Are Simple Power Laws Adequate for the Description of Ternary Polymer Solutions? An Analysis of Special Experimental Situations

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ABSTRACT: For ternary polymer solutions we use the renormalization group to analyze special experimental situations close to scaling limits. Specifically we concentrate on scattering experiments under optical Θ-conditions or in a solvent isorefractive to one polymer component. We suggest a modification of the optical Θ-condition, based on renormalization theory. In addition we suggest and analyze osmotic pressure compensation experiments equivalent to the scattering experiments mentioned above. We find that in general a simple evaluation using power law scaling is not justified. To exclude a misinterpretation of the data, one always needs additional information on the binary polymer–solvent subsystems. Furthermore, Flory's χ_{12}-parameter in general is not the appropriate quantity for an analysis of the experiments. It is a nonuniversal quantity typically dominated by contributions of the binary subsystems.

1. Introduction

New experimental and theoretical developments recently led to increasing interest in the physics of ternary polymer solutions. On the theoretical side the renormalization group is expected to explain in detail the properties of weak solutions of any number of chemically different macromolecular species in a common solvent. On the experimental side a new light-scattering method using an "optical Θ-solvent" has led to promising results. This method was developed[1] on the basis of Flory's theory of polymer solutions, which interprets the experimental phenomena in terms of the "χ-parameters". Two parameters $\chi_{\text{o}a}$ represent the interaction of monomers of polymer species $a = 1,2$ with the solvent and thus are characteristic for binary polymer–solvent systems. The third parameter χ_{12} measures the effective interaction of the two polymer species in solution, and it thus contains the new physics specific for the ternary system. Much experimental work has aimed at its precise determination, which turned out to be a difficult task. The optical Θ-method is distinguished by its ability to determine χ_{12} from dilute solution data directly, without knowledge of the binary solution parameters $\chi_{\text{o}a}$. This great progress resulted in the first reliable estimates of χ_{12}.

In contrast to the original assumptions of Flory's theory the χ-parameters experimentally are found to depend on concentrations and molecular weights, and they therefore do not play the originally expected role of proper microscopic parameters. To a large part, their variation is due to the excluded-volume effect, and some attempts to analyze χ_{12}-data on the basis of traditional theories of the excluded volume can be found in the literature.[2,3] A modern approach to excluded-volume effects is based on the renormalization group[4] (RG). For binary solutions RG theory has led to an almost quantitative explanation of many experimental results,[4–6] far beyond the familiar phenomena of scaling and power law behavior. For ternary solutions only some qualitative features of the RG have been tested so far. Experimental work is restricted to the tentative verification[7] of power laws which hold under very restricted conditions.

RG theory of ternary polymer solutions[8–10] shows a very rich structure. Several fixed points with their associated scaling regions are connected by nontrivial crossover behavior. To test the complete picture, it needs an extensive set of measurements for some typical systems, which in general cover some range of the crossover regime. The analysis of such data would be a major and not quite trivial task, a challenge both to experiment and to theory. A more modest program consists in the analysis of well-defined limiting situations, and the present contribution is concerned with this task. *We search for experimentally realizable situations which allow for a simplified theoretical evaluation.* The optical Θ-condition was proposed exactly with this goal in mind, and we analyze it in detail in light of the RG. We propose a modification adequate for such ternary solutions where excluded-volume effects dominate both the binary polymer–solvent subsystems (good-solvent scaling limit). If one polymer species ($a = 2$) is at Θ-conditions, the other one ($a = 1$) being dominated by the excluded-volume interaction, we reach a strongly asymmetric scaling limit where the optical Θ-condition is not appropriate. Then a simple analysis results if the solvent happens to be isorefractive to species 1. Osmotic measurements also can be designed such that a simple evaluation is feasible in these scaling regimes.

Our analysis goes beyond the formulation of limiting power laws which can be derived on the basis of scaling assumptions.[10,11] We use lowest order renormalized perturbation theory ("tree approximation") as a first step toward quantitative expressions for the scaling functions, and we include enough results of the RG to reconstruct the full crossover behavior. This extension of the simple scaling approach is necessary and most important under two different aspects. The first aspect deals with the fact that in the analysis of a given experiment we must verify that the scaling region is reached. This cannot be judged just from the observation of "power law" behavior. The physics of ternary solutions is rich enough to simulate power laws also in parameter regions where they are unfounded theoretically. Even close to a scaling limit, it therefore is important to check the data against quantitative predictions in order to get a complete and consistent picture. The second aspect concerns the original motivation of the experiments, which a priori aim at the determination of the interaction parameter of the two polymer species. In RG theory the Flory parameter, χ_{12}, is replaced by an interaction parameter, $g_{12,\text{o}}$, which holds the microscopic information of inter-

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est. However, in the scaling limits the data in general become insensitive to this parameter, and it needs a detailed quantitative analysis including also corrections to leading power laws to extract $g_{12,o}$.

To summarize, it is the aim of the present contribution to suggest experiments that allow for a simplified theoretical treatment and to analyze the information on the basic interaction parameters contained in such experiments. We here concentrate on the neighborhood of the scaling regions. A presentation of the general theory can be found in ref 12.

The organization of our paper is as follows. In section 2 we recall the optical Θ-method. In section 3 we present results of the renormalized theory. The derivation of these results is a standard problem of renormalized perturbation theory, and no details will be given. Some aspects of the derivation are discussed in ref 12. In section 4 we analyze the expression for χ_{12}, which results from renormalized theory, we formulate a renormalized version of the optical Θ-condition, and we discuss scattering experiments using an isorefractive solvent. Section 5 is devoted to the osmotic pressure. Our results are summarized in section 6.

2. Optical Θ-Method

2.1. Notation. We denote by c_{pa} the number per unit volume of macromolecules of species a. N_a (or N_{wa}) is the number-(or weight-)average degree of polymerization ("chain length") and $c_a = N_a c_{pa}$ is the monomer concentration of species a. $\nu_a = \partial n / \partial c_a$ stands for the scattering index increment. Introducing the monomer number densities, ρ_a, of liquid polymer (and the density, ρ_0, of pure solvent), we easily can relate our variables to those introduced in refs 1 and 2.

$$c_a = \rho_a \varphi_a \qquad \nu_a = \psi_a / \rho_a \tag{2.1}$$

Here φ_a is the volume fraction of polymer a in solution and ψ_a is the scattering index increment related to a change of φ_a. (The volume excess upon mixing has been ignored; i.e., $v = v_{id}$ in the notation in ref 2.)

To describe a scattering experiment, we introduce the matrix of intensities, $\mathbf{I}_{ab}(q)$, which is defined as the Fourier transform of the (a) monomer-, (b) monomer–density correlation function. The scattering intensity is proportional to

$$I(q,\nu_1,\nu_2) = \sum_{a,b=1}^{2} \nu_a \mathbf{I}_{ab} \nu_b \tag{2.2}$$

It is useful to express the matrix $\mathbf{I}$ in terms of its inverse $\check{I}$

$$\mathbf{I}_{ab} = (-1)^{a+b} \frac{\check{I}_{\bar{a}\bar{b}}}{\check{I}_{11}\check{I}_{22} - \check{I}_{12}^{\,2}} \tag{2.3}$$

where here and in the sequel we use the notation

$$\bar{c} = 1 \quad \text{if } c = 2 \qquad \bar{c} = 2 \quad \text{if } c = 1 \tag{2.4}$$

Identifying $I(0,\nu_1,\nu_2)$ with R_0/K^* of ref 2, which is the scattering intensity at $q = 0$, normalized to $R_0/K^* \to \sum_a \nu_a^2 c_a N_{wa}$ for $c_1 + c_2 \to 0$, we can use eqs 8 and 12 of ref 2 to introduce the χ-parameters as a mere reparametrization of the experimental information

$$\check{I}_{12} = \frac{\rho_0}{\rho_1 \rho_2}\left[\left(1 - \frac{c_1}{\rho_1} - \frac{c_2}{\rho_2}\right)^{-1} - \chi_{01} - \chi_{02} + \chi_{12}\right] \tag{2.5}$$

2.2. Scattering Intensity under Optical Θ-Conditions. To derive the optical Θ-condition, we consider the virial expansion of $\mathbf{I}_{ab}(q{=}0)$.

$$\mathbf{I}_{aa}(0) = c_a N_{wa} + A_{aa} c_a^{\,2} + A_{a\bar{a}} c_a c_{\bar{a}} + O(c^2) \tag{2.6i}$$

$$\mathbf{I}_{12}(0) = \bar{A}_{12} c_1 c_2 + O(c^3) \tag{2.6ii}$$

Thus

$$I(0,\nu_1,\nu_2) = \sum_{a=1}^{2} \nu_a^{\,2} c_a N_{wa} + A + O(c^3)$$

$$A = \sum_{a=1}^{2} \nu_a^{\,2} c_a^{\,2}\left(A_{aa} + A_{a\bar{a}}\frac{c_{\bar{a}}}{c_a}\right) + 2\nu_1\nu_2 c_1 c_2 \bar{A}_{12} \tag{2.7}$$

