Simulation and Theoretical Perspectives of the Phase Behaviour of Solids, Liquids and Gases using the Mie Family of Intermolecular Potentials

by

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Abstract

The Mie ($\lambda_r, \lambda_a$) intermolecular pair potential has been suggested as an alternative to the traditional (12,6) Lennard-Jones potential for modelling real system both via simulations and theory. Its implementation as a molecular-based equation of state for the fluid phase has led to accurate derivative thermophysical properties, which cannot be obtained when potentials of fixed exponents are considered. In this work, the effect the attractive and repulsive exponents have on the solid-liquid-vapour phase behaviour of this class of potentials is studied. A novel simulation technique, involving use of a direct interfacial methodology, is presented and is used to obtain the solid-fluid phase boundaries of monomer and chain systems of Mie potentials. The methodology is used in conjunction with simulation techniques for vapour-liquid and solid-vapour coexistence to determine the global phase behaviour of a number of potentials of this family. The application of the principle of corresponding states is discussed, with the focus of obtaining a unified view of the thermodynamic equilibrium properties of the Mie potential. A three parameter corresponding states model is presented, where a third parameter $\alpha$, which corresponds to the mean-field integrated energy is proposed. A unique relationship between the stable fluid range and $\alpha$ is presented, which can be used to predict exponent parameters of the Mie models that can be used to treat real systems. An equation of state (EOS) for the solid phase of Mie spheres and chains is presented by extending Wertheim’s thermodynamic perturbation theory (TPT1) to the solid phase. The SAFT-VR framework (on which TPT1 is based) is used in conjunction with the perturbation theory of Kang et al. for treatment of simple spherical solids to develop the SAFT-VR Mie solid EOS. This EOS is used with the recently presented SAFT-VR Mie fluid EOS of Lafitte et al., to solve for coexistence and determine the global phase behaviour of a host of Mie potentials of varying range of attraction. The accuracy of the theory is validated against the simulation results of this work and following this, the limiting behaviour of Mie chain systems is determined using the theory.
I, Nina Ramrattan, declare that the work in this thesis is my own, and that work from others has been referenced appropriately.

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Dedicated to Uncle
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Chapter 1

Scope of Work

The use of equations of state to determine phase equilibrium properties of fluids have accelerated the development of engineering tools in industry. Petrochemical industries for example, rely heavily on van der Waals-type equations of state for the design and operation of processes and in particular, the equilibrium properties obtained from these equations form the underlying basis of a large number of unit operations [1]. However, with respect to solid phases and solidification within industrial processes, there is little reliable technology available which can facilitate prediction of these events. As a point-wise example, this can be a particular challenge for the oil industry as unwanted precipitation in pipelines and refinery kit can result in costly and potentially hazardous effects [2]. Subsea pipelines, for example, experience extreme conditions of temperature and pressure in which the solidification of mixtures of crude oil components is a serious issue to address. Similar examples can be drawn in other industries such as the pharmaceutical, food and personal care products. The development of reliable equations of state for the prediction of the solid-fluid transition boundaries of compounds of relevance to industry can therefore be seen as a viable option to address such challenges.
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Probably the most obvious method of tackling such an issue is by experimental analysis. Correlating experimental data to an equation of state is indeed the most accurate method for the determination of solid-fluid phase transitions. Experimental measurements of melting points however, possess a number of challenges in terms of cost and time. The extreme operating conditions required to observe some of these phase transitions can be expensive. Additionally, the magnitude of experiments required for a robust correlation over a reasonable range of data can be time intensive.

Rather than approaching the problem by treatment of bulk systems through experimental analysis, an alternative is to determine phase equilibrium properties from a molecular modelling approach; by computer simulation or by development of theoretical molecular-based equations of state. At this level, the interactions between the molecules in the real system is approximated to a mathematical molecular model. Following the statistical mechanical machinery, the microscopic properties can be related to bulk observable equilibrium properties. The cost and time required for computer simulations are considerably reduced by comparison to experiments and even further reduced for theoretical equations of state. Table 1.1 summarises updated, estimated time and cost (equipment and labour) associated with a single vapour-liquid equilibrium point through the three forms of analysis [3].

Table 1.1: Cost and time estimates comparing the experimental, computer simulation and theoretical determination of a single data point for vapour-liquid equilibrium.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Time</th>
<th>Cost per annum (£)</th>
<th>Cost (£)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>1 week</td>
<td>$10^5$</td>
<td>1918</td>
</tr>
<tr>
<td>Simulation</td>
<td>6 hours</td>
<td>3.5x10^4</td>
<td>24</td>
</tr>
<tr>
<td>Theory</td>
<td>1 minute</td>
<td>1.5x10^4</td>
<td>0.029</td>
</tr>
</tbody>
</table>

It is obvious from this brief estimation, that there are vast advantages to determining equilibrium properties through computer simulation or theoretical analysis. While there has been significant advances in developing molecular models and theories for
fluids [4], comparatively less progress has been made for the solid phases and determination of solid-fluid transitions in the same context. Here, a very successful model first proposed by Wertheim is followed to explore its use in the development of an EOS for solid-fluid boundary determination. In doing so, a fast solution to determining these boundaries is presented. In the following sections more details are provided related to the study on a molecular level and its manifestation of the bulk thermodynamics equilibrium properties through application of statistical mechanics.

1.1 Statistical Mechanics

Statistical mechanics provides the link between the macroscopic properties of substances and the molecular-level interactions [5]. The objective of this section is to present an overview of the relevant equations which are used to describe the molecular interactions of particles and their manifestation in the observable properties of macroscopic systems.

The thermodynamic state of a macroscopic pure component can be defined by a small set of parameters e.g., the number of particles ($N$), the temperature ($T$) and the pressure ($P$) of the system. All other thermodynamic properties can be obtained from fundamental thermodynamic relations and knowledge of the equation of state. Characterisation of a thermodynamic state therefore is dictated by a few state variables ($NPT$) rather than by a unique mechanical state of the particles in the system. On the other hand, microscopic properties are dependent on the instantaneous state of a system. Averages of all the instantaneous states must be taken to obtain the measured (average) bulk property. In Section 1.3 the type of averaging for different simulation methods is explained in greater depth.

Given sufficient time a particle defined by its position and momentum will occupy a phase space with a probability distribution function which is independent of time. To obtain the functional form of the distribution function, in statistical mechanics it
is useful to consider the concept of an ensemble. Rather than considering a single
system which evolves in time through a set of states in phase space, an infinite number
of replicas of the system each with its own distribution of allowable microstates (i.e.,
position and momenta) which are restricted to the macroscopic thermodynamic condi-
tions (such as \(N, P\) and \(T\)) are considered. Each state of all these exact copies is called
an ensemble. Each ensemble is essentially a collection of points in phase-space, it will
evolve over time and consequently the phase space density will also change. The state
properties chosen give rise to four main ensemble types in chemical thermodynamics;

1. Microcanonical \(NVE\), closed system with constant number of particles, volume
and total energy

2. Grand Canonical \(\mu VT\), open system with constant temperature, volume and
chemical potential

3. Canonical \(NVT\), closed system with constant number of particles, volume and
temperature

4. Isobaric/isothermal, \(NPT\), closed system with constant number of particles,
pressure and temperature

If for example, the canonical ensemble is considered, the probability distribution of
states will follow a Boltzmann distribution given by;

\[
P_N(E_i) = \frac{e^{(-\beta E_i)}}{\sum_i e^{(-\beta E_i)}},
\]

(1.1)

where \(E_i\) is the energy of state \(i\) of the particles in a system, \(P_N\) is the probability of
the \(N\) particles existing at the energy state \(i\) and \(\beta = \frac{1}{k_B T}\).

The denominator is a normalisation factor that represents the sum over all allowable
states of the distribution. It has a key role in statistical mechanics as it allows a
convenient way to express all classical thermodynamic variables, this is known as the canonical partition function \(Q_{NVT}\),

\[
Q_{NVT} = \sum_i e^{(-\beta E_i)}, \tag{1.2}
\]
where the summation extends over \(i\) allowable energy states. The ensemble averaged energy \(<E>\) over all \(i\) states therefore is,

\[
<E> = \sum_i E_i e^{(-\beta E_i)}/Q_{NVT}. \tag{1.3}
\]

\(Q_{NVT}\) can be constructed to a probability distribution in terms of phase space continuum and the summation of the kinetic and potential energies which is represented by the Hamiltonian operator \(\mathcal{H}\). This is given by;

\[
Q_{NVT} = \frac{1}{\hbar^{3N}N!} \int \cdots \int e^{[\beta \mathcal{H(r^N,p^N)}]}/d\mathbf{r}^N, d\mathbf{p}^N, \tag{1.4}
\]
where \(\mathbf{r}^N\) represents the position of \(N\) particles and \(\mathbf{p}^N\) is their momenta. The factor \(\hbar^{3N}N!\) has been added to account for the phase-space volume of each quantum state and the indistinguishability of particles.

In the isothermal-isobaric ensemble, the probability density is proportional to;

\[
P \propto e^{-\beta(\mathcal{H(r^N,p^N)}+PV)}, \tag{1.5}
\]
which leads to the appropriate partition function,

\[
Q_{NPT} = \frac{1}{\hbar^{3N}N! V_0} \int dV \int e^{[\beta \mathcal{H(r^N,p^N)}+PV]}/d\mathbf{r}^N, d\mathbf{p}^N, \tag{1.6}
\]
where in order for \(Q_{NPT}\) to be dimensionless a unit of volume \(V_0\) must be chosen.

In order to have a physical understanding of the state of the system, the partition function is related to the Helmholtz free energy \((\mathcal{A})\) of the system. To do this the
derivative of the partition function \( Q_N \) (Equation (1.2)) with respect to \( \beta \) is used:

\[
\frac{\delta Q_N}{\delta \beta} = - \sum_i E_i e^{-\beta E_i}.
\] (1.7)

Moreover, for simple systems the internal energy \( U \) is equal to the average energy \( < E > \), therefore (Equation 1.3),

\[
U = < E > = \frac{\sum_i E_i e^{-\beta E_i}}{Q_N}.
\] (1.8)

On substitution of Equation (1.7) into Equation (5.11),

\[
U = -(\frac{\delta Q_N}{\delta \beta}) \frac{1}{Q_N} = - \frac{\delta \ln Q_N}{\delta \beta},
\] (1.9)

and by substituting this equation into the Gibbs fundamental relation,

\[
\frac{A}{T} = \frac{U}{T} - S,
\] (1.10)

where \( S \) is the entropy of the system. By differentiating with respect to \( T \);

\[
\frac{\delta}{\delta T} \left( \frac{A}{T} \right) = - \frac{U}{T^2} = \frac{1}{T^2} \left( \frac{\delta \ln Q_N}{\delta \beta} \right) = -k_B \left( \frac{\delta \ln Q_N}{\delta T} \right).
\] (1.11)

So the Helmholtz free energy \( (A) \), can be determined from the canonical partition function and temperature alone,

\[
A = -k_B T \ln Q_{NVT}.
\] (1.12)

Thus, the Helmholtz free energy provides the link between the molecular system and the bulk thermodynamic properties in the \( NVT \) (canonical) ensemble. All other macroscopic properties of the system can be determined from standard thermodynamic relations.
Thus far the link between the molecular and bulk properties has been elucidated. The interacting forces between the particles however, have yet to be discussed. These intermolecular models can be determined from quantum mechanics (e.g., ab intio calculations) or by fitting from experimental measurements of the thermophysical properties. The full interaction energy ($\Phi$) can be defined as a summation of the forces/energies of individual atoms due to an external field ($\phi(r_i)$), followed by a pairwise interaction between molecules ($\phi(r_i, r_j)$), followed by a triplet contribution, followed by a many body interaction:

$$
\Phi = \sum_{i} \phi(r_i) + \sum_{i} \sum_{j>i} \phi(r_i, r_j) + \sum_{i} \sum_{j>i} \sum_{k>j>i} \phi(r_i, r_j, r_k) + \ldots \quad (1.13)
$$

For the purpose of solving the macroscopic properties of a system, this full potential proves to be too computationally taxing to deduce and it is typical to truncate the interaction and propose an effective potential by assuming pair-wise additivity,

$$
\Phi \simeq \sum_{i} \sum_{j>i} \phi^{eff}(r_i, r_j; \theta) \quad (1.14)
$$

where $\theta$ represents a parameter set specific to a given potential. This has been discussed in greater depth in several texts [6] [7] [5]. The assumption is a common one in molecular physics, as little is known about the 3rd, 4th and higher-body interactions. While there is no rigorous proof, it proves to be accurate particularly with larger system sizes [8]. There have been multiple pairwise interaction potential functions studied throughout the 20th century. In the following section some of the best known potentials and the contributions each model has made to phase behaviour description is reviewed.
1. Scope of Work

1.2 Intermolecular Pair Potentials

There have been numerous intermolecular potential models developed to describe molecular interactions with the common focus of finding a general potential which, with parameter fitting, can reproduce experimentally observed phase behaviour for a host of real molecular systems of a given classification, e.g., noble gases, polar solvents etc.

Due to its simplicity and range of application by far the most studied potential by the early simulation community is the hard-sphere intermolecular potential model. Its functional form is expressed mathematically as:

\[
\phi_{HS}(r) = \begin{cases} 
\infty & r \leq \sigma \\
0 & r > \sigma,
\end{cases}
\]  

(1.15)

where \(\sigma\) corresponds to the particle diameter, \(\phi(r)\) is the intermolecular potential and \(r\) is the centre-centre inter particle distance between two particles. At least 22 equations of state have been published for this potential [9] and of these equations the most widely implemented have been the Carnahan and Starling EOS [10] for the fluid phase and the Hall EOS for the solid phase [11]. These equations have provided vital reference systems for many perturbation theories of soft core systems [12] [13] [14] [15] to name a salient few. Hard sphere models have also been particularly useful to the determination of solid-fluid and solid-solid phase transitions in simulation studies. They have been important for validating the stability of crystal structures for dumbells [16], nonlinear triatomic molecules [17], mixtures of benzene and hexafluorobenzene [18] and n-alkanes [19] [20] [21]. In particular the relative stability of the face centred cubic (fcc) crystal with respect to the hexagonal close packed (hcp) crystal was clarified by analysis of the free energy of the hard spheres [22]. A disadvantage of the hard-sphere model is that it is athermal i.e., no attractive interaction is incorporated into the model and therefore hard-sphere systems do not exhibit vapour liquid coexistence.
The square well intermolecular potential model is the simplest hard potential incorporating attractions. Its functional form is given by,

\[ \phi^{SW}(r) = \begin{cases} 
\infty & r \leq \sigma \\
-\epsilon & \sigma < r \leq \lambda \sigma \\
0 & r > \lambda \sigma, 
\end{cases} \]  

(1.16)

where \( \lambda \) is a parameter that defines the range of the attraction of the potential well of depth \( \epsilon \). As attractive forces are taken into account in the SW model, it is possible to calculate vapour-liquid-solid transitions with this potential. Similar potentials such as the Yukawa [23] and Sutherland [24] have been proposed; these are variations of the square well potential in that they are hard spheres with attractions, though the attractive tails differ in shape. The discontinuous nature of these potentials is not truly representative of the behaviour of real molecular systems and more sophisticated continuous models such as the Buckingham [25] or Lennard-Jones (LJ) potential [26] are preferred for modelling of real compounds.

The LJ model is a continuous potential which possesses a functional form which is thought to describe more accurately the interaction of real molecules by comparison to the discontinuous potentials; SW, Yukawa, etc. It is given by [26];

\[ \phi^{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]. \]  

(1.17)

The attractive exponent was determined from the London theory of dispersion [27] [28]. The repulsive exponent was given the arbitrary value of 12 for computational simplicity. The model itself has now become a benchmark through which many other models are compared as there is substantial data available in the literature for comparisons to be made. With respect to contributions to theoretical developments, the original framework of the statistical associating fluid theory (SAFT) for example, which is a theoretical EOS based on Wertheims perturbation theory, was first presented by
application of the LJ potential [29] [30]. In recent years, from a simulation perspective, the potential has also been implemented in numerous studies and is typically used to test the accuracy of novel simulation methodologies as there is appreciable data available for comparisons to be made [31] [32] [33] [34] [35]. Extensive simulation data for the LJ model have also been used to present correlations for the free energy of the LJ monomer system, the most notable being the works of van der Hoef [36] for the solid and Johnson et al [37] for the fluid. Such equations prove to be accurate over a wide range of conditions and have been useful in determining the VLE and SFE boundaries of chain systems in combination with the Wertheim’s thermodynamic perturbation theory for fluid and solid states [38]; this will be discussed in greater depth in Chapter 4. Although the LJ potential has proven to reproduce accurately the thermophysical properties of simple systems it is less accurate for describing more complex systems and therefore for such cases a more complex functional form needs to be considered.

The Mie intermolecular potential has long been recognised as superior to the LJ model as the additional number of parameters present in the function form are thought to allow for greater flexibility of the potential. This potential is mathematically expressed by [39]:

$$\phi_{Mie}(r) = \left( \frac{\lambda_r}{\lambda_r - \lambda_a} \right) \left( \frac{\lambda_r}{\lambda_a} \right)^{\lambda_a/(\lambda_r - \lambda_a)} \epsilon \left[ \left( \frac{\sigma}{r} \right)^{\lambda_r} - \left( \frac{\sigma}{r} \right)^{\lambda_a} \right]$$  \hspace{1cm} (1.18)

where $\lambda_r$ is the repulsive exponent and $\lambda_a$ is the attractive exponent of the potential.

The Mie intermolecular potential actually predates the LJ model; it was first suggested by Gustav Mie in 1903 [39]. The LJ potential is essentially a functional form of the Mie with a reduction in the number of degrees of freedom by using a fixed set of exponent parameters 12 and 6. These additional degrees of freedom is what is thought to make the Mie superior to LJ when describing the phase behaviour of complex systems. Mie force fields have been recently shown in a simulation study by Potoff and Bernard-Brunel [40] to be more accurate in the description of the phase
behaviour of \(n\)-alkane systems and perfluoroalkane systems. These authors noted that the real failure in using the LJ model is that regardless of the parameterisation of the potential it is not possible to obtain good descriptions of the vapour pressures while still obtaining an accurate density saturation curve. This is unsurprising as the vapour pressure had not traditionally been of particular interest in the development of robust force fields. In a more recent study by Aveñáno et al. [41] a case study of the \(\text{CO}_2\) molecule is presented, as well as a review of all former efforts to attempt to model this system with a LJ potential. None of the multiple parameterisations discussed are capable of reproducing all the thermophysical and transport properties of the system. A single-site coarse grained model with a Mie force field is proposed in the work of Aveñáno in which all thermophysical properties evaluated are in good agreement with experimental data. These results showcase the advantages of using the Mie potential over the traditional LJ.

In addition to fitting to experimental data for molecular model development, there has been a conscious effort to understand on a more fundamental level, how the Mie potential can be used in the classification of molecular systems. The works of Okumura and Yonezawa [42], Orea et al. [43] and Bulavin and Kulinski [44] in particular account for this by application of the principle of corresponding states to several thermophysical properties of a host of Mie potentials of varying range of exponents. This aspect is discussed in greater depth in Chapter 3. Much of the current studies on the Mie potential have been aimed at fitting of parameters to experimental data and application of the corresponding states (CS) principle to Mie fluids; only a few studies however [45] [46] [47], have attempted to determine the solid-fluid behaviour of Mie systems. The scarcity of studies in this region of the phase diagram accounts for the limited understanding of the global phase behaviour (SFE, VLE and SVE) of Mie systems. As such, the true capability of the Mie potential for prediction of the phase behaviour of more complex systems has yet to be explored. It is an aim of this work to address this and thereby provide an insight into the phase behaviour of this family of systems.
1.3 Computer Simulations

Computer simulation allows for the exact determination of the macroscopic thermophysical properties through averaging of the instantaneous thermodynamic properties of various microstates of the specific phase space. Simulations thus, provide a means for validating and analysing theoretical models. It is through this validation that reliable theoretical models can be proposed to approximate better the behaviour of real systems. In essence computer simulations are very similar to an experimental procedure in the sense that a system of a given size must be defined (\(N\) number of particles), and fixed thermodynamic relevant properties such as temperature and pressure must be applied to it. Once a simulation is started the system is allowed to equilibrate before averaged equilibrium output properties can be obtained. There are two main methods of performing a molecular simulation; Molecular Dynamics (MD) and Monte Carlo (MC). The MD approach implements time averaging for the computation of thermodynamic properties while MC uses ensemble averaging. An MD and MC simulation with identical input conditions (e.g., \(NVT\)) produce the same averaged output properties in the thermodynamic limit, as given by the ergodic hypothesis [48]. This hypothesis states that in an MD simulation, the time averaged thermodynamic property of a fluid, e.g., the free energy \(A\), given a sufficiently long time at which the thermodynamic limit is approached, is independent of the initial configuration of the simulation. Therefore the time-averaged result would not change if for example, a large number of simulations of the same conditions (\(NVT\)) but different starting configurations are used. Averaging the free energy of the fluid over all possible initial configurations rather than time is known as an ensemble average. Therefore averaging over the time evolved phase-space coordinates is equivalent to averaging over all initial phase-space coordinates in the thermodynamic limit [48].

In this section an overview of the two simulation methods is presented. In this work MD is used and therefore more emphasis is placed on this algorithm while the MC
1. Scope of Work

method is only briefly summarised.

1.3.1 Monte Carlo (MC) Method

MC is a stochastic method to generate a sequence of configurations by successive random displacements. By doing so, it is possible to sample configurational space for a given ensemble and from this, obtain ensemble-averaged macroscopic properties. Typically, configurational space is sampled by generating successive states that are determined by specifying random positions of particles. Rather than exploring all phase space it is possible to reduce this to only an area of interest which is known as importance sampling. This type of sampling is used in the Metropolis MC method [49] which is a widely used variation of MC. It is particularly useful as it reduces the timeframe of simulations. The movement of a particle follows a random walk in such a way that the probability of the position of a particle \( r^N \), is proportional to the Boltzmann factor \( e^{-\beta U(r^N)} \). As the probability of a configuration is a function of the Boltzmann factor, the instantaneous thermodynamic property \( \kappa(n) \) is also a function of this. Ensemble averaged thermodynamic properties \( \langle \kappa \rangle \) are therefore taken as the average of instantaneous properties over all possible configurations, given by:

\[
\langle \kappa \rangle = \frac{\sum_n \kappa(n)e^{-\beta U(r^N)}}{\sum_n e^{-\beta U(r^N)}}.
\]

Further details on this technique and applications can be found elsewhere [48] [50].

1.3.2 Molecular Dynamics (MD)

MD simulations mimic molecular motion by solution of Newton’s equations of motion in an isolated closed system of \( N \) particles of mass, \( m \), within a volume, \( V \). By solving classical Newtonian mechanics it is possible to obtain the position and momenta of each particle in the closed system which are key to determining observable properties of the system [50] [48]. As the core principle of MD follows classical mechanics, the acceleration of a particle \( i \) in a system can be expressed as a function of the force
acting on the particle which is given by,

$$\frac{d^2 \mathbf{r}_i(t)}{dt^2} = \frac{1}{m_i} \sum_{i<j}^N \mathbf{F}_{ij}(r_{ij}(t)), \quad (1.20)$$

where $\frac{d^2 \mathbf{r}_i(t)}{dt^2}$ is the acceleration of particle $i$, $m_i$ is the mass of that particle and $\mathbf{F}_{ij}(r_{ij}(t))$ is the force between particles $i$ and $j$ at a distance $r_{ij}(t)$ at a time $t$. In using this equation pairwise additivity of a classical system of interacting particles is assumed. For each molecule, $i$ the acceleration at a particular time $t$ is approximated as a function of the summation of the interaction force between the particle $i$ and its pairing to all other particles $j$ in the system. As the particles are interacting with each other via an intermolecular pair potential $\phi_{ij}(r)$ the force can be determined directly from the derivative of the intermolecular potential energy,

$$F_i(t) = \sum_{i<j}^N \mathbf{F}_{ij}(r_{ij}(t)) = -\sum_{i<j}^N \nabla \phi_{ij}(r_{ij}(t)) \quad (1.21)$$

where $-\nabla \phi_{ij}(r_{ij}(t))$ is the derivative of the intermolecular potential energy between particles $i$ and $j$ at a distance $r_{ij}$ at a particular time $t$. Typically in simulations a cutoff radius is implemented for which the interactions outside this defined distance are ignored because the interacting forces are considered to be negligible by comparison to the interaction of the particles within the radius. The choice of the cutoff radius is an important one as one which is too small may result in inaccuracies in the force calculation while a radius which is unnecessarily long is computationally too taxing.

In an MD simulation Equations (1.20) and (1.21) are coupled to determine the force and acceleration, which is now required to integrate the equations of motion to determine the trajectories for each particle in the system at each increment of time. There are several algorithms available for this integration, of which the Verlet algorithm is one of the most popular and the chosen algorithm used in the molecular dynamics package DL_POLY [51] used in this work.
Verlet Algorithm

This method is based on positions at time $t$, acceleration, and the positions of the particles from the previous step, $r(t-\delta t)$. The derivation starts with a Taylor expansion of the coordinates of a particle at time $t$,

$$r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t + \frac{F_i(t)}{2m} \Delta t^2 + ....$$  \hspace{1cm} (1.22)

similarly,

$$r_i(t - \Delta t) = r_i(t) - v_i(t)\Delta t + \frac{F_i(t)}{2m} \Delta t^2 + ....$$  \hspace{1cm} (1.23)

If these two equations are summed,

$$r_i(t + \Delta t) = 2r_i(t) - r(t - \Delta t) + \frac{F_i(t)}{m} \Delta t^2 + ....$$  \hspace{1cm} (1.24)

Therefore, the trajectory of the particle can be determined from the intermolecular force acting on it and knowledge of the particles current position as well as its position in the previous time step i.e., the Verlet algorithm does not require the velocity to compute the motion of the particle.

The stepwise procedure for a MD program can be summarised as follows [50] [48];

1. Initialisation: At the start of a simulation as the force calculation has yet to be performed, the particles of a given configuration are initially assigned random velocities. These velocities are then rescaled to ensure the consistency of the kinetic energy of the system with the required temperature.

2. Equilibration: The force is determined from Equation (1.21) and using the Verlet algorithm (Equation (1.24)) the equations of motion are integrated to assign new positions and velocities of each particle. This loop is restarted until equilibration is attained.
3. Sampling: The force is determined from Equation (1.21) and using the Verlet algorithm (Equation (1.24)) the equations of motion are integrated to assign new positions and velocities of each particle. Samples of averages are collected to determine the properties at a given time step. The loop is restarted at a subsequent time step.

**Thermostats and Barostats**

As in experiments, in order to maintain a system at constant conditions, thermostats and/or barostats need to be implemented in simulations to minimise fluctuations of temperature and pressure. In this work the Nose-Hoover thermostat [52] is used for simulation in the canonical ensemble ($NVT$). By rescaling the velocities, the thermostat acts like a heat bath which ensures the system temperature is maintained close the required value. This is done by modifying the equations of motion such that:

\[
\frac{dr_i(t)}{dt} = v_i(t),
\]

(1.25)

and

\[
\frac{dv_i(t)}{dt} = \frac{F_i(t)}{m} - \chi(t)v_i(t),
\]

(1.26)

where $\chi$ is the friction coefficient which is controlled by a first order differential equation;

\[
\frac{d\chi(t)}{dt} = \frac{N_f k_B}{Q} (T(t) - T_{req}),
\]

(1.27)

where $Q = N_f k_B T_{req} T_T^2$ is the effective ‘mass’ of the thermostat, $T_T$ is a specified time constant, $N_f$ is the number of degrees of freedom of the system, $T(t)$ is the instantaneous temperature and $T_{req}$ is the required temperature.
For the isothermal-isobaric ensemble ($NPT$) the Hoover barostat which maintains the required pressure ($P_{\text{req}}$) is coupled to a Nose-Hoover thermostat [53]. As with the thermostat, the equations of motion are modified as follows:

$$\frac{dr_i(t)}{dt} = v_i(t) + \eta_r(r_i(t) - R_0),$$

(1.28)

$$\frac{dv_i(t)}{dt} = F_i(t) \frac{m}{m} - [\chi(t) + \eta(t)]v_i(t),$$

(1.29)

$$\frac{d\chi(t)}{dt} = \frac{N_f k_B}{Q} \left( T(t) - T_{\text{req}} \right) + \frac{1}{Q} \left( W \eta(t)^2 - k_B T_{\text{req}} \right),$$

(1.30)

$$\frac{d\eta(t)}{dt} = \frac{3}{W} V(t)(P(t) - P_{\text{req}} - \chi(t)\eta(t),$$

(1.31)

$$\frac{dV(t)}{dt} = [3\eta(t)]V(t),$$

(1.32)

where, $W = N_f k_B T_{\text{req}} T_P^2$ is the effective ‘mass’ of the barostat, $\eta$ is the barostat friction coefficient, $R_0$ is the system centre of mass, $T_P$ is the specified time constant for the pressure fluctuations and $V$ is the volume of the system.

1.4 Theoretical Developments

Although simulations can be used to solve the thermophysical properties of a molecular model accurately, they can be time consuming in the determination of phase transitions. This is of greater concern for simulations of the solid-fluid region due to the complexity of the techniques required to stabilise solid phases by simulation. It is prudent therefore, to consider the development of reliable equations of state also, as they can provide results which are significantly faster by comparison to simulations (refer to Table 1.1). Theories also provide the advantage of easy implementation into programs, an aspect which is vital for modelling of industrial processes [54].
There are multiple routes through which theories of fluids can be developed. Cubic equations of state such as the Peng-Robinson [55] and Soave-Redlich-Kwong [56] are widely used in the petrochemical industries. Semi-empirical equations such as that of Johnson et al [37] and of Kolafa and Nezbeda [57] which are specific to the LJ potential and use computer simulation data, are also well known examples. Perturbation theory approaches, which are inherently derived from statistical mechanics, are also viable options. Wertheim’s perturbation theory [58] [59] [60] [61] [62] [63] in particular has been the basis for the development of the statistical associating fluid theory (SAFT) [29] [30]. This molecular-based equation of state was used early on to model over 100 pure components and 60 binary mixtures [64] [65]. To date, there are multiple versions of SAFT available, however, in this work the variable range version SAFT-VR [66] [67] will be discussed in greater depth. This contribution in particular has proven to be a versatile tool for the prediction of thermophysical properties as all intermolecular potentials which possess variable ranges e.g, Yukawa, [68] LJ [69], Mie [70] and square well [71] [72] to name a few, have been applied to SAFT-VR to predict a range of real systems. More detailed explanations on the different versions of SAFT and its development can be found in several review works by Muller and Gubbins [54], Economou [73] and a recent text by Kontogeorgis and Folas [4].

Theoretical equations of state for the solid phase and determination of SFE are, by comparison, less prevalent. Density functional theory (DFT) is one such example that has been used to determine SFE [74] [75] [76] [77]. Another option is to use cell theory for the solid phase and a theoretical equation of state for the fluid phase. On comparison to Monte Carlo simulation data, the use of cell theories with fluid equations of state appear to be more accurate than the use of DFT [78]. This approach has in particular been used successfully to study several different systems including; hard spheres [79], LJ spheres [80], hard dumbbells [78], hard chains [19], mixtures of hard spheres [81] [82], mixtures of LJ spheres [83] ionic systems [84] and a four site model for water [85] to name a few. In this work however, rather than use cell theory, we
choose instead to develop an equation of state that can be applied to the solid phase for the Mie potential using perturbation theory.

With the success of perturbation theories to describe fluid state properties it is logical to attempt to apply the method to solid state systems, as was first carried out by Longuet-Higgins and Widom [86]. In this thesis, the extension of Wertheim’s theory to the solid phase, originally proposed by Vega and McDowell [87] is used to determine the solid equation of state for tangentially bonded fully flexible chains interacting through a Mie potential. The extension of Wertheim’s theory to the solid phase has been applied to several potentials, the most complex of which is the LJ and when compared to simulation data the accuracy of the theory is confirmed. A crucial contribution to the development of this EOS is determining the free energy of the monomer system. In the SAFT-VR treatment [66], perturbation theory is used to split the potential into a reference hard sphere and attractive perturbation terms which are then summed, and in this work the same methodology is adopted; in SAFT-VR fluid the Barker and Henderson split is followed. In fluids, the Weeks Chandler Anderson (WCA) [88] perturbation theory is accurate, however, as first noted by Weis [89], this is not true for the solid phase. He attributed this to the inaccuracies in the treatment of the reference system in the WCA theory. The problem was later overcome in studies by Kang et al. [12] [13] who suggested a modification to the division of the intermolecular potential in the WCA theory. This will be discussed in greater depth in Chapter 4. The modified WCA theory proves to be accurate when compared to free energy data from simulations for the LJ and exp-6 spherical monomer systems and in this work it is used to treat the Mie potential. By using the extension of Wertheim’s theory to solids, the SAFT-VR treatment and the modified WCA theory an equation of state is presented for fully flexible tangentially bonded chains systems interacting through a Mie intermolecular potential. The solid EOS is then used in conjunction with the SAFT-VR Mie EOS (developed using the SAFT-VR treatment) [90] to determine the SFE boundaries of a host of Mie systems.
1.5 Thesis Layout

Through computer simulation and theoretical analysis, the global phase behaviour of the Mie intermolecular potential is explored. In Chapter 2 a novel simulation technique involving the use of a direct interfacial methodology to evaluate solid-fluid equilibrium is presented. This method has been developed in the spirit of modern techniques which exploit the available increase in computational power [91] [32]. The technique is initially tested on the LJ potential (monomer and chain systems) for which there is appreciable data in the literature for comparisons to be made. In Chapter 3 this methodology along with standard simulation techniques for evaluating vapour-liquid equilibrium and solid-vapour equilibrium are applied to determine the global phase behaviour of a host of Mie potentials of varying range of attraction. In applying the principle of corresponding states, a unified view of the Mie potential is proposed, which clarifies the dominating parameters that affect the phase behaviour of this class of potentials.

