SMOOTHED PARTICLE SIMULATION OF THE LIQUID-VAPOUR PHASE TRANSITION

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DRAFT! Submitted for the award of Master of Applied Science

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Andrew Charles: Smoothed Particle Simulation of the Liquid-Vapour Phase Transition, DRAFT! Submitted for the award of Master of Applied Science, © July 2009

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The more we learn about the world, and the deeper our learning, the more conscious, specific, and articulate will be our knowledge of what we do not know, our knowledge of our ignorance. For this, indeed, is the main source of our ignorance - the fact that our knowledge can be only finite, while our ignorance must necessarily be infinite. — Karl Popper (Conjectures and Refutations: The Growth of Scientific Knowledge, 1963)

Dedicated to .
1939 – 2005
ABSTRACT

The vapour-liquid phase transition is a familiar phenomenon: the condensation of clouds to form rain, the evaporation of an open container of fuel and the boiling of a kettle. While the equilibrium thermodynamics of vapour-liquid phase transitions are well understood, the non-equilibrium thermodynamics and kinetics are still fields of current investigation.

Molecular dynamics simulations can provide realistic models that achieve phase transitions, but they are still limited in sizes and timescales smaller than the thermodynamic limit.

Smoothed Particle Hydrodynamics (SPH) is a meshfree particle method for solving continuous partial differential equations (PDEs). In SPH the system is represented by ‘particles’ whose properties are ‘smoothed’ over space. The natural application of SPH is to the equations of continuum mechanics. By carefully applying SPH interpolation formulae to the PDEs of continuum mechanics, a set of ordinary differential equations (ODEs) governing an n-body system of particles is obtained.

An advantage of SPH over grid methods is a more natural handling of deformation and free boundaries.

This work details the application of SPH to a continuum system modelled by the homogeneous van der Waals equation of state and linear constitutive relations for viscosity and heat flux. The SPH code has been tested in various droplet formation scenarios.

In a series of constrained expansion simulations, phase transitions are observed, and stable coexisting vapour and liquid phases, with densities in good agreement with theory, are produced.
Science may be described as the art of systematic over-simplification.
— Karl Popper, quoted in Observer, London, 1 Aug 1982

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ACRONYMS

SPH  Smoothed Particle Hydrodynamics
FDM  Finite Difference Method
NEMD  Non-equilibrium Molecular Dynamics
Part I

PART 1 - MASTERS THESIS
INTRODUCTION

Phase transitions are an interesting problem. The liquid vapour phase transition is in many ways the simplest and easiest to study.

In chapter 2 the continuum dynamic equations for a phase separating fluid are presented. A standard set of linear non-equilibrium constitutive relations are used, with the homogeneous van der Waals equation of state providing the equilibrium pressure.

In chapter 3 the smoothed particle technique is explained. While SPH is general enough to solve arbitrary PDEs, its natural application is to continuum mechanics and non-equilibrium thermodynamics. Methods of symmetrisation, which are essential to ensure conservation are detailed. An overview of the varied applications of SPH is also supplied.

In SPH, the fluid is represented by a set of particles. Each particle represents a macroscopic mass element, and carries mechanical properties of mass and velocity as well as thermodynamic properties such as temperature. The continuum equations of motion are converted into a set of equations describing forces between particles.

Chapter 4 describes an implementation of the smooth particle technique to the model presented in chapter 2. The symmetrisation techniques given in chapter 3 are applied to obtain the standard set of SPH continuum mechanics equations. Test calculations for the formation of a liquid drop, following [?] and [?] are given. Results of tests demonstrating energy conservation, and the formation of droplets after a quench are also presented.

Chapter 5 provides details of a simulation of the formation of a planar vapour-liquid interface.

Chapter 6 is a discussion of results. Good agreement with predicted densities - the phase diagram is reproduced almost in its entirety. The interface itself is poorly resolved, and does not increase in width close to the critical point to the extent predicted by diffuse interface theory.

In conclusion, future directions and interesting potential applications are outlined.
In this chapter the equations of change of a viscous, heat conducting, phase separating fluid are presented. The general equations for the time derivatives of density, momentum and internal energy are explained.

