

Theory of semi-dilute polymer solutions. II. Correlation functions in a good solvent

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1985 J. Phys. A: Math. Gen. 18 127

(<http://iopscience.iop.org/0305-4470/18/1/024>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 17:03

Please note that [terms and conditions apply](#).

Theory of semi-dilute polymer solutions: II. Correlation functions in a good solvent

Akira Nakanishi[†] and Takao Ohta[‡]

[†] Department of General Education, Osaka Institute of Technology, Osaka 535, Japan

[‡] Department of Physics, Kyushu University, Fukuoka 812, Japan

Received 30 March 1984, in final form 31 July 1984

Abstract. We study the static correlations of monomer density fluctuations in semi-dilute polymer solutions in a good solvent. By means of the conformation space renormalisation theory, the universal scaling form of the scattering functions is obtained up to order $\epsilon = (4 - d)$ with d the dimensionality of space. In a dilute limit agreement with the experiment is improved over the mean field theory. The correlation length and the osmotic compressibility obtained previously are also compared with the recent light scattering experiment. These theoretical results exhibit a very good agreement with the experimental observation without any adjustable parameters.

1. Introduction

Statistical properties of semi-dilute polymer solutions have been studied for many years both theoretically and experimentally. In a good solvent earlier theories were mainly based on the perturbation expansion in terms of the excluded volume parameter or the mean field approximation (e.g. Yamakawa 1971). However the theory breaks down below four dimensions for sufficiently large values of the polymerisation index N where the universal features of polymer solutions are revealed. One of the results which are still relevant at present is Flory's self-consistent method of evaluating the exponent ν for the mean square end-to-end distance of an isolated polymer chain (Flory 1971). Although a recent advanced theory (Le Guillou and Zinn-Justin 1980) yields a slightly different value of ν , the Flory value $\nu = \frac{3}{5}$ in three dimensions is practically very accurate and has been confirmed experimentally (Louchex *et al* 1958). A generalisation to evaluate thermodynamic quantities such as the osmotic pressure has been attempted recently (Muthukumar and Edwards 1982).

An essentially new progress was initiated by the development of the theory of phase transition. The concept of the universality and the scaling law have been found to be very useful in polymer problems as well (de Gennes 1979). A renormalisation group approach (Wilson and Kogut 1974, Brezin *et al* 1976) is mostly suitable for formulating the scaling law and computing the asymptotic universal quantities. Application of the renormalisation group theory to polymer solutions was first achieved by the polymer-magnet analogy (de Gennes 1972, des Cloizeaux 1975). Indeed the correspondence has been used successfully by various authors (Daoud and Jannink 1976, Moore 1977, Witten and Schäfer 1981, Knoll *et al* 1981). The scaling law has been observed to some extent experimentally (Daoud *et al* 1975, Chu and Nose 1980, Amirzadeh and McDonnel 1982, Oyama *et al* 1982). However the analogy has its own limitation. One

has to deal with the n -component magnetic system with $n \rightarrow 0$ limit. Thus it is quite difficult, especially for polymer chemists, to follow intuitively the theory. Furthermore the magnet analogy is not capable of treating the dynamics. These disadvantages are avoided by a sort of direct renormalisation group methods (Al-Noaimi *et al* 1983, Jasnow and Moore 1978, des Cloizeaux 1981, Shiwa and Kawasaki 1982). In particular the conformation space renormalisation group theory has been applied to both statics and dynamics in the dilute limit (Oono 1979, Oono *et al* 1981, Oono and Kohmoto 1983, Oono 1983).

It has been shown in a previous paper (Ohta and Oono 1982) that Edwards' mean field approach (Edwards 1966) is a good starting point for constructing the conformation space renormalisation group theory of semi-dilute polymer solutions. The calculation of the osmotic pressure and the correlation length ξ of monomer density fluctuations in a good solvent enables us to compare with experiments without any adjustable parameters (Ohta and Nakanishi 1983, hereafter referred to as I). Freed (1983) has also calculated the quantities similar to those obtained in I. It seems to us, however, that the expression of ξ is erroneously simplified. As was criticised by the author himself it does not exhibit the proper scaling behaviour in the semi-dilute limit. Later but independently by means of the polymer-magnet analogy a similar study has been done by Schäfer (1984) including a temperature crossover.

In this paper we present our calculation of the correlation functions by a renormalisation group theory in a good solvent. This is the first attempt to study the scaling function of the non-uniform quantities in the semi-dilute region. The scaling form of the scattering function $G(q)$ of a test chain and $S(q)$ of the full monomer density fluctuations is obtained up to order $\varepsilon = (4 - d)$ with d the spatial dimension of a system.

The qualitative behaviours of the correlation functions can be obtained by the scaling argument (de Gennes 1979). In the region $q > \xi^{-1}$, $S(q)$ reduces to $G(q)$ which is then given by (Edwards 1966)

$$G(q) \sim q^{-1/\nu}. \quad (1.1)$$

This relation has been checked experimentally in the dilute limit (Okano *et al* 1974) and in the semi-dilute regime (Cotten *et al* 1974, Farnoux *et al* 1975). An extensive review of the scattering experiments on polymers has been made by Higgins (1978). For $q < \xi^{-1}$, $S(q)$ is screened and is given approximately by

$$S(q) \sim (q^2 + \xi^{-2})^{-1}. \quad (1.2)$$

Thus there is a crossover from (1.1) to (1.2) with changing wavenumber. A quantitative study of this crossover has not been available except for the recent experiment by Noda *et al* (1983) in a dilute limit. Therefore the renormalisation group calculation of the scaling form of $G(q)$ and $S(q)$ is of much interest for further understanding the polymer solutions in a good solvent.

In § 2 we summarise the results obtained in I. The renormalisation group analysis of the correlation functions will be given in § 3. Comparison with the experiment by Noda *et al* (1983) is made in § 4. Quite recently Wiltzius *et al* (1983) have measured the concentration dependence of the correlation length ξ and the osmotic compressibility. Their results are compared with our theory. In § 5 we discuss the relationship between our theory and Schäfer's approach.