In Chapter 4 Wertheim’s thermodynamic perturbation theory is extended to the solid phase, as originally proposed by Vega and MacDowell [87]. The SAFT-VR theoretical framework [66] is applied to the Mie potential in order to determine the monomer contribution to the free energy. This framework is used in conjunction with the perturbation theory outlined by Kang et al. [13] for the treatment of simple spherical solids systems. The resulting solid closed-form EOS obtained is rigorously tested against simulation data for the LJ system. In Chapter 5, the solid EOS is coupled to the recently presented EOS for the fluid phase by Lafitte et al. (SAFT-VR Mie) [90] to solve for the solid-fluid coexistence boundaries. This result is tested against simulation results for LJ monomer, dimer and trimer systems. The simulation results presented in Chapter 3 are used to validate the accuracy of the theoretical predictions of the solid-fluid boundaries for a host of Mie potentials of varying range of attraction. Finally, the true capability of the theory is tested for longer chain systems of varying
range of attraction and the trends which arise from variation of chain length and inter-
molecular attraction are discussed. In the final chapter, Chapter 6, the contributions of this thesis is summarised and recommendation for future work are outlined.
Chapter 2

Determination of the Solid-Fluid Phase Boundaries Using Molecular Dynamics Simulations

Difficulties in attaining solid-fluid equilibrium (SFE) through computer simulation has spurred the development of unique techniques to facilitate the computation of the coexistence properties in a reasonable time scale and with the required accuracy. In this chapter a review of the recent efforts in this field is provided and a new method is presented which is aimed at addressing these issues. The proposed methodology is used to obtain the SFE of the LJ monomer system and is compared with results available in the literature. Further to this, the versatility and robustness of the technique is analysed by application of the method to flexible LJ chain systems and to spherical Mie particles. The Mie potential provides a choice of intermolecular potential exponents where the vapour liquid equilibrium (VLE) region of the phase diagram is expected to be metastable with respect to the solid phase. In such systems a solid-fluid transition is obtained where a continuous change from solid-supercritical fluid to solid-gas coexistence at low temperature is seen.
2. MD Simulation Technique for Solid Fluid Equilibrium

2.1 Introduction

Computer simulations have been essential to understand the fundamentals of the phase behaviour of molecular systems such as dumbbells [16] [92], charged particles [84] [93] and chains [94] [40]. However, available computational power has not been the sole reason for the success of these simulations. Credit must also be given to the simulation techniques that have been developed over the last few decades that have been vital to calculating phase boundaries. Techniques such as the Gibbs Ensemble Monte Carlo (GEMC) [1] for VLE, Rahman-Parrinello techniques for the solid phases [95], thermodynamic integration [22] and Gibbs-Duhem techniques [96] for SFE are just a few that have become standard tools for investigating phase transitions.

Although the fluid phase equilibria of model systems has been extensively studied, [1] [97] [37] [98] (to name a few), the solid-fluid boundary of the phase diagram has been studied less by comparison. One might presume that this has been due to a lack of computational power and the inability to attain phase separation over a reasonable time scale, hence making the task of direct interfacial simulations taxing. The crux of the problem lies in the high energy barrier required to attain the solid-fluid interface. These strongly first order transitions are associated with a high degree of hysteresis and consequent inaccuracies in determining equilibrium. Observing this coexistence can be facilitated, as stated previously, by applying simulation techniques that can either impose an interface onto the system or remove the interface entirely.

The Gibbs Ensemble Monte Carlo (GEMC) method proposed by Panagiotopolous [1] for the VLE region is an example that allows for the determination of phase coexistence properties through a single computer experiment without the presence of an interface. This is done by performing a simulation simultaneously in two distinct regions of differing density under a new ensemble (the Gibbs ensemble). The basis of the technique is that the simulation can be performed for two regions of density in such a way that the criteria for equilibrium (i.e., equal pressure and chemical potential)
between the two are satisfied in a statistical sense. An exchange of particles between the two regions ensures an equal and opposite change in the volume of the two regions such that equality of the pressure and chemical potential is achieved. This methodology has proven to be very accurate and has been used extensively in determining the coexistence properties of fluid equilibria in model systems such as: homo- and heteronuclear LJ chains [99], LJ dimers [100], linear rigid and flexible LJ chains [101], LJ mixtures [102], Yukawa spheres [103], square well spheres [97] and Mie spheres [104].

The absence of the interface makes this method viable for evaluation of solid-fluid transitions, as this appears to address the limiting step in these simulation studies. However, at very high fluid densities and densities in the solid phase the probability of particle insertion/exchange into the distinct density regions is very low, making the technique infeasible for application to solid-fluid transition studies.

Another technique that removes the interfacial region is the Gibbs-Duhem Integration (GDI) method [96], the keystone of which is the Clausius-Clapeyron equation for two coexisting phases. It is based on two independent simulations of separate coexisting phases, which allows for a direct mapping of the saturation line (details of the methodology are given in Section 2.3.1). This method does not require particle insertions as in GEMC and can therefore be used to evaluate solid-fluid boundaries. The disadvantage of this technique is that it requires an initial known coexistence point in order to map the phase boundary lines and as such needs to be used in tandem with another technique. Regardless, the methodology proves to be very accurate and has been implemented in several studies of the solid-fluid boundary;[101] [105] [94] [103] [106] [107] [108] [109] [110].

The development of free energy calculations has in many ways been crucial to determining solid fluid coexistence by computer simulation. This involves the transition of a system from one state of known free energy to another, along a reversible path and calculating the free energy difference involved in the change. A typical example
2. MD Simulation Technique for Solid Fluid Equilibrium

is the integration along a fluid isotherm to zero density where, the system behaves as an ideal gas (of which the free energy is known). However, for solid phases, a problem arises as the expansion of a solid involves crossing a first order transition (melting) which is irreversible [111].

Hoover and Ree [111] were the first to suggest that rather than performing thermodynamic integration along a natural pathway, a more convenient method would be to perform an analogous integration along an artificial reversible pathway. Frenkel and Ladd [22] followed this suggestion and presented a method to compute the free energy of arbitrary solids by constructing a reversible path from the solid phase under consideration to an Einstein crystal (for which the free energy is known) with the same crystallographic structure. To obtain a reversible thermodynamic pathway, virtual harmonic springs are slowly turned on to bind the atoms to their lattice sites until the structure is an Einstein crystal. As the reference state is structurally identical to the real crystal structure it is reasonable to infer that no phase transitions have occurred, i.e., the pathway is reversible. This is expressed as [22];

\[ A(\omega) - A(\omega = 0) = \int_{0}^{\omega} \left( \frac{\delta H(\omega')}{\delta \omega} \right) d\omega', \tag{2.1} \]

where \( \omega \) is the coupling constant that is slowly changed to switch on the harmonic springs that bind the atoms to their lattice sites, \( H \) is the Hamiltonian which represents the energy of the crystal and \( A \) is the Helmholtz free energy of the crystal at a given coupling constant. In the original work [22], the methodology is used to study solid-solid phase transitions of the face centred cubic (fcc) and hexagonal closed packed (hcp) structures of hard spheres. The method has been widely used to evaluate the solid-fluid boundaries of systems such as: hard sphere dumbbells [16], hard sphere chain molecules [112] [19], semi flexible cut and shifted LJ chains [94], six site potential models for water [113] and colloidal electrolytes [93]. Solid-fluid boundaries are determined by comparing the solid branch (Equation 2.1) to a reversible path of the fluid phase i.e.,
from an ideal gas to the fluid phase of a given density ($\rho$) at the same temperature, $T$. The free energy of the fluid branch can be determined using,

$$\frac{A(\rho, T)}{Nk_B T} = [\ln(\rho \sigma^3) - 1] + \int_0^\rho \frac{[Z(\rho', T) - 1]}{\rho'} d\rho',$$

where $Z$ is the compressibility factor and $[\ln(\rho \sigma^3) - 1]$ represents the ideal free energy of the fluid. The remainder of the equation represents the residual free energy determined between the two limits of an ideal gas and a given density of the fluid phase. Matching of the solid and fluid branches and equating the pressures, results in a unique state of equal chemical potential and pressure of the two independent phases indicating coexistence. This method proves to be computationally taxing and is typically used in conjunction with the GDI method; the free energy calculation is used to determine an initial coexistence point and the GDI method is implemented to trace the entire coexistence boundary. These two methods have been implemented in numerous works including, [101], [105], [103], [106], [109], [114], [115].

Determining solid-fluid coexistence by a direct method is also a viable option. Some of the first simulations of this nature were presented by Ladd and Woodcock [116] [117] [118] in which coexistence is achieved in the $NVE$ ensemble using MD simulations. The initial results on the LJ and inverse 12 power systems however, were not very accurate; most likely due to small system sizes and simulation timescales being too short [119]. Such limitations, have been slowly disappearing with the steady increase in available computational power [120]. Consequently, direct SFE simulations have become more prevalent in recent years e.g., studies on simple molecular models [121] [122] [123], ionic systems [124] [125], and water [126] [127] [128] [129] to name a few. Particularly in the last decade several works have been published to present simulation techniques that ‘induce’ solid-fluid phase separation in a reasonable time frame; here we review in more detail a few methodologies relevant to our work.
Agarwal and Escobedo [91] have recently presented a methodology for simulating the SFE of polyhedral particles using a ‘direct’ approach. Initially, anisotropic expansions of a solid along an isobar using the Rahman-Parinello technique [95] of constant stress ($N\sigma T$ ensemble) and isotropic compressions of a liquid (along the same isobar) using the $NPT$ ensemble are carried out at stepwise increments of temperature to observe melting of the solid and freezing of the liquid phase. For cases where hysteresis is present (i.e., when the melting and freezing temperatures do not coincide), direct interfacial $NVT$ simulations are performed to determine the coexisting conditions at a given temperature. The coexisting $NVT$ system is generated from an initial structure taken from the expansion (solid) branch close to the transition point (within the hysteresis region). The solid is duplicated and placed next to the original crystal. The simulation cell is then expanded to a lower density to induce melting of the duplicated solid which is exposed to a vacuum. The size of the expansion is averaged such that the density of the entire system lies within the expected metastable region. The size of the metastable region is estimated as the midpoint of the overlapping solid and fluid isobars. Under the $NVT$ ensemble the simulation is performed for $3 \times 10^7$ timesteps. At the end of the simulation, melting of the crystal exposed to the vacuum is noted and two phases (solid and fluid) separated by an interface are recorded. The coexisting densities and pressure are obtained directly from the simulation results. This final $NVT$ simulation step, in particular, requires considerable computational time for melting of the solid and formation of the interface. A variation of the Agarwal and Escobedo methodology is implemented in this thesis, which reduces the time of the final step considerably.

A similar method has been proposed by Morris and Song [32]. Herein, a solid is achieved by performing pure-phase $NPT$ simulations close to the estimated melting temperature of the chosen system. A corresponding liquid is obtained by duplicating the solid and applying large amplitude displacements to the system by increasing the temperature to approximately 150% of the estimated melting temperature. The solid
and liquid boxes are combined and run under the $NVT$ ensemble creating a solid-fluid interface. However a major source of error, which has been recognised by the authors, is that the hydrostatic equilibrium pressure obtained is probably incorrect, as the two boxes are at very different conditions prior to being combined and as a result, the stress at each axis differs. To treat the problem, the pressure is obtained by manually adjusting the system box size so that the stress components are approximately equal and from here an average of the stresses obtained from the stress tensor is used as the coexistence pressure. The method in general, is similar to the Agarwal and Escobedo method in the sense that phase separation is ‘induced’ by the initially creating a solid which is then duplicated and by melting the copy, solid-fluid coexistence can be observed. The generation of the liquid phase in the Morris and Song method allows for a faster simulation ($1.5 \times 10^5$ timesteps) although it suffers from the accuracies in the coexistence pressure discussed above.

Vega et al. [130] have presented a technique to determine the melting line of different water models. An initial ice structure is created using the Rahman-Parinello [95] technique i.e., $N\sigma T$ ensemble, at zero pressure, to ensure the solid attains an equilibrated structure which is not stressed. Following this, an ice-vacuum interface is created by expansion of the simulation cell in one direction. For this study, it was particularly important to consider the crystal plane of the ice exposed to the vacuum, as this is expected to influence the properties of the ice-vacuum interface. The elongated system is then run under the $NVT$ ensemble to observe melting at the interface of the solid structure and the vacuum. The objective was to determine the start point of melting for different water models i.e., the start point of melting of ice. This was observed to occur at the surface of the solid, forming a thin layer of liquid over a stable solid block. Melting eventually propagates through to the bulk, however, the system only entirely melts at the melting temperature. The method was developed specifically to obtain the melting line of different water models and no attempt was made to obtain coexisting densities or pressures of these systems.
The focus of this chapter is to present a new direct method to determine SFE with MD. An adaptation of the Agarwal and Escobedo [91] methodology is proposed that allows for accurate determination of solid-fluid coexisting properties in a shorter time scale. The reduction in computational time is achieved by following the methodology of Morris and Song [32], which combines the pure solid and fluid phases at estimated coexisting conditions. This reduces the time required for the liquid phase to melt and for the formation of a stable interface. The present technique, however, does not possess the flaws seen in the Morris and Song methodology related to the equilibrium hydrostatic pressure. The key difference resides in the way the liquid phase is generated: The fluid phase, constructed to be placed in contact with the solid, is obtained by reduction of the density of the replicated solid by removal of particles rather than by a drastic increase in temperature. As a result, the two systems are at similar temperature and pressure conditions, prior to being combined. The methodology is applied here to a LJ monomer system (Equation 1.17) as a benchmark and subsequently used to obtain the SFE boundary conditions of a more complex fully flexible LJ trimer system. Finally, the robustness of technique is tested using the Mie potential (Equation 1.18) for a very short range attractive potential at which the VLE region becomes metastable with respect to the solid phase.

2.2 Calculation of Solid-Fluid coexistence boundaries

As mentioned previously, attaining solid-fluid equilibrium in molecular simulation is a particular challenge due to the very long timescales involved in both the freezing and the melting processes [91]. The method presented here is referred to as the Freeze method. The procedure for obtaining SFE can be summarised by the following scheme (Figure 2.1). Throughout this section a LJ system is used as the model and we use throughout reduced units where $T^* = \frac{kT}{\epsilon}$, $P^* = \frac{P\sigma^3}{\epsilon}$ and $\rho^* = \rho\sigma^3$. 
2. MD Simulation Technique for Solid Fluid Equilibrium

STEP 1

NPT/NσT isobaric compression/expansion simulations to identify region of solid-fluid coexistence

Identify solid on expansion branch close to expected transition region, replicate and place next to original i.e., $N \rightarrow 2N$

STEP 2

Remove molecules from replicated solid to reduce the overall density of the system to a density which lies within the estimated coexistence region

Increase/decrease number of molecules removed depending on freezing/melting

STEP 3

Using $(P_0, T_0)$ and the Gibbs Duhem Integration method, trace the SFE phase boundaries

In the NVT ensemble, perform the freeze method

Solid-Fluid Coexistence $(P_0, T_0)_{coexist}$

Melting/freezing of system

Figure 2.1: Scheme showing the steps implemented in the presented technique to evaluate solid-fluid transition boundaries. Each step is highlighted by a different coloured box for clarity.
2.2.1 Step 1: Fluid and Solid phase Isobars

In the first step, a crystalline solid is heated at constant pressure in the \( N\sigma T \) ensemble until melting occurs. The system (now in the liquid phase) is then cooled at constant pressure until it refreezes to a solid. To determine the phases of each state point along the isobar, the radial distribution function of each simulation is analysed. As mentioned previously, freezing/melting transitions are highly first order and are associated with a strong degree of hysteresis, therefore the exact melting temperature can not be obtained via this route. This is better exemplified in Figure 2.2 where the hysteresis region of a LJ monomer system at \( P^*=8.12 \) is shown within the solid purple lines (\( T^*=1.2-1.35 \)). Hysteresis can be attributed to factors such as system-size effects or the high free-energy barriers associated with these transitions, which lead to the metastable state points shown in Figure 2.2 and the inability to obtain an accurate transition temperature. Although an exact melting temperature can not be attained, the advantage to this method is that the expected region of the phase transition is narrowed to within the boundaries of the hysteresis region which can then be analysed in more detail.

To identify the expected solid-fluid coexistence region, extensive isothermal-isobaric simulations are performed in the temperature range of \( T^*=0.675-2.7 \). The pressure of each isobar is selected by creating a solid system of a density that is in the stable solid phase and performing a simulation under the \( NVT \) ensemble. The output pressure obtained through the virial route and final configuration of this simulation is then used as the fixed pressure of the isobar and the starting configuration for the heating isobar.
Figure 2.2: $T^* - \rho^*$ Diagram showing the heating (red crosses) and cooling (blue open diamonds) compression and expansion respectively, isobars at $P^*=8.12$ for the LJ monomer, the green dashed lines are a guide to the eye. The boundaries of the hysteresis region are highlighted by the solid purple lines. The solid black lines are the solid-fluid coexistence boundaries determined by Mastny and de Pablo [35] for the LJ monomer.

2.2.2 Step 2: Identification of solid-fluid coexistence point: The ‘Freeze’ Method

The freeze method is carried out in three stages as shown in Figure 2.3. An initial solid close to the boundary required for the freeze methodology is obtained from careful heating of a high density solid along an isobar. Each simulated solid along this isobar represents a thermodynamically stable solid configuration at constant pressure and temperature. Of these heated solids, the one closest to the transition of melting (i.e.,
the configuration obtained just before the phase transition to the liquid phase) is considered to be closest to the expected phase transition region. Therefore it is selected as the configuration to be implemented in the freeze methodology.

This configuration is replicated four times in the z-direction. Half of this larger system is ‘frozen’ (i.e., fixed in space) into its position such that the presence of these molecules has no effect on the other half of the simulation cell. Some of the remaining ‘unfrozen’ molecules are removed [131], to reduce the overall system density to a metastable density. As the actual coexistence region is yet to be determined this density is averaged as the midpoint of the expected saturated liquid and solid states. The actual value used is unimportant as the next step in the procedure will self-correct the densities. The combined system is then relaxed under the $NVT$ ensemble, the unfrozen half melts to a fluid while the frozen particles remain stationary. $10^6$ timesteps are deemed sufficient for the melting to this fluid phase.

Finally, the stationary molecules are ‘unfrozen’ (i.e, all particles in the system take part in the simulation) and the entire system is run in the canonical ($NVT$) ensemble for a period of $5 \times 10^6$ timesteps, 20% of which is discarded for equilibration. The density profile of a successful simulation shows two well-defined plateaus corresponding to the coexisting phases. The densities of each phase are obtained by taking averages of the plateaued regions of the density profile.
This methodology requires an approximate knowledge of a transition point. This is discussed following Figure 2.4. The isobars calculated in the previous section provide estimates of lower and upper temperature boundaries corresponding to the phase transitions upon cooling a liquid and heating a solid respectively. The estimated fixed temperature of the simulation is taken as the upper temperature (that of the heated solid) \( T_{\text{est}} = T_{\text{upp}} \) and the estimated fixed density of the system is the average of the upper and lower densities \( \rho_{\text{est}} = \frac{\rho_{\text{upp}} + \rho_{\text{low}}}{2} \). The outcome of the procedure is independent of the density of the solid structure in as long as it is a relaxed solid (without stress) close to the melting line. For the second stage of the procedure, it is plausible that the removal of particles to create the fluid provokes a situation where the copied solid becomes unstable and melts at the fixed temperature. Generation of a fluid phase in this manner, allows for the system to be at very similar conditions of temperature and pressure to the original solid, and as such, errors in the equilibrium pressure are avoided as no manual calculations are required to readjust the size of the simulation cell to equate the stress at each axis, as was done previously in the work of Morris and Song [32].
2. MD Simulation Technique for Solid Fluid Equilibrium

Figure 2.4: Schematic showing how the estimated conditions \( T \) and \( \rho \) are chosen for the freeze method to be carried out. The dashed green lines are the fluid and solid isobars (as shown in Figure 2.2), the red crosses show the highest temperature simulation along the heating isobar before the solid melts \( (T_{\text{upp}}, \rho_{\text{upp}}) \), the lowest temperature simulation along the cooling isobar before the fluid freezes \( (T_{\text{low}}, \rho_{\text{low}}) \) and the purple lines show the region of hysteresis. The blue closed circle is the system at the estimated \( T_{\text{est}} \) and \( \rho_{\text{est}} \) used in the freeze method.

During the final stage when the solid is in contact with the fluid, the interface will rearrange (melt or freeze) to accommodate the corresponding equilibrium densities. With this procedure, it is found that typically only one trial is required to obtain the coexisting properties, as although the individual phases are not at the correct coexisting densities at the start of the simulation, the deviation from equilibrium conditions is small enough that the system rearranges itself to obtain these properties. Additionally, the initial estimate of the overall metastable density of the system is a good one, as it is taken as the midpoint of the region of hysteresis and therefore melting or freezing of the entire system is unlikely to occur. In the event that the two coexisting phases are not equilibrated (stable) in the first iteration of the freeze method, the choice of the
metastable density is adjusted to accommodate for this. For the case where the system solidifies, more molecules are removed in the third stage of the algorithm, conversely if the system melts, less molecules are removed. This shift in the estimated metastable density is repeated until coexistence is obtained.

This technique is tested on five coexisting points of the Lennard-Jones spherical system and compared to the Mastny and de Pablo [35] equation of state. This EOS is chosen because solid-fluid coexistence is solved by combining the Johnson EOS [37] for the fluid and the van der Hoef EOS [36] for the solid to determine the solid-fluid boundaries of the LJ monomer system. Both the Johnson and Van der Hoef equations are a fit to a deluge of simulation points over a wide density and temperature range for the fluid and solid phases respectively. In the work of Mastny and de Pablo, an improvement on one of the constants of the van der Hoef EOS ($C_{tr}$) is presented by simulation at a longer cutoff radius ($6\sigma$). The resulting correlation for the SFE boundaries are in excellent agreement with simulation data and, as such, is ideal for comparison with the presented simulation methodology.

The coexistence pressures are obtained as an output of the canonical ensemble simulation. The pressure is obtained as the normal component of the pressure tensor, i.e., $P_{zz}$. To ensure the accuracy of the output pressures, independent simulations are run in the $NVT$ ensemble at the coexisting temperature and fluid densities determined from the density profile. The output pressure obtained corresponds to the coexistence pressure at the fixed density and temperature conditions. These additional simulations prove to be slightly more accurate than the coexisting pressures obtained from the normal component of the pressure as the effect of the interface is removed. This result has been used for comparison of the pressures to the work of Mastny and de Pablo (Figure 2.7). With this known coexistence point the Gibbs-Duhem integration technique can be implemented to complete the coexistence boundary for the solid-fluid region.
2.2.3 Step 3: Gibbs Duhem Integration (GDI)

The GDI method [96] involves thermodynamic integration along a path coinciding with the saturation line. One coexistence point must be known to initialise the procedure. Integration according to the Claussius-Clapyeron formula (a first order differential equation) is implemented to determine the change in pressure with temperature to maintain coexistence. For the case of the solid-fluid boundary this can be expressed as,

\[
\frac{dP}{d\beta} = -\frac{\Delta h_{\text{melting}}}{\beta \Delta v_{\text{melting}}}. \tag{2.3}
\]

where \( \beta = \frac{1}{k_B T} \) and \( \Delta h \) and \( \Delta v \) are the enthalpy and volume differences, respectively, per particle between the fluid and solid phases and the differentiation is taken along the saturation boundary line \( \sigma \). Values for \( \Delta h \) and \( \Delta v \) can easily be obtained from molecular simulation [96], and the differential equation can be solved stepwise by numerical integration e.g., by predictor-corrector methods.

An example of an integration step proceeds as follows: Given a known initial coexistence point \((P_0, T_0)\), an increment in temperature is chosen (in this work \( \Delta \beta = \frac{1}{k_B T_1} - \frac{1}{k_B T_0} = 0.01 \) and 0.5) and the saturation pressure \( (P_1) \) at a new temperature \( (T_1) \) is predicted using the calculated \( \Delta h \) and \( \Delta v \) at \((P_0, T_0)\) and the Claussius-Clapyeron equation i.e., simulation data is used to solve the right hand side of Equation 2.3 and a new pressure, \( P_1 \) is predicted:

\[
P_1 = P_0 + \Delta \beta \frac{\Delta h_{\text{melting}}(P_0, T_0)}{\beta_0 \Delta v_{\text{melting}}(P_0, T_0)}. \tag{2.4}
\]

With these predicted conditions \((P_1, T_1)\) independent simultaneous single phase (solid and fluid) \(NPT\) simulations are run for the coexisting solid and fluid phases. The starting configuration of each phase is taken from a previously equilibrated system from the previous step i.e. \((P_0, T_0)\). \(NPT\) calculations allow the determination of new enthalpies \( \Delta h_{\text{melting}}(P_1, T_1) \) and specific volumes \( \Delta v_{\text{melting}}(P_1, T_1) \) needed to
evaluate the right hand side of Equation 2.3 and thus update Equation 2.4, therefore,

$$P_c = P_0 + \Delta \beta \frac{\Delta h_{melting}(P_1, T_1)}{\Delta v_{melting}(P_1, T_1)}. \quad (2.5)$$

The updated or corrected pressure, $P_c$, is then compared to the original predicted pressure, $P_1$. If the difference between $P_c$ of the simulation and the predicted pressure ($P_1$) is within a certain accepted tolerance (for this work 1% deviation is acceptable), $P_c$ is accepted as the correct advancement ($P_1 = P_c$) along the coexistence curve for the solid-fluid boundary. Following this, the temperature advances by another increment and the process is repeated.

If the difference is above the 1% criteria, an average of the predicted and corrected pressure is taken and another pair of simulations are carried out to update Equation 2.5. If the new corrected pressure, $P_{c2}$ is within a 1% deviation then $P_{c2}$ is accepted as the correct advancement (i.e, $P_1 = P_{c2}$) and the procedure advances to another temperature increment. If not, an iterative process is carried out to continually ‘correct’ the pressure until the criteria is met [132].

2.3 Results

The phase diagrams of four model systems are obtained by MD simulation with the objective of testing the validity of the presented Freeze method. A simple LJ monomer, a linear rigid tangentially bonded trimer, a fully flexible tangentially bonded LJ trimer and a Mie spherical system. Initially the LJ monomer system is tested as there is appreciable data available for a comparison to be made for the SFE boundaries. Following this, the technique is extended to chain systems; initially the method is applied to the LJ linear rigid tangentially bonded trimer as the solid-fluid boundaries have previously been determined [101]. The SFE of the fully flexible LJ trimer is calculated next. Finally the technique is used to determine the phase boundaries of the Mie intermolecular potential at a choice of exponents for which the VLE region is
expected to be metastable with respect to the solid phase.

2.3.1 Simulation Details

Molecular dynamics simulations are performed to evaluate the phase boundaries of the LJ monomer system. The molecular dynamics code DL-POLY (version 2.20), is used in this study to perform all simulations and the Nose-Hoover thermostat is implemented to ensure an average constant temperature throughout the timescale of each simulation. The usual periodic boundary conditions are employed. The system sizes are chosen such that finite size effects are negligible and a cutoff radius of $5\sigma$ are employed \cite{133}. No long range corrections are implemented, however the choice of cutoff radius of $5\sigma$ incorporates 99.94% of the interacting energy which is deemed sufficient for study of the LJ system. Additionally, to confirm that the cutoff radius is a prudent choice, a simulation of the presented technique is tested at a longer cut off radius ($7\sigma$) in which a negligible change in the coexisting properties are noted. All properties are represented in reduced units where;

$$T^* = \frac{k_B T}{\epsilon}, \quad \text{(2.6)}$$

$$\rho^* = \rho \sigma^3 \quad \text{(2.7)}$$

and,

$$P^* = \frac{P \sigma^3}{\epsilon}. \quad \text{(2.8)}$$

For all simulations performed, the error in the calculation is also determined. For pure phase $NPT$ or $N\sigma T$ simulations, the associated error in the density is obtained from the fluctuation in the size of the simulation cell. For pure phase $NVT$ simulations the error in the pressure is obtained from the fluctuations in the pressure tensor. For $NVT$ phase coexistence simulations, the error in the coexisting densities is calculated
2. MD Simulation Technique for Solid Fluid Equilibrium

as the maximum deviation from the averaged coexistence value obtained from the density profile.

2.3.2 LJ monomer

In Figure 2.6 the $T^* - \rho^*$ phase diagram of a monomer (1-centre) LJ system is shown where the symbols correspond to simulation data of this work and the lines to phase boundaries calculated from analytical equations of state from the literature. The vapour liquid boundary and supercritical isobars are obtained from the Johnson EOS [37]. This EOS is a fit to a wide range of simulation data over a temperature range, $T^* = 0.7$-$6.0$ and density range, $\rho^* = 0.1$-$1.25$. The solid-vapour boundary is obtained from the van der Hoef EOS [134], which is also a fit to MD simulation data over a large number of state points. The SFE boundaries are taken from the work of Mastny and de Pablo [35] which is obtained by solving for the phase coexistence conditions of the LJ monomer using the Johnson EOS [37] and the van der Hoef EOS for the solid [36]. A constant in the van der Hoef EOS ($C_{Tr}$), which is dependent on the triple point temperature of the LJ monomer, is improved upon in the Mastny and de Pablo study by performing the simulations at a longer cutoff radius ($6\sigma$). Adjustment of this constant was originally suggested by van der Hoef [36], and in doing so led to a more accurate EOS for the solid, which consequently leads to a more accurate prediction of the SFE boundaries.

The supercritical isobars are evaluated using single phase $NPT$ simulations over a temperature and density range, $T^* = 1.0$-$2.7$ and $\rho^* = 0.01$-$0.97$. The pressures and simulation data points of each isobar can be found in Appendix A. The VLE of the LJ monomer system has been extensively analysed and a thorough review of these studies has been presented in the works of Johnson et al [37] and Lotfi et al [135]. There are a few established methods which have been used to determine the coexisting properties of the VLE region; the GEMC developed by Panagiotopoulos [1], as mentioned previously, the $NPT$ plus test particle method [135], and the direct method [136] [120]; which is
used in this work. \textit{NVT} simulations under the Nose-Hoover thermostat are carried out on a system size of 2400 particles of a metastable density (i.e, lies within the expected coexistence region), in a parallelepiped box with sides $L_x = L_y = \frac{1}{3}L_z$ over a temperature range of $T^* = 0.7 - 0.9$. $10^6$ timesteps are employed with 20\% being discarded to ensure equilibration. The coexistence densities are calculated by plotting the particle density along the $z$-axis of the simulation box and using the plateaued region of this density profile for both phases (see Figure 2.5). The tabulated simulation data for this procedure is given in Appendix A.

Figure 2.5: (a) Schematic showing the vapour liquid phase separation of LJ spheres at $T^*$=0.8 using the direct method (b) Density profile of the system shown in (a), the coexisting densities are determined from an average of the plateaued regions and are highlighted by the dotted lines.
To evaluate the solid-vapour phase boundary the Rahman-Parinello technique of constant stress is implemented. The stable crystal structure of spherical particles packed in a lattice is known to be face centred cubic (fcc) [95]. In the Rahman-Parinello technique the $NPT$ ensemble is modified to allow for non isotropic changes of the sides and angles of the simulation cell throughout the timescale of the simulation; this is known as the $NσT$ ensemble i.e, constant number of particles, temperature and stress ($σ$). This method is essential for crystalline solid systems where the equilibrium structure is not known $a$ $priori$ as periodic boundary conditions as well as the imposition of a simulation cell shape, which is incommensurate with the unit cell of the solid can distort the crystal from its equilibrium structure. This technique has been used in MD studies [94] and in MC simulations [137] [16] [115] to determine the solid vapour transitions and solid-solid transitions. To calculate the solid-vapour boundary an fcc configuration at a density which is well within the stable solid region is run in the $NσT$ ensemble at temperature and pressure conditions which are below the expected triple point $T^*_t$ and $P^*_t$ of the system. The simulation is run for $10^6$ timesteps, 40% of which is discarded for equilibration. The final configuration of this simulation is then expanded to zero pressure at constant temperature in the $NσT$ ensemble again for $10^6$ timesteps, 40% of which is discarded for equilibration. The final configuration of this second run is an expanded solid at a density just above where the phase coexistence boundary is expected i.e. the solid vapour boundary. The procedure is repeated for several different temperatures up to the expected triple point temperature.

