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THE EFFECTS OF MOLECULAR STRUCTURE AND DESIGN ON THE PLASTICIZER PERFORMANCE THROUGH COARSE-GRAINED MOLECULAR SIMULATION

BY

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THESIS

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Abstract

Plasticizers are a commonly used additive used in the polymer industry to make the plastic more pliable by reducing the glass transition temperature, T_g and Young's modulus, Y. As the plasticizer aids in polymer process-ability and making it suitable for applications from industrial cables to sensitive medical equipment, the mechanism of plasticization is not fully understood. There are three theories used to explain plasticization: lubricity theory, gel theory, and free volume theory. The latter is a fundamental concept of polymer science that is used to calculate many polymer properties, but they all do not give a clear picture on plasticization. With molecular dynamics (MD) simulation, a coarse-grained (CG) model which consist of a simple bead-spring model that generalizes particles as a bead and connects them via a finite spring is used to explore the impact of plasticizer size throughout the polymer system. The interaction characteristics of the plasticizer is explored by representing the plasticizer molecules as a single bead of varying size. This gives better control on the variability of the mixture and pinpoint the significant contributions to plasticization. A path to understanding the the mechanism of plasticization will give insight in glass formation, and can later be used to find an optimal plasticizer architecture to minimize the migration of the additive by tuning the compatibility. Current results show a decoupling between the ${\cal T}_g$ and Y of the polymer-additive system. The overall understanding of finite-size effects shows: as additive of increasing size is added, the polymer free volume increases which in-turn would decrease the Y, but T_g is shown to increase because the polymer and additive are not as mobile to reduce caging effect of monomeric units.

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List of Abbreviations

MD	Molecular Dynamics
MSD	Mean Square Displacement
LJ	Lennard-Jones
NVE	Constant number, volume, and energy
NVT	Constant number, volume, and temperature/isothermal-isochoric ensemble
NPT	Constant number, pressure, and temperature/isothermal-isobaric ensemble
FENE	Finite Extension Nonlinear Elastic
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
DPD	Dissipative Particle Dynamics
RDF	Radial Distribution Function
PDF	Probability Density Function
HPC	High Performance Computing

List of Symbols

- T_q Glass transition temperature
- Y Young's Modulus
- σ_B or $\sigma_{BB}\,$ Additive bead size
- σ_P or σ_{AA} Polymer bead size

$$\sigma_s \qquad \sigma_B = 0.5$$

$$\sigma_b \qquad \sigma_B = 1.0$$

- $\langle u^2 \rangle$ Propensity
- ϕ_N Fraction of additive at constant system atom number
- ϕ_M Mass fraction of additive
- T_m Melting temperature
- U_{LJ} Lennard-Jones Potential
- r Distance between particles in simulation box
- r_c Cut-off distance for potential
- ε LJ Unit of energy
- σ LJ unit of distance
- k Spring constant of FENE poential, 30 $[\varepsilon/\sigma^2]$
- R_0 Maximum bond length, $[1.5\sigma]$
- au LJ unit of time
- δt Timestep, $[0.001\tau]$
- m LJ unit of mass

- k_B Boltzmann constant
- T^* Reduced temperature, $[\varepsilon/k_B]$
- U_{soft} Cosine soft potential
 - A Amplitude of cosine soft potential
- U_{DPD} DPD soft potential
 - *a* Maximum repulsion parameter of DPD soft potential
 - P^* Reduced pressure
 - \dot{e} True strain rate
 - L Simulation box length
 - L_0 Initial box length (before tensile deformation)
 - σ_{ts} Tensile Stress
 - P_x Tensile stress at x direction
 - P_y Tensile stress at y direction
 - P_z Tensile stress at z direction
 - ϵ_{ts} Tensile strain

Chapter 1 Introduction

1.1 Manipulating Polymer Properties

The glass transition is one of the most intriguing phenomena observed in any condensed soft matter. This phenomenon has been studied for decades but very little is understood about the behaviour; making it an elusive property. The glass transition temperature is found to be a range; there is a non-linear change in the volume (free volume) of the system (also correlated through the expansion coefficient, heat capacity, and other thermodynamic properties). The glass transition temperature, T_g , is not a thermodynamic quantity - the system is never truly at equilibrium, making it a dynamic phenomenon, as stated famously by Nieuwenhuizen, "*Thermodynamics does not work for glasses, because there is no equilibrium*" [7]. The basic understanding of this phenomena is when solidification of a glass, crystal, or gel occurs, their constituent particles become localized; there is limited room to freely explore the total space.

The dynamics and characteristics of polymers and polymeric liquids have been a problem of interest and to this day trying to be fundamentally understood. While liquids are consisting of small molecules, polymeric liquids, at times, show a unique and unusual non-Newtonian behaviour whereas ordinary liquids are primarily known to be Newtonian. The reason for this unusual behaviour is due to the topological constraints subjected to the polymer. All simple molecules have atomic and molecular constraints, but polymers also exhibit entanglement when in the long chain regime [8]. This characteristic limits the motion of polymers greatly because they cannot easily pass through one another. This is an important concept to grasp because it all comes back to understanding the dynamic transition region. This becomes very interesting when looking at heterogeneous dynamics for glass-forming materials. This is where highly mobile particles (smaller, easier to diffuse particles) can coexist alongside regions of immobile particles (the polymer) [8]. This is where relaxation of the system is important to study for better understanding the behaviour during the glass transition [8][9].

Plasticizers are a commonly used additive in the plastics industry to help manipulate the mechanical features of a polymer and also aid in the process-ability. By IUPAC the general definition of plasticizers, given in 1951 is: a substance incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility [9]. Plasticizers are used to make plastics flexible and durable; characteristically this reduces the polymer melt viscosity, elastic modulus, and most interestingly the glass transition temperature. By having such a small molecule in low quantities aid in manipulation of an entire polymer system, this concept alone makes it a very intriguing topic, and since they play a large role in glass transition temperature reduction, they can further lead to gains in a fundamental understanding on the glass transition [8].

When looking at particles as hard spheres and ordering their packing randomly within a system, the simplicity of this model leads to many fundamental questions such as: is there an ideal glass transition, is the glass transition based on the nature of the random packing or jamming of particles, and the understanding of the entropy crisis or Kauzmann paradox when the transition from liquid to crystal occurs: all these remain relevant questions to understand the fundamentals of glass transition [10]. Figure 1.1 shows the basic understanding of how a plasticizer works and will be used as a guide to further discuss the details of its impact on T_g .



Figure 1.1: Schematic of polymer exposed to non-solvent plasticizer. Reproduced from [1].

1.1.1 Mechanism of Plasticizers

To have an effective plasticizer, the additive will be fully incorporated in to the polymer system to obtain a homogeneous material. As the plasticizer is penetrated into the system by adsorption and diffusion, the polymer chain interactions would be altered essentially softening the system to aid in the reduction of the T_g , elastic modulus, and relaxation time of the system; effects of the additive can be captured by the change in the α - and β relaxation times through their structural changes.

There are many theories to understand plasticization ranging from the effectiveness of the plasticizer in polymer processing to the mechanistic understanding of plasticization. The three main theories in practice are: lubrication theory, gel theory, and free volume theory. The latter will be discussed in-depth to understand glass transition better [11].

Lubricity Theory

As the system is heated the plasticizer molecules diffuse through the polymer and weaken the polymer-polymer self interactions (van der Waals forces), this is the non-bonding potential that is disrupted by increasing the free volume with the addition of the plasticizer [12]. The plasticizer molecule is also said to act as a shielding mechanism to reduce the polymer-polymer interactive forces and reduce the formation of a rigid entangled system. By this, the phenomenon of T_g is reduced allowing the polymer chains to move rapidly, thus increasing flexibility, softness, and elongation at a lower temperature than pure polymer [12][13].

Gel Theory

The plasticized polymer is neither in a solid or liquid, but in an intermediate state, in which the polymer system is loosely held together by a secondary bonding force. These secondary bonding forces formed between plasticizer and polymer are easily overcome by applying external stresses that allow the plasticized polymer to induce mechanical loading like flexion, elongation, and compression [12].

Free Volume

The free volume theory is most commonly used to understand the nave behaviour of the T_g . Typically, the T_g is calculated as specific volume plotted against temperature to see the change in volume - where the intersection between the linear regression of the liquid and glassy regions correspond to the T_q . When additives are mixed into the polymer system, the free volume would increase leading to an upward shift in specific volume versus temperature curve. However, to understand the caging effect and how the entropy changes within the system, especially if its entangled, relaxation time of the polymer and how its fragility is affected will help to understand the structural and topological changes in the polymer system [14]. To look at molecular motion in a polymeric system, associated with the largescale motion of the entire polymer itself, the timescale jumps from microseconds to minutes. Understanding of timescales is important because the observable and processing time scales are on the same order, making this ratio a good guideline [15]. The meaning of relaxation time is the amount of time the system takes to move from an existing equilibrium with a disturbance, to the new equilibrium post-disturbance [14]. When calculating T_g , the pressure is kept constant but polymer system is being cooled at a constant cooling rate, varying the temperature to see the change in volume, heat capacity, and expansion coefficient.

Relaxation and Fragility

Relaxation time distribution is a widely used system property as a function of time that helps to measure the general dynamics of the glass-forming material. A very simple model used to understand the supercooled regime, C(t) is the Kohlrausch-Williams-Watts (KWW).

$$C(t) = C_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$
(1.1)

In this equation C_0 is the pre-exponential factor, τ is the characteristic relaxation time of the polymer, and β describes the relaxation time distribution and the fragility index, where $\beta \leq 1$. When looking at structural relaxation of any glass-material, there is generally a two-step process that the system is shown to observe [16]. The β -relaxation is a very short length time-scale relaxation process that corresponds to high localization of relaxation and is weakly dependent on the temperature. The α -relaxation, on the other hand is defined as the longer length time-scale, corresponding to the complete structural relaxation of the supercooled regime.

When looking at temperatures above T_g , a polymer system is very similar to a generic glassy-liquid, and according to Kohlrausch-Williams-Watts the function would show an exponential decay with β being equal to one this relaxation time is more commonly referred to as the Arrhenius equation. The temperature dependence of the relaxation time can be found using the Vogel-Fulcher-Tammann-Hesse (VFTH) equation [16].

$$\tau(T) = \tau_0 \exp\left[\frac{DT_0}{T - T_0}\right]$$
(1.2)

The high-temperature relaxation time, τ_0 is typically on the order of 10 - 13 seconds, T_0 is the temperature found when extrapolating relaxation time to infinity, and D is a measure of the strength of the temperature dependence on τ and the classification of the type of liquid behaviour being observed. The classification of supercooled liquids is referred to as

their *fragility*, this relates to how the dynamic properties of the glassy material deviates from the Arrhenius temperature dependence. A strong glass former shows very little deviation from Arrhenius behaviour, while a *fragile* glass former, exhibit substantial deviation from Arrhenius behaviour, as observed in Figure 1.2 [2].



Figure 1.2: Angell equation representation to show strong-fragile pattern in liquid viscosities. Strong liquids show Arrhenius behaviour. Fragile liquids show super-Arrhenius behaviour, the activation increases as temperature decreases. Reproduced from [2].

The nature of glass formation can be explained by the potential energy landscape, and the Adam-Gibbs theory [17]. There are other theories to explain glass-formation like modecoupling theory, random first-order transition theory, and the activated barrier-hopping model [12].

To understand how the long and short time-scales play a significant role in the understanding of how the polymer structure is affected and thus affecting the glass transition, the potential energy landscape (PEL) is a good measure for this. Figure 1.3 shows how the PEL of both a strong and fragile glass-former is formed with many local minima and local maxima [15]. The graph shows the potential energy of the system as the configurational coordination of the system changes, to sample all configurations of the glass-former. When the temperature is very high, the total energy of the system is well above the PEL. This allows for no impedance in the dynamics and leads to the structural relaxation time to have Arrhenius dependence on the temperature. However, as the temperature is decreased, the PEL plays a significant role. The higher potential energy barrier is an obstacle for the system to overcome, this makes the exploration of the configurational-space less likely. With this decreased likelihood of the system to explore its configurational-space, the two relaxation times play a prominent role. The β -relaxation time is seen when the system is exploring at the short time-scales, while the jumps between valleys or jumps from valley-to-valley needs more energy, which causes α -relaxation. As the system is further cooled and within the glass transition region, the dynamic properties are significantly slowed down due to larger energy barriers for relaxation [14]. Figure 1.3 shows the graphs being in respect to the Kauzmann temperature (T_K) which is the cross-over temperature where the entropy of the glass and crystal intersect. This means that the entropy of the glass-former would become lower than that of a stable crystal resulting in negative entropy this violates the third law of thermodynamics and thus called the entropy crisis (Kauzmann Paradox) [10][18].



Figure 1.3: Potential energy of system versus configurational coordination of a) strong glass-former and b) fragile glass-former. T_K is the Kauzmann temperature. Reproduced from [3].

The Adam-Gibbs framework is similar to PEL; there is a drastic decrease in configurational entropy of the molecular configurational states as the temperature is lowered to T_g . This leads to Adam-Gibbs theorizing that the cooperative motion of the local particles nearby must move since only a few configurational states can be made, so as temperature decreases there is higher cooperative rearrangement regions making the system as a whole, exhibit slower dynamic [14].

