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Crossover effects on the osmotic pressure and the diffusion coefficient in moderately concentrated polymer solutions

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The effects of a finite volume fraction of polymer on the reduced osmotic pressure and the reduced diffusion coefficient in solutions, covering an extended concentration range, are analysed in the framework of a recent theoretical approach, which incorporates a renormalization group treatment of a modified interaction Hamiltonian. The resulting analytical functions are consistent with the large amount of experimental data accumulated from the literature. In the interpretation of the diffusion behaviour, over a large concentration interval, the concept of hydrodynamic screening plays a crucial role in obtaining a uniform picture. In the region of strongly overlapping chains a breakdown of the universal features of the reduced osmotic pressure and the reduced diffusion coefficient can be inferred from the theoretical relations.

(Keywords: osmotic pressure; diffusion; semidilute and concentrated polymer solutions; crossover effects; hydrodynamic screening)

Introduction

It has been known for some years that renormalization group theory provides a framework for a universal description, in the form of explicit analytical functions, of static properties[1-8] (e.g. osmotic pressure) and transport phenomena[9-11] (e.g. cooperative diffusion and sedimentation) of flexible polymer chains in the 'effective' semidilute regime. Some of the theoretical predictions have been compared[12-16] with experimental results, and many essential features of the theoretical models have been endorsed.

An 'effective' semidilute solution may be viewed as a solution in which the polymer coils strongly overlap each other but still occupy a small volume fraction Φ of polymer ($\Phi \ll 1$). In this concentration region the theoretical approaches resort to the Edwards Hamiltonian[17], extended to a many-chain system, to describe the large and strongly correlated fluctuations in the segment density as well as the gradual screening of the excluded-volume interactions. However, it should be recognized that the use of the Hamiltonian is legitimate only if the monomer density is sufficiently small. If this prerequisite is violated departures between experimental results and the theoretical prediction can be anticipated, and eventually (at sufficiently high concentration) a concomitant breakdown of the universality is expected. In a recent work[15] it was found that the theoretical values of the reduced osmotic pressure $\Pi M/RTc$ [where Π is the osmotic pressure, M is the molar mass, R is the gas constant, T is the absolute temperature and c is the mass concentration (mass/volume)] became gradually smaller than the corresponding experimental values for polystyrene at good solvent conditions with increasing degree of coil overlapping. This trend has been reinforced by a previous osmotic pressure study[18] of polystyrene at good solvent conditions, covering an extended concentration range (concentrations up to $\sim 0.8\,\mathrm{g\,cm^{-3}}$), where a palpable breakdown of the universal behaviour of the reduced osmotic pressure was revealed at high concentrations. In order to account for the effects of a finite volume fraction of polymer (Φ), Shiwa *et al.*[19] constructed a generalized Edwards Hamiltonian, incorporating mean field ideas of the Flory–Huggins type[20,21], and with the aid of a renormalization group formalism calculated the osmotic pressure of moderate and concentrated solutions of flexible chains in good solvents.

Since the translational diffusion process is governed by the interplay between hydrodynamic and thermodynamic properties through the relationship[22] $D \cong s\,\partial\Pi/\partial c$ (where s is the sedimentation coefficient and $\partial\Pi/\partial c$ is the inverse osmotic compressibility), analogous concentration related crossover effects as for the osmotic pressure are expected to show up in a comparison between experimental results and the theoretical diffusion models, where the original Edwards Hamiltonian has been invoked as a theoretical tool. The surmise is that if the effects of a finite polymer volume fraction are not accounted for, a gradual deviation between the experimental results and the theoretical diffusion predictions will occur with increasing polymer concentration.

The aim of the present study is to construct, guided by the theoretical advances of Shiwa *et al.*[19], tractable analytical functions in terms of experimentally accessible variables, without any adjustable parameter, to analyse experimental osmotic pressure and diffusion data, covering a wide concentration range. In this report a large amount of experimental osmotic pressure data and diffusion data, collected from the literature, for polystyrene at good solvent conditions are compared with the corresponding theoretical predictions.