2. General formulation

In this section we briefly summarise the results obtained in I. Especially we present the formulae for the correlation functions $G(q)$ of a test chain and $S(q)$ of the full monomer density fluctuations up to first order of the excluded volume parameter.

Edwards' transformation (Edwards 1966) enables us to represent the Hamiltonian of a semi-dilute polymer solution in terms of a continuous scalar field variable $\phi(\mathbf{r})$,

$$\begin{aligned}
 H\{\phi\} = & \frac{1}{2} \int_{\mathbf{k}} (u^{-1} + 2c\hat{\Gamma}^{(2)}(k)) \phi_{\mathbf{k}} \phi_{-\mathbf{k}} + ic \int_{\mathbf{q}, \mathbf{p}} \phi_{\mathbf{q}} \phi_{\mathbf{p}} \phi_{-\mathbf{q}-\mathbf{p}} \hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p}) \\
 & + c \int_{\mathbf{q}, \mathbf{p}, \mathbf{k}} \phi_{-\mathbf{q}} \phi_{\mathbf{p}-\mathbf{q}} \phi_{\mathbf{k}} \phi_{\mathbf{q}-\mathbf{p}} \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}, \mathbf{k}) \\
 & - \frac{c}{2V} \int_{\mathbf{q}, \mathbf{p}} \phi_{\mathbf{q}} \phi_{-\mathbf{q}} \phi_{\mathbf{p}} \phi_{-\mathbf{p}} \hat{\Gamma}^{(2)}(q) \hat{\Gamma}^{(2)}(p) + \dots
 \end{aligned} \quad (2.1)$$

where $\int_{\mathbf{k}} = \int d^d k / (2\pi)^d$. The constant $u (> 0)$ is the excluded volume parameter, c the polymer number density and V the system volume. The Fourier transform of $\phi(\mathbf{r})$ is defined by

$$\phi_{\mathbf{k}} = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \phi(\mathbf{r}). \quad (2.2)$$

The vertex function $\hat{\Gamma}^{(n)}$ is given by the n -point monomer density correlation of a single Gaussian chain:

$$\hat{\Gamma}^{(2)}(k) = N^2 \{ 2/k^2 N - (2/k^2 N)^2 [1 - \exp(-k^2 N/2)] \} \quad (2.3)$$

$$\begin{aligned}
 \hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p}) = & \frac{1}{6} \int_0^N d\tau_1 \int_0^N d\tau_2 \int_0^N d\tau_3 \exp[-q^2|\tau_1 - \tau_2|/2 \\
 & - \mathbf{q} \cdot \mathbf{p} (|\tau_1 - \tau_2| + |\tau_1 - \tau_3| + |\tau_3 - \tau_2|)/2 - p^2|\tau_2 - \tau_3|]
 \end{aligned} \quad (2.4)$$

$$\begin{aligned}
 \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}, \mathbf{k}) = & \int_0^N d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \\
 & \times \exp[-q^2(\tau_1 - \tau_2)/2 - p^2(\tau_2 - \tau_3)/2 - k^2(\tau_3 - \tau_4)/2]
 \end{aligned} \quad (2.5)$$

where N stands for the polymerisation index. We are concerned with the monodisperse limit. Effects of the polydispersity can readily be taken into account in the present formalism as was shown in a previous paper (Ohta and Oono 1982). Recently Oono (1982) has studied the correlation function $G(q)$ of a polydisperse system.

Now we examine the order estimation of (2.1). Noting the fact that $\phi_{\mathbf{q}} \sim u^{1/2} N^{d/4}$ and $\hat{\Gamma}^{(n)} \sim N^n$ the term with the m th power of ϕ is of order

$$cu^{m/2} N^{dm/4} N^{-d(m-1)/2} N^m = cuN^2 (uN^{2-d/2})^{-1+m/2} \quad (m > 1) \quad (2.6)$$

where the factor $N^{-(m-1)/2}$ comes from the integral over $\{\mathbf{q}\}$. In the semi-dilute regime one has to assume that $cuN^2 \sim O(1)$. This is analogous to the case of the theory of phase transitions where the square of the order parameter times the coupling constant is of order unity below a second-order transition point (e.g. Brezin *et al* 1976). Equation (2.6) indicates that (2.1) is indeed the expansion in powers of $(uN^{2-d/2})^{1/2}$. Thus one may apply the loop expansion (Amit 1978) where each loop carries the factor of $uN^{2-d/2}$.

The formula for the scattering function $S(q)$ has been given in I by

$$S(q) = u^{-1} - u^{-2} \langle \phi_q \phi_{-q} \rangle \quad (2.7)$$

where the average is taken with respect to $H\{\phi\}$. Up to the one-loop order $S(q)$ is given by

$$S(q) = cJ(q)/(1 + cuJ(q)) \quad (2.8)$$

where

$$J(q) = G(q) + 18cu^2 \int_p \frac{(\hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p}))^2}{(1 + 2cu\hat{\Gamma}^{(2)}(p))(1 + 2cu\hat{\Gamma}^{(2)}(|\mathbf{q} + \mathbf{p}|))}. \quad (2.9)$$

The function $G(q)$ is the scattering function of a test chain which is given up to $O(u)$ by

$$G(q) = 2\hat{\Gamma}^{(2)}(q) - 2u \int_p (\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) - \hat{\Gamma}^{(2)}(q)\hat{\Gamma}^{(2)}(p))(1 + 2cu\hat{\Gamma}^{(2)}(p))^{-1} \quad (2.10)$$

where

$$\begin{aligned} \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) = & \hat{\Gamma}^{(4)}(\mathbf{p}, 0, \mathbf{q}) + \hat{\Gamma}^{(4)}(\mathbf{p}, \mathbf{p} + \mathbf{q}, \mathbf{q}) + \hat{\Gamma}^{(4)}(\mathbf{p}, \mathbf{p} + \mathbf{q}, \mathbf{p}) \\ & + \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p} + \mathbf{q}, \mathbf{q}) + \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p} + \mathbf{q}, \mathbf{p}) + \hat{\Gamma}^{(4)}(\mathbf{q}, 0, \mathbf{p}). \end{aligned} \quad (2.11)$$

Each of these six terms which contribute to the intrachain correlation has a definite physical meaning as was shown pictorially in figure 1 of Ohta *et al* (1982).

