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# On the diffusion coefficient of a polymer chain in theta solvents

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**Abstract.** The path integral formulation of polymer dynamics is used to derive the perturbation expansion of the diffusion coefficient of a polymer chain in theta solvents in powers of the hydrodynamic interaction. The perturbation expansion of the diffusion coefficient has been renormalised to second order of the hydrodynamic interaction. The ratio of the hydrodynamic radius to the gyration radius is given to second order in  $\epsilon = 4 - d$ , where  $d$  is the space dimension.

## 1. Introduction

The diffusion coefficient of a polymer chain in theta solvents has been investigated both theoretically and experimentally. The classical investigations by Kirkwood and Riseman (1948), Kirkwood (1954) and Zimm (1956) (see also Yamakawa 1971) provide the basis for understanding the dynamical behaviour of the dilute polymer solutions. However, the methods of Kirkwood and Zimm use the pre-averaging of the hydrodynamic interaction ( $\zeta_0$ ). In this connection, the natural question about the effects of the fluctuating  $\zeta_0$  arises. The interest in the effects of the fluctuating  $\zeta_0$  has increased after the finding of Schmidt and Burchard (1981) that the prediction of the Kirkwood theory for the ratio of the gyration radius to the hydrodynamic radius is at variance with experiment. At present the Monte Carlo simulations by Zimm (1980), Fixman (1981, 1983) and Freire *et al* (1986) studying the effects of the fluctuating  $\zeta_0$  on the diffusion coefficient are available.

So far, these effects have not been theoretically investigated in a satisfactory way. The first theoretical study of the effects of the fluctuating  $\zeta_0$  was carried out by Oono and Kohmoto (1983). Their approach is based on the treatment of the Kirkwood diffusion equation using the Kirkwood-Riseman formalism. Carrying out the iterative solution of the Kirkwood-Riseman scheme, Oono and Kohmoto obtained the perturbation expansion of the friction coefficient of the polymer chain in powers of the fluctuating  $\zeta_0$ . Since the critical dimension of this expansion is four, Oono and Kohmoto applied the renormalisation group to analyse the perturbation expansion in the vicinity of four dimensions. However, as a matter of fact, the  $\epsilon$  result for the diffusion coefficient in theta solvents obtained by Oono and Kohmoto does not go beyond the Kirkwood result. The extension of the calculations of Oono and Kohmoto up to second order in powers of the hydrodynamic interaction was recently carried out by Wang *et al* (1986).

However, the Kirkwood-Riseman formalism is an approximate treatment of the Kirkwood diffusion equation. The rigorous description has to be formulated using the

Green-Kubo formalism or, equivalently, has to start with the Einstein formula for the diffusion coefficient. The last formulations lead to expressions of the diffusion coefficient ( $D$ ) as a time correlation function (Fixman 1981, Ackcasu 1982). The calculation of the diffusion coefficient starting from the expression of  $D$  as a time correlation function was done by Stepanow (1984), Oono (1985) and quite recently by Wang and Freed (1986).

In the present paper we give the theory of the translational diffusion coefficient of a polymer chain in theta solvents on the basis of the path integral formulation of polymer dynamics (Stepanow 1984), which is assumed to be governed by the Kirkwood diffusion equation. The idea of the path integral formulation consists of the following. The Kirkwood diffusion equation is a Fokker-Planck equation, which is the differential equation for Markovian processes. The transition probability for these processes is, indeed, a path integral. The application of path integrals to the stochastic processes has been the subject of numerous articles in recent years.

We use the method of Langouche *et al* (1979) which closely follows the path integral formulation of the quantum field theory. Recently this method was used by Elderfield (1985) for kinetic growth models. The connection to the field theory originates from the formal analogy between the Schrödinger equation and the Fokker-Planck equation.

The path integral formulation of the Kirkwood diffusion equation is an efficient tool for deriving the perturbation expansion of the dynamical quantities of dilute polymer solutions. The starting point for the calculation of the translational diffusion coefficient is the well known Einstein formula. A different but equivalent way is the expression for the mobility of the polymer chain which is obtained using the linear response theory (Fixman 1981). The path integral method enables one to interpret in a rigorous manner the Einstein formula for  $D$  in terms of the perturbation expansion. To our knowledge this is done in the present paper for the first time. Here we extend the work of Stepanow (1984) to give a general representation of the perturbation expansion of the diffusion coefficient in powers of the  $\eta_1$  by means of diagrams. To achieve this we follow the standard method of obtaining perturbation series in the quantum field theory (for example, see Huang 1982). The representation of the whole perturbation expansion of  $D$  by means of diagrams is an advantage by which our method differs from that of Oono (1985) and Wang and Freed (1986). Furthermore, working with the generating functional, which plays a central role in the path integral method, enables one to consider the inelastic scattering function, the translational diffusion coefficient and the intrinsic viscosity in a unified way. The practical aim of this paper is the computation of the diffusion coefficient of a polymer chain in theta solvents up to second order in powers of the  $\eta_1$  and renormalisation of  $D$  to  $\epsilon^2$ .

The paper is organised as follows. Section 2 introduces the derivation of the perturbation expansion of  $D$ . Section 3 gives the solution of the Zimm model with pre-averaging  $\eta_1$  in  $d$  dimensions. Section 4 introduces the calculation of the two-loop contribution of the fluctuating  $\eta_1$  to  $D$ . Section 5 introduces the renormalisation group analysis of the diffusion coefficient. Section 6 contains the discussion.

## 2. Perturbation expansion

As a model we use the continuous model of the polymer chain by Edwards. Instead of the configuration of the chain  $\mathbf{r}(s)$  it is advisable to introduce its Fourier transform

$\xi_k$  defined as follows:

$$r(s) = \sum_{k=0}^{\infty} Q_{sk} \xi_k$$

$$Q_{s0} = L^{-1/2} \quad Q_{sk} = (2/L)^{1/2} \cos(\pi sk/L)$$

where  $L$  is the contour length of the chain. The Kirkwood diffusion equation for the transition probability density  $P(\xi, t; \xi^0, t^0)$  ( $\xi = \xi_0, \xi_1, \dots$ ) can be written in the form of a Schrödinger equation (Stepanow 1984)

$$i\partial P(t, t^0)/\partial t = H(\hat{p}, \xi)P(t, t^0). \tag{1}$$

The Hamilton operator

$$H(\hat{p}, \xi) = H_0(\hat{p}, \xi) + H_{int}(\hat{p}, \xi)$$

is given by

$$H_0(\hat{p}, \xi) = -D_0 \lambda_{(k)} \hat{p}_k \xi_k - iD_0 \hat{p}_k^2 \tag{2}$$

$$H_{int}(\hat{p}, \xi) = -i\hat{p}_k^\mu \hat{p}_n^\nu T_{kn}^{\mu\nu} - \hat{p}_k^\mu T_{kn}^{\mu\nu} \lambda_{(n)} \xi_n^\nu \tag{3}$$

where

$$\lambda_{(k)} = (d/l)(\pi k/L)^2 \quad D_0 = kTl/\zeta_0 \quad \hat{p}_k = -i\nabla_k \tag{4}$$

$$T_{kn}^{\mu\nu} = kT\eta^{-1} \int_q \int_0^L ds_1 \int_0^L ds_2 Q_{ks_1} T^{\mu\nu}(q) Q_{s_2n} \exp(iq\xi_m(Q_{s_1m} - Q_{s_2m}))$$

$\int_q = \int d^d q / (2\pi)^d$ ,  $\eta$  is the solvent viscosity,  $k$  is the Boltzmann constant,  $T$  is the temperature and  $\zeta_0$  is the monomer friction coefficient. The Fourier transform of the Oseen tensor  $T^{\mu\nu}(q)$  is given by

$$T^{\mu\nu}(q) = q^{-2}(\delta^{\mu\nu} - q^\mu q^\nu / q^2).$$

In (2)-(4) the Einstein sum convention is used. The excluded volume interaction is omitted in (2) and (3).