The SFE boundaries are obtained using the freeze methodology and the GDI technique, which are both presented in Figure 2.6. The freeze method is performed to determine 5 solid-fluid coexistence points, tabulated values can be found in Table 2.1. The solid ($N=3375$) chosen from Step 2 of the methodology is replicated 4 times and placed successively next to the original to create an elongated simulation cell. The freeze method is carried out over $10^6$ timesteps for the ‘frozen’ simulation and $5 \times 10^6$ timesteps for the ‘unfrozen’ simulation. One of the five coexistence points ($T^*_0=1.351$,
$P_0^*=9.416$) is chosen as the initial known coexistence point required to perform the GDI method, to complete the SFE boundaries. Simultaneous single phase $NPT$ and $N\sigma T$ simulations of the fluid and solid at $(T_0^*, P_0^*)$ are performed over $10^5$ timesteps, 20% of which is discarded for equilibration. The simulation results are used to solve the Clausius-Clapyeron formula to trace the entire phase boundary via the iterative predictor-corrector procedure previously outlined in Section 2.2.3. The simulation results are in good agreement with the SFE boundaries determined by Mastny and de Pablo [35]. Additionally, in Figure 2.7, the $P^*-T^*$ solid-fluid phase diagram is shown; again good agreement is noted between the simulation results and the EOS from the literature. The deviation from the work of Mastny and de Pablo is presented in Figure 2.8, which allows for an augmented view of the deviation between the simulation data and EOS. The good agreement of all the presented simulation results with the correlation for the phase boundaries of the LJ monomer indicate that the simulations presented are accurate.
Figure 2.6: $T^* - \rho^*$ Global phase diagram for Lennard Jones particles showing the comparison of the simulation results (symbols) with available correlations; Mastny and de Pablo [35] for the SFE curves, Johnson et al [37] for the VLE and the supercritical isobars and Van der Hoef [134] for the solid-vapour boundary. The diamonds are the supercritical simulations, triangles are the VLE from direct simulations and squares the $N\sigma T$ simulations at zero pressure for the solid vapour boundary. The circles represent the SFE obtained from the freeze methodology, and the crosses are obtained from the GDI of this work. Solid lines represent the phase coexistence boundaries and the dashed lines represent the supercritical isobars.
Figure 2.7: \( P^* - T^* \) solid-fluid coexistence curve of the LJ monomer. The solid lines correspond to empirical equations of state developed by Mastny and de Pablo [35]. The blue diamonds represent simulation results using the freeze methodology of this work and the green crosses are obtained from the Gibbs Duhem integration technique the initial point of which is taken at \( T^*=1.351 \) and \( P^*=9.416 \).

Table 2.1: Coexisting pressures (\( P^* \)) and densities for the 1 centre LJ system calculated using the Freeze Technique compared with results of Mastny and de Pablo [35]. The error is given in the square parentheses where 2.034[53]=2.034\pm0.053.

<table>
<thead>
<tr>
<th>( T^* )</th>
<th>This work</th>
<th>Reference [35]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P^* )</td>
<td>( \rho^*_l )</td>
<td>( \rho^*_s )</td>
</tr>
<tr>
<td>0.844</td>
<td>2.034[53]</td>
<td>0.902[3]</td>
</tr>
</tbody>
</table>
Figure 2.8: Deviation of the simulation pressure; normal component of pressure from the freeze method, (blue diamonds) and the pressure obtained from the GDI technique (green crosses) compared to the pressure from the correlated work of Mastny and de Pablo [35].

2.3.3 LJ linear rigid tangentially bonded trimer

Encouraged by the good agreement between the simulation results using the Freeze method and GDI with previous data from the literature, the SFE of LJ trimer systems are evaluated. The global phase diagram of the linear rigid LJ trimer has been simulated previously: the SFE has been determined using free energy calculations and the GDI technique [101]. In Table 2.2 tabulated values of three solid-fluid coexistence points carried out on the linear rigid LJ trimer using the new ‘Freeze’ method, compared to the results of [101] are shown. The initial solid used in the simulation is taken as the most thermodynamically stable configuration [137] i.e, a fcc lattice of tangentially bonded spheres in which all the molecular axes oriented in the same direction. Other simulation details are the same as those of the LJ monomer case. The coexisting
properties are in good agreement with the previous work of free energy calculations and GDI, confirming the validity of the method when applied to chain systems.

Table 2.2: Tabulated coexisting pressures and densities of 3 state points calculated using the ‘Freeze’ technique for the LJ rigid trimer compared with results of [101]. The error is given in the square parentheses.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho_i^*$</th>
<th>$\rho_s^*$</th>
<th>$P^*$</th>
<th>$\rho_i^*$</th>
<th>$\rho_s^*$</th>
<th>$P^*$</th>
</tr>
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<td>9.57[10]</td>
<td>0.3305</td>
<td>0.3723</td>
<td>10.98</td>
</tr>
<tr>
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<td>0.376[4]</td>
<td>14.80[12]</td>
<td>0.341</td>
<td>0.383</td>
<td>16.15</td>
</tr>
</tbody>
</table>

2.3.4 LJ flexible tangentially bonded trimer

In comparison to other molecular models, simulations of the SFE of flexible chain systems are scarce. Malanoski and Monson [112] have calculated the SFE boundaries of fully flexible tangentially bonded hard sphere chain models of $n$-alkane molecules and Polson and Frenkel [94] determined the SFE of semiflexible tangentially bonded LJ chains of $n$-alkane molecules. The solid phase of flexible chain systems are of interest as they are typically used as models of alkane molecules that are known to exhibit the solid phase at room temperature and pressure. Evaluation of these phase transitions are particularly important to industrial processes which deal with solid-fluid separation of alkane mixtures. In this work the fully flexible tangentially bonded LJ trimer molecule is studied. The monomer segments are connected by harmonic springs with the following potential:

$$U_{\text{stretch}}(r_i) = \frac{1}{2}k_b(r_i - r_b)^2$$  \hspace{1cm} (2.9)

where $r_i$ is the distance between the $(i-1)^{th}$ and the $i^{th}$ monomer segment, $r_b$ is the equilibrium bond length which is fixed at the value of $\sigma$ for tangentially bonded
molecules and $k_b$ is the bonding stretching harmonic force constant. $k_b$ is given a large value of 2500 to ensure that the segments do not stretch i.e., remain tangential.

In the case of a LJ fully flexible tangentially bonded trimer chain molecules, the thermodynamically stable solid configuration is not easily attained. Wojciechowski et al. [138] [139] were the first to suggest that for flexible molecules formed by tangentially bonded spherical segments, the most stable configuration is one which exhibits an fcc close-packed arrangement of the monomer spherical segments with a random bond order, i.e., no long-range orientational order is present in such a system; the structure is known as a disordered solid. In a recent study of the LJ tangential bonded dimer (2CLJ), a crystal was generated in an fcc lattice with a random bond orientation and the solid-fluid phase boundary was determined from free energy calculations and the GDI method [38]. Additionally the phase transition between the disordered and ordered phases was also presented. The ordered solid is noted to only become stable relative to the disordered solid at very low temperatures. For the case of the flexible trimer, the generation of a disordered crystal is significantly more complex as there are a greater number of bond angles and molecular orientations to consider. In this work, an attempt is made to generate the disordered crystal structure by cooling and freezing of an isotropic fluid.

A system of flexible trimers consisting of $N=768$ chains ($N_s=2304$ where $N_s$ is the number of monomer segments) is equilibrated under constant temperature and pressure at supercritical conditions. Stepwise, the system is cooled at constant pressure under the $NPT$ ensemble until it freezes (refer to Figure 2.9). Freezing is confirmed by analysis of the radial distribution function. At this point the ensemble is changed to the constant stress ensemble, $N\sigma T$, to ensure that the solid is not ‘stressed’ due to restriction of the box dimensions i.e., the stable equilibrium state of lowest free energy is obtained. The solid is further cooled and a structural analysis is carried out on the final configuration. To characterise the final configuration, the radial distribution
function and Steinhardt [140] order parameters are determined. In Figure 2.10 the site-site radial distribution function, $g(r)$ in a final configuration at $T^* = 0.8$, $P^* = 8.0$ and $\rho^* = 0.375$ is shown.

Figure 2.9: Snapshot of the solid fully flexible tangentially bonded trimer

Figure 2.10: Site-site radial distribution function of the fully flexible tangentially bonded trimer structure formed after cooling of a supercritical fluid to a temperature $T^* = 0.8$, $P^* = 8.0$ and $\rho^* = 0.375$
The sharp peaks, particularly the double peak found between $r^* = r/\sigma = 1.5-1.8$ indicate that the system has indeed frozen into a solid crystalline state rather than an amorphous structure. Steinhardt order parameters allow the crystal structure morphology to be tested and compared to reference histograms [140]. The result (Figure 2.12) is in excellent agreement of a structure corresponding to an fcc lattice. Furthermore, the randomness of the bond distribution of the trimer molecules is determined with respect to a reference vector (1,0,0). The angle ($\theta$) between a trimer bond and the reference vector (1,0,0) is expressed as $\cos \theta$. In Figure 2.11 the probability distribution of $\cos \theta$ is presented to show the bond distribution with respect to the reference vector. This indicates, that there is an approximately equal probability of obtaining three different types of bond angles with respect to the reference vector. It is reasonable to conclude that within the crystal structure there is an approximately equal distribution of bonds i.e., the bond order is disordered.

Figure 2.11: Diagram showing the frequency of bond orientation with respect to a reference vector (1,0,0) in the crystal structure of the fully flexible trimer at $T^*=0.8$, $P^*=8.0$ and $\rho^*=0.375$
Figure 2.12: Steinhardt order parameters of several reference crystal structures presented in [140] (blue histograms). The histogram on the right illustrates the Steinhardt order parameters for the flexible trimer crystal which corresponds to the fcc crystal structure, structure (b).
Using this initial crystal structure, heating followed by cooling isobars, are evaluated, using $N\sigma T$ and $NPT$ MD simulations over a temperature range of $0.8 < T^* < 1.6$ at a fixed pressure $P^*=8$ to outline the general region of the solid-fluid transition boundaries. The freeze method procedure is then implemented using the same simulation details as seen in the previous cases to obtain a coexistence point at $T^*=1.202$ and $P^*=6.601$ and coexisting densities $\rho_s=0.362$ and $\rho_l=0.335$. From here, the GDI technique is implemented to trace the solid-fluid phase boundary. The vapour-liquid region and solid-vapour regions are also simulated and the results are compared to the thermodynamic perturbation theory for LJ systems (TPT1-LJ) and the extension of TPT1 to the solid phase (TPT1-LJ solid) proposed by Vega et al [38] [101]. TPT1-LJ solid will be discussed in greater depth in Chapter 4. The $T^* - \rho^*$ theoretical predictions for the fully flexible trimer model are shown in Figure 2.13 and are compared to the simulation results of this work. As expected, excellent agreement is seen between the simulation data and the theoretical predictions of TPT1-LJ in the VLE region. It is interesting to see that there is also good agreement between simulation results and TPT1-LJ solid for the SFE and SVE boundaries. A slight over-prediction of the theory for the coexisting solid densities in the SVE boundary is observed, however the differences in density are not significant ($\rho_{\text{theory}} - \rho_{\text{sim}}=0.005$). There is a negligible difference between the predicted theoretical triple point and the simulation triple point temperatures. Tabulated values of the coexisting properties obtained from the Freeze method and GDI are listed in Table 2.3. The solid-fluid $P^* - T^*$ phase diagram is also shown in Figure 2.14 in which good agreement between the simulation results and theory is noted again. To date TPT1-LJ solid has been compared to simulation data of the 2CLJ system [105], however there has been no simulation data available for the solid-fluid boundaries of longer flexible chain systems and therefore the theory remained untested for systems longer than the dimer. The simulation results of this work allow for the theory to be compared with the simulation results and the excellent agreement noted between the two provides further evidence of the accuracy of TPT1-LJ solid for flexible chain systems.
Table 2.3: Solid-Fluid coexistence properties for the fully flexible tangentially bonded LJ trimer obtained with the Freeze technique and GDI. The points which are obtained from the freeze method and used in the initial points for the GDI are denoted with a. The error is given in the square parentheses.

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</tr>
<tr>
<td>1.608</td>
<td>0.350[3]</td>
<td>0.376[9]</td>
<td>12.77[94]</td>
</tr>
<tr>
<td>1.743</td>
<td>0.354[3]</td>
<td>0.381[1]</td>
<td>14.87[90]</td>
</tr>
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</table>
Figure 2.13: $T^* - \rho^*$ Global phase diagram of LJ fully flexible trimer. The vapour liquid points are obtained by Sanz et al [137] using GEMC (squares) and this work (crosses) via the direct MD simulation technique. The solid-vapour region is obtained from $N\sigma T$ simulations at zero pressure (triangles) and the solid-fluid region is obtained from the freeze technique (asterisks) and the Gibbs Duhem Integration method (circles). The solid lines are SAFT-LJ predictions for the fully flexible LJ trimer [101].
Figure 2.14: $P^* - T^*$ solid-fluid saturation curve of the fully flexible tangentially bonded LJ trimer. The simulation data for the solid-fluid coexistence pressure is obtained from the freeze method (blue diamonds) and GDI (green crosses). The solid lines are TPT1-LJ predictions [101]

2.3.5 Mie monomer

The Mie intermolecular potential [39] as discussed in Chapter 1 is a generalised form of the LJ model (Equation 1.18). Adjustment of the attractive and repulsive exponent parameters can result in molecular models with shorter range attractive wells which are known to exhibit a metastable VLE region with respect to the solid phase [46] [47]. In order to test the capability of the Freeze method to obtain this type of phase transition, a Mie potential at attractive and repulsive exponents which result in a short range attractive well was chosen. In two previous studies by Hasegawa [46] and Hasegawa and Ohno [47] it was shown that the phase diagrams of Mie potentials
(24,12) and (28,14), exhibit a metastable VLE region with respect to the solid phase. For the purpose of this work, a monomer interacting via a (44.2,9) Mie potential is chosen to test the simulation method as the short range attraction is similar to [46] and [47].

The freeze method is performed as outlined in Sections 2.2.1 and 2.2.2. Heating and cooling isobars at $P^* = 1.085$ are carried out to determine the general region of expected coexistence. The freeze method is used to obtain an initial coexistence point at $P^* = 0.582$, $T^* = 0.6$, $\rho_s = 1.075$, $\rho_f = 0.817$. As the solid-fluid phase boundaries of a highly repulsive potential are very steep, small increments in temperature result in large predicted pressures in the GDI method. The algorithm outlined in Section 2.3 would require multiple iterations before convergence and therefore it is found to be more computationally efficient to heat/cool the equilibrated system obtained from the freeze method. The full scheme (Figure 2.1) is not carried out, but rather, the first two steps are implemented and the equilibrated system obtained from the freeze method is heated and cooled in the NVT ensemble for $3 \times 10^6$ timesteps, 20% of which is discarded for equilibration, to determine the coexisting properties at the new set temperature.

The phase diagram of the (44.2,9) Mie potential is presented in Figure 2.15 and tabulated values of the coexistence points are given in Table 2.4. On cooling of the equilibrated solid-fluid system (where the fluid is in the supercritical state) a transition from supercritical fluid to vapour phase is observed. This smooth transition indicates that no stable liquid phase exists and the triple point temperature is above the critical point temperature. The VLE region is expected to lie below the transition shown in Figure 2.15 i.e., it is metastable with respect to the solid phase. The ability of the simulation methodology presented to obtain this more complex phase behaviour is particularly remarkable. This result showcases the robustness of the simulation technique to capture more complex phase transitions which are otherwise not easily
attained.

Table 2.4: Coexisting densities at given temperature of a (44.2,9) Mie potential calculated using the freeze Technique. The error is given in the square parentheses. The phases present are highlighted in the final column.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho_{f,v}^*$</th>
<th>$\rho_s^*$</th>
<th>$P^*$</th>
<th>phases</th>
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<tr>
<td>0.450</td>
<td>0.007[1]</td>
<td>1.110[7]</td>
<td>0.002[70]</td>
<td>SVE</td>
</tr>
<tr>
<td>0.500</td>
<td>0.026[1]</td>
<td>1.104[9]</td>
<td>0.009[75]</td>
<td>SVE</td>
</tr>
<tr>
<td>0.520</td>
<td>0.049[1]</td>
<td>1.102[9]</td>
<td>0.019[74]</td>
<td>SVE</td>
</tr>
<tr>
<td>0.530</td>
<td>0.092[3]</td>
<td>1.100[6]</td>
<td>0.030[81]</td>
<td>SVE</td>
</tr>
<tr>
<td>0.535</td>
<td>0.138[1]</td>
<td>1.098[8]</td>
<td>0.032[75]</td>
<td>SVE</td>
</tr>
<tr>
<td>0.540</td>
<td>0.562[2]</td>
<td>1.095[6]</td>
<td>0.034[74]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.550</td>
<td>0.678[6]</td>
<td>1.093[6]</td>
<td>0.040[76]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.563</td>
<td>0.742[2]</td>
<td>1.091[5]</td>
<td>0.140[75]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.572</td>
<td>0.780[11]</td>
<td>1.085[12]</td>
<td>0.275[70]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.600</td>
<td>0.816[9]</td>
<td>1.075[6]</td>
<td>0.581[82]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.800</td>
<td>0.884[12]</td>
<td>1.083[10]</td>
<td>2.802[98]</td>
<td>SFE</td>
</tr>
</tbody>
</table>
2. MD Simulation Technique for Solid Fluid Equilbrium

2.4 Conclusion

A new methodology referred to as the ‘Freeze’ method has been presented for the determination of solid-fluid coexistence. The methodology has been used with the LJ intermolecular potential as this molecular model provides an ideal benchmark. The freeze method is found to be accurate in determining the solid-fluid boundaries of the LJ monomer system. Five state points have been analysed all of which are in good agreement with previous data. The GDI technique has been implemented to complete the SFE phase boundaries and the results are found to be in good agreement with previous data in terms of coexisting densities and pressures.

Encouraged by the good agreement of these results with former work the method is applied to the LJ flexible trimer system for which the solid-fluid boundary has been
presented with theoretical predictions [101]. These predictions however, had yet to be confirmed by simulation data due to the difficulties in obtaining a thermodynamically stable configuration for the solid phase. By cooling and subsequently freezing of an isotropic fluid (along an isobar) a stable crystal structure is obtained that corresponds to the so-called ‘disordered’ solid. The solid structure is analysed in detail and is found to correspond to a random bond distribution in which the monomer segments form an fcc arrangement. The entire phase boundary is obtained with the freeze method and GDI for which excellent agreement with previous theoretical predictions [101] is observed. The technique is also used to study the phase behaviour of a particular set of parameter values for which the Mie potential exhibits a VLE region that is metastable with respect to the solid phase. This type of phase behaviour has been observed in fullerene molecules ($C_{60}$) and this methodology can be useful for determining the phase behaviour of coarse grained models of such systems.
Chapter 3

Phase Behaviour of Solid, Liquid and Gases of the Mie family of Intermolecular Potentials

Using the simulation methodologies outlined in Chapter 2 the global (VLE, SVE and SFE) phase diagrams of a number of Mie potentials over a wide range of intermolecular attraction are presented. Due to the additional parameters which are present in the functional form of the Mie potential, there is essentially an infinite number of model fluids available which can be used in modelling of real substances. To address this, a few works [42] [43] [44] [141] in recent years have attempted to unify view of this family of non conformal fluids using the principle of corresponding states (CS). The conclusions of these works are conflicting and therefore it is still not clear how the CS principle can be applied to the Mie family of potentials. In this Chapter, we attempt to rationalise and clarify the holistic behaviour of this family of fluids through analysis of the free energy of each system and propose an application of the CS principle to Mie fluids.
3. Phase behaviour of solid, liquid and gases of the Mie family

3.1 Introduction

The intermolecular pair potential describes the potential energy change between two molecules as a function of the distance between them. It forms the basis of statistical mechanical theories in which a link between the microscopic and macroscopic properties are made. The calculation of phase diagrams of model molecules is a pre requisite to determining robust parameter sets, that can be used to describe the interaction of real molecules. Spherical models, where both the repulsive and attractive interactions are taken into account, are more accurate in describing the behaviour of real molecular systems. Examples of these are the Sutherland [24] [142], Yukawa [23], Morse [143], Buckingham [25] and LJ [26] potentials.

Amongst these, the Lennard-Jones (LJ) potential [26], is the most widely used model for describing the interaction of simple nonpolar molecules. The functional form was discussed in Chapter 1 (Equation (1.17)) It consists of two terms, a repulsive term proportional to $r^{-12}$ and an attractive one proportional to $r^{-6}$. While there are theoretical arguments to support the form of the attractive exponent [27] [28], there is no basis for the choice in the repulsive form and there has been much debate regarding 12 as being an effective choice for describing the phase behaviour of real substances [104]. Lennard-Jones himself suggested the use of a repulsive exponent of 14 for modelling Argon. It makes sense then to recognise the empirical nature of the LJ potential and to use the exponents as adjustable parameters. This form of the extended LJ form is known as the Mie potential,

\[
\phi^{Mie}(r) = \left( \frac{\lambda_r}{\lambda_r - \lambda_a} \right) \left( \frac{\lambda_r}{\lambda_a} \right)^{\lambda_a/(\lambda_r - \lambda_a)} \epsilon \left[ \left( \frac{\sigma}{r} \right)^{\lambda_r} - \left( \frac{\sigma}{r} \right)^{\lambda_a} \right]. \tag{3.1}
\]

In recent years the Mie potential has become increasingly popular for molecular modelling of real systems [40] and coarse grained models [41] [144] [145] as it usually provides greater flexibility in correlating data due to the additional number of parameters.
From a fundamental perspective, recent studies of the Mie potential have elucidated the effect that the exponents have on the macroscopic thermophysical properties of this family of fluids by development of fluid equations of state and simulation analysis. A number of studies [146] [147] [148] [149] have been presented concerning the vapour liquid coexistence of the Mie potential for various sets of attractive-repulsive exponents. Adamenko et al. [147] studied by MD simulation the influence of the repulsive exponent on derivative properties of the (24,6) Mie fluid compared to the LJ fluid. On the other hand, the work of Paricaud [149], a perturbation approach was presented for the development of an EOS for the study of the fluids phases of model systems interacting via a Mie potential, the results presented were found to be in excellent agreement with simulation data. Similarly, Galliero et al. [148] tested the SAFT-VR Mie EOS of Lafitte et al. [70] on Mie fluids ((λ_r-6 ) where λ_r=8,10 and 12) for the liquid and supercritical states. The direct and derivative thermodynamic properties from the theory were compared to MD simulation data for which good agreement was found between the two.

While the previously mentioned studies investigated the development of fluid equations of state to describe the phase behaviour of model systems interacting via a Mie potential, other works investigate the use of the Mie potential to model the thermophysical properties of real molecular systems [40] [70] [104] [150]. The work of Nasrabad [104] presented an analysis of the Mie (λ_r, 6) in the range λ_r =10-20 and the (14,7) potential. The (14,7) potential in particular is found to be a good molecular model for describing the vapour-liquid behaviour of Argon. Remarkably this exponent pair had been suggested approximately a century ago by Lennard-Jones [26] and by Mie [39] as a model for Argon. Lafitte et al. [70] presented an EOS for Mie fluids which accurately predicts the fluid phase behaviour and derivative properties of n-alkane systems up to C_{36} in which an accurate fit of the theory to experimental data is noted. In a simulation study Potoff and Bernard-Brunel [40] apply the Mie potential to describe the thermophysical properties of several alkane and perfluoroalkanes, in which they find
that the variable range of attraction which the potential allows for, leads to excellent predictions of vapour pressure as well as reproducing the saturated liquid curve to a high degree of accuracy. The model proves to be a remarkable improvement to the LJ potential, which cannot reproduce accurately both of these thermophysical properties. They obtain their results using MC simulations in the GEMC for alkanes from methane to tetradeane and perfluorocarbons from perfluoro-methane to -octane. The vapour pressures were found to be within 3% to 6% of experiments while saturated liquid densities are within 1%. A similar study has been carried out by Gordon [150] for the prediction of transport properties of \( n \)-paraffins, again with good agreement with experimental results. In general, the added flexibility of being able to fine-tune the repulsive exponents in the Mie potential (as opposed to a fixed functional form such as the LJ) allows an overall better fit of both the slope of the saturation curve and the correct representation of secondary derivative properties, e.g., heat capacities and the speed of sound which proves to be useful for modelling of real substances.

As compared to the fluid phases, the global phase behaviour (i.e., incorporation of the solid-fluid transitions) has been studied significantly less. In the study of Ahmed and Sadus [45] softer Mie potentials in which the upper limit of the repulsive range considered was \( \lambda_r = 12 \) using MD simulation were investigated. The effect of the repulsive exponent on the solid-fluid coexistence was examined and the triple point properties were estimated by extrapolation of molecular simulation data of the \( (12,6) \), \( (11,6) \), \( (10,6) \), \( (9,6) \), \( (8,6) \) and \( (7,6) \) potentials. These approximated values are then used to determine the triple point data for the infinitely repulsive case (\( \lambda_r \to \infty \)). Other studies of the solid-fluid transitions have typically analysed the effect of the repulsive exponents on the stability of the vapour-liquid region. It has been shown that the critical point temperature is lowered by increasing the repulsive interaction of the potential. A simulation study by Vliegenthart et al. [151] shows this dramatic decrease in the critical point for an increasingly repulsive potential and in a subsequent work, Vliegenthart and Lekkerkerker [152] propose a predictive method of finding the critical
point of any Mie potential by use of the 2nd virial coefficient, which they show to be insensitive to the repulsive exponent at the critical temperature.

Other studies on solid-fluid transitions of Mie systems are those by Hasegawa [46] and Hasegawa and Ohno [47] who carry out a variation perturbation calculation and apply density functional theory of freezing to analyse the \((\lambda_r = 2\lambda_a, \lambda_a)\) systems. The two approaches produced similar results showing the dependency of the VLE region on the degree of attraction between particles interacting via a Mie potential. They also suggest a Mie potential which can be used to model the buckminsterfullerene (C\(_{60}\)) as an alternative to the Girifalco potential [153] which has a more complex functional form. The results for the C\(_{60}\) model with the Mie parameters are qualitatively in good agreement with a simulation study by Hagen and Frenkel [103] who perform GEMC for the fluids phases and free energy calculations coupled with the Gibbs Duhem integration technique for the solid-fluid transitions. With an increasing degree of repulsion, the metastable solid-fluid region is found to widen in terms of the densities of the transition while the vapour liquid region is seen to shrink. Incidentally, although not explicitly acknowledged in the study of Ahmed and Sadus (mentioned previously), the shrinking of the vapour-liquid region is also observed with an increasingly repulsive exponent. The disappearance of the stable VLE region, however, is not noted as the range of repulsion studied is smaller \((\lambda_r \leq 12)\).

One of the most recent studies on the stability of the liquid phase with variation of inter particle repulsive is an experimental study by Larsen and Zukoski [154]. Through analysis of colloidal interactions they find that the range of attraction plays a critical role in determining whether a system will possess a stable liquid phase hence, confirming the previous simulation studies. Altering the range of repulsion is found to have a pronounced effect on the stability of the liquid phase. They propose the use of a critical variable which is a ratio of the energies of the liquid and solid phases, which can be used to determine the stability of the liquid phase. Unfortunately, the
Mie potential is not explicitly studied in this work, but this analysis provides sound experimental evidence which elucidates the mechanisms through which a system will exhibit a metastable liquid state, liquid-like or solid-like behaviour.

The works presented thus far have been attempts to study Mie systems at a fundamental level seeking validation of equations of state developed with computer simulations, studying the effect of exponents on thermophysical properties or applications of Mie fluids for modelling of real substances. In addition to these works, there have been several publications which aim at rationalising the behaviour of the Mie family of potentials using the principle of corresponding states. The Mie potential is characterised uniquely by four parameters: the energy well depth, $\epsilon$, the diameter of the particle $\sigma$ and the exponents which dictate the overall potential form $\lambda_r$ and $\lambda_a$. It is unclear however, to what extent these four parameters are independent of each other and if a corresponding states principle may be applied to study this family of potentials.

In the context of the CS principle, Orea et al. [43] have studied the VLE of a wide range of Mie fluids $(24,12)$, $(18,9)$, $(14,7)$, $(18,6)$, $(32,6)$ and LJ, using computer simulations. They reduced the saturated vapour-liquid curve, surface tension plots and pressure-density plots with respect to critical properties of the respective fluids ($T_r = T/T_c$, $P_r = P/P_c$, $\rho = \rho/\rho_c$ and $\gamma_r = \frac{\gamma}{\gamma_c}$) and noted that the curves roughly aligned to a single master curve for each of the properties considered, suggesting that independent of the repulsive and attractive exponents, all Mie fluids follow a 2-parameter CS model. The authors advocate that independent of the potential exponents ($\lambda_r$ and $\lambda_a$) all Mie fluids can be characterised by two parameters $\sigma$ and $\epsilon$. This result is particularly surprising as it is known for example that the SW fluids are non conformal. The findings of Orea et al. seem to be in accordance with a previous study by Okumura and Yonezawa [42] who analyse the $(\lambda_r,6)$ fluids over a range $\lambda_r = 7-32$. They show that the vapour-liquid curve of all Mie fluids tested collapse to a master curve when reduced with respect to critical properties, however they also recognise a
linear dependence of the critical properties on the range of attraction of the potential model. There is strong emphasis that these critical properties are in themselves dependent of the exponents of the potential and this dependency will be analysed in greater depth in this work.

In stark contrast to the works of Orea et al. and Okumura and Yonezawa, there have been a few studies which suggest that the Mie systems will not follow a 2 parameter CS model. A study by Bulavin and Kulinskii [44] and subsequently Kulinskii [141] suggest that when reduced with respect to the critical properties, the $T - \rho$ fluid range of Mie systems will not align to a master curve (in accordance for example with the behaviour exhibited by the SW family) i.e., all Mie systems will not follow a two parameter model independent of the potential exponents. Through a theoretical analysis (which is confirmed by simulation data of Vliegenthart et al [151]) the authors suggest that Mie systems will align to a master curve if a three parameter CS model is used. The parameter $z$, which is dependent on the critical temperature of a given Mie fluid, is defined, and is used in essence as a third parameter which is required for the Mie to be applied to the CS principle. A final study which also disagrees with the argument for a two parameter CS model for the Mie is an investigation presented by Galliero et al. [155], who find a dependence of the reduced pressure (for $(\lambda_r,6)$ fluids ranging from $\lambda_r=10-20$) on the repulsive exponent. The reduced pressure ($P_r = P^*/P^{*c}$) of a given Mie fluid differs from the reduced pressure of the LJ model (used as a reference for comparison) and therefore the vapour-pressure curves will not align to a unique master curve. This difference is noted to increase with increasing density. These results suggest that Mie fluids will not follow the CS principle unless they have the same repulsive exponent and therefore will follow a three parameter ($\sigma$, $\epsilon$ and $\lambda_r$) CS model.

In this chapter we carry out systematic MD simulations to determine solid-vapour, liquid-vapour and solid-fluid boundaries for a host of Mie potentials with a varying
range of attraction and repulsion. A CS principle is applied by examining the free energy of the system using a perturbation approach. This treatment is used to classify the phase behaviour of these systems and to characterise it under a CS principle framework.

