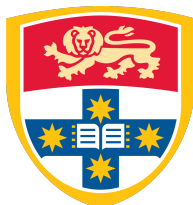


**The Role of Molecular Shape on the Properties
of the Condensed Phase:
A Simulation Study**

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A thesis submitted in partial fulfillment of
the requirements for the degree of
B.Sc. (Honours)

School of Chemistry
The University of Sydney



March 2015

Abstract

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Statement of Contribution

Write: Contributions

I certify that this report contains work carried out by myself except where otherwise acknowledged

Signed:

Malcolm Ramsay

March 2015

Acknowledgements

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CHAPTER 1

Introduction

Manipulating the formation of a condensed phase is a critical part of both nature and technology. From molluscs controlling crystal formation¹, to molecular glasses to increasing the solubility of drugs², to plastics, silicon in photovoltaic cells, and many other materials that we rely on every day. As the devices we use become smaller the need to understand the processes that form them becomes more important. A complete theory of glass formation is still elusive and our ability to control crystal formation is far from what is available to nature. To better understand the formation of the solid phase, we need an understanding of the molecular rearrangements that take place as we move from a molecular liquid, through a supercooled liquid to either a glass or molecular crystal.

The goal of my project is to explore fundamental features of molecular shape; asymmetry and concavity, influence the properties of the various condensed phases; liquid, crystal, glass and supercooled-liquid. This requires the characterisation of a new set of molecular models for computer simulation. I will be addressing how the molecular orientation and translational motion couple during crystal growth, how the degree of concavity in the molecular shape determines the dynamics of rotations and translations in the low temperature liquid phase and, to find stable structures that determine the properties of crystals and glasses and how these structures are influenced by molecular shape.

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1.1 Molecular Crystals

The unit cell is the building block of a crystal, as such it is a useful tool to be able to describe the type of crystal. It is commonly used to describe metal salts, there is the CsCl structure, or NaCl, Zinc blende and many others. These are used because they are common materials characteristic of their unit cell structure, however the names do not directly inform us of the properties of the underlying unit cell. The simplest descriptor of the unit cell is the shape of the lattice system. There are 7 of these systems representing the different shapes that can be used to pack three dimensional space. Some of these lattice systems can then be combined with a lattice centering, an extra point or points on which a molecule is placed within the lattice. Taking the cubic lattice system as an example, there is the primitive (P) lattice centering where there are only lattice points on the corner of the unit cell which is the lattice of the primitive cubic packing of spheres. The second lattice centering is body centered (I) where there is an additional lattice point in the center of the lattice system resulting in the face centered cubic lattice. There is also the face lattice centering (F) where there is an additional lattice point on each face of the unit cell, for spheres this gives the densest known packing, the face centered cubic packing. The final lattice centering is the base (C) where there is an extra lattice point on one pair of opposing sides. This lattice centering is not present in the cubic lattice system. The combination of these lattice systems and lattice centerings gives the 14 *Bravais lattices* (Figure 1.1).

While extensive, the Bravais lattices are not a complete description of the unit cell, especially in the case of molecules. There is no information on the relative orientation of molecules at each of the lattice points, the orientation of each molecule would have to be defined separately. There is a more complete description of the unit cell known as

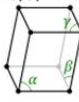
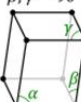
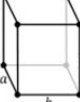

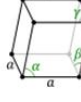

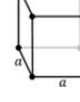


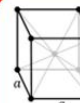


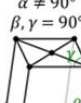

Important Bravais lattices							
	Triclinic	Monoclinic	Orthorhombic	Tetragonal	Rhombohedral	Hexagonal	Cubic
P	$\alpha, \beta, \gamma \neq 90^\circ$ 	$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ 	$a \neq b \neq c$ 	$a \neq c$ 	$\alpha, \beta, \gamma \neq 90^\circ$ 	$a \neq c$ 	
I			$a \neq b \neq c$ 	$a \neq c$ 			
F			$a \neq b \neq c$ 				
C		$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ 	$a \neq b \neq c$ 				

Figure 1.1: Modifying the seven lattice systems with lattice centerings gives the 14 Bravais lattices. TO LICENCE

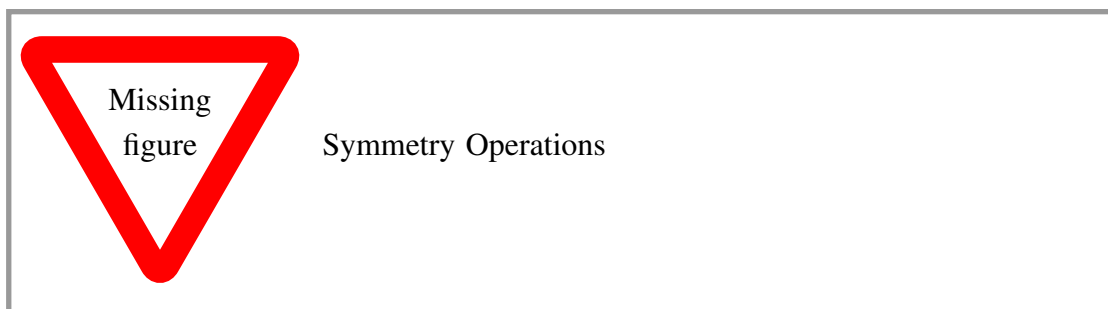


Figure 1.2: Diagram showing the symmetry operations

the *space group*. The unit cell can be completely recreated from the space group, the unit cell parameters, and the position and orientation of a single molecule within the unit cell. Space groups are the combination of a set of symmetry operations and one of the Bravais lattices resulting in 219 space groups, 230 when including chiral copies. There are five symmetry operations that are important to space groups: reflection, rotation, improper rotation (a rotation combined with a mirror plane), screw axis (rotation and translation), and glide plane (reflection and translation) (Figure 1.2). This complete description of unit cells using space groups allows simple comparisons of crystal structures.