The path integral formulation of the Kirkwood diffusion equation is based on the following representation of the transition probability density for the infinitesimal time  $\Delta t$ :

$$P(\xi, t^0 + \Delta t; \xi^0, t^0) = \int_p \exp(i\mathbf{p}(\xi - \xi^0) - i\Delta t h(\mathbf{p}, \xi^0)) \tag{5}$$

where  $\mathbf{p}\xi$  is the abbreviation for  $\mathbf{p}_k \xi_k$  and  $\int_p$  means the integration over  $\mathbf{p}_0, \mathbf{p}_1, \dots$ .  $h(\mathbf{p}, \xi)$  is the classical Hamiltonian associated with the Hamilton operator  $H(\hat{p}, \xi)$ . For the finite time interval, we partition the time axis  $t^0 < t_1 < \dots < t_n = t$  and get

$$P(\xi, t; \xi^0, t^0) = \int d^d \xi_{n-1} \dots \int d^d \xi_1 P(\xi, t; \xi_{n-1}, t_{n-1}) \dots P(\xi_1, t_1; \xi^0, t^0). \tag{6}$$

Using (5) and (6) and taking the limit  $\Delta t = t_j - t_{j-1} \rightarrow 0$  we arrive at the path integral representation of the transition probability density (Stepanow 1984)

$$P(\xi, t; \xi^0, t^0) = \int D\mathbf{p} \int D\xi \exp\left(i \int_{t_0}^t dt [\mathbf{p}(t') \dot{\xi}(t') - h(\mathbf{p}(t'), \xi(t'))]\right) \times \delta(\xi - \xi(t)) \delta(\xi^0 - \xi(t_0)). \tag{7}$$

Following Langouche *et al* (1979), instead of  $P(t, t^0)$  we consider the generating functional  $Z(\mathbf{j}, \mathbf{j}^*)$  which is defined as follows:

$$Z(\mathbf{j}, \mathbf{j}^*) = \int D\mathbf{p} \int D\boldsymbol{\xi} \exp\left(iS(T, t^0) + i \int_{t_0}^T dt' \boldsymbol{\xi}_k(t') \mathbf{j}_k(t') + i \int_{t_0}^T \mathbf{p}_k(t') \mathbf{j}_k^*(t')\right) \delta(\boldsymbol{\xi}^0 - \boldsymbol{\xi}(t_0)). \tag{8}$$

The 'action'  $S(T, t^0)$  is the integral in the exponent of (7).  $T$  is an arbitrary time which must be large enough. The functional differentiation of  $Z$  with respect to the external sources  $\mathbf{j}$  and  $\mathbf{j}^*$  enables one to obtain different correlation functions. For example, the correlation function

$$\langle \xi_k^\mu(t_2) \xi_m^\nu(t_1) \rangle = \int d^d \boldsymbol{\xi}(t_2) \int d^d \boldsymbol{\xi}(t_1) \xi_k^\mu(t_2) P(t_2, t_1) \xi_m^\nu(t_1) P(t_1, t^0) \quad (t_2 > t_1)$$

can be expressed as a functional derivative of the generating functional as follows:

$$\langle \xi_k^\mu(t_2) \xi_m^\nu(t_1) \rangle = i^{-2} \delta^2 Z(\mathbf{j}, \mathbf{j}^* = 0) / \delta j_k^\mu(t_2) \delta j_m^\nu(t_1) |_{\mathbf{j}=0}.$$

The time correlation function

$$\langle \xi_k^\mu(t_2) \exp(i\mathbf{q}_2 \boldsymbol{\xi}_1(t_2)) \xi_m^\nu(t_1) \exp(i\mathbf{q}_1 \boldsymbol{\xi}_p(t_1)) \rangle$$

is expressed by  $Z$  as follows:

$$\langle \dots \rangle = i^{-2} \delta^2 Z(\mathbf{j}, \mathbf{j}^* = 0) / \delta j_k^\mu(t_2) \delta j_m^\nu(t_1) |_{j_n(t) = \mathbf{q}_2 \delta_{nk} \delta(t-t_2) + \mathbf{q}_1 \delta_{np} \delta(t-t_1)}.$$

The generating functional  $Z^0(\mathbf{j}, \mathbf{j}^*)$  associated with the Hamiltonian  $H_0$  (Rouse model) which was obtained by Stepanow (1984) is

$$Z^0(\mathbf{j}, \mathbf{j}^*) = \exp\left(i \boldsymbol{\xi}_k^0 \int_0^T dt' \mathbf{j}_k(t') D_{(k)}(t') - i \int_0^T dt' \int_0^T dt'' \mathbf{j}_k(t') D_{(k)}(t' - t'') \mathbf{j}_k^*(t'') - \frac{1}{2} \lambda_{(k)}^{-1} \int_0^T dt' \int_0^T dt'' \mathbf{j}_k(t') \Delta_{(k)}(t', t'') \mathbf{j}_k(t'')\right) \tag{9}$$

where

$$D_{(k)}(t) = \theta(t) \exp(-D_0 \lambda_{(k)} t)$$

$$\Delta_{(k)}(t, u) = D_{(k)}(t - u) + D_{(k)}(u - t) - D_{(k)}(t + u)$$

and  $\theta(t)$  is the step function.  $Z^0(\mathbf{j}, \mathbf{j}^*)$  given by (9) can be represented graphically as follows:

$$Z^0(\mathbf{j}, \mathbf{j}^*) = \exp\left(- \square \longrightarrow \bullet + \times \longrightarrow \bullet + \bullet \text{ wavy line } \bullet\right) \tag{9'}$$

where the black circle is associated with the source  $\mathbf{j}_k(t)$ , the cross with the source  $\mathbf{j}_k^*(t)$ , the square with  $\boldsymbol{\xi}_k^0$ , the full line (propagator) with  $-D_{(k)}(t' - t'')$  and the wavy line with  $-\lambda_{(k)}^{-1} \Delta_{(k)}(t', t'')$ . The time integrations are associated with the ends of lines. The symmetry numbers of the diagrams in (9') have to be taken into account. The symmetry number of the first two diagrams is one, whereas that of the third diagram

is two. The generating functional for a polymer chain with hydrodynamic interaction obtained by Stepanow (1984) can be represented graphically as follows:

$$Z(j, j^*) = \exp\left( \text{loop diagrams} \right) \times \exp\left( \text{propagator diagrams} \right) \quad (10)$$

where the arrows and the black circle in the first exponent are associated with  $-i\delta/\delta j_k^*(\tau)$  and  $\delta/\delta j_k(\tau)$ , respectively. They act on the cross and the black circles in the second exponent respectively. The loops in (10) are respectively associated with  $-iT_{kn}\lambda_{(n)}$  and  $iT_{kn}$ , where  $T_{kn}$  is given by (4) without the exponent. The second diagram in the first exponent of (10) has the symmetry number one. The time integration  $i \int_0^T d\tau$  is associated with each loop. To facilitate 'reading' the diagrams we will give below analytical expressions associated with some diagrams. Two diagrams in the first exponent of (10) are associated, respectively, with the following expressions:

$$i \int_0^T d\tau i^{-1}(\delta/\delta j_k^{*\mu}(\tau))(-i)T_{kn}^{\mu\nu}\lambda_{(n)}(\delta/\delta j_n^\nu(\tau))$$

$$i \int_0^T d\tau i^{-1}(\delta/\delta j_k^{*\mu}(\tau))iT_{kn}^{\mu\nu}i^{-1}(\delta/\delta j_n^\nu(\tau)).$$

