Phase change of a block copolymer molecule

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Abstract. Polymer molecules can be so large that they may individually be considered as systems amenable to the methods of statistical mechanics. On this basis the configurational statistics of a block copolymer is considered, the polymer being of the form (A–A–A . . . –A–)–(B–B . . . –B) where the AA, BB and AB interactions are different. The mathematics becomes very easy in the special case of potentials $V_{AA} = V_{BB} = -V_{AB}$, and it is shown that when $V_{AA}(= V_{BB})$ is attractive, V_{AB} repulsive a phase change can take place in the structure of the molecule. For short molecules (or weak V) the structure is that of a random flight with small local fluctuations. At a critical length (or critical V) the molecule takes up a statistical dumb-bell configuration which becomes more pronounced with increasing length (or increasing V). The theory is developed at the equivalent of a mean field theory level of accuracy. The equations are discussed for the general case $V_{AA} \neq V_{BB} \neq V_{AB}$, but the solution is there hampered by the intervention of an excluded volume problem.

1. Introduction

The following problem was posed to the author by Professor Benoit. Suppose one has a solution of a block copolymer molecule of the type A^{N_A}–B^{N_B}, where A and B can be rather different monomers, say a styrene and a butadiene. For very long chains one might expect, with suitable solvent and temperature, that one or both will condense. Certainly the degree of separation of glass-like and rubber-like constituents in a Kraton type material, ie the solid state of such block copolymers, is remarkable. In spite of the chemical bond between the two blocks, sharp surfaces appear separating spherical, rod-like, or planar regions, according to conditions. The problem posed is to find out whether a *single* block copolymer will undergo a phase change. Consider for simplicity always $N_A = N_B = N$, for it is easy but tiresome to look at the general case. Then for a small number of monomers, N, the dominant thing will be the entropy associated with the many configurations. Again for simplicity, freely-hinged chains will be assumed. However, the number of interactions possible will go up much faster than N if a non-uniform probability in space is taken up by the molecule. So providing the signs of the intermonomer forces are appropriate one can expect a critical N_c to exist at which the molecule will cease to be a random flight, and take up a non-uniform configuration. The level of technique of this paper will be that of replacing the true configurational integrals by their averages, ie the spirit is that of a mean field theory, though it is more complicated than the mean field theories of magnetism or of the Van der Waals liquid. This is a dangerous thing to have faith in, because in some aspects the polymer is one dimensional, and one-dimensional mean field theories are false. However, this is due to the enhancement of fluctuations by the sparse phase space of one dimension, and in the present problem one really is in the three-dimensional world. Thus although the

phase change discovered here will not be treated exactly at the critical point (as usual), it is believed that the effect is real and indeed portrayed with some accuracy.

2. The self-consistent field method

The forces present between the monomers making up the polymer chain will be repulsive at short distances, and attractive at long distances. Both types of forces are short-ranged compared with the end-to-end distance of the polymer or indeed of segments of it. Unless one is concerned with phenomena involving the fine structure of the forces, for example crystallization, one need not treat these effects separately but define an effective or pseudopotential which incorporates both features. The pseudopotential is defined so that the interaction in statistical equilibrium between monomer n and monomer m will be $\exp(-V_{nm}/kT)$ and V_{nm} will have a short-range form

$$\frac{V_{nm}}{kT} \sim -v_{nm}\delta(\mathbf{r}_n - \mathbf{r}_m). \tag{2.1}$$

The value v_{nm} will be positive if attractive forces predominate and negative if the short-range force is strongest. Clearly v will be a function of temperature and its value is the concern of polymer solution theory. As far as the present work is concerned it will be taken as a given parameter. At this point we give an outline argument for the basic equation (2.11), whilst putting a formal derivation in an appendix. Now consider one particular monomer, labelled 1 say. The Boltzmann factor weighting its role in the problem will be $\exp[+\Sigma_n v_{n1}\delta(\mathbf{r}_1 - \mathbf{r}_n)]$. The basic approximation will be to replace the variable $\mathbf{r}_n$ in this by the probability of finding $\mathbf{r}_n$ at a particular point in space. Let the probability of finding the nth monomer at $\mathbf{r}$ be $p_n(\mathbf{r})$. The self-consistent field approximation is to say that the Boltzmann factor for the Kth monomer is

$$\exp\left(-\int \sum_n v_{nK}\delta(\mathbf{r}_K - r)p_n(r)\,\mathrm{d}^3r\right) = \exp\left(-\sum_n v_{nK}p_n(\mathbf{r}_K)\right). \tag{2.2}$$