When metallic crystals are grouped into their respective space groups there is a fairly even distribution amongst all the space groups (Figure 1.3). Do the same with molecular crystals and there is a very different distribution, the $P2_{1/c}$ space group contains over a third of all molecular crystals and the five most populous space groups contain 75 % of all molecular crystals. To explain why molecules prefer these space groups over all the others we look to the simpler case of 2D. Using two dimensions has many benefits over a three dimensional system. Computations are far quicker in two dimensions, the complexity of the calculation is often to the power of the dimension, instead of dealing with n^3 calculations there are only n^2 ; a big difference when n is large. The

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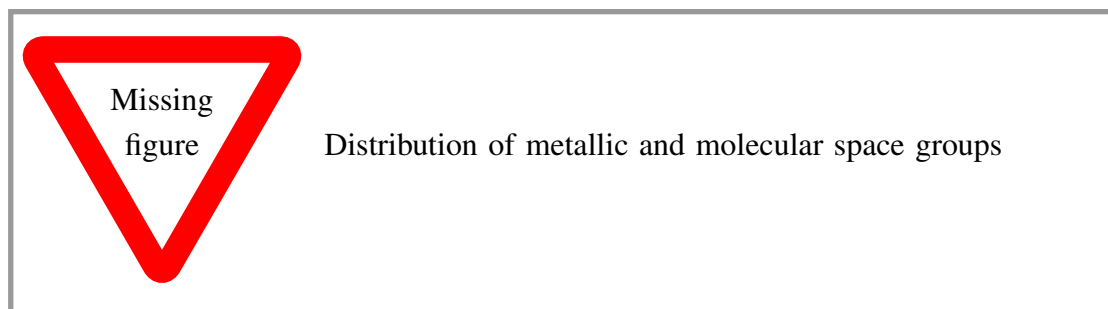


Figure 1.3: Showing the distribution of molecular crystals amongst the space groups

visualisation of a two dimensional system on a two dimensional interface such as a computer monitor or a piece of paper is also simpler, not having to deal with issues such as perspective. This makes visual identification of a pattern or property that incites Issac Asimov’s famous “that’s funny” response far more likely. Another benefit of working in 2D is that there are only 17 *wallpaper groups* (Figure 1.4), the 2D equivalent of space groups. Wallpaper groups are constructed in the same way as space groups and it is easier to identify the symmetry operations. In a similar manner to 3D we can group all the 2D molecular shapes that have been studied into their wallpaper groups (Figure 1.5). In this case there are two wallpaper groups that contain the vast majority of molecules, the p2 and the p2gg wallpaper groups. As a general guideline for the packing of 2D molecules without central symmetry, Torquato and Jiao³ suggest that the molecules will pair such that the pair will have an inversion center (Figure 1.6). The only wallpaper groups that support pairs of molecules with this inversion center are the p2 and the p2gg, suggesting that the pairing of molecules has reasonable basis. This concept of an inversion center also applies to the 3D system, the $P2_{1/c}$ space group also has an inversion center and generally inversion centers are favoured⁴.

The way that molecular crystals pack space is an important problem in simulating crystal structures. One of the methods used to find the optimal crystal structure is to model

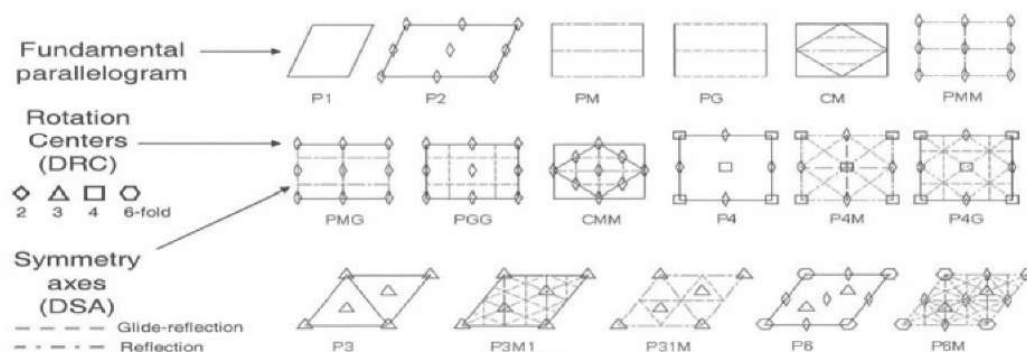


Figure 1.4: Showing all the wallpaper groups and the symmetry operations that comprise them. TODO LICENCE