The action of the first exponent in (10) on  $Z^0(j, j^*)$  produces the perturbation expansion of  $Z(j, j^*)$  in powers of the  $\text{HI}$  which can be represented by means of diagrams. The result of the action of the second loop of (10) on  $Z^0(j, j^*)$  is

$$Z(j, j^*) = \exp\left( \text{loop diagrams} \right) \times \exp\left( \text{propagator diagrams} \right). \quad (11)$$

As an example we give the analytical expression associated with the third diagram in the second exponent of (11):

$$\int_0^T dt' \int_0^T dt'' i \int_0^T d\tau j_k^\mu(t') D_{(k)}(t' - \tau) iT_{kn}^{\mu\nu} D_{(n)}(t'' - \tau) j_n^\nu(t'').$$

The action of the loop in the first exponent of (11) on the first three diagrams in the second exponent changes the propagator  $D_{(k)}(t)$  as follows:

$$\text{propagator diagrams} \rightarrow \text{propagator diagrams} + \text{loop diagrams} + \dots = \text{propagator diagrams}. \quad (12)$$

We note that the loop with two outgoing lines is associated with  $iT_{kn}$ , whereas the loop with an outgoing and an incoming line is associated with  $-iT_{kn}\lambda_{(n)}$ , where  $\lambda_{(n)}$

belongs to the incoming line. Equation (12) defines the effective propagator  $\mathcal{D}_{n,k}^{\mu\nu}(t)$ . It is easy to check that  $\mathcal{D}_{n,k}^{\mu\nu}(t'-t'')$  satisfies the following equation:

$$\text{---} \rightarrow \square \text{---} + \text{---} \circ \text{---} \quad (13)$$

which has the following analytical representation:

$$\mathcal{D}_{k,n}^{\mu\nu}(t_2-t_1) = \delta^{\mu\nu} \delta_{kn} D_{(n)}(t_2-t_1) - i \int_{t_1}^{t_2} d\tau D_{(n)}(\tau-t_1) (-i) \lambda_{(n)} T_{nm}^{\mu\sigma} \mathcal{D}_{k,m}^{\sigma\nu}(t_2-\tau). \quad (14)$$

The result of the action of the operators in the first exponent of (11) on the last diagram in the second exponent is

$$\text{---} \circ \text{---} + \text{---} \circ \text{---} + \text{---} \circ \text{---} \circ \text{---} \quad (15)$$

Taking into account (12) and (15) we obtain for  $Z(j, j^* = 0)$

$$Z(j) = \exp\left( -i \text{---} \square \text{---} + \text{---} \circ \text{---} + \text{---} \circ \text{---} \text{---} + \text{---} \circ \text{---} \text{---} \text{---} + \text{---} \circ \text{---} \text{---} \right) \sim \quad (16)$$

As an example we give the analytical expression associated with the third diagram in (16):

$$\int_0^T dt' i \int_0^T d\tau \int_0^T dt'' j_k^\mu(t') \mathcal{D}_{k,n}^{\mu\sigma}(t', \tau) (-i) T_{nm}^{\sigma\nu} \lambda_{(m)} \lambda_{(n)}^{-1} \Delta_{(m)}(\tau, t'') j_m^\nu(t'').$$

The symbol  $\sim$  in (16) means that the sources  $j_k(t)$  have to be modified step by step in the perturbation expansion as follows (Stepanow 1984):

(a) first order

$$j_k(t) \rightarrow j_k(t) + q_1(Q_{ks_1} - Q_{ks_2}) \delta(t - \tau_1)$$

(b) second order

$$j_k(t) \rightarrow j_k(t) + q_1(Q_{ks_1} - Q_{ks_2}) \delta(t - \tau_1) + q_2(Q_{ks_3} - Q_{ks_4}) \delta(t - \tau_2) \quad (17)$$

and so on.  $q_i, s_{2i-1}, s_{2i}$  and  $\tau_i$  are the variables associated with the  $i$ th loop. Representing the wavy line in (16) in the graphic form

$$\text{---} \circ \text{---} = \text{---} \leftarrow + \text{---} \rightarrow + \text{---} \leftarrow \rightarrow$$

instead of (16) we arrive at

$$Z(j) = \exp\left( -i \text{---} \square \text{---} + \text{---} \leftarrow + \text{---} \rightarrow + \text{---} \leftarrow \rightarrow + \text{---} \circ \text{---} \right) \sim \quad (18)$$

The third diagram in the exponent of (18) is associated with the following expression:

$$\frac{1}{2} \int_0^T dt' \int_0^T dt'' j_k^\mu(t') \mathcal{D}_{k,n}^{\mu\sigma}(t', 0) \lambda_{(n)}^{-1} \mathcal{D}_{m,n}^{\nu\sigma}(t'', 0) j_m^\nu(t'').$$

Performing the average over the  $\xi_k^0$  ( $k = 1, \dots$ ) according to the formula

$$Z(j)_a = \int d^d \xi Z(j) \exp\left( -\frac{1}{2} \sum_{k=1}^{\infty} \lambda_{(k)} (\xi_k^0)^2 \right) \left[ \int d^d \xi \exp\left( -\frac{1}{2} \sum_{k=1}^{\infty} \lambda_{(k)} (\xi_k^0)^2 \right) \right]^{-1}$$

we get

$$Z(j)_a = \exp\left( \text{---} \leftarrow \rightarrow + \text{---} \text{---} + \text{---} \circ \text{---} \right) \sim \quad (19)$$







Using (28) one gets for  $D_p$

$$D_p = L^{-1}(H_{00} - (H(\Lambda H)^{-1}\Lambda H)_{00}). \tag{29}$$

The matrix  $H_{kn}$  is defined as follows:

$$H_{kn} = D_0(\delta_{kn} + ht_{kn})$$

where  $h = (\zeta_0/\eta)(d-1)(d/2\pi l)^{d/2}/d^2(d-2)$  and

$$t_{kn} = \int_0^L ds_1 \int_0^L ds_2 Q_{ks_1}|s_1 - s_2|^{-1+\epsilon/2} Q_{s_2n}.$$

It can be shown that (29) coincides with the Zimm formula

$$D_p = L^{-1}/H_{00}^{-1}. \tag{30}$$

Thus we have shown that by using the pre-averaging approximation our perturbation expansion for  $D$  reduces to the Zimm expression of the diffusion coefficient, which was obtained by the exact solution of the Kirkwood diffusion equation (Zimm 1956).

