of ‘particles’ representing macroscopic fluid elements and carrying mass, momentum and thermal energy. SPH is one member of a family of particle methods, including dissipative particle dynamics (DPD) and vortex particle methods. A review by Koumoutsakos \cite{63} describes a number of such methods. Lagrangian particle methods such as SPH are capable of simulating flows with complex structure naturally. Because irregular particle arrangements are permitted, the particles can track inhomogeneities in the simulated material, for example in the impact fracture of a solid \cite{49} or turbulent magnetohydrodynamics \cite{96}.

DPD is a particle based method, in which interparticle forces are combined with random and dissipative forces in an attempt to model continuum systems at the small scales in which random thermal effects are important. As discussed previously by Warren, and more recently by Espanol \cite{36}, DPD has been used to model liquid vapour systems \cite{122, 41, 9}. Recently DPD was used by Ghoufi et al. \cite{41} to investigate the surface properties of water \cite{9} at a very small length scale: the DPD particles used in their study represented only a small number of molecules. A limitation of the traditional DPD approach used by these authors is that the relationship between the inter-particle forces and the underlying continuum mechanical system is empirical. Recent reformulations of DPD have adopted many aspects of SPH \cite{36}, \cite{121}, \cite{122} and have developed a more systematic relationship between the continuum description and the particle equations.

Another simulation method which has been used for liquid-vapour systems is Lattice-Boltzmann (LB) \cite{30, 120}. As an extension of cellular automata models of gases, LB models the fluid as a collection of particles on a fixed lattice. It is described by practitioners as a method for solving a discretisation of the continuous Boltzmann equation. LB has been used to study domain growth in liquid-vapour phase transitions \cite{92}.

In SPH, the particles are interpolation points at which the mechanical and thermodynamic fields are evaluated. Particles interact via a soft, ‘smooth’ potential. The equations of motion governing the smoothed particles are derived from the continuum equations describing the system to be modelled. The essential feature of SPH is that it converts a set of partial differential equations into a set of ordinary differential equations governing an N-body particle system. Two complementary introductions to smoothed particle methods are found in the books of Hoover \cite{49} and Liu \cite{71}.

While the SPH numerical method is general enough to solve arbitrary Partial Differential Equations (PDEs), its natural application is to the continuum mechanics of systems in which complicated flow is present, because significant particle disorder is tolerated without instability. Another benefit of the smoothed particle method for quantitative modelling is that it provides a clear relationship between the continuum equations and the numerical
model, and so allows measured material coefficients to be used as input.

1.5 Smoothed particle modelling of phase transitions and surface tension

While grid based continuum methods have been successfully applied to the study of the short-time growth of density fluctuations in the van der Waals squared gradient model \[66\], particle based methods provide a clear way of incorporating terms important for hydrodynamics such as viscosity, heat conduction, latent heat, external body forces and boundary effects, terms which are often neglected for simplicity.

SPH has previously been used to model multiphase systems, systems with phase transitions and systems with surface tension. Such treatments of surface tension using smoothed particles either make use of a ‘colour’ function \[84\], use a longer smoothing length for the cohesive force \[88\], use arbitrary ‘particle-particle’ forces \[109\], or model the surface tension of a free surface and do not model vapour liquid phase coexistence arising from a single equation of state \[49\].

Nugent and Posch \[88\] used the homogeneous van der Waals equation of state to model coexisting liquid and vapour in two dimensions. They used the frequency of oscillation of droplets to compute the surface tension of a liquid vapour system and compared this with the surface tension calculated from the difference in pressure between the droplet and the atmosphere. They found that at low temperatures the droplets that were formed contained clustering of SPH particles in concentric rings. Later work has sought to develop methods for removing such structures which were considered to be artifacts \[104\]. Nugent and Posch \[88\] showed that the van der Waals equation of state can be used to model liquid vapour phase separation with SPH. Their work was completed in two dimensions, which presents difficulties for verification against results for real materials and for using properties derived from real materials. Their work also neglected the liquid-vapour interface itself. Most liquid-vapour modelling with other numerical methods has been for two dimensional systems. The extension of this work to three dimensions is an outstanding problem, the solution of which is required for many practical applications.

The study of the kinetics of the liquid vapour phase transition using particle methods has received limited investigation. Existing grid based solutions have used the isothermal continuum equations \[66\] and this raises the question of whether aspects such as the growth parameters would be different if the full set of equations were solved.

The work presented in this thesis extends existing work in three novel ways: i) by solving the equations in three dimensions; ii) considering density gradient contributions to the equilibrium pressure; and iii) using experimentally derived values of parameters to simulate a specific substance. Despite the volume of prior work, few have used diffuse interface theory to simulate the liquid-vapour interface.

Also outstanding is the role of the gradient term, whether its solution by the SPH
method is possible and whether it will enhance the accuracy of the solution. Does the gradient term affect the interfacial width as expected, and what is its effect on the growth parameters during the transition period?

1.6 Thesis outline

Chapter 2 sets out a continuum model describing a phase separating fluid. This model is used in the rest of the thesis. A standard set of linear non-equilibrium constitutive relations are used. The homogeneous van der Waals equation of state provides the local equilibrium pressure and the properties of the interface are predicted by the van der Waals squared gradient model. Further detail is provided on liquid vapour phase separation, the van der Waals equation of state, the squared gradient model and the theory of phase separation due to thermal quenching.

Chapter 3 introduces particle methods for solving continuum equations and establishes the details of the smoothed particle numerical method. Methods of symmetrisation, which are essential to ensure conservation of energy and momentum, are discussed along with other technical issues.

In Chapter 4 the specifics of applying the method to liquid-vapour systems are given. A set of symmetrised smoothed particle equations corresponding to the continuum model presented in Chapter 2 are developed. These equations form the basis of simulation codes developed for numerical experiments.

In Chapter 5 the implementation in code of the smoothed particle model outlined in Chapter 4 is discussed. General principles for the design of N-Body solvers are outlined, and important details of the software are given.

Chapter 6 provides results for the simulation of the formation of liquid and vapour systems in two dimensions. Test calculations for the formation of a liquid drop, following [88] and [76] are given. Simulations of phase transitions in response to temperature quenches are presented. It is shown that the mechanical instability of the fluid in the spinodal region of the phase diagram is reproduced, resulting in the formation of droplets coexisting with vapour at varying densities. The formation of liquid vapour interfaces by volume expansion, with accurate reproduction of the theoretical phase diagram at various temperatures is demonstrated. The squared gradient term is introduced in a series of simulations, and shown to increase the interfacial width close to the critical point in proportion to the gradient energy coefficient.

In Chapter 7 the growth exponents for liquid droplets growing in a spinodally quenched vapour in two dimensions are studied. The effect of the gradient term on the growth exponents is examined.

Chapter 8 outlines the software design for a three dimensional smoothed particle solver.

Chapter 9 presents simulations of the development of three dimensional liquid vapour systems using parameters for water. It is shown conclusively that the code and method can simulate water, and produce coexisting phases at the correct densities. It is shown that
increased resolution in the interfacial region is a solution to the problem of underestimation of the surface tension.

In Chapter 10 the thesis concludes and the results of this research are summarised and discussed. Future directions and interesting potential applications are outlined.
2 Continuum dynamics of a phase separating fluid

Modelling the dynamics of matter in the continuum limit involves solving the equations of change governing the fluxes of mass, momentum and energy. In this chapter a Lagrangian form of these equations suitable for modelling a phase separating fluid is developed.

First the van der Waals equation of state and the van der Waals square gradient model are outlined. The van der Waals equation of state provides a simple, elegant model for the coexistence of vapour and liquid. The application of the Maxwell construction in the van der Waals region of negative compressibility provides a model for vapour-liquid phase coexistence and predicts the densities of the coexisting phases. The van der Waals squared gradient theory predicts that the interface between coexisting vapour and liquid is diffuse, and increases in width as the critical point is approached. van der Waals capillary theory states that if the interface is continuous, mechanical and thermodynamic stability requires additional terms in the pressure and free energy that depend on the density gradient. The van der Waals squared gradient model [116] describes the interfacial region as smoothly varying in density.

Next, the general equations for the time derivatives of mass density, momentum and internal energy are explained. A model for the pressure tensor is developed, using: linear constitutive relations for viscosity; the van der Waals equation of state for equilibrium pressure and internal energy; the van der Waals squared gradient model for density inhomogeneity; and Fourier’s law for the heat flux. All constants in this model may be set to values determined by experiment or by molecular dynamics simulation.

2.1 van der Waals’ equation of state

The simplest continuum model that exhibits liquid-vapour coexistence is one in which the equilibrium pressure is given by the van der Waals equation of state [116]. This equation of state is based on the assumption of a long range mean field attraction $a$ between molecules and a hard core excluded volume $b$, giving it a sound although simplified microscopic basis. It gives the pressure $p$ as a function of number density $n$ and temperature $T$, with Boltzmann’s constant $k_B$, as:

$$p = \frac{nk_BT}{1 - nb - an^2}.$$  (2.1)
The van der Waals equation of state can be derived using statistical mechanics by taking the mean field limit of an intermolecular potential composed of a short range, hard repulsion and a long range attraction. Specific internal energy (per unit mass) $u$ is related to temperature by the caloric equation of state

$$u = \frac{d}{2} k_B T - an$$

(2.2)

where $d$ is the number of dimensions.

Figure 2.1: Left: The van der Waals equation of state in the pressure-volume plane, with the Maxwell construction tie line. Right: The phase diagram in the temperature density plane for a quenched one component van der Waals fluid. The spinodal points are where $dp/dV$ is zero. The binodal points are where the constant-pressure line intersects the $p(V)$ curve. The blue regions are the van der Waals loops. A temperature quench into the unstable region is shown.

This equation of state, along with constitutive equations for the stress, heat flux and internal energy can be used to close the Lagrangian conservation equations for mass, momentum and internal energy.

The free energy of the homogeneous van der Waals equation of state has a ‘double well’ at temperatures less than the critical temperature. This is a sufficient requirement for the phase separated system to be more thermodynamically stable. While other, more accurate equations of state exist, the van der Waals equation provides a suitable test case for numerical modelling of coexisting vapour and liquid, because of its simplicity, the ready availability of parameters for real materials and the amount of existing work that has used it.

The van der Waals equation of state has a number of limitations for the quantitative description of real systems. The term $nk_BT/(1 - nb)$ is correct for hard spheres in one dimension but Widom notes that it must be replaced by a more accurate expression for
three dimensional hard spheres \[124\]. Further, the accuracy of the \(-an^2\) term depends on molecules having many neighbours such that the attractive forces mostly cancel.

Even for idealised molecular systems, the van der Waals equation is only exact in the mean field limit and it is in a mean-field sense that the long range interactions (molecular attraction) enter. In their derivations of this relation both van Kampen \[117\] and Espanol \[35\] make use of a mean field approximation in which the system is divided up into cells. Within a cell both the short range and long range terms are taken into account. In considering interactions between particles in different cells, only the long range part of the potential is taken into account and the interaction is computed with respect to the centre of the other cell.

The natural variable to use for SPH is the mass density \(\rho\), rather than the molar or number density. The equation of state (Equation 2.3) may be expressed in terms of \(\rho\) by introducing the parameters \(\bar{a} = a/m^2\), \(\bar{b} = b/m\) and \(k_B = k_B/m\) where \(m\) is the molecular mass and \(\rho = mn\), resulting in the equations

\[
p = \frac{\rho k_B T}{1 - \rho b} - \bar{a} \rho^2, \tag{2.3}
\]

and

\[
u = \frac{d}{2} k_B T - \bar{a} \rho. \tag{2.4}
\]

The critical temperature is the temperature above which there is no distinction between vapour and liquid. In the \(pV\) plane below the critical temperature the isotherms of the van der Waals equation of state have two stationary points known as spinodal points (where \(dp/dV\) is zero) and a kink known as a van der Waals loop in which the pressure decreases with increasing density, shown in Figure 2.1. Such van der Waals loops are also present in molecular fluids that are constrained to be homogeneous \[45\]. The implied decrease of pressure with increasing density in the region of the van der Waals loops (negative compressibility) is not displayed by real substances at equilibrium. Instead, the system separates into coexisting vapour and liquid phases, with densities given by the Maxwell construction.

The van der Waals equation of state as written above is a cubic polynomial in \(\rho\). Below the critical point this equation has three real roots, giving rise to the van der Waals loops. At the critical point there is only a single root and the variables take on their critical values \(p_c\), \(T_c\) and \(\rho_c\). The critical properties themselves are found by noting that, for volume \(V = Nm/\rho\), with number of molecules \(N\), \((V - V_c)^3\) is zero at the critical point. Expansion of this produces three simultaneous equations that can be solved for \(p_c\), \(V_c\), \(\rho_c\) and \(T_c\) to yield

\[
V_c = 3Nb, \tag{2.5}
\]

\[
p_c = \frac{a}{27b^2}, \tag{2.6}
\]
The van der Waals equation of state can then be written in reduced form where each variable is scaled by its critical value, \( p^* = p/p_c, T^* = T/T_c \) and \( \rho^* = \rho/\rho_c \): 

\[
p^* = \frac{8\rho^*T^*}{3 - \rho^* - 3\rho^*^2}.
\]  

(2.9)

This equation is universal, as the material-specific constants \( a \) and \( b \) no longer appear.

The Maxwell construction is based on the equilibrium requirements that a) both the vapour and liquid phase must coexist at equal mechanical pressure, with equal chemical potential and b) that the total free energy \( A \) (given by the area under the pressure-volume curve) is minimised. The combination of the constant pressure constraint and common tangent in the volume-free energy plane requires the pressure to be minimised subject to 

\[
\int_{V_l}^{V_g} p dV = p V (V_g - V_l)
\]

with volume of gas \( V_g \) and liquid \( V_l \).

The Maxwell construction is usually represented as a constant pressure line in the equation of state. The binodal points, which give the volumes of coexisting liquid and vapour, are the intersections of this line with the equation of state in the \( pV \) plane. The binodal line consists of the set of points created in this manner and bounds the region where the vapour and liquid phase coexist. Figure 2.1 shows the region of two phase coexistence, with areas labelled A and B equal. A method of numerically solving for the binodal line is presented in Chapter 9.

In the mechanically unstable spinodal region the derivative \( \partial p/\partial \rho \) is negative. Here the system is susceptible to spontaneous phase separation initiated by infinitesimal fluctuations. The metastable region between the spinodal and binodal is stable under small fluctuations, but will phase separate subject to sufficiently large fluctuations. The latent heat associated with this phase transition is accounted for implicitly by the equation of state.

The main limitation of the van der Waals equation of state’s predictions, for the purpose of the current study, is that the critical exponents that determine how coexistence densities scale with temperature are quantitatively wrong [123] due to the mismatch between the critical exponents obtained from the universal van der Waals equation and those found in real fluids. The liquid-vapour coexisting densities predicted by the Maxwell construction can be fit by the relation 

\[
\frac{\rho_l - \rho_v}{\rho_c} = \frac{7}{2} \left( 1 - \frac{T}{T_c} \right)^{\frac{1}{3}},
\]

(2.10)

which is due to Guggenheim [44]. The critical exponent characterising the relationship between coexisting densities and temperature is found to systematically differ from that

\[
T_c = \frac{8ab}{27b^2k_B},
\]

(2.7)

\[
\rho_c = \frac{m}{3b}.
\]

(2.8)
found in real materials \cite{15, 41}. For real substances, the exponent is closer to 1/2 \cite{10}.

### 2.2 van der Waals’ squared gradient model

When the Maxwell construction is applied to the van der Waals equation of state, it predicts the formation of coexisting phases, but does not make any predictions about the nature of the interface between the liquid and vapour.

The van der Waals squared gradient model \cite{116} is a density gradient theory of the liquid-vapour interface. It makes predictions about the forces acting in a region of continuously inhomogeneous density. In this model, the vapour-liquid interface is a diffuse region where the density varies smoothly between the bulk liquid and vapour densities. It is an example of a density functional theory in which a property (in this case the free energy) is expressed as a series expansion in the density and density gradients \cite{38}. Korteweg, a collaborator of van der Waals, incorporated a density gradient term into the stress tensor \cite{94, 8}. A similar squared gradient model was developed by Cahn and Hilliard \cite{22} to treat phase interfaces in mixtures. Anderson \cite{8} presented a concise review of diffuse interface theories with references to modern applications.

Recently, Kjelstrup and Bedeaux \cite{58} used the squared gradient model to investigate the properties of the liquid vapour interface. In this work the value of the gradient term coefficient for water was determined. Bedeaux et al. \cite{14} devised a numerical solution for the squared gradient model and presented the effects of changes to temperature and pressure boundary conditions on the density profile, discussing the dependence of the constitutive relations for fluxes (such as Fourier’s law) on the spatial derivatives of the density.

Several studies have solved the van der Waals squared gradient model using grid based methods. One recent study is by Lamorghese, who examined isothermal quench-induced phase separation in liquid vapour systems \cite{66}. Turski and Langer \cite{115} used the van der Waals squared gradient model to derive capillary wave solutions and solutions for droplet growth. They found that coupling to the internal energy equation was required for these solutions in order to account for the effect of the latent heat of condensation.

More recently, Kong et al. \cite{62} examined the squared gradient model in several molecular dynamics simulations, and found that it gave a reasonably accurate description of density fluctuations for long wavelengths to short wavelengths of the scale of atomic sizes. This suggested that the gradient coefficient in many liquid states could be negative and that the density dependence of this coefficient needs to be taken into account in order to accurately estimate the surface tension of the interface.

### 2.3 The continuum conservation equations

The equations of Lagrangian continuum mechanics describe the co-moving evolution of mass density $\rho$, velocity $\mathbf{v}$ and specific internal energy $u$ (internal energy per unit mass).
In the Lagrangian description, the only way the density of a mass element can change is by expansion or contraction of that element as indicated by the velocity gradient $\nabla \cdot \mathbf{v}$. This conservation of mass is expressed by the mass continuity equation:

$$\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v},$$ \hfill (2.11)

where $\rho = \rho(r)$ is the density at position $r$. The momentum equation

$$\frac{d\mathbf{v}}{dt} = -\frac{1}{\rho} \nabla \cdot \mathbf{P}$$ \hfill (2.12)

describes the acceleration of a mass element in terms of the divergence of the pressure tensor $\mathbf{P}$, defined such that the force $d\mathbf{F}$ acting on an area element $d\mathbf{A}$ is

$$d\mathbf{F} = -\mathbf{P}^T \cdot d\mathbf{A}.$$ \hfill (2.13)

The energy balance equation describes the temporal change in the internal energy of an element of mass

$$\frac{du}{dt} = \frac{1}{\rho} \left( -\nabla \cdot \mathbf{J}_q - \mathbf{P}^T : \nabla \mathbf{v} \right)$$ \hfill (2.14)

in terms of the heat flux $\mathbf{J}_q$ and work done by stresses.

Specific substances are modelled by the selection of an equation of state to describe the equilibrium pressure and the selection of parameters for the other constitutive relations that describe the pressure tensor $\mathbf{P}$ and heat flux vector $\mathbf{J}_q$ [49]. When applied to Newtonian fluids, which exhibit a linear relationship between stress and rate of strain, these are also known as the Navier-Stokes equations. For a more complete discussion of the development of continuum mechanics for non-equilibrium systems the reader is referred to the references [32, 37]. These are the basic equations of continuum mechanics which will be used throughout the rest of this work.

### 2.4 The pressure tensor

In the equilibrium ideal gas model the pressure is an isotropic scalar function directly proportional to the density. In general, the pressure tensor is not isotropic and is here represented as a second rank tensor. In materials such as solids and non-Newtonian liquids, the off-diagonal components of the pressure tensor become important. The pressure tensor can be divided into equilibrium (reversible) and non-equilibrium (irreversible) components:

$$\mathbf{P} = \mathbf{P}_{eq} + \Pi.$$ \hfill (2.15)

If the equilibrium pressure $\mathbf{P}_{eq}$ is isotropic it is typically a function of the local density and temperature. It becomes a second rank tensor when non-local terms involving the spatial gradients of $\rho$ are included. The non-equilibrium component $\Pi$ is generally associated with
viscosity and with gradients in the temperature $T$.

In general, the equilibrium pressure $P_{eq}$ has local (homogeneous) and non-local (inhomogeneous) components,

$$ P_{eq} = p 1 + C. $$  \hfill (2.16)

The homogeneous pressure $p$ is a function of local mass density $\rho$ and temperature $T$ and is multiplied by the identity tensor $1$. By this definition the local equilibrium pressure is isotropic:

$$ p = p(\rho(r), T(r)). $$  \hfill (2.17)

$C$ is the part of the equilibrium pressure which depends on non-local contributions, usually expressed as spatial gradients. The inhomogeneous pressure $C$, associated with capillary or elastic forces is here a function of the density gradient $\nabla \rho$:

$$ C = C(\nabla \rho). $$  \hfill (2.18)

The functions used to define $P$ and $\Pi$ are called constitutive relations and are discussed in Sections 2.5 and 2.6.

