

A unified model for the structure of polymers in semidilute solution*

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A model is developed to analyse the concentration dependence of the range ξ_p of the monomer pair correlation function. In semidilute solution, three concentration regimes are found for semiflexible molecules and the crossover points between the various regimes are predicted in terms of the characteristic ratio of the chains in dilute solution and in terms of the Flory interaction parameter χ . A simple physical interpretation is given which explains the concentration dependence of ξ_p based on binary contacts initially and then ternary contacts at higher concentration. Temperature-concentration diagrams are developed for several common polymer-solvent systems.

Keywords Semidilute; polymer; solutions; correlations; theory; scaling

INTRODUCTION

The application of scaling methods^{1,2} to polymers in solution led to a dramatic increase in theoretical and experimental interest in polymers in semidilute solution. Scaling provides a simple scheme to predict the concentration dependence of various observables such as radius of gyration of entangled polymers. When coupled with the concepts of hydrodynamic screening and reptation, dynamic quantities such as chain mobility and solution viscosity can also be predicted within numerical factors. Scaling methods unfortunately apply only to systems which display strong swelling due to excluded volume or, stated differently, these methods only apply in the asymptotic limit $N \rightarrow \infty$, where N is the degree of polymerization.

Following the proclamation of scaling laws, a burst of experimental data on static and dynamic properties confirmed the validity of scaling predictions²⁻⁶. Subsequent experimental investigation, however, revealed numerous violations⁷⁻¹³ of scaling laws and questions concerning the sovereignty of the scaling hierarchy inevitably followed^{7,8,14,15}. Based on dynamic data on polystyrene (PS) in various solvents, Schaefer, Joanny and Pincus⁸ (SJP) traced the breakdown of scaling to chain stiffness and demonstrated that most of the experimentally accessible solutions are best treated by perturbation theory in the mean-field approximation consistent with the scheme originally proposed by Edwards¹⁶.

The purpose of the present contribution is to provide a conceptually simple yet predictive scheme to analyse the properties of semidilute solutions from thermodynamic parameters. Although the more simplistic aspects of the SJP scheme are avoided, the basic of SJP conclusions remain: namely that the mean-field formulation covers

most experimentally accessible systems.

Before considering semidilute systems, the single chain problem is reviewed. The purpose of this exercise is to relate the thermodynamic parameters χ and χ_s in Flory theory with the corresponding parameters in the so-called blob model⁶ of chain statistics. This correlation is done for semiflexible molecules where the flexibility is defined by a Kuhn segment length¹⁷ or persistence length.

The analysis of semidilute solutions is based on the postulation of various concentration-dependent crossovers which separate regimes where different physical models are needed to describe solution properties. These crossovers, such as the overlap concentration, are now well known except for that describing the onset of marginal behaviour (the concentration where scaling analysis breaks down). This crossover is traced to chain rigidity and is predictable when based on the thermodynamic properties of the particular polymer-solvent system.

Confirmation of the ideas presented here comes from a large body of experimental data on the structure and dynamics of polymer systems. In subsequent papers, literature data on sedimentation and cooperative diffusion is analysed. These data not only demonstrate the predicted crossovers but also show that marginal behaviour is widespread. In the case of polystyrene (PS) in benzene, new data²³ are reported which in conjunction with existing results show that scaling exponents previously reported for this system result from fitting the data in a crossover regime. Static structural data are also reported⁴⁶ on PS in cyclopentane near the theta point and on PS in butanone. These data are consistent with the model developed here.

Elsewhere the model is used to treat reptation-based quantities such as viscosity and self-diffusion constant²⁴. In most cases, exponents describing the concentration dependence of experimental properties are correctly predicted⁴⁹.

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SWELLING OF A SINGLE SEMIFLEXIBLE CHAIN

In the subsequent description of semidilute solutions, the degree of chain expansion due to excluded volume plays a critical role. In semidilute solution, highly swollen chains are best described by scaling theory whereas weakly swollen coils are best modelled by a perturbation approach¹⁴. In this section the degree of swelling is quantified using the so-called blob model⁶ in which short sequences are presumed to be ideal whereas long sequences are fully swollen due to the repulsive inter-monomer forces which give rise to the excluded volume effect.

The critical parameter in the blob picture is N_τ , the temperature-dependent bond index which marks the transition from ideal to swollen behaviour. The actual chain is viewed as a sequence of blobs or subchains of radius ξ_τ , each containing N_τ bonds in an ideal (random flight) sequence

$$\xi_\tau = (nN_\tau)^{1/2}a \quad (1)$$

where a is the bond length. The parameter n is the number of bonds in a persistence length¹⁷, so the semiflexible chain is modelled as a random sequence of rigid rods of length $b = na$.

The rigidity index n is proportional to the number of bonds in a Kuhn segment⁴⁸. The normal Kuhn definition⁴⁸ of the persistence length is not used because chain-specific factors related to bond angles would have to be introduced. In addition n is defined with respect to the radius of gyration in SJP rather than the end-to-end distance. As a result of these differences we find⁶ $n = (0.83)^2 n'/6$ where n' is the number of bonds per equivalent Kuhn segment and the constant 0.83 is specific to a tetrahedrally bonded chain.