1.2 Additive Packing

When having additives mixed into the polymer system, the packing density is taken into consideration when understanding the cooperative motions of the system. For a strong glass former, the molecules are packed much more efficiently compared to a fragile glass former, where is a large degree of packing frustration [19]. As strong glass formers have higher configurational entropy and smaller cooperative rearrangements due to the restriction in movement, and smaller deviation in Arrhenius behaviour.

There are two main categories plasticizers are categorized in: internal and external plasticizers. Internal plasticizers increase free volume by having loose packing, this would decrease the T_g . This is achieved by the plasticizer being copolymerized with the polymer molecules, causing the structural order to decrease. External plasticizers are the generally preferred method because these low vapour pressure compounds are more adaptable by a manufacturer and can be tuned to the formulation to achieve desired properties [19][20].

1.3 Plasticizer Migration

Plasticizers have no doubt advanced process-ability of many other polymers. However, one huge area of research and concern deals with the migration of plasticizers within the system. Referring to Figure 1.4 on the triangle of plasticizer characterization: compatibility, efficiency, and permanence, all three of these components play a key role with each other. The larger the plasticizer molecule, the lower its volatility, resulting in a greater permanence (tendency to remain in the plasticized material). There are many other factors: chemical, processing and product environment conditions that influence the rate of plasticizer movement. To design an efficient plasticizer, high rates of diffusion are known to provide greater efficiency but low plasticizer permanence. This compromise is a hard barrier to overcome and affects the end product greatly [19].



Figure 1.4: Schematic representation of relationships between three important properties of the plasticizer: compatibility, efficiency, and permanence. Reproduced from [4].

After the material is processed, the material is exposed to either air, liquid, or another contact surface that the plasticizer can migrate to. This migration is a challenging concept to solve since it causes the product to become brittle and eventually degrade over time due to the transport of the plasticizer to the interface. Not only is this a problem for the material, but it is also a problem to the environment and human health [21]. Traditionally, phthalates are used as the backbone of a plasticizer molecule. Commonly used plasticizers worldwide are: DINP (diisononyl phthalate), and DEHP (di-2-ethylhexyl phthalate) [21]. All

these plasticizers have been banned by the European Union (EU) in some applications for having hazardous properties specifically having negative effects on cardiac and reproductive development [22][23]. Plasticizer volatility greatly compromises the use of it in polymer when it becomes a dilemma as great as this.

Solutions for non-phthalate "green" based plasticizers are developed, but still not as dominant in the market as a phthalate based plasticizer is. Current research is being done to develop methods to better screen plasticizers and understand the behaviour between the polymer system and plasticizer entity to truly grasp the transport phenomena occurring during processing and post-processing.

Study of glass transition has been an active field for many years. It is both a practical and fundamental significance to understand and characterize this unusual behaviour. With amorphous solids being ubiquitous to everyday life and having an impact on many applications from engineering applications in semiconductors and simple window panes to biological preservers, understanding their behaviour is an on-going scientific challenge [24].

The understanding of plasticizers and mechanism of plasticization is yet to be fully understood. It is difficult to characterize because the additive is intimately tied within the polymer system, and the polymer itself is dependent on its previous configurational state (experimentally), simulation work would alleviate the difference in crystallinity when producing the polymer.

All the factors that affect plasticization are: degree of compatibility, architecture of the plasticizer in the system within all processing temperatures, plasticizer efficiency in order to effectively reduce the T_g and elastic modulus, and the plasticizer should be permanent should not be easily diffused out of the system, making them usually have a property of low vapour pressure and larger architecture [25].

The applications of plasticizers is pertinent and understanding the age old problem of the glass transition would help to advance the study in its entirety. The PEL and Adam-Gibbs theory gives a basis to understand how the additive-polymer system behaves when the glass transition region is reached and within it, but there still is more to be discovered and understood about the process.

1.4 Chain Dynamics and Entanglement

Polymers are a complex and ubiquitous molecule that is embedded in our everyday lives, from DNA and proteins, to plastics. These natural and synthetic materials are characterized for their multitude of applications, for instance their rigidity plays a key role in the polymer dynamics, biological functionality, and polymer processing and reliability. Polymer chain dynamics is a complex multi-body problem that takes into account many factors such as: chain entanglement, cooperative bead motion, and even segmental chain motion.

The understanding and fundamental basis of polymer melt dynamics is widely built upon the *Rouse model* and the *repetition model*. The Rouse model is a simple case of unentangled chains, where a Gaussian chain made of beads and connected by springs interact in a stochastic medium to represent the presence of other chains within the system [26][27][28]. This sort of system behaves similarly like a particle with the center-of-mass of the chain under-going particle-like diffusion. In-turn, the self-diffusion coefficient, D scales with the length of the chain, N as $D \propto N^{-1}$. The repetition model confines the polymer chain inside a "tube", this confinement is induced by the entanglement with the other surrounding chains. The self-diffusion coefficient is one of the main predictions of this theory and its set to N^{-2} for chains longer than the entanglement length, $N > N_e$.

In a pioneering study by Kremer and Grest, they performed a coarse-grained MD simulation of polymer melts which results in an entanglement length, $N_e \approx 35$ which gives a diffusion coefficient close to the scaling factor of $N^{-\nu} \rightarrow \nu \approx 2$ [29]. But later was, reanalysis of this did show improvement in a refined entanglement length of $N_e \approx 30$ and $N_e \approx 70$ based on mean-square displacement and diffusion coefficient, respectively, shows dependence on chain length. For this study all polymer chains are above the entanglement length of $N_e \approx 32$ by [30].

There is no obvious consensus in the scientific literature on the scaling of the self-diffusion coefficient with chain length, nor is it clear what the value is of the entanglement length corresponding to the crossover between Rouse and repetition regimes. It is noted that the disparity is partly the result of a non-unanimous definition of N_e . Since it is a peculiar theoretical concept that cannot be measured directly, one can only see its effects on different macroscopic properties of the melt (self-diffusion, plateau modulus, polymer melt dynamics viscosity, structure factor). Inconsistent values of N_e are found based on these different properties. Furthermore, N_e depends on the level of coarse-graining used, a factor that makes comparisons even more difficult.

1.5 Effects of Additives on Polymer Properties

The canonical behaviour observed when a low molecular weight additive is mixed with a polymer is that of a plasticizer. This class of behaviours takes place when the additive reduces T_g , the density, and softens the material. The physical picture surrounding plasticization is that the low molecular weight additive increases the free volume, which leads to enhanced dynamics and softens material [31][32].

1.6 Motivation and Outline

From the discussion above, it is clear that glass formation is a complex problem with poorly understood origins. In addition, for the plastics industry, especially polyvinyl chloride (PVC), it is important to predict behaviours of the polymer when additives are needed in the product for processing. PVC is the third largest commodity plastic in the world, behind polyethylene and polypropylene, it is a widely used polymer from applications in a lot of our everyday lives. It's funny how such a large industry still has some unanswered questions, the biggest one being the migration or movement of plasticizers. This issue leads to material breakage, and plasticizer leaching is known to be toxic to humans and the environment.

The end goal is to be able to predict plasticization using computer simulations to understand the movement of these particles and their compatibility with the plastic.

Three main factors taken into consideration when finding the best plasticizer are: (1) The size, how well the particles are able to fit in and pack in together (2) The interaction between the plasticizer and plastic by tuning the attraction and repulsion between them (3) the design the molecules added into the system are straight or branched

Traditionally plasticization studies are done experimentally, which are both time and resource intensive. Its a lot like dating for humans, such a complex system with so many variables, where we all have a target but don't know what's really made for us. We have an app for dating, so why not have an e-Harmony for our plastics?

Using molecular simulation, we are able to look at interactions at the atomic level, change variables much more easily, and most importantly in the future be able to devise an algorithm to make the predictability of plasticizer-plastic compatibility effortless.

With the use of a low level molecular simulation, we would be able to explore systematically how the polymer-plasticizer system works, by modifying design of the low molecular weight additive to employ control over certain finite size effects. In this report we develop a coarse-grained model with small molecule additives to explore its glass-forming properties and their effect on glass transition temperature, elastic modulus, free volume, and spatial arrangement within the system.

The overall contributions made would be exploring a fundamental understanding of plasticization where molecular simulation has shown to have a decoupling of T_g and the Young's modulus, Y. There is a significant limitation in size on the T_g reduction for polymer when the additive reaches the same bead-size (Kuhn length) as the polymer. With on-going research on tune-ability and compatibility of additives in a polymer system, it will lead to a better understanding of the mechanics of plasticization.

Chapter 2 Methodology

2.1 Molecular Dynamics

Molecular Dynamics (MD) is a type of simulation that utilizes N-bodies to represent atoms and molecules with point particles of interest. The basis of MD simulations is to solve Newton's equation of motion, which models the classical physics of motion for particleparticle interactions. This captures the relevant thermodynamics, dipoles, and some reaction pathways/mechanisms. The most important component of accurate MD simulations is the *potential function* (also known as the force-field or interatomic potential). This potential describes how each atom interacts based on their coordinates. Incidentally, evaluating the potential function is also the most expensive computational component of MD simulations. The potential must account for all the different forms of energy within the molecular system; which include bonded (bond stretching, valence angle bending, and dihedral torsions) and non-bonded (electrostatics and van der Waals/Lennard-Jones forces).

Given topological information - initial coordinates and velocities - of the ensemble of particles are placed under a certain condition and integration of the equation of motion takes place to provide a new set of coordinates and velocities at each timestep. MD is a well suited tool for studying polymeric systems because of the strict control of the internal motion. As MD was developed for ideal systems in mind before (gases, liquids or crystals) the chain behaviour inside a polymer is extremely complex, not allowing for the complete picture to be theoretically understood.

2.2 Periodic Boundary Condition

Due to computational complexity scaling with number of particles of the system, $\mathcal{O}(n)$, the size of the simulation is relatively small compared to the macroscopic system. To overcome this scaling issue and make any simulation relevant is to employ a periodic boundary condition (PBC) to the simulation box. What this does is cause a repeated image of the primary box to continue around itself. These identical images are along the central/principle box.

2.3 Coarse-grained models of polymers

Coarse-graining a model is to remove the details of the chemical structure and generalize the chemical model. Generically working with a dense system consisting of many long polymer chains, in which all the atoms are considered, with detailed chemical interactions, for a long time, to a obtain realistic characteristics of the polymer. However, this task requires an exhaustive amount of knowledge of the interaction potentials between all atomic species and a considerable amount of computational power that cannot be surveyed even by the fastest supercomputers. This makes coarse-graining imperative because while it does reduce the complexity of the simulation system it more importantly reduces the amount of computation for the model to access longer time scales and larger length scales. Figure 2.1 illustrates this concept.

There are various methods of coarse-graining that are developed, but the basic formula leads to grouping together atoms or monomeric units into a bigger chain sub-unit that would absorb all the molecular detail. These new repeat units will now befriend each other through interactions as resulted from the realistic replaced parts. This coarse-graining is suggested by the nature of the polymer as they are known to clearly exhibit a time and length scaling for their static and dynamic properties [33]. Even if polymer topologies are very different that react universally to temperature modifications, of even a similar but "scaled" glass transition [34].



Figure 2.1: Schematic representation of different levels of modelling for a polymer chain. From top to bottom: PVC chain is represented by its chemical structure which is directly translated into a chemically specific/all-atom model which is then coarse-grained to a generic bead-spring model.



Figure 2.2: Schematic view of the topology breakdown and how the force field is represented for a system of linear chain molecules: bonded potentials act on a group of two (bonds), three (angles) or four (dihedrals) neighbours connected by chemical bonds; non-bonded potentials act on particles, which are close to each other in space, but not involved in a joint bonded interaction.

2.4 Equations of Motion

The conventional basis of MD is based on the stepwise time integration of Newton's equations of motion for a set of N particles:

$$\frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$
(2.1)

$$\mathbf{F}_{i}(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N}) = -\nabla_{\mathbf{r}_{i}} U_{i}(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N})$$
(2.2)

Where \mathbf{r}_i is the trajectory (position vector) of particle *i*, \mathbf{F}_i is the total force acting on particle *i* and U_i is the total potential energy - derived from the force. Solving Newton's equation conserves the total energy of the system and the time averages obtained during the simulations are equivalent to the averages in micro-canonical ensemble, NVE, explained in detail in Table 2.1. However, most often this ensemble is not practical when it comes to comparing between experiments and theory, so other ensembles are preferably employed depending on the thermodynamic quantity.

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Representation	Ensemble	Constant Parameters
NVE	microcanoical	n umber of particles, v olume, e nergy
NVT	canonical	number of particles, volume, temperature
NPT	isothermal-isobaric	number of particles, pressure, temperature
μVT	grand canonical	chemical potential, volume, temperature

2.5 Force Field

To understand and predict the macroscopic properties of a polymeric system with interactions within and between the polymer chain and the chain topology, makes the choice of potentials governing the interactions (force field) very crucial in MD simulations. The forces between the particles have to be realistic as possible while being able to obtain a feasible simulation because it is the most time consuming to calculate the forces for N particles. MD potentials can be split into two major contributing factors:

$$U(r) = U_{non-bonded}(r) + U_{bonded}(r)$$
(2.3)

where r is the position of each individual particle and U is the potential function. The most familiar pair interaction potential used is the LJ potential:

$$U_{LJ}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & r < r_c \\ 0 & r \ge r_c \end{cases}$$
(2.4)

where $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the interacting particles *i* and *j*, ε is the minimum energy and σ is the length at which $U_{LJ}(r) = 0$. LJ potential is made up of two terms, the strongly repulsive core ($\propto 1/r^{12}$) and a weak attractive tail ($\propto 1/r^6$) [35]. To constrain the potential and avoid extensive computation of the potential a truncation value is employed at a specific distance, r_{cut} .

