SINGLE CHAIN STATISTICS OF A POLYMER IN A CRYSTALLIZABLE
SOLVENT

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SINGLE CHAIN STATISTICS OF A POLYMER IN A CRYSTALLIZABLE SOLVENT

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Dissertation

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ABSTRACT

The main goal of this dissertation is to develop a simulation methodology to investigate the thermodynamic and structural behavior of a polymer in a crystallizable solvent. In addition to the polymer chain in a crystallizable solvent, two other models are analyzed, including the monodispersed and polydispersed solvent configurations.

The study of the monodispersed solvent is motivated by a recent publication that employed a hybrid technique utilizing both Molecular Dynamics (MD) and Wang-Landau (W-L) Monte Carlo (MC) in order to determine the solid-liquid equilibrium of Lennard-Jones (LJ) spheres. In this work, the hybrid method is modified by replacing the W-L MC method with a new MC scheme. It is found that there is a first order phase transition due to a discontinuity in both the entropy and volume as a function of temperature and pressure. Moreover, based on the simulation results, the crystalline state of the solvent displayed a face-centered cubic (FCC) symmetry.

This model is then extended by introducing varying degrees of polydispersity into the solvent. The first order phase transition observed in the monodispersed solvent disappears due to the imperfect packing in these systems, causing the formation of an amorphous solid state. Specifically, as the width of the atom sphere size distribution is increased, there is a significant reduction in the crystalline order.
Next, the monodispersed solvent model is modified by placing a polymer chain in the solvent. In order to sample different chain conformations in the crystalline solvent, a new reptation move for the polymer chain is developed. The introduction of this chain did not disrupt the crystalline order in the system, thus enabling a first order phase transition to be observed. However, compared to the monodispersed spheres model, this transition disappears at high pressures due to the different responses of the various inter-atomic potentials to compression. The FCC symmetry of this system is enhanced due to the co-crystallization of the polymer with the solvent. There is more crystalline order in this model compared to the monodispersed solvent because the atom distance ranges have been restricted by the chain bonding potential.
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CHAPTER I
INTRODUCTION

1.1 An overview of previous experimental studies

The competition of liquid-liquid phase separation and crystallization or glass transition in polymer solutions and blends is not fully understood and remains a challenge to the polymer physics community. In this dissertation, we study the coupling of these transitions. The following sections in this overview explain in greater detail through the use of examples, in polymer solutions and blends, the competition between liquid-liquid phase separation (LLPS) and crystallization, the competition between LLPS and glass transition as well as systems comprised of polymers immersed in crystallizable solvents.

1.1.1 Liquid-liquid phase separation coupled with crystallization in polymer solutions and blends

According to Cheng [1], when a polymer solution undergoes liquid-liquid phase separation, two phases are created as the composition crosses the binodal line of the phase envelope, creating a polymer-rich as well as a solvent-rich phase. In polymer
blends, the solvent-rich phase is replaced by another polymer-rich phase. However, in these systems, if one of the components can crystallize, this phase separation may also intersect with the melting curve, causing a complex interplay between liquid-liquid phase separation and crystallization.

In polymer solutions, Cheng suggests that the first discovery of these competing phase transformations occurred because many researchers found strange crystal morphologies derived from solution crystallization of polymers [1]. For example, Garber and Geil [2] as well as Hay and Keller [3] both reported the appearance of small spherical globules of polyethylene. Furthermore, other interesting crystal morphologies such as elongated globules possessing cigar shapes have been obtained in binary mixtures of polyamides in benzoic acid [4]. In addition, bowl or cup shaped crystals have also been observed in mixtures of poly (4-methyl-1-pentene) [5], polyoxymethylene [6] and polychlorotrifluoroethylene [7] in different solvents as well as in trans-1,4-polyisoprene in amyl acetate [8-9]. It was ultimately deduced, according to Cheng, that the formation of these abnormal morphologies were due to the competition between liquid-liquid phase separation of the polymer from the solvent and the crystallization of the polymer from solution [1]. Schaaf and collaborators performed a detailed study of this competition, illustrating their results in Figure 1.1 for a binary mixture of a monodisperse polymer in a poor solvent as well as in a good solvent [10]. In Figure 1.1, Region I corresponds to the high temperature state where the polymer is miscible in the solvent, causing a single liquid phase to be formed. In Region II, liquid-liquid phase separation occurs once the system crosses the binodal curve in this upper critical solution temperature phase
diagram. Region III represents the state below the melting curves for both the poor solvent (M-N) as well as the good solvent (U-V). From this diagram, it is clear that at high polymer concentrations, the system crystallizes from the liquid state without undergoing phase separation. However, by decreasing the polymer concentration, this melting curve is continuously depressed and ultimately intersects the binodal curve for the polymer in a poor solvent [1].

![Equilibrium phase diagram for a binary mixture of a monodisperse polymer with a poor solvent (M-N) and a good solvent (U-V)](http://www.sciencedirect.com/science/journal/00323861. Image redrawn.)

Based on Figure 1.1 above, once the melting curve crosses the binodal, the equilibrium melting temperature within this phase separation region becomes constant.
According to Cheng, this invariant temperature phenomenon is due to the intervention of liquid-liquid phase separation that leads to the formation of the polymer-rich as well as solvent-rich states [1]. Thus, when the concentration of the polymer in the solution is low, the polymer-rich state is the minority phase within the solvent-rich majority phase, possessing a fixed composition at N after the liquid-liquid phase separation [10]. As the solvent in a binary mixture becomes increasingly compatible with the polymer, the binodal curve will be suppressed to lower temperatures. On the other hand, Cheng elucidates that if the liquid-liquid phase separation curve is only slightly lower than the melting curve, phase separation is still possible through rapid quenching if crystallization does not occur rapidly [1]. This condition is illustrated in Figure 1.2 below [1, 11].

Figure 1.2: Phase diagram for a fully miscible polymer solution possessing a liquid-liquid phase separation curve below the crystal melting curve (BP is Berghmans’ point) (Reprinted from Ref. [11] “The role of metastability in polymer phase transitions”. Copyright 1998, with permission from Elsevier Limited). http://www.sciencedirect.com/science/journal/00323861
In Figure 1.2, the upper line corresponds to the melting curve while the lower curve depicts the binodal line with an upper critical solution temperature. Berghmans’ point is defined as the intersection point of the glass transition line with the binodal curve of the phase envelope. Based on Figure 1.2, it is clear that for a low level of undercooling, represented by $\Delta T_1$, a single phase liquid undergoes crystallization without any phase separation. Thus, when the blend is quenched into a region outside of the binodal and spinodal curves, crystallization occurs from the homogeneous single phase. However, at a larger degree of undercooling $\Delta T_2$, the system phase separates, creating either a droplet-rich phase morphology if a nucleation and growth type mechanism happens in the metastable region or an interconnected, bicontinuous morphology if the system is in the unstable, spinodal decomposition region of the phase diagram, as explained by Cheng [1]. This phenomenon of sequential liquid-liquid separation and crystallization has been observed experimentally by Berghmans and collaborators in binary mixtures of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) in cyclohexanol. These results are shown in Figures 1.3 and 1.4 [1, 12] where the melting curve lies above the binodal curve represented by the cloud points.
Figure 1.3: Temperature-concentration phase diagram for PPE1 (molecular weight $= 30 \times 10^3$ g/mol) in cyclohexanol (Reprinted from Ref. [12] “Phase behavior and structure behavior in solutions of poly(2,6 dimethyl-1,4-phenylene ether”. Copyright 1995, with permission from Elsevier Limited).

http://www.sciencedirect.com/science/journal/00323861
Figure 1.4: Temperature-concentration phase diagram for PPE2 (molecular weight= $350 \times 10^3$ g/mol) in cyclohexanol (Reprinted from Ref. [12] “Phase behavior and structure behavior in solutions of poly(2,6 dimethyl-1,4-phenylene ether”. Copyright 1995, with permission from Elsevier Limited).

http://www.sciencedirect.com/science/journal/00323861
Another system investigated experimentally is the more complicated mixture of syndiotactic polystyrene in a cyclohexanol solvent. This complication arises from the fact that this polymer forms different crystal forms or polymorphs when crystallized from solution [1]. The phase diagram for this system is shown in Figure 1.5 [1, 13].

![Phase diagram for syndiotactic polystyrene in cyclohexanol](http://www.sciencedirect.com/science/journal/00323861)

Figure 1.5: Phase diagram for syndiotactic polystyrene in cyclohexanol (Reprinted from Ref. [13] “Phase behavior and structure formation in the system syndiotactic polystyrene/cyclohexanol”. Copyright 1999, with permission from Elsevier Limited).

In Figure 1.5 above, the liquid-liquid phase separation binodal curve is below the crystal melting curve. According to Cheng, if the system undergoes a large degree of
undercooling into the unstable region below the glass transition, only amorphous aggregates are obtained. However, he further states that if the mixture is cooled slightly, the single phase state forms crystals with the \( \beta \) phase. Further cooling leads the system to the \( \gamma-\beta \) transition line, causing recrystallization of the system into the \( \gamma \) phase [1, 13].

If the solvent in a polymer-solvent mixture is now replaced by another polymer, we can observe this competition between liquid-liquid phase separation and crystallization in polymer blends where one component is crystallizable. Tanaka and Nishi first studied this phenomenon in polymer blends by analyzing systems of poly(\( \varepsilon \)-caprolactone) (PCL) and polystyrene (PS), where PCL is the crystallizable component while PS remains amorphous. In Figure 1.6 below, six different phase diagrams are considered for various types of crystalline-amorphous polymer blends [1, 14].

![Figure 1.6: Phase diagrams for various crystalline-amorphous polymer blends. \( \phi \) is the concentration of one component in the mixture, T is the temperature (Reprinted Figure 1 with permission from Ref. [14]. Copyright 1989 by the American Physical Society).](http://prola.aps.org/abstract/PRA/v39/i2/p783_1)
In all these cases, the binodal as well as melting curves are represented by the solid lines while the spinodal curves are drawn as dotted lines. These diagrams are presented based on the relative position of the melting curve with respect to the binodal and spinodal lines of the phase diagram. In cases (a), (b) and (c), a system with an upper critical solution temperature is presented while a lower critical solution temperature system is shown in cases (d), (e) and (f). Moreover, in cases (a) and (d), the melting curve intersects with the phase diagram, in cases (b) and (e), the melting curve lies tangent to the phase diagram while in cases (c) and (f), the melting curve does not intersect with the phase diagram but instead lies either above, as in case (c), or below, as in case (f) [14]. Tanaka and Nishi also considered four different cases of undercooling, A, B, C and D as illustrated in Figure 1.7 [15].

