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1983 J. Phys. A: Math. Gen. 16 4155

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# Theory of semi-dilute polymer solutions: I. Static property in a good solvent

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Received 4 May 1983

**Abstract.** We study the static property of semi-dilute polymer solutions in a good solvent. Edwards' transformation is employed to develop the conformation space renormalisation group theory in semi-dilute solutions. We are primarily concerned with the crossover behaviour from a dilute to semi-dilute regime. The first-order calculation on  $\varepsilon = (4 - d)$  with  $d$  the dimensionality of space is performed for the asymptotic scaling functions of the radius of gyration, osmotic compressibility and the correlation length of the monomer density fluctuations.

## 1. Introduction

The current understanding of semi-dilute polymer solutions in a good solvent is mainly based on the scaling theory (de Gennes 1979). In a dilute limit the radius of gyration  $R_{GD}$  is the characteristic length of the problem.  $R_{GD}$  depends on the polymerisation index  $N$  for large values of  $N$  as

$$R_{GD} \sim N^\nu \quad (1.1)$$

which defines the exponent  $\nu$ . If one increases the monomer concentration  $C$  the polymer chains begin to overlap each other at the concentration

$$C^* = N/R_{GD}^d, \quad (1.2)$$

where  $d$  is the spatial dimension of the system. The scaling theory assumes for sufficiently large values of  $N$  that a thermodynamic quantity  $X$  behaves as

$$X = N^\gamma F(C/C^*) \quad (1.3)$$

with an exponent  $\gamma$ . The asymptotic behaviour of  $F(C/C^*)$  for  $1/C^* \gg C/C^* \gg 1$ , which is the definition of the semi-dilute limit, can be determined if one specifies the  $N$  dependence of  $X$ . The results thus obtained have shown good agreement with experiments (Daoud *et al* 1975, Chu and Nose 1980, Amirzadeh and McDonnell 1982). Despite these successful predictions one cannot help getting an impression that the theory is still rather limited. In order to confirm the scaling law (1.3) one needs to obtain the full concentration dependence of  $F(C/C^*)$ . So far few works have been available in this direction. Quite recently the scaling function of the osmotic pressure has been calculated by a renormalisation group method (Knoll *et al* 1981, Ohta and

Oono 1982). On the other hand Noda *et al* (1981) have performed a precise light scattering measurement of the osmotic pressure. If one allows one parameter to be adjusted, the theory by Ohta and Oono shows good agreement with experimental observation in a wide range of concentration. See also the analysis by Schäfer (1982).

In this paper we would like to extend our theory to cover other quantities. The correlation length of the monomer density fluctuations is of particular interest. Since the light scattering technique provides us with information about the osmotic pressure and the correlation length simultaneously, one can compare the theory with experimental observation without any adjustable parameters. If such an analysis could be made, it would be a quantitative test of the scaling law (1.3).

Here we study the concentration dependence of the correlation length of the monomer density fluctuations in a good solvent. For simplicity we restrict ourselves to a monodisperse case. By means of the conformation space renormalisation group theory (Oono 1979, Oono *et al* 1981) the scaling form of the correlation length is obtained up to first order of  $\varepsilon = (4 - d)$ . In the course of the calculation the radius of gyration of a test chain is also evaluated.

The conformation space renormalisation method was first introduced in the study of a single chain where the model is written in terms of chain conformation. Such a direct application of a renormalisation theory is possible in the dilute limit but difficult technically to cover the semi-dilute regime. A similar attempt has been made by des Cloizeaux (1981). However, the results obtained have been limited to a dilute regime. As was shown in a previous paper (Ohta and Oono 1982), Edwards' (1966) transformation of the model is most suitable to study semi-dilute solutions by the conformation space renormalisation method. Edwards represents the model with a continuous scalar field variable. The feature of chain connectedness or the information of chain conformation then enters in the vertex functions. Thus this representation is capable of using the renormalisation theory transparently.

In § 2 we describe the Edwards approach in a manner appropriate to the present purpose. The scattering function of the full monomer density fluctuations is obtained formally in § 3 up to first order of the excluded volume parameter. The scattering function consists of two parts. One is due to the intrachain correlation while the other comes from the correlation between different chains. In § 4 we derive the radius of gyration and the correlation length by expanding the scattering function in powers of the wavenumber. Our renormalisation group procedure is presented in § 5. The  $\varepsilon$  expansion of the radius of gyration and the correlation length is carried out in § 6. The final section is devoted to a summary and discussions. In the appendix we summarise the formulae used in the derivation of the correlation length.

## 2. General formulation

We consider the system of a semi-dilute solution with  $n$  polymer chains in a box  $V$  in  $d$  dimensions. The model which we start with is defined by the Hamiltonian

$$H\{\mathbf{c}\} = \frac{1}{2} \sum_i^n \int_0^N d\tau \left( \frac{d\mathbf{c}_i}{d\tau} \right)^2 + \frac{u}{2} \sum_{i,j}^n \int_0^N d\tau \int_0^N d\tau' \delta(\mathbf{c}_i(\tau) - \mathbf{c}_j(\tau')), \quad (2.1)$$

$|\tau - \tau'| > a$

where  $\mathbf{c}_i(\tau)$  represents the continuous chain conformation of the  $i$ th chain with the contour length  $\tau$ ,  $u (> 0)$  is the excluded volume parameter,  $a$  is the microscopic cut-off,

and  $N$  is the measure of the chain length. In this paper we restrict ourselves to the monodisperse case. Although the model (2.1) has an intuitively definite meaning it makes the actual calculation complicated. Thus a more convenient representation is necessary. One of the methods is to introduce a new Hamiltonian equivalent with (2.1) but written with a continuous field variable (Edwards 1966). First introduce the local monomer density

$$\rho(\mathbf{r}) = \sum_i \int_0^N d\tau \delta(\mathbf{r} - \mathbf{c}_i(\tau)) = \int_q \rho_q e^{i\mathbf{q}\mathbf{r}} \quad (2.2)$$

where

$$\rho_q = \sum_i \int_0^N d\tau \exp[-i\mathbf{q}\mathbf{c}_i(\tau)], \quad (2.3)$$

$$\int_q = \int d^d q / (2\pi)^d. \quad (2.4)$$

The partition function may be written as

$$\begin{aligned} Z &= \int d\{\mathbf{c}\} \int d\{\rho\} \prod_k \delta\left(\rho_k - \sum_i \int_0^N d\tau \exp[-i\mathbf{k}\mathbf{c}_i(\tau)]\right) e^{-H(\mathbf{c})} \\ &= \int d\{\mathbf{c}\} \int d\{\rho\} \int d\{\phi\} \exp\left[i \int_k \phi_k \rho_k - i \sum_i \int_0^N d\tau \phi(\mathbf{c}_i(\tau)) \right. \\ &\quad \left. - \frac{1}{2} \sum_i \int_0^N d\tau \left(\frac{d\mathbf{c}_i}{d\tau}\right)^2 - \frac{u}{2} \int_k \rho_k \rho_{-k}\right], \end{aligned} \quad (2.5)$$

where

$$\phi(\mathbf{c}_i(\tau)) \equiv \int_k \phi_k \exp[i\mathbf{k} \cdot \mathbf{c}_i(\tau)].$$

