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Perturbation expansions for the transport quantities of dilute polymer solutions

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Abstract. The dynamics of a single polymer chain in solution is formulated in the framework of path integrals. The method enables one to obtain the perturbation expansions of the transport quantities in powers of the excluded volume and the hydrodynamic interactions. The inelastic scattering function and the diffusion coefficient are considered in the first-order perturbation theory.

1. Introduction

The conformational and dynamic properties of long polymer chains in a solvent have been the subject of several experimental and theoretical investigations in recent years. The conformational properties of dilute and semi-dilute polymer solutions had been successfully investigated in the framework of the renormalisation group approach. The theoretical description of the dynamical properties does not exhibit such success. The phenomenological scaling (de Gennes 1979) provides a simple basis for arriving at the power law dependence of varicus quantities (i.e. diffusion coefficient, viscosity) on the number of segments per chain N and the monomer concentration. Quantitative calculations carried out as in the static case do not exist. The dynamical renormalisation group calculations given by Jasnow and Moore (1978) and Al-Noaimi *et al* (1978) and recently by Oono and Kohmoto (1983) are not performed strictly in the framework of the dynamical theory. The static blob concept is used by Jasnow and Moore and Al-Noaimi *et al*, whereas the approach used by Oono and Kohmoto is based on approximative expressions for the intrinsic viscosity and diffusion coefficient and not on the corresponding Kubo formulae.

One of the reasons for such a situation is, in our opinion, connected with the fact that for the dynamic quantities in comparison with those in the static case, there do not exist good perturbation expansions in powers of the excluded volume strength. In the present work we give a method enabling us to obtain the perturbation expansions of the transport quantities such as the inelastic scattering function $S(\boldsymbol{k}, t)$ and the diffusion coefficient D in powers of the excluded volume and the hydrodynamic interactions. These perturbation expansions will be subsequently used to analyse $S(\boldsymbol{k}, t)$ and D in good solvents. We assume that the dynamic properties are governed by the Kirkwood diffusion equation. It is well known that this equation is a Fokker–Planck equation. Recently the Fokker–Planck equation was formulated in the framework of path integrals (Langouche *et al* 1979). This formulation gives a natural way to arrive at the perturbation expansions for the dynamic quantities under consideration. The perturbation solution of the Kirkwood equation was earlier used (Fixman 1965, see also Yamakawa (1971)) in connection with the investigation of the intrinsic viscosity. This approach corresponds, in fact, to the usual quantum mechanical perturbation theory. The perturbation expansions appearing in the framework of path integrals are like those in the quantum field theory. The advantages of these expansions are: (1) they can be represented by graphs and (2) they are suitable for the performance of the renormalisation program.

The paper is organised as follows. Section 2 briefly reports the polymer formalism. The path integral formulation of the Kirkwood equation is represented in § 3. The technique of the generating functional is reported in § 4. The evaluation of the generating functional for the Rouse model is given in § 5. In § 6 the evaluation of the inelastic scattering function for the Rouse model is carried out. Section 7 introduces the perturbation expansion of the generating functional. Section 8 gives the first-order correction to $S(\boldsymbol{k}, t)$. Section 9 reports on the evaluation of the diffusion coefficient.

2. Model

As a model of a polymer the continuous limit of the bead–spring model with excluded volume and hydrodynamic interactions between segments is used. The time evolution of the probability density $P(\boldsymbol{r}(s), t)$ for a conformation $\boldsymbol{r}(s)$ ($0 \leqslant s \leqslant L$, L is the contour length of the chain) is governed by the Kirkwood diffusion equation

$$\frac{\partial P}{\partial t} = \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \frac{\delta}{\delta \boldsymbol{r}(s_1)} [D_0 \boldsymbol{I} \delta(s_1 - s_2) + \boldsymbol{T}(\boldsymbol{r}(s_1) - \boldsymbol{r}(s_2))] \times [\delta F / \delta \boldsymbol{r}(s_2) + \delta / \delta \boldsymbol{r}(s_2)] P \tag{1}$$

where $D_0 = kTl/\zeta$, k is the Boltzmann constant, T the temperature, ζ the segment friction coefficient, and l the statistical segment length. The Oseen tensor $T^{\mu\nu}(\boldsymbol{r}(s_1) - \boldsymbol{r}(s_2))$ is defined in d dimensions by

$$T^{\mu\nu}(\boldsymbol{r}(s_1) - \boldsymbol{r}(s_2)) = \frac{kT}{\eta} \int \frac{\mathrm{d}^d \boldsymbol{q}}{(2\pi)^d} \frac{1}{q^2} \left(\delta^{\mu\nu} - \frac{q^\mu q^\nu}{q^2} \right) \exp[\mathrm{i}\boldsymbol{q}(\boldsymbol{r}(s_1) - \boldsymbol{r}(s_2))]$$

where η is the shear viscosity of the solvent. The free energy in units of kT for a continuous chain is given by

$$F = \frac{d}{2l} \int_0^L \mathrm{d}s (\partial \boldsymbol{r}(s)/\partial s)^2 + \tfrac{1}{2} v_0 l^{-2} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta^d(\boldsymbol{r}(s_1) - \boldsymbol{r}(s_2)) \tag{2}$$

where v_0 is the excluded volume strength. Instead of the continuous variable $\boldsymbol{r}(s)$ it is advisable to introduce the Fourier components $\boldsymbol{\xi}_k$ (normal coordinates), which are defined as follows:

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

$$Q_{sk} = (2/L)^{1/2} \cos(\pi s k / L), \qquad k = 1, 2, \ldots; \qquad Q_{s0} = L^{-1/2}.$$