To simplify this potential even further and have only the purely repulsive term of the potential, by setting the cut-off distance to the minimum of U_{LJ} ($r_{cut} = 2^{1/6}\sigma$) and shifting the potential such that it vanishes at this distance (and there is no discontinuity in the potential). This results in the Weeks-Chandlers-Andersen, WCA potential [36][37].

$$U_{WCA}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] & r < 2^{1/6} \\ 0 & r \ge 2^{1/6} \end{cases}$$
(2.5)

Both the LJ and WCA potential are shown in Figure 2.3. Particle interactions by a simple LJ potential act like a relatively soft spheres in a narrow range of separation and act as a hard sphere as they are driven closer together. For polymeric systems, which are characteristically made with high particle density, particle bead connectivity, and excluded volume interactions - this potential is a great choice due to the computational simplicity while retaining the essential physics.

For chemically bonded beads along the polymer chain a combination of potentials is



Figure 2.3: LJ-based potentials: 12-6 LJ (Eq. 3.2) and WCA (Eq. 2.5). r stands for r_{ij} .

used: WCA potential to account for excluded volume interaction and the attractive Finite Extensible Non-Linear Elastic (FENE) potential, to keep the consecutive beads along the chain bonded together [35].

The very common FENE potential for bead-spring polymers is represented as such [35]:

$$U_{FENE}(r) = \begin{cases} -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] & r < R_0 \\ \infty & r \ge R_0 \end{cases}$$
(2.6)

This bonded potential has the form of a simple harmonic potential for small extensions $r/R_0 < 0.2$ and limits the spring extension to R_0 .

By super-imposing FENE and LJ potentials, as shown in Figure 2.4, it yields an anharmonic spring interaction between connected beads with an equilibrium bond length b_0 and an ultimate bond length r_{max} . This makes bond crossing in polymer chains energetically


unfavourable and chain entanglement is naturally obtained [35].

Figure 2.4: Bond potentials: LJ + FENE (dashed blue line), LJ (solid black line), FENE (solid red line).

2.6 Equilibration Protocol

2.6.1 Melt Equilibration

The polymer chains and additives are initially randomly placed into the simulation box with a number density of 1.0. The particles are allowed to overlap. To reduce finite size effects and to make system-to-system comparability 10 000 atoms are used for various concentrations. To make sure the system is well equilibrated two different methods, namely fast push-off and Dissipative Particle Dynamics (DPD) push-off algorithms are employed to prepare a well-equilibrated melt [38]. The produces are using these two methods for melt equilibration are briefly introduced as follows. More details can be found in the literatures [39] [40]. Considering the small molecular weights of the monomers and polymer chains above the entanglement length, a fast push-off method is used for equilibration. In this method, a weak excluded volume interaction is introduced to separate the highly-overlapped monomers from each other. One of the soft potentials, named cosine potential, is often used for this purpose.

$$U_{soft}(r) = \begin{cases} A \left[1 + \cos\left(\frac{\pi r}{r_c}\right) \right] & r < r_c \\ 0 & r \ge r_c \end{cases}$$
(2.7)

Where the cut-off distance is $r_c = \sqrt[6]{2}\sigma$. In the fast push-off process, the initial amplitude A is increased from 4ε to 200ε over a short time interval of 10τ . The system is then switched to full LJ potential and equilibrated for a short MD run.

However, this fast push-off method is not feasible for equilibration of long polymer chains, as it result sin deformation of the polymers on short to intermediate length scales during the push-off step [41]. Due to the slow repetition dynamics of long chains, it requires an extremely long MD run to fully relax the molecules. Therefore, a different equilibration protocol, known as DPD-push-off, is used to equilibrate the long chain system. The method uses a different soft repulsion potential with a cuff-off distance of $r_c = \sigma$.

$$U_{DPD}(r) = \begin{cases} \frac{a_{DPD}}{2} r_c \left(1 - \frac{r}{r_c}\right) & r < r_c \\ 0 & r \ge r_c \end{cases}$$
(2.8)

Where maximum repulsion parameter a_{DPD} is selected at $25k_BT$ initially. The system is then simulated for 500τ before increasing the parameter a_{DPD} from $25k_BT$ to $1000k_BT$ over a time interval of 5.5τ . Finally, MD simulation with full LJ potential is performed for $10^4\tau$.

To understand the mapping of LJ units, table 2.2 identifies the meaning of physical quantities with the reduced LJ unit form.

Physical quantity	LJ unit
length	σ
energy	ε
mass	m
time	$\sigma(m/\varepsilon)^{1/2}$
temperature	ε/k_B
pressure	$arepsilon/\sigma^3$
velocity	$(\varepsilon/m)^{1/2}$
force	ε/σ
number density	$1/\sigma^3$

Table 2.2: A mapping of how the physical quantity is expressed in Lennard-Jones reduced units.

2.6.2 Molecular Model

As the initial polymer system is setup has a 100 bead by 100 chain system, every consecutive system is made with a constant number of atoms at n = 10000. The polymer chains are modelled as freely jointed bead-spring molecules, and the additives are represented by single beads [42]. The pair interaction between topologically unconnected particles is described by the standard truncated 12-6 Lennard-Jones(LJ) potential as modelled by the following equation:

$$U_{LJ}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + C & r < r_c \\ 0 & r \ge r_c \end{cases}$$
(2.9)

where r is the distance between the particles, r_c is the cut-off distance chosen at 2.5, and ε and σ are LJ units of energy and distance, respectively. A constant C is used to ensure that the LJ potential is continuous everywhere. For connected particles, and anharmonic interaction known as the finite extension nonlinear elastic (FENE) potential is applied in addition to LJ interaction.

$$U_{FENE}(r) = \begin{cases} -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] & r < R_0 \\ \infty & r \ge R_0 \end{cases}$$
(2.10)

Where r is a distance between neighboring segments, k is a spring constant and R_0 is maximum length of the spring. Standard parameters are used for the maximum bond length $R_0 = 1.5\sigma$, at which the elastic energy of bond is infinite, and the spring constant $k = 30\varepsilon/\sigma^2$, which is small enough to allow using a relatively large timestep while sufficiently large to prevent bonds from cutting through each other [42]. In the simulation, the equations of motion are intergrated by the velocity-Verlet algorithm with a timestep of $\delta t = 0.001\tau$, where τ is LJ unit of time expressed by $\tau = \sigma \sqrt{\frac{m}{k_B T}}$, where m is the unit mass, $T = \varepsilon/k_B$ is the temperature, and k_B is the Boltzmann constant. Periodic boundary conditions (PBC) is applied in all studied process, and simulations are carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) developed by Sandia National Laboratories [43].

Chapter 3 Results and Discussion

3.1 Single-bead additives with varying σ

3.1.1 Introduction

As polymer materials are ubiquitous in our everyday life and found abundantly in nature, their full behaviours are yet to be understood. Their low density relative to metallic materials, low thermal and electric conductivities, and plethora of applications in coatings and insulators, and nanotechnology gives rise to electrical components - transistors, with ever on-going research to better them. To manipulate these polymeric materials, the addition of small molecules to the system normally leads to the depression of the glass transition temperature T_g and a softening of the polymeric material. This phenomenon is widely known as *plasticization* which is widely exploited in applications, especially amongst materials made out of polyvinyl chloride (PVC). One of the major issues of small molecule additives in regards to the environment are the uncontrollable change in thermal and mechanical properties of the polymer. Under usual conditions, polymer materials are in contact with a gas or liquid environment, this allows for further penetration of other small molecules. This uncontrolled uptake of low molecular weight substances by the polymer leads to accelerated degradation and reduction in its life span.

There are a variety of theories suggested for plasticization [44]. Three major theories being: lubricity theory, gel theory, and free volume theory, that merely show a vague understanding of a complicated phenomena of a glass-forming material. The lubricity theory takes into account the resistance of a polymer to deformation i.e. rigidity, from intermolecular friction [45] [46]. Gel theory considers the rigidity of a polymer is resulting from a three dimensional structure formation - loose attachments along the polymer chain due to van der Waals forces, hydrogen bonding, or crystalline crosslinking [47][48]. The free volume theory explains the progressive transition from rigid to flexible due to the increase in polymer molecule mobility due to the facilitated increase in free volume brought on by plasticizer [49] [50].

While these theories draw a vague path towards the direction of mechanistically understanding plasticization, there is a lot still to explore, even from a purely finite-size effect model. Typically, a small molecule additive that has a strong interaction with the polymer melt is known to behave like an antiplasticizer, primarily at low concentrations. This phenomena is responsible for the hardening effect, explained by Chang et. al. [51]. At low concentrations these molecules are involved in a "hole-filling" mechanism involving the filling of "holes" created under high stress/deformation environments with these small molecule additives, which would effectively reduce the free volume of the system. The latter hypothesis is particularly important because in antiplasticization effect, it is generally observed when these properties are obtained by large deformation tests, whereby plasticization effects occur on small deformation thermal properties. To understand plasticization as a whole, we have stripped down the typical model to only look at how the size of a single Lennard-Jones (LJ) bead affects the overall dynamics of the polymer. It is generally understood that as the size of an additive in the system increases, the polymer chains would move apart further from the generation of increased free volume for the system. As the polymer has more space to move, it causes the polymer to soften at a lower temperature. That theory is tested with a simple LJ coarse-grained model to see the effect of small molecules on polymer melts.

The goal of this work is to develop and characterize a plasticizer model from a finite size perspective. In this work, an additive molecule from lower limit of $\sigma_B = 0.5$ to the limit of the polymer bead-size of $\sigma_B = 1.0$ are added to a coarse-grained polymer melt at varying atom fraction, ϕ_N , at typical plasticizer concentrations of 5% to 40%. The polymer model is chosen to be a fragile glass-former, that has been characterized extensively [35]. We begin by presenting the model set-up, then obtaining characteristic information of the various systems that are built and equilibrated. To understand the behaviour of these systems, characteristic temperatures and Young's modulus of the various additive manipulated systems are obtained. We find that the polymer-additive system decreases in T_g with decreasing size of additive, with respect to the polymer bead-size at unity. Interestingly, we also find that the effectiveness of the additive to reduce the Young's modulus with decreasing size of the additive to increase, with respect to the polymer bead-size of unity. This is what we observe, a decorrelation in the T_g and Young's modulus with varying size of additive at the limit of 5% to 40% additive concentration to mimic a plasticized system.

Additionally, we investigate how the additive molecules modify the polymer by characterizing certain tendencies of the system from free volume, molecular neighbours, and particle mobility. Free volume of the system is explored through the use of Voronoi tessellation to understand the spacial occupancy of the polymer and additive beads. The molecular neighbouring of the system is examined with the radial distribution function (RDF) to see packing and cluster formation of additives with the polymer chains. Finally, we investigate the structural indicator of fast dynamics in the system. By looking at the mean-square displacement, this gives an indicator at long times-scale dynamics, but short-time mean-square displacement ("propensity" or *local* Debye-Waller factor $\langle u^2 \rangle$) also shows sensitivity to the long-time mobility of the system. All these methods give insight into understanding and exploring the decorrelation in the system.

3.1.2 Methods

Molecular dynamics (MD) simulations were carried out for a coarse-grained model, in which the polymer is treated as a linear chain of N beads of mass m, which we refer to as monomers, connected by a stiff anharmonic springs that prevent chain crossing and breaking [35]. The coarse-grained polymer representation is based on the Kremer - Grest model, where both a polymer melt with and without small molecule additives are simulated. The pure polymer melt is an extensively studied and characterized model [52][53][54][55]. Polymer beads are connected by anharmonic springs modelled by Finite Extensible Non-Linear Elastic (FENE) potential equation

$$U_{FENE}(r) = \begin{cases} -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] & r < R_0 \\ \infty & r \ge R_0 \end{cases}$$
(3.1)

With the spring constant, $k = 30\epsilon/\sigma^2$, and spring extension limit, $R_0 = 1.5\sigma$.