For coils whose radius of gyration is small compared to ξ_τ , the coil is assumed to be ideal so that the radius of gyration is given by the random flight result

$$R_0 = a(nN)^{1/2} = a\left(\frac{C_\infty}{6} N\right)^{1/2}; \quad N < N_\tau \quad (2)$$

where N is the number of bonds and where the subscript θ denotes ideal statistics which are characteristic of chains at the so-called θ temperature. The characteristic ratio C_∞ has been introduced to show that the stiffness n can be extracted from tabulated data⁴⁷, $n = C_\infty/6$.^{*} The characteristic ratio is measured at the theta temperature where $N_\tau = N$.

Chains of sufficiently high molecular weight will deviate from (2) due to excluded-volume-induced swelling. The radius of gyration of a swollen semiflexible chain can be obtained from a generalization of Flory's formula¹⁸ which becomes^{8,20}

$$R_g = a(1 - 2\chi)^{1/5} n^{1/5} N^{3/5}; \quad R \gg \xi_\tau, N \gg N_\tau \quad (3)$$

where $v/a^3 \equiv 1 - 2\chi$ is the excluded volume per monomer, χ being Flory's reduced residual partial-molar free energy of dilution¹⁹. This parameter is generally referred to as the Flory interaction parameter.

* The parameter n depends on the particular measure of chain dimensions being considered. Equation (2) refers to radius of gyration because this length rather than say the end-to-end distance is a reasonable length to use to define the overlap concentration ϕ^*

In the simple blob picture of polymer coils, the transition from (2) to (3) occurs at the critical bond index polymerization N_τ occurring in (1). The parameter N_τ can therefore be found by equating (1) and (3), with the result

$$N_\tau = \frac{n^3}{(1 - 2\chi)^2} \approx \frac{n^3}{(1 - 2\chi_s)^2 \tau^2} \quad (4)$$

The right-hand side of (4) presumes that the excluded volume parameter $(1 - 2\chi)$ is linear in the deviation from the theta temperature, $\tau = (T - \theta)/T$. The parameter χ_s is Flory's reduced residual partial-molar entropy of dilution¹⁹.

Equation (4) shows that the parameter N_τ is directly related to Flory's interaction parameter χ so that in the highly swollen state the two models (blob and Flory) are identical. Near the transition $N = N_\tau$, however, the blob model presumes an unrealistically sharp transition between ideal and self-avoiding statistics²¹. Since the simplicity of the blob picture compensates for the unrealistic nature of the transition near $N = N_\tau$, the treatment below is cast in terms of the blob model. The inadequacies of this approach are corrected by realizing that 'sharp' transitions predicted are in reality broad and smooth changes in statistical properties.

Various classes of thermodynamic and structural data can be used to determine N_τ . N_τ can, for example, be extracted from the molecular weight dependence of any property which depends on the size of the isolated molecule in dilute solution²⁸. Table 1 shows N_τ extracted²³ from the molecular weight dependence of the diffusion constant D using the expression of Akcasu and Han²⁵ for D within the blob model.

Given N_τ , the Flory interaction parameter χ can be found using (4) provided the rigidity index n is known. This parameter, however, can be obtained from the characteristic ratio C_∞ with the result $n = C_\infty/6 = 1.67$ for polystyrene (see previous footnote). Column 9 of Table 1 shows χ calculated on the basis of N_τ in column 8 using (4). For comparison, χ obtained from thermodynamic measurements is shown in column 10. The entropic contribution χ_s to the Flory interaction parameter χ is shown in column 11 assuming $(1 - 2\chi) = (1 - 2\chi_s)\tau$.

There is substantial uncertainty in the value of the parameter χ . Thermodynamic measurements are generally interpreted using some type of mean-field equation coupled with the assumption $w = a^6$. The mean-field assumption is best satisfied at high concentration where errors in the choice of the ternary coupling constant (w) are most severe. Generally values of χ in the table are taken from extrapolations into the dilute regime.

In this section, the basic ideas of the blob model have been extended to semiflexible coils and the parameter N_τ was related to Flory's thermodynamic interaction parameter χ . Either of these parameters, which are related by (4), can be used to characterize chain swelling due to excluded volume. Excluded volume coupled with chain stiffness characterized by n provides the basis for the theory of semidilute solutions outlined below.

The present treatment differs from the previous analysis of SJP⁸ in that SJP assumed that the excluded volume effect was attributed entirely to the geometric contact of Kuhn segments so that $v/a^3 = n^2\tau$. This assumption leads to unrealistic variation of stiffness with solvent quality. In the present treatment n is independent of solvent quality as it should be.

