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## The size of a polymer molecule in a strong solution

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**Abstract.** It is well known that a polymer molecule will tend to take up an ideal random flight configuration in a strong solution, because the expansion due to self-interaction is masked by the many other interactions with other molecules. In this paper the actual expression for the probability distribution is deduced as a function of temperature and solute density, since experiment is now reaching the point where such systems can be studied, and also because the problem is one of the rare problems in polymer theory which can be solved, and is non-trivial. If the effective repulsive interaction near the Flory  $\theta$  temperature is  $v = \omega(T - \theta)$ ,  $\rho$  is the solute density and  $l$  is the step length of the polymer, the end-to-end distance

$$\langle (R(L) - R(0))^2 \rangle = Ll[1 + a\omega(T - \theta)^{1/2}\rho^{-1/2}]$$

under conditions in which the correction term is small, where  $a$  is a constant. This expression vanishes at  $T = \theta$  and  $\rho = \infty$ , as it must.

### 1. Introduction

When polymer solution theory was first developed by Flory and by Huggins, it was already realized that when a solution became dense the many interactions between chains masked the self-interaction of any one chain, and a chain took up a random flight configuration and no longer posed the problem of the self-interacting walk which hampered very dilute solution theory. The latter is eased by studying near the Flory temperature  $\theta$ , where positive and negative interactions cancel, so that at  $T = \theta$  even in dilute solution a random flight may be assumed. When  $T > \theta$  the dense solution turns out to be a soluble problem in statistical mechanics having analogies with the electrolyte theory of Debye and Huckel (Edwards 1968), and the dynamics also turns out to be soluble, so that the viscosity of a strong solution (providing it is not so strong as to gel) is a soluble problem and simpler than the dilute solution theory (Edwards and Freed 1975). Recent experimental developments show that neutron scattering, particularly using deuterated samples, can estimate the size of molecules (Cotton *et al* 1971, 1972) and it becomes worthwhile to get an accurate expression for the size of a polymer molecule, even if the correction does not dominate the answer as it does in dilute solution.

Thus whereas a free flight will have

$$\langle (R(L) - R(0))^2 \rangle = Ll \tag{1.1}$$

where  $L = Nl$ ,  $N$  is the number of Kuhn step lengths in the polymer and  $l$  is the step

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length, in a dilute solution one of the favoured expressions is:

$$v^{2/5} L^{6/5} l^2 \tag{1.2}$$

where  $v$  is the effective interaction between monomers which, when one is near  $\theta$ , has the form  $\omega(T - \theta)$ , ie

$$\langle (R(L) - R(0))^2 \rangle \propto \omega^{2/5} (T - \theta)^{2/5} L^{6/5}. \tag{1.3}$$

In a strong solution one can expect the answer to return to (1.1), and the form derived in this paper will be

$$Ll[1 + a\omega^{1/2}(T - \theta)^{1/2}\rho^{-1/2}] \tag{1.4}$$

which gives a correction vanishing at  $T = \theta$  or at  $\rho = \infty$ , and clearly fails as  $\rho \rightarrow 0$ . In fact we shall derive rather wider expressions than this, but whereas a general theory for (1.3) and (1.4) is difficult one appears to be on firm ground in (1.4). For a very dense system (1.4) will fail because the system will gel. Mathematically it is very easy to produce a theory without gelation by putting no cross links in, or by ignoring entanglements. If there are no cross links the former is trivially correct except for transient hydrogen bonds perhaps. Provided chains are not extremely long, they will slip by one another in time, and so even the phenomenon of gelation will not spoil the present calculation which relies entirely on equilibrium statistical mechanics.

In § 2 a plausible derivation of the answer will be given. A systematic derivation allowing higher corrections is relegated to an appendix, since it involves more difficult mathematics and it agrees with the simple derivation in the region of interest.