Proceeding slightly more general than necessary for the discussion of this subsection, we now impose the condition

$$\nu_1 c_1 \alpha_1 + \nu_2 c_2 \alpha_2 = 0 \tag{2.8}$$

where the α_a will be fixed below. Equation 2.7 can be rewritten as

$$A = \nu_1\nu_2 c_1 c_2\left[2\bar{A}_{12} - \frac{\alpha_1}{\alpha_2}\left(A_{22} + A_{21}\frac{c_1}{c_2}\right) - \frac{\alpha_2}{\alpha_1}\left(A_{11} + A_{12}\frac{c_2}{c_1}\right)\right] \tag{2.9}$$

Using eqs 2.1, 2.4, and 2.5, we can relate the virial coefficients to the χ-parameters, evaluated at zero concentration.

$$A_{aa} + A_{a\bar{a}}\frac{c_{\bar{a}}}{c_a} = -N_{wa}^{\;2}\frac{\rho_0}{\rho_a^{\,2}}(1 - 2\chi_{0a})$$

$$\bar{A}_{12} = -N_{w1}N_{w2}\frac{\rho_0}{\rho_1\rho_2}(1 - \chi_{01} - \chi_2 + \chi_{12}) \tag{2.10}$$

(Note that the first equation in general implies a dependence of χ_{0a} on the composition of the solution.) Choosing now

$$\alpha_a = N_{wa}/\rho_a \tag{2.11}$$

we find that A becomes proportional to χ_{12}

$$A = -\nu_1\nu_2 c_1 c_2 \frac{\rho_0}{\rho_1\rho_2} N_{w1} N_{w2} (2\chi_{12}) \tag{2.12}$$

This is the desired result, which opens a way for direct measurement of χ_{12} in the dilute limit. With eq 2.11, eq 2.8 becomes the optical Θ-condition (ref 2, eq 17):

$$\nu_1 \frac{c_1}{\rho_1} N_{w1} + \nu_2 \frac{c_2}{\rho_2} N_{w2} = 0 \tag{2.13}$$

3. Renormalized Theory

3.1. General Scheme. The renormalization group exploits the fact that the microscopic unit of the polymer chain is not uniquely fixed. As defined above we think of the monomer as a microscopic unit, but an equivalent chain can be constructed by combining several monomers into one effective segment. In RG theory one proves that macroscopic properties of sufficiently dilute solutions of sufficiently long chains are invariant under a transformation of the microstructure, provided the effective segment size, l, the elementary interactions, $g_{ab,0}$, the chain lengths, N_a, and the concentrations, c_{pa}, are changed appropriately.

$$l \to l_R(\lambda) = l/\lambda \qquad c_{pa} \to c_{pR}^{(a)}(\lambda)$$

$$N_a \rightarrow N_{\mathrm{R}}^{(a)}(\lambda) \qquad g_{ab,0} \rightarrow g_{ab}(\lambda) \tag{3.1}$$

The intensity matrix $\mathbf{I}_{ab}$ transforms as[12]

$$\mathbf{I}_{ab}(q,N_c,c_{\mathrm{p}c},g_{cd,0},l) = (c_aN_a)^{1/2}\bar{I}_{\mathrm{R}ab}(ql_{\mathrm{R}}(\lambda),N_{\mathrm{R}}^{(c)}(\lambda),c_{\mathrm{pR}}^{(c)}(\lambda),g_{cd}(\lambda))(c_bN_b)^{1/2} \tag{3.2}$$

where the arguments N_c, etc., stand for the whole set N_1, N_2, etc.

To proceed, we need an explicit form of the mapping (eq 3.1). Since basically this mapping is a dilatation of the elementary length l by a factor $1/\lambda$, the transformation of the polymer concentrations is trivial

$$c_{\mathrm{pR}}^{(a)}(\lambda) = (l/\lambda)^3\, c_{\mathrm{p}a} = l_{\mathrm{R}}^{3}c_{\mathrm{p}a} \tag{3.3}$$

For the other parts of the mapping we use results[6] of second-order renormalized perturbation theory

$$\frac{s_l^{(a)}}{l_{\mathrm{R}}} = (1-f_a)^{1/\omega}f_a^{-1} \tag{3.4}$$

$$N_{\mathrm{R}}^{(a)} = (1-f_a)^{1/\nu\omega}f_a^{-2}s_N^{(a)}N_a \tag{3.5}$$

Equation 3.4 determines

$$f_a = g_{aa}/g^* \tag{3.6}$$

as a function of $\lambda = l/l_{\mathrm{R}}$. Here the fixed point coupling, g^*, is the limiting value of $g_{aa}(\lambda)$ for $\lambda \rightarrow 0$, which for $g_{aa,0} > 0$ is independent of $g_{aa,0} = g_{aa}(\lambda{=}1)$: $g^* \approx 4.8$.[6] Once $f_a = f_a(\lambda)$ is known, eq 3.5 determines $N_{\mathrm{R}}^{(a)}(\lambda)$. Equations 3.4 and 3.5 involve nonuniversal scale factors $s_l^{(a)}$ and $s_N^{(a)}$. These parameters depend on $g_{aa,0}$ and thus on temperature and microstructure but are independent of concentration or molecular weight. They are taken as fit parameters of RG theory. The critical exponents ω and ν take the values

$$\nu = 0.588 \qquad \omega = 0.790$$

derived from higher order calculations.

We finally need an expression for $f_{12}(\lambda) = g_{12}(\lambda)/g^*$. A first-order calculation yields (in three dimensions)

$$\frac{\mathrm{d}\ln f_{12}}{\mathrm{d}\ln\lambda} = -1 + \frac{1}{4}(2f_{12} + f_{11} + f_{22}) \tag{3.7}$$

Third-order results have recently been derived.[13] This equation in general cannot be integrated analytically. Special solutions have been given in ref 9 and will be exploited in subsection 3.4.

3.2. Tree Approximation for the Intensity Matrix. To lowest order renormalized perturbation theory we find[12] for the inverse $\check{I}_{\mathrm{R}}$ of the matrix $\bar{I}$ (eq 3.2)

$$\check{I}_{\mathrm{R}ab} = \frac{\delta_{ab}}{D_a((ql_{\mathrm{R}})^2N_{\mathrm{R}}^{(a)})} + (c_{\mathrm{R}}^{(a)}c_{\mathrm{R}}^{(b)}N_{\mathrm{R}}^{(a)}N_{\mathrm{R}}^{(b)})^{1/2} \tag{3.8}$$

$$c_{\mathrm{R}}^{(a)} = c_{\mathrm{pR}}^{(a)}N_{\mathrm{R}}^{(a)} \tag{3.9}$$

Here δ_{ab} denotes Kronecker's symbol and $D_a(y)$ is the generalized Debye function. Introducing the Laplace transform $\tilde{p}_a(x)$ of the normalized chain length distribution $p_a(N)$ of species a

$$\tilde{p}_a(x) = \sum_{N=1}^{\infty} e^{-xN/N_a}p_a(N) \tag{3.10}$$

we define $D_a(x)$ as

$$D_a(x) = \frac{2}{x^2}(\tilde{p}_a(x) - 1 + x) \tag{3.11}$$

Equation 3.8 is the renormalized form of the standard RPA result as given, for instance, in ref 14. From eqs 3.2 and 3.8 we find

$$I_{aa}(q) = c_aN_aD_a(1 + g_{\bar{a}\bar{a}}c_{\mathrm{R}}^{(\bar{a})}N_{\mathrm{R}}^{(\bar{a})}D_{\bar{a}})\Delta^{-1} \tag{3.12i}$$

$$I_{12}(q) = -c_1c_2l_{\mathrm{R}}^{3}N_{\mathrm{R}}^{(1)}N_{\mathrm{R}}^{(2)}D_1D_2g_{12}\Delta^{-1} \tag{3.12ii}$$

where

$$\Delta = 1 + g_{11}c_{\mathrm{R}}^{(1)}N_{\mathrm{R}}^{(1)}D_1 + g_{22}c_{\mathrm{R}}^{(2)}N_{\mathrm{R}}^{(2)}D_2 + (g_{11}g_{22} - g_{12}^{2})c_{\mathrm{R}}^{(1)}c_{\mathrm{R}}^{(2)}N_{\mathrm{R}}^{(1)}N_{\mathrm{R}}^{(2)}D_1D_2 \tag{3.13}$$

$$D_a = D_a((ql_{\mathrm{R}})^2N_{\mathrm{R}}^{(a)}) \tag{3.14}$$

3.3. Choice of the Renormalization Point. If the number of interacting segments is large, i.e., for long chains or higher concentrations, perturbation theory breaks down. Renormalization is a way to overcome this problem. An isolated chain of length $N \gg 1$, for instance, can be mapped onto a renormalized chain of length $N_{\mathrm{R}} \sim 1$, and for such a short chain perturbation theory is valid. In terms of length scales $N_{\mathrm{R}} \sim 1$ imples $l_{\mathrm{R}} \sim R_g$, i.e., the size of the renormalized segment is of the order of the radius of gyration of the chain.