Performing the integral over  $\{\rho\}$  one obtains

$$Z = AZ_0 \int d\{\phi\} G\{\phi\} \exp\left(- (2u)^{-1} \int_k \phi_k \phi_{-k}\right), \quad (2.6)$$

where

$$A = \int d\{\rho\} \exp\left(-\frac{1}{2}u \int_k \rho_k \rho_{-k}\right), \quad (2.7)$$

$$Z_0 = \int d\{\mathbf{c}\} \exp\left[-\frac{1}{2} \sum_i \int_0^N d\tau \left(\frac{d\mathbf{c}_i}{d\tau}\right)^2\right], \quad (2.8)$$

$$G\{\phi\} = \left\langle \exp\left(-i \int_0^N d\tau \phi(\mathbf{c}(\tau))\right) \right\rangle_0. \quad (2.9)$$

The bracket  $\langle \dots \rangle_0$  means the canonical average with respect to the Hamiltonian (2.1) with  $u = 0$ . The subscript  $i$  of  $\mathbf{c}_i(\tau)$  has been omitted in (2.9) since this representation factorises out each chain. Thus one obtains the new Hamiltonian

$$\mathcal{H}\{\phi\} = (2u)^{-1} \int_k \phi_k \phi_{-k} - \ln G\{\phi\}, \quad (2.10)$$

where an additive constant has been ignored.

The correlation function of the monomer density fluctuations can also be written with the  $\phi$  field:

$$S(q) \equiv \int d\{c\} \rho_q \rho_{-q} e^{-H(c)} / Z = u^{-1} - u^{-2} \langle \phi_q \phi_{-q} \rangle, \tag{2.11}$$

where  $\langle \dots \rangle$  indicates the average with respect to (2.10).

So far our treatment is general and exact. In order to obtain the explicit form of  $G\{\phi\}$  one has to employ an approximation. Here we expand  $G\{\phi\}$  in powers of  $\phi$ :

$$\ln G\{\phi\} = n \ln \left[ \sum_{m=0}^{\infty} \frac{(-i)^m}{m!} \int_0^N d\tau_1 \dots \int_0^N d\tau_m \int_{k_1 \dots k_m} \phi_{k_1} \dots \phi_{k_m} \times \left\langle \exp \left( i \sum_{i=1}^m \mathbf{k}_i \cdot \mathbf{c}(\tau_i) \right) \right\rangle_0 \right]. \tag{2.12}$$

Note the formula that

$$\left\langle \exp \left( i \sum_j \mathbf{k}_j \cdot \mathbf{c}(\tau_j) \right) \right\rangle_0 = \exp \left( -\frac{1}{2} \sum_{i,j} \mathbf{k}_i \cdot \mathbf{k}_j \chi(\tau_i, \tau_j) \right), \tag{2.13}$$

where

$$\chi(\tau_i, \tau_j) = \langle c^\alpha(\tau_i) c^\alpha(\tau_j) \rangle_0 = N \left\{ \frac{1}{4} (N^{-1}(\tau_i + \tau_j) - 1)^2 - \frac{1}{12} + \frac{1}{4} (N^{-1}|\tau_i - \tau_j| - 1)^2 - \frac{1}{12} \right\}. \tag{2.14}$$

By neglecting the wall effect the system must have translational invariance in space. Furthermore one may put  $\phi_0 = 0$  without loss of generality. With these in mind (2.12) is evaluated up to fourth order of  $\phi$  as

$$\begin{aligned} \ln G\{\phi\} = & -c \int_{\mathbf{k}_1, \mathbf{k}_2} \phi_{\mathbf{k}_1} \phi_{\mathbf{k}_2} \Gamma^{(2)}(\mathbf{k}_1, \mathbf{k}_2) + ic \int_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \phi_{\mathbf{k}_1} \phi_{\mathbf{k}_2} \phi_{\mathbf{k}_3} \Gamma^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\ & + c \int_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} \phi_{\mathbf{k}_1} \phi_{\mathbf{k}_2} \phi_{\mathbf{k}_3} \phi_{\mathbf{k}_4} [\Gamma^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) \\ & - (2V)^{-1} \Gamma^{(2)}(\mathbf{k}_1, \mathbf{k}_2) \Gamma^{(2)}(\mathbf{k}_3, \mathbf{k}_4)], \end{aligned} \tag{2.15}$$

where

$$\begin{aligned} \Gamma^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) &= \frac{(2\pi)^d}{n!} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_n) \int_0^N d\tau_1 \dots \int_0^N d\tau_n \exp \left( -\frac{1}{2} \sum_{i,j} \mathbf{k}_i \cdot \mathbf{k}_j \chi(\tau_i, \tau_j) \right) \\ &\equiv (2\pi)^d \delta(\mathbf{k}_1 + \dots + \mathbf{k}_n) \hat{\Gamma}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_{n-1}) \end{aligned} \tag{2.16}$$

and  $c = n/V$  is the polymer number density.

Substitution of (2.15) into (2.10) gives us the final form of  $\mathcal{H}\{\phi\}$ . It can be shown by a dimensional argument that the approximation used in the derivation of (2.15) is actually the expansion in terms of  $uN^{2-d/2}$  with  $cuN^2$  fixed. Hence one can develop the loop expansion for  $\mathcal{H}\{\phi\}$  just as in the theory of phase transitions (e.g. Brézin *et al* 1976). In fact the calculation of the scattering function described in § 3 is correct up to one-loop order.

The above fact on the expansion parameter indicates that in the scaling limit  $N/a \gg 1$  the naive expansion (2.12) breaks down below four dimensions. The renormalisation method is thus indispensable to make the approximation controllable and to obtain reliable scaling results, which will be discussed in § 5.