Table 1 Parameters for polymer systems

System	T (°C)	θ (K)	τ	$10^2 \eta$ (Poise)	ν_h	L (Å)	N_r	χ_D	χ	χ_s	$\bar{\phi}$
PS in											
CH ³²	35	307 ¹⁹	0	0.762	0.491	8.19	—	0.5	0.51 ¹⁹	0.21 ¹⁹	—
EA ⁸	25	229 ³⁹	0.232	0.426	0.515	8.66	5240	0.49	0.49 ¹⁸	0.47 ¹⁹	0.001
MEK ³³	25	0 ¹⁹	1	0.38	0.525	8.78	1312	0.47	0.494 ¹⁹	0.50 ¹⁹	0.002
BZ ³	20	(100) ¹⁹	(0.66)	0.649	0.537	9.73	964	0.46	0.44 ¹⁸	0.41 ¹⁸	0.006
CCl ₄ ⁴⁴	22	—	—	0.94	0.520	8.29	550	0.45	—	—	0.006
THF ³⁴⁻³⁶	25	—	—	0.46	0.559	10.13	160	0.41	—	—	0.01
TOL ^{37,38}	20	(160) ¹⁹	(0.46)	0.589	0.567	8.03	100	0.39	0.36 ⁴⁰	0.39 ¹⁸	0.01
EBZ	25	—	—	—	—	—	—	—	0.40 ¹⁹	0.42 ¹⁹	0.01
PAMS in											
TOL ⁴³	25	—	—	0.522	0.534	7.92	386	0.43	0.36 ⁴¹	—	0.03
BZ ⁴³	30	—	—	0.561	0.536	7.87	326	0.43	—	—	0.03
PDMS in											
TOL	20	—	—	—	—	—	—	—	0.43 ⁴²	—	0.03

The parameters L and N_r are extracted from light scattering data on the molecular weight dependence of the diffusion constant D in dilute solution. The parameters are taken from Akcasu and Han's²⁵ expression for D within the blob model. L is roughly the segment length and N_r the crossover bond number. χ is the Flory interaction parameter¹⁹ obtained from thermodynamic measurements. χ_D is obtained from N_r using (4). $\bar{\phi}$ is the volume fraction for the onset of marginal behaviour calculated by (13). η , θ , τ are the viscosity, theta temperature and reduced temperature. ν_h is the effective hydrodynamic exponent: $\nu_h = -(d \log D)/(d \log N)$. χ_s is Flory's entropy parameter. PAMS is poly(α -methyl styrene) ($n = 1.84$) and PDMS is poly(dimethyl siloxane) ($n = 1.0$). The solvents are cyclohexane (CH), ethyl acetate (EA), methyl ethyl ketone (MEK), benzene (BZ), carbon tetrachloride (CCl₄), toluene (TOL) and ethyl benzene (EBZ).

SEMIDILUTE SOLUTIONS

Preliminaries

In dilute solutions, chain statistical properties are adequately described by the blob model outlined above. Although the detailed description of the properties of internal sequences is incorrect in the blob model^{21,22}, it is fair to say that the global properties of dilute chains are understood both experimentally and theoretically. In semidilute solutions, where the chains overlap, the situation is less clear with conflicting experimental data and lack of consensus on theoretical models²³. The basic motivation of this and subsequent papers is to clarify this situation and to harmonize existing data within a unified model which incorporates both scaling and mean-field concepts. The key to success of this approach is the recognition that the limits of validity of scaling can be defined through the parameters which characterize the single chain, namely n , χ and χ_s .

Length scales

Just as in the case of dilute solutions, length parameters form the basis for theoretical analysis of various measurable factors which characterize chain statistics. In dilute solutions, the characteristic lengths are ξ_r and R_g which define chain statistics and overall chain dimensions. Knowledge of the temperature dependence of these lengths allows prediction of the salient features of the scattering structure factor, the diffusion constant, the solution viscosity, etc. In most cases, the persistence length b is inconsequential to the functional dependence of any of these observable factors.

In semidilute solution, the overall size of the constituent chains is no longer the significant length scale for most static and dynamic solution properties. The pair correlation function (or its Fourier inverse, the structure factor), for example, no longer depends on R_g but rather is characterized by a smaller N -independent but concentration-dependent length, ξ_p , the range of the pair

correlation function. The radial dependence of the monomer pair correlation falls off faster in semidilute solutions (i.e. $\xi_p < R_g$) because the concentration of monomers a distance r from any given monomer is dominated by other chains whenever r exceeds the mean distance ξ_2 between monomer-monomer contacts. For $r > \xi_p = \xi_2$ the pair correlation function is dominated by interchain processes which occur at random. This situation is illustrated in Figure 1 which schematically displays the pair correlation function for dilute and semidilute solutions.

In good solvents ξ_p is the screening length which was first introduced by Edwards¹⁶ and is fundamental to all

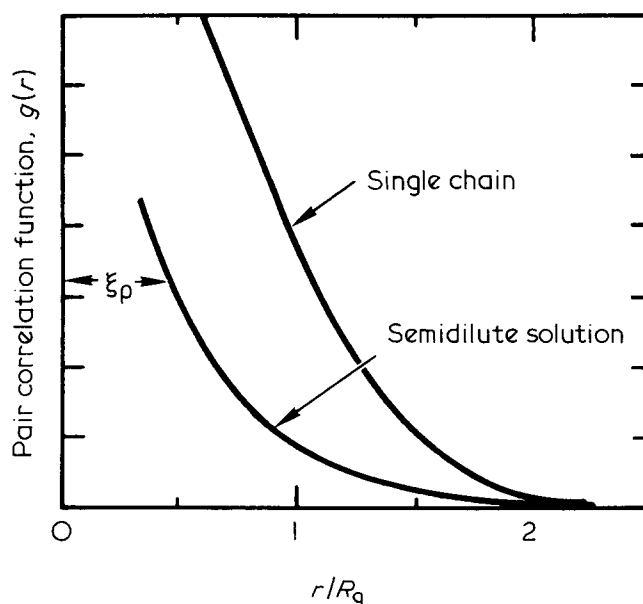


Figure 1 The pair correlation function in dilute and semidilute solution. For dilute solutions $g(r) \sim \exp(-r/R_g)^2$ for $r \gg R_g$ whereas in semidilute solution $g(r) \sim r^{-1} \exp(-r/\xi_p)$ for $r \gg \xi_p$. R_g is the radius of gyration and ξ_p is the screening length. At short distances, $r \ll \xi_p$, both function go as r^{-1} (not shown). In this example $\xi_p = 0.4 R_g$

