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Polymer chain in good solvents under elongational flow

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Abstract. The properties of a single polymer chain under steady elongational flow are investigated by means of a renormalisation group method. Based on the Rouse–Zimm model, the asymptotic scaling function of the end-to-end distribution is calculated by the $\varepsilon = 4 - d$ expansion approximation with d being the spatial dimension of the system. The corrections due to the excluded-volume effect and the hydrodynamic interaction are evaluated up to the order of ε. The effect of the flow on the scattering function is also described with a simple approximation.

1. Introduction

There have been extensive studies of the polymer problem for many years. Especially, recent application of a renormalisation group theory has made it possible to investigate systematically the universal properties of the polymer system. As far as the static problems of a single polymer chain are concerned, the various scaling functions have been calculated explicitly (Oono *et al* 1981, Ohta *et al* 1981a, b, Witten and Schäfer 1980). On the contrary, the dynamic aspects of a single chain have not been studied intensively by a reliable theory. Only the elegant phenomenological scaling arguments (de Gennes 1979) and the calculation of the dynamic exponent by renormalisation group methods (Al-Noaimi *et al* 1978, Jasnow and Moore 1977, Oono and Freed 1981b) have been available.

In this paper we study the properties of a polymer chain in a good solvent submitted to the steady elongational flow. The flow pattern $\boldsymbol{u}$ is displayed in figure 1, which takes the form

$$\boldsymbol{u} = (SX, -SY, \boldsymbol{0}) \tag{1.1}$$

with $S > 0$, where X and Y are the cartesian coordinates of the system. In the present non-equilibrium steady-state problem we have to consider two nonlinearities of the excluded-volume effect and the hydrodynamic interaction. The choice of the flow (1.1) has an advantage that it satisfies automatically the integrability condition of the Fokker–Planck equation at least in the absence of the hydrodynamic interaction (see § 3). Moreover the elongational flow would produce more extensional effects on a real chain than the simple shear flow $\boldsymbol{u} = (SY, 0, \boldsymbol{0})$, because the latter contains the rotating degree of freedom (de Gennes 1979).

We are primarily concerned with the end-to-end distribution function $G(N, \boldsymbol{R}, S)$ of a polymer chain with the number of monomers N under the flow. The asymptotic behaviour of G for large values of N can be obtained by the following argument. The characteristic length of the problem is the mean radius of the chain ξ which is assumed

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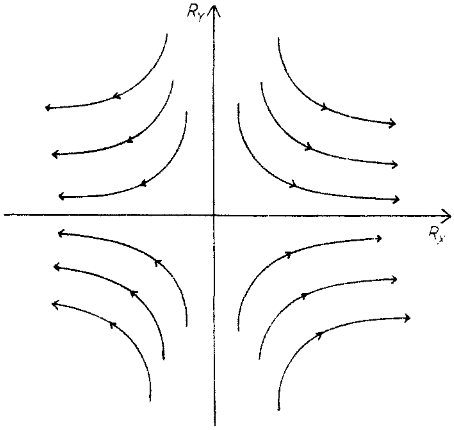

Figure 1. Elongational flow in X–Y plane

$\xi \sim N^{\nu}$ with the positive exponent ν. Since the rate of shear S has a dimension of frequency, we need the characteristic frequency Ω which is given by the diffusion rate of a polymer chain. Assuming that $\Omega \sim \xi^{-z}$ with the dynamic exponent z, the dimensional analysis leads us to the asymptotic form of $G(N, \boldsymbol{R}, S)$ in d dimensions:

$$G(N, \boldsymbol{R}, S) = N^{-d\nu}\hat{G}(\boldsymbol{R}/N^{\nu}, SN^{z\nu}). \tag{1.2}$$

On the basis of the Rouse–Zimm model (Rouse 1953, Zimm 1956) we calculate the scaling function $\hat{G}(\hat{\boldsymbol{R}}, \hat{S})$ as well as the exponents ν and z by means of the conformational space renormalisation group method (Oono 1979, Oono and Freed 1981a, b). We do not use the polymer–magnet analogy (de Gennes 1972, des Cloizeaux 1975, Emery 1975, Jasnow and Fisher 1976, Gujrati 1981) since the method has not been developed for the dynamic problems so far.

The Rouse–Zimm model has an artifact that it cannot be applied in the strong shear regime of the elongational flow, where the steady solution of the Fokker–Planck equation does not exist. In order to avoid this difficulty we have to consider the anharmonicity between the nearest-neighbour monomer interaction, which will be considered in a future work. The present investigation is restricted to the weak shear regime $\hat{S} \leqslant 1$.

In § 2 we start with the Rouse–Zimm model and describe the application of the dynamic renormalisation group method. Without assumptions used in the derivation of (1.2) we can discuss the scaling property by solving the renormalisation group equation for $G(N, \boldsymbol{R}, S)$. The scaling function $\hat{G}$ with the excluded volume interaction is calculated in § 3. We employ the $\varepsilon \equiv 4-d$ expansion approximation and obtain the correction of $\hat{G}$ up to $O(\varepsilon)$. The effects of the hydrodynamic interaction are studied in § 4. Since the function $\hat{G}$ for the general values of $\hat{S}$ (but with the above mentioned restriction) is very complicated, we expand the corrections due to the hydrodynamic interaction in powers of $\hat{S}$ and retain only the leading terms. In § 5 we briefly describe the scattering function with finite $\hat{S}$ neglecting the nonlinear interactions. The scattering function for $\hat{S} = 0$ has been calculated up to $O(\varepsilon)$ (Ohta *et al* 1981a, b). The result shows that the correction due to the excluded-volume effect is, if scaled properly, small in magnitude although it does appreciably change the non-symmetry coefficient. Hence we may expect that the obtained anisotropic nature of the scattering function by the flow is qualitatively correct. Section 6 is devoted to discussions. The various correlation functions are summarised in appendix 1, while in appendix 2 we describe our derivation of the steady-state solution of the Fokker–Planck equation in the presence of the hydrodynamic interaction.

2. Model and renormalisation group analysis

We consider a dilute polymer system in a good solvent under the elongational flow. There are two nonlinear interactions in a single polymer chain. One is the excluded-volume effect. The monomer density fluctuations excite a velocity field in the solvent. A long-range interaction mediated by this velocity field appears between monomers which is called the hydrodynamic interaction. The static properties in equilibrium are not affected by the hydrodynamic interaction. In the steady state submitted by the flow, however, both interactions are equally important.

