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Submitted on 1 Jan 1977

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THEORY OF SEMI-DILUTE POLYMER SOLUTIONS

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(Reçu le 29 octobre 1976, accepté le 24 novembre 1976)

Abstract. — Some properties of semi-dilute poor and good solvent polymer solutions are examined within the framework of the field-theoretic formulism. The uncontrollable polydispersivity inherent in the field-theoretic formulism is shown to produce no errors if the quantity under investigation is molecular weight independent. A renormalization group cross-over calculation correct to order $\varepsilon^3$ is performed to obtain an expression for the osmotic pressure which holds in both poor and good solvent limits for the special case where the ternary cluster integral vanishes.

1. Introduction. — Recently, considerable advances have been made in our understanding of semi-dilute polymer solutions. This has been brought about through neutron scattering experiments [1] and their interpretation by means of scaling ideas [2, 3, 4]. In particular, Daoud and Jannink [4] have attempted to delineate all possible regions in the temperature-concentration diagram of polymer solutions using a scaling analysis based on the analogy with tricritical behaviour [5]. They find five regions, in each of which quantities like the mean-square end-to-end distance of each polymer, the osmotic pressure and screening length, etc., have distinctive asymptotic behaviour as functions of molecular weight or concentration. Such scaling analyses, while very useful, only give qualitative information. In this paper, we shall study in detail two of the regions described by Daoud and Jannink [4] — the semi-dilute good solvent region and the semi-dilute poor (theta) solvent region (regions II and III in their notation).

The semi-dilute poor solvent region was studied by Edwards [6] who obtained an expression for the screening length as a function of the concentration of polymer segments, which at first sight completely differs from that derived by Daoud and Jannink [4] by means of scaling arguments. We shall find that the expression given by Edwards is valid when the ternary cluster integral (or third virial coefficient at the $\theta$-point) vanishes or is very small, otherwise the expression given by Daoud and Jannink is appropriate.

To discuss the matter further, we must first introduce some terminology. Let $v$ be the excluded volume parameter as used by Edwards [6] and let $\beta$ be the ternary cluster integral. Near the $\theta$-point, $v$ varies with temperature as

$$ v = v_0(1 - \theta/T) . $$

and so vanishes when $T = \theta$. $v_0$ is a constant of order $I d$ where $d$ is the dimensionality of the system and $I$ is a polymer segment length. $\beta$ would be expected to be of order $l^{2d}$. In terms of $v$ and $\beta$, the osmotic pressure $\Pi$ has the virial expansion near the $\theta$-point

$$ \frac{\Pi}{kT} = \frac{c}{N} + \frac{1}{2} vc^2 + \beta c^3 + \cdots . $$

$c$ is the concentration of polymer segments of which there are $N$ per polymer. (N.B. Our definition of $c$ is different to that of ref. [1].) In section 2, we shall show that the screening length $\xi$ in the semi-dilute region near the $\theta$-point is given by

$$ \xi = l[(12 \ v c + 36 \ \beta c^2)^{-1/2} . $$

When $\beta$ is zero, (1.3) reduces to the result of Edwards. If $v \ll l^{2d}$, one is in the poor solvent semi-dilute
region, while for \( v \gg c \ell^6 \), one is in the good solvent semi-dilute region (Daoud and Jannink [4]; see also section 2). Bearing this condition on \( v \) in mind, it seems likely that unless \( \beta \) is very much smaller than its natural size of \( \ell^9 \), the Edwards [6] form for \( \xi \) will not be experimentally observable. There seem to be very few, if any, reliable experimental determinations of \( \beta \).