### 2.5 The equation of state and coexistence

In its simplest form the van der Waals equation of state (Equation 2.3) describes homogeneous systems as it has no non-local contributions. In an inhomogeneous fluid the density gradient contributes to the free energy, and thus to the equilibrium pressure. The form of the non-local contribution to the pressure tensor is discussed in Section 2.7.

### 2.6 Non-equilibrium constitutive relations

The non-equilibrium pressure $\Pi$ is associated with irreversible processes such as viscosity. It is broken up into isotropic, symmetric traceless and antisymmetric components for convenience:

$$ \Pi = \Pi^{\alpha \alpha} + \Pi^I + \Pi^a. $$  \hfill (2.19)

$\Pi^{\alpha \alpha}$, the symmetric traceless component, is associated with viscous shear. $\Pi^I$, the isotropic irreversible pressure, is associated with deformations leading to changes in volume (bulk stress). The last term $\Pi^a$ is antisymmetric and will typically only be non-zero for structured molecules, transient states or states with unbalanced body torques. In this work we set

$$ \Pi^a = 0, $$  \hfill (2.20)

which implies that $\Pi = \Pi^T$. The shear viscosity $\eta$ is defined by

$$ \Pi^{\alpha \alpha} = -2\eta \nabla \nu^{\alpha \alpha}, $$ \hfill (2.21)
with coefficient $\eta$ where $\nabla \mathbf{v}^{os}$ is the symmetric-traceless velocity gradient given by

$$
\nabla \mathbf{v}^{os} = \frac{1}{2} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{1}{d} (\nabla \cdot \mathbf{v}) \mathbf{1},
$$

(2.22)

with number of dimensions $d$. The bulk viscosity $\eta_v$ is defined by

$$
\Pi = -\eta_v \nabla \cdot \mathbf{v}.
$$

(2.23)

The heat flux is defined by Fourier’s law

$$
\mathbf{J}_q = -\lambda \nabla T,
$$

(2.24)

where $\lambda$ is the coefficient of thermal conductivity. This captures the heat flux due to conduction. Convection of heat is included implicitly as a consequence of the flow of matter, while radiation is neglected.

### 2.7 The liquid-vapour interface and surface tension

A capillary pressure tensor $\mathbf{C}$, dependent on the spatial gradient of the density is incorporated into the total pressure tensor (Equation 2.16). This gradient term expresses the contribution to the pressure tensor due to density inhomogeneities as a function of the density gradient and accounts for the energy required to form and maintain density inhomogeneities. The contribution of the gradient term to the pressure tensor is given by

$$
\mathbf{C} = -M \left( \rho \nabla^2 \rho + \frac{1}{2} \left| \nabla \rho \right|^2 \right) \mathbf{1} + M \nabla \rho \nabla \rho,
$$

(2.25)

with coefficient $M$. This expression for the density gradient contribution to the equilibrium pressure is described by Felderhoff [39] and Anderson [8]. A key prediction of the van der Waals gradient theory is that the interface between vapour and liquid becomes infinite in width as the critical temperature is approached [90].

The effect of this term is to minimise density gradients by imposing an energy penalty which modulates the pressure in the region of density inhomogeneity. Felderhof [39] derived the expression for the profile of an equilibrium planar interface perpendicular to coordinate $z$ in the vicinity of the critical point:

$$
\rho(z) = \frac{1}{2} (\rho_l + \rho_g) - \frac{1}{2} (\rho_l - \rho_g) \tanh \left( \frac{\kappa z}{2} \right)
$$

(2.26)

with

$$
\kappa = \left( 2kM^{-1} (\rho_l - \rho_g)^2 \right)^{\frac{1}{2}}
$$

(2.27)

where $k$ is a constant.

This equation can be fitted to observed or modelled interfaces. It does not give a predictive density profile because the interfacial width, dependent on $\kappa$ is one of the fitted
parameters, determined entirely by a fit to obtain the desired surface tension and interfacial width.

The density profile described by Equation 2.26 is shown in Figure 2.2. The width of the interface increases with $M$ from an infinitely thin interface with $M = 0$. Molecular dynamics simulations can be used to determine the values of $M$ for specific fluids, or the known surface tension can be used to compute the value. While frequently $M$ is assumed independent of temperature (e.g. by [90] and [14]), this is not the case in general. In this work the temperature and density dependence of the phenomenological coefficients are neglected, however it is recognised that quantitatively correct modelling will require them to be included.

![Figure 2.2: The hyperbolic tangent fit of the liquid vapour interface in the squared gradient model. The width of the interface increases with $M$.](image)

At most pressures and temperatures the interfacial width is microscopic. For example at 300 K, Townsend [113], [114] reported widths of 3.45 Å for molecular dynamics simulations of water, in good agreement with the value determined from X-ray reflectance measurements of 3.30 Å.

The surface tension $\gamma$ can be obtained from the interfacial profile [116] as

$$\gamma = M \int \left( \frac{d\rho(z)}{dz} \right)^2 dz. \quad (2.28)$$

As the critical temperature is approached, the density profile becomes flatter and the integral in Equation 2.28, and thus the surface tension, approaches zero.

Van der Waals also showed that the surface tension is also given by the integral of the difference between parallel pressure $P_\parallel$ and normal pressure $P_\perp$ across the interface [39]:

$$\gamma = -\int_{-\infty}^{\infty} (P_\parallel - P_\perp) \, dz. \quad (2.29)$$

The orientation of the conventions used here for ‘parallel’ and ‘normal’ is shown in
Figure 2.3: The liquid vapour interface showing the directions of normal and parallel pressure.

Figure 2.4 shows a hyperbolic tangent density profile where the interfacial width has been selected to produce the correct surface tension for water as calculated by the area under the normal minus parallel pressure curve. In the lower-right panel of this figure, the equilibrium pressure from the equation of state and the normal component of $C$ are plotted. For mechanical stability, these two pressures must sum to a constant throughout the interface.

2.8 Atomistic modelling of liquid-vapour phenomena

A number of molecular dynamics (MD) studies have examined the structure and properties of liquid-vapour interfaces. Here several that have focussed on water are briefly reviewed.

Townsend used MD to examine the properties of the liquid vapour interface for water [114, 113]. Yang argued that a strictly correct description of the structure of the liquid vapour interface of water is only possible with a molecular treatment, because of the importance of the dipole moment [127]. Estimates of interfacial width and properties generated from such molecular experiments are given by Yang in [128]. Alejendre [5] determined that the SPC/E MD potential produced more accurate surface tensions, across a range of temperatures from 300 to 600 K, for liquid-vapour water interfaces than the SPC or TIP4P models.

Ghoufi [42], reported good agreement between molecular models and experimentally computed surface tensions, discussed in relation to studies applied to CO$_2$ storage in wetted rocks. Ismail compared several different MD force-field models of water [55], and
examined the sensitivity of surface tension estimates to the form of the interface fitting function, finding that an error function provided a good fit.

Other recent atomistic studies of the liquid-vapour interface include Kuo [65] and Schwalback [102], who used phase-field methods to study the dynamics of liquid droplets in nanowire growth.
In general while MD provides information about the structure of interfaces at an atomic resolution, it is limited in its ability to access the hydrodynamic regime because of the number of molecules and simulation time required.

2.9 Continuum modelling of liquid-vapour phenomena

As discussed, Lagrangian particle methods such as SPH are capable of simulating flows with complex structure naturally, because particle arrangements track inhomogeneities in the simulated material. Warren used Dissipative Particle Dynamics (DPD) with density dependent attractive and repulsive interparticle forces to model liquid-vapour coexistence [121], and to study bubble coarsening [122]. The version of DPD Warren used incorporated a simple linear weight function, dependent on particle density, with attractive and repulsive particle interactions structured to produce a cubic equation of state. Ghoufi et al. [41] extended this approach, using a similar version of DPD to investigate the surface properties of water [9]. A distinction between the work of Ghoufi et al. and this thesis is that the DPD particles used in their study [41] represent only a handful of molecules while the SPH particles used in this study represent thousands. At a fully macroscopic scale the width of the liquid-vapour interface is effectively zero.

As discussed in the introduction, a limitation of traditional linear weight function DPD is that the relationship between the inter-particle forces and the underlying continuum mechanical system is not clear, in other words there is no systematic method for deriving the DPD forces from continuum mechanics. In SPH, material properties are input parameters, while in DPD they are emergent. In recent reformulations of DPD, for example [36] have adopted the more systematic relationship between the continuum description and the particle equations used in SPH.

In SPH, the fluid is represented by a set of particles which represent macroscopic mass elements, and carry mechanical properties of mass and velocity as well as thermodynamic properties such as internal energy. The particles are interpolation points, at which the mechanical and thermodynamic fields are evaluated. The equations of motion governing the particles are derived from the continuum equations describing the system to be modelled, converting a set of partial differential equations into a set of ordinary differential equations governing an N-body particle system. For the simulation of simple hydrodynamic flows SPH has proven successful. Morris compared SPH and finite element simulations of Poiseuille and Couette flow [85] and found the SPH simulations generated accurate solutions.

Particle methods bring their own set of numerical challenges including the need to use artificial viscosity to manage shockwaves, troublesome particle clumping, and computational expense. One particular problem is ‘tensile instability’ where the numerical simulation using particles is unstable under tension [64, 80]. This problem has been attacked using a range of methods, including the use of different length scales for different terms of the equation of state [88]. In a formulation of SPH for general fluid flows, Kum discussed the
tendency of smoothed particles to appear to freeze under tension [64].

While the movement of the interpolation points is a strength of the method, it can also be a weakness, resulting in reduced resolution in regions of low density, or an excessive number of particles and hence neighbours in regions of high density. In an N-body system the number of interacting pairs is the main determinant of computational time. Particle reconfiguration (analogous to ‘remeshing’ in a mesh based method) has been proposed as a solution to this [63]. Bergdorf [18] proposed a wavelet based method for the redistribution of particles. Such remeshing techniques are said to improve the handling of diffusive terms in the equations of motion [23].

The clear relationship between the continuum equations and the numerical model is an advantage of SPH, because it allows measured material coefficients to be used. In competing methods such as Lattice Boltzmann and DPD, the relationship between the model dynamics and the continuum equations is less clear [92].
2.10 Conclusions

In this chapter a continuum model for a fluid with a vapour liquid phase transition and a diffuse liquid vapour interface was developed. The key features of the model are the van der Waals equation of state and the van der Waals squared gradient term. The explicit appearance of the internal energy equation is notable because it allows the model to be solved non-isothermally. In later chapters we will discuss numerical solutions using this model. The continuum equations for our model are summarized here. The remainder of the thesis deals with using the smoothed particle technique to generate solutions of this model under a variety of boundary conditions.

The model consists of the mass continuity equation:

\[ \frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v}, \]  

(2.30)

the momentum equation:

\[ \frac{d\mathbf{v}}{dt} = -\frac{1}{\rho} \nabla \cdot \mathbf{P}, \]  

(2.31)

and the energy equation:

\[ \frac{du}{dt} = \frac{1}{\rho} \left( -\nabla \cdot \mathbf{J}_q - \mathbf{P} : \nabla \mathbf{v} \right), \]  

(2.32)

with

\[ \mathbf{J}_q = -\lambda \nabla T. \]  

(2.33)

The internal energy is related to the temperature and density by

\[ u = \frac{d}{2} k_B T - \bar{a} \rho. \]  

(2.34)

The equilibrium pressure tensor at a point in a fluid in terms of mass density \( \rho \) is

\[ \mathbf{P} = p\mathbf{1} + \mathbf{C} + \Pi, \]  

(2.35)

with the equilibrium pressure

\[ p = \frac{\rho k_B T}{1 - \rho b} - \bar{a} \rho^2, \]  

(2.36)

the capillary pressure

\[ \mathbf{C} = -M \left( \rho \nabla^2 \rho + \frac{1}{2} |\nabla \rho|^2 \right) \mathbf{1} + M \nabla \rho \nabla \rho, \]  

(2.37)

and the non-equilibrium viscous terms

\[ \Pi = -2\eta \nabla \mathbf{v}^{os} - (\eta_v \nabla \cdot \mathbf{v}) \mathbf{1}. \]  

(2.38)
3 Smoothed particle hydrodynamics

The complex structure of a condensing quenched vapour suggests Lagrangian particle methods like Smoothed Particle Hydrodynamics (SPH) and Dissipative Particle Dynamics (DPD) as suitable numerical techniques. Because of their grid-free nature, Lagrangian particle methods allow for arbitrarily complex flows, do not suffer from mesh tangling and avoid unstable modes associated with grid methods [51].

In smoothed particle methods the fluid is represented as a set of particles that carry the properties of the fluid and interact according to particle equations of motion. These smoothed particle equations are derived in a clear and consistent way from the continuum equations and constitutive relations for the system.

In this chapter the SPH method of solving partial differential equations is introduced, explained and key elements are derived. The properties of smoothing kernels are discussed. Interpolation formulae for arbitrary properties and for derivatives are developed. The symmetrisation of SPH expressions for derivatives is introduced. The deleterious effect of tensile instability is discussed and solutions to this problem, including the use of artificial viscosity and adaptive smoothing length, are outlined.

Lessons from previous work using SPH to model phase transitions and surface tension are recalled to set the scene for the development of an SPH model for liquid vapour phase transitions in the next section.

3.1 Introduction to smoothed particle hydrodynamics

SPH is a numerical technique for solving partial differential equations (PDEs) in continuum mechanics, independently developed by Monaghan [82] and Lucy [73] for astrophysical modelling. It has also been abbreviated as SPAM (Smoothed Particle Applied Mechanics) in its applications to computational statistical mechanics [48]. While the most commonly modelled equations are the Navier-Stokes equations for viscous fluid flow, or its variants, SPH is general enough to solve arbitrary PDEs.

In SPH the fluid is represented by particles that have macroscopic attributes including density, mass, velocity and temperature. The particles are interpolation points, and their movement represents the motion of mass in the fluid. Field variables are mapped by this set of arbitrarily distributed particles. Particle properties are smoothed over space by an interpolation kernel. Particles move with a velocity close, but not identical, to the fluid’s local velocity.

In the SPH representation, the partial differential equations (PDEs) of continuum me-
Mechanics are transformed into a set of ordinary differential equations (ODEs) governing the motion of particles. The problem can then be solved as a standard N-body system using techniques familiar from molecular dynamics or astrophysical N-body simulation. The mathematical basis for the method is the approximation of a field variable by an integral. Field properties at any point \( \mathbf{r} \) are calculated by a weighted summation over neighbouring particles with a density dependent weighted kernel summation over \( N \) particles

\[
f(\mathbf{r}) = \sum_{i=1}^{N} \frac{f_i m_i}{\rho_i} W(\mathbf{r} - \mathbf{r}_i; h),
\]

where \( \rho_i, m_i \) and \( \mathbf{r}_i \) are the density, mass and position of particle \( i \). The smoothing kernel \( W \) is usually a cubic spline of Gaussian-like shape and a range of \( h \) also called the smoothing length. This weighted summation is used to recover the field variables at any point in space as shown in Figure 3.1.

Particle equations of motion are derived using this integral approximation of the continuum equations. Because the particles move with the streaming velocity of the fluid, we are able to use the simpler Lagrangian formulation of the continuum equations.

![Figure 3.1: Left: The 'Lucy' smoothing kernel. Centre: Particle positions. Right: Continuum smoothing of the particle plot generated using software described in [95].](image)

### 3.2 Derivation of the smoothed particle approximation

The essence of the SPH method is the approximation of a continuous function by an integral. This integral over space is then approximated by a sum over discrete particles [78]. The identity

\[
f(\mathbf{r}) = \int f(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r}',
\]

is known as the integral representation of a function. Here \( \delta \) is the Dirac delta function defined by

\[
\int_{-\infty}^{+\infty} f(x) \delta(x) dx = f(0).
\]
The delta function in Equation 3.2 can be replaced with a smoothing kernel with the property
\[
\lim_{h \to 0} W(\mathbf{r}; h) = \delta(\mathbf{r}).
\] (3.3)

This smoothing kernel also shares the normalisation property of the delta function
\[
\int W(\mathbf{r}; h) d\mathbf{r} = 1.
\] (3.4)

A normalised Gaussian is one function that fits these criteria, and is a natural choice given we have defined the Dirac \(\delta\) function as a Gaussian in the limit of the width going to zero. With the substitution of the kernel for the delta function, the integral interpolant representation of \(f(\mathbf{r})\) becomes
\[
f(\mathbf{r}) = \int f(\mathbf{r}') W(\mathbf{r} - \mathbf{r}'; h) d\mathbf{r}'.
\] (3.5)

Having substituted a smoothed kernel for the delta function, the integral over all space can be approximated with an integral over a finite number of interpolation points:
\[
f(\mathbf{r}) = \int \left[ \frac{f(\mathbf{r}')}{\rho(\mathbf{r}')} \right] W(\mathbf{r} - \mathbf{r}'; h) \rho(\mathbf{r}') d\mathbf{r}',
\] (3.6)

where \(d\mathbf{r}' = dx'dy'dz'\) is a volume element \((d\mathbf{r}' = dV')\). Using the usual continuum definition of density we have
\[
dV' = \frac{dm(\mathbf{r}')}{\rho(\mathbf{r}')}.\]

If the matter is divided into small elements of mass \(m_i\) with positions \(\mathbf{r}_i\), the contribution of the \(i^{th}\) element to the integral is
\[
f(\mathbf{r}_i) \frac{m_i}{\rho(\mathbf{r}_i)} W(\mathbf{r} - \mathbf{r}_i; h).
\] (3.7)

The contributions of such distributed mass elements are summed to produce the approximation to the integral, resulting in the SPH particle approximation for any field variable at an arbitrary position:
\[
f(\mathbf{r}) = \sum_{i=1}^{N} m_i \frac{f_i}{\rho_i} W(\mathbf{r} - \mathbf{r}_i; h).
\] (3.8)

Any field property can be computed at an arbitrary point in space via the smoothed particle interpolation. In Equation 3.8, the sum is over all particles. It is important to note that the smoothed value of a property at a point \(f(\mathbf{r})\) is not always equal to the property \(f\) of the particle located at \(\mathbf{r}\). That is to say, in general, \(f(\mathbf{r}_i) \neq f_i\). An important exception to this is the particle density which is always equal to the field density at the particle’s position: \(\rho_i = \rho(\mathbf{r}_i)\).
3.3 The smoothing kernel

The smoothing kernel can be likened to the weight function used in the finite element method. The kernel is always normalised (Equation 3.4), is always even and is usually radially symmetric \(W(|r|; h)\), although some studies have used kernels with an elliptical shape that respond to the anisotropy of the simulated system [104]. For computational efficiency it is preferable for the kernel to have finite extent.

The simplest smoothing kernel is the Gaussian kernel in \(d\) dimensions

\[
W(r; h) = \frac{1}{h^d \pi^{d/2}} \exp \left( -\frac{r^2}{h^2} \right),
\]

where \(r = |r|\) is the distance from the center of the kernel and \(h\) is a smoothing length associated with the range of the kernel. It has the advantage of being continuously differentiable and easily normalised, but the computational disadvantage that it is not finite in extent. The derivative of this Gaussian kernel in one dimension is

\[
\frac{dW(r; h)}{dr} = -\frac{2r}{h^2} W(r).
\]

Most serious applications of SPH use cubic splines with compact support which are computationally cheaper to compute than the Gaussian [81]. Another popular kernel [88, 75, 54] is Lucy’s quartic spline kernel \(W_{lucy}\) [73],

\[
W_{lucy}(r; h) = \frac{5}{\pi h^2} \left( 1 + 3 \frac{r}{h} \right) \left( 1 - 3 \frac{r}{h} \right)^3.
\]

Lucy’s kernel is computationally cheap and finite in extent being zero for \(r > h\). The derivative of \(W_{lucy}\) is

\[
\frac{\partial W_{lucy}}{\partial r} = \frac{5}{12 \pi h^2} \left( -\frac{12r^3}{h^4} + \frac{24r^2}{h^3} - \frac{12r}{h^2} \right).
\]

For radially symmetric kernels, the spatial gradient of the kernel \(\nabla W(r)\) is a function of vector \(r\) such that

\[
\nabla W(r; h) = \sum_i \nabla_i W(r - r_i; h),
\]

where the operator

\[
\nabla_i = \frac{r - r_i}{|r - r_i|} \frac{\partial}{\partial r},
\]

is used to compute the kernel gradient at the location of particle \(i\) with respect to a kernel centred at \(r\).

In most formulations of the SPH equations, the kernel gradient is calculated particle-wise, such that each neighbour’s contribution to the gradient is calculated separately:

\[
\nabla_i W(r) = \frac{r_{ji}}{r} \frac{\partial}{\partial r} W(r),
\]

26
where \( r = |r_{ij}|, \ r_{ij} = r_j - r_i \) and \( r_{ji} = r_i - r_j \).

