Liquid–Liquid Phase Separation in Polydisperse Polymer Solutions: The Distribution Coefficient†

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ABSTRACT: Phase separation in polymer solutions is highly asymmetric: an inhomogeneous dilute phase of isolated coils is in equilibrium with a homogeneous concentrated solution. Many deviations from the simple Flory–Huggins predictions, found experimentally, can be traced back to this fact. Here, a previously introduced improved description obtained by an explicit coupling of configurational statistics to thermodynamics is extended to polydisperse polymer solutions. It is shown to predict a chain length dependence of the distribution of polymer molecules over the two phases that differs from the original F–H predictions but agrees well with experimental results.

1. Introduction

The common discussion about liquid–liquid phase separation in polydisperse polymer solutions is based on the classical Flory–Huggins expression for the free energy of mixing. Within the quasibinary approach, this expression takes the form

$$\frac{\Delta G}{RT} = N_s \ln \phi_s + \sum_n N_n \ln \phi_n + gN_s\phi \qquad (1)$$

where N_s and ϕ_s are the number and volume fraction of solvent molecules, N_n and ϕ_n are the number and volume fraction of polymer molecules with chain length n, ϕ is the volume fraction of all polymer molecules together, and g is a dimensionless interaction function, which will in general depend on temperature and concentration but not on chain length.[1–3] In its most simple form, g will even be independent of concentration; however, already the introduction of contact surfaces per core volume as the interaction determining entity will make g concentration dependent.[4] The most obvious deficiency of eq 1 in relation to polymer solutions is the implicit assumption of a homogeneous segment distribution. In reality, a phase-separated system consists of a diluted phase in equilibrium with a concentrated phase. The diluted phase is characterized by the presence of isolated polymer coils in a sea of solvent for which the assumption of a homogeneous segment distribution is clearly violated. As a consequence, various predictions based on this free energy function turn out to be wrong.

In this paper we will concentrate on one particular aspect of phase separation in polydisperse solutions: the distribution of polymers of a given chain length over the two phases. This property is of major interest for the process of fractionation[5] and consequently attracted considerable interest in the past.[6–8] According to the simple Flory–Huggins approach, the distribution of component n with chain length n over the two phases, the distribution coefficient, satisfies

$$\phi_n''/\phi_n' = \exp(-\sigma n) \qquad (2)$$

where ϕ_n'' and ϕ_n' represent the volume fraction of the polymer component with chain length n in the diluted and concentrated phases of volumes V'' and V', respectively. σ is a complicated constant, which is, however, independent of the specific polymer component (i.e. chain length) considered. In practice, this equation is often written in the following way, introduced by Breitenbach and Wolf[6]

$$\ln(w_n''/w_n') = \ln r - \sigma n \qquad (3)$$

where r is the phase volume ratio V''/V' and w_n denotes the mass of polymer species n. Hence, this approach predicts a linear chain length dependence of the logarithm of the distribution coefficient. Experimentally, this is clearly not found. Extensive research by Koningsveld and co-workers[8,9] on polystyrene with a broad molecular weight distribution in cyclohexane confirmed older experimental data, indicating a much weaker chain length dependence.

The most apparent deficiency of the Flory–Huggins expression for dilute solutions is the Van Laar type exchange interaction contribution, which presupposes a homogeneous segment distribution. In order to have a description that covers the entire concentration regime from dilute to concentrated, Stockmayer and co-workers[7] proposed a "bridging" expression for the interaction parameter g

$$g = g_{dil}P + g_{conc}(1 - P) \qquad (4)$$

where P is defined as the probability that a small volume element in the solution contains no polymer segments. As a first approximation, an expression for P is derived using the unperturbed random walk size of the coils. This leads to

$$P = \exp(\lambda_0 \sum_n \phi_n \sqrt{n}) = \exp(-\lambda_w \phi) \qquad (5)$$

where λ_0 and λ_w are constants, the latter being inversely proportional to the critical overlap concentration under θ conditions. Next, eq 4 is simplified to

† It is a pleasure to dedicate this paper to Professor Ron Koningsveld on the occasion of his 70th birthday.

