A Unified Description of the Transport Properties of Dilute and Semidilute Polymer Solutions

S. Stepanow* and G. Helmis

Technische Hochschule Merseburg, Fachbereich Physik, 0-4200 Merseburg, Germany

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ABSTRACT: By using the renormalization group method, we give to the first order of $\epsilon = 4 - d$ (d is the space dimensionality) a unified description of the effects of the excluded-volume interaction and the hydrodynamic interaction on the self-diffusion coefficient and the viscosity of dilute and semidilute polymer solutions in Θ and good solvents.

1. Introduction

The classical basis of the dynamics of dilute polymer solutions has been developed by Kirkwood,[1] Kirkwood and Riseman,[2] Zimm,[3] and Rouse.[4] The concentration dependence of the transport quantities has been the subject of numerous investigations.[5-7] A special attention in the polymer dynamics has been paid to the question of the screening of the hydrodynamic interaction.[8-12] An important success in the theory of polymer dynamics is connected with the experience that the hydrodynamic interaction can be treated with the aid of the renormalization group method.[13-18] Initially, the RG method was applied to the study of the transport quantities of dilute polymer solutions. This method was used in ref 19 to describe the concentration dependence of the transport quantities such as the viscosity and the self-diffusion coefficient in Θ solvents. In the present article we extend the RG method to include the excluded-volume effects on the transport coefficients. The RG represents a new basis, which permits us to describe the transport coefficients in a broad concentration range (without the entanglements) in a unified way.

2. Calculation Scheme

The self-diffusion coefficient can be represented as a function of the excluded-volume interaction and the hydrodynamic interaction as follows

$$D_s = kTl/(\zeta_0 L) f_D(z, w_0, \zeta_0 lLc/\eta_s, v_0 l^3 c, 1/\epsilon) \qquad (1)$$

where $z = \bar{v}_0 L^{\epsilon/2}$ is the excluded-volume parameter, $w_0 = \bar{\zeta}_0 L^{\epsilon/2}$ is the parameter of the hydrodynamic interaction, $\bar{v}_0 = (d/2\pi l)^{d/2} v_0 l^{-2}$, and $\bar{\zeta}_0 = \zeta_0 (d/2\pi l)^{d/2}/d\eta_s$. l is the statistical segment length, and L is the contour length of the polymer chain. ζ_0 is the monomer friction coefficient, and v_0 is the excluded-volume strength. c is the monomer concentration.

In an analogous way the viscosity $\delta\eta = \eta - \eta_s$ can be written as

$$\delta\eta = \zeta_0 N_A L^2/(12 d\eta_s M) c f_\eta(z, w_0, \zeta_0 lNc/\eta_s, v_0 l^3 c, 1/\epsilon) \quad (2)$$

where M is the molecular weight of the polymer.

The structure of (1) and (2) can be justified as follows. In the dilute solution ($c \rightarrow 0$) the expansion parameters of the transport coefficients are z and w_0.[12] The concentration corrections due to the excluded-volume interaction are prescribed by the theory of the conformational properties.[20] The parameter describing the concentration corrections due to the hydrodynamic interaction is obtained by the dimensional arguments.

The $1/\epsilon$ in (1) and (2) indicates that there in the perturbation expansions of D_s and $\delta\eta$ appear the $1/\epsilon$ poles. It is well-known[12,13] that the renormalization group enables one to remove these poles from the perturbation expansions by redefining the parameters ζ_0, v_0, and L. By carrying out the renormalization of (1) and (2), we obtain

$$D_s = kT/\zeta L' f^{r}_{D}(g, w, \zeta lL'c/\eta_s, vl^3 cL'/L) \qquad (3)$$

$$\delta\eta = \zeta N_A L'^2/12 d\eta_s M c f^{r}_{\eta}(g, w, \zeta lL'c/\eta_s, vl^3 cL'/L) \quad (3')$$

The effective dimensionless interaction constants of the excluded-volume interaction, g, and of the hydrodynamic interaction, w, are defined by

$$g = \bar{v} \lambda_m^{\epsilon/2}, \quad w = \bar{\zeta} \lambda_m^{\epsilon/2} \qquad (4)$$

where λ_m is the final value of the parameter of the renormalization group (see refs 17 and 18). The parameters L', v, and w have been computed to the first order of ϵ as[17]

$$L'/L = Q^{1/4}, \quad v = v_0/Q \qquad (5)$$

$$w = 4zw_0 Q^{-1/4} (\lambda_m/L)^{\epsilon/2}/(4z + w_0(Q^{3/4} - 1)) \qquad (5')$$

with $Q = 1 + (8/\epsilon)\bar{v}_0 \lambda_m^{\epsilon/2}$. From (5) it follows for large λ_m

$$L'/L \simeq \lambda_m^{(2\nu-1)/2\nu} \qquad (6)$$

where $\nu = {}^1/_2 + \epsilon/16 + ...$ is the critical exponent ν computed to the first order of ϵ.