This simple choice of l_{R} is valid only for a very dilute system. At higher concentrations polymer coils strongly interpenetrate, and the overlapping of many chains suppresses the effect of the interaction. We can define a screening length,[15] ξ_{E} (the blob size of the scaling theories), so that the interactions are negligible for correlations on the scale of $r \gg \xi_{\mathrm{E}}$. A detailed analysis of the screening effect (see, for instance, ref 16) shows that a valid choice of l_{R} for a binary system is $l_{\mathrm{R}} \sim \xi_{\mathrm{E}}$. In the dilute limit ξ_{E} approaches R_g.

In generalizing these considerations to a ternary system, we have to identify an appropriate screening length. In ref 12 we show that the effective interactions in a ternary system involve two length scales. One scale diverges on the spinodal and thus governs the critical phenomena at the two-fluid phase separation, which is not our problem here. The other length is finite everywhere and takes the form

$$\xi = l_{\mathrm{R}}\xi_{\mathrm{R}} \tag{3.15}$$

$$\xi_{\mathrm{R}}^{-2} = \frac{1}{2N_{\mathrm{R}}^{(1)}} + \frac{1}{2N_{\mathrm{R}}^{(2)}} + g_{11}c_{\mathrm{R}}^{(1)} + g_{22}c_{\mathrm{R}}^{(2)} + \left[\left(\frac{1}{2N_{\mathrm{R}}^{(1)}} - \frac{1}{2N_{\mathrm{R}}^{(2)}} + g_{11}c_{\mathrm{R}}^{(1)} - g_{22}c_{\mathrm{R}}^{(2)}\right)^2 + 4g_{12}^{2}c_{\mathrm{R}}^{(1)}c_{\mathrm{R}}^{(2)}\right]^{1/2} \tag{3.16}$$

For identical polymer species where $N_1 = N_2$ and $g_{11} = g_{22} = g_{12}$, this length reduces to the screening length of the binary system. Generalizing our treatment of binary solutions, we therefore fix $\lambda = l/l_{\mathrm{R}}$ such that

$$\xi_{\mathrm{R}}^{-2} = 1 \tag{3.17}$$

This condition constitutes the final input to our scheme. Equations 3.3–3.7 and 3.17 allow for the determination of all renormalized variables in terms of unrenormalized variables N_a and $c_{\mathrm{p}a}$ and microscopic parameters $s_l^{(a)}$, $s_N^{(a)}$, and $g_{12,0}$. (We should note that in ref 9 we used a somewhat different length scale, which is equivalent from the RG point of view but yields more complicated expressions. Compare[9] eq 4.14.)

We finally want to point out some problems related to the choice of eqs 3.16 and 3.17 in a case in which the two chains are of very different size: $N_R^{(a)} \gg N_R^{(a)}$. Taking the dilute limit $c_R^{(1)}$ and $c_R^{(2)} = 0$, we find that our condition distinguishes the smaller chain:

$$1 = \min [N_R^{(1)}, N_R^{(2)}]$$

Combined with low-order expressions for the scaling functions, our method in the dilute limit therefore will give distinctively better results for the *small* chains than for the *large* chains. This problem is inherent in the theory, which possesses a single adjustable length scale whereas in the dilute solution in fact both radii of gyration are of equal importance. It cannot be avoided as long as we insist on having a smooth crossover prescription connecting the dilute and semidilute limits.

3.4. Scaling Limits. The mapping from microscopic to renormalized parameters in general has to be evaluated numerically. An analytical evaluation is possible only if the coupling constants $g_{ab}(\lambda)$ approach their fixed point values. We here evaluate the mapping in the two most relevant of these scaling regimes.

A. Both Binary Subsystems Are Close to the Excluded-Volume Fixed Point. Of all the limiting cases, this one is easiest to reach experimentally. It is realized that both binary polymer–solvent subsystems are found in the good-solvent scaling regime, which for $g_{aa,0} > 0$ can always be reached by increasing the molecular weight.

Formally, this limit is defined by

$$(1 - f_a) \ll 1$$

and eliminating f_a among eqs 3.4 and 3.5, we find

$$N_R^{(a)} = [B_a/l_R]^{1/\nu} N_a \tag{3.18}$$

Here

$$B_a = s_l^{(a)} (s_N^{(a)})^{\nu} \tag{3.19}$$

is the only combination of the nonuniversal parameters for polymer a occurring in this limit. Equations 3.3, 3.9, and 3.18 yield

$$c_R^{(a)} = [B_a/l_R]^{1/\nu} l_R^{\,3} c_a \tag{3.20}$$

An interpretation of B_a can be given in terms of the radius of gyration. Equations 3.12 and 3.13 yield for a single chain of length N

$$\begin{aligned} R_{g,a}^{\,2}(0) &= \lim_{c_1,c_2 \to 0} \left[-\frac{1}{2} \Delta_q \ln I_{aa}(q)\Big|_{q=0} \right] \\ &= l_R^{\,2} N_R^{(a)} \end{aligned} \tag{3.21}$$

Using eq 3.18 with $N_R^{(a)} = 1$, as appropriate in the single chain limit, we can eliminate l_R^2 to find

$$R_{g,a}^{\,2}(0) = B_a^{\,2} N_a^{\,2\nu} \tag{3.22}$$

which provides us with the most direct interpretation of B_a.

Replacing in eq 3.7 f_a by 1, a = 1, 2, we can integrate this equation[13] to find a solution valid within the accuracy of a second-order calculation.

$$s_l^{(12)}/l_R = |f_{12} - 1|^{1/\omega_{12}} f_{12}^{\,1/\omega_{12}(0)} \tag{3.23}$$

Here $\omega_{12} = 13/64$ and $\omega_{12}(0) = -21/64$ to second order. Higher order calculations yield the improved estimate $\omega_{12} = 0.37$ ($\nu\omega_{12} = \gamma = 0.22$ in the notation of ref 11). $s_l^{(12)}$ is the nonuniversal parameter characteristic for the polymer 1–polymer 2 interactions, replacing

$$g_{12,0} = g_{12}(\lambda{=}1)$$

The renormalization condition (eq 3.17) simplifies only in the dilute or semidilute limits. Without loss of generality we may take $N_R^{(1)} \le N_R^{(2)}$ to find in the dilute limit $c_1 \sim c_2 \to 0$

$$1 = 1/N_R^{(1)} \tag{3.24}$$

With eq 3.18 this fixes l_R and thus all the renormalized variables. In particular, if f_{12} is close to its fixed point value $f_{12} = 1$, we find from eq 3.23

$$|f_{12} - 1| = \left[\frac{s_l^{(12)}}{l_R}\right]^{\omega_{12}} = \left[\frac{s_l^{(12)}}{B_1}\right]^{\omega_{12}} N_1^{\,-\nu\omega_{12}} = \left[\frac{s_l^{(12)}}{R_{g1}(0)}\right]^{\omega_{12}} \tag{3.25}$$

In the semidilute limit of strongly overlapping chains $1/N_R^{(a)}$ is negligible and for $f_{12} \sim 1$ the normalization condition (eq 3.17) reduces to

$$1 = 2g^*(c_R^{(1)} + c_R^{(2)}) \tag{3.26}$$

which yields

$$(B_1 B_2)^{1/2}/l_R = [2g^*\hat{c}]^{\nu/(3\nu-1)} \tag{3.27}$$

$$\hat{c} = (B_1 B_2)^{3/2} [(B_1/B_2)^{1/2\nu} c_1 + (B_2/B_1)^{1/2\nu} c_2] \tag{3.28}$$

$$|f_{12} - 1| = \left(\frac{s_l^{(12)}}{(B_1 B_2)^{1/2}}\right)^{\omega_{12}} (2g^*\hat{c})^{\nu\omega_{12}/(3\nu-1)} \tag{3.29}$$

We note that the scaling theories found in the literature[8,10,11] mainly are concerned with the dilute or semidilute excluded-volume limit as discussed here, imposing the additional symmetry conditions $N^{(1)} = N^{(2)}$, $B_1 = B_2$, and $\rho_1 = \rho_2 = \rho_0$.

B. Strongly Asymmetric Solution. We now consider a solution where polymer 2 is at its Θ-point, $f_2 \to 0$, whereas polymer 1 is under good-solvent conditions, $f_1 \to 1$. It should not be too hard to find systems satisfying the necessary conditions $g_{11,0} > 0$, $g_{22,0} = 0$.

