Phase transition in a polymer chain in dilute solution

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Abstract. The order of the phase transition within a long polymer molecule in dilute solution brought about by the intramolecular forces is investigated within the context of a lattice model. It is found that the entropy is continuous at the transition but that the density changes discontinuously, implying that the transition has features of both first- and second-order transitions.

1. Introduction

A long standing problem in the theory of polymer chains in solution is the effect of intramolecular forces on the shape and size of the chain. These intramolecular forces will usually be of van der Waals type consisting of a hard-core repulsion at short distances and a longer range attractive interaction. Domb (1974) has suggested that the problem is mathematically analogous to the condensation of a gas of molecules with van der Waals forces, except that the existence of the chain imposes restrictions on the configurational space of the molecules.

One expects to find, using this analogy, that at sufficiently high temperatures the repulsive forces will dominate; the chain will be in the 'gaseous' state and its 'density' ρ will be very low. Just how low can be judged as follows. Estimate the density ρ as

$$\rho \sim N/D^3, \tag{1.1}$$

where D is a typical dimension of the N-link chain such as its radius of gyration. For a random walk chain, $D \sim \sqrt{N}b$, where b is the length of a link of the chain. For a self-avoiding walk, or a polymer in which excluded volume forces are taken into account, $D \sim N^{\nu}b$, with $\nu \simeq 0.6$ (McKenzie and Moore 1971). In either case, the density ρ tends to zero as the number of links N tends to infinity.

At low temperatures, the analogy with the gas–liquid condensation suggests that the attractive forces between the links of the chain will become dominant and cause a phase transition to a higher density (ie 'liquid') phase. The chain will not now be extended and of vanishingly low density, but instead exist in the form of a globule of given density which remains finite in the limit of large N. The temperature T_c at which the transition takes place from the 'gaseous' to the 'globule' phase would be expected to be lower than the Flory Θ temperature, and close to the temperature at which the polymer or polymer-rich solution separates out of a very dilute solution. Of course, a true phase transition within an N-link chain can only take place in the limit of infinite N. For finite N, the phase transition will be 'rounded-off'.

The main purpose of this note is to examine the order of the transition. Domb (1974), Edwards (1970) and Lifshitz (1969) have argued on various grounds that the transition should be first order and there is both numerical (Domb 1974) and experimental evidence (McIntyre and Mazur 1974) that the density does indeed change discontinuously at the transition temperature from zero to some finite value. Such behaviour is usually thought characteristic of a first-order transition. We shall also find such behaviour for the density in our model calculation. On the other hand, the entropy in our calculation turns out to be continuous at the transition temperature but with a discontinuity in its temperature derivative. This would imply that the transition was second order in the Ehrenfest sense (Pippard 1957). It looks therefore that this polymer phase transition, while technically second order, may be somewhat unusual, as the obvious candidate for the order parameter of the transition—the density—does not decrease continuously to zero as the temperature approaches T_c from below.

The model we employ of the polymer chain in solution is a variation on the widely used Orr (1947) model (see also Fisher and Hiley 1961). In that model, an N-link polymer chain is represented by an N-step self-avoiding walk on a regular lattice, with attractive forces between nearest neighbours. In a self-avoiding walk, no lattice site is visited more than once. In our model, which we shall call the crossing model, the walks are such that no lattice bond is used more than once. This restriction on the walks, like the restriction that no site is visited more than once in a self-avoiding walk, is to be thought of as a consequence of the short range excluded volume forces. In our model, a lattice site can be visited several times, the maximum number of times depending on the coordination number of the lattice. If the coordination number of the lattice is four, the walk can cross itself only once at any given site. From now on, we shall suppose that we are always dealing with lattices of such coordination number, noting that the best lattice for individual polymer chains of carbon atoms is the tetrahedral lattice (DiMarzio and Gibbs 1958). Attractive forces are incorporated in the model in interactions which occur only at sites at which the polymer touches or crosses itself. Let V be the energy associated with such a 'crossing' or 'touching'. The configurational partition function of an N-link chain is then

$$Q_N(w) = \sum_t c_{N,t} w^t \tag{1.2}$$

where $w = \exp(-V/kT)$, and $c_{N,t}$ is the number of walks of N steps with t 'crossings' or 'touchings', in which no lattice bond is used more than once in the walk. It is to be supposed that if the walk begins or ends at a site which has been already visited during the walk, then there is a 'touching' at that site. $V < 0$ corresponds to attractive interactions. Note that the crossings are not permanent links; their average number $\langle t \rangle$ is given by

$$\langle t \rangle = \sum_t t c_{N,t} w^t / Q_N(w) = \partial \ln Q_N / \partial \ln w. \tag{1.3}$$