The sense of direction implied by the gradient operator subscript is shown in Figure 3.2.

This direction is a matter of convention, and care is needed to ensure consistency, because
\[ \nabla_i W(r) = -\nabla_j W(r) \]

With the distance between two particles \( r_{ij} = |r_j - r_i| \), the kernel gradient between two particles is given as
\[ \nabla_i W_{ij} = \frac{r_{ji}}{r_{ij}} \frac{\partial W_{ij}}{\partial r_{ij}}. \]  \hspace{1cm} (3.16)

This amounts to taking the position of particle \( i \) as the reference or origin. \( \nabla_i W_{ij} \) is the directional derivative with respect to the coordinates of particle \( i \).

Figure 3.2: Lucy kernel and gradient with respect to other particles.

### 3.4 Smoothed field properties

Field properties computed at particle locations are given by
\[ f(r_i) = \sum_{j=1}^{N} m_j \frac{f_j}{\rho_i} W_{ij}, \]  \hspace{1cm} (3.17)
and $W_{ij}$ is the kernel computed over a pair of particles:

$$W_{ij} = W(|\mathbf{r}_j - \mathbf{r}_i|; h). \quad (3.18)$$

This expression for a field at an arbitrary location (Equation 3.17), is not unique. There are a multitude of possible smoothed approximations. Hoover [49] points out that applying the SPH rule Equation 3.17 to $\rho f$, $f$ and $f/\rho$ yields the following approximations for field variable $f$:

$$f_0(r) = \frac{1}{\rho(r)} \sum_i f(r_i)m_iW(r - r_i; h); \quad (3.19)$$

$$f_1(r) = \sum_i f(r_i)\frac{m_i}{\rho_i}W(r - r_i; h); \quad (3.20)$$

$$f_2(r) = \sum_i f(r_i)\frac{\rho(r)}{\rho_i^2}m_iW(r - r_i; h); \quad (3.21)$$

The difference is in the involvement of the particle density and the density of the neighbouring particles in the summation. Each of Equations 3.19, 3.20 and 3.21 are equally valid, so that the choice of one particular version is motivated by computational ease, or by its accuracy under particular conditions.

### 3.4.1 Smoothed approximation of density

There are two ways to calculate the density at a point in the simulated fluid using SPH. The most straightforward is the ‘summation density’ approach, obtained by applying Equation 3.17 to the density.

$$\rho(r) = \sum_{j=1}^{n} m_jW(r - r_j; h). \quad (3.22)$$

The summation density approach explicitly conserves mass. The alternative is to make an SPH approximation of the continuity equation as proposed by Monaghan [79],

$$\frac{d\rho}{dt} = \sum_i m_i\mathbf{v}_{ij} \cdot \nabla W_{ij}. \quad (3.23)$$

The continuity density rule only gives the evolution of density with time, so an initial density needs to be assigned either arbitrarily or using the summation method. A benefit of the continuity density approach is increased stability for highly incompressible flows. Summation density produces density gradients at free surfaces, which in turn produce pressure gradients. In modelling vapour and liquid in coexistence, density gradients are desirable, as the whole point of the exercise is to resolve the forces in the density interface. In this thesis only the summation density method is used.
3.5 Smoothed approximation of derivatives

The smoothed approximation of the gradient of a field function can be taken by analytically differentiating the interpolation formula as follows \[77\]:

\[
\nabla f(r) = \sum_{i=1}^{N} \frac{m_i}{\rho_i} f_i \nabla W(r - r_i; h). \tag{3.24}
\]

The gradient operator \( \nabla \) can simply be taken inside the sum and applied to \( W \) as all other factors are independent of \( r \). There are some caveats on this, the main one being that this is not valid near the boundary where there is a deficit of particles. This boundary inconsistency issue is explored in detail by Liu \[71\]. In the current work periodic boundary conditions are used throughout, so boundary truncation is less of an issue, although it may increase the errors in smoothed approximations of gradients around the liquid-vapour interface. From Equation \[3.24\] the density gradient is given by

\[
\nabla \rho(r) = \sum m_j \nabla W(r - r_j). \tag{3.25}
\]

The same technique used for the gradient operator can be used for the divergence of a vector field:

\[
\nabla \cdot \mathbf{f}(r) = \sum_{j=1}^{N} \frac{m_j}{\rho_j} \mathbf{f}(r_j) \cdot \nabla_i W_{ij}. \tag{3.26}
\]

3.6 Symmetrisation of smoothed properties

The direct application of the SPH approximation can lead to a set of particle equations with undesirable asymmetry. For example applying Equation \[3.17\] to the momentum equation (Equation \[2.12\]) produces

\[
\frac{d\mathbf{v}_i}{dt} = -\frac{1}{\rho_i(r_i)} \sum_j m_j \mathbf{P}_j \cdot \nabla_i W_{ij}, \tag{3.27}
\]

where \( \mathbf{v}_i \) is the velocity of particle \( i \), and \( \mathbf{P}_i \) is the pressure tensor of particle \( i \). The force on particle \( i \) due to particle \( j \) is

\[
f_{ij} = \frac{m_i m_j}{\rho_i \rho_j} \mathbf{P}_j \nabla_i W_{ij},
\]

while the force on particle \( j \) due to particle \( i \) is

\[
f_{ji} = \frac{m_i m_j}{\rho_i \rho_j} \mathbf{P}_i \nabla_i W_{ij}.
\]
It is clear that unless $P_i = P_j$, using this naive SPH form of the momentum equation results in $F_{ij} \neq F_{ji}$.

This lack of symmetry between the mutual forces acting on pairs of particles was recognised by Monaghan [78], who developed the first symmetrised SPH discretisations of the equations of motion. General methods of symmetrising SPH expressions were introduced by Monaghan [77] and are discussed by Hoover [49]. The two most widely used methods make use of the product and quotient rules for derivatives and will now be outlined.

### 3.6.1 Product rule symmetrisation

The product rule for gradients can be used to derive symmetrised SPH expressions. The expression

$$\nabla (\rho f) = \rho \nabla f + f \nabla \rho,$$

can be arranged as

$$\nabla f(r) = \frac{1}{\rho} \left[ \nabla (\rho f(r)) - f(r) \nabla \rho \right]. \tag{3.28}$$

Taking smoothed approximations of the each term, using Equation 3.24 gives

$$\nabla (\rho f(r)) = \nabla \sum_j \rho_j {m_j \rho_j \over \rho} f(r_j)W(r-r_j) \tag{3.29}$$

$$= \sum_j m_j f(r_j) \nabla W(r-r_j), \tag{3.30}$$

which combined with Equation 3.25 produces

$$\nabla f(r) = \frac{1}{\rho} \left[ \sum_j m_j f(r_j) \nabla W(r-r_j) - \sum_j f(r) m_j \nabla W(r-r_j) \right]. \tag{3.31}$$

In order for particle pair contributions to be symmetric, the mean mass and density must be used. For calculating the gradient at the location of a particle

$$\hat{\nabla} f(r_i) = \sum \frac{m_{ij}}{\rho_{ij}} (f(r_j) - f(r_i)) \nabla_i W_{ij} \tag{3.32}$$

where

$$m_{ij} = \frac{m_i + m_j}{2}$$

and

$$\rho_{ij} = \frac{\rho_i + \rho_j}{2}$$

A similar identity holds for the divergence of a vector field

$$\nabla \cdot (\rho \mathbf{F}) = (\nabla \rho) \cdot \mathbf{F} + \rho (\nabla \cdot \mathbf{F}). \tag{3.33}$$
3.6.2 Quotient rule symmetrisation

To symmetrise the gradient of a second rank tensor field using the quotient rule, quotient identity is rearranged as
\[
\nabla \mathbf{F} = \rho \left( \nabla \frac{\mathbf{F}}{\rho} + \frac{\mathbf{F}}{\rho} \nabla \rho \right). 
\]
(3.34)

If we take smoothed approximations of each term, use Equation 3.25 for the density gradient and note that
\[
\nabla \hat{\mathbf{F}} \rho = \sum_j m_j \mathbf{F}_j \rho_j^2,
\]
(3.35)
and then substitute these to obtain the symmetrised SPH expression for \( \nabla \mathbf{F} \), we find
\[
\nabla \mathbf{F} = \rho \left[ \sum_j m_j \left( \frac{\mathbf{F}_j}{\rho_j^2} + \frac{\mathbf{F}}{\rho^2} \right) \nabla W \left( \mathbf{r} - \mathbf{r}_j \right) \right].
\]
(3.36)

The corresponding rule for the divergence of a second rank tensor is
\[
\nabla \cdot \mathbf{F} = \rho \left( \nabla \cdot \frac{\mathbf{F}}{\rho} \right) + \frac{\nabla \rho \cdot \mathbf{F}}{\rho}.
\]
(3.37)

3.7 Issues and limitations of smoothed particle hydrodynamics

Another potential deficiency of SPH is instability under tensile forces [80], which may lead to particle clumping as noted by Hoover [49]. While smoothed particles may clump together or form string-like phases, these structures may not have a great impact on the continuum interpolation of the field. They may however affect the dynamics of the solution if the particles become unphysically ‘stuck’, or if it leads to spuriously large forces and ‘blow up’. To explain this tensile instability, Morris [85] studied the dispersion properties of SPH particles in one dimension. A key finding was that stability changed with the sign of the background pressure.

When boundaries are not periodic, the truncation of the smoothing function at a boundary must be taken into account for the solution to remain accurate.

Kitsionas [57] notes that SPH is typically not as accurate as finite difference methods using nested grids for simulating strong density gradients. They propose a particle splitting method to deal with this [57]. While particle reconfiguration has the potential to create spurious perturbations which may affect the simulation dynamics, Kitsionas and Whitworth found that the perturbations were transient, and rapidly damped. Issues with the resolution of density gradients will be discussed in Chapter 9.

Morris also found that the growth rate of instabilities was smaller for kernels whose Fourier transform fell off more rapidly and that the inclusion of artificial viscosity slowed the growth of these instabilities [85].
3.7.1 Artificial viscosity

When using grid-based solvers, artificial viscosity may be required to deal with shock waves of smaller spatial scale than the resolution of the numerical method, otherwise unphysical particle interpenetration may occur. Sound speed is typically an increasing function of density. This leads to the high density (and thus high pressure) parts of a wave overtaking the slower parts. In real systems, dissipative forces prevent shock waves from becoming infinitely steep. However, the dissipation occurs at very small (atomic) length scales. Molecular dynamics studies have confirmed that a shock wave is a region with a width of the order of a few mean free atomic paths. Hoover [49] provides a simple calculation of the order of the shock front size. Artificial viscosity is used in most popular macroscopic continuum models.

In order to correctly conserve mass and energy in a macroscopic-scale simulation, pressure waves must be artificially spread over a few mesh points or particle spacings [125]. Von Neumann-Richtmeyer artificial viscosity accomplishes this by increasing the bulk viscosity for compression, determined by negative velocity divergence \( \nabla \cdot v < 0 \). It is usually implemented as a linear term and a quadratic term in the velocity divergence. The artificial viscosity contributions to the pressure tensor are given by a linear term

\[
\Pi_{erv} = -\rho \alpha_1 h c \nabla \cdot v
\]

and a quadratic term

\[
\Pi_{ervq} = \alpha_2 h^2 \rho (\nabla \cdot v)^2
\]

In the linear term \( c \) is the speed of sound, and \( h \), the smoothing length is the desired shockfront width. \( \alpha_1 \) and \( \alpha_2 \) are coefficients that can be tuned to the particular system, usually set to around 1 for convenience.

Another problem in SPH is that particles may penetrate each other unphysically, due to tension or simply due to large accelerations. This is also alleviated by using an artificial viscosity term.

3.7.2 Core repulsion

To further prevent particle interpenetration and clumping, a core potential was suggested by Hoover [49]. Using

\[
\phi = \sum_{r_{ij} < \sigma} c_r \frac{r_{ij}}{4} \left( 1 - \left( \frac{r_{ij}}{\sigma} \right)^2 \right)^4,
\]

The force \(-d\phi/dr\) is

\[
F_c = \sum_{r_{ij} < \sigma} -c_r \frac{2 r_{ij}}{\sigma^2} \left( -\frac{r_{ij}^2}{\sigma^2} + 1 \right)^3 \frac{r_{ij}}{|r_{ij}|},
\]
where \( c_r \) is a coefficient that determines the strength of the repulsion, and \( \sigma \) gives the core size. This force is zero for large distances. Its effects are included in the pressure-volume work by treating this term as part of the reversible pressure tensor.

### 3.8 Applications of smoothed particle hydrodynamics

SPH has been used to simulate systems ranging in scale from the microscopic to the galactic. Initially conceived for astrophysical simulations by Monaghan [82] and Lucy [73], the method continues to be popular in astrophysical modelling [57]. A widely cited outline of the technique has been written by Monaghan [78], in which symmetrised SPH forms of the continuity, momentum, and thermal energy equations are derived in detail.

The method was applied in the field of non-equilibrium statistical mechanics by Hoover, using a new acronym SPAM (Smooth Particle Applied Mechanics) [48]. Among many studies by Hoover was an investigation of the entropy increase of an ideal gas undergoing confined expansion [54] and also more philosophical works about the potential for particle methods to bridge the gap between molecular and continuum mechanics [48]. A recent review by Koumoutsakos [63] discusses the application of particle methods to multi-scale problems and the potential to couple continuum particle methods with molecular dynamics.

Hoover and Posch [53] used the isomorphism of SPH with molecular dynamics to understand the artificial transport of momentum and kinetic energy in smoothed particle systems as a form of numerical heat conductivity, and related this to phenomenological turbulence models for parameterising the transport of momentum and energy by turbulent eddies.

Hoover showed that complex flows such as Rayleigh-Bernard convection have been modelled with SPH [50]. The problem of incorporating heat conduction was studied in depth by Cleary [26] and separately by Jeong [56]. SPH has also found traction in the field of computer graphics. For example, Muller uses SPH to generate visual models of blood flow for surgical simulations [86]. Geophysical applications have included modelling of Arctic ice movement [70]. SPH is a popular method for modelling flows with free surfaces such as the coalescence of microscopic droplets [76] and high pressure die cast moulding [27]. Flow through complex geometry is also treated naturally, see for example Klapp’s [59] study of flow through a wellhead.

A detailed presentation of SPH with an exhaustive list of references is provided by Liu and Liu [71], who include derivations of SPH models for heat conduction, non-viscous fluids, viscous fluids and explosions.
3.9 Smoothed particle modelling of phase transitions and surface tension

While grid based continuum methods have been successfully applied to the study of short-time growth of fluctuations in van der Waals squared gradient and Cahn-Hilliard models, these applications have typically been for isothermal systems. Particle based methods provide a clear way of incorporating terms important for hydrodynamics such as viscosity, heat conduction, latent heat, external body forces and boundary effects.

Existing work provides a range of methods for how the interfacial properties and kinetics of phase transitions can be modelled with SPH. Such treatments of surface tension using smooth particles either make use of a ‘colour’ function [84], use a longer smoothing length for the cohesive force [88], use arbitrary ‘particle-particle’ forces [109], or do not model liquid-vapour phase coexistence [49]. Each of these approaches has limitations and they are discussed in more detail below.

In other work, modelling of multiple phases using SPH has been achieved by using separate equations of state for the different system components or by utilising a single equation of state capable of describing both phases. Colagrossi et al. [29], in their study of a cavitating fluid use different particles governed by different equations of state for the gas and liquid components. Benz [17] used a single equation of state with solid and liquid phases to study hypotheses of the formation of the moon by a planetary impact. Monaghan’s work on crystallisation falls somewhere in between, modelling the solidification of a fluid by means of a set of water particles and a set of ice particles where mass is transported from the liquid particles to the ice particles [83].

SPH was used to model the equilibrium properties of liquid-vapour coexistence in two dimensions by Nugent and Posch [88]. The work presented in this thesis relies heavily on their foundation, extending it by solving the equations in three dimensions, considering density gradient contributions to the equilibrium pressure and using experimental parameters to simulate a specific substance.

Nugent and Posch used standard SPH forms of the momentum and energy equations, with a van der Waals equation of state, to simulate liquid drop formation without the need for tracking the surface. The droplets formed in their simulations do not exhibit uniform density, suffering from a clustering in concentric rings [88]. Simply using the van der Waals equation of state for the pressure was found to lead to instability, and to result in numerical artifacts in the form of tightly bound structures. The solution applied by Nugent and Posch was to use a longer smoothing length (and hence a longer range) for the cohesive part of the pressure (and thus the attractive forces between particles). They found instabilities were reduced, and stable interfaces formed. This same approach was previously used by Hoover for surface tension forces. This approach has been criticised [112] for ‘numerically inducing’ surface tension. In Nugent and Posch’s approach, the surface tension appears as a consequence of the calculation of equilibrium pressure. Nugent and Posch found that the coexisting densities were a good fit to those predicted by the Maxwell construction for
temperatures away from the critical point. Closer to the critical point they found that the equilibration time was too long to obtain a good fit.

Other approaches have modelled surface tension directly by ad-hoc attractive forces between particles. To model surface tension, Hoover incorporated simple attractive terms in an equation of state similar to the embedded atom method potential \[47\]. Tartakovsky and Meakin incorporated a separate ‘particle-particle’ force to the standard SPH force to model surface tension, and used attractive-repulsive boundary particle interactions to simulate wetting of a solid surface \[110\] \[109\]. Surface tension is modelled by adding this pair potential to the potential between particles due to the equation of state and was verified by observing that the Young-Laplace equation and the surface tension implied by oscillation gave similar results \[111\]. The attractive and repulsive interparticle forces used by Warren with DPD are another example of this approach \[121\].

A third approach is to track the interface and impose a surface tension force directly. Morris modelled surface tension by tracking the fluid interface and applying a surface tension force \[84\]. To achieve this, Morris used a colour function which provided a measure of interfacial curvature to resolve the effects of surface tension in a fluid SPH model. This colour function is superficially similar to a density gradient term. In Morris’ method, multiphase flow is modelled by adding an additional particle type.

Following closely on from Nugent and Posch’s work, Melean and Sigalotti \[103\] \[76\] sought to correct the particle inhomogeneity, displayed with the formation of concentric ring like structures in liquid droplets, using the van der Waals equation of state. They attributed the formation of these structures to tensile instability and applied an artificial stress correction term. The application of this numerical correction produced a similar liquid droplet to Nugent and Posch’s lowest temperature, but with a more homogeneous distribution of particles.

Other attempts to correct for tensile instability include Monaghan’s use of dispersion relations to derive the form of an artificial repulsive term \[80\], and Hoover’s use of a density dependent weight function to reduce the tensile instability in simulations of solids \[52\].

The van der Waals equation of state has since been used for a number of SPH studies focussed on questions not related to phase transitions. For example Melean studied low energy collisions of Van der Waals droplets. \[75\]. Lopez investigated the oscillation of Van der Waals droplets, using the oscillation period to determine a surface tension, and studied the oscillation behaviour for different values of Reynold’s number \[72\].

Further work by Sigalotti \[104\] used a method of ’Adaptive Kernel Estimation’ (ADKE) to adjust the kernel width as a function of particle density. This reduced the range of the smoothing function in regions of high particle density. This was shown to reduce the width of the surface in a free droplet.

Despite the volume of work, only a few have used diffuse interface theory to model the liquid-vapour interface directly. Ghoufi \[41\] extended this approach to use DPD to investigate the surface properties of water \[9\]. Recent work by Espanol \[34\] has reformulated DPD using the SPH method of deriving particle potentials from the hydrodynamic...
equations.

3.10 Conclusions

In this chapter, the smooth particle hydrodynamics method of numerical solution of the continuum equations was introduced. The mathematical basis of the method was presented and limitations of the technique were discussed. In later chapters the application of the method to the particular problem of liquid-vapour phase separation will be outlined.
In this chapter the construction of a SPH approximation for solving the model for a phase separating fluid outlined in Chapter 2 is presented. This chapter describes the development and exposition of the SPH model as implemented in the code described in Chapter 5. In this smoothed particle model the energy equation is solved explicitly and heat conduction is included. To produce stable coexistence, the cohesive part of the pressure operates at a longer range than the repulsive part. While it may appear at first that this is required for consistency with mean-field theory, closer examination shows that it is related to the stability of the forces in the smooth particle approximation.