For polymer 1 equations 3.18–3.20 hold. For the second species equations 3.4, 3.5, and 3.9 yield

$$N_R^{(2)} = (\tilde{l}_2/l_R)^2 N_2 \tag{3.30}$$

$$c_R^{(2)} = l_R \tilde{l}_2^{\,2} c_2 \tag{3.31}$$

$$\tilde{l}_2 = s_l^{(2)} (s_N^{(2)})^{1/2} \tag{3.32}$$

$\tilde{l}_2$ again can be related to the radius of an isolated chain. Equations 3.21 and 3.30 yield for $N_R^{(2)} = 1$

$$R_{g,2}^{\,2}(0) = \tilde{l}_2^{\,2} N_2 \tag{3.33}$$

Again eq 3.7 can be integrated[13] to yield

$$s_l^{(12)}/l_R = |f_{12} - \tilde{f}_{12}^{\,*}|^{1/\tilde{\omega}_{12}} f_{12}^{\,1/\tilde{\omega}_{12}(0)} \tag{3.34}$$

where $\tilde{\omega}_{12} = 49/128$, $\tilde{\omega}_{12}(0) = -85/128$, and $\tilde{f}_{12}^{\,*} = 47/32$ to second-order approximation. Neither $\tilde{\omega}_{12}$ nor $\tilde{f}_{12}^{\,*}$ has been calculated with the same precision as in limit A. We note that our result for $\tilde{\omega}_{12}$ differs from the results of ref 8, a point which will be clarified in ref 13. As before, the renormalization condition (eq 3.17) simplifies in the dilute or semidilute limits. For $c_R^{(1)} \to 0$, $g_{22} = 0$ we find $N_R^{(2)} = 1$ or

$$\tilde{l}_2/l_R = N_2^{\,-1/2} \tag{3.35}$$

(We assumed $N_R^{(2)} < N_R^{(1)}$, which will be the case in general for $N_1 \sim N_2$.) In the semidilute limit $c_R^{(1)}$ dominates ξ_R to yield $2g^*c_R^{(1)} = 1$ or

$$B_1/l_R = (2g^*B_1^3c_1)^{\nu/(3\nu-1)} \qquad (3.36)$$

Equations 3.35 and 3.36 again yield simple expressions for all renormalized quantities in terms of unrenormalized variables, but up to now this scaling limit has not found much interest.

It sometimes is useful to express the results in terms of scaling variables. By definition these quantities are combinations of the basic variables which are independent of l_R, provided the binary couplings g_{aa} take fixed point values. The previous results suggest the following combinations:

(i) Overlap for species a

$$\begin{aligned} s_a = c_{pa}R_{ga}^3(0) &= B_a^3c_aN_a^{3\nu-1} \quad \text{if } f_a = 1 \\ &= \hat{l}_a^3c_aN_a^{1/2} \quad \text{if } f_a = 0 \end{aligned} \qquad (3.37)$$

(ii) Ratio of the radii of gyration

$$\begin{aligned} \frac{R_{g1}(0)}{R_{g2}(0)} &= \frac{B_1}{B_2}\left(\frac{N_1}{N_2}\right)^{\nu} \quad \text{limit A} \\ &= \frac{B_1}{\hat{l}_2}\frac{N_1^{\nu}}{N_2^{1/2}} \quad \text{limit B} \end{aligned} \qquad (3.38)$$

Note, that in all these expressions $R_{ga}(0)$ by definition is the radius of an isolated chain of fixed length N_a under Θ- or excluded-volume conditions. If all couplings including g_{12} take fixed point values, then all scaling functions, which by definition depend only on renormalized variables, can be expressed in terms of these scaling variables.[12]

The limits A and B considered so far represent the experimentally most relevant scaling regions. The further limit $f_1 \sim f_2 \rightarrow 0$ considered in the literature[10] needs a common Θ-solvent for both polymer species, which is a very special case not explicitly treated here. (We mention in passing that our choice of the renormalized length scale, which is dictated by the screening effect, in the semidilute Θ-limit yields results that differ from those of ref 10.)

4. Scattering Experiments

4.1. The χ-Parameter. Comparing eqs 2.4 and 2.5 to eqs 3.2 and 3.8, we find

$$\left(1 - \frac{c_1}{\rho_1} - \frac{c_2}{\rho_2}\right)^{-1} - 2\chi_{0a} = \frac{\rho_a^2}{\rho_0}l_R^3\frac{(N_R^{(a)})^2}{N_a^2}g_{aa} \qquad (4.1)$$

$$\chi_{12} = \frac{\rho_1\rho_2}{2\rho_0}l_R^3\frac{N_R^{(1)}N_R^{(2)}}{N_1N_2}\left[2g_{12} - U(\lambda)g_{11} - \frac{g_{22}}{U(\lambda)}\right] \qquad (4.2)$$

$$U(\lambda) = \frac{\rho_1N_R^{(1)}N_2}{\rho_2N_1N_R^{(2)}} \qquad (4.3)$$

It is easily checked that these expressions coincide with our previous results derived from thermodynamic quantities, except that in ref 9 we took $\rho_1 = \rho_2 = \rho_0$.

Equation 4.2 shows that χ_{12} is not simply a measure of the (renormalized) interaction of the two polymer species. To determine g_{12}, we need information on the parameters of the binary subsystems. A simplification occurs insofar as the ratio $N_R^{(a)}/N_a$ via eqs 3.4 and 3.5 depends only on λ, $s_N^{(a)}$, and $s_l^{(a)}$. Thus, except for the trivial term $(1 - (c_1/\rho_1) - (c_2/\rho_2))^{-1}$, the χ-parameters depend on chain lengths and concentrations only implicitly via λ. This feature, however, is lost in higher order perturbation theory.

We now consider the scaling limits.

Limit A. Equations 3.18 and 4.2 yield

$$\chi_{12} = \frac{\rho_1\rho_2}{\rho_0}(B_1B_2)^{1/\nu}g^*l_R^{3-2/\nu}(f_{12} - 1 - \Delta U) \qquad (4.4)$$

$$\Delta U = \frac{1}{2}\left[\frac{\rho_1}{\rho_2}\left[\frac{B_1}{B_2}\right]^{1/\nu} + \frac{\rho_2}{\rho_1}\left[\frac{B_2}{B_1}\right]^{1/\nu}\right] - 1 \qquad (4.5)$$

For $|f_{12} - 1| \ll 1$ we find from eqs 3.24 and 3.25, or eqs 3.27 and 3.29

$$\chi_{12} = \frac{\rho_1\rho_2}{\rho_0}B_1^3\left[\frac{B_2}{B_1}\right]^{1/\nu}g^*N_1^{3\nu-2}\left[\left[\frac{s_l^{(12)}}{B_1}\right]^{\omega12}N_1^{-\nu\omega12} - \Delta U\right] \qquad (4.6)$$

$$2 - 3\nu = 0.24; \quad \nu\omega_{12} = 0.22; \quad \text{dilute limit}$$

$$\chi_{12} = \frac{\rho_1\rho_2}{\rho_0}(B_1B_2)^{3/2}g^*(2g^*\hat{c})^{(2-3\nu)/(3\nu-1)} \times \left[\left[\frac{s_l^{(12)}}{(B_1B_2)^{1/2}}\right]^{\omega12}(2g^*\hat{c})^{\nu\omega12/(3\nu-1)} - \Delta U\right] \qquad (4.7)$$

$$\frac{2 - 3\nu}{3\nu - 1} = 0.31; \quad \frac{\nu\omega_{12}}{3\nu - 1} = 0.29; \quad \text{semidilute limit}$$

The nonuniversal parameter ΔU is positive and vanishes only if the additional symmetry condition $\rho_1B_1^{1/\nu} = \rho_2B_2^{1/\nu}$ is fulfilled.

In general, the limiting behavior of χ_{12} as $f_{12} \rightarrow 1$ is dominated by the contribution of $\Delta U > 0$ and thus by the properties of the *binary* subsystems. χ_{12} will reach its asymptotic value $\chi_{12} = 0$ from below, the limiting power law being independent of ω_{12} or $s_l^{(12)}$. To get information specific for the *ternary* system, we have to consider the corrections to the leading power law, and the analysis becomes quite delicate. We illustrate this in Figure 1 where we have plotted log χ_{12} against log $(c_1 + c_2)$, as evaluated from eq 4.4. We use parameters $B_1 = 2.49 \times 10^{-8}$ cm, $B_2 = 2.31 \times 10^{-8}$ cm, and $s_l^{(12)} = 1.06 \times 10^{-11}$ cm as suggested by a rough preliminary evaluation of the data of ref 2, but to show the effect of ΔU we used $\Delta U = 0.0035$, a value 5 times larger than that found for this system. (An accurate evaluation of these data within the framework of our theory is given in ref 12.) The asymptotic curve representing the semidilute limit (eq 4.7) shows definite curvature, but for finite chain lengths and larger concentrations the data can be well represented by a straight line. A naive interpretation indicates the asymptotic power law log $\chi_{12} \approx 0.68$ log $(c_1 + c_2) - 0.35$. Evaluating this result in the spirit of simple scaling models, i.e., using eq 4.7 with $\Delta U = 0$, we find $\omega_{12} = 0.48$ and $s_l^{(12)} = 7.5 \times 10^{-11}$ cm, to be compared to the correct values $\omega_{12} = 0.37$ and $s_l^{(12)} = 1.06 \times 10^{-11}$ cm. Note that just from such data we have no chance to uncover the failure of our power law analysis, since clearly we can attribute the deviations from the "asymptotic power law" occurring for small $c_1 + c_2$ to a violation of the semidilute limit, and possible deviations for large $c_1 + c_2$ would be taken to indicate that the experiments leave the region $|f_{12} - 1| \ll 1$.