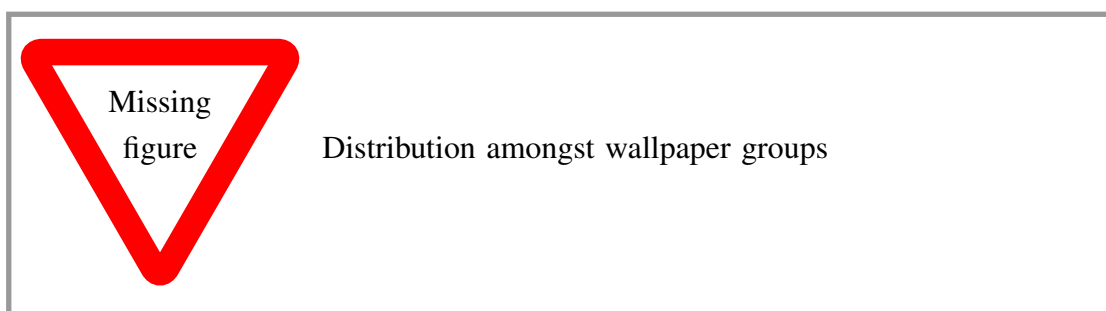


Figure 1.5: Distribution of 2D molecules amongst the 17 wallpaper groups

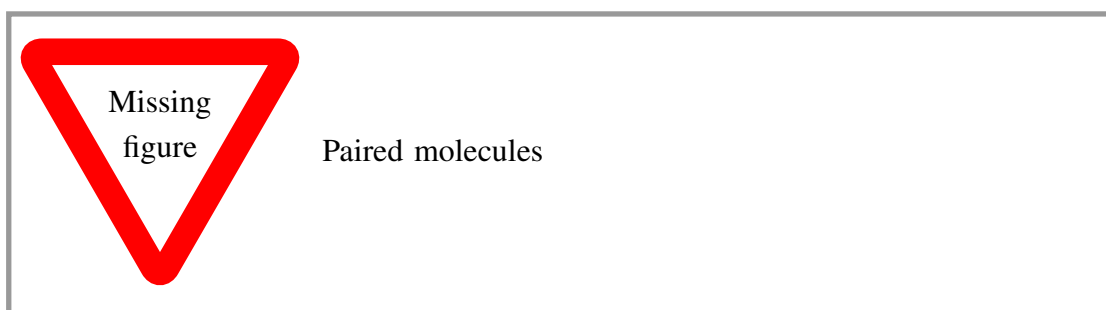


Figure 1.6: When molecules are non centrally symmetric they tend to pair creating an inversion center

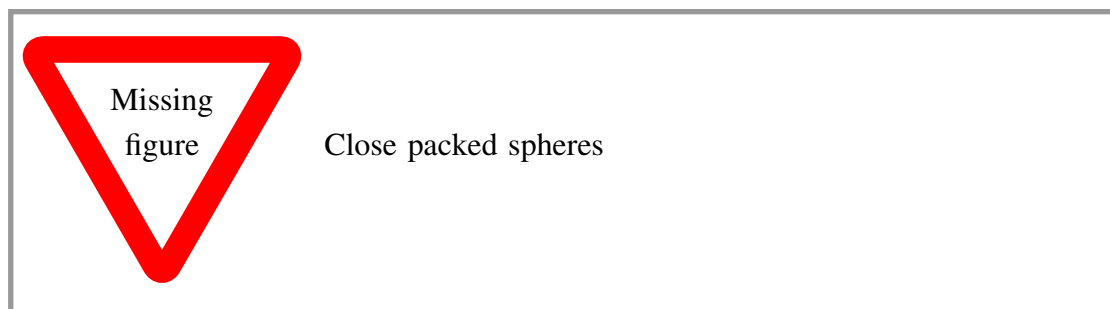


Figure 1.7: There are two structurally distinct closest packings of spheres, the hexagonal close packed structure and the cubic close packed structure

the molecule as an arrangement of hard spheres and find the arrangement of molecules that occupies the largest volume of space⁵, also known as the *packing fraction*. The simplest example of this is packing spheres, to which Kepler proposed that the hexagonal close packed structure was the most efficient in 1611⁶. The hexagonal close packed structure has the same packing fraction as the face centered cubic structure despite being structurally distinct. While these structures have been considered the best possible packing of spheres in space for hundreds of years there has not been a mathematical proof until recently. In 2005 Hales⁷ published a 400 page proof of this problem of which mathematicians were 99% certain was correct. Nearly 10 years later Hales *et al.*^{hales:14} announced the completion of a project to completely satisfy the proof, using computers to check all possible configurations.