This approximation was introduced by the present author to study the excluded volume problem (Edwards 1965, 1966, also Freed 1971) and has recently been successfully applied to interfacial problems by Helfand and Tagami (1972). It is convenient to think of the label n replaced by a continuous variable s, ie $\mathbf{r}_n \rightarrow r(s)$. If the number of configurations of a force-free chain between s' and s when $r(s') = \mathbf{r}'$ and $r(s) = \mathbf{r}$ is called $G_0(\mathbf{r}, \mathbf{r}'; s, s')$, then G_0 satisfies the diffusion equation

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2\right)G_0(\mathbf{r}, \mathbf{r}'; s, s') = \delta(\mathbf{r} - \mathbf{r}')\delta(s - s') \tag{2.3}$$

$$G_0 = \exp\left(-\frac{3}{2l}\frac{(\mathbf{r}-\mathbf{r}')^2}{|s-s'|}\right)(s-s')^{-3/2}\left(\frac{3}{2l\pi}\right)^{3/2}. \tag{2.4}$$

The number of configurations will be modified by the Boltzmann factor, and by changing n to $n+1$ one sees a change $\Sigma_n v_{n,K+1}p_n(\mathbf{r}_{K+1})$, so moving to the continuous notation a factor

$$\exp\left(\mathrm{d}s \int v(s, s')p_s(r(s))\,\mathrm{d}s'\right), \tag{2.5}$$

ie $\partial/\partial s$ now brings down an extra factor $\int v(s, s')p_{s'}(r)\,ds'$, ie

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 - \int v(s, s_1)p_{s_1}(r)\,ds_1\right)G(r, r'; s, s') = \delta(r - r')\delta(s - s'). \qquad (2.6)$$

At this point the particular model is chosen of an AB block copolymer with monomers $1 \ldots N$ being A's, $N + 1 \ldots 2N$ being B's, and

$$v(s, s') = v \qquad \begin{array}{l} s, s' < N \\[6pt] s, s' > N \end{array}$$

$$v(s, s') = -v \qquad \begin{array}{l} s < N < s' \\[6pt] s' < N < s. \end{array} \qquad (2.7)$$

It is convenient to take the join of the A and B blocks as the origin and define

and
$$\begin{array}{ll} G_A(r, s) \text{ as } G(r_0, s_0) & 0 < s < N \\[6pt] G_B(r, s) \text{ as } G(r_0, s_0) & 2N > s > 0. \end{array} \qquad (2.8)$$

$$P_A(r, s) = \frac{G_A(r, s)}{\int G_A(r_1, s)\,d^3r_1} \qquad \int P_A(r, s)\,d^3r = 1$$

$$P_B(r, s) = \frac{G_B(r, s)}{\int G_B(r_1, s)\,d^3r} \qquad \int P_B(r, s)\,d^3r = 1 \qquad (2.9)$$

and finally the densities

$$\rho_A(r) = \int_N^0 P_A(r, s)\,ds$$

$$\rho_B(r) = \int_0^N P_B(r, s)\,ds. \qquad (2.10)$$

The diffusion equation is now

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 - v(\rho_A(r) - \rho_B(r))\right)G_A(r, s) = \delta(r)\delta(s)$$

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 - v(\rho_B(r) - \rho_A(r))\right)G_B(r, s) = \delta(r)\delta(s), \qquad (2.11)$$

which is the basic equation of this paper.