Now we compute  $D_p$ , which is given by (30), in  $d$  dimensions. First we introduce the function  $l(s)$  as follows:

$$H_{mn}^{-1} = \int_0^L ds_1 \int_0^L ds_2 Q_{ms_2} l(s_2 - s_1) Q_{s_1n}.$$

The requirement that  $H_{mn}^{-1}$  is the inverse of  $H$  leads to the following equation for  $l$ :

$$l(s_2 - s_1) + h \int_0^L ds_3 l(s_2 - s_3)|s_3 - s_1|^{-1+\epsilon/2} = \delta(s_2 - s_1). \tag{31}$$

It is convenient to introduce the function

$$\varphi(s_1) = \int_0^L ds_2 l(s_2 - s_1).$$

Then, from (31) we obtain

$$\varphi(x) + h \int_0^L dy |x - y|^{-1+\epsilon/2} \varphi(y) = 1. \tag{32}$$

The last equation can be rewritten in the symmetrical form as follows:

$$\tilde{\varphi}(t) + hL^{\epsilon/2}2^{-\epsilon/2} \int_{-1}^1 du |t - u|^{-1+\epsilon/2} \tilde{\varphi}(u) = 1. \tag{33}$$

In the asymptotic region  $L \rightarrow \infty$  (33) gives

$$\int_{-1}^1 du |t - u|^{-1+\epsilon/2} \tilde{\varphi}(u) = (2/L)^{\epsilon/2}/h. \tag{34}$$

The last equation can be solved by means of the method of Lata (Cochran 1972, see also Fixman 1981). The solution is

$$\tilde{\varphi}(x) = h^{-1}(2/L)^{\epsilon/2}\Gamma^{-1}(\epsilon/4)\Gamma^{-1}(d/4)(1-x^2)^{-\epsilon/4} \tag{35}$$

where  $\Gamma(x)$  is the gamma function. Using  $\tilde{\varphi}(x)$  we can compute  $H_{00}^{-1}$ :

$$H_{00}^{-1} = \frac{1}{2} \int_{-1}^1 dt \tilde{\varphi}(t)$$

and in accordance with (30) the diffusion coefficient  $D_p$ . The result is

$$D_p = (kT/\zeta_0 N)[(d-1)/d](2/\varepsilon)2^{-\varepsilon/2}\Gamma(1+\varepsilon/4)\Gamma((6-\varepsilon)/4)/(\Gamma(\frac{3}{2})(1-\varepsilon/2))\xi_0 L^{\varepsilon/2} \tag{36}$$

where  $\xi_0 = (d/2\pi l)^{d/2}\zeta_0/\eta d$  is introduced. In three dimensions (36) yields

$$D_p = \frac{kT}{\zeta_0 N} \frac{8}{3\sqrt{2}} \frac{\Gamma^2(\frac{5}{4})}{\Gamma(\frac{3}{2})} \xi_0 L^{1/2}. \tag{37}$$

Equation (37) was first obtained by Auer and Gardner (1955) by solving the integral equation (34), using the Gegenbauer polynomials. Recently (37) was rederived by Fixman (1981) using the Lata method of solving the integral equation (34). Expanding (36) in the vicinity of four dimensions one gets

$$D_p = \frac{kT}{\zeta_0 N} \left( \frac{3}{2\varepsilon} \xi_0 L^{\varepsilon/2} - \frac{1}{8} \xi_0 L^{\varepsilon/2} + \dots \right). \tag{38}$$

To first order in  $\varepsilon$  the expression of the diffusion coefficient obtained by the summation of the pre-averaged perturbation expansion (36) coincides with the Kirkwood formula for  $D$  (see (40)).

**4. Perturbative calculation of the diffusion coefficient**

The exact formula for the diffusion coefficient in theta solvents is given by (23). This formula gives the perturbation expansion of  $D$  in powers of the fluctuating  $\eta_1$ . The diffusion coefficient to second order in the  $\eta_1$  is given by (24). The contributions of different orders to  $D$  can be represented as follows:

$$D = kT/\zeta_0 N + D_1 + D_2 + \dots$$

$D_1$  is the first-order contribution to  $D$  which is associated with the first diagram in (24)

$$D_1 = (kT/\zeta_0 N)[(d-1)/d]\xi_0 L^{-1} \int_0^L ds_2 \int_0^L ds_1 \int d^d q q^{-2} \exp(-q^2|s_2-s_1|). \tag{39}$$

Computing the integrals in (39) gives

$$N\zeta_0 D_1/kT = [(d-1)/d][1/(1-\varepsilon^2/4)](2/\varepsilon)w_0 \tag{40}$$

where  $w_0 = \xi_0 L^{\varepsilon/2}$  is the dimensionless expansion parameter of the hydrodynamic interaction. Equation (40) can be represented as follows:

$$N\zeta_0 D_1/kT = \frac{3}{2\varepsilon} w_0 + k(\varepsilon)w_0$$

where  $k(\varepsilon)$  is given by

$$k(\varepsilon) = (-1+3\varepsilon-3\varepsilon^2/4)[8(1-\varepsilon/4)(1-\varepsilon^2/4)]^{-1}. \tag{40'}$$

The first two-loop diagram in (24) is associated with the following expression:

$$(kT/\zeta_0 N)\xi_0^2 I_3/2d\pi^d$$

where  $I_3$  is given by

$$I_3 = \int d^d q_1 \int d^d q_2 \int_0^L ds_1 \int_0^L ds_2 \int_0^L ds_3 \int_0^L ds_4 \int_0^x d\tau [(q_1 q_2)^3/q_1^4 q_2^4 - q_1 q_2/q_1^2 q_2^2] \times Q_{s_2 n}(Q_{s_3 n} - Q_{s_4 n})D_{(n)}(\tau)Q_{s_4 m}(Q_{s_1 m} - Q_{s_2 m})D_{(m)}(\tau)Z^0(\tau) \tag{41}$$

where

$$Z^0(\tau) = \exp(-q_1^2 |s_2 - s_1| - q_2^2 |s_4 - s_3| - \mathbf{q}_1 \mathbf{q}_2 t_{12}(\tau)) \tag{42}$$

is obtained from the generating functional of the Rouse model with sources fixed in accordance with (17). The function  $t_{12}(\tau)$  in (42) is given by

$$t_{12}(\tau) = \frac{2d}{l} \sum_{m=1}^{\infty} \lambda_{(m)}^{-1} D_{(m)}(\tau) (Q_{s_1 m} - Q_{s_2 m})(Q_{s_3 m} - Q_{s_4 m}) \tag{43}$$

$$t_{12}(0) = 2(\max(s_1, s_4) - \max(s_1, s_3) + \max(s_2, s_3) - \max(s_2, s_4)). \tag{44}$$

Introduction of the variable transformations

$$\mathbf{q}'_1 = \mathbf{q}_1 (|s_2 - s_1|)^{1/2} \quad \mathbf{q}'_2 = \mathbf{q}_2 (|s_4 - s_3|)^{1/2}$$

converts (41) to

$$I_3 = \int_0^{\infty} d\tau \int_0^L ds_1 \int_0^L ds_2 \int_0^L ds_3 \int_0^L ds_4 Q_{s_2 n} (Q_{s_3 n} - Q_{s_4 n}) D_{(n)}(\tau) Q_{s_4 m} (Q_{s_1 m} - Q_{s_2 m}) \\ \times D_{(m)}(\tau) (|s_2 - s_1| |s_4 - s_3|)^{-3/2 + \epsilon/2} f(t_{12}(\tau) / (|s_2 - s_1| |s_4 - s_3|)^{1/2}) \tag{45}$$

where  $f$  is given by

$$f = \int d^d \mathbf{q}_1 \int d^d \mathbf{q}_2 [(q_1 q_2)^3 / q_1^4 q_2^4 - q_1 q_2 / q_1^2 q_2^2] \\ \times \exp[-q_1^2 - q_2^2 - \mathbf{q}_1 \mathbf{q}_2 t_{12}(\tau) / (|s_2 - s_1| |s_4 - s_3|)^{1/2}].$$

It is important to ascertain if (45) possesses the  $1/\epsilon$  singularities, which are substantial for the renormalisation group analysis of the perturbation series of the diffusion coefficient. To check if  $I_3$  has the  $1/\epsilon$  poles we proceed as follows. For  $\tau > 0$  the function  $t_{12}(\tau)$  defined by (43) transforms as the product of  $s_2 - s_1$  and  $s_4 - s_3$  in the limit that these differences are small. When  $\tau = 0$ , then in dependence on the order of  $s_1, \dots, s_4$ ,  $t_{12}(0)$  is zero or transforms as the first power of one of the differences  $s_i - s_j$ . This is the consequence of the non-uniform convergence of the sum in (43) for  $\tau \geq 0$ . When  $\tau > 0$ , the function  $f$  in (45) transforms as  $(|s_2 - s_1| |s_4 - s_3|)^{1/2}$  for small  $s_2 - s_1$  and  $s_4 - s_3$ .