All beads in the system interact through a conventional 12-6 Lennard-Jones potential that is truncated at 2.5σ times the particle diameter (the tiny discontinuity of the force at the cut-off distance, less than 1% of the maximal attractive part, has no consequences).

$$U_{LJ}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & r < r_c \\ 0 & r \ge r_c \end{cases}$$
(3.2)

The non-bonded potential parameters in the Lennard-Jones equation for the polymer beads (A) are taken to be unity; for the small molecule additive (B), we use $\varepsilon_A = \varepsilon_B = 1.0$ and σ_B varies in size from 0.5 to 1.1. Equal values of ε helps to promote entropic mixing in the system, while the varying values in additive size explores the effect of packing efficiency upon addition of the additive particles. The cross interaction is captured through the Lorentz-Berthelot mixing rule. The mass of the polymer beads are at unity, and the additive particles are taken to be $m_B \propto \sigma_B^3$, keeping consistent with the relative volume of the species. All quantities will be reported in units of Lennard-Jones length scale σ and energy scale ϵ , and the characteristic time is $\tau_{LJ} = \sqrt{m\sigma^2/\epsilon}$. Newton's equations of motion are integrated with the velocity-Verlet method and a time step of $\delta t = 0.001$. If ε is taken to be approximately $300k_B$, and σ_A as approximately 2 nm (a typical statistical segment size for PVC), then the unit time is roughly 20 ps [56]. Periodic simulation cells of initial size $L_x(0) = L_y(0) = L_z(0)$ containing a constant number of particles at n = 10000 with variable polymer chain number and constant polymer chain length, N = 100 beads are used with Nosé -Hoover thermostat and barostat, *i.e.* in the NVT ensemble for equilibration and NPT ensemble for production runs. All samples were generated using freely-joint-chain algorithm from the chain.py tool provided by LAMMPS in the Pizza Toolkit, thereafter all simulations are performed with LAMMPS [43]. Once generated the system is relaxed from its non-physical state, *i.e.* bead overlap, the system is first put through long chain fast-push-off DPD dynamics at T = 1.0. To enforce appropriate non-bonded interactions, the system is then equilibrated with appropriate LJ conditions for both the polymer and additive particles in an NVT ensemble at T = 1.0 and P = 0 for 10^6 MD steps, then the temperature is risen in an NVT ensemble at T = 2.0 and P = 0 for 10^7 MD steps, and finally allow the box size to relax to appropriate density of $\rho \approx 0.85$ in an NPT ensemble at T = 1.0 and P = 0 for 10^7 MD steps. The equilibration criterion is: the mean square displacement of the additive particles have explored the entirety of the simulation box twice $(\langle r^2 \rangle \propto L^2)$ or the polymer chains are well in the linear diffusive regime $(\langle r^2 \rangle \propto t)$, this ensures that every particle has had ample time to explore the entirety of the box.



Figure 3.1: A change in σ_B shifts the LJ potential along the *x*-axis. From $\sigma_B = 1.0$, decreasing the size of the intermolecular force-field shifts the LJ potential to the left.

3.1.3 Glass Transition

Glass transition is a gradual reversible transition found in amorphous materials, from a hard and brittle glassy state to a viscous/rubbery state upon heating. An explanation of this phenomena is illustrated in figure 3.2. When an amorphous polymer is cooled, the volume decreases with decreasing temperature until a glass transition temperature, T_g , is reached at which the material passes from elastomeric/rubbery regime to glassy. As the temperature is further decreased, the decrease in volume continues, however at a slower rate. If the elastomeric region of the curve is linearly extrapolated to absolute zero, giving a specific volume of V_1° , the obtained hypothetical specific volume will be too small to represent the material. If glassy region is linearly extrapolated to absolute zero, giving a specific volume of V_g° , the hypothetical specific volume is too large to present the material. To appropriately represent this hypothetical volume of the material between V_1° and V_g° , V_o is determined by the intersection point to represent the true occupied volume, while assuming V_o remains constant with temperature.



Figure 3.2: Thermal expansion and free volume diagram of a amorphous polymer. V is the specific volume; V° is the specific volume of pure and perfectly ordered material at absolute zero; V_G° and V_L° are specific volumes of glass and liquid, respectively, extrapolated to 0°K. Adapted from [5].

In essence, the free volume of the material remains constant at all temperatures below T_g and has been calculated to remain approximately constant in this region at a calculated volume which constitutes from 12% to 17% of the total volume [57]. However, with plasticization the free volume permits an increase, causing the polymer molecules to become more mobile. Traditional theories of free volume come to explain free volume by the contribution of (1) motion of the chain ends, (2) motion of the side chains, (3) motion of the main chain. To increase these motions the free volume can be increased by increasing:

- increasing the number of chains (decreasing molecular weight)
- increasing the number of side chains (increasing branching)

- increasing the chance for main chain movement by decreasing the steric hindrance and the intermolecular attraction (internal plasticization or copolymerization)
- inclusion of compatible compounds of lower molecular weight that act as if they do all the three points above (external plasticization)
- increasing the temperature

There is a derived relation by Kanig to predict the lowering of T_g of a pure polymer by the addition of plasticizers [50]. His predictions are:

- the smaller the plasticizer molecule, the more efficient it is in lowering T_g
- the efficiency of plasticizers in lowering T_g decreases with increasing concentration (the first amounts of plasticizers are more effective and increasing the amounts are progressively less effective)
- within limits, the smaller the affinity between polymer/plasticizer, as compared to polymer/polymer, the more efficient is the plasticizer (a good plasticizer is a poor solvent)
- within limits, the smaller the affinity between plasticizer/plasticizer, as compared to polymer/polymer, the more efficient is the plasticizer (the viscosity of the plasticizer should be low)

Taking the same approach from an MD point-of-view, a lot is taken into consideration. The preparation of the configurations for the system requires care. To initialize the system, polymers and small molecules are randomly arranged in a box and simulations are performed at constant temperature and pressure for a sufficiently long time in order to allow the polymer to melt and reach the corresponding equilibrium state. The temperature at the initial stage is set to $T = 1.0\epsilon/k_B$, so the thermodynamics driving force from the initial regular structure to the disordered liquid is not too high in order to avoid numerical instabilities. After the system is equilibrated at T = 1.0 and stable in the melt state, the temperature is increased to T = 2.0 and equilibrated inorder to enhance dynamics of structural relaxation. This step is useful for an efficient generation of statistically independent samples since the structural relaxation time, which determines the time-scale between independent samples, which decreases with T [58]. The extracted configurations are then cooled to T = 1.0, and are equilibrated at this temperature. Samples prepared in this way are then cooled a constant rate of $\dot{T} = 10^{-7}$ at P = 0 and the volume is allowed to fluctuate. The glass transition temperature is then determined by analysing the recorded system volume versus temperature.

To avoid undesired effects of the preparation history on T_g , the equilibrium state of the system has to be reached prior to the cooling simulations. This is achieved by a survey of the dynamics of structural relaxation, shown by the autocorrelation function of the chain's end-to-end vector (calculated with equation 3.3 and the mean-square displacement [59]. A survey of these two quantities is shown in figure 3.3 of the pure polymer system at T = 2.0. To ensure the system is relaxed appropriately by the autocorrelation function decaying to zero and the polymer beads explored the entirety of the simulation box and well within the linear diffusion region ($\langle r^2 \rangle \propto t$) as seen in figure 3.3(b). This provides evidence that the statistical independence of the samples are indeed ensured.

$$R_{EE}(t) = \frac{\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle}{\langle \mathbf{R}^2 \rangle}$$
(3.3)



Figure 3.3: Equilibration verification for pure polymer system at a temperature of T = 2.0: (a) chain end-to-end autocorrelation function is calculated and normalized for the system; (b) mean square displacement of polymer chains in the system.

Using the prepared configurations, the polymer-additive mixture is cooled under constant pressure at a rate of $\dot{T} = 10^{-7}$ and the system volume, energy, and various other parameters are recorded. A survey of the system volume versus temperature shows two linear regimes corresponding to the high-temperature liquid and low-temperature solid states. Both regions are linearly regressed, independently, and using the intersection of the two straight lines to define the glass transition temperature, as illustrated in figure 3.4. The T_g of the pure polymer system is found to be $0.423 \pm 1 \times 10^{-3}$ which is in agreement with previous study results for entangled polymers of similar sizes [35].



Figure 3.4: Specific volume and temperature plot of pure polymer to calculate glass transition temperature.

Evidently, as seen by Riggleman *et. al.*, we do see a reduction in T_g with an additive $\sigma_B = 0.5$ [14]. However, as the size of the additive is shown to increase, the T_g of the mixture becomes very close to that of the pure polymer melt, as seen in figure 3.5. There is an imposed limitation to the reduction in T_g as the size limit of the LJ bead becomes that of the polymer bead. While the reduction in T_g is significantly seen in small additive size (smaller than the polymer bead size) and increase additive concentration, ϕ_N , there is a slight decrease in T_g with the addition of additive size equal to polymer bead size. The drop in T_g for the aforementioned system is also shown to not be a jump in the system from 0% additive to 5% additive.



Figure 3.5: Glass transition temperature for additive concentration from 5% to 40% of various additive sizes. Error bars represent standard error over three independent samples.

Figure 3.6 illustrates the size effect on the T_g at an additive concentration of $\phi_N = 30\%$. Theoretically, with a non-bonded bead roaming the entirety of the simulation box, the additive should be moving polymer chains apart and causing an increase in free volume that would induce a lower T_g to occur due to more dynamic movement happening in the system. The packing efficiency of a small molecule does induce better plasticization properties, by allowing the small molecule to hop out of the cages created by the polymer melt and induce better *lubrication* between the chains to aid in softening the melt. But even with this theory, at small sizes of an additive, it holds, but this theory breaks-down as the additive size reaches the limit of the polymer bead size. This can also be explained by the viewpoint of the compatibility based on Flory-Huggins parameter, χ , of the polymer and increasing alcohol moiety chain length - the larger the alkyl chain on the alcohol moiety the compatibility drastically decreases [60]. Also, looking at a study of PMMA with residual monomeric units, if small amounts of monomer are left, it does not significantly reduce the T_g [61]. This limitation is also seen by Honary *et.al.*, using hydroxypropylmethylcellulose (HPMC) with varying plasticizer concentrations of increasing molecular weights of polyethylene glycol (PEG) showed ineffective reduction in T_g when larger plasticizers were used [62]. Physically interpreting these scaling of this problem, the statistical segmental size of the plasticizer reaching the statistical segmental size of the polymer would result in ineffective reduction to T_g .



Figure 3.6: Glass transition temperature for 30% additive concentration of varying additive sizes. Error bars represent standard error over three independent samples.

To verify that this phenomena is not an anomaly in calculation, figure 3.7 explores the behaviour of the T_g fitting based on the points chosen above and below the glass transition region and how the shift in transition comes about. The graph is constructed by looping

through all possible combinations of points above and below the glass transition zone, T > 0.5 and T < 0.3, respectively. The number of points sampled above the glass transition region are plotted with a varying number of points below the glass transition zone with the gradient representing the change in T_g calculated from the intersection point of the various linear regressions over the fluctuation of points. From the results, all T_g values, for consistency across all systems, uses 60 points in total, which allows for the T_g to be in the same statistical significance as found in literature for polymer systems of this size.



Figure 3.7: The fluctuation in Tg is captured by the number of points chosen above and below the glass transition temperature. The x-axis are the number of points above glass transition region, while the spread of points (in increasing circle size from bottom to top) represents the number of increasing points below glass transition region. The colour-bar represents the variation in T_g as the number of points below the glass transition region increases.

There is a very interesting find in how the change in the size of an additive is giving interesting dynamics. However, this limitation does challenge the general free volume theory intuitively understood for plasticization.

3.1.4 Tensile Test

Elastic moduli of the various polymer systems with different concentrations and size of the small molecular additives are measured by conducting tensile deformation simulations. For this test, the simulation box is deformed in the positive and negative z-directions with a constant true strain rate of $\dot{e} = 0.0327/\tau$ [63]. This change in box dimension, elongation of simulation cell, with respect to time is modelled by equation 3.4, with L_0 being the box length before deformation.

$$L(t) = L_0 \exp\left(\dot{e}\Delta t\right) \tag{3.4}$$

The deformation simulations were conducted under NPT condition with the no pressure applied on the x and y directions. This allows for a dynamic response to occur in one dimension and the fluctuation in pressures can be used in the tensile deformation calculations. The tensile stress σ_{ts} and the engineering strain ϵ_{ts} are calculated by equation 3.5 and 3.6, respectively.

$$-\sigma_{ts} = P_z - \frac{1}{2} \left(P_x + P_y \right)$$
 (3.5)

$$\epsilon_{ts} = \frac{L - L_0}{L_0} \tag{3.6}$$

Equation 3.5 uses pressure: P_x , P_y , and P_z in the Cartesian coordinates to calculate the stress induced by the deformed box. In equation 3.6 correlates the final box length in z-direction, L, to calculate percent elongation or induced strain. The resultant curve is shown in figure 3.8. The Young's modulus for the pure polymer system is found to be 34.3 ± 3.4 .



Figure 3.8: Resultant stress-strain curve of pure polymer system at T = 0.1.

To investigate the mechanical properties induced by the small molecule additive component, tensile deformation tests were performed. This is processed in MD as an elongation of the simulation box at a constant true strain rate. To calculate the Young's modulus of the system, entire stress-strain curve is examined and focus is put on the elastic region. Due to high levels of noise when deforming the system, system averaging is done to filter the noise without losing important artifacts from the signal. To achieve better signal processing, signal averaging is achieved by running the same simulation with varying initial velocity seed numbers. By changing the initial velocity of the un-strained system, it allows for changes in initial momentum of the system to aid in signal-to-noise ratio reduction. This signal averaging is done approximately 50 times. Not all the noise can be eliminated from these curves (without intervention of external signal filtering processes), hence to fluctuations in modulus values. The final signal is then examined in the elastic region and a linear regression is done < 2% of the elastic region by both statistical and visual inspection of the curve. Figure 3.9 shows the cumulative result of all the system and their respective Young's modulus at T = 0.1. With increasing concentration of additive the modulus is shown to decrease, and with increase size of the additive the modulus is shown to decrease. Larger additive size is



Figure 3.9: Young's modulus calculated for T = 0.1 at varying additive size and concentration. Error bars represent standard error over three independent samples.

shown to be better polymeric softeners but not as effective at T_g reduction.