### 3. Scattering function

Before applying the renormalisation procedure we wish to derive the formal expression of the correlation function  $S(q)$  up to first order of  $uN^{2-d/2}$ . The correlation  $\langle \phi_q \phi_{-q} \rangle$  is calculated by the Hamiltonian (2.10) with (2.15):

$$\begin{aligned} \mathcal{H}\{\phi\} = & \frac{1}{2} \int_{\mathbf{k}} (u^{-1} + 2c\hat{\Gamma}^{(2)}(\mathbf{k})) \phi_{\mathbf{k}} \phi_{-\mathbf{k}} + ic \int_{\mathbf{k}_1, \mathbf{k}_2} \phi_{\mathbf{k}_1} \phi_{\mathbf{k}_2} \phi_{-\mathbf{k}_1-\mathbf{k}_2} \hat{\Gamma}^{(3)}(\mathbf{k}_1, \mathbf{k}_2) \\ & + c \int_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \phi_{-\mathbf{k}_1} \phi_{\mathbf{k}_2-\mathbf{k}_3} \phi_{\mathbf{k}_3} \phi_{\mathbf{k}_1-\mathbf{k}_2} \hat{\Gamma}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\ & - (c/2V) \int_{\mathbf{k}_1, \mathbf{k}_2} \phi_{\mathbf{k}_1} \phi_{-\mathbf{k}_1} \phi_{\mathbf{k}_2} \phi_{-\mathbf{k}_2} \hat{\Gamma}^{(2)}(\mathbf{k}_1) \hat{\Gamma}^{(2)}(\mathbf{k}_2). \end{aligned} \quad (3.1)^\dagger$$

It should be noted that the vertex function  $\hat{\Gamma}^{(n)}$  defined by (2.16) is the  $n$ -point monomer density correlation of a single Gaussian chain. For instance  $\hat{\Gamma}^{(2)}(\mathbf{k})$  is given from (2.13) and (2.16) by

$$\hat{\Gamma}^{(2)}(\mathbf{k}) = N^2 \{ 2/k^2 N - (2/k^2 N)^2 [1 - \exp(-k^2 N/2)] \}. \quad (3.2)$$

This is the scattering function of a Gaussian chain. Calculation of other vertex functions is more involved. Those precise forms are, however, not necessary for the present purpose (see appendix).

The zeroth-order correlation  $\langle \phi_q \phi_{-q} \rangle_0$  is obtained by

$$\langle \phi_q \phi_{-q} \rangle_0 = u / (1 + 2cu\hat{\Gamma}^{(2)}(q)). \quad (3.3)$$

The correction  $\langle \phi_q \phi_{-q} \rangle_1$  from the  $\hat{\Gamma}^{(3)}$  term of (3.1) is shown to be given up to the leading order by

$$\langle \phi_q \phi_{-q} \rangle_1 = -18c^2 \langle \phi_q \phi_{-q} \rangle_0^2 \int_{\mathbf{p}} \langle \phi_{\mathbf{p}} \phi_{-\mathbf{p}} \rangle_0 \langle \phi_{\mathbf{q}+\mathbf{p}} \phi_{-\mathbf{q}-\mathbf{p}} \rangle_0 \hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p}) \hat{\Gamma}^{(3)}(-\mathbf{q}, -\mathbf{p}), \quad (3.4)$$

where we have used the fact that  $\phi_0 = 0$ . The last two terms of (3.1) produce another correction  $\langle \phi_q \phi_{-q} \rangle_2$  given by

$$\langle \phi_q \phi_{-q} \rangle_2 = 2cu \langle \phi_q \phi_{-q} \rangle_0 \int_{\mathbf{p}} \{ \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) - \hat{\Gamma}^{(2)}(q) \hat{\Gamma}^{(2)}(p) \} \langle \phi_{\mathbf{p}} \phi_{-\mathbf{p}} \rangle_0, \quad (3.5)$$

where  $\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p})$  consists of six terms which arise from the factorisation of  $\phi_{-\mathbf{k}_1} \phi_{\mathbf{k}_2-\mathbf{k}_3} \phi_{\mathbf{k}_3} \phi_{\mathbf{k}_1-\mathbf{k}_2}$ :

$$\begin{aligned} \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) = & \hat{\Gamma}^{(4)}(\mathbf{p}, 0, \mathbf{q}) + \hat{\Gamma}^{(4)}(\mathbf{p}, \mathbf{p} + \mathbf{q}, \mathbf{q}) + \hat{\Gamma}^{(4)}(\mathbf{p}, \mathbf{p} + \mathbf{q}, \mathbf{p}) \\ & + \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p} + \mathbf{q}, \mathbf{q}) + \hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p} + \mathbf{q}, \mathbf{p}) + \hat{\Gamma}^{(4)}(\mathbf{q}, 0, \mathbf{p}). \end{aligned} \quad (3.6)$$

Now let us consider the meaning of the corrections (3.4) and (3.5). Note that the factor  $c\hat{\Gamma}^{(3)}$  appears twice in (3.4). Since  $\hat{\Gamma}^{(3)}$  is the three-point correlation of a single Gaussian chain this indicates that (3.4) gives the interchain correlation of the scattering function. On the other hand (3.5) with  $c\hat{\Gamma}^{(4)}$  gives rise to the intrachain correlation.

† The wavenumber dependence of the third term of (3.1) has been chosen to be consistent with  $\hat{\Gamma}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$  given by (A7).

If one tentatively ignores (3.4) the formula (2.11) gives the scattering function as follows:

$$S(q) = cG(q)/(1 + cuG(q)) \quad (3.7)$$

with

$$G(q) = 2\hat{\Gamma}^{(2)}(q) - 2u \int_{\mathbf{p}} (\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) - \hat{\Gamma}^{(2)}(q)\hat{\Gamma}^{(2)}(p))(1 + 2cu\hat{\Gamma}^{(2)}(p))^{-1}. \quad (3.8)$$

The function  $G(q)$  is the scattering function of a test chain in the semi-dilute solution. Equation (3.7) was first derived by Edwards (1966). The scaling form of  $G(q)$  has been obtained recently with including the polydispersity effect (Oono, private communication). If one takes the dilute limit  $c \rightarrow 0$ ,  $S(q)/c$  reduces to the scattering function of a single chain studied previously (Ohta *et al* 1082).

The proper scattering function up to  $O(u)$  must incorporate the correction (3.4):

$$S(q) = cG(q)/(1 + cuG(q)) + cS_1(q), \quad (3.9)$$

where

$$S_1(q) = 18u \frac{cu}{(1 + 2cu\hat{\Gamma}^{(2)}(q))^2} \int_{\mathbf{p}} \frac{\hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p})\hat{\Gamma}^{(3)}(-\mathbf{q}, -\mathbf{p})}{(1 + 2cu\hat{\Gamma}^{(2)}(\mathbf{p}))(1 + 2cu\hat{\Gamma}^{(2)}(\mathbf{q} + \mathbf{p}))}. \quad (3.10)$$