The elastic term in the free enrgy expressed through $\boldsymbol{\xi}_k$ becomes

$$F_{\mathrm{el}}=\tfrac{1}{2}\sum_{k=0}^{\infty}\lambda_{(k)}\boldsymbol{\xi}_k^2$$

where $\lambda_{(k)}=(d/l)(\pi k/L)^2$. After introducing the normal coordinates, (1) takes the form

$$\partial P/\partial t=\boldsymbol{\nabla}_k(D_0\lambda_{(k)}\boldsymbol{\xi}_k+D_0\boldsymbol{\nabla}_k)P+\boldsymbol{\nabla}_k[D_0(\boldsymbol{\nabla}_kF_{\mathrm{ex}})+\boldsymbol{T}_{kn}(\lambda_{(n)}\boldsymbol{\xi}_n+(\boldsymbol{\nabla}_nF_{\mathrm{ex}})+\boldsymbol{\nabla}_n)]P \qquad (3)$$

where $\boldsymbol{\nabla}_n=\partial/\partial\boldsymbol{\xi}_n$, F_{ex} is the second term on the right-hand side of (2), and

$$T_{kn}^{\mu\nu}=\int_0^L \mathrm{d}s_1\int_0^L \mathrm{d}s_2\; Q_{ks_1}T^{\mu\nu}(\boldsymbol{r}(s_1)-\boldsymbol{r}(s_2))Q_{s_2n}.$$

The Einstein sum convention is used in (3) ($k, n=0,1,2,\ldots$). Equation (3) remains valid also for discrete chains with the difference that the indices k and n run from zero to $N-1$, where N is the segment number of the chain.

3. Representation as a path integral

Equation (3) can be represented after introducing the momentum and position operators $\hat{\boldsymbol{p}}_k=(1/\mathrm{i})\boldsymbol{\nabla}_k$ and $\hat{\boldsymbol{\xi}}_k=\boldsymbol{\xi}_k$ respectively, as a Schrödinger equation (Langouche *et al* 1979)

$$\mathrm{i}\,\partial P/\partial t=\hat{H}P \qquad (4)$$

where the Hamilton operator $\hat{H}=\hat{H}_0+\hat{H}_{\mathrm{int}}$ is given by

$$\hat{H}_0=-D_0\lambda_{(k)}\boldsymbol{p}_k\boldsymbol{\xi}_k-\mathrm{i}D_0\boldsymbol{p}_k^2, \qquad (5)$$

$$\hat{H}_{\mathrm{int}}=-D_0\hat{\boldsymbol{p}}_k(\boldsymbol{\nabla}_kF_{\mathrm{ex}})-\hat{\boldsymbol{p}}_k\boldsymbol{T}_{kn}\lambda_{(n)}\boldsymbol{\xi}_n-\hat{\boldsymbol{p}}_k\boldsymbol{T}_{kn}(\boldsymbol{\nabla}_nF_{\mathrm{ex}})-\mathrm{i}\hat{\boldsymbol{p}}_k\hat{\boldsymbol{p}}_n\boldsymbol{T}_{kn}+\hat{\boldsymbol{p}}_k(\boldsymbol{\nabla}_n\boldsymbol{T}_{kn}). \qquad (6)$$

The $\hat{\boldsymbol{p}}_k$ operators are contained in (5)–(6) on the left-hand side of $\boldsymbol{\xi}_k$. In order to obtain the ordered Hamiltonian, the term $T_{kn}^{\mu\nu}\nabla_n^{\nu}P$ in (3) was transformed as follows:

$$T_{kn}^{\mu\nu}\nabla_n^{\nu}P=\mathrm{i}\hat{p}_n^{\nu}(T_{kn}^{\mu\nu}P)+(-\nabla_n^{\nu}T_{kn}^{\mu\nu})P \qquad (7)$$

where the term $-\nabla_n^{\nu}T_{kn}^{\mu\nu}$ is explicitly given by

$$\delta(0)\int\frac{\mathrm{d}^d\boldsymbol{q}}{(2\pi)^d}\,T^{\mu\nu}(\boldsymbol{q})\mathrm{i}q^{\nu}\int_0^L\mathrm{d}s_1\int_0^L\mathrm{d}s_2\;Q_{ks_1}\exp[\mathrm{i}\boldsymbol{q}(Q_{s_1m}-Q_{s_2m})\boldsymbol{\xi}_m]$$

where $T^{\mu\nu}(q)$ is the Fourier transformation of the Oseen tensor and $\delta(0)=Q_{sn}^2=\infty$. This infinity appears as a consequence of the transform (7) and must be reduced in the final expressions. On that account we treat $\delta(0)$ in the intermediate stage as a finite quantity.

The eigenfunctions of $\hat{\boldsymbol{\xi}}_k$ and $\hat{\boldsymbol{p}}_k$ in the coordinate representation are respectively

$$|\boldsymbol{\xi}\rangle=\delta(\boldsymbol{\xi}-\boldsymbol{\xi}_0), \qquad |\boldsymbol{p}\rangle=(2\pi)^{-3/2}\exp(\mathrm{i}\boldsymbol{p}\boldsymbol{\xi}).$$

The transfer matrix is

$$\langle\boldsymbol{\xi}|\boldsymbol{p}\rangle=(2\pi)^{-3/2}\exp(\mathrm{i}\boldsymbol{\xi}\boldsymbol{p}).$$

Further, for $\boldsymbol{\xi}_0,\ldots,\boldsymbol{\xi}_m,\ldots$ the abbreviation $\boldsymbol{\xi}$ is used. $\boldsymbol{\xi}\boldsymbol{p}$ means $\Sigma_{i=0}^{\infty}\boldsymbol{\xi}_i\boldsymbol{p}_i$ (for a discrete chain, $\Sigma_{i=0}^{N-1}\boldsymbol{\xi}_i\boldsymbol{p}_i$).