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$$g = g_{\text{conc}} + g^{*}P \tag{6}$$

with

$$g^{*} = \lim_{\phi \to 0}(g_{\text{dil}} - g_{\text{conc}}) \tag{7}$$

Then an expression for g^* is derived on the basis of dilute solution theory.[10] It amounts to equating the virial expansion for the chemical potential (or osmotic pressure) obtained within the dilute solution theory to the corresponding expression obtained using eqs 1 and 6. Ultimately, this leads to

$$g^{*} = \frac{\left(\frac{1}{2} - \chi_1\right)\left(1 - \sum_n \sum_m w_n w_m h(z_{nm})\right)}{1 + \lambda_{\text{w}}} \tag{8}$$

where $h(z_{nm})$ denotes the excluded volume function representing the effect of the molecular weight distribution on the second virial coefficient. Various expressions for $h(z_{nm})$ are available. Stockmayer and co-workers[8] used the following semi-empirical function introduced by Stockmayer[11]

$$h(z) = \frac{1}{(1 + 2.865z)} \tag{9}$$

For polydisperse solutions z_{nm} is given by the Flory–Krigbaum[12] expression

$$z_{nm} = C\left(\frac{1}{2} - \chi_1\right)\left[\frac{1}{2}\left(\frac{\sqrt{n}}{m}\right)^{2/3} + \left(\frac{\sqrt{m}}{n}\right)^{2/3}\right]^{-3/2} \tag{10}$$

Furthermore, χ_1 is defined by

$$\chi_1 = \lim_{\phi \to 0}\left[g_{\text{conc}} - \phi_{\text{s}}\left(\frac{\partial g_{\text{conc}}}{\partial \phi}\right)\right] \tag{11}$$

Since for various polymer/solvent systems semi-empirical expressions for g_{conc} are available, these equations provide a complete description of the thermodynamics of polydisperse polymer solutions. As far as the distribution coefficient is concerned, the final result can be cast in the form

$$\ln\left(\frac{w_n''}{w_n'}\right) = \ln r - D - An - Bn^{3/2} - C_n n \tag{12}$$

where A, B, C, and D represent complicated functions of which only C depends on n. Using this procedure, the authors[8] observed that although improved agreement with the experimentally determined phase boundary and distribution coefficient is obtained, much more remains to be done.

In the above description the derivation of eq 5 for P is based on the assumption that the polymer coils have their unperturbed Gaussian size. It is well-known that in reality the polymer coils are somewhat collapsed in the diluted phase compared to the concentrated phase. In a later stage[13] the above given description has been extended to include explicitly the concentration dependence of the polymer coil size. Still, it turned out to be impossible to describe all thermodynamic findings for a given polymer/solvent pair with a single free energy expression. For instance, the influence of the molecular weight distribution on the spinodals could be described with one set of parameter values, which, however, failed to describe the distribution coefficient and vice versa.

In this paper we will introduce a new approach to this old problem, based on a model formulated some years ago by one of us.[14] In the present paper our objective is to demonstrate that the explicit coupling of the configurational statistics to the thermodynamics, characteristic of this approach, leads to a distribution coefficient that depends on the chain length in a way observed experimentally.

2. Theoretical Approach

The theoretical approach that we apply in this study is based on looking at a single chain with all its intramolecular interactions exactly taken into account and the intermolecular interactions taken in a mean-field approximation. This approach, originally developed to treat surfactant molecules in amphiphilic aggregates[15] and later generalized to bulk[14] and inhomogeneous polymeric systems,[16] has been shown to provide excellent quantitative predictions for conformational and thermodynamic properties. Furthermore, it is the first theoretical approach that predicted the variation of the critical volume fraction with molecular weight found experimentally for polymer solutions.

One of the main advantages of the theory is that it treats explicitly the coupling between the conformational degrees of freedom of the chains with the thermodynamic behavior. Thus, the two types of properties can be studied within the same theoretical framework. This will be shown to be very important in the understanding of the polydisperse solutions on which we concentrate our attention in this work.