theories of semidilute solutions. As the concentration increases, intrachain excluded volume interactions are screened by the intervening monomers from other chains, thus weakening the intrachain interaction. In good solvents ξ_p is the distance beyond which there is no excluded volume swelling.

In theta solvents ξ_p should not be thought of as a screening length because there is no effective two-body excluded volume effect to be screened. Nevertheless, correlations exist over distances comparable to ξ_3 , the mean distance between ternary contacts. Therefore in theta solvents $\xi_p \approx \xi_3$ retains its meaning as the range of the pair correlation function.

Since correlations in semidilute solution have been clearly reviewed by de Gennes¹, the point here is merely to justify the derivation of the concentration dependence of ξ_p for semidilute solutions. If ξ_p is known then factors such as the collective diffusion constant, the chain friction constant and the sedimentation constant follow.

Concentration crossovers

Since ξ_p is the fundamental length for semidilute solutions, it is reasonable that changes or crossovers in solution properties occur when ξ_p is comparable to the other lengths such as ξ_r , ξ_2 and ξ_3 . The first such crossover occurs when the chains overlap. Overlap occurs when the range of the pair correlation function (R_g in dilute solution) is equal to the mean distance between chains. This condition defines the overlap monomer concentration ρ^* (monomers/unit volume) and volume fraction $\phi^* = \rho^* a^3$, which specify the boundary between dilute and semidilute solution. For an ideal chain

$$\phi_g^* = \frac{3 N a^3}{4\pi R_g^3} = N^{-1/2} n^{-3/2} \quad (5)$$

For a swollen chain,

$$\begin{aligned} \phi_g^* &= (3/4\pi) N^{-4/5} n^{-3/5} (1-2\chi)^{-3/5} \\ &\approx (3/4\pi) N^{-4/5} n^{-3/5} (1-2\chi_s)^{-3/5} \tau^{-3/5} \end{aligned} \quad (6)$$

The crossover which occurs at ϕ_g^* is schematically illustrated in Figure 2 which shows the characteristic length as a function of volume fraction for a swollen chain. Below ϕ^* this length is just the radius of gyration which, apart from perturbative corrections (virial effects), is concentration independent. Above ϕ^* , the characteristic length is ξ_p which is described above and which decreases as a function of concentration.

Other crossover points $\tilde{\phi}$, ϕ^+ , ϕ_b , are also shown in Figure 2. Although most of the remainder of this paper is devoted to defining these crossovers, it is worthwhile to preview the situation here. Between ϕ_g^* and $\tilde{\phi}$, scaling analysis is valid and the concentration dependence of ξ_p can be found by a variety of scaling arguments. Scaling, however, is an asymptotic theory which applies strictly to an infinite chain. Translated into the present context this limitation requires that ξ_p is much larger than any other length in the problem such as ξ_r or b . Scaling fails, therefore, when $\xi_p = \xi_r$, the condition which defines $\tilde{\phi}$.

Above $\tilde{\phi}$ the chains are nearly ideal and the excluded volume is screened and very weak. Clearly a perturbation approach is indicated¹⁴ and indeed the concentration dependence of ξ_p calculated by linear response theory is in agreement with a considerable body of experimental

data⁸. The perturbation regime where excluded volume effects are weak but not absent is called the marginal regime. In this paper we show that the results of the perturbation calculation can be obtained on the basis of a simple identification of ξ_p with the distance between binary contacts ξ_2 or at higher concentration, the distance between ternary contacts ξ_3 . This analysis provides both conceptual simplicity and also provides the framework for identification of the crossover $\tilde{\phi}$ where $\xi_p \approx \xi_2 = \xi_r$, and another crossover ϕ^+ where ternary interactions dominate ($\xi_p \approx \xi_3$).

In summary, semidilute solutions are analysed by three different approaches under the names good, marginal and theta. These regimes are tabulated in Table 2 which lists the assumptions concerning chain statistics and monomer interaction which apply in each case. In the good solvent, semidilute case, for example, the chains are considered fully swollen and the monomer interaction is a strong two-body effect. In the marginal regime, the chains are ideal within perturbative corrections and weak two-body interactions control the thermodynamics. Finally, in the theta case, ideal chains interact via three-body forces.

At some rather high concentrations the range of the pair correlation function becomes comparable to the persistence length b . At this point, the system is essentially close packed and is no longer tractable by theories which presume each monomer is surrounded by solvent. The crossover ϕ_b defines the upper limit of semidilute behaviour.