If finding a proof for the simplest of shapes was so difficult, how hard is it going to be to find closest packings for arbitrary shapes. While having a mathematical proof of the closest packed structure is nice, it is not necessary to perform useful chemistry, using the closest known packed structure is a reasonable alternative. Without the requirement for proof of correctness the problem of finding the closest known packing of arbitrary shapes becomes far simpler. The degrees of freedom of the particles can be considered

a multidimensional space with the value at each point in space being the packing fraction (Figure 1.8), finding the solution is now a case of finding the global minimum of this multidimensional function. Finding the global minimum of a function is a problem that appears in many fields, including computer science. As such there are a number

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of algorithms that can be used in an attempt to find the global minimum . It should be noted that the only method that guarantees finding the global minimum is to evaluate packing fraction at every possible configuration. This is not computationally possible for any reasonably sized system, the number of points required scales exponentially with the number of molecules, quickly running into calculations that would take longer than the age of the universe. Many of these approximations use the concept of sim-

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ulated annealing . This is the process by which the configuration is given an amount of energy to move around the configuration space, moving out of a configuration that has a low packing fraction happens with a high probability, while moving out of a well where the packing fraction is high occurs with low probability. The probability of the configuration moving scales with the energy, as the energy is slowly reduced only the best configurations are sampled. If the energy is reduced slowly enough the global minimum is the final configuration, however there is no way to determine beforehand what slowly enough is. This concept comes from the process of glass formation which will be discussed in (Section ??) and many of the same concepts hold.

Much of the work that has been done in determining best packed structures has dealt with convex particles. These are fairly easy to pack efficiently. The shape with the worst packing efficiency of a centrally symmetric convex shape in 2D is the curved octahedron

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with a packing efficiency of 0.90 . While dealing with the packing of convex shapes is suitable for metallic crystal, when dealing with molecules concavities appear when holding two touching spheres in any orientation (Figure 1.9).

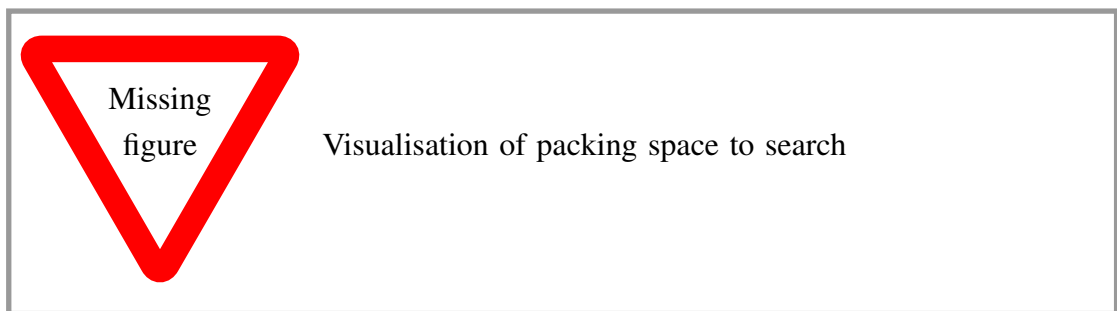


Figure 1.8:

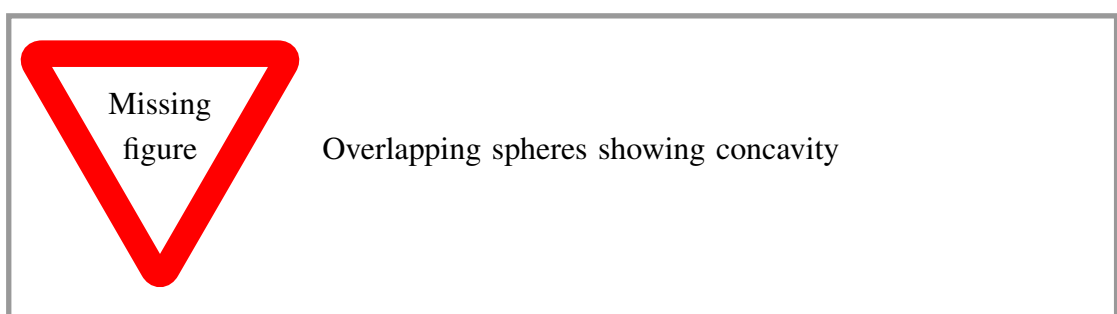


Figure 1.9:

Write: results of packing stuff

Along with categorising the crystal structure the unit cell of a crystal structure is also responsible for many of the properties of the resulting material.

Write: Properties of solids, magnetic, conductivity, brittleness, piezoelectric

Write: Link to liquids - Properties of the crystal degrade when transitioning to the liquid phase

1.2 Molecular Liquids

The liquid phase is defined by its incompressibility and its ability to flow. There are two forces at play that define this behaviour. The ability to flow is comes from the energy of the particles, they have enough energy to move out of their local environments, but not enough to escape the attractive forces of the neighbouring particles as they flow around them. This attractive force is integral to the liquid phase, if the force is too short range or not present then the liquid phase does not exist, only the solid and gas phases will form.

When considering the process that occurs when a liquid flows, molecules must move away from their optimal position and around neighbouring molecules. If the attraction is too small at these larger distances there is nothing stopping the molecule flying off and becoming a gas. The other important force in a liquid is the repulsive force which is responsible for the structure of the liquid. A common measure of the structure of the liquid phase is the *radial distribution function* (Figure 1.10) denoted $G(r)$. It can be calculated by