Some further simplification can now be obtained by defining

$$G = \frac{G_A + G_B}{2} \qquad F = \frac{G_A - G_B}{2}, \qquad (2.12)$$

and

$$\phi(s) = \int G_A(r, s)\,d^3r = \int G_B(r, s)\,d^3r \qquad (2.13)$$

by symmetry, so that the mean probability

$$P = \frac{G}{\phi}, \qquad (2.14)$$

and usefully one can also define

$$Q = \frac{F}{\phi}, \tag{2.15}$$

with

$$\rho(r) = \rho_A - \rho_B = \int Q(r, s) \, ds. \tag{2.16}$$

The basic equations can be rewritten as

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2\right)G - v\rho F = \delta$$
$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2\right)F - v\rho G = 0, \tag{2.17}$$

or in integral form

$$G(r, s) - v \int G_0(r, r_1; s, s_1)\rho(r_1)F(r_1, s_1) \, d^3r_1 \, ds_1 = G_0(r, s)$$
$$F(r, s) - v \int G_0(r, r_1; s, s_1)\rho(r_1)G(r_1, s_1)d^3r_1 \, ds_1 = 0. \tag{2.18}$$

If now the equation for P is integrated over r, since

$$\int G_0 \, d^3r = 1$$

one gets

$$\phi(s) - v \int \rho(r_1)\phi(s_1)Q(r_1, s_1) \, ds_1 \, d^3r_1 = 1. \tag{2.19}$$

Hence ϕ must be a constant with the value

$$\phi = \frac{1}{1 - v \int \rho^2(r) \, d^3r}, \tag{2.20}$$

since $\int Q(r_1, s_1) \, ds_1 = \rho(r_1)$. This greatly simplifies the analysis leaving

$$P(r, s) - v \int G_0(r, r_1; s, s_1)\rho(r_1)Q(r_1, s_1) \, d^3r_1 \, ds_1 = \left(\frac{G_0(r, s)}{\phi}\right)$$
$$Q(r, s) - v \int G_0(r, r_1; s, s_1)\rho(r_1)P(r_1, s_1)d^3r_1 \, ds_1 = 0. \tag{2.21}$$

There is one trivial solution,

$$Q = 0, \qquad \rho = 0, \qquad P = P_0, \qquad G = G_0. \tag{2.22}$$

The question is : is there another solution?

3. The phase change

It will now be shown that when $v(Ll)^{1/2}$ exceeds a numerical constant α, there is another solution and this solution represents a lower free energy than the random flight solution above. To see this firstly in general terms, the problem can be simplified by guessing the forms of Q and ρ within a scale factor and studying the scale factor. The boundary condition $Q(r, 0) = 0$, $\rho(0) = 0$ shows that if the second solution exists it must have at least a plane of antisymmetry, ie it will look something like $\mu x P_0$ where the plane of antisymmetry is chosen to be the y, z plane without loss of generality, and μ is a magnitude. To reduce (2.22) to an equation for μ alone, one may note that

$$\phi = \frac{1}{1 - v\mu^2\beta} \tag{3.1}$$

where $\beta = \int \rho^2 \, d^3r$. Hence

$$P = v \int G_0\rho Q + G_0(1 - v\mu^2\beta) \tag{3.2}$$

and

$$Q - v \int G_0\rho \left(v \int G_0\rho Q + G_0(1 - v\mu^2\beta) \right) = 0. \tag{3.3}$$

Substituting the trial $\mu x P_0$ for Q and ρ and multiplying (3.3) by $x P_0$ and integrating over all r, s yields

$$\mu - v\mu[v\mu^2\epsilon + \gamma(1 - v\mu^2\beta)] = 0 \tag{3.4}$$

where

$$\mu^3\epsilon = \int G_0\rho G_0\rho Q \tag{3.5}$$

and

$$\gamma = \int G_0\rho G_0. \tag{3.6}$$

The three quantities ϵ, γ, β are functions of L, l alone. The solution of (3.4) is either $\mu = 0$ or