3.2 The Corresponding States Principle

The corresponding states principle for describing thermophysical properties of fluids is based on the underlying assumption that there is a common functional form that can describe these properties regardless of the fluid. The pioneering experimental studies of Guggenheim [156] and Su [157] provide proof that simple fluids follow a unique master curve when reduced with respect to their critical properties. The work of Guggenheim in particular is noteworthy as it was the first experimental work to analyse thermophysical properties such as the vapour-liquid curve, 2\textsuperscript{nd} virial coefficient, Boyle point, vapour pressure, entropy of vapour, coefficients of thermal expansion, triple point properties and surface tension of liquid argon, krypton, xenon and neon. All of these thermodynamic properties were found to follow the CS principle. Nitrogen, oxygen, carbon monoxide and methane were also analysed [156] and were also found to conform to a unique vapour-liquid curve. Additionally, Guggenheim observed that although the fluid phases follow the CS principle this is not true for the solid phase. Before these experimental studies however, the CS principle had been suggested theoretically by van der Waals [158] who derived it from his EOS in the form;

\[ P_r = \frac{8T_r}{(3V_r - 1)} - \left( \frac{3}{V_r^2} \right), \]  

(3.2)

where, \( T_r = T/T_c \), \( V_r = V/V_c \) and \( P_r = P/P_c \), the reduced pressure. A major contribution of this theory is that the experimentally known configurational properties of a few substances can be used to predict the values of the same properties for fluids which have not been studied experimentally. In fact it was by following these suggestions
that Kamerlingh-Onnes [159] was able to liquify Helium; a notable example of theory guiding experimental discovery. It is important to note that the CS principle is not a universal law but rather an experimental observation valid within a range of conditions and for substances of similar morphology. This is noted by the excellent agreement shown by the noble gases when tested against the list of properties investigated by Guggenheim. For more complex fluids this conformal behaviour is not followed as precisely. For example, even simple almost spherical compounds such as CH$_4$ do not follow quantitatively the reduced properties of the noble gases.

Although the CS principle was originally an empirical observation, it can also be inferred from statistical mechanics under a set of well defined approximations [6]. The advantage of such a route (by comparison to macroscopic derivations such as that of van der Waals) is that it clarifies the approximations made and confirms that the CS principle should be extendable to more complex systems [6]. The derivation of the CS principle from statistical mechanics along with the assumptions which are applied can be found in a review by Leland and Chapplear [160] and in [6]. The fundamental issue is the assumption of the existence of a universal function of a pairwise potential which can be nondimensionalised such that:

$$u \left( \frac{r}{\sigma} \right) = \epsilon \phi \left[ \frac{r}{\sigma} \right]$$  \hspace{1cm} (3.3)

where $\phi$ is the dimensionless potential function of the position of the particle, $r$ and the parameters $\epsilon$ and $\sigma$ are constant and characteristic for a given substance. The underlying assumption is that for most simple spherical fluids only repulsive and dispersive forces are important hence two scales, one of energy and the other distance are deemed sufficient to map the fluid behaviour. The molecular requirements that must be satisfied for a system to obey the CS principle in its simplest form have been previously outlined by Pitzer [161]. These two independent scaling parameters ($\epsilon$ and $\sigma$) may then be employed to non-dimensionlise macroscopic properties. The dimen-
sionless critical properties $T^*_c = k_B T_c / \epsilon$, $P^*_c = P_c \sigma^3 / \epsilon$ and $\rho^*_c = \rho_c \sigma^3$ are then related to the intermolecular potential parameters $\epsilon$ and $\sigma$ thereby providing the link between experimental approaches and statistical mechanics. Using non-dimensional variables the EOS can be expressed in the form:

$$P^* = f(T^*, V^*).$$

(3.4)

One application of this concept is to estimate the model parameters ($\epsilon$ and $\sigma$) from a wide range of experimental data by using the EOS to find the best fit to the vapour pressure and saturated liquid density [6].

For fluids with more complexity than an isotropic repulsion and dispersion, more detailed intermolecular functions need to be implemented, this is reflected in the intermolecular potential being characterised by a larger number of parameters, e.g., the Kihara potential [162], given by:

$$\phi(r) = \epsilon \left[ \frac{\lambda_a}{\lambda_r - \lambda_a} \left( \frac{r_m}{r} \right)^{\lambda_r} - \frac{\lambda_r}{\lambda_r - \lambda_a} \left( \frac{r_m}{r} \right)^{\lambda_a} \right],$$

(3.5)

where $\lambda_r > \lambda_a > 3$, and $r_m$ in the distance between two particles at the potential well minimum. This potential can be made to describe the phase behaviour of polar polyatomic fluids particularly well by comparison to simpler models [6] and therefore a two-parameter CS approach is no longer valid. This aspect has been thoroughly reviewed by Leland and Chapplear [160]. The increase in the number of parameters is dependent on the severity of the deviation from the original assumption outlined by Pitzer [161] for the CS principle. For example, weakly polar molecules can be modeled with a three parameter CS model while moderately polar molecules with appreciable asymmetry require four parameters. The addition of parameters indicates a change in the choice of the intermolecular potential used to describe the fluid. It is also understood that molecular fluids that conform to the CS principle must interact via an intermolecular potential that is commensurate in terms of the parameter set used to
describe it, i.e., a three-parameter CS model should be mappable to an intermolecular potential with at least three characteristic parameters. An example are families of hard potentials with attractive variable ranges such as Sutherland, square well and Yukawa potentials.

Analyses have also been carried out on the conformality of experimental fluids to a given potential, LJ [148], square well [163] and hard core attractive Yukawa potentials [164] [165]. In addition to this, there has been a recent interest in applying the CS principle to Mie systems, as discussed earlier [42] [43] [155] [44] [141]. In two of these studies with the Mie potential a two parameter CS approach was used [42] [43]. The authors advocate that all Mie fluids, independent of exponent, follow a universal trend when reduced with respect to the critical properties i.e., a two-parameter CS model. As shown in the previous section however, there have been a number of works [44] [141] [155] which dispute this. Bulavin and Kulinskii [44] and the later work of Kulinskii [141] propose a parameter $z$, which is a function of the critical temperature, which can be used as a classification of Mie intermolecular potentials such that the potentials of the same $z$ parameter exhibit conformal properties i.e., a three-parameter CS model. Galliero et al [155], have also discussed the invalidity of a two-parameter CS model for the Mie family of fluids by showing that the reduced pressure of a host of $(\lambda_r, 6)$ systems do not conform to reduced pressure of the $(12, 6)$ model. They suggested that for Mie fluids to follow the CS principle the repulsive exponent of the Mie potential must be the same.

In this work an analytical expression for the Helmholtz free energy of the fluid based on perturbation theory is used to present a conformal mapping of Mie fluids. The proposed scaling is validated using MD data of the solid, liquid and gas phase boundaries of a range of Mie fluids of variable range of attraction.
3.2.1 Conformality through the free energy

For two or more fluids to be conformal (i.e., exhibit the same macroscopic thermodynamic properties), they must, in essence, have the same free energy. Assuming then that the Barker and Henderson (BH) [14] [166] perturbation theory can be used to obtain an accurate description of the free energy of the fluid (and implicitly of the solid) it is possible to obtain an expression for the free energy of a given fluid. The theory of BH originates from treating the attractive potential as a perturbation of a hard sphere system with an effective diameter. This is written as;

\[ a = a^{id} + a^{HS} + \beta a_1 + \beta^2 a_2 + \ldots \]  

(3.6)

where, \( a^{id} \) is the free energy of an ideal gas, \( a^{HS} \) is the free energy of a hard sphere reference system of diameter \( d \), \( \beta \) is the inverse of temperature \( \beta = \frac{1}{kT} \), \( a_1 \) is the first order perturbation term and \( a_2 \) is the second order perturbation term. By approximating the total free energy to the first term only, the free energy can be expressed by,

\[ a = a^{id} + a^{HS} + \beta a_1. \]  

(3.7)

The first perturbation term \( a_1 \) is given by;

\[ a_1 = -2\pi \rho \int_{\sigma}^{\infty} g^{HS}(r)\phi(r)r^2 dr, \]  

(3.8)

where \( g^{HS}(r) \), is the radial distribution function of the hard sphere system, \( \rho \) is the density and \( \phi(r) \) is the intermolecular potential as shown before. If a mean field approximation is assumed where the fluid is homogeneously distributed, (i.e. \( g(r)^{HS} = 1 \)) and the Mie potential is substituted in the integral, the mean field energy of a Mie fluid can be written as;

\[ a_1 = 2\pi \rho \sigma^3 \epsilon \alpha, \]  

(3.9)
which as is often implemented in mean field approaches. \( a_1 \) is a function of density and three parameters \( \epsilon, \sigma \) and \( \alpha \), which is given by,

\[
\alpha = \frac{1}{\epsilon \sigma^3} \int_\sigma^\infty \phi(r)r^2dr = C \left[ \left( \frac{1}{\lambda_a - 3} \right) - \left( \frac{1}{\lambda_r - 3} \right) \right].
\]

(3.10)

where \( C \) is given by;

\[
C = \left( \frac{\lambda_r}{\lambda_r - \lambda_a} \right) \left( \frac{\lambda_r}{\lambda_a} \right)^{\lambda_a/(\lambda_r - \lambda_a)}.
\]

(3.11)

Examining Equation (3.9) it can be seen that fluids of the same \( \epsilon, \sigma \) and \( \alpha \) will have the same free energy, hence, the same properties and therefore will be conformal. The parameter \( \alpha \) depends solely on the repulsive and attractive exponents and it constitutes a dimensionless third parameter that determines the free energy of the Mie fluid under consideration. This derivation suggests that the Mie potential is not conformal for any given pair of exponents \( (\lambda_r, \lambda_a) \) but rather only the those that yield the same value of \( \alpha \). This result also suggests that the Mie family can not be mapped to a unique master curve as suggested by Orea et al. [43] and Okumura and Yonezawa [42]. These issues are further discussed in Section 3.4.

### 3.3 Simulation Details

MD simulations are performed to determine the phase boundaries of the Mie fluids studied. The different simulation strategies outlined in Chapter 2 are implemented. For the VLE region \( NVT \) simulations of \( N=2400 \) particle were run for \( 10^6 \) timesteps with the first 40% of the configurations discarded to ensure equilibration. The critical temperature and density values were calculated by fitting to subcritical data, using the simulation results for the liquid and vapour densities and the relations,

\[
\rho^*_l = \rho^*_c + C_2 \left| 1 - \frac{T^*_c}{T^*_e} \right| + \frac{1}{2} B_0 \left| 1 - \frac{T^*_a}{T^*_e} \right|^2
\]

(3.12)
and

\[ \rho_v^* = \rho_c^* + C_2|1 - \frac{T^*}{T_c}| - \frac{1}{2}B_0|1 - \frac{T^*}{T_c}|^\beta, \]  

(3.13)

where \( \rho_l^* \) and \( \rho_v^* \) are the liquid and vapour coexistence densities at temperature \( T^* \). \( \rho_c^* \), \( B_0 \) and \( C_2 \) are constants and \( \beta \) is the critical exponent. The universal value determined from renormalisation group theory shows a cubic shaped coexistence curve \( \beta = 0.325 \).

Details of the methodology are outlined by Vega et al. [97].

The SVE boundary was determined using the Rahman-Parrinello [95] technique of constant stress. We refer to these as \( N\sigma T \) simulations, at zero pressure over a period of \( 10^6 \) timesteps with the first 40% being discarded to ensure equilibration. The SFE boundaries were determined with the Freeze technique (Section 2.2), run in the \( NVT \) ensemble for \( 5 \times 10^6 \) timesteps, 20% of which are discarded for equilibration.

As mentioned previously no long-range corrections have been implemented in these simulations however it has been shown for the LJ potential that a cut-off radius of \( 5\sigma \) is sufficient to take into account 99.94% of the interaction energy and when tested against a longer cut-off radius (\( 7\sigma \)) there is no change in the calculated coexisting densities (within the simulation error). As the functional form of the Mie allows slow decaying attractive tails, for potentials ‘softer’ than LJ it is also prudent to analyse whether \( 5\sigma \) is still a valid choice. For the softest potential analysed (8-6) a cut-off of \( 5\sigma \) takes into account 99.89% of the energy. Additionally we have tested the freeze method on the (9.84-6) potential with a cutoff radius of \( 7\sigma \) for which a negligible difference between the coexisting densities of the solid and fluid phases from those obtained using \( 5\sigma \) is found. This result confirms that the cut-off radius of \( 5\sigma \) is sufficiently large for testing of all Mie potentials in this study.
3.4 Results

The proposed parameter $\alpha$ is used to select two Mie fluids expected to exhibit conformal phase behaviour given the discussion in Section 3.2. MD simulation are used to determine the phase boundaries of the selected Mie systems. In addition, a range of Mie systems spanning a range of the parameter $\alpha$ are also studied and the effect the parameter has on the fluid range is analysed. A relationship is proposed between $\alpha$ and the size of the stable VLE region. The use of $\alpha$ to model coarse-grained spherical models is also discussed.

3.4.1 Validation of $\alpha$ to determine conformal Mie fluids

To validate the proposal that Mie fluids exhibit conformal behaviour provided that they possess the same value of $\alpha$, we study the fluid range and the vapour pressures of two Mie fluids of different exponents that share a common $\alpha$ value which we choose to be 0.52; fluid 1 has exponents (23, 6.66) and fluid 2 is a (14.65, 8) Mie (refer to Figure 3.1).

![Figure 3.1: Intermolecular potentials of 3 Mie fluids. Two fluids with the same $\alpha$ value, 0.52; fluid 1, (23,6.66) (green solid line) and fluid 2, (14.65,8) (purple solid line). The third fluid is LJ (solid blue line) with a corresponding $\alpha$ value of 0.89.](image-url)
For comparison the phase behaviour of these two fluids are compared to that of the LJ model (12,6) which has an \( \alpha = 0.89 \). In Figure 3.2(a) the \( T^* - \rho^* \) coexistence curve of the fluid region of all three fluids are compared using reduced units in terms of their critical properties \( (T_r = T^*/T_c^*) \) which are presented in Table 3.1. The coexistence density curves of the fluid region of the three systems appear to align which is in accordance with findings of Orea et al. [43] and Okumura and Yonezawa [42]. On closer inspection however if one plots the fluid properties in terms of their natural reduced properties (Figure 3.2(b)) it is evident that the LJ system exhibits a very different phase behaviour and therefore can not be said to be conformal with respect to the other two Mie fluids considered. Fluid 1 and 2 (of the same \( \alpha \)) on the other hand do display a close-to-conformal behaviour. There is a slight deviation with respect to the critical temperature between these two fluids which can be accounted as due to the assumptions made in the definition of \( \alpha \) i.e., the free energy is approximated to a first order expansion (Equation (3.7)). Additionally a mean field approximation of the \( g(r) \) has been made for the fluids which although reasonable is not formally exact.

Table 3.1: Tabulated values of three Mie systems used to analyse the conformal behaviour of Mie fluids.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \alpha )</th>
<th>( \lambda_r )</th>
<th>( \lambda_a )</th>
<th>( T_c^* )</th>
<th>( \rho_c^* )</th>
<th>( P_c^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.52</td>
<td>23.00</td>
<td>6.66</td>
<td>0.87</td>
<td>0.334</td>
<td>0.085</td>
</tr>
<tr>
<td>2</td>
<td>0.52</td>
<td>14.65</td>
<td>6.00</td>
<td>0.83</td>
<td>0.333</td>
<td>0.065</td>
</tr>
<tr>
<td>LJ</td>
<td>0.89</td>
<td>12.00</td>
<td>6.00</td>
<td>1.33</td>
<td>0.300</td>
<td>0.135</td>
</tr>
</tbody>
</table>

The vapour pressures are also studied for these fluids as shown in Figure 3.3. In Figure 3.3(a) the properties are scaled with respect to their own critical points. In this representation Fluid 1 and 2 present very similar (if not mathematically identical) properties, however the LJ fluid presents very different values of vapour pressures. Scaling the data with respect to the potential parameters \( \epsilon \) and \( \sigma \) (Figure 3.3(b)) confirms the excellent agreement of the two conformal fluids (1 and 2), with a significant
deviation of the vapour pressure of the LJ model. This result explains in part the findings of Galliero et al. [155] who suggests that the vapour pressures of the Mie will not follow the CS principle for any arbitrary pairing of exponents; this is in essence analogous to the current proposal of the parameter $\alpha$. Reiterating, only those pairs of $\lambda_r$ and $\lambda_a$ corresponding to the same $\alpha$ will follow the CS behaviour.

The global phase diagram (solid, liquid and vapour phase boundaries) of all three potentials are also compared. In Figure 3.4(a) the phase boundaries reduced with respect to the critical properties are shown. This is a particularly noteworthy result as this representation highlights how the fluid ranges of all Mie potentials are not conformal as previously suggested [43] [42]. The triple point temperatures of fluids 1 and 2 are essentially equal and therefore the fluid range $T_c^*/T_t^*$ of these fluids are also the same. The LJ model however has a distinctly larger fluid range by comparison to fluids 1 and 2, and clearly does not exhibit conformal behaviour. In Figure 3.4(b), in different units, a similar result is observed: a much more expanded fluid range is evident for the LJ model by comparison to the $\alpha_1$ and $\alpha_2$ models. These global phase diagrams show the non-conformal nature of the solid phase which as previously mentioned was originally suggested by Guggenheim [156] and is again confirmed in this work. The $\alpha$ parameter is defined strictly from the integration of the average cohesive energy of the potential, evidenced by the fact the integration is made from a value of $\sigma$ (for which the potential is zero) spanning into the attractive well of the potential. The particles of a solid, however will on average explore the repulsive ($r < \sigma$) region of the potential. The repulsive component contributes heavily to the shape of the potential in this region but is not included in the evaluation of $\alpha$; leading to differences in the solid-fluid phase behaviour of fluids 1 and 2.
Figure 3.2: a) Vapour-liquid coexistence densities plotted in reduced units with respect to critical properties for the LJ potential (blue diamonds), $\alpha_1$ (23.66) potential (green triangles) and $\alpha_2$ (14.65,8) potential (purple circles). b) Vapour liquid coexistence densities expressed in reduced units, symbols as in (a). The estimated critical points are highlighted by crosses of each respective colour.
Figure 3.3: a) Vapour-pressure curve presented in reduced units with respect to critical properties for the LJ potential (blue diamonds), $\alpha_1 (23,6.66)$ potential (green triangles) and $\alpha_2 (14,65,8)$ potential (purple circles). b) Vapour-pressure curve expressed in reduced units, symbols as in (a). The estimated critical points are highlighted by crosses of each respective colour. Black solids lines are a guide to the eye.
Figure 3.4: a) Global phase diagram presented in reduced units with respect to critical properties for the LJ potential (blue diamonds), $\alpha_1$ (23,6.66) potential (green triangles) and $\alpha_2$ (14.65,8) potential (purple circles). The triple point temperature of each potential is highlighted by black dashed lines b) Global phase diagram expressed in reduced units, symbols the same as previous figure. The estimated critical points are highlighted by crosses of each respective colour.
3.4.2 Phase behaviour trends of the Mie potential

Figure 3.5: Variation of $\alpha$ as a function of repulsive exponent $\lambda_r$. The purple curve corresponds to ($\lambda_r$, 8.8) potentials, the blue curve to ($\lambda_r$, 7.5) potentials, the red curve to ($\lambda_r$, 6.66) potentials and the green curve to ($\lambda_r$, 6) potentials. The black crosses indicate the potentials chosen for simulations with the individual exponents used.

A host of Mie potentials of varying range of attraction characterised by unique values of the $\alpha$ parameter have been studied spanning a wide range of the intermolecular interaction (from a soft, slow-decaying, attractive tail to a very short-ranged attraction). In order to obtain a good spread of data we refer to the plot in Figure 3.5 which shows the chosen Mie potentials ($\lambda_r$, $\lambda_a$) with their corresponding $\alpha$ value. The range of $\alpha$ chosen for analysis is 0.279-1.26. The individual Mie potentials studied are highlighted in Figure 3.5. The softest potential studied is the (8,6) model (corresponding to $\alpha$=1.26) and the most repulsive potential considered is (42,8.8) (corresponding
3. Phase behaviour of solid, liquid and gases of the Mie family

to $\alpha=0.279$). Using the simulation methodology outlined in the previous chapter the solid, liquid and vapour phase boundaries of these Mie potentials are obtained by MD simulation. As an example, Figure 3.6 highlights the key aspects of the phase diagram of one such Mie potential studied (32.53-6). The critical point properties are determined from fitting to subcritical data and using Equations (3.12) and (3.13). For the given Mie potential the critical properties are found to be $T^*_c=0.869$ and $\rho^*_c=0.341$. The triple point temperature is obtained by observation of the intersection of the vapour liquid coexistence curve with the solid-fluid boundary, which occurs at $T^*_t=0.635$. The tabulated simulation data for this potential is presented in Table 3.2.

Seven systems interacting via Mie potential are presented, the specific values of the exponents ($\lambda_r, \lambda_a$), the critical point temperatures, triple point temperatures and fluid ranges are listed in Table 3.3. The simulation data of each potential are presented in Appendix B. In each case the $T^*$ and $\rho^*$ is plotted reduced with respect to critical properties (Figure 3.7(a)). As discussed previously, it has been confirmed that conformal behaviour is only applicable to the fluid region of the phase diagram and therefore the fluid properties alone are presented in the subsequent graph (Figure 3.7(b)) to analyse this behaviour in more detail. By plotting the properties reduced with respect to $T^*_c$ and $\rho^*_c$ it is expected that the VLE envelopes will align however it is also observed that the triple point temperatures do not and therefore the fluid ranges ($T^*_c/T^*_t$) are different. The triple point temperature of each fluid studied is determined by the intersection point of the solid-fluid phase boundary and the vapour-liquid curve; as shown in Figure 3.7(b), this occurs at varying temperatures. It is also evident that reducing the value of $\alpha$, and hence reducing the range of attraction of the potential results in a decrease in the size of the stable fluid coexistence range ($T^*_c/T^*_t$). For the softest potential, $\alpha=1.26$ corresponds to a fluid range of $T^*_c/T^*_t=2.47$, however on the other extreme, $\alpha=0.279$ the fluid range decreases significantly to 1.04. The shrinking of the VLE region with a decreasing value of $\alpha$ is better seen in Figure 3.8 where the phase diagrams of six Mie systems are presented. The gradual decrease in $\alpha$ clearly results
in the shrinking of the fluid range until, it becomes entirely metastable with respect to the solid phase.

Figure 3.6: Global phase diagram corresponding to $\alpha = 0.538$ (35.63,6). Diamonds represent the VLE envelope obtained from direct $NVT$ simulation with the estimated critical point represented by a cross, triangles are $N\sigma T$ simulations at zero pressure to obtain the solid-vapour boundary and the circles represent the solid-fluid boundary obtained from the freeze method. The open points represent the metastable simulations and the dashed line represents the triple point obtained from intersection of the solid-gas line with the solid-fluid line as well as the intersection of the saturated liquid curve with the solid-fluid boundary.
Table 3.2: Tabulated values of the coexistence properties at $\alpha=0.538$. The metastable points are highlighted with parentheses and the type of equilibrium is shown in the last column along with the estimated (*) triple and critical point. The error estimation is in square parentheses.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho_g^*$</th>
<th>$\rho_l^*$</th>
<th>$\rho_s^*$</th>
<th>phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.300</td>
<td>$\sim0$</td>
<td>1.125[1]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.350</td>
<td>$\sim0$</td>
<td>1.115[1]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.400</td>
<td>$\sim0$</td>
<td>1.104[2]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.450</td>
<td>$\sim0$</td>
<td>1.092[1]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.490</td>
<td>(0.002[8])</td>
<td>(0.939[3])</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>$\sim0$</td>
<td>1.079[2]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.527</td>
<td>(0.003[4])</td>
<td>(0.912[6])</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.550</td>
<td>$\sim0$</td>
<td>1.066[3]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.565</td>
<td>0.006[7]</td>
<td>(0.883[4])</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
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<td>$\sim0$</td>
<td>1.048[4]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.600</td>
<td>(0.794[6])</td>
<td>(1.047[9])</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.602</td>
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<td>(0.853[4])</td>
<td>VLE</td>
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</tr>
<tr>
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<td>$\sim0$</td>
<td>0.816</td>
<td>1.046</td>
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</tr>
<tr>
<td>0.640</td>
<td>0.017[5]</td>
<td>0.819[7]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.650</td>
<td>0.828[1]</td>
<td>1.045[9]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.650</td>
<td>$\sim0$</td>
<td>1.045[4]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.678</td>
<td>0.026[2]</td>
<td>0.785[4]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.700</td>
<td>0.844[4]</td>
<td>1.044[12]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.715</td>
<td>0.040[3]</td>
<td>0.746[5]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.750</td>
<td>0.859[6]</td>
<td>1.041[9]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.753</td>
<td>0.061[7]</td>
<td>0.704[1]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.791</td>
<td>0.087[2]</td>
<td>0.646[9]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.800</td>
<td>0.871[6]</td>
<td>1.041[9]</td>
<td>SFE</td>
<td></td>
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<td>0.850</td>
<td>0.878[7]</td>
<td>1.043[9]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.869</td>
<td>0.341</td>
<td>0.341</td>
<td>critical pt*</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.899[3]</td>
<td>1.049[8]</td>
<td>SFE</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.7: (a) Comparison of global phase diagrams reduced with respect to the critical properties at all potentials \((\lambda_r, \lambda_a)\). \((8,6)\) (crosses), \((9.85,6)\) (T-crosses), \((12,6)\) (open diamonds), \((15.6,6)\) (open circles), \((32.53,6)\) (closed triangles), \((23,6.66)\) (closed diamonds), \((19.02,8.8)\) (closed circles), \((42.8,8.8)\) (horizontal dashes). (b) same as (a) with the saturated solid boundary data removed for clarity.
Figure 3.8: Variation of the \((T^* - \rho^*)\) global phase diagrams with a decrease in the parameter \(\alpha\) a) (9.85,6), b) (12.6), c) (15.58,6), d) (19.02,8.8), e) (42.5,8,8) and f) (44.2,9). Symbols as in Figure 3.6. No triple point or vapour-liquid critical point is observed for the system with \(\alpha=0.269\) (44.2,9).
The relationship between the triple point \((T_t^*)\) and critical point \((T_c^*)\) with respect to \(\alpha\) is shown in Figure 3.9. A positive linear trend in the critical point with respect to \(\alpha\) is observed. The triple point also increases with increasing \(\alpha\) although, with a smaller gradient. The intersection of these two lines provides a value of \(\alpha\) below which the VLE region is predicted to be metastable. The shaded region in between these two lines provides a physical representation of the decrease in size of the stable VLE region with a decreasing value of \(\alpha\). The critical point \((T_c^*)\) appears to be most heavily influenced by a change in \(\alpha\) which may be explained by the fact that \(\alpha\) quantifies the size of the attractive well of the potential and consequently the degree of repulsion of the potential. This dependence of \(T_c^*\) has previously been reported by several authors [42] [44] [152].

Even more remarkable is the proposed linear relationship which has been observed between the fluid range, \((T_c^*/T_t^*)\) and the parameter \(\alpha\). The graph presented in Figure 3.10 suggests that for any value of \(\alpha\), and by association any Mie potential chosen, the corresponding fluid range can be directly determined with this linear relationship which is expressed by the following correlation;

\[
\frac{T_c}{T_t} = 1.464\alpha + 0.608. \tag{3.14}
\]
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Table 3.3: Tabulated values of the Mie potentials used, individual exponents $\lambda_r$ and $\lambda_a$ and the corresponding $\alpha$ value, the critical point, triple point and fluid range of all Mie potentials simulated in this work.

<table>
<thead>
<tr>
<th>$\lambda_r$</th>
<th>$\lambda_a$</th>
<th>$\alpha$</th>
<th>$T_c^*$</th>
<th>$T_t^*$</th>
<th>$\frac{T_c^<em>}{T_t^</em>}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00</td>
<td>6.00</td>
<td>1.26</td>
<td>1.74</td>
<td>0.706</td>
<td>2.47</td>
</tr>
<tr>
<td>9.85</td>
<td>6.00</td>
<td>1.04</td>
<td>1.46</td>
<td>0.680</td>
<td>2.14</td>
</tr>
<tr>
<td>12.00</td>
<td>6.00</td>
<td>0.89</td>
<td>1.33</td>
<td>0.694</td>
<td>1.92</td>
</tr>
<tr>
<td>15.58</td>
<td>6.00</td>
<td>0.75</td>
<td>1.11</td>
<td>0.670</td>
<td>1.66</td>
</tr>
<tr>
<td>32.53</td>
<td>6.00</td>
<td>0.54</td>
<td>0.869</td>
<td>0.635</td>
<td>1.37</td>
</tr>
<tr>
<td>23.00</td>
<td>6.66</td>
<td>0.52</td>
<td>0.86</td>
<td>0.636</td>
<td>1.35</td>
</tr>
<tr>
<td>19.02</td>
<td>8.80</td>
<td>0.40</td>
<td>0.735</td>
<td>0.600</td>
<td>1.23</td>
</tr>
<tr>
<td>42.50</td>
<td>8.80</td>
<td>0.28</td>
<td>0.585</td>
<td>0.563</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Figure 3.9: Variation of the critical point, $T_c^*$ (closed diamonds) and the triple point $T_t^*$ (closed triangles) with $\alpha$. Solid lines are a guide to the eye. The shaded region indicates the stable VLE region.
3. Phase behaviour of solid, liquid and gases of the Mie family

Figure 3.10: Variation of the fluid range $T_c^*/T_t^*$ with $\alpha$ (diamonds). The $\alpha$ value of the potentials at which the VLE region becomes metastable with respect to the solid has been determined by Hasegawa [46] with a variational perturbation theory (circle) and by Hasegawa and Ohno [47] with density functional theory of freezing (asterisk) have been plotted for comparison. The linear trend intersects with the line $T_c^*/T_t^*=1$ (dashed line) at $\alpha=0.269$ indicating that below this value of $\alpha$ the VLE region is metastable.

From Figures 3.9 and 3.10 the potential at which the VLE region becomes metastable with respect to the solid can be determined. In Figure 3.9, the phenomenon is expected to occur at the $\alpha$ value at the intersection of the two lines, while in Figure 3.10 the intersection of the linear trend of $\alpha$ with the line $T_c^*/T_t^*=1$ also indicates that this is the limiting potential at which a VLE region is no longer stable. The point of
intersection occurs at $\alpha=0.269$. This result is compared to the potentials determined by Hasegawa [46] and Hasegawa and Ohno [47] who also investigated the limiting potential of the Mie for a stable VLE region. Hasegawa and Ohno determined such a potential using a density functional theory of freezing and find the potential to be $(24,12)$. This corresponds to $\alpha=0.254$. Hasegawa determined the potential for the metastability of the VLE region using variational perturbation theory and found the potential to be $(28,14)$ ($\alpha=0.204$). Both these points have been included in Figure 3.10 as a comparison to the potential determined in this work. The agreement is reassuring, notwithstanding, the former studies use the $(\lambda_r = 2\lambda_a, \lambda_a)$ classification which only allows for discrete potentials to be analysed. The result presented here is more general in nature and not restricted to integer exponents as seen in the former works.

In Figure 3.8(f) the global phase diagram of the limiting potential for VLE stability predicted from the linear relationship (Equation (3.14)) $\alpha=0.269$ is shown. Using the freeze methodology the global phase behaviour is determined with simulation as previously discussed in Chapter 2. As predicted no stable liquid region is observed and the VLE region is metastable with respect to the solid phase. This result in particular showcases the flexibility of the Mie potential for analysing a wide range of complex systems and its capacity for modelling real systems which exhibit this anomalous phase behaviour. This phase diagram also provides confidence that the linear relationship proposed provides an accurate representation of the variation of the fluid range with $\alpha$.

### 3.4.3 Application to real fluids and coarse-grained potentials

An added benefit of the new proposed parameter $\alpha$ which determines the extent of the fluid range is that it can be used to propose Mie potentials for modelling of anisotropic coarse grained models for both simple and complex fluid systems. This can be explained with the aid of Figure 3.11; the fluid range of carbon dioxide ($T_c^{\text{exp}}=304.25$, $T_l^{\text{exp}}=216.55\text{K}$) for example can be mapped to a corresponding $\alpha$ value which can then
be used to determine a host of corresponding exponents that can be used to describe the fluid with a Mie potential consistent with the fluid range of the experimental fluid. The dashed CO\textsubscript{2} line labeled “CO\textsubscript{2}” corresponds to the fluid range for CO\textsubscript{2}; $T_c/T_t=1.405$. This intersects the curves which correspond to $(\lambda_r, 6)$, $(\lambda_r, 7)$ and $(\lambda_r, 8)$ Mie potentials give an indication of the values of the repulsive exponent $\lambda_r$ at each intersection point. From this plot it is possible to estimate the exponents that could be used to fit the fluid range of a given experimental fluid. For example this suggests that the thermodynamic properties of CO\textsubscript{2} can be accurately described using a sphere with a (31,6), or an (18,7) or a (13.5,8) potential with equivalent accuracy. Although the parameters may be obtained from least square fitting of experimental data such as vapour pressure and densities [41] the parameter space is large and the solution is not unique. Being able to propose exponent pairs \textit{a priori} which are self-consistent will enable more robust parameters to be obtained from this fitting procedure.