## 2. The collective view of a strong solution

It will be recalled that in the theory of electrolytes, the Coulomb potential  $1/r$  becomes screened to the value  $e^{-r/\lambda}/r$  where  $\lambda = (4\pi\rho e^2/\kappa T)^{-1/2}$  is the Debye-Huckel screening length. This is usefully written in terms of the Fourier transform

$$\int \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r} d^3r = \frac{4\pi}{k^2} \quad \int \frac{e^{-r/\lambda}}{r} e^{i\mathbf{k}\cdot\mathbf{r}} d^3r = \frac{4\pi}{k^2 + \lambda^{-2}}$$

so that the screening alters  $1/k^2$  to  $1/(k^2 + \lambda^{-2})$ . Now in a polymer solution the interaction is local compared to the very large distances involved in the end-to-end distances which concern the present paper. Thus one can summarize both attractive and repulsive parts of the interaction by a pseudopotential  $U(r)$  such that the Fourier transform of  $U$  is effectively a constant, ie

$$\int e^{i\mathbf{k}\cdot\mathbf{r}} U(r) d^3r = u_k \quad \text{to a good approximation} \tag{2.1}$$

$$\simeq v\kappa T \tag{2.2}$$

where  $v$  is, to a good approximation, a constant in  $k$ . The result obtained earlier (Edwards 1966) confirmed that  $U_k$  is screened into

$$u_k - \frac{u_k}{1 + k^2 l^3 \kappa T / 12\rho u_k} \tag{2.3}$$

or

$$v \rightarrow v \frac{k^2}{k^2 + 12\rho v/l^3} = \frac{\tilde{U}_k}{\kappa T} \quad (\text{say}). \tag{2.4}$$

The screening therefore alters  $U(r)$  from  $v\kappa T\delta(r)$  to

$$\tilde{U} = v\kappa T \left( \delta(r) - \frac{e^{-\mu r}}{4\pi\mu^{-2}r} \right) \tag{2.5}$$

where

$$\mu^2 = 12\rho v/l^3. \tag{2.6}$$

This screening has the effect that now

$$\int \tilde{U}(r) d^3r = 0 \tag{2.7}$$

since this is the value of  $U_k$  when  $k = 0$ .

To see how the screening occurs, one notes the Boltzmann factor between links  $n$  of chain  $\alpha$  and  $m$  of chain  $\beta$ :

$$\exp \left( - \sum_{\alpha\beta} \sum_{nm} U(r_n^{(\alpha)} - r_m^{(\beta)}) / \kappa T \right) = \exp \left( -v \sum_{\alpha\beta} \sum_{nm} \delta(r_n^{(\alpha)} - r_m^{(\beta)}) \right). \tag{2.8}$$

The exponent can be split up studying one particular chain, call it  $r_n^{(1)}$ :

$$\sum \sum U(r_n^{(\alpha)} - r_m^{(\beta)}) = \sum_{nm} U(r_n^{(1)} - r_m^{(1)}) + \sum_n \sum'_{\beta m} U(r_n^{(1)} - r_m^{(\beta)}) + \sum'_{\alpha\beta} \sum_{nm} U(r_n^{(\alpha)} - r_m^{(\beta)}) \tag{2.9}$$

where  $\Sigma'$  means that  $r_n^{(1)}$  is now excluded. The important effects involve large distances, hence it is fruitful to consider chain 1 interacting with a polymer density:

$$\rho(r) = \sum_{\beta} \sum_n \delta(r - r_n^{(\beta)}) \tag{2.10}$$

or in the Fourier transform

$$\rho_k = \sum_{\beta} \sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n^{(\beta)}}. \tag{2.11}$$

Thus

$$\sum \sum U = \sum_{nm} U(r_m^{(1)} - r_n^{(1)}) + \sum_n \int U_k e^{i\mathbf{k}r_n^{(1)}} \rho_k d^3k + \int \rho_k \rho_k^* U_k d^3k \tag{2.12}$$

and the Boltzmann factor becomes

$$\exp \left( -v \sum_{nm} \delta(r_m^{(1)} - r_n^{(1)}) - v \sum_n \int \rho_k e^{i\mathbf{k}r_n^{(1)}} d^3k - v \int d^3k \rho_k \rho_k^* \right). \tag{2.13}$$