$$1 - v[v\mu^2\epsilon + \gamma(1 - v\mu^2\beta)] = 0.$$

Thus

$$1 - v\gamma + v^2\mu^2(\beta\gamma - \epsilon) = 0$$

that is

$$\mu^2 = \frac{v\gamma - 1}{v^2(\beta\gamma - \epsilon)}. \tag{3.7}$$

The distributions Q, ρ are of course real, so μ must be real, which implies that $\gamma v > 1$ for the second solution to be possible, it being possible to show that $\beta\gamma > \epsilon$ by the Schwarz inequality. The critical value comes at $1 = \gamma v$ when Q, ρ are still zero and P is P_0. At this point γ can be evaluated and is a numerical constant times $(Ll)^{1/2}$, ie

$$v(Ll)^{1/2} = \alpha l^2,$$

or

$$Nv^2 = \alpha^2 l^2. \tag{3.8}$$

With this introduction a more rigorous treatment can be given, for the critical point will arise when, putting $P = P_0$, a solution for Q, ρ just becomes possible, ie

$$Q(r, s) - v \int G_0(r, r_1; s, s_1)\rho(r_1)G_0(r_1, s_1)\, d^3r_1\, ds_1 = 0 \tag{3.9}$$

has a solution with $\rho(0) = 0$. Equation (3.9) can be written in the differential form

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2\right)Q(r, s) - v\rho(r)G_0(r, s) = 0. \tag{3.10}$$

This can be integrated from 0 to L to give

$$-\frac{l}{6}\nabla^2\rho(r) - vg_0(r)\rho(r) = Q(r, L) \tag{3.11}$$

where

$$g_0(r) = \int G_0(r, s)\, ds = \frac{1}{r} - \text{Ei}\left[\left(\frac{r^2}{Ll}\right)^{1/2}\right]. \tag{3.12}$$

But $Q(r, L)$ is a very small quantity and can be safely ignored, so the problem is to find when the equation

$$\left(E - \frac{l}{6}\nabla^2 - vg_0(r)\right)\rho(r) = 0 \tag{3.13}$$

has a solution with $\rho(0) = 0$ and $E = 0$. The equation is written this way in analogy with the Schrödinger equation where E is the eigenvalue and $vg_0(r)$ the potential. The lowest eigenvalue with $\rho(0) = 0$ will be the p state $\rho = \cos\theta\sigma(|r|)$, so the problem is to discover the values of v, L for which the first p state emerges. The 'potential' $vg_0(r)$ looks like v/r at the origin and is experimentally small when $r^2 > Ll$. Without doing a detailed calculation it is clear on dimensional grounds that the condition is as above $v^2L = \alpha^2 l^3$, and it is well known from studies of this kind of equation that with a quite regular function $vg_0(r)$ appearing, the p state does indeed emerge. Detailed calculations can readily be done by say the Rayleigh–Ritz method, but obviously α is of order unity.

Now the pseudopotential will vanish at the temperature where the attractive potential just counterbalances the entropy due to short-range repulsions, the θ temperature of Flory. At this temperature the critical length is infinite. In general near $T = \theta$ one has, since

$$v(\theta) = 0$$

$$v(T) = v(\theta + T - \theta) = v(\theta) + (T - \theta)v' + \ldots.$$

Therefore near $T = \theta$

$$[v'(T - \theta)]^2 L = \alpha^2 l^3.$$

Thus as $T \to \theta$, $L \to L_c$ where

$$L_c \propto \frac{1}{(T - \theta)^2} = lN_c \qquad T < \theta. \tag{3.14}$$

One can expect that a more elaborate theory will give some slightly different power, following recent developments in the theory of critical phenomena, where mean field

theories have been shown to give powers which, though not rigorously correct, are reasonably near the truth.

If the length becomes much longer than L_c or v much larger, one can reach a point where $\phi \to 0$ and the polymer collapses into an absurd kind of 'dipole' near $r = 0$. This is of course due to an approximation of using a pseudopotential which is now attractive. A return to the realistic force with long- and short-range components will mean physical sense being maintained, but of course the real predominance of the attractive parts will lead to crystallization of the two blocks separately, touching at $r = 0$. The mathematics of this paper is inadequate to deal with that problem.

