Molecular order in soft condensed matter

R.A.L.Jones

November 15, 2002

1 Introduction

Most of the materials that are studied in the field of "hard" condensed matter physics - metals, semiconductors and ceramics - are crystalline; the atoms or molecules of which they are composed are arranged with near-perfect long ranged order over distances that are many orders of magnitude greater than the distance between molecules. Single crystals of metals or semiconductors of macroscopic size are not uncommon, but even where these materials are described as "polycrystalline" the fraction of the molecules that do not partake in the long ranged order is very small (though, of course, this small fraction of atoms associated with grain boundaries and defects such as dislocations may have an effect on bulk properties out of proportion to their number).

The situation in soft condensed matter is rather different. Crystallinity involving full long-ranged positional order - is important in soft matter, but in most soft matter systems the degree of molecular ordering falls somewhere between the full positional order of a single crystal and the complete positional disorder of a liquid or a glass. In fact, there are two distinctly different types of intermediate order in soft matter systems:

- liquid crystallinity. These are *equilibrium* phases in which molecules are arranged with a degree of order intermediate between the complete disorder of a liquid and the long-ranged, three dimensional order of a crystal.
- partial crystallinity. This is a *non-equilibrium* state of matter in which the system is prevented from reaching its equilibrium state of full longranged order for kinetic or other reasons, and in which microscopic

regions of crystalline order coexist with disordered regions, often in a complex hierarchical structure.

Liquid crystalline phases are found in

- certain organic compounds with a highly anisotropic molecular shapes. These are the materials used in liquid crystalline displays;
- polymers composed of units having a high degree of rigidity, either in the backbone or attached to the backbone as side-chains;
- polymers or molecular aggregates which form rigid-rod like structures in solution.

Partial crystallinity is typical of many flexible polymers, such as polyethylene or poly(ethylene terephthalate).

2 Crystallinity in polymers

The most common state of molecular order in polymers is the crystalline state, with full three dimensional positional order. However, in contrast to the situation in elemental solids and small molecules, very few polymer systems can attain a state of complete crystallinity. Instead, almost all polymers are *semi-crystalline*, consisting of a composite of very small crystals in a matrix of much less ordered material, with a total of between 20being present in the crystalline state. The amorphous material can either be glassy (as for example in polyethylene terephthalate, familiar from bottles for carbon ated soft drinks) or rubbery, that is to say liquid like, but effectively crosslinked by the small crystals. This is the situation in polyethylene. The reasons for this partial crystallinity are:

- Slow kinetics. Polymers are entangled, so it takes a long time for the molecules to arrange themselves in perfect crystals. Even quite modest cooling rates allow one to produce a glass.
- Quenched disorder. Polymers may have disorder built in to the polymer chain. This can take the form of randomness in the sterochemistry or tacticity (polystyrene for example is usually atactic and does not readily crystallise at all), or a random sequence of monomers in a random copolymer.



Figure 1: A chain-folded lamella, the basic unit in semi-crystalline polymers. The lamellar thickness l is much smaller than the contour length of a polymer chain.

• Branching. If the polymer chains have many branches, this makes it more difficult to pack the chains into regular crystals. This is why low density polyethylene, which is branched, is less crystalline than high density polyethylene, which is strictly linear.

2.1 Hierarchies of structure

Crystalline polymers have a hierarchical structure - that is there are different structures on different length scales.

The basic unit of most polymer crystals is the *chain-folded lamella*. The lamellar thickness l is independent of molecular weight, as we shall see it is a function of the supercooling when the crystal was formed. A typical value for l would be about 10 nm. Lamellae are separated by amorphous regions; individual chains may be involved in more than one lamella as well as the amorphous regions in between.

The chain folded lamellae are themselves organised in larger scale structures called *spherulites*. These structures, which may be many microns in size, consist of a sheaves of individual lamellae which grow out from a central nucleus, until finally the whole of space is filled by these structures.