In addition to the Boltzmann factor, there will also be a probability weighting of the  $\rho_k$  simply due to the fact that they are the density fluctuations associated with a collection of random flight molecules, randomly distributed in space. It is well known, and will in effect be rigorously developed in the appendix, that such a distribution will give rise to a normal distribution of the  $\rho_k$  with the standard deviation which is obtained directly from the random flight statistics. (These need not be corrected by including the potential

effects on chains 2 ... since we only work to the first approximation; the appendix however is indeed self-consistent.) Directly then

$$\langle \rho_k \rho_j^* \rangle = \sum_{\alpha\beta} \sum_{mn} \langle e^{ik(r_n^{(\alpha)} - jr_m^{(\beta)})} \rangle \delta_{kj} \tag{2.14}$$

$$= \sum_{mn} e^{-k^2|m-n|l^2/6} \sum_{\alpha\beta} \delta_{\alpha\beta} \delta_{kj} \tag{2.15}$$

$$\simeq \rho_n \sum_{x=-\infty}^{\infty} e^{-k^2|x|l^2/6} \tag{2.16}$$

$$\simeq \rho_n \int_{-\infty}^{\infty} dx e^{-k^2|x|l^2/6} \delta_{kj} \quad \text{since } k \text{ is small and } L \text{ is large} \tag{2.17}$$

$$= 12\rho_n \delta_{kj} / k^2 l^2 \tag{2.18}$$

where  $\rho_n = Nn = NL/l$  and there are  $N$  chains of  $n$  links, which corresponds to a distribution:

$$\exp\left(-\int \rho_k \rho_k^* d^3k \frac{k^2 l^2 V}{12\rho_n (2\pi)^3}\right) \tag{2.19}$$

since  $\delta_{kj} \rightarrow \delta(k+j)(2\pi)^3/V$  and

$$\exp\left[-\left(\frac{V}{(2\pi)^3}\right)^2 \int d^3k d^3j \frac{(2\pi)^3}{V} \delta(k+j)\right]$$

is the joint probability. The total distribution in the  $\rho_k$  is then

$$\exp\left[-v \sum_n \frac{1}{(2\pi)^3} \int \rho_k e^{ikr_n^{(1)}} d^3k - \frac{1}{(2\pi)^3} \int \left(\frac{k^2 l^3}{12\rho} + v\right) \rho_k \rho_k^* d^3k\right] \prod d\rho \tag{2.20}$$

where  $\rho = NL/V$  is proportional to physical density. When the  $\rho_k$  are integrated out by completing the square, this gives

$$\begin{aligned} &\exp\left(+\sum_{mn} \frac{1}{(2\pi)^3} \int \frac{v^2}{v+k^2 l^3/12\rho} e^{ik(r_n^{(1)} - r_m^{(1)})} d^3k\right) \\ &\times \int \exp\left[-\frac{1}{(2\pi)^3} \int \left(\frac{k^2 l^3}{12\rho} + v\right) \tilde{\rho}_k \tilde{\rho}_k^* d^3k\right] \prod d\tilde{\rho} \end{aligned} \tag{2.21}$$

where  $\tilde{\rho} = \rho - v \sum e^{ikr_m^{(1)}}$ .

The remaining terms in  $r^{(1)}$  are therefore in the screened form

$$\exp\left[-\sum_{mn} \int \frac{d^3k}{(2\pi)^3} e^{ik(r_m^{(1)} - r_n^{(1)})} \left(v - \frac{v^2}{v+k^2 l^3/12\rho}\right)\right] \tag{2.22}$$

which equals

$$\exp\left(-\sum_{mn} \tilde{U}(r_m^{(1)} - r_n^{(1)}) / \kappa T\right). \tag{2.23}$$