$$G(r) = \text{maths} \quad (1.1)$$

where $g(r)$ is defined. In essence it maps the probability of finding molecules at a distance r from any particle, however unlike a probability the radial distribution function is normalised to $N - 1$ where N is the total number of particles in the system. It can also be expressed as the term that when multiplied by the density ρ gives the local density around a particle. The radial distribution function gives a very clear distinction between the crystal, and liquid and gas phases (Figure 1.10). In the liquid phase we can see there is a region of excluded volume at small r , this is the result of the repulsive force, the apparent size of the molecule. Beyond the excluded region there is a sharp peak corresponding to the shell of nearest neighbours around the central molecule. It is the excluded region and short range ordering that results in the incompressibility, there is nowhere for the particles to move upon compression because of the repulsive force. The final part of the radial distribution function is the long range behaviour, for liquids there is no long range ordering, while for crystals there are peaks out to very large r . The radial distribution function is very useful when modelling systems where it is easy to calculate the distance between each particle, for experimental systems this is not possible. The usefulness of the radial distribution function is that it can be linked to a directly measurable quantity, the *static structure factor* by a Fourier transform

$$G(r) = \text{some function, structure factor} \quad (1.2)$$

The static structure factor can be experimentally determined by taking the x-ray diffraction pattern of a sample providing the link between experimental and theoretical systems. Along with the structural differences between a liquid and a crystal there are also significant dynamical differences.

Two common dynamic properties of a liquid are the viscosity and diffusion. The viscosity (η) of a liquid is a property of the bulk liquid measured in P or *units of poise*.

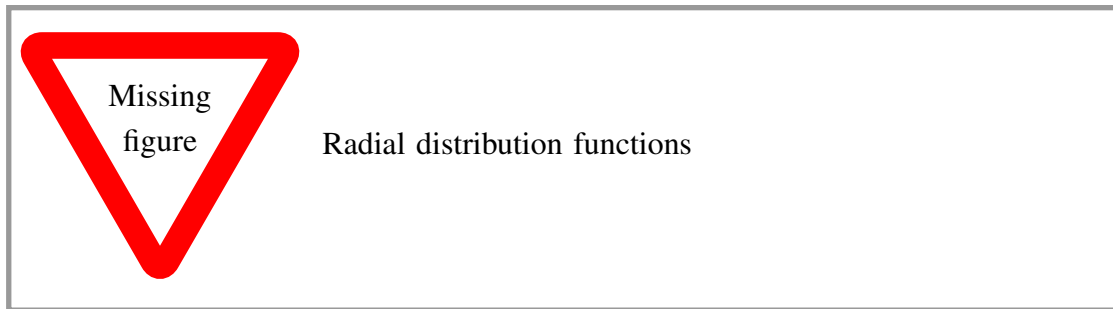


Figure 1.10:

The viscosity is a temperature dependent quantity, following an Arrhenius curve

$$\eta = \text{Arrhenius} \quad (1.3)$$

where T_0 is the viscosity at a known temperature T_0 , K_B is the Boltzmann constant, and E_a is the activation energy. In this case the activation energy can be considered the energy required to move past the nearest neighbours. The Arrhenius relation holds because this activation energy remains constant throughout the temperature range. The viscosities of some common liquids are shown in (Table ??) showing the range that viscosities take. The other dynamic property is diffusion, this is a property of individual molecules. Diffusion in liquids is described by *Brownian motion*, first postulated by

[Check Einstein in 1911](#). The motion of particles is described by a differential equation

$$\text{Brownian motion} \quad (1.4)$$

which is broken into two parts, a stochastic function ($A(t)$) responsible for the randomness of the motion as well as a term for the force a particle requires to move through the liquid, a similar concept to the activation energy. The stochastic nature of this differential equation requires that it be solved as an ensemble average, with the motion of any single

particle being random solving for a particular particle results in a random solution. This ensemble averaged solution gives the result that at short times relative to ζ^{-1} the mean squared displacement (MSD) is dominated by ballistic motion from the local vibrations of particles. However looking to longer times we get a relation

$$\text{Diffusion constant relation} \quad (1.5)$$

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where . This can be simplified by

Write: define diffusion constant

Write: Link diffusion constant and viscosity

When dealing with molecules, along with the motion of the molecules the rotations of the molecules is also important.

Write: rotational relaxations

1.3 Supercooled Liquids

Supercooled liquids are an important part of forming the solid phase. At the melting point of a crystal T_m both the liquid phase and the solid phase have the same free energy, there is no preferred state. However along with the energy of each phase there is also an energy penalty at the boundary of each phase, this means that for crystal formation to occur there has to be free energy gained by the formation of the crystal that offsets the penalty of the surface effects. The free energy of the crystal phase is only lower than the liquid phase when the liquid is supercooled. The free energy