To avoid unnecessary repetition, we shall suppose in the rest of this paper that the term 'walk' means a walk in which no lattice bond is used twice. We believe that the crossing model on a tetrahedral lattice captures the physics of a polymer chain in solution as satisfactorily as does the Orr model.

As might have been expected, the partition function, $Q_N(w)$, cannot be calculated without resorting to approximation. The scheme we have adopted is to 'approximate' the tetrahedral lattice by the modified cactus Bethe lattice of figure 1. Technically, this is a Husimi tree, each block of which is a triangle. On this lattice, $Q_N(w)$ can be obtained
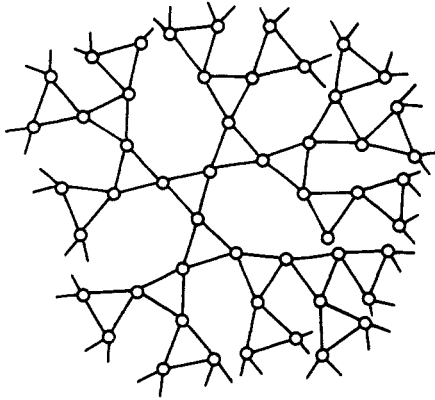
Figure 1. Portion of a triangle cactus Bethe lattice of coordination number four.

exactly in the limit of large N. Nagle (1974) has pointed out that the widely-used Flory–Huggins approximation for polymers in solution is exact for a plain, that is, non-cactus Bethe lattice. Thus our approximation scheme follows closely the traditional calculations of the thermodynamics of polymers in solution, and so has their virtues and defects.

It proves convenient not to evaluate $Q_N(w)$ directly, but to find the generating function

$$G(z, w) = \sum_{N=1}^{\infty} Q_N(w)z^N. \tag{1.4}$$

Having obtained $G(z, w)$, $Q_N(w)$ can be found from the inversion formula

$$Q_N(w) = \frac{1}{2\pi i} \oint \frac{G(z, w)}{z^{N+1}} \, dz. \tag{1.5}$$

The evaluation of $G(z, w)$ and its inversion to get $Q_N(w)$ is performed in §2. The thermodynamics of the phase transition are derived in §3, special attention being devoted to the entropy and density of the polymer chain both above and below the transition.

2. The generating function

We shall first study the partition function $A_N(w)$ for all walks of N steps which terminate at the origin, their starting point, and which return to the origin via the same triangle as they started out. $A_N(w)$ is defined by

$$A_N(w) = \sum_t a_{N,t} w^t \tag{2.1}$$

where $a_{N,t}$ is the number of walks of N steps which return to the origin via the same triangle as they set out in and which have t 'crossings' or 'touchings'. Thus $a_{3,1} = 2$, $a_{6,2} = 8$ etc and it is clear that N must be a multiple of three and that $t = \frac{1}{3}N$. Hence

$$A_N(w) = a_{N,N/3}w^{N/3} \equiv a_N w^{N/3}. \tag{2.2}$$

The generating function for $A_N(w)$ is

$$A(z, w) \equiv A = \sum_{N=3}^{\infty} z^N A_N(w)$$

$$= 2wz^3 + 8w^2z^6 + \dots . \tag{2.3}$$

A closed form expression for $A(z, w)(\equiv A)$ can be found. Let us label the origin O, and the other two vertices of the triangle which contains the origin and are visited by the N-step walk, X and Y. Starting from the origin, the walk could go first to site X, then take M steps into the lattice beyond X before returning to X. After returning to X the walk must continue to Y (it cannot return to O directly as this would mean using the bond OX twice). At Y, the walk could take $(N - M - 3)$ steps into the lattice beyond Y before returning to Y and then go on back to O (it cannot go back to X as this would involve using the bond XY twice). This walk could of course be undertaken in the opposite direction, that is first to Y rather than X. The number of such walks is