There is evidently temperature dependence on the modulus value, with increasing temperature the modulus would decrease due to the softening of the material with the introduction of more energy causing mobility of the particles to increase. To illustrate the temperature dependence on Young's modulus for additive sizes of $\sigma_s = 0.5$ and $\sigma_b = 1.0$ at additive concentrations of 5% and 30% are shown in 3.10 in reference to the pure polymer Young's Modulus. This is to show how the antiplasticization effects are more pronounced at a concentration of 5% for the σ_s case, which is validated by Riggleman *et.al.*. The signicance of the temperature cross-over shown between small molecule additive and pure polymer shows the small additive becomes softer when closer to the T_g of the pure polymer [17]. The antiplasticizer is indeed stiffer in the glassy state, The σ_b is obvious in showing plasticization effects from glassy to rubber state by always being below the pure polymer modulus values and having no cross-over points occur during the T_g period. The temperature dependence of Y is obvious, but it also shows when the additive system is most likely to change in stiffness; σ_s is stiff in the glass region until the glass region of the pure polymer is reached, while the σ_b is always a softer system.



Figure 3.10: Temperature dependence of Young's modulus of systems with small, $\sigma_B = 0.5$ (blue) and large, $\sigma_B = 1.0$ (red) additive sizes in comparison to pure polymer (green). Error bars represent standard error over three independent samples.

As the modulus of the polymer depend on both the cohesive energy and mobility of the system; this explains at temperatures below T_g there is lower molecular mobility which could be resulting in a higher T_g , but the opposite is noticed above T_g . This is intuitively understandable as the system is heated it becomes more pliable due to higher molecular mobility and increase in free volume for the chains the move freely in - especially in the case of an amorphous polymer. Even with a system built with entanglements, the temporary crosslink nodes do play a role in gelation and increasing strength but are all factors that would be temperature dependent.

To further explore the continuity of the system by varying the size of the additive for values between $\sigma_B = 0.5$ to $\sigma_B = 1.0$, figure 3.11 the change in Y with temperature with reference to the pure polymer Y at the respective temperature. At the two concentrations of 5% and 30% there is shift in behaviour of the system and especially how pliable it becomes with the addition of the additive which does induce plasticizer abilities. Although it is much harder to calculate the Y at $T > T_g$ (melt state deformation induces a lot more noise), increasing the additive concentration does reduce the Y and larger additive size does still induce greater Y reduction compared to its smaller counter-part.



Figure 3.11: Temperature dependence of Young's modulus of systems with varying additive size. Error bars represent standard error over three independent samples.

To summarize the findings from the first two sections: figure 3.12 shows a clear decoupling between T_g and Young's modulus for increasing additive size. There is a size limit to the amount of plasticization the polymer melt can experience by an attractive additive molecule. There needs to be a balance in size with the polymer monomeric unit size to ensure sufficient reduction in both T_g and Y.



Figure 3.12: Glass transition temperature and Young's modulus for 30% additive concentration of varying additive sizes.

3.1.5 Voronoi Volume Fluctuations

The concept of free volume has been long utilized to explain glass transition phenomena and behaviour of glassy materials. It is a concept that is widely accepted by its simplicity and intuitive plausibility. The approach to calculating the unoccupied space surround the particle (molecule) is found using the technique of Voronoi tessellation [64]. The algorithm subdivides the space into space-filling convex polyhedra surrounding each atom [65]. With positional information about the atomic centers, the Voronoi polyhedra are unambiguously defined and the distribution of free volume is calculated in reference to the size distribution of the constructed polyhedra.

Following suit with previous reports the structural properties are investigated using a Voronoi tessellation of the space [66][67][68][69]. The focus is both on the pure polymer and the pure additive species within the system. Looking at both species gives insight into volume occupancy, especially when looking at the system below the glass transition temperature which makes it exhibit a very high degree of cooperativity. Using the trajectory files of various additive sizes at concentrations from 5% to 40% and at temperatures of T = [0.1, 0.2, 0.3, 0.4]. All Voronoi distributions are normalized by the volume of the central particles (polymer or additive size) of interest.

Figure 3.13 shows the probability distribution function (PDF) of how the system volume occupancy is distributed by additive and polymer bead size. The systems are normalized to their respective bead size. At lower concentrations of additive the polymer system shows more variance in volume distribution as the concentration of the additive is shown to increase. However, for the polymer with an additive size of $\sigma_B = 1.0$ shows negligible change in volume.



Figure 3.13: Probability distribution function of Voronoi volume from systems with additive sizes of $\sigma_B = 0.5$ and $\sigma_B = 1.0$ at a temperature of T = 0.1.

The rest of the systems are compared in figure 3.14 by seeing the change in average Voronoi volume at its respective additive size and additive concentration. As particle size increases, the polymer free volume increases to a region where the polymer Voronoi volume of the mixture is now that of the pure polymer species. As the concentration of the additive increases, the polymer volume is also decreasing, this is due to the system size being the same allowing for the number of particles to be placed in the same box, so as the additive fraction increases the number of polymer chains decrease for consistency of the system size. The additive Voronoi volume has the same sort of trend, but obviously the spacial volume per atom decreases as more are packed together and size increases.



Figure 3.14: Mean Voronoi volume of (a) polymer and (b) additive, for T = 0.1 at varying additive size and concentration.

As figure 3.14 shows the influence of additive size on polymer and additive Voronoi volumes at a temperature in the glassy state, figure 3.15 explores the temperature dependence of the system. As the temperature is increased, the obvious trend of the polymer free volume increasing is noticed while the opposite is seen for the additive particles - this is due to the packing density from the number of particles in the system and how the particles size influence spacial distribution in their confined spaces. For the case of $T > T_g$, found in Appendix A.1, there is a monotonic trend in Voronoi volume since at higher temperatures, higher the energy of each particle resulting in more movement to allow the particle to occupy more volume.



Figure 3.15: Mean Voronoi volume at 30% additive concentration for polymer and additive below T_g at varying additive size.

It is understood that particle free volume has a large influence on the modulus of the system, and that is also seen to in the behaviour of our system as well. Figure 3.16 shows the polymer mean Voronoi volume of both polymer and additive, and as the Voronoi volume is shown to increase with additive size, the Y is shown to decrease, this is directly correlated to the trend shown in the proposed decoupling model. Also, the particle size dependence seen from both the polymer and additive $\langle V_v \rangle$ resonates with the decorraltion between T_g and Y.



Figure 3.16: Young's modulus as a function of Voronoi volume in terms of both the polymer and additive, a concentration of 30% additive at a temperature of T = 0.1.

3.1.6 Radial Distribution Function

Radial distribution function (RDF) or known as g(r) is a type of pair correlation function that defines the probability of finding a particle at a distance r from a reference particle. The RDF is strongly dependent on the state of matter in question. This is calculated by taking the ratio of density of atoms at a distance r, over a control area dr, by the overall density - this gives a relative density of atoms as a function of radius. Figure 3.17 illustrates the calculation to find the location and density of neighbouring particles with respect to a reference point.

$$g(r) = \frac{\rho(r)}{\rho} \tag{3.7}$$



Figure 3.17: Schematic of how g(r) is computed, with the red being a reference atom, the blue being the atoms found within the force cut-off.

As the RDF gives probability of finding an atom in reference to another, within these shells the *number* of atoms interacting with the reference particle can be calculated. This value is known as the coordination number, defined by equation 3.8 [70]. This equation shows the calculations for the number of particles in the first solvation shell defined as the integral of the first peak of g(r) bounded between r = 0 at $g(r) \approx 0$ to the first minimum, r_1 .

$$n_1 = 4\pi \int_{r_0}^{r_1} r^2 g(r) \rho dr \tag{3.8}$$

Particle packing and distribution gives an insight to how the particles influence each other in the system. For the cases of $\sigma_B = 0.5$ and 1.0, the RDF plots at varying concentration are down in figure 3.18 at T = 0.1. The polymer interacting with the additive has the most interesting RDF - at small additive size, there is prominent aggregation shown in the second solvation shell, but that disappears as the additive size increases. This can be explained by the mobility of a smaller particle being much higher than larger ones and with the argument of particle spatial occupancy, more smaller additives would be able to occupy the polymer cages formed, compared to its counterpart.



Figure 3.18: Radial distribution function between polymer beads and polymer-additive from systems with additive sizes of $\sigma_B = 0.5$ and $\sigma_B = 1.0$ at a temperature of T = 0.1.

For all the concentrations and sizes tested in the model, it is interesting to see the trends as shown in figure 3.19. The static properties of the confined polymer shows a decrease in coordination number of a polymer, while the opposite is seen with the additive. This is a good measure of conformational properties of polymer melts. It is well understood that the coordination number of a linear polymer grows with $N^{1/2}$ [71][72]. For this case, the number of contacting molecular pairs per polymer is defined by the coordination number, where two polymers of which at least one monomer-monomer pair is closer in space than σ are regarded as contacting pairs. The decrease in the coordination number with increasing additive size in figure 3.19(a) shows how the polymer is not able to see more molecules of its own type causing potential break in the glass-forming ability of the polymer melt - the presence of a T_q comes from the polymer melt and minor reduction would be exhibited from very weak molecular interactions. As the mixture RDF seen in 3.19(c) also confirms how the polymer is in contact with more additive molecules with increasing additive size and the additive molecules clearly show a larger neighbouring effect as the size increases in 3.19(b), there is a disturbance associated with the polymer to become a better glass-former at a lower temperature even with the increase in free volume shown in the polymer Voronoi volume plot in 3.14.



Figure 3.19: Coordination number calculated from the first solvation shell at additive concentration of $\phi_N = 0.30$ between respective atoms: (a) Polymer-Polymer, (b) Additive-Additive, (c) Polymer-Additive.

3.1.7 Particle Mobility

As the dynamics of the molecules in the associated volume collide and re-collide with each other, the observational trajectories of any given molecule in the system will find that it meanders erratically and randomly. There is no directed motion due to the Newtonian behaviour implied on the imposed particles, to quantify the dynamics of such transport can be captured through the mean-square displacement. This is the measure of the average distance a molecule travels with the definition given from equation 3.9.

$$MSD(t) = \langle \Delta \mathbf{R}_i(t)^2 \rangle = \langle \left(\mathbf{R}_i(t) - \mathbf{R}_i(0)^2 \right) \rangle$$
(3.9)

This equation calculates the vector distance, $\mathbf{R}_i(t) - \mathbf{R}_i(0)$, travelled by molecule *i* over a time interval of length *t*. Where this distance is then averaged over all molecules in the system. To understand the motion of the molecule over the desired time evolution, there are distinct regions of the MSD curve that characteristically explain the motion of the molecule. Figure 3.20 illustrates how the polymer melt moves over time. It first starts off by encountering no other molecules causing it to travel ballistically, and then the distance it travels would be proportional to the time interval making the distance increase quadratically with *t*. For dense systems and especially glass-forming systems, like a polymer melt, there is a plateau region where caging effect of the polymer occurs, this region decreases significantly with increasing temperature. Also, as the system becomes denser the quadratic region becomes shorter, the molecules are then in the linear region of the MSD $\propto t$, this will be the diffusive region (as correlated to the Stokes-Einstein equation for diffusivity). The growth rate of the MSD is dependent on the molecules suffering collisions. As the density increases so does the molecules impedance to movement which causes longer to achieve the diffusive region.



Figure 3.20: Mean square displacement schematic for the Rouse model. Reproduced from [6].

Glassy systems take longer to achieve a full MSD curve, especially at such low temperatures - it is nearly impossible. Figure 3.21 shows how the system with different additive sizes affect the polymer dynamics at small and large additive sizes, as well as concentration effects on the polymer melt, all measured at a temperature of T = 0.1. Observing the behaviour deep in the glassy regime reveals interesting results for the aforementioned decorrelation. Figure 3.21(a) shows the system at $\sigma_B = \sigma_s = 0.5$, and as the concentration of the small additive increases, the plateau region decreases. But, for the system with $\sigma_B = \sigma_b = 1.0$, increasing concentration there results in very minimal increase in the plateau region. The dynamics of the polymer with σ_b does not change significantly compared to the dynamics with σ_s . Figure 3.21(c) shows with increasing additive size the plateau also increases. The mobility of the smaller particle increases mobility of the polymer. To search further in mobilization of the particles, figure 3.22 shows the polymer system at T = 0.3, 0.4, 0.8, this represents the polymer within the glass transition region, just above the glass transition temperature, and as a full polymer melt, respectively. From figure 3.22 at T = 0.3, although σ_b has a greater plateau than σ_s , the latter escapes the plateau region first. This is more pronounced in the T = 0.4 case. This means the small additive case allows the polmyer to

escape the caging earlier even though the plateau region from the MSD is lower than that of a larger additive. This can further help to explain why smaller additives are better at reducing T_g while not being as effective at reducing Y. The high temperature cause from figure 3.22 shows as increasing the additive size, the polymer melt increases in dynamics.