Equations 4–6 fulfill the ultraviolet regularization of the perturbation expansions. They are worthy for dilute solutions and for the semidilute ones and also for renormalization of the dynamical viscosity in the large frequency limit.[17,18] In order to apply (4) and (5) to the study of the scaling behavior, we have to use the matching condition for λ_m.[17,18]

In the dilute limit, semidilute Θ regime, and the semidilute good solvent regime, λ_m is, respectively, given by

$$\lambda_m = L' \qquad (7)$$

$$1/\lambda_m = \zeta lc/12 d\eta_s \qquad (8)$$

$$1/\lambda_m = vl^{-1} cL'/L \qquad (9)$$

In order to obtain (8) and (9), the concentration-dependent renormalization point is used.[19] In that procedure the main effect of the concentration corrections to the transport quantities consists of changing the infrared behavior of their perturbation expansions. As a consequence, the matching condition changes from (7) to (8) and (9). To first order in ϵ, the diffusion coefficient and

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the viscosity are given, respectively, by the prefactors in (3) and (3′) in combination with (4)–(9). In the good solvent semidilute scaling regime, $L \to \infty$, $c \to 0$, the concentration corrections due to the excluded-volume dominate over that due to the hydrodynamic interaction, and for the matching condition we have to use (9). Then, the diffusion coefficient is obtained from (3) and (4) and (9) as

$$D_s \simeq kT/(Lc^{(1-\nu(d-2))/(\nu d-1)}) \qquad (10)$$

With respect to the dependence on L, D_s behaves as prescribed by the Rouse theory. We note that in this paper we do not consider the entanglements. (10) coincides with the well-known scaling prediction for D_s in the semidilute nonentangled concentration regime.

Equations 7–9 enable one to describe, respectively, the dilute regime, the semidilute Θ regime, and the semidilute good solvent regime. In order to describe these three regimes in a united way, we have to combine (7)–(9). The simple way to do this can be achieved as follows:

$$1/\lambda_m = 1/L' + \upsilon l^{-1} cL'/L + l\zeta c/(12d\eta_s) \qquad (11)$$

λ_m is the final value of the parameter of the RG, which is an arbitrary quantity in the ultraviolet renormalized theory. Whereas the ultraviolet behavior is the same in both dilute and semidilute solutions, the infrared behavior is quite different. The consequences of this are (7)–(9). The matching condition[17,18] [(7)–(9) or (11)] are necessary in order to take into account the infrared behavior of the theory, which is responsible for the scaling behavior of the polymer quantities, within the RG method. The arbitrariness of λ_m is a property of the RG method. This arbitrariness does not influence the physical quantities in the exact theory, but it affects them if one carries out the calculations by using the perturbation theory. Thus, the concrete choice of λ_m affects the practical calculations of the transport quantities. Despite this, (11) is fully acceptable from the fundamental point of view.

The different choice of the numerical prefactors in (7)–(9) corresponds to using the different renormalization schemes.[37] We note that (11) (without the third term in the right-hand side) is analogous to that used by Schäfer[21] to describe in a unified way the conformational properties of dilute and semidilute polymer solutions.

Since L', ζ, and υ in (11) are functions of λ_m, (11) yields a nonlinear equation for λ_m, which can be solved numerically.

Using (4)–(6) and introducing the variable $x = \lambda_m/L$, we rewrite (11) as

$$x = Q(x)^{1/4}/(1 + f(Q(x)/Q(x_0))^{-1/2}c/c^*) + (1/12)(\zeta(x)/\zeta(x_0))(Q(x)/(Q(x_0))^{1/4}(c^*/c^*_h)(c/c^*)) \qquad (12)$$

where $c^* = 1/(\upsilon l^{-1}L'^2/L)$ is the overlap concentration for the excluded-volume interaction, $c^*_h = 1/(lw(2\pi l/d)^{d/2}L'^{(d-2)/2})$ is the critical concentration above which the hydrodynamic interaction becomes screened, f is a fit parameter, and x_0 is x for $c = 0$.

The parameter f introduced in (12), which will be considered below as a fit parameter, reflects the above-mentioned ambiguity in the choice of the matching condition. The ratio of c^*/c^*_h is obtained as

$$c^*/c^*_h = (w(x_0)/g(x_0))Q(x_0)^{-1/4}$$

c is the concentration in grams per cubic centimeter.

In order to compare the present theory with experiment, we must not compute c^* and c^*_h for the polymer under consideration but identify c/c^* with the experimental values.