The field theoretic formulism of Des Cloizeaux [2] is valuable in that it can be used to support the heuristic scaling arguments employed by Daoud et al. [1]. However, it is not expected to provide a general formulism in which quantitative calculations of the properties of polymer solutions can be made because of the inherent polydispersivity it introduces. It constructs an ensemble of polymer chain lengths whose distribution is broad and alters with concentration \( c \) and temperature, i.e. \( v \). In the very dilute limit the difficulty can be overcome by assigning to each polymer present in the solution its own set of field variables [7]. For semi-dilute solutions such a procedure becomes unwieldy. In the poor solvent semi-dilute region it is possible to evaluate directly using straightforward perturbation theory all quantities of physical interest and compare the results with those derived from the field-theoretic approach. The discrepancies can be large (by factors of 2 in certain cases), but disappear if the quantity calculated is not dependent on molecular weight (i.e. \( N \)). Thus, the field-theoretic formulism also gives (1.3) for the screening length as (1.3) is \( N \) independent. We shall use the field-theoretic formulism to obtain the correction of order \((v c)^{1/3} l^{-3}\) to the osmotic pressure virial expansion of eq. (1.2). The calculation in the field-theoretic language is trivial and amounts to no more than a calculation of the effective potential at the one-loop level. The numerical coefficient of the correction term is consistent with that of Edwards [6], when a trivial error in his calculation is removed.

The calculations in section 2 are essentially perturbation expansions in the variable \( v / c \ell^6 \) and therefore fail in the good solvent region where \( v \gg c \ell^6 \). To study the osmotic pressure in the good solvent regime one can employ the renormalization group and improve the equation of state by a matching procedure [8, 9]. The basic idea is to integrate the RG recursion relations out of the region in which perturbation theory cannot be used until the effective coupling constant is sufficiently small so that perturbation theory can once again be used. By this procedure an expression is obtained in section 3 for the osmotic pressure, which is valid to order \( \varepsilon \) in both the good and poor solvent semi-dilute regions.

The basic quantities which are determined experimentally are the density-density correlation functions of the polymer segments. (By deuterating a small number of the polymers in the solution, it has recently become possible to determine the density-density correlation function of the segments belonging to a single polymer molecule [1].) In the poor solvent, the form of the overall density-density correlation function was first given by Edwards [6] and in section 2 we shall obtain his result and the leading corrections to it. The study of the density correlation functions in the good solvent region looks a difficult problem, although a promising start has been made by Schäfer and Witten [10].

2. The semi-dilute poor solvent region. — 2.1 Field theoretic formulism. — We shall just quote the results of the Des Cloizeaux [2] field theoretic formulism which we shall actually be needing. Given the effective potential \( \Gamma(M, t) \) of an \( O(n) \) symmetric field theory in the limit \( n \to 0 \), polymer quantities can be extracted from it by the relations

\[
c = \frac{\partial \Gamma}{\partial t}.
\]

\[
cN = \frac{1}{2} M \frac{\partial \Gamma}{\partial M}
\]

and

\[
\Pi \frac{kT}{N} = \frac{c}{N} \ln \frac{N}{\Gamma}.
\]

Notice that \( c/N \) is the concentration of polymer molecules. In the Des Cloizeaux formulism the monomers are in an equilibrium characterized by the monomer chemical potential \( t \); this entails a broad (polydisperse) distribution of chain lengths. \( N \) in this formulism is an average chain length, which unfortunately varies with the concentration \( c \) of the segments. The \( O(n) \) symmetric field theory has Lagrangian density

\[
\frac{A}{kT} = \frac{l^2}{4d} (\nabla \varphi)^2 + \frac{1}{2} \varphi^2 + \frac{\varepsilon}{8} (\varphi^2)^2 + \frac{\beta}{16} (\varphi^3)^3 - h \varphi
\]

\( \varphi \) is the \( n \)-component field variable \( (\varphi^{(1)}, \ldots , \varphi^{(n)}) \). The unusual normalization of the gradient term is needed in order to make contact with the conventional definitions employed in the polymer literature [6]. \( h \) is a magnetic-field variable needed to generate a non-vanishing concentration of monomers.

From (2.4), it follows that the mean-field approximation to the effective potential is

\[
\Gamma(M, t) = \frac{1}{2} t M^2 + (\varepsilon/8) M^4 + (\beta/16) M^6.
\]

where \( \langle \varphi \rangle = M \). Using (2.1), one has

\[
c = \frac{1}{2} M^2
\]

and from (2.2)

\[
t = 1/N - \nu c - (3/2) \beta \varepsilon^2.
\]
Hence the osmotic pressure according to (2.3) is just

$$\Pi = c \frac{N}{kT} = c \left( 1 + \frac{1}{2} v c^2 + \beta c^3 \right)$$  \hspace{1cm} (2.8)

in the mean-field approximation. This coincides with the virial expansion in the poor solvent region, eq. (1.2).