The pressure tensor is then decomposed and a model developed, using linear constitutive relations for heat flux and viscosity and the van der Waals equation of state (to first order in the density) for equilibrium pressure. This first order van der Waals model is the simplest to display vapour-liquid phase coexistence, with the densities of coexisting phases given by the Maxwell construction. The interface between coexisting vapour and liquid is expected to be diffuse, and to increase in width as the critical point is approached.

2.1 THE CONTINUUM EQUATIONS

The equations of Lagrangian continuum mechanics (Navier-Stokes equations) describe the comoving evolution of density \( \rho \), velocity \( \mathbf{v} \) and specific internal energy \( u \) in terms of the position \( \mathbf{r} \) and the gradients of the velocity \( \nabla \mathbf{v} \), pressure tensor \( \mathbf{P} \) and heat flux vector \( \mathbf{J}_q \). [? , Hoover 2006]

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

2.2 THE PRESSURE TENSOR

The equilibrium, or hydrostatic pressure \( p \) is a state variable, and is a function of local density and temperature, although more generally can include non-local terms that enter via the spatial gradients of \( \rho \) and \( T \). It usually assumed to be isotropic, but becomes a second rank tensor...
when gradient terms are included.

\[ P = p_{eq} + \Pi \] (2.4)

2.2.1 Equilibrium pressure (reversible?)

The equilibrium pressure has an isotropic and a non-isotropic component.

\[ p = p(\rho(r), T(r)) \] (2.5)

\[ p_{eq} = p(\rho(r), T(r)) + C \] (2.6)

C is the non-isotropic part of the equilibrium temperature, which depends on non-local contributions, usually expressed as spatial gradients. This is the expression used by Anderson (ref) and Felderhoff. Kortweg introduced this form of the gradient term in the pressure tensor but for binary mixtures. The idea for the gradient term appears to be due to van der Waals, Rayleigh and others.

\[ C = -M \left( \rho \nabla^2 \rho - \frac{1}{2} |\nabla \rho|^2 \right) + M \nabla \rho \nabla \rho \] (2.7)

2.2.2 Non-equilibrium pressure

The second term \( \Pi \) is the non-equilibrium pressure, usually associated with irreversible sources like viscosity. It is broken up into \( \Pi^{os} \), the symmetric traceless component associated with viscous shear, and \( \Pi^I \), the isotropic, irreversible pressure, associated with bulk stress. The last term \( \Pi^a \) is antisymmetric. Typically this term will only be non-zero when treating structured molecules, and in this work is neglected.

\[ \Pi = \Pi^{os} + \Pi^I + \Pi^a \] (2.8)

This implies that \( P = P^\text{transpose} \)

\[ \Pi^a = 0 \] (2.9)

2.3 Constitutive relations

2.3.1 The homogeneous van der Waals equation of state

The equilibrium pressure can be given by the van der Waals equation of state. It needs to be noted that this equation of state applies to homogeneous systems as it has no non-local contributions. In a non-homogeneous fluid the density gradient contributes to the free energy, and thus to the equilibrium pressure.

\[ p = \frac{\rho k_B T}{1 - \rho b} - a \rho^2 \] (2.10)
In this reduced form of the usual van der Waals equation of state, a and b play the role of the usual van der Waals attractive and repulsive parameters.

2.3.2 The van der Waals caloric equation of state

The temperature is given by the caloric van der Waals equation of state.

\[ T = \frac{u + a\rho}{k_b} \]  
(2.11)

2.3.3 Constitutive relations for viscosity

\[ \Pi^0s = -2\eta \nabla \nu^0s \]  
(2.12)

\[ \Pi^1 = -\eta_v \nabla \cdot \nu \]  
(2.13)

2.3.4 Constitutive relations for the energy equation

\[ J_q = -\lambda \nabla T \]  
(2.14)

2.4 The van der Waals equation of state

Describe equation 2.10 in more detail.