Figure 3.21: Mean-square displacement at T = 0.1 of polymer for the following systems: (a) additive size of $\sigma_B = 0.5$; (b) additive size of $\sigma_B = 1.0$; (c) additive concentration of $\phi_N = 0.30$. Pure polymer melt MSD is represented at $\phi_N = 0$.


Figure 3.22: Mean-square displacement of polymer with 30% additive for the following systems at T = 0.3, 0.4, 0.8.

To explore the dynamics of the additive particles in the system, figure 3.23 shows the MSD of additives in the system at T = 0.1, 0.3, 0.4, 0.8. Similar to figure 3.22, the systems are showing the behaviour of the additive particles in the deep glassy region, the glass transition region, just above the glass transition region, and the system as a pure liquid, respectively. The additive at T = 0.1 has a higher plateau at σ_s compared to σ_b , and this result is consistent with increasing temperature. The smaller particle has greater mobility, which is understandable by the nature of the size and mass of the particle the diffusivity would be greater than that of a larger particle.



Figure 3.23: Mean-square displacement of additive with 30% additive for the following systems at T = 0.1, 0.3, 0.4, 0.8.

From looking at dynamics at the glass transition region from both the polymer and additive MSD, the smaller particle gives rise to escaping the caging regime earlier. This is seen in figure 3.22 with the polymer MSD at σ_s , with a lower plateau, moves in to α relaxation earlier - this is further validated by figure 3.23 with the smaller additive particle having greater mobility in comparison to its counter-part. This is also consistent with the study by Li, *et. al.*, explaining that plasticization is reflected in the long-time relaxation of the polymer where the plasticized polymer chains escape the dynamically arrested stage at shorter time scales [73]. The smaller additive is able to move and jump to more polymer cages produced from the entanglement of the chains. This aids in the reduction of T_q much more easily by separating more chains compared to the larger additive case.

For a more comparative approach of MSD curves, the Debye-Waller factor, the meansquare particle displacements $\langle u^2 \rangle$ in some caging time, provides a short-time relation for particles in various system and also a local measure of stiffness of the material [74]. An ideal model would have particles assumed to be localized by a harmonic potential in their confined space - where the reciprocal of stiffness would be a measure of the compliance of a material, the $\langle u^2 \rangle$ can be interpreted as a measure of molecular compliance $\langle u^2 \rangle$. This quantity is a measure that can qualitatively capture the true elastic moduli of the material at temperatures below T_g . By looking at the measure for both polymer and additive for the desired system, it can reveal microscopic information about the macroscopic phenomena at question. The findings of $\langle u^2 \rangle$ are also advantageous due to the measures being able to be captured experimentally through the means of inelastic neutron or x-ray scattering.

The determination of the Debye-Waller factor, is based on the "isoconfigurational ensemble" in order to calculate $\langle u^2 \rangle$ [74][75]. This factor is also referred to as the "propensity". Typically the $\langle u^2 \rangle$ is calculated as the mean-square displacement at the average collision time, t_c for each trajectory of particles. The average collision time is defined as the time when the velocity autocorrelation function is first found to become negative, however due to the nature of the systems in this work, multiple systems with different additive sizes and concentrations gives rises to multiple t_c . To simplify this case and have a basis of comparison, $t_c = 1.0\tau$ for both additive and polymer beads. By using isoconfigurational ensemble, it allows for the system to not deviate too far from the starting point; for each trajectory a short runs of $t \approx 100t_c$ are simulated to calculate the MSD and extract the $\langle u^2 \rangle$. With multiple systems of varying additive size and concentrations, figure 3.24 shows variation in propensity of the systems. Propensity does not show dependence on concentration as much as it shows a dependence on the additive size. As the additive size is increased the propensity increases dramatically as well, this short time mobility factor gives an insight into the long-time mobility of the particles which would help in understanding how the particles behave

without all the computation effort. The main observation abstracted from the $\langle u^2 \rangle$ shows a general decrease in polymer mobility at the short time-scale with increased concentration of additive, and decreased polymer mobility with decreasing additive size (in reference to polymer bead size at unity). It is similarly seen in the additive $\langle u^2 \rangle$ as well, with increasing additive concentration the $\langle u^2 \rangle$ decreases - due to more clusters of mobile particles creating more collisions, while the additive size decreases the $\langle u^2 \rangle$ is shown to increase - smaller particles are able to move more freely in confined spaces.



Figure 3.24: Propensity values of (a) polymer and (b) additive with varying additive size a T = 0.1.

As mentioned before, the $\langle u^2 \rangle$ gives information on the local stiffness of the material as well. To explore the spatial distribution of $\langle u^2 \rangle$, figure 3.25 shows the local $\langle u^2 \rangle$ of the pure polymer melt, mixture with σ_s and system with σ_b . Each contour map are produced from the glassy configuration at T = 0.1, which local averaging of $\langle u^2 \rangle$ is found at a side length of $L \approx 2.0\sigma$. An interpretation of the Debye-Waller factor can provide a measure of the local stiffness, where $k_B T / \langle u^2 \rangle$ is an elastic constant defining the localization of the particles on time-scales between the ballistic regime and structural relaxation. This interpretation is based on the simple basiss that the particles are being harmonically confined with an idealized elastic matrix, this provides a measure of local stiffness in a qualitative sense. In reference to the pure polymer melt, the σ_s case has darker regions (small fluctuations in $\langle u^2 \rangle$), by reciprocating the $\langle u^2 \rangle$, the local stiffness would be higher. With more yellow regions in cause of σ_b , the larger fluctuations results in regions with lower local stiffness.



(a) Pure Polymer



Figure 3.25: (Colour) Local propensities in: (a) pure polymer; (b) $\sigma_B = 0.5$ system; (c) $\sigma_B = 1.0$ system. All values are calculated at T = 0.1 and at a concentration of $\phi_N = 0.30$. Values are averaged over areas of $L = 2.0\sigma$.

To correlate the decorrelation seen with the varying additive size, the lower $\langle u^2 \rangle$ would imply a higher local stiffness, which complies to the findings from the system with σ_s . To further the argument figure 3.26 compares the T_g at 30% additive with the $\langle u^2 \rangle$ of the polymer at 30% additive at T = 0.1. The relation observed is similar in nature to the nature of the T_g with increasing additive size; T_g increases with polymer $\langle u^2 \rangle$ with increasing σ_B . This counter-intuitive nature shines light on the observed decorrelation, while T_g is increasing with additive size the $\langle u^2 \rangle$ is actually correlated with Y. Polymer is shown to be stiffer in the glassy regime and less mobile at smaller additive size. The limitation seen in the larger additive size is shown to have better Y reduction but terrible T_g reduction due to the nature of the bulkiness of the additive. It is generally understood that as free volume increases - T_g decreases - Y decreases - particle mobility increases, however there is a hiccup in this knowledge from how the system is being modelled with a finite-size dependence showing a correlation break in T_g and $\langle u^2 \rangle$ being related as intuitively as it would be.



Figure 3.26: T_g as a function of propensity for polymer at a concentration of 30% additive at a temperature of T = 0.1.

The MSD results show two characteristic factors that would aid in explaining the dynamics of the system. As the $\langle u^2 \rangle$ is a measure of the height of the MSD curve, this parameter correlates well with Y. Another characteristic value of the MSD curve is the length of the plateau region - the σ_s has a shorter plateau region allowing for the polymer the escape out of caging, in comparison to σ_b , this would lead to the correlation of plateau length being correlated to T_g . Shorter MSD height and plateau region leads to increased Y and reduced T_g .

3.2 Single-Bead Additive: Ternary System

3.2.1 Overview

We explored how the T_g and Y are affected by additive size, but to check continuity and tunability of our system, a ternary system is made by varying the concentration of $\sigma_s = 0.5$ in a system with polymer and $\sigma_b = 1.0$ all at the name atom number of 10 000 beads. The same decorrelation between the T_g and Y are exhibited as shown in figure 3.30. This phenomena is shown to be persistent with varying size and concentration of a combination of sizes in a blend. This concept can be thought of as the tunability of plasticizers in a polymer blend - typically a blend of plasticizers are used to a polymeric system to fine adjust the desired parameters in the system. This adjustment in concentration of large and small molecule additives give rise to tunability in a system that would give control over processing temperature and stiffness of the resulting polymer blend.



Figure 3.27: Glass transition temperature and Young's modulus at 30% additive concentration with increasing amount of additive size σ_s .

3.2.2 Static Variable Exploration

The Voronoi volume of the ternary mixture results allow for verification of model validity. Figure 3.28 shows the temperature dependence on mean Voronoi volume as the concentration of the ternary mixture varies. The typical result is seen and verified in the previous section that discusses Voronoi volume with a decrease in mean Voronoi volume with increasing concentration of σ_s . Increasing temperature would influence larger Voronoi volumes due to potential energy of the particles increasing.



Figure 3.28: Mean Voronoi volume for temperatures below T_g of system with 30% total additive at varying σ_s fraction.

The spatial distribution of the particles gives insight into neighbouring particles. The coordination number calculated from the first solvation shell gives an idea of the number atoms in direct relation to the reference atom. Figure 3.29 (a), (b), (c) show an increase in

coordination number as the fraction of σ_s increases. This is intuitive since a larger number of σ_s would be able fill the voids created between polymer chains with an increasing number of them, which in turn would increase its self interaction as well. The opposite is seen for the σ_b atoms and its interaction with the polymer and itself.



Figure 3.29: Coordination number of all possible molecular neighbours in ternary system at temperatures below T_g .

The second solvation shell in the the $\sigma_p - \sigma_s$ interaction shows aggregation like previously

at higher concentrations of σ_s . The aggregation for the smaller additive particle explains the influence it has one entirety of the system to plasticize it at higher concentrations. The smaller particle is able to induce both a drop in T_g but not a significant drop in Y, while σ_b is able to show a drop in Y but not a significant drop in Y. The understanding of this tune-ability is important in applications of molecular blends to make adjustment for desired properties.



Figure 3.30: RDF for $\sigma_p - \sigma_s$ at T = 0.1.

3.2.3 Particle Mobility

As previously explored, the $\langle u^2 \rangle$ shows the fluctuation of the particles in short-time mobility to give an idea of the system's long-time mobility. It also shows a qualitative measure of local stiffness. Figure 3.31 compares all components of the ternary system at various temperatures to see the influence it has on the mobility and local stiffness of the particles. Generally, for all temperatures below T_g , σ_s has lower $\langle u^2 \rangle$ than σ_b and σ_p . While, σ_b is always above the $\langle u^2 \rangle$ of the polymer. This would mean the measure of the local stiffness would always be lower due to the higher induced $\langle u^2 \rangle$ of σ_b and even with a arithmetic average of the two $\langle u^2 \rangle$ from the additives, it would always be above the polymer $\langle u^2 \rangle$; consistently having a



higher fluctuation resulting in lower local stiffness.

Figure 3.31: Propensity comparison at temperatures below T_g .

To understand the particle mobility at $T < T_g$ and $T > T_g$, figure 3.32 shows the MSD of the polymer (σ_p), small additives (σ_s), and large additives (σ_b) at varying concentrations of small additives. Similar to the binary mixture, the polymer MSD shows to escape the caging region with the presence of more σ_s . Even though the plateau of system with the higher concentration of σ_s is smaller, the mobility of the particles is higher. This is validated by the dynamics of only the σ_s particle and the σ_b particle. The presence of the decorrelation is same as the binary system, and the dynamics is very similar to that of the binary system.



Figure 3.32: MSD of polymer, small additive, and large additive for $T = 0.1 < T_g$ and $T = 0.4 > T_g$ at varying small additive concentration.

Chapter 4

Conclusions and Future Work

4.1 Summary

As described above, there is a strong need to understand the dimension dependent properties of polymers not only for fundamental reasons, but also for the practical applications in the plastics industry; plasticizer size effect with a mechanistic understanding. Polymeric materials are the least understood materials, and a glass - especially the concept of glass transition - is even more vaguely understood. With the decorrelation results presented between T_g and Y, it goes to show how very little is understood about additive interactions in polymeric materials. It is necessary to design and understand schemes to eliminate effects of confinement such that the amorphous materials in confined geotries can be anticipated from their bulk properties. The work presented here helps to explore an avenue through polymer physics to meet potential goals in understanding a mechanistic view of additive size to alter behaviour of polymers.