Theoretical considerations

In the theoretical treatments of the static correlations of monomer density fluctuations in the 'effective' semidilute regime (low volume fraction of polymer), the many-chain version of the Edwards Hamiltonian constitutes a good starting point to develop renormalization group ideas.

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Previously, a conformation space renormalization group formalism together with the $\varepsilon = 4 - d$ (where d is the spatial dimensionality) expansion has been employed to derive[1,4] an explicit analytical function, in terms of a universal static overlap parameter X, for the reduced osmotic pressure in the 'effective' semidilute range (Π_{SD})

$$\frac{M\Pi_{SD}}{RTc} = 1 + (X/2)\exp\left\{(\varepsilon/4)\left[\frac{\mu^2}{X^2}\ln\mu + \left(1 - \frac{\mu^2}{X^2}\right)\ln(\mu + X) + \frac{\mu}{X}\right]\right\} \quad (1)$$

where $\mu = M_n/M_w$ is a polydispersity parameter. In order to recover the correct scaling behaviour in the asymptotic limit and to account partially for the higher-order corrections of ε the usual augmentation procedure[2–4,9] is adopted here by replacing the factor $(\varepsilon/4)$ by $A \equiv (2 - d\nu)/(d\nu - 1)$ with $d = 3$. The parameter ν is the excluded-volume exponent characterizing the molecular weight dependence of the radius of gyration. For flexible polymers at good solvent conditions, ν assumes a value of 0.588 (the most accurate theoretical value)[23]. The dimensionless static scaling variable X may be expressed as $X \sim c/c^* \sim A_2Mc$ (where c^* denotes the overlap threshold concentration and A_2 is the second virial coefficient). In order to be able to make a direct comparison, without any adjustable parameter, between the theoretical prediction [equation (1)] and the experimental results, the following relation was derived[12]

$$X = [16A_2Mc - 8A\ln(\mu)]/9 \quad (2)$$

In the good 'effective' semidilute regime equation (1) with $(\varepsilon/4)$ substituted by $A = 0.3089$ has been found to be in good agreement with experimental data, and a universal picture emerged.

In this domain where the density fluctuations are strong the mean field theory (e.g. the classical Flory–Huggins theory) fails. However, as the monomer concentration increases the fluctuations will gradually become small and can be treated by a simple mean field theory. Quite recently, Shiwa *et al.*[19] utilized a generalized interaction Hamiltonian, elaborated from the Edwards form of the Hamiltonian in combination with the Flory–Huggins theory, together with a renormalization group scheme for the calculation of the generalized osmotic pressure Π_G for polymer solutions covering a wide concentration range

$$\Pi_G = \Pi_{SD}(X) - k_BTn_0[\ln(1 - \Phi) + \Phi + \Phi^2/2] \quad (3)$$

where k_B is Boltzmann's constant and n_0 is the solvent number density. The second term on the right-hand side of equation (3), represents the Flory–Huggins contribution. The polymer volume fraction can be cast into the following form

$$\Phi = pXM^{1-3\nu} \quad (4)$$

where p is a parameter which depends on the chemical nature of the polymer and solvent, but not on the molar mass of the polymer. In the treatment of Shiwa *et al.*[19], p was considered to be an adjustable variable of the theory. However, for a given polymer/solvent system, where A_2, M, μ and c or Φ all are known, p can easily be determined. In the present study this latter procedure has been adopted.