### 2.2 CORRELATIONS BETWEEN THE CHAIN ENDS

This is a topic fully discussed by Daoud et al. [1]. We repeat their calculations here, as it serves to introduce certain correlation functions which will be needed throughout the paper. Suppose that the magnetic field (and hence $M$) are in the 1-direction of field space. Then the Gaussian approximation expression [11] for the longitudinal correlation function is

$$\langle \varphi^{(1)}(q) \varphi^{(1)}(-q) \rangle - M^2 = \left[ q^2 l^2/2 d + \left( t + 3 v M^2/2 + 15 \beta M^4/8 \right) \right]^{-1}$$

$$= \left[ q^2 l^2/2 d + (1/N + 2 v c + 6 \beta c^3) \right]^{-1}.$$  \hspace{1cm} (2.9)

This result can be obtained by changing (2.4) to new field variables $\varphi^{(1)} = M + \sigma$ where $\langle \sigma \rangle = 0$, and then retaining in the Lagrangian density only term quadratic in the field variables. By similar methods the transverse correlation function is found to be

$$\langle \varphi^{(2)}(q) \varphi^{(2)}(-q) \rangle = \left[ q^2 l^2/2 d + (t + v M^2/2 + 3 \beta M^4/8) \right]^{-1}$$

$$= \left[ q^2 l^2/2 d + 1/N \right]^{-1}.$$  \hspace{1cm} (2.10)

The transverse correlation function is related to the correlations between the two ends of the same chain [2]. From (2.10), it follows that the mean-square end-to-end distance is

$$\langle R^2 \rangle = N l^2.$$  \hspace{1cm} (2.11)

which shows that the interactions between the segments cancels to leading order in the poor solvent semi-dilute region. The interpretation of the longitudinal correlation function is that it is the correlation function between the ends of all the chains. It could be studied experimentally by attaching at both ends of each chain atoms or groups which strongly scatter neutrons. Notice that according to (2.9) this correlation function will decay exponentially at large spatial separations of the ends with a correlation length given by (1.3) in the semi-dilute region (when the $1/N$ term is negligible compared to the other two terms). However, the behaviour of this correlation function is completely modified when one goes beyond mean-field approximation and includes the effects of the transverse modes [1]. Discussion of these problems does not seem worthwhile given the present dearth of experimental data.

### 2.3 THE DENSITY-DENSITY CORRELATION FUNCTIONS

There are two kinds of density correlation function of experimental interest in polymer solutions. The first is the overall density-density correlation function of the segments, regardless of which polymer they belong to:

$$S(r) = \langle c(r) c(o) \rangle = c^2.$$  \hspace{1cm} (2.12)

and the second is the density-density correlation function of segments which belong to the same polymer. Schäfer and Witten [10] have given an extensive discussion of how both can be discussed within the framework of the field-theoretic formalism. From (2.1) and (2.4) it is obvious that

$$S(r) = \left[ \langle \psi^2(r) \psi^2(o) \rangle - \langle \varphi^2(r) \rangle \langle \varphi^2(o) \rangle \right]/4.$$  \hspace{1cm} (2.13)

Eq. (2.13) can be re-written in terms of the new field variable $\sigma = \varphi^{(1)} - M$. when it becomes

$$S(r) = M^2 \langle \sigma(r) \sigma(o) \rangle + M \langle \sigma(r) \psi^2(o) \rangle + \left[ \langle \psi^2(r) \psi^2(o) \rangle - \langle \psi^2(r) \rangle \langle \psi^2(o) \rangle \right]/4$$

$$= \left[ M^2 l^2/2 d + (1/N + 2 v c + 6 \beta c^3) \right]^{-1}.$$  \hspace{1cm} (2.14)

where $\psi = (\sigma, \varphi^{(2)}, \ldots \varphi^{(n)})$. The leading term in $S(r)$ is given by the first term on the right-hand side of (2.14). Defining the Fourier transform

$$S(q) = \int d\mathbf{r} S(r) e^{i\mathbf{qr}}.$$  \hspace{1cm} (2.15)

the leading term in $S(q)$ (see (2.9)) is then

$$S(q) = M^2 \left[ q^2 l^2/2 d + (t + 3 v M^2/2 + 15 \beta M^4/8) \right]^{-1}$$

$$= 2 c [q^2 l^2/2 d + (1/N + 2 v c + 6 \beta c^3)]^{-1}.$$  \hspace{1cm} (2.16)

The cross-over concentration between dilute and semi-dilute behaviour in poor solvents is usually defined as occurring at [4]

$$C^* \sim \frac{N}{R^3} \sim \frac{N}{N^{3/2} l^{3/2}} \sim N^{-1/2} l^{-3}.$$  \hspace{1cm} (2.17)

in three dimensions.

We shall find it instead more useful to define the cross-over as that concentration $c^*$ at which

$$\frac{1}{N} = 2 v c^* + 6 \beta (c^*)^2.$$  \hspace{1cm} (2.18)
for then, when \( c \gg c^* \), it is possible to neglect the \( 1/N \) term in (2.16). When it reduces to
\[
S(q) = 4\pi d[q^2 l^2 + 4 dve + 12 d\beta c^2]^{-1}.
\]
(2.19)

\( c^* \) has the physical interpretation as that concentration at which the screening length of (1.3) equals the root-mean square end-to-end distance. Eq. (2.19) for \( S(q) \) is equivalent to the result of Edwards for \( S(q) \) if \( \beta \) is set equal to zero.

Eq. (2.16) was derived within the framework of the field-theoretic formalism and it is interesting to determine the errors which arise from the uncontrollable polydispersivity. There is a sum rule \[1\] which states that
\[
\lim_{n \to 0} S(q) = kTc \frac{\partial c}{\partial n}.
\]
(2.20)
The right-hand side of this equation equals
\[
c[1/N + ve + 3 \beta c^2]^{-1}
\]
according to (1.2) while the left-hand side equals
\[
c[1/2 N + ve + 3 \beta c^2]^{-1}
\]
according to (2.16). Thus, in the semi-dilute concentration region where \( c > c^* \) and where the \( N \) dependence can be neglected the field-theoretic expression for \( S(q) \) satisfies the sum rule. In the opposite dilute limit where \( c < c^* \) the field-theoretic formalism is out by a factor of 2. Therefore in the semi-dilute region it seems likely that when calculating \( N \) independent expression the polydispersivity of the field-theoretic formalism produces no errors.

Taking this to be the case, it would seem worthwhile to evaluate the corrections to (2.19) in the poor solvent semi-dilute region. This calculation involves writing down the leading terms for the second and third terms in (2.14), together with the first correction to the first term. The details of such a calculation are given in a paper by A. J. Bray \[12\]. Specializing to the case of \( \beta = 0 \), the results are, in the limit \( n \to 0 \).

\[
S(q) = M^2/[q^2 l^2/2 + r_L] + \frac{1}{2} \Pi(q, r_L) (q^2 l^2/2 + t - 3 vM^2/2)^2 (q^2 l^2/2 + r_L)^{-2} - \frac{1}{2} \Pi(q, r_T) (q^2 l^2/2 + r_T)^2 (q^2 l^2/2 + r_T)^{-2} - \frac{1}{2} (3 F(r_L) - F(r_T)) vM^2 [3t + 3 vM^2/2 + 2 q^2 l^2/2 d) r_L^{-1}(q^2 l^2/2 + r_L)^{-2},
\]
where
\[
r_L = t + 3 vM^2/2, \quad r_T = t + vM^2/2,
\]
\[
\Pi(q, r) = \frac{1}{2(\pi)^4} \int d^4 p \frac{1}{p^2 l^2/2 d + r} \frac{1}{q + p} l^2/2 d + r
\]
and
\[
F(r) = \frac{1}{2(\pi)^4} \int d^4 p \left[ \frac{1}{p^2 l^2/2 d + r} - \frac{1}{p^2 l^2/2 d} \right].
\]
(2.21)

One uses the mean-field values for \( M^2, r_L \) and \( r_T \) in (2.21) as (2.21) already contains the leading corrections to these quantities beyond the mean-field approximation.