The central quantity of the theory is the probability distribution function (pdf) of chain conformations, $P_n(\alpha_n)$, where the subscript n denotes the chain length of the molecules and α_n is the conformation of the chain. From the knowledge of the pdf we can calculate any desired average conformational and thermodynamic property. In ref 14 it was shown how one can derive the theory by explicitly looking at the many chain partition function of the system. Here we present a simpler, alternative, derivation that leads to identical results. The idea is to write the Helmholtz free energy of the system in terms of the pdf and from its minimization to find the functional form of the pdf to be used in the calculations.

Consider a mixture of polymer molecules composed by the same monomers with N_n polymer molecules of chain length n in a lattice with total number of sites M. We assume that all the lattice sites are occupied by polymer chains or solvent molecules, i.e. $M = \sum_{\{n\}} nN_n + N_s$, where $\{n\}$ denotes the set of different chain lengths and N_s is the number of solvent molecules. The volume fraction of species n is given by nN_n/M, and due to the lattice filling condition the solvent volume fraction is given by $\phi_s = 1 - \sum\phi_n$.

The Helmholz free energy of the system can be written as

$$\beta F = \sum_{\{n\}}[N_n \ln \phi_n + N_n \sum_{\{\alpha_n\}} P_n(\alpha_n) \ln P(\alpha_n) + \chi N_n \langle n_n \rangle \phi_s] + N_s \ln \phi_s \tag{13}$$

where the first term is the translational entropy of the chain molecules, the second term is the conformational entropy of the polymers, and the third term represents

the interactions between the polymer molecule of size n and the solvent molecules. The fourth term in the free energy expression is the translational entropy of the solvent molecules.

In the systems treated here there are only two types of species, i.e. solvent and monomers of polymer; then in a filled lattice there is only one relevant interaction parameter, which in our case is $\chi = [\epsilon_{ps} - 1/2(\epsilon_{pp} + \epsilon_{ss})]/k_BT$ with ϵ_{ij} denoting the interaction between monomer of type i and that of type j, T the absolute temperature, and k_B the Boltzmann constant. Therefore, the interaction of a polymer chain of length n in configuration α_n is given by the number of possible contacts of the chain in that conformation with solvent molecules, $n_n(\alpha_n)$, multiplied by the probability of finding a solvent molecule at the neighboring site of the chain. This probability, within a mean-field approximation, is given by the volume fraction of solvent molecules, ϕ_s. The third term in the right-hand side (rhs) of eq 13 is the average of this quantity over all the possible conformations of the chains summed for all the possible chain lengths.

Minimizing the free energy, eq 13, with respect to the pdf, one obtains

$$P_n(\alpha_n) = \frac{1}{q_n} \exp[-\chi n_n(\alpha_n)\phi_s] \tag{14}$$

where q_n is the single chain partition function that ensures the normalization of the pdf for each molecular weight. This expression for the pdf shows the coupling between the chain conformations and the thermodynamic state of the system through the Boltzmann exponent. It can be seen that different conditions of temperature and composition change the probability of the different configurations. As will be shown in the next section, this has important effects on the average conformational properties of the chains as well as on the partition coefficients between different phases.

Now that we have an explicit expression for the pdf, eq 14, it is convenient to introduce it into the free energy expression, eq 13, to obtain

$$\beta F = \sum_n [N_n \ln \phi_n - N_n \ln q_n] + N_s \ln \phi_s \tag{15}$$

where for notational simplicity the summation over $\{n\}$ has been replaced by a summation over n. It is important to recognize that the single chain partition function for each chain length, q_n, is a function of the composition and temperature of the system. Note also that if we consider the energy per chain to be independent of the chain conformation, eq 15 transforms into the well-known Flory–Huggins expression (1) for a polydisperse polymer solution.

We are interested in determining the phase diagram and the distribution coefficients between the equilibrium phases. Then, we need to evaluate the chemical potentials of the chains. This is readily obtained by taking the derivative of the free energy, eq 15, with respect to the number of molecules of chain of length n, to obtain

$$\mu_n = \ln \phi_n - \ln q_n - \sum_{n'} \phi_{n'}\chi\langle n_{n'}\rangle\phi_s + (1 - n)\phi_s \tag{16}$$

and for the solvent chemical potential

$$\mu_s = \ln \phi_s + (1 - \phi_s) - \sum_n \frac{\phi_n}{n} - \sum_n \frac{\phi_n}{n}\chi\langle n_n\rangle(1 - \phi_s) \tag{17}$$

where for both equations we have used the fact that $\phi_s = 1 - \Sigma\phi_n$.