Equations (2.8) and (2.10) yield the complete expressions of $S(q)$ and $G(q)$ respectively up to $O(u)$. In I we have restricted ourselves to the small wavenumber regime to obtain the correlation length and the radius of gyration. Here we wish to study the full scaling form of the correlation functions by the first-order ε -expansion.

3. Renormalisation group analysis and the scaling function

The expansions of $G(q)$ and $S(q)$ up to order $uN^{(4-d)/2}$, obtained in (2.10) and (2.8) respectively, break down below four dimensions in the asymptotic limit where $uN^{(4-d)/2} \gg 1$. In order to defeat this difficulty we resort to the renormalisation group method with $\varepsilon (= 4 - d)$ expansion. Scaling functions of $G(q)$ and $S(q)$ will be obtained up to first order of ε . The integration over \mathbf{p} in (2.9) and (2.10) may be carried out in four dimensions.

Here we define for later convenience

$$F^{(3)}(\mathbf{Q}, \mathbf{P}) = \Gamma^{(3)}(\mathbf{q}, \mathbf{p})/N^3 \quad (3.1)$$

$$F^{(4)}(\mathbf{Q}, \mathbf{P}) = (\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) - \hat{\Gamma}^{(2)}(q)\hat{\Gamma}^{(2)}(p))/N^4 \quad (3.2)$$

where

$$\mathbf{Q} = \mathbf{q}(N/2)^{1/2}, \quad \mathbf{P} = \mathbf{p}(N/2)^{1/2}. \quad (3.3)$$

For sufficiently large values of P we find from (A1) and (A2) that

$$F^{(3)}(\mathbf{Q}, \mathbf{P}) = 2g(Q^2)/3P^2 \quad (3.4)$$

$$F^{(4)}(\mathbf{Q}, \mathbf{P}) = (g_D(Q^2)/Q^2)\{-2\mathbf{P} \cdot \mathbf{Q}/P^4 + (2\mathbf{P} \cdot \mathbf{Q})^2/P^6\} \quad (3.5)$$

with

$$g(x) = 1/x - 1/x^2 + e^{-x}/x^2 \quad (3.6)$$

$$g_D(x) = 1/x - 2/x^2 + (1/x + 2/x^2) e^{-x}. \quad (3.7)$$

The first term in the bracket of (3.5) was omitted in I since it does not contribute to the correlation length calculated there. The above asymptotic forms for $P \gg 1$ yield the logarithmically divergent parts of $G(q)$ and $J(q)$ at $d = 4$ as follows,

$$[G(q)]_{\text{div}} = -8uN^2(g_D(Q^2)/Q^2) \int_P [(2\mathbf{P} \cdot \mathbf{Q})^2/P^6] \quad (3.8)$$

$$[J(q)]_{\text{div}} = -8uN^2(g_D(Q^2)/Q^2) \int_P [(2\mathbf{P} \cdot \mathbf{Q})^2/P^6] + 32uN^2(cuN^2)[g(Q^2)]^2 \int_P 1/P^4 \quad (3.9)$$

where the integral should be understood to have the ultraviolet cut-off $(N/2a)^{1/2}$ with a , a microscopic cut-off parameter. These logarithmic anomalies will be shown to be renormalised into the zeroth term of $G(q)$ and $S(q)$. We do not describe the details of our renormalisation procedure which has already been given in I.

Hereafter we employ a renormalised perturbation theory. The excluded volume parameter u is replaced by its fixed point value u^* and N should be understood to be renormalised. First we derive the scaling form of scattering function of a test chain $G(q)$. Extracting the singular part of (2.10) $G(q)$ is expressed up to $O(u^*)$ with cu^*N^2 fixed,

$$\begin{aligned} G(q) = & 2N^2g(Q^2) - 8u^*N^2g_D(Q^2)(1/4\pi^3) \int_0^{(N/2\kappa)^{1/2}} dP P^3 \int_0^\pi d\theta \sin^2 \theta \frac{4 \cos^2 \theta}{P^4 + 2} \\ & - 8u^*N^2(1/4\pi^3) \int_0^\infty dP P^3 \int_0^\pi d\theta \sin^2 \theta \left(\frac{F^{(4)}(\mathbf{Q}, \mathbf{P})}{(1 + 2cu^*N^2g(P^2))} \right. \\ & \left. - g_D(Q^2) \frac{4P^2 \cos^2 \theta}{P^4 + 2} \right) \end{aligned} \quad (3.10)$$

where κ is the reference short distance cut-off parameter. With use of the fixed point value $u^*(\pi^2\varepsilon)/2 + O(\varepsilon^2)$ the scaling form of $G(q)$ is given by

$$G(q) = 2N^2\{g(Q^2) + \varepsilon M(Q, X)\}, \quad (3.11)$$

where

$$\begin{aligned} M(Q, X) = & (g_D(Q) \ln 2)/16 - (1/2\pi) \int_0^\infty dP P^3 \int_0^\pi d\theta \sin^2 \theta \left(\frac{F^{(4)}(\mathbf{Q}, \mathbf{P})}{(1 + 2Xg(P^2))} \right. \\ & \left. - g_D(Q^2) \frac{4P^2 \cos^2 \theta}{P^4 + 2} \right), \end{aligned} \quad (3.12)$$

$$X = cu^*N^2(N/2\kappa)^{-\varepsilon/4}. \quad (3.13)$$

In this derivation the logarithmic anomaly in the second term of (3.10) has been absorbed into $g(Q^2)$ with modification $q(N/2)^{1/2} \rightarrow q(N/2)^{1/2+\varepsilon/16}$. The argument Q

in (3.11) is now defined by

$$Q = q(N/2)^{1/2 + \epsilon/16}. \quad (3.14)$$

The origin of the exponent $\epsilon/4$ in (3.13) will be described in the next paragraph.