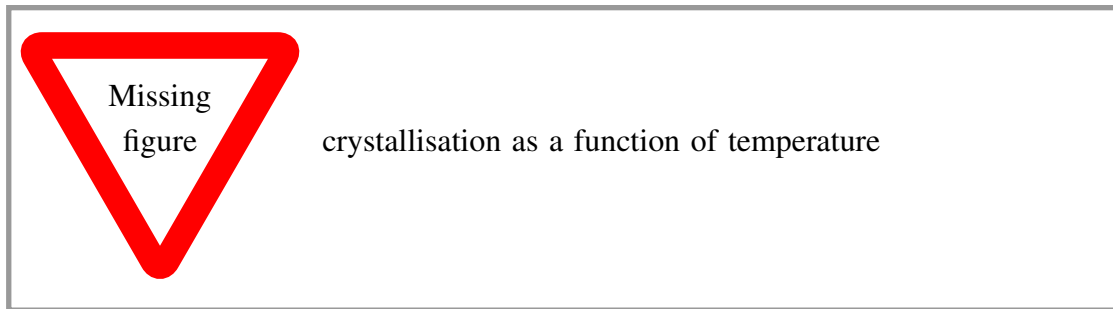


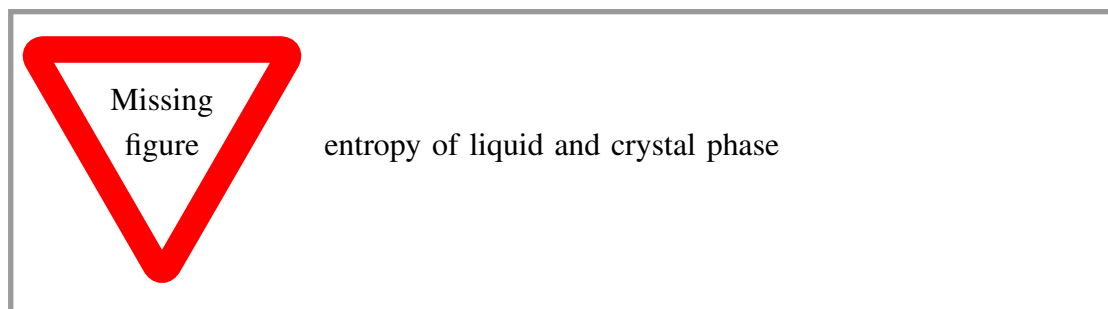
Figure 1.11:

gained by the crystal phase scales with the supercooling, increasing the speed of crystal growth just requires reducing the temperature. Reducing the temperature will increase the growth rate of the crystal while the nucleation event is limiting the growth. As the temperature decreases the diffusion constant increases (Section ??), this also means that the movements at the interface of the crystal to get molecules to align become slower, this is also well pronounced in the rotations of molecules. These two competing forces result in a temperature dependence on the rate of crystallisation that for some supercooling has a maximum rate of crystallisation (Figure 1.11).

If we are dealing with a system containing a constant number of particles, constant temperature and constant pressure, the standard conditions when working in a laboratory, the free energy that we are concerned with is the *Gibbs free energy* (G). The change in free energy can be calculated using

$$\Delta G = \Delta H - T\Delta S \quad (1.6)$$

where ΔH is the change in enthalpy and ΔS is the change in entropy. The temperature dependence on the entropy is the reason that larger supercoolings promote nucleation. The entropy of the system is also a temperature dependent quantity which scales with



the number of degrees of freedom. In a crystal molecules are far more constrained than in a liquid giving the temperature dependence of entropy a more gradual slope (Figure 1.3). The result of this is that if the supercooled liquid can be kept in the liquid state there is a point at which the entropy of the liquid is below that of the crystal. Continuing this down to absolute zero the entropy will at worst track the slope of the crystal meaning there is a lower entropy state than the crystal at 0 K. This is known as the Kauzmann paradox⁸ and the temperature at which the entropy of the supercooled liquid is projected to cross that of the crystal is the Kauzmann temperature (T_k). Another important temperature when dealing with supercooled liquids is the *glass transition temperature* (T_g), defined as the temperature at which the viscosity of the supercooled liquid reaches 10^{13} P. One of the theories of glass formation⁹ is that the glass transition is the system providing a solution to the paradox, undergoing dynamical arrest above T_k reducing the number of degrees of freedom.

When dealing with dynamics of supercooled liquids in most cases the viscosity observes Arrhenius behaviour just like a liquid. When approaching the glass transition temperature (T_g) there are a number of supercooled liquids that display super-Arrhenius behaviour (Figure 1.12) where there is a temperature dependence in the activation energy^{angell:91}. Supercooled liquids that display this temperature dependence on the activation energy are known as *fragile* liquids, they are interesting because they suggest