Figure 2: The assembly of a *spherulite* from chain folded lamellae radiating and branching from a central nucleus.

2.2 Chain folded crystals

Why is the chain folded lamellar crystal the basic unit of semi-crystalline polymers? These are not equilibrium structures; the fold surface is considerably disordered, and there is a substantial interfacial energy σ_f associated with it. This means that the melting point of a lamellar crystal of thickness $l, T_m(l)$ is depressed from the ideal thermodynamic value, $T_m(\infty)$. This can be seen by considering the change in free energy δg when one polymer stem, of length l, joins the crystal. If the cross-sectional area of the stem is a^2 , then we can write this change in energy as

$$\Delta g = -\frac{\Delta H_m \Delta T}{T_m(\infty)} lla^2 + 2a^2 \sigma_f, \qquad (1)$$

where ΔH_m is the latent heat of melting per unit volume, and the undercooling $\Delta T = T_m(\infty) - T$. So the melting point of this crystal of finite thickness is given by the condition $\Delta g = 0$, which yields the expression

$$T_m(l) = T_m(\infty) \left(1 - \frac{2\sigma_f}{\Delta H_m L} \right).$$
⁽²⁾

Thus at equilibrium we would anticipate crystals in which the participating chains were fully extended. In fact, it turns out that the finite thickness of chain-folded polymer lamellar crystals arises from kinetic considerations, not equilibrium thermodynamics. In short, polymers form lamellae of a welldefined thickness because crystals with this thickness grow the fastest.



Figure 3: Free energy changes when a stem of polymer joins the growing crystal from the melt.

Where does this mechanism of length-scale selection come from? The important insight is that in order for a section of a polymer chain to join the crystal as a linear stem of length l, it has first to *unfold*; this requires a temporary loss of entropy, whose probability decreases exponentially with the length of the stem required. Thus we can see that:

- crystals that are too thick grow slowly because the probability of a long enough length of polymer straightening itself out from its random coil configuration is too small, while
- crystals that are too thin involve too much unfavourable energy from their fold surfaces, leading to smaller thermodynamic driving forces for the growth of the crystal.

We can make this argument more quantitative with a simple model calculation. The energetics involved when one stem is added to the crystal are sketched in figure 3. In order to join the crystal, a length of chain, which in the melt has a random coil configuration, must first straighten itself out. This leads to a reduction in entropy ΔS . Only when a random fluctuation has produced such a straight length of chain can the stem join the growing crystal face, finishing up with a free energy Δg lower than its energy in the melt.

Now we can estimate both the rate at which chain segments join the growing crystal from the melt, and the rate at which segments leave the crystal to rejoin the melt. We have

melt
$$\rightarrow$$
 crystal rate $= \tau^{-1} \exp\left(-\frac{\Delta S}{k_B}\right)$
crystal \rightarrow melt rate $= \tau^{-1} \exp\left(-\frac{(T\Delta S - \Delta g)}{k_B T}\right),$ (3)

where τ^{-1} is a microscopic frequency (recall also that in equation 1 we defined Δg to be negative when the crystal was stable). The difference between these two rates gives us the net crystallisation rate u, defined as the number of stems attached to a given site per unit time:

$$u = \tau^{-1} \exp\left(-\frac{\Delta S}{k_B}\right) \left[1 - \exp\left(\frac{\Delta g}{k_B T}\right)\right].$$
 (4)

To simplify things we will assume that $\Delta g/k_BT$ is small enough to expand the exponential; writing for the velocity of crystal growth v = ua, (where a is the cross-sectional diameter of the polymer chain), we find

$$v = a\tau^{-1} \exp\left(-\frac{\Delta S}{k_b}\right) \frac{\Delta g}{k_B T}.$$
(5)