Now we calculate the scaling form of $S(q)$. $J(q)$ is obtained by adding the interchain correlation term to $G(q)$ as given (2.9). Therefore manipulation similar to the above yields the following form,

$$J(q) = 2N^2[g(Q^2) + \epsilon(g(Q^2))^2 \ln((N/2\kappa)^{1/2} + \epsilon N(Q, X))] \quad (3.15)$$

where Q is again given by (3.14). The non-singular part $N(Q, X)$ takes the following form,

$$N(Q, X) = M(Q, X) - (X/2)(\ln 2 + 1)(g(Q^2))^2 + \frac{9X}{2\pi} \int_0^\infty dP P^3 \\ \times \int_0^\pi d\theta \sin^2 \theta \left(\frac{(F^{(3)}(Q, P))^2}{(1 + 2Xg(P^2))(1 + 2Xg((P+Q)^2))} - \frac{4(g(Q^2))^2}{9(P^2 + 2)^2} \right). \quad (3.16)$$

Substituting $J(q)$ into (2.8) we obtain the scattering function $S(q)$. It should be noted that the extra divergence which appeared in the second term of (3.15) can be eliminated by replacing cu^*N^2 with $cu^*N^2(N/2\kappa)^{-\epsilon/4}$. This has been used in (3.13). Thus the scaling form of $S(q)$ is written up to $O(\epsilon)$ as

$$S(q) = \frac{2cN^2(g(Q^2) + \epsilon N(Q, X))}{1 + 2X(g(Q^2) + \epsilon N(Q, X))}. \quad (3.17)$$

The wavenumber of the scattering functions obtained in (3.11) and (3.17) are scaled by the quantity proportional to the radius of gyration in the dilute limit (see(3.14)). However the characteristic lengths in a semi-dilute solution are the concentration dependent radius of gyration and the correlation lengths. Therefore the scaling with these quantities would be more convenient.

We employ the radius of gyration R_G for the scaling form of $G(q)$. R_G is obtained in I as follows,

$$R_G^2 = R_{GD}^2[1 + \epsilon\eta(X)] \quad (3.18)$$

where

$$R_{GD}^2 = (N/2)(d/3)(N/2\kappa)^{\epsilon/8}(1 - h\epsilon) \quad (3.19)$$

and

$$\eta(X) = -\frac{1}{4} \int_0^\infty dy y^5 V(y) \frac{2Xg(y^2)}{1 + 2Xg(y^2)} \quad (3.20)$$

with

$$V(y) = \frac{30}{y^{12}} - \frac{6}{y^{10}} - \frac{3}{y^8} + \frac{1}{y^6} + \left(-\frac{30}{y^{12}} - \frac{24}{y^{10}} - \frac{6}{y^8} + \frac{1}{4y^4} \right) \exp(-y^2) \quad (3.21)$$

$$h = \ln(2/16) - \frac{1}{4} \int_0^\infty dy \left(y^5 V(y) - \frac{y^3}{y^4 + 2} \right). \quad (3.22)$$

R_{GD} is the radius of gyration of a polymer chain in the dilute limit. We introduce

$$\hat{Q} = qR_G = Q\xi'_M[(1 + \epsilon\eta(X))(1 - \epsilon h)]^{1/2} \quad (3.23)$$

with

$$\xi'_M = d/3. \quad (3.24)$$

Substitution of the relation derived from (3.18), $Q = \hat{Q}/\{\xi'_M[(1 + \varepsilon\eta(X))(1 - \varepsilon h)]^{1/2}\}$, into (3.11) gives $G(q)$ in the following form up to $O(\varepsilon)$

$$G(q) = 2N^2 g(\hat{Q}^2/\xi_M'^2) \exp\left(\frac{\varepsilon \hat{M}(\hat{Q}, X)}{g(\hat{Q}^2/\xi_M'^2)}\right) \quad (3.25)$$

where

$$\hat{M}(\hat{Q}, X) = M(\hat{Q}/\xi'_M, X) + (\eta(X) - h)g_D(\hat{Q}^2/\xi_M'^2). \quad (3.26)$$

In (3.25) the correction of order ε has been exponentiated.

Now we examine various limiting behaviours of (3.25). In the limit of $X \rightarrow \infty$ (3.26) gives the result

$$\hat{M}(\hat{Q}, X) \rightarrow 0 \quad (3.27)$$

so that $G(q)$ reduces to $2N^2 g(\hat{Q}^2/\xi_M'^2)$. It reflects the fact that when $X \rightarrow \infty$ the excluded volume interaction in a test chain is screened by the surrounding chains. In the limit of $\hat{Q} \rightarrow \infty$ (3.26) yields

$$\hat{M}(\hat{Q}, X) \rightarrow \ln \hat{Q}/(4(\hat{Q}^2/\xi_M'^2)). \quad (3.28)$$

Thus $G(q)$ may be put into the form

$$G(q) \sim \hat{Q}^{-2(1-\varepsilon/8)}. \quad (3.29)$$

This is consistent with the scaling argument $G(q) \sim \hat{Q}^{-1/\nu}$ and indicates that in this limit $G(q)$ exhibits the wavevector dependence of scattering function of the isolated chain with excluded volume effect. We define $I_{\text{self}}(q)$ as

$$I_{\text{self}}(q) = G(q)/G(0) = G(q)/N^2 \quad (3.30)$$

and also the zeroth-order scattering function $I_{\text{self}}^0(q)$ as

$$I_{\text{self}}^0(q) = 2g(\hat{Q}^2). \quad (3.31)$$

The curves of $(I_{\text{self}}(q))^{-1}$ for a few values of X and $(I_{\text{self}}^0(q))^{-1}$ as a function of \hat{Q}^2 are depicted with $\varepsilon = 1$ ($d = 3$) in figure 1. It is found that $(I_{\text{self}}^0(q))^{-1}$ and $(I_{\text{self}}(q))^{-1}$ for each X , cross each other at some value of \hat{Q} . This has been observed in a previous study in a dilute solution (Witten and Schäfer 1981, Ohta *et al* 1982). The intersecting point shifts to larger \hat{Q} as X increases.