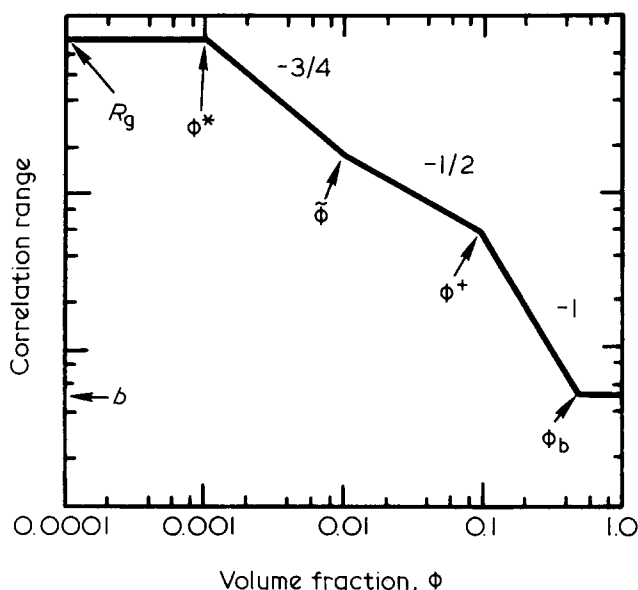


Figure 2 Schematic representation of the concentration dependence of the range of the pair correlation function. The sharp breaks are a consequence of the model and are not expected in real systems

Table 2 Chain statistics and monomer interactions for various concentration regimes

Regime	Statistics $R \sim N^\nu$	Thermodynamics $F/RT = \nu\rho^2 + w\rho^3 + \dots$
Good	$\nu = 3/5$	$w = 0$ (2 body)
Marginal	$\nu = 1/2$	$w = 0$ (2 body)
Theta	$\nu = 1/2$	$\nu = 0$ (3 body)

It needs to be re-emphasized that the crossovers ϕ^* , $\bar{\phi}$ and ϕ^+ do not represent sharp transitions. Indeed all experimental data suggest that the transitions are smooth. Although the present theory predicts a smooth transition at ϕ^+ , a substantially more complex analysis is required to treat the other transition regions. Such an analysis lies beyond the intent of this paper, the aim of which is to understand the properties of semidilute solutions on the basis of conceptually simple physical ideas. In fact theories exist^{26,27} to treat the transition $\bar{\phi}$, and although these treatments are not entirely consistent with the present model, they do show that the transitions are within the scope of current theoretical methods.

The good solvent regime, $\phi^ < \phi < \bar{\phi}$*

In the concentration domain between overlap ϕ^* and marginal behaviour $\bar{\phi}$ the assumptions of scaling theory^{1,2} are valid. Here the concentration dependence of ξ_ρ can be obtained by forcing ξ_ρ to follow power-law behaviour above ϕ^* and to approach R_g correctly when $\phi = \phi^*$ (see Figure 2)

$$\xi_\rho \sim R_g \left(\frac{\phi}{\phi^*} \right)^x \quad (7)$$

The exponent x follows from the known N dependence of R_g and ϕ^* (equations (3) and (6)) coupled with the requirement that ξ_ρ is independent of N

$$\xi_\rho \sim a\phi^{-3/4}n^{-1/4}(1-2\chi)^{-1/4} \quad (8)$$

Although only one small-angle scattering measurement² shows the $\phi^{-3/4}$ power law for ξ_ρ , indirect measurements based on quasielastic light scattering seem to be consistent with this result²³.

It is instructive to show that ξ_ρ in (8) is proportional to ξ_2 , the average distance between binary contacts. This proportionality follows from the scaling law¹ for osmotic pressure π

$$\pi \sim \rho^{9/4} \sim \phi^{9/4} \quad (9)$$

In the semidilute regime π is proportional to the number of binary contacts between chains. Since ρ/N is the chain density, $\rho^{9/4}(N/\rho) = N\rho^{5/4}$ is proportional to the number of binary contacts/chain. If g_2 is the number of monomers between interchain contacts, N/g_2 is also the number of binary contacts/chain, so recalling that $\rho \sim \phi$,

$$\frac{N}{g_2} \sim N\phi^{5/4} \quad (10)$$

or

$$g_2 \sim \phi^{-5/4} \quad (11)$$

Knowing g_2 , the distance between contacts follows from the Flory law:

$$\xi_2 \simeq g_2^{3/5}a \sim a\phi^{-3/4} \sim \xi_\rho \quad (12)$$

The proportionality $\xi_\rho \sim \xi_2$ is important because this relation is not expected to be dependent on chain swelling but only on the fact that binary interactions dominate the thermodynamics. The proportionality can therefore be exploited above $\bar{\phi}$ where scaling assumptions are no longer valid.

The marginal regime, $\bar{\phi} < \phi < \phi^+$

The breakdown of scaling at some concentration $\bar{\phi}$ is

due to the fact that chains are ideal at small length scales in contradiction to (3) which underlies (12). We know from the second section that swelling is found only for distances greater than ξ_2 : the temperature-dependent length which characterizes single chain swelling. The volume fraction $\bar{\phi}$ where (12) fails is found by equating (8) with (1):

$$\bar{\phi} = \frac{3}{4\pi} \frac{(1-2\chi)}{n^3} \quad (13)$$

Since χ is typically about 0.4 and n typically about 2, (13) shows that scaling is valid for volume fractions typically below 0.01. This fact alone explains most of the confusion in the literature concerning the validity of scaling in semidilute solutions.