The condition of thermodynamic equilibrium between two phases is given by the equality of chemical potential for each species in the two phases. Let, as before, $'$ and $''$ denote the two phases at coexistence for a given temperature. Then the phase equilibrium between the two phases will be given by

$$\mu_n' = \mu_n'' \quad \text{for all } n$$

$$\mu_s' = \mu_s'' \tag{18}$$

which can be readily calculated using the explicit forms, i.e. eqs 16 and 17. From eq 16 we have that the distribution coefficient will be given by

$$\ln \frac{\phi_n''}{\phi_n'} = -\ln \frac{q_n(\phi_n')}{q_n(\phi_n'')} + (1 - n)(\phi_s' - \phi_s'') - \chi\sum_{n'}[\phi_{n'}'\langle n_{n'}\rangle'\phi_s' - \phi_{n'}''\langle n_{n'}\rangle''\phi_s''] \tag{19}$$

From this expression we can see that if there is a nonlinear dependence of the distribution coefficient on n it must arise from the first term in the rhs of eq 19. Therefore, it arises from the explicit consideration of the distribution of chain conformations and their dependency on the thermodynamic state of the system. As will be shown in the Results, this is clearly the case.

Once we know the coexistence curve we can calculate any desired average conformational property of the chain molecules at the points of phase equilibrium. In particular we will show the average radii of gyration for a given coexistence state, to see how the different environments and the polydispersity affects the average size of the polymer molecules. This quantity is calculated from

$$\langle R_g^2\rangle_n = \sum_{\alpha_n} P(\alpha_n) \sum_{i=1}^{n} [r_i(\alpha_n) - r_{cm}(\alpha_n)]^2 \tag{20}$$

where $r_i(\alpha_n)$ is the coordinate of segment i in a chain of n segments in conformation α_n and r_{cm} denotes the location of the center of mass of the chain in configuration α_n.

3. Results and Discussion

Phase separation in polymer solutions is characterized by equilibrium between two essentially different phases, a dilute and a concentrated phase. For the polymer conformations this has important consequences. In the dilute phase the chains are isolated and somewhat collapsed, whereas in the concentrated phase the polymer segments are distributed homogeneously and the individual chains have their unperturbed size. A slightly collapsed state of isolated coils obviously implies many more polymer segment–segment interactions than the mean-field estimation of the simple Flory–Huggins theory. To what extent the explicit coupling between configurational degrees of freedom and thermodynamics, introduced in the previous section, can explain the most striking differences between the experimentally observed and theoretically predicted phase behavior of polymer solutions remains to be seen. We already know that it predicts a chain length dependence of the critical concentration in monodisperse polymer solution which differs essentially from the Flory–Huggins prediction but agrees well with experimental observations. The chain length dependence of the distribution coefficient in polydisperse polymer

Table 1. Initial Distributions

	n	10	20	30	40	50	60	70	80	90	100
$\phi = 0.25$	$100\phi_n =$	0.5	1.5	2.5	3.5	4.5	4.5	3.5	2.5	1.5	0.5
$\phi = 0.125$	$100\phi_n =$	0.25	0.75	1.25	1.625	2.25	2.25	1.625	1.25	0.75	0.25

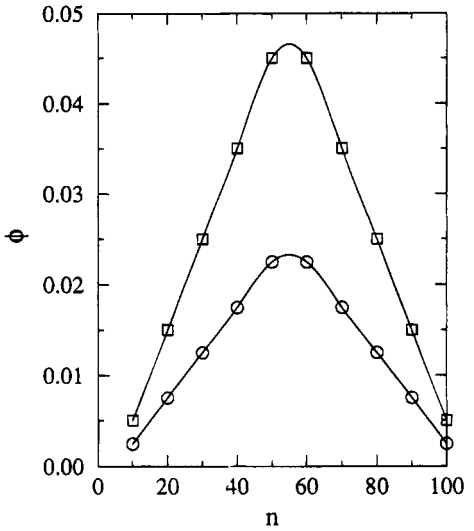

Figure 1. Initial distribution for $\phi = 0.25$ (squares) and for $\phi = 0.125$ (circles).