The van der Waals equation of state can be derived from statistical mechanics, by taking the mean field limit of an intermolecular potential composed of a short range, hard repulsion and a long range attraction.\[?\] Despite its simplicity, the van der Waals equation of state displays a realistic vapour-liquid phase transition. It is not considered accurate enough to model real materials quantitatively. [, Hill]

Nice three dimensional plot of \(p, \rho, T\)
Location of the spinodal, binodal and critical points
Figure 1: van der Waals equation of state for density (T=0.75)

Figure 2: van der Waals equation of state for pressure (T=0.75)
Below the critical temperature the van der Waals phase diagram exhibits loops, in which the pressure decreases with increasing density. This negative compressibility is not displayed by real substances in the bulk. Instead, the system separates into coexisting vapour and liquid phases, with pressures given by the Maxwell construction [, Huang, p45]. It is worth noting, though, that when a fluid is constrained to be homogeneous [, Verlet], van der Waals loops are displayed by molecular systems.

In the language of the Ehrenfest classification, the liquid vapour phase transition is a first order phase transition, in which the first derivative of the Gibbs free energy is discontinuous across the phase boundary.

The Maxwell construction is based on the recognition that both the vapour and liquid phase must coexist at equal mechanical pressure, with equal free energy and chemical potential.

The locus of curves obtained by applying the maxwell construction over the range of temperatures defines the binodal curve, which defines the boundary between the liquid and vapour phases.


2.6 THE LIQUID-VAPOUR INTERFACE

A brief outline of diffuse interface theory.

Early theories of gas-liquid interfaces, for example those of Young and Gauss, treated the dividing surface as infinitesimal, with properties such as surface tension inherent in the interface and physical quantities discontinuous across it. While others recognised that the interface was not in fact of zero thickness, it was van der Waals and Rayleigh who developed the first detailed gradient theories to predict the thickness of the interface.

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. A capillary pressure tensor, with constitutive relations based on the spatial gradient of the density, can be incorporated into the total pressure tensor in order to capture this interfacial model. For a concise review of diffuse interface theories see Anderson [?, Andersen 1998].
3

THE SMOOTHED PARTICLE TECHNIQUE

The SPH approximation is introduced, explained and derived. The properties of smoothing kernels are discussed. Interpolation formulae for arbitrary properties and for derivatives are developed. Symmetrisation of SPH expressions in the context of derivatives is introduced. Several applications of SPH are surveyed, with some historical perspective on the development of the method. Issues affecting stability, accuracy and consistency are briefly covered, in particular tensile instability, artificial viscosity, adaptive smoothing length, and normalisation.

3.1 INTRODUCTION TO SPH

SPH is a particle method for solving the continuum equations of motion. The most commonly modelled equations are the Navier Stokes equations for viscous fluid flow, or its variants. SPH is general enough, though, to solve arbitrary PDEs.

In SPH the fluid is represented by particles that carry properties including mass and velocity. The particles are interpolation points, and their movement represents the motion of the fluid. The partial differential equations of motion describing the fluid system are converted into a set of ordinary differential equations, from which the forces acting on each particle are calculated. Field properties at any point are calculated by a weighted summation over neighbouring particles. The system can then be solved as a standard n-body system.

3.2 DERIVATION OF THE SP APPROXIMATION

The essence of the SPH approximation is that using the integral representation, a continuous function is approximated by an integral over space. This integral over space is then approximated by a sum over discrete particles. [?]

The identity

\[ f(r) = \int f(r') \delta(r - r')dr' \]  

(3.1)

where \(\delta\) is the dirac delta function, defined as the limit of a sequence (ref), is known as the integral representation [].

Replace the dirac \(\delta\) function in equation 3.1 with a smoothing kernel with the property

\[ \lim_{h \to 0} W(r, h) = \delta(r) \]

The smoothing kernel also shares the normalisation property of the delta function.
\[ \int W(r, h) dr = 1 \]

A normalised Gaussian is one function that fits these criteria, and is natural 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 \( f(r) \) becomes

\[
f(r) = \int f(r') W(r - r', h) dr'
\]  

(3.2)

**Particle Approximation**

Having substituted a smoothed kernel for the delta function we proceed to approximate an integral over all space with an integral over a finite number of interpolation points.

\[
f(r) = \int \left[ \frac{f(r')}{\rho(r')} \right] W(r - r', h) \rho(r') dr'
\]

(3.3)

\[ dr' = dV' \]

\[ dV' = \frac{dm(r')}{\rho(r')} \]