Above $\bar{\phi}$, the chains are nearly ideal on all length scales. For distances less than ξ_2 , they are ideal because the binary contacts are too sparse to lead to significant swelling. For lengths greater than ξ_ρ , however, ideality is a consequence of the screening effect described above. Above $\bar{\phi}$ binary contacts between monomers occur at random so the system cannot obtain a more energetically favourable situation by chain swelling. The statistics are therefore ideal at all length scales greater than b .

In the situation of random chain statistics it is reasonable to treat the weak excluded volume effect as a perturbation on an ideal chain. This is basically what Edwards¹⁶ and Moore¹⁴ have done for flexible chains and SJP⁸ for semiflexible chains. The concentration dependence of the correlation range ξ_ρ , however, can be obtained by simple physical argument. ξ_ρ should scale with the mean distance ξ_2 between binary contacts so long as the system is sufficiently dilute that ternary contacts are negligible. In this situation the logic leading to (12) implies

$$\pi \sim \phi^2 \quad (14)$$

$$g_\rho \sim g_2 \sim \phi^{-1} \quad (15)$$

$$\xi_\rho \sim \xi_2 \sim \frac{n^{3/2}a}{(1-2\chi)^{1/2}} \phi^{-1/2} \quad (16)$$

The ϕ dependence of ξ_ρ in (16) follows from the present argument although the coefficient requires a full perturbation treatment and is inferred from a straightforward extension of SJP's calculation⁸.

Expressions (15) and (16) are expected to apply between $\bar{\phi}$ and the concentration ϕ^+ at which ternary contributions to the free energy are comparable to two-body effects. The region $\bar{\phi} < \phi < \phi^+$ is called the marginal regime, denoting behaviour intermediate between a good solvent where scaling applies and the theta regime where the effective two-body interaction vanishes. In the original formulation of semidilute solutions by the French school², the marginal regime was not found and a direct transition from good solvent to theta behaviour was predicted (i.e. $\bar{\phi} = \phi^+$). As shown below the absence of a marginal regime is a direct consequence of the assumption of complete chain flexibility.

An attempt has been made to treat the marginal regime by tinkering with scaling laws^{28,29}. Although in some cases it is possible to predict reasonable effective concentration exponents assuming direct crossover from good to theta behaviour, this approach has little experimental or theoretical justification. In addition, temperature predictions for ξ_ρ for this model are at variance with experimental results⁷.

The theta regime

The essential physics of the marginal semidilute regime is random chain statistics and weak binary interactions. As the monomer volume fraction increases, the first assumption is more perfectly satisfied whereas binary interactions are eventually dominated by ternary contributions. By analogy with the theta point in dilute solution, the concentration regime in semidilute solution where three-body effects dominate is called the theta regime. Indeed, at the theta temperature a direct crossover from dilute to semidilute theta behaviour is observed with no intervening marginal or good solvent regime.

The concentration dependence of ξ_p in the theta regime follows from the same argument that led to (12) and (16), except that in this case the osmotic pressure and the number of ternary contacts between chains scale as ϕ^3 and the correlation range ξ_p scales with the mean distance ξ_3 between ternary contacts

$$\pi \sim \phi^3 \tag{17}$$

$$\frac{N}{g_3} \sim N\phi^2 \tag{18}$$

$$\xi_p \sim \xi_3 \sim \frac{an^2}{(wa^{-6})^{1/2}} \phi^{-1} \tag{19}$$

Once again the coefficients in (19) do not follow from (17) and (18) but arise from a straightforward generalization of the linear response calculation^{8,14}. The parameter w is the three-body excluded volume. In Flory theory¹⁹ $w = a^6$ but it is left as a parameter here.

Expression (19) is expected to apply in all semidilute systems where effective three-body effects dominate: at the theta point and at high concentration. At the theta point (19) will apply above ϕ^* in (5). In this case the concentration dependence of ξ_p also follows from scaling arguments³⁰.

Above the theta temperature a good and/or marginal regime lies between the overlap concentration ϕ^* and the concentration ϕ^+ where theta behaviour is expected. The crossover ϕ^+ occurs where two-body contributions to ξ_p are exactly equal to three-body contributions. This concentration is found by equating (16) and (19)

$$\phi^+ = na^3vw^{-1} \simeq 1 - 2\chi \tag{20}$$

assuming $vw^{-1} = (1 - 2\chi)n^{-1}$. Little is known about third virial coefficients but for rod-like segments vw^{-1} should scale⁴⁵ as n^{-1} .