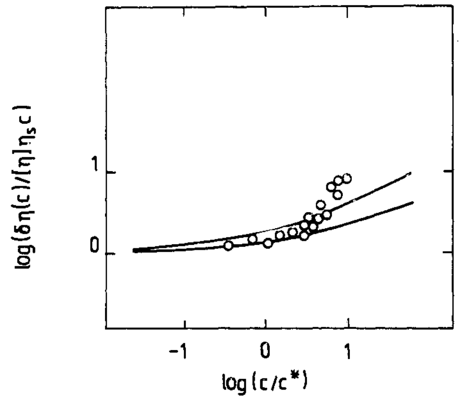

Figure 1. Polymer viscosity versus concentration. The upper and lower curves correspond, respectively, to the excluded-volume parameters $z = 0.3$ and $z = 4$. The parameter of the hydrodynamic interaction, w_0, is 30. Open circles are experimental results due to Takahashi et al.[36] The factor f in (12) is 0.5.

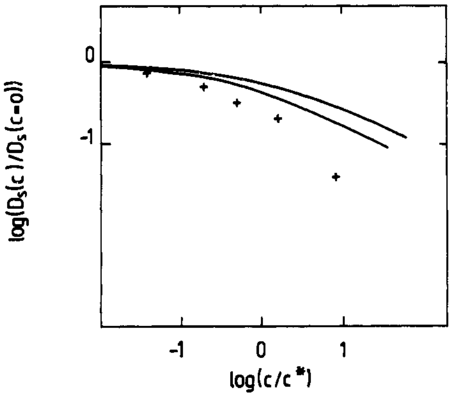

Figure 2. Self-diffusion coefficient versus concentration for $z = 4$ (the upper curve) and $z = 0.3$. $w_0 = 30$. The crosses are experimental data of Leger et al.[22] on polystyrene in benzene for the molecular weight $M = 78\,300$. The data for this M are available for sufficiently low c.

The computation of D_s and $\delta\eta$ occurs as follows. To the first order of $\epsilon = 4 - d$, the functions f^r_D and f^r_η in (3) have to be put equal to 1. The reason for this is that, in the scaling regime, the quantities g, w, ζ, and υ in (3) are proportional to ϵ. To the first order of ϵ, we have the Rouse-like expressions for D_s and $\delta\eta$ with the quantities L' and ζ being renormalized. The latter are given by (5) and (5′) ($\zeta = w\lambda_m^{-\epsilon/2}$) with λ_m obtained by solving (12). The concentration dependences of ζ and L', which determine the concentration dependences of the transport quantities under consideration, are taken into account through the dependence of λ_m on c. Thus D_s and $\delta\eta$ are obtained as

$$\delta\eta(c)/[\eta]\eta_s c = (\zeta(x)/\zeta(x_0))(Q(x)/Q(x_0))^{1/2} \qquad (13)$$

$$D_s(c)/D_s(c{=}0) = (\zeta(x_0)/\zeta(x))(Q(x_0)/Q(x))^{1/4} \qquad (14)$$

$[\eta]$ is the intrinsic viscosity. x_0 in (13) and (14) is $(\lambda_m/L)_{c=0}$.

In Figures 1 and 2 we represent the result of computing the viscosity and the self-diffusion coefficient based on (12)–(14).

The present theory does not take into account the entanglement effects. Thus, comparison with the experiment must be performed in the concentration region where the entanglements are not important. The parameter f is adjusted to achieve the best agreement with the viscosity data. In (13) and (14) we used f as the only fit parameter.

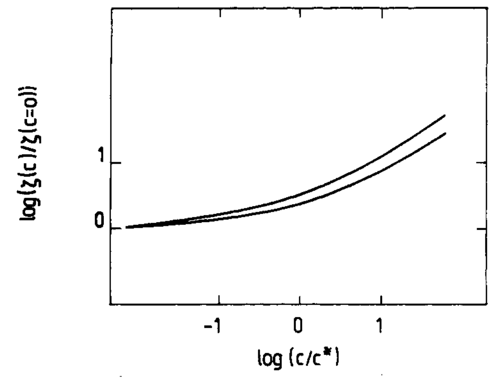

Figure 3. Reduced effective monomer friction coefficient versus concentration for $z = 0.3$ (upper curve) and $z = 4$.

The high values of w_0 are reasoned by the fact that the hydrodynamic interaction seems to be very strong, which in other words means that the nondraining case takes place. Within the RG formalism the strength of the hydrodynamic interaction means that w lies in the vicinity of its fixed point value $w^* \simeq \epsilon$, which demands the high values of w_0. The two values for the excluded-volume parameter z used in Figures 1–3 have to show the dependence of the transport quantities on the quality of the solvent. It is known how to determine z for polymer–solvent systems from experimental data.[25] We are not aware if such a determination of w_0 is also possible.