Similar results are found in the dilute limit. In Figure 2 we plot log χ_{12} as function of log N_1 for the parameter values given above. Again the curve does not confirm the naively expected power law, and a power law analysis of some finite intermediate range of N_1 yields

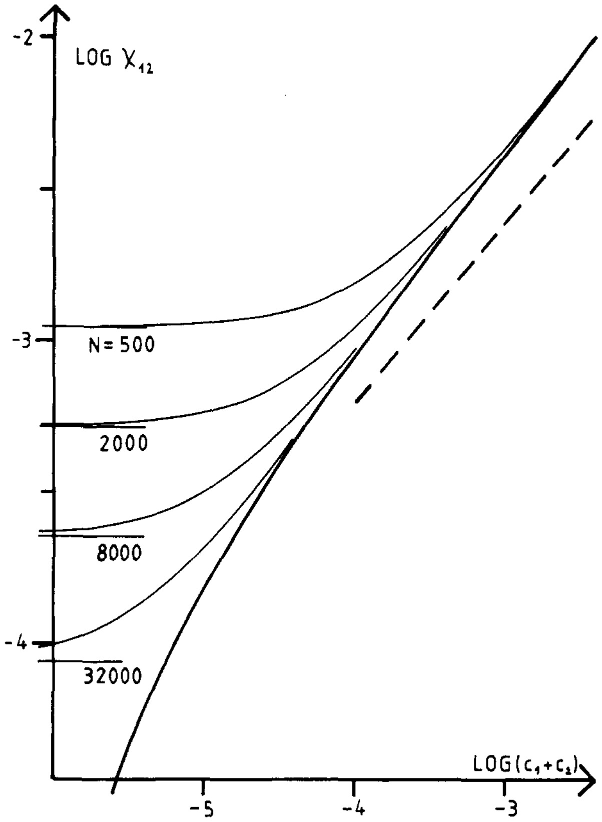

Figure 1. log χ_{12} as a function of log $(c_1 + c_2)$ close to the symmetric fixed point (limit A). The fat line represents the semidilute limit $N_R \to \infty$. Thin lines give results for finite N. The slope of the broken line indicates the ideal power law for $\Delta U = 0$. The curves are calculated with the full crossover form for f_{12}, using parameter values given in the text.

completely wrong parameters.

This discussion shows that a simple scaling analysis of χ_{12} is justified only if $\Delta U \approx 0$. Fortunately ΔU is not very sensitive to small deviations $\rho_1 B_1^{1/\nu} \neq \rho_2 B_2^{1/\nu}$, and furthermore $\Delta U \approx 0$ can be checked on the values of χ_{0a}: From eq 4.1 we find in the excluded-volume limit

$$\frac{\chi_{01}}{\chi_{02}} = \left[\frac{\rho_1 (B_1)^{1/\nu}}{\rho_2 (B_2)^{1/\nu}}\right]^2$$

and therefore a simple power law analysis of χ_{12} is justified from $\chi_{01} \approx \chi_{02}$. However, a quantitative formulation of this criterion again needs additional information since from eq 4.4 the deviation $\chi_{01} - \chi_{02} \neq 0$, which can be tolerated, depends on $f_{12} - 1$ and thus on $s_l^{(12)}$! Furthermore, any error in the parameters α_a of the Θ-condition (eq 2.8), for instance due to a wrong estimate of N_{wa}, can result in an increase of ΔU. In summary, the consistency of a power law analysis for χ_{12} in the good-solvent scaling regime cannot be checked intrinsically. It needs a more precise evaluation using additional data and the full RG result.

Limit B. Equations 3.18, 3.30, and 4.2 yield

$$\chi_{12} = \frac{\rho_1\rho_2}{\rho_0} B_1^{2/\nu} g^* l_R^{3-2/\nu} \left[\hat{l}_2^{\,2} B_1^{-1/\nu} l_R^{1/\nu-2} f_{12} - \frac{\rho_2}{2\rho_1} \right] \quad (4.8)$$

The scaling limit $l/l_R = \lambda \to 0$ is dominated by the second term in the square brackets, again involving the parameters of the binary subsystems only. The first correction results from replacing f_{12} by its fixed point value $\tilde{f}_{12}^*$ and thus is still independent of $\tilde{\omega}_{12}$ and $s_l^{(12)}$. In the extreme dilute or semidilute limits we find

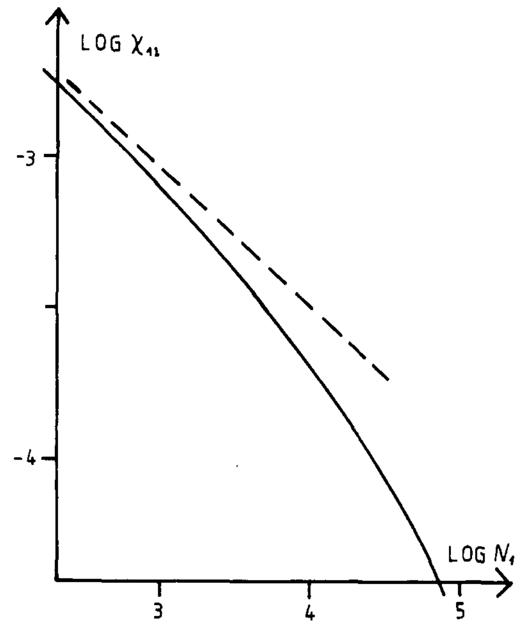

Figure 2. log χ_{12} as a function of log N_1 in the dilute limit. The slope of the broken line indicates the power law for $\Delta U = 0$. Parameter values as in Figure 1.

$$\chi_{12} = \frac{\rho_1\rho_2}{\rho_0} \tilde{l}_2^{\,3} \left[\frac{B_1}{\tilde{l}_2}\right]^{2/\nu} g^* N_2^{3/2-1/\nu} \times \left[\left[\frac{B_1}{\tilde{l}_2}\right]^{-1/\nu} \tilde{f}_{12}^* N_2^{1/2\nu-1} - \frac{\rho_2}{2\rho_1}\right] \quad (4.9)$$

$$\frac{1}{\nu} - \frac{3}{2} = 0.20; \quad 1 - \frac{1}{2\nu} = 0.15; \quad \text{dilute limit}$$

$$\chi_{12} = \frac{\rho_1\rho_2}{\rho_0} B_1^{\,3} g^* (2g^* B_1^{\,3} c_1)^{(2-3\nu)/(3\nu-1)} \times \left[\left[\frac{\hat{l}_2}{B_1}\right]^2 \tilde{f}_{12}^* (2g^* B_1^{\,3} c_1)^{(2\nu-1)/(3\nu-1)} - \frac{\rho_2}{2\rho_1}\right] \quad (4.10)$$

$$\frac{2-3\nu}{3\nu-1} = 0.31; \quad \frac{2\nu-1}{3\nu-1} = 0.23; \quad \text{semidilute limit}$$

Since we have no way to suppress the leading contribution $\sim\rho_2/(2\rho_1)$, it is clear that a reliable determination of $s_l^{(12)}$, which measures the deviations of f_{12} from $\tilde{f}_{12}^*$, needs data far outside the scaling limit. Furthermore, the exponents of the correction terms in eqs 4.9 and 4.10 are quite small so that an analysis of χ_{12} by a single power law will never be justified in practice.

4.2. Renormalized Optical Θ-Condition. The previous analysis suggests that we search for a modification of the optical Θ-condition that in limit A eliminates the leading contribution ΔU. In the spirit of the derivation of the optical Θ-condition we first consider the dilute limit. The virial coefficients can be expressed in terms of renormalized quantities via eqs 2.6 and 3.12.

$$A_{aa} = l_R^{\,3} (N_{wR}^{(a)})^2 g_{aa} \quad (4.11)$$

$$A_{a\bar{a}} = 0 \quad (4.12)$$

$$\bar{A}_{12} = -l_R^{\,3} N_{wR}^{(1)} N_{wR}^{(2)} g_{12} \quad (4.13)$$

Choosing $\alpha_a = N_{wR}^{(a)}$, we find from eq 2.9

$$A = -\nu_1\nu_2 c_1 c_2 l_R^{\,3} N_{wR}^{(1)} N_{wR}^{(2)} (2g_{12} - g_{11} - g_{22}) \quad (4.14)$$

to be compared to eq 2.12 with eq 4.2 taken for χ_{12}. Obvi-

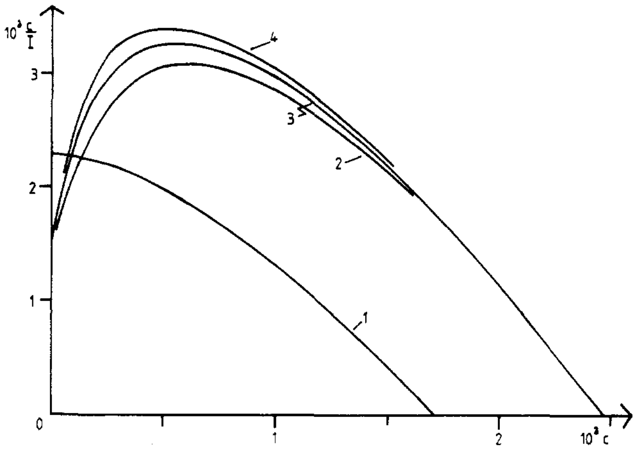

Figure 3. $10^3c/I(q{=}0)$ as a function of 10^3c. Curve 1 uses parameter values of Figure 1 and a composition x corresponding to renormalized optical Θ-conditions. Curves 2–4 use a different composition and show the effect of varying $B_1 = B_2 = B$ and $s_l^{(12)}$ as explained in the text.

ously the annoying factors $U(\lambda)$ are absent.