Since the argument is all on the assumption that  $\tilde{U}$  is weak, the change in  $\langle (R(L) - R(0))^2 \rangle$  can be calculated in perturbation theory. This was done long ago by Fixman for short-range forces and gives corrections involving  $vL^{1/2}$ , which will not be small for large

enough  $L$ , but in the present case the screening gives an answer which is independent of  $L$ , and in a quite straightforward calculation (given in the appendix) gives

$$\langle (R(L) - R(0))^2 \rangle = Ll(1 + a_0 \rho^{-1/2} v^{1/2}) \tag{2.24}$$

where  $a_0$  is the constant  $2\sqrt{3}/\pi l^{5/2}$ . A self-consistent approach would have given

$$\begin{aligned} \langle (R(L) - R(0))^2 \rangle &= Ll\epsilon \\ \epsilon^{-1} &= 1 - a\rho^{-1/2} v^{1/2} \epsilon^{-5/2} \end{aligned} \tag{2.25}$$

but this does not represent a sound basis for a theory when  $\rho \sim 0$ , serving simply to reassure that  $\epsilon \simeq 1$  is a valid basis for approximation.

Near the  $\theta$  temperature one may expand  $v$  in terms of  $T - \theta$ ,

$$v = \omega(T - \theta). \tag{2.26}$$

(The  $\kappa T$  absorbed into the definition of  $v$  would only affect  $\omega$  to order  $(T - \theta)^2$ ; moreover, since  $v$  represents both repulsive and attractive parts of the potential, the  $\kappa T$  is partly conventional.) One then obtains the final form

$$\langle (R(L) - R(0))^2 \rangle = Ll[1 + a\rho^{-1/2}(T - \theta)^{1/2}] \tag{2.27}$$

where  $a = a_0\omega$ .

### 3. Extrapolation to dilute solutions

It is well known that in a dilute solution the end-to-end distance satisfies a power law

$$\langle (R(L) - R(0))^2 \rangle = L^\beta$$

where  $\beta \sim 1.2$  experimentally and certain theories give  $\beta$  analytically, eg  $\beta = \frac{6}{5}$ . Although this paper is not concerned with dilute solution it is of interest to produce an analytical formula which extrapolates between (2.27) and a dilute solution approach. To this one must choose some really simple dilute solution approach, and this we do by taking a very crude model in which an effective step length  $l/\alpha$  is used to model the polymer, ie

$$\langle (R(L) - R(0))^2 \rangle = Ll/\alpha, \quad \alpha = \alpha(L, v, \rho). \tag{3.1}$$

The work above has calculated  $\epsilon = \alpha^{-1}$ , but  $\alpha$  is a better parameter as we now show. The mathematical problem is that of a random walk with a potential in Fourier transform

$$U = v - \frac{v^2}{v + k^2 l^2 / 12\rho\alpha} \tag{3.2}$$

where now we are explicitly including  $\alpha$  in the  $k$  dependence of  $U$ . Mathematically we must evaluate

$$\int (R_1(L) - R_1(0))^2 \exp\left(-\frac{3}{2l} \sum \int R_n'^2(s) ds - \sum \sum v \iint \delta(R_n - R_m)\right) \tag{3.3}$$

which we have shown reduces to a single-chain model:

$$\exp\left(-\frac{3}{2l} \int R_n'^2 ds - \iint U(R_1(s_1) - R_1(s_2)) ds_1 ds_2\right). \tag{3.4}$$

The calculation for  $\alpha$  is now made by simulating this by putting

$$\exp\left(-\frac{3\alpha}{2l} \int R'^2 - \left\{ \frac{3}{2l} (1-\alpha) \int R'^2 + \iint U \right\}\right) \quad (3.5)$$

and treating the expression in braces as something whose effect will be made zero by the choice of  $\alpha$ . (Alternatively a variational calculation can be adopted—it yields the same results.) Calculating  $\langle (R(L) - R(0))^2 \rangle$  from (3.5) by expansion, one gets

$$\frac{Ll}{\alpha} = \langle (R(L) - R(0))^2 \rangle = \frac{Ll}{\alpha} + \left\{ \frac{(1-\alpha)}{\alpha^2} Ll + A(\alpha, \rho, L) \right\} \quad (3.6)$$

where the term in braces stems from the one in (3.5) and is calculated to first order in that expression, in (3.5), and