We now need to see how this growth velocity depends on the thickness of the crystal l. Equation 1 gives us the variation of Δg on l. The entropy loss ΔS on straightening out a length l of the chain is proportional to the number of segments in the length to be straightened; we write $\Delta S = \mu l/a$ where μ is a dimensionless constant. This gives us

$$v(l) = (\text{constant}) \left(2a^2 \sigma_f - \frac{\Delta H_m \Delta T}{T_m(\infty)} l_f a^2 \right) \exp\left(-\frac{\mu l}{a}\right).$$
(6)

The shape of this function is plotted in figure 4. Crystals of thickness l_c are at equilibrium with the melt at a given temperature and do not grow at all; on the other hand there is a certain thickness l^* for which the growth rate is a maximum, and it is crystals of this thickness which we expect to dominate the final morphology. We can find l^* by differentiating equation 6; this yields

$$l^* = \frac{a}{\mu} + \frac{2\sigma_f T_m(\infty)}{\Delta H_m(T_m(\infty) - T)}.$$
(7)



Figure 4: The crystal growth rate as a function of crystal thickness. At a given temperature, crystals of thickness l_c are in equilibrium with the melt and do not grow at all. Crystals of thickness l^* have the maximum growth rate and dominate the morphology.

We see that the deeper the quench the thinner the resulting crystals will be. This is what is observed experimentally, and indeed the functional form of equation 7 gives a good fit to the data, as shown in figure 5.

We can also use this approach to predict the temperature dependence of the crystal growth rate. To do this we simply substitute our expression for the fastest growing crystal thickness l^* from equation 7 into our expression for the crystal growth velocity, equation 5. An important point that we have up to now glossed over is the question of what determines the microscopic frequency τ^{-1} . This gives a measure of the rate of conformational rearrangements of a polymer coil in a melt. These conformational rearrangements involve the complicated internal dynamics of a polymer chain; luckily, however, even in the absence of a detailed analysis of these modes we know from the principle of time-temperature superposition that all such modes have the same temperature dependence, which we can write in the Vogel-Fulcher form; thus we can write

$$\tau^{-1} = \tau_0^{-1} \exp\left(\frac{-B}{T - T_0}\right),\tag{8}$$

where B is a positive coefficient and T_0 is the Vogel-Fulcher temperature, a material constant which is typically around 50° below the experimental glass transition temperature.



Figure 5: Crystal thickness as a function of undercooling for polyethylene, showing good agreement with the functional form of equation 7. Data from P.J. Barham et al., J. Mater Sci, **20** 1625 (1985).

Putting this all together, we find for the temperature dependence of the crystal growth velocity

$$v = \frac{a\tau^{-1}}{e k_B T} \frac{a^3}{\mu} \frac{\Delta H_m \Delta T}{T_m(\infty)} \exp\left(\frac{-B}{T - T_0}\right) \exp\left(-\frac{2\mu\sigma_f T_m(\infty)}{a\Delta H_m \Delta T}\right).$$
(9)

The temperature dependence of this expression is dominated by the two exponentials, which combine to give a very strong peak in the growth rate as a function of temperature. At high temperatures, it is the size of the thermodynamic driving force that controls the growth rate, via the second exponential function in equation 2.2. At lower temperatures, it is the rapidly decreasing mobility as the glass transition approaches that suppresses the growth of crystals. In practise, it is not at all uncommon to observe changes in crystal growth rates of three or four orders of magnitude, so great is the temperature dependence predicted by equation .

To conclude this section, it is worth making some general observations. We have seen that when polymers crystallise, kinetic considerations mean that the final morphology is a long way from equilibrium, and indeed the equilibrium morphology, in the sense of the morphology with overall lowest free energy, is practically unattainable. If a semi-crystalline polymer is kept at a temperature at which the chains are still mobile, there is some evolution of the morphology which is reflected in a very slow increase in the crystalline fraction. The crystalline lamellae do thicken; new lamellae are nucleated and grow in the interstices between existing lamellae. But to achieve the equilibrium state, of fully chain extended crystals, would require such a wholesale rearrangement of chains, which would involve such a huge energy barrier that it is practically unattainable. Here we see the limits of equilibrium thermodynamics.