We see that, by using the ratio c/c^* in order to plot the concentration dependence of the transport quantities, experimental data as well as the theoretical curves do depend on the molecular weight and on the solvent quality. In connection with the study of the cooperative diffusion coefficient, the plotting of the data by using the dynamical overlap concentration produces a universal plot.[23,24] By representing the experimental data on $\delta\eta$ and D_s through the dynamical overlap concentration, one expects to obtain the universal plot, too. The dynamical overlap concentration corresponds to the variable k_Dc in (15). Figure 3 gives the effective monomer friction coefficient versus concentration.

To compute the transport quantities to the order ϵ^2, the computation of $f^r{}_D$ and $f^r{}_\eta$ is necessary. Such a computation has to occur within the dynamical theory of the transport quantities based on the RG method. Such a theory does not exist so far. The theory presented here as well as in ref 19 has to be considered as a precursor of a such dynamical theory. A theory developed by Oono et al.[24] deals with the cooperative diffusion coefficient where the screening of the hydrodynamic interaction does not have a meaning. We note that the theory of the screening of the hydrodynamic interaction developed by Edwards and co-workers[5-7] has quite a different basis. It does not operate with the monomer friction coefficient but starts with the hydrodynamic equations of the solvent coupled to the Langevin equation of polymer chains. The theory developed by Shiwa et al.[10] does not use the RG concept in describing the effects of the hydrodynamic interaction and seems to be related to that of Edwards and co-workers (see refs 34 and 35). The theory developed by Shiwa[26] takes into account the entanglements as well as both the excluded-volume interaction and the hydrodynamic interaction. Regarding the treatment of both latter interactions, this theory does not consider them in a unified way. As analogous to ref 10, the excluded-volume effects are considered on the basis of the RG method whereas the hydrodynamic interaction is considered by using the mode coupling theory. The theory recently developed by Semenov[27] has the aim to describe the influence of the entanglements on the polymer dynamics and do not overlap with the present approach.

For small concentrations (14) gives

$$D_s(c) = D_s(c{=}0)(1 - k_D\bar{c} + ...) \tag{15}$$

where

$$k_D = (3/4)w(1/(1-g))(fz/w_0 Q^{-1/2} + (\zeta/\zeta_0)Q^{1/4}) \tag{16}$$

w, g, and ζ are taken by $c = 0$. In Θ solvents $k_D\bar{c}$ can be represented as

$$k_D\bar{c} = (3/4)w[\eta]c$$

where $\bar{c} = c(N_A/M_s)l^2\zeta_0/12d\eta_s$ is introduced. $[\eta]$ is the intrinsic viscosity. Using the fixed point value for the effective interaction constant of the hydrodynamic interaction to the first order of ϵ, $w^* = (2/3)\epsilon$, we obtain

$$k_D\bar{c} = 0.5[\eta]c \tag{17}$$

Comparing (17) with the expression[9]

$$D_s(c) = D_s(c{=}0)(1 - k_t[\eta]c + ...)$$

we obtain $k_t = 0.5$.

The experimental value of k_t lies in the range of 0.7–0.8 (see refs 9 and 29). k_t was computed previously by other authors. Muthukumar and DeMeuse[28] obtained the value $k_t = 0.75$, Yamakawa, $k_t = 0.2$,[25] Freed,[29] $k_t = 1$, and Perico and Freed,[8] $k_t = 0.58$.

3. Conclusion

By extending the renormalization group description of the dilute solutions to nonzero concentrations, we give a unified description of the transport quantities such as the self-diffusion coefficient and the viscosity in the broad concentration region for both good and Θ solvents. The concentration corrections due to both excluded-volume interaction and hydrodynamic interaction are taken into account.

The proposed description of the transport quantities relies on the Rouse expressions of the transport coefficients for dilute solutions in which the parameters L, v_0, and ζ_0 are replaced by the renormalized ones. The universality of the description is due to the fact that the RG equations for these parameters are the same in both dilute and semidilute limits. The physics, which is different in both regimes, is governed by the value of the final parameter of the renormalization group, i.e., the matching condition. The form of the matching condition can be determined without carrying out the quantitative corrections in the semidilute regime. However, there remains the ambiguity in the choice of the prefactors in the matching condition. These prefactors can be considered as fit parameter.

We note that the proposed approach is an extension of the RG description of the dilute polymer solutions to nonzero concentrations and differs from that proposed in refs 5–10 and 30–35. We consider the approach proposed here as a precursor of a dynamical theory of the transport quantities that treats both the excluded-volume and hydrodynamic effects in the framework of the RG concept.

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