![Figure 1.7: Phase diagram for a polymer blend of PCL and PS. φ is the concentration of PS in the mixture, T is the temperature (Reprinted Figure 1 with permission from Ref. [15]. Copyright 1985 by the American Physical Society).](http://prola.aps.org/abstract/PRL/v55/i10/p1102_1)
In Figure 1.7 above, the melting-point curve cannot be defined thermodynamically in the two-phase region while the binodal line cannot be defined below the melting curve. Moreover, in this blend, the melting point is dependent on the fraction of amorphous polymer present. Therefore, if the amount of PS increases in the system, a melting point depression occurs because the interaction parameter between these compatible polymers becomes negative [15]. In cases A & B, the crystallization and phase separation processes take place simultaneously. In case A, the system is quenched below the melting curve into the unstable region of the phase diagram, causing spinodal decomposition type phase separation to occur. This leads to the creation of a periodically modulated structure that appears in the initial stage of phase separation with no induction time. In contrast, case B involves the quenching of the system below the melting curve into the metastable region of the phase diagram, leading to nucleation and growth type phase separation and the creation of a droplet-like structure that possesses an induction time. On the other hand, in case C, crystallization can actually induce phase separation because the amorphous polymer (PS) is removed by crystallization. The amorphous polymer acts as an impurity for crystallization of the crystalline polymer. The non-crystalline polymer is rejected from the crystalline lamellae and trapped in the interlamellar region. Thus, the concentration of PS in the interlamellar region becomes larger until it exceeds the binodal line, causing nucleation and growth type phase separation to occur at the growth front, forming droplets of a PS-rich phase. In addition, in case D, phase separation at a temperature above the melting curve can create a crystalline polymer-rich region. Thus, crystallization takes place in this region because
the liquid-liquid separation produces a region where the content of the crystalline polymer is high enough for primary nucleation of the crystal. Nevertheless, crystallization becomes more difficult as the content of the crystalline polymer becomes lower [15]. Nojima and co-workers also investigated this polymer blend in order to better understand the competition between liquid-liquid phase separation and crystallization, but utilized PCL with a narrower molecular weight distribution as well as a polystyrene oligomer [16]. Other studies of polymer blends with competing phase transitions have also been conducted by various researchers. Crist and Hill have analyzed the experimental and theoretical aspects of liquid state miscibility for blends of saturated hydrocarbon polymers [17]. Inaba and collaborators have also investigated the interplay of liquid-liquid phase separation (LLPS) and crystallization in blends of polypropylene (PP) and ethylene-propylene rubber (EPR), where PP is the crystallizable component. This study involves demixing the system above the melting temperature as well as subsequent crystallization from this phase-separated blend. This is illustrated in Figure 1.8 [18].
In Figure 1.8, the system, initially at point Q, is heated to a temperature $T_s$ and allowed to demix through spinodal decomposition for a period of time. Subsequently, the system is rapidly quenched to point C below the melting curve. If the crystallization occurs rapidly, the “structure memory” of the liquid-liquid phase separation, which involves a modulated, bicontinuous and periodic structure, is maintained in the spherulites formed. In this mixture, crystallization occurs through the PP-rich domains without rejection of the EPR component to the interlamellar region because this crystallization process is faster than the rate of EPR diffusion to the crystal front. But the structure formed during phase separation is not maintained in the spherulites if the crystallization rate becomes...
lower [18]. Moreover, another widely investigated blend has been a mixture of two statistical block copolymers, poly(ethylene-co-butene) (PEB) and poly(ethylene-co-hexene) (PEH), where PEH is the crystallizable component [19-21]. This interplay between liquid-liquid phase separation and crystallization is illustrated in Figure 1.9 below [21].

Figure 1.9: Schematic of (a) phase diagram for PEH/PEB blends, (b) liquid-liquid phase separation-assisted nucleation, (c) concentration fluctuation of the PEH/PEB mixture in the intermediate stage and (d) concentration fluctuation of the PEH/PEB blend in the late stage (Reprinted from Ref. [21] “Fluctuation-Assisted Crystallization: In a Simultaneous Phase Separation and Crystallization Polyolefin Blend System”. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).
In Figure 1.9 above, the phase diagram for the polymer blend is presented in part (a), together with a schematic illustrating a crystallization mechanism termed “fluctuation assisted crystallization” in part (b). In this mechanism, the concentration fluctuation growth caused by spinodal decomposition during liquid-liquid separation is spontaneous, thus it does not need to overcome any energy barrier, unlike homogeneous crystallization. This process involves inter-diffusion of PEH chains toward PEH-rich domains and PEB chains toward PEB-rich domains. The moving PEH or PEB chains induce certain chain segmental alignment and orientation, becoming precursors of nuclei for crystallization. The corresponding morphology for crystallization and phase separation in this case are volume-filling spherulites and bicontinuous and interconnected tubes, respectively. This phase separation assisted crystallization occurs at the domain interfaces. However, as the system spends more time in the liquid-liquid separation region of the phase diagram, the crystallization rate as well as the number and size of spherulites formed would decrease due to the smaller interphase volume between domains, as evidenced by parts (c) and (d) in Figure 1.9 above [20]. In addition, another blend that exhibits this competition between phase transitions with an upper critical solution temperature is the mixture of isotactic polypropylene (iPP) and hydrogenated (polystyrene-co-butadiene) (hSBR) that has been studied by Otsuka and co-workers [22].

In addition to the mixtures mentioned previously that exhibit upper critical solution temperature behavior, there are also blends that possess lower critical solution temperature properties where phase separation occurs at high temperatures while the polymer mixture remains fully miscible at low temperatures. For example,
poly(vinylidene fluoride) (PVDF) / poly(ethyl acrylate) (PEA) blends exhibit this phenomenon, with the phase diagram intersecting the melting curve as illustrated in Figure 1.10 below [1, 23].

Figure 1.10: Phase diagram for the PVDF/PEA mixture possessing a lower critical solution temperature. (●) binodal curve, (○) spinodal curve and (■) melting line (Springer and the original publisher Ref. [23] “Studies on phase separation and coarsening in blends of poly(vinylidene-fluoride) and poly(ethyl-acrylate)”, original copyright notice is given to the publication in which the material was originally published, by adding; with kind permission from Springer Science and Business Media).
Moreover, the poly(ε-caprolactone) (PCL) / polycarbonate (PC) [24-25] system also exhibits a lower critical solution temperature behavior, as shown in Figure 1.11 below [1, 24].

![Figure 1.11: Phase diagram of the PCL/PC system showing a lower critical solution temperature (Reprinted with permission from Ref. [24]. Copyright 1994 American Chemical Society).](image)

From Figure 1.11 above, it can be observed that each component of the blend has a separate melting curve but only a single glass transition line. Furthermore, binary blends of poly(vinylidene fluoride) (PVDF) and poly(1,4-butylene adipate) (PBA) [26-
Also exhibit lower critical solution temperature behavior. The phase behavior for this mixture is illustrated in Figure 1.12 below [1, 26]. Similar to the previous blend, there are two melting curves in this system, one for each component.

Figure 1.12: Temperature-concentration phase diagram of PVDF/PBA mixtures. A binodal line, B melting curve of PVDF, C melting curve of PBA and D glass transition of the mixture (Reprinted with permission from Ref. [26]. Copyright 1996 American Chemical Society).
There are also polymer blends that exhibit both upper as well as lower critical solution temperature behavior. Svoboda and collaborators have studied this phenomenon in blends of poly(ε-caprolactone) (PCL) and poly(styrene-ran-acrylonitrile) (SAN). For this PCL/SAN binary blend, both phase envelopes create a closed miscibility area in the temperature-composition plane. In addition, this unique phase separation behavior was also intersected by the melting curve [29]. This phenomenon was also seen in poly(vinylidene fluoride) (PVDF) / poly(methyl methacrylate) (PMMA) blends [30-31], as shown in Figure 1.13 [1, 30].

Figure 1.13: Phase diagram illustrating both upper critical and lower critical solution temperature behavior in blends of PVDF/PMMA (Reprinted from Ref. [30] “Upper Critical Solution Temperature Behavior in Poly(vinylidene fluoride)/Poly(methyl methacrylate) Blends”. Copyright The Society of Polymer Science, Japan. Reproduced with permission)
Based on Figure 1.13, PVDF could crystallize in the one-phase region below the melting curve or in the two-phase region below the upper critical solution temperature curve. However, Cheng explains that Bernstein and collaborators, unlike Saito and co-workers, only found a lower critical solution temperature around 350 °C and did not notice the existence of upper critical solution temperature behavior at low temperatures [1, 31].

These experimental studies of polymer blends show the need for more work in order to develop a solid understanding of the competition between liquid-liquid phase separation and crystallization. The next section discusses the interplay between liquid-liquid phase separation and glass transition, another complex phenomenon present in polymer solutions and blends.

1.1.2 Liquid-liquid phase separation coupled with glass transition in polymer solutions and blends

In addition to the interplay between liquid-liquid phase separation and crystallization, the competition between glass transition or vitrification and liquid-liquid separation has also been analyzed in polymer solutions and blends. In these cases, the formation of the glass interrupts the phase separation and vitrifies the polymer in its non-equilibrium state [1].

For polymer solutions, the glass transition curve was already included with the melting curve in Figs. 1.2, 1.3, 1.4. and 1.5. Cheng explains that for such systems, when
both the segmental volume occupancy as well as the interaction between the solvent and polymer are equal to the solvent-solvent and polymer-polymer interactions, the glass transition temperature varies linearly with polymer concentration. However, he further adds that as the polymer-solvent interactions increasingly differ from the interactions between similar species, this glass transition temperature would either exhibit a concave or convex shape with respect to polymer concentration [1]. The influence of vitrification on liquid-liquid phase separation in polymer solutions is illustrated in Figure 1.14 below [1, 11].

Figure 1.14: Phase diagram illustrating liquid-liquid phase separation coupled with glass transition (Reprinted from Ref. [12] “Phase behavior and structure behavior in solutions of poly(2,6 dimethyl-1,4-phenylene ether”. Copyright 1995, with permission from Elsevier Limited). http://www.sciencedirect.com/science/journal/00323861
In Figure 1.14 above, as the temperature is decreased, a two-phase liquid, is formed as the system enters the liquid-liquid phase separation region. As the temperature tie line meets the Berghmans point, Cheng elucidates that the polymer-rich phase becomes vitrified. In addition, he also clarifies that as the glass transition temperature intersects the phase diagram, the $T_g$ of the polymer-rich phase becomes constant and invariant with concentration [1]. This is shown in the binary mixture of amorphous polystyrene and cyclohexanol. The phase diagram for this solution, together with the glass transition temperature curve, is shown in Figure 1.15 below [1, 32].

![Figure 1.15: Phase diagram for atactic polystyrene in cyclohexanol. (●) binodal curve, (○) experimental glass transition temperature, (----) theoretical extrapolation of the glass transition curve beyond the phase diagram. (Reprinted from Ref. [32] “Thermoreversible gelation of atactic polystyrene: Phase transformation and morphology”. Copyright 1988, with permission from Elsevier Limited).](http://www.sciencedirect.com/science/journal/00323861)
Therefore, in Figure 1.15, it is clear that as soon as the Berghmans point is reached, the experimental glass transition temperature becomes constant with respect to concentration. Moreover, Figure 1.16 below also shows that the glass transition temperature becomes invariant with concentration once it intersects the phase boundary [33].

Figure 1.16: (a) Phase diagram for a model polymer-solvent system with the glass transition temperature curve. (b) The corresponding morphology development in the binodal region. (c) The corresponding morphology development in the spinodal region (Springer and the original publisher Ref. [33] “Microphase separated semi-interpenetrating polymer networks from atactic polystyrene and methacrylates – a novel route”, original copyright notice is given to the publication in which the material was originally published, by adding: with kind permission from Springer Science and Business Media). Image redrawn.

Figure 1.16 also depicts the morphological development of the polymer-solvent mixture. If the polymer-rich phase is the minority phase, solid droplets would form in a liquid matrix. On the other hand, if the polymer-rich state is the majority phase, a system
possessing liquid droplets in a solid matrix would be created, as described by Cheng [1]. However, at intermediate concentrations where neither is the majority phase, both the liquid phase and vitrified solid state would form interconnected, bicontinuous phases [1, 33]. But if the polymer-solvent system is quenched rapidly below the Berghmans point, Cheng suggests that thermodynamic phase separation can no longer be achieved. This is because the system would separate but fail to reach the final equilibrium concentration state, with the polymer-rich phase solidifying before reaching the binodal curve. However, above this glass transition temperature region, there is no effect on liquid-liquid phase separation and even below this curve, phase separation still occurs in constrained local areas within this vitrified state [1].

For polymer blends, the glass transition line was included with the melting curve in Figs 1.11 and 1.12 above. The competition between phase separation and glass transition, similar to the interplay between crystallization and phase separation discussed previously, necessitates further experimental as well as theoretical work in order to fully comprehend this complicated phenomenon. The next section discusses a phenomenon that is garnering experimental interest and is the primary motivation for this research, a system where the polymer resides in a crystallizable solvent.

1.1.3 Polymer in solution with a crystallizable solvent

An emerging field of experimental investigation is currently focusing on cases where a polymer resides in a solvent that crystallizes. The systems analyzed include
poly(vinyl methyl ether) (PVME) in deuterium oxide (D$_2$O) [34-36], PVME in water [37-41] and poly(vinylpyrrolidone) (PVP) in water [42]. These binary mixtures possess very intriguing phase behavior. The phase diagram for the PVME/D$_2$O system is presented in Figure 1.17 below [1, 34].