3 Liquid crystallinity

3.1 Introduction to liquid crystal phases

A crystal has *long ranged, three dimensional, positional order*, while a liquid has neither positional order nor orientational order. Liquid crystalline phases posess order intermediate between these two extremes. The most disordered type of liquid crystalline phase is the *nematic* phase, which has no positional order, but in which the molecules are, on average, oriented about a particular direction, called the *director*. The transition between the isotropic phase and the nematic phase is sketched in figure 6. The absence of positional order in a nematic phase means that if one plotted the centres of mass of the molecules the arrangement would be indistinguishable from an isotropic liquid; the only ordering is in the orientation of the molecules, and even this ordering is, as sketched, not perfect. This point will emerge more clearly when we consider statistical mechanical theories of the transition from an isotropic to a nematic liquid, in the next section.

A variant of the nematic phase occurs in systems where the system is composed of molecules which are *chiral*; that is in which the molecule differs from its own mirror image. In these systems there may be a slight tendency for neighbouring molecules to align at a slight angle to one another. This weak tendency leads to director to form a helix in space, with a well-defined pitch which is usually much longer than the size of a single molecule. these phases are called *chiral nematics*, or perhaps more commonly *cholosterics*. In many cases the pitch of the helix is of the same order as the wavelength of light, and so these materials can display striking optical effects.

There are still more phases that are intermediate in order between nematics and crystals. In a *smectic* phase, the molecules arrange themselves in sheets. Within each layer, the molecules are aligned, but have no positional order. Thus in going from a nematic to a smectic, we go from a situation of no positional order, to long-range positional order in one dimension only. two



Figure 6: A sketch of the transition between the isotropic liquid phase, in which there is neither positional nor orientational order, to a nematic phase, in which there is orientational order, but still no positional order.

Phase	positional order	orientational order
Liquid	None	None
Nematic	None	Yes
Smectic	One-dimensional	Yes
Columnar	Two-dimensional	Yes
Crystalline	Three-dimensional	Yes

Table 1. Degrees of order in liquid crystalline phases.

common sub-classes of smectic ordering are the *smectic* A phase, in which the director is parallel to the layer normal, and the *smectic* C phase, in which the director and the layer normal make an angle. Thus a smectic C phase is made up of layers of tilted molecules.

Finally, it is possible to have a phase which has positional order in two dimensions as well as orientational order. This kind of phase is found in molecules that are disk-like, rather than rod-like; in a *columnar* phase such molecules stack into long columns. Within each column there is no long-ranged order in the position of the molecules, but the columns arrange themselves into a regular two-dimensional hexagonal lattice (figure 8).

These different levels of positional and orientational order are summarised in table1.



Figure 7: A sketch of the transition between the nematic phase, in which there is orientational order but no positional order, to a smectic A phase, in which there orientational order and long-ranged positional order in one dimension.

3.2 The nematic/isotropic transition

The simplest and least ordered liquid crystal phase is the *nematic* phase, in which there is no positional order, but in which there is long range order of the direction of the molecules. In going from an *isotropic* state, in which both position and orientation are random, to a *nematic* state, in which position is random but there is a preferred orientation, there must be a reduction in the orientational entropy of the system. So in order for the nematic state to have a lower free energy than the isotropic state, there must be another term in the free energy which favours orientation. Then, as the temperature changes, the relative importance of the two terms changes, leading to a phase transition.

How can we describe the state of orientational order of a molecule in a quantitative way? For a rod like molecule we can introduce a single preferred direction, the *director*, and we introduce an *orientation function* $f(\theta)$; $f(\theta)d\Omega$ is the fraction of molecules in a solid angle $d\Omega$ which are oriented at an angle of θ to the director. For a completely randomly oriented molecule, there is an equal chance that the molecule points anywhere in a solid angle of 4π , and $f(\theta)$ is constant. For a more ordered system the function becomes more peaked around the angles 0 and π , as shown in figure 9. In all known nematics, the directions 0 and $+\pi$ are identical, so $f(\theta) = f(\pi - \theta)$.

the distribution function contains all the information about the state of



Figure 8: A sketch of a columnar phase, in which disk-shaped molecules are arranged with orientational order and long-ranged positional order in two dimensions. Within each column there is no long-ranged positional order.