We here employ the Rouse–Zimm model (e.g. Yamakawa 1971) which describes the time development of the probability distribution function $P(\{c\}, t)$ where $c(\tau)$ is the position vector of the monomer with the contour length τ. The model is written explicitly as

$$\frac{\partial P\{c\}, t)}{\partial t} = \int_{\substack{0 \\ |\tau-\tau'|>a}}^{N_0} \mathrm{d}\tau \int_0^{N_0} \mathrm{d}\tau' \sum_{\alpha,\beta} \frac{\delta}{\delta c^{\alpha}(\tau)} \left[\left(\frac{1}{\zeta_0}\delta_{\alpha\beta}\delta(\tau-\tau') + g_0 T^{\alpha\beta}_{(\tau,\tau')}\right)\right.$$

$$\left. \times\left(\frac{\delta \mathcal{H}}{\delta c^{\beta}(\tau')} + \frac{\delta}{\delta c^{\beta}(\tau')} - v^{\beta}\delta(\tau-\tau')\right)\right] P(\{c\}, t) \tag{2.1}$$

where

$$\mathcal{H} = \frac{1}{2}\int_0^{N_0} \mathrm{d}\tau \left(\frac{dc}{d\tau}\right)^2 + \frac{u_0}{2}\int_{\substack{0 \\ |\tau-\tau'|>a}}^{N_0} \mathrm{d}\tau \int_0^{N_0} \mathrm{d}\tau' \, \delta(c(\tau) - c(\tau')). \tag{2.2}$$

The subscript 0 denotes the bare quantities, ζ_0 is the inverse of the friction coefficient, g_0 stands for the strength of the hydrodynamic interaction and u_0 is the excluded-volume parameter. N_0 is the total monomer length of a chain. The short distance cut-off parameter a is introduced in (2.2). The Oseen tensor $T^{\alpha\beta}$ is defined in d dimensions by

$$T^{\alpha\beta}(\tau, \tau') = \int_k \frac{1}{\eta k^2}\left(\delta_{\alpha\beta} - \frac{k^{\alpha}k^{\beta}}{k^2}\right) \exp[\mathrm{i}k(c(\tau) - c(\tau'))] \tag{2.3}$$

where $\int_k \equiv \int \mathrm{d}^d k/(2\pi)^d$. η is the shear viscosity of the solvent. The external velocity field v is given by

$$v = (Sc^x, -Sc^y, 0). \tag{2.4}$$

We here generalise the Gell-Mann–Low-type renormalisation group method used in the static problem (Oono *et al* 1981). We first perform the dimensional consideration for the parameters in (2.1):

$$\begin{aligned} &[N_0] \equiv L \qquad [c] = L^{1/2} \qquad [u_0] = L^{(d-4)/2} \\ &[g_0\zeta_0/\eta] = L^{(d-4)/2} \qquad [S\zeta_0] = L^{-2}. \end{aligned} \tag{2.5}$$

If we calculate some macroscopic quantity by the model (2.1), the primitive divergences will appear in four dimensions. In order to eliminate these divergences we introduce the renormalised parameters together with the renomalisation factors Z_s':

$$N_0 = N/Z_1 \tag{2.6}$$

$$\zeta_0 = \zeta Z_\zeta \tag{2.7}$$

$$u_0 = u\kappa^{(d-4)/2} Z_2 \tag{2.8}$$

$$g_0\zeta_0/\eta = g\kappa^{(d-4)/2} Z_\zeta \tag{2.9}$$

with κ being the short distance reference cut-off, where u and g are the dimensionless renormalised coupling constants. Note here that we did not introduce an additional renormalisation factor for g. In the critical dynamics the streaming interaction coefficient has been shown to be unchanged by renormalisation transformation (Kawasaki and Gunton 1977, Gunton and Kawasaki 1976). The calculation of the dynamic exponent z (Oono and Freed 1981b) also shows that there is no renormalisation of g.

We have *assumed* the renormalisability of the model (2.1). It is shown up to the first order of u and g, that the above renormalisation factors are indeed sufficient.

Now we wish to see the scaling behaviour of some observable quantity in the limit $a/N \to 0$. We illustrate it with the normalised end-to-end distribution function

$$G_B(N_0, \boldsymbol{R}, S\zeta_0, u_0, g_0, \alpha) = \langle \delta(\boldsymbol{c}(0) - \boldsymbol{c}(N_0) - \boldsymbol{R})\rangle, \tag{2.10}$$

where the average is taken with respect to the steady solution of (2.1). The explicit parameter dependence of G_B is shown in (2.10). By noting (2.6)–(2.9), G_B is related to the renormalised distribution G in the limit $a/\kappa \to 0$ as

$$G_B(N_0, \boldsymbol{R}, S\zeta_0, u_0, g_0, a) = ZG(N, \boldsymbol{R}, S\zeta, u, g, \kappa), \tag{2.11}$$

where we have provided Z for the renormalisation of $\boldsymbol{c}(\boldsymbol{r})$, although Z will be shown to be unity up to $O(u)$. Since G_B should not depend on the reference parameter κ, we may impose the condition

$$\kappa(\mathrm{d}G_B/\mathrm{d}\kappa) = 0. \tag{2.12}$$

From (2.11) and (2.12) we have the renormalisation group equation for G:

$$\left(\kappa\frac{\partial}{\partial\kappa} + \beta_u(u)\frac{\partial}{\partial u} + \beta_g(u, g)\frac{\partial}{\partial g} + \kappa\frac{\mathrm{d}\ln Z}{\mathrm{d}\kappa} + \kappa\frac{\mathrm{d}\ln Z_1}{\mathrm{d}\kappa}N\frac{\partial}{\partial N} - \kappa\zeta\frac{\mathrm{d}\ln Z_\zeta}{\mathrm{d}\kappa}\frac{\partial}{\partial\zeta}\right)G = 0, \tag{2.13}$$

where

$$\beta_u(u) = \kappa(\mathrm{d}u/\mathrm{d}\kappa) \tag{2.14}$$

$$\beta_g(u, g) = \kappa(\mathrm{d}g/\mathrm{d}\kappa). \tag{2.15}$$

At the fixed-point values $u = u^*$ and $g = g^*$ defined by $\beta_u(u^*) = 0$ and $\beta_g(u^*, g^*) = 0$, (2.13) reduces to

$$\left(\kappa\frac{\partial}{\partial\kappa} + A + BN\frac{\partial}{\partial N} - C\zeta\frac{\partial}{\partial\zeta}\right)G = 0, \tag{2.16}$$

where

$$\begin{aligned} A &= \kappa(\mathrm{d}\ln Z/\mathrm{d}\kappa)|_{u=u^*,g=g^*} \\ B &= \kappa(\mathrm{d}\ln Z_1/\mathrm{d}\kappa)|_{u=u^*,g=g^*} \\ C &= \kappa(\mathrm{d}\ln Z_\zeta/\mathrm{d}\kappa)|_{u=u^*,g=g^*}. \end{aligned} \tag{2.17}$$

The general solution of (2.16) is given by

$$G(N, \boldsymbol{R}, S\zeta, \kappa) = \kappa^{-A}\hat{G}(\boldsymbol{R}, \kappa N^{-1/B}, \kappa(S\zeta)^{1/C}), \tag{2.18}$$

where $\hat{G}$ is an arbitrary but well defined function. The usual dimensional analysis, on the other hand, shows that G should satisfy

$$G(N, \boldsymbol{R}, S\zeta, \kappa) = \lambda^{-d/2}G(N/\lambda, \boldsymbol{R}\lambda^{-1/2}, S\zeta\lambda^2, \kappa/\lambda), \tag{2.19}$$

where λ is a positive parameter. It is found from (2.18) and (2.19) and after some manipulations that G takes the form

$$G(N, \boldsymbol{R}, S\zeta) = N^{(2A-d)/2(1-B)}\hat{G}(\boldsymbol{R}N^{-1/2(1-B)}, S\zeta N^{(2-C)/(1-B)}), \tag{2.20}$$

where we have put κ to be unity. The expression (2.20) is the final scaling form of the normalised end-to-end distribution function under the flow. The explicit function $\hat{G}(\boldsymbol{x}, y)$ with the exponents A, B and C are obtained by a perturbation expansion of G and by the evaluation of Z factors and the fixed-point values u^* and g^*. This program will be performed in the subsequent sections.