By using standard definitions and standard thermodynamics[24] for binary systems the solvent number density may be expressed in terms of experimentally accessible quantities as

$$n_0 = \frac{N_A}{v_0M_0}(1 - \Phi) \quad (5)$$

where N_A is Avogadro's number, M_0 is the solvent molar mass and v_0 is the partial specific volume of solvent. By combining equations (1), (3) and (5) the reduced osmotic pressure may be written in the form

$$\frac{M\Pi_G}{RTc} = 1 + (X/2) \times \exp\left\{A\left[\frac{\mu^2}{X^2}\ln(\mu) + \left(1 - \frac{\mu^2}{X^2}\right)\ln(\mu + X) + \frac{\mu}{X}\right]\right\} - \frac{M}{v_0M_0c}\left[(1 - \Phi)\ln(1 - \Phi) + \Phi(1 - \Phi) + (1 - \Phi)\frac{\Phi^2}{2}\right] \quad (6)$$

It is clear from relation (6) that at sufficiently high concentrations, where the effects of a finite volume fraction of polymer cannot be ignored, the reduced osmotic pressure loses its universal feature due to the influence of the second term on the right-hand side of equation (6), and the equation of state will depend on system related properties.

Let us now discuss diffusion properties and the effects of a finite polymer volume fraction on the diffusion behaviour. The reduced diffusion coefficient D/D_0 (where D_0 is the diffusion coefficient at infinite dilution) may be expressed as[14]

$$(D/D_0) = (S/S_0)\frac{M}{RT}(\partial\Pi/\partial c) \quad (7)$$

Recently, Shiwa[10] devised a scheme for a universal description of the reduced diffusion coefficient as a function of a scaling variable. This approach incorporates renormalization group calculations of both hydrodynamic and thermodynamic quantities as well as kinetic equations of the Ginzburg–Landau type for an analytical description of the effect of gradual screening of both hydrodynamic and excluded-volume interactions on polymer solution dynamics. The analysis yields a relationship which may be written in the following functional form

$$(D/D_0) = \frac{(1 + X)^{-3\varepsilon/8}}{H(X)}\frac{M}{RT}(\partial\Pi/\partial c) \quad (8)$$

Here the hydrodynamic screening effect is captured through an enhancement factor $H(X)$, which describes the dragging effect of screening. The factor $H(X)$ is given by[10]

$$H(X) = \alpha^{-(3\varepsilon/8)[\alpha/(1-\alpha)]} \quad (9)$$

with $\alpha = k^2/2(1 + X)$. The parameter k is the inverse of the normalized hydrodynamic screening length[11], which directly describes the influence of hydrodynamic screening on polymer solution dynamics. In the framework of a mode-coupling scheme and renormalization group calculations with the $\varepsilon = 4 - d$ expansion, expressions for the evaluation of the quantity k as a function of the overlap parameter for polymer solutions of flexible chains with and without excluded-volume interactions, were developed[11]. In the absence of hydrodynamic screening $k \to 0$ and $H(X) \to 1$.

Let us now consider the reduced inverse osmotic compressibility $(M/RT)(\partial\Pi/\partial c)$ for the two situations. In the region of 'effective' semidilute behaviour the following relation is obtained[9] by differentiating equation (1)

$$\frac{M}{RT}(\partial\Pi/\partial c)_{\mathrm{SD}}$$

$$= 1 + \left\{\left(1 + \frac{A}{2}\right)X + A\left[\frac{\ln(\mu + X)}{X} - 1\right]\right\}$$

$$\times \exp\left\{A\left[\frac{\mu^2}{X^2}\ln(\mu) + \left(1 - \frac{\mu^2}{X^2}\right)\ln(\mu + X) + \frac{\mu}{X}\right]\right\} \tag{10}$$

In this context it should be mentioned that in the model of Shiwa[10] an expression with a different appearance to equation (10) was devised for the calculation of the reduced osmotic compressibility. A slightly different renormalization group technique, namely, a cut-off method instead of the dimensional regularization scheme to calculate the reduced osmotic compressibility, was utilized. However, the theoretical models of Ohta and Oono[1,4] and Shiwa[10] are identical except for the detail of computation methods, which have different ways to treat higher-order corrections. Since it has been recognized[15,16] that the model of Ohta and Oono is in better agreement with experimental results than the relationship of Shiwa, we have chosen the former approach [equation (10)] in the present work.