We take up the correlation length ξ to make a scaling from of $S(q)$. ξ can be written up to $O(\varepsilon)$ from I as

$$\xi^2 = \xi_0^2(1 + \varepsilon\zeta(X)) \quad (3.32)$$

with

$$\xi_0^2 = R_{GD}^2/(1 + X) \quad (3.33)$$

and

$$\begin{aligned} \zeta(X) = \frac{X}{2(X+1)} \left\{ -(1 + \ln 2)/2 + \int_0^\infty dy y^3 \left(\frac{(g(y^2))^2}{(1 + 2Xg(y^2))^2} - \frac{1}{(y^2 + 2)^2} \right) \right\} \\ - (1/4) \int_0^\infty dy y^5 V(y) \frac{2Xg(y^2)}{(1 + 2Xg(y^2))} + (6J_2/dN - 2J_1)/(8\varepsilon), \end{aligned} \quad (3.34)$$

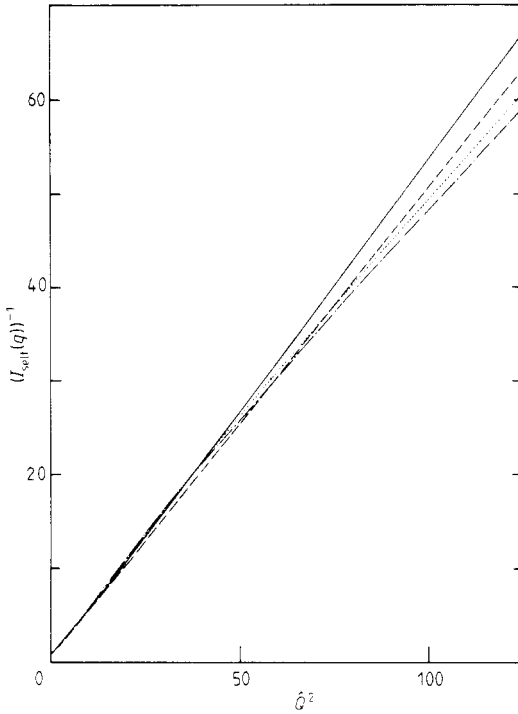


Figure 1. Plots of $(I_{\text{seif}}(q))^{-1}$ for a few values of X and $(I_{\text{seif}}^0(q))^{-1}$ against \bar{Q}^2 . The broken line indicates $(I_{\text{seif}}^0(q))^{-1}$ and the chain line, the dotted line and the full line denote $(I_{\text{seif}}(q))^{-1}$ for $X = 0.05, 1.0$ and 100 respectively.

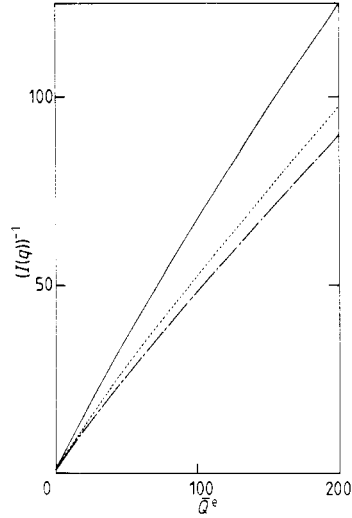


Figure 2. Plots of $(I(q))^{-1}$ for a few values of X against \bar{Q}^2 . The chain line, the dotted line and the full line denote $(I(q))^{-1}$ for $X = 0.05, 1.0,$ and 100 respectively.

where it is noted that $6J_2/dN - 2J_1 = O(\epsilon)$. The expressions of J_1 and J_2 have been given in the appendix of I. We define

$$\bar{Q} = q\xi = Q\xi_M\{(1 + \epsilon\xi(x))(1 - \epsilon h)\}^{1/2} \tag{3.35}$$

where

$$\xi_M^2 = (d/3)/(1 + X). \tag{3.36}$$

Q in the RHS of (3.17) is replaced with $Q = \bar{Q}/\{\xi(1 + \epsilon\eta(X))(1 - \epsilon h)\}^{1/2}$. Thus $S(q)$ is given up to $O(\epsilon)$ by

$$S(q) = \frac{2cN^2g(\bar{Q}^2/\xi_M^2)}{1 + 2Xg(\bar{Q}^2/\xi_M^2)} \exp\left(\epsilon \frac{L(\bar{Q}, X)}{g(\bar{Q}^2/\xi_M^2)(1 + 2Xg(\bar{Q}^2/\xi_M^2))}\right) \tag{3.37}$$

with

$$L(\bar{Q}, X) = N(\bar{Q}/\xi_M, X) + g_D(\bar{Q}^2/\xi_M^2)(\zeta(X) - h). \tag{3.38}$$

We have again exponentiated the first-order correction. Introducing the osmotic compressibility through the thermodynamic relation

$$cN^2/S(0) = \partial\pi/\partial c \tag{3.39}$$

we can write (3.37) in a normalised form:

$$I(q) = \frac{S(q)}{S(0)} = \frac{\partial \pi}{\partial c} \frac{2g(\bar{Q}^2/\xi_M^2)}{1+2Xg(\bar{Q}^2/\xi_M^2)} \exp\left(\varepsilon \frac{L(\bar{Q}, X)}{g(\bar{Q}^2/\xi_M^2)(1+2Xg(\bar{Q}^2/\xi_M^2))}\right), \quad (3.40)$$

where

$$\frac{\partial \pi}{\partial c} = (1+X) \exp\left\{-\varepsilon \frac{X}{2(X+1)} \left[-(1+\ln 2)/2 + \int_0^\infty dy y^3 \left(\frac{(g(y^2))^2}{(1+2Xg(y^2))} - \frac{1}{(y^2+2)^2} \right) \right] \right\}. \quad (3.41)$$

In the limit $\bar{Q} \rightarrow \infty$ (3.38) becomes

$$L(\bar{Q}, X) \rightarrow \ln \bar{Q}/(4(\bar{Q}^2/\xi_M^2)). \quad (3.42)$$

Hence $I(q)$ behaves as

$$I(q) \sim \bar{Q}^{-2(1-\varepsilon/8)}. \quad (3.43)$$

Thus for the large scattering wavenumber $I(q)$ becomes the same as $G(q)$ as expected. We carried out the numerical calculation of (3.40). The curves of $(1/I(q))$ as function of \bar{Q}^2 for several values of X are shown with $\varepsilon = 1$ ($d = 3$) in figure 2.