According to Cheng, in this PVME/D$_2$O mixture, the system exhibits bimodal lower critical solution temperature behavior. In addition, at lower temperatures, an upper
critical solution temperature is obtained with a narrow distribution, encompassing the PVME weight fraction from approximately 0.7 to 1.0 [1]. The melting curve for the solvent is also present in the system and exists below the bimodal lower critical solution temperature but above the unimodal upper critical solution temperature. Furthermore, the glass transition curve intersects the upper critical solution temperature at the Berghmans point, decreasing with higher D$_2$O content in the system. Cheng postulates that there should be two glass transition temperatures within this narrow region from 0.7 to 1.0 in Figure 1.17 above, but explains that since this region is narrow, both of these temperatures are sufficiently close to cause overlap. Thus, there is only one glass transition obtained for the system. Moreover, he suggests that this apparent decrease of the glass transition temperature, instead of being invariant with polymer concentration, may be due to the different composition partitions in the two phases obtained from liquid-liquid phase separation [1].

It is these intriguing polymer systems that we seek to understand further through computer simulation techniques. A review of the simulation methods utilized in this work is presented in the following section.

1.2 An overview of computer simulation methods [43]

Computer simulations continue to play an integral role in the exploration and pursuit of science. In the past, science was defined by a complex interplay between theory and experiment. But in the early days of theoretical models, only system behavior
in a few selected cases and circumstances were simple enough to be calculated, albeit with a multitude of approximations.

This scenario was forever changed with the introduction of high speed computing in the 1950s by inserting a bridge between experiment and theory, called computer simulations. Using this technique, calculations were performed by the computer based on an algorithm written in a programming language. Thus, by using more and more powerful machines, a greater deal of complexity could be introduced while paving the way for a better understanding of experiments through the investigation of more realistic systems. Therefore, computer simulations provided the motivation for more theoretical models to be developed as well as the ability to verify results from experiments. When these simulation models are shown to be sufficiently accurate, they possess the capability of analyzing regions of systems that are not accessible experimentally, either due to cost or physical constraints. Moreover, another benefit of computer simulations is the ability to perform ‘thought experiments’, which are investigations that are impossible to perform realistically but would lead to a richer and deeper understanding of the phenomenon being analyzed.

The two broad classes of simulation techniques utilized in this work are Molecular Dynamics as well as Monte Carlo methods. Each will be discussed in more detail in the following sections.
1.2.1 An overview of Molecular Dynamics simulations [44]

Molecular Dynamics (MD) is a computer simulation technique involving the integration of the equations of motion in order to track the time evolution of a set of interacting atoms in the system. In MD, Newton’s Law is utilized, as shown below.

\[ F_i = m_i a_i \]  

(1.1)

where \( F_i \) is the force acting on each atom \( i \), \( m_i \) is the mass of each atom \( i \) and \( a_i \) is the acceleration for each atom \( i \). MD is a deterministic technique, which means that atom positions at every timestep can be determined because the rate and direction of motion are controlled by the forces atoms exert on one another. Under specific conditions, these atoms would behave in ways that are very similar to particles in real, physical materials. Therefore, a trajectory or series of structural change ‘snapshots’ over time can be obtained. Consequently, from MD, physical quantities such as thermodynamic variables can be represented by averages over configurations distributed based on a particular ensemble.

The design of the system being studied in MD (including number of particles, timestep and duration) should be appropriate in order for the simulation to finish in a reasonable period of time. However, the duration of the simulation should be adequate for the technique to properly probe the phenomenon of interest.
In this work, we utilize the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) MD software package, developed by Sandia National Laboratories. This MD package was used to create the initial configurations for all the systems studied subsequently with Monte Carlo (MC) techniques. A detailed discussion of MC methods is presented in the following sections.

1.2.2 An overview of Monte Carlo simulations

The Monte Carlo (MC) simulation method is named after the famous city and gambling haven in Monaco because, similar to gambling, probabilities are also utilized in this method. It was first developed in Los Alamos National Laboratory to solve the problem of neutron diffusion in fissionable material. The technique involves the generation of random moves in order to explore a certain search space. Every MC technique begins with a source of uniformly distributed random numbers. In the first MC method, once a random move was performed, the new configuration was accepted if it resulted in an energy decrease. However, if the system energy increased, the new configuration was only accepted if it survived a criteria biased by the Boltzmann factor. If rejection occurred, the old configuration of the system was restored. This traditional MC technique became known as the Metropolis method in 1953. It incorporated the system temperature into the acceptance criteria in order to calculate the Boltzmann average of a particular system property [45]. This method, being the foundation for all subsequent MC methods, will be discussed below.
1.2.2.1 An overview of the Metropolis method

At a particular instant during the simulation, the current state, state 0, has an energy value, $\varepsilon_0$. After a random move is performed, the system moves into state 1, with energy $\varepsilon_1$. The energies of both states are now compared by utilizing a random number generator between 0 and 1, leading to a value of $R$. If $\varepsilon_1 < \varepsilon_0$, the new state is accepted and becomes the new state 0 for the next move in the system. Nevertheless, if $\varepsilon_1 > \varepsilon_0$, there are two possible outcomes:

$$\exp\left(\frac{-(\varepsilon_1 - \varepsilon_0)}{kT}\right) > R$$ \hspace{1cm} (1.2)

$$\exp\left(\frac{-(\varepsilon_1 - \varepsilon_0)}{kT}\right) < R$$ \hspace{1cm} (1.3)

If Equation 1.2 is satisfied, the energy difference is thus small enough to be accepted. However, if Equation 1.3 is fulfilled, the energy difference is sufficiently large to be rejected [45].

Although the Metropolis algorithm has been utilized successfully to study numerous systems in the past, it has several drawbacks. The main problem with this method is that the system becomes trapped in an energy valley if the search space regions are separated by extremely large energy barriers, making it impossible to explore the entire system space. Thus, various improved MC methods have been developed to
overcome the disadvantages of the Metropolis scheme. One of these enhanced MC techniques is the Wang-Landau algorithm, which is discussed in the following section.

1.2.2.2 An overview of the Wang-Landau Monte Carlo method

The Wang-Landau sampling scheme was developed in order to improve the performance and overcome the obstacles inherent in traditional MC methods. In addition to this algorithm, other new MC techniques have been developed as well, including parallel tempering, multicanonical sampling and umbrella sampling [46].

The technique of Wang and Landau has numerous advantages over the Metropolis method as well as other MC techniques. For instance, it does not become trapped in any energy minima throughout the system, thus overcoming the drawback of the Metropolis algorithm. Therefore, this method can overcome simulation slow down near a transition point, causing it to be able to study first and second order transitions. In addition, unlike the Metropolis method as well, there is no temperature dependence of the acceptance criteria, enabling system properties to be obtained for any temperature. Moreover, using this scheme, both the Gibbs free energy and the entropy can be computed directly from the simulation, unlike conventional MC methods. Furthermore, from a single simulation, one can obtain all relevant thermodynamic properties, including phase behavior [47].

The Wang-Landau scheme involves the estimation of the density of states (DOS), which is the degeneracy of energy levels available to the system. This quantity is directly related to the entropy and can be utilized to determine thermodynamic properties at any
conditions of interest. The DOS corresponding to a particular energy state is inversely proportional to the probability of achieving a specific atomic configuration. These values are not known beforehand but instead successively approximated by modification at every simulation step in order to ensure uniform distribution. The Wang-Landau method differs from traditional MC techniques due to the dynamic update of its acceptance criterion, where this successive update of the DOS values, at each timestep rather than between various runs, results in a violation of the microscopic detailed balance equation. Nevertheless, this undesirable situation is resolved because the DOS modification factor magnitude continuously decreases throughout the simulation until the fluctuations are within the precision of the computer. At this stage, the detailed balance is essentially satisfied [48].

In order to illustrate this scheme, let us assume for discussion purposes that the quantity of interest is the energy in the system. At the beginning of a Wang-Landau simulation, all the DOS values are not known, thus all of them are set to 1. When a random move is performed to bring the system from a state with energy $E_1$ to a state with energy $E_2$, the transition probability is given by the equation below.

$$p(E_1 \rightarrow E_2) = \min \left( \frac{g(E_1)}{g(E_2)}, 1 \right)$$  \hspace{1cm} (1.4)

The entire energy landscape can be broken up into bins of equivalent size. Therefore, each time a particular energy state is visited, the DOS value for that particular energy bin is updated by a factor $f$. The initial value of $f$ is set equal to $e$ (2.71828...). Furthermore,
the histogram bin for that energy is also incremented by 1. The random walk is continued throughout the system until the total histogram becomes “flat”, which means that all histogram values are not less than 80 percent of the average histogram value, \(\langle H(E) \rangle\) at that particular instant. Once this criterion is fulfilled, the value of \(f\) is reduced by taking its cubic root and all histogram values for the energy bins are reset to 0. This Wang-Landau scheme proceeds using the new value of \(f\) and all the steps above are repeated until the value of \(f-1\) is less than \(10^{-8}\) [49]. This is the stoppage condition for the method. This technique could also be further improved by performing multiple random walks in parallel on different segments of the system space. Thus, the resulting pieces of the DOS could then be joined together and utilized to calculate quantities for the overall system [46]. This is further explained by Shell and collaborators, where the total energy range for the system was divided and the DOS calculated for each section. Subsequently, the DOS for the entire range was acquired by matching values in overlapping regions. Furthermore, they claim that if this procedure is not employed, the simulation time required for algorithm convergence could become extremely long for regions with high entropy gradients, similar to “ergodicity times” or “tunneling times” in multicanonical techniques [50-51] introduced by Berg and collaborators. Consequently, improvements to the Wang-Landau MC method that significantly reduce the time needed to reach the stoppage condition as well as speed up the convergence of the algorithm have been implemented. These enhancements are discussed in the section below.
1.2.2.3 An overview of the improvements to the Wang-Landau method

Although the traditional Wang-Landau MC sampling scheme is more efficient than previous methods, the limiting factor to this technique is the flatness criterion, which causes the simulation to require a long period of time to reach the stoppage condition. Therefore, due to this fact, improvements to the Wang-Landau method have been proposed, including the recycling of rejected states [52-53]. Using this method, there is a considerable increase in statistical accuracy [52]. In addition, Nguyen and collaborators devised a method that first estimates the initial DOS using a smoothed potential energy surface. They claim that these seeded simulations were found to converge faster and with higher accuracy than the standard Wang-Landau method [54]. Moreover, Zhou and co-workers have proposed a technique where a kernel function is adopted as a local update together with another global update for the DOS values in the system. This scheme is particularly useful for models with a joint density of states (JDOS) as a function of two or more variables [55]. Furthermore, Tröster and Dellago have introduced a self-adjusting Wang-Landau method that is applicable for the computation of multidimensional and structurally complicated DOS where the boundaries of the system are not known a priori [56]. Shell and co-workers have also proposed a refinement to the Wang-Landau algorithm by utilizing transition matrix MC techniques, where the calculations employ a record of proposed transitions between macrostates instead of visits to these states. They claim that this scheme results in DOS estimates that possess higher statistical accuracy compared to the original algorithm [57]. Yan and de Pablo have also suggested
improvements to the original Wang-Landau algorithm by including a running estimate of the DOS obtained from the instantaneous configurational temperature of the system, calculated from either the gradient of the forces or the kinetic contribution to the total energy in the system [58]. Other related improvements to the method involve the $N$-fold way Monte Carlo [59] as well as the round trip time optimization method [60].

However, in this work, we utilize a brand new method proposed by Belardinelli and Pereyra [61] that circumvents the use of this flatness criterion, causing the simulation to reach this stoppage condition much faster. This new DOS algorithm is described in the section below.