$$2a_M a_{N-M-3}$$

with a_N as in (2.2) and $a_0 \equiv 1$. The factor of 2 arises from the possibility of taking the walk in either direction. M can have the values $0, 3, 6, \dots, N-3$, so the total number of walks of N steps of this kind is given by

$$a_N = 2 \sum_{M=0}^{N-3} a_M a_{N-M-3} . \tag{2.4}$$

Multiplying both sides of (2.4) by $w^{N/3}$ and using (2.2) we get

$$A_N(w) = 2w \sum_{M=0}^{N-3} A_M(w) A_{N-M-3}(w). \tag{2.5}$$

(2.5) is a typical convolution. It can be solved by multiplying both sides of it by z^N and summing over N. Using the definition of $A(z, w)$ in (2.3), one obtains

$$A(z, w) = 2wz^3(1 + A(z, w))^2 \tag{2.6}$$

so, solving this quadratic equation in $A(z, w)$ and taking the root which recovers (2.3),

$$A(z, w) \equiv A = [1 - 4wz^3 - \sqrt{(1 - 8wz^3)}]/4wz^3. \tag{2.7}$$

The method used to find $A(z, w)$ can be extended to obtain $G(z, w)$ and so we shall only outline the rest of the argument. Walks can be classified by the number of steps their endpoint lies from the origin. The generating function for walks which terminate at the origin, regardless of whether or not the walk returns to the origin in the same triangle as it started out, is

$$2A(1 + A). \tag{2.8}$$

(The factor of two arises because the walk could start in either of the two triangles at the origin; the factor $(1 + A)$ arises because in a walk which starts in a given triangle, it may or may not return to the origin via the other triangle at the origin.)

The generating function for the partition function of walks which terminate one step from the origin is

$$[z + z^2(1 + A)](1 + A)^2. \tag{2.9}$$

(The generating function for a 'direct' step is $(1 + A)z(1 + A)$, while the generating

function for the 'indirect' step is $(1+A)z(1+A)z(1+A)$; their sum gives (2.9).) There are four lattice sites which can be reached by one step from the origin, so that these lattice sites give a contribution to $G(z, w)$ of

$$4[z+z^2(1+A)](1+A)^2. \tag{2.10}$$

Similarly, the contribution to $G(z, w)$ made by walks which terminate at the eight sites two steps from the origin is

$$8[z+z^2(1+A)]^2(1+A)^2. \tag{2.11}$$

$G(z, w)$ is the sum of the generating functions of the partition functions of walks which terminate 0, 1, 2, 3, ... steps from the origin, and hence can be seen to be

$$G(z, w) = 2A(1+A) + \frac{4[z+z^2(1+A)](1+A)^2}{1-2[z+z^2(1+A)]}. \tag{2.12}$$

On substituting the expression (2.7) for A, (2.12) becomes

$$G(z, w) = \frac{(-16wz^5+8wz^4-12wz^3+4z^2+2)-(8wz^4-4wz^3+4z^2+2)\sqrt{(1-8wz^3)}}{4wz^5[-4wz^2+2wz-1+\sqrt{(1-8wz^3)}]}. \tag{2.13}$$

Multiplying top and bottom by $[-4wz^2+2wz-1-\sqrt{(1-8wz^3)}]$, we have

$$G(z, w) = \frac{\begin{aligned}&[-8wz^5+4(4w-1)z^4-2(3w+2)z^3-2z+1]\\&\quad+[8wz^5-4(2w-1)z^4+2(w+2)z^3+2z-1]\sqrt{(1-8wz^3)}\end{aligned}}{2wz^5[8wz^3-(8w-4)z^2+(2w+4)z-2]}. \tag{2.14}$$