The formal solution of (4) is

$$P_t = \exp[-\mathrm{i}(t-t_0)\hat{H}]P_{t_0}. \tag{8}$$

The matrix element

$$P(\boldsymbol{\xi}, t; \boldsymbol{\xi}^0, t_0) = \langle \boldsymbol{\xi} | \exp[-\mathrm{i}(t-t_0)\hat{H}] | \boldsymbol{\xi}^0 \rangle \tag{9}$$

gives the transition probability from the state $(\boldsymbol{\xi}^0, t_0)$ to the state $(\boldsymbol{\xi}, t)$. The path integral representation of $P(\boldsymbol{\xi}, t; \boldsymbol{\xi}^0, t_0)$ is accomplished as follows. As a consequence of the ordering of $\boldsymbol{p}$ and $\boldsymbol{\xi}$ in H,

$$\langle \boldsymbol{p} | \hat{H} | \boldsymbol{\xi} \rangle = h(\boldsymbol{p}, \boldsymbol{\xi}) \langle \boldsymbol{p} | \boldsymbol{\xi} \rangle$$

applies, where $h(\boldsymbol{p}, \boldsymbol{\xi})$ is identical with $H(\hat{\boldsymbol{p}}, \hat{\boldsymbol{\xi}})$, and $\boldsymbol{p}$ and $\boldsymbol{\xi}$ are c-numbers. Then for the matrix element $\langle \boldsymbol{\xi} | \exp(-\mathrm{i}\Delta t \hat{H}) | \boldsymbol{\xi}^0 \rangle$ for small Δt we obtain

$$\langle \boldsymbol{\xi} | \mathrm{e}^{-\mathrm{i}\Delta t \hat{H}} | \boldsymbol{\xi}^0 \rangle = \int \frac{\mathrm{d}\boldsymbol{p}}{(2\pi)^3} \exp[\mathrm{i}\boldsymbol{p}(\boldsymbol{\xi} - \boldsymbol{\xi}^0) - \mathrm{i}\Delta t h(\boldsymbol{p}, \boldsymbol{\xi}^0)]$$

where $\int \mathrm{d}\boldsymbol{p}/(2\pi)^3$ abbreviates $\int \mathrm{d}\boldsymbol{p}_0/(2\pi)^3 \ldots \int d\boldsymbol{p}_k/(2\pi)^3 \ldots$. After writing the right-hand side of (9) as

$$\langle \boldsymbol{\xi} | (\mathrm{e}^{-\mathrm{i}\Delta t \hat{H}})^n | \boldsymbol{\xi}^0 \rangle \qquad (\Delta t \cdot n = t - t_0)$$

and using the completeness of the set $|\boldsymbol{\xi}\rangle$ we get

$$\begin{aligned} P(\boldsymbol{\xi}, t; \boldsymbol{\xi}^0, t_0) = \int \frac{\mathrm{d}\boldsymbol{p}_n}{(2\pi)^3} \int\int \frac{\mathrm{d}\boldsymbol{p}_{n-1}\,\mathrm{d}\boldsymbol{\xi}_{n-1}}{(2\pi)^3} \ldots \int\int \frac{\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{\xi}_1}{(2\pi)^3} \\ \times \exp[\mathrm{i}\boldsymbol{p}_n(\boldsymbol{\xi} - \boldsymbol{\xi}_{n-1}) + \mathrm{i}\boldsymbol{p}_{n-1}(\boldsymbol{\xi}_{n-1} - \boldsymbol{\xi}_{n-2}) + \ldots + \boldsymbol{p}_1(\boldsymbol{\xi}_1 - \boldsymbol{\xi}^0) \\ -\mathrm{i}\Delta t h(\boldsymbol{p}_n, \boldsymbol{\xi}_{n-1}) - \mathrm{i}\Delta t h(\boldsymbol{p}_{n-1}, \boldsymbol{\xi}_{n-2}) - \ldots - \mathrm{i}\Delta t h(\boldsymbol{p}_1, \boldsymbol{\xi}^0)]. \end{aligned} \tag{10}$$

In the limit $\Delta t \to 0$, equation (10) gives the path integral

$$\begin{aligned} P(\boldsymbol{\xi}, t; \boldsymbol{\xi}^0, t_0) = \int\int \mathscr{D}\boldsymbol{p}\, \mathscr{D}\boldsymbol{\xi} \exp\left(\mathrm{i} \int_{t_0}^{t} dt' \,[\boldsymbol{p}(t')\dot{\boldsymbol{\xi}}(t') - h(\boldsymbol{p}(t'), \boldsymbol{\xi}(t'))] \right) \\ \times \delta(\boldsymbol{\xi} - \boldsymbol{\xi}(t)) \delta(\boldsymbol{\xi}^0 - \boldsymbol{\xi}(t_0)). \end{aligned} \tag{11}$$

The delta function in (11) is the abbreviation for

$$\delta(\xi_0^0 - \xi_0(t_0)) \delta(\xi_1^0 - \xi_1(t_0)) \ldots.$$

In the deduction of (11) we followed Slavnov and Fadeev (1978). Equation (11) was earlier obtained for the Fokker–Planck equation by Langouche *et al* (1979).