The price paid is some complication of the optical Θ-condition. With $\alpha_a = N_{wR}^{(a)}$ eq 2.8 yields

$$\nu_1 c_1 N_{wR}^{(1)} + \nu_2 c_2 N_{wR}^{(2)} = 0 \tag{4.15}$$

This "renormalized optical Θ-condition" even in the dilute limit implicitly depends on the f_a (compare eq 3.5). In limit A it simplifies by virtue of eq 3.18:

$$\nu_1 c_1 B_1^{1/\nu} N_{w1} + \nu_2 c_2 B_2^{1/\nu} N_{w2} = 0 \tag{4.16}$$

Equations 4.16 and 2.13 become identical only for $\rho_1 B_1^{1/\nu} = \rho_2 B_2^{1/\nu}$, which is the exceptional case $\Delta U = 0$ where the unrenormalized Θ-condition yields simple power laws for χ_{12} (compare eqs 4.6 and 4.7). With the renormalized Θ-condition these simple laws hold in all the scaling regime A, with no additional symmetry requirements.

The expression for the scattering intensity at $q = 0$ also simplifies. Assuming $f_a = 1$ and $|1 - f_{12}| \ll 1$, we can reduce the tree approximation for $I(q{=}0,\nu_1,\nu_2)$ to the form

$$-\frac{\nu_1 \nu_2 c}{I(0,\nu_1,\nu_2)} = Y^{-1} - 2 l_R^{3-\omega_{12}-2/\nu} (s_l^{(12)})^{\omega_{12}} (B_1 B_2)^{1/\nu} g^* x(1-x) N_{w1} N_{w2} Y^{-2} c \tag{4.17}$$

valid for all concentrations. Here

$$Y = x[B_1/B_2]^{1/\nu} N_{w1} + (1-x)[B_2/B_1]^{1/\nu} N_{w2} \tag{4.18}$$

$$c = c_1 + c_2 \qquad c_1 = xc \tag{4.19}$$

Quite generally this behavior is reached for very long chains. According to eq 4.17, c/I depends almost linearly on concentration, some small curvature being due to the implicit c-dependence of l_R, which is to be determined by the renormalization condition. The typical shape is shown in Figure 3, curve 1, which compares favorably to the typical shape of experimental results of ref 2. (A semiquantitative analysis is given in ref 12.) To show the effect of the Θ-condition (eq 4.16), we also calculated c/I for a different composition x (curve 3 in Figure 3). Typically c/I passes through a maximum which is suppressed by the Θ-condition. In unrenormalized theory the same effect was found in ref 1 subject to the additional symmetry condition $c_1 = c_2$.

From eq 4.17 it is obvious that the renormalized Θ-condition fixes a concentration particularly suited for a determination of $s_l^{(12)}$. It is of interest to discuss the sensitivity of $s_l^{(12)}$, as derived from such data, to errors in B_a or N_{wa}. To simplify the analysis, we take $B_1 = B_2 = B$ and $N_{w1} = N_{w2} = N_w$. We first consider the spinodal, given by the zero of c/I, which is most sensitive to $s_l^{(12)}$. Since the spinodal is found in the semidulute region, we can use the renormalization condition in the form of eq 3.26 to find

$$0 = 1 - (s_l^{(12)})^{\omega_{12}} B^{(3+\omega_{12})/(3\nu-1)} x(1-x) N_w [2g^* c]^{(1+\nu\omega_{12})/(3\nu-1)} \tag{4.20}$$

$$\omega_{12} = 0.37; \quad \frac{3+\omega_{12}}{3\nu-1} = 4.41; \quad \frac{1+\nu\omega_{12}}{3\nu-1} = 1.60$$

This result is consistent with our previous work.[9] Clearly eq 4.20 fixes only a special combination $\sim (s_l^{(12)})^{0.37} B^{4.41}$ of the nonuniversal parameters. The numerical evaluation shows that with the renormalized optical Θ-condition c/I in all the concentration regime to a very good approximation is sensitive only to this combination. For instance, a 10% change of B can be compensated by a change of $s_l^{(12)}$ within the accuracy of our plot (Figure 3, curve 1). $s_l^{(12)}$ is extremely sensitive to B. Due to the numerically very different exponents a 10% change of B induces a change of $s_l^{(12)}$ by a factor of 3! Thus errors in B_a make an important source of uncertainly for $s_l^{(12)}$. The sensitivity to errors in N_w is not as large, but still not negligible.

The need for precise values of B_a and N_a seems to be a general feature, not restricted to scattering under optical Θ-conditions. To illustrate this, we in Figure 3 have included two more curves (2 and 4) differing from curve 3 only by the choice of B and a compensating change of $s_l^{(12)}$. Curves 2–4 cannot be distinguished in the semidilute region. Only the maximum at intermediate concentrations is sensitive to B separately. The renormalized Θ-condition suppresses exactly this region.

If we leave the scaling limit A the renormalized Θ-condition becomes less useful since it depends on f_a and thus implicitly on concentrations and chain length. In scaling limit B it simplifies again:

$$\nu_1 c_1 \left[\frac{B_1 N_1^{\nu}}{l_2 N_2^{1/2}}\right]^{1/\nu} + \nu_2 c_2 = 0$$

For $N_1 \sim N_2 \rightarrow \infty$ this yields $\nu_1 c_1 \sim 0$; i.e., the renormalized optical Θ-condition naturally leads to an isorefractive solvent.

4.3. Isorefractive Solvent in the Strongly Asymmetric Limit. In limit B, where polymer species 2 is at its Θ-temperature whereas species 1 is in good-solvent conditions, we expect results interpreted most simply if the solvent happens to be isorefractive to species 1: $\nu_1 = 0$. In this situation eqs 2.1 and 3.12 yield

$$1 - \frac{\nu_2^2 c_2 N_{w2}}{I(0,0,\nu_2)} = g_{12}^2 \frac{c_R^{(1)} c_R^{(2)} N_{wR}^{(1)} N_{wR}^{(2)}}{1 + g^* c_R^{(1)} N_{wR}^{(1)}} \tag{4.21}$$

A particularly simple result is found by taking the dilute limit with respect to component 1. According to section 3.4, the renormalization condition in general will reduce to $N_R^{(2)} = 1$ to give

$$\lim_{c_1 \to 0} \left[1 - \frac{\nu_2^2 c_2 N_{w2}}{I(0,0,\nu_2)}\right] c_1^{-1} = g_{12}^2 \tilde{l}_2^{6-2/\nu} B_1^{2/\nu} \tilde{p}_1'' \tilde{p}_2'' N_1 N_2^{2-1/\nu} c_2 \tag{4.22i}$$

where $\tilde{p}_a''$ denotes the second moment of the reduced

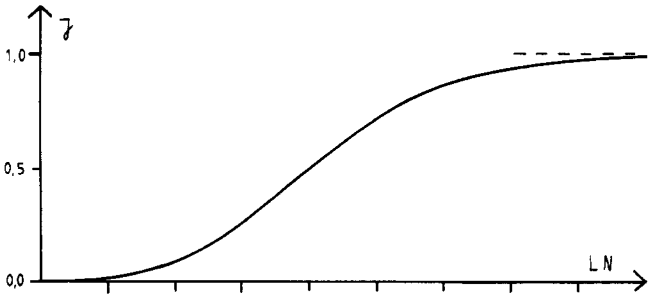

Figure 4. $J = [1 - \nu_2{}^2 c_2 N_{w2}/I(0,0,\nu_2)](g_{12}{}^{*2} s_1 s_2)^{-1}$ for $R_{g1} = R_{g2}$ as a function of $LN = \log\,[[\hat{l}_2/s_l{}^{(12)}]^2[g_{12}{}^*/g^*]^{(2/\omega_{12})-(8/3)}N_2]$ for an unsymmetric system $g_{11} = g^*$ and $g_{22} = 0$, in the limit $s_1 \to 0$. The variation is due to the change of g_{12} with N_2 from $g_{12} \to 0$ ($N_2 \to 0$) to $g_{12} \to g_{12}{}^*$ ($N_2 \to \infty$).