Figure 9: The distribution function $f(\theta)$ for a nematic phase with various degrees of order. The order parameter S takes the value 0.82, 0.71 and 0.44 for the solid, dashed and dotted lines respectively.

order in the material, but it would be convenient to represent this state of order no aas a function but as a simple number — an order parameter — which took the value 0 for complete disorder, and 1 for complete order. One might think of taking the average of $\cos(\theta)$, but this is zero because $f(\theta) = f(\pi - \theta)$. Instead we must take another average; $1/2 < 3\cos^2 \theta - 1 >$ has the right properties. Thus we define the order parameter S by

$$\mathcal{S} = 1/2 < 3\cos^2\theta - 1 > = \int \frac{1}{2} \left(3\cos^2(\theta) - 1 \right) f(\theta) \, d\Omega. \tag{10}$$

Why should a liquid adopt a nematic phase? In going from an isotropic state to a state of orientational order, there must be a loss of the entropy associated with the freedom of a molecule to be oriented in any arbitrary direction. If the nematic phase is to be at equilibrium, the positive contribution to the free energy arising from this loss of orientational entropy must be outweighed by some other factor that causes the free energy to be lowered when the molecules are aligned. This is likely to occur in melts of rod like objects for two reasons:

- favourable attractive interactions arising from van der Waals forces between the molecules will be maximised when they are aligned;
- it is easier to pack rod-like molecules when they are aligned.

The first factor is perhaps most important for melts of relatively small molecules which form nematic phases; the second factor is the major factor underlying the transitions that occur as a function of concentration for very long rigid molecules and supramolecular assemblies. In both cases, simple statistical mechanical theories can be formulated on the basis of these ideas. These theories, which yield predictions about the nature of the transition between the isotropic and nematic states, are both *mean-field* theories, and as such are similar in spirit to theories introduced elsewhere in this book to describe other phase transitions.

The starting point for both theories is to write down an expression for the entropy lost when molecules become oriented. We can write the contribution to the entropy of a molecule due its orientational freedom using the Boltzmann formula as

$$S_{orient} = -k_B \int f(\theta) \ln f(\theta) \, d\Omega. \tag{11}$$

In the isotropic state, $f(\theta) = 1/4\pi$, so the change in entropy per molecule on going from the isotropic state to an ordered state is given by

$$\Delta S = -k_B \int f(\theta) \ln \left[4\pi f(\theta)\right] d\Omega.$$
(12)

In the first theory we consider, which is known as the *Maier-Saupe theory*, we make the phenomenological assumption that the energetic interaction between molecules is simply a quadratic function of the order parameter, so we write the total free energy change per molecule on going from the isotropic to the nematic state as

$$\Delta F = -u\mathcal{S}^2/2 + k_B T \int f(\theta) \ln\left[4\pi f(\theta)\right] d\Omega, \qquad (13)$$

where u is a parameter that expresses the strength of the favourable interaction between two neighbouring molecules. Of course, S is defined in terms of the distribution function $f(\theta)$. What we now need to do is find the function $f(\theta)$ which minimises the free energy.

We do this in two stages. First, for a given value of the order parameter S, we find the most probable distribution function $f(\theta)$ by maximising the entropy associated with $f(\theta)$ subject to the constraint of a fixed value of S. From this most probable distribution function we can calculate the entropy. In this way we can find the orientational entropy as a function of the order parameter.