Considering now, non-negligible effects of Φ the reduced inverse osmotic compressibility may be obtained by differentiating equation (6). The resulting expression may be cast into the following generalized form

$$\frac{M}{RT}(\partial\Pi/\partial c)_{\mathrm{G}} = \frac{M}{RT}(\partial\Pi/\partial c)_{\mathrm{SD}} + \frac{M}{v_0 M_0}$$

$$\times\left[\ln(1 - \Phi) + \frac{\Phi(3\Phi + 2)}{2}\right] \tag{11}$$

Before we display the final relations for the reduced diffusion coefficient some relevant modifications will be introduced. Adopting the usual augmentation procedure[9] the factor $(3\varepsilon/8)$ appearing in equations (8) and (9) is substituted by $B \equiv -[(d-2)\nu - 1]/[d\nu - 1]$. With $d = 3$ and $\nu = 0.588$ the factor $B = 0.5393$. The static overlap parameter X is known to constitute a universal variable in displaying static properties of polymer solutions in the 'effective' semidilute regime. However, when it comes to dynamic features, such as the reduced diffusion coefficient, the static overlap parameter X has been found[9,13] to be unable to condense the experimental data in a universal manner. In this case the dimensionless variable $k_{\mathrm{D}}c$ [k_{D} expresses the first-order concentration dependence of D; $D = D_0(1 + k_{\mathrm{D}}c)$] was reported[13] to be a more appropriate parameter in the description of universal dynamic behaviour [e.g. in a plot of (D/D_0) *versus* $k_{\mathrm{D}}c$]. In order to facilitate a direct comparison between experimental diffusion data and the theoretical prediction [equation (8) combined with equation (10)] a dynamic scaling parameter x, analogous to the static variable X is introduced by an identification process[9]. If polydispersity effects are neglected the result is

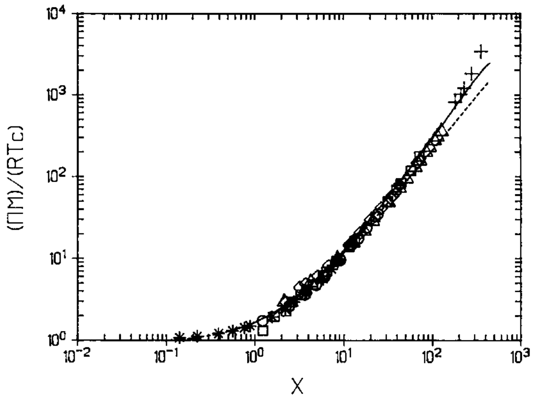

Figure 1 Reduced osmotic pressure as a function of the scaled static variable X, which is given by $X = 2.809 \times 10^{-2}cM^{0.714}$ for polymer–good solvent systems. Polystyrene/toluene[18,28,29]: (✱) $M = 5.1 \times 10^4$; (○) $M = 1.19 \times 10^5$; (△) $M = 6.9 \times 10^5$; (□) $M = 9.0 \times 10^5$; (+) $M = 9.0 \times 10^5$; (◇) $M = 1.9 \times 10^6$. The broken and the solid curves represent equations (1) and (6), respectively

$$x = \frac{k_{\mathrm{D}}c}{\exp(A/2) - B} \tag{12}$$

In light of the above considerations we may now construct explicit functional forms for the reduced diffusion coefficient by combining equation (8) with equation (10) ['effective' semidilute solution behaviour (superscript SD)] and with equation (11) [incorporating the effects of a finite volume fraction of polymer (superscript G)], respectively. The expressions may be presented on the following experimentally tractable forms

$$(D/D_0)^{\mathrm{SD}}_{\mathrm{exp}}/(1 - vc) = \frac{1}{(1 + x)^B H(x)}$$

$$\times\left[1 + \left\{(1 + A/2)x + A\left[\frac{\ln(\mu + x)}{x} - 1\right]\right\}\right.$$

$$\left.\times \exp\left\{A\left[\frac{\mu^2}{x^2}\ln(\mu) + \left(1 - \frac{\mu^2}{x^2}\right)\ln(\mu + x) + \frac{\mu}{x}\right]\right\}\right] \tag{13}$$