$$A = v \iint_0^L d^3k \frac{k^2 l^2}{36\alpha^2} s^2 ds e^{-k^2 l s / 6\alpha} \left( 1 - \frac{v}{v + k^2 l^2 / 12\rho\alpha} \right), \quad (3.7)$$

ie redefining  $k \rightarrow k\alpha^{1/2}$ ,

$$\frac{1-\alpha}{\alpha^2} = \int_0^L ds \int d^3k \alpha^{1/2} s^2 \frac{k^4 l^4}{12\rho k^2 l^2 / 12\rho + v} e^{-k^2 l s / 6} \quad (3.8)$$

or

$$1 = \alpha + b v \alpha^{5/2} \int_0^L \int \frac{k^6}{k^2 l^2 + 12v\rho} e^{-k^2 l s / 6} s^2 ds dk \quad (3.9)$$

where  $b$  is a constant, or

$$1 = \alpha + b \left( \frac{v}{\rho} \right)^{1/2} \alpha^{5/2} \int_0^\infty dj \frac{j^6}{j^2 + 1} \left( \frac{\partial^2}{\partial(j^2)^2} \right)^{\delta/2} \frac{1 - e^{-j^2 Ll}}{j^2/6} \quad (3.10)$$

$$= \alpha + c \left( \frac{v}{\rho} \right)^{1/2} \alpha^{5/2} \int_0^\infty \frac{dj}{j^2 + 1} [1 - e^{-j^2 Ll} (1 + Lj^2 + L^2 j^4)]. \quad (3.11)$$

This integral is not available in simple form, but a crude evaluation to illustrate its properties is given by

$$1 = \alpha + c \left( \frac{v}{\rho} \right)^{1/2} \alpha^{5/2} (1 - e^{-(Lv\rho)^{1/2}}). \quad (3.12)$$

If  $Lv\rho \rightarrow \infty$ , then

$$\alpha = 1 - c \left( \frac{v}{\rho} \right)^{1/2}. \quad (3.13)$$

If  $Lv\rho \rightarrow 0$ , then

$$\alpha = v^{-2/5} L^{-1/5}. \quad (3.14)$$

This calculation is offered merely as being indicative of what might be a starting point for a more elaborate theory. Other results could follow, for example the correlation function.

$$\int_0^\infty ds \delta(\mathbf{r} - \{\mathbf{R}(s) - \mathbf{R}(0)\})$$

has the values

$$r^{-4/3} \quad \text{for the dilute case}$$

and

$$\frac{1 + c^{(v/\rho)^{1/2}}}{r} \quad \text{for the concentrated case.} \quad (3.16)$$

#### 4. Conclusion

This paper has aimed to give a precise form to statements commonly made in the literature, particularly by Flory, which have not always been fully accepted. It fully confirms Flory's statement that in a concentrated solution a polymer takes random flight configuration, by explicitly calculating the extent to which it does not do so.

The results of this paper have consequences in neutron diffraction from polymers, since the quasi-elastic coherent scattering will tend to revert to Lorentzian form due to interactions. The results also will permit a more detailed study of polymer viscosity in concentrated solutions than that given by Edwards and Freed (1975). Dr Freed and I hope to return to these points in later papers.

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#### Appendix

Using the exact expression for the partition function of a system of  $N$  interacting chains ( $\alpha$ ):

$$Z = e^{-F/kT} = \mathcal{N} \int \delta r_\alpha \exp \left( \frac{-3}{2l} \sum_\alpha \int r_\alpha^2 ds_\alpha - \frac{v}{2l^2} \sum_{\alpha\beta} \iint ds_\alpha ds_\beta \delta(r_\alpha - r_\beta) \right)$$

where  $\mathcal{N}$  is the normalization,  $\alpha, \beta$  are chain labels,  $l$  is the step length and, as before,  $v\delta(r-r')$  is the pseudopotential term (§ 2). One may formally parametrize this interaction by noting that