4.1 Smoothed approximation of the momentum equation

The density of each particle is computed using Equation 3.22, using Lucy’s quartic spline (Equation 3.11). Using Equation 3.36 for the divergence of the pressure tensor, a symmetrised version of the SPH momentum equation is obtained that guarantees conservation of momentum by ensuring that pairs of particles exert equal and opposite forces on each other:

\[
\frac{dv_i}{dt} = -\sum_{j=1}^{N} m_j \left( \frac{P_j}{\rho_i^2} + \frac{P_i}{\rho_j^2} \right) \cdot \nabla_i W_{ij},
\]

where the summation is over \( j \) neighbouring particles, with particle velocity \( v_i \). The unsymmetrised form of the spatial derivative is used for the velocity gradient at the position of particle \( i \),

\[
(\nabla v)_i = \frac{1}{\rho_i} \sum_{j=1}^{N} m_j (v_j - v_i) \nabla W_{ij}.
\]

This form ensures that for any two particles, \( \nabla v_{ij} = 0 \) when \( v_i = v_j \). The divergence is calculated as

\[
(\nabla \cdot v)_i = \frac{1}{\rho_i} \sum_{j=1}^{N} m_j (v_j - v_i) \cdot \nabla W_{ij}.
\]

The temperature gradient is interpolated using the product rule symmetrised expression.
\[ \nabla T_i = \sum_j \frac{m_{ij}}{\rho_{ij}} (T_j - T_i) \nabla W_{ij}, \quad (4.4) \]

with \(m_{ij}\) and \(\rho_{ij}\) given by the arithmetic means of the pair of particles' masses and densities.

### 4.2 Smoothed particle approximation of the energy equation

#### 4.2.1 The work term

Using the product rule for divergence and the above expression for the velocity gradient, a simple smoothed interpolant of the pressure part of the energy equation (Equation 2.14) can be constructed by applying the \(f_0\) SPH approximation of Equation 3.19,

\[ \frac{du_i}{dt} = -\frac{1}{\rho} P^T_i : \frac{1}{\rho_i} \sum_j m_j (v_j - v_i) \nabla W_{ij} \quad (4.5) \]

This suffers from a symmetrisation problem, which can be remedied by expanding \(P^T : v\) as

\[ -P^T : \nabla v = -\nabla \cdot (P \cdot v) + v \cdot (\nabla \cdot P) \quad (4.6) \]

so that

\[ \frac{du}{dt} = -\left[ \nabla \cdot \left( \frac{P}{\rho} \cdot v \right) - v \cdot \left( \nabla \cdot \frac{P}{\rho} \right) \right]. \]

Smoothed approximations for each term (at the position of particle \(i\)) are

\[ \nabla \cdot \left( \frac{P}{\rho} \cdot v \right) = \sum_j m_j \frac{P_j}{\rho_j} \cdot v_j \cdot \nabla W_{ij} \]

and

\[ \left( v \cdot \nabla \frac{P}{\rho} \right)_i = v_i \cdot \sum_j m_j \frac{P_j}{\rho_j} \cdot \nabla W_{ij}, \]

which are added together to give a second version of the SPH energy equation

\[ \frac{du}{dt} = \sum_j m_j \frac{P_j}{\rho_j^2} \cdot (v_j - v_i) \cdot \nabla W_{ij}. \quad (4.7) \]

which can be written using the identity \(v \cdot (\nabla \cdot P) = v \nabla : P\) to

\[ \frac{du}{dt} = \sum_j m_j \frac{P_j}{\rho_j^2} : (v_j - v_i) \nabla W_{ij}. \quad (4.8) \]

This is also not symmetric, but Equations (4.5) and (4.8) are averaged to obtain the final, symmetrised work term (Equation 4.9). In most of the literature the pressure tensor appears as \(P_i\), not transposed. In most practical applications and throughout this work the
The pressure tensor is symmetric but in general it may contain asymmetric terms.

\[
\frac{du_i}{dt} = -\frac{1}{2} \sum_{j}^{N} m_j \left( \frac{P_T^i}{\rho_i^2} + \frac{P_j}{\rho_j^2} \right) : v_{ij} \nabla W_{ij}. \tag{4.9}
\]

The SPH interpolant of the heat flux vector \( \mathbf{J}_q \) (Equation 2.24) is simply

\[
\mathbf{J}_q = -\lambda \nabla T.
\]

Using the above expression for temperature gradient and the quotient symmetrisation, the heat conduction contribution to the change in internal energy is

\[
\nabla \cdot \mathbf{J}_q = \sum_{j} m_j \left( \frac{J_{qi}}{\rho_i^2} + \frac{J_{qj}}{\rho_j^2} \right) \cdot \nabla W_{ij}. \tag{4.10}
\]

The complete SPH energy equation is

\[
\frac{du_i}{dt} = \frac{1}{2} \sum_{j=1}^{N} m_j \left( \frac{P_i}{\rho_i^2} + \frac{P_j}{\rho_j^2} \right) : v_{ij} \nabla W_{ij} - \sum_{j=1}^{N} m_j \left( \frac{J_{qi}}{\rho_i^2} + \frac{J_{qj}}{\rho_j^2} \right) \cdot \nabla W_{ij}. \tag{4.11}
\]

4.3 Separation of attractive and repulsive components of pressure

Figure 4.1: Terms in the pressure tensor that result in an attractive interparticle force operate on a longer range (H) than the terms that are repulsive.

To avoid unstable attractive forces the cohesive and repulsive components of the pressure are treated separately, using a longer range for the attractive forces. This is shown in Figure 4.1 where the central particle is shown interacting with another particle only through attraction with smoothing length \( H \). Figure 4.2 shows interparticle forces at various temperatures and background densities. The left panel shows the interparticle force
with \( h = 2.0 \) and \( H = 4.0 \). The right panel shows the interparticle force with \( h = H = 2.0 \). Negative forces are attractive. It is clear from this plot that the \( h = H \) case results in uniformly attractive and thus unstable forces between particles for some temperatures and densities. Stability of the simulation requires that interparticle forces become repulsive at a sufficiently high density (close distance). The instability of attractive forces suggests that unless the squared density gradient term is explicitly incorporated, this separation of smoothing lengths is required to obtain well behaved liquid vapour coexistence with SPH.

![Figure 4.2: Interparticle force as a function of separation. Left: with long range attraction and short range repulsion. Right: Attractive and repulsive components with the same smoothing length. Top panels show the forces between two isolated particles, while bottom panels show forces between two particles with a background density of 1.0.](image)

Sigalotti [104] has suggested that the separation of the attractive and repulsive components is sufficient to model surface tension. This argument is motivated by the similarity of the attractive force term with the density gradient term used for grid based methods and by Morris [84] for phenomenological surface tension in SPH between two fluids in which a ‘colour’ property is used to distinguish between phases and the curvature of the colour field determines the surface tension force. Both these studies show that the attractive force acts to oppose density gradients. Morris also determined that a long smoothing length was required for this colour term to ensure stability. Morris [84] determined that SPH stability was improved by varying the range of the kernel, which tended to damp out spurious periodic modes. In another study, Morris used different smoothing lengths to compute the pressure and the curvature term from which a surface tension force was calculated [84].
The use of a longer attractive smoothing length is not the only way to induce surface tension or phase separation. To model surface tension with SPH particles, Tartakovsky and Meakin [109] made use of an additional interparticle force to generate long-ranged attraction and short-ranged repulsion, effectively superimposing a molecule-like model for surface tension onto the SPH particles. The existence of the liquid-vapour phase transition has been argued to be a result of competition between the long range attraction and short range repulsion between particles [69] [117].

Therefore the separation of the long and short smoothing lengths has a similar effect to superimposing a long ranged attractive potential, creating the conditions whereby the smoothed particles can phase separate. When the smoothing lengths are separated in this way, the long smoothing length determines the minimum thickness of the interface. As such, any attempt to model diffuse interfaces must target regimes where the interface is broader than $H$, such as near the critical point.

Separated into short and long range components, the momentum and energy equations for smooth particles are

$$\frac{dv_i}{dt} = -\sum_{j=1}^{N_s} m_j \left( \frac{P_{si}}{\rho_{si}^2} + \frac{P_{sj}}{\rho_{sj}^2} \right) \cdot \nabla_i W_{sij} - \sum_{j=1}^{N_L} m_j \left( \frac{P_{Li}}{\rho_{Li}^2} + \frac{P_{Lj}}{\rho_{Lj}^2} \right) \cdot \nabla_i W_{Lij}, \quad (4.12)$$

and

$$\frac{du_i}{dt} = -\frac{1}{2} \sum_{j=1}^{N_s} m_j \left( \frac{P_{si}}{\rho_{si}^2} + \frac{P_{sj}}{\rho_{sj}^2} \right) : \mathbf{v}_{sij} \nabla_i W_{sij} + \frac{1}{2} \sum_{j=1}^{N_L} m_j \left( \frac{P_{Li}}{\rho_{Li}^2} + \frac{P_{Lj}}{\rho_{Lj}^2} \right) : \mathbf{v}_{Lij} \nabla_i W_{Lij}$$

$$- \sum_{j=1}^{N_s} m_j \left( \frac{J_{qi}}{\rho_{si}^2} + \frac{J_{qj}}{\rho_{sj}^2} \right) \cdot \nabla_i W_{sij}, \quad (4.13)$$

where $N_s$ and $N_L$ are used to indicate the number of interacting neighbours for the short and long range pressure tensors. $P_s$ represents the short range and $P_L$ the long range pressure. The isotropic pressure is given by the van der Waals equation of state using the particle density (Equation 3.22) and is separated into short range repulsive and long range attractive components. A long range density is also computed for use in expressions involving the long range force using a longer smoothing length $H$. The short range pressure is computed as

$$P_{si} = \left( \frac{\rho_{si} \bar{K}_{si} t}{1 - \rho_{si} b} \right) \mathbf{1} + \tilde{M} \left( \rho_{si} \nabla^2 \rho_{si} + \frac{1}{2} \left| \nabla \rho_{si} \right|^2 \right) \mathbf{1} + M \nabla \rho_{si} \nabla \rho_{si} - 2\eta \nabla v^\rho_{si} - (\eta_v \nabla \cdot \mathbf{v}_i) \mathbf{1}, \quad (4.14)$$

where $v^\rho_{si} = \frac{1}{2} \left( \nabla \mathbf{v}_i + (\nabla \mathbf{v}_i)^T \right) - \frac{1}{d} (\nabla \cdot \mathbf{v}_i) \mathbf{1}$ with the relevant SPH approximations to
each term, using the corresponding range kernel, where \( \rho_{si} \) is the density computed using the short range smoothing length. The velocity gradient is given by Equation 4.2, the kernel gradient by Equation 3.16 and the velocity divergence by Equation 4.3.

The density gradient force was incorporated into the short range term because accurate resolution of density gradients depends on smoothing lengths being as fine as possible. This point will be discussed further in Chapter 9. One potential objection to this methodology is that two different estimates of the density are calculated at each point. The long range pressure is computed as

\[
P_{Li} = -\bar{a} \rho_{Li}^2,
\]

with the density computed using the long range kernel \( \rho_L \). Where a longer ranged kernel is used for part of the force it is used to compute all smoothed properties that go into computing that force.

### 4.3.1 Stability to singularities in the equation of state

The van der Waals equation of state imposes some stability constraints on SPH particle solutions: certain particle mass settings will prevent the system from reaching certain densities even though these densities are the optimal equilibrium state, while others will allow particles to reach the density threshold \( (\rho_b = 1) \) beyond which interparticle forces are unstable. The maximum density attained by particles in regular lattices is plotted in Figure 4.3 along with the unstable density threshold.

To prevent particles attaining these densities which are not plausible physically and not practical to simulate numerically a hard collision is imposed at a distance of 0.6 scaling lengths. It is also necessary to create particles with sufficient mass that the densities desired to be resolved can be attained by particles further apart than this minimum separation. Other means to prevent numerical degeneration of the simulation include artificial viscosity and artificial repulsive forces which were described in Sections 3.7.1 and 3.7.2.

Previous studies have attempted to solve van der Waals droplets isothermally [66]. However, Langer and Turski [115] found that coupling to the thermal part of the equations of motion is important to account for the latent heat of condensation. A significant advantage of the SPH methodology developed here is that the energy equation is handled naturally.

### 4.4 Conclusions

In this chapter an application of smoothed particle hydrodynamics for the modelling of single component liquid-vapour systems was developed.
Figure 4.3: The summation density calculated for a grid of particles with regular separation. The unstable threshold for the van der Waals repulsive term with $\tilde{b} = 0.5$ is shown with a dotted line. Once densities exceed this threshold the equation of state is unstable.
5 A two dimensional smooth particle code

There is a rich variety of algorithmic variations for smooth particle numerical methods, and often no clear means of selecting the best combination of techniques for a particular problem without experimentation. This experimentation with algorithmic variations requires a software implementation of a software implementation of a flexible, configurable solver for the equations of motion for smooth particle systems. In this chapter, a design for a smooth particle solver is developed, and its implementation in the Fortran programming language is described.

As the code was written with the particular goal of modelling liquid-vapour phase transitions using the methods outlined in Chapter 4, it supports the separation of equations of states into attractive and repulsive components and the use of different smoothing lengths for these components. This chapter presents the design and gives a broad overview of the software structure.

5.1 Design of an N-body code

The smooth particle algorithm is in essence the same as algorithms for classical molecular dynamics or N-body gravity solvers, with additional steps to compute the particle density using Equation 3.22 and a more complicated inter-particle force calculation. As such many of the same software patterns are applicable, and the general design is that of a generic N-body solver.

The smoothed particle code is conceptually divided into six main components: particle systems, forces, neighbour lists, an integrator and a time stepping algorithm.

The particle system contains coordinates, velocities and other properties for a given number (\(N\)) of particles, which may vary as the simulation progresses. Particle coordinates may be updated in a number of ways, including body forces, interparticle forces and boundary conditions.

A force computes rates of change of the particle properties. Most forces are pairwise additive and are calculated by iteration over a neighbour list. In the software implementation a 'force' is interpreted broadly as any operation that changes the velocity, acceleration or rate of change of the internal energy of the particles. Particle collisions are implemented as a special case of a force, as is the thermostat. The force components are stateless.

A neighbour list tracks interacting pairs of particles from a given particle system (or several systems) and maintains pair properties such as interparticle displacements. The list of pair properties depends on the type of particle system. If the particle system has
only positions and velocities then the position and velocity differences are the only two pair properties. For a smooth particle system there are additional pair properties such as kernel and kernel gradient values. Because the number of pairs in the worst case grows as $N^2$, the neighbour finding and pair property calculations are the most expensive computational step in the integration of the smooth particle system. As square root operations are expensive it is important to only compute distances as often as necessary.

A **containing box** provides the spatial reference for the particle positions, and enables boundary conditions to be implemented. The simplest implementation is a fixed size box.

An **integrator** is a general purpose component that operates on an array of system state variables, performing numerical integration. It calls subroutines which calculate the rates of change of the state variables, and calculates the consequent change in state variables based on the timestep.

The **time stepper** orchestrates the particle system. Its main functions are to call the numerical integration component, and to update the particle system’s properties to reflect its progression.

For a fixed size containing box, the data structures in the **particle system** and **neighbour list** components store all of the information about the system state. Other components can be designed using functional programming methods.

### 5.2 Software structure

The software is structured in four tiers. Fortran 90 provides powerful data structure capabilities, but the use of custom data structures comes at a cost to portability and reusability. At the peak (Tier 1), an executable module initialises data structures for particles and neighbour lists, and controls the main loop. The second tier (Tier 2) is composed of modules with subroutines which carry out time stepping or other complicated algorithms such as boundary handling which are dependent on the abstractions defined in the third tier (Tier 3), where the particle and neighbour list structures are defined. In the lowest tier (Tier 4) are modules that use only primitive arguments for their subroutines. Most of the key SPH calculations are implemented in primitive modules, as are operations like the calculation of pair separations. This allows them to be exposed to other programming languages such as C and Python, and reduces their coupling to the abstractions used in Tier 3.

In **Tier 1**, the main module for running 2D simulations is `fsph.f90`. This module is responsible for data structure initialisation and main loop running. The main loop primarily calls functions in the `sphstep.f90` module.

**Tier 2** contains modules that use the **neighbour list** and **particle system** structures. These modules implement moderately complex algorithms. They include `density.f90`, `adaptive_timestep.f90`, `boundary.f90`. This is the level at which the time stepper and integrator components sit.

**Tier 3** consists of modules in which the higher level abstractions are defined. These are
particle system, neighbour list, and containing box.

In Tier 4 there are only stand-alone modules with only primitive argument subroutines. Most of the basic smooth particle calculations are implemented in this tier. The primary reason for this is so that they can be exposed to other programming languages. For example when generating a plot using the Python language, it is desirable to use the same smoothing kernel implementation as was used for the simulation. Another reason for ensuring the building blocks calculations have only primitive arguments is to reduce their coupling to the implementations of the abstractions for particle systems and neighbour lists. This means the abstractions can be redeveloped without risking introducing errors in the fundamental calculations. Modules at this tier include art viscosity.f90, collision.f90, core potential.f90, eos.f90 and boundary.f90. The key module in this tier is splib.f90, which implements most of the basic smooth particle calculations of symmetrised pressures and forces.

The design of the software was heavily influenced by the smoothed particle code made available by Liu and Liu [71], and made use of neighbour list modules from molecular dynamics code developed at RMIT [31, 74].

5.2.1 Smoothed particle solution

The precise sequence of operations in the solution algorithm depends on the selection of numerical integrator. In this section the solution process using a modified leapfrog algorithm similar to that used by Melean [75] is described. The system is specified by the positions \( x \), velocities \( v \) and internal energies \( u \) of the particles. For each timestep of size \( h = t_{i+1} - t_i \), a time-centred projection of the system is computed, using the previous step’s time-centred state:

\[
\begin{align*}
x_{n+\frac{1}{2}} &= x_{n-\frac{1}{2}} + h v \\
v_{n+\frac{1}{2}} &= v_n + \frac{h}{2} a_n \\
u_{n+\frac{1}{2}} &= u_n + \frac{h}{2} \dot{u}_n
\end{align*}
\] (5.1)

Particle separations, kernel values, densities, temperatures and finally the rates of change \( a_{n+\frac{1}{2}}, \dot{u}_{n+\frac{1}{2}} \) are computed for the time-centred state. Then the time centred values are used to project the system a full timestep.

\[
\begin{align*}
x_{n+1} &= x_n + h v_{n+\frac{1}{2}} \\
v_{n+1} &= v_n + h a_{n+\frac{1}{2}} \\
u_{n+1} &= u_n + h \dot{u}_{n+\frac{1}{2}}
\end{align*}
\] (5.4)

A scaling thermostat keeps the average temperature constant while allowing fluctua-
tions. The average temperature $T_A$ is calculated over all particles by

$$T_A = \sum_{i}^{n} \frac{T_i}{n},$$

and then for all particles the thermostat is applied by

$$T_{i,scaled} = \frac{T_D}{T_A} T_i. \quad (5.7)$$

The full integration step proceeds as follows:

1. calculate time centred position and velocity using 5.1, 5.2, 5.3;
2. apply periodic and/or reflective boundary conditions;
3. check neighbour list reformation condition and reform if indicated;
4. calculate pair separations using time centred positions, and compress neighbour list;
5. calculate kernels, kernel gradients for all pairs;
6. calculate summation density;
7. recalculate temperature with new density;
8. calculate time-centred rates of change;
9. update x,v,u using 5.4, 5.5, 5.6;
10. update temperatures;
11. apply thermostat;
12. apply boundary conditions;
13. calculate smoothed values at particle locations.

### 5.2.2 Configuration

Program options are set in a plain text key-value text file, and are read and used to set global module variables which control which branches of the code are executed. The configuration file sets the options to be used for a simulation run. The full set of options are outlined in a manual distributed with the source code. What follows here is a descriptive summary.

Simple parameters such as the number of particles $N$, timestep size $dt$, interaction cutoff radius $r_c$ and number of timesteps are configurable. Several experimental adaptive timestep methods can be selected. The output of a previous run may be designated as the input file for a further run, with or without a re-setting of particle temperatures.
Integration methods can be selected from a two step predictor-corrector method, a modified leapfrog integration method described in [76] and a fourth order Runge Kutta method described in [49]. A set of test configurations solving for condensation in gravity with a lower boundary is used to demonstrate that the choice of integrator does not affect the solution’s accuracy provided the appropriate timestep for the solver is chosen.

Two distinct methods of calculating the viscous part of the stress tensor can be selected from: an approximate viscous stress calculation as used in Liu and Liu [71], or a full calculation of viscous stress as used in [103]. Artificial viscosity may be set to none, a basic von Neumann-Richtmeyer viscosity [49], or the Mongahan beta term [71]. The heat flux can be computed using the algorithm developed by Monaghan and Cleary [20], or the full heat flux as described in Equation 2.24.

A repulsive core force may be used to prevent unphysical inter-penetration, and to reduce simulation instability. Core size and repulsion strength are both input parameters [49]. If this repulsion is nonzero it makes a contribution to the pressure-volume work, to maintain consistency. A velocity averaging scheme based on the algorithm in [78] is implemented.

For the van der Waals equation of state a density of 2.0 or greater leads to unrecoverable instability. Options for managing this are to ignore, halt, or set the pressure of the particle to zero when the threshold is crossed. The last option has little basis in physics, but prevents the unstable collapse of the simulation.

The temperature of the scaling thermostat may be set for the particle system and up to two boundary systems.