4. Generating functional

Following Langouche *et al* (1979), instead of $P(\boldsymbol{\xi}, t; \boldsymbol{\xi}^0, t_0)$ we consider the generating functional $Z(j, j^*)$ which is defined as follows:

$$\begin{aligned} Z(j, j^*) = \int\int \mathscr{D}\boldsymbol{p}\, \mathscr{D}\boldsymbol{\xi} \exp\bigg(\mathrm{i}S(T, t_0) + \mathrm{i} \int_{t_0}^{T} \mathrm{d}t'\, \xi_k(t') j_k(t') \\ + \mathrm{i} \int_{t_0}^{T} \mathrm{d}t'\, p_k(t') j_k^*(t') \bigg) \delta(\boldsymbol{\xi}^0 - \boldsymbol{\xi}(t_0)). \end{aligned} \tag{12}$$

The 'action' $S(T, t_0)$ is the integral in the exponent of (11). T is an arbitrary time which must only be large enough. The functional differentiation of Z with respect to j and j^* enables us to obtain different correlation functions. For example, the correlation function

$$\langle \xi_k^\mu(t_2)\xi_m^\nu(t_1)\rangle = \int \mathrm{d}\boldsymbol{\xi}(t_2)\int \mathrm{d}\boldsymbol{\xi}(t_1)\, \xi_k^\mu(t_2)\xi_m^\nu(t_1)P(\boldsymbol{\xi}(t_2),\boldsymbol{\xi}(t_1))P(\boldsymbol{\xi}(t_1),\boldsymbol{\xi}(t_0))$$

($P(\ldots)$ is the transition probability given by (11)) can be expressed as a functional derivative from the generating functional

$$\langle \xi_k^\mu(t_2)\xi_m^\nu(t_1)\rangle = \frac{1}{\mathrm{i}^2}\frac{\delta^2 Z(\boldsymbol{j},\boldsymbol{j}^*)}{\delta j_k^\mu(t_2)\delta j_m^\nu(t_1)}\bigg|_{j=j^*=0} \qquad (T \geq t_2 \geq t_1 \geq t_0). \tag{13}$$

It can be directly proved that the following boundary conditions are satisfied (Langouche *et al* 1979):

$$\langle \boldsymbol{\xi}_k(t_0)\rangle = \boldsymbol{\xi}_k^0 Z(\boldsymbol{j},\boldsymbol{j}^*), \qquad \langle \boldsymbol{p}_k(T)\rangle = 0.$$

Tne average over the initial conditions is not carried out in (13). The correlation function $S_{ss'}(\boldsymbol{k}, t-t_0) = \langle \exp[\mathrm{i}\boldsymbol{k}(\boldsymbol{r}_s(t)-\boldsymbol{r}_{s'}(t_0))]\rangle_{\mathrm{a}}$ can be expressed through $Z(\boldsymbol{j},\boldsymbol{j}^*)$ as follows:

$$S_{ss'}(\boldsymbol{k}, t-t_0) = Z(\boldsymbol{j},\boldsymbol{j}^*=0)_{\mathrm{a}} \tag{14}$$

where

$$\boldsymbol{j}_m(t') = \boldsymbol{k}(Q_{sm}\delta(t-t') - Q_{s'm}\delta(t'-t_0)). \tag{15}$$

The symbol a in (14) denotes the average over $\boldsymbol{\xi}(t_0)(\boldsymbol{\xi}_1(t_0),\ldots,\boldsymbol{\xi}_n(t_0),\ldots)$ which is to be carried out by means of the free energy F,

$$(O)_{\mathrm{a}} = \int \mathrm{d}\xi\, O\exp(-F)\bigg/\int \mathrm{d}\xi \exp(-F).$$

The generating functional $Z^0(\boldsymbol{j},\boldsymbol{j}^*)$ for the Hamiltonian H_0 (Rouse model) will be calculated in § 5.

Now we show that the perturbation expansion of $Z(\boldsymbol{j},\boldsymbol{j}^*)$ in powers of h_{int} can be represented in a closed form. In the nth order in h_{int} we have to deal with the average

$$\int\int \mathscr{D}\boldsymbol{p}\,\mathscr{D}\boldsymbol{\xi}\, h_{\mathrm{int}}(\tau_1)\ldots h_{\mathrm{int}}(\tau_n)$$
$$\times\exp\left(\mathrm{i}S(T,t_0) + \int_{t_0}^{T}\mathrm{d}t'\,(\boldsymbol{j}(t')\boldsymbol{\xi}(t') + \boldsymbol{j}^*(t')\boldsymbol{p}(t'))\right).$$

The dependence of h_{int} on $\boldsymbol{\xi}_k$ appearing through the terms $\boldsymbol{\nabla}_k F_{\mathrm{ex}}$ and $\boldsymbol{T}_{kn}$, which are supposed to be developed in Fourier integrals, can be represented in the form $\exp[\mathrm{i}\boldsymbol{q}(Q_{s_1m}-Q_{s_2m})\boldsymbol{\xi}_m(\tau)]$. These terms can be taken into account through the modification of the source $\boldsymbol{j}_m(t')\to\boldsymbol{j}_m(t')+\boldsymbol{q}(Q_{s_1m}-Q_{s_2m})\delta(t'-\tau)$. $\boldsymbol{p}_k(\tau_1)$ and the remaining $\boldsymbol{\xi}_k(\tau_j)$, which are not contained in $\boldsymbol{\nabla}_k F_{\mathrm{ex}}$ and $\boldsymbol{T}_{kn}$, are represented as correlation functions from the powers of $p_k^\mu(\tau_i)$ and $\xi_m^\nu(\tau_j)$ which are again expressed as functional derivatives of $Z^0(\boldsymbol{j},\boldsymbol{j}^*)$. Then we arrive at the following expression for $Z(\boldsymbol{j},\boldsymbol{j}^*)$:

$$Z(\boldsymbol{j},\boldsymbol{j}^*)_{\mathrm{a}} = \exp\left(-\mathrm{i}\int_{t_0}^{T}\mathrm{d}t'\, h_{\mathrm{int}}(\boldsymbol{p}(t'),\boldsymbol{\xi}(t'))\right)^{\sim} Z^0(\boldsymbol{j},\boldsymbol{j}^*)_{\mathrm{a}}. \tag{16}$$

The tilde in (16) means that ξ_k which are contained in $\nabla_m F_{ex}$ and T_{lm} cause the modification of $j_k(t')$ in $Z^0(j, j^*)$ in each order of the perturbation expansion (see (21)–(22)) and the remaining $\xi_k(t')$ and $p_m(t'')$ must be replaced by

$$(1/\mathrm{i})\delta/\delta j_k(t') \qquad \text{and} \qquad (1/\mathrm{i})\delta/\delta j_m^*(t'')$$

respectively.