4. The general case

The case chosen was so chosen for simplicity. It would be surprising to find a system where $v_{AA} = v_{BB} = -v_{AB}$ and in general the diffusion–mean field equation becomes a matrix equation. This matrix of equations will not have the elegant properties of the system above, and it will take the form

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 - v_{AA}\rho_A + v_{AB}\rho_B \right) G_A = \delta$$

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 - v_{BB}\rho_B - v_{AB}\rho_A \right) G_B = \delta. \tag{4.1}$$

One can at least keep the boundary condition $\rho(0) = 0$ if one defines ρ, G, F, P, Q as before, but in addition introduces

$$\eta = \tfrac{1}{2}(\rho_A + \rho_B). \tag{4.2}$$

Then the forms are

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 + C_{11}\rho + C_{12}\eta \right) G = \delta$$

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 + C_{22}\rho + C_{12}\eta \right) F = 0. \tag{4.3}$$

If $F = \rho = 0$, one still has the non-linear problem

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla^2 + C_{12}\eta \right) G_1 = \delta. \tag{4.4}$$

which to the self-consistent field equation of the excluded volume problem as originally derived by Edwards (1965, 1966) (see also Freed 1971). The equation for the critical field is still (3.9), but with the G_1 of (4.4) used in it instead of G_0. Let us suppose all the $|v_{ij}|$ are of the same order of magnitude v. If the excluded volume mean square radius of the polymer is taken to be $L^{1+\xi}v^{\lambda}$, then the critical equation becomes

$$vL^{1+\xi}v^{\lambda} = l^{\psi}, \tag{4.5}$$

in particular the self-consistent equation (4.4) leads to $v^{2/5}L^{6/5}l^{2/5}$ so that

$$v(v^{2/5}L^{6/5}l^{2/5})^{1/2} \sim l^2. \tag{4.6}$$

Thus $v^{6/5}L^{3/5} = l^{9/5} \times$ constant and as before

$$L_c \propto \frac{1}{(T-\theta)^2}. \tag{4.7}$$

But if, however, one introduces v_e for the excluded volume and v_i for the coefficient of η,

$$v_i v_e^{1/5} L^{3/5} \sim l^{9/5}. \tag{4.8}$$

Thus the peculiar form

$$L_c \propto \frac{1}{(T-\theta)^{5/3}} \tag{4.9}$$

results.

It must be emphasized that solving (4.4) is *much* more difficult than solving (3.9).

5. Conclusion

It appears that in suitable circumstances block copolymer molecules can undergo phase changes. The present work prompts the idea that the solid state of such polymers might be tackled by similar methods and the author hopes to return to this in a later paper.

Acknowledgments

Appendix

The exact form for the entire distribution can be written

$$\mathcal{N} \exp\left(-\frac{3}{2l} \int R'^2(s)\, ds - \int \int \frac{V}{kT}(R(s_1) - R(s_2))\, ds_1\, ds_2 \right). \tag{A.1}$$

where the polymer is designated $R(s)$ and the interaction V which may be infinite in hard-core repulsions. If the two segments are designated $L, 0$ and $0, L$, we have

$$\left(-\frac{3}{2l} \int_{-L}^{0} R_A'^2\, ds - \frac{3}{2l} \int_{0}^{L} R_B'^2\, ds - \int_{-L}^{0} \int_{-L}^{0} \frac{V_{AA}}{kT}(R_A - R_A) \right.$$

$$\left. - \int_{-L}^{0} \int_{0}^{L} \frac{V_{AB}}{kT}(R_A - R_B) - \int_{0}^{L} \int_{0}^{L} \frac{V_{BB}}{kT}(R_B - R_B) \right). \tag{A.2}$$

If now the pseudopotential is substituted for V/kT and the self-consistent fields introduced, ie

$$\delta(R_A(s_1) - R_A(s_2)) = \int d^3r \delta(R_A(s_1) - r)\delta(r - R_A(s_2)) \, ds_1 \, ds_2$$

$$\simeq \int d^3r \delta(R_A(s_1) - r)P(r, s_2) \, ds_2$$

$$= \int p(R_A(s_1), s_2) \, ds_2$$

$$= \rho(R_A(s_1)). \tag{A.3}$$

The Wiener integral is now markovian and can be considered taken up to s rather than L, and the differential equations follow in the normal way.

References

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