The equation of state may be selected from the ideal gas equation, van der Waals equation, the separated form of the van der Waals equation, and the van der Waals equation (separated) with the density gradient term.

Physical parameters that may be set are the shear and bulk viscosities $\eta, \eta_v$, the van der Waals coefficients $\bar{a}, \bar{b}, \bar{k}_g$ and the gradient energy coefficient $\bar{M}$.

The kernel function may be selected to be Gaussian, Lucy’s quartic spline, a ‘spiky’ spline devised by Desbrun [33], and a combination of ‘spiky’ repulsion and Lucy’s for attraction.

The particle smoothing length is an input parameter, and optionally this smoothing length may be adapted using the adaptive density kernel estimation algorithm detailed in [105]. As both attractive and repulsive smoothing lengths are input parameters, they may be set to the same value to recover the non-separated van der Waals equation of state, if it is desired to use that formulation along with the gradient term.

Boundaries may be reflective boundaries, and boundary particles may be added with their own repulsive interaction. Systems of boundary particles may be initialised, which interact with the primary system particles through a simplified force, the purpose of which is to simulate a solid boundary and also model the transfer of heat from a boundary of fixed temperature.

A body force may be applied to all particles to model the effects of gravity.
The neighbour list may be configured by setting the type of condition for reformation (particle displacements or particle separations), the maximum number of neighbours, and the tolerance shell used to determine when a recalculation of pairs is needed. These options have a major effect on the simulation run time and should be chosen carefully for sizable simulations.

5.2.3 Program Output

The program primarily outputs particle positions, masses and velocities. From these quantities, all other derived smooth particle quantities can be calculated. The output file is a simple space delimited text format. Further processing utilities were developed to convert this to a netCDF format based on the schema used by the AMBER molecular dynamics software.
6 Liquid vapour coexistence in two dimensions

This chapter describes the use of the smoothed particle hydrodynamics code described in Chapter 5 to solve for the formation of liquid and vapour in equilibrium coexistence. In Section 6.1, a regular grid of particles is allowed to relax to a circular droplet in order to validate the model against previous work. In a second numerical experiment outlined in Section 6.2, a system is equilibrated at vapour density and then quenched into the unstable part of the phase diagram, to discover whether a temperature quench would induce a phase separation as expected. Results show that quench driven phase separation is feasible using SPH. In Section 6.3, a formed droplet is subjected to changes in the repulsive and cohesive smoothing length to determine the sensitivity of the equilibrium droplet structure to the difference between cohesive and repulsive range and gain insight into the effect of the practice of using different smoothing lengths for attractive and repulsive forces.

In Section 6.4, the formation of a planar liquid-vapour interface in a two-dimensional Navier-Stokes-van der Waals fluid is modelled, in an attempt to reproduce the coexisting densities predicted by theory, showing that a thermostat constrained smooth particle system can achieve expansion-driven phase separation. To induce the formation of a planar liquid-vapour interface, an equilibrated liquid is subjected to a sudden increase in available volume. The consequent drop in pressure causes it to expand to fill the available volume. The system is thermostatted in order to keep it in the region of thermodynamic phase space in which two phases can coexist. Because of the periodic boundaries a two phase system forms with a rectangular geometry - a liquid and a vapour separated by a planar interface. The densities of the two coexisting equilibrium phases are in good agreement with those predicted by the Maxwell construction for a range of temperatures.

In Section 6.5, a gas in a long periodic box is quenched. In this experiment the interconnected domains characteristic of spinodal decomposition are observed, with indications that short time liquid-gas domain growth and long time hydrodynamic domain coalescence are present as distinct regimes. The asymmetry of the containing box and periodic boundary conditions leads to a planar interface being the equilibrium state. Phase separating systems equilibrate to domains of coexisting vapour and liquid at the expected densities for the van der Waals model. In the experiments outlined in this chapter, the vapour liquid interface itself is not modelled explicitly and no density gradient term is included to model it implicitly.

Finally, an experiment in which the gradient term of van der Waals original theory [116]
is explicitly incorporated into the pressure tensor is carried out. It is found that larger values of the gradient term result in a broader liquid-vapour interface, as predicted by theory.

6.1 Formation of droplets from an initial grid

In an initial experiment designed to validate the smooth particle code, a regular grid of particles is initialised at a liquid temperature and forms a single liquid droplet in the same manner as reported by Nugent and Posch [88] and Melean and Sigalotti [76]. The equations of motion solved for this experiment are those developed in Chapter 2, with the omission of the density gradient term, so that the pressure tensor is simply

$$P = \left( \frac{\rho k_b T}{1 - \rho b} - \bar{a} \rho^2 \right) \mathbf{1} - 2\eta \nabla \mathbf{v}^o - \left( \eta_v \nabla \cdot \mathbf{v} \right) \mathbf{1}. \quad (6.1)$$

Momentum and energy were evolved using the symmetrised particle equations of motion, with standard smoothed velocity and temperature derivatives and summation density as described in Section 3.6. Following Nugent and Posch [88] the constants were set to $\bar{a} = 2.0$, $\bar{b} = 0.5$ and $\bar{k}_b = 1$ in reduced units. In these units the critical temperature is $T_c \approx 1.2$.

The Lucy kernel (Equation 3.11) was used. The separated van der Waals equation of state was used with a smoothing length $h = 5$ for the repulsive component of the pressure and long smoothing length $H = 10$ for the cohesive component of the pressure. 900 particles were set up on a regular grid with a separation of 0.75 of the length units defined by the choice of $\bar{a}$, $\bar{b}$ and $\bar{k}_b$. The initial configuration is shown in Figure 6.1a. Using a timestep size of 0.005, the system was advanced 1200 steps. No thermostat was used in this experiment. A simple leapfrog integrator was used to solve the smooth particle equations as described in Section 5.2.1.

The rectangular grid is not stable and immediately begins to collapse, as shown in Figure 6.1b which shows the system after 100 timesteps. The exchange of kinetic and potential energy is close to symmetric, with a small amount of noise in the total energy apparent at the beginning of the simulation which can be explained by the instability of the initial configuration of particles and by the fact that the initial values of half-step quantities, initialised to zero, are not correct.

The final particle distribution shown in Figure 6.1c displays a clustered ringed structure. Such structures are well known in SPH simulations and their appearance here validates this simulation as being structurally identical to similar work by Nugent and Posch [88] and by Melean et al. [76]. These particle structures may be considered artifacts to the extent that they produce errors in the field estimates, or that they bind the system in unphysical states. In Figure 6.1d the density at each pixel is interpolated using neighbouring particles. It is apparent that although the particles themselves are clustered, the resulting density profile is quite smooth and does not exhibit an exaggerated ringed structure, because the extent by which the particle mass is smoothed over space is greater than the extent of the...
Figure 6.1: The formation of a droplet at a reduced temperature of 2.0. 
a: Start positions. b: Positions after 100 timesteps. c: Final stable positions. d: Final smoothed
density profile. Note that the smoothing property of the particles means the
ring structures apparent in the particle plot are reduced.

Odd particle structures, for example the concentric rings in Figure 6.1 related to tensile
forces seem to be a persistent feature of condensation using smooth particles. While the
structures sometimes formed by SPH particles may seem problematic, the effect of this
structure on the interpolated field may be minimal. As discussed in Chapter 3 there are
standard methods for alleviating these artifacts, although the extent to which they are
of consequence for the dynamics once the particle properties are interpolated to a grid is
unclear.
6.2 Droplet coalescence in response to quench

A system was initialised as a homogeneous vapour and then quenched into the spinodal region of density-pressure phase space. Small fluctuations in the density became sites for the coalescence of liquid droplets in coexistence with a vapour. The purpose of this experiment was to determine whether the SPH model could respond to a temperature quench as expected.

In this experiment, 900 particles were equilibrated to an almost homogeneous density at a scaled temperature of 1.5 in a periodic box of size $50 \times 50$ scaling lengths. The Lucy kernel (Equation 3.11) was used, with repulsive and cohesive smoothing lengths $h = 5$ and $H = 10$ units respectively. A scaling thermostat is used to keep the mean temperature constant. The average temperature $T_A$ is calculated over all particles, and the scaling thermostat given by Equation 5.7. Again, the squared density gradient term is not present in this experiment.

The initial distribution of particles shown in Figure 6.2 looks homogeneous, especially when the smoothed field is plotted, but contains variations in the density due to the random distribution of particles in the gas state shown in Figure 6.3. Upon quenching into the unstable region, it is the regions of high density in which density perturbations grow and around which the rest of the fluid begins to gather, forming liquid regions which initially take the form of long filaments. The sequence in Figure 6.4 shows the formation of filaments, their breakup and coalescence into droplets.

The final state of the system quenched to a temperature of 0.4 is virtually all at the liquid density, with the exception of a few boundary particles. When the system is quenched to a higher, but still unstable, temperature of 0.9 most of the mass of the system is still in the liquid droplets, but there is now an atmosphere (Figure 6.5). This demonstrates the generation of coexisting liquid and vapour via a spinodal quench.

This droplet condensation simulation provides evidence that the model conserves energy, is stable and is consistent. This demonstrates that the smooth particle model of a van der Waals liquid responds to a spinodal quench via spontaneous phase separation. The results have extended the earlier work of Nugent and Posch [88] and Melean et al. [76] by showing that the methodology used can respond appropriately to changes in the thermodynamic state of the system.

In these experiments the van der Waals square gradient term is not included explicitly. It is interesting that the system appears to minimise surface energy without an explicit contribution of surface tension in the equations of motion. An explanation for the existence of a surface tension is that it is due to the ‘trick’ of increasing the range of the attractive part of the pressure, which has the effect of imposing a density gradient penalty.

When the same simulation was run with equal repulsive and cohesive smoothing lengths, no phase separation occurred. This confirms the importance of the separation of attractive and repulsive smoothing lengths for phase separation, at least for simulations in which the gradient term is not included.
6.3 Short and long smoothing lengths, are they really necessary?

In this section, the apparent requirement to set the cohesive pressure smoothing length longer than the repulsive smoothing length is further investigated. To recap: in the simulations so far, the attractive part of the pressure from the equation of state has been treated with a longer smoothing length than the repulsive pressure. A series of computational experiments were carried out to determine whether a simulated liquid-vapour system, once equilibrated, is sensitive to a change of the ratio of SPH smoothing lengths used for attractive and repulsive components.

At a reduced temperature of 0.2, starting from a regular configuration, with the repulsive smoothing length set to 2.5 and the cohesive smoothing length set to 5.0 a droplet was formed. The cohesive smoothing length was then changed to 2.5 and the system evolved...
Figure 6.3: A low density gas, used as the initial condition for the experiment shown in Figure 6.2. Note the small density inhomogeneity in the initial state. Immediately after the quench, the higher density regions begin to coalesce until a new equilibrium was reached. The cohesive smoothing length was then changed back to 5.0, and after the system was once again equilibrated, the repulsive smoothing length was changed to 5.0. Finally, from the initial state, both smoothing lengths were set to 5.0. The results of this investigation are shown in Figure 6.6.

When the cohesive smoothing length was changed to 2.5, the droplet deformed into a droplet with less symmetry and more clustering (Figure 6.6c). Changing the smoothing length back to 5.0 recovered the original droplet (Figure 6.6d). The change of the repulsive smoothing length to 5.0 did not seem to affect the configuration of particles at all. Setting both smoothing lengths to 5.0 at the beginning of the run does not produce a spherical droplet of uniform density as shown in Figure 6.6f.

This indicates that a formed equilibrium interface may be stable to an increase of the repulsive smoothing length, but that it is not stable to a decrease of the cohesive smoothing length. At the temperature studied the system was fully condensed. This confirms similar findings by Nugent and Posch [SS], who found that the setting of repulsive and cohesive smoothing lengths to the same value led to a numerically unstable simulation that did not result in stable droplets.

Nugent and Posch [SS] used this method to study the formation and oscillation of liquid droplets. Hoover [49] used an attractive density gradient force to model surface tension. A similar technique is used in other particle-based methods when a surface tension is required, for example with DPD simulations, Warren [121] enforced a density dependent interparticle potential with a long range attractive and short range repulsive central force. Tartakovsky et al. [109] have used SPH to model capillary forces in fluid flow through
Figure 6.4: Smoothed plot of the gas quench shown in Figure 6.2 at a reduced temperature of $T=0.4$. Smoothed densities are calculated at each grid point.

...pores by superimposing additional attractive and repulsive interparticle forces. While this method of using different smoothing lengths for different components of the pressure produces good results, it is somewhat unsatisfying as the behaviour could be considered an artifact rather than arising from the physics of the problem. It is not clear what determines the correct values for repulsive and attractive smoothing length, other than the requirement that the simulation phase separates and looks correct.
Figure 6.5: Quench of a vapour to a reduced temperature of $T = 0.9$. The color scale highlights the small density inhomogeneities present at the outset of the simulation. Immediately after the quench, the higher density regions begin to coalesce.

6.4 Formation of a liquid-vapour film in two dimensions by expansion

A phase transition may also be induced via a change in the volume available to a system. Figure 6.7 shows the binodal curve on the density temperature plane, with the state point of the initial liquid state, and the post-expansion state (in this case for $T=0.75$).

Initially, a fluid consisting of 1,984 particles is brought to a stable state at liquid density in a box with dimensions 25 by 25 by 50. The box length is then increased to 100, reducing the average density such that the system state is in the coexistence region. The fluid is allowed to expand into the available volume, maintained at a constant average temperature with a scaling thermostat. After a time, equilibrium is reached.

The SPH equations of motion are the same as for the two dimensional droplet simulations presented in the previous chapter (Equation 6.1), using the following values for the van der Waals parameters: $\bar{a} = 2, \bar{b} = \frac{1}{2}, \bar{k}_b = 1$. Once again the squared density gradient term is neglected.
Figure 6.6: Sensitivity to changes in repulsive/cohesive smoothing length. Arrows show the particle accelerations. a) Initial state. b) Droplet formed with short/long smoothing lengths 2.5 and 5.0. c) The cohesive smoothing length from B. is changed to 2.5. d) The cohesive smoothing length is changed back to 5.0. e) The repulsive smoothing length is changed to 5.0. f) From the initial state, both smoothing lengths are set to 5.0.

Periodic boundary conditions are imposed. A scaling thermostat is used to keep the average temperature constant. A smoothing kernel with a greater range for the cohesive contribution to the pressure tensor and internal energy is used. The repulsive smoothing length is set to 5 while the attractive smoothing length is set to 10.

A leapfrog algorithm (Section 5.2.1) is used to advance the positions and energies of the particles in time. No artificial viscosity and no repulsive corrections for particle clumping
Figure 6.7: Equilibrated and expanded states for the film formation experiment. Red: the binodal curve in the temperature-density plane. The point outside the curve is the initial liquid state. The system is moved instantaneously to the point inside the curve by an increase in available volume, which decreases the average mass density.

are applied. The scaling thermostat (Equation 5.7) is applied to keep the mean temperature constant.

Figure 6.8 shows the development of the system after the available volume is increased. After a period of oscillation shown by the system energy curves in Figure 6.9, a vapour liquid interface with a smoothly varying density profile forms. Final densities lie close to the binodal line in good agreement with the Maxwell construction. Equilibration is much slower close to the critical point, which may be because the wavelength of perturbations for which growth is favourable is comparable too, and possibly larger than, the box size.

Figure 6.10 shows the final coexistence densities. The final spread of densities is plotted against the expected binodal curve. The coexisting densities are correctly related to the system temperature. Systems that are forced into the coexistence region by the change in volume separate spontaneously into vapour and liquid phases, with densities closely matching those calculated using the equal area rule. Final profiles at several temperatures are shown in Figure 6.11.

The idea that the smoothing length itself, rather than the thermodynamic state of the system, determines the interfacial width is supported by observations in the literature [104]. In free boundary problems this is undesirable as the interfacial width is usually effectively zero. In diffuse boundary problems this is undesirable because the boundary region itself is the object of interest. This behaviour is particularly undesirable around the
region of the critical point, where the width of the interface is expected to increase. This limitation is addressed in Section 6.5 with the inclusion of the gradient term.
Figure 6.9: Total kinetic and internal energies over time for a typical system. Kinetic energy decays over time while internal energy oscillates towards the constant value associated with the thermostat temperature.

Figure 6.10: Densities of the equilibrated coexisting phases, plotted against the binodal curve

6.5 Quench of a vapour

The next series of experiments involved a temperature quench, of a box geometry designed so that a liquid film with planar symmetry would be the most stable equilibrium state. A set of simulations were run without a gradient term, and then another set where the
gradient term was varied in order to test for the broadening of the interface expected by theory. These experiments were described in [24]. The structure of these experiments is similar to the quench discussed in Section 6.2 although the box geometry and other details are different.

The full equations of change given in Equations 3.22, 4.12, 4.13 are used with a fourth order Runge-Kutta integrator for timestepping. The fourth order integrator was chosen to allow a greater timestep than the leapfrog methods of the previous experiments. As in the previous experiments, $\bar{a} = 2.0$, $\bar{b} = 0.5$ and $\bar{k}_b = 1$. In these units the critical temperature $T_c \approx 1.2$.

The temperature rescaling thermostat (Equation 5.7) was used to maintain a constant mean temperature. To reduce particle clumping a short range repulsive force is added [49]. To reduce the formation of ring structures and string like artifacts found by Nugent and Posch [88] we use the ADKE adaptive smoothing length technique reported by Sigalotti [105].
Initially equilibrated to a homogeneous density above the critical point, the system is temperature quenched and maintained at the quenched temperature using a scaling thermostat. The mass density field is rendered using the smooth particle summation (Equation 3.22) for each pixel. The normalised distribution of particle density is overlayed on the phase diagram to show the close agreement of the final densities with predictions.

The condensation process is shown in Figure 6.12. The system begins to condense in the direction of high density fluctuations. Such fluctuations are always present except for contrived cases due to the effectively random configuration of particles. Over time the domains phase separate more decisively with density peaks (Figure 6.12, left) appearing at the expected densities. The two phase regions coalesce slowly into larger pockets and the system flows into a new configuration that minimises its surface area. The liquid density is represented quite well. At low temperatures the method has difficulty resolving the lowest density of the equilibrium vapour phase due to the fixed masses of the particles. Adaptive particle mass and particle splitting algorithms could help solve this problem.

Figure 6.13 shows final equilibrium configurations for quenches at a range of temperatures. As the critical point is approached the system takes longer to phase separate.

The runs with greater values of the gradient energy coefficient $M$ took longer to phase separate, and displayed an increased interfacial width as shown in Figure 6.14. These results exhibit the broadening of the interface predicted by theory.

The smooth particle model obeys the equation of state reasonably well in the coexistence region and generates a plausible representation of a phase separating fluid. The interfacial width responds correctly to increases in the gradient energy coefficient, but greater resolution is needed to analyse the interfacial profile.

A 'freezing' of SPH particles is something that was observed in some temperature quenches where there were no restrictions on particle proximity. Kum and Hoover [64] identified that the pressure itself enters the smooth particle momentum equation - when the pressure is too high particles are prevented from moving, even if the gradient of the pressure should cause them to move. The idea of frozen smoothed particles was explored further by Hoover [52], but from a perspective where stable lattice structures were desirable.

### 6.6 Conclusions

The numerical experiments presented in this chapter have validated the smooth particle code described in Chapter 5. Using this code we are able to perform spinodal quenches of vapour resulting in growth of density perturbations and the formation of separate liquid and vapour phases.

This phase separation is performed for configurations and set-ups similar to those presented in other work [88, 76], and for novel configurations using a scaling thermostat. Coexistence densities are a good reproduction of those predicted by the van der Waals equation of state.
Figure 6.12: Condensation of a 2D smooth particle fluid. Elapsed time is denoted by $t$. The timestep size is 0.05. Plots on the left show the distribution of density by particle, while plots on the right show the spatially rendered mass density field. The binodal line is shown in blue. The black horizontal line shows the thermostat temperature.
Figure 6.13: Coexisting vapour and liquid in equilibrium at a range of temperatures.

A spinodal quench in a long box leads to a planar interface forming, capturing each aspect of the phase transition outlined in Chapter 1: correct response to thermodynamic instability; a transition process incorporating hydrodynamic flow; equilibrium phase separation; and a liquid-vapour interface with surface tension. The density gradient term has been explicitly included, and the effect of increasing the gradient term is to broaden the
Figure 6.14: Vapour-liquid interfaces for different values of the gradient coefficient. Top: $M = 1.0$, Center: $M = 8.0$, Bottom: $M = 21.0$

interface, as predicted by theory. The results in this chapter have gone beyond previous work by performing temperature quenches, using a thin geometry to cause a film to form and by explicitly incorporating the density gradient term.


7 Domain growth kinetics in two dimensions

In this chapter the kinetics of the phase transition in a quenched vapour are studied using the SPH method detailed in Chapter 4 and software documented in Chapter 5. Regimes in which the growth of liquid domains is characterised by power law behaviour are identified, and the effect of the inclusion of a density gradient term and of the quench depth on the domain growth exponents are discussed.