5. Evaluation of $Z^0(j, j^*)$

As $h_0(p, \xi)$ is a quadratic function relative to p_k and ξ, $Z^0(j, j^*)$ is a Gauss integral. The Gauss integral, according to a well known property (Feynman and Hibbs 1965), is equal to the integrand with 'action' evaluated for the classical path

$$Z^0(j, j^*) = \int\int \mathscr{D}p\, \mathscr{D}\xi\, \exp[\mathrm{i}S^0(T, t_0)] \sim \exp(\mathrm{i}S^0_{\mathrm{cl}})$$

where the 'action' S^0 is given by

$$S^0 = \int_{t_0}^{T} \mathrm{d}t' \, [p_k(t')\dot{\xi}_k(t') + \mathrm{i}D_0 p_k^2(t') + D_0\lambda_{(k)} p_k(t')\xi_k(t') + j_k(t')\xi_k(t') + j_k^*(t')p_k(t')].$$

S^0_{cl} is obtained from S^0 by replacing $\xi_k(t)$ and $p_k(t)$ by the solution of the 'classical movement equations'

$$\delta S^0/\delta \xi_k(t) = 0, \qquad \delta S^0/\delta p_e(t) = 0. \tag{17}$$

The solution of (17) with the boundary conditions $\xi_k(0) = \xi_k^0$, $p_k(T) = 0$ (later we put $t_0 = 0$) is

$$p_k(t) = -\int_t^T \mathrm{d}t' \, j_k(t') \exp[-D_0\lambda_{(k)}(t' - t)],$$

$$\xi_k(t) = \xi_k^0 \exp(-D_0\lambda_{(k)}t) - \int_0^t \mathrm{d}t' \, j_k(t') \exp[-D_0\lambda_{(k)}(t - t')] - 2\mathrm{i}D_0 \int_0^t \mathrm{d}t' \, p_k(t') \exp[-D_0\lambda_{(k)}(t - t')].$$

Finally for $Z^0(j, j^*)$ one obtains

$$Z^0(j, j^*) = \exp\biggl(\mathrm{i}\xi_k^0 \int_0^T \mathrm{d}t' \exp(-D_0\lambda_{(k)}t) j_k(t') - \mathrm{i}\int_0^T \mathrm{d}t' \int_0^T \mathrm{d}t'' \, j_k(t') D_{(k)}(t' - t'') j_k^*(t'') - \tfrac{1}{2}(\lambda(k))^{-1} \int_0^T \mathrm{d}t' \int_0^T \mathrm{d}t'' \, j_k(t') \Delta_{(k)}(t', t'') j_k(t'')\biggr), \tag{18}$$

where $D_{(k)}(t) = \theta(t) \exp(-D_0\lambda_{(k)}t)$ ($\theta(t)$ is the step function and

$$\Delta_{(k)}(t', t'') = D_{(k)}(t' - t'') + D_{(k)}(t'' - t') - \exp[-D_0\lambda_{(k)}(t' + t'')].$$

(18) coincides with the result obtained using the method stated by Langouche *et al* (1979).

6. Inelastic scattering function for the Rouse model

In the Rouse model the excluded volume and hydrodynamic interactions are absent ($h_{\text{int}} = 0$). The generating functional is given by (18). The correlation function $S_{ss'}(\boldsymbol{k}, t)$ is obtained by means of (14), (15) and (18). The inelastic scattering function is obtained from $S_{ss'}(\boldsymbol{k}, t)$ as follows:

$$S(\boldsymbol{k}, t) = l^{-2} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \, S_{ss'}(\boldsymbol{k}, t).$$

Substituting $\boldsymbol{j}_m(t')$ given by (15) in (18) one obtains for $Z^0(\boldsymbol{j}, \boldsymbol{j}^* = 0)$

$$\exp[\mathrm{i}\boldsymbol{\xi}_m \boldsymbol{k}(Q_{sm} \exp(-D_0\lambda_{(m)}t) - Q_{s'm}) - \tfrac{1}{2}(\boldsymbol{k}^2/\lambda_{(m)}) Q_{sm}^2 \Delta_{(m)}(t, t)]. \tag{19}$$

The average of (19) over the initial conditions

$$S_{ss'}^0(\boldsymbol{k}, t) = \int \ldots \int \ldots \mathrm{d}\boldsymbol{\xi}_1 \ldots \mathrm{d}\boldsymbol{\xi}_n \ldots \exp(-F_{\text{el}}) Z(\boldsymbol{j}, \boldsymbol{j}^* = 0)$$

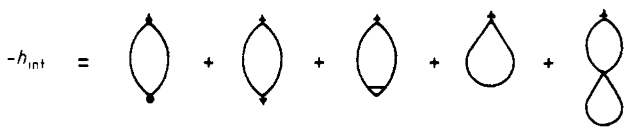
gives after separation of the $m = 0$ mode and some elementary transformations

$$S_{ss'}^0(\boldsymbol{k}, t) = \exp\left(-\frac{kT}{\zeta N} \boldsymbol{k}^2 t\right) \times \exp\left(-\tfrac{1}{2}\boldsymbol{k}^2 \sum_{m=1}^{\infty} \frac{1}{\lambda_{(m)}} [Q_{sm}^2 + Q_{s'm}^2 - 2Q_{sm}Q_{s'm} \exp(-D_0\lambda_{(m)}t)]\right).$$

This expression is identical with the result obtained in a different way by Pecora (1963, 1965).