Thus we need to find the function $f(\theta)$ that gives a stationary value of the integral $\int f(\theta) \ln f(\theta) \sin \theta \, d\theta$ subject to the constraint that the integral $\int \frac{1}{2} (3\cos^2(\theta) - 1) f(\theta) \sin \theta \, d\theta = S$ is a constant. The Euler-Lagrange equation resulting from this problem in the calculus of variations is

$$\ln f + \frac{3\lambda}{2}\cos^2\theta + 1 - \frac{\lambda}{2} = 0, \qquad (14)$$

which has the solution

$$f(\theta) = \exp(3\lambda\cos(\theta)^2), \tag{15}$$

where λ is the Lagrange multiplier that sets the value of the order parameter \mathcal{S} . Now, for a given value of λ , and thus a given value of \mathcal{S} , we can evaluate the entropy using equation 12. The resulting curve showing the change in orientational entropy per molecule ΔS_{orient} on going to an oriented state with order parameter \mathcal{S} is shown in figure 10.



Figure 10: The change in orientational entropy per molecule on going from an isotropic state to an ordered state as a function of the order parameter S.

We can now plot the free energy as predicted by equation 13 as a function of order parameter for various values of u/k_BT . This is shown in figure 11. For relatively small values of the u/k_BT , the minimum free energy is found for a value of the order parameter of zero - here the free energy is dominated by the orientational entropy term, and the equilibrium state is isotropic. But as the coupling parameter is increased a minimum of the free energy is found for a non-zero value of S - the equilibrium phase is *nematic*. The critical value of u/k_BT for the transition is around 4.55.

By calculating the value of the order parameter S as a function of u/k_BT we can investigate the character of the transition. This is shown in figure 12; at a value of $u/k_BT = 4.55$ there is a discontinuous change of the order parameter from S = 0 to S = 0.44. This is the nematic/isotropic phase transition; because it is a discontinuous change it is a *first order* phase transition, but as the change in degree of order at the transition is not very great it the transition can be said to be only weakly first order.

In order to compare the predictions of the Maier-Saupe theory with experiment we would need to have some theory about the way in which the coupling parameter u varied with temperature. The simplest assumption is that u is independent of temperature; this would be the case if the coupling arose entirely from van der Waals forces. This turns out to be quite a reasonable first approximation for small molecule liquid crystals; figure compares experimentally measured ordered parameters for the molecule p-azoxyanisole (PAA) with the prediction of Maier-Saupe theory assuming that u takes the



Figure 11: The free energy as a function of the order parameter S for various values of the coupling parameter u/k_BT , as given by the Maier-Saupe theory (equation 13).



Figure 12: The order parameter S as a function of the coupling parameter u/k_BT , as given by the Maier-Saupe theory. There is a weak first order phase transition at $u/k_BT = 4.55$.

temperature independent value that reproduces the experimentally observed transition temperature (i.e. this is a one-parameter fit). There is quite good qualitative agreement; while the theory captures the relatively small degree of order at the transition and gives a good account of the development of order with decreasing temperature, there are clearly systematic deviations from the predictions of theory, particularly close to the transition.

There are a number of reasons why there are discrepancies between the experimental data and the predictions of Maier-Saupe theory. Two such possible factors are:

- intrinsic temperature dependence of u. This could arise, for example, because the excluded volume interaction is significant.
- neglect of fluctuations. The Maier Saupe theory is a *mean-field theory*, and like all such theories it neglects the effects of fluctuations in the order parameter. These are likely to become important close to the transition point.



Figure 13: The order parameter S as a function of temperature for pazoxyanisole (PAA), as measured by refractive indices (circles - from S. Chandrasekhar and N.V. Madhusudana, Applied Spectroscopy Reviews, **6** 189 (1972)) and diamagnetic anisotropy (squares - from H. Gasparoux, B. Regaya and J. Prost, C.R. Acad. Sci. **272B** 1168 (1971)). The solid line is the prediction of Maier-Saupe theory assuming u is independent of temperature and takes a value which reproduces the experimental transition temperature.