The partition function $Q_N(w)$ is obtained from $G(z, w)$ by using (1.5). For large N the integral will be dominated by the singularity of $G(z, w)$ closest to the origin in the complex z plane. From (2.14), it can be seen that the singularities of $G(z, w)$ are the three poles arising from the vanishing of the denominator and the three branch cuts from the term $\sqrt{(1-8wz^3)}$. For small w, that is, high temperatures, there is a pole on the positive real axis at $z = \alpha(w)$ which lies closer to the origin than the other two poles, and also than the branch cuts, which start at a distance $\beta(w) = 1/2w^{1/3}$ from the origin. As w increases, the branch cuts and pole change their relative distances from the origin until at a certain critical value of w, which we shall call w_c and which corresponds to the phase transition temperature T_c, they are the same distance from the origin. For $w > w_c$, that is, at temperatures less than the phase transition temperature T_c, the pole $\alpha(w)$ disappears. It is cancelled by a zero in the numerator, leaving the branch cuts as the nearest and dominant singularities. Thus in the limit as $N \to \infty$,

$$Q_N(w) \sim C(w)/\alpha^N(w), \qquad w < w_c \quad \text{or} \quad T > T_c \tag{2.15}$$

and

$$Q_N(w) \sim D(w)/\beta^N(w)N^{3/2}, \qquad w > w_c \quad \text{or} \quad T < T_c \tag{2.16}$$

where $C(w)$ and $D(w)$ are rather complicated functions of w which we shall not specify, as in the large N limit (see (3.2)) they do not affect the thermodynamics of the polymer.

The critical value, w_c, at which the transition takes place can be found as follows. Let z_c be the common distance of the pole and branch cut from the origin when they coincide at $w = w_c$. There

$$\sqrt{(1-8w_c z_c^3)} = 0 \tag{2.17}$$

which means, using (2.7), that $A(z_c, w_c) = 1$. The denominator of (2.12) then implies that

$$1 - 2(z_c + 2z_c^2) = 0 \tag{2.18}$$

with $z = z_c$. The value of z_c is given by the positive root of this quadratic equation, and equals $(\sqrt{5} - 1)/4$. Hence, from (2.17)

$$w_c = \frac{1}{8z_c^3} = \frac{8}{(\sqrt{5} - 1)^3} \simeq 4\cdot2. \tag{2.19}$$

3. The phase transition

The free energy can be related to the partition function $Q_N(w)$, by the bridge equation

$$F = -kT \ln Q_N(w) \tag{3.1}$$

so for $T < T_c$, the free energy of the polymer, which will be in the 'globule' or 'liquid' phase, is using (2.16)

$$F \simeq -kT \ln D(w) - \tfrac{3}{2} \ln N + NkT \ln \beta(w)$$

$$\Rightarrow NkT \ln \beta(w) \qquad \text{as } N \Rightarrow \infty$$

$$= \tfrac{1}{3} NV - NkT \ln 2. \tag{3.2}$$

Given the free energy, the thermodynamics of the 'globule' phase is easily worked out. Using (1.3) the average number of 'crossings' or 'touchings' within a configuration in this phase is given by

$$\langle t \rangle = \frac{\partial \ln Q_N}{\partial \ln w} = \tfrac{1}{3} N \tag{3.3}$$

and the fluctuations about the mean are measured by the magnitude of

$$\langle t^2 \rangle - \langle t \rangle^2 = \frac{\partial^2 \ln Q_N}{\partial \ln w^2}. \tag{3.4}$$

which, from (3.3), is zero. Therefore, when in the 'globule' phase, the polymer has taken up those configurations which have the maximum possible number of 'crossings' $\tfrac{1}{3}N$. Unfortunately the concept of density is not well defined for a Bethe lattice, as such lattices are in some senses infinite dimensional (Nagle 1974). That the mean number of 'crossings' equals the maximum possible number of 'crossings' would, on a normal lattice, imply that the globule was of non-vanishing density. It would seem very reasonable to claim that our approximation predicts a finite globule density.

From (3.2), the globule entropy S has the simple form

$$S = Nk \ln 2 \tag{3.5}$$

and the specific heat

$$C = T \frac{\partial S}{\partial T} = 0. \tag{3.6}$$

The vanishing of the specific heat in the 'globule' phase suggests that the polymer configurations within this phase are effectively 'frozen-in'. 'Frozen-in' behaviour

observed in other model systems is often accompanied by a first-order transition (Domb 1974). We shall, however, show that the entropy is continuous at the transition.