By adjusting the size parameter in the LJ potential, the coarse-grained model presented results that question our understanding of additive confinement and interaction between polymer-small molecule systems. While at low concentration for very small additive sizes there is the exhibited antiplasticization effect as studied by Riggleman *et* al., however there is also an observed decorrelation between the T_g of the system with the Y. It is demonstrated that not only is the glass transition temperature of the system reaching the limit of the polymer while the size of the additive increases, but the Y decreases with an increase in size of the additive in the glassy regime. Upon further inspection, while Y is shown to be

correlated with the free volume of the system. The full MSD curve of the system below, at, and above T_g shows the height of the plateau $(\langle u^2 \rangle)$ correlates well with Y while the length of the plateau correlates best with T_g . The decoupling in the nature of the results is extremely interesting yet difficult to interpret the counter-intuitive nature of this behaviour. The free volume argument does not hold for the T_g due to $\sigma_p = \sigma_b$ having no change in Voronoi volume, this results in this strange limitation in results. The particle mobility and MSD illustrate the behaviour of σ_s affect on the polymer but with varying size show the counter-intuitive nature of its relation with Y rather than T_g . The overall understanding of finite-size effects shows: as additive of increasing size is added, the polymer free volume increases which in-turn would decrease the Y - making it softer and pliable, but T_g is shown to increase because the polymer and additive are not as mobile to reduce caging effect of monomeric units. With tune-ability being another avenue of understanding, the ternary system comprised of both σ_s and σ_b gives results very similar to the size effect system. The potential of exploration with this study leads to new avenues on understand polymeric materials and liquid glasses with insight into factors affect small molecule additives and their limitation on being a true plasticizer.

4.2 Future Directions

4.2.1 Complex Architecture

With the generation of such a coarse-model, a lot of detail is stripped and only the bare-bone physics is taken into account. However, to refine the model, it is an on-going battle to make the architecture more complex with the addition of bond stiffness, other types of atoms to characterize, and various other potentials to implement in the cross-interaction. However, to find potentials and parameters are always a challenge to appropriately describe the system in focus. Figure 4.1 shows the basis of a very commonly used phthalate based plasticizer. In order to understand the interaction between polymer and additive in a more detailed aspect and to not have an all-atom system built (due to an increase in computational complexity) it would be ideal to have a simple structure that can be easily equilibrated and the microand macroscopic behaviours can be studied. This can be done by the having different types of beads being expressed to characterize interaction it will possess.



Figure 4.1: Palatinol (phthalate-based) chemical structure and method to coarse-grain molecule. The different colours represent different bead types for definition in the molecular system, (blue) would be bead type 1 with different parameters from (red) bead type 2.

Another common method used to ensure appropriate chemical detailing is achieved to have desired behaviours, forward and backward mapping can be applied to have chemical species identified by it's all-atom system counter-part. This obviously requires the existence of an all-atom system, or at least have access to the applied force-field in the system to be applied to the coarse-grain model by methods like: force-matching, iterative Boltzmann, entropic matching, etc. [76][77][78].

4.2.2 Polarity Model and Potential Tune-ability

To make the model more realistic it is important to achieve a level of defined coarse-grain parameters that can help to bring a better understanding of interactions with generic polymer materials. One way to do this is to apply different polarity to the beads in order to have it represent a polymer like PVC with a hydrophobic and hydrophilic region. This can be done by changing the cut-off radius of the LJ potential to the minimum of the potential $(r_c = 2^{1/6})$. However, do keep in mind the equilibration protocol would need to be revised in order to accommodate the highly repulsive beads now introduced into the system.

With the coarse-grain model, the variability and adjustments are quite vast, this allows for the introduction of various architectures of polar plasticizers also possible. Figure 4.2 shows a generic model of what the polarity systems would entail: a bead-spring polymer with a repeating polar/non-polar backbone with additives that can be assembled in various polarity combinations in a distinct number to learn chain length effect and polarity effect from one model. This would help to understand how phthalate based plasticizers behave in a system of PVC chains.



Figure 4.2: Small chain polarity configurations.

With tuning the system with different polarities, and already exploring the tune-ability of a polymer system with two different additive bead sizes, there is also the option to tune the LJ potential itself. This can be achieved by having a LJ potential with coefficients in the attraction and repulsive terms to tune the intensity of both components. Equation 4.2.2 is used for the cross interaction to tune how the polymer and additive molecules would interact with each other - weak or strong interactions an be customized for various polymers with different χ parameters as well [79] [76]. With variable interaction potential between the two components in the system it would allow for more exploration into specific types of plasticizer interactions and even tuning σ_b to make it much more weakly attractive to the polymer - would that results in better plasticization?

$$U_{1-2}(r) = \begin{cases} 4\beta\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \alpha \left(\frac{\sigma}{r}\right)^6 \right] & r < r_c \\ 0 & r \ge r_c \end{cases}$$
(4.1)

Understanding the mechanism of plasticization with the coarse-grain model is an ideal tool to understand how the different facets of interaction, size, architecture, and system design all affect the vaguely understood phenomena.

Appendix A

Raw Data Plots of Systems

- A.1 Voronoi Volume Distribution
- A.1.1 Additive Voronoi Volume



Figure A.1: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.5, 0.6, 0.7, 0.8\}.$



Figure A.2: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.90, 0.95, 0.98, 1.0, 1.1\}.$



Figure A.3: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.4: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.5: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.6: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.7: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}.$



Figure A.8: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.9: Voronoi volume of additive at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.8, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



A.1.2 Polymer Voronoi Volume

Figure A.10: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.5, 0.6, 0.7, 0.8\}.$



Figure A.11: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.90, 0.95, 0.98, 1.0, 1.1\}.$



Figure A.12: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.13: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}$.



Figure A.14: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.15: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}$.



Figure A.16: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}.$



Figure A.17: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.18: Voronoi volume of polymer at additive concentrations from 5% to 40%. System conditions: $P = 0, T = 0.8, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.

A.2 Radial Distribution Function



A.2.1 Additive-Additive RDF

Figure A.19: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.5, 0.6, 0.7, 0.8\}.$


Figure A.20: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.90, 0.95, 0.98, 1.0, 1.1\}.$



Figure A.21: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.5, 0.6, 0.7, 0.8.0.9.1.0\}.$



Figure A.22: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.23: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.5, 0.6, 0.7, 0.8.0.9.1.0\}.$



Figure A.24: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.25: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.5, 0.6, 0.7, 0.8.0.9.1.0\}.$



Figure A.26: Additive-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



A.2.2 Polymer-Polymer RDF

Figure A.27: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.5, 0.6, 0.7, 0.8\}.$



Figure A.28: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.90, 0.95, 0.98, 1.0, 1.1\}.$



Figure A.29: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}.$



Figure A.30: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.31: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.32: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.33: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.34: Polymer-Polymer RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



A.2.3 Polymer-Additive RDF

Figure A.35: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.5, 0.6, 0.7, 0.8\}.$



Figure A.36: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.1, \sigma_B = \{0.90, 0.95, 0.98, 1.0, 1.1\}.$



Figure A.37: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.38: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.2, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.39: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.40: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.3, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



Figure A.41: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$.



Figure A.42: Polymer-Additive RDF at additive concentration from 5% to 40%. System conditions: $P = 0, T = 0.4, \sigma_B = \{0.95, 0.98, 1.0, 1.1\}.$



A.2.4 RDF Summary

Figure A.43: RDF between polymer-polymer and its first coordination number and maximum g(r) value compared between temperatures below T_g .



Figure A.44: RDF between polymer-polymer and its first coordination number and maximum g(r) value compared between temperatures below T_g .



Figure A.45: RDF between additive-additive and its first coordination number and maximum g(r) value compared between temperatures below T_g .



Figure A.46: RDF between polymer-additive and its first coordination number and maximum g(r) value compared between temperatures below T_g .

A.3 Mean Square Displacement

A.3.1 MSD of Polymer



Figure A.47: MSD of polymer value compared between temperatures below T_g .



Figure A.48: MSD of polymer value compared between temperatures below T_g .

A.3.2 MSD of Additive



Figure A.49: MSD of additive value compared between temperatures below T_g .



Figure A.50: MSD of additive value compared between temperatures below T_g .

Appendix B

LAMMPS Scripts for Simulation

```
_{1} \# Mar 26, 2016
3 # Kremer-Grest model
5 # =====
  # These settings are stored in restart
7 # system ------
           1 j
9 units
   atom_style bond
special_bonds lj/coul 0 1 1
13 # read lammps data file —
15 read_data unequil-pol-add.data
  #mass 2 0.125
17
  # force field styles ------
19
   pair_style dpd 1.0 1.0 122347  # very soft pair-potential
  pair_coeff * * 25 4.5 1.0
21
23 bond_style fene
   bond_coeff * 30.0 1.5 1.0 1.0
```

```
27 # simulation parameters -
  neighbor 0.4 bin
29
   neigh_modify every 1 delay 1
   comm_modify mode single vel yes
31
   timestep 0.01
          mydump all dcd 50000 equil.dcd
33
  dump
35 # log file -----
   thermo
             1000
37 thermo_modify
                  norm no
39
   velocity all create 1.0 17786140
41
  # bonds in initial datafile are unphysically close
43 # fix nve/limit doesn't let the system to explode during the equilibration run
45 fix
        1 all nve/limit 0.001
        500
  run
47 fix
        1 all nve/limit 0.05
  run
        500
49 fix
       1 \text{ all nve/limit } 0.1
  run
        500
51 unfix 1
  fix
        1 all nve
        50000
53 run
55 write_data tmp.restart_dpd.data
57 pair_coeff * * 50.0 4.5 1.0
```

```
velocity all create 1.0 15086120
59 run
        50
  pair_coeff * * 100.0 4.5 1.0
61 velocity all create 1.0 15786120
  run
      50
  pair_coeff * * 150.0 4.5 1.0
63
  velocity all create 1.0 15486120
65 run
        50
  pair_coeff * * 200.0 4.5 1.0
67 velocity all create 1.0 17986120
      100
  run
69 pair_coeff * * 250.0 4.5 1.0
  velocity all create 1.0 15006120
      100
71 run
  pair_coeff * * 500.0 4.5 1.0
73 velocity all create 1.0 15087720
  run
        100
75 pair_coeff * * 1000.0 4.5 1.0
  velocity all create 1.0 15086189
      100
77 run
  write_data tmp.restart_dpd1.data
79
  pair_style hybrid/overlay lj/cut 1.122462 dpd/tstat 1.0 1.0 1.122462 122347
81 pair_modify shift yes
  pair_coeff * * lj/cut 1.0 1.0 1.122462
83 pair_coeff * * dpd/tstat 4.5 1.122462
85 velocity
            all create 1.0 1508612013 \# this velocity reset is repeated 10 times
        50
  run
            all create 1.0 1508614013
87 velocity
  run
        50
<sup>89</sup> velocity all create 1.0 1508617013
```

```
run
         50
91 velocity
             all create 1.0 1508619013
         50
  run
93 velocity
             all create 1.0 1508610013
         50
  run
             all create 1.0 1508712013
  velocity
95
         50
  run
             all create 1.0 1508212013
97 velocity
  run
         50
99 velocity
             all create 1.0 1508912013
  run
         50
             all create 1.0 1508112013
101 velocity
         50
  run
             all create 1.0 1508616013
  velocity
103
  run
         50
105
   write_data tmp.restart_push.data
107
   velocity all create 1.0 15086125
  run
         2000000
109
  write_data equil.data
111
   write_restart equil.restart
```