$$\frac{v}{2l^2} \sum_{\alpha\beta} \iint ds_\alpha ds_\beta \delta(r_\alpha - r_\beta) \equiv \frac{v}{2l^2} \int \frac{d^3k}{(2\pi)^3} \sum_\alpha \int ds_\alpha e^{ikr_\alpha} \sum_\beta \int ds_\beta e^{-ikr_\beta} \equiv \int d^3k f(k)f(-k)$$

so that

$$\exp \left( - \int d^3k f(k)f(-k) \right) = \mathcal{N}' \int \delta \phi_k \exp \left( - \int \phi^2(k) d^3k - 2i \int \phi(k)f(k) d^3k \right)$$



where  $\delta\phi_k$  means an integral over the whole set of variables  $\phi_k$ . Then one has

$$\begin{aligned}
 e^{-F/\kappa T} &= \mathcal{N} \int \delta r_\alpha \delta \phi_k \exp \left( \frac{-3}{2l} \int \sum_\alpha \dot{r}_\alpha^2 ds_\alpha - \int \phi(k)^2 d^3 k - 2i \int \phi(k) f(k) d^3 k \right) \\
 &= \mathcal{N} \int \delta r_{\alpha\omega} \delta \phi_k \exp \left( \frac{-3}{2l} \sum_\alpha \int g^{-1}(\omega) d\omega - \int \phi(k) \Delta_k^{-1} \phi(k) d^3 k \right) \\
 &\quad \times \exp \left( \frac{-3}{2l} \sum_\alpha \int r_{\alpha\omega}^2 (\omega^2 - g^{-1}(\omega)) - \int \phi(k) (1 - \Delta_k^{-1}) \phi(k) \right) \\
 &\quad \times \exp \left( -2i \int \phi(k) f(k) d^3 k \right) \quad (\text{an identity}). \quad (\text{A.1})
 \end{aligned}$$

The corrections to  $g$  and  $\Delta$  are of the order of the square of the term in  $i \int \phi(k) f(k) d^3 k$  and are of course real. This means that we are unable to use the Feynman variational principle. Nevertheless we can get a good systematic procedure which is justified *post hoc* by expanding the expression

$$\left\{ \frac{-3}{2l} \sum_\alpha \int |r_{\alpha\omega}^2| (\omega^2 - g^{-1}(\omega)) d\omega - \int |\phi_k|^2 (1 - \Delta_k^{-1}) d^3 k \right\}$$

to order  $m$  say, and expression

$$\left( 2i \int \phi_k f_k d^3 k \right)$$

to order  $2m$ , and minimizing their joint effect, as was done in the version in § 2. In fact we just take the term in braces to order one and the term in parentheses to order two, but a study of higher-order terms shows that within logarithms the procedure amounts to an expansion in  $(T - \theta)^{1/2} \rho^{-1/2}$ . Evaluating the terms one finds

$$\begin{aligned}
 \exp \left( \frac{-F(\Delta_k, g(\omega))}{\kappa T} \right) &= \int d\omega \frac{3LN}{4\pi} \ln \left( \frac{2lg(\omega)}{3} \right) + \int \frac{d^3 k}{(2\pi)^3} \frac{V}{2} \ln \Delta_k - \frac{3LN}{4\pi} \int d\omega (\omega^2 g(\omega)^{-1} - 1) \\
 &\quad - \frac{V}{2(2\pi)^2} \int d^3 k \Delta_k^{-1} - \xi^2 N l \int d^3 k \Delta_k \int ds \exp \left( -\frac{k^2 l}{3\pi} \int \frac{d\omega \sin^2(\frac{1}{2}\omega s)}{g^{-1}(\omega)} \right) \quad (\text{A.2})
 \end{aligned}$$

where  $\xi^2 = v/2l^2(2\pi)^3$  was from the definition of  $f(k)$ :

$$f(k) = \xi \sum_\alpha \int ds_\alpha e^{+ik \cdot r_\alpha(s_\alpha)}. \quad (\text{A.3})$$