In order to show that the contribution to the integral in (45) from the small differences  $s_2 - s_1$  and  $s_4 - s_3$  does not cause the  $1/\epsilon$  singularities, we omit  $f$  in (45). Then we can perform the integration over  $\tau$ . Afterwards we consider the sum over the modes in (45), which we denote by  $i(s_1, \dots, s_4)$ . In the limit  $s_2 - s_1 \rightarrow 0$  and  $s_4 - s_3 \rightarrow 0$ ,  $i(\dots) / [(s_2 - s_1)(s_4 - s_3)]$  is proportional to

$$\sum_{n=1}^{\infty} n \cos(\pi n s_1 / L) \sum_{m=1}^{\infty} [m / (m^2 + n^2)] \cos(\pi m s_3 / L).$$

Because the integral sum behaves as  $n^{-2}$  for large  $n$ , the above expression is finite when  $s_1 \neq 0$  and  $s_3 \neq 0$ . It can be shown that the integrals over  $s_1$  and  $s_3$  converge at small  $s_1$  and  $s_3$ . Therefore, in the integral over  $s_1, \dots, s_4$  the differences  $s_2 - s_1$  and  $s_4 - s_3$  have the power  $-\frac{1}{2} + \epsilon/2$ . Thus, the  $s$  integration in (45) is finite in four dimensions, and consequently (45) is free of  $1/\epsilon$  poles in  $d$  dimensions.

The contribution to  $D$  of the second two-loop diagram in (24) is

$$-(1/dL^2)(2d/l)^{d-2}(2\pi)^{-2d} \int d^d \mathbf{q}_1 \int d^d \mathbf{q}_2 \int_0^L ds_1 \int_0^L ds_2 \int_0^L ds_3 \int_0^L ds_4 \int_0^{\infty} d\tau (kT/\eta)^2 \\ \times T^{\mu\nu}(\mathbf{q}_1) Q_{s_2 n} \lambda_{(n)} D_{(n)}(\tau) T^{\mu\nu}(\mathbf{q}_2) Q_{s_4 n} Z^0(\tau). \tag{46}$$

In order to transform (46) we look at the time integral

$$\int_0^x d\tau \lambda_{(n)} D_{(n)}(\tau) \exp[-\mathbf{q}_1 \mathbf{q}_2 t_{12}(\tau)].$$

Integrating it by parts we obtain

$$D_0^{-1} \exp(-\mathbf{q}_1 \mathbf{q}_2 t_{12}(0)) (\delta(s_2 - s_4) - 1/L) + \mathbf{q}_1 \mathbf{q}_2 D_0^{-1} 2d l^{-1} \int_0^x d\tau \sum_{m=1}^{\infty} D_{(m)}(\tau) (Q_{s_1 m} - Q_{s_2 m}) (Q_{s_3 m} - Q_{s_4 m}).$$

Then, the contribution to  $D$  of the second two-loop diagram in (24) can be represented as follows:

$$-(kT/\zeta_0 N) \xi_0^2 \pi^{-d} L^{-1} (I_1 + 2I_2)/4d \tag{47}$$

where

$$I_1 = \int d^d \mathbf{q}_1 \int d^d \mathbf{q}_2 [d - 2 + (\mathbf{q}_1 \mathbf{q}_2)^2 / q_1^2 q_2^2] / q_1^2 q_2^2 \int_0^L ds_1 \int_0^L ds_2 \int_0^L ds_3 \int_0^L ds_4 \times \exp(-q_1^2 |s_2 - s_1| - q_2^2 |s_4 - s_3| - \mathbf{q}_1 \mathbf{q}_2 t_{12}(0)) (\delta(s_2 - s_4) - 1/L) \tag{48}$$

$$I_2 = \int_0^x d\tau \int_0^L ds_1 \int_0^L ds_2 \int_0^L ds_3 \int_0^L ds_4 (|s_2 - s_1| |s_4 - s_3|)^{-3/2+\epsilon/2} \times \sum_{n=1}^{\infty} Q_{s_2 n} Q_{s_4 n} D_{(n)}(\tau) \sum_{m=1}^{\infty} D_{(m)}(\tau) (Q_{s_1 m} - Q_{s_2 m}) (Q_{s_3 m} - Q_{s_4 m}) \times g(t_{12}(\tau) / (|s_2 - s_1| |s_4 - s_3|)^{1/2}). \tag{49}$$

The function  $g$  in (49) is defined by

$$g = \int d^d \mathbf{q}_1 \int d^d \mathbf{q}_2 [(d - 2) \mathbf{q}_1 \mathbf{q}_2 + (\mathbf{q}_1 \mathbf{q}_2)^3 / q_1^2 q_2^2] / q_1^2 q_2^2 \times \exp[-q_1^2 - q_2^2 - \mathbf{q}_1 \mathbf{q}_2 t_{12}(\tau) / (|s_2 - s_1| |s_4 - s_3|)^{1/2}].$$

For the same reason as for the integral  $I_3$  we conclude that  $I_2$  does not contain the  $1/\epsilon$  poles. The complete two-loop contribution to the diffusion coefficient is given by

$$D_2 = -(kT/\zeta_0 N) \xi_0^2 L^{-1} \pi^{-d} (I_1/4d + (I_2 - I_3)/2d). \tag{50}$$

We note that that  $I_1$ ,  $I_2$  and  $I_3$  given by (48), (49) and (45), respectively, are derived without using the pre-averaging approximation. We have checked that the Kirkwood-Riseman formalism gives another expression for  $D_2$ .