If the matter is divided into small elements of mass \( m_i \) and positions \( r_i \), the contribution of the \( i \)th element to the integral is

\[
f(r_i) \frac{m_i}{\rho(r_i)} W(r - r_i, h)
\]

(3.4)

Summing these contributions, the approximation to the integral gives us the SPH particle approximation for any field variable at an arbitrary position

\[
f(r) = \sum_{i=1}^{N} m_i \frac{A_i}{\rho_i} W(r - r_i, h)
\]

(3.5)

, where the sum is over all particles. It is important to note that the smoothed value of a property at a point \( A(r) \) is not always equal to the property \( A \) of the particle located at \( r \). That is to say, in general, \( f(r_i) \neq f(j) \). An important exception to this is that \( \rho_i = \rho(r_i) \). In fact, some works [Hoover] attach physical significance to the difference between the two.
3.2.1 non-uniqueness of SPH interpolants

There are a multitude of possible smoothed approximations. Hoover uses an ‘f’ terminology to identify the first three ‘orders’ of sph approximation. The following three are obtained by applying the sph rule to \( \rho \), \( f \) and \( \frac{f}{\rho} \):

\[
\hat{f}_0(x) = \frac{1}{\rho(x)} \sum_b f(x_b) m_b W(x - x_b, h) \tag{3.6}
\]

\[
\hat{f}(x) = \sum_b f(x_b) \frac{m_b}{\rho_b} W(x - x_b) \tag{3.7}
\]

\[
\hat{f}_2(x) = \sum_b f(x_b) \frac{\rho(x)}{\rho_b} m_b W(x - x_b) \tag{3.8}
\]

3.3 DENSITY APPROXIMATION

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 ?? to the density.

\[
\rho(r) = \sum_{j=1}^{n} m_j W(r - r_j, h) \tag{3.9}
\]

The summation density approach explicitly conserves mass. The alternative is to make an SPH approximation of the continuity equation. [? , p547]

\[
\frac{d\rho}{dt} = \sum_i m_i v_{ij} \cdot \nabla W_{ij} \tag{3.10}
\]

The continuity density rule only gives the evolution of density with time - an initial density needs to be assigned either arbitrarily or using the summation method. Benefits of the continuity density approach include increased stability for highly incompressible flows. Summation density produces density gradients at free surfaces, which in turn produce pressure gradients. In modelling the vapour and liquid in coexistence density gradients are unavoidable.

3.4 THE SMOOTHING KERNEL

The smoothing kernel can be likened to the weight function used in the FEM. The kernel is always normalised, is always even and is usually radially symmetric. For computational efficiency it is preferable for the kernel to have finite extent.
The simplest smoothing kernel is the Gaussian kernel. It has the advantage of being continuously differentiable and easily normalised, but the disadvantage that it is not finite in extent.

\[
W(r) = \frac{1}{h^{d/2} \sqrt{\pi^d}} \exp\left(-\frac{r^2}{h^2}\right) \tag{3.11}
\]

The derivative of this Gaussian kernel (in one dimension) is

\[
\frac{dW(r)}{dr} = -\frac{2r}{h^2}W(r) \tag{3.12}
\]

The simplest smoothing kernel is the Gaussian kernel. It has the advantage of being continuously differentiable and easily normalised, but the disadvantage that it is not finite in extent.

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\]

The derivative of this Gaussian kernel (in one dimension) is

\[
\frac{dW(r)}{dr} = -\frac{2r}{h^2}W(r) \tag{3.12}
\]

**Lucy kernel**

3.4.1 **kernel gradient**

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.

\[
\nabla_i W(r_j) = \frac{\partial W}{\partial r} \frac{1}{r} |r_{ij}|
\]

where \( r = |r_{ij}| \) and \( r_{ij} = r_j - r_i \)

3.5 **Smoothed approximation of derivatives**

3.5.1 **Smoothed approximation of the gradient**

The smoothed approximation of the gradient of a field function can be taken by analytically differentiating the interpolation formula. [

\[
\nabla f(r) = \sum_{i=1}^{N} \frac{m_i}{\rho_i} f_i \nabla W(r - r_i, h) \tag{3.14}
\]

The grad operator can simply be taken inside and applied to \( W \) as all other terms 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 in Liu [? ]. In the current work periodic boundary conditions are used throughout, so boundary truncation is not an issue.