7. Perturbation expansion

The development of the exponent in (16) in powers of h_{int} produces the perturbation expansion of $Z(\boldsymbol{j}, \boldsymbol{j}^*)_{\text{a}}$ in powers of the excluded volume and the hydrodynamic interactions. It is convenient to represent this expansion by means of diagrams. To achieve this we first represent h_{int} graphically



(20)

Figure 1.

where the arrows and the full circle are associated with $p_k(\tau)=(1/\mathrm{i})\delta/\delta j_k^*(\tau)$ and $\lambda_{(n)}\xi_{(n)}(\tau)=\lambda_{(n)}(1/\mathrm{i})\delta/\delta j_n(\tau)$ respectively. The different loops in (20) are associated with analytical expressions as follows:

$$=\int \frac{\mathrm{d}^d \boldsymbol{q}}{(2\pi)^d}\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, Q_{ks_1} T^{\mu\nu}(\boldsymbol{q}) Q_{ns_2},$$

$$=\mathrm{i}\int \frac{\mathrm{d}^d \boldsymbol{q}}{(2\pi)^d}\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, Q_{ks_1} T^{\mu\nu}(\boldsymbol{q}) Q_{ns_2},$$

$$=\delta(0)\int \frac{\mathrm{d}^d \boldsymbol{q}}{(2\pi)^d}\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, Q_{ks_1} T^{\mu\nu}(\boldsymbol{q})\mathrm{i}q^\nu,$$

$$=\tfrac{1}{2}v_0 l^{-2} D_0 \int \frac{\mathrm{d}^d \boldsymbol{q}}{(2\pi)^d}\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \mathrm{i}\boldsymbol{q}(Q_{ns_1}-Q_{ns_2}),$$

$$=\tfrac{1}{2}v_0 l^{-2} D_0 \int \frac{\mathrm{d}^d \boldsymbol{q}_1}{(2\pi)^d}\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \int \frac{\mathrm{d}^d \boldsymbol{q}_2}{(2\pi)^d}\int_0^L \mathrm{d}s_3 \int_0^L \mathrm{d}s_4\, Q_{ks_1}$$
$$\times T^{\mu\nu}(\boldsymbol{q}_1) Q_{s_2 n}\mathrm{i}q_2^\nu (Q_{ns_3}-Q_{ns_4}).$$

The factors associated with the full circle and the arrows are not written. The ξ_m which are contained in T_{kn} and F_{ex} modify the sources $j_m(t)$ step by step in the perturbation theory as follows;

first order

$$j_m(t)\to j_m(t)+\boldsymbol{q}(Q_{ms_1}-Q_{ms_2})\delta(t-\tau); \tag{21}$$

second order

$$j_m(t)\to j_m(t)+\boldsymbol{q}_1(Q_{ms_1}-Q_{ms_2})\delta(t-\tau_1)+\boldsymbol{q}_2(Q_{ms_3}-Q_{ms_4})\delta(t-\tau_2), \tag{22}$$

and so on. The result of the average of $Z^0(j,j^*)$ over the initial conditions can be represented as follows,

$$Z^0(j,j^*)_{\mathrm{a}}=(1+I(j))Z^0(j,j^*)^0_{\mathrm{a}}$$

where $Z^0(j,j^*)^0_{\mathrm{a}}$ is given by

$$Z^0(j,j^*)^0_{\mathrm{a}}=\exp\bigg(-\tfrac{1}{2}\sum_{m=1}^{\infty}\frac{1}{\lambda_{(m)}}\int_0^T \mathrm{d}t'\int_0^T \mathrm{d}t''\, j_m(t')$$
$$\times[D_{(m)}(t'-t'')+D_{(m)}(t''-t')]j_m(t'')$$
$$-\mathrm{i}\int_0^T \mathrm{d}t'\int_0^T \mathrm{d}t''\, j_m(t')D_{(m)}(t'-t'')j_m^*(t'')$$
$$-\tfrac{1}{2}\lim_{m\to 0}\frac{1}{\lambda_{(m)}}\int_0^T \mathrm{d}t'\int_0^T \mathrm{d}t''\, j_m(t')\Delta_{(m)}(t',t'')j_m(t'')\bigg).$$

In the first-order perturbation theory for $I(\boldsymbol{j})$ we obtain

$$I^1(\boldsymbol{j}) = \tfrac{1}{2}v_0 l^{-2} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \int \frac{\mathrm{d}^d \boldsymbol{q}}{(2\pi)^d} \exp\left(-\frac{l}{2d}\boldsymbol{q}^2|s_2 - s_1|\right)$$
$$\times\left[1 - \exp\left(-\int_0^T \mathrm{d}t' \exp(-D_0\lambda_{(m)}t')\boldsymbol{j}_m(t')\frac{\boldsymbol{q}}{\lambda_{(m)}}(Q_{ms_1} - Q_{ms_2})\right)\right]. \tag{23}$$

$I(\boldsymbol{j})$ gives the correction to $Z(\boldsymbol{j}, \boldsymbol{j}^*)$ which appear through the average over the initial conditions.