The term  $\mathbf{q}_1 \mathbf{q}_2 t_{12}(0)$  in the exponent of (48) and the terms  $\mathbf{q}_1 \mathbf{q}_2 t_{12}(\tau)$  in the exponents of the expressions defining  $g$  and  $f$  result from the modification of the sources. As was pointed out at the beginning of § 3, the sources  $j_m(t)$  must not be modified by using the pre-averaging approximation. As a result, by using the pre-averaging approximation, the terms  $\mathbf{q}_1 \mathbf{q}_2 t_{12}(0)$  and  $\mathbf{q}_1 \mathbf{q}_2 t_{12}(\tau)$  do not appear. Then, in this case  $I_2$  and  $I_3$  become zero and  $I_1$  can be computed exactly. The result is

$$\pi^{-d} I_1^p = L^{1+\epsilon} (32/\epsilon^2) (d - 1)^2 / [d(d - 2)^2] \times [\Gamma^2(1 - \epsilon/2) / \Gamma(2 + \epsilon) + 1/(1 + \epsilon) - 2/(1 + \epsilon/2)^2] \tag{51}$$

where the superscript p denotes pre-averaging. We note that  $I_1^p$  has a finite limit in four dimensions, i.e. it does not contain  $1/\epsilon$  poles. To second order in  $w_0$  the diffusion coefficient with pre-averaged hydrodynamic interaction is given by

$$D_p = (kT/\zeta_0 N)(1 + \frac{16}{9}w_0 - 0.0135w_0^2 + \dots) \quad (d = 3). \tag{52}$$

We computed  $I_1$  and  $I_2 - I_3$  numerically in three dimensions without using the pre-averaging approximation. The result for the diffusion coefficient in three dimensions up to second order in powers of the fluctuating  $\mathbf{H}_1$  is

$$D = (kT/\zeta_0 N)(1 + \frac{16}{9}w_0 - 0.14w_0^2 + \dots). \tag{53}$$

Comparing (52) with (53) we see that the fluctuating  $\mathbf{H}_1$  drastically changes the two-order contribution to  $D$ .

Next, we start computing the  $1/\epsilon$  poles of  $I_1$ . It is convenient to use the representation of  $I_1$  by means of diagrams

$$I_1 = 2 \left( \text{diagram } j_1 + \text{diagram } j_2 + \text{diagram } j_3 \right) - \frac{8}{L} \left( \text{diagram } j_4 + \text{diagram } j_5 + \text{diagram } j_6 \right). \tag{54}$$

For example,  $j_4$  is associated with the following expression:

$$j_4 = \int d^d \mathbf{q}_1 \int d^d \mathbf{q}_2 [(d-2)/q_1^2 q_2^2 + (\mathbf{q}_1 \mathbf{q}_2)^2 / q_1^4 q_2^4] \int_0^L ds_4 \int_0^{s_4} ds_2 \int_0^{s_2} ds_1 \int_0^{s_1} ds_3 \\ \times \exp[-(s_4 - s_2)q_2^2 - (s_2 - s_1)(\mathbf{q}_1 + \mathbf{q}_2)^2 - (s_1 - s_3)q_2^2] \tag{55}$$

and analogously for other diagrams. To select the  $1/\epsilon$  poles of  $j_i$  we proceed as follows. First we carry out the Laplace transform of  $j_i$ :

$$j_i(m) = \int_0^\infty dL \exp(-mL) j_i.$$

For example,  $j_4(m)$  is given by

$$j_4(m) = m^{-2} \int d^d \mathbf{q}_2 \frac{1}{q_2^2 (q_2^2 + m)^2} \int d^d \mathbf{q}_1 \frac{d-2 + (\mathbf{q}_1 \mathbf{q}_2)^2 / q_1^2 q_2^2}{q_1^2 [(\mathbf{q}_1 + \mathbf{q}_2)^2 + m]}. \tag{56}$$

The  $1/\epsilon$  pole of  $j_4(m)$ , which we are searching for, is connected with the ultraviolet logarithmic divergence of the integral over  $q_1$  in four dimensions. At large  $q_1$  the integral over  $q_1$  behaves like  $\int dq_1/q_1$ , i.e. its ultraviolet behaviour does not depend on  $q_2$  and  $m$ . If we put both  $q_2$  and  $m$  to zero in the propagator  $1/[(\mathbf{q}_1 + \mathbf{q}_2)^2 + m]$  the integral would diverge at the lower limit. In order to compute the  $1/\epsilon$  pole of the integral it is convenient to put  $m$  equal to zero in the propagator. This method of computing  $1/\epsilon$  poles is a special case of the general method proposed by Vladimirov (1980) with which the singularities of the four-loop diagrams in the field theory were calculated. The integral over  $q_1$  in (56) can be computed by means of the formulae (A2) and (A3) of the appendix. The integral over  $q_2$  is computed by means of (A1). In the vicinity of four dimensions  $j_4(m)$  is obtained as

$$j_4(m) = \pi^d m^{-3-\epsilon} 18/4\epsilon + \dots \tag{57}$$

Carrying out the inverse Laplace transform of (57) we obtain

$$j_4 \approx \pi^d (9/4\epsilon) L^{2+\epsilon} + \dots \tag{58}$$

In an analogous way one can check that  $j_\varepsilon$  does not contain the singularity at  $\varepsilon = 0$ , whereas for  $j_6$  one gets

$$j_6 = \pi^d L^{2+\varepsilon} \left( \frac{9}{2\varepsilon^2} - \frac{33}{8\varepsilon} \right) + O(\varepsilon^0). \tag{59}$$

In order to compute  $j_1 + j_2 + j_3$  we transform it as follows:

$$j_1 + j_2 + j_3 = 2j_1 + j_2 + j_3 - j_1.$$

The computing of  $j_1$  is similar to that of  $j_6$ . Keeping only the singular terms we get

$$j_1 = \pi^d L^{1+\varepsilon} \left( \frac{9}{\varepsilon^2} - \frac{15}{4\varepsilon} \right) + O(\varepsilon^0). \tag{60}$$

With the same precision as above from (59) and (60) it follows that

$$j_6 = \frac{1}{2}j_1 - j_4. \tag{61}$$

After an elementary transformation we get for  $j_2(m) + j_3(m) - j_1(m)$ :

$$m^{-2} \int d^d \mathbf{q}_1 \int d^d \mathbf{q}_2 \frac{-2\mathbf{q}_1 \mathbf{q}_2 + m}{(q_1^2 + m)(q_2^2 + m)[(\mathbf{q}_1 + \mathbf{q}_2)^2 + m]} \times [d - 2 + (\mathbf{q}_1 \mathbf{q}_2)^2 / q_1^2 q_2^2] / q_1^2 q_2^2. \tag{62}$$

To compute the  $1/\varepsilon$  pole all masses in (62) are put to zero, with the exception of the mass in the propagator  $1/(q^2 + m)$  and in the prefactor. Then, the computation of the integrals in (62) can be carried out by means of the formulae (A3), (A5) and (A1). The result is

$$j_2 + j_3 - j_1 = \pi^d L^{1+\varepsilon} \frac{21}{4\varepsilon} + O(\varepsilon^0). \tag{63}$$

Taking into account (54), (61) and (63) we get

$$I_1 = \pi^d L^{1+\varepsilon} \frac{21}{2\varepsilon} + O(\varepsilon^0).$$

The contribution to the diffusion coefficient is obtained as

$$D_2 = -(kT/\zeta_0 N) w_0^2 \frac{21}{32\varepsilon} + O(\varepsilon^0). \tag{64}$$

We also calculated  $D_2$  using the Kirkwood-Riseman formalism. Although our perturbation expansion gives an expression for  $D_2$ , which differs from that of the Kirkwood-Riseman formalism, the  $1/\varepsilon$  pole of  $D_2$  is the same and is given by (64).  $D_2$  was also independently computed by Wang *et al* (1986) using the Kirkwood-Riseman formalism. Their result coincides with (64).