7.1 Coarsening and domain growth in phase transitions

After a thermal quench into an unstable state, the separation of phases involves up-hill diffusion against concentration gradients in a two component system, and wave growth against density gradients in a one component system. This wave growth, superimposed on thermal noise and modified by hydrodynamic flow is responsible for the kinetics and morphology of the phase separating system.

The Cahn-Hilliard equation has been extensively studied in the context of phase transitions in binary systems. It represents the evolution of an order parameter as a combination of a diffusive and a convective term. Abraham performed molecular dynamics studies of phase separation of a simple fluid [2] and used a Cahn-Hilliard like expression for the free energy to examine the thermodynamics of non-uniform one component fluids [1]. In these papers Abraham argues that the van der Waals and Cahn Hilliard theories are fundamentally the same, and derives an expression for the gradient term coefficient in terms of the interatomic potential and correlation function. Coelho also applied the Cahn-Hilliard theory of spinodal decomposition to one-component systems [28], but found that it was not a suitable model for the spinodal decomposition of a one-component Lennard-Jones fluid.

Cahn and Hilliard quantified the details of domain growth in two component fluids, and at the same time Landau and Ginsburg developed a similar theory, both following van der Waals’ key insight about the gradient term. Their work led to what has become known as the Landau-Ginsburg functional [87] for a change in the free energy $G$:

$$\Delta G = \int_V \left\{ g + k (\nabla \rho)^2 \right\} dV,$$

where $g$ is the change in bulk free energy due a change in the order parameter, in this case density $\rho$. The constant $k$ can be obtained by measuring the surface tension or from mean field theories. The relevance of this functional to the present work is the dependence of
the change in free energy on the squared density gradient. The effect of this is to create a trade-off between minimising the bulk free energy by phase separation and minimising the surface free energy. Analysis of this functional can produce solutions for the form of the interface, and for the minimum bifurcation and droplet sizes [87]. Solutions for the growth of spatial structure modes by wavenumber can be obtained by linearised stability analysis [87], in which the fastest growing wavelength dominates short times and gives a characteristic domain size.

Interconnected worm-like patterns arise as a consequence of the fastest growing solutions of the linearised equations. This structure of interconnected domains was reproduced by Cahn by generating a Fourier series consisting of normally distributed amplitudes, with uniformly distributed phase (0 to \(\pi\)) and random direction cosines [1].

Analyses of spinodal decomposition as it relates to one component fluids have focused on the diffusion-like growth of small amplitude long wavelength density fluctuations at the beginning of the process [1]. These complex structures are aesthetically and theoretically interesting, and may be used for commercially interesting materials such as microdispersions and membranes [98]. Morphologies can be categorised as particulate, in which disconnected domains dominate, or co-continuous which may also be described as ‘worm-like’. In two-component systems, the volume fraction is a determinant of this morphology, Nauman gives 35% as the rough threshold beyond which co-continuous domains are expected [87]. More recently, Ahmad used molecular dynamics simulations to study phase separation kinetics [3, 4].

In spinodal decomposition, the growth of small amplitude long wavelength fluctuations is expected, whereby long-range correlations are established and lead to the spontaneous growth of density waves. The main types of domain growth in condensation are nucleation, ripening and aggregation (coalescence).

Nucleation refers to the establishment of microscopic regions of one of the phases. The growth of the separated phases is called ripening. When this happens by diffusion, as in two component systems, it is called Ostwald ripening. At longer time-scales hydrodynamic terms become important in the description of domain coalescence [67]. As noted earlier, it is difficult for molecular dynamics to access these longer time-scales and for experiment to access the early time-scale. Consequently there is a need for simulation methodologies that bridge the gap.

The kinetics of a phase transition describe the rate at which regions of a phase grow for both binary and single-component systems. Typically this process is governed by a power law, where the domain lengths grow as some power of elapsed time. The key metrics of a spinodal decomposition process are these growth parameters, which were studied by Alexander for different regimes [6]. Analysis of such scaling problems requires quantification of the fluid structure, either using the density-density correlation function, or methods from image analysis such as described in Sofonea et al. [106]. Power law behaviour is tested by the analysis of log-log plots. The critical exponents are well studied for the case of binary systems [67], but less well for liquid-vapour systems due to the difficulties
Analytical methods make predictions for both diffusion driven Ostwald ripening and Brownian motion induced coalescence, with predicted expected growth proportional to $t^{1/3}$. This is independent of the averaging method used to determine domain size and of whether the system is two or three dimensional [92]. Osborn notes that this value of $1/3$ is for quiescent systems and may be considerably faster in systems with hydrodynamics. This is also an asymptotic result and so may not be observed with finite grids or small systems.

Although well studied for binary systems [97], there is still little concrete agreement on the values of the exponents for single component systems. Noting this, Osborn et al. [92] used the Lattice Boltzmann method of simulation to investigate the growth rate of liquid droplets. For the growth rate at short time, where the phase separation is governed by surface tension, they find an exponent of 1/2, increasing to 2/3 for later times where hydrodynamic coalescence is the primary mechanism for domain growth. Osborn notes that ‘for fluids with hydrodynamic modes the situation is far from clear’, citing studies where power laws of the order of 0.4 were found.

Recently Lamorgese [66] obtained a similar result using a grid-based finite difference numerical method to model liquid-vapour phase separation, finding a late-stage growth exponent of 2/3. Koch [61] distinguished two main regimes: an initial regime of wave creation and growth, which proceeded until the liquid densities were reached by parts of the system; this was followed by wave necking and breakup in which the system decomposes into clusters. Based on DPD simulation results, Warren [122] suggests three main regimes: an initial diffusive regime where the exponent is 1/3, followed by acceleration due to hydrodynamic modes, initially dominated by viscosity, with an exponent of 1, followed by an inertial regime with an exponent of 2/3. In particle dynamics studies he reproduced the 1/3 power law behaviour for the early stages of bubble growth.

Several experimental studies of spinodal decomposition in liquid-vapour systems exist. Klein et al. used light scattering to study the spinodal decomposition of sulfur hexafluoride [60]. Beysens [19] studied the vapour-liquid and two-component phase transitions in a variety of experiments, including in free-fall and space to reduce the effects of gravity. For quenched single component systems they find the late stages of coalescence are characterised by a 1/3 power law, although the power laws vary depending on the quench depth and the volume fractions of the coexisting phases. Very early time regimes are not yet accessible experimentally due to the very short time-scales involved in the phase transition.

**7.2 Domain growth simulation design**

In order to investigate the kinetics of phase transition in a two-dimensional van der Waals SPH system a series of temperature quench simulations were performed. A system of 1600 particles was equilibrated to a vapour state at a reduced temperature of 1.5, in the same reduced units as the experiments in Chapter 6. It was then subjected to quenches of varying...
depths, using the scaling thermostat (Equation 5.7) to drop and control the temperature. Three variants of the experiment were conducted. The first set used the separated van der Waals equation of state (SEP). The second set added a gradient term to the separated equation of state (GRAD-SEP). The third set used the same smoothing lengths for attraction and repulsion, with a gradient term (GRAD). Table 7.1 gives the smoothing lengths and gradient terms used for the variants. Each variant was run for the temperatures 0.5, 0.6, 0.7, 0.8. The experiments where the cohesive and attractive smoothing lengths were equal made use of a small interparticle repulsive force, and collisions at a distance of 0.5 to limit instability. All runs used leapfrog integration, a timestep of 0.001, an interaction cutoff of 5.0 and box dimensions $66 \times 66$. A timestep size of 0.0001 is used for early-time simulations, and 0.001 for longer time runs. Simulations are run for 100,000 steps.

Table 7.1: Experimental configuration.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$h$</th>
<th>$H$</th>
<th>$M$</th>
<th>rcoef</th>
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</thead>
<tbody>
<tr>
<td>SEP</td>
<td>2.5</td>
<td>5.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>GRAD-SEP</td>
<td>2.5</td>
<td>5.0</td>
<td>10.0</td>
<td>0.0</td>
</tr>
<tr>
<td>GRAD</td>
<td>5.0</td>
<td>5.0</td>
<td>10.0</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

7.3 Analysis of structure

At each step, the particle distribution was used to compute a continuum density on a $100 \times 100$ cell grid. The density-density correlation function

$$H(r, r') = \langle (\rho(r) - \langle \rho(r) \rangle)(\rho(r') - \langle \rho(r') \rangle) \rangle,$$

(7.1)

is calculated, and then radially averaged for each snapshot to produce the radial two-point density correlation function. The first zero of a polynomial fit to this correlation function is chosen as representative of a characteristic domain size. This number is referred to as the mean domain size, which can also be obtained from a Fourier transform of the radially averaged two-point correlation function. It provides a measure of spatial ordering or structure and gives the average size of the liquid regions in the decomposing fluid. Figure 7.1 shows this measure of structure applied to a synthetically generated field of liquid and vapour densities in a checkerboard pattern.

The time series of mean domain size was compared for runs at a range of temperatures using log-log plots to determine whether power laws were operative. Multiple, competing processes operate (wave decomposition, diffusion, hydrodynamic flow) to change the structure of the fluid, thus it is difficult to clearly identify regimes.

Two distinct linear regimes were identified in the structure factor time series plot, an example of which is shown in Figure 7.2. The first is associated with the initial ‘decomposition’ of the homogenous system into liquid and vapour domains, as described by Koch et
al. [61]. This regime involves the creation and growth of density waves. After an intermediate regime of wave necking and breakup, a second phase of power law domain growth is found. This second regime involves the growth of the droplets composing the liquid phase and is called ‘coarsening’.

Some subjective analysis was required in choosing the start and end points of each regime for further analysis. Example time series curves are shown in Figure 7.2.

Figure 7.2: Time series of characteristic domain size for quenches to reduced temperatures 0.5, 0.6, 0.7 and 0.8. Lines for power law growth with constants 1/3, 1/2, 2/3, 1 are shown as a guide. The abcissa shows time, with characteristic domain size shown on the ordinate.
Figure 7.3: Snapshots of domain decomposition at reduced temperature of 0.5 for indicated times (t).

Figure 7.4: Snapshots of domain coarsening at reduced temperature of 0.5 for indicated times (t).
7.4 Domain growth simulation results

Figure 7.3 shows the density field at timesteps as marked for an early-time simulation. This regime is characterised by the growth in amplitude of interconnected regions of high density.

Figure 7.4 shows similar snapshots for a longer time simulation. This longer time regime is associated with the development of droplets, the growth of these droplets and then by hydrodynamic flow driven coalescence.

In the regimes studied, the growth exponent shows a linear dependence on the quench temperature $T$. For the decomposition regime the growth exponent is approximated by $0.18T$. For the coarsening regime the growth exponent is approximated by $1.5T$. The effect of the quench depth is more pronounced for the coarsening regime. The inclusion of a gradient coefficient changes the growth exponents, but the number of experiments was too small to quantify this relationship accurately.

Table 7.2: Mean growth coefficients over the range of temperatures

<table>
<thead>
<tr>
<th>Regime</th>
<th>SEP</th>
<th>GRAD-SEP</th>
<th>GRAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition</td>
<td>-0.34</td>
<td>-0.30</td>
<td>-0.30</td>
</tr>
<tr>
<td>Coarsening</td>
<td>0.41</td>
<td>0.66</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Table 7.3: Decomposition growth exponent by quench depth

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Decomposition Exponent</th>
<th>Coarsening Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-0.350</td>
<td>0.292</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.338</td>
<td>0.435</td>
</tr>
<tr>
<td>0.7</td>
<td>-0.312</td>
<td>0.615</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.299</td>
<td>0.732</td>
</tr>
</tbody>
</table>

7.5 Conclusions

Lamorgese [68] suggested three distinct regimes for the development of a quenched vapour. The first regime involves the development of regions of liquid phase, and may proceed quite slowly, depending on the quench depth and the intensity of initial noise. Once separation is established, the distinction between phases increases rapidly and sharp interfaces form with nuclei not growing appreciably in size. This process reaches a local equilibrium and is followed by a much slower regime of domain growth dominated by inertial flow, where the balance of capillary and inertial forces leads to $2/3$ power law behaviour. The domain growth observed in the smoothed particle simulations presented here displays these three regimes.

The range of exponents in the decomposition regime is in broad agreement with Warren’s value of 1 for the viscous hydrodynamic regime and $2/3$ for the inertial hydrodynamic
regime [122]. Osborn [92] found a power law of $1/2$ for an initial surface tension driven regime and a power law of $2/3$ for the subsequent hydrodynamic regime. The decomposition exponents are also in very good agreement with Lamorgese’s [68], value of $2/3$ for the late stage growth of liquid-vapour phase separation. The decomposition rate is faster than that found by Abraham et al. [2], but the general picture of smaller exponent for decomposition and larger for coarsening is consistent.

It is encouraging to note that the separation of smoothing lengths for attraction and repulsion did not appreciably affect the domain growth exponents. Incorporating the gradient term alone was sufficient to observe phase separation. This overcomes a key concern with the SPH methodology developed in this thesis: that the use of different smoothing lengths for different terms is arbitrary and that the dynamics may be more influenced by these arbitrary decisions, made for reasons of numerical stability, than by the physical parameters.

The study of domain growth in three dimensions will require larger systems than are practical with the code developed for this work. However, Lamorgese [68] has shown that 2D simulations return results for domain growth scaling quantitatively similar to 3D.

Figure 7.5: Domain growth exponents related to quench temperature in SPH quenches.
8 Development of a three dimensional SPH code

A smoothed particle simulation and analysis system for performing three dimensional calculations is described in this chapter. This code is conceptually similar to that described in Chapter 5 but architecturally different. In this chapter the software architecture of a three dimensional SPH code is described. The architecture uses Python for all high level control and to decompose the system into modules, with Fortran or C extensions used for computationally expensive components, extending the two dimensional code described in Chapter 5. The agile, discovery-led development methodology used for the project is described.

The conceptual model of a smoothed particle system is outlined along with a set of software objects for key components: particle structure; neighbour list; force application; and numerical integration.

The performance of several neighbour list implementations is compared, and reflections on the next steps to improve performance are provided.

8.1 Development methodology

The scientific process is unforgiving of traditional software development lifecycles, primarily because of the difficulty of verifying that software requirements were correct until after the software is built. In this work, an agile, discovery-led development technique was followed. Rich data output and visualisation for short runs was used to fine tune the implementation and pick up any problems with minimal computation time. In the early stages of development, real-time visual output is especially helpful in this regard as it assists with manually ending a simulation once the developer has the subjective sense it has reached a dead end, either through variables blowing up to infinities, or the system being trapped in an unphysical state.

In this process, the use of version control software is a crucial means of preserving the history of the source code, which ensures that past results are reproducible even (especially!) if the software is shown to contain bugs which were later fixed.
8.2 System languages

The primary language in which the system is written is Python, and it is at the Python level that simulation runs are scripted. Initially, smoothed particle calculations were implemented in pure Python. The use of high level languages for improved efficiency of software development is supported by empirical research, some of which is reviewed by Wilson [126].

The benefits of high level languages are speed of development, easy integration with analysis code and the capability to interactively execute sub-components, which improves testing and bug discovery.

A multi-language strategy was employed, making use of the improved efficiency afforded by the high level language Python for run configuration and management while making use of the greater efficiency of compiled languages for core numerical calculations.

Later, some computationally intensive routines were converted to compiled extensions using the Cython language. Cython, a Python-like language for creating C extensions for Python is used to speed up computationally important elements, described by Behnel [15]. Optimisation with Cython is straightforward and leads to code that runs at C speed.

It is also straightforward to integrate simple Fortran code such that it can be called from Python. Others were modified to use subroutines in the Fortran code described earlier, which were wrapped using the tool F2PY [93] such that they could be called from within the Python code.

This approach allows the speed benefits of compiled code to be realised, coupled to the convenience of high level analysis and plotting routines, and an interactive programming console.

The time investment required to validate and debug numerical routines should not be underestimated, and as such there is considerable benefit in creating implementations of algorithms that can be studied at a more granular level before committing to large and computationally intensive simulations. Strict functional decomposition also eases the task of replacing functions and sub-modules with third party implementations. Below the replacement of custom built neighbour list structures with freely available, highly optimised and open source code will be described. These points very much support a functional programming paradigm, in which operations are contained in functions whose output depends only on their input.

As discussed in Chapter 5 in order to support portability and interoperability, the use of complex data structures as function arguments should be avoided, at least for the low level computationally expensive operations. There are several reasons for this. This first is that automated interface generators such as F2PY do not support custom data structures. The second is that by coupling a function to a data structure definition, its portability is reduced and reimplementation is more difficult.
8.3 Design

The same conceptual N-Body design is used as described in Chapter 5. Object oriented design is used to group data with the methods that operate on that data.

8.3.1 Particles

ParticleSystem objects store the states of the particles. Currently their update() method is responsible for integrating the model forward in time. One ParticleSystem can be operated on by multiple forces, and can have multiple interaction lists. In principle this supports coupling between different particle systems.

8.3.2 Forces

In the program design, a Force is an object that implements the right hand side of the differential equation $\dot{X} = f(X)$, where $X$ represents the vector of all variables necessary to store the state of the system. A Force alters the rates of change of a ParticleSystem. It is the mapping from the particle attributes to the $X$ and $\dot{X}$ state vectors that tells you which variables are modified by a force, and which are not. For example if the state vector was composed of particle positions and velocities such that $X = \{x, v, \dot{v}\}$, and was operated on by a body force, the computational Force operation would update $\dot{v}$ to equal the body force divided by the particle mass.

If a force depends on a rate of change then we have a potential ordering problem where the application of one force before another alters the outcome of the other force calculation. Such a situation is rare. Most applications will only require the update of $dv/dt$ and $dc/dt$ and most forces will not have terms that depend on these values, so each force will simply add to an accumulator of the total rate of change for each variable in the state vector. A collision operator is a special class of force, because it is expected to alter the particles’ properties instantaneously. When a collision is detected, velocities are changed immediately and positions are adjusted for interpenetration. Forces are stateless, their sole function is to update the rates of change in the ParticleSystem object.

8.3.3 Integrator

Because the Python programming language supports functional programming, the functions that return the system rates of change can themselves be an input, allowing the integrator to be quite generic. The logic to translate particle properties into a state vector, and to compute the rates of change, is contained in the particle class, which has methods for dumping its properties into a large array, and then retrieving them from the array once the integrator has updated it. These methods do not seem to carry a high overhead, especially when compared to the crushing cost of N-body distance calculations.

Integrators are also stateless, their sole function is to update variables in the ParticleSystem object based on their rates of change, for a given timestep.
8.3.4 Time stepper

In the implementation described here references to the forces to be applied are contained in the particle system. This allows the list of forces to be iterated over, and for multiple particle systems to be operated on by different sets of forces. For example boundary particles might have fixed positions, while fluid particles might interact via a smoothed particle hydrodynamics force with the boundary.

The TimeStepper is also stateless, its function is to orchestrate the calls to Forces and Integrators to maintain the internal consistency of the ParticleSystem object.

8.4 Complexity and performance

Particle-based methods can be much more computationally intensive than grid-based methods. The operation that dominates the computational expense is the calculation of distances between pairs of particles. The next largest computational cost is the string of calculations that must be carried out for each pair. Next to the cost of these operations, the cost of execution of the code that orchestrates the calculations is negligible. However such orchestration code is a prime source of errors. As such, implementation of high level orchestration in as high a level language as possible is desirable. Several resons for this are: high level languages are more terse; high level languages are more testable, with testing libraries often built into the default set of libraries; and high level languages provide more built-in control through native data structures such as linked lists and hash tables.

In this software, control code is implemented in Python to take advantage of flexibility, while all neighbour list loops and most particle loops are implemented in Fortran or Cython to take advantage of their raw speed. Because so much of the computational cost is concentrated in the inner loops over pairs this strategy is possible with little sacrifice of speed.

The code scales reasonably well to large system sizes, especially once systems are large enough that the interaction cutoff reduces the scaling of particle pairs with the number of particles to be less than $N^2$.

The practical limit of this code is probably several thousand particles. At sizes larger than this additional effort in reducing the computational effort in resolving pair separations would seem worthwhile. In order to make significant ground in this area multipole or tree methods should be investigated.

Construction of the list is a minor cost compared to the major cost is the computation of interparticle distances. Brute force, Verlet list [119] and KDtree [16] neighbour list schemes are implemented. The Verlet and Brute lists are order $N^2$ for list construction method, the KDtree is able to construct the list in $N \log(N)^2$ time. Another notable method for constructing a neighbour list is the cell method. This was tested but found to not provide significant advantage due to the small number of particles used and the long interaction radius.
The build process iterates over particles and determines which meet the criteria for being neighbours. This built list is then pruned according to a cutoff or other criterion. Typically the build process, being computationally expensive, is run less frequently than the compress process, which serves to prune pairs that are outside of the interaction range. The computational cost of pair separation calculation is dominated by the need to take the square root of the squared distance.