Using the equations (2.6) and (2.7) for \( M^2 \) and \( t \), (2.21) can be written in polymer variables for \( \beta = 0 \) as
\[
S(q) = \frac{2c}{q^2 l^2/2 d + 2 ve} + \frac{1}{2} \Pi(q, 2 ve) (q^2 l^2/2 d - 4 ve)^2 (q^2 l^2/2 d + 2 ve)^{-2} - 3 F(2 ve) q^2 l^2/2 d (q^2 l^2/2 d + 2 ve)^{-2} - \frac{1}{2} \Pi(q, 1/N) (q^2 l^2/2 d + 1/N)^2 (q^2 l^2/2 d + 2 ve)^{-2}
\]
(2.22)

provided \( 2 ve \gg 1/N \). In the limit \( q \to 0 \), the \( N \) dependent terms are negligible in (2.22), which gives in that limit
\[
S(0) = ve^{-1} + R \Pi(2 ve)
\]
(2.23)
where
\[
R = \frac{\pi}{2} \frac{1}{\sin \pi \varepsilon/2} K_d
\]
(2.24)
and
\[
K_d = (2 d l^2)^{1/2} \pi d^2/(\Gamma(d/2) (2 \pi)^d).
\]
(2.25)
Notice that for $q^2 l^2/2 d > 1/N$, the $N$ dependent terms will be again negligible in (2.22).

One sees from (2.23) that the perturbation expansion is in the variable $(v/\ell^6)(vc)^{-\xi/2}$, which for $v = 1$ is equivalent to $(v/c\ell^6)$. Provided this is small, the approximation (2.19) should be adequate.

The density-density correlation function for the segments belonging to one given polymer cannot be calculated accurately in the field-theoretic formalism because of polydispersivity problems. It is, however, easy to see why its behaviour should be close to that of just an isolated chain at the $\theta$-point. The effective interaction between two segments of a given chain will consist of a direct term $v$ and an indirect term involving interactions with segments from other polymers. In the limit $\beta = 0$, at wavevector $q$, the effective interaction is just

$$v - v^2 \langle c(q) c(-q) \rangle = v - v^2 \frac{2}{c/(q^2 l^2/2 d + 2 vc)} = \frac{A}{q^2 l^2/2 d (q^2 l^2/2 d + 2 vc)},$$

which vanishes as $q \to 0$ and is much smaller than the direct interaction.

2.4 The Osmotic Pressure. — We shall now calculate the osmotic pressure within the framework of the field-theoretic formalism, but go beyond the mean-field approximation (which leads to (2.8)) to a one-loop correction [13]. We shall then compare our result with the result Edwards [6] obtained by a functional integral calculation and also with the sum-rule (2.20).

From ref. [13] the one-loop corrections to the effective potential are readily calculated. In the limit $n \to 0$, the effective potential then becomes

$$\Gamma(M, t) = \frac{t}{2} M^2 + (v/8) M^4 - (2 R_d/d) \times \left[ (t + 3 v M^2/2) - (t + v M^2/2)^2 \right].$$

(2.26)

(We shall again work in the limit $\beta = 0$.) The propagators needed for this calculation are just the correlation functions (2.9) and (2.10). The parameters $t$ and $M$ can be eliminated in favour of polymer variables by the usual relations

$$e = \frac{\partial \Gamma}{\partial t} = \frac{1}{2} M^2 - R_d(2 vc)^{1-\xi/2}$$

(2.27)

and (2.2), which gives

$$t = 1/N - vc + 2 v R_d(2 vc)^{1-\xi/2}.$$  

(2.28)

Substituting $t$ and $M$ into (2.26) for $\Gamma$ and using (2.3), the osmotic pressure is in the limit when $2 vc \gg 1/N$,

$$\frac{\Pi}{kT} = \frac{c}{N} + \frac{1}{2} vc^2 - \frac{R_d}{d} (2 - e) (2 vc)^{2-\xi/2}.$$  

(2.29)

For $\varepsilon = 1$ (three dimensions), (2.29) becomes

$$\frac{\Pi}{kT} = \frac{c}{N} + \frac{1}{2} vc^2 - \frac{3}{\pi} \xi (vc)^{3/2}.$$  

(2.30)

The correction to the mean-field expression is just twice that given by Edwards [6]. I believe that the discrepancy is entirely due to a trivial error in his paper on going from his eq. (3.16) to (3.17). Eq. (2.30) is consistent with the sum-rule (2.20) and the expression (2.23) for $S(\sigma)$. Notice again that polydispersivity effects are absent in terms which are $N$ independent.