1.2.2.4 An overview of the new density of states Monte Carlo method [61]

This new DOS MC method is similar to the Wang-Landau scheme at the beginning, where the DOS values for all the energy bins are not known and are thus set equal to 1. The transition probability of moving from state 1 with energy $E_1$ to state 2 with energy $E_2$ is given by Equation 1.4 once again.

In addition, the DOS value for a particular energy bin is updated by a factor $f$ while the histogram value is incremented by 1 every time that energy bin is visited. However, the major difference between this new method and the previous Wang-Landau scheme is the recording of a MC time. This time is the ratio of the number of trial moves at that particular instant to the number of energy and volume bins discovered in a pre-simulation run for approximately two weeks. This pre-simulation is explained in more
detail in Section 3.2. The histogram is checked after a fixed MC time interval. If all the
histogram values for the feasible energy bins have been populated (all values are non-
zero), the value of $f$ is reduced by taking its cubic root and all histogram values are reset
to zero. It is important to note that there is no use of the “flatness” criterion in this
method. The random walk throughout the system is continued with this new value of $f$
and the steps above are repeated. However, once the value of $f$ becomes less than or equal
to $\exp(1/\text{MC time})$, the value of $f$ is set equal to $\exp(1/\text{MC time})$. Thus, the factor $f$ is
updated after each MC move while the histogram is now no longer used for the rest of the
simulation. This method continues until the value of $f$$^{-1}$ is less than $10^{-8}$, indicating the
stoppage condition.

After implementing this new MC method, we have utilized umbrella sampling in
order to refine the DOS results obtained from this algorithm. The technique of umbrella
sampling is discussed in the next section.

1.2.2.5 Use of umbrella sampling

Due to the fact that the method developed by Belardinelli and Pereyra is new, has
not been tested extensively and was only proven for the Ising model, we perform
umbrella sampling simulations with single histogram reweighing utilizing the DOS
results from this method [62]. This is similar to the work of Nguyen and collaborators,
but instead of utilizing a guess based on calculations of an energy surface, the initial
values are derived from this new DOS scheme. During these simulations, the generated
random moves are accepted based on the previously defined Wang-Landau criterion while the histogram is incremented for each visited bin. The DOS values are only updated at the end of these simulations, based on the equation below [62].

\[
\ln[g(E)]_{\text{new}} = \ln[g(E)]_{\text{old}} + \ln[H(E)]
\]  

(1.5)

These simulations are then terminated after a large fixed number of MC trial moves, giving the method ample time to sample the entire system search space. Thus, by utilizing umbrella sampling, we can refine the DOS results acquired from the new Belardinelli and Pereyra method in order to obtain more accurate values of the DOS for all the models studied in this work.
2.1 An overview of the common neighbor analysis method

The three simulation models built in our work generate numerous particle configurations that have different structural characteristics. Consequently, in order to obtain information regarding these structures, the common neighbor analysis (CNA) method is utilized. The technique used in this work is based on the method utilized by Cleveland and collaborators [63], which is slightly different from the other scheme employed by Honeycutt and Andersen [64]. The following sections in this chapter explain and illustrate this CNA method.

Cleveland and co-workers summarize CNA signatures for various atomic arrangements in a table which is used as a reference for identifying structures in our research [63]. These three integers in the CNA signature act as a type of identification number and are calculated by first breaking down a structure into a collection of atom pairs, with only pairs within a cutoff distance been considered. The cutoff distance is always larger than the nearest neighbor distance but less than the next nearest neighbor distance in a particular system. Therefore, once a particular pair of atoms is within the
cutoff distance and accepted, a set is defined around this pair. Thus, the three integers of the CNA method describe the characteristics of this set. The first integer identifies the number of atoms in the set, ignoring the two atoms that form the accepted pair. A particular atom is in the set if its distance from both members of the accepted pair is less than the cutoff distance. The second integer calculates the total number of bonds in the set. A bond is formed between two atoms in the set (once again, ignoring the bond between the atoms of the accepted pair) if the distance between both atoms is less than the cutoff distance. The third integer calculates the number of bonds in the largest continuously bonded cluster surrounding the accepted pair [63]. For this third integer, a cluster analysis method is utilized in order to determine the largest cluster. There are a large number of different cluster analysis techniques available but, the particular scheme chosen for this work is an agglomerative hierarchical clustering method, which is described in the next section.

2.1.1 An overview of the agglomerative hierarchical clustering technique [65].

The agglomerative hierarchical clustering technique is illustrated in Figure 2.1 below.
This technique is a bottom-up clustering method and termed agglomerative because it begins with every individual particle \( (p, q, r, s, t) \) in a single cluster. Subsequently, with each successive iteration, it agglomerates (merges) the closest pair of clusters by satisfying certain criteria (in this case the cutoff distance). In addition, this method is known as hierarchical because it involves different levels of clustering. For example, the first level indicates that each particle is its own cluster. Thus, as additional particles are added to the cluster, the system now reaches the next level and proceeds further until all particles that are continuously bonded and within the cutoff distance from the accepted pair are members of a single cluster. The algorithm for this method is defined below.

Figure 2.1: Graphical depiction of the agglomerative hierarchical clustering technique.
1. Assign each particle (p, q, r, s, t) to a separate cluster
2. Evaluate all distances between particle clusters
3. Look for the pair of particle clusters within the cutoff distance
4. Merge the pair of particle clusters into a new, larger cluster
5. Evaluate all distances from each member of this new cluster to all other particle clusters
6. Continue adding particles that are within the cutoff distance to any member of this cluster until there are no more particle clusters within the cutoff distance from members of this cluster

In order to illustrate the use of this agglomerative hierarchical clustering method, a theoretical set of atoms around an accepted pair is considered as an example in Figure 2.2 below.

Figure 2.2: Illustration of a theoretical set of atoms around an accepted pair used as an example for the agglomerative hierarchical clustering technique.
Based on Figure 2.2 above, the black circles represent the accepted pair while the white circles are the set of atoms surrounding the pair. For the clustering technique, only the atoms in the set (A, B, C, D, E, F) are considered. Utilizing the algorithm above, particles A, B, C, D, E and F are in separate clusters at first. The bonds drawn in Figure 2.2 are not chemical, but merely geometrical; indicating that the distance between two particles is less than the cutoff distance. B is then added to cluster A to create cluster A-B because B is within the cutoff distance from A. Next, the distance between both members of the cluster and all other particles in the set are analyzed to determine whether any other particle lies within the cutoff distance from cluster A-B. It is found that C satisfies this criterion. Therefore, C is added to cluster A-B to form cluster A-B-C. This continues until cluster A-B-C-D-E is created. However, because F is not within the cutoff distance from cluster A-B-C-D-E, it is not added to the cluster but remains a separate, individual particle cluster. In the example above, there are 5 particles in the largest cluster around the accepted pair (A-B-C-D-E) while the number of bonds in that cluster is equal to 4.

This clustering technique is integral for the CNA method because although in perfect crystals, the ordered configuration leads to simple clusters only, there are a plethora of different cluster configurations for imperfect crystal structures as well as disordered states. Therefore, a method that can accurately identify all these clusters needs to be implemented.
2.1.2 An example illustrating the use of the common neighbor analysis method

A set is defined around an accepted pair of atoms as shown in Figure 2.2 below.

Figure 2.3: Graphical depiction of an example illustrating the use of the common neighbor analysis method.

The black atoms are part of the accepted pair while the white atoms are part of the set that surround the pair. The bonds drawn in Figure 2.3 are not chemical, but merely geometrical; indicating that the distance between two particles is less than the cutoff distance. The first integer, which calculates the total number of atoms in the set, is equal to 4 in this case because there are 4 atoms surrounding the accepted pair. The second integer is 2 because there are 2 total bonds in the set around the pair while the third integer in this example is 1 because there is only one bond in the largest continuously bonded cluster around the pair. Therefore, based on the example in Figure 2.3, the result of the CNA method for this case is \{4 2 1\}. 
Therefore, the CNA result for a perfect face centered cubic (FCC) crystal structure is all pairs in that system having the identification number of \{4 \ 2 \ 1\}. On the other hand, for a perfect body centered cubic (BCC) structure, there is a mixture of \{6 \ 6 \ 6\} and \{4 \ 4 \ 4\} pairs in the system, depending on whether the atom in the middle of the unit cell or the atoms at the cell edges constitute a particular accepted pair [63].

2.2 An overview of structural results from the common neighbor analysis method

In the three simulation models, the cutoff distance used did not vary and was based on the parameters for a perfect Lennard-Jones (LJ) FCC crystal. In this system, the nearest neighbor \(r\) distance is \(2^{1/6} \sigma (1.122\sigma)\) while the next nearest neighbor distance is equal to \(\sqrt{2} \times 2^{1/6} \sigma (1.59\sigma)\) [66]. Thus, the cutoff distance chosen for our work was set as \(1.3\sigma\). In order to obtain the number of \{4 \ 2 \ 1\} pairs for a perfect LJ FCC crystal, we use the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) Molecular Dynamics (MD) software package to generate this configuration with 256 atoms. Once this configuration was generated, we employ the CNA method to calculate these three integers. It was found that for this structure, there are 1536 pairs with the designation \{4 \ 2 \ 1\}. Therefore, based on this result, we have defined an order parameter called \(\eta\), which is the ratio of the number of \{4 \ 2 \ 1\} pairs for a particular configuration obtained from our simulations to 1536, the number of \{4 \ 2 \ 1\} pairs for a perfect crystal structure. The structural results for each model built are presented in Chapters 3, 4 and 5.
CHAPTER III

SIMULATION OF SOLID-LIQUID EQUILIBRIUM FOR MONODISPERSED LENNARD-JONES SPHERES

3.1 An overview of previous simulation studies regarding solid-liquid equilibrium

The solid-liquid phase transition is one of the most fundamental material properties in nature. However, theoretical techniques to determine solid-liquid equilibrium have lagged behind the determination of fluid phase equilibria such as vapor-liquid and liquid-liquid coexistence even though simulation methods have enabled a better understanding of the thermodynamic and structural properties of solids. In fact, various techniques such as Gibbs Ensemble Monte Carlo, proposed by Panagiotopoulos [67], as well as Multicanonical Monte Carlo, introduced by Berg and Neuhaus [68], while enabling researchers to investigate liquid-gas and liquid-liquid phase transformations in a plethora of fluid simulation models [69], are unsuitable to be utilized for the determination solid-liquid equilibrium [70].

Early simulation methods that were developed to sample this solid-liquid phase coexistence calculated the free energy difference between a reference state and the desired state [71-73]. These schemes can be classified based on the approach...
used to calculate this free energy difference as well as the reference state chosen for both the liquid and solid states [74]. These approaches are based upon techniques such as thermodynamic integration [75], Landau free energy [76], free energy perturbation as well as “parameter hopping” in umbrella sampling [71]. Moreover, the reference state for the solid could be chosen as an Einstein crystal [77] while an ideal gas [78] or a metastable fluid configuration [76, 79-80] could be selected as the liquid reference state.

In thermodynamic integration, laborious and time-consuming simulations have to be performed iteratively in order to calculate the free energy change between the reference state and the system of interest and match these two branches of the calculated free energy until a suitable point where the chemical potential, pressure and temperature of both phases are identical, signifying solid-liquid coexistence [78]. In addition, along this reversible integration path, real as well as artificial singularities could be encountered such as in the single-occupancy cell model of Hoover and Ree [81], causing corrections to be implemented if the path fails to achieve the desired state [77]. Therefore, due to this difficulty of using thermodynamic integration in order to determine solid-liquid phase equilibria, only a small number of specific systems have been investigated until now [78].

Furthermore, the Gibbs-Duhem integration method, first introduced by Kofke, has also been utilized to identify the melting/freezing curve [82-83]. This technique, refined by him as well as Agrawal, uses an initial coexistence point determined from the hard sphere estimate of Hoover and Ree [75] and extends it to a soft sphere system [84-85]. Agrawal and Kofke have also extended their work with a subsequent integration that includes the attractive term from the Lennard-Jones potential [86]. This method was also
employed in the work by Eike and collaborators in order to determine the solid-liquid coexistence curve for the Lennard-Jones fluid system [87]. However, similar to the thermodynamic integration scheme, these serial methods could ultimately cause the determination of an incorrect coexistence line if a wrong initial coexistence point is employed in the calculation. The Gibbs-Duhem technique could also lead to errors due to the inadequate numerical integration of the Gibbs-Duhem equation [71].