One may write (3.9) in another form

$$S(q) = cJ(q)/(1 + cuJ(q)) \quad (3.11)$$

with

$$J(q) = G(q) + 18cu^2 \int_{\mathbf{p}} \frac{\hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p})\hat{\Gamma}^{(3)}(-\mathbf{q}, -\mathbf{p})}{(1 + 2cu\hat{\Gamma}^{(2)}(\mathbf{p}))(1 + 2cu\hat{\Gamma}^{(2)}(\mathbf{q} + \mathbf{p}))} \quad (3.12)$$

which is equivalent to (3.9) up to  $O(u)$ . The scattering function in the limit  $q \rightarrow 0$  must be related to the osmotic compressibility. This is verified in the following. The osmotic pressure  $\Pi = \partial \ln Z / \partial V$  is calculated from (3.1) and is given up to first order of  $u$  by ( $k_B T = 1$ )

$$\Pi = c + \frac{1}{2}uc^2N^2 - \frac{1}{2} \int_{\mathbf{p}} \ln[1 + 2cu\hat{\Gamma}^{(2)}(p)] + cu \int_{\mathbf{p}} \frac{\hat{\Gamma}^{(2)}(p)}{1 + 2cu\hat{\Gamma}^{(2)}(p)}, \quad (3.13)$$

where the first term appears from the additive constant neglected in (2.10). On the other hand note the facts obtained from (2.16) that

$$\lim_{q \rightarrow 0} \hat{\Gamma}^{(2)}(q) = \frac{1}{2}N^2, \quad (3.14)$$

$$\lim_{q \rightarrow 0} \hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p}) = \frac{1}{3}N\hat{\Gamma}^{(2)}(p). \quad (3.15)$$

Furthermore one can show that (see appendix)

$$\lim_{q \rightarrow 0} (\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) - \hat{\Gamma}^{(2)}(q)\hat{\Gamma}^{(2)}(p)) = 0. \quad (3.16)$$

Therefore (3.11) becomes

$$\lim_{q \rightarrow 0} cN^2/S(q) = 1 + cuN^2 - 2cu^2 \int_{\mathbf{p}} \frac{(\hat{\Gamma}^{(2)}(p))^2}{(1 + 2cu\hat{\Gamma}^{(2)}(p))^2}. \quad (3.17)$$

It is readily shown from (3.13) that the RHS of (3.17) is  $\partial\Pi/\partial c$  up to  $O(u)$ . Note that the last term of (3.17) comes from  $S_1(q)$ . Thus the interchain correlation is important to satisfy the thermodynamic relation consistently up to  $O(u)$ .

#### 4. Radius of gyration and correlation length

In a semi-dilute polymer solution there are three types of characteristic lengths. One is the root mean square end-to-end distance of a test chain, which has been studied in a previous paper (Ohta and Oono 1982). The radius of gyration  $R_G$  also characterises the form of a test chain. These two quantities are accessible by a neutron scattering experiment. The third characteristic length is the correlation length  $\xi$  of monomer density fluctuations. In a dilute regime the correlation length  $\xi$  is the same as  $R_G$ . However, if one increases the polymer concentration, the chains overlap each other. The average contact length specifies the correlation length. Thus one may expect that the correlation length  $\xi$  is generally shorter than the radius of gyration  $R_G$  in semi-dilute solutions.

First we wish to derive the expression of  $R_G$  up to  $O(u)$ . The radius of gyration  $R_G$  is defined with the correlation function  $G(q)$  of a test chain by

$$G(q)/G(0) = 1 - (q^2/d)R_G^2 + O(q^4). \quad (4.1)$$

One may expand  $G(q)$  given by (3.8) in powers of  $q$ :

$$G(q) = N^2 - \frac{1}{3}N^2Q^2 - \frac{1}{3}uN^4(2/N)^{d/2} \int_{\mathbf{P}} (2\mathbf{P} \cdot \mathbf{Q})^2 V(\mathbf{P})(1 + 2cu\hat{\Gamma}^{(2)}(\mathbf{p}))^{-1} + O(Q^4), \quad (4.2)$$

where

$$Q = q(N/2)^{1/2}, \quad P = p(N/2)^{1/2}, \quad (4.3)$$

and  $V(P)$  is defined by

$$\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) - \hat{\Gamma}^{(2)}(\mathbf{q})\hat{\Gamma}^{(2)}(\mathbf{p}) = \frac{1}{6}N^4(2\mathbf{Q} \cdot \mathbf{P})^2 V(\mathbf{P}) + O(Q^4). \quad (4.4)$$

The explicit form of  $V(P)$  is given by (A9) in the appendix. Comparing (4.2) with (4.1), some manipulations yield

$$R_G^2/R_{GD}^2 = 1 - uN^2 \left(\frac{2}{N}\right)^{d/2} \frac{4}{d} \int_{\mathbf{P}} P^2 V(\mathbf{P}) \frac{2cu\hat{\Gamma}^{(2)}(\mathbf{p})}{1 + 2cu\hat{\Gamma}^{(2)}(\mathbf{p})}, \quad (4.5)$$

where  $R_{GD}$  is the radius of gyration in the dilute limit:

$$R_{GD}^2 = \frac{1}{6}dN \left(1 + uN^2(2/N)^{d/2}(4/d) \int_{\mathbf{P}} P^2 V(\mathbf{P})\right). \quad (4.6)$$

The calculation of the correlation length  $\xi$  can be performed in a similar way. The definition of  $\xi$  is given through the relation

$$S(q)/S(0) = 1 - (q^2/d)\xi^2 + O(q^4). \quad (4.7)$$

In order to obtain  $\xi$  up to  $O(u)$  one may use  $S(q)$  derived in (3.11) with (3.12). Let us expand  $J(q)$  in terms of  $q$ :

$$J(q) = N^2 - (q^2N^2/d)R_G^2 + N^2J_1 - (N^2q^2/d)J_2 + O(q^4), \quad (4.8)$$



where the terms with  $J_1$  and  $J_2$  arise from the second term of (3.12). The formulae of  $J_1$  and  $J_2$ , which are of order  $u$ , are given in (A14) and (A15) respectively in the appendix. The scattering function  $S(q)$  may be written up to  $O(q^2)$  as

$$S(q) = \frac{cN^2}{(\partial\Pi/\partial c)} \left( 1 - \frac{q^2}{d} \frac{(R_G^2 + J_2)(1 - 2J_1)}{\partial\Pi/\partial c} \right). \quad (4.9)$$

Thus the correlation length  $\xi$  is given by

$$\xi^2/R_{GD}^2 = \left( \frac{\partial\Pi}{\partial c} \right)^{-1} (R_G^2/R_{GD}^2 + 6J_2/dN - 2J_1), \quad (4.10)$$

where we have used the fact that  $J_1 \sim J_2 \sim O(u)$ .