The result of action of the functional derivatives $(1/\mathrm{i})\delta/\delta\boldsymbol{j}_n(\tau)$ and $(1/\mathrm{i})\delta/\delta\boldsymbol{j}_m^*(\tau)$ on the exponential $Z^0(\boldsymbol{j}, \boldsymbol{j}^*)_{\mathrm{a}}^0$ can be represented graphically as follows:

$$\lambda_{(n)}\boldsymbol{\xi}_n(\tau) \sim\!\sim\!\sim = \bullet - - - (\sim\!\sim\!\sim)$$
$$\boldsymbol{p}_k(\tau) \sim\!\sim\!\sim = \bullet\!\!-\!\!\leftarrow\!\!-(\sim\!\sim\!\sim)$$

The wavy line is associated with $Z^0(\boldsymbol{j}, \boldsymbol{j}^*)_{\mathrm{a}}^0$. The full circles are associated with $\boldsymbol{j}_k(t')$, and the full and broken lines (propagators) with $-D_{(k)}(t'-\tau)$ and $-(1/\mathrm{i})(D_{(k)}(t'-\tau) + D_{(k)}(\tau - t'))$, respectively. The integration over t' is performed. The other ends of propagators correspond to the time τ. Figure 2 shows the diagrams contributing to $Z(\boldsymbol{j}, \boldsymbol{j}^*)_{\mathrm{a}}$ in the first-order perturbation theory.

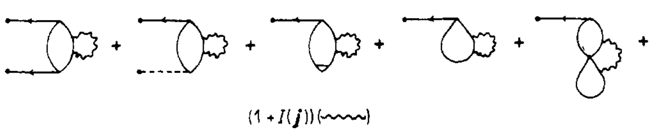


Figure 2. The diagrams contributing to $Z(\boldsymbol{j}, \boldsymbol{j}^*)_{\mathrm{a}}$ in the first-order perturbation theory.

The propagators begin at the vertices of the loops. With each loop the integration $\mathrm{i}\int_0^T \mathrm{d}\tau$ is associated. The wavy line is $Z^0(\boldsymbol{j}, \boldsymbol{j}^*)_{\mathrm{a}}^0$ with the sources which are modified for the first four diagrams according to (21). The fifth diagram is of first order with respect to h_{int} and of second order with respect to the excluded volume and the hydrodynamic interactions. Its sources are modified according to (22) with $\tau_1 = \tau_2 = \tau$.

In the perturbation expansion of the generating functional there appear terms which are proportional to $D_{(n)}(0)$ (tadpoles). Going to the discrete version of the path integral for the generating functional (this must be done in the same way as for the transition probability $P(\boldsymbol{\xi}, t; \boldsymbol{\xi}_0, t_0)$), we see that $D_{(n)}(0)$ is to be interpreted as $D_{(n)}(-0)$ and thus is zero.

8. Inelastic scattering function

Bringing the sources in the diagrams shown in figure 2 in accordance with (15) we obtain the first-order correction to the correlation function $S_{ss'}(\boldsymbol{k}, t)$ (Stepanow 1983),

$$S_{ss'}(\boldsymbol{k}, t) = S_{ss'}^0(\boldsymbol{k}, t)(1 + I_{ss'}^1(\boldsymbol{k}, t) + I_{ss'}^2(\boldsymbol{k}, t)). \tag{24}$$

$I^1_{ss'}(\boldsymbol{k}, t)$ is given by (23) with source fixed according to (15). The function $I^2_{ss'}(\boldsymbol{k}, t)$ is

$$I^2_{ss'}(\boldsymbol{k}, t) = \int_0^t \mathrm{d}\tau \int_0^L \mathrm{d}s_2 \int_0^{s_2} \mathrm{d}s_1 \int \frac{\mathrm{d}^d \boldsymbol{q}}{(2\pi)^d} [D_0 v_0 l^{-2} \boldsymbol{qk}(Q_{ms_1} - Q_{ms_2}) Q_{sm} D_{(m)}(t-\tau)$$
$$- 2 Q_{sk} D_{(k)}(t-\tau) Q_{ks_1} k^\mu T^{\mu\nu}(\boldsymbol{q}) k^\nu Q_{s_2 n} Q_{ns'} D_{(n)}(\tau)] \exp(-A) \tag{25}$$

where A is given by

$$A = \frac{l}{2d} \boldsymbol{q}^2 (s_2 - s_1) + \boldsymbol{kq} \sum_{m=1}^{\infty} \frac{1}{\lambda_{(m)}} (Q_{ms_1} - Q_{ms_2})(Q_{sm} D_{(m)}(t-\tau) - Q_{s\,m} D_{(m)}(\tau)).$$

The scattering function $S(\boldsymbol{k}, t)$ can be represented in the following form:

$$S(\boldsymbol{k}, t) = S^0(\boldsymbol{k}, t) + v_0 l^{-4} S_0^{\varepsilon/2} f_1(S_0 \boldsymbol{k}^2, D_0 l t / S_0^2)$$
$$+ \boldsymbol{k}^2 S_0 (\zeta l^{-1}/\eta) S_0^{\varepsilon/2} f_2(S_0 \boldsymbol{k}^2, D_0 l t / S_0^2)$$

where $S_0 = Ll$. The functions f_1 and f_2 are given by (23)–(25).