code/equil.lmpscript

```
\# Mar 26, 2016
2
  \# insert comment
4
  shell mkdir analconf
6
  # read restart file ------
8
  variable name string pol100L-add-eq
10 read_restart equil.restart # change restart file
12 # variables —
14 variable rcut equal "2.5"
  variable sigma equal "1.0"
16 variable rmin equal "2^{(1/6)}"
18
  variable max_loop equal "3"
20 variable n_tseries index 100
  variable var_tseries_freq index ${n_tseries}
22
  # =====
24 # These settings are stored in restart
 # system -
            # default:
26
 # units lj # lj
 {}_{28} \# \text{ boundary } p p p \qquad \# p p p 
 \# atom_style bond \# CG
30
  # force field styles -----
32
```
```
34 pair_style lj/cut ${rcut}
   pair_modify shift yes mix arithmetic
            2
_{36} \# \text{ mass}
                  0.125
_{38} # polymer – full-size and long-range
40 pair_coeff 1 1 1.0 1.0 ${rcut}
   pair_coeff 2 2 1.0 ${sigma} ${rcut}
42
44 bond_style
               fene
   bond_coeff * 30.0 1.5 1.0 1.0
  special_bonds fene dihedral no extra 300
46
  # =
48
_{50} # simulation parameters –
                             # default (for LJ units): 0.4 bin
   neighbor
                0.4
                      bin
52 neigh_modify
                    delay 1 every 1 check yes # default: delay 1 every 1 check
      yes once no include all exclude none page 100000 one 2000 binsize 0.0;
     binsize = 0.0 would be automatically set to 1/2 cutoff.
   timestep
                0.001
                            # set to 0.001-tau
54 run_style
                              # default: verlet; use respa for multi-time-scale
               verlet
     problems, see documentation.
  # min_style
              cg
                          # default: cg
56
  # log file -
58
   thermo
                   1000
60 thermo_style custom step temp emol pe etotal pxx pyy pzz press lx ly lz vol
     density
```

```
\# redefine temp and press
62
   compute cpt_temp all temp/com
   compute cpt_press all pressure cpt_temp
64
66
   reset_timestep
                     0
68
   group
               grp_pol
                          type 1
                          type 2
   group
               grp_add
70
72 #group chain ends to calculate end-to-end distance
74
   variable
               \mathrm{nf}
                      equal
                              count(grp_pol)
  group
               chainend1
                            id 1:${nf}:100
76
   group
               chainend2
                            id 100:${nf}:100
                            union chainend1 chainend2
   group
               chainends
78
80
  # fix/compute styles -
82
           fix_nve all nve
   fix
           100000
  run
84
   unfix
             fix_nve
86
           fix_nvt_first all nvt temp 1.0 1.0 0.5 tchain 3 drag 0.0
   fix
           100000
   run
88
             fix_nvt_first
   unfix
90
   compute
               cpt_chunk_pol
                                grp_pol chunk/atom molecule #type
                                     grp_add chunk/atom molecule
               cpt_chunk_add
   compute
92
```

```
compute
               cpt_com_all
                              all com
94
                              grp_pol com/chunk cpt_chunk_pol
   compute
               cpt_com_pol
               cpt_rg_pol
                              grp_pol gyration/chunk cpt_chunk_pol
96
   compute
                              grp_add com/chunk cpt_chunk_add
   compute
               cpt_com_add
98
             cpt_all all
                            msd com yes
   compute
100
   compute
             cpt_pol grp_pol msd com yes
   compute
             cpt_add grp_add msd com yes
102
    fix
           fix_msd_all all ave/time 1 1 500 c_cpt_all[*] file msd_all.dat
           fix_msd_pol all ave/time 1 1 500 c_cpt_pol[*] file msd_pol.dat
    fix
104
           fix_msd_add all ave/time 1 1 500 c_cpt_add [*] file msd_add.dat
    fix
           dmp_ee chainends custom 500
                                          trajee.dump type id x y z
   dump
106
   fix
           fix_nvt_high all nvt temp 2.0 2.0 0.5 tchain 3 drag 0.0
108
           10000000
   run
                      analconf/${name}.restart.*
    write_restart
110
   unfix
             fix_msd_all
112
    unfix
             fix_msd_pol
             fix_msd_add
    unfix
114
    unfix
             fix_nvt_high
             dmp_ee
   undump
116
118
  #
  # Get multiple configurations at high temperature for statistical independence
120
   label
                      loop
                              ${max_loop}
122
   variable
                   a loop
                 ^{"}A = a"
   print
                 "$a > ${max_loop}" then "jump equil-nvt.lmpscript break"
   i f
124
```

```
"Temperature = 2.0"
    print
126
    fix
           fix_nvt_cycle all nvt temp 2.0 2.0 0.5 tchain 3 drag 0.0
           100000
    run
128
              fix_nvt_cycle
    unfix
                   analconf/${name}-${a}.restart
    write_restart
130
132
   next
                  a
    jump
                  equil-nvt.lmpscript loop
   label
                  break
134
    variable
                        delete
                    a
136
   #-
138
     fix
           fix_npt all npt temp 1.0 1.0 0.5 iso 0 0 5 tchain 3 pchain 3 drag 0.0
140 # fix
           fix_nvt_last all nvt temp 1.0 1.0 0.5 tchain 3 drag 0.0
142
  # output -
   print "----- Run 0 step to initialize some outputs. -----"
144
    run 0
    print "----- Done. -----"
146
148
  \# thermo variables
                var_xlo
                          equal
150
    variable
                                   xlo
    variable
                var_xhi
                          equal
                                   xhi
    variable
               var_ylo
                          equal
                                   ylo
152
    variable
               var_yhi
                          equal
                                   yhi
                          equal
154
    variable
               var_zlo
                                   zlo
    variable
               var_zhi
                          equal
                                   zhi
    variable var_vol
                        equal
                                 vol
156
```

variable var_pe equal pe variable var_etotal equal etotal variable var_emol equal emol variable var_epair equal epair

- ¹⁶² # these outputs are all performed BEFORE rescaling velocity/box in thermostat/ barostat, different from thermo outputs in log.lammps
- 164 fix fix_thermo_out all ave/time \${var_tseries_freq} 1 \${
 var_tseries_freq} v_var_vol c_cpt_temp c_cpt_press v_var_pe v_var_etotal
 v_var_emol v_var_epair mode scalar file thermo.dat ave one start 0
 - fix fix_boundaries_out all ave/time \${var_tseries_freq} 1 \${
 var_tseries_freq} v_var_xlo v_var_ylo v_var_ylo v_var_ylo v_var_zlo
 v_var_zhi mode scalar file boundaries.dat ave one start 0
- 166 fix fix_com_all_out all ave/time \${var_tseries_freq} 1 \${
 var_tseries_freq} c_cpt_com_all[1] c_cpt_com_all[2] c_cpt_com_all[3] mode
 scalar file com_all.dat ave one start 0
 - fix fix_com_pol_out grp_pol ave/time \${var_tseries_freq} 1 \${
 var_tseries_freq} c_cpt_com_pol[*] mode vector file com_pol.dat ave one
 start 0
- 168 fix fix_rg_pol_out grp_pol ave/time \${var_tseries_freq} 1 \${
 var_tseries_freq} c_cpt_rg_pol mode vector file rg_pol.dat ave one start 0

fix fix_com_add_out grp_add ave/time \${var_tseries_freq} 1 \${
 var_tseries_freq} c_cpt_com_add[*] mode vector file com_add.dat ave one
 start 0

```
170
```

dump dmp_pol grp_pol h5md 10000 poltraj.h5 position 172 dump dmp_add grp_add h5md 10000 addtraj.h5 position

174 **# run**

run 10000000

```
176 write_restart ${name}.restart
```

write_data \${name}.data.* pair ij

 ${\rm code/equil-nvt.lmpscript}$

```
_{1} \# Mar 26, 2016
_{3} # heating and cooling sequence to randomize system before constant cooling to
     find glass transition temperature
5 shell mkdir analres
7 # read restart file —
9 read_restart pol100L-add-eq.restart # change restart file
11 # variables -
  variable rcut
                    equal
                             "2.5"
13
   variable sigma
                      equal "0.5"
  variable rmin
                               "2^{(1/6)}"
                       equal
15
  variable s1
                             "step"
                     equal
17
                             "temp"
   variable t1
                     equal
19 variable p1
                     equal
                             "press"
                             "vol"
   variable v1
                     equal
   variable d1
                     equal
                             "density"
21
23 variable max_loop
                         equal
                                  " 6"
   variable run_step_1
                          equal
                                  1.0\,\mathrm{e5}
  variable run_step_2
                           equal
                                  1.0\,\mathrm{e6}
25
   variable tg_press
                                  0.0
                         equal
27
  # ===
29 # These settings are stored in restart
  # system -
              # default:
31
```

```
# units
         lj # lj
33 # boundary ppp #ppp
 \# atom_style bond
                          # CG
35
 \# force field styles -
37
39 pair_style lj/cut ${rcut}
  pair_modify shift yes mix arithmetic
         2
             0.125
  {\rm mass}
41
43 # polymer - full-size and long-range
45 pair_coeff 1 1 1.0 1.0 ${rcut}
  pair_coeff 2 2 1.0 \{sigma\} \{rcut\}
47
49 bond_style fene
  bond_coeff * 30.0 1.5 1.0 1.0
  special_bonds fene dihedral no extra 300
51
 # ==
53
_{55} # simulation parameters –
  neighbor
               0.4 bin
                           \# default (for LJ units): 0.4 bin
                   delay 1 every 1 check yes # default: delay 1 every 1 check
  neigh₋modify
57
     yes once no include all exclude none page 100000 one 2000 binsize 0.0;
     binsize = 0.0 would be automatically set to 1/2 cutoff.
                      \# set to 0.001-tau
  timestep
               0.001
             verlet # default: verlet; use respa for multi-time-scale
59
 run_style
     problems, see documentation.
 \# \min_{style} cg \# default: cg
```

```
61
  # log file -
63
                    1000
   thermo
   thermo_style custom step temp emol epair etotal pxx pyy pzz press lx ly lz \,
65
     vol
  \# redefine temp and press
67
   compute cpt_temp all temp/com
  compute cpt_press all pressure cpt_temp
69
71
   reset_timestep
                   0
73
               grp_pol
                        type 1
   group
  group
               grp_add
                        type 2
75
77 # fix/compute styles -----
  fix
           fix_npt all npt temp 1.0 1.0 0.5 iso ${tg_press} ${tg_press} 5 tchain
79
     3 pchain 3 drag 0.0
           \{run\_step\_1\}
   run
81
  unfix
            fix_npt
83
  # output -----
<sup>85</sup> print "----- Run 0 step to initialize some outputs. -----"
   run 0
  print "----- Done. -----"
87
_{89} # Heating/Cooling by changing temperature in NPT ensemble – Main Run
```

```
label
                      loop
91
                    a loop \{\max_{loop}\}
    variable
                  ^{"}A = a"
    print
93
                  "$a > ${max_loop}" then "jump anneal.lmpscript break"
    i f
                  b equal a^{\infty}_{a}
    variable
95
    if "\{b\} = 0" then "variable temp equal 1.0" else "variable temp equal 0.6
     ,,
             "Temperature = \{temp\}"
97
   print
    fix
            fix_npt all npt temp ${temp} ${temp} 0.5 iso ${tg_press} ${tg_press} 5
99
       tchain 3 pchain 3 drag 0.0
            \{ run_step_2 \}
    run
    unfix
              fix_npt
101
                      analres/tg.equilibrim-${a}.restart
    write_restart
103
    next
                  \mathbf{a}
                  anneal.lmpscript loop
    jump
105
    label
                  break
                         delete
    variable
                   \mathbf{a}
107
109 # run -
                       tg.equilibrim.restart
    write_restart
111
    write_data
                  tg.equil.data.*
```

code/anneal.lmpscript

```
_{1} \# Mar 26, 2016
_{3} # heating and cooling sequence to randomize system before constant cooling to
     find glass transition temperature
5 shell mkdir coolrestart
   shell mkdir tvp
  # read restart file --
9
  read_restart pol100L-add-eq.restart #tg.equilibrim.restart # change restart
      file
  # variables -
13
   variable rcut
                               "2.5"
                       equal
                         equal "1.0"
  variable sigma
15
                                "2^{(1/6)}"
   variable rmin
                       equal
17
   variable s1
                     equal
                              "step"
19 variable t1
                              "temp"
                     equal
   variable p1
                     equal
                              "press"
   variable v1
                     equal
                              "vol"
21
   variable d1
                              "density"
                     equal
23
   variable
               name
                         string polAdd-cooled
25
   variable run_step_tgeq
                                equal
                                         5.0e5
  variable tg_press
                         equal
                                  0.0
27
   variable maxTemp
                         equal
                                  1.0
  variable lowTemp
                         equal
                                  0.1
29
```

```
31 # ===
 # These settings are stored in restart
33 # system -
             # default:
35 # units lj # lj
 # boundary ppp #ppp
37 # atom_style bond # CG
39 # force field styles -
41
  pair_style lj/cut ${rcut}
43 pair_modify shift yes mix arithmetic
           2 0.125
 # mass
45
 # polymer - full-size and long-range
47
   pair_coeff 1 1 1.0 1.0 ${rcut}
49 pair_coeff 2 2 1.0 ${sigma} ${rcut}
51
   bond_style
              fene
  bond_coeff * 30.0 1.5 1.0 1.0
53
   special_bonds fene dihedral no extra 300
55 # ==
57
 # simulation parameters -----
                           # default (for LJ units): 0.4 bin
59 neighbor
               0.4
                     bin
   neigh_modify delay 1 every 1 check yes # default: delay 1 every 1 check
      yes once no include all exclude none page 100000 one 2000 binsize 0.0;
     binsize = 0.0 would be automatically set to 1/2 cutoff.
```

```
timestep
                  0.001
                               \# set to 0.001-tau
61
                                 \# default: verlet; use respa for multi-time-scale
   run_style
                  verlet
      problems, see documentation.
63 # min_style
                               # default: cg
                    cg
65 # log file ----
   thermo
                     1000
67
   thermo_style custom step temp emol epair etotal pxx pyy pzz press lx ly lz
      vol density
69
   \# redefine temp and press
  compute cpt_temp all temp/com
71
   compute cpt_press all pressure cpt_temp
73
   reset_timestep
                      0
75
               grp_pol
                          type 1
   group
77
   group
               grp_add
                          type 2
79
  # fix/compute styles -
<sup>81</sup> # Constant cooling from T^* = 1.1 to T^* = 0.1
   variable dt
                    equal 0.01
83
                               {\rm maxTemp}-{\rm dt}
   variable
               \mathbf{a}
                      equal
   variable
               \mathbf{b}
                      equal
                               ${a}
85
   label
             loop
87
   fix
           fix_print all print 1000 "${s1} ${t1} ${p1} ${v1} ${d1}" file tvp/tg-
89
      pn2-${b}.txt screen no
```

```
fix_npt all npt temp ${b} ${b} 0.5 iso ${tg_press} ${tg_press} 5
    fix
91
      tchain 3 pchain 3 drag 0.0
           ${run_step_tgeq}
    run
    unfix
              {\rm fix}\,\_\,n\,p\,t
93
    unfix
              fix_print
    write_restart coolrestart/cooling_runover-${b}.restart.*
95
                             {b} - {dt}
    variable c
                    equal
97
         "$c < ${lowTemp}" then "jump tg_coolcycle.lmpscript break"
   i f
99
    variable b
                    equal
                             \{c\}
101
   jump
            tg\_coolcycle.lmpscript loop
103
    label
              break
105
  # run -
   write_restart cooling_runover - $ {name }. restart.*
107
```

 $code/tg_coolcycle.lmpscript$

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