chain length distribution: $\tilde{p}_a'' = N_{wa}/N_a$. This result takes a simpler form if we introduce the appropriate scaling variables (eqs 3.37 and 3.38). We find

$$\lim_{s_1 \to 0} \left[1 - \frac{\nu_2{}^2 c_2 N_{w2}}{I(0,0,\nu_2)}\right] s_1{}^{-1} = g_{12}{}^2 \tilde{p}_1'' \tilde{p}_2'' s_2 \left[\frac{R_{g1}}{R_{g2}}\right]^{2/\nu - 3} \qquad (4.22\text{ii})$$

$$2/\nu - 3 = 0.40$$

valid in tree approximation for all s_2. Simple expressions also result if we add a small amount of species 2 to a semidilute solution of species 1. Since in the limit $g^* c_R{}^{(1)} N_R{}^{(1)} \gg 1$, the variables $c_R{}^{(1)} N_{wR}{}^{(1)}$ cancel in eq 4.21. From eqs 3.30 and 3.31 together with the renormalization condition $2g^* c_R{}^{(1)} = 1$, we find

$$1 - \frac{\nu_2{}^2 c_2 N_{w2}}{I(0,0,\nu_2)} = \frac{g_{12}{}^2}{g^*}[B_1{}^{1/\nu} 2 g^* c_1]^{\nu/(3\nu-1)} \hat{l}_2{}^4 c_2 N_{w2}$$

$$= \frac{g_{12}{}^2}{g^*}(2g^* s_1)^{\nu/(3\nu-1)} s_2 \frac{R_{g2}}{R_{g1}} \tilde{p}_2'' \qquad (4.23)$$

$$\frac{\nu}{3\nu - 1} = 0.77$$

In contrast to the results (eqs 4.9 and 4.10, of the unrenormalized optical Θ-method, eqs 4.22 and 4.23 contain no leading term independent of $f_{12} = g_{12}/g^*$. An isorefractive solvent—if it can be found—in scaling limit B therefore clearly is superior to the Θ-method. For long chains g_{12} of course will tend to its fixed point value, independent of $s_l{}^{(12)}$, but information on $\tilde{\omega}_{12}$ and $s_l{}^{(12)}$ can be extracted from the leading corrections. In Figure 4 we show the crossover behavior predicted by eq 4.22 in terms of appropriately reduced variables.

5. Osmotic Pressure Compensation Experiments

A standard experiment in the thermodynamics of solutions consists of the determination of the osmotic pressure, π. For ternary solutions lowest order renormalized theory predicts

$$\frac{\pi}{k_B T} = c_{p1} + c_{p2} + \frac{1}{2} l_R{}^{-3} \sum_{ab=1}^{2} g_{ab} c_R{}^{(a)} c_R{}^{(b)} \qquad (5.1)$$

This result looks like a virial expansion carried to second order. Due to the occurrence of renormalized variables which depend nonlinearly on the physical concentrations, it, however, describes the *whole crossover* from the dilute to the semidilute regimes. Results for the second virial coefficients can be found in refs 8, 9, and 17.

In general, the pressure due to 1–2 contacts will be of the same order of magnitude as the pressure due to a–a contacts. Measuring the pressure of the ternary solution not against pure solvent but against a carefully chosen binary solution, we might be able to compensate uninteresting contributions to π and to concentrate on effects specific for the interaction among the different polymer species. We thus assume that a ternary solution (system II) is measured against a binary solution (system I), the experimental result being

$$\Delta\pi = \left[\frac{\pi}{k_B T}\right]^{\text{II}} - \left[\frac{\pi}{k_B T}\right]^{\text{I}} \qquad (5.2)$$

We concentrate on the two scaling limits discussed throughout this paper.

5.1. Good Solvent Scaling Limit. For $g_{aa} = g^*$ and $a = 1$ and 2, we can rewrite eq 5.1 in the form

$$\left[\frac{\pi}{k_B T}\right]^{\text{II}} = c_{p1}{}^{\text{II}} + c_{p2}{}^{\text{II}} + g^*(l_R{}^{\text{II}})^{-3}\left[\frac{1}{2}[c_R{}^{\text{II}}]^2 + (f_{12} - 1)c_R{}^{(1)\text{II}} c_R{}^{(2)\text{II}}\right] \qquad (5.3)$$

where

$$c_R{}^{\text{II}} = c_R{}^{(1)\text{II}} + c_R{}^{(2)\text{II}} \qquad (5.4)$$

and the superscript II refers to the ternary solution. The interesting information is contained in the term proportional to $f_{12} - 1$, and we thus look for a binary solution I compensating the contribution proportional to $(c_R{}^{\text{II}})^2$. Ideally solution I should obey

$$c_R{}^{(1)\text{I}} \equiv c_R{}^{\text{II}} \qquad c_R{}^{(2)\text{I}} \equiv 0 \qquad l_R{}^{\text{I}} \equiv l_R{}^{\text{II}} \qquad (5.5)$$

These relations are too restrictive, however. Due to the difference of the binary solution renormalization condition

$$1 = [N_R{}^{(1)\text{I}}]^{-1} + 2g^* c_R{}^{(1)\text{I}} \qquad (5.6)$$

as compared to conditions in eqs 3.16 and 3.17, the postulates $l_R{}^{\text{I}} \equiv l_R{}^{\text{II}}$, $c_R{}^{(1)\text{I}} \equiv c_R{}^{\text{II}}$ cannot be fulfilled simultaneously. The difference in the renormalization conditions is reduced if we adjust the molecular weights such that

$$N_R{}^{(1)\text{II}} \equiv N_R{}^{(2)\text{II}} = N_R{}^{\text{II}} \qquad (5.7\text{i})$$

or (see eq 3.21)

$$R_{g1}(0) \equiv R_{g2}(0) = R_g(0) \qquad (5.7\text{ii})$$

equivalently. Restricting ourselves to this situation and assuming $|f_{12} - 1| \ll 1$, we can expand the renormalization condition of the ternary system to find

$$1 = [N_R{}^{\text{II}}]^{-1} + 2g^* c_R{}^{\text{II}} + 4g^*(f_{12} - 1)\frac{c_R{}^{(1)\text{II}} c_R{}^{(2)\text{II}}}{c_R{}^{\text{II}}} + O(f_{12} - 1)^2 \qquad (5.8)$$

We now impose the compensation condition

$$c_1{}^{\text{I}} = c_1{}^{\text{II}} + \left[\frac{B_2}{B_1}\right]^{1/\nu} c_2{}^{\text{II}} \qquad (5.9)$$

which guarantees that eq 5.5 is fulfilled to zero order in $f_{12} - 1$. (Compare eqs 5.6 and 5.8.) With eq 5.7, eq 5.9 implies that the total polymer concentrations c_p in both solutions are identical.

$$c_{p1}{}^{\text{I}} = c_{p1}{}^{\text{II}} + \left[\frac{R_{g2}(0)}{R_{g1}(0)}\right]^{1/\nu} c_{p2}{}^{\text{II}} = c_{p1}{}^{\text{II}} + c_{p2}{}^{\text{II}} \qquad (5.10)$$

With eq 5.6 fixing l_R^{I}, we can solve eq 5.8 to find the ratio l_R^{II}/l_R^{I} to first order in $f_{12} - 1$. Substituting the result into eqs 5.2 and 5.3, we find after some straightforward algebra

$$\Delta\pi = g^*(f_{12} - 1)l_R^{d-2/\nu}(B_1B_2)^{1/\nu}\frac{x(1-x)(c^{II})^2}{1 + (3\nu - 2)2g^*c_R^{II}} \quad (5.11)$$

where $l_R = l_R^{I} = l_R^{II} + 0(f_{12} - 1)$ and $x = c_1^{II}/c^{II}$ (compare eq 4.19). In the dilute or semidilute limits our result reads

dilute limit

$$\begin{aligned}\pm\Delta\pi &= g^*[s_l^{(12)}]^{\omega12}B_1^{3-\omega12-1/\nu}B_2^{1/\nu}N_1^{3\nu-\nu\omega12-2}x(1-x)(c^{II})^2 \\ &= g^*\left[\frac{s_l^{(12)}}{R_g(0)}\right]^{\omega12}R_g^3(0)c_{p1}^{II}c_{p2}^{II} \quad (5.12)\end{aligned}$$

semidilute limit

$$\begin{aligned}\pm\Delta\pi &= \frac{1}{6\nu-2}(2g^*)^{(1+\nu\omega12)/(3\nu-1)}[s_l^{(12)}]^{\omega12} \times \\ &(B_1B_2)^{[(3+\omega12)/(3\nu-1)](1/2)}x(1-x)\left[\left(\frac{B_1}{B_2}\right)^{1/2\nu}x + \left(\frac{B_2}{B_1}\right)^{1/2\nu} \times \right. \\ &\left.(1-x)\right]^{(1+\nu\omega12)/(3\nu-1)-1}(c^{II})^{\nu(3+\omega12)/(3\nu-1)} \\ &= \frac{1}{6\nu-2}\left[\frac{s_l^{(12)}}{R_g(0)}\right]^{\omega12}[2g^*(s_1 + s_2)]^{(1+\nu\omega12)/(3\nu-1)}\frac{c_{p1}^{II}c_{p2}^{II}}{c_{p1}^{II} + c_{p2}^{II}}\end{aligned} \quad (5.13)$$

$$\frac{1+\nu\omega_{12}}{3\nu-1} = 1.60$$

The sign in front of $\Delta\pi$ refers to an incompatible (+; $f_{12} > 1$) or compatible (−; $f_{12} < 1$) ternary solution, respectively.