4. Comparison with experiments

Recently there have been several attempts to detect the scaling law quantitatively. Noda *et al* (1981) have measured the concentration dependence of the osmotic compressibility of poly(α -methylstyrenes) in a good solvent by a light scattering experiment. Their data obtained in the samples having the different but sufficiently large values of molecular weight clearly show the scaling behaviour. The theory (Ohta and Oono 1982) exhibits a good agreement with the experiments with one unknown parameter adjusted. A more definite comparison is possible if we use the experimental results by Wiltzius *et al* (1983). They have performed the light scattering measurement of the correlation length and the osmotic compressibility of polystyrenes in good and marginal solvents. These are the very same quantities that we have calculated in I. Thus one can compare our theory with the experiment uniquely without any adjustable parameters.

The scaling form of the scattering function itself has also been measured in the dilute limit by Noda *et al* (1983). Figure 3 displays $S(q)$ for $X = 0$ with the experimental data. The theoretical result by the naive ε -expansion which yields $S(q) \sim \bar{Q}^{-2(1-\varepsilon/8)}$ ($\varepsilon = 1$) for $\bar{Q} \gg 1$ is also plotted. This agrees with the previous one obtained directly in the dilute limit (Ohta *et al* 1982). Figure 3 shows that the present theory improves agreement with the experiment over the zeroth-order result. However there is still a discrepancy for large values of \bar{Q} . Although we expect that this discrepancy is partially understood by the difference between $2\nu = 1 + \varepsilon/8 = 1.125$ and $2\nu = 1.176$ (Le Guillou and Zinn-Justin 1980) we do not have a satisfactory method of replacement at present.

Now we make a comparison with the results by Wiltzius *et al* (1983). The osmotic compressibility has been given up to $O(\varepsilon)$ by (3.41) and is exhibited in figure 4. As was done in I the factor $\varepsilon/4$ in the exponentiated function is replaced by $(2-d\nu)/(d\nu-1)$ with $d = 3$ and $\nu = 0.588$ so that $\partial \pi / \partial c \sim X^{1/(d\nu-1)}$ for $X \gg 1$. The exponentiation procedure of the order ε correction is slightly different from that in I. However the

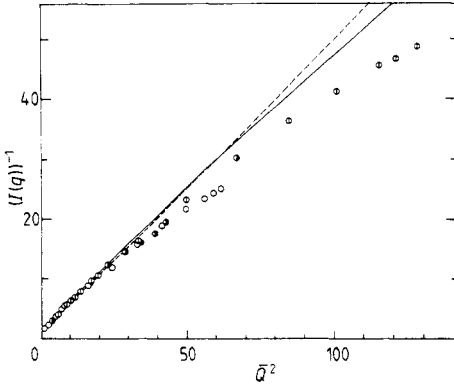


Figure 3. $(I(q))^{-1}$ for $X = 0.0$ against \bar{Q}^2 and the experimental data by Noda *et al* (1983) together with the zeroth-order result $(2g(Q^2))^{-1}$. \circ , \bullet and \square mean the data points for several samples having the different values of molecular weights. The full line; $(I(q))^{-1}$ for $X = 0.0$ and the broken line; $(2g(Q^2))^{-1}$.

difference for $\partial\pi/\partial c$ is at most 1% in the range $10^{-2} < X < 10^2$. In figure 4 the data by Wiltzius *et al* are also plotted. Our X was chosen to be the same as their X . Since Wiltzius *et al*, have determined the unknown proportionality constant between X and c through the second virial coefficient we may say that there is no adjustable parameter in figure 4.

The correlation length is given by (3.30) which may be written as

$$\xi^2 = K(X)R_G^2(\partial\pi/\partial c)^{-1} \tag{4.1}$$

where $K(X)$ and R_G have been obtained numerically in I. The first-order correction of R_G given by (3.18) has been exponentiated. Our ξ differs from the definition by Wiltzius *et al* by a factor of $\sqrt{3}$. Figure 5 displays the result together with the experimental data. Since the horizontal axis has been fixed in figure 4 there is no adjustable parameter in these comparisons. The agreement is shown to be very good.

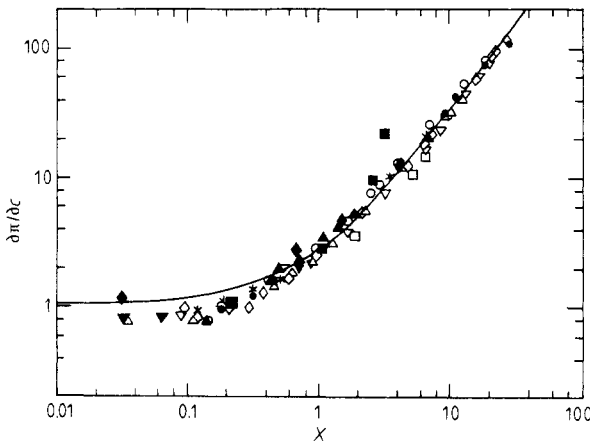


Figure 4. Calculated $\partial\pi/\partial c$ against X and the experimental data by Wiltzius *et al* (1983). \circ , \bullet , \triangle , \blacktriangle and so on denote the data points for several samples with the different values of molecular weights and solvents of different quality.

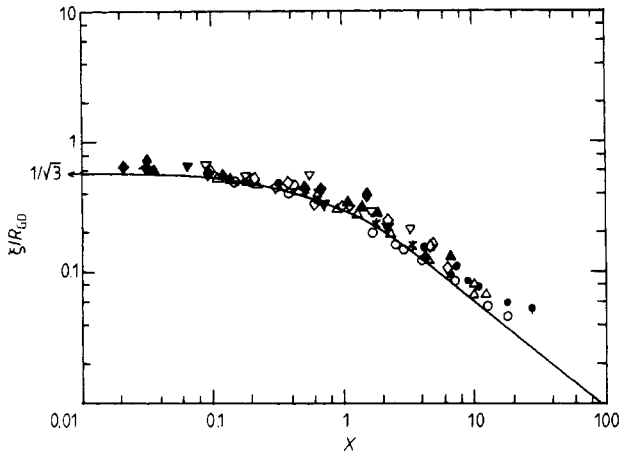


Figure 5. Calculated ξ against X and the experimental data by Wiltzius *et al* (1983). The meaning of symbols is given in figure 4.