In the present model, the transition at ϕ^+ is smooth. The complete expression for ξ_p throughout the marginal and theta regime follows from linear response theory as in ref. 8:

$$\xi_p = \frac{n^2a}{[n(1 - 2\chi)\phi + wa^{-6}\phi^2]^{1/2}} \tag{21}$$

Concentrated solutions

When the correlation range becomes comparable to the persistence length b , no further concentration dependence is expected since a rod is always correlated over its length. The condition $\xi_p = b = na$ defines the concentrated regime and different crossover concentrations ϕ_m and ϕ_θ occur depending on whether crossover occurs from the marginal or theta regime. From (16) and (19)

$$\phi_m = \frac{n}{1 - 2\chi} \tag{22}$$

$$\phi_\theta = \frac{n}{(wa^{-6})^{1/2}} \simeq n^{-1/2} \tag{23}$$

where $w = n^3a^6$ is the assumed third virial coefficient for the interaction of rod-like segments. Little is known experimentally about concentrated systems and no theory exists to treat such systems.

T-C DIAGRAMS

The various regimes described above can be collected graphically through a temperature-concentration diagram (T - C diagram) as proposed by Daoud and Jannink³¹. Such a diagram is shown in Figure 3 for a 20-unit chain with $n = 1.5$ and $(1 - 2\chi) = \tau$. The various lines in the figure represent the approximate transition regions where the nature of polymer dynamics changes. The line τ^* , for example, separates dilute theta system (region I) from dilute swollen systems (region II). The equation for this line follows from (4) with $N_r = N$. Lines ϕ_θ^* and ϕ_G^* represent the overlap crossover to semidilute solution and follow from (5) and (6) for theta and good solvents.

As discussed above, the semidilute regime is subdivided into good (II), marginal (III) and theta (IV) domains with the crossovers $\tilde{\phi}$ and ϕ^+ defined by (13) and (20). Finally, the crossover ϕ_b to the concentrated regime V is determined by the condition $\xi_p = na$ and follows directly from (22) and (23).

A more universal form of the T - C diagram can be constructed by use of the parameter $(1 - 2\chi) = va^{-3}$ instead of temperature on the ordinate. The semilog version of such a plot is shown in Figure 4 for $N = 3000$ and $n = 1.67$. This value of n is chosen for PS where $n = C_\infty/6 = 1.67$. The behaviour of PS in various solvents can be predicted from horizontal lines at the appropriate values of $(1 - 2\chi)$ obtained from Table 1. Lines appropriate to PS in several solvents are included. Plots like Figure 4 should accurately reflect trends with temperature, chain rigidity and solvent quality, but caution should be exercised in quantitative predictions based on the

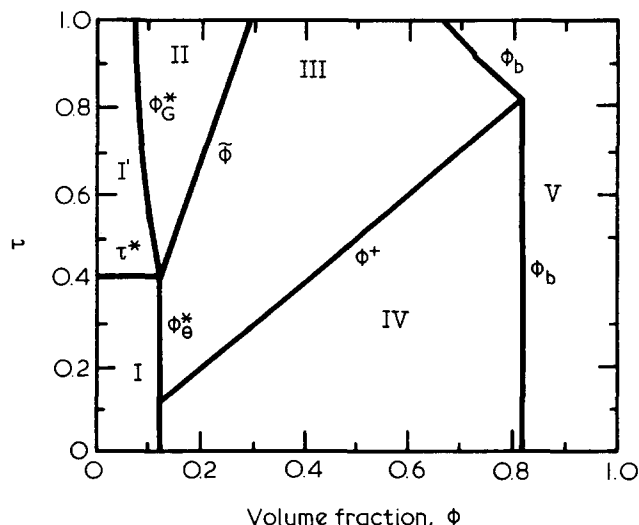


Figure 3 T - C diagram for a 20-unit chain with $n = 1.5$. The excluded volume parameter v is assumed to be linear in the reduced temperature increment $\tau = (T - \theta)/T$

diagrams. After all, the assumptions leading to the diagram are crude and although power-law exponents are probably accurate, the coefficients required for quantitative analysis are largely unknown.

A considerable body of experimental data has accumulated on collective diffusion in semidilute solution²³. These data yield the concentration

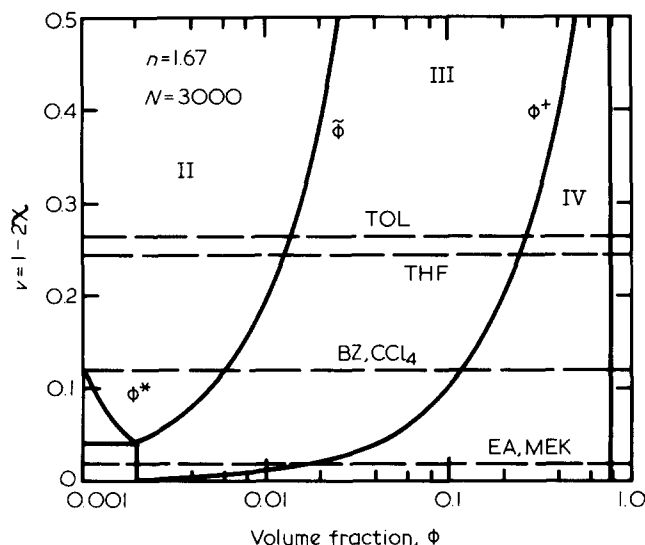


Figure 4 T-C diagram for PS. The ordinate is the coupling constant $(1 - 2\chi) = v a^{-3}$ and various solvents are represented by the horizontal lines. The diagram is drawn for $N = 3000$, $n = 1.67$