3. End-to-end distribution with the excluded-volume interaction under the flow

Here we calculate the end-to-end distribution function up to the first order of u_0 and carry out the renormalisation procedure to obtain the scaling function. The hydrodynamic interaction will be considered in the next section.

The model (2.1) with the velocity field (2.4) satisfies automatically the potential condition (the detailed balance condition). Therefore when g_0 is absent, we easily obtain the steady-state probability function $\partial P_s/\partial t = 0$:

$$P_s \equiv P_0P_1 = \exp\left[-\frac{1}{2}\int \mathrm{d}\tau\left(\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}\tau}\right)^2 + \frac{S\zeta_0}{2}\int \mathrm{d}\tau\{(c^x)^2-(c^y)^2\} - \frac{u_0}{2}\int \mathrm{d}\tau\int \mathrm{d}\tau'\,\delta(\boldsymbol{c}(\tau)-\boldsymbol{c}(\tau'))\right] \tag{3.1}$$

where

$$\boldsymbol{c} = (c^x, c^y, \boldsymbol{c}_\perp). \tag{3.2}$$

P_0 and P_1 denote the quadratic parts and the interaction part of the exponential respectively. In order for the variance $\langle c(\tau)c(\tau')\rangle$ to be finite, we note the restriction that $\zeta_0SN^2 < \pi^2$. See equation (A1.2) in appendix 1.

By expanding P_s in powers of u_0, we obtain the following form of the end-to-end distribution:

$$G_B(N, \boldsymbol{R}, S) = G_B^{[0]}(N, \boldsymbol{R}, S) + G_B^{[1]}(N, \boldsymbol{R}, S) + \mathrm{O}(u_0^2) \tag{3.3}$$

where

$$G_B^{[0]}(N, \boldsymbol{R}, S) = \langle\delta(\boldsymbol{c}(0)-\boldsymbol{c}(N)-\boldsymbol{R})\rangle_0 \tag{3.4}$$

$$G_B^{[1]}(N, \boldsymbol{R}, S) = -\frac{u_0}{2}\int \mathrm{d}\tau\int \mathrm{d}\tau'\{\langle\delta(\boldsymbol{c}(0)-\boldsymbol{c}(N)-\boldsymbol{R})\delta(\boldsymbol{c}(\tau)-\boldsymbol{c}(\tau'))\rangle_0$$
$$-G_B^{[0]}(N, \boldsymbol{R}, S)\langle\delta(\boldsymbol{c}(\tau)-\boldsymbol{c}(\tau'))\rangle_0\}. \tag{3.5}$$

The average $\langle \ldots \rangle_0$ is taken over the probability function P_0. In the evaluation of (3.4) and (3.5) we need various correlation functions, such as $\langle(c^x(\tau)-c^x(\tau'))^2\rangle$ and $\langle(c^x(0)-$

$c^x(N))(c^x(\tau)-c^x(\tau')))$. The expressions of these correlation functions will be provided in appendix 1. The zeroth-order distribution $G_B^{[0]}$ is given by

$$G_B^{[0]}(N, \boldsymbol{R}, S)=\frac{(F(w)F(\mathrm{i}w))^{1/2}}{(2\pi N)^{d/2}}\exp[-r_x^2F(w)-r_y^2(F(\mathrm{i}w)-r_\perp^2] \tag{3.6}$$

where

$$w^2=\zeta SN^2 \tag{3.7}$$

$$r_i^2=R_i^2/(2N) \tag{3.8}$$

$$F(w)=\tfrac{1}{2}w\cot\tfrac{1}{2}w. \tag{3.9}$$

The vector $\boldsymbol{r}_\perp$ is the perpendicular part of the scaled end-to-end distance. In the limit $S\to 0(w\to 0)$, $F(0)=1$ so that (3.6) becomes the Gaussian form. The calculation of the first-order correction $G_B^{(1)}$ is tedious but straightforward. The final form is given by

$$\begin{aligned}G_B^{[1]}(N, \boldsymbol{R}, S)&=-[N^2u_0/(2\pi N)^{d/2}]G_B^{[0]}(N, \boldsymbol{R}, S)\tfrac{1}{2}w(\sin\tfrac{1}{2}w\sinh\tfrac{1}{2}w)^{1/2}\\&\quad\times\int_0^1\mathrm{d}x\int_x^1\mathrm{d}y\,\{x^{(d-2)/2}[\sin\tfrac{1}{2}wx\sinh\tfrac{1}{2}wx\sin\tfrac{1}{2}w(1-x)\\&\quad\times\sinh\tfrac{1}{2}w(1-x)]^{1/2}\}^{-1}\{(1-x)^{(2-d)/2}\exp[-r_x^2F(w)K(x, y, w)\\&\quad-r_y^2F(\mathrm{i}w)K(x, y, \mathrm{i}w)-r_\perp^2x/(1-x)]\\&\quad-(1+K(x, y, w))^{-1/2}(1-K(x, y, \mathrm{i}w))^{-1/2}\}\end{aligned} \tag{3.10}$$

where

$$K(x, y, w)=\sin\tfrac{1}{2}wx[\cos\tfrac{1}{2}w(1-y)]^2/[\cos\tfrac{1}{2}w\sin\tfrac{1}{2}w(1-x)]. \tag{3.11}$$

Now we apply the renormalisation procedure. Since the renormalised value of u_0 turns out to be of order $\varepsilon=4-d$, we may perform the integrals of (3.10) in four dimensions. In order to eliminate the strong cut-off dependence of (3.10), we extract the divergent part in (3.10) which contains the multiplicative factor of $\ln(a/N)$:

$$\begin{aligned}G_B^{[1]}(N, \boldsymbol{R}, S)_{\mathrm{div}}&=-\frac{u_0}{(2\pi)^2}G_B^{[0]}(N, \boldsymbol{R}, S)\ln(N/a)\\&\quad\times\left[1+\frac{1}{4}(1-2r_x^2F(w)\left(\frac{w}{\sin w}+1\right)+\frac{1}{4}(1-2r_y^2F(\mathrm{i}w))\left(\frac{w}{\sinh w}+1\right)-r_\perp^2\right].\end{aligned} \tag{3.12}$$

Now we can determine the renormalisation factors Z_1, Z and Z_ζ, which may be expanded as

$$Z=1+bu+\ldots \tag{3.13}$$

$$Z_1=1+b_1u+\ldots \tag{3.14}$$

$$Z_\zeta=1+b_\zeta u+\ldots. \tag{3.15}$$

From (2.11) the renormalised G is written as

$$G(N, \boldsymbol{R}, S\zeta, u, g, \kappa)=Z^{-1}G_B(N/Z_1, \boldsymbol{R}, S\zeta Z_\zeta, u_0, g_0, a). \tag{3.16}$$