The methods implemented and tested from the `pyticles.neighbour_list` module are as follows: NeighbourList: reference implementation in pure Python; VerletList: extends the brute force neighbour list with a pruning of pairs outside interaction radius; FortranVerletList: uses a Fortran pair separation function with an interface generated by f2py, passing the position arrays; CythonVerletList: a Cython implementation that passes the particle data structure to the pair separation function; FastVerletList: a Cython implementation that passes the position arrays directly to the pair separation function; KDList: Extends the FastVerletList class to use the scipy.spatial.KDTree function to build the list; BruteScipy: brute force list using the scipy.spatial.pdist function. Uses the FastVerletList pair separations function.

When the number of pairs is greater than 50000, the total time to build, compress and compute pair separations is 30 percent faster with the KDtree implementation than the Verlet implementation. This is due to a shorter build and compress time. Because the pair separations are the same for a given number of neighbours, and the KDtree does not systematically find fewer pairs than the Verlet procedure, it does not compute the pair separations any faster.

Figure 8.1 shows the times to compute pair separations using three of the tested implementations. The primary result is that when optimised aggressively, the Cython implementation was faster than the wrapped Fortran implementation. A pure Python brute force implementation was also used but is not shown because the performance is not competitive. All methods are implemented with a Python interface, which abstracts the main steps of neighbour list construction and use: building, compression and pair calculation. Note that the pair separation calculation is independent of the method used to build the list, as most methods will cull pairs outside of the maximum interaction radius.

On a HPZ400 (CPU) a 1000 particle system took approximately 4.3 seconds to compute pair separations, a 4000 particle system with double the volume took approximately 5.2 seconds to compute pair separations. This suggests that the code will scale reasonably well to large system sizes, especially once systems are large enough that the interaction cutoff reduces the scaling of particle pairs with the number of particles to be less than N².

With the caveat that performance will vary depending on machine architecture and compiler, the general performance of the code is as follows: a typical 2000 particle simula-
Figure 8.1: Timing of different neighbour list implementations.
tion with approximately 400,000 pairs consumes less than 320 MB of memory and executes a single simulation step in approximately 26 seconds on a 2.5 Ghz processor of which 23.5 is spend computing pair separations.

As an N-body method, strategies for improving performance in other N-body simulations such as gravitational or molecular dynamics are applicable to SPH. It is clear that for very large systems, say of the order of millions of particles, parallelism is required in order to achieve tractable compute times.

Improvements to neighbour list performance is possible with the use of multi-pole or tree methods that reduce the effective number of pairs by averaging distant neighbours. Such methods are popular in production quality SPH codes [107, 43], but require significant effort to implement.

### 8.5 Conclusions

A flexible, extensible three dimensional SPH code was developed. Results using this code to simulate liquid-vapour phase transition in three dimensions will be presented in the following chapters.
9 Three dimensional modelling of the condensation of water

A limitation of the work described in previous chapters was that the van der Waals parameters were chosen purely for convenience, limiting the use of experimental data to validate the theoretical predictions and the simulated results. In this chapter we first describe how the model developed in Chapter 4 was parameterised for water. This parameterised model is used to simulate several liquid-vapour processes. The motivation for using parameters derived from real fluids is to allow for direct verification against experimental results and is a step towards making predictions for fluids on which physical experimentation is impractical.

To validate the three dimensional model and solver, an equilibrated gas was quenched and observed to form a droplet and then a film under periodic boundary conditions. Having established the stability of the solver, the questions of the quantitative accuracy of the coexisting densities and the interfacial tension were addressed. Previous work by Nugent and Posch [88] has established that coexistence at the predicted bulk densities can be attained for two dimensional systems at a range of temperatures, but little work has been done on the properties of the interface, especially in comparison to experimentally measured quantities. A series of volume expansion film formation simulations were conducted, with the resulting coexisting densities and surface tensions compared against experimental values, and against the theoretical predictions for the van der Waals square gradient model.

To further investigate the ability of SPH to model the liquid-vapour interface, idealised interfaces are generated and studied.

9.1 Parameterisation of a smoothed particle model for water

Values for the parameters of the van der Waals equation of state given by Kjelstrup and Bedeaux [58] are converted to units expressed in terms of mass density. Convenient scaling values are chosen so that numerical solutions are not complicated by extremely large or small numbers and the equation rewritten in terms of scaled variables. These scaling parameters are given in Table 9.2 and are close to those selected by Kjelstrup and Bedeaux [58].

A numerical solution for the binodal line was obtained using Brentq optimisation [21], a fast, robust root finding method implemented in the Scipy package [89] for the Python
Table 9.1: van der Waals equation of state parameters for water (Kjelstrup and Bedeaux [58]).

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals attraction</td>
<td>$\bar{a}$</td>
<td>$1.045 \times 10^4$</td>
<td>Jm$^3$/kg$^2$</td>
</tr>
<tr>
<td>van der Waals excluded volume</td>
<td>$\tilde{b}$</td>
<td>$1.038 \times 10^{-3}$</td>
<td>m$^3$/kg</td>
</tr>
<tr>
<td>Density gradient coefficient</td>
<td>$\bar{M}$</td>
<td>$9.244 \times 10^{-17}$</td>
<td>m$^2$/s$^3$K</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>$\bar{k}_B$</td>
<td>$4.615 \times 10^2$</td>
<td>Jm$^5$/kg$^2$</td>
</tr>
</tbody>
</table>

Table 9.2: Scaled parameters for smoothed particle simulations of water condensation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scaling length</td>
<td>$x_{scl}$</td>
<td>$2.81$</td>
<td>nm</td>
</tr>
<tr>
<td>Scaling mass</td>
<td>$m_{scl}$</td>
<td>$1.247 \times 10^{-23}$</td>
<td>kg</td>
</tr>
<tr>
<td>Scaling temperature</td>
<td>$T_{scl}$</td>
<td>$562$</td>
<td>K</td>
</tr>
<tr>
<td>Scaling time</td>
<td>$t_{scl}$</td>
<td>$1 \times 10^{-9}$</td>
<td>s</td>
</tr>
<tr>
<td>Scaling mass density</td>
<td>$\rho_{scl}$</td>
<td>$5.629 \times 10^2$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Scaled van der Waals attraction</td>
<td>$\bar{a}$</td>
<td>$7.446 \times 10^4$</td>
<td>-</td>
</tr>
<tr>
<td>Scaled van der Waals repulsion</td>
<td>$\tilde{b}$</td>
<td>$5.842 \times 10^1$</td>
<td>-</td>
</tr>
<tr>
<td>Scaled gradient coefficient</td>
<td>$\bar{M}$</td>
<td>$8.345 \times 10^2$</td>
<td>-</td>
</tr>
<tr>
<td>Scaled Boltzmann’s constant</td>
<td>$\bar{k}_B$</td>
<td>$3.285 \times 10^4$</td>
<td>-</td>
</tr>
</tbody>
</table>

programming language. The pressure satisfying the equal area constraint is found by optimisation of the area function between the two spinodal pressures. The solution for water, using the parameters in Table 9.2 is shown in Figure 9.1.

9.2 Experimental properties of the water liquid vapour interface

As outlined in Section 2.8, the interfacial width of liquid-vapour water has been studied using molecular dynamics as well as experimentally. Usually the measurement quoted for interfacial width is the 10-90 width, which is the width of the region from where the density is 0.1 of the liquid density $\rho_l$ to 0.9 $\rho_l$.

Estimates of interfacial width vary and are complicated by considerations of the effect of capillary waves on X-rays in the case of experimental studies, and on the details of the molecular models used in the case of numerical studies. A distinction must be made between intrinsic width of the interface and the apparent width due to the presence of capillary waves which have a broadening effect [108]. Ismail reported molecular dynamics results with intrinsic interfacial widths from 0.8 Å at 300K to 1.5 Å at 500K, and total widths of 0.2-0.24 nm [55]. At 300 K, Townsend reported 10-90 widths of 3.45 Å for molecular dynamics simulations of water, in good agreement with the value determined from X-ray reflectance measurements of 3.30 Å [114, 113]. Yang reported a wider 10-90 interfacial width at 300 K of 5.75 Å based on density functional theory predictions.
Figure 9.1: The van der Waals equation of state, with the Maxwell construction tie line, parameterised for water. Green points: binodal points for temperatures given by the scale on the right. Red: vapour, homogeneous and liquid densities at 562K, Black: spinodal points at 562K. Blue line: pressure-volume curve for T=562K, pressure is given by the scale on the left. Blue shading: areas equalised by the Maxwell construction.
These results are summarised in Table 9.3. Surface tensions have been measured in experiment, MD and DFT modelling, with Yang reporting surface tensions from density functional theory at 325 K as 170 mN/m and from molecular dynamics as 149 mN/m, compared with the experimental value of 68 mN/m. This and other measurements of the modelled surface tension of water are summarised in Table 9.4. Vargaftik documented a simple empirical relationship between temperature and surface tension for water.

Table 9.3: Molecular dynamics (Alejandre, Ismail, Townsend), density functional theory (Yang) and experimental (Brausla) properties for liquid-vapour interfaces of water.

<table>
<thead>
<tr>
<th>Method</th>
<th>T (K)</th>
<th>Interface Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ismail (SPC/E)</td>
<td>300K</td>
<td>0.8 Å</td>
</tr>
<tr>
<td>Alejandre (SPC/E)</td>
<td>300K</td>
<td>2.99 Å</td>
</tr>
<tr>
<td>Townsend (MD)</td>
<td>300K</td>
<td>3.45 Å</td>
</tr>
<tr>
<td>Yang (DFT)</td>
<td>325K</td>
<td>5.75 Å</td>
</tr>
<tr>
<td>Brausla (X-ray measurement)</td>
<td>300K</td>
<td>3.24 Å</td>
</tr>
<tr>
<td>Townsend (X-ray measurement)</td>
<td>300K</td>
<td>3.30 Å</td>
</tr>
</tbody>
</table>

Table 9.4: Experimental, simulation and van der Waals model properties for the surface tension of water.

<table>
<thead>
<tr>
<th>Method</th>
<th>T (K)</th>
<th>γ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ismail (MD)</td>
<td>300K</td>
<td>47-61 mN/m</td>
</tr>
<tr>
<td>Alejandre (SPC/E)</td>
<td>328K</td>
<td>66.0 ± 3.0 mN/m</td>
</tr>
<tr>
<td>Yang (DFT)</td>
<td>325K</td>
<td>170 mN/m</td>
</tr>
<tr>
<td>Yang (MD)</td>
<td>325K</td>
<td>149 mN/m</td>
</tr>
<tr>
<td>Yang (Experiment)</td>
<td>325K</td>
<td>68 mN/m</td>
</tr>
<tr>
<td>Ismail (Experiment)</td>
<td>300K</td>
<td>71.7 mN/m</td>
</tr>
</tbody>
</table>

9.3 Condensation of vapour quenched into an unstable state

In an initial test of the three dimensional model a small smoothed particle system in a periodic box was temperature quenched. 1000 particles were initialised in a cubic box of a side 10 \( x_{scl} \) long where each particle has a mass of 0.4 \( m_{scl} \), was equilibrated at a temperature of 1.5 \( T_{scl} \) (Table 9.2). This is a very small system, of the order of the size of a virus, and smaller by an order of magnitude than engineered nanoparticles (≈200-500 nm). Simulation of larger systems could be accomplished by using a larger number of particles, or assigning a larger mass to each particle, however a larger particle mass reduces the spatial resolution of the simulation.
This produced a system with a small range of particle densities (calculated using Equation 3.22) shown in Figure 9.2 (top left). This temperature is above the critical temperature for the system. The system is then quenched into the unstable region of the phase diagram, with a scaling thermostat used to keep the mean temperature constant.

This vapour was then quenched to a temperature of $0.5 \ T_{scl}$ for 3000 timesteps with a timestep size of $0.001 \ t_{scl}$ from an initial temperature of $1.5 \ T_{scl}$. The simulated quench time is $3.0 \times 10^{-10}$ seconds with the film configuration attained at roughly $5 \times 10^{-11}$ seconds.

The phase separation of the water develops naturally from the solution of the model as shown in Figure 9.2 with no explicit tracking of the vapour-liquid interface. Density histograms, shown in the top left panels of Figure 9.2 were generated by binning the particle densities and then normalising the resulting distribution. As the droplets equilibrated, oscillations were observed. Two distinct phases formed, although the vapour phase is barely resolved due to the large density difference between vapour and liquid. The liquid phase adopted a curious cylindrical configuration. No particular significance should be attached to this shape other than to note that it is a minimum of the surface area compatible with the periodic boundary conditions. These boundary conditions stabilise configurations that would not minimise the free energy in unbounded space, just as they did for the two dimensional planar interface.

The liquid density predicted by the Maxwell construction is 1.45. The maximum particle density is 1.53. The peak of the density distribution of the final state is between 1.3 and 1.35. The initial and final states are shown in Figure 9.2. This agreement is close enough to be encouraging, although the attained densities are not as a good a fit of expectations as for the two dimensional systems previously studied. Larger simulations are required in order to ensure that a true bulk state has been attained because in this simulation the width of the liquid film is less than the smoothing length ($H = 4.0$).

### 9.4 Formation of a droplet in three dimensions

To demonstrate the condensation of a water droplet, an equilibrated vapour was quenched into an unstable state. The 42 nm side periodic box contains 3375 particles each with a mass of 1800 atomic mass units and a spatial resolution of 4 nm. The mean system density is $0.3 \ \rho_{scl}$. After equilibration at a temperature above the critical point it is quenched to $0.9 \ T_{scl}$. After the quench the system is simulated for 100,000 timesteps of length $1.0 \times 10^{-5}$, with core force parameters $c_r = -1000$ and $\sigma = 1.0$. Hard collisions occur at $0.3 \ x_{scl}$. The van der Waals parameters, including the gradient term, are set to the values give in Table 9.2.

Figures 9.3 - 9.8 show the development of water droplets from the quenched vapour. The initial density is slightly inhomogeneous, with a density maxima near the centre of the cell. It is towards this perturbation that the mass gathers after the quench (Figure 9.4).
Figure 9.2: Particle position plot of the quench of a gas to a cylindrical film at (a) 1500, (c) 2500 timesteps, with normalised particle density distribution histogram (top left of each frame). Frames show particle positions as seen from the $xy$, $xz$ and $yz$ planes \[25]\.
Figure 9.3: Initial vapour state. Boundaries are periodic. Left: positions. Right: density maximum in xy plane with arrows indicating the acceleration vectors (smoothed) along a slice in the z plane.

Figure 9.4: Quenched to an unstable temperature of 0.9 reduced units (timestep 100).
Figure 9.5: Density perturbations grow into a droplet.

Figure 9.6: Two separate droplets are formed.
Figure 9.7: Droplets begin to coalesce.

Figure 9.8: Droplets have coalesced.
The simulation was terminated while the liquid configuration was still a droplet. This experiment validates that the model and simulation methodology are able to resolve instability driven phase separation, and demonstrates that the model and code can generate droplet formation in three dimensions, including the coalescence of two smaller droplets into a single liquid phase.

According to the Maxwell construction this quenched state should produce a liquid with a mean density of 1.13 and a vapour with a density of 0.13. In the experiment final density distribution was bimodal with liquid and vapour densities 1.35 and 0.05 respectively. This failure to obtain quantitatively correct densities will be discussed further in the next section.

9.5 Formation of a film in three dimensions by expansion

The next set of experiments attempted to reproduce in three dimensions the planar interface experiments outlined in Chapter 6.4. In this experiment an equilibrium liquid is subjected to an instantaneous increase in the available volume and held at a temperature for which two phase coexistence is stable. Three discrete steps are involved: liquid relaxation, liquid equilibration at the thermostatted temperature, and expansion driven phase separation. The objective of the experiment is to generate two stable phases separated by a planar interface.

A near equilibrium liquid was prepared, with a mean density of about 1.5 $\rho_{scl}$. The size of the initial liquid box is $10 \times 5 \times 5$ $\times_{scl}$, or $28.0 \times 14.0 \times 14.0$ nm or $5.55 \times 10^{-24}$ m$^3$. For 1000 particles, with a scaling density of $5.629 \times 10^2$ kg/m$^3$ and thus a mean system density of 844 kg/m$^3$ the mass of this system is $3.75 \times 10^{-21}$ kg, with each SPH particle representing 125 water molecules. For this number of molecules, our parameter for the van der Waals $b$ (excluded volume per atom, $3.105 \times 10^{-29}$ m$^3$) implies a minimum volume of $3.88 \times 10^{-24}$ m$^3$.

In the liquid equilibration the particles are initialised in an FCC crystal configuration. FCC was chosen because it is more tightly packed than a simple cubic lattice and so positions the particles closer to their equilibrium positions, allowing for a shorter relaxation stage. The objective of this step is to fill the container uniformly and to allow the particles to relax to equilibrium positions. Next the liquid is equilibrated at the temperature which will be maintained for the expansion and separation without changing the size of the box.

For a range of scaled temperatures (0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.02, 1.04, 1.06) the system is again brought to equilibrium, thermostatted at the prescribed temperature such that the density distribution is unimodal. The objective of this step is to separate the temperature change from the volume expansion. For some of the lower temperatures the box size and hence the mean system density is such that the system phase separates into a liquid and an unresolved (very low density) vapour. Finally in the expand stage, the size of the $x$ dimension of the box is doubled to 20 scaled length units. For thermostat settings below the critical temperature, the liquid expanded to fill the box and separated
into coexisting liquid and vapour, forming a film (stabilised by the periodic boundary conditions), in the same manner as the 2D planar interface experiments described in Chapter 6.

Figure 9.10 shows the system kinetic energy in the process of formation of a film, for a temperature of 0.8 $T_{scl}$. It shows that an equilibrium state has been reached. The final state of this simulation is shown in Figure 9.11. The final densities are close to the expected densities.

Table 9.5: van der Waals equation of state (vdW) and smoothed particle (SPH) densities for coexisting liquid and vapour.

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature</th>
<th>Reduced Temperature</th>
<th>Liquid Density</th>
<th>Vapour Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>vdW</td>
<td>281K</td>
<td>0.5</td>
<td>1.44</td>
<td>0.000</td>
</tr>
<tr>
<td>SPH</td>
<td>281K</td>
<td>0.5</td>
<td>1.55</td>
<td>0.000</td>
</tr>
<tr>
<td>vdW</td>
<td>337K</td>
<td>0.6</td>
<td>1.38</td>
<td>0.01</td>
</tr>
<tr>
<td>SPH</td>
<td>337K</td>
<td>0.6</td>
<td>1.47</td>
<td>0.00</td>
</tr>
<tr>
<td>vdW</td>
<td>449K</td>
<td>0.8</td>
<td>1.17</td>
<td>0.11</td>
</tr>
<tr>
<td>SPH</td>
<td>449K</td>
<td>0.8</td>
<td>1.23</td>
<td>0.07</td>
</tr>
<tr>
<td>vdW</td>
<td>505K</td>
<td>0.9</td>
<td>1.13</td>
<td>0.130</td>
</tr>
<tr>
<td>SPH</td>
<td>505K</td>
<td>0.9</td>
<td>1.03</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The resulting coexistence densities were calculated by taking the peak density in the vapour and liquid regions respectively and are presented in Table 9.5 where they are compared against coexistence densities calculated using the van der Waals equation of state and against the coexistence densities obtained for the smoothed particle expansion simulations. There is a difference between the coexisting densities predicted for the van der Waals $a$ and $b$ parameters, and the densities obtained by molecular dynamics. Using molecular dynamics with the SPC/E model, Ismail et al. found a liquid density of 1.76 at 300 K, in contrast to the 1.43 predicted by the Maxwell construction. In the present work we have used the predictions of the van der Waals equation of state as verifying data. These coexistence densities are plotted in Figure 9.12.

At low temperatures (up to 0.7 $T_{scl}$) the liquid density is a very good fit of the predicted density, while the density of the vapour phase is too low to be resolved. At temperatures of 0.8 to 1.0 the coexisting densities, are a good fit to the expected densities considering the large smoothing length (low spatial resolution) and the fact that there is a broad distribution of particle densities. Some difficulty is apparent with the phase separation at higher temperatures. It is unclear if the system is getting stuck in a thermodynamically metastable state, if more time is required, or if the numerical method is trapped in a local minimum. The region in Figure 9.12 between the red and blue lines is the metastable region: a system in this state is much less likely to phase separate. At higher temperatures the system took longer to equilibrate, simply because the forces produced by the thermo-dynamic instability are smaller. At the higher temperatures of 1.04 and 1.06 there were in
Figure 9.9: Planar liquid-vapour interface formed by expansion, using water parameters, at a reduced temperature of 0.9. Smoothed fields are shown for slice in the z dimension: (a) density; (b) acceleration; (c) density gradient; (d) temperature; (e) difference between normal and parallel pressure; and (f) cross-sectional mean of e).
Figure 9.10: System kinetic energy for film expansion at a reduced temperature of 0.8.