The density gradient is given by

\[ \nabla \rho(r) = \sum m_j \nabla W(r - r_j) \]  

(3.15)

3.5.2 Smoothed approximation of the divergence

The same technique used for the gradient operator can be used for the divergence.

3.6 Symmetrisation (derivatives, momentum)

3.6.1 Symmetrisation using the product rule

Symmetrisation techniques for SPH were pioneered by Monaghan [? , p544]. A compact treatment can be found also in Hoover [? , Hoover p88].

Using the product rule for gradients, we can arrange

\[ \nabla (\rho f) = \rho \nabla f + f \nabla \rho \]

as

\[ \nabla f(r) = \frac{1}{\rho} [\nabla (\rho f(r)) - f(r) \nabla \rho] \]  

(3.16)

Taking smoothed approximations of the each term, using equation 3.14 gives

\[ \nabla (\rho \hat{f}(r)) = \nabla \sum_j \frac{m_j}{\rho_j} f(r_j) W(r - r_j) \]  

\[ = \sum_j m_j f(r_j) \nabla W(r - r_j) \]  

(3.17)

(3.18)

Combining with 3.15 produces

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

(3.19)

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

\[ \nabla \hat{f}(r_i) = \sum \frac{m_{ij}}{\rho_{ij}} (f(r_j) - f(r_i)) \nabla \cdot W_{ij} \]

(3.20)
The smoothed particle technique

\[ m_{ij} = \frac{m_i + m_j}{2} \]

\[ \rho_{ij} = \frac{\rho_i + \rho_j}{2} \]

A similar identity holds for the divergence.

\[ \nabla \cdot (\rho F) = (\nabla \rho) \cdot F + \rho (\nabla \cdot F) \]

(3.21)

3.6.2 Symmetrisation using the quotient rule

To symmetrise the gradient of a second rank tensor field using the quotient rule, rearrange the quotient identity

\[ \nabla F = \rho \left( \nabla \frac{F}{\rho} + \frac{F}{\rho} \nabla \rho \right) \]

(3.22)

Take smoothed approximations of each term, using equation 3.15 for the density gradient and note that

\[ \nabla \hat{F} = \sum_j \frac{m_j F(r)}{\rho_j^2} \]

(3.23)

substitute these to obtain the symmetrised sph expression for \( \nabla F \)

\[ \nabla F = \rho \left[ \sum_j m_j \left( \frac{F_j}{\rho_j^2} + \frac{F}{\rho^2} \right) \nabla W(r - r_j) \right] \]

(3.24)

The corresponding rule for the divergence of a second rank tensor is

\[ \nabla \cdot F = \rho \left( \frac{\nabla \cdot F}{\rho} \right) + \frac{\nabla \rho \cdot F}{\rho} \]

(3.25)

3.7 Applications of SPH

SPH has been used to simulate many varieties of systems in fields including astrophysics [?], non equilibrium statistical mechanics and materials science.

In [? ] Hoover studies the entropy increase of an ideal gas undergoing confined expansion.

Muller uses SPH to generate visual models of blood flow for surgical simulations [?]. Smoothed particle techniques have been used to simulate droplet coalescence [?], arctic ice movement [?], high pressure die cast moulding [?] and interstellar gases [?]
3.8 Issues with SPH (Accuracy, Consistency)

- tensile instability
- artificial
- viscosity
- adaptive smoothing length (typical variation to keep constant number of neighbours, alternative variation to reduce influence near density gradients)
- normalisation
- density gradients ([? ])
- boundary truncation
- clumping
- symmetrisation

3.9 Modelling Surface Tension with SPH

Attempts to model surface tension using SPH have included: using a 'colour' function to measure interfacial curvature [? , Morris]; incorporating simple attractive terms in the equation of state [? , Hoover early paper]; incorporating separate 'particle-particle' forces to the force calculating [? ]; and using the homogenous van der Waals equation of state [? ].
The most natural approach is for the surface tension to appear as a consequence of the calculation of equilibrium pressure, as with Nugent and Posch’s approach. However it turns out that this can lead to instability, and causes the formation of tightly bound structures. By using a longer smoothing length (and hence a longer range) for the cohesive part of the pressure (and thus the attractive forces between particles) instabilities are reduced, and the behaviour of the particles more accurately reflects expected fluid behaviour.
4