Up to the first order of u, we can use (3.6) for G_B. Then we expand the right-hand side of (3.16) in terms of u and compare it with (3.12). Thus the factors Z'_s are given up to order u by

$$b = 0 \tag{3.17}$$

$$b_1 = b_\zeta = (1/4\pi^2)\ln(\kappa/a). \tag{3.18}$$

In order to determine the remaining renormalisation factor Z_2, a second-order calculation is necessary. We here simply employ the result obtained by Ohta *et al* (1981b):

$$Z_2 = 1 + (u/\pi^2)\ln(\kappa/a). \tag{3.19}$$

Putting (2.8), (2.14) and (3.19) together we have up to order u,

$$\beta_u(u) = u(\mathrm{d}\ln u/\mathrm{d}\ln\kappa) = u(\tfrac{1}{2}\varepsilon - u/\pi^2). \tag{3.20}$$

Thus the fixed-point value u^* is given by

$$u^* = \tfrac{1}{2}\pi^2\varepsilon + \mathrm{O}(\varepsilon^2). \tag{3.21}$$

Accordingly the exponents A, B and C defined by (2.17) are evaluated up to order ε as

$$A = 0 \tag{3.22}$$

$$B = C = u^*/4\pi^2 = \varepsilon/8. \tag{3.23}$$

Thus the end-to-end distribution (2.20) takes the form with the usual static exponent ν and the dynamic exponent z

$$G(N, \boldsymbol{R}, S\zeta) = N^{-d\nu}\hat{G}(\boldsymbol{R}N^{-\nu}, N^{z\nu}S\zeta) \tag{3.24}$$

where

$$\nu = \tfrac{1}{2}(1 + \tfrac{1}{8}\varepsilon + \mathrm{O}(\varepsilon^2)) \tag{3.25}$$

$$z = 4 - \tfrac{1}{4}\varepsilon + \mathrm{O}(\varepsilon^2). \tag{3.26}$$

These agree with the result by Al-Noaimi *et al* (1978). In the absence of the hydrodynamic interaction the phenomenological scaling argument (de Gennes 1979) predicts

$$z = 2 + 1/\nu. \tag{3.27}$$

See also Oono and Freed (1981b). Equations (3.25) and (3.26) are consistent with (3.27).

Before performing the numerical computation of $\hat{G}$, we evaluate the analytic form for sufficiently small values of $N^{z\nu}\zeta S$. From (3.6) and (3.10) $G(N, \boldsymbol{R}, S)$ is written up to $\mathrm{O}(w^2)$ as

$$G(N, \boldsymbol{R}, S) = (2\pi N)^{-d/2}\exp\left(-\frac{R^2}{2N}\right)\left\{1 - \frac{\varepsilon}{8}I(R) + \frac{w^2}{24}\frac{R_x^2 - R_y^2}{N}\left[1 - \frac{\varepsilon}{8}I(R) + \exp\left(\frac{R^2}{2N}\right)\mathrm{Ei}\left(-\frac{R^2}{2N}\right)\right]\right\} \tag{3.28}$$

where

$$I(R) = \left(\frac{R^2}{2N} - 2\right)\ln\left(\frac{a}{N}\right) + \left(\frac{R^2}{2N} - 1\right)\left(\ln\frac{R^2}{2N} + \gamma\right) - \frac{R^2}{2N}. \tag{3.29}$$

We have used the fixed-point value u^* of (3.21). $\mathrm{Ei}(x)$ is the exponential integral. γ is Euler's constant (0.5771 . . .). Thus we have

$$\hat{G}(\hat{\boldsymbol{R}}, \hat{S}) = (2\pi)^{-d/2}\hat{R}^{\varepsilon/4}\exp\left\{-\hat{R}^{2+\varepsilon/4}+\frac{\varepsilon}{8}[\hat{R}^2+\gamma(1-\hat{R}^2)]\right\}$$

$$\times\left\{1+\frac{1}{12}\hat{S}(\hat{R}_x^2-\hat{R}_y^2)\left[1-\frac{\varepsilon}{8}\mathrm{e}^{\hat{R}^2}\,\mathrm{Ei}(-\hat{R}^2)\right]\right\} \tag{3.30}$$

where

$$\hat{\boldsymbol{R}} \equiv \frac{\boldsymbol{R}}{2N^{\nu}} \tag{3.31}$$

$$\hat{S} = N^{z\nu}\zeta S. \tag{3.32}$$

In the limit $\hat{S} = 0$ we recover the result by Oono *et al* (1981).

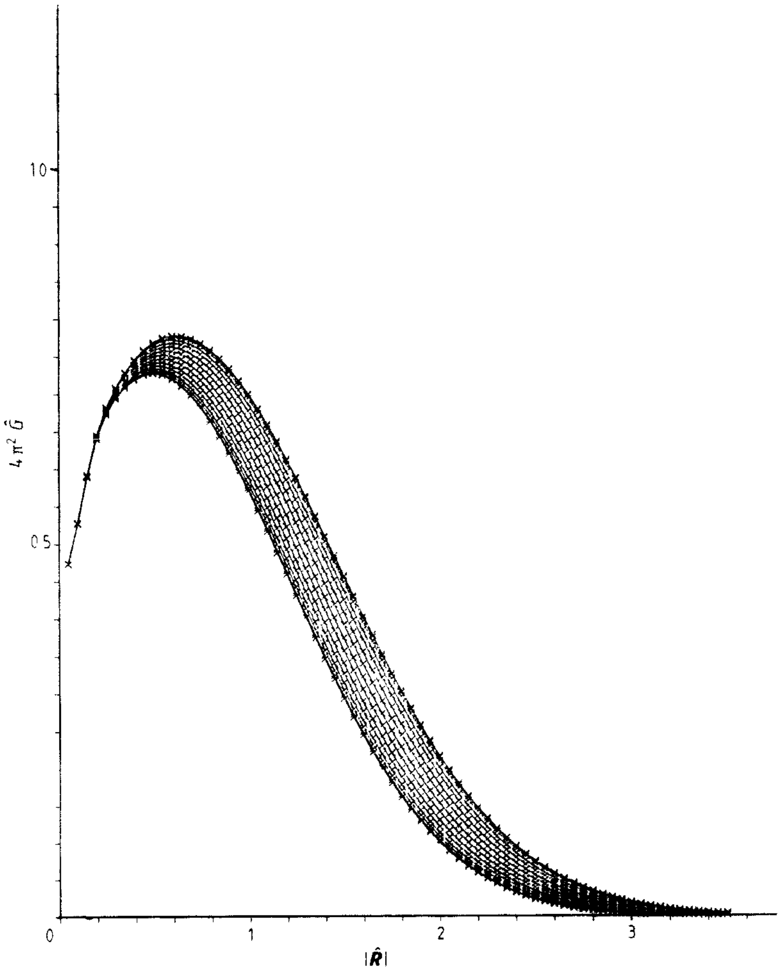

Figure 2. The end-to-end distribution function $4\pi^2\hat{G}(\hat{\boldsymbol{R}}, \hat{S})$ for the parameters $\hat{w} = 1.5$ and $\hat{\boldsymbol{R}} = 0$. The curves represent the distribution function for the polar angles $\theta = n\pi/30$ ($n = 0, \ldots, 15$) defined through $\hat{R}_\alpha = |\hat{\boldsymbol{R}}|\cos\theta$. The intensity of the distribution decreases with increasing θ.