Sweatman introduced a new self-referential Monte Carlo method that still utilizes a reference state, but is substantially different from previously described techniques. This is because the reference state is now the desired crystalline solid, but possessing a different number of unit cells. Therefore, the free energy difference in this case is between two crystal structures that vary based on size. Thus, because the reference state is similar in nature to the final state, this method is termed “self-referential.” According to Sweatman, this technique is faster and more efficient compared to older methods incorporating reference states [74]. This self-referential scheme is a reinvention of the technique proposed by Barnes and Kofke for a system of one dimensional hard rods on a line [88]. This method is also similar to the work of Mon and collaborators, who studied lattice systems such as the lattice gas model [89-90].

New simulation techniques have recently been devised that do not require a previous knowledge of an initial point in order to determine the coexistence curve. For example, Morris and Song have utilized large scale Molecular Dynamics simulations to calculate the free energy difference between a reference state and the system studied in order to identify a point where the coexisting solid and liquid states have equivalent
chemical potential, temperature and pressure values [91]. In addition, Shetty and Escobedo have employed a method involving virtual Gibbs ensembles in order to calculate these coexistence points [92].

Another new direct simulation method is the phase-switch Monte Carlo scheme that can sample both solid as well as liquid phases in a single simulation through biased sampling techniques [70, 93]. In the work by Errington, this scheme directly acquires coexistence information by introducing order parameters which define a path connecting the crystalline and fluid phases. Subsequently, transition matrix methods are utilized in order to bias the sampling while the coexistence properties are obtained from this biased sampling through an analysis of specific volume probability distributions [93]. However, the drawback of this method is the fact that the solid phase configuration has to be known \textit{a priori} and technique can be difficult to implement. Moreover, the coexistence pressure calculated using this method were lower than values reported by Agrawal and Kofke, which utilized the Gibbs-Duhem technique for the Lennard-Jones fluid [86]. Furthermore, in the work by Wilding, it is stated that another prerequisite of this method is that the transition has to be first order without any spontaneous transitions between coexisting phases [70].

Due to these reasons, Mastny and de Pablo have devised a new scheme to calculate the solid-liquid equilibria for the Lennard-Jones fluid using the Wang-Landau density of states (DOS) Monte Carlo method. This new Monte Carlo technique has already been used to study the behavior of Lennard-Jones liquids [61-62] as well as the vapor-liquid coexistence of Lennard-Jones fluids [52, 94]. The validity of this scheme for
vapor-liquid coexistence has already been verified by comparing the obtained results with literature values [95]. Specifically, this technique employs a random walk in energy and volume space in order to directly estimate the DOS for the system as a function of both energy and volume. Therefore, by acquiring the DOS over the phase space, the melting curve can be subsequently determined over the temperature and pressure range of interest. The advantages of this scheme are the conceptual simplicity, computational efficiency as well as its general applicability for a diverse variety of systems [78]. This method has been proven accurate for the determination of solid-liquid equilibrium by comparing the results obtained to other techniques such as Gibbs-Duhem integration [86] and phase-switch Monte Carlo [93].

Another DOS Monte Carlo method utilized for the study of solid-liquid phase transitions was developed by Chopra and co-workers, with a special emphasis on crystallization studies. In this work, they performed a random walk in order parameter space to calculate the free energy profile between these two coexisting phases. The identification of the phase transition was performed for a purely repulsive Lennard-Jones fluid [46]. They claim this method is useful for the determination of crystallization, which still poses challenges in the field of computer simulations, either with Monte Carlo techniques [96], Molecular Dynamics methods [97-98] or through a combination of both schemes [99]. In addition, according to them, this order parameter determination of crystallization is either comparable or better to other techniques such as phase switch Monte Carlo, self-referential Monte Carlo, thermodynamic integration, Gibbs-Duhem integration as well as a recent study of crystallization by Moroni and collaborators.
utilizing transition path sampling [100]. They discovered that the stable nuclei at melting for this Lennard-Jones system was found to be face centered cubic, similar to previously reported results in literature by Hsu and Rahman [101] as well as by Swope and Andersen [102].

In our work, we utilize the DOS Monte Carlo method used by de Pablo and collaborators as well as the new Monte Carlo scheme proposed by Belardinelli and Pereyra [61] in order to determine the solid-liquid phase transition for a system of Lennard-Jones spheres. The details of the simulation model and scheme will be presented in the following section.

3.2 Simulation model and protocol

We utilize the work of Mastny and dePablo as a basis for studying this model of monodispersed Lennard-Jones (LJ) spheres that later becomes the crystallizable solvent for the polymer chain. The potential between all the particles in this system is defined by Equation 3.1 [78]

\[
\phi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \quad (3.1)
\]

where \( \phi \) is the LJ interaction energy while \( \varepsilon \) and \( \sigma \) are the LJ energy and size parameters, respectively.
The initial configurations for this model were built using the LAMMPS Molecular Dynamics (MD) software package. In our LAMMPS input script file, we built a face-centered cubic (FCC) lattice comprising 256 atoms with a LJ soft potential between each particle at the temperature and pressure for both the solid and liquid phases. These temperature and pressure conditions were taken from the phase diagram in the paper by Mastny and dePablo [78]. Thus, the solid state had a temperature of 1.5 LJ units and a pressure of 21.5 LJ units while the liquid phase had a temperature of 2.5 LJ units and a pressure of 21.5 LJ units.

The LJ spheres with $\varepsilon$ and $\sigma$ values equal to 1.0 for each atom are then allowed to equilibrate in the isothermal-isobaric (NPT) ensemble. The outputs from this LAMMPS simulation are LJ energy ($E$) and LJ volume ($V$), indicating a range of energy and volume for the entire system. Figure 3.1 illustrates the entire $E$-$V$ range for this system of LJ spheres. The cluster at high volume and high energy corresponds to the liquid configurations while the low energy and volume cluster represents the solid configurations.
Next, in order to make the simulation more efficient, we utilize the method from Mastny and dePablo of dividing this landscape into several energy-volume windows which are run simultaneously and in parallel [78]. Figure 3.2 illustrates the $E-V$ range for the system divided into various $E-V$ windows. The windows need to overlap with one another in order to avoid “edge” effects at the window boundaries for the restricted energy-volume range [103].
Figure 3.2: Plot of the different windows used to divide the energy-volume range of interest

The configurations obtained from LAMMPS that possess energy and volume values in a particular window were then used as seed configurations for the subsequent DOS Monte Carlo simulations performed in that window. Therefore, with a smaller energy and volume range to explore, the Monte Carlo simulation would converge faster.

In this work, the DOS, $g$, is a function of both energy and volume. Moreover, because the simulations are performed in the NPT ensemble, the Wang-Landau acceptance criteria is modified as shown in Equation 3.2 below [78]

$$p(E_1, V_1 \rightarrow E_2, V_2) = \min \left[ \left( \frac{V_2}{V_1} \right)^N \frac{g(E_1, V_1)}{g(E_2, V_2)} \right]$$

(3.2)
where \( N \) is the number of particles in the system, \( E \) is the system energy and \( V \) is the system volume.

For all \( E-V \) windows, periodic boundary conditions are implemented in order to overcome boundary effects at the edges of the simulation box. Two types of Monte Carlo moves are performed on the system; local moves as well as global moves. In the local move, an atom is chosen at random and displaced by a fixed amount in a random direction. The LJ energy change after each local move is computed in order to bin the energy value after every move. In addition to the local move, global moves are also implemented in the system, including a volume change move with coordinate rescaling as well as volume changes without any coordinate rescaling. In the first type of global move, the box volume is changed to a random value in the volume range for that specific window and the coordinates of the atoms are rescaled to the new box volume. However, in the second global move, the atom coordinates are not rescaled to the new box volume, but remain at their original positions before the volume change. If this volume change causes any of the atoms to be outside the box however, the move is rejected.

However, before running the actual DOS MC scheme, a pre-simulation has to be performed in all the windows in order to sample the feasible energy and volume bins for the subsequent full MC simulations. The technique for these pre-simulations are similar to the full DOS MC method, but do not involve checking for histogram “flatness” or modification of the factor, \( f \). These pre-simulations are allowed to run for approximately two weeks. At the end of this duration, the histogram values for all energy-volume bins, \( H(E,V) \), in a specific window are checked to determine whether a particular bin is
feasible. The criterion for feasibility in this case is a value of \( H(E,V) > 0.0 \) for the E-V bin. Thus, once all the feasible bins have been ascertained, the DOS MC simulations over all the windows are restarted. It is clear that because the duration of these full simulations are much longer than the pre-simulations, there will be states discovered that were not detected in the pre-simulations, particularly in the low volume, low energy windows. Therefore, if the simulation enters a particular energy and volume state not discovered in the pre-simulation, the move is automatically rejected and the configuration written to a separate file. The DOS values for these states are not included in our final results.

After the simulation reaches the stoppage condition (discussed in Section 1.2.2.2. and 1.2.2.4 of Chapter I) for all the windows, the resulting pieces of the DOS surface in the various windows are then joined together to obtain the overall DOS result for the system, discussed in the next section.

Based on these Monte Carlo simulations, we can graphically observe the low energy and volume states produced in order to confirm the existence of a crystal structure. We utilize the Visual Molecular Dynamics (VMD) software package to view these configurations and find that there is indeed the presence of an FCC structure, illustrated in Figures 3.3 and 3.4. This structure is confirmed by the previously published work [100-101].
Figure 3.3: Graphical depiction of the low energy, low volume structure indicating a FCC crystal configuration when viewed along the x-axis.
3.3 Density of states results

As mentioned previously, the density of states (DOS) values are the desired output from our Monte Carlo simulations. The DOS corresponds to the degeneracy of energy levels present in the system [48]. Once the DOS is obtained, we interpolate these values to obtain additional points between the various energy and volume bins on our surface. This surface is plotted in Figure 3.5 below.
Based on Figure 3.5, the natural logarithm of the DOS varies with energy and volume. It decreases with decreasing energy and increases with increasing volume. This is to be expected because the number of states with a specific energy decreases as the energy decreases. In other words, it becomes more difficult to obtain many different configurations with a particular energy at a fixed volume as the energy is reduced because the atoms become closely packed and can only assemble into a small number of different arrangements with equal energy. Moreover, as the volume increases, more space is available to sample various dissimilar configurations at a fixed energy value. This ability to form many different configurations at higher volumes leads to a larger number of states, i.e. higher value for the DOS. Thus, the DOS is small at low energies and low
volumes as there are a very small number of possible configurations. The flat region in
the DOS surface indicated in Figure 3.5 above that has a \( \ln g(E,V) \) value of 0 occurs
because our pre-simulation did not find any feasible bins that correspond to these very
low values of energy and volume. Thus, these bins are not included in the subsequent full
DOS MC simulations that calculate DOS values. The ranges for the energy and volume
in Figure 3.5 correspond to the ranges of energy and volume in Figure 3.1.

Once the overall DOS surface has been obtained, we can utilize it to calculate
thermodynamic results, which we present in the next section.