$$(D/D_0)^{\mathrm{G}}_{\mathrm{exp}}/(1 - vc)$$

$$= (D/D_0)^{\mathrm{SD}}_{\mathrm{exp}}/(1 - vc) + \frac{1}{(1 + x)^B H(x)}\frac{M}{v_0 M_0}$$

$$\times\left[\ln(1 - \Phi) + \frac{\Phi(3\Phi + 2)}{2}\right] \tag{14}$$

where the dimensionless dynamic scaled variable x is defined by equation (12). The factor $(1 - vc)$, where v is the partial specific volume of the solute, is introduced to approximately correct the experimental diffusion coefficients for backflow effects[25].

Results and discussion

In *Figure 1*, reduced osmotic pressure data for polystyrene of different molecular weights in toluene, over an extended X range, are plotted on log–log axes as a function of the static variable X. The variable $X = 2.809 \times 10^{-2}cM^{0.714}$ has been evaluated using equation (2) (with $\mu = 1$) together with the relation A_2 (cm^3 mol g^{-2}) $= 1.58 \times 10^{-2}M^{-0.286}$ reported[26] for the system polystyrene/toluene. Since the data represent molecular weights with narrow molecular weight distri-

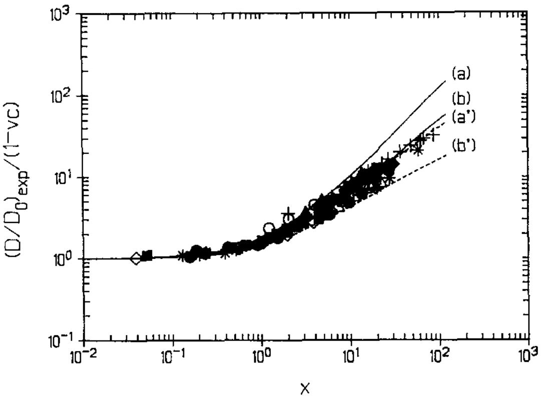

Figure 2 Reduced diffusion coefficient for polystyrene systems at good solvent conditions as a function of the scaled dynamic variable x which is related to k_D by $x = 1.593k_Dc$. Polystyrene/benzene[30–32]: (●) $M = 7.0 \times 10^5$; (✱) $M = 3.8 \times 10^6$; (▲) $M = 8.42 \times 10^6$. Polystyrene/toluene[33,34]: (◇) $M = 2.0 \times 10^5$; (△) $M = 7.6 \times 10^5$; (□) $M = 2.88 \times 10^6$. Polystyrene/tetrahydrofuran[35–38]: (■) $M = 3.9 \times 10^5$; (◆) $M = 9.0 \times 10^5$; (+) $M = 8.42 \times 10^6$; (○) $M = 1.0 \times 10^7$. The broken curves (a') and (b') represent equation (13) in the absence and presence of hydrodynamic screening, respectively. The solid curves (a) and (b) represent equation (14) in the absence and presence of hydrodynamic screening, respectively

butions and it has been shown[1] that the polydispersity effect has a very minor influence on the numerical results of the reduced osmotic pressure, $\mu = 1$ is used in this work. The broken curve is calculated from equation (1), representing the 'effective' semidilute range. At a low degree of chain overlap the agreement between the experimental data and the theoretical representation is good, but at higher values of X a gradual and significant departure is revealed. Obviously, the theoretical model, based on the 'pure' Edwards Hamiltonian, seriously underestimates the values of the reduced osmotic pressure in the domain of high X values. As indicated in the theoretical section this trend is attributed to the effects of a finite volume fraction of polymer.