The assumptions $R_{g1}(0) = R_{g2}(0)$ and $|f_{12} - 1| \ll 1$, which lead to the simple result in eq 5.11, are not very crucial. If $R_{g1}(0) = R_{g2}(0)$ but f_{12} is not close to 1, then our straightforward evaluation fails, but the experimental effect still is totally due to the deviation $f_{12} - 1$. If furthermore the radii of gyration differ, then we still can evaluate the dilute or semidilute limits. In the semidilute limit and for $|f_{12} - 1| \ll 1$ we find the same result as given in the first line of eq 5.13—a result that in fact is independent of the chain lengths. Also in the dilute limit we essentially recover the first line of eq 5.12, provided the compensating solution I contains the species of smaller radius of gyration: $N_R^{(1)} < N_R^{(2)}$; i.e., $R_{g1}(0) < R_{g2}(0)$.

$$\lim_{c^{II}\to 0}\left[\Delta\pi + \left(\left[\frac{R_{g2}(0)}{R_{g1}(0)}\right]^{1/\nu} - 1\right)c_{p2}^{II}\right][c^{II}]^{-2} = g^*(s_l^{(12)})^{\omega12}B_1^{3-1/\nu-\omega12}B_2^{1/\nu}N_1^{3\nu-\nu\omega12-2}x(1-x) \quad (5.14)$$

This shows that a compensation experiment with c_1^{I} chosen according to eq 5.9 fulfills its task of compensating the leading contribution to π, measuring essentially $f_{12} - 1$.

Comparing eqs 4.17 and 5.11, we find that the compensation method suggested here yields results of the same structure as scattering under renormalized optical Θ-conditions. The osmotic method has some interesting advantages and one great disadvantage. The benefits are obvious: The solvent is not restricted by the condition $\nu_1\nu_2 < 0$, and we are free to change the composition of the solution. The problem arises from the order of magnitude of the different terms in the expression 5.3 for the osmotic pressure. In general, the interesting term $\sim f_{12} - 1$ is only a small correction, comparable in magnitude to the ideal gas term. Thus the compensation has to be done very carefully, based on precisely known values of B_a.

5.2. Strongly Asymmetric Limit. Simple limiting results are found if polymer species 2 is at its Θ-temperature ($g_{22} = 0$) whereas species 1 is in good-solvent conditions ($g_{11} = g^*$). We first consider a case in which a small amount of polymer 1 is added to a solution of polymer 2, the so produced ternary system II being measured against the binary solution I of polymer 2.

$$c_{p2}^{I} = c_{p2}^{II} \qquad c_{p1}^{I} = 0 \qquad c_{p1}^{II} > 0 \quad (5.15)$$

Provided $N_R^{(1)} > N_R^{(2)}$ the renormalization condition reduces to $N_R^{(2)} = 1$. A simple calculation yields

$$\begin{aligned}\lim_{c_1^{II}\to 0}\left[\frac{\Delta\pi}{c_{p1}^{II}} - 1\right] &= g_{12}\hat{l}_2^{d-1/\nu}B_1^{1/\nu}N_2^{1/2-1/2\nu}N_1c_2^{II} \\ &= g_{12}\left[\frac{R_{g1}(0)}{R_{g2}(0)}\right]^{1/\nu}s_2^{II} \quad (5.16)\end{aligned}$$

This holds for all s_2^{II}.

Another experiment of interest consists in adding a small amount of species 2 to a semidilute solution of species 1.

$$c_1^{I} = c_1^{II} \qquad c_2^{I} = 0 \qquad c_2^{II} > 0 \quad (5.17)$$

Here the screening lengths and thus the renormalization conditions differ in both solutions. As in the previous subsection we can treat this effect perturbatively to find

$$\lim_{c_2^{II}\to 0}\left[\frac{\Delta\pi}{c_{p2}^{II}} - 1\right] = \frac{2-3\nu}{3\nu-1}\frac{g_{12}^2}{4g^*} + \frac{g_{12}}{2g^*}\left[1 + \frac{2-3\nu}{3\nu-1}\frac{g_{12}}{2g^*}\right] \times \left[\frac{R_{g2}(0)}{R_{g1}(0)}\right]^2[2g^*s_1^{II}]^{2\nu/(3\nu-1)} \quad (5.18)$$

These results should be compared to eqs 4.22 and 4.23, established for a solvent isorefractive to polymer species 1. Clearly the two types of experiments carry the same information. However, the osmotic pressure can be determined for any solvent obeying $g_{22} = 0$, $g_{11} = g^*$ without need for the additional very restrictive constraint of isorefractivity.

The experiments proposed above allow for a determination of the renormalized coupling constant g_{12}. For long chains and small concentrations g_{12} tends to its fixed point value $g^*\tilde{f}_{12}^*$, and we may ask whether we can compensate the fixed point behavior to measure only the deviations from the scaling limit, in complete analogy to the compensation experiment discussed in the previous subsection. A fairly simple compensation condition can be given only in the dilute limit, provided $N_R^{(1)} \le N_R^{(2)}$, i.e., $R_{g1}(0) \le R_{g2}(0)$, so that the renormalization condition takes the form $l_R^{I} = l_R^{II} = R_{g1}(0)$. Choosing

$$c_1^{I} = c_1^{II}\left[1 + 2\tilde{f}_{12}^*\left[\frac{R_{g2}(0)}{R_{g1}(0)}\right]^2\frac{c_{p2}^{II}}{c_{p1}^{II}}\right]^{1/2} \qquad c_2^{I} = 0 \quad (5.19)$$

we find in the dilute limit of both components

$$\Delta\pi = c_{p1}^{II} + c_{p2}^{II} - c_{p1}^{I} + g^*(f_{12} - \tilde{f}_{12}^*)\left[\frac{R_{g2}(0)}{R_{g1}(0)}\right]^2c_{p2}^{II}s_1^{II} \quad (5.20)$$

Assuming $f_{12} < \tilde{f}_{12}^*$, we can solve eq 3.34 to find the leading behavior

$$f_{12} - \tilde{f}_{12}^* = -\left[\tilde{f}_{12}^{*4/3}\frac{s_l^{(12)}}{R_{g1}(0)}\right]^{\tilde{\omega}_{12}} \qquad (5.21)$$

This method suffers from the fact that the not precisely known quantity $\tilde{f}_{12}^*$ occurs in the compensation condition. ($\tilde{f}_{12}^* = 47/32$ only to second order.) Thus in practice the compensation will only be approximate, and the experimental result should not be evaluated assuming eqs 5.19–5.21.

6. Summary and Conclusions

In this paper we have discussed compensation experiments which aim at a determination of features characteristic for a ternary polymer solution. Often such experiments are evaluated assuming simple power law scaling. We have stressed that this might be quite misleading. In a situation where the solvent is equally excellent for both polymer species, all the interesting effects are due to the corrections to the leading scaling behavior. We then have to check carefully whether a simple power law indeed does dominate the effects. In particular, for an optical Θ-solvent we have found that, in general, the representation of the data by a single power law cannot be justified. We have proposed a modification of the optical Θ-condition, which to leading order yields simple power laws, and we have suggested an equivalent osmotic pressure measurement. We want to stress that even for the evaluation of such experiments, we need additional information: We need to know the parameters of the binary subsystems polymer (a)–solvent both to judge whether we are in the good-solvent limit and to evaluate the experiment quantitatively. If this information can be provided, we can extract the basic parameter $s_l^{(12)}$ of the polymer–polymer interaction. Its precision, however, strongly depends on the precision of the binary solution parameters.

We also considered a strongly asymmetric situation in which one polymer species is at its Θ-temperature, the other one being in good-solvent conditions. We proposed both osmotic and light-scattering experiments adequate for this scaling limit, which to our belief should find more interest.

To fix the experimental conditions, the different experiments need information on the binary subsystems on a very different level. For the isorefractive solvent method as well as for the first two osmotic experiments in the strongly asymmetric limit we only have to guarantee that the Θ-condition or the condition of isorefractivity is met. In contrast, all experiments in the symmetric limit as well as an osmotic measurement aiming at compensation of the fixed point behavior in the asymmetric case need precise values of the binary solution parameters in order to set up the ternary solutions. Thus these latter experiments should be evaluated using our general results, not assuming a priori that the relevant conