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Polymers in poor solvents : loop expansion of irreducible diagrams (II)

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Abstract. — Properties of polymers in poor solvent are found by calculating irreducible diagrams to the order of one-loop. This approximation is valid for dilute and semi-dilute solutions. Expressions are given for the osmotic pressure, the size of a polymer in a solution and the density-density correlation function. A result obtained previously by S. F. Edwards and M. A. Moore is reproduced. However, as the method used here is more direct and flexible, it gives the possibility of calculating easily polydispersion effects.

1. Introduction. Polymers in poor solvent and the one-loop approximation. — In a preceding article [1] (to be referred as I), we discussed the application of the grand canonical formalism to the study of polymer solutions, we introduced the concept of reducibility with respect to the interaction lines and we showed that the main physical quantities can be expressed in terms of irreducible diagrams (the so-called I-irreducible diagrams).

To calculate such quantities we have now to evaluate these irreducible diagrams and this task is particularly simple for poor solvents because, in this case, the interaction is weak. Therefore, the relevant diagrams may contain many polymer lines but these polymer lines must be connected by a relatively low number of interaction lines. Let us be more specific: if a connected diagram contains \( N \) polymer lines and \( J \) interaction lines, it contains \( \ell \) loops where

\[
\ell = J - N + 1 \geq 0.
\]

If for a given \( N \), \( J \) is low, \( \ell \) must be low. Thus, polymers in poor solvents can be studied by considering only the diagrams with \( \ell = 0 \) and \( \ell = 1 \). This is the one-loop approximation which is worked out in this article.

The basic formalism is recalled in section 2. We calculate the osmotic pressure in section 3, the size of a polymer in section 4 and the density-density correlation function in section 5. These calculations apply to dilute or semi-dilute solutions of mono-disperse or polydisperse polymers.

2. Basic formalism and notation. — The notation used here is the same as in article I. By definition a diagram is I-irreducible if and only if it cannot be separated into two pieces by cutting an interaction line carrying a zero wave vector.

The I-irreducible partition function of \( N \) dissymmetric polymers made of \( N_1, \ldots, N_N \) monomers respectively is denoted by \( \mathcal{Z}_I(N_1, \ldots, N_N) \). If restrictions \( \mathcal{R} \) are applied to the polymers, we define in the same way a restricted partition function \( \mathcal{Z}_I(N_1, \ldots, N_N ; \mathcal{R}) \).

The coefficients which are introduced for calculating in wave space the diagrams contributing to \( \mathcal{Z}_I(N_1, \ldots, N_N) \) depend on a characteristic length \( l \) and on the excluded volume \( u \). We have

1) for each polymer segment of \( n \) links, carrying a wave vector \( k \), a factor \( \exp[- nk^2 l^2/2] \);
2) for each interaction line, a factor \( -u(2\pi)^{-d} \);
3) for the whole diagram, a factor \( (2\pi l^{-1})^{dN-1} \).

As was explained in I, the calculations can be made in the continuous limit and by eliminating the short
range divergences, we obtain the regularized partition functions

\[ \mathcal{Z}_f(N_1, \ldots, N_n) \text{ and } \mathcal{Z}_f(N_1, \ldots, N_n, R) \].

The corresponding grand partition functions are

\[ \mathcal{Z}_f(\{ h \}; R) = \sum_{N=1}^{\infty} \frac{1}{N!} \times \]

\[ \times \sum_{N_1, \ldots, N_n} h_{N_1} \cdots h_{N_n} \mathcal{Z}_f(N_1, \ldots, N_n; R) . \] (2.2)

The renormalized fugacities \( h_N \) can be considered as parameters. All the physical quantities will be expressed in terms of them.

Among these quantities, we have for instance the number \( C_N \) of \( N \) link polymers per unit volume, the total number \( C \) of polymers per unit volume and the total number of monomers \( c \) per unit volume

\[ C = \sum_{N} C_N \]
\[ c = \sum_{N} NC_N . \] (2.3)

Thus, the average number \( N' \) of links per polymer can be defined by

\[ N' = c/C . \] (2.4)

Results will be often expressed in terms of the classical dimensionless parameter

\[ z_N = \frac{u l^{-d} N^{2-d/2}}{(2\pi)^{d/2}} \] (2.5)

where \( d \) is the space dimension (actually \( d = 3 \)).

Since we deal here with rather poor solvents \( z_N \) will be considered as small \( (u l^{-3} N^{1/2} \ll (2\pi)^{3/2}) \).

In this case, a loop expansion is valid and in the following sections, we shall calculate in this way interesting physical quantities.

3. Osmotic pressure and concentrations. — As was shown in I, the number \( C_N \) of polymers with \( N \) links and the osmotic pressure \( \Pi \) are given by

\[ C_N = l^{-d} h_N \partial h_N \mathcal{Z}_f(\{ h \}) \]
\[ \Pi \beta = l^{-d} \mathcal{Z}_f(\{ h \}) \text{ } + \text{ } \frac{1}{2} c^2 u \quad (d = 3) . \] (3.1)

The simple tree approximation or zero loop approximation is trivial (see Fig. 1). The corresponding contribution to \( \mathcal{Z}_f(N_1, \ldots, N_n) \) is the one polymer term \( \mathcal{Z}_f^0(N) = \mathcal{Z}_f^0(N) = 1 \).

Fig. 1. — The trivial diagram corresponding to the zero loop approximation.

Fig. 2. — Calculation of \( \Pi \) : one-loop diagrams. The first diagram \((N = 1)\) is divergent and must be renormalized. The other ones are convergent \((N = 2, 3, 4, \ldots)\).

We may now proceed one step further. Let \( \mathcal{Z}_f^0(N_1, \ldots, N_n) \) be the contribution of the one-loop diagrams which are represented on figure 2.

We find by applying the rules given in I and summarized in section 2

\[ \mathcal{Z}_f^0(N_1, \ldots, N_n) = \frac{l^d}{(2\pi)^d} (ul^{-d})^N 2^{N-1}(N-1)! \int d^d k \prod_{j=1}^{N} G_{N}^0(k) , \] (3.2)

where \( 2^{N-1}(N-1)! \) is a counting factor.

The function \( G_{N}^0(k) \) is

\[ G_{N}^0(k) = \int_0^N d n (N-n)e^{-nk^{3/2}} \]
\[ = (N-n_0)e^{-n_0k^{3/2}} - \frac{e^{-n_0k^{3/2}} - e^{-nk^{3/2}}}{(k^2 l^2/2)^2} , \] (3.3)

where \( n_0 \) is a small cut-off.
For \( N > 1 \), we may calculate \( \gamma_1(N_1, \ldots, N_N) \) by putting \( n_0 = 0 \) and by replacing \( G_N^0(k) \) in equation (3.2) by
\[
G_N(k) = \frac{N}{k^2 l^2/2} - \frac{1 - e^{-N k^2/2}}{(k^2 l^2/2)^2},
\]
because in this case \( \int d^d k \, I_j \, G_N(k) \) converges.

However this cannot be done for \( N = 1 \) and, as was pointed out by S. F. Edwards [3] in 1966, this case has to be treated separately. Actually \( \int d^d k \, G_N(k) \) diverges and the terms of this integral which become infinite when \( n_0 \to 0 \), are
\[
(N - n_0) \int d^d k \frac{e^{-N k^2/2}}{k^2 l^2/2} c \frac{N - n_0}{n_0^2 + \delta^2}.
\]
Thus for calculating \( \gamma_1(N) \) from \( \gamma_2(N) \), we have to subtract this term as was explained in 1.

This can be done by replacing \( G_N^0(k) \) by \( G_N(k) = \frac{2N}{k^2 l^2} \). As a consequence we have:

for \( N = 1 \)
\[
\gamma_1^0(N) = 1
\]
\[
\gamma_1^1(N) = \frac{1}{2(2 \pi)^d/2} (-2 u l^{-d}) \int d^d k \, \left[- \frac{1}{k^4} + \frac{e^{-N k^2}}{k^4}\right],
\]
for \( N > 1 \)
\[
\gamma_1^0(N_1, \ldots, N_N) = 0
to I \left( \frac{N}{k^2 l^2} - \frac{1 - e^{-N k^2/2}}{(k^2 l^2/2)^2}\right).
\]

Let us bring these results in the expression of \( \gamma_1(\{h\}) \) (see Eq. (2.1)); we find the one loop approximation.

\[
\gamma_1(\{h\}) = \sum_N h_N + \frac{1}{2(2 \pi)^d/2} \int d^d k \left\{ (2 u l^{-d}) \frac{1}{k^2} \sum_N N h_N - \log \left[ 1 + 2 u l^{-d} \sum_N h_N \left( \frac{N}{k^2} - \frac{1}{k^4} + \frac{e^{-N k^2}}{k^4}\right) \right] \right\}.
\]

In particular for \( d = 3 \)
\[
\gamma_1(\{h\}) = \sum_N h_N + \frac{1/2}{2 \pi^2} \int_0^\infty dx \left\{ 2 u l^{-3} \sum_N N h_N - \chi^2 \log \left[ 1 + 2 u l^{-3} \sum_N h_N \left( \frac{N}{\chi^2} - \frac{1}{x^4} + \frac{e^{-N x^2}}{x^4}\right) \right] \right\}
\]
and this expression can be used in equation (5.2), to obtain a parametric representation of \( \Pi \) and \( \mathcal{C}_N \). In particular, we can study the limits of small \( h_N \) or large \( h_N \).

A) For small \( h_N \), we have
\[
\gamma_1(\{h\}) = \sum_N h_N + \frac{4}{(2 \pi)^3/2} (u l^{-3}) \sum_N N^{1/2} h_N + \frac{16}{15 (2 \pi)^3/2} (u l^{-3})^2 \sum_{A,B} [5 A B^{3/2} - (A + B)^{3/2} + 2 A^{3/2}] h_A h_B.
\]

In this case, the value of the osmotic pressure depends on the polydispersity of the polymer and by bringing (3.8) in (3.1), it would not be difficult to show explicitly such effects.

However, for reasons of simplicity, we shall assume here that the system is monodisperse. Each polymer has \( N \) links and we may set \( h_N = h \) and \( C_N = C \). In this case, it is convenient to write
\[
\gamma_1(h) = (u l^{-3} N^2)^{-1} w(h u l^{-3} N^2),
\]
where
\[
w(t) = (1 + 4 z_N) t + \frac{16}{15} (7 - 4.2 l^{-1}) z_N i^2.
\]
On the other hand, equation (3.1) gives
\[ \Pi \beta = \frac{w(t)}{\nu N^2} + \frac{1}{2} \sigma^2 u N^2 \]  
(3.10)
\[ CuN^2 = \tau \frac{\partial}{\partial t} w(t) . \]

Thus, for small concentrations (CuN^2 \ll 1), we find
\[ \Pi \beta \approx C \left\{ \frac{1}{2} + \frac{1}{2} \frac{CuN^2}{C} + CuN^2 \left[ 1 + \left( 1 + \frac{128(7 - 4.2^{1/2})}{15(1 + 4 \zeta_2)^2} CuN^2 \right)^{1/2} \right]^{-1} \right\}^2 . \]  
(3.11)

B) For large values of hN, the large k regions are dominant in the integral which appears on the right hand side of equation (3.6). In this case, which corresponds to large concentrations (CuN^2 \gg 1), we may write
\[ \tilde{\gamma}(h) \approx \sum_{N} h_N + \frac{2^{1/2}}{2 \pi^2} \int_{0}^{\infty} dx \left\{ 2 u l^{-3} \sum_{N} Nh_N - x^2 \ln \left[ 1 + \frac{2 u l^{-3}}{x^2} \sum_{N} Nh_N \right] \right\} , \]

(3.12)
or more explicitly
\[ \tilde{\gamma}(h) \approx \sum_{N} h_N + \frac{2}{3 \pi} \left( u l^{-3} \sum_{N} Nh_N \right)^{3/2} . \]

(3.13)
Using this result in equation (3.1), we find
\[ C_N l^3 = h_N + \frac{1}{\pi} Nh_N \left( u l^{-3} \sum_{N} Nh_N \right)^{1/2} . \]
\[ \Pi \beta l^3 = \sum_{N} h_N + \frac{2}{3 \pi} \left( u l^{-3} \sum_{N} Nh_N \right)^{3/2} + \frac{1}{2} \sigma^2 u l^3 . \]
\[ = \frac{2}{3} \frac{C l^3}{\sigma} + \frac{1}{3} \sum_{N} h_N + \frac{1}{2} \sigma^2 u l^3 . \]
(3.14)
It is convenient to introduce a new variable \( \alpha \) defined by
\[ \alpha^2 = u l^{-3} \sum_{N} Nh_N . \]
(3.15)
Now equation (3.13) may be written in the form
\[ h_N = \frac{C_N l^3}{1 + N \pi^{-1} (u l^{-3}) \alpha} . \]
(3.16)
and \( \alpha \) is determined by the implicit equation:
\[ \alpha^2 = u \sum_{N} \frac{NC_N}{1 + N \pi^{-1} (u l^{-3}) \alpha} . \]
(3.17)

On the other hand, the osmotic pressure is given by
\[ \Pi \beta = \frac{2}{3} C + \frac{1}{2} \sigma^2 u + \frac{1}{3} \sum_{N} \frac{C_N}{1 + N \pi^{-1} (u l^{-3}) \alpha} . \]
(3.18)
and polydispersion effects appear clearly on this formula. Now, two different situations may occur.

For moderately large concentrations or rather poor solvents \( \mathcal{N}(u l^{-3}) \) is small (Cu^3 \ll \nu^2 \ll \nu^2) and we have \( \alpha^2 \approx \sigma \)
\[ \Pi \beta \approx C + \frac{1}{2} \sigma^2 u - \frac{1}{3 \pi} (Cu)^{3/2} l^{-3} . \]
(3.19)

Thus, we find exactly the result obtained by S. F. Edwards [2] and M. A. Moore [3]. Moreover, we check the prediction made by Moore, that in this case polydispersion effects disappear.

In the monodisperse case, the preceding equation can be also written in the form
\[ \Pi \beta = C \left[ 1 + \frac{1}{2} CuN^2 - \frac{2}{3} (2 \pi)^{1/2} \zeta_6 (CuN^2) \right] \]
(3.20)
On the contrary, for rather large concentrations and moderately poor solvents \( \mathcal{N}(u l^{-3}) \alpha \) is large (Cu^3 \ll \nu^2 \ll \nu^2) and we have
\[ \alpha = (\pi C l^3)^{1/3} \]
\[ \Pi \beta = \frac{2}{3} C + \frac{1}{2} \sigma^2 u + \frac{1}{3} (2 \pi)^{-1/3} \left( \sum_{N} \frac{C_N}{N} \right) u^{-1} l^2 . \]
(3.21)
We see again in this case that the polydispersion effects are taken into account in a simple way. In the monodisperse case, we may also write the preceding equation in the form
\[ \Pi \beta = C \left[ \frac{2}{3} + \frac{1}{2} CuN^2 + \frac{\pi^{-1/3}}{6} (\zeta_6)^{-2/3} (CuN^2)^{-1/3} \right] \]
(3.22)
However, the validity of the one loop approximation for these rather high concentrations is doubtful.
4. **End to end distance.** — Let us consider the configurations in which the vector joining the origin of an $N$ link polymer to the extremity of the same polymer has a given value $r$.

The corresponding restricted irreducible partition function will be denoted by $\tilde{\mathcal{Z}}_\ell(N, N_1, \ldots, N_N; r)$ and we shall be essentially interested in the Fourier transform of the regularized partition function

$$\tilde{\mathcal{Z}}_\ell(N, N_1, \ldots, N_N; \mathbf{k}) = \int \mathcal{D}r \ e^{i \mathbf{k} \cdot \mathbf{r}} \tilde{\mathcal{Z}}_\ell(N, N_1, \ldots, N_N; r).$$  \hspace{1cm} (4.1)

![Fig. 3. — Calculation of $P_N(k)$: one-loop diagrams.](image)

The corresponding grand partition function is

$$\mathcal{Z}_\ell(\{ h \}; N, \mathbf{k}) = \sum_{N_{\alpha}=1}^{\infty} \frac{1}{N_{\alpha}!} h_{N_{\alpha}} h_{N_{\alpha}} \ldots h_{N_{\alpha}} \tilde{\mathcal{Z}}_\ell(N, N_1, \ldots, N_N; \mathbf{k}).$$  \hspace{1cm} (4.2)

It is easy to verify from equations (2.2) and (3.1) that

$$C_N l^d = \mathcal{Z}_\ell(\{ h \}; N, 0).$$  \hspace{1cm} (4.3)

Let $P_N(r)$ be the probability distribution of $r$ and $\tilde{P}_N(k)$ its Fourier transform

$$\mathcal{P}_N(k) = \langle e^{i k \cdot \mathbf{r}} \rangle.$$  \hspace{1cm} (4.4)

We have

$$C_N l^d \mathcal{P}_N(k) = \mathcal{Z}_\ell(\{ h \}; N, \mathbf{k}).$$  \hspace{1cm} (4.5)

Thus

$$R_N^2 \equiv \langle r^2 \rangle = -2 d \frac{\partial}{\partial (k^2)} \left[ \ln \mathcal{Z}_\ell(\{ h \}; N, \mathbf{k}) \right]_{k=0}.$$  \hspace{1cm} (4.6)

The one loop contribution to $\tilde{\mathcal{Z}}_\ell(\{ h \}; N, \mathbf{k})$ is (see Fig. 3)

$$\tilde{\mathcal{Z}}_\ell(\{ h \}; N, \mathbf{k}) = \frac{f^d}{(2 \pi)^d} (u l^{-d})^{N+1} 2^N N! \int \mathcal{D}q \ J(k, q) \prod_{j=1}^{N} G_{k^j}(q)$$  \hspace{1cm} (4.7)

where $G_{k^j}(q)$ is defined by (3.3) and

$$J_0(k, q) = \int_{n_0}^{N} \mathcal{D}n \ (N - n) \ e^{-N - n(q+n)/2} e^{-n(k+q)(n/2)}.$$  \hspace{1cm} (4.8)

In the limit $n_0 \to 0$, we have

$$J_0(k, q) = \left[ \frac{N}{(k+q)^2/2} - 1 - e^{-N(k+q+q/2)^2/2} \right] e^{-Nk/2/2}.$$  \hspace{1cm} (4.9)

Thus, after regularization and a scale transformation, we find:

for $N = 1$

$$\tilde{\mathcal{Z}}_\ell(0, N; k, 2^{-1/2}) = e^{-Nk^2}$$  \hspace{1cm} (4.10)

$$\tilde{\mathcal{Z}}_\ell(1, N; k, 2^{-1/2}) = \frac{e^{-Nk^2}}{2(2 \pi)^d} \left( -2 u l^{-d} \right) \int \mathcal{D}q \left( -\frac{2 Nkq}{q^2 + 2kq} - 1 \right) + e^{-N(q^2 + 2kq)}.$$  \hspace{1cm} (4.11)
As a consequence, we find

\[
\frac{\Delta \mu(N, N_1, \ldots, N_N; k/2^{1/2})}{N!} = \frac{\Delta \mu(N, N_1, \ldots, N_N; k/2^{1/2})}{N!} = \frac{e^{-N\xi^2}}{2(2\pi)^{d/2}} \left( -2u^{1/2} \right)^{N+1} \times \int d^d q \left[ \frac{N}{q^2 + 2\kappa q} - \frac{1}{(q^2 + 2\kappa q)^2} + \frac{e^{-Nq^2 + 2\kappa q}}{(q^2 + 2\kappa q)^2} \right] \times \prod_{j=1}^{N} \left[ \frac{N_j}{q^2 - \frac{1}{q^2} + \frac{e^{-N_j\xi^2}}{q^2}} \right].
\] 

(4.12)

As a consequence, we find

\[
\Delta \mu(h; N, k/2^{1/2}) = e^{-N\xi^2} \left[ 1 + \frac{u^{1/2}}{(2\pi)^{d/2}} \right] \int d^d q \left\{ \frac{N}{q^2} - \left( \frac{N}{q^2 + 2\kappa q} - \frac{1}{(q^2 + 2\kappa q)^2} + \frac{e^{-N(q^2 + 2\kappa q)}}{(q^2 + 2\kappa q)^2} \right) \left[ 1 + \frac{2}{u^{1/2}} \sum_{A} h_{A} \left( \frac{A}{q^2} - \frac{1}{q^2} + \frac{e^{-A\kappa q}}{q^2} \right) \right]^{-1} \right\}.
\] 

(4.13)

Let us bring this expression in (4.6), we find

\[
R^2_N = d^2 \left\{ N + 2 \frac{h_N}{C_N} \frac{u^{1/2}}{(2\pi)^{d/2}} \times \int d^d q \left[ \frac{2N}{q^2} - 6 \left\{ 2 - 4 \frac{N}{q^2} + 4 \frac{N^2}{q^2} \right\} \left( \frac{N}{q^2 + 2\kappa q} - \frac{1}{(q^2 + 2\kappa q)^2} + \frac{e^{-N(q^2 + 2\kappa q)}}{(q^2 + 2\kappa q)^2} \right) \right] \times \left[ 1 + \frac{2}{u^{1/2}} \sum_{A} h_{A} \left( \frac{A}{q^2} - \frac{1}{q^2} + \frac{e^{-A\kappa q}}{q^2} \right) \right]^{-1} \right\}.
\] 

(4.14)

Like the osmotic pressure, this quantity can be studied in different limiting cases for which simple calculations are possible.

Thus, we may consider here the semi-dilute region which is particularly interesting. In this case, the parameters \( h_A \) are large and the relevant values of \( q \) are also large.

Consequently, for \( uN^2 \gg 1 \) and \( d = 3 \), we may unite

\[
R^2_N = 3 \frac{I^2}{N!} \left\{ N + 2 \frac{h_N}{C_N} \frac{u^{1/2}}{\pi^2} \int d^d q \left[ 2N - 6 \left\{ 2 - 4 \frac{N}{q^2} + 4 \frac{N^2}{q^2} \right\} \left( \frac{N}{q^2 + 2\kappa q} - \frac{1}{(q^2 + 2\kappa q)^2} + \frac{e^{-N(q^2 + 2\kappa q)}}{(q^2 + 2\kappa q)^2} \right) \right] \times \left[ 1 + \frac{2}{u^{1/2}} \sum_{A} h_{A} \left( \frac{A}{q^2} - \frac{1}{q^2} + \frac{e^{-A\kappa q}}{q^2} \right) \right]^{-1} \right\}.
\] 

(4.15)

This equation, the definition (3.15) of \( \epsilon \) and equation (3.16) give

\[
R^2_N = 3 \frac{I^2}{N!} \left\{ N + (u^{-1})^{-1} \frac{\pi}{\alpha} + (u^{-1})^{-1} \frac{N}{N^2} H(2N\kappa) \right\},
\] 

(4.16)

where

\[
H(x) = x + 3 + \pi^{-1/2} x^{1/2} \left( \frac{x}{2} - 6 \right) - \pi^{-1/2} \left( \frac{x}{2} - 2x + 3 \right) \int_{0}^{x} \frac{e^{-t}}{(t + x)^{1/2}} dt.
\] 

(4.17)

We note that

\[
H(x) \approx x \quad x \gg 1.
\] 

(4.18)

Incidentally, we see from equations (3.15) and (4.13) that the screening length \( \xi \) introduced by S. F. Edwards [4] can be defined here by the equality

\[
\xi = I^2/2N.
\] 

(4.19)

In particular for moderately large concentrations and rather poor solvents (\( Cu^3 l^{-3}; N^3 \approx 1 \)), \( N^{(u^{-1})} \alpha \) is small and we have

\[
\alpha = cu.
\]

\[
R^2_N = 3 \frac{I^2}{N!} \left\{ N + \pi^{-1} e^{-3} u^{-2} l^{-3} H(2N^2\kappa^2) \right\}.
\] 

(4.20)

This result is valid for monodisperse and polydisperse solutions. The result is particularly simple if the chain is long (\( N\kappa^2 u^2 \gg 1 \)) and in this case

\[
R^2_N = 3 \frac{I^2}{N!} \left\{ N + 2(\pi N^3)^{-1} \right\}.
\] 