The solid curve in *Figure 1* has been constructed with the aid of equation (6) with $v_0 = 1.160$, $M_0 = 92.13$, $M = 9.0 \times 10^5$ (this molecular weight was chosen because the experimental data for this sample give rise to the highest values of X) and $\Phi = 63.55XM^{-0.764}$ [cf. equation (4)]. The value of p (63.55) was determined by combining equations (2) and (4) and using experimental data for the system polystyrene/toluene. The agreement between the experimental osmotic pressure data and the generalized theoretical model [equation (6)] is good over an extended X region. Due to the enhanced influence of the last term on the right-hand side of equation (6) with increasing values of Φ, a gradual breakdown of the universality is expected. This effect has already clearly been demonstrated[18,19] for concentrated solutions of polystyrene in good solvents.

Figure 2 compares the experimental results (the same data as in ref. 15) for the reduced diffusion coefficient of polystyrene at good solvent conditions with the theoretical predictions, without any adjustable parameter, given by equations (13) and (14), respectively. The scaled dynamic variable $x = 1.593k_Dc$ has been calculated from equation (12) in combination with the relationships k_D (cm^3 g^{-1}) $= 4.60 \times 10^{-3}M_w^{0.76}$ ($M_w \leqslant 4 \times 10^6$) and k_D (cm^3 g^{-1}) $= 0.519M_w^{0.44}$ ($M_w > 4 \times 10^6$) reported[27] from a systematic study of experimental data of polystyrene in good solvent.

Let us first discuss the features of the theoretical prediction representing the 'effective' semidilute regime [equation (13); broken curves] with [curve (b')] and without [curve (a'); $H(x) = 1$] hydrodynamic screening effects incorporated. Curve (a') is consistent with the experimental data, whereas curve (b') exhibits a progressive deviation from the experimental results at higher values of x. Judging from the picture depicted by only these two curves, one may be tempted to suggest that hydrodynamic screening should not be invoked in the description of diffusion behaviour in solutions of flexible chains at good solvent conditions.

The above assumption is at variance with some experimental and theoretical evidence. However, we argue that the observed trend is merely fortuitous due to an underestimation of the thermodynamic factor in equation (13) [see also equation (11)]. This view is reinforced by the solid curves in *Figure 2*, which are constructed with the aid of equation (14), without any adjustable parameter, for the same system (polystyrene/toluene) and for the same molecular weight ($M = 9.0 \times 10^5$) as were employed in the above analysis of the osmotic pressure results. In this case the relation between Φ and x is given by $\Phi = 133.3xM^{-0.764}$. The numerical difference between this value of p and that used in connection with the evaluation of the osmotic pressure data is due to the difference between the static and dynamic scaling variables. The curve representing the generalized diffusion equation [equation (14)], without hydrodynamic screening [curve (a)] exhibits a marked divergence from the experimental points at high values of x, whereas curve (b) (hydrodynamic screening considered) conforms with the experimental data. In light of this observation and the findings for the reduced osmotic pressure, a uniform picture of the diffusion behaviour over a wide concentration range emerges, if the effects of a finite volume fraction of polymer on the thermodynamic factor is taken into account as well as the effect of hydrodynamic screening. In analogy with the observation for the osmotic pressure, a gradual breakdown of the universality of diffusion with increasing concentration is expected also in this case.

Conclusions

Based on the theoretical model of Shiwa *et al.*, expressions on explicit functional forms in terms of experimentally accessible quantities have been presented to analyse reduced osmotic pressure data and reduced diffusion coefficients of flexible polymer chains at good solvent conditions over an extended concentration regime. It is shown that a much better agreement between the experimental osmotic pressure data and the theoretical prediction, in the region of strongly overlapping chains, may be accomplished by utilizing a generalized relation, incorporating the effects of a finite volume fraction of polymer, for the reduced osmotic pressure, instead of the original uncorrected expression [equation (1)]. Analogous crossover effects were also observed to play an important role in the description of the diffusion behaviour in moderately concentrated solutions. The model that emerges is consistent with the experimental results only if the effect of hydrodynamic screening is taken into account. However, it should be noted that by introducing the effects of a finite volume fraction of polymer in the theoretical models, with the aid of a

Flory–Huggins type interaction Hamiltonian, a breakdown of the universality for the reduced osmotic pressure as well as for the reduced diffusion coefficient is expected at higher concentrations.

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