While we prepared the revised version of this paper the article by Wang and Freed (1986) was published. These authors studied the translational diffusion coefficient of a polymer chain in theta solvents starting with the formula for  $D$  which was derived by Fixman (1981) by use of the linear response theory. In our notation this formula for  $D$  is (continuous chain, theta solvents)

$$D = \frac{1}{dL} (H_{00}^{\mu\mu})_a - \frac{1}{dL} \int_0^\infty dt \langle T_{0n}^{\mu\sigma}(t) \lambda_{(n)} \xi_n^\sigma(t) \lambda_{(m)} \xi_m^\beta(0) T_{m0}^{\beta\mu}(0) \rangle_a. \tag{65}$$

The second term in (65) contains the perturbation expansion in powers of the  $\eta_1$  in a closed form. We checked that (65) is equivalent to (23), which was obtained starting from the Einstein formula for  $D$ . Contrary to our result (64), Wang and Freed found that  $D_2$  ( $D^{(1)}$  in their notations) does not contain the  $1/\epsilon$  pole. They did not explicitly compute  $D^{(1)}$  but checked that the quantity  $\langle B_\nu | \psi_{\beta(n)} \rangle$  (see Wang and Freed 1986) is regular in four dimensions ( $\epsilon = 0$ ). Because  $D^{(1)}$  is quadratical in  $\langle B_\nu | \psi_{\beta(n)} \rangle$  the regularity of this quantity only means that  $D^{(1)}$  (in agreement with our result (64)) does not contain a  $1/\epsilon^2$  pole. But the regularity of  $\langle B_\nu | \psi_{\beta(n)} \rangle$  does not eliminate the possibility of the existence of the  $1/\epsilon$  pole of  $D^{(1)}$ . The latter can appear by the 'interference' of both terms  $\langle B_\nu | \psi_{\beta(n)} \rangle$  in  $D^{(1)}$  which is caused by the summation on  $n$ .

**5. Renormalised perturbation calculation**

In the vicinity of four dimensions the diffusion coefficient is obtained as

$$D = (kT/\zeta_0 N) \left( 1 + \frac{3}{2\epsilon} w_0 + k(\epsilon) w_0 - \frac{21}{32\epsilon} w_0^2 + O(w_0^3) \right). \tag{66}$$

The goal of the regularisation is to remove the  $1/\epsilon$  singularities from the perturbation series by the redefinition of the parameter of the theory. Following Oono and Kohmoto (1983) we assume that  $1/\epsilon$  singularities renormalise the friction constant  $\zeta_0$ . To first order of  $\zeta_0$  equation (66) gives

$$\xi = \xi_0 \left( 1 - \frac{3}{2\epsilon} \xi_0 L^{\epsilon/2} + \dots \right)$$

where  $\xi = (d/2\pi l)^{d/2} \zeta / \eta d$ . The regular part of the first-order contribution to  $D$  does not depend on  $\zeta_0$  and on that account it will not be renormalised. Then, the two-loop singularity in (66) renormalises  $\zeta_0$  in the prefactor

$$\xi = \xi_0 \left( 1 - \frac{3}{2\epsilon} \xi_0 L^{\epsilon/2} + \frac{21}{32\epsilon} (\xi_0 L^{\epsilon/2})^2 + \dots \right). \tag{67}$$

Equation (67) diverges if  $\epsilon$  tends to zero. To make it finite at  $\epsilon = 0$  we modify (67) as follows:

$$\xi = \xi_0 [ 1 - \frac{3}{2} \xi_0 (L^{\epsilon/2} - \Lambda^{-\epsilon}) / \epsilon + \frac{21}{32} \xi_0^2 (L^\epsilon - \Lambda^{-2\epsilon}) / \epsilon + \dots ].$$

$\Lambda$  can be interpreted as a cutoff which cuts the integrals over 'momenta' at the upper limit. To introduce the renormalisation group we carry out the regularisation step by step:

$$\Lambda \rightarrow \Lambda_1 \rightarrow \dots \rightarrow \Lambda_{\min} \equiv L^{-1/2}.$$

The renormalisation of  $\xi$  at the step  $\Lambda_1 \rightarrow \Lambda_2$  is given by

$$\xi_2 = \xi_1 [ 1 - \frac{3}{2} \xi_1 (\Lambda_2^{-\epsilon} - \Lambda_1^{-\epsilon}) / \epsilon + \frac{21}{32} \xi_1^2 (\Lambda_2^{-2\epsilon} - \Lambda_1^{-2\epsilon}) / \epsilon ]. \tag{68}$$

Differentiating (68) with respect to  $\Lambda_2$  and putting  $\Lambda_2 = \Lambda_1 = \Lambda' = \Lambda/t$  we obtain, after the introduction of the dimensionless interaction constant  $w = \xi \Lambda^{1-\epsilon}$ ,

$$t \partial w / \partial t = \epsilon w - \frac{3}{2} w^2 + \frac{21}{16} w^3 \equiv \beta(w). \tag{69}$$



For small  $\varepsilon$  the Gell-Mann-Low function  $\beta(w)$ , in addition to the root at  $w=0$ , has a root at

$$w^* = \frac{2}{3}\varepsilon(1 + \frac{7}{12}\varepsilon). \quad (70)$$

This result coincides with that obtained by Wang *et al* (1986) after an appropriate redefinition of the interaction constant. For large  $L$  the interaction constant  $w$  tends to its fixed point  $w^*$ , the effective friction coefficient  $\xi$  scales as  $w^*L^{-\varepsilon/2}$ . The renormalised perturbation expansion of the diffusion coefficient is obtained as

$$D = (kT/\eta N)(d/2\pi l)^{d/2}d^{-1}L^{\varepsilon/2}(1 + k(\varepsilon)w^*)/w^* \quad (71)$$

where  $k(\varepsilon)$  is given by (40'). The friction coefficient of the polymer chain  $f$  is obtained from (71) by using the Einstein relation  $f = kT/D$ . The renormalisation group predicts that  $f$  is independent on the monomer friction coefficient  $\zeta_0$ . Because  $w^*$  is proportional to  $\varepsilon$ , the expansion parameter of the renormalised perturbation expansion of the friction coefficient becomes small in the vicinity of four dimensions. The common use of the renormalised perturbation expansion consists in expanding  $f$  or  $D$  in powers of  $\varepsilon$  ( $\varepsilon$  expansion). The transition to three dimensions is carried out by putting  $\varepsilon = 1$  in the  $\varepsilon$  expansion. With the aid of (71), we get for the friction coefficient to order  $\varepsilon^2$

$$f = \eta NL^{-\varepsilon/2}(2\pi l/d)^{d/2}d^{\frac{2}{3}}\varepsilon(1 + \frac{2}{3}\varepsilon). \quad (72)$$

In three dimensions the hydrodynamic radius of the polymer chain is defined by

$$R_H = kT/6\pi\eta D.$$

Next we consider the dimensionless ratio  $\rho = R_G/R_H$  of the gyration radius  $R_G = (Ll/6)^{1/2}$  to the hydrodynamic radius. Using (72) in three dimensions we obtain for  $1/\rho$

$$1/\rho = \frac{4}{3}\pi^{1/2}\varepsilon(1 + \frac{2}{3}\varepsilon). \quad (73)$$

However, according to Marqusee and Deutch (1981) the hydrodynamic radius in  $d$  dimensions is defined by

$$R_H^{d-2} = kT/6\pi\eta D. \quad (74)$$

On that account (73) is defined in three dimensions only. To define  $\rho$  in  $d$  dimensions we have to use (74) with the consequence that the  $\varepsilon$  expansion of  $1/\rho$  will be non-analytic in  $\varepsilon$ . To avoid this shortcoming we proceed as follows. In  $d$  dimensions, instead of  $\rho$  we introduce the ratio  $\rho_d = (R_G/R_H)^{d-2}$ , which coincides with  $\rho$  in three dimensions. The  $\varepsilon$  expansion of  $1/\rho_d$  is obtained as

$$1/\rho_d = 6^{-\varepsilon/2}\pi^{-1}d(2\pi/d)^{d/2}\frac{2}{3}\varepsilon(1 + \frac{2}{3}\varepsilon). \quad (75)$$