Another example is also the buckminsterfullerene, C\textsubscript{60} molecule. This molecule consists of 60 carbon atoms held together by covalent bonds where the molecules interact with each other via van der Waals forces. There is limited available experimental data for this system however, Girifalco [153] has proposed an analytic potential to describe the interaction of these molecules:

$$\phi(r) = -b \left[ \frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4} \right] + c \left[ \frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{2}{s^{10}} \right], \quad (3.15)$$

where $s = 2\sigma_{C_{60}}$, $\sigma_{C_{60}}$ is the radius of a C\textsubscript{60} sphere ($\sigma_{C_{60}}=3.55$ \textup{A}). The values of $b$ and $c$ were determined by Girifalco by fitting to experimental data of the sublimation energy and lattice parameter of the $C_{60}$ solid. The thermophysical properties of this model are found to be consistent with the experimental data available. The function form of the Girifalco model however is complex and therefore finding parameters for the Mie potential which are capable of reproducing the phase behaviour observed with
C$_{60}$ molecules can be a viable option for determining the thermophysical properties in a shorter time scale. Parameters for a Mie spherical system have been fit to molecular properties obtained from the Girifalco potential and have been recently presented by Avendaño et al. [41] who report $\epsilon=3213.5$K, $\sigma=9.05\text{Å}$, $\lambda_r=42.46$ and $\lambda_a=8.8$. In this work, we use the potential parameters of Avendaño et al. to determine the global phase diagram via simulation. The result (Figure 3.8(e)) is consistent with the findings of Girifalco in the sense that the VLE region is very small ($T^*_c/T^*_t=1.04$) and with the experimental observations that the vapour-liquid transition is suppressed [106]. In Figure 3.11 it is also shown that there are multiple combinations of exponents of the Mie potential that can be used to model C$_{60}$ molecules.

Figure 3.11: Variation of $\alpha$ and corresponding fluid range ($T^*_c/T^*_t$) with Mie fluids of fixed attractive exponents; ($\lambda_r, 6$) is represented by a solid orange line, ($\lambda_r, 7$) with a red line, ($\lambda_r, 8$) with a purple line and ($\lambda_r, 10$) a blue line. The dashed lines indicate the experimental fluid range of H$_2$O and CO$_2$ and reference potentials, LJ and that of the coarse grained model for C$_{60}$. 
It is clear that this methodology has great potential to propose molecular models for real systems. Very little experimental data ($T_c$ and $T_t$) is required to determine a Mie model which can be used in conjunction with parameter fitting to evaluate the thermodynamic properties of the system either by simulation or theoretical analysis. Either route proves to provide a faster and cheaper solution to determining properties of a given system than via traditional experimental analysis.

### 3.5 Conclusion

In this chapter the phase behaviour of solids, liquids and gases of the Mie intermolecular potential has been studied with the aim of obtaining a unified view of this family of fluids. By analysis of the free energy using a BH perturbation expansion to the first order a parameter is proposed which characterises the free energy of a given Mie fluid. Mie potentials with the same value of this parameter $\alpha$, have been shown to display a close-to-conformal phase behaviour. Slight deviations between the phase boundaries are noted and can be accounted for within the approximations made in the derivation of $\alpha$. This result contradicts the reports of Orea et al. [43] and Okumura and Yonezawa [42] who suggest the Mie family will follow a two parameter CS model. It is however in agreement with the works of Galliero et al. [148], Bulavin and Kulinskii [44] and Kulinskii[141] who suggest that three parameters are needed. The use of the $\alpha$ parameter also presents the advantage that it provides a rationalisation for characterising the Mie family of fluids.

By characterising the potential through the $\alpha$ parameter, a host of Mie potentials of varying range of attraction have been presented. The choice of $\alpha$ has been observed to have a strong influence of the critical point, which is in accordance with the works of Vliegenthart and Lekkerkerker [152], Okumura and Yonezawa [42] and Bulavin and Kulinskii [44]. The parameter is noted to have a less significant influence on the triple point temperature. The overall result shows that there is a linear relationship between
α and the size of the stable fluid range i.e. smaller values of α, which corresponds to an increase in the repulsive nature of the interaction, results in a decrease in the size of the stable fluid range. This result is in agreement with the findings of several other authors [44] [141] [46] [47] [151]. The relationship can ultimately be used to propose a limit at which the VLE region becomes metastable with respect to the solid phase. The resulting potential is found to be in good agreement with simulation data and with the predictions of Hasegawa [46] and Hasegawa and Ohno [47].

The relationship between α and the stable fluid range has also presented an added advantage of proposing exponents for the Mie that can be used to model real systems. The method shown reduces the parameter space which is typically explored in order to find reliable molecular models to mimic the behaviour a given real system. By proposing several combinations of exponents more robust parameters can be obtained from the fitting procedure.
Chapter 4

SAFT-VR Mie equation of state for the solid phase

4.1 Introduction

Even considering today’s software and hardware standards, detailed molecular simulations can be computationally taxing, time consuming and system specific. These problems are magnified when considering the solid phases and solid-fluid equilibrium, as in these cases simulation techniques are not as well developed as in the fluid case, and on average, require greater computational time. Equations of state can be used as predictive tools that are computationally efficient to evaluate the phase transitions of unexplored potentials. In Chapter 1, theories such as density function theory [76] [74] [75] [77] and cell theories [79] [80] [78] [81] [82] [83] [84] [85] [19] were acknowledged as viable methods to developing theoretical equations of state for the solid phase, however in this work we choose to develop a molecular based equation of state for solids interacting via a Mie potential using perturbation theory. In this chapter, some of the reported efforts to obtain reliable equations of state for the solid phase of simple molecular models through perturbation theory are reviewed.
Longuet-Higgins and Widom [86] were the first to use perturbation theory to determine solid-fluid equilibrium. In its simplest form, they determined the free energy of the fluid and solid phases of a system of hard spheres with a mean field attraction which enabled the evaluation of solid-fluid coexistence boundaries. More recently, Vega and MacDowell showed that Wertheim’s Thermodynamic Perturbation Theory (TPT1) could be applied to the treatment of chain systems in the solid phase [87]. TPT1 was originally presented in a series of seminal papers by Wertheim, in which the key contribution was showing that the free energy of a chain system requires only a knowledge of the free energy of a system of spherical segments (monomers) and the structure of the monomer system (radial distribution function) [58] [59] [60] [61] [62] [63]. There is no explicit mention of a specific phase and as such, this is the basis of the extension of the theory, originally used for fluids, to the solid phase. The extension to TPT1 was first employed to the most straightforward case of hard sphere chains by Vega and MacDowell [87] in which excellent agreement is found when compared to the simulation data of Malanoski and Monson [19]. Encouraged by these findings, this work led to the study of Blas et al. [167] for the analysis of the solid-fluid coexistence of fully flexible hard-chains molecules with a segment-segment attractive interaction treated at the mean field level of van der Waals. The effect of flexibility on the phase behaviour of chains was accounted for by calculation of the phase diagram of fully flexible chains and linear rigid chains [168] [169] [170], as well as, the two dimensional study of hard discs chains [171].

Another potential applied to TPT1 extended to the solid was the LJ model, proposed by Vega et al. [38] (referred herein as TPT1-LJ solid). They carried out simulations for 134 state points to determine the radial distribution function at $\sigma$ of the solid LJ system over a temperature range of $T^*=0.4-2.7$ and density range, $\rho^*=0.9-1.3$ and presented a 25 coefficient polynomial to correlate the values. The Helmholtz free energy of the monomer LJ system is taken from the van der Hoef EOS for the solid LJ sphere which itself is also a fit to 877 simulation state points [36]. This EOS is used in conjunction
with TPT1-LJ for the fluid to solve for coexistence of the LJ fully flexible chain SFE boundaries. The calculated boundaries were found to be in excellent agreement with simulation data for the LJ tangentially bonded dimer [105] and most recently for the fully flexible trimer as shown in Chapter 2. As explained in Chapter 2, the global phase diagram (VLE, SVE and SFE) of fully flexible LJ chains had not been evaluated via simulation (with the exception of the tangentially bonded dimer), due to difficulty in attaining a thermodynamically stable configuration of the solid crystal structure. Therefore, in the absence of this data, the calculations of Vega et al. [38] were used to predict the global phase behaviour of fully flexible chains of varying length. These predictions were then used as a comparison to the simulation data of rigid linear LJ chain system presented in [101] and therefore, the effect of flexibility on the phase diagram of LJ chain systems was studied.

The extension of TPT1 to the solid phase of LJ systems described above makes use of the van der Hoef EOS [36], which provides the Helmholtz free energy of the solid monomer system, as well as, the correlation of the radial distribution function at \( \sigma \), presented by Vega et al. [38]. For the TPT1-LJ fluid, the properties (free energy and \( g(r) \)) are obtained from the Johnson EOS [37]. All of the above are empirical fits to simulation data and have come at the expense of correlation efforts. Additionally, the nature of these fitted equations do not guarantee accurate extrapolations, on the contrary, they are only valid over a given temperature and density range. Furthermore, they are obviously not applicable to any potential other than the LJ. The multiparametric nature of the Mie potential precludes the use of these ‘brute force’ methods to determine the EOS for all possible combinations of exponents (\( \lambda_r, \lambda_a \)) of the Mie potential. Hence, in this work we aim to obtain the Helmholtz free energy of the solid Mie monomer system by following a more theoretical route as given in the SAFT-VR treatment [66], where the free energy of the monomer is obtained from the Barker and Henderson [14] [166] perturbation theory. The key advantage to this method is that the free energy of any monomer of a potential with a variable range of attraction can
be determined through a summation of the repulsive and attractive components in the high temperature expansion originally proposed by Zwanzig [172]. The resulting EOS can then be used in conjunction with the recently presented EOS for the fluid phase of the Mie (SAFT-VR Mie) [90] to determine the SFE for monomer and chain systems for a host of Mie potentials. The objective here is to develop a molecular-based theoretical solid EOS for fully flexible tangentially-bonded chains systems interacting via a Mie potential, based on the SAFT-VR (variable range) framework [66]. In SAFT-VR the free energy of the monomer is obtained from the Barker and Henderson perturbation theory [14] [166] for spherical systems. Lafitte et al. [70] applied this framework to the study of the Mie potential in the fluid phase and have presented an analytical EOS. Recently, an improved EOS which takes a more rigorous approach to the determination of the free energy and the radial distribution function ($g(\sigma)$) has also been presented for Mie fluids [90]. The theory, which proves to be in excellent agreement with simulation data, will be discussed in more depth in Section 4.6.

On analysis of the literature, it is apparent that for treatment of the solid phase, a modified Weeks-Chandler-Anderson (WCA) perturbation approach must be used in preference to the BH theory [173] [12] [13]. This was originally suggested by Ree [173] who proposed that a modification of the WCA theory can be used to treat high-density fluids with perturbation theory. The methodology was later perfected in the subsequent papers of Kang et al. [12] and extended to the solid phase [13]. The EOS presented can be used to treat simple spherical solids interacting through a continuous intermolecular potential and has been tested against the LJ model and a soft core repulsive model. The results are found to be in very good agreement with simulation data. The theory was used by Jackson and van Swol [15] to study the solid-solid transitions of hcp and fcc phases of the cut-and-shifted LJ model, Adidharma and Radosz [174] to predict the solid-solid and solid-fluid phase transitions of mixtures of noble compounds, and by Zhou [175] to study the formation of multiple solid phases. In Section 4.2 a review by Verlet and Weis [176] for different proposals for splitting
a continuous potential is summarised and the approach best suited for treatment of simple solid spherical systems is presented.

By implementation of a modified WCA theory into the SAFT-VR framework, we present an EOS for the solid phase of the Mie intermolecular potential. At present, the perturbation expansion is taken to the first order only. The EOS is tested using the LJ parameters (12,6), as there is significant data available for a comparison of these results, particularly the residual free energy of the monomer system determined by van der Hoef [36]. As the solid EOS is developed for the fcc crystal structure, an EOS for the hcp solid is also presented with a view for determining the solid-solid phase transitions of different Mie systems. Finally, our fcc solid theory is used in conjunction with a fluid EOS for the Mie potential [90] to determine SFE, however, this will be discussed in greater depth in Chapter 5.

4.2 Theories for splitting continuous potentials

The generic form for split an attractive potential can be expressed as:

\[
\phi(r) = V_0(r) + W(r),
\]

where \( V_0(r) \) contains the repulsive part of the potential and \( W(r) \) contains the attractive part of the potential which is treated as a perturbation.

Arguably the most renowned factorisation is the one underlying the BH perturbation theory [14] [166] which proposes that the potential is split at the intersection with the \( x \) axis i.e. when total energy changes sign (Figure 4.1). This can be expressed as:

\[
V_0(r) = \begin{cases} 
\phi(r) & r \leq \sigma \\
0 & \sigma > r,
\end{cases}
\]
\[ W(r) = \begin{cases} \phi(r) & r \geq \sigma \\ 0 & \sigma < r. \end{cases} \quad (4.3) \]

In the BH formulation, the repulsive part of the potential is approximated to a reference system of hard spheres which have the effective diameter of the soft sphere system. This diameter of the effective hard sphere is known as the Barker and Henderson diameter \((d_{BH})\). Rather than taking a unique value one can consider a temperature dependency given by:

\[ d_{BH} = \int_{0}^{\sigma} (1 - e^{-\beta \phi(r)}) dr. \quad (4.4) \]

\[ \frac{\phi(r)}{\varepsilon} \]
\[ \frac{V_{p}(r)}{\varepsilon} \]
\[ \frac{W(r)}{\varepsilon} \]

Figure 4.1: Diagrams showing the splitting of the LJ potential at the contact value \(\sigma\) in the BH Perturbation theory. a) The full LJ potential, b) the repulsive component of the potential and the approximation to the hard sphere with an effect diameter (red dashed line) which has a dependence on temperature c) the attractive component of the potential is treated as a summation of perturbation terms.

There are a few analytical expressions available to solve the above integral [177] however none are considered sufficiently accurate on comparison to the numerical solution and as such \(d_{BH}\) is typically determined through quadrature methods. This potential split proves very accurate for determining the Helmholtz free energy of the fluid phases.
4. SAFT-VR Mie equation of state for the solid phase

and as mentioned previously is the choice implemented in the SAFT-VR framework for determination of the free energy of monomer systems \([66] [67]\) including the fluid SAFT-VR Mie equation of state \([70] [90]\). It is known however, that in the high density region, the BH diameter becomes inaccurate \([178]\) and therefore is not suitable for treatment of the solid phase.

In the WCA theory \([88] [179]\) the potential is split at the energy well minimum, \(r_m\) rather than at \(\sigma\) so that,

\[
V_0(r) = \begin{cases} 
\phi(r)^{\text{Mie}} + \epsilon & r \leq r_m \\
0 & r > r_m,
\end{cases}
\]

and,

\[
W(r) = \begin{cases} 
\phi(r)^{\text{Mie}} & r \geq r_m \\
-\epsilon & r < r_m.
\end{cases}
\]

This procedure has proven successful in describing the fluid phase but becomes less accurate at densities close to the freezing line \([12]\). The effective hard sphere diameter \((d_{WCA})\) determined by the WCA theory is given by,

\[
\int dr (e^{-\beta V_0(r)} - e^{-\beta V_{HS}(r)}) y_{HS}(r/d_{WCA}) = 0,
\]

where \(y^{HS}(r/d_{WCA})\) is the background correlation function with an effective hard sphere diameter \(d_{WCA}\). The inaccuracy at high-density is a consequence of the reference potential \((V_0(r))\) becoming too stiff at these high densities which results in unrealistically large equivalent hard sphere diameters. To overcome this problem Ree \([173]\) and subsequently Kang et al \([12] [13]\) have proposed a new method for splitting the potential at a (variable) distance \(\lambda\) which is dependent on density, this is known as the Modified WCA theory.

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At lower densities the value of $\lambda$ reduces to that of the WCA theory which describes the fluid phase accurately [180], i.e., ($\lambda = r_m$). At higher densities and for the solid phase, $\lambda = a_c$ which is the nearest neighbour distance determined in an fcc lattice, i.e., $a_c = 2^{1/6}/\rho^{1/3}$. The reasoning behind this is that at high densities, molecules are more likely to collide with their nearest neighbour and a steep repulsion induces a neighbour-neighbour separation of $r_m$ which is highly improbable whereas a hard sphere diameter evaluated at $\lambda=a_c$ is a more reasonable approach [173]. Under equilibrium conditions $\lambda$ will lie closer to the $a_c$ rather than $r_m$ for high densities [12] and with this potential split the molecule is ‘confined’ to a cage formed by the repulsive forces of its neighbours.

In a later paper by the same authors, the discontinuity of the choice in $\lambda$ i.e. ($\lambda=a_c$ or $r_m$) is addressed by introducing several functions such that;

$$\lambda = r_m + S(\rho)(a_c - r_m), \quad (4.8)$$

$$S(\rho) = \begin{cases} 
0 & \rho < \rho_1 \\
\left(\frac{(\rho-\rho_1)^3(6\rho^2-3(5\rho_2-\rho_1)\rho+10\rho^2-5\rho_1\rho_2+\rho_2^3)}{(\rho_2-\rho_1)^3}\right) & \rho_1 < \rho < \rho_2 \\
1 & \rho_2 < \rho. 
\end{cases} \quad (4.9)$$

Therefore, at densities which are less than $\rho_1$ (where $\rho_1 = 0.97\rho_c$) the value of $\lambda$ is equal to the $r_m$ (i.e. reduces to the WCA theory) and at densities higher than $\rho_2$ (where $\rho_2 = 1.01\rho_c$), $\lambda = a_c$ and for the narrow range between $\rho_1$ and $\rho_2$ either value will work. $\rho_c$ is the density at which $r_m = a_c$, therefore $\rho_c = \sqrt{2}/(r_m)^3$. As we are considering the solid phase, the density will always be above $\rho_2$ therefore $\lambda$ will always hold a value of $a_c$. In Figure 4.2 the potential split using the modified WCA theory with the parameter $\lambda$ is presented.

This potential split can be expressed mathematically as,

$$\phi(r) = V_0(r) + W(r), \quad (4.10)$$
with,

\[
V_0(r) = \begin{cases} 
\phi(r) - F(r) & r \leq \lambda \\
0 & r > \lambda,
\end{cases}
\]

(4.11)

and

\[
W(r) = \begin{cases} 
F(r) & r < \lambda \\
\phi(r) & r \geq \lambda.
\end{cases}
\]

(4.12)

Figure 4.2: Diagram showing the splitting of the LJ potential with the modified WCA theory using the parameter \(\lambda\). (a) is the full potential highlighting the relevant points at which the potential can be cut (b) is repulsive component which has been cut for a solid i.e at \(\lambda = a_c\) and shifted by the appropriate energy \(F(r)\) (c) is the attractive component which is the tail of the potential starting at the distance \(\lambda\).

The potential split is dependent on an arbitrary function \(F(r)\) which is expressed as,

\[
F(r) = \phi(\lambda) - \phi'(\lambda)(\lambda - r).
\]

(4.13)

In the first work for a high-density fluid theory [12], several functions were tested to describe this arbitrary function, and Equation (4.13) was found to be most accurate. This expression must be substituted at the required \(\lambda\) into Equation (4.11) in order to solve for the effective hard sphere diameter.
The repulsive part of the potential can now be mapped to a reference hard sphere potential with an effective diameter which is expressed by the density and temperature dependent, WCA diameter,

\[
\int dr (e^{-\beta V_0(r)} - e^{-\beta V_{HS}(r)}) y_{HS}(r/d) = 0,
\]

where \( d \) is the effective hard sphere diameter determined from the modified WCA theory. The expression can be solved using the Verlet-Weis approximation (Equations 4.15-4.17) which produce results which are nearly identical to the WCA diameter [13],

\[
d = dB(1 + (\sigma_1/2\sigma_0)\delta),
\]

\[
\sigma_0 = y_{HS}(r = d),
\]

\[
\sigma_1 = 2\sigma_0 + \left( \frac{dy_{HS}(x)}{dx} \right)_{x=r; d=1}.
\]

\( \delta \) is generally very small in magnitude (\( \simeq 10^{-3} \)). The exact value can be found using the expression,

\[
\delta = \int_0^\lambda \left( \frac{r}{dB} - 1 \right)^2 \frac{d}{dr} \left( e^{-\beta V_0(r)} \right) dr.
\]

It is important to note that \( dB \) in Equation (4.15), which is analogous to the BH diameter \((dB_H)\) is represented by a different equation to what has been shown in Equation (4.4). This is primarily due to the way the potential is split. The limits of the integral are now between \( \lambda \) and 0, rather than \( \sigma \) and 0, but more importantly, the functional form of the reference potential \((V_0)\) has changed, it is expressed by Equation (4.11),

\[
d_B = \int_0^\lambda dr (1 - e^{-\beta V_0(r)}).
\]
Equation (4.19) is solved with numerical integration. With this solution, an iterative process is applied to Equations (4.15-4.17) to solve for the effective hard sphere diameter, $d$. The numerical evaluation of the derivative in Equation (4.17) is very sensitive to the $g_{HS}(r/d)$, therefore, it is imperative that the expressions used are accurate. Fortunately, as will be shown in Section 4.35, a robust analytical expression has been obtained [181] that covers the necessary range of validity relevant to the solid phase ($\eta=0.52-0.73$) for the $g_{HS}(r/d)$ which is in excellent agreement with simulation results and as such the need to test the sensitivity is eliminated. The modified WCA theory has been applied to the LJ and soft core repulsive spheres and the free energy of the solid systems are found to be in very good agreement with the simulation data especially by comparison to the WCA theory [13]. Using the most accurate expression for $g_{HS}(r/d)$ [181] the modified WCA is used here to determine reference hard sphere diameters over a range of temperatures and densities for the LJ monomer and compared to the original results of Kang et al. [13]. The comparison can be found in Appendix C in which excellent agreement is noted.

For completeness, an alternative potential split presented by McQuarrie and Katz [182] is discussed. In this case the $r^{-12}$ is chosen as the reference system and the $r^{-6}$ is treated as a perturbation term. The approach only proves to be accurate at high temperatures ($T^* \approx 3$) as the reference potential is considerably softer than the full potential close to the potential well minimum [183]; as such, this method will not be discussed in any greater depth. On analysis of the perturbation theories available, the Modified WCA theory appears to be best suited for treatment of the solid phase. Consequently, this theory is chosen to be implemented into the SAFT approach, following the SAFT-VR framework in order to develop an EOS for the solid phase.
4.3 The SAFT approach

The SAFT equation of state was developed by Chapman et al. [29] [30] on the basis of the TPT1 theory of Wertheim for associating fluids. Since its development this molecular-based EOS has constituted a major advancement towards a theoretical framework for modelling complex fluids and has been used extensively to correlate and predict experimental results for a wide variety of substances. From a brief overview of the current literature it is can be seen that SAFT is a versatile tool in the description of fluid phase equilibria [54] [73] [4].

The formulation of SAFT for non-associating fluids expressed in terms of the Helmholtz free energy $A$ of $N$ chains at a temperature $T$ formed from $m$ monomer segments and is given by [29] [30],

$$A = A_{\text{ideal}} + A_{\text{mono}} + A_{\text{chain}}$$

where,

$$A_{\text{ideal}} = Nk_B T \ln(\rho \Lambda^3) - 1$$

The ideal term takes into account the free energy of an ideal gas and is given by;

$$A_{\text{ideal}} = \ln(\rho \Lambda^3) - 1$$

where $\rho$ is the number density of chain molecules ($\rho = N/V$).
Figure 4.3: Diagram illustrating the SAFT contributions for non associating fluids. From top, the ideal fluid, followed by the monomer contribution which consists of hard sphere segments to which dispersion forces are added. This is followed by taking into account the corresponding energy contribution due to the formation of chain molecules.

The monomer contribution can be written in terms of the number of segments $N_s$:

$$\frac{A^{\text{mono}}}{Nk_B T} = m \frac{A^M}{N_s k_B T}$$

(4.22)

where $N_s$ is the total number of spherical monomer segments and $A^M$ is the residual (with respect to the ideal energy) Helmholtz free energy per monomer. For cases where empirical equations are available for the Helmholtz free energy of the monomer system, determination of $A^{\text{mono}}$ is relatively straightforward. This is the case for the LJ model where correlations are available for the fluid phase [37] [57] and the solid phase [36].
for the LJ systems as mentioned in the introduction. Alternatively, the monomer free energy can be found at the level of the mean-field approximation described in terms of an augmented van der Waals expression, splitting the contributions into a hard sphere $A^{HS}$ and a mean field attraction term $\alpha^{VDW}$ [86] [184],

$$\frac{A^M}{N_s k_B T} = \frac{A^{HS}}{N_s k_B T} - \frac{\alpha^{VDW} \rho_s}{k_B T}.$$  \hspace{1cm} (4.23)

For example $A^{HS}$ may be obtained from the Carnhan and Starling [10] equation for the fluid phase or by Hall [11] for the solid phase. The van der Waals attractive constant which characterises the dispersion interaction is given by;

$$\alpha^{VDW} = 2\pi \epsilon \int_0^\infty \sigma \phi(\sigma) r^2 dr.$$  \hspace{1cm} (4.24)

Equations (4.23) and (4.24) have been used to describe the monomer free energy in the generalised van der Waals theory presented by Longuet-Higgins and Widom [86] and in the SAFT-HS approach [184]. In more recent years however, there have been efforts to improve the agreement of the EOS with experimental data through a better description of the dispersion forces. In the last two decades, more realistic reference fluids such as SW, LJ, Yukawa and sutherland fluids have been used to develop SAFT models. This can done through treatment with the SAFT-VR framework [66] [67] in which the free energy of the monomer contribution is determined using the Barker and Henderson perturbation theory.

The contribution to the free energy due to chain formation of $m$ monomer segments, $A^{\text{chain}}$ is expressed as [30]:

$$\frac{A^{\text{chain}}}{Nk_B T} = -(m - 1) \ln y^m(\sigma),$$  \hspace{1cm} (4.25)

where $y^m(\sigma)$ is the monomer-monomer background correlation function evaluated at the bonding distance.
SAFT as mentioned previously, is based on TPT1 developed by Wertheim, and does not explicitly state the phase for which the theory is valid, therefore SAFT can be extended to treat solid systems. By following the methodology of Vega and MacDowell [87], who applied the TPT1 to the solid phase for hard sphere and LJ chain systems, we present a solid equation of state for Mie chain systems using the SAFT approach.

4.3.1 SAFT-VR framework

The SAFT-VR equations of state [66] [67] was developed for the treatment of chain and/or associating molecules consisting of a hard-core segment with an attractive potential of variable range. A crucial contribution of this methodology is determination of the free energy of the monomer system with the Barker and Henderson perturbation theory [14] [166] [185] which expresses the monomer free energy as a series expansion in inverse temperature;

\[ a_{\text{mono}} = a^{HS} + \beta a_1 + \beta^2 a_2 + \ldots, \quad (4.26) \]

where \( a_{\text{mono}} = \frac{A_{\text{mono}}}{Nk_B} \) is the free energy of the monomer system, \( a^{HS} = \frac{A^{HS}}{Nk_B} \) is the free energy of the reference hard sphere system, \( \beta = \frac{1}{k_BT} \) and \( a_1 \) and \( a_2 \) are first and second order attractive perturbation terms respectively. This high temperature Taylor expansion was originally proposed by Zwanzig [172] to account for the full intermolecular interaction as the sum of a hard-sphere reference contribution in which the attractive terms are perturbations which can be summed. The other crucial step in the SAFT-VR formulation is the determination of a compact analytical expression for the \( a_1 \) perturbation term using the mean value theorem and a mapping for the radiation distribution functions. This framework was applied to a host of variable range potentials, such as SW, LJ, Sutherland and the Mie potential [66]. The perturbation approach has lead to the development of several fluid equations of state for LJ [69], Hard core attractive Yukawa [68], SW [71] and most recently the Mie [70] [90].
In Section 4.2 the Barker and Henderson perturbation theory was introduced, where the continuous potential is division at the contact value \( \sigma \). Also mentioned previously, is that this division of the potential is not accurate for the treatment of the solid phase. Instead, in this work the modified WCA theory is used to determine the Helmholtz free energy of the monomer. At present, our theory is approximated to a first order expansion only. The mean value theorem and mapping of the radial distribution function for the evaluation of the first perturbation term is not implemented at this point and therefore the proposed theory requires quadrature methods in order to calculate the monomer free energy. Development of an entirely analytical equation of state will however, be the focus of future work. The solid EOS using the SAFT-VR framework with the modified WCA perturbation theory is presented in the following section.

### 4.4 SAFT-VR Mie Solid Equation of State

#### 4.4.1 Residual Helmholtz free energy of monomer, \( a_{\text{mono}} \)

In order to calculate the free energy of the solid phase following the SAFT-VR treatment, the free energy is approximated using only the first term in the perturbation expansion,

\[
a_{\text{mono}} = a_0 + \beta a_1,
\]

where \( a_0 \) is the free energy of the reference system and \( a_1 \) is the first perturbation term.

**Reference system, \( a_0 \)**

The reference system is taken to be a hard sphere with an effective hard sphere diameter. The approximated free energy is given by;

\[
a_0 \approx a^{HS},
\]
where $a^{HS}$ is the free energy of the hard sphere system which has an effective diameter of $d$. The diameter is determined from the modified WCA theory [13] as shown in Section 4.2. For a system of hard spheres, the free energy is explicitly dependent on the packing fraction $\eta$ (where $\eta = \frac{\omega d^3}{6}$ and $\rho$ is the number density). $a^{HS}$ for the solid can be obtained from the work of Hall [11], in terms of the compressibility,

$$Z^{solid} = \frac{3}{\alpha} + 2.557696 + 0.1253077\gamma + 0.1762393\gamma^2 - 1.053308\gamma^3 + 2.818621\gamma^4 - 2.921934\gamma^5 + 1.118413\gamma^6,$$

(4.29)

where $Z^{solid}$ is the compressibility factor ($\frac{PV}{NkT}$). Upon integration of the pressure Equation (4.29) can be expressed in terms of the Helmholtz free energy;

$$a^{HS} = -S_0 + \ln \rho_0 - 3\ln \frac{2\alpha}{3} + \int_0^\gamma (Z_{HS} - Z_{ref}) \frac{d\gamma}{\gamma - 4},$$

(4.30)

where

$$\alpha = \frac{\rho_0}{\rho} - 1,$$

(4.31)

and

$$\gamma = 4(1 - \frac{\rho}{\rho_0}),$$

(4.32)

and

$$Z_{ref} = 3 + 3/\alpha,$$

(4.33)

where $\rho_0$ is a constant which corresponds to the number density at the close-packing fraction, $\eta_c = 0.74$, therefore $\rho_0 = \frac{6\eta_c}{d^3\pi}$. $Z_{ref}$ is the high-density limit of the hard sphere compressibility factor in the Lennard-Jones-Devonshire cell theory [186] [187]. The value of $S_0$ is obtained from simulation analysis by Alder et al [188] : $S_0 = -0.24 \pm 0.04$
Perturbation term, $a_1$

The first perturbation term $a_1$ can be expressed as \[ a_1 = 2\pi \rho_s \epsilon \int_\sigma^\infty \phi^{Mie}(r)r^2 dr, \] \[ (4.34) \]

where $g^{HS}(r)$ is the radial distribution function of the hard sphere reference system. As the potential is split using the modified WCA theory rather than BH as is in the original SAFT-VR framework, the integration cannot be carried out at $\phi^{Mie}(r)$ but rather the attractive component ($W(r)$) in Equation (4.10), therefore,

\[ a_1 = 2\pi \rho_s \epsilon \int_d^\infty g^{HS}(r)W(r)r^2 dr. \] \[ (4.35) \]

In the fluid phase, the $g^{HS}(r)$ is obtained from the Malijevsky and Labik formula [189]. In the original SAFT-VR treatment, Equation (4.34) is first solved numerically which is followed by a mapping [66] to determine an analytical expression which is more useful for practical engineering applications. Here we present a numerical method for determining the monomer free energy of the solid; the development of an analytical expression through mapping may be the focus of future work. A reliable analytical expression for the $g^{HS}(r)$ in the solid phase is required to solve Equation (4.35) numerically. Naturally, the expression will depend on the varying crystallographic structure of the solid in question. For the purpose of this work and with a view of eventually coupling this equation to the fluid expression to determine the solid fluid equilibrium of Mie molecules, we use the expression for the fcc lattice structure, as it has been accepted as the most common crystal structure which is in equilibrium with the fluid phase [138] [139]. Works by Weis [89], Kincaid and Weis [190], Kang et al. [13], Jackson and van Swol [15] and most recently Zhou [175] have all presented analytical expressions for the radial distribution function of the hard sphere fcc lattice, however, none of these are superior to the work of Choi et al. [181] who has presented an expression which is a correlation of simulation data over the widest range of packing fraction.
(\eta=0.52-0.73) at the greatest distance \( r/d = 3.3 \). This expression is given by a series of equations by a summation of neighbouring shells:

\[
g^{HS}(r/d, \eta) = \sum_{i=0}^{\infty} g^{(i)},
\]

(4.36)

where,

Table 4.1: Distances \( r_i \) and number of molecules, \( n_i \) in the \( i^{th} \) shell of a face centered cubic crystal. \( d_0 \) is the distance between the nearest neighbours and can be expressed as \( d_0 = 2^{1/6}v_0^{1/3} \), where \( v_0 \) is the volume of the crystal \( (v_0 = \frac{n d^3}{6\eta}) \) [191].