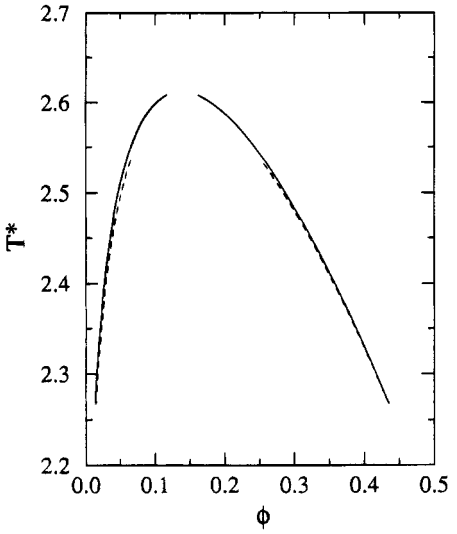

Figure 2. Coexistence curves for a polydisperse polymer solution with the chain length distribution given in Table 1. The full line is the result for overall polymer concentration $\phi = 0.125$, while the dashed line is for overall polymer concentration $\phi = 0.25$.

solutions is another property which shows a strikingly different behavior.

To discuss polydisperse polymer solutions, assumptions about the initial chain length distribution are required. Since our objective here is merely to show that the theory can predict the curvature of the distribution coefficient, we chose quite arbitrarily as a starting point two polymer solutions with a volume fraction of polymer $\phi = 0.25$ and $\phi = 0.125$ and with chain length distributions as given in Figure 1. Table 1 presents this distribution in terms of chain lengths and volume fractions. The corresponding moments are given by $n_n = 44.3$, $n_w = 55.0$, and $n_z = 62.7$.

Before we turn to the distribution coefficient, the phase diagram will be considered first. The coexistence curve is found by determining the two phases for which the chemical potentials for each chain length, eq 16, and the solvent, eq 17, are the same in the two phases. As these equations show, this requires the generation of representative samples of self-avoiding conformations for the chain lengths involved, which, using the Rosenbluth and Rosenbluth method, is standard practice by now.[14,17] In all cases 10^6 conformations per chain length were generated. If the number of different chain lengths present equals k, the number of equations involving the $2k$ different polymer concentrations and the 2 different solvent concentrations is $k + 1$. However, fixing the initial overall polymer concentration and the initial chain length distribution reduces the number of unknowns to $k + 1$ as well. This follows from

$$\phi_n' = \frac{N_n'}{V'} = \frac{V}{V'}\frac{N_n}{V}\frac{N_n'}{N_n} = (1 + r)\phi_n x_n \qquad (21)$$

and

$$\phi''_n = \left(1 + \frac{1}{r}\right)\phi_n(1 - x_n) \qquad (22)$$

where x_n refers to the fraction of molecules with chain length n of all molecules with chain length n in the concentrated phase. These equations demonstrate that the $k + 1$ unknowns are r and $\{x_n, n = 1,..., k\}$. Alternatively

$$\phi'_n V' + \phi''_n V'' = \phi_n V \qquad (23)$$

demonstrates the same property.

Since for polydisperse polymer solutions, the coexisting phases depend on the overall polymer concentration, a coexistence curve can only be calculated for a fixed initial concentration. In the situations considered here ϕ was chosen to be $\phi = 0.25$ and $\phi = 0.125$. The former value is higher than the critical concentration for the given chain length distribution while the latter is lower. The value of the critical volume can be estimated from the Flory–Huggins expression[18,19]

$$\phi_c = \frac{1}{1 + n_w n_z^{-1/2}} \qquad (24)$$

Inserting the values of n_w and n_z given before leads to $\phi_c = 0.126$. The predictions of the theory presented here give $\phi_c = 0.14$ which is 10% higher than predicted from the simpler Flory–Huggins approach. As a consequence, the concentrated right branch of the coexistence curve ends at $\phi' = 0.25$ and the diluted branch at the concentration ϕ'' calculated to be in equilibrium with this value. On the other hand for the total volume fraction $\phi = 0.125$ the dilute branch ends at $\phi'' = 0.125$ while the concentrated branch enters at the corresponding calculated value ϕ'. The next figure (Figure 2) shows the phase diagram in a (ϕ,T^*) plane, where $T^* = 1/2\chi$ and χ is the Flory–Huggins parameter defined before. Note that even though the two distributions have the same moments, the different overall concentrations of polymer manifest themselves in the phase diagram.