The concentration dependence of the mean square end-to-end distance  $[R^2]$  has been studied previously (Ohta and Oono 1982). Here we present the result up to  $O(u)$  without derivation:

$$[R^2]/[R^2]_D = 1 - \frac{2u}{d} N^2 \left( \frac{2}{N} \right)^{d/2} \int_{\mathbf{P}} P^2 U(P) \frac{2cu\hat{\Gamma}^{(2)}(p)}{1 + 2cu\hat{\Gamma}^{(2)}(p)}, \quad (4.11)$$

where

$$[R^2]_D = dN + 2uN^3(2/N)^{d/2} \int_{\mathbf{P}} P^2 U(P), \quad (4.12)$$

$$U(x) = \frac{2}{x^6} - \frac{6}{x^8} + \left( \frac{1}{x^4} + \frac{4}{x^6} + \frac{6}{x^8} \right) \exp(-x^2). \quad (4.13)$$

## 5. The renormalisation group analysis

The expressions of  $R_G$  and  $\xi$  obtained in § 4 are correct up to order  $uN^{(4-d)/2}$ . In the asymptotic scaling limit where  $uN^{(4-d)/2} \gg 1$ , however, the expansion breaks down below four dimensions. In order to overcome this difficulty we here employ the renormalisation group method together with the  $4-d(=\varepsilon)$  expansion. The scaling functions for  $R_G$  and  $\xi$  will be calculated up to  $O(\varepsilon)$ .

The results (4.5), (4.6) and (4.10) obtained by naive perturbation contain key information for renormalisation. Since we are concerned with the order  $\varepsilon$  corrections the integral over  $P$  may be performed in four dimensions. For sufficiently large values of  $P$  with  $cuN^2$  fixed one can show that

$$\hat{\Gamma}^{(2)}(p) \approx N^2/P^2, \quad V(P) \approx 1/P^6. \quad (5.1)$$

Therefore the integral in (4.6) diverges logarithmically whereas the RHS of (4.5) does not exhibit divergence as long as  $cuN^2$  is finite. The osmotic compressibility in (4.10) contains a divergent integral, which is easily seen from (3.17). As is shown in the appendix the factors  $J_1$  and  $J_2$  also diverge logarithmically. However, these divergences are found to cancel each other in the combination  $6J_2/Nd - 2J_1$ . This must be the case, otherwise the exponent associated with  $\xi$  depends on the polymer concentration. Thus the divergent integrals appear only in  $R_{GD}$  and  $\partial\Pi/\partial c$ . In fact the divergent parts

of these quantities are given for  $d = 4$  by

$$[R_{GD}^2]_{\text{div}} = \frac{1}{6}dN \left( 1 + 4u \int_{\mathbf{P}} P^{-4} \right), \quad (5.2)$$

$$[\partial\Pi/\partial c]_{\text{div}} = 1 + cuN^2 - cuN^2(8u) \int_{\mathbf{P}} P^{-4}, \quad (5.3)$$

where the integrands have been approximated by the asymptotic form for  $P \gg 1$ . Therefore an infrared cut-off should be understood. On the other hand the ultraviolet cut-off is given by  $(N/2a)^{1/2}$  with  $a$  defined in (2.1). Here we do not use the dimensional regularisation since the present approach is simpler, at least for the calculations up to  $O(\varepsilon)$ .

In order to eliminate the logarithmic anomaly we introduce the renormalisation factors  $Z_N$  and  $Z_u$ ;

$$N = N_R / Z_N, \quad (5.4)$$

$$u = u_R \kappa^{(d-4)/2} Z_u, \quad (5.5)$$

where  $N_R$  is the renormalised polymerisation index and  $u_R$  is the dimensionless renormalisation coupling constant.  $\kappa$  is the reference short distance cut-off parameter. The renormalisation of  $c$  or  $c_i(\tau)$  is not necessary since any divergences can be shown to be absorbed into  $Z_N$  and  $Z_u$ . The renormalisation group equation for the characteristic length  $A(N, c, u, a)$  which stands for  $R_G$  or  $\xi$  is constructed as follows. The renormalised length  $A_R(N_R, c, u_R(u), \kappa)$  should be related to  $A(N, c, u, a)$  as

$$A_R(N_R, c, u_R(u), \kappa) = \lim_{a/\kappa \rightarrow 0} A(N_R/Z_N, c, u_R \kappa^{(d-4)/2} Z_u a), \quad (5.6)$$

where we have used the relations (5.4) and (5.5). Impose the condition that  $A$  is independent of the arbitrary chosen reference cut-off  $\kappa$  ( $N > \kappa > a$ ) so that one obtains

$$\left( \kappa \frac{\partial}{\partial \kappa} + \beta(u_R) \frac{\partial}{\partial u_R} + \kappa N_R \frac{\partial \ln Z_N}{\partial \kappa} \frac{\partial}{\partial N_R} \right) A_R(N_R, c, u_R, \kappa) = 0, \quad (5.7)$$

where use of (5.4) has been made. The Gell-Mann-Low function  $\beta(u_R)$  is given by

$$\beta(u_R) \equiv \kappa \left( \frac{\partial u_R}{\partial \kappa} \right)_{a, u, N} = u_R \left( \frac{4-d}{2} - \frac{\partial \ln Z_u}{\partial \ln \kappa} \right). \quad (5.8)$$

The renormalisation factors  $Z_N$  and  $Z_u$  can be obtained by a perturbation expansion in terms of  $u_R$ ;

$$Z_N = 1 + b_1 u_R + O(u_R^2), \quad Z_u = 1 + b_2 u_R + O(u_R^2). \quad (5.9)$$

The coefficients  $b_1$  and  $b_2$  are determined in such a way that the ultraviolet divergences in (5.2) and (5.3) should be eliminated by  $Z_N$  and  $Z_u$ . Thus one obtains

$$b_1 = (4\pi^2)^{-1} \ln(\kappa/a), \quad (5.10)$$

$$b_2 - 2b_1 = (2\pi^2)^{-1} \ln(\kappa/a), \quad (5.11)$$

where the relation  $u = u_R + O(u_R^2)$  has been used. The function  $\beta(u_R)$  is then given up to  $O(u_R^2)$  by

$$\beta(u_R) = u_R(\frac{1}{2}\varepsilon - \pi^{-2}u_R). \quad (5.12)$$

The condition  $\beta(u_R) = 0$  yields the fixed point value  $u_R^*$

$$u_R^* = \frac{1}{2}\pi^2 \varepsilon + O(\varepsilon^2), \tag{5.13}$$

which agrees with that obtained in the dilute limit (Oono *et al* 1981, Ohta *et al* 1982).