We have performed the numerical computations of $\hat{G}$ for general values of $\hat{S}$ ($\hat{S} < \pi^2$). As shown above the divergent part (3.12) can be absorbed in the zeroth-order term with modification of the exponents. Therefore, we may calculate (3.10) with the subtraction of (3.12) so that no divergences appear in four dimensions. Figure 2 displays $4\pi^2\hat{G}(\hat{\boldsymbol{R}}, \hat{S})$ for the parameters $\hat{w} = 1.5$, $\varepsilon = 1$ and $\boldsymbol{R}_\perp = 0$. The curves represent the distribution functions for the angles $\theta = n\pi/30$ with $n = 0, 1, \ldots 15$ defined by $\hat{R}_x = |\hat{\boldsymbol{R}}| \cos\theta$. The contour lines of $\hat{G}(\hat{\boldsymbol{R}}, \hat{S})$ are shown in figure 3. The broken lines show $\hat{G}(\hat{\boldsymbol{R}}, 0)$ for comparison. Thus we can see that the end-to-end distribution is distorted and is very anisotropic due to the flow.

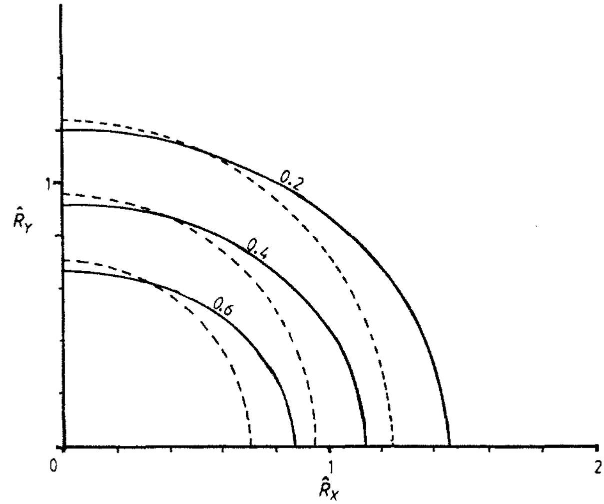

Figure 3. The contour lines of $4\pi^2\hat{G}(\hat{\boldsymbol{R}}, \hat{S}) = 0.2$, 0.4 and 0.6 with $\hat{w} = 1.5$ and $\boldsymbol{R} = 0$. $\hat{G}(\hat{\boldsymbol{R}}, 0)$ for the respective values are plotted by the broken curves.

4. Effects of the hydrodynamic interaction

The hydrodynamic interaction does not affect any static properties in equilibrium. However, in the steady-state sustained by the flow the interaction is very important. Here we wish to study the effects to the end-to-end distribution up to the first order of the interaction strength.

First we need to obtain the steady-state probability function P_{st} in the presence of the hydrodynamic interaction. Since we are interested in the first-order corrections, we do not consider the cross-effects of the excluded-volume interaction and the hydrodynamic interaction. Therefore we put $u_0 = 0$ in (2.2). We do not use the simple pre-averaged Oseen tensor approximation. The expression of P_{st} is obtained by the expansion with the functional Hermite polynomials. The calculation will be represented in appendix 2. Unfortunately since the final form of P_{st} is very complicated we have to employ a further approximation. Namely, we take account only of the leading nontrivial eigenstates. In the terminology of the boson representation of the Fokker–Planck equation (Fixman 1965) this means that only the two-particle excited states are considered. As described in appendix 2 we can show exactly that no logarithmic anomaly appears from other states. The two-particle excited state includes the pre-averaged Oseen tensor term only where the logarithmic divergence appears. Under these approximations P_{st} is given as follows:

$$P_{st}=P_0-(g_0\zeta_0^2/2)\sum_{\alpha,\beta}S^\beta\int d\tau\int d\tau'\Big\{\langle T^{\alpha\beta}(\tau,\tau')\rangle_0\Big[c^\beta(\tau)c^\beta(\tau')-\langle c^\beta(\tau)c^\beta(\tau')\rangle_0\Big]$$
$$+U^{\alpha\beta}(\tau,\tau')\Big[c^\alpha(\tau)(c^\alpha(\tau)-c^\alpha(\tau'))-\langle c^\alpha(\tau)(c^\alpha(\tau)-c^\alpha(\tau'))\rangle_0$$
$$-\sum_{p,q}V^\alpha(p,q,\tau,\tau')c_p^\alpha c_q^\alpha\Big]\Big\}P_0 \tag{4.1}$$

with

$$\boldsymbol{S}=(S,-S,\boldsymbol{0})$$

where U and V are given by (A2.16) and (A2.17) in appendix 2. The first term of (4.1) is same as obtained by the pre-averaged Oseen tensor approximation.

Now we calculate the correction $G_H^{(1)}(N,\boldsymbol{R},S)$ of $G(N,\boldsymbol{R},S)$ by the hydrodynamic interaction. The average of (2.10) is taken with respect to (4.1) so that we obtain

$$G_H^{[1]}(N,\boldsymbol{R},S)=-G^{[0]}(N,\boldsymbol{R},S)(g_0\zeta_0^2/2)\sum_{\alpha,\beta}S^\beta\frac{1}{\chi_{0N}^\alpha}\left(\frac{(R^\alpha)^2}{\chi_{0N}^\alpha}-1\right)$$
$$\times\int d\tau\int d\tau'\Big[\langle T^{\alpha\beta}(\tau,\tau')\rangle_0\langle(c^\beta(0)$$
$$-c^\beta(N))c^\beta(\tau)\rangle_0\langle(c^\beta(0)-c^\beta(N))c^\beta(\tau')\rangle_0$$
$$+U^{\alpha\beta}(\tau,\tau')\Big\{\langle(c^\alpha(0)-c^\alpha(N))c^\alpha(\tau)\rangle_0\langle(c^\alpha(0)-c^\alpha(N))(c^\alpha(\tau)-c^\alpha(\tau'))\rangle_0$$
$$-\frac{16}{N^2}\sum_{\substack{p,q\\ \text{odd}}}V^\alpha(p,q,\tau,\tau')/(\lambda_p^\alpha\lambda_q^\alpha)^2\Big\}\Big] \tag{4.2}$$

where χ_{0N}^α and λ_p^α are defined by (A1.6) and (A1.2) in appendix 1. The divergent part of (4.2) is extracted as

$$G_H^{[1]}(N,R,S)_{div}=\frac{3g_0\zeta_0}{64\pi^2\eta}\ln(N/a)G_B^{[0]}(N,R,S)$$
$$\times\left[(1-2r_x^2F(w))\left(\frac{w}{\sin w}-1\right)+(1-2r_y^2F(iw))\left(\frac{w}{\sinh w}-1\right)\right]. \tag{4.3}$$