The corresponding phase volume ratio $r = V''/V'$ is presented in Figure 3 as a function of T^*, demonstrating the expected approach to 0 for increasing values of T^* for $\phi = 0.25$. For the case of overall concentration $\phi = 0.125$ the volume ratio is always larger than 1 and increases very sharply for the cases in which the dilute branch approaches the total overall concentration, since

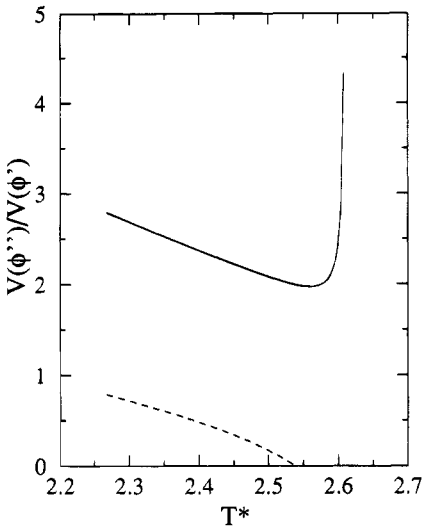

Figure 3. Phase volume ratio $r = V(\phi'')/V(\phi')$ as a function of T^*. The full line is the result for overall polymer concentration $\phi = 0.125$, while the dashed line is for overall polymer concentration $\phi = 0.25$.

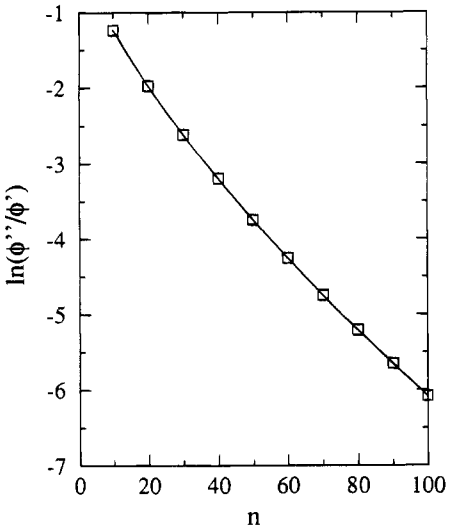

Figure 4. Distribution coefficient for $T^* = 2.2676$.

in this case the phase-separated solution will have a dilute phase of a much larger volume than that of the concentrated phase. The nonmonotonic behavior of the volume ratio is due to the different curvature of the concentrated and dilute branches as they approach the critical point.

Having calculated the coexisting phases as a function of T^*, all information to calculate the fractionation characteristics is available. The following results are for overall concentration $\phi = 0.25$; the results for the other concentration shown in Figures 2 and 3 are qualitatively very similar and thus, not shown.

The following figure (Figure 4) shows our main result, the distribution coefficient as a function of chain length n for a value $T^* = 2.2676$, considerably below the onset value for phase separation. Clearly, the deviation from a linear dependence found experimentally is also present in our model, even though the initial distribution chosen is quite narrow compared to most experimental examples. Hence, the difference in average conformation of polymer molecules in the dilute and concentrated phases, which is the essential new ingredient of our approach, must be responsible for this behavior. Figure 5 demonstrates this difference.