SMOOTHED PARTICLE MODELLING OF A PHASE SEPARATING VAN DER WAALS FLUID

In this chapter the construction of an SPH approximation for solving the model outlined in chapter 2 is presented. Smoothed approximations for all terms are derived and presented. Where required tensors are detailed componentwise to expose the detail of implementation. This chapter comprises the development and exposition of the SPH model as implemented in code. A droplet condensation simulation matching results produced by (cite nugent and posch and Sigalotti) provides evidence that the model conserves energy, is stable, and is consistent.

4.1 THE MOMENTUM EQUATION

Applying equation 3.5 to the momentum equation (2.2) produces

\[
\frac{dv_i}{dt} = -\frac{1}{\rho_i(r_i)} \sum_j m_j \frac{P_j}{\rho_j} \cdot \nabla_i W_{ij}
\]  

(4.1)

where \( v_i \) is the velocity of particle i, and \( P_i \) is the pressure tensor of particle i calculated using the constitutive relations (below) on particle properties.

The force on particle i due to particle j is

\[
F_{ij} = \frac{m_i m_j P_j}{\rho_i \rho_j} \nabla_i W_{ij}
\]

while the force on particle j due to particle i is

\[
F_{ji} = \frac{m_i m_j P_i}{\rho_i \rho_j} \nabla_i W_{ij}
\]

Unfortunately \([?]\) using this level of approximation, unless \( P_{ij} = P_j \),

\[
F_{ij} \neq F_{ji}
\]

4.1.2 Symmetrised version of the momentum equation

The simplest way to guarantee momentum conservation is to ensure forces between particles are equal and opposite. Using equation 3.24 for the divergence of the pressure tensor, a symmetrised version of the
SPH momentum equation is obtained that guarantees pairs of particles exert equal and opposite forces on each other.

\[ \frac{dv_i}{dt} = \sum_{j=1}^{N} m_j \left( \frac{P_j}{\rho_j} + \frac{P_i}{\rho_i} \right) \cdot \nabla_i W_{ij} \quad (4.2) \]

### 4.2 Smoothed Approximation of Spatial Derivatives

The symmetrised forms of the spatial derivatives below ensures that for any two particles, \( \nabla v_{ij} = 0 \) when \( v_i = v_j \)

#### 4.2.1 Velocity Gradient

\[ (\nabla v)_i = \frac{1}{\rho_i} \sum_{j=1}^{N} m_j (v_j - v_i) \nabla W_{ij} \quad (4.3) \]

#### 4.2.2 Velocity Divergence

\[ (\nabla \cdot v)_i = \frac{1}{\rho_i} \sum_{j=1}^{N} m_j (v_j - v_i) \cdot \nabla W_{ij} \quad (4.4) \]

#### 4.2.3 Temperature Gradient

The temperature gradient is interpolated in the same manner as the velocity gradient

\[ \nabla T = \sum_j \frac{m_{ij}}{\rho_{ij}} (T_j - T_i) \nabla W_{ij} \quad (4.5) \]

### 4.3 The SPH Energy Equation

#### 4.3.1 The Work Term

Using the product rule for divergence and the above expression for the velocity gradient, a simple smoothed interpolant of the energy equation 2.3 can be constructed by applying the fo SPH approximation.

\[ \frac{du}{dt} = -\frac{1}{\rho} P_T : \sum_j m_j (v_j - v_i) \nabla W_{ij} \quad (4.6) \]

This suffers from a symmetrisation problem, which can be remedied by noting that

\[ \frac{-P_T}{\rho} : \nabla v = -\nabla \cdot \left( \frac{P}{\rho} \cdot v \right) + v \cdot \left( \nabla \cdot \frac{P}{\rho} \right) \]

[September 22, 2008 at 13:50]
Applying the quotient identity for divergences gives

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

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

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

and

\[
v \cdot \nabla \frac{P}{\rho} = v_i \cdot \sum_j m_j \frac{P_j}{\rho_j} \cdot \nabla W_{ij}
\]

to give a second potential SPH version of the energy equation

\[
\frac{du}{dt} = \sum_j m_j \frac{P_j}{\rho_j} \cdot v_j - v_i \cdot \nabla W_{ij}
\] 