At the fixed point  $u_R = u_R^*$  the renormalisation group equation (5.7) simplifies to

$$(\kappa \partial / \partial \kappa + N_R B \partial / \partial N_R) A_R(N_R, c, u_R^*, \kappa) = 0, \tag{5.14}$$

where

$$B \equiv \kappa (\partial \ln Z_N / \partial \kappa)_{u_R = u_R^*} = \frac{u_R^*}{4\pi^2} = \frac{1}{8}\varepsilon + O(\varepsilon^2). \tag{5.15}$$

Equation (5.14) and the dimensional analysis give the scaling form of  $A_R$

$$A_R(N_R, c, u_R^*, 1) = N_R^\nu F(cN_R^{d\nu}, u_R^*), \tag{5.16}$$

where

$$\nu \equiv [2(1 - B)]^{-1} = \frac{1}{2}(1 + \frac{1}{8}\varepsilon + O(\varepsilon^2)). \tag{5.17}$$

In (5.16) we have put  $\kappa = 1$ . The exponent  $\nu$  given by (5.17) agrees with the value obtained by various methods. The scaling function  $F(x, u_R^*)$  will be evaluated in § 6.

### 6. Scaling form of the correlation length

Although our final aim is to evaluate the universal scaling function of the correlation length  $\xi$  many kinds of other quantities can be obtained as a byproduct in the course of the calculation. Hereafter we omit the subscript R of  $N$  and  $u^*$  which should be understood to be the renormalised variables.

First we wish to derive the scaling form of the radius of gyration. In the dilute limit  $R_{GD}^2$  is given from (4.6) up to  $O(\varepsilon)$  by

$$R_{GD}^2 = \frac{d}{6} \left\{ N + \frac{Nu^*}{2\pi^2} \left[ \int_0^{(N/2\kappa)^{1/2}} dx \frac{x^5}{x^6 + 30} + \int_0^\infty dx x^5 \left( V(x) - \frac{1}{x^6 + 30} \right) \right] \right\}, \tag{6.1}$$

where the last term is a convergent integral. Using (A9) for  $V(x)$  and the fixed point value (5.13) one obtains  $R_{GD}$  in the limit  $N/\kappa \gg 1$

$$R_{GD}^2 = \frac{1}{6} dN(N/2\kappa)^{\varepsilon/8} (1 - \frac{31}{96}\varepsilon + \frac{1}{8}\gamma\varepsilon + O(\varepsilon^2)), \tag{6.2}$$

where  $\gamma$  is the Euler constant  $\gamma = 0.577 \dots$ . Equation (6.2) does not agree with the previous result obtained by a slightly different method (Ohta *et al* 1982). This is not surprising because  $R_{GD}$  itself is not a universal quantity. In fact one can verify that the ratio  $R_{GD}^2/[R^2]_D$ , which is universal, does agree with that obtained in the above paper if one calculates  $[R^2]_D$  given by (4.12) in the same way as described here.

The scaling form of the radius of gyration is given from (4.5) by

$$R_G^2/R_{GD}^2 = \exp \left( -\frac{\varepsilon}{4} \int_0^\infty dy y^5 V(y) \frac{2Xg(y^2)}{1 + 2Xg(y^2)} + O(\varepsilon^2) \right), \tag{6.3}$$

where

$$g(z) = z^{-1} - z^{-2} + z^{-2} e^{-z}, \tag{6.4}$$

$$X = cu^* N^2 (N/2\kappa)^{-\varepsilon/4}. \tag{6.5}$$

In (6.3) the correction of order  $\epsilon$  has been exponentiated. Furthermore we have introduced a scaled variable  $X$  instead of  $cuN^2$ . These are allowed in the spirit of the  $\epsilon$  expansion. The origin of the exponent  $\epsilon/4$  in (6.5) will be described below. In the semi-dilute limit where  $X \gg 1$  equation (6.3) becomes

$$R_G^2/R_{GD}^2 \approx \exp\left(-\frac{\epsilon}{4} \int_{(2X)^{-1/2}}^{\infty} dy \frac{1}{y(y^2+1)}\right) \approx (2X)^{-\epsilon/8} \tag{6.6}$$

so that  $R_G^2$  depends on  $N$  and  $c$  as

$$R_G^2 \approx N(cN)^{-\epsilon/8}. \tag{6.7}$$

This is consistent with the scaling argument (de Gennes 1979)

$$R_G^2 \approx N(cN)^{(1-2\nu)/(d\nu-1)}. \tag{6.8}$$

We have performed a numerical computation to obtain the full  $X$  dependence of  $R_G^2$ . The result is displayed in figure 1. Note that the factor  $\epsilon/4$  in (6.3) has been replaced by  $2(1-2\nu)/(d\nu-1)$  with  $d=3$  and  $\nu=0.588$  (Le Guillou and Zinn-Justin 1980) so that the higher-order corrections of  $\epsilon$  are partially taken into account.

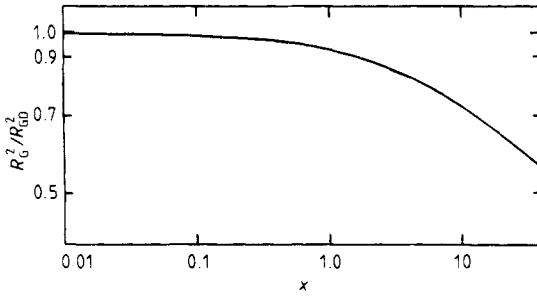


Figure 1. Scaling function of  $R_G^2/R_{GD}^2$ .

We have also evaluated  $[R^2]$ . The ratio  $R_G^2/[R^2]$  is found to be almost independent of the concentration in the entire range of  $X$ . Daoud *et al* (1975) have studied this ratio theoretically and found a strong  $c$  dependence when  $c$  is close to the overlapping concentration  $c^*$ . However, this is probably due to the rough approximation used there.

We have restricted ourselves to the monodisperse limit. The calculation of  $R_G$  in a polydisperse system has been carried out recently by Oono (private communication).

Now we discuss the scaling form of  $\xi$ . One needs to obtain the osmotic compressibility  $\partial\Pi/\partial c$ . Using (3.17) one gets

$$\begin{aligned} \frac{\partial\Pi}{\partial c} &= 1 + cu^*N^2 - \frac{u^*}{\pi^2} cu^*N^2 \int_0^{(N/2\kappa)^{1/2}} dx \frac{x^3}{(x^2+2)^2} \\ &\quad - \frac{u^*}{\pi^2} cu^*N^2 \int_0^{\infty} dx x^3 \left( \frac{g(x^2)^2}{(1+2cu^*N^2g(x^2))^2} - \frac{1}{(x^2+2)^2} \right). \end{aligned} \tag{6.9}$$

The third term produces  $\frac{1}{2} \ln(N/2\kappa)$  which is absorbed into the second term by replacing  $cu^*N^2$  by  $cu^*N^{2-\epsilon/4}$ . This fact has been used in (6.5). Equation (6.9) is thus written

up to  $O(\epsilon)$  as

$$\frac{\partial \Pi}{\partial c} = 1 + X \exp \left\{ -\frac{2(2-d\nu)}{d\nu-1} \left[ c_1 + \int_0^\infty dx x^3 \left( \frac{g(x^2)^2}{(1+2Xg(x^2))^2} - \frac{1}{(x^2+2)^2} \right) \right] \right\}, \quad (6.10)$$

where

$$c_1 = -\frac{1}{2}(1 + \ln 2), \quad (6.11)$$

$$\frac{2(2-d\nu)}{(d\nu-1)} = \frac{1}{2}\epsilon + O(\epsilon^2). \quad (6.12)$$

For sufficiently large values of  $X$ , (6.10) is shown to be given by

$$\partial \Pi / \partial c \approx X^{1/(d\nu-1)}, \quad (6.13)$$

which is in agreement with the scaling arguments (des Cloizeaux 1975). The numerical result of (6.10) with  $d = 3$  and  $\nu = 0.588$  is exhibited in figure 2.