The free energy of the high-temperature phase is given by, using (2.15)

$$F \simeq -kT \ln C(w) + NkT \ln \alpha(w)$$
$$\Rightarrow NkT \ln \alpha(w) \qquad \text{as } N \to \infty \tag{3.7}$$

For general $w < w_c$, $\alpha(w)$ can be obtained by finding the smallest root of the cubic expression in the denominator of (2.14). We shall not need the full expression for $\alpha(w)$ as our main interest is in the entropy as $T \to T_c$.

At T_c, $\alpha(w_c) = \beta(w_c)$. It can be seen that the condition for the entropy itself being continuous at the transition is that

$$\frac{d\alpha(w)}{dw}\bigg|_{w=w_c} = \frac{d\beta(w)}{dw}\bigg|_{w=w_c} = -\frac{\beta(w_c)}{3w_c} = -\frac{\alpha(w_c)}{3w_c}. \tag{3.8}$$

From (2.13), $\alpha(w)$ must satisfy the equation

$$-4w\alpha^2 + 2w\alpha - 1 + \sqrt{(1-8w\alpha^3)} = 0. \tag{3.9}$$

If one employs this expression to calculate $d\alpha(w)/dw$, one sees that as $w \Rightarrow w_c$ and $\alpha \Rightarrow z_c$, that through $\sqrt{(1-8wz^3)} \Rightarrow 0$ in this limit, one has

$$\frac{d\alpha(w)}{dw}\bigg|_{w=w_c} = -\frac{\alpha(w_c)}{3w_c} \tag{3.10}$$

and (3.8) follows. The entropy is continuous at the transition and equal to $Nk \ln 2$.

In figure 2 we have plotted the entropy per link as a function of temperature for both $T > T_c$ and $T < T_c$ in the limit of $N \Rightarrow \infty$. We have also plotted the entropy per link for chains of 12 steps and 30 steps in order to illustrate the rounding of the transition that takes place in a polymer of finite length. One can see some of the features of the infinite N limit such as the discontinuity in the derivative of the entropy at w_c building
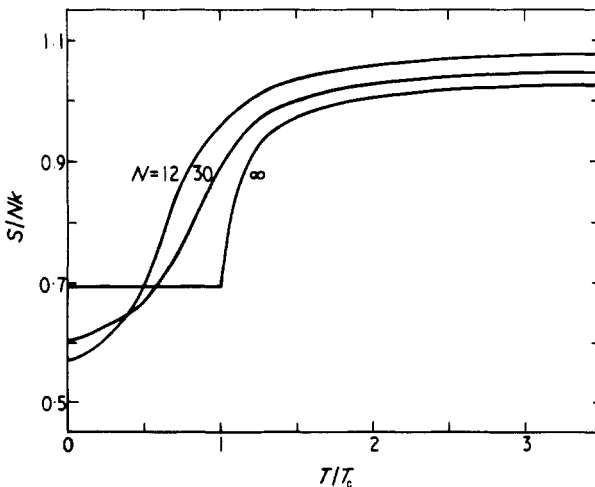

Figure 2. Configurational entropy per link as a function of temperature for chains of 12, 30 and infinite numbers of links.

up as N gets large. The convergence to the large N limit is slowest at $w \simeq w_c$ and greatest well away from the transition, as of course might have been expected.

The density of the polymer in the high-temperature or 'gaseous' phase is not easily derived from the behaviour on a Bethe lattice. However, as the polymer in this phase is rather similar to a self-avoiding walk, there seems no reason to suppose that the density does not vanish in the large N limit.

4. Conclusions

The transition has characteristics of both first- and second-order transitions. The entropy is continuous at the transition, which implies that the transition is of second order. The density, the probable order parameter of the system, jumps from zero in the 'gaseous' phase to a finite value in the 'globule' phase which is typical of first-order behaviour. The polymer configurations in the 'globule' phase are 'frozen-in', a feature which would normally be expected to produce first-order behaviour. The jump in density is consistent with the sudden change with temperature of the radius of gyration of high molecular weight polystyrene in cyclohexane reported by McIntyre and Mazur (1974).

Nagle (1974) has studied a variety of models for the melting of polymers and found that the 'classical' Flory–Huggins type of approximation employed in this paper is a reasonable first approximation, but misses many important features of the various models he examined. We suspect that a similar conclusion will eventually be drawn about the polymer phase transition in dilute solution studied in this note.

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