(4.21)

On the contrary, for fairly large concentrations and moderately poor solvents (\( Cu^3 l^{-3}; N^3 \gg 1 \)), \( N^{(u^{-1})} \alpha \) is large; we have

\[
\alpha = (\pi N^3)^{1/3}
\]

\[
R^2_N = 3 \frac{I^2}{N!} \left\{ N + N^{-1}(\pi N^3)^{4/3} H(2N(\pi N^3)^{1/3}) \right\},
\] 

(4.22)

and if the chain is very short

\[
R^2_N = 3 \frac{I^2}{N!} \left\{ N + 2(\pi N N^3)^{-1} \right\}.
\] 

(4.23)
If the system is monodisperse, we may also express $c l^3$ and $NC l^3$ in terms of the current parameters $z_N$ and $C u N^2$.

5. Density-density correlation function. — The same method can be used to calculate the density-density correlation function for polymers of link numbers $A$ and $B$. This function $C_G(r; A, B)$ is of the form ($A \neq B$)

$$C_G(r; A, B) = C_A C_B + C(r; A, B). \quad (5.1)$$

Here $r$ is the vector joining a point of a polymer with $A$ links to a point of a polymer with $B$ links.

The relevant quantity is the Fourier transform of $C(r; A, B)$

$$\tilde{C}(k; A, B) = \int d^d r \ C(r; A, B) e^{i k \cdot r}. \quad (5.2)$$

The calculation of the one loop approximation is straightforward but not very simple in the general case. For this reason, we shall calculate only the zero loop approximation.

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Fig. 4. — The zero loop diagram corresponding to the calculation of the density correlation function.

The corresponding I-irreducible diagram is shown on figure 4. We use a grand canonical formalism and as was shown in I, the correlation function is given by an I-irreducible grand partition function

$$C(k; A, B) = l^{-d} \gamma_1(\{h\}; k; A, B). \quad (5.3)$$

Using the same notation as before, we find

$$\gamma_1(\{h\}; k; A, B) = h_A h_B G_A^0(h) G_B^0(k) \times$$

$$\times \sum_{p=0}^{\infty} (-2u l^{-d})^p \sum_N h_N G_N^0(k). \quad (5.4)$$

and after passing to the limit $n_0 \to 0$

$$C(k; A, B) = h_A h_B (2u l^{-d}) G_A(k) G_B(k) \frac{1}{1 + 2u l^{-d} \sum_N h_N G_N(k)}. \quad (5.5)$$

On the other hand, the zero loop approximation gives $C_N l^4 = h_N$.

We obtain in this way

$$C(k; A, B) = -\frac{2u C_A C_B G_A(k) G_B(k)}{1 + 2u \sum_N C_N G_N(k)}. \quad (5.6)$$

where $G_N(k)$ is given by equation (3.4).

6. Conclusion. — In this article, we have shown that the properties of polymer solutions in poor solvents can be studied by using loop expansions. As examples, we gave formulas for the osmotic pressure, the end to end distance of a polymer and the density-density correlation functions.

The method used here is elementary but powerful. In particular, we have been able to reproduce a formula concerning the osmotic pressure and obtained previously by Edwards and Moore.

This formula has been derived here under the assumption that the effect of the excluded volume is small $(u l^{-3} N^{1/2} \ll (2\pi)^{3/2})$. However, it seems clear that the same restriction applies to the derivations of Edwards and Moore. In fact, one loop expansion are not sufficient to describe strong excluded volume effects.

Our method has the advantage of using straightforward perturbation theory for the calculation of simple irreducible diagrams. Thus all the simple tree diagrams are automatically eliminated. This technique is also very flexible and many other physical quantities could be calculated by using the same approach. In particular, we must emphasize the fact that polydispersion effects can be easily calculated.

However, more sophisticated methods must be used if the interaction is not small and, for determining the properties of good solvents, renormalization processes have to be introduced. The problem has been already studied by many physicists. However the methods used so far are not completely satisfactory: more work has to be done concerning the critical domain and we intend to come back later to this interesting question.

References