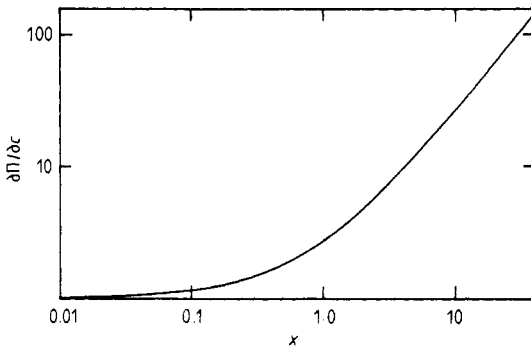


Figure 2. Scaling function of  $\partial \Pi / \partial c$ .

Using (4.10), (6.3) and (6.10) one may write the correlation length as

$$\xi^2 = K(X) R_G^2 (\partial \Pi / \partial c)^{-1}, \quad (6.14)$$

where

$$K(X) = \exp(6J_2/dN - 2J_1 + O(\epsilon^2)). \quad (6.15)$$

(6.14) is our final formula for  $\xi$  which is exact up to  $O(\epsilon)$ .  $J_1$  and  $J_2$  are complicated functions of  $X$ . In the limit  $X \rightarrow 0$ ,  $K(X)$  becomes unity. On the other hand in the semi-dilute limit where  $X \gg 1$  one can evaluate  $K(\infty)$  analytically (see appendix)

$$K(\infty) = \exp\left[\frac{(1-2\nu)}{(d\nu-1)}\right] \approx 0.376, \quad (6.16)$$

where we have put  $d = 3$  and  $\nu = 0.588$ . Thus  $\xi^2$  behaves for  $X \gg 1$  as

$$\xi^2 \approx (cN)^{2\nu/(1-d\nu)}, \quad (6.17)$$

where (6.6), (6.8) and (6.13) have been used. The scaling relation (6.17) is consistent with that obtained by Daoud *et al* (1975). However, our concern is the full scaling form of (6.14). The explicit concentration dependence of  $K(X)$  and (6.14) was evaluated numerically and is shown in figures 3 and 4 respectively. The numerical

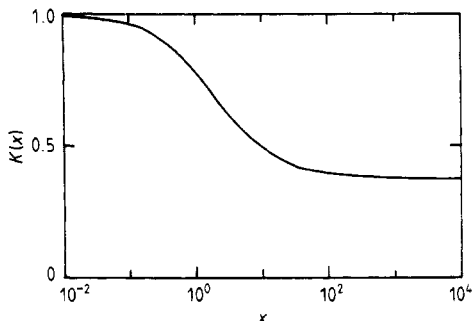


Figure 3. Semi-log plot of  $K(X)$ .

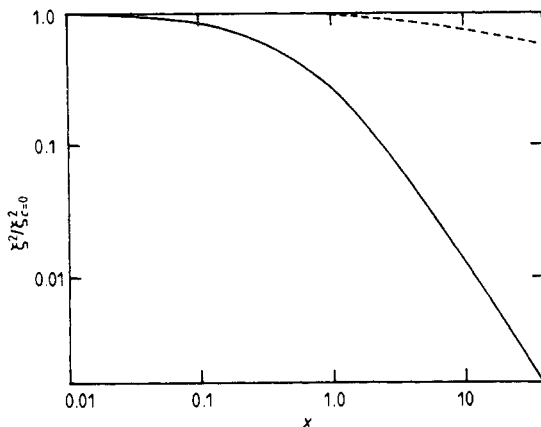


Figure 4. Scaling function of  $\xi^2/\xi_{c=0}^2$  (full line). The radius of gyration  $R_G^2/R_{OD}^2$  is also exhibited by a broken line.

result indicates that  $K(X)$  approaches the asymptotic value (6.16) only when  $X \approx 10^4$ . In figure 4 note the strong concentration dependence of  $\xi$  compared with  $R_G$ . Since the correlation length in the dilute limit is of order of several hundred Å in a typical experimental situation it becomes comparable to the microscopic length at about  $X \approx 30$ . There universal scaling does not hold and the microscopic degrees of freedom which have been eliminated in the present theory must be taken into account.

### 7. Discussions

In the preceding sections we have studied the asymptotic scaling behaviour of semi-dilute polymer solutions. When the polymerisation index  $N$  is sufficiently large, a system in a good solvent should obey the scaling law in the concentration regime where the correlation length  $\xi$  is well separated from the microscopic distance  $a$  ( $\xi \gg a$ ). Although the scaling behaviour of the osmotic pressure has been confirmed experimentally (Noda *et al* 1981), the available data of the correlation length seem to be insufficient for comparison with theory. For instance, the light scattering measurement by Chu and Nose (1980) covers a wide range of concentration as well as of temperature. However, they were little concerned with the scaling function. Thus a precise experiment focused on the scaling form of the correlation length is highly desirable.

It has been shown that Edwards' transformation plays an important role in constructing the renormalisation group theory of semi-dilute polymer solutions. In fact the theory enables us to study the scaling behaviour systematically beyond the phenomenological argument for the semi-dilute limit and the low density expansion. Besides these features the present theory provides us with a new field-theoretic model (2.10) which is renormalisable in four dimensions. This model is quite different in its structure from the so-called  $\phi^4$  model. First of all the interaction is not of short range. The  $\phi^4$  term of (3.1) is approximately given by

$$\frac{1}{2} \int_q [u^{-1} + 2cN^2/(1 + Nq^2)] \phi_q \phi_{-q} \tag{7.1}$$

whereas the usual  $\phi^4$  model contains

$$\frac{1}{2} \int_q (q^2 + r) \phi_q \phi_{-q}. \quad (7.2)$$

Thus the wavenumber dependence of the vertex functions is relevant in the present case. Secondly although (3.1) is truncated up to fourth order of  $\phi$  this does not imply that the higher-order terms are irrelevant as is the case in the  $\phi^4$  model of the ordinary second-order phase transition. In the calculation of a higher-order scaling function one needs to retain the terms neglected in (3.1).