Although our result is correct up to $O(\varepsilon)$ we have partially taken account of the higher-order correction in such a way that $\partial\pi/\partial c$ and ξ exhibit the correct scaling behaviour for $X \gg 1$ in three dimensions. This is one of the reasons of the above good agreement.

Schäfer (1984) has also obtained the scaling forms of $\partial\pi/\partial c$ and ξ by means of the polymer-magnet correspondence. The results for a monodisperse and good solvent case are quite similar in magnitude to those obtained in I except for one important point: in the limit $X \rightarrow \infty$ the universal ratio in (4.1) is given by

$$K(\infty) = \exp[17[1 - 2\nu]/(d\nu - 1)/4] = 1 - 17\varepsilon/32 + O(\varepsilon^2) \quad (4.2)$$

which yields $K(\infty) = 0.47$ for $\varepsilon = 1$. If we use $d = 3$ and $\nu = 0.588$ we get $K(\infty) = 0.376$. Schäfer has not evaluated $K(\infty)$ analytically. From his expressions of $\partial\pi/\partial c$ and ξ , however, one can estimate $K(\infty)$ in three dimensions which is found approximately to be

$$K(\infty) = 0.8. \quad (4.3)$$

Thus there is a difference of about a factor of 2 between two results. At present the origin of this discrepancy is not clear since Schäfer has not described his derivation of $\partial\pi/\partial c$ and ξ in detail.

5. Discussions

We have shown our renormalisation group calculation of the scaling form of the scattering functions. The results up to $O(\varepsilon)$ exhibit agreement with the available experiments better than the mean field result. However, there is still room to improve the theory such that it deals systematically with the high q behaviour of $S(q)$ in three dimensions.

In a recent paper Schäfer (1984) has made a comment on our papers (Ohta and Oono 1982, Ohta and Nakanishi 1983) that some specific features of the collective effects in the semi-dilute limit are ignored in our work. Since Schäfer does not specify

what we have really ignored† it is hard to reply to his comment. It should be emphasised that our results are exact up to $O(\varepsilon)$. With the exponentiation procedure all the quantities show the proper asymptotic behaviour in the semi-dilute limit: $\partial\pi/\partial c \sim X^{1/(d\nu-1)}$ and $\xi \sim X^{\nu/(1-d\nu)}$ with $d = 4 - \varepsilon$ and $2\nu = 1 + \varepsilon/8$. As was mentioned in § 4 the scaling form is insensitive to choice of the exponentiation procedure. Schäfer employs the double expansion in terms of ε and $w(w^{-\varepsilon/2} - 1)$ where $w \rightarrow 0$ in the semi-dilute limit. In the osmotic pressure there appears an anomalous term like $w(w^{-\varepsilon/2} - 1)/(8(1 - w))$ which signifies the breakdown of the expansion in terms of w in the semi-dilute regime. Our theory also incorporates this anomaly in the form of $-(\varepsilon/16)X^{-1} \ln(X + 1)$ (see equation (8) of Ohta and Oono 1982). Furthermore it should be noted that this anomalous term is negligible in the semi-dilute *limit* compared to the leading term $X^{1/(d\nu-1)}$. As was described in § 4 a true discrepancy appears in the universal ratio $K(\infty)$. If treated correctly both theories should yield the same value of $K(\infty)$ irrespective of the exponentiation procedure or the double expansion.

Acknowledgments

The authors are grateful to Professor Y Oono for a number of valuable discussions. Thanks are also due to Professor L Schäfer for sending us his preprint prior to publication.

Appendix

$\hat{F}^{(3)}(\mathbf{Q}, \mathbf{P})$ and $\hat{F}^{(4)}(\mathbf{Q}, \mathbf{P})$ defined by (3.4) and (3.5) have been given up to $O(q^2)$ in I. Here their full expressions are needed for the numerical calculation of scattering functions. From (2.3), (2.4), (2.5) and (2.11) they are finally put with a tedious but straightforward calculation in the forms,

$$F^{(3)}(Q, P) = \frac{1}{3} \left[\frac{1}{(\mathbf{P} + \mathbf{Q})^2} \left(\frac{1}{Q^2} + \frac{1}{P^2} \right) - \frac{e^{-(\mathbf{P} + \mathbf{Q})^2} - 1}{(\mathbf{P} + \mathbf{Q})^4} \left(\frac{1}{2\mathbf{P} \cdot \mathbf{Q} + P^2} + \frac{1}{2\mathbf{P} \cdot \mathbf{Q} + Q^2} \right) \right. \\ \left. + \frac{1}{(2\mathbf{P} \cdot \mathbf{Q} + P^2)Q^4} (e^{-Q^2} - 1) + \frac{1}{(2\mathbf{P} \cdot \mathbf{Q} + Q^2)P^4} (e^{-P^2} - 1) \right. \\ \left. + \frac{1}{P^2 Q^2} - \frac{1}{P^4(P^2 - Q^2)} (e^{-P^2} - 1) + \frac{1}{Q^4(P^2 - Q^2)} (e^{-Q^2} - 1) \right], \quad (\text{A1})$$

$$F^{(4)}(Q, P) = \left[\frac{2}{(P^2 - Q^2)} \left(\frac{e^{-P^2} - 1}{P^6} - \frac{e^{-Q^2} - 1}{Q^6} \right) + \frac{1}{P^2 Q^2} - \frac{2}{P^4 Q^2} - \frac{2}{P^2 Q^4} + \frac{2}{P^2(\mathbf{P} + \mathbf{Q})^2 Q^2} \right. \\ \left. + \frac{2}{(P^2 - Q^2)} \left(\frac{e^{-Q^2} - 1}{Q^4(P^2 + 2\mathbf{P} \cdot \mathbf{Q})} - \frac{e^{-P^2} - 1}{P^4(Q^2 + 2\mathbf{P} \cdot \mathbf{Q})} \right) \right. \\ \left. + \frac{2(e^{-(\mathbf{P} + \mathbf{Q})^2} - 1)}{(\mathbf{P} + \mathbf{Q})^4(Q^2 + 2\mathbf{P} \cdot \mathbf{Q})(P^2 + 2\mathbf{P} \cdot \mathbf{Q})} \right. \\ \left. + \frac{1}{P^4(\mathbf{P} + \mathbf{Q})^2} + \frac{1}{Q^4(\mathbf{P} + \mathbf{Q})^2} + \frac{e^{-Q^2}}{Q^4(P^2 + 2\mathbf{P} \cdot \mathbf{Q})} + \frac{e^{-P^2}}{P^4(Q^2 + 2\mathbf{P} \cdot \mathbf{Q})} \right]$$