This value is now minimized by differentiating  $F(\Delta_k, g(\omega))$ :

$$\begin{aligned}
 \frac{\delta F}{\delta g(\sigma)} &= \frac{3LN}{4\pi} g^{-1}(\sigma) - \frac{3LN}{4\pi} \sigma^2 \\
 &\quad + \xi^2 LN \int d^3 k \Delta_k \frac{k^2 l}{3\pi} \int ds \sin^2 \frac{s\sigma}{2} \exp \left( -\frac{k^2 l}{3\pi} \int \frac{d\omega \sin^2(\frac{1}{2}\omega s)}{g^{-1}(\omega)} \right) = 0 \quad (\text{A.4})
 \end{aligned}$$

$$\frac{\delta F}{\delta \Delta_\rho} = \frac{V \Delta_\rho^{-1}}{2(2\pi)^3} - \frac{V}{2(2\pi)^3} - 2\xi^2 LN \int_{-\infty}^{\infty} ds \exp\left(\frac{-\rho^2 l}{3\pi} \int \frac{d\omega \sin^2(\frac{1}{2}\omega s)}{g^{-1}(\omega)}\right) = 0. \tag{A.5}$$

(coupled equations for  $\Delta_\rho$  and  $g(\sigma)$ ).

These equations are analogues of familiar forms in quantum field theory, the additional terms being ‘self-energy’ and ‘polarization’ terms. To get an approximate solution, we write  $g^{-1}(\omega) = \epsilon\omega^2$ , the Gaussian assumption. We use this in (A.5) to get a form for  $\Delta_\rho$ , then put  $\Delta_\rho$  in (A.4) and it is found that the result for  $g$  is consistent with the original assumption (ie we require a self-consistent argument):

$$\begin{aligned} \Delta_\rho^{-1} &= 1 + \beta^2/\rho^2 & \beta^2 &= 24(2\pi)^3 \xi^2 (LN/V)\epsilon/l \\ \Delta_\rho &= \rho^2/(\rho^2 + \beta^2) \end{aligned}$$

back in equation (A.4):

$$\epsilon\sigma^2 = \sigma^2 - \frac{4\pi}{9} \xi^2 l/\pi \int \frac{dk k^6 4\pi}{k^2 + \beta^2} \int ds \sin^2(\frac{1}{2}\sigma s) \exp\left(\frac{-k^2 l|s|}{2\epsilon}\right). \tag{A.6}$$

In the small- $\sigma$  region, we expand  $\sin^2(\frac{1}{2}\sigma s) \simeq (\frac{1}{2}\sigma s)^2$  and get a consistent result

$$g^{-1}(\sigma) = \sigma^2 - \sigma^2 f(\epsilon)$$

and this consistency gives a relation for  $\epsilon$ :

$$\epsilon = 1 - f(\epsilon).$$

From (A.6)

$$\begin{aligned} \epsilon &= 1 - \frac{4\pi}{9} \xi^2 l \int \frac{dk k^6 4\pi}{k^2 + \beta^2} \left(\frac{6\epsilon}{k^2 l}\right)^3 \\ \epsilon &= 1 - \left(\frac{v}{\rho}\right)^{1/2} \left(\frac{\epsilon}{l}\right)^{5/2} \frac{2\sqrt{3}}{\pi} \end{aligned} \tag{A.7}$$

where  $\rho = LN/V$ , proportional to the physical density.  $\epsilon \simeq 1$ . We put  $\epsilon = 1$  in the right-hand side. Also, near the  $\theta$  point we can express

$$v = a(T - \theta) + O[(T - \theta)^2].$$

Absorbing  $a$  and other constants,

$$\epsilon = 1 - b \left(\frac{T - \theta}{\rho}\right)^{1/2}.$$

*A.1. Regions of validity of the above derivation*

One must have

$$\begin{aligned} \left(\frac{v}{\rho}\right)^{1/2} \frac{1}{l^{5/2}} \frac{2\sqrt{3}}{\pi} &\ll 1 \\ \left(\frac{v}{l^3}\right)^{1/2} \left(\frac{V}{N}\right)^{1/2} 1.11 &\ll (Ll^2)^{1/2} \\ (Ll)^{3/2} &\sim v_0 \end{aligned}$$