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The constant $J$ is constrained to satisfy the virial theorem and relates to the compressibility factor:

$$\frac{PV}{NkT} = 1 + 4\eta g_{HS}(1/\eta),$$

(4.38)

where $\frac{PV}{NkT}$ is obtained from the Hall EOS (Equation 4.29).

$$g^{(i)} = \frac{K(\eta)}{24\eta\sqrt{\pi}} \frac{n_i d^2}{r_{ri}} e^{-|K(r-r_i)/d|}, i \geq 2$$

(4.39)

where $n_i$ is the number of particles in the $i^{th}$ nearest neighbour lattice sites and $r_i$ is the distance of the $i^{th}$ shell and $i$ is the number of neighbouring shells ($i=1-65$) in an fcc lattice. The number of particles and distances of each shell can be found in Table 4.1, and

$$K_1(\eta) = \frac{1.5338}{\eta^*} - 0.37687e^{[-989.6(\eta-0.52)^2]} - 2.5146 - 1.3574\eta^* - 8.5038\eta^{*2}$$

(4.40)

$$K_2(\eta) = \frac{0.80313}{\eta^*} - 1.208e^{(5.6128\eta^*)} + 67.808\eta^{*2} - 67.918\eta^{*3}$$

(4.41)

and,

$$K(\eta) = \frac{1.9881}{\eta^*} - 3.5276 + 6.9762\eta^* - 26.205\eta^{*2}$$

(4.42)

and,

$$r_1(\eta) = \frac{(1 - 8.0521\eta^* + 18.003\eta^{*2})}{1 - 8.2973\eta^* + 20.546\eta^{*2} - 13.828\eta^{*3} + 103.95\eta^{*4} - 582.74\eta^{*5} + 1245.7\eta^{*6}}$$

(4.43)
where $\eta^* = \eta_c - \eta$.

On analysis, the presented expression (of Choi et al. [181]) produces results which are in excellent agreement with the simulation results of Zhou [175] for the radial distribution of the hard spheres at a packing fraction ranging from $\eta = 0.52 - 0.73$ (see Figure 4.4) and simulation results of Weis [89] (see Figure 4.5). The analytical expression from Choi et al. fits remarkably better to simulation data of Zhou at a packing fraction of 0.52 in comparison to the analytical expression of Zhou. This validates the superiority of the Choi expression against the expression of Zhou despite the work of Zhou being more recent. It also provides evidence that the expression of Choi et al. will be accurate at lower packing fractions ($\eta < 0.565$) as this is within the range of expected solid-fluid coexistence and as such it is important to have an accurate fit.
Figure 4.4: Comparison of the radial distribution functions of the hard sphere fcc solid lattice with simulation data from Zhou [175] (black circles). The solid black lines denote the analytical expression for the radial distribution function of an fcc lattice at different packing fractions presented by Zhou [175] and the solid blue lines correspond to the analytical radial distribution function used in this work (Equation (4.36)) i.e. the work of Choi et al. [181].
Figure 4.5: Comparison of the analytical radial distribution functions of the hard sphere fcc solid lattice used in this work (Equation (4.36)) (solid blue lines) with simulation data from Weis (red closed diamonds) [89].
A pertinent issue to consider at this point, is the number of neighbouring particles and the distances of each neighbouring shell that needs to be incorporated in Equation (4.36). Data for these shells within an fcc lattice is taken from [191]. The table is presented again here (Table 4.1) and provides the number of neighbours and relevant distances up to the $65^{th}$ shell of an fcc lattice. To ensure a high level of accuracy, all 65 shells have been incorporated to the determination of the Helmholtz free energy of the solid phase. With this analytical expression for the $g^{HS}(r)$, the integral in Equation (4.35) can be solved using numerical integration. In this work, either the extended Simpson’s rule or 64 point Gauss-Legendre integration method has been used, both produce results of equal accuracy.

4.4.2 Free energy Chain contribution, $a^{chain}$

In order to account for the energy contribution due to the formation of chains of tangentially bonded segments (Equation 4.25), the background correlation function of the reference monomer system, $y^m(\sigma)$ can be determined by relation to the radial distribution function at contact,

$$y^m(\sigma) = g^m(\sigma)e^{(-\beta u^m(\sigma))}. \quad (4.44)$$

At contact, $\sigma$ the potential reduces to zero and in the case of the Mie the above expression is simplified to,

$$y^m(\sigma) = g^{Mie}(\sigma). \quad (4.45)$$

To obtain the radial distribution function of soft core potentials (in this case $g^{Mie}(\sigma)$) a first order WCA perturbation theory is used [192],

$$g^{Mie}(\sigma) = y^{HS}(\sigma)e^{(-\beta V_0(\sigma))}, \quad (4.46)$$

where $V_0(\sigma)$ is defined in equation 4.11 and $y^{HS}(\sigma) = g^{HS}(\sigma)$ for $\sigma > d$. 

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As the potential is split at $\lambda$ rather than $\sigma$ and since $\lambda$ is density and temperature dependent the effective hard sphere diameter, $d$ can be found to be larger than $\sigma$ and as such the assumption that $y^{HS}(\sigma) = g^{HS}(\sigma)$ for $\sigma > d$ is not valid for all values. In such situations the $y^{HS}(\sigma)$ must be evaluated by extending the Henderson and Grundke [193] scheme for the hard sphere solid as proposed by Choi et al. [181] where,

$$\ln y^{HS}(\sigma, \eta) = \sum_{n=0}^{3} a_n(\sigma)^n,$$  \hspace{1cm} (4.47)

where,

$$a_0 = \ln y^{HS}(0, \eta) = \frac{A^e}{NkT} + \frac{PV}{NkT} - 1,$$  \hspace{1cm} (4.48)

$$a_1 = \frac{\partial \ln y^{HS}(\sigma, \eta)}{\partial r} = -6\eta y^{HS}(1, \eta)$$  \hspace{1cm} (4.49)

where $\frac{A^e}{NkT}$ is the excess Helmholtz free energy of the hard-sphere solid and $\frac{PV}{NkT}$ is defined in Equation (4.29) which follows the Hoover and Poirier proof [194]. Equation (4.49) was obtained by Meeron and Siegert [195] and is equal to $(\frac{PV}{NkT} - 1)/4\eta$. The coefficients $a_2$ and $a_3$ are determined by requiring that $y^{HS}(r/d, \eta)$ and $\delta y^{HS}(r/d, \eta)/\delta r$ are continuous at $r = d$. For the purpose of this work however, it is found that for the temperature and density range analysed, the approximation $y^{HS}(r/d) = g^{HS}(r/d)$ holds as for all cases studied $d$ is not significantly larger than $\sigma$ and therefore the approximation remains valid and therefore Equations (4.47) to (4.49) are not used; they are nonetheless, included for completeness.

### 4.5 SAFT-VR Mie Solid Equation of state for an hcp crystal structure

In the previous section the solid EOS presented is specific to the fcc crystal structure however there are multiple other crystal structures that have not been considered. The
fcc structure was chosen as it is typically accepted as the stable structure that is in
equilibrium with the fluid phase for spherical systems and the objective of this work
is to ultimately use this EOS to determine the solid fluid coexistence boundaries of
Mie monomer and chain systems. In this Section an EOS for the hcp solid is also
presented as this crystal is very similar to the fcc in structure and the difference in
the free energy between both crystals is small. For these reasons there has been much
debate surrounding the dominating stable crystal structure [196] [197] [22] [181] and
which crystal coexists with the fluid phase. We therefore also study this aspect of the
phase diagram to evaluate which structure is stable with the fluid phase. The hcp EOS
is be determined using the SAFT-VR framework approximated to the first expansion
term only, and the modified WCA theory for treatment of the evaluation of the free
energy of the monomer term, as before. Therefore,

\[ a = a^{id} + a^{mono} + a^{chain}, \]  

(4.50)

where \( a^{id} \) and \( a^{chain} \) are evaluated using Equations (4.21) and (4.25). The free energy
of the monomer system is given by,

\[ a^{mono} = a_0 + \beta a_1, \]  

(4.51)

where the reference term is a system of hard spheres with an effective diameter deter-
mined using the modified WCA theory and the first perturbation term is determined
using,

\[ a_1 = 2\pi \rho_s \epsilon \int_0^\infty g^{HS}(r)W(r)r^2dr. \]  

(4.52)

In Section 4.4, \( g^{HS}(r) \) for an fcc lattice was determined using the expression developed
by Choi et al. [181]. The authors also presented an expression for the \( g^{HS}(r) \) for the
hcp lattice however we use instead the expression from the work of Jackson and van
Swol [15]. This expression is chosen over Choi et al., as on comparison of the two it
was found that the Jackson and van Swol expression was fit to simulation data over a larger neighbour-neighbour distance (up to $r/d=4.5$) over the same range of packing fractions as Choi et al., hence making the expression superior.

Jackson and van Swol also use the theory proposed by Kang et al. to study the hcp and fcc solid-solid transitions and as such they present expressions for the hcp phase which are consistent with the functional form of Equation 4.36 i.e.,

$$g^{HS}(r/d, \eta) = \sum_{i} g^{(i)}(r/d, \eta), \quad (4.53)$$

where,

$$g^{(1)} = \frac{Jd}{r} e^{-[K_1(\eta)(r/d-r_1/d)]^2-\frac{[K_2(\eta)(r/d-r_1/d)]^4}{2}}, \quad (4.54)$$

The constant $J$ is constrained to satisfy the virial theorem and relates to the compressibility factor;

$$\frac{PV}{NkT} = 1 + 4\eta_gHS(1/\eta), \quad (4.55)$$

where $\frac{PV}{NkT}$ is obtained from the Hall EOS (Equation 4.29).

$$g^{(i)} = \frac{K(\eta) n_i d^2}{24\eta \sqrt{\pi}} \frac{n_i d^2}{r r_i} e^{-[K(r-r_i)/d]^2}, i \geq 2 \quad (4.56)$$

where,

$$K_1(\eta) = \frac{1.5389}{\eta^*} - 2.0901e^{8.4547\eta^*} + 197.57\eta^{*2}, \quad (4.57)$$

$$K_2(\eta) = (0.78530 - 1.1122\eta^* - 1.2291\eta^{*2} - 0.79157\eta^{*3})/\eta^*, \quad (4.58)$$

$$K(\eta) = (1.0 - 2.4447\eta^{*1.3317})/[0.53828\eta^*]^{1.0048} \quad (4.59)$$
and,

\[
   r_1(\eta) = \frac{1 + 2.2580\eta^* - 26.384\eta^{*2}}{1 + 2.0212\eta^* - 26.860\eta^{*2} + 11.232\eta^{*3} - 8.5635\eta^{*4} + 13.966\eta^{*5} - 125.60\eta^{*6}}
\]

(4.60)

The radial distribution function of the hcp phase at different packing fractions are plotted in Figure 4.6. At present there was no simulation data available to compare the results of Jackson and van Swol. It is important to mention that although very similar in structure there are distinct differences in the packing of the fcc and hcp phases which is reflected in the number of particles of neighbouring shells and corresponding distances which is presented in Table 4.2. The data of neighbouring shells and corresponding distances is taken from the same source as the fcc lattice [191].

![Figure 4.6: The Radial distribution function of the hard sphere hcp solid at varying packing fractions obtained from the analytical expression proposed by Jackson and van Swol [15]](image)
Table 4.2: Distances $r_i$ and number of molecules, $n_i$ in the $i^{th}$ shell of a hexagonal close packed crystal. $d_0$ is the distance between the nearest neighbours and can be expressed as $d_0 = 2^{1/6}v_0^{1/3}$, where $v_0$ is the volume of the crystal ($v_0 = \frac{\pi d_0^3}{6\sqrt{2}}$) [191].

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4.6 SAFT-VR Mie Fluid Equation of state

An equation of state based on the SAFT-VR framework for Mie fluids has been presented by Lafitte et al. [90] In this formulation the Barker and Henderson perturbation theory is taken up to a third order expansion;

$$a_{mono} = a^{HS} + \beta a_1 + \beta^2 a_2 + \beta^3 a_3.$$  (4.61)

The reference fluid $a^{HS}$ is a system of hard spheres which have an effective diameter $d_B$ obtained from Equation (4.4). The free energy of this term can be obtained from the Carnahan and Starling EOS [10] for the HS fluid;

$$a^{HS} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}.$$  (4.62)

In the first work of Lafitte et al. [70] an approximation of the BH perturbation theory was used in which the first and second order terms are integrated between the effective hard sphere diameter $d_B$ and $\infty$ rather than $\sigma$ and $\infty$ as the original theory suggest. In the later work [90] a more rigorous approach is taken in which no such simplification is made. This robust EOS is presented in a purely analytical form as it is more useful for practical applications, additionally it does not suffer from loss of accuracy when compared to integral equation theories. In order to do this, the mean value theorem (MVT) and a mapping for the radial distribution function is applied to the first two terms as was done by Gil Villegas et al., [66] in the original SAFT-VR treatment. It should be noted that it is more straightforward to apply the MVT to a potential with a hard core repulsion rather than the soft core (as is the case with the Mie potential) and as such the functional form presented in this work is considerably more complex. The analytical function for the first perturbation term is given by;

$$a_1 = C[x_0^{\lambda_a} \{a_1^s(\eta; \lambda_a) + B(\eta; \lambda_a)\} - x_0^{\lambda_r} \{a_1^s(\eta; \lambda_r) + B(\eta; \lambda_r)\}]$$  (4.63)
where \( x_0 = \sigma / d \) and,

\[
B(\eta; \lambda) = 12\eta \left( \frac{1 - \eta/2}{(1 - \eta)^3} I_\lambda(\lambda) - \frac{9\eta(1 + \eta)}{2(1 - \eta)^3} J_\lambda(\lambda) \right). \tag{4.64}
\]

\( a_1^s(\eta; \lambda) \) is the Helmholtz free energy of a system of hard spheres of diameter, \( d \), interacting through a Sutherland potential of range \( \lambda \). It is through this term that the MVT and mapping of the radial distribution function, can be applied and is presented as an expression which is a function of an effective packing fraction (\( \eta_{eff} \)). The evaluation of this function is explained in great depth in the work of Lafitte et al. [90]. The analytical expression is given by:

\[
a_1^s(\eta; \lambda) = -12\epsilon \eta \left( \frac{1}{\lambda - 3} \right) \frac{1 - \eta_{eff}/2}{(1 - \eta_{eff})^3} \tag{4.65}
\]

where,

\[
\eta_{eff} = c_1\eta + c_2\eta^2 + c_3\eta^3 + c_4\eta^4 \tag{4.66}
\]

and,

\[
\begin{pmatrix}
c_1 \\
c_2 \\
c_3 \\
c_4
\end{pmatrix} = \begin{pmatrix}
0.81096 & 1.7888 & -37.578 & 92.284 \\
1.0205 & -19.341 & 151.26 & -463.50 \\
-1.9057 & 22.845 & -228.14 & 973.92 \\
1.0885 & -6.1962 & 106.98 & -677.64
\end{pmatrix} \begin{pmatrix}
1 \\
1/\lambda \\
1/\lambda^2 \\
1/\lambda^3
\end{pmatrix}, \tag{4.67}
\]

where the range of applicability is \( 5 < \lambda < 100 \). The remaining terms are given by the following expressions:

\[
I_\lambda(\lambda) = \int_1^{x_0} \frac{x^2}{x^\lambda} dx = -\frac{(x_0)^{-\lambda + 3} - 1}{\lambda - 3}, \tag{4.68}
\]

\[
J_\lambda(\lambda) = \int_1^{x_0} \frac{(x^3 - x^2)}{x^\lambda} dx = -\frac{(x_0)^{-\lambda + 4}(\lambda - 3) - (x_0)^{-\lambda + 3}(\lambda - 4) - 1}{(\lambda - 3)(\lambda - 4)}. \tag{4.69}
\]
The second order term is evaluated in a similar manner to the first,

\[
a_2 = \frac{1}{2} K^{HS} (1 + \chi) \epsilon C^2 \left( x_0^{2\lambda_a} (a_1^s(\eta; 2\lambda_a) + B(\eta; 2\lambda_a)) \right) \\
-2x_0^{2\lambda_a+\lambda_r} (a_1^s(\eta; \lambda_a + \lambda_r) + B(\eta; \lambda_a + \lambda_r)) \\
+x_0^{2\lambda_r} (a_1^s(\eta; 2\lambda_r) + B(\eta; 2\lambda_r))
\]  
\[(4.70)\]

where \( K^{HS} \) is the isothermal compressibility of the HS fluid in the Carnahan and Starling equation [10],

\[
K^{HS} = \frac{(1 - \eta)^4}{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4}.
\]  
\[(4.71)\]

and \( \chi \) is an empirical function of \( \eta \) obtained from Monte Carlo simulation;

\[
\chi = f_1(\alpha) \eta x_0^3 + f_2(\alpha) (\eta x_0^3)^5 + f_3(\alpha) (\eta x_0^3)^8
\]  
\[(4.72)\]

where \( \alpha \) has been previously defined in Equation (3.10).

The third perturbation term of the Helmholtz free energy is given by the following empirical function;

\[
a_3 = -\epsilon^3 f_4(\alpha) \eta x_0^3 \exp(f_5(\alpha) \eta x_0^3 + f_6(\alpha) \eta^2 x_0^6),
\]  
\[(4.73)\]

where,

\[
f_i(\alpha) = \sum_{n=0}^{n=3} \phi_{i,n} \alpha^n / \left[ 1 + \sum_{n=4}^{n=6} \phi_{i,n} \alpha^{n-3} \right] \]  
\[(4.74)\]

the coefficients \( \phi_{i,n} \) are given in Table 4.3.
In addition to this Lafitte et al. also present a more robust equation for the contact value of the radial distribution function $g^{Mie}(\sigma)$. This is determined from a BH perturbation expansion;

$$g^{Mie}(\sigma) = g_d^{HS}(\sigma) \exp\left(\beta \epsilon_{g_1}(\sigma)/g_d^{HS}(\sigma) + (\beta \epsilon)^2 g_2(\sigma)/g_d^{HS}(\sigma)\right)$$ (4.75)\n
where,

$$g_d^{HS}(\sigma) = \exp(k_0 + k_1 x_0 + k_2 x_0^2 + k_3 x_0^3)$$ (4.76)\n
and the density-dependent coefficients are given by;

$$k_0 = -\ln(1 - \eta) + \frac{42\eta - 39\eta^2 + 9\eta^3 - 2\eta^4}{6(1 - \eta)^3},$$ (4.77)\n
$$k_1 = \frac{\eta^4 + 6\eta^2 - 12\eta}{2(1 - \eta)^3},$$ (4.78)\n
$$k_2 = \frac{-3\eta^2}{8(1 - \eta)^2},$$ (4.79)
The first and second expressions are given by:

\[ g_1(\sigma) = \frac{1}{2\pi\epsilon d^3} \left[ 3 \frac{\delta a_1}{\delta \rho_s} \frac{\lambda_a x_0^\lambda_a a^s_1(\eta; \lambda_a) + B(\eta; \lambda_a)}{\rho_s} + C \lambda_r x_0^\lambda_r a^s_1(\eta; \lambda_r) + B(\eta; \lambda_r) \right] \]

\[ g_2(\sigma) = (1 + \gamma_c) g^MCA_2(\sigma), \]

where \( g^MCA_2(\sigma) \) is the corrected macroscopic compressibility approximation (MCA) [185],

\[ g^MCA_2(\sigma) = \frac{1}{2\pi\epsilon^2 d^5} \left[ \frac{\delta}{\delta \rho_s} \frac{a_2}{1 + \chi} \right] \]

\[ = \epsilon K^{HS} C^2 \frac{\lambda_a x_0^{2\lambda_a} (a^s_1(\eta; 2\lambda_r) + B(\eta; 2\lambda_r))}{\rho_s} \]

\[ + \epsilon K^{HS} C^2 (\lambda_a + \lambda_r) x_0^{\lambda_a + \lambda_r} \]

\[ \times \left( a^s_1(\eta; \lambda_a + \lambda_r) + B(\eta; \lambda_a + \lambda_r) \right) \rho_s \]

\[ - \epsilon K^{HS} C^2 \frac{\lambda_a x_0^{2\lambda_a} a^s_1(\eta; 2\lambda_a) + B(\eta; 2\lambda_a)}{\rho_s} \]

and,

\[ \gamma_c = \phi_{7,0}(- \tanh(\phi_{7,1} (\phi_{7,2} - \alpha)) + 1) \eta x_0^3 \theta \exp(\phi_{7,3} \eta x_0^3 + \phi_{7,4} \eta^2 x_0^6)). \]
4.7 Results

In this Section the presented EOS for the fcc solid referred to herein as SAFT-VR Mie solid is compared to data in the literature for the solid LJ monomer system and simulation data of other Mie potentials.

4.7.1 LJ monomer systems

Residual Helmholtz free energy, \(a^{\text{res}}\)

![Graph showing the comparison of residual Helmholtz free energy between SAFT-VR Mie solid and van der Hoef's correlation for LJ monomer solid at different temperatures.]

Figure 4.7: Comparison of the residual Helmholtz free energy of the LJ monomer solid from SAFT-VR Mie solid (red dashed lines) with the residual Helmholtz free energy obtained from the correlation of van der Hoef for the LJ monomer solid phase [36] (solid black lines) at temperatures \(T^*\) = 0.75, 0.8, 0.9, 1.0, 1.15, 1.35 and 1.5.
In Figure 4.7 the residual Helmholtz free energy ($a^{res}$) determined using SAFT-VR Mie solid is compared to residual Helmholtz free energy obtained from the correlation of van der Hoef [36] for the LJ solid monomer system. $a^{res}$ is tested over a range of temperatures from $T^* =$0.75-1.5. The solid black lines are the isotherms obtained from the van der Hoef equation and the red dashed lines are the residual free energy determined from the SAFT-VR Mie solid. Excellent agreement is seen between the isotherms specifically at the lower temperatures. At high temperatures however, particularly $T^* > 1.0$ there is a slight discrepancy at lower densities values of the free energy which is reflected in a change in gradient which becomes more pronounced with increasing temperature.

**Compressibility, Z**

The compressibility ($Z = \frac{\partial A}{\partial P}$) obtained from SAFT-VR Mie fcc solid, is compared to the derivative of the free energy from the van der Hoef equation. In Figure 4.8 we note that the slight deviation in the free energy results in a magnified deviation of the derivative property. The isotherms are re-represented in Figure 4.9 to highlight more clearly at what conditions the deviation is occurring. For isotherms of a lower temperature (Figure 4.9(a)) a good agreement is noted with the van der Hoef isotherms while there is greater deviation of the theory at higher temperatures (Figure 4.9(b)). For the purpose of SSE these deviations will not be an issue as the phase transitions occur at higher densities, i.e., in a density range where there is no deviation between our expression and the expression of van der Hoef. For SFE, an increase in temperature also results in a corresponding increase in the coexisting density of the solid phase and for the case of LJ we find that the required coexisting density is in a density range such that the free energy in the solid phase given by SAFT-VR Mie solid is still in agreement with the van der Hoef isotherms, i.e. the SAFT-VR Mie solid is appropriate for the determination of SFE boundaries.
Figure 4.8: Comparison of the theoretical compressibility of the LJ solid (dashed lines) in comparison to the derivative of the EOS for solid phase presented by van der Hoef (solid black lines) [36] at temperatures $T^*=0.75$ (green), $T^*=0.8$ (brown), $T^*=0.9$ (orange), $T^*=1.0$ (purple), $T^*=1.15$ (blue), $T^*=1.35$ (red) and $T^*=1.5$ (dark blue).

Figure 4.9: Magnification of the deviation of the compressibility at a) lower isotherms $T^*=0.75$, 0.8, 0.9 and 1.0 and b) higher isotherms $T^*=1.15$, 1.35 and 1.5. $T^*=0.75$ (green), $T^*=0.8$ (brown), $T^*=0.9$ (orange), $T^*=1.0$ (purple), $T^*=1.15$ (blue), $T^*=1.35$ (red) and $T^*=1.5$ (dark blue)
4. SAFT-VR Mie equation of state for the solid phase

4.7.2 Mie monomer; fluid and solid isotherms

It is useful to assess the accuracy of the two independent EOS presented for the fluid and the solid, as on solving for coexistence this aspect can not be tested. To investigate this, isotherms obtained from the equations of state are compared to simulation data. This provides an insight into the range at which each theory is accurate and consequently the conditions at which they may breaks down.

Isobaric-isothermal simulations (NPT and NσT) are performed at increasing pressure increments along an isotherm to obtain simulation data for which a comparison can be made. Solid and fluid systems of Mie spheres of varying exponents which span the α parameter (α=0.392-1.26) are created in order to cover a wide range of intermolecular attractions. In the NPT ensemble for the fluid and the NσT ensemble for the solid the pressure is increased at a constant temperature which is at 1.1T_t of the individual Mie potential tested. The triple point values used are those presented in Chapter 3 (Table 3.3). Each simulation of N=3375 was run for 10^6 timesteps 20% of which were discarded for equilibration. The density of the system is obtained from the output final configuration of the simulation cell.

In Figure 4.10 a comparison of the simulation results and the calculations from the SAFT-VR Mie solid and fluid equations of state for 5 different Mie potentials at T^*=1.1T_t is presented. Overall there is good agreement between the simulation results and the theory for all potentials studied. With respect to the solid isotherms, at lower densities, deviation from the simulation results is particularly more pronounced for the (8,6) potential. For exponents which result in a more repulsive potential the theory appears to be in better agreement with simulation results along the entire isotherm. This result suggests a limitation to the presented EOS at very low densities for very ‘soft’ potential. As the remaining isotherms show good agreement with simulation data it is reasonable to assume that the EOS is accurate for systems which are more repulsive than the (8,6) potential.
4. SAFT-VR Mie equation of state for the solid phase

With respect to the liquid isotherms, the comparison between simulation data and the SAFT-VR Mie fluid EOS predictions show overall good agreement. Here, the theory is seen to deviate from simulation data at the higher densities (especially for the softer Mie potentials (8,6) and (9,85,6)). In SAFT-VR Mie fluid as explained in Section 4.6, the monomer term is developed using a Barker and Henderson perturbation theory which is taken to a third order expansion. The reference term \(a_0\) is a hard sphere systems with an effective diameter \((d)\). \(a_0\) is calculated using the Carnahan and Starling EOS for hard spheres in the fluid phase [10] and \(a_1\) is evaluated via a purely theoretical approach. The evaluation of the 2\textsuperscript{nd} and 3\textsuperscript{rd} order terms on the other hand required several variables in the expression for \(a_2\) and \(a_3\) being fit to simulation data. At the point of its development, these variables required to determine \(a_2\) and \(a_3\) were fit to simulation data which took into account densities up to a maximum of \(\rho^*\)=0.8. This density is too low for consideration of the solid fluid transition region and therefore will account for the deviations of the isotherms. To correct this, the \(a_2\) and \(a_3\) terms would have to be refit to simulations that incorporate a higher density range. For Mie potentials with a greater degree of repulsion it is surprising to note the good agreement along the entire isotherm, even at densities above \(\rho^*=0.8\).
4. SAFT-VR Mie equation of state for the solid phase

Figure 4.10: Liquid and solid isotherms of several Mie potentials: simulation at $T^* = 1.17 T$ for all potentials. Solid theory isotherms are represented by blue lines, and the liquid theory by green lines. The solid simulations are red diamonds and the liquid simulations by purple circles: a) (8,6), b) (9.85,6), c) (15.58,6), d) (23,6.66), e) (19.02,8,8).
4. SAFT-VR Mie equation of state for the solid phase

4.8 Summary

In this chapter, an EOS has been presented for spherical and chain solid systems interacting via a Mie potentials. The EOS follows the extension of TPT1 to the solid phase, originally presented by Vega and MacDowell [87]. The SAFT-VR framework (which is based on TPT1) is implemented to determine the Helmholtz free energy of the solid system and the modified WCA theory proposed by Kang et al [13] is applied to determining the free energy of the monomer contribution in the solid phase. This perturbation theory is used in preference to the BH theory, which is typically used in the SAFT-VR methodology, as the modified WCA theory has proven to be more accurate in treating the solid phase.

The EOS is developed using the above methodology and the radial distribution function of the hard sphere of an effective diameter. $g^{HS}(r/d)$ is required to evaluate the $a_1$ perturbation term and is obtained from the work of Choi et al. [181] for an fcc crystal structure. The resulting EOS is tested against the excess free energy of the LJ monomer solid obtained from the van der Hoef EOS [36], which is a correlation to 877 state points in the solid phase over a temperature range $T^*=0.1-2.0$ and density $\rho^*=0.94-1.20$. The EOS is in good agreement with the correlation, although a slight discrepancy is noted at lower densities of higher temperature isotherms. This error becomes augmented when derivative properties (compressibility) are analysed. The aim of obtaining such an EOS for the solid phase is to ultimately predict the SFE and SSE boundaries for a host of Mie potentials, and the inaccuracies observed at higher temperature isotherms are out of the density range required to evaluate both SSE and SFE for the LJ system and, therefore, the EOS is still considered accurate for this purpose. The SAFT-VR Mie solid EOS for the hcp phase was presented and the SAFT-VR Mie fluid EOS [90] was briefly reviewed.

The SAFT-VR Mie equations of state for solid and fluid phases are tested against simulation data for Mie potentials other than the LJ. For the individual equations of
state, it is found that SAFT-VR Mie fluid equation deviates from simulation data at higher densities for potentials with longer attractive tails i.e. ‘softer’ potentials. The deviation can be accounted for by analysis of the $a_2$ and $a_3$ terms of the free energy that are fits to simulation data, which only considered a maximum density range of $\rho^*=0.8$ which is below the required density range for SFE. In spite of this however, the theory still appears to be sufficiently accurate when compared to simulation data particularly as the degree of repulsion of the potential is increased. The solid EOS is also tested against simulations and it is found that the theory begins to deviate at lower densities for the ‘softer’ potentials however, in all other cases tested the theory is in good agreement with the simulation results. With the good agreement of the theoretical calculations with the simulation data of the independent equations of state, the next step is to use both equations to solve for solid-fluid coexistence.
Chapter 5

Global phase behaviour of the Mie family of model molecules

5.1 Introduction

For a pure substance, the coexistence of two phases can be described by consideration of an isolated system of a constant volume $V$ containing a total number of particles $N$. Within this system two phases, $A$ and $B$ exist in which particles can be exchanged via an interface (Figure 5.1) [198]. Given that entropy ($S$), volume and the number of particles are extensive variables and the system is closed;

\[ S = S^A + S^B, \quad (5.1) \]

\[ V = V^A + V^B, \quad (5.2) \]

and

\[ N = N^A + N^B. \quad (5.3) \]
According to the 2\textsuperscript{nd} law of thermodynamics for a system to be in equilibrium, the total entropy must be at a maximum i.e., \( dS=0 \). Given that the complete system is isolated and therefore \( dV=0,\ dN=0 \) and \( dU=0 \) the following relationship can be derived:

\[
dS = 0 = dS^A + dS^B, \tag{5.4}
\]

\[
dV = 0 = dV^A + dV^B, \tag{5.5}
\]

\[
dN = 0 = dN^A + dN^B, \tag{5.6}
\]

and,

\[
dU = 0 = dU^A + dU^B. \tag{5.7}
\]
\[ dS^A = -dS^B, \]  \hspace{1cm} (5.8)

\[ dV^A = -dV^B \]  \hspace{1cm} (5.9)

\[ dN^A = -dN^B \]  \hspace{1cm} (5.10)

and

\[ dU^A = -dU^B. \]  \hspace{1cm} (5.11)

Entropy can be expressed as a function of the internal energy, volume and number of particles,

\[ dS = \frac{dU}{T} + \frac{PdV}{T} - \frac{\mu}{T} dN, \]  \hspace{1cm} (5.12)

where \( \mu \) is the chemical potential which is defined as the molar Gibbs free energy, \( \mu = \left( \frac{\partial G}{\partial N} \right)_{P,T} = \left( \frac{\partial A}{\partial N} \right)_{T,V} \). Given the relations in Equations (5.8) to (5.11) and since \( dS = dS^A + dS^B \) the total entropy can be written as;

\[ dS = \left( \frac{1}{T^A} - \frac{1}{T^B} \right) dU^A + \left( \frac{P^A}{T^A} - \frac{P^B}{T^B} \right) dV^A - \left( \frac{\mu^A}{T^A} - \frac{\mu^B}{T^B} \right) dN^A. \]  \hspace{1cm} (5.13)

Since the internal energy, volume and number of particles are independent variables, the expression \( dS = 0 \) is only satisfied if;

\[ \left( \frac{1}{T^A} - \frac{1}{T^B} \right) = 0, \]  \hspace{1cm} (5.14)

\[ \left( \frac{P^A}{T^A} - \frac{P^B}{T^B} \right) = 0 \]  \hspace{1cm} (5.15)
and,

\[
\left( \frac{\mu^A}{T^A} - \frac{\mu^B}{T^B} \right) = 0. 
\]  \tag{5.16}

Therefore, for equilibrium between phases \( A \) and \( B \) the following conditions must be met;

\[
T^A = T^B, \quad \tag{5.17}
\]

\[
P^A = P^B, \quad \tag{5.18}
\]

and

\[
\mu^A = \mu^B. \quad \tag{5.19}
\]

In order to complete the phase diagram of any model system, these conditions must be satisfied for any two coexisting phases, i.e., solid-fluid, vapour-liquid, solid-vapour and any solid-solid equilibrium. Solving for coexistence using two independent equations of state is exemplified in Figure 5.2. At a given temperature, the equation of state of each phase is used to evaluate the corresponding pressures and chemical potential over a given density range. This relationship is represented in Figure 5.2 by the two solid lines, each corresponding to a different phase. The unique coexistence point is found on the intersection of the two lines. At this point, the chemical potentials and pressures of each phase are equal to each other at a constant temperature; therefore the conditions for phase equilibrium are met. On either side of this transition the phase which possesses the lower chemical potential will be more stable with respect to the other i.e., Phase A is more stable at higher pressures however after the phase transition, Phase B is seen to become more stable with respect to Phase A.
Figure 5.2: Schematic diagram illustrating how coexistence between two independent phases (A and B) is evaluated. The solid lines represent the chemical potential versus pressure relationship of each phase. The intersection of these two lines (green circle) indicates the unique conditions at which phases A and B will coexist at constant temperature.