3.4 Thermodynamic results

Thermodynamic variables such as free energy, enthalpy, entropy, average
volume, heat capacity, isothermal compressibility and thermal expansion coefficient can
be calculated from the DOS results based on Equation 3.3 below.

\[
<X> = \frac{1}{Z} \sum_{E,V} V^N g(E,V) \exp \left( \frac{-(E + PV)}{kT} \right) X
\]

(3.3)

where \( N \) is the number of atoms in the system, \( g \) is the DOS as a function of energy \( E \) and
volume \( V \), \( T \) is the system temperature, \( P \) is the system pressure, \( k \) is the Boltzmann
constant and \( X \) is the thermodynamic variable of interest such as average volume. \( Z \) is the
partition function for the system and is given by Equation 3.4 below with the same
variables as Eqn. 3.3 also used in Eqn. 3.4.
\[ Z = \sum_{E,V} V^N g(E,V) \exp \left( -\frac{(E + PV)}{kT} \right) \]  \hspace{1cm} (3.4)

Therefore, using the DOS presented in the previous section in Eqs. 3.3 and 3.4, thermodynamic variables such as the average volume, \(<V>\) and entropy, \(S\) can be calculated. The average volume, \(<V>\), is calculated by replacing \(X\) in Eqn. 3.3 with \(V\). The internal energy of the system, \(U\) is equivalent to \(<E>\) and can be computed by replacing \(X\) with \(E\) in Eqn. 3.3. In addition, the Gibbs free energy, \(G\), can be obtained from Eqn. 3.5 below.

\[ G = -kT \ln \left( \sum_{E,V} V^N g(E,V) \exp \left( -\frac{(E + PV)}{kT} \right) \right) \]  \hspace{1cm} (3.5)

Once these values are determined, the entropy can be calculated from Eqn. 3.6 below.

\[ S = \frac{<E> + P <V> - G}{T} \]  \hspace{1cm} (3.6)

The average volume and entropy for this model of monodispersed spheres are plotted as a function of temperature, \(T\) and pressure, \(P\) in Figures 3.6 and 3.7 below.
Figure 3.6: Plot of average volume, $<V>$ as a function of temperature, $T$ and pressure, $P$ for the system of monodispersed Lennard-Jones spheres.

In Figure 3.6, the average volume for the system of monodispersed Lennard-Jones spheres shows a discontinuity as a function of temperature and pressure. This discontinuity illustrates a first-order phase transformation because average volume is a first derivative of the free energy and is to be expected since this system of
monodispersed spheres is able to form crystalline structures from the disordered fluid state. The reason a section of the plot has to be removed is because the volume is artificially constrained between the volume bounds for this system, based on Figures 3.1 and 3.5. Furthermore, a phase transition is also clearly shown in Figure 3.7 where the entropy is plotted as a function of temperature and pressure.

Figure 3.7: Plot of entropy, $S$ as a function of temperature, $T$ and pressure, $P$ for the system of monodispersed Lennard-Jones spheres.
The discontinuity observed in Figure 3.7 is because the entropy is also a first order derivative of the free energy. The empty region in the plot is due to the removal of a section due to artificial volume constraints, as mentioned previously.

Two-dimensional slices of the average volume plot in Figure 3.6 and entropy plot in Figure 3.7 at both constant temperature and constant pressure are plotted in Figures 3.8, 3.9, 3.10 and 3.11 below in order to present a better illustration of the crystallization transition.

Figure 3.8: Two-dimensional plot of average volume, \( <V> \) as a function of temperature, \( T \) at a constant pressure value of 20 LJ units for the system of monodispersed Lennard-Jones spheres.
Figure 3.9: Two-dimensional plot of average volume, $\langle V \rangle$ as a function of pressure, $P$ at a constant temperature value of 1.5 LJ units for the system of monodispersed Lennard-Jones spheres.
Figure 3.10: Two-dimensional plot of entropy, $S$ as a function of temperature, $T$ at a constant pressure value of 20 LJ units for the system of monodispersed Lennard-Jones spheres.
Figure 3.11: Two-dimensional plot of entropy, $S$ as a function of pressure, $P$ at a constant temperature value of 1.5 LJ units for the system of monodisperse Lennard-Jones spheres.

Based on Figures 3.8, 3.9, 3.10 and 3.11 above, there is a clear first-order transition in average volume and entropy, thus validating the discontinuity due to crystallization depicted in Figures 3.6 and 3.7.

3.5 Structural results from the common neighbor analysis (CNA) method

The CNA method was used to study the crystalline configurations for monodisperse spheres and compare these configurations with the ones obtained for the
liquid states. In order to obtain these results, 10 configurations were selected from the low energy, low volume window in the MC simulation for the crystalline state while 10 configurations were chosen from the high volume, high energy window for the liquid state. The mean and standard error of the CNA results for these crystalline and liquid states are summarized in Table 3.1 below.

Table 3.1: Comparison of the number of {4 2 1} pairs for two different configurational states investigated in this model of monodispersed Lennard-Jones spheres.

<table>
<thead>
<tr>
<th>Monodispersed LJ Spheres Configuration</th>
<th>No. of {4 2 1} pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline state</td>
<td>708 ± 7</td>
</tr>
<tr>
<td>Liquid state</td>
<td>50 ± 2</td>
</tr>
</tbody>
</table>

In addition, based on the results presented in Table 3.1 above, we can also present these findings in terms of the order parameter $\eta$, defined previously in Chapter II. Table 3.2 presents the mean and standard error of these results.

Table 3.2: Order parameter values for two different configurational states investigated in this model of monodispersed Lennard-Jones spheres.

<table>
<thead>
<tr>
<th>Monodispersed LJ Spheres Configuration</th>
<th>Order parameter, $\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline state</td>
<td>0.461 ± 0.005</td>
</tr>
<tr>
<td>Liquid state</td>
<td>0.033 ± 0.002</td>
</tr>
</tbody>
</table>

Based on Tables 3.1 and 3.2, it is clear that the crystalline states generated through this simulation model have considerably more order than the corresponding fluid configurations, thus validating the ordered FCC structures present at low volume and energy.
CHAPTER IV
SIMULATION OF SOLID-LIQUID EQUILIBRIUM FOR POLYDISPERSED LENNARD-JONES SPHERES

4.1 An overview of previous simulation studies regarding solid-liquid equilibrium of glass-forming systems

In the previous chapter we discussed the crystallization transition of the system of monodispersed spheres. Another transition that has been as extensively investigated as the crystallization transition is the glass transition where a fluid freezes into an amorphous solid. This transition has been studied theoretically, experimentally and with computer simulation methods.

Theoretical models have been developed to explain the characteristics of glass formation. For example, Ediger and collaborators have examined the thermodynamic features of supercooled liquids and glasses and have presented various models that attempt to describe the basic features of these systems [104]. Debenedetti and Stillinger have also used theory to study supercooled liquids and their corresponding glass transition [105]. Furthermore, Stillinger and Weber interpreted the thermodynamic properties of the glass-formers in terms of the inherent structure formalism which
involves the stable disordered packing configuration of these liquids [106]. Another approach was proposed by Mezard and Parisi who developed a first principles theoretical calculation of the thermodynamics of simple fragile glasses. This work indicates that the liquid-glass transformation is a consequence of an underlying equilibrium phase transition [107]. Sciortino and co-workers also investigated the properties of glasses by introducing a model of binary Lennard-Jones mixtures [108-109]. On the other hand, the effect of polydispersity in the solid-liquid equilibrium has been investigated by McRae and Haymet theoretically with the introduction of a polydisperse hard sphere model [110].

Based on these theoretical studies, researchers have used simulation techniques to probe the solid-liquid equilibrium of glass-forming systems. Kob and collaborators performed Molecular Dynamics simulations [111-112] while Parisi and co-workers used Monte Carlo techniques [113-116] based on the theoretical model developed by Sciortino and co-workers. These researchers attempted to analyze the phase behavior as well as the thermodynamic properties of a Lennard-Jones system where crystallization is strongly inhibited. In addition, traditional Monte Carlo schemes have been implemented based on the theory developed by McRae and Haymet. For example, Bolhuis and Kofke have used the Gibbs-Duhem Monte Carlo technique in their simulation work on polydisperse systems [117-118] while Blaak and collaborators have compared their Monte Carlo simulations with analytical estimates based on the Percus-Yevick equation of state [119-120]. Based on these works, a terminal polydispersity limit has been identified, above which no crystallization occurs in the system. In fact, the upper limit of this maximum
polydispersity has been defined in the range of 5-15 percent in terms of the sphere size standard deviation [118]. This fact is confirmed in the simulation work by Wilding, who also mentions this terminal polydispersity level [70].

In this work, the investigation of disordered solid characteristics is performed using simulation techniques through the introduction of polydispersity into the system of Lennard-Jones spheres. This method utilizes the density of states Monte Carlo scheme proposed recently by de Pablo and collaborators [121-122] combined with previously mentioned studies on polydisperse systems. The simulation model and protocol for this system is explained in the next section. However, we hesitate to name the disordered solid state discovered a glass due to the lack of evaluation of dynamic and kinetic system properties in our research.

4.2 Simulation model and protocol

The second model built in our work involves extending the previous model of monodispersed Lennard-Jones (LJ) spheres in order to investigate the behavior of disordered solid systems. This is done by introducing polydispersity into the previous model through a Gaussian distribution. The spheres still possess a LJ energy parameter (ε) value of 1.0 but the LJ size parameter (σ) values now deviate from an average of 1.0. The amount of deviation from this average is quantified in the standard deviation (SD) for the Gaussian function. The equation for this function is given as follows [123]:
with $a$ being the mean of $\sigma$. Thus, by varying the SD value, we have the ability to study systems with different levels of polydispersity in their sphere sizes. In this work, we consider four cases, SD=0.1, SD=0.2, SD=0.3 and SD=0.4. The distributions for all these four cases are illustrated in Figures 4.1, 4.2, 4.3 and 4.4 which contain both the histogram and cumulative distribution function for the Gaussian distribution.

\[
f(x) = \frac{1}{\sqrt{2\pi(\text{SD})^2}} \exp\left(-\frac{(x-a)^2}{2(\text{SD})^2}\right)
\]  

(4.1)

Figure 4.1: Plot of the cumulative distribution function and histogram for the polydisperse system with a standard deviation of 0.1.
Figure 4.2: Plot of the cumulative distribution function and histogram for the polydisperse system with a standard deviation of 0.2.
Figure 4.3: Plot of the cumulative distribution function and histogram for the polydisperse system with a standard deviation of 0.3.
Figure 4.4: Plot of the cumulative distribution function and histogram for the polydisperse system with a standard deviation of 0.4.

These sphere size distributions were generated and then entered into LAMMPS for the four cases at temperatures and pressures corresponding to both solid and liquid phases. These values were once again equivalent to the previous model of monodispersed spheres, with a temperature of 1.5 and a pressure of 21.5, both in LJ units, for the solid state while the liquid state had a temperature of 2.5 and a pressure of 21.5 both in LJ units. These Molecular Dynamics (MD) simulations were run in the isothermal-isobaric (NPT) ensemble and allowed to equilibrate. The result from these runs is the energy-volume range for all the four cases studied. They are presented in Figures 4.5, 4.6, 4.7 and 4.8. The configurations obtained from LAMMPS are plotted in these figures, with the
high energy, high volume states corresponding to the liquid phase and the configurations possessing low energy and low volume analogous to the solid state.

![Energy-volume scatter plot](image)

**Figure 4.5**: Plot of the energy-volume range for the system of polydisperse Lennard-Jones spheres with a standard deviation of 0.1 obtained from the LAMMPS Molecular Dynamics package.
Figure 4.6: Plot of the energy-volume range for the system of polydispersed Lennard-Jones spheres with a standard deviation of 0.2 obtained from the LAMMPS Molecular Dynamics package.
Figure 4.7: Plot of the energy-volume range for the system of polydisperse Lennard-Jones spheres with a standard deviation of 0.3 obtained from the LAMMPS Molecular Dynamics package.
Based on Figures 4.5, 4.6, 4.7 and 4.8, it is clear that as the polydispersity in sphere size is increased, both the overall volume and energy of the system rises for all cases considered. This is due to the fact that the system is unable to achieve perfect packing and requires a larger volume to exist in a particular configuration. Moreover, due to this imperfect packing, the distances between atoms become larger, thus leading to higher values of the LJ potential. Therefore, these systems allow us to study the behavior of disordered solids that lack crystalline order.

Once the volume and energy ranges for the four cases have been obtained, the overall $E-V$ landscape is again broken up into various windows in order to speed up the convergence of the Monte Carlo (MC) simulations. The configurations that have energy
and volume values within a particular window range are used as initial seed configurations for the MC density of states (DOS) method.