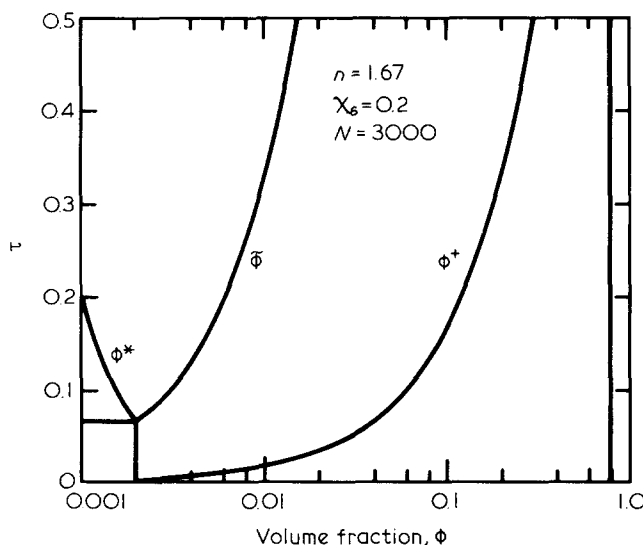


Figure 5 T-C diagram for PS in cyclohexane. This diagram assumes $\chi_s = 0.2$ and that $(1 - 2\chi)$ is linear in the reduced temperature increment $\tau = (T - \theta)/T$. $N = 3000$, $n = 1.67$

Table 3 Predicted dependences of ξ_p , R_g and g_p on various parameters

Regime		ξ_p	R_g	g_p
I	Dilute - theta	—	$(Nn)^{1/2}$	—
I'	Dilute - good	—	$N^{3/5} v^{1/5}$	—
II	Semidilute - good	$\phi^{-3/4} v^{-1/4} n^{-1/4}$	$N^{1/2} \phi^{-1/8} v^{-1/8}$	$\phi^{-5/4} v^{-3/4} n^{-3/4}$
III	Semidilute - marginal	$\phi^{-1/2} v^{-1/2} n^{3/2}$	$N^{1/2}$	$\phi^{-1} v^{-1}$
IV	Semidilute - theta	$\phi^{-1} w^{-1/2} n^2$	$N^{1/2}$	$\phi^{-2} w^{-1}$
V	Concentrated	n	$N^{1/2}$	n

ϕ is the volume fraction, n is the number of monomers in a persistence length, v and w are the two- and three-body excluded volume parameters. For rod-like monomers $v = (1 - 2\chi)a^3 \approx n^2 a^3 \tau$ and $w \approx n^3 a^6$

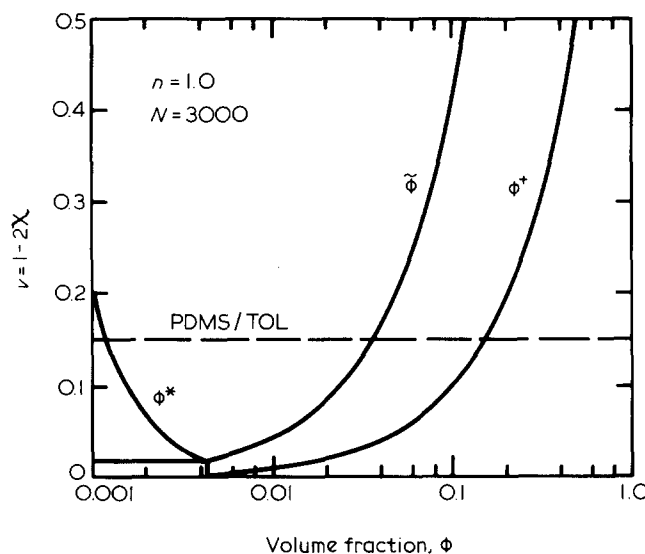


Figure 6 T-C diagram for a very flexible chain $N = 3000$, $n = 1$. This diagram should be appropriate for PDMS. $1 - 2\chi$ for PDMS in toluene is shown as horizontal line

dependence of ξ_p and generally exponents of $-1/2$ are found in concentration regimes near the predicted crossover ϕ . These results suggest therefore that the ϕ line should occur at lower concentration than shown in Figure 4.

For systems like PS in cyclohexane (CH) where $(1 - 2\chi)$ is a strong function of temperature, it is possible to construct a temperature-concentration diagram as shown in Figure 5. This diagram assumes $\chi_s = 0.2$ and $1 - 2\chi = (1 - 2\chi_s)\tau$. The diagram should be reasonably accurate for PS in CH and probably is fairly close for PS in cyclopentane as well.

The marginal regime (III) is found only in stiff polymer chains. Figure 6 shows the T-C diagram appropriate to a highly flexible chain such as PDMS where $n = C_\infty/6 = 1.0$. For $n = 1$ region III is very small and it is conceivable that the crossover occurs directly from good to theta regime so the marginal regime would not be observed.

The n , N , v , w and ϕ dependences of g_p , ξ_p and R_g are collected in Table 3 for the various temperature-concentration regimes.

CONCLUSIONS

The model presented in this paper attempts to predict the behaviour of polymer systems from dilute solution to bulk. On the basis of structural and thermodynamic data, the parameters χ , χ_s and n can be found for any polymer system. These parameters can then be used to generate T-C diagrams similar to Figure 4.

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