In the previous chapter, two separate equations of state have been presented for the fluid and solid phases of tangentially bonded flexible chains interacting via Mie potentials; the EOS for the fluid phase (SAFT-VR Mie fluid) presented by Lafitte et al. [90] and the EOS for the solid phases presented in this work. The SAFT-VR Mie solid equation for the fcc phase will be used in conjunction with the SAFT-VR Mie fluid EOS to solve for coexistence and thereby determine the SFE boundary of monomer and chain systems. Additionally, the SSE hcp-fcc boundary is calculated using the SAFT-VR Mie solid equations of state for the respective phases. Combining these calculations with calculations for the VLE boundary obtained from SAFT-VR Mie fluid EOS and the SVE boundary, we obtain the global phase diagram of the tangentially bonded flexible chain systems interacting via the Mie potential. Our results are compared to previously reported simulation data of the LJ potential, monomer [35], dimer [105] and
5. Global phase behaviour of the Mie family

5.2 LJ monomer: calculation of coexistence boundaries

Coexistence between the fcc solid phase and fluid phase of a LJ sphere is considered first. Equilibrium is evaluated by equating the pressures and chemical potentials of the two phases at specified temperatures. In Figure 5.3, isotherms of the SAFT-VR Mie solid and SAFT-VR Mie fluid at a given temperature are presented. The intersection of the two lines indicates the point of equilibrium of the phases for a given temperature. To the right of the intersection, the fcc solid phase is more stable (lower chemical potential), on the left of the intersection the fluid becomes more stable with respect to the solid. By performing this calculation over a wide temperature range the SFE boundaries are evaluated. In our implementation, coexistence is solved over a given temperature range by inputting an initial ‘guess’ of the coexisting densities of the solid and fluid phases at the initial temperature. The fluid and solid EOS are solved independently to determine the pressure and chemical potential. If coexistence is found i.e. \( P_{\text{liq}} = P_{\text{sol}} \) and \( \mu_{\text{liq}} = \mu_{\text{sol}} \) the program advances to the next temperature increment. If the differences in \( P \) and \( \mu \) are outside a given tolerance, the Newton-Raphson method is implemented to update the initial guesses until the differences between the properties is within the accepted tolerance.

In Figure 5.4 the phase diagram of the LJ monomer system including VLE, SVE, SFE and SSE phase boundaries is presented. The VLE region is obtained from SAFT-VR Mie fluid EOS [90] and the SFE and SVE are obtained from solving for coexistence with the SAFT-VR Mie solid and fluid equations. The SSE boundary is evaluated from the solid theory coupled with differing fcc and hcp crystal structures. With respect to SFE and SVE the theoretical predictions are in good agreement with simulation data although the Mastny and de Pablo EOS [35] is seen to be slightly more accurate for the solid-fluid region in comparison to our theory. This is to be expected as they use the
excess free energy of the LJ monomer in the solid phase, obtained from the correlation of Van der Hoef to simulation data [36] while in our current EOS a perturbation theory is taken to a 1st order expansion only. The SVE predictions however, appear to be equivalent in accuracy to the correlation of van der Hoef [134]. The SAFT-VR Mie equations yield a triple point which is 3.4% lower than the triple point temperature obtained from the intersection of the saturated liquid branch of the Johnson EOS and the solid-fluid boundary of the Mastny and de Pablo EOS. With respect to the critical point, SAFT-VR Mie fluid EOS [90] is seen to also predict a value slightly lower when compared to the critical point obtained from the Johnson EOS[37].

The solid-solid phase transitions are also depicted in Figure 5.4. The phase transition is found to be weakly first order (continuous) with a difference between coexisting densities of approximately 0.002 in reduced units. This result is in qualitative agreement with the findings of Jackson and van Swol [15] who also suggested a weakly first order phase transition for the cut and shifted LJ potential where the potential is cut and shifted at the cutoff radius \(r_c\) which is taken to be \(2.5\)\(\sigma\). The fcc phase is found to be stable at lower densities and coexists with the liquid phase while the hcp phase becomes more stable at higher densities. This result is also in agreement with the findings of several other authors [196] [197] [22] [94].
Figure 5.3: $\mu^* - P^*$ plots indicating the phase coexistence conditions of the fcc solid and fluid phases for the LJ monomer system at temperatures, $T^*$=2.0, 1.8, 1.4, 1.2, 1.0 and 0.8. The fcc solid isotherms (blue lines) are determined for the SAFT-VR Mie solid and the fluid isotherms (red lines) are determined for the SAFT-VR Mie fluid. The intersection of two lines indicates the point of coexistence between the two phases at the given temperature.
Figure 5.4: Comparison of the global phase behaviour of the LJ monomer as determined by the Johnson EOS [37] for the fluid phases and the Mastny and de Pablo [35] for SFE (dashed line) and the SAFT-VR Mie EOS for the fluid phases [90] and the fluid theory coupled with the solid EOS of this work (solid line). Simulation data points presented previously in Chapter 2 are represented by the green diamonds. The Solid-solid phase transition from fcc to hcp is highlighted by the solid line with the stable hcp phase lying to the right and fcc to the left. The different phases of the diagram are highlighted for clarity.
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5.3 Mie monomer global phase diagram

Model systems interacting with a Mie potential have been of considerable interest with respect to development of coarse-grained models. In a recent work by Avendaño et al. [41], a case study of the CO$_2$ model was presented in which it was shown that use of a simpler model such as the LJ was incapable of reproducing multiple thermophysical properties regardless of the parameterization i.e., a parameter set accurately describing the liquid densities will fail to predict correctly the vapour pressures. A coarse grained spherical model of CO$_2$ interacting via a (23,6.66) potential was found however, to reproduce a wide range of experimentally observed properties of CO$_2$ in the fluid phase. This result in particular showcases the robust nature of the Mie potential where simpler models such as LJ have failed. Similar coarse-grained studies by Shelley et al. [145] McCallagh et al. [144] and Potoff and Bernard [40] have yielded similar conclusions on the viability of the Mie potential for use in coarse-grained models.

Given this increased interest in using the Mie as a force field for coarse-graining, we employ the EOS presented in Chapter 4 to calculate the phase diagram of several other Mie potentials. The theoretical calculations are compared to simulation results presented in Chapter 3 as the phase diagrams presented in this chapter span Mie potentials with a wide range of exponents and intermolecular attraction. The inherent speed of computations using the theory, by comparison to simulations also enables us to further test the relationship between the parameter $\alpha$ and the fluid range of different Mie potentials. In previous chapters only seven potentials spanning different values of $\alpha$ had been chosen to study the compression of the fluid range, however having an analytical equation of state, this relationship can be analysed with different parameter combinations. This will be discussed in greater depth in Section 5.3.2.

Having shown that the calculated isotherms from the proposed EOS (Figure 4.10) are in good agreement with simulation data we use the two independent equations of state to solve for solid-fluid coexistence for five monomer Mie systems of varying range.
of attraction. The vapour-liquid predictions from SAFT-VR Mie fluid and the vapour-solid predictions from SAFT-VR Mie fluid and solid are also included. The triple point temperature is obtained on observation of the intersection of the vapour-liquid curve with the solid-fluid phase boundaries. In Figure 5.5 the global phase diagrams of several Mie potentials of varying range of attraction are presented. The exponents are chosen such that they are consistent with the chosen Mie potentials used in Chapter 3 to carry out the simulation analysis. Overall, the theoretical calculations are in good agreement with simulation data for all Mie potentials studied. The theory can accurately determine the triple point of Mie systems within a maximum percentage error of 4%. Although there is good agreement between theory and simulation for phase diagrams (a) to (e), the deviation of the theory from the simulation data is most pronounced at the most repulsive potential studied (42,8.8). As observed in the simulation analysis for these potentials, the critical point is more sharply affected by an increase in the repulsive nature of the potential in comparison to the triple point for which the change is more subtle. Overall the theoretical calculations are consistent with the simulation results as a more repulsive potential corresponds to a sharp decrease in the critical point temperature with a more subtle decrease in the triple point temperature.

It is interesting to note the ability of the theory to predict the disappearance of the stable fluid range, a phenomenon that has been noted by several experimental [154], simulation [151] and theoretical [47] [46] works. From Figure 5.5 we see the shrinking of the fluid range with an increase in the repulsive nature of the potential which is in accordance with our previous findings (Chapter 3). This suggests that the theory is robust enough to also predict the behaviour of a Mie potential where the destabilisation of the VLE region with respect to the solid phase is seen. This aspect will be discussed in Section 5.3.2.
Figure 5.5: Global phase behaviour of the Mie intermolecular potential, theoretical prediction from this work (black lines) compared to simulation data (green diamonds).
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5.3.1 SSE hcp-fcc transitions of Mie particles

For the six systems selected, the hcp-fcc phase transition is studied in more detail here. There is currently no simulation data for the fcc-hcp phase transition boundaries for Mie monomer systems and therefore the theoretical calculations can not be confirmed. However, on a qualitative basis; our results are similar to the findings of Jackson and van Swol [15] for the cut and shifted LJ potential.

In a study by Somasi et al.[199] it was suggested that the difference between the hcp and fcc phases only begins at the 3rd nearest neighbour shell (refer to Table 4.1 and 4.2), and therefore it is the attractive tail of the potential that will influence the relative stability of the phases. As our solid theory has been developed for both the fcc and hcp phases, the SSE boundaries can be determined and the suggestion of Somasi et al. can be analysed over a range of attractive tails of Mie potentials. In Figure 5.6 the fcc-hcp phase transitions of the Mie potential at a varying range of attraction is presented. The phase transitions, as in the case of the LJ monomer, are found to be weakly first order (continuous) where the difference in coexisting densities is approximately 0.002 (in reduced units) for all potentials studied. In Figure 5.6 the stable hcp phase is highlighted by the shaded region and the solid-solid phase transition boundary is represented by the solid line. The stability of the fcc structure at lower densities with respect to the hcp phase is in agreement with the findings of previous works; the early simulation works of Alder et al. [196] [197], the theoretical study of Jackson and van Swol on spheres interacting via a cut and shifted LJ potential [15], the simulation study of Frenkel and Ladd on hard sphere monomers [22], the theoretical predictions of Choi et al. on the LJ spherical system [181] and the simulation study of Polson and Frenkel on semi-flexible LJ chains [94] to name a few.

The phase diagrams in Figure 5.6 show that a change in the attractive tail of the potential (i.e., a change in exponents and therefore a change in $\alpha$) of the Mie potential does indeed affect the SSE boundary; though the change is subtle. On examination
of the first phase diagram (a), the phase boundary of the potential with the softest attractive tail (corresponding to $\alpha=1.04$) has a positive gradient. A decrease in the value of $\alpha$, which corresponds to shorter attractive tail, is found to increase the steepness of the gradient; this is reflected by the near-vertical phase boundaries at the most repulsive potential $(42,8.8)$ i.e., $\alpha=0.269$. This suggests, in this high temperature region, a slight stabilisation of the hcp phase with respect to fcc with a decrease in the size of the attractive tail (i.e., decrease in attractive energy). Additionally a general shift of the transition boundaries to lower densities for a decrease in $\alpha$ is also observed, again suggesting the stabilisation of the hcp phase at lower densities for potential with shorter attractive tails. These trends can therefore provide some insight into the effect the tail of the pair potential has on the stability of differing crystal phases which has been suggested previously [199].
Figure 5.6: SSE of the spheres interacting with a Mie potential of variable range. The stable hcp phase is highlighted by the shaded region and the phase transition boundary is represented by the adjacent solid line. All other symbols are as in Figure 5.5.
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5.3.2 Further considerations on the conformality of Mie potentials

Figure 5.7: Comparison of two Mie potentials of the same $\alpha$ value ($\alpha = 0.75$) but different individual exponents (11.15,7) solid green lines and (15.6,6) solid black lines

In Chapter 3, upon analysis of simulation data, we observed an apparent conformality within the Mie potentials based on an analysis of the Helmholtz free energy of the fluid. Using the theory it is also possible to test the extent to which this conformal behaviour holds. In Figure 5.7 two Mie potentials (11.15,7) and (15.6,6) of the same $\alpha$ value ($\alpha=0.75$) are shown. On inspection of the two phase diagrams a close-to-conformal fluid behaviour of the two potentials is observed, with a negligible difference in the critical point. However, a difference in triple point of 0.04 (in reduced units) and a mismatch of the solid-vapour and solid-fluid equilibria of the two potentials is also observed. In Chapter 3 the non-conformal nature of the solid phase through simulation analysis were discussed; the EOS results reflect the same behaviour. The parameter $\alpha$, is defined as an integral from $\sigma$ to $\infty$ and hence it does not take into account difference in the potential at distances less than $\sigma$, corresponding to the repulsive branch of the potential. Whilst for most fluid states molecules will rarely explore such close
distances, the interaction energy profile at these distances needs to be considered in the solid.

In Chapter 3 a linear relationship was proposed between $\alpha$ (Equation 3.10) and the stable fluid range ($T_c/T_t$) through a simulation study of seven potentials. Here, SAFT-VR Mie solid and fluid are used to determine the phase diagrams of several other Mie potentials. The correlations and the range of validity for these trends is given in Appendix D. In Figure 5.8 the fluid range is plotted as a function of $\alpha$ at varying exponent combinations; the ($\lambda_r$,6), ($\lambda_r$,7) and ($\lambda_r$,8) potential families were chosen where the repulsive exponent was varied to span the range of $\alpha$. In calculating the fluid range with the theory it is seen that the trend is not linear as inferred from the simulation results; instead, there is narrow range of possible $T_c/T_t$ values for different Mie potentials which correspond to the same $\alpha$ value. This refinement of the results confirms that $\alpha$ is not an exact parameter in defining conformal fluids. Mie potentials of the same $\alpha$ display only a ‘close-to-conformal’ behaviour due to the approximations made in the derivation of $\alpha$ in Equation 3.7. It can be inferred that the discrepancy lies within the definition of $\alpha$ as an integral covers only the cohesive energy (from $\sigma$ to $\infty$) while neglecting the close range effects. While two fluids with the same $\alpha$ value exhibit very similar properties in the fluid phase, they are not exact, particularly in terms of their solid phase behaviour.

The theory does clearly show a non linear decrease in the size of the stable fluid range with $\alpha$ and predicts the loss of the stable fluid at an $\alpha$ value of 0.279. This is within a 3.6% deviation of that $\alpha$ value predicted by the simulation data presented in Chapter 3. The trends are also consistent with the work of Ahmed and Sadus [45] who determine the global phase behaviour of Mie potentials ($\lambda_r$,6) where $\lambda_r$ =11, 10, 9, 8 and 7. The corresponding $\alpha$ values were determined and plotted against the $T_c/T_t$ ratio (Figure 5.8). It is found that the simulation results of Ahmed and Sadus are in excellent agreement with the simulation results of Chapter 3 and also good agreement.
with the theoretical predictions for the $(\lambda_r,6)$ systems.

Figure 5.8: Comparison of the fluid range $T_c/T_t$ with a change in $\alpha$. The solid purple lines correspond to the fluid ranges of $(\lambda_r,6)$ potentials, the blue dashed-dotted lines to the $(\lambda_r,7)$ potentials and the red dashed lines to the $(\lambda_r,8)$ potentials. The black closed points are the fluid ranges obtained from simulation data points (see Chapter 3) and the dashed black line is the correlation obtained from the simulation results. The green crosses are obtained from simulation data from Ahmed and Sadus [45].

On closer analysis of the calculations with the different Mie fluids i.e., $(\lambda_r,6)$, $(\lambda_r,7)$ and $(\lambda_r,8)$, it is noted that the $(\lambda_r,6)$ fluids (purple line) will span a range from very ‘soft’ potential to moderately repulsive potentials ($\alpha=0.503-1.26$). $(\lambda_r,8)$ potentials (red dashed line) on the other hand span moderately repulsive potentials to highly repulsive systems ($\alpha=0.27-0.77$). The $(\lambda_r,7)$ fluids (blue dash-dotted line) however, are seen to cover the widest range of $\alpha$ values ($\alpha=0.366-1.01$) and will therefore allow
for a clearer representation of the data when studying trends of the parameter $\alpha$. As such, potentials of the form $(\lambda, \gamma)$ are chosen for further analysis of chain systems, using our theory.

5.4 Chain systems

5.4.1 Dimers

The global phase behaviour of the tangentially bonded LJ dimer system has previously been calculated by Vega et al. [105] using MC simulation and a TPT1 approach. The VLE region was determined using the GEMC method [1], the SVE region using the Rahman-Parinello technique at zero pressure and the SFE region using free energy calculations [22] and the GDI method [96]. The theory used was TPT1-LJ for the fluid and TPT1-LJ extended to the solid phase [87] for the solid. The two equations of state were used to solve for coexistence and the global phase diagram. Here, we compare the simulation and theoretical results of TPT1-LJ [105] against the theory developed in Chapter 4 for the case of the tangentially bonded dimer system. In Figure 5.9 the global phase diagram of the LJ tangentially bonded dimer is shown using: simulations (green diamonds), TPT1-LJ proposed by Vega et al. (black dashed lines) and the current theory presented in this work (solid black lines). On comparison of our theoretical calculations to the simulation results, good agreement is noted between the two, although as seen in the monomer case the theoretical predictions of Vega et al. [105] are slightly more accurate than the present theory. This is attributed to the excess free energy of the reference monomer solid in the work of Vega et al. being obtained from the van der Hoef EOS [36]. The predicted triple point temperature is found to be in very good agreement with the calculations using TPT1-LJ and simulation results of Vega et al. Finally, the SSE boundary has also been included. The phase transition is found to be continuous with a difference in the coexisting densities of the two phases being very small. At present there is no simulation data available to test the accuracy of our calculations for the SSE boundary.
Figure 5.9: Global phase diagram of the LJ dimer as determined by TPT1-LJ for the fluid phase and the TPT1-LJ extension to the solid phase (dashed line) [105] and the SAFT-VR Mie EOS for the fluid phases and the fluid theory coupled with the solid EOS of this work (solid line). The solid-solid phase transition from fcc to hcp is highlighted by the solid line with the stable hcp phase lying to the right and fcc to the left. The symbols are simulation results obtained from [105].
Given the good agreement between the simulation data and the calculations of our theory for the LJ tangentially bonded dimer system the next step was to evaluate the global phase diagram using the theory for other Mie dimer systems. In Figure 5.10 five other Mie potentials in addition to the LJ dimer are presented. The exponents were chosen in order to span the range of the parameter $\alpha$ and therefore determine the effect varying the range of intermolecular attraction will have on dimer systems. As a further test of our theory, two of the five Mie dimer systems (Figure 5.10 (c) (f)) were also analysed with computer simulations and the results compared to the theoretical calculations. On comparison of the simulation results with the theory; the VLE calculations were found to be accurate with negligible differences between the critical and triple point temperatures for both potentials studied. The solid-fluid boundaries were also in good agreement although there is a slight over prediction of the coexisting densities of the solid boundary for the more repulsive potential (19.02,8.8).

On analysis of all the phase diagrams in Figure 5.10, it is evident that decreasing $\alpha$ and therefore making the potential more repulsive results in a reduction in the size of the stable fluid range. An increase in the repulsion results in a sharp decrease in the critical point temperature with a less steep decrease in the triple point which consequently compresses the fluid range. The gradient of the SFE boundaries are seen to become more steep with an increase in repulsion as well as an increase of the width the metastable solid-fluid region. These results follow the trends observed for the monomer.
Figure 5.10: Global phase diagram of tangentially bonded dimers interacting via a Mie potential where the exponents are: (a) (8,7) (b) LJ (c) (15.58,6) (d) (16,7) (e) (20,7) (f) (19.02-8.8). Solid black lines are theoretical predictions obtained from SAFT-VR Mie solid and fluid. The green symbols are simulation data b) simulation data of Vega et al [105], c) and f) this work.
5.4.2 Trimers

The phase diagram of flexible tangentially bonded LJ trimers is considered next. Simulation data was presented in Chapter 2 for the VLE, SVE, and SFE regions of the phase diagram and this result is used to test the accuracy of our theory. In addition to the simulation data, a comparison is also made to the TPT1-LJ applied to the LJ flexible trimer system [38]. In Figure 5.11 a comparison of the simulation data and TPT1-LJ to the current theoretical calculations is shown, in which good agreement is noted once again. There is a slight under prediction of the triple point when compared to the simulation data and the calculations of Vega et al. [38]. The calculations of the SFE boundaries using TPT1-LJ is found to be more accurate than our current theory when both are compared to the simulation data; a result which has been noted in the monomer and dimer cases. As mentioned previously, this is to be expected as the Helmholtz free energy of the monomer term in TPT1-LJ solid is obtained from the van der Hoef EOS [36], which is a fit to simulation data. The SSE boundaries of the trimer system are also plotted for completeness although there is no simulation data available for a comparison to be made to test its accuracy. The transition is predicted to be continuous with the differences in the coexisting densities of the hcp and fcc phases being very small. The fcc is stable at lower densities while the hcp is seen to become more stable with respect to the fcc at higher densities. With an increase in temperature, the SSE boundary shifts to higher densities suggesting that the fcc is more stable relative to the hcp at higher temperatures.

Using the SAFT-VR Mie theory, the phase diagram of five fully flexible trimer systems interacting via Mie potentials of varying range of attraction are presented in Figure 5.12. The exponents are chosen to span the range of the parameter $\alpha$. Similar to the monomer and dimer cases, increasing the repulsive nature of the potential results in a reduction of the stable fluid range. The critical point is seen to be most heavily influenced by an increase in repulsion while the triple point by comparison is relatively constant and shrinking of the fluid range is a direct consequence. With respect to the
SFE region and a more repulsive potential is seen to increase the width of the solid-fluid metastable region as well as increase in the steepness of the SFE boundaries, a result which is consistent with the monomer and dimer cases.
Figure 5.11: Global phase diagram of the LJ flexible trimer as determined by TPT1-LJ for the fluid phase and the TPT1-LJ extension to the solid phase (dashed line) [38] and the SAFT-VR Mie EOS for the fluid phases and the fluid theory coupled with the solid EOS of this work (solid line). Simulation data (green diamonds) for the VLE region obtained from Galindo et al. [101] and the SFE region obtained from Chapter 2. The solid-solid phase transition from fcc to hcp is highlighted by the solid line with the stable hcp phase lying to the right and fcc to the left.
Figure 5.12: Global phase diagram of the fully flexible tangentially bonded trimers interacting via a Mie potential; (a) (8,7) (b) LJ c) (13,7) d) (16,7) e) (21,7) f) (35,7). Solid black lines are theoretical predictions obtained from SAFT-VR Mie solid and fluid. The green symbols represent the LJ trimer phase boundaries, the VLE region is obtained from Galindo et al. [101] and the SFE is obtained from simulation data of this work using the methodology outlined in Chapter 2.
5. Global phase behaviour of the Mie family

5.5 Longer Chain Model Systems and Limiting Phase Behaviour

$n$-alkane systems, polymers and other chain-like molecules which can be modelled using tangentially bonded chains interacting with a Mie potential, are known to exhibit the solid phase at room temperature and pressure. Therefore, it is particularly interesting to consider the use of the proposed methods to study the phase behaviour of these molecules. In Figure 5.13 and Figure 5.14 the $T^* - \rho^*$ and $T^* - \rho^*_s$ (where $\rho^*_s$ is the segment density) global phase diagrams of LJ fully flexible chains systems for $m=1, 2, 4, 8$ and $16$ is shown. The SSE boundaries are only included in Figure 5.14 for clarity. The increasing chain length has a more pronounced effect on the VLE region by comparison to the rest of the phase diagram. An increase in the critical point temperature with an increase in chain length is noted which is in accordance with expected trends [38] [105] [101]. There is a slight decrease in the triple point temperature with increasing chain length, as well as a general shift of the SFE boundaries to higher densities which suggests an increase in stability of the fluid phase for longer chains. In Figure 5.14 it is also possible to compare the effect that chain length has on the SSE boundary. With increasing chain length the transition from fcc to hcp occurs at higher densities. The most marked effect is between the monomer and dimer cases and at chain lengths greater than $m=4$ there is a negligible change in the density i.e. for an infinitely long fully flexible LJ chain the limiting SSE boundary is almost indistinguishable to the SSE boundary at $m > 4$. Furthermore, at lower temperatures ($T^* < 0.64$), all LJ chains converge to the same SSE boundary.
Figure 5.13: $T^\ast - \rho$ global phase diagram of LJ chain systems using the SAFT-VR Mie equations of state. The VLE region is obtained from SAFT-VR Mie for the fluid phase and the SVE and SFE are obtained from the presented equation for the solid phase (SAFT-VR Mie solid) coupled with SAFT-VR Mie fluid. The chain lengths presented are $m = 1$ (blue lines), $m = 2$ (black lines), $m = 4$ (purple lines), $m = 8$ (orange lines) and $m = 16$ green lines.
Figure 5.14: $T^* - \rho_s$ global phase diagram of LJ chain systems using the SAFT-VR Mie equations of state. The phase boundaries are obtained as explained in Figure 5.13, and the SSE boundary is obtained from by coupling the SAFT-VR Mie solid EOS for fcc and hcp phases. The chain lengths presented are $m = 1$ (blue lines), $m = 2$ (black lines), $m = 4$ (purple lines), $m = 8$ (orange lines) and $m = 16$ green lines. The triple point temperatures are highlighted by a dotted line in each respective colour. The Solid-solid phase transition from fcc to hcp is highlighted by the solid line with the stable hcp phase lying to the right and fcc to the left.
5.5.1 Analysis of Trends

The temperature-density and temperature-segment density \((T^* - \rho^*\) and \(T - \rho^*_s\)) phase diagrams for six different Mie potential \((\lambda_r,7)\) of varying chain length over a wide range of intermolecular attraction, where \(\lambda_r=9, 11, 14, 20, 27\) and 37 has been calculated. Critical and triple point data of each diagram can be found in Table 5.1. An attractive exponent of seven is employed in order to span an extensive range of \(\alpha\) values (Figure 5.8). The chain systems analysed, are fully flexible models which are tangentially bonded with \(m=1, 2, 4, 8, 16\) being the number of segments per chain. The VLE region is obtained by solving for coexistence using the SAFT-VR Mie fluid equation of state, the solid-fluid and solid vapour boundaries are obtained from solving for coexistence using the SAFT-VR Mie solid and SAFT-VR Mie fluid equations and the solid-solid boundaries are obtained by solving for coexistence using the SAFT-VR Mie solid EOS for the fcc and hcp crystal structures. It is found that it was not possible to solve for the solid-vapour boundary of the \(m=16\) chain due to numerical problems as the coexisting densities of the vapour phase are too small (to the order of magnitude of \(10^{-40}\)). It is also observed that for the potential with the longest attractive tail i.e, the ‘softest’ potential (9-7), it is not possible to obtain the VLE for the \(m=16\) chain for the same reasons mentioned above and therefore the phase diagram of the chain \(m=16\) is not included in Figure 5.15.

The phase diagrams are a projection of the phase behaviour of Mie systems of variable chain length and intermolecular attraction. In Figure 5.15 the \(T^* - \rho^*\) phase diagram of chains of varying length of the softest potential (9-7) is presented, the subsequent diagrams (Figures 5.16 to 5.20) are for Mie potentials with a gradual increase in the overall repulsion (decreasing values of \(\alpha\)). For all Mie potentials there are a number of trends to the phase diagram that are common and these will be addressed first. With respect to the effect of chain length, an increase in the number of segments results in a more pronounced effect on the vapour-liquid curve than for either the solid-vapour or solid-fluid phase boundaries. This observation has previously been
reported for the fully flexible LJ chains [38] [105] [101] and for hard sphere fully flexible chains with segment-segment attraction at the mean field level of van der Waals [170] [167]. This is represented by the marked increase in the critical point temperature and the progressively more expanded vapour-liquid envelope with an increase in $m$. With respect to the solid-fluid transitions, in general, an increase in temperature results in an increase in the densities of the solid-fluid boundaries. The effect of increasing chain length however is found to be more subtle than in the vapour-liquid region. The triple point temperature is seen to decrease slightly with increasing chain length which is consistent with studies on LJ fully flexible systems [38] [105] [101] but is in contrast to the hard sphere fully flexible chain with segment-segment attraction, for which an increase in chain length results in an increase in the triple point temperature [170] [167]. As the models are fully flexible chains the subtle variation of the triple point with increasing chain length is to be expected by comparison to linear rigid molecules, for which the triple point is known to be very sensitive to an increase in chain length [101]. $T_t$ is also noted to approach an asymptotic value with increasing chain length; this result is also consistent with previous work on LJ systems [38]. The solid-vapour and solid-fluid boundaries both shift towards higher densities for increasing chain length, which is in agreement with studies on flexible LJ chains [38] [105] [101] and hard-sphere chains with segment-segment attraction [170] [167]. For the solid-solid transitions, all potentials exhibit a weakly first order phase transition, with the fcc phase being stable at lower densities with respect to the hcp phase. This is qualitatively consistent with the finding of Jackson and van Swol for the cut-and-shifted LJ monomer [15]. The difference in density of the solid-solid boundaries for different chain length is subtle where an increase in chain length results in a shift in the SSE boundaries to higher densities at higher temperatures. The most marked increase occurs between the monomer and dimer cases. There is a negligible further increase in density of the SSE boundary for a chain length greater than $m=4$. The SSE boundaries for all chain lengths converge at lower temperatures.
Next a comparison is made between the different Mie chain systems and the trends that arise from increasing the repulsive interaction of the potential. As expected from former works [46] [47] [45] and as discussed in Chapter 3 an increase in the repulsive nature of the potential results in a shrinking of the VLE region. For chain systems, the increase in the repulsive exponent is seen to reduce the typically pronounced decrease in the critical point and therefore the size of the stable fluid range varies less drastically for the more repulsive potentials. This is reflected for example, in the smaller increase in critical point between the $m=8$ chain and monomer system of the (37,7) potential ($\Delta T^*_c=0.489$) in comparison to the change in critical point temperature between the $m=8$ and monomer system of the (9,7) potential ($\Delta T^*_c=1.6$).

As mentioned previously the triple point temperature is observed to decrease with increasing chain length which eventually approaches an asymptotic value. The trend is also observed for an increasingly repulsive exponent. It is also noted however, that for more repulsive potentials, the triple point temperature approaches the asymptotic value at successively shorter chain lengths (refer to Table 5.1). For the (20,7) and (27,7) potential the limiting triple point temperature is $T^*_t=0.605$ and 0.56 respectively and occurs at a chain length of $m=8$ however the limiting triple point for the (37,7) potential ($T^*_t=0.56$) occurs at a chain length of $m=4$. Additionally, the solid-fluid boundaries that increase in density with increasing temperature become less pronounced with an increase in the degree of repulsion i.e. the solid-fluid transitions become more steep. This effect is also observed for an increase in chain length and therefore for the boundaries of the (37,7) potential for $m>1$ are almost vertical. Finally, the solid-solid phase transitions for the softest potential are more dispersed, and the individual transition boundaries can be identified. For an increase in the repulsive exponent, the SSE boundaries for the various chain lengths appear to converge and at the most repulsive potential (37,7) hence the individual boundary lines are almost indistinguishable. An increase in the repulsive exponent also results in a shift in the phase boundary towards lower densities indicating a stabilisation of the hcp phase at lower densities for more
repulsive potentials.