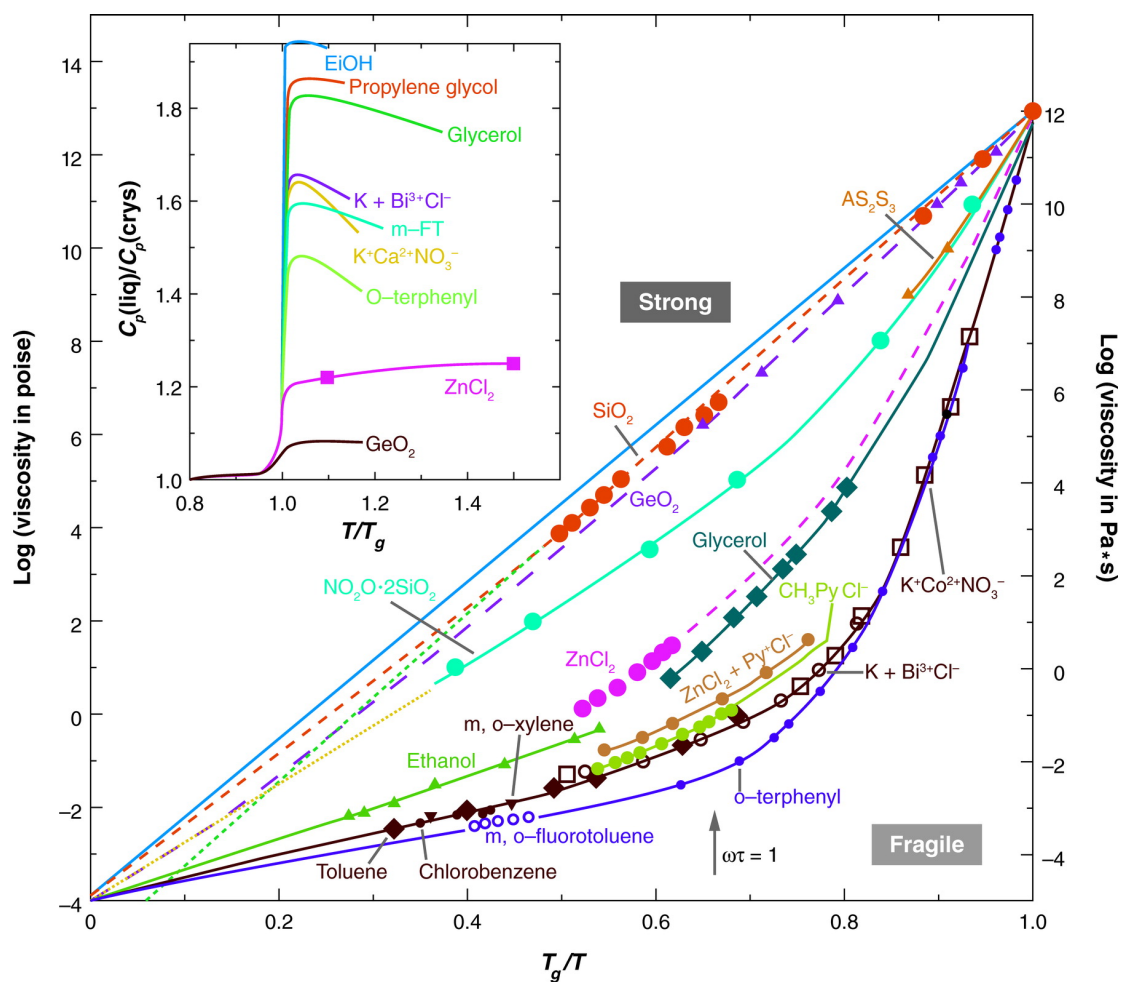
that the glass transition temperature is not just an arbitrary concept but an inherent property of a material. The typical example of a fragile liquid is *o*-terphenyl which has been widely studied¹⁰. The liquids that keep the Arrhenius behaviour over the entire temperature range are known as *strong* liquids, with the prototypical example being silica (SiO₂). The fragility (m) of a supercooled liquid can be given by the slope given in (Figure 1.12),

$$m = \text{stuff here} \quad (1.7)$$

Check This gives a range of fragilities from silica, $m = 1$ to *o*-terphenyl, $m = ??$ with everything in between (Table ??). It is interesting to note that along with *o*-terphenyl many of the fragile supercooled liquids are molecular, this feeds the hypothesis that glass forming ability is in some way related to shape, it can not be the only contributing factor but is a line of investigation to pursue.

Along with the fragility of molecular glass formers, they are also interesting due to their rotational motion. In supercooled liquids below approximately $1.2 T_g$ there is a decoupling between rotational and translational diffusion. It has been found that molecules translate faster than expected for their viscosity by as much as two orders of magnitude⁹. This results in molecules being able to move past each other but unable to rotate, limiting the range of states that can be sampled by the supercooled liquid. This is not the only decoupling present as close to T_g , there is also a splitting of the relaxation

Cite frequency into two bands, the slow α relaxation and fast β relaxation. This decoupling in the relaxation can be explained by interpreting the supercooled liquid as a point on a multidimensional potential energy landscape, just like for the packing problem (Section ??). Here the way that the supercooled liquid moves through the potential energy landscape is a function of the temperature. At high temperatures the liquid moves freely about the potential energy landscape, the energy of the molecules is often above any of




 Lubchenko V, Wolynes PG. 2007.
Annu. Rev. Phys. Chem. 58:235–66

Figure 1.12: Angell plot (from Lubchenko and Wolynes [11], used with permission from Annual reviews)

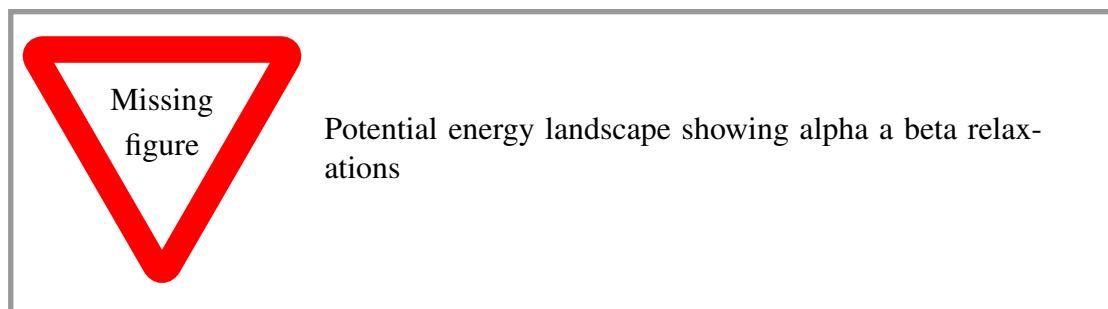


Figure 1.13:

the potential energy barriers. As the temperature gets lower the space of configurations available to the system gets smaller, there are potential energy barriers which only have a low probability of crossing. Close to the glass transition temperature the space of configurations is limited, there are many small local potential energy minima separated by larger energy minima. Moving between these larger minima requires a large number of rearrangements in the structure of the system, these movements correspond to the slow α relaxations (Figure 1.13). The motion between the smaller energy minima are the β relaxations resulting from small particle shifts.