We can easily verify that this divergence is completely absorbed into the renormalisation factor of Z_ζ. By the same method described in § 3, Z_ζ is found to be given by

$$Z_\zeta=1+\frac{u}{4\pi^2}\ln(\kappa/a)+\frac{3g}{16\pi^2}\ln(\kappa/a). \tag{4.4}$$

This is correct up to the first order of u and g. The fixed-point value g^* is obtained by the relation $\beta_g=0$ with

$$\beta_g(u,g)=g\frac{d\ln g}{d\ln\kappa}=g\left(\frac{\varepsilon}{2}-\frac{u}{4\pi^2}-\frac{3}{16\pi^2}g\right) \tag{4.5}$$

where we have used (2.9). From (3.21) and (4.5) we have

$$g^*(3/16\pi^2)=\tfrac{3}{8}\varepsilon. \tag{4.6}$$

The constant b_ζ evaluated in § 3 without the hydrodynamic interaction is now modified as follows

$$b_\zeta = \tfrac{1}{8}\varepsilon + \tfrac{3}{8}\varepsilon = \tfrac{1}{2}\varepsilon. \tag{4.7}$$

Hence the dynamic exponent z introduced in the scaling function (3.24) is given by

$$z = 4 - \varepsilon + \mathrm{O}(\varepsilon^2). \tag{4.8}$$

This is consistent with the phenomenological prediction by de Gennes (1979) $z = d$. (4.8) also agrees with the result by Al-Noaimi *et al* (1978). See Oono and Freed (1981b) also.

The correction to the scaling function is obtained by putting $g_0\zeta_0/\eta = g^*$ in (4.2) and by subtracting the divergent term (4.3). When w is small enough, we can easily evaluate the correction. If we combine it with (3.30), the first-order term of $\hat{S}$ in (3.30) has an additive correction so that it reads

$$\tfrac{1}{12}\hat{S}(\hat{R}_x^2 - \hat{R}_y^2)[1 - \tfrac{1}{8}\varepsilon \mathrm{e}^{\hat{R}^2}\,\mathrm{Ei}(-\hat{R}^2) + \tfrac{7}{8}\varepsilon + \tfrac{1}{4}\varepsilon(-\tfrac{1}{24} + J)] \tag{4.9}$$

where

$$J = \frac{32}{N^4}\int_0^1 \mathrm{d}x \int_x^1 \mathrm{d}y \frac{y-2}{x} \sum_{\substack{p,q\\ \mathrm{odd}}} V(p, q, \tau, \tau')/(\lambda_p\lambda_q)^2$$

$$\simeq 0.0765. \tag{4.10}$$

The exponent z contained in $\hat{S}$ is now given by (4.8). We can see from (4.9) that both of the two nonlinearities have a tendency to strengthen the anisotropy of the distribution function. In particular, the hydrodynamic interaction is found up to $\mathrm{O}(\hat{S})$ to give the multiplicative correction to $\hat{S}$ of the zeroth-order distribution.

5. Anisotropic scattering function

In this section we will study the effect of the flow to the polymer scattering function. This is a quantity directly measurable by a light scattering technique. Since the monomer density $\rho(\boldsymbol{r})$ is given by

$$\rho(\boldsymbol{r}) = \int \mathrm{d}\tau\,\delta(\boldsymbol{c}(\tau) - \boldsymbol{r}) \tag{5.1}$$

the normalised scattering function $I(\boldsymbol{k})$† is written as

$$I(\boldsymbol{k}) = \frac{1}{N^2}\int \mathrm{d}\tau \int \mathrm{d}\tau' \langle \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{c}(\tau) - \boldsymbol{c}(\tau'))]\rangle. \tag{5.2}$$

When the flow is absent, $I(\boldsymbol{k})$ has been calculated up to order ε by taking account of the excluded-volume effect (Ohta *et al* 1981a, b). The result shows that the excluded-volume effect produces about 5% correction to the zeroth-order scattering function. When S is finite, the calculation becomes very complicated. In the present calculation of $I(\boldsymbol{k})$ we ignore both the excluded-volume effect and the hydrodynamic interaction. Even in this simplest case we cannot obtain a closed analytic form of $I(\boldsymbol{k})$.

† The function $I(\boldsymbol{k})$ should not be confused with $I(R)$ defined by (3.29).

The average in (5.2) is now taken with respect to the probability distribution $P_0(\{c\}, S)$ given by (3.1). Thus we have the anistropic scattering function:

$$I(\boldsymbol{k}) = \hat{I}(K_x, K_y, K_z, w)$$
$$= 2\int_0^1 dx \int_x^1 dy \exp(-K_x^2 F(x, y, w) - K_y^2 F(x, y, \mathrm{i}w) - K_z^2 x) \tag{5.3}$$

where

$$K_i^2 = k_i^2 \langle G^2 \rangle \tag{5.4}$$

with $\langle G^2 \rangle$ the mean-square radius of gyration in three dimensions. The function F has been defined in (3.9). In the regime where the K_i are small enough we may expand (5.3) in terms of K_i. Thus we obtain

$$\hat{I}(\boldsymbol{K}, w) = 1 - \frac{K_z^2}{3} - \frac{K_x^2}{w \sin w}\left(\frac{\sin w}{w} - \cos w\right) + \frac{K_y^2}{2 \sinh w}\left(\frac{\sinh w}{w} - \cosh w\right) + \ldots . \tag{5.5}$$

The scattering function is distorted by the flow so that it exhibits an ellipse on the K_x–K_y plane. In order to see the behaviour for arbitrary values of K_i we have performed a numerical computation of (5.3). Figure 4 represents the result for $w = 1.5$. The scattering function with $w = 0$

$$\hat{I}(K, 0) = 2\left(\frac{1}{K^2} - \frac{1}{K^4} + \frac{1}{K^4} \mathrm{e}^{-K^2}\right) \tag{5.6}$$

is also shown for comparison by the broken curves. We expect that the qualitative features of the flow effect do not change by the nonlinear interactions neglected here.

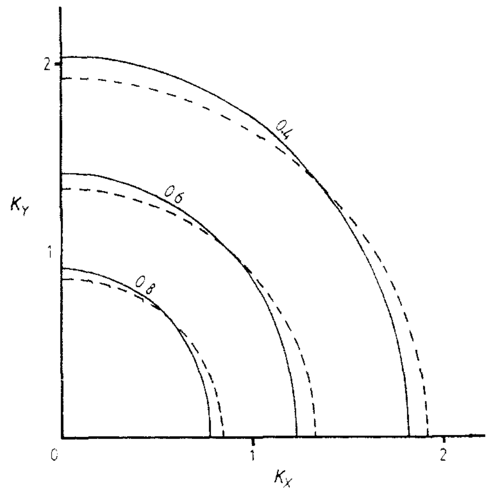

Figure 4. The anisotropic scattering function $\hat{I}(\boldsymbol{k}, w)$ with $w = 1.5$. The broken curves represent $\hat{I}(\boldsymbol{k}, 0)$.