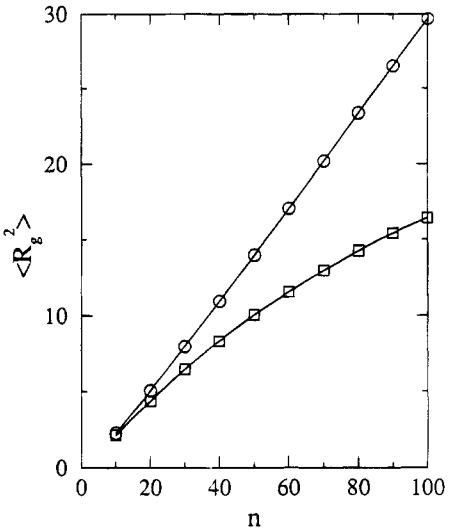

Figure 5. Average radius of gyration as a function of n in the concentrated (○) and diluted (□) phases.

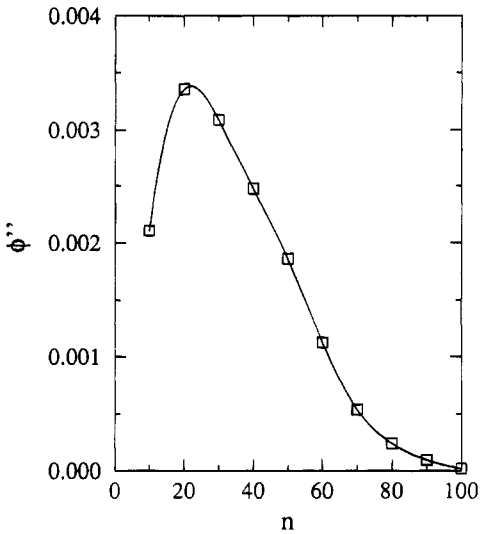

Figure 6. Chain length distribution in the diluted phase; $T^* = 2.2676$.

As is obvious from this figure, the coil size satisfies the random walk statistics in the concentrated phase, i.e. $\langle R_g^2 \rangle \sim n$, whereas the coils start to collapse in the diluted phase, in complete agreement with current theories.[20] Note that the different behaviors observed in the two phases are a result of the coupling between the thermodynamic state and the conformational properties of the chains. All the results shown in Figure 5 are obtained with the same sets of conformations, but with the appropriate weight which is a function of temperature and composition, as discussed following eq 14.

Finally, the last two figures (Figures 6 and 7) show the chain length distribution in the diluted and concentrated phases, demonstrating fractionation in a more pictorial way.

4. Concluding Remarks

The specifics of phase behavior in polymer solutions is often quite different from the simple Flory–Huggins predictions. Attempts to improve this situation were so far mainly based on a semi-empirical bridging approach combined with a more complicated concentration and temperature dependence of the χ parameter. Our

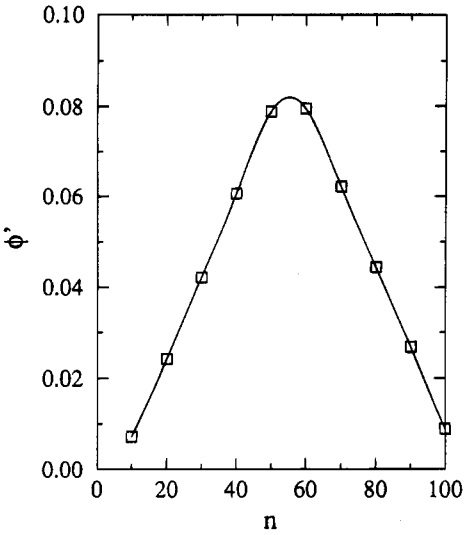

Figure 7. Chain length distribution in the concentrated phase; $T^* = 2.2676$.

approach addresses the most obvious inadequacy of a simple mean-field description: the inhomogeneity of the diluted phase. Thermodynamics is explicitly coupled to configurational statistics, and apart from a true interaction parameter, no additional parameters are involved. Previously, it was demonstrated that this approach predicts a chain length dependence of the critical concentration in monodisperse polymer solutions $\phi_c \sim 1/(1 + n^{0.4})$, differing from the F–H predictions but in good agreement with experimental observations. In the present paper we demonstrate that it also accounts for the observed chain length dependence of the distribution coefficient in polydisperse solutions. From the work of Koningsveld and co-workers it is well-known how complicated phase behavior in polydisperse polymer solutions can be. It remains a challenge to see how far we can get with the present single parameter approach.

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