(4.7)

Average equations 4.6 and 4.7 to obtain the final, symmetrised work term.

\[
\frac{du_i}{dt} = \frac{1}{2} \sum_j m_j \left( \frac{P_i^T}{\rho_i^2} + \frac{P_j}{\rho_j^2} \right) : \mathbf{v}_{ab} \nabla W_{ij}
\] 

(4.8)

4.3.2 The heat term

The SPH interpolant of the heat flux 2.14 is simply

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

Using the expression for the temperature gradient given above. This is symmetrised using the quotient identity to give the heat conduction contribution to the change in internal energy of

\[
\frac{du_i}{dt} = - \sum_j m_j \left( \frac{J_{qi}}{\rho_i^2} + \frac{J_{qj}}{\rho_j^2} \right) : \nabla W_{ij}
\] 

(4.9)

\[
\frac{du_i}{dt} = \frac{1}{2} \sum_j m_j \left( \frac{P_i^T}{\rho_i^2} + \frac{P_j}{\rho_j^2} \right) : \mathbf{v}_{ab} \nabla W_{ij} - \sum_j m_j \left( \frac{J_{qi}}{\rho_i^2} + \frac{J_{qj}}{\rho_j^2} \right) : \nabla W_{ij}
\] 

(4.10)
4.4 COMPONENTS OF THE PRESSURE TENSOR

4.4.1 Reduced units

\[ k_B^- = \frac{k_B}{m} \]

\[ \bar{a} = \]

\[ \hat{b} = \]

4.5 EVALUATION OF MODEL

4.5.1 Droplet formation at low temperature

Simulations were conducted using the same parameters as Nugent and Posch \cite{Nugent99} and Melean and Sigalotti \cite{Melean01}.

The clustering, ringed structure in figure 5 is typical of gaussian shaped kernels.

Plots of total energy, kinetic and internal energy are displayed for a non-thermostatted condensation simulation.

4.5.2 Droplet coalescence in response to quench
Figure 6: Starting positions
Figure 7: Positions at midway in the run
Figure 8: Stable positions. A droplet has formed.

Figure 9: Final smoothed density profile. Note that the smoothing property of the particles means the rung structures apparent in the particle plot are reduced.
Figure 10: Note the smooth exchange between kinetic and internal energy, and the very small error in total energy.

Figure 11: A low density, high temperature gas.
Figure 12: Immediately after the quench, the higher density regions begin to coalesce.
Liquid droplets form

Figure 13: Liquid droplets form
In this chapter a simulation of a liquid exposed to a sudden increase in available volume, and consequent drop in pressure and allowed to expand presented. The details required to replicate the experiment are given, and expected behaviour is discussed.

5.1 Description of Experiment

Figure 5.1 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).
Figure 14: The binodal curve in the temperature-density plane. The point outside the curve is the initial liquid state. The system is moved instantaneous to the point inside the curve by an increase in available volume, which decreases the total mass density.

5.2 SIMULATION PARAMETERS

Any details not made clear in chapter 4 go here.

5.2.1 Periodic boundary conditions

Periodic boundary conditions are implemented, as described in [? ]

5.3 THERMOSTAT

A scaling thermostat is used to keep the average temperature constant. The average temperature $T_A$ is calculated over all particles by

$$ T_A = \frac{1}{n} \sum_{i} T_i $$

For all particles the thermostat is applied by

$$ T_{i,\text{scaled}} = \frac{T_D}{T_A} T_i $$

(5.1)

5.4 NUMERICAL INTERGRATION

A leapfrog algorithm is used to advance the positions and energies of the particles in time.

5.4.1 SPH step procedure

1. check neighbour list reformation, and reform if necessary
2. calculate $x(t+1/2)$, $v(t+1/2)$, $u(t+1/2)$
3. calculate pair separations and compress neighbour list
4. calculate kernels, kernel gradients for all pairs
5. summation density
6. recalculate temperature with new density
7. call sphforce on ‘guess’ variables
8. update $x,v,u$
9. update temperatures
10. apply thermostat
11. apply boundary conditions
12. calculate smoothed values are particle locations

5.5 SMOOTHING LENGTHS

The justification for using a separate smoothing length for the attractive pressure is given.