where  $v_0$  is the volume of space explored by a randomly walking chain,

$$(Ll^2)^{1/2} = v_0^{1/2}(l/L)^{1/4}$$

$$\frac{V}{N} = v_c = \frac{\text{volume of solvent}}{\text{length of chain}}.$$

Hence one must have

$$1.11 \left(\frac{v}{l^3}\right)^{1/2} v_c^{1/2} \ll v_0^{1/2} \left(\frac{l}{L}\right)^{1/4}$$

where

$$\left(\frac{l}{L}\right)^{1/4} \sim 10^{-1.25}, \quad \left(\frac{v}{l^3}\right)^{1/2} \in (1, 10^{-3})$$

and the condition becomes roughly:  $v_c \ll v_0$ . This means we have to be in regions (i) and (ii) of the density classification given in Edwards (1966).

### A.2. Validity of the small- $\sigma$ expansion

We evaluate the integrals in (A.6) exactly:

$$\epsilon\sigma^2 = \sigma^2 - \frac{16\pi l \zeta^2}{9} \int_0^\infty \frac{dk k^6}{k^2 + \beta^2} \int_{-\infty}^\infty ds \sin^2(\frac{1}{2}\sigma s) \exp\left(\frac{-k^2 l |s|}{6\epsilon}\right)$$

and

$$\int ds \sin^2(\frac{1}{2}\sigma s) \exp\left(\frac{-k^2 l |s|}{6\epsilon}\right) = \frac{6\epsilon\sigma^2}{k^2 l (k^4 l^2 / 6^2 \epsilon^2 + \sigma^2)} = \left(\frac{6\epsilon}{l}\right)^3 \frac{\sigma^2}{k^2 [k^4 + (6\epsilon\sigma/l)^2]}.$$

Therefore,

$$\epsilon\sigma^2 = \sigma^2 - \frac{16\pi \zeta^2 6^3 \epsilon^3}{9l^2} \sigma^2 \int_0^\infty \frac{dk k^4}{(k^2 + \beta^2)(k^4 + \alpha^4)}$$

where  $\alpha^2 = 6\epsilon\sigma/l$  and

$$\int_0^\infty \frac{dk k^4}{(k^2 + \beta^2)(k^4 + \alpha^4)} = \frac{\pi}{\alpha^4 + \beta^4} \frac{1}{2} \left( \beta^3 + \frac{\alpha}{\sqrt{2}} (\beta^2 - \alpha^2) \right)$$

$$\epsilon\sigma^2 = \sigma^2 - \sigma^2 \frac{16\pi^2 \zeta^2 6^3 \epsilon^3}{9l^2} \frac{1}{2} \left( \frac{\beta^3 + (\alpha/\sqrt{2})(\beta^2 - \alpha^2)}{\alpha^4 + \beta^4} \right).$$

The conditions for self-consistency are:

- (a) for small  $\sigma$ , the correction term is small and has  $\sigma^2$  dependence;
- (b) for large  $\sigma$ , the correction term has  $\sigma^2$  dependence so that the relation is

$$\epsilon\sigma^2 = \sigma^2 - a\sigma^\alpha$$

and for large enough  $\sigma$  we have  $\sigma^2 \gg a\sigma^\alpha$ ;

- (c) for all intermediate values of  $\sigma$ ,  $1/L < \sigma < 1/l$ , we have the situation that, if  $\epsilon\sigma^2 = \sigma^2 - a\sigma^\alpha - b\sigma^2$  then

$$a \ll \sigma^{2-\alpha} \quad a = a(\rho, v).$$

Now since  $\rho = Nl/V$  and since the condition for self-consistency is  $\rho \gg 4(v/l_0^3)$  one finds for polydimethylsiloxane with  $l_0 \sim 3 \text{ \AA}$  and a typical degree of polymerization of 2250, the value  $(v/l_0^3)$  in the range 1 to  $10^{-1}$  and hence  $\rho \sim 1\%$ .

## References

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