6. Discussion

We have studied the properties of a polymer chain in the non-equilibrium steady state. Although calculations of the exponent z have been performed by several authors, to our knowledge this is the first attempt of a systematic application of the renormalisation group theory to the polymer dynamics†.

The anisotropic end-to-end distribution has been obtained up to $O(\varepsilon)$ with the inclusion of corrections from the excluded-volume and hydrodynamic interactions. The end-to-end distribution of a single chain would be observed by the neutron scattering experiment of a dilute polymer solution labelled at the end-points by isotopes. However, accurate experiments seem to be necessary in order to detect the anisotropy due to flow.

Extension of the present calculation to other quantities such as the intrinsic viscosity will be reported in a separate paper.

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Appendix 1

Here we wish to summarise the correlation functions for $\boldsymbol{c}(\tau)$. The zeroth-order solution P_0 of equation (2.1) can be written as

$$P_0 = \prod_{p,\alpha} (\lambda_p^\alpha/\sqrt{2\pi}) \exp[-(\lambda_p^\alpha c_p^\alpha)^2/2] \tag{A1.1}$$

where

$$(\lambda_p^\alpha)^2 = (\pi p/N)^2 - S^\alpha \zeta \tag{A1.2}$$

and c_p^α is the Rouse coordinate defined by

$$c_p^\alpha = \sqrt{2/N} \int_0^N \mathrm{d}\tau\, c^\alpha(\tau) \cos(\pi p \tau/N) \qquad (p = 1, 2, \ldots, \infty). \tag{A1.3}$$

From (A1.1) we have

$$\langle c_p^\alpha c_q^\beta \rangle = (\lambda_p^\alpha)^{-2} \delta_{p,q} \delta_{\alpha,\beta}. \tag{A1.4}$$

In this Appendix the average is taken with respect to P_0. The inverse Fourier transform of (A1.4) gives us

$$\langle c^x(\tau) c^x(\tau') \rangle = -\frac{N}{2w \sin w}[\cos w(y-1) + \cos w(x-1)] + \frac{2N}{w^2} \tag{A1.5}$$

where $x = |\tau - \tau'|/N$ and $y = (\tau + \tau')/N$ and w has been defined by (3.7). Based on (A1.5) we can write various formulae:

$$\begin{aligned}\chi_{\tau,\tau'}^x &\equiv \langle (c^x(\tau) - c^x(\tau'))^2 \rangle \\ &= 2N \sin(wx/z) \sin[(1-x)w/2](1 + K(x, y, w))/(w \sin(w/2))\end{aligned} \tag{A1.6}$$

† The evaluation of the exponent z has been performed by Oono and Freed (1981b) from the general point of view of the Wilson–Kadanoff-type renormalisation group theory.

$$\langle (c^x(0) - c^x(N))^2 \rangle = N/F(w) \tag{A1.7}$$

$$\langle (c^x(0) - c^x(N))(c^x(\tau) - c^x(\tau')) \rangle$$
$$= -2N \sin(wx/2) \cos[w(y-1)/2]/(w \cos(w/2)) \tag{A1.8}$$

where $F(w)$ and $K(x, y, w)$ have been given by (3.9) and (3.11) respectively. The following formulae are also useful:

$$\langle c^x(\tau)(c^x(\tau) - c^x(\tau')) \rangle$$
$$= -\frac{N}{2w \sin w} \left\{ \cos w\left(1 - \frac{2\tau}{N}\right) + \cos w - \cos w(y-1) - \cos w(x-1) \right\} \tag{A1.9}$$

$$\langle c^x(\tau)(c^x(0) - c^x(N)) \rangle = N \sin[(1 - 2\tau/N)w/2]/(w \cos(w/2)). \tag{A1.10}$$

The correlation functions for $c^y(\tau)$ are obtained if we replace w by $\mathrm{i}w$ in the above expressions.

Appendix 2

Here we describe the derivation of the steady probability distribution function P_{st} and the end-to-end function $G_{\mathrm{H}}^{(1)}$ used in § 4. P_{st} is defined by

$$(\mathscr{L}^0 + \mathscr{L}^{\mathrm{h}})P_{\mathrm{st}} = 0 \tag{A2.1}$$

where $\mathscr{L}^0$ is the Fokker–Planck operator of (2.1) for $u = g = 0$. $\mathscr{L}^{\mathrm{h}}$ consists of the hydrodynamic interaction

$$\mathscr{L}^{\mathrm{h}} = g \sum_{\alpha,\beta} \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \frac{\delta}{\delta c^\alpha(\tau)} T^{\alpha\beta}(\tau, \tau') \left(-\ddot{c}^\beta(\tau') + \frac{\delta}{\delta c^\beta(\tau')} \right). \tag{A2.2}$$

P_{st} is to be obtained by the expansion in powers of g:

$$P_{\mathrm{st}} = P_0(1 + P_1 + \ldots) \tag{A2.3}$$

$$\mathscr{L}^0 P_0 = 0 \tag{A2.4}$$

$$\mathscr{L}^{\mathrm{h}} P_0 = -\mathscr{L}^0 P_0 P_1 \tag{A2.5}$$

where P_{st} and P_0 are properly normalised, i.e. $\int \mathrm{d}\{\boldsymbol{c}\} P_{\mathrm{st}} = \int \mathrm{d}\{\boldsymbol{c}\} P_0 = 1$. In order to get the first-order correction P_1 we utilise the method of the functional Hermite polynomial expansion (Yamakawa 1971). We can easily check that $\mathscr{L}^0$ satisfies the following eigen-equation:

$$(\mathscr{L}^0 - E_{\{n_p^\alpha\}}) P_0 \prod_{p,\alpha} H_{n_p^\alpha}(\lambda_p^\alpha c_p^\alpha) = 0 \tag{A2.6}$$

with

$$(\lambda_p^\alpha)^2 = (\pi p/N)^2 - S^\alpha \zeta \tag{A2.7}$$

where $H_n(x)$ is the nth-order Hermite polynomial. The eigenvalue is given by

$$E_{\{n_p^\alpha\}} = -(1/\zeta) \sum_{p,\alpha} n_p^\alpha (\lambda_p^\alpha)^2. \tag{A2.8}$$

Now P_1 is expanded in terms of these eigenfunctions

$$P_1=\sum_{\{n_p^\alpha\}}\Big(\prod_{p,\alpha}H_{n_p^\alpha}(\lambda_p^\alpha c_p^\alpha)\Big/n_p^\alpha!\Big)D\{n_p^\alpha\}\Big/\sum_{\{n_p^\alpha\}}n_p^\alpha(\lambda_p^\alpha)^2 \tag{A2.9}$$

where the coefficients $D\{n_p^\alpha\}$ are given by

$$D\{n_p^\alpha\}=g\zeta^2\sum_{\alpha,p}S^\beta\int \mathrm{d}\tau\int \mathrm{d}\tau'\Big\langle \ddot{c}^\alpha(\tau)T^{\alpha\beta}(\tau,\tau')c^\beta(\tau')\prod_{p,\alpha}H_{n_p^\alpha}(\lambda_p^\alpha c_p^\alpha)\Big\rangle_0. \tag{A2.10}$$