† In the published version Schäfer has added (2.30) and several sentences which were not in his preprint. However those are similar to the description in this section.

$$\begin{aligned}
& + \frac{2}{Q^6(2\mathbf{P} \cdot \mathbf{Q} + P^2)}(e^{-Q^2} - 1) + \frac{2}{P^6(2\mathbf{P} \cdot \mathbf{Q} + Q^2)}(e^{-P^2} - 1) \\
& - \frac{1}{Q^4(2\mathbf{P} \cdot \mathbf{Q} + P^2)^2}(e^{-Q^2} - 1) - \frac{1}{P^4(2\mathbf{P} \cdot \mathbf{Q} + Q^2)^2}(e^{-P^2} - 1) \\
& + \frac{e^{-(\mathbf{P} + \mathbf{Q})^2} - 1}{(\mathbf{P} + \mathbf{Q})^4} \left[\frac{1}{(2\mathbf{P} \cdot \mathbf{Q} + P^2)^2} + \frac{1}{(2\mathbf{P} \cdot \mathbf{Q} + Q^2)^2} \right] - g(Q^2)g(P^2) \quad (\text{A2})
\end{aligned}$$

where \mathbf{Q} and \mathbf{P} are defined in (3.3) and $g(x)$ is given in (3.6).

References

- Al-Noaimi G F, Martinez-Mekler G C and Velasco R M 1983 *J. Chem. Phys.* **78** 3316
 Amirzadeh J and McDonnell M E 1982 *Macromolecules* **15** 927
 Amit D J 1978 *Field Theory, the Renormalization Group and Critical Phenomena* (New York: McGraw-Hill)
 Brezin E, Le Guillou J C and Zinn-Justin J 1976 *Phase Transitions and Critical Phenomena* vol 6, ed
 C Domb and M S Green (New York: Academic)
 Chu B and Nose T 1980 *Macromolecules* **13** 122
 Cotten J P, Decker D, Farnoux B, Jannink G, Ober R and Picot C 1974 *Phys. Rev. Lett.* **32** 1170
 Daoud M, Cotton J P, Farnoux B, Jannink G, Sarma G, Benoit H, Duplessix R, Picot C and de Gennes
 P G 1975 *Macromolecules* **8** 804
 Daoud M and Jannink G 1976 *J. Physique* **37** 973
 de Gennes P G 1972 *Phys. Lett.* **38A** 339
 — 1979 *Scaling Concepts in Polymer Physics* (Ithaca: Cornell University Press)
 des Cloizeaux J 1981 *J. Physique* **42** 635
 — 1975 *J. Physique* **36** 281
 Edwards S F 1966 *Proc. Phys. Soc.* **88** 265
 Farnoux B, Daoud M, Decker D, Jannink G and Ober R 1975 *J. Physique* **36** L35
 Flory P J 1971 *Principles of Polymer Chemistry* (Ithaca: Cornell University Press)
 Freed K F 1983 *J. Chem. Phys.* **79** 6357
 Higgins J S 1978 *J. Appl. Cryst.* **11** 345
 Jasnaw D and Moore M A 1978 *J. Physique* **38** L467
 Knoll A, Schäfer L and Witten T A 1981 *J. Physique* **42** 767
 Le Guillou J C and Zinn-Justin J 1980 *Phys. Rev. B* **21** 3976
 Loucheux C, Weil G and Benoit H 1958 *J. Chem. Phys.* **43** 540
 Moore M A 1977 *J. Physique* **38** 265
 Muthukumar M and Edwards S F 1982 *J. Chem. Phys.* **76** 2720
 Noda I, Imai M, Kitano T and Nagasawa M 1983 *Macromolecules* **16** 425
 Noda I, Kato N, Kitano T and Nagasawa M 1981 *Macromolecules* **14** 668
 Ohta T and Nakanishi A 1983 *J. Phys. A: Math. Gen.* **16** 4155
 Ohta T and Oono Y 1982 *Phys. Lett.* **89A** 460
 Ohta T, Oono Y and Freed K F 1982 *Phys. Rev. A* **15** 2801
 Okano K, Wada R, Taru Y and Hiramatsu H 1974 *Rep. Prog. Polym. Phys. Japan* **17** 145
 Oono Y 1979 *J. Phys. Soc. Japan* **47** 683
 — 1982 Private communication
 — 1983 *J. Chem. Phys.* **79** 4629
 Oono Y and Kohmoto M 1983 *J. Chem. Phys.* **78** 520
 Oono Y, Ohta T and Freed K F 1981 *J. Chem. Phys.* **74** 6458
 Oyama T, Shiokawa K and Baba K 1982 *Polym. J.* **14** 667
 Schäfer L 1984 *Macromolecules* **17** 1357
 Shiwa Y and Kawasaki K 1982 *J. Phys. C: Solid State Phys.* **15** 5345
 Wilson K G and Kogut J 1974 *Phys. Rep.* **12** 75
 Wiltzius P, Haller H R, Cannell D S and Schäfer D W 1983 *Phys. Rev. Lett.* **51** 1183
 Witten T A and Schäfer L 1981 *J. Chem. Phys.* **74** 2582
 Yamakawa H 1971 *Modern Theory of Polymer Solutions* (New York: Harper)