We see that in three dimensions (75) coincides with (73). In three dimensions (75) gives  $\rho = 0.76$ . This value is considerably smaller than the experimental value  $\rho_e = 1.28$  reported by Schmidt and Burchard (1981). If, instead of (75) we use the  $\varepsilon$  expansion of  $\rho_d$ , we will obtain the worse value  $\rho = 0.42$ . It is noted that the value of  $\rho$  to order  $\varepsilon$  ( $\rho = 9/4\pi^{1/2}\varepsilon$ ) gives the best agreement with experiment. Apparently, the summation of the  $\varepsilon$  series, which has been successful in the physics of the critical phenomena and in the equilibrium excluded-volume problem, has to be performed to make a more accurate prediction of the effect of the fluctuating  $H_1$  on the diffusion coefficient. The

next terms in the  $\varepsilon$  expansion of  $1/\rho_d$ , which are necessary for performing the summation of the  $\varepsilon$  series, can be computed using the perturbation expansion (23).

## 6. Discussion

In the present paper we have extended the path integral formulation of polymer dynamics, which was earlier developed by one of the authors, to derive the perturbation expansion of the translational diffusion coefficient of a polymer chain in dilute solutions in powers of the hydrodynamic interaction. Our method of deriving the perturbation expansion is analogous to that used in quantum field theory. The diagram representation of the perturbation expansion, which has been obtained in the present paper, is of great importance for the analysis of the general properties of perturbation series, such as renormalisability and for performing higher-order calculations of the diffusion coefficient.

To first order of the hydrodynamic interaction, our perturbation expansion coincides with that of Oono and Kohmoto (1983) which was obtained by the iterative solution of the Kirkwood-Riseman scheme. Jagannathan *et al* (1985) also showed that the correct Green-Kubo formalism and the Kirkwood-Riseman theory to first order of the  $\eta_1$  both give the same result for  $D$ . To second order of the  $\eta_1$ , the field theoretic perturbation expansion deviates from that of Oono and Kohmoto. Nevertheless, the  $1/\varepsilon$  poles of the two-order correction to the diffusion coefficient coincide in both approaches. Consequently, the friction coefficient of the polymer chain to  $\varepsilon^2$  also coincides in both theories. This result is at variance with the result obtained by Wang and Freed (1986). In our opinion their arguments do not prove the absence of the  $1/\varepsilon$  pole in the two-order contribution of the hydrodynamic interaction to the diffusion coefficient.

The perturbation expansion of  $D$  derived in the present paper has been summed within the pre-averaging approximation to give the Zimm formula for  $D$ . Here, we have computed the diffusion coefficient given by the Zimm formula in  $d$  dimensions. To first order in  $\varepsilon$  the whole perturbation expansion (Zimm formula) coincides with its first-order term, giving the Kirkwood formula for  $D$ . In three dimensions the deviation between the Zimm formula and the Kirkwood formula amounts to 2%.

The present work elucidates the question of the quality of the pre-averaging approximation. The consequence of pre-averaging is that the perturbation expansion of  $D$  does not contain  $1/\varepsilon$  singularities, with the exception of the first-order term. The  $1/\varepsilon$  pole of the two-loop contribution to  $D$ , which does not appear within the pre-averaging approximation, indicates the importance of the fluctuations of the hydrodynamic interaction. The effect of the fluctuating  $\eta_1$  to order  $\varepsilon^2$  is found to be rather strong. Despite this, it is possible to ascribe the experimental value  $\rho_e = 1.28$  of the ratio of the gyration radius to the hydrodynamic radius to the fluctuations of the  $\eta_1$ . The renormalised calculations of  $1/\rho$  to the next orders in  $\varepsilon$  with the subsequent resummation of the  $\varepsilon$  series are necessary to obtain a more accurate prediction of the effect of the fluctuating  $\eta_1$  on the translational diffusion coefficient. The perturbation expansion of  $D$  derived in the present work is the basis for performing the high-order calculations. We note that the recent MC simulations by Freire *et al* (1986) attribute the difference between the Kirkwood result  $\rho = 1.504$  and the experiment  $\rho_e = 1.28$  to the fluctuating  $\eta_1$ . Wang *et al* (1986) discuss other possible reasons to explain this deviation.

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### Appendix

To compute the singularities of the two-loop contribution to  $D$  the following formulae are used (Vladimirov 1980):

$$\int \frac{d^d p}{(p^2)^a (p^2 + m)^b} = \frac{\pi^{d/2}}{m^{a+b-2+\epsilon/2}} \frac{\Gamma(a+b-2+\epsilon/2)\Gamma(2-a-\epsilon/2)}{\Gamma(2-\epsilon/2)\Gamma(b)} \quad (\text{A1})$$

$$\int \frac{d^d p}{(p^2)^a [(k-p)^2]^b} = \frac{\pi^{d/2}\Gamma(a+b-2+\epsilon/2)\Gamma(2-a-\epsilon/2)\Gamma(2-b-\epsilon/2)}{(k^2)^{a+b-2+\epsilon/2}\Gamma(a)\Gamma(b)\Gamma(4-a-b-\epsilon)} \quad (\text{A2})$$

$$\int \frac{d^d p p^\mu}{(p^2)^a [(k-p)^2]^b} = \frac{\pi^{d/2}k^\mu\Gamma(a+b+2+\epsilon/2)\Gamma(3-a-\epsilon/2)\Gamma(2-b-\epsilon/2)}{(k^2)^{a+b-2+\epsilon/2}\Gamma(a)\Gamma(b)\Gamma(5-a-b-\epsilon)} \quad (\text{A3})$$

$$\int \frac{d^d p p^\mu p^\nu}{(p^2)^a [(k-p)^2]^b} = \frac{\pi^{d/2}\Gamma(a+b-3+\epsilon/2)\Gamma(3-a-\epsilon/2)\Gamma(2-b-\epsilon/2)}{(k^2)^{a+b-2+\epsilon/2}\Gamma(a)\Gamma(b)\Gamma(6-a-b-\epsilon)} \\ \times [(a+b-3+\epsilon/2)(3-a-\epsilon/2)k^\mu k^\nu + \frac{1}{2}(2-b-\epsilon/2)\delta^{\mu\nu}k^2] \quad (\text{A4})$$

$$\int \frac{d^d p p^\mu p^\nu p^\lambda}{(p^2)^a [(k-p)^2]^b} = \frac{\pi^{d/2}\Gamma(a+b-3+\epsilon/2)\Gamma(4-a-\epsilon/2)\Gamma(2-b-\epsilon/2)}{(k^2)^{a+b-2+\epsilon/2}\Gamma(a)\Gamma(b)\Gamma(7-a-b-\epsilon)} \\ \times [(a+b-3+\epsilon/2)(4-a-\epsilon/2)k^\mu k^\nu k^\lambda \\ + \frac{1}{2}(2-b-\epsilon/2)k^2(k^\mu\delta^{\nu\lambda} + k^\nu\delta^{\lambda\mu} + k^\lambda\delta^{\mu\nu})] \quad (\text{A5})$$

where  $\delta^{\mu\nu}$  is the Kronecker symbol in  $d$  dimensions ( $\delta^{\mu\mu} = d$ ). The above formulae are taken from Vladimirov (1980) and are reduced here to a form convenient for our calculations.

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