The average in the integrand can be evaluated if we note the formula

$$(2\pi)^{-1/2}\int_{-\infty}^{+\infty}\mathrm{d}x\,\exp\Big[-\frac{x^2}{2}+fx\Big]H_n(x)=(-f)^n\exp\Big[\frac{f^2}{2}\Big]. \tag{A2.11}$$

After a lengthy but straightforward transformation, $D\{n_p^\alpha\}$ is found to be given by

$$\begin{aligned}D\{n_p^\alpha\}=-g\zeta^2\sum_{\alpha,\beta}S^\beta\int\mathrm{d}\tau\int\mathrm{d}\tau'\int_k\frac{1}{k^2}\Big(\delta_{\alpha\beta}-\frac{k^\alpha k^\beta}{k^2}\Big)\exp\Big[-\frac{1}{2}\sum_\gamma(k^\gamma)^2\chi^\gamma_{\tau,\tau'}\Big]\\
\times\prod_{p,\delta}(-\sqrt{2/N}A^\delta(p,\tau,\tau')/\lambda_p^\delta)^{n_p^\alpha}\Big\{\sum_{p'}n_p^\alpha(\lambda_{p'}^\alpha)^2\cos\frac{\pi p'}{N}\tau\Big/A^\alpha(p',\tau,\tau')\\
\times\Big[\sum_{p''}n^\beta_{p''}\cos\frac{\pi p''}{N}\tau'\Big/A^\beta(p'',\tau,\tau')+\mathrm{i}k^\beta\langle c^\beta(\tau')(c^\beta(\tau)-c^\beta(\tau'))\rangle_0\Big]\\
-\delta_{\alpha\beta}\sum_{p'}n_{p'}^\alpha(\lambda_{p'}^\alpha)^2\cos\frac{\pi p'\tau}{N}\cos\frac{\pi p'\tau'}{N}\Big/(A^\alpha(p',\tau,\tau'))^2\Big\}\end{aligned} \tag{A2.12}$$

where

$$A^\alpha(p,\tau,\tau')=\mathrm{i}k^\alpha\Big(\cos\frac{\pi p}{N}\tau-\cos\frac{\pi p}{N}\tau'\Big) \tag{A2.13}$$

and $\chi^\alpha_{\tau\tau'}$ has been defined by (A1.6). Substituting (A2.12) into (A2.9) we obtain the exact expression of P_1. Although (A2.12) is complicated somehow, it provides us with important information on the renormalisation property of the hydrodynamic interaction. Since the divergence will come from the short distance part of $t\equiv|\tau-\tau'|/N\ll 1$, we expand the integrand of (A2.12) in powers of t. Then, after carrying out the integral over $s\equiv|\tau+\tau'|/N$, (A2.12) is shown to have the factor

$$\int_{a/N}^1\mathrm{d}t\,t^{(\Sigma_{p,\alpha}n_p^\alpha-d)/2}. \tag{A2.14}$$

Thus it is verified exactly up to $\mathrm{O}(g)$ that the logarithmic divergence exists only in the states with $\Sigma\, n_p^\alpha=2$ in four dimensions. If we restrict oursleves to the two-particle excited states $\Sigma\, n_p^\alpha=2$, P_1 is given by

$$\begin{aligned}P_1=-(g\zeta^2/2)\sum_{\alpha,\beta}S^\beta\int\mathrm{d}\tau\int\mathrm{d}\tau'\Big\{\langle T^{\alpha\beta}(\tau,\tau')\rangle_0[c^\beta(\tau)c^\beta(\tau')-\langle c^\beta(\tau)c^\beta(\tau')\rangle_0]\\
+U^{\alpha\beta}(\tau,\tau')\Big[c^\alpha(\tau)(c^\alpha(\tau)-c^\alpha(\tau'))-\langle c^\alpha(\tau)(c^\alpha(\tau)-c^\alpha(\tau'))\rangle_0\\
-\sum_{p,q}V^\alpha(p,q,\tau,\tau')c_p^\alpha c_q^\alpha\Big]\Big\}\end{aligned} \tag{A2.15}$$

where

$$U^{\alpha\beta}(\tau,\tau')=\frac{\langle c^{\alpha}(\tau)T^{\alpha\beta}(\tau,\tau')c^{\beta}(\tau')\rangle_0-\langle T^{\alpha\beta}(\tau,\tau')\rangle_0\langle c^{\beta}(\tau)c^{\beta}(\tau')\rangle_0}{\langle c^{\alpha}(\tau)(c^{\alpha}(\tau)-c^{\alpha}(\tau'))\rangle_0} \tag{A2.16}$$

$$V^{\alpha}(p,q,\tau,\tau')=\frac{(\lambda_p^{\alpha})^2-(\lambda_q^{\alpha})^2}{(\lambda_p^{\alpha})^2+(\lambda_q^{\alpha})^2}\cos\frac{\pi p}{N}\tau\cos\frac{\pi p}{N}\tau'. \tag{A2.17}$$

Note that the states with $\Sigma\, n_p^{\alpha}=0, 1$, do not contribute to P_1. Finally, $G_{\mathrm{H}}^{[1]}(N,\boldsymbol{R},S)$ for $\Sigma\, n_p^{\alpha}=2$ is obtained by

$$\begin{aligned}G_{\mathrm{H}}^{[1]}(\mathrm{N},\mathbf{R},S)&=\langle\delta(\boldsymbol{c}(0)-\boldsymbol{c}(N)-\boldsymbol{R})P_1\rangle_0\\&=-G^{[0]}(N,\boldsymbol{R},S)(g\zeta^2/2)\sum_{\alpha,\beta}S^{\beta}\left(\frac{(R^{\alpha})^2}{\chi_{0N}^{\alpha}}-1\right)\Big/\chi_{0N}^{\alpha}\\&\quad\times\int\mathrm{d}\tau\int\mathrm{d}\tau'\Big\{\langle T^{\alpha\beta}\rangle_0\langle(c^{\beta}(0)-c^{\beta}(N))c^{\beta}(\tau)\rangle_0\langle(c^{\beta}(0)-c^{\beta}(N))c^{\beta}(\tau')\rangle_0\\&\quad+U^{\alpha\beta}(\tau,\tau')\Big[\langle(c^{\alpha}(0)-c^{\alpha}(N))c^{\alpha}(\tau)\rangle_0\langle(c^{\alpha}(0)-c^{\alpha}(N))(c^{\alpha}(\tau)-c^{\alpha}(\tau'))\rangle_0\\&\quad-\frac{16}{N^2}\sum_{\substack{p,q\\ \mathrm{odd}}}V^{\alpha}(p,q,\tau,\tau')\Big/(\lambda_p^{\alpha}\lambda_q^{\alpha})^2\Big]\Big\}\end{aligned} \tag{A2.18}$$

where the summations over p and q are restricted to the positive odd integers.

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