2.5 Validity of Perturbation Theory. — Perturbation theory will be useful, provided the one-loop corrections are small compared to the mean-field terms. This means that $(v/\ell^8)(vc)^{-\xi/2}$ must be small or in three dimensions that $v \ll c\ell^6$. If $v \gg c\ell^6$ ordinary perturbation theory fails and one is in the good solvent region. For the Edwards expression for $\xi$ to be valid one also needs $v \gg \beta c$ and as $\beta$ is of order $l^6$, it seems unlikely that the conditions for the validity of perturbation theory ($v \ll c\ell^6$ and the neglect of the ternary cluster integral ($v \gg \beta c$) will be simultaneously realized, unless $\beta$ is anomalously small.

An alternative way of expressing the condition on the utility of perturbation theory is the Ginzburg criterion that [8]

$$v l^{-d} r_T^{-\xi/2} \ll 1.$$  

(2.31)

It might be thought that a further condition for the validity of perturbation theory would be

$$vl^{-d} r_T^{-\xi/2} \ll 1$$

where in this case $r_T = 1/N$. In fact. this is the condition for the validity of the Fixman perturbation expansions in dilute solution [14]. For certain quantities (e.g. osmotic pressure, the overall density-density correlation function) in the semi-dilute region the effects of the transverse modes (i.e. those involving $r_T$) are negligible and so no condition of validity other than (2.31) is required. However, in other quantities (such as the overall end-to-end correlation function (2.10)) the influence of the transverse modes is profound and modifies completely the mean-field expressions as given in (2.10).

3. The semi-dilute good solvent region. — In this section we shall obtain an expression. correct to order $e = (4 - d)$, for the osmotic pressure which is simultaneously valid in both the poor solvent and good solvent regions and in the intermediate region of temperature. (that is. $\nu$). as one crosses over from one region to the other. A large number of authors have discussed how such cross-over calculations can be performed [8. 9. 14. 15. 16. 17]. We shall employ here the matching procedure of Riedel and Wegner [9], but in an $\varepsilon$ expansion framework as used by Nelson and Rudnick [8].
The RG recursion relations arise from considering the variations of the coupling constants under the action of the RG. They are for $t$ and $v$ in the $n \to 0$ limit to first order in $\varepsilon$

$$\frac{dt}{d\tau} = 2t - 2K_d v t$$

$$\frac{dv}{d\tau} = \nu = 8K_d v^2$$

When the RG parameter $\tau$ is set equal to zero, $t(0) = t$, $v(0) = v$, their physical values. The solutions of (3.1) and (3.2) in terms of the initial values $t$ and $v$ are

$$v(\tau) = v e^{\nu \tau}$$

$$t(\tau) = t e^{\nu \tau}$$

where $\nu = 1/4$ for $n = 0$ and

$$Q(\tau) = 1 + 8K_d v/\varepsilon (e^{\nu \tau} - 1)$$

The longitudinal correlation function is

$$M^2(\tau) = e^{2\nu \tau}$$

where $M^2(\tau) = e^{2\nu \tau} M^2$ [8]. Mean-field approximations such as (2.9) are valid when the screening length is of the order of the inverse wave-vector cut-off ($l$). The idea of the matching procedure is to continue the solution of (3.2) and (3.3) until $v(\tau)$ and $t(\tau)$ are in a region in which mean-field theory is applicable. This will be when $\tau = \tau^*$ where

$$t(\tau^*) + (3/2)v(\tau^*) M^2(\tau^*) = 1$$

(The precise number adopted on the right-hand side of (3.6) is immaterial to order $\varepsilon$) [8]. The improved value of the effective potential is then just [8]

$$\Gamma(M, t) = e^{-\nu \tau} \left[ \frac{1}{2} t(\tau^*) M^2(t^*) + (v(\tau^*)/8) M^4(t^*) \right]$$

$$= \frac{1}{2} tQ^{-\nu}(\tau^*) M^2 + (v/8) Q^{-1}(\tau^*) M^4$$

To order $\varepsilon^{-1}$ (N.B. $M^2$ itself is of this order). 