Figure 5.15: a) $T^* - \rho^*$ and b) $T^* - \rho_s^*$ diagrams of a (9,7) Mie potential for chain lengths $m=1, 2, 4$ and 8. $m=1$ (blue) $m=2$ (black), $m=4$ (green) and $m=8$ (purple). The triple point of each system is represented by a dotted line of the corresponding colour. The SSE boundaries are excluded from diagram (a) for clarity.
Figure 5.16: \( T^* - \rho^* \) and b) \( T^* - \rho_{s}^* \) diagrams of a (11,7) Mie potential for chain lengths \( m=1, 2, 4, 8 \) and 16. \( m=1 \) (blue), \( m=2 \) (black), \( m=4 \) (green), \( m=8 \) (purple) and \( m=16 \) (orange). The triple point of each system is represented by a dotted line of the corresponding colour. The SSE boundaries are excluded from diagram (a) for clarity.
Figure 5.17: $T^* - \rho^*$ and b) $T^* - \rho_s^*$ diagrams of a (14,7) Mie potential for chain lengths $m=1, 2, 4, 8$ and 16. $m=1$ (blue), $m=2$ (black), $m=4$ (green), $m=8$ (purple) and $m=16$ (orange). The triple point of each system is represented by a dotted line of the corresponding colour. The SSE boundaries are excluded from diagram (a) for clarity.
Figure 5.18: $T^* - \rho^*$ and b) $T^* - \rho_s^*$ diagrams of a (20,7) Mie potential for chain lengths $m=1, 2, 4, 8$ and 16. $m=1$ (blue), $m=2$ (black), $m=4$ (green), $m=8$ (purple) and $m=16$ (orange). The triple point of each system is represented by a dotted line of the corresponding colour. The SSE boundaries are excluded from diagram (a) for clarity.
5. Global phase behaviour of the Mie family

Figure 5.19: \( T^* - \rho^* \) and b) \( T^* - \rho_s^* \) diagrams of a (27,7) Mie potential for chain lengths \( m=1, 2, 4, 8 \) and 16. \( m=1 \) (blue), \( m=2 \) (black), \( m=4 \) (green), \( m=8 \) (purple) and \( m=16 \) (orange). The triple point of each system is represented by a dotted line of the corresponding colour. The SSE boundaries are excluded from diagram (a) for clarity.
Figure 5.20: \( T^* - \rho^* \) and b) \( T^* - \rho_s^* \) diagrams of a (37,7) Mie potential for chain lengths \( m=1, 2, 4, 8 \) and 16. \( m=1 \) (blue), \( m=2 \) (black), \( m=4 \) (green), \( m=8 \) (purple) and \( m=16 \) (orange). The triple point of each system is represented by a dotted line of the corresponding colour. The SSE boundaries are excluded from diagram (a) for clarity.
Table 5.1: Critical point temperature, triple point temperatures and fluid range 
\( (T^*_c/T^*_t) \) of chain systems interacting with a Mie potential of variable range \((\lambda_r, 7)\) obtained from the SAFT-VR Mie equations of state.

| \((\lambda_r, 7)\)| \(m\) | \(T^*_c\) | \(T^*_t\) | \(T^*_c/T^*_t\) | \((\lambda_r, 7)\)| \(m\) | \(T^*_c\) | \(T^*_t\) | \(T^*_c/T^*_t\) |
|---|---|---|---|---|---|---|---|---|
| 1  | 1.340 | 0.600 | 2.233 | 1  | 0.873 | 0.660 | 1.323 |
| 2  | 1.830 | 0.560 | 3.268 | 2  | 1.120 | 0.620 | 1.806 |
| (9,7) | 4  | 2.380 | 0.540 | 4.407 | (20,7) | 4  | 1.360 | 0.605 | 2.248 |
| 8  | 2.940 | 0.520 | 5.653 | 8  | 1.580 | 0.600 | 2.633 |
| 16 | 1.800 | 0.600 | 3.000 | 16 | 1.800 | 0.600 | 3.000 |
| 1  | 1.160 | 0.620 | 1.871 | 1  | 0.789 | 0.650 | 1.214 |
| 2  | 1.540 | 0.560 | 2.750 | 2  | 1.000 | 0.620 | 1.613 |
| (11,7) | 4  | 1.960 | 0.540 | 3.630 | (27,7) | 4  | 1.200 | 0.580 | 2.069 |
| 8  | 2.390 | 0.535 | 4.467 | 8  | 1.380 | 0.560 | 2.464 |
| 16 | 2.790 | 0.520 | 5.365 | 16 | 1.560 | 0.560 | 2.786 |
| 1  | 1.020 | 0.650 | 1.569 | 1  | 0.741 | 0.620 | 1.195 |
| 2  | 1.320 | 0.600 | 2.200 | 2  | 0.910 | 0.580 | 1.569 |
| (14,7) | 4  | 1.640 | 0.580 | 2.828 | (37,7) | 4  | 1.080 | 0.560 | 1.929 |
| 8  | 1.960 | 0.565 | 3.469 | 8  | 1.230 | 0.560 | 2.196 |
| 16 | 2.270 | 0.560 | 4.054 | 16 | 1.390 | 0.560 | 2.482 |

In Figure 5.21 the variation of the size of the stable VLE region \((T_c/T_t)\) with a change in the range of attraction for different chain lengths is shown. These correlations and the corresponding range of validity is given in Appendix D. As expected for increasing chain length, the size of the VLE region also increases and therefore the Mie potential at which the VLE region becomes metastable with respect to the solid phase also changes. From this diagram it can be concluded that an increase in chain length results in an increase in the required degree of repulsion of the Mie potential required for the VLE region to be metastable with respect to the solid phase i.e., a more repulsive potential.
is required for a longer chain in order for the VLE region to be entirely metastable with respect to the solid.

Figure 5.21: Diagram showing the $T_c/T_t$ relationship with the parameter $\alpha$ for Mie chains systems. The solid line corresponds to the $m=1$ system, dotted line for the $m=2$ system, dash-dotted for the $m=4$ system, dashed line for the $m=8$ system and dash-double dotted for the $m=16$ system.

In order to evaluate the effect of the range of attraction of the potential on the critical temperature of different Mie systems, a Schultz-Flory diagram is presented in Figure 5.22. In this diagram a linear relationship is obtained between the critical temperature and the number of segments in the chain. It is worth mentioning that the critical temperature of an infinitely long chain can also be determined from the 2nd virial coefficient being zero for an infinitely long chain as shown previously by Vega and MacDowell [200]. The Schultz-Flory representation allows us to determine the critical temperature of a chain of infinite length for the different Mie potentials analysed. For the (9,7) potential the infinite chain would correspond to one having $T_c^* = 5.405,$
for (11,7) $T^*_c = 4.029$, for (14,7) $T^*_c = 3.063$, for (20,7) $T^*_c = 2.084$, for (27,7) $T^*_c = 1.965$ and for (37,7) $T^*_c = 1.883$. From this diagram we note that Mie potentials with longer attractive tails or ‘softer’ Mie systems will have the highest critical point temperature, while the infinitely long chain of Mies systems with an increase in repulsion will have progressively lower critical point temperatures. As the triple point temperatures are seen to remain relatively constant by comparison to the sharp variation of $T_c$ it is reasonable to conclude the the stable fluid range is also most expanded for the (9,7) potential and increasing the range of repulsion results in shrinking of the fluid range.

Figure 5.22: Schultz-Flory diagram comparing the critical temperature of Mie chain systems of varying range of attraction. The closed diamonds correspond to a (9,7) potential, the square correspond to a (11,7) potential, triangles to a (14,7) potential, circles to a (20,7) potential, crosses to a (27,7) potential and the asterisks to a (37,7) potential. The solids lines are guides to the eye.
5.6 Summary

The SAFT-VR Mie solid and SAFT-VR Mie fluid equations of state are used to calculate the phase diagrams of a large range of Mie monomer and chain model systems. SSE boundaries are found by combining the fcc form of SAFT-VR Mie solid and the hcp form of the equation. In the case of a LJ system, good agreement is found in the SFE region when compared to simulation results of Chapter 2 and the theoretical predictions of Mastny and de Pablo [35]. The agreement between the Mastny and de Pablo EOS with simulation data, however, is found to be slightly better than our current theory at higher temperatures. In addition, the hcp-fcc phase transition is calculated and the results are in qualitative agreement with the findings of Jackson and van Swol [15] in which a weakly first order phase transition is noted with the difference in the coexisting densities being approximately $\Delta \rho^* = 0.002$. The fcc phase is also found to be stable at lower densities with respect to the hcp and is identified as the solid phase in coexistence with the fluid.

The phase diagrams of monomer systems interacting via a variety of Mie potentials have also been obtained with theoretical calculations. The solid-fluid and solid-vapour boundaries were calculated using the SAFT-VR Mie solid and fluid theories and the results are in good agreement with the simulation results obtained from the freeze methodology and $N\sigma T$ simulation at zero pressures respectively. Additionally, the predicted triple point is within an 4% deviation from the simulation triple point for all Mie potentials studied. The relationship with the fluid range and the parameter $\alpha$ is also investigated with the theory. Through this analysis we confirm that $\alpha$ is not an exact parameter in defining conformal fluids. It is however useful for determining a close to conformal behaviour of two Mie fluids. The relationship is found to be slightly more complex (non-linear) and therefore differs to the linear relationship proposed using the simulation analysis. In spite of this, the theory also predicts the loss of the stable fluid range (Figure 5.8) which is in agreement with the simulation results.
The SSE transitions are also investigated for varying sizes of the attractive tail of the potential. It is found that this feature will indeed have an effect of the stability of the crystal phases though it is not significant. A decrease in the size of the attractive tail and therefore a decrease in the attractive energy of the potential results in a shift of the SSE phase boundary to lower densities (at higher temperatures) which suggest a stabilisation of the hcp phase with respect to the fcc in this region.

The phase behaviour of flexible LJ chain systems has previously been obtained via simulation analysis (Vega et al. [105] and Chapter 2) and theoretical predictions of TPT1-LJ solid and fluid [38] [105]. The theoretical calculations of the tangentially bonded LJ dimer and flexible tangentially bonded LJ trimer obtained from the SAFT-VR Mie EOS are compared to these former results in which good agreement with simulation data and TPT1-LJ is noted. The theoretical calculations of Vega et al [38] are in slightly better agreement with simulation data in comparison to our presented theory. This can be attributed to the free energy of the monomer being obtained from the van der Hoef EOS which is a fit to simulation data of the LJ monomer solid [36]. Several other Mie dimer and trimer systems of varying range of attraction were calculated with the theory to determine the trends which arise from these chain systems. Overall, an increase in the repulsive nature of the potential results in a most pronounced decrease of the critical point temperature with a less sharp decrease in the triple point temperature. The fluid range is seen to become compressed with a more repulsive potential. The SFE boundaries are seen to become more steep with an increase in repulsion in addition to an increase in the width of the metastable region.

The theory is further tested for chain lengths up to \( m=16 \). The trends of the key features of the phase diagram are similar to the findings of Vega et al [38] [105] and Galindo et al [101] for LJ flexible chains i.e. an increase in chain length results in a pronounced increase in the critical point and a slight decrease in the triple point. There is a general shift of the SFE boundaries to higher densities with increasing chain
length suggesting the increased stability of fluid phase with longer chains. The effect of the chain length of the SSE boundary is also analysed. Increasing chain length results in an increase in the density of the SSE boundary at higher temperatures i.e. an increased stability of the fcc structure. The most marked increase occurs between the monomer and dimer cases. There is a negligible further increase in density of the SSE boundary for a chain length greater than \( m = 4 \). The SSE boundaries for all chain lengths converge at a temperature below \( T^* = 0.64 \).

The SAFT-VR Mie equations of state are implemented to predict the phase boundaries (VLE, SFE, SVE and SSE) of a host of flexible tangentially bonded chain systems of chain length \( m = 2, 4, 8, 16 \) interacting with a Mie potential of varying range of attraction. The trends of the key aspects of the phase diagram have been discussed; features such as the variation of critical point, triple point and the shifting of the phase boundaries with increasing chain length to higher densities are in agreement with the findings of other work on the LJ fully flexible chain system [38] [105] [101]. An increase in repulsive nature of the Mie potential has been found to have subtle effects on the solid-fluid phase boundaries with a more pronounced effect on the vapour-liquid region which is in accordance with simulation results of this work (Chapter 3) and previous reports [46] [47] [45].

The effect of the chain length on the critical point temperature of the VLE region is seen to be reduced with an decrease in the value of \( \alpha \) (i.e., increased repulsive nature of the potential) and therefore makes the increase in critical temperature less drastic with increasing chain length. There is a limiting value to the decrease in the triple point temperature with an increase in chain length. This is noted to occur at shorter chains lengths for more repulsive Mie potentials. The trend of the solid-fluid boundaries to increase in density with increasing temperature becomes less pronounced with an increase in chain length and an increase in the repulsive nature of the potential. Therefore, for the most repulsive potential analysed the phase boundaries for the sys-
tems $m > 1$ are near vertical. The solid-solid boundaries of all chain lengths are noted to converge with an increase in the short range attraction with a general shift in the phase boundaries to lower densities indicating a stabilisation of the hcp phase at lower densities.

The variation of the size of the fluid range ($T_c^*/T_t^*$) with an increase in the degree of repulsion for different chain lengths is also analysed. It is concluded that for longer chain systems the required Mie potential that would result in the VLE region being metastable with respect to the solid phase would be at successively lower values of $\alpha$ for a longer chain system. A Schultz-Flory representation is used to determine the critical point temperature of the infinitely long fully flexible chain interacting through the six different Mie potentials presented in this work. As expected, the highest critical temperature of the infinite chain occurs for the softest potential (9-7) ($T_c^* = 5.405$) and the lowest critical temperature of the infinite chain occurs for the most repulsive potential (37-7) ($T_c^* = 1.883$)
Chapter 6

Conclusions and Future Work

At the start of this document, unwanted solidification of waxes was highlighted as being problematic to the oil and petrochemical industries. Equations of state for the fluid phases are currently heavily used in operation and design in industry. It is therefore logical to assume that a reliable EOS to predict solid-fluid phase transitions would also vastly benefit these industries by avoiding events such as wax precipitation. In recent years, the Mie intermolecular potential has been used in preference to other molecular models as it describes the phase behaviour of real molecular systems more accurately. This seems a logical extension to the traditional intermolecular potential models, as three (or four) parameters can be used to fit properties in the Mie potential, as opposed to only the two parameters available in, for example, the LJ model. The Mie pair potential was chosen in our work for the development of an EOS with a view for its future application to industry. A robust EOS which was developed for chain systems interacting via a Mie potential in the fluid phase has recently been presented [90], however no equivalent EOS existed to treat the solid phase. This thesis therefore, has been dedicated towards addressing this issue.

Presented in this work is a solid EOS for Mie flexible tangentially-bonded chain systems. This EOS can be used in conjunction with the fluid EOS of Lafitte et al.
6. Conclusions and Future Work

[90], to determine the solid-fluid transitions of model molecular systems. Our results at present, are centred on obtaining a theory which is in agreement with simulation data. Further implementation of the theory to describe the solid-fluid phase transitions of the real molecules should be the focus of future work. As such, this work is a first step towards developing a robust EOS for predicting solid-fluid transitions in real systems and its use in the future as a predictive tool in industry.

Combining the predicted solid-fluid equilibrium (SFE) and solid-vapour equilibrium (SVE) boundaries with the vapour-liquid equilibrium (VLE) boundaries (using the SAFT-VR Mie fluid EOS) the global phase behaviour of any Mie system can be obtained. The accuracy of the theoretical predictions has been validated by comparison of simulation results for each region of the phase diagram. In doing so we find that Mie systems will exhibit a close-to-conformal behaviour when reduced with respect to $\epsilon$, $\sigma$ and $\alpha$ (which is explicitly dependent on $\lambda_r$ and $\lambda_a$). It is then possible to suggest a three-parameter corresponding states model for the Mie potential. This result provides a more unified view of the phase behaviour of this family of non-conformal fluids than previously available and more importantly reduces the number of parameters required in parameter fitting of real substances. In addition to this we also find a unique linear relationship between the parameter $\alpha$ and the stable fluid range. For analysis of real substances, fitting of parameters to a potential requires exploration of a large parameter space for the Mie potential. This linear relationship can assist in narrowing down the choice of the Mie exponents required and thereby allow for more robust parameters to be obtained for a given substance provided the experimental fluid range is known.

At present the solid EOS has been compared to simulation data and is found to be in good agreement. Therefore, it is reasonable to conclude that the EOS will accurately describe the phase behaviour of simple real solid systems or spherical coarse-grained models. For more complex systems however more robust approaches need to be implemented into the current theory and this should be a major focus of the future...
work.

6.1 Key Contributions

1. An MD simulation technique to determine the solid-fluid phase boundaries of soft potentials has been developed. Monomer and chain systems have been tested with a variety of exponent pairs for the Mie family of potentials. An unusual phase diagram where the VLE coexistence region is metastable with respect to the solid phases has also been obtained via the simulation method for one of the Mie systems studied.

2. A unified view of the Mie family of potentials is given by proposing a parameter $\alpha$ which can be used in conjunction with parameters $\epsilon$ and $\sigma$ to develop a three-parameters corresponding states model for the Mie potential.

3. A unique relationship between $\alpha$ and the stable fluid range that can be used to predict exponents of the Mie which can be used to appropriately model real systems has been presented.

4. A molecular based EOS (SAFT-VR Mie solid) for the solid phase of fully flexible tangentially bonded chains interacting via Mie potentials has been developed.

5. The global phase behaviour of Mie chain systems of varying range of attraction and evaluation of limiting behaviour of these systems has been studied.

6.2 Direction of Future Work

The flexibility provided by the Mie intermolecular potential makes it a viable option to model a wide variety of substances and for modelling complex systems in a coarse-grained context. The EOS proposed, based on a tangentially-bonded chain model, is solved numerically in the present work. Obtaining an entirely analytical expression for the EOS following a SAFT-VR-like mapping as presented by Gil Villegas et al
would be a useful contribution to this work. This approach has already been implemented in the SAFT-VR Mie fluid EOS [90] and has proven to be more practical for use in engineering applications.

As was shown in Chapter 4, the SFE boundaries although in good agreement with simulation data, are not of the quality of the equations of state which obtain the Helmholtz free energy from fitting to simulation data (TPT1-LJ solid) [38]. This can be attributed to either inaccuracies in the Helmholtz free energy of the monomer or inaccuracies in the radial distribution function needed in the chain contribution of the free energy. With respect to the monomer contribution, the current theory is approximated to the first-order term of perturbation only and to improve upon this the second and third perturbation terms could be added. Additionally, it would be useful to develop the theory from a more rigorous approach as was done by Lafitte et al [90] in which no simplification to the BH theory is made to the $a_1$ term and the integration is taken from between $\sigma$ and $\infty$ rather than $d$ and $\infty$.

Regarding the chain contribution, the deviation of the theory from simulation data at higher temperatures does not appear to increase with increasing chain length. Therefore it can be concluded that the $g(\sigma)$ obtained from a first order WCA perturbation expansion is accurate and the error does indeed lie with the Helmholtz free energy of the monomer contribution. However for completeness, it is worth mentioning that in the fluid EOS (SAFT-VR Mie fluid) [90] $g^{mie}(\sigma)$ was developed by using a BH perturbation theory up to the second order expansion and therefore a second order WCA expansion could also be applied to our EOS.

In nature, molecules such as $n$-alkanes and polymers are not fully flexible; introducing semiflexibility into the current model of chain systems and developing a theory would be important to obtain more accurate thermophysical properties of experimental systems. This last implementation would be highly useful for applying this EOS to model more complex systems such as these. A problem that arises here however,
is that the thermodynamically stable configuration of such a structure will no longer
be an fcc lattice as the segments would be restricted due to torsional and bending
potentials and therefore will not be able to form a close-packed arrangement.

A further avenue to develop is the use of the theory presented to the study of the
solid phase equilibria of mixtures. Potoff and Bernard-Brunel [40], have shown that
the Mie potential can be used to describe accurately the properties of \( n \)-alkane and
perfluoro-alkane systems. It is pertinent however, to acknowledge that at present
the radial distribution function of hard spheres is for an fcc solid system of equal
segment size \( \sigma \). Hence, at present the current EOS can only be extended to mixtures
of equal segment size. The predictions will have to be compared to simulation data
of mixtures and therefore the freeze method will have to be applied to mixtures to
validate the accuracy of the theory. The work of Lamm and Hall [2] would provide
a useful starting point to determine the transition boundaries of these more complex
systems via simulation as in this work, the global phase diagram of binary LJ systems
has been presented.

6.3 Publications

1. A molecular dynamics simulation technique to determine solid-fluid phase equi-
librium; in preparation (2013)

2. Global phase behaviour of the Mie family of intermolecular potentials and its use
in molecular modelling of real substances; in preparation (2013)

3. SAFT-VR Mie Equation of state for the solid phases and solid fluid equilibrium
of flexible tangentially bonded chain systems; in preparation (2013)
6.4 Posters and Presentations

1. Presentation: Global Phase Behaviour of the Mie family of intermolecular potentials and its use in molecular modelling of real substances, Boulder Colorado 2012

2. Poster: Global Phase Behaviour of the Mie family of intermolecular potentials and its use in molecular modelling of real substances, Imperial College London, Chemical Engineering Symposium 2012
Bibliography


6. Conclusions and Future Work


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Appendix A

Simulation results for Chapter 2

Table A.1: VLE ($T^* - \rho^*$) simulation data of the LJ monomer system obtained from the direct method.

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<th>$\rho^*_l$</th>
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<td>0.0023[9]</td>
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<td>0.0625[1]</td>
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Table A.2: SVE ($T^* - \rho^*$) simulation data of the LJ monomer system obtained from the Rahman Parinello constant stress technique.

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<th>$\rho^*_s$</th>
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### Table A.3: $T^\ast - \rho^\ast$ supercritical isobars of LJ monomer system

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<th>$P^\ast$</th>
<th>$T^\ast$</th>
<th>$\rho^\ast$</th>
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Appendix B

Simulation results for Chapter 3

Table B.1: Tabulated values of the global phase behaviour of the (8,6) potential. The type of equilibrium is shown in the last column along with the estimated (*) triple and critical point. The error is given in the square parentheses.

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<th>$T^*$</th>
<th>$\rho^*_l$</th>
<th>$\rho^*_i$</th>
<th>$\rho^*_s$</th>
<th>phases</th>
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<td>$\sim 0$</td>
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<td>$\sim 0$</td>
<td>1.000[7]</td>
<td>SVE</td>
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</tr>
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<td>$\sim 0$</td>
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210
Table B.2: Tabulated values of the global phase behaviour of the (9.85,6) potential. The metastable points are highlighted with parenthesis and the type of equilibrium is shown in the last column along with the estimated (∗) triple and critical point. The error is given in the square parentheses.

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<th>$\rho_g^*$</th>
<th>$\rho_l^*$</th>
<th>$\rho_s^*$</th>
<th>phases</th>
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<td>SVE</td>
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<tr>
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<td>~0</td>
<td>0.999[1]</td>
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<td>SVE</td>
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<td>SVE</td>
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<td>(0.895)</td>
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The error is given in the square parentheses.
## Table B.3: Tabulated values of the global phase behaviour of the (15.58,6) potential.

The metastable points are highlighted with parenthesis and the type of equilibrium is shown in the last column along with the estimated (*) triple and critical point. The error is given in the square parentheses.

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<th>( \rho_g^\ast )</th>
<th>( \rho_l^\ast )</th>
<th>( \rho_s^\ast )</th>
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<td>0.996[9]</td>
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\( \sim \): Approximately equal.
Table B.4: Tabulated values of the global phase behaviour of the (19.02,8.8) potential. The metastable points are highlighted with parenthesis and the type of equilibrium is shown in the last column along with the estimated (*) triple and critical point. The error is given in the square parentheses.

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<th>$\rho_s^*$</th>
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<td>0.450</td>
<td>~0</td>
<td>1.049[8]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>~0</td>
<td>1.037[2]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.522</td>
<td>(0.0114[8])</td>
<td>(0.864[4])</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.545</td>
<td>(0.0158[4])</td>
<td>(0.842[1])</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.550</td>
<td>~0</td>
<td>1.018[7]</td>
<td>SVE</td>
<td></td>
</tr>
<tr>
<td>0.568</td>
<td>(0.0222[3])</td>
<td>(0.819[5])</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.600</td>
<td>0.030</td>
<td>0.779</td>
<td>1.008</td>
<td>triple pt*</td>
</tr>
<tr>
<td>0.613</td>
<td>0.040[6]</td>
<td>0.764[1]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.635</td>
<td>0.055[7]</td>
<td>0.736[7]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.650</td>
<td>0.803[2]</td>
<td>1.004[4]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.658</td>
<td>0.077[3]</td>
<td>0.694[4]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.681</td>
<td>0.102[6]</td>
<td>0.646[7]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.700</td>
<td>0.827[1]</td>
<td>1.001[1]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.704</td>
<td>0.131[9]</td>
<td>0.579[4]</td>
<td>VLE</td>
<td></td>
</tr>
<tr>
<td>0.735</td>
<td>0.359</td>
<td>0.359</td>
<td>critical pt*</td>
<td></td>
</tr>
<tr>
<td>0.800</td>
<td>0.856[6]</td>
<td>1.005[7]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>0.900</td>
<td>0.875[9]</td>
<td>1.010[2]</td>
<td>SFE</td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td>0.886[6]</td>
<td>1.017[1]</td>
<td>SFE</td>
<td></td>
</tr>
</tbody>
</table>
Table B.5: Tabulated values of the global phase behaviour of the (42.5, 8.8) potential. The metastable points are highlighted with parenthesis and the type of equilibrium is shown in the last column along with the estimated (*) triple and critical point. The error is given in the square parentheses.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho_u^*$</th>
<th>$\rho_l^*$</th>
<th>$\rho_s^*$</th>
<th>phases</th>
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<tbody>
<tr>
<td>0.450</td>
<td>~0</td>
<td>0.944[8]</td>
<td></td>
<td>SVE</td>
</tr>
<tr>
<td>0.500</td>
<td>~0</td>
<td></td>
<td>0.931[6]</td>
<td>SVE</td>
</tr>
<tr>
<td>0.500</td>
<td>(0.043[2])</td>
<td>(0.830[1])</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.510</td>
<td>(0.052)</td>
<td>(0.821)</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.520</td>
<td>(0.062)</td>
<td>(0.791)</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.530</td>
<td>(0.076)</td>
<td>(0.774)</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.540</td>
<td>(0.092)</td>
<td>(0.741)</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.545</td>
<td>(0.0158)</td>
<td>(0.842)</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.550</td>
<td>(0.113)</td>
<td>(0.708)</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.550</td>
<td>~0</td>
<td></td>
<td>0.921[5]</td>
<td>SVE</td>
</tr>
<tr>
<td>0.560</td>
<td>(0.140)</td>
<td>(0.675)</td>
<td></td>
<td>VLE</td>
</tr>
<tr>
<td>0.563</td>
<td>(0.589[3])</td>
<td>(0.920[1])</td>
<td></td>
<td>SFE</td>
</tr>
<tr>
<td>0.572</td>
<td>0.190</td>
<td>0.602</td>
<td>0.919</td>
<td>triple pt*</td>
</tr>
<tr>
<td>0.585</td>
<td>0.393</td>
<td>0.393</td>
<td></td>
<td>critical pt*</td>
</tr>
<tr>
<td>0.600</td>
<td></td>
<td>0.649[7]</td>
<td>0.917[7]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.625</td>
<td></td>
<td>0.666[6]</td>
<td>0.915[4]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.650</td>
<td></td>
<td>0.687[7]</td>
<td>0.912[5]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.700</td>
<td></td>
<td>0.703[3]</td>
<td>0.906[6]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.750</td>
<td></td>
<td>0.716[5]</td>
<td>0.908[4]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.850</td>
<td></td>
<td>0.732[1]</td>
<td>0.909[4]</td>
<td>SFE</td>
</tr>
<tr>
<td>0.950</td>
<td></td>
<td>0.745[9]</td>
<td>0.906[1]</td>
<td>SFE</td>
</tr>
</tbody>
</table>
Appendix C

Comparison of $\eta$ determined in this work to Kang et al.

Table C.1: Table showing the parameter $\lambda$ which corresponds to $\rho^* = \rho \sigma^3$ and $T^*$, the BH diameter as determined by equation 4.19, the effective hard sphere diameter as determined from equations 4.15 to 4.17, the corresponding packing fraction $\eta$, ($\eta = \frac{\rho \pi d^3}{6}$) and the value of $\eta$ as determined by the work of Kang et al for the LJ monomer system [13].

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho \sigma^3$</th>
<th>$\lambda$</th>
<th>$d_{BH}$</th>
<th>$d$</th>
<th>$\eta$</th>
<th>$\eta$ (Kang et al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>1.0</td>
<td>1.1225</td>
<td>1.0258</td>
<td>1.0267</td>
<td>0.567</td>
<td>0.567</td>
</tr>
<tr>
<td></td>
<td>1.025</td>
<td>1.1133</td>
<td>1.0219</td>
<td>1.0230</td>
<td>0.575</td>
<td>0.575</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.0874</td>
<td>1.0097</td>
<td>1.0119</td>
<td>0.596</td>
<td>0.596</td>
</tr>
<tr>
<td>1.15</td>
<td>1.05</td>
<td>1.1044</td>
<td>1.0035</td>
<td>1.0040</td>
<td>0.557</td>
<td>0.557</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.0874</td>
<td>0.9908</td>
<td>0.9916</td>
<td>0.562</td>
<td>0.562</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.0563</td>
<td>0.9763</td>
<td>0.9776</td>
<td>0.587</td>
<td>0.587</td>
</tr>
<tr>
<td>1.35</td>
<td>1.2</td>
<td>1.0563</td>
<td>0.9528</td>
<td>0.9531</td>
<td>0.544</td>
<td>0.544</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>1.0285</td>
<td>0.9405</td>
<td>0.9413</td>
<td>0.568</td>
<td>0.568</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>1.0034</td>
<td>0.9279</td>
<td>0.9292</td>
<td>0.588</td>
<td>0.588</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>0.9597</td>
<td>0.9029</td>
<td>0.9051</td>
<td>0.621</td>
<td>0.620</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>0.9227</td>
<td>0.8787</td>
<td>0.8818</td>
<td>0.646</td>
<td>0.644</td>
</tr>
</tbody>
</table>
Appendix D

Correlations of the relationship between the fluid range and $\alpha$.

The correlation showing the relationship between the fluid range and $\alpha$ for the $(\lambda_r, 6)$ monomer systems over a range, $\alpha=0.503$-1.26 is given by:

$$\frac{T_c}{T_t} = -1.7961\alpha^3 + 4.1562\alpha^2 - 1.2962\alpha + 1.0611. \quad (D.1)$$

The correlation showing the relationship between the fluid range and $\alpha$ for the $(\lambda_r, 7)$ monomer systems over a range, $\alpha=0.366$-1.01 is given by:

$$\frac{T_c}{T_t} = -2.8581\alpha^3 + 6.127\alpha^2 - 2.2274\alpha + 1.2269. \quad (D.2)$$

The correlation showing the relationship between the fluid range and $\alpha$ for the $(\lambda_r, 8)$ monomer systems over a range, $\alpha=0.27$-0.77 is given by:

$$\frac{T_c}{T_t} = 0.7083\alpha^3 - 0.2225\alpha^2 + 1.4227\alpha + 0.602. \quad (D.3)$$

The correlations obtained from the relationship between the fluid range and $\alpha$ as determined by the theoretical predictions of this work are presented below. The correlation is valid over a range of attraction of $\alpha=0.4$-0.9. Each correlation corresponds
to a Mie system of varying chain length; the monomer, m=1, m=2, m=4, m=8 and finally the m=16 chain system.

\[
\frac{T_c}{T_l} = 7.369\alpha^4 - 24.431\alpha^3 + 30.008\alpha^2 - 13.712\alpha + 3.2303 \quad (D.4)
\]

\[
\frac{T_c}{T_l} = -5.6137\alpha^4 - 2.301\alpha^3 + 21.533\alpha^2 - 14.472\alpha + 4.2032 \quad (D.5)
\]

\[
\frac{T_c}{T_l} = -71.467\alpha^4 + 168.09\alpha^3 - 138.1\alpha^2 + 51.028\alpha - 5.3194 \quad (D.6)
\]

\[
\frac{T_c}{T_l} = -68.916\alpha^4 + 176.5\alpha^3 - 159.65\alpha^2 + 66.577\alpha - 8.4294 \quad (D.7)
\]

\[
\frac{T_c}{T_l} = 26.939\alpha^3 - 36.876\alpha^2 + 22.821\alpha - 2.4779 \quad (D.8)
\]