9. Diffusion coefficient

Now we show how the diffusion coefficient of the polymer chain can be expressed through the generating functional. The starting point is the Einstein formula for the diffusion coefficient

$$D = \frac{1}{2d} \lim_{t\to\infty} t^{-1} L^{-2} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \langle (\boldsymbol{r}_s(t) - \boldsymbol{r}_{s'}(0))^2 \rangle_{\mathrm{a}}. \tag{26}$$

It can be shown that (26) is equivalent to the well known Kubo formula for the diffusion coefficient. Expressing $\boldsymbol{r}_s(t)$ through $\boldsymbol{\xi}_k(t)$, equation (26) gives

$$D = \frac{1}{2dL} \lim_{t\to\infty} \frac{1}{t} \left(\sum_{k=0}^{\infty} \langle \boldsymbol{\xi}_k^2(t) \rangle_{\mathrm{a}} + \sum_{k=0}^{\infty} \langle \boldsymbol{\xi}_k^2(0) \rangle_{\mathrm{a}} - 2 \langle \boldsymbol{\xi}_0(t) \boldsymbol{\xi}_0(0) \rangle_{\mathrm{a}} \right). \tag{27}$$

The second and third terms an the right-hand side of (27) do not contribute to D. The third term becomes zero if one chooses the origin of the coordinates system in the centre of gravity of the chain ($\boldsymbol{\xi}_0(0) = 0$). Taking into account that in the first term only the $k = 0$ mode gives the required contribution, we obtain

$$D = (2dL)^{-1} \lim_{t\to\infty} t^{-1} \langle \boldsymbol{\xi}_0^2(t) \rangle_{\mathrm{a}}. \tag{28}$$

Equation (28) can also be rewritten equivalently as

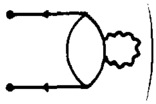
$$D = (2dL)^{-1} \lim_{t\to\infty} t^{-1} \langle (\boldsymbol{\xi}_0(t) - \boldsymbol{\xi}_0(0))^2 \rangle_{\mathrm{a}}$$

which resembles the diffusion coefficient for one particle. Expressing $\boldsymbol{\xi}_0^2(t)$ through $Z(\boldsymbol{j}, \boldsymbol{j}^*)$ in accordance with (13), we obtain for the diffusion coefficient

$$D = -\frac{1}{2dL} \lim_{t\to\infty} \frac{1}{t} \left. \frac{\delta^2 Z(\boldsymbol{j}, \boldsymbol{j}^*)_{\mathrm{a}}}{\delta \boldsymbol{j}_0(t) \delta \boldsymbol{j}_0(t)} \right|_{\boldsymbol{j}^* = 0}. \tag{29}$$

Differentiating in accoradance with (29) the diagrams shown in figure 2 for the diffusion coefficient, it follows that

$$D=\frac{kT}{\zeta N}-\frac{1}{dL}\lim_{t\to\infty}\frac{1}{t}. \tag{30}$$



The remaining diagrams do not contribute to D. In (30) the full line with the open circle is associated with $-D_{(0)}(t-\tau)$. The diagram in (30) corresponds to the following expression:

$$\mathrm{i}\int_0^t \mathrm{d}\tau\, D^2_{(0)}(t-\tau)\int\frac{\mathrm{d}^d\boldsymbol{q}}{(2\pi)^d}\,2\int_0^L \mathrm{d}s_2\int_0^{s_2}\mathrm{d}s_1\; Q_{0s_1}\mathrm{i}T^{\mu\mu}(q)Q_{0s_2}$$
$$\times\exp[-(l/2d)\boldsymbol{q}^2(s_2-s_1)]. \tag{31}$$

The exponential function in (31) (wavy loop in (30)) is

$$Z^0(j,j^*=0)^0_{\mathrm{a}}|_{j_m(t)}=\boldsymbol{q}(Q_{ms_1}-Q_{ms_2})\delta(t-\tau).$$

After carrying out the integration in the expression (31) we obtain

$$D=\frac{kT}{\zeta N}\left(1+\frac{d-1}{d}\,\frac{1}{1-\varepsilon^2/4}\,\frac{2}{\varepsilon}\,\xi L^{\varepsilon/2}+\ldots\right) \tag{32}$$

where

$$\xi=(\zeta/\eta)(d/2\pi l)^{d/2}l/d.$$

(32) coincides with the expression following from the well known equation of Kirkwood (Yamakawa 1971, p 280).

For example, in figure 3 we represent the diagrams contributing to D up to second order in the excluded volume strength. The numbers in the diagrams are the factors which must be taken into account in the analytical expressions associated with diagrams. The analytical expression which is associated with the second diagram is given by

$$-\mathrm{i}^2\int_0^t \mathrm{d}\tau_1\int_0^{\tau_1}\mathrm{d}\tau_2\int\frac{\mathrm{d}^d\boldsymbol{q}_1}{(2\pi)^d}\,\frac{2}{L}\int_0^L \mathrm{d}s_2\int_0^{s_2}\mathrm{d}s_1\;\mathrm{i}T^{\mu\mu}(\boldsymbol{q}_1)v_0 l^{-2}D_0$$
$$\times\int\frac{\mathrm{d}^d\boldsymbol{q}_2}{(2\pi)^d}\int_0^L \mathrm{d}s_4\int_0^{s_4}\mathrm{d}s_3\;\mathrm{i}\boldsymbol{q}_2(Q_{ns_3}-Q_{ns_4})$$
$$\times\int_0^T \mathrm{d}t'\,j_n(t')D_{(n)}(t'-\tau_2)Z^0(j,j^*)=0)^0_{\mathrm{a}}$$

where the source j is given by (22).

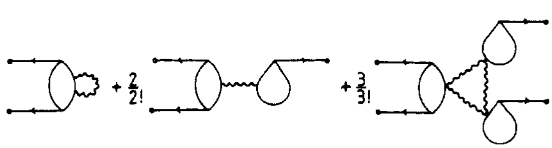


Figure 3. The diagrams contributing to D up to second order in the excluded volume strength.

10. Conclusion

In the present work we have, for the first time, formulated the dynamics of a single polymer chain in a solution in the framework of the path integral. In this way we arrive at the perturbation expansions for the transport quantities such as the inelastic scattering function and the diffusion coefficient in powers of the excluded volume and the hydrodynamic interactions. The author has shown that the intrinsic viscosity can also be expressed through the generating functional, and the present method thus enables one to obtain also the perturbation expansion for the intrinsic viscosity.

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