In this MC scheme, the trial moves on the system (particle displacement, volume change with coordinate rescaling and volume change without coordinate rescaling) are similar to the previous model of monodispersed spheres. These moves are accepted or rejected based on Equation 3.1. First, pre-simulations are run in all the energy-volume windows for approximately two weeks in order to obtain the feasible bins for each window as explained in Section 3.2 of Chapter III. Subsequently, once the stoppage criterion for the MC DOS technique is fulfilled in all the windows, the resultant pieces of the DOS are joined together to obtain the overall DOS for each of the four cases.

4.3 Density of states results

Interpolation is once again performed on the DOS results acquired for the four cases considered. These DOS surfaces are plotted in Figures 4.9, 4.10, 4.11 and 4.12 below.
Figure 4.9: Plot of the density of states for the system of polydispersed Lennard-Jones spheres with a standard deviation of 0.1.
Figure 4.10: Plot of the density of states for the system of polydispersed Lennard-Jones spheres with a standard deviation of 0.2.
Figure 4.11: Plot of the density of states for the system of polydisperse Lennard-Jones spheres with a standard deviation of 0.3.
The same trend for the DOS seen in Figure 3.5 is also observed in Figures 4.9, 4.10, 4.11 and 4.12. The natural logarithm of the DOS increases with increasing volume as well as decreases with decreasing energy. In addition, as the sphere size distribution becomes broader, both the energy and volume of the system increases. As mentioned previously, this is due to the fact that the system needs a larger volume to pack closely and this imperfect packing causes an energy increase. Thus, as the standard deviation of the sphere size increases, a larger volume is required for this greater degree of packing imperfection and the energy of this disordered state would further rise due to a higher deviation from the perfect crystalline state. The flat region of the DOS surface at low energy and low volume in Figures 4.9, 4.10, 4.11 and 4.12 are due to the fact that those
bins were not discovered during the pre-simulations and were not included in the calculation of the DOS values in the subsequent full DOS MC simulations, as explained previously in Section 3.3. The ranges for the energy and volume in Figures 4.9, 4.10, 4.11 and 4.12 correspond to the energy and volume values in Figures 4.5, 4.6, 4.7 and 4.8, respectively.

Once the overall DOS surfaces had been obtained for the four cases, we calculated the thermodynamic results which will be discussed in the next section.

4.4 Thermodynamic results

Once the DOS values for all the four cases are acquired, we use Eqns. 3.3, 3.4, 3.5 and 3.6 in order to calculate average volume, \(<V>\) and entropy, S as a function of temperature, T and pressure, P, similar to the procedure for the previous model of monodispersed spheres. These thermodynamic results are plotted for each of the four cases separately.
Figure 4.13: Plot of average volume, $<V>$ as a function of temperature, $T$ and pressure, $P$ for the system of polydispersed Lennard-Jones spheres with standard deviation of 0.1.
Figure 4.14: Plot of entropy, $S$ as a function of temperature, $T$ and pressure, $P$ for the
system of polydispersed Lennard-Jones spheres with standard deviation of 0.1.
Figure 4.15: Plot of average volume, $<V>$ as a function of temperature, $T$ and pressure, $P$ for the system of polydisperse Lennard-Jones spheres with standard deviation of 0.2.
Figure 4.16: Plot of entropy, $S$ as a function of temperature, $T$ and pressure, $P$ for the system of polydispersed Lennard-Jones spheres with standard deviation of 0.2.
Figure 4.17: Plot of average volume, \(<V>\) as a function of temperature, T and pressure, P for the system of polydispersed Lennard-Jones spheres with standard deviation of 0.3.
Figure 4.18: Plot of entropy, $S$ as a function of temperature, $T$ and pressure, $P$ for the system of polydisperse Lennard-Jones spheres with standard deviation of 0.3.
Figure 4.19: Plot of average volume, $<V>$ as a function of temperature, $T$ and pressure, $P$ for the system of polydispersed Lennard-Jones spheres with standard deviation of 0.4.
Figure 4.20: Plot of entropy, $S$ as a function of temperature, $T$ and pressure, $P$ for the system of polydispersed Lennard-Jones spheres with standard deviation of 0.4.
Based on Figures 4.13, 4.14, 4.15, 4.16, 4.17, 4.18, 4.19 and 4.20 above, as the standard deviation of the sphere size increases from zero, the first-order phase transition seen in Figures 3.6 and 3.7 for the monodispersed spheres system disappears completely, even for the polydispersed spheres model with a SD of 0.1. This discontinuous disappearance is explained by Kofke and Bolhuis, who state that there is a terminal polydispersity limit, above which no crystallization occurs [120]. This terminal polydispersity, in the range of 5-15 percent, is consistent with our findings where by slightly increasing the SD to 0.1 or above, this crystallization transition vanishes and a disordered solid forms due to the imperfect packing caused by this polydispersity.

4.5 Structural results from the common neighbor analysis method

The common neighbor analysis method was used to study the configurations of polydispersed spheres with different sphere size standard deviation values. Once again, 10 configurations were selected from the low energy, low volume window in the MC simulation for each of the four SD cases considered. The mean and standard error of the CNA results for these different sphere size standard deviation cases are summarized in Table 4.1 below.
Table 4.1: Comparison of the number of \{4 2 1\} pairs for the different sphere size standard deviation cases investigated in this model of polydispersed Lennard-Jones spheres.

<table>
<thead>
<tr>
<th>Sphere Size Standard Deviation of Polydisperse LJ Spheres</th>
<th>No. of {4 2 1} pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>106 ± 4</td>
</tr>
<tr>
<td>0.2</td>
<td>52 ± 2</td>
</tr>
<tr>
<td>0.3</td>
<td>32 ± 2</td>
</tr>
<tr>
<td>0.4</td>
<td>17 ± 1</td>
</tr>
</tbody>
</table>

In addition, based on the results presented in Table 4.1 above, we can also present these findings in terms of the order parameter \(\eta\). Table 4.2 presents the mean and standard error of these results.

Table 4.2: Order parameter values for the different sphere size standard deviation cases investigated in this model of polydispersed Lennard-Jones spheres.

<table>
<thead>
<tr>
<th>Sphere Size Standard Deviation of Polydisperse LJ Spheres</th>
<th>Order Parameter, (\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.069 ± 0.003</td>
</tr>
<tr>
<td>0.2</td>
<td>0.034 ± 0.001</td>
</tr>
<tr>
<td>0.3</td>
<td>0.021 ± 0.001</td>
</tr>
<tr>
<td>0.4</td>
<td>0.011 ± 0.001</td>
</tr>
</tbody>
</table>

Based on Tables 4.1 and 4.2 and comparing them to Tables 3.1 and 3.2, it is clear that the crystalline order in the system is significantly reduced when even a small degree of polydispersity is introduced into the monodispersed LJ spheres model. When the sphere size standard deviation is increased from 0 to 0.1, the number of \{4 2 1\} pairs (indicating FCC structure) drops dramatically from 742 to 122, with an order parameter reduction from 0.483 to 0.079. Subsequently, these values are further reduced as the standard deviation is raised from 0.1 to 0.4. Thus, this disruption in crystalline packing
due to the presence of spheres with differing sizes causes the formation of configurations that possess amorphous characteristics (low number of FCC pairs and low order parameter values). Furthermore, the CNA results for this model of polydispersed spheres are close in value to the liquid state derived from the monodispersed spheres system, indicating considerably disordered structures.
CHAPTER V

STATISTICS OF A POLYMER CHAIN IN A SOLVENT OF
MONODISPERSED LENNARD-JONES SPHERES

5.1 A brief overview of previous simulation studies of polymer chains

Molecular simulations, including both Molecular Dynamics (MD) and Monte Carlo (MC) techniques, have been extensively utilized in order to investigate the numerous properties of polymers in various systems. Binder and collaborators have extensively elucidated the use of both methods in the field of polymer physics [124-125].

Moreover, it was Binder and co-workers who first extended MC methods for polymer chains from a lattice system to an off-lattice model [126]. In this work, we simulate a polymer chain based on a coarse-grained bead-spring model [127] in real space instead of on a lattice. This work utilizes both the Wang-Landau Monte Carlo (MC) density of states (DOS) scheme as well as the new DOS MC technique proposed by Belardinelli and Pereyra [61] in order to simulate a single chain residing in a Lennard-Jones solvent that crystallizes.
The detailed simulation model and protocol for this system is explained in the following section.

5.2 Simulation model and protocol

The third model we have studied is a system consisting of a short polymer chain in a solvent of monodispersed Lennard-Jones (LJ) spheres. The properties of this solvent have been studied in our first model. The polymer was built based on the bead-spring model and consists of 10 beads. The number of solvent atoms surrounding the polymer chain is set to 246, causing the system to contain a total number of 256 atoms. This is done so that we can compare the results obtained from this model with the previous models based on a similar number of system particles.

For the generation of initial configurations, a polymer chain was built using the LAMMPS Molecular Dynamics (MD) software package and subsequently added to both liquid and solid state configurations of the monodispersed LJ spheres system. The interaction between solvent atoms in the system is modeled using the LJ potential with the energy parameter ($\varepsilon$) equivalent to 1.0 and the size parameter ($\sigma$) equal to 1.0. In addition, this potential is also used between non-bonded beads along the chain as well as between bead and solvent atoms; with $\varepsilon$ and $\sigma$ values still equal to 1.0. However, for the interaction between bonded beads along the chain, the Finitely Extensible Nonlinear Elastic (FENE) potential in LAMMPS was used with a spring constant, $K = 40.0$, a
maximum bond length, $R_0=1.2$ as well as $\varepsilon=1.0$ and $\sigma=1.0$ for the repulsive LJ term in the equation. The combined potential is described by the equation below [128].

$$V_{\text{FENE}}(R) = -0.5KR_0^2 \ln \left(1 - \frac{R^2}{R_0^2}\right) + 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon \quad (5.1)$$

$R$ is the distance between consecutive beads along the chain. The repulsive LJ interaction term was added to the FENE potential in order to avoid the overlap of beads during the LAMMPS MD simulation run. In addition, the FENE potential was designed in such a way that when the consecutive bead distance along the polymer chain became equal to $2^{1/6}\sigma$, the potential had a value of 0. This setup was done in order for the polymer chain to co-crystallize with the solvent. In addition, the chain was modeled as a freely-joined, fully flexible chain, which means that all bond and torsion angles for the polymer are equally probable. For future work, we can tune Equation 5.1 with different parameters to allow the polymer chain to remain in an amorphous state as well as describe the chain with other, more elaborate models.

For the LAMMPS MD run, the pressure and temperature values were once again equivalent to the previous model of monodispersed spheres with a temperature of 1.5 and pressure of 21.5, both in LJ units, for the solid state while the liquid state had a temperature of 2.5 and pressure of 21.5 both in LJ units. These Molecular Dynamics (MD) simulations were run in the isothermal-isobaric (NPT) ensemble and allowed to
equilibrate. The output from this simulation is the energy and volume range, as illustrated in Figure 5.1 below.

![Plot of the energy-volume range](image)

**Figure 5.1:** Plot of the energy-volume range for the polymer chain in a crystallizable solvent obtained from the LAMMPS Molecular Dynamics package.

The clusters in Figure 5.1 correspond to both the solid (low energy, low volume) and liquid (high energy, high volume) states. Subsequently, this entire range was once again divided into various windows in order to enhance the convergence of the MC simulations. Furthermore, initial configurations that had energy and volume values in a particular window range were used to seed these MC simulations.

During the subsequent MC simulations, the interactions between solvent atoms, non-bonded beads as well as between beads and solvent atoms were modeled using the
LJ potential with $\varepsilon$ and $\sigma$ values equal to 1.0. For the bonded beads along the chain, the FENE potential was utilized with $K=40.0$ and $R_o=1.2$.