5.6 INITIALISATION

5.7 EXPECTED BEHAVIOUR

Where on the phase diagram we start, and where we expect to end up based on the Maxwell construction.
Figure 15: The binodal curve in the density-pressure plane (red) and the equation of state (blue). The points of intersection of the two lines give the densities and pressures of the coexisting liquid and vapour.
Results for the simulation described in chapter 4 are presented. The time development of a typical run is detailed, and the final spread of densities plotted against the expected binodal curve. We find that the 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.

6.1 General Results
Figure 16: Near equilibrium coexistence densities, against the expected binodal curve.

Figure 17: A typical near-equilibrium planar interface
6.2 DETAILS OF A TYPICAL RUN

This section follows the time evolution more closely.

6.3 COEXISTENCE DENSITIES

The final, near-equilibrium densities for the result set.

- [Image: images/75_d.png]
- [Image: images/120_1.png]
- [Image: images/110_1.png]
- [Image: images/90_1.png]
RESULTS AND DISCUSSION

images/70_1.png

images/50_1.png

images/120_2.png

images/120_1.png

images/80_1.png

images/60_1.png

[September 22, 2008 at 13:30]
6.3 COEXISTENCE DENSITIES

[Images of data points and lines plotted on a graph, labeled as images/40_1.png, images/20_2.png, images/20_1.png, images/100_1.png, and images/100_0.png]
6.3 Coexistence Densities

[September 22, 2008 at 13:50]
6.3 COEXISTENCE DENSITIES

[September 22, 2008 at 13:30]
Comparison of the expected interfacial profile with the simulated profile.

6.4 INTERFACIAL PROFILE

Comparison of the expected interfacial profile with the simulated profile.
CONCLUSION

The smoothed particle technique is clearly capable of simulating the phase separation and formation of a planar interface in a two dimensional van der Waals-Navier-Stokes-Fourier fluid.

I recap the significant results, outline potential improvements to the implementation and outline how the inclusion of the gradient term could improve the system.
Part II

APPENDICES
A.1 LIST OF APPENDICES

Fortran code details C code details Matlab code details Literature survey

<table>
<thead>
<tr>
<th>SYMBOLS</th>
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Table 1: Autem usu id.
This thesis was built on the Classic Thesis \LaTeX template by Andre Miede. The notes below are his.

This thesis was typeset with \LaTeX using Hermann Zapf’s \textit{Palatino} and \textit{Euler} type faces (Type 1 PostScript fonts \textit{URW Palladio L} and \textit{FPL} were used). The listings are typeset in \textit{Bera Mono}, originally developed by Bitstream, Inc. as “Bitstream Vera”. (Type 1 PostScript fonts were made available by Malte Rosenau and Ulrich Dirr.)

The typographic style was inspired by ?’s genius as presented in \textit{The Elements of Typographic Style} [?]. It is available for \LaTeX via \texttt{CTAN} as “classicthesis”.

\textbf{Note:} The custom size of the textblock was calculated using the directions given by Mr. Bringhurst (pages 26–29 and 175/176). 10 pt Palatino needs 133.21 pt for the string “abcdefghijklmnopqrstuvwxyz”. This yields a good line length between 24–26 pc (288–312 pt). Using a “\textit{double square textblock}” with a 1:2 ratio this results in a textblock of 312/624 pt (which includes the headline in this design). A good alternative would be the “\textit{golden section textblock}” with a ratio of 1:1.62, here 312:505.44 pt. For comparison, \texttt{DIV9} of the \textit{typearea} package results in a line length of 389 pt (32.4 pc), which is by far too long. However, this information will only be of interest for hardcore pseudo-typographers like me.

To make your own calculations, use the following commands and look up the corresponding lengths in the book:

\begin{verbatim}
\settowidth{\abcd}{abcdefghijklmnopqrstuvwxyz}
\the\abcd\ % prints the value of the length
\end{verbatim}

Please see the file \texttt{classicthesis.sty} for some precalculated values for Palatino and Minion.

[September 22, 2008 at 13:50]
DECLARATION

Put your declaration here.

Melbourne, July 2009

Andrew Charles