Figure 9.11: Particle positions and density distribution for film expansion at reduced temperature of 0.8. The red dotted line shows the target vapour density and the green dotted line shows the target liquid density.

Fact multiple peaks of density and clearly distinguishing the liquid and vapour phases was more challenging. A similar difficulty in obtaining the correct orthobaric densities using molecular dynamics was found by Alejandre [5].

The final profile for one of these experiments is shown in Figure 9.9. While these experiments generated a stable liquid-vapour interface, the surface tension of the interface is dramatically underestimated (Figure 9.13). The surface tensions were found to be orders of magnitude too small. The smoothed particle surface tensions do display the expected relationship with temperature, such that increased temperatures lead to reduced surface tensions, but the data are quite noisy and represent a small number of experiments. Therefore it is not possible to state with a high degree of confidence that the relationship is re-
Figure 9.12: Coexisting densities from three dimensional film formation simulations. Blue dots: SPH simulations using 1000 particles. Blue line: solution to Maxwell construction using water parameters given in the main text. Red dashed line: Spinodal line of the equation of state for water.

Figure 9.13: Left: surface tensions for 3D smoothed particle interfaces (red) and observed surface tensions (black). Right: smoothed particle surface tensions plotted alone to show the temperature/surface tension relationship obtained in the experiments.

produced. To investigate the deficiencies in the representation of surface tension, smoothed particle systems were fitted to idealised interfaces.
Figure 9.14: The smoothed approximation, for any smoothed field property, in the vicinity of a density gradient. Each particle is assigned the same value of the field (blue asterix). The red open circle shows the value of interpolated field property. Notice the perturbation in the interpolated field property around the density gradient, which is an artifact of increased errors in the SPH summation around the density gradient.

9.6 Ideal liquid-vapour interfaces with smoothed particles

Can we obtain realistic surface tensions and interfacial widths from such coarse-grained continuum mechanical models? In this section this question is addressed using smoothed particle model fitted to the ideal interface, in an attempt to determine whether the failure to capture the temperature related variation in surface tension in the previous section was a failure of the SPH method or of the dynamics.

The representation of density gradients by SPH is examined, using particle distributions fitted to the analytical profile in order to understand the best possible smoothed particle representation. Figure 9.14 shows how a density inhomogeneity creates an inconsistency in the smoothed property (any field property, for example temperature) near the inhomogeneity, even though the field properties are set to be equal for all particles.

Previously, in Figure 2.4, a regular grid was initialised with densities given by the analytical expression for the density gradient in the interfacial region. The width was chosen to yield a value for the surface tension in agreement with the value given by the Maxwell construction for the water parameters. One approach to setting up a distribution of SPH
particles to match a density gradient is to distribute particles uniformly and set the masses such that the desired density is achieved. Another approach is to use particles of constant mass and to alter the distance between them to achieve the desired density. The smoothed properties that are obtained do not differ greatly between these approaches.

In Figure 9.15 a regular grid of particles is initialised with masses to fit the idealised density gradient shown in Figure 2.4. The Laplacian of the density is computed using the product rule symmetrised formulation. The unsymmetrised and quotient rule expressions were examined and found to yield a less satisfactory fit than the product rule formulation.

Figure 9.15: Smooth particle representation of a density gradient: a) Green: target density profile, Blue: Smoothed density, Black: particle positions and densities; b) Green: density gradient, Blue: Laplacian of density; c) Squared density gradient terms; d) Normal and perpendicular capillary pressure; e) Difference between normal and perpendicular pressure; f) Normal pressure (green) and temperature (blue).
compared with the density gradient estimated using grid-based methods. Comparing Figures 2.4 and 9.15 shows a qualitative agreement, but also a significant difference in the Laplacian. There are also significant differences in the magnitude of the density gradient. While the difference between the normal and parallel pressure is of the correct shape, it is of a magnitude significantly less than in the gridded interface.

Panel e) of Figure 9.15 shows the smoothed estimate of the normal pressure, which should be constant over the interface but is clearly not. This strange feature also appears in the dynamical SPH film formation simulations, and would seem at first to be physically implausible: how can the system be mechanically stable when the pressure is not constant? One explanation is that small errors in the estimation of high liquid densities can lead to large errors in the estimate of pressure. This is noted as a problem for future consideration.

The next step was to examine the surface tension of such analytically fitted interfaces at a range of temperatures, and to investigate whether the smoothing length (spatial resolution) played a role in determining the accuracy of this surface tension. Analytically prescribed density profiles for a range of temperatures, fitted with smoothed particle by adjusting particle masses are shown in Figures 9.16 - 9.17.

The surface tension can be calculated as the integral of the difference between normal and parallel pressure across the interface [39]. Next the surface tension is compared against the observed temperature dependent surface tension [118].

It is noted that the hyperbolic tangent fit to the liquid-vapour interface derived by Felderhof is only strictly valid in the region of the critical point. Ismail [55] compared surface tension results obtained by fitting hyperbolic tangent functions with results from fitting error functions to molecular dynamics generated interfaces, and found that the fitted hyperbolic tangent function systematically underestimated the surface tension.

For $h$ larger than the scale of density discontinuities, large errors in the estimation of density gradients are present (Figure 9.16). These errors lead to an underestimation of the magnitude of the surface tension (Figure 9.18). When the smoothing length is of a comparable scale to the density gradient, both the density gradient (Figure 9.17) and the surface tension (Figure 9.19) are well estimated.

This shows that accurate estimates of the density gradient requires a particle smoothing length of the order of the interfacial width. With a fine (short) smoothing length, the surface tension has the right temperature dependence and a magnitude close to the observed values documented by Vargaftik [118]. A smoothing length greater than the length scale of the density interface lead to gross errors in the estimate of the density gradient. With a coarse smoothing length, the surface tension has the right temperature dependence but is grossly underestimated. Insufficient spatial resolution is the reason the dynamical simulations did not capture the surface tension correctly.

A clear conclusion that the spatial resolution (particle smoothing length) must be of the order of the liquid-vapour interfacial width in order to accurately resolve density gradients and surface energy. The surface tension of water (72 mN/m at 300K) implies that the interface is microscopically narrow away from the critical temperature. These findings are
Figure 9.16: Coarse resolution SPH density gradient. (10nm smoothing). In the upper panel the green line in the top figure is the smoothed approximation to the correct field shown in black. The solid blue line shows the smoothing kernel. In the lower panel the red line is the smoothed particle approximation to the true density gradient (black).

Figure 9.17: Fine spatial resolution SPH density gradient (2 nm smoothing). Description as for Figure 9.16.
Figure 9.18: Coarse resolution smoothed particle representation of surface tension.

Figure 9.19: Fine spatial resolution SPH surface tension.
consistent with those of Ghoufi et al [40], who were successful at producing quantitatively accurate surface tensions using DPD. The spatial resolution of their simulation was such that each DPD particle represented only a handful of molecules, in contrast to the work presented in this chapter where SPH particles represented hundreds of water molecules. The failure of the expansion simulations to produce the correct temperature dependence of surface tension is explained by a combination of small system size and low spatial resolution (long smoothing length).

### 9.7 Improved representation of density gradients using adaptive kernels

An examination of the errors in SPH interpolation when resolving density gradients is performed. A new method for adapting particle smoothing lengths is proposed in which the smoothing length is adaptively reduced in regions of density gradients. This density gradient-based adaptive smoothing length outperforms both a naive constant smoothing length and a density-based adaptive smoothing length in the accuracy of estimation of the density gradient.

Several methods for adapting particle smoothing lengths in order to adaptively deal with particle disorder and inhomogeneity have been proposed in the literature. The ADKE method proposed by Sigalotti was shown to reduce the concentric circular clustering found in SPH droplet condensation simulations at low temperatures [105]. In this section we compute smoothing lengths using ADKE and a novel density gradient-based method of smoothing length adjustment.

A set of particles is initialised in three dimensions, with positions and masses on a regular grid. To create a density gradient, the masses of half the particles are set to 0.5, creating a density gradient without a discontinuity in particle separation.

The smoothed particle density and density gradient is then computed using a constant smoothing length, and this estimate is then fed into the two smoothing length adaptation algorithms.

This results in three density estimates, one for constant smoothing length, one for the ADKE adjusted smoothing length, and one for the density gradient adjustment. Figure 9.20 shows these three density estimates. The top panel of the figure shows the adjusted smoothing lengths, averaged in the y dimension. The ADKE reduces the smoothing in regions of high density and increases it in regions of low density. The density gradient adjustment decreases the smoothing length in regions of large density gradients.

It can be seen in the centre panel that the density profile is sharper using the density gradient adjustment, which is closer to the sharp interface we have created by setting up a discontinuity in particle masses.

The lower panel of Figure 9.20 shows the estimate of a field property, in this case the temperature, which is set to a constant value for all particles. It demonstrates that near
density gradients, errors appear in the SPH estimate of field properties. The root mean square error (RMSE) between the assigned field properties and the kernel estimates of those properties. For constant smoothing length the error in temperature over the interface was 0.051 while for the ADKE estimate it was a larger 0.065. The density gradient adjustment produced the lowest error of 0.048.

The density gradient based kernel adjustment was found to result in an improved estimate of field properties across the density inhomogeneity. This would suggest that in simulations in which the density gradient is of critical importance, the particle resolution should respond adaptively to the gradient of the density. This result does not establish the superiority of this means of adjusting smoothing lengths for anything other than the error in field properties across a density gradient. In several papers, Sigalotti et al. [105, 75] have demonstrated benefits from the ADKE estimate.

## 9.8 Conclusions

Using the smoothed particle code to solve the continuum equations of motion for this model of water we have used a temperature quench to produce an instability driven decomposition
into coexisting liquid and vapour with a cylindrical-planar interface.

This chapter extended the modelling of liquid-vapour phase transitions using the simple van der Waals model from two dimensions to three dimensions. The modelling of coexisting phases with densities close to theoretical values for a smoothed particle model parameterised for water was demonstrated. Further work using molecular dynamics and experimental studies is needed to determine if the dynamics of phase transitions are captured correctly.

It was found that the ADKE method, which adjusts smoothing lengths based on particle density, was not as effective at improving the resolution of density gradients as an adaptive kernel method that adjusted the smoothing lengths based on the magnitude of the density gradient.

When a liquid-vapour system is modelled using a diffuse interface model, and represented by smoothed particles, an artificial broadening of the interface has consequences for the accurate representation of density gradient forces. It was found that at coarse spatial resolution the interface is artificially broadened, leading to spuriously low surface tension. If the spatial resolution cannot resolve phenomena of interest, then there is an argument for other mechanisms to be included in the model to parameterise the unresolved behaviour. This is the motivation behind interface tracking schemes.

The condensation of a simple fluid can be modeled using continuum equations solved using SPH. The quench-induced decomposition of a vapour into a liquid in three dimensions was demonstrated. As was previously found for two dimensions, droplets of liquid will form under appropriate boundary conditions. The formation of a stable film was demonstrated. The discrepancy between the predicted densities using the van der Waals equation of state, and those obtained from molecular dynamics models was noted. For quantitative applications, more accurate equations of state are needed, such as the Barker-Henderson-Abraham equation of state [13]. However difficulties may arise using equations of state for which the repulsive and cohesive terms cannot be easily separated. This film demonstrated a qualitatively correct surface tension which was orders of magnitude lower than the expected, observed surface tension. Ideal interfaces were studied with SPH and it was determined that spatial resolution was the source of the surface tension problems. Inaccuracies in the estimation of the density gradient were identified as the source of the underestimated surface tension. The smoothed particle interpolated interfaces described by the van der Waals square gradient model are accurate at fine resolution. At coarse spatial resolution the interface is artificially broadened, leading to spuriously low surface tension. The spatial resolution (particle smoothing length) must be of the order of the liquid-vapour interfacial width in order to accurately resolve density gradients and surface energy.
10 Conclusion

10.1 Recap

In this thesis the potential of the smooth particle hydrodynamics numerical method to model liquid-vapour phase separation was investigated. This question was addressed for simple fluids in two and three dimensions using the van der Waals equation of state and the van der Waals square gradient model for the diffuse interface. A set of partial differential equations describing the dynamics of a phase separating liquid was developed and a formulation of Smooth Particle Hydrodynamics was used to solve these equations numerically. The liquid-vapour interface is intrinsically diffuse in the analytical model and the numerical method. Several computational codes were developed to solve this model. These codes are single-processor codes and can solve systems of several thousand particles comfortably. The time complexity of the solution increases linearly with the number of interacting pairs, which is the main computational limiting factor. In the worst case, where all particles interact with all other particles, the number of pairs increases with $N^2$.

The smooth particle solution generates liquid and vapour in coexistence under periodic boundary conditions in both two and three spatial dimensions. A fluid quenched into the unstable region of the phase diagram will phase separate, with a flow that appears realistic and without gross artifacts. Droplets and bubbles can be realised and these droplets coalesce when driven together by flow. With sufficient resolution, the density gradient and associated surface tension can be resolved.

In two dimensions, the numerical model was used to study temperature and volume driven phase changes. The resulting coexisting liquid and vapour densities were compared favourably against the analytical values for the van der Waals equation of state. The density gradient term was found to contribute to a broadening of the interface as expected. The kinetics of decomposition and coarsening were studied in two dimensions, at a range of temperatures with and without the inclusion of the square gradient term and the separation of attractive and repulsive smoothing lengths.

In three dimensions the numerical model, parameterised for water, was used to study: temperature and volume driven phase changes; coexisting densities of liquid and vapour resulting from the phase transition; the accuracy of the surface tension in the stable liquid-vapour systems; and the utility of adaptive smoothing for resolving density gradients.
10.2 Conclusions

The first question to be addressed was the selection and construction of a set of continuum equations capable of modelling liquid-vapour transition and coexistence. While it is limited for quantitative applications, the van der Waals equation of state was selected for its simplicity and because the separate treatment of repulsive and attractive terms is numerically advantageous. The van der Waals square gradient model was selected as a simple diffuse interface model.

The next question was whether the chosen numerical method, SPH, could solve this model. Through a series of experiments it was demonstrated that with the right configuration, SPH can model the liquid-vapour phase transition. Carrying the calculation out successfully requires attention to appropriate symmetrisation of the smooth particle interactions. Under some conditions, additional numerical techniques such as artificial viscosity and particle collisions are required to maintain stability of the simulation. In two and three dimensions SPH can model coexisting phases, with hydrodynamic waves and flow. Unlike previous studies, the use of different particle types or different equations of state to represent the two phases is not required. Instead the phase separation of the one component fluid arises naturally out of the van der Waals equation of state and squared gradient model. No explicit tracking of the liquid-vapour interface is required.

One aspect of the modelling results presented here that needs to be noted again is the use of different smoothing lengths for attractive and repulsive parts of the pressure. It is to be expected that a system governed by long range attractive and short range repulsive interactions should exhibit a liquid-vapour phase separation, because it is this quality of the intermolecular potential that is responsible for phase transition. Most of the results presented in this thesis use this method, with the exception of several of the kinetics experiments, which demonstrate that phase transitions can be modelled without this method. Reassuringly, when kinetics for models with and without separated attractive and repulsive smoothing lengths were compared, the domain growth exponents were similar. This is a significant result, as the arbitrary requirement to separate the attractive and repulsive components of pressure complicates the application of the method to different equations of state. However it is clear from these results that much of the surface tension which maintains smooth phase boundaries arises from the difference in range between the inter-particle attraction and repulsion. Surface tension was apparent in simulations where the smoothing lengths were separated, even in the absence of a density gradient term. The only source of this surface energy is from the different ranges used for attraction and repulsion which indicates that it is in fact an artificial surface tension. Further work in understanding this numerical phenomenon would assist in determining whether the effect needs to be compensated for.

A key question for any numerical method is that of the tractability of performing useful simulations. The computational complexity of the calculation is dominated by the size of the neighbour list, in particular the computation of pair separations. Because the in-
teraction range is usually finite, this complexity will be bounded by \( N \) squared. Particle amalgamation algorithms may be especially useful in improving this aspect of the method.

In two dimensions, coexisting liquid and vapour are produced at the correct density and with visually realistic dynamics. In three dimensions phase separation occurs, and the liquid density is reproduced, however at temperatures closer to the critical point long equilibration times and a numerical ‘freezing’ prevents the correct coexistence densities from being reached. The system appears to become trapped in a local energy minimum. This may be due to insufficient resolution or lack of thermal fluctuations. It was confirmed, in two dimensions, that standard SPH techniques reproduce the van der Waals liquid-vapour transition correctly for a range of temperatures, provided the attractive part of the pressure is treated as longer range than the repulsive part.

Using the SPH solution of the momentum and energy equations with the van der Waals equation of state and the squared density gradient interface model we can produce temperature driven phase transitions with hydrodynamic coalesence. The kinetics of the phase transition shows three distinct regimes, an initial decomposition into liquid and vapour domains, followed by a coarsening of those domains, followed by a regime that appears to be dominated by the flow of droplets with no systematic change in the characteristic domain size except by coalescence caused by collisions.

In two dimensions volume and temperature quenches produce phases at the right densities. The shock-type response to volume expansion, and the development of worm-like structure in response to the quench are both expected behaviour.

Surface tension arises through the attractive part of the van der Waals equation of state and the van der Waals square gradient term. The existence of droplet oscillations is evidence of a surface tension, and is present even when the gradient term is not modelled. To quantitatively model the interface and the surface energy the contribution of the density gradient to the energy and momentum equations must be considered. The diffuse interface in the three dimensional simulations has a surface tension which is of the same nature as that in the van der Waals square gradient model. Using the water parameterisation the surface tension, found from the integral of the difference between parallel and normal pressure over the interface, is roughly a tenth of the experimental value. This discrepancy is explained by coarse spatial resolution. Actual surface tension across the interface is underestimated due to coarse spatial resolution. It is hard to see how to resolve this without modelling at close to atomic scale, or parameterising the interface, that is by empirically fitting the density gradient term to produce the correct surface tension.

Provided the resolution is fine enough, the density gradient can be modelled accurately. If the smoothing length is greater than the width of the interface then it will not be well resolved. This is a weak point of the method and is expected to affect any method of solving the continuum equations that relies on a coarse resolution grid. Errors in field interpolants near density gradients can be reduced by adaptive kernel methods. An advantage of diffuse interface models is that they remove the need to explicitly track the interface between phases, however in circumstances where the interface cannot be modelled at a very high
spatial resolution, the tracking and parameterisation of the interface may be the best computational solution.

A simple method was devised for improving the accuracy of the density gradient approximation, by adapting the particle spatial resolution to the density gradient.

10.3 Future directions

Future work on this topic could focus on improving the technique and on simulating more complex systems, including:

- Developing particle splitting and amalgamation algorithms, or mass transfer between particles, to better model phase separated systems with large density gradients;
- Driving condensation and boiling with boundary conditions;
- The use of constitutive relations and parameters obtained by molecular dynamics (MD) to model complex polymeric fluids;
- The modelling of interesting flow regimes, such as Rayleigh-Benard convection in three dimensions;
- Exploring the practical application of adaptive smoothing and higher particle resolution;
- Phase transitions in multiple component solutions;
- The use of different equations of state for modelling materials not well described by the van der Waals equation of state;
- Parallelisation of the smoothed particle code; and
- Parameterisation of the liquid-vapour interface to account for the reduction in surface tension due to coarse spatial resolution.

Validation of the SPH results against large-scale MD experiments would allow the errors associated with the numerical method to be isolated from the limitations of the continuum model. The quantitative limitations of the van der Waals equation of state could be bypassed by constructing a MD model using a potential such as Lennard-Jones with a well-understood equation of state and physical properties. The equation of state of this MD system and physical properties could be exactly matched in the SPH simulations, allowing the accuracy of the SPH approximation to be tested precisely against MD.

Accurate continuum modelling of phase transitions could be an input into the design of controlled phase transitions for the manufacture of membrane structures. Phase transitions have applications in manufacturing, for example the production of membrane structures by quenching a fluid into the spinodal region. Structured membrane materials have applications in many technological fields, including medicine.
The liquid-vapour phase transition is in many ways the simplest and easiest to study. Successfully modelling the kinetics and interface of liquid-vapour phase transitions is an important step towards modelling the kinetics of solidification.

Phase transitions to play a role in the formation of many biological structures. Appropriate equations of state and constitutive relations could be incorporated into a multi-phase SPH code in order to computationally explore the phase behaviour of biological molecules.

The accuracy is resolution dependent. One strength of the methodology we have presented is that a range of temporal and spatial scales may be investigated using this single modelling framework.

The smooth particle framework we have used can be extended to handle concentration gradients, arbitrary boundary conditions, and other equations of state. The model can be naturally extended to handle concentration, with the appropriate constitutive relations, which would allow the inclusion of osmotic flow. This simple extensibility to more complicated physical systems is the major strength of the SPH method, which promises to provide a single framework for the modelling of phenomena at a range of length and time scales.
Bibliography