The reptation move was designed in order to generate different chain conformations in the solvent. There are other efficient moves that have been designed for a polymer chain which we used as inspiration for our reptation algorithm, including the pivot algorithm for isolated polymer chains undergoing self-avoiding random walks [129], the double-pivot move utilized in dense polymer melts [127], the “slithering snake” move [130], a configurational bias Monte Carlo move that allows large scale conformational changes of the chain in a single trial move [131-132] together with further extensions of this algorithm [133] as well as a “wormhole” move that allows a polymer chain to reptate through a hole in space [134]. In our move, the polymer chain undergoes reptation by first identifying if there is a solvent atom in the bond length range from the end bead of the chain. If there is a solvent particle in that range, this solvent atom is converted into the new end bead for the chain. Subsequently, because the number of beads and solvent particles are set to be constant in the system, the first bead is thus converted to a solvent atom. Our reptation move was created as such due to the difficulty of bead random movement in such a close packed solvent. If we attempted to displace beads randomly in the system, a large majority of the moves would have been rejected. However, we have not analyzed our reptation move to see if it specifically obeys detailed balance. This move is illustrated in Figure 5.2 below.
Figure 5.2: Depiction of the reptation move.

On the other hand, the trial moves attempted for the solvent were similar to the first model of monodispersed spheres, including particle displacement moves, volume change moves with coordinate rescaling as well as volume change moves without rescaling. For all the moves in the system (both for the solvent as well as the bead), the acceptance criterion is based on Equation 3.1.

Once again, pre-simulations are run in all the energy-volume windows for approximately two weeks in order to obtain the feasible bins for each window as explained in Section 3.2 of Chapter III. Subsequently, once the stoppage criterion for the MC DOS technique is fulfilled in all the windows, the resultant pieces of the DOS are joined together to obtain the overall DOS surface for this system.
Based on these MC methods, we can graphically observe the low energy and volume states produced in order to confirm the existence of a crystalline solvent with the polymer chain co-crystallizing with the surrounding solvent. We utilize the Visual Molecular Dynamics (VMD) MD software package to view these configurations and find that the polymer chain does indeed co-crystallize with the solvent which possesses a face centered cubic-like structure, as evidenced by Figures 5.3 and 5.4 below.

Figure 5.3: Graphical depiction of the low energy, low volume structure indicating the polymer chain co-crystallizing with the solvent which adopts a FCC crystal configuration when viewed at an offset angle of 45° along the x-axis.
Figure 5.4: Graphical depiction of the low energy, low volume structure indicating the polymer chain co-crystallizing with the solvent which adopts a FCC crystal configuration when viewed along the z-axis, with a 45° degree angle between the y-axis and x-axis.

5.3 Density of states results

In order to obtain the overall DOS surface for the polymer chain in a crystallizable solvent system, interpolation is performed on the DOS results acquired from our MC simulations of this model and plotted in Figure 5.5 below.
Based on Figure 5.5, the energy and volume values for this system are close to the monodispersed spheres system but lower than the polydispersed spheres model. This is to be expected, since the solvent for the chain consists of monodispersed spheres, thus enabling it to form close-packed configurations with lower values of both volume and energy. In addition, the polymer chain beads are equivalent in size to the solvent atoms and the bonding potential is designed in such a way that the polymer co-crystallizes with the solvent. Therefore, the distance between consecutive beads is equivalent to the distance between neighboring solvent atoms when the solvent becomes crystalline. Thus, the polymer chain does not disrupt the structure of the crystalline solvent, allowing it to crystallize into the face-centered cubic (FCC) configuration. The natural logarithm of the
DOS for this system also exhibits the trend of increasing with higher volume values and decreasing with lower energy values as seen in Figures 3.5, 4.9, 4.10, 4.11 and 4.12. The flat region of the DOS surface at low energy and low volume in Figure 3.5 is due to the fact that those bins were not discovered during the pre-simulations and were not included in the calculation of the DOS values in the subsequent full DOS MC simulations, as explained previously in Section 3.3. The energy and volume ranges shown in Figure 5.5 correspond to the values in Figure 5.1.

5.4 Thermodynamic results

For the polymer chain in a solvent of monodispersed LJ spheres system, the first order phase transition seen in Figures 3.6 and 3.7 is once again observed in the plots of average volume and entropy, as shown in Figures 5.6 and 5.7 below.
Figure 5.6: Plot of average volume, $<V>$ as a function of temperature, $T$ and pressure, $P$ for the polymer chain in a crystallizable solvent system.
Figure 5.7: Plot of entropy, $S$ as a function of temperature, $T$ and pressure, $P$ for the polymer chain in a crystallizable solvent system.
Nevertheless, unlike the previous system of monodispersed spheres, this discontinuity disappears at high pressures, as illustrated in Figures 5.6 and 5.7. The absence of this transition at elevated pressures is due to the fact that the interactions in the system are modeled by two different potentials, the LJ potential as well as the Finitely Extensible Nonlinear Elastic (FENE) potential. Consequently, these potentials react differently with respect to pressure. In fact, the value of the FENE potential becomes very large if the bond length between consecutive atoms deviates from $2^{1/6}\sigma$, the length corresponding to the nearest neighbor distance in an FCC crystal as well as the minimum of the FENE potential in our model. Thus, due to this bonding potential, the beads along the chain are very difficult to compress together, thus this transition vanishes at high pressures where the system becomes extremely close-packed. Therefore, because these bead interactions are not described by the LJ potential, they are unable to be packed as close together as soft spheres.

Two-dimensional slices of the average volume plot in Figure 5.6 and entropy plot in Figure 5.7 at both constant temperature and constant pressure are plotted in Figures 5.8, 5.9, 5.10 and 5.11 below in order to present a better illustration of this first-order phase transformation.
Figure 5.8: Two-dimensional plot of average volume, $\langle V \rangle$ as a function of temperature, $T$ at a constant pressure value of 10 LJ units for the polymer chain in a crystallizable solvent system.
Figure 5.9: Two-dimensional plot of average volume, $\langle V \rangle$ as a function of pressure, $P$ at a constant temperature value of 1.5 LJ units for the polymer chain in a crystallizable solvent system.
Figure 5.10: Two-dimensional plot of entropy, $S$ as a function of temperature, $T$ at a constant pressure value of 10 LJ units for the polymer chain in a crystallizable solvent system.
Figure 5.11: Two-dimensional plot of entropy, $S$ as a function of pressure, $P$ at a constant temperature value of 1.5 LJ units for the polymer chain in a crystallizable solvent system.

Based on Figures 5.8, 5.9, 5.10 and 5.11 above, there is a clear first-order transition in average volume and entropy, thus validating the discontinuity due to crystallization of the polymer-solvent model depicted in Figures 5.6 and 5.7.

5.5 Structural results from the common neighbor analysis method

The common neighbor analysis method was utilized in order to study the configurations for this polymer chain in a crystallizable solvent system and compare it to
crystalline pure solvent configurations. Once again, 10 configurations were selected from the low energy, low volume window in the MC simulation for this polymer-solvent model. The results for the pure monodispersed solvent were obtained by removing the polymer chain from the system and reanalyzing these 10 configurations. The mean and standard error of the CNA results for both configurational states are summarized in Table 5.1 below.

<table>
<thead>
<tr>
<th>Polymer in Crystallizable Solvent System</th>
<th>No. of {4 2 1} pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monodispersed Solvent Only</td>
<td>714 ± 8</td>
</tr>
<tr>
<td>Monodispersed Solvent + Polymer chain</td>
<td>904 ± 11</td>
</tr>
</tbody>
</table>

In addition, based on the results presented in Table 5.1 above, we can also present these findings in terms of the order parameter \( \eta \), defined previously in Chapter II. Table 5.2 presents the mean and standard error of these results.

<table>
<thead>
<tr>
<th>Polymer in Crystallizable Solvent System</th>
<th>Order parameter, ( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monodispersed Solvent Only</td>
<td>0.465 ± 0.006</td>
</tr>
<tr>
<td>Monodispersed Solvent + Polymer chain</td>
<td>0.589 ± 0.007</td>
</tr>
</tbody>
</table>

Based on Tables 5.1 and 5.2 above, it is clear that the pure solvent in this system has similar structural characteristics to the crystalline state of the monodispersed spheres.
model summarized in Tables 3.1 and 3.2, even with the reduction in the number of particles from 256 to 246. However, when the polymer chain is introduced into this pure crystalline solvent, the degree of order in the system increases appreciably. This is due to the fact that the chain co-crystallizes with the solvent. This co-crystallization enhances the crystalline order in the system because the FENE potential restricts the consecutive bead distance along the chain to approximately $2^{1/6}\sigma$, corresponding to the nearest neighbor distance in a LJ FCC crystal. Therefore, this causes both the number of \{4 2 1\} pairs as well as the order parameter value to rise. In contrast, for the pure solvent model, the LJ soft potential allows for a broader range of inter-atom distances, thus leading to a lower degree of order in the system.
CHAPTER VI

CONCLUSIONS

In this dissertation, a novel simulation method to investigate the behavior of a polymer in a crystallizable solvent has been developed and analyzed. The model was built to understand polymer blends with crystallizable components or to investigate polymer solutions where the solvent can crystallize. In addition to this model, two other models for monodispersed and polydispersed Lennard-Jones spheres were developed and analyzed.

Thermodynamic results for these three systems were obtained through the use of a new density of states (DOS) Monte Carlo (MC) method developed by Belardinelli and Pereyra [61] while the structural characteristics of the models were analyzed with the common neighbor analysis (CNA) technique designed by Cleveland and co-workers [63]. In order to utilize the CNA method, agglomerative, hierarchical cluster analysis techniques [65] were used to detect a plethora of different cluster formations which were especially prevalent in disordered states. Thus their acquisition enabled us to correctly ascertain structural behavior.
Our first model of monodispersed Lennard-Jones spheres was based on a hybrid technique motivated by recent work utilizing a combination of Molecular Dynamics and Monte Carlo methods. The purpose of this study was to determine solid-liquid phase coexistence. Thus, based on thermodynamic results, there is a crystallization transition observed by discontinuities in first order derivatives such as entropy and average volume. This transition leads to the formation of face-centered cubic (FCC) crystalline structures. Therefore, this model could be utilized to study nanoparticles of various materials. This work is currently being performed in our research group. Therefore, by altering the Lennard-Jones parameters to mimic specific nanoparticle interactions such as between gold or silver particles, a particular nanoparticle system can be investigated.

Our second model addressed the behavior of polydispersed Lennard-Jones spheres and was designed to analyze the behavior of amorphous materials based on imperfect packing in these systems. The disappearance of the discontinuity in these first-order derivatives prove that this interruption of packing disrupts the crystallization transition previously observed in the case of monodispersed Lennard-Jones spheres. Moreover, based on our findings, as the standard deviation of the sphere size distribution becomes larger, the system moves further away from a perfect FCC structure. This model could be further extended by introducing a polymer chain into the system of polydispersed spheres acting as a solvent, thus enabling the investigation of a polymer residing in a solvent that vitrifies.
Our third model involves the introduction of a polymer chain into the monodispersed solvent system. We developed a new reptation move for the polymer chain because it was extremely difficult to randomly move the chain in a close-packed solvent. Therefore, with this move, different chain conformations could be investigated. We found that there is a first order phase transition in this model, thus proving that the introduction of the chain does not disrupt the crystallinity of the solvent. Nevertheless, compared to the monodispersed spheres system, this solid-liquid coexistence disappears at high pressures due to the different responses of the various inter-particle potentials in this system to compression. Furthermore, we observed that the FCC symmetry is enhanced because the polymer co-crystallizes with the solvent. This increased level of crystalline order in the model is due to the fact that the interatomic distances have been restricted by the FENE bonding potential, when compared to the broader distances allowed by the soft Lennard-Jones potential in the pure monodispersed solvent.

In the future, we could introduce more polymer chains in the crystallizing or vitrifying solvent as well as increase the chain lengths studied. Moreover, different chain models such as to freely-rotating chain model, the hindered rotation model, the rotational isomeric state (RIS) model and the Kratky-Porod worm-like chain model [135] could be utilized to describe the polymer. In conclusion, this area of research has a broad scope and immense potential in understanding the behavior of polymer solutions as well as polymer blends.
BIBLIOGRAPHY


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