This topological view of the relaxation is consistent with a growing dynamic length scale, a property observed when approaching the glass transition¹². At low temperatures the ability of the system to rearrange is very limited and requires coordinated rearrangement of a number of particles to move between each of the larger potential energy wells. Moving back into real space this growing dynamic length scale was first theorised when looking at dynamic heterogeneity¹³ in model glass formers. These simulations showed areas of glasses that were highly mobile, where other regions were completely stationary. The mobile regions are those that are cooperatively moving as the liquid relaxes. As the supercooled liquid moves to lower temperatures larger regions have to move cooperatively, in the topological view this is where there is a barrier that is insurmountable

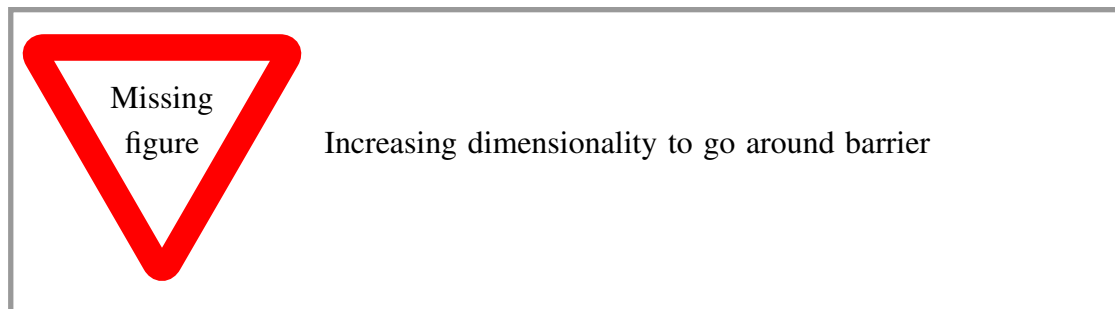


Figure 1.14: In 2D space there is a barrier that is impassable, by including the 3rd dimension the traversal of the barrier is just a simple case of going around.

in one direction, however by incorporating more particles and increasing the dimensionality the supercooled liquid can just move around the barrier (Figure 1.14).

Taking these dynamic quantities to their limit, the glass transition temperature results in the formation of the glassy phase.

1.4 Molecular Glasses

The structure of a glass is indistinguishable from that of a liquid, the difference is that a

Cite

glass has a viscosity of 10^{13} P. Despite the liquid like structure, and urban legends the glassy phase is most definitely solid, it would require a timescale of 100 million years

Cite

for a glass with a viscosity at the glass transition to appreciably flow . Much of the misunderstanding of the glassy phase is related to the lack of a first order phase transi-

Cite

tion . None of the thermodynamic properties change upon transition, all the structural properties of the liquid phase apply to the glass phase, however the dynamics of the glass phase are far slower than any liquid. What does this mean for the glass phase?

Write: Molecular glasses

CHAPTER 2

Method

2.1 Molecules

Degrees of freedom

2.1.1 Interaction Potentials

Intermolecular - LJ potential from each atom Intramolecular - harmonic potential between atoms, large potential to model rigid atoms Constraints due to software

2.2 LAMMPS

Freely available software Molecular dynamics Noose-Hoover thermostating

2.2.1 Rahman-Parinello

Allowing simulation cell to adjust to shape of crystal

2.3 Crystal Structures

Toby's structures Converting to large unit cell, squaring the edges The starting unit cells

2.4 Melting Points

Heat up slowly until melting More points around melting

2.5 Interface Kinetics

Region of liquid, region of crystal. Liquid created by holding the crystal region in place and heating the liquid above melting point.

CHAPTER 3

Packing shapes on a Plane

3.1 Effect of shape on packing

3.2 Some ideal packings

3.3 Why I chose these particular shapes

CHAPTER 4

Liquid Dynamics

4.1 $d=1$

4.2 $d=1+r$

4.3 Oh hey they are different

CHAPTER 5

Noncrystalline Ordering

5.1 This is a thing we saw

5.2 Plastic Crystals

CHAPTER 6

Crystallisation

6.1 Nothing crystallised

6.2 Here's why

CHAPTER 7

Conclusion

7.1 Yeah I did stuff

7.2 Future Work

Appendix A: Appendix A

A.3 Stuff I couldn't fit in the Introduction

A.4 Other cool stuff just because

Appendix B: Appendix B

B.5 Some code, cause I want to put it somewhere

Appendix C: Appendix C

C.6 A whole bunch of figures I felt like including

C.7 testing

Appendix D: Appendix D

D.8 I don't know what I am doing any more

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