$$c = \frac{\partial \Gamma}{\partial t} \approx \frac{1}{2} M^2 Q^{-\nu}(\tau^*) + O(1)$$

$$c = \frac{1}{2} M^2 \frac{\partial \Gamma}{\partial M} = \frac{1}{2} M^2 tQ^{-\nu} + (v/4) M^4 Q^{-1}$$

i.e.

$$\Gamma = t + \nu c Q(\tau^*)$$

Hence, from (2.3), the osmotic pressure is

$$\Pi = \frac{c}{N} + \frac{1}{2} \nu c^2 Q(\tau^*)$$

Unfortunately, (3.3)-(3.6) form a set of transcendental equations for $Q(\tau^*)$ which cannot be solved in closed form. They only yield simple expressions in the extreme poor solvent and good solvent limits.

In the poor solvent limit, $Q \approx 1$. so that (3.6) can be approximated as follows:

$$t + (3/2) vM^2 = e^{-2\nu} \approx 2 \nu c$$

and hence from (3.5), taking $e^{\nu \tau} \gg 1$.

$$Q(\tau^*) \approx 1 + 8K_d v/\varepsilon (2 \nu c)^{-1/2}$$

which implies

$$\frac{\Pi}{kT} = \frac{c}{N} + \frac{1}{2} \nu c^2$$

(1/\nu = 2 - \epsilon A, $\nu$ is the exponent which describes the dependence of the mean-square end-to-end distance on segment number $N$. viz. $< R^2 > \sim N^{2\nu}$). (3.12) can be substituted into (3.10) to give the osmotic pressure in the good solvent region

$$\Pi = \frac{c}{N} + \frac{1}{2} \nu c^2$$

(3.13)

Aside from these limiting cases (and expansions about them), no closed-form solution can be written down. However, one can easily see that in general

$$\Pi = \frac{c}{N} + \frac{1}{2} \nu c^2$$

The argument of the function $f$ is, apart from numerical factors, just the parameter of section 2, part (2.5), which governed whether or not conventional perturbation theory was applicable. If it is small, one can use perturbation theory and indeed our RG calculation reduces to the perturbation theory results in
that limit (Eq. (3.11)). If it is large, perturbation theory cannot be used and one is in the good solvent region. However (3.13) is consistent with the result predicted by Daoud and Jannink [4] on the basis of scaling arguments.

The calculation of the density-density correlation functions in the good solvent region is a difficult problem which we hope to discuss in a future paper. From scaling arguments one expects the overall density-density correlation function to have the form

\[ S(q) = q^{-a_v} F \left( q^\xi, \frac{8 K_d}{\xi} (2 v c)^{-a_s^2} \left( v/\xi^4 \right)^{-\frac{1}{2}(2a_v - 1)} \right) \]

with \( a = 2 - dv \). Schäfer and Witten [10] have examined the large \( q^\xi \) behaviour of \( S(q) \) and have found that it is dominated by the single chain contribution in this limit, as might be expected on physical grounds. However, obtaining an expression for \( S(q) \) which is valid for all values of \( q^\xi \) and in both good and poor solvents appears a non-trivial problem.

So far in this section we have completely ignored the effects of \( \beta \) — the ternary cluster integral. For \( \epsilon < 1 \) it is an irrelevant operator and under the RG transformation rapidly becomes negligible. However, at \( \epsilon = 1 \), which is the case of most interest, \( \beta(\tau) \) falls off only logarithmically with \( \tau \) in the poor solvent region [18], so that it will probably always play an important role there in determining the size of screening lengths, etc. In the good solvent region it is of much less importance and no serious error is likely to be encountered by setting it equal to zero from the outset. The fact that for \( \epsilon = 1 \) one should really be including contributions from \( \beta \) in the cross-over calculation means that an accurate solution will be difficult to achieve.

Acknowledgments. — I am indebted to Dr. P. R. Gerber for his persistent questions about the validity of perturbation theory in semi-dilute solutions, which led to the writing of this paper, and to Dr. A. J. Bray for showing me how to get a sensible answer when calculating the density-density correlation function.

References