Although our treatment is exact up to first order of  $\varepsilon$ , the calculation of the scaling functions is very involved, mainly because of the complicated wavenumber dependence of the vertex functions. Simplification of those but keeping the essence would be useful to discuss the scaling form of other quantities such as the scattering function itself. Further study in this direction and also of dynamics will be published in future.

### Acknowledgments

We are grateful to Professors Y Oono and M Oyama for valuable discussions. We are also indebted to Mr H Shibata for providing figure 2.

### Appendix

Here we describe the formulae of the vertex functions. From the definition of  $\Gamma^{(n)}$  given by (2.16) one obtains

$$\begin{aligned} \hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p}) = & \frac{1}{6} N^3 \int_0^1 d\tau_1 \int_0^1 d\tau_2 \int_0^1 d\tau_3 \exp[-Q^2|\tau_1 - \tau_3| \\ & - \mathbf{P} \cdot \mathbf{Q}(-|\tau_1 - \tau_2| + |\tau_1 - \tau_3| + |\tau_3 - \tau_2|) - P^2|\tau_2 - \tau_3|], \end{aligned} \quad (A1)$$

where  $P$  and  $Q$  have been introduced in (4.3). Expansion in terms of  $Q$  yields up to  $O(Q^2)$

$$\hat{\Gamma}^{(3)}(\mathbf{q}, \mathbf{p}) = \frac{1}{6} N^3 [Y_0(P) + Y_1(P)(2\mathbf{P} \cdot \mathbf{Q}) + Y_2(P)Q^2 + Y_3(P)(2\mathbf{P} \cdot \mathbf{Q})^2], \quad (A2)$$

where

$$Y_0(P) = \frac{2}{P^2} - \frac{2}{P^4} + \frac{2}{P^4} \exp(-P^2), \quad (A3)$$

$$Y_1(P) = -\frac{1}{P^4} + \frac{2}{P^6} - \left(\frac{1}{P^4} + \frac{2}{P^6}\right) \exp(-P^2), \quad (A4)$$

$$Y_2(P) = -\frac{2}{3P^2} + \frac{1}{P^4} - \frac{2}{P^6} + \frac{4}{P^8} - \left(\frac{1}{P^4} + \frac{2}{P^6} + \frac{4}{P^8}\right) \exp(-P^2), \quad (A5)$$

$$Y_3(P) = \frac{1}{P^6} - \frac{4}{P^8} + \frac{4}{P^{10}} + \left(\frac{1}{3P^4} + \frac{1}{P^6} - \frac{4}{P^{10}}\right) \exp(-P^2). \quad (A6)$$

The fourth-order vertex function  $\hat{\Gamma}^{(4)}$  is given by

$$\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}, \mathbf{k}) = \int_0^N d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \times \exp\left(-\frac{q^2}{2}(\tau_1 - \tau_2) - \frac{p^2}{2}(\tau_2 - \tau_3) - \frac{k^2}{2}(\tau_3 - \tau_4)\right), \quad (\text{A7})$$

which is not symmetrised about the interchange of the arguments. This point is, however, harmless since  $\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p})$  given by (3.6) is symmetric with the proper prefactor. By using (3.6) a tedious but straightforward calculation leads to

$$\hat{\Gamma}^{(4)}(\mathbf{q}, \mathbf{p}) - \hat{\Gamma}^{(2)}(q)\hat{\Gamma}^{(2)}(p) = \frac{1}{6}N^4 V(P)(2\mathbf{P} \cdot \mathbf{Q})^2, \quad (\text{A8})$$

where

$$V(P) = \frac{30}{P^{12}} - \frac{6}{P^{10}} - \frac{3}{P^8} + \frac{1}{P^6} + \left(-\frac{30}{P^{12}} - \frac{24}{P^{10}} - \frac{6}{P^8} + \frac{1}{4P^4}\right) \exp(-P^2). \quad (\text{A9})$$

This formula was used to evaluate the radius of gyration (4.5). The relations (3.15) and (3.16) are verified by (A2) and (A8) respectively.

In order to obtain  $J(q)$  given by (3.12) up to  $O(Q^2)$  we make use of the expansion  $(1 + 2cu\hat{\Gamma}^{(2)}(\mathbf{q} + \mathbf{p}))^{-1}$

$$= W_0(P) + W_1(P)(2\mathbf{P} \cdot \mathbf{Q}) + W_1(P)Q^2 + W_2(P)(2\mathbf{P} \cdot \mathbf{Q})^2 + O(Q^4) \quad (\text{A10})$$

where

$$W_0(P) = (1 + 2cu\hat{\Gamma}^{(2)}(p))^{-1}, \quad (\text{A11})$$

$$W_1(P) = 2cuN^2 W_0(P)^2 \left[ \frac{1}{P^4} - \frac{2}{P^6} + \left( \frac{1}{P^4} + \frac{2}{P^6} \right) \exp(-P^2) \right], \quad (\text{A12})$$

$$W_2(P) = W_0(P)^{-1} W_1(P)^2 - 2cuN^2 W_0(P)^2 \left[ \frac{1}{P^6} - \frac{3}{P^8} + \left( \frac{1}{2P^4} + \frac{2}{P^6} + \frac{3}{P^8} \right) \exp(-P^2) \right]. \quad (\text{A13})$$

Using (A1) and (A10),  $J(q)$  is found to be given by (4.8) with

$$J_1 = \frac{1}{2}uN^2(2/N)^{d/2}cuN^2 \int_{\mathbf{P}} W_0(P)^2 Y_0(P)^2, \quad (\text{A14})$$

$$J_2 = -\frac{dN}{2} \frac{uN^2}{2} \left( \frac{2}{N} \right)^{d/2} cuN^2 \int_{\mathbf{P}} \left\{ W_0(P) W_1(P) Y_0(P)^2 + 2W_0(P)^2 Y_0(P) Y_2(P) + (4/d)P^2 \left[ 2W_0(P)^2 Y_0(P) Y_3(P) + W_0(P)^2 Y_1(P)^2 + W_0(P) W_2(P) Y_0(P)^2 + 2W_0(P) W_1(P) Y_0(P) Y_1(P) \right] \right\}. \quad (\text{A15})$$

The integrand of (A14) behaves as  $4/P^4$  for large values of  $P$  while that of (A15) is like  $-8/3P^4$ . Therefore these logarithmic divergences do not appear in the combination of  $6J_2/Nd - 2J_1$ .



When  $X$  is large enough one may approximate the integrands of (A14) and (A15) by the expressions of large values of  $P$  so that the integrals are evaluated analytically. The universal amplitude ratio  $K(\infty)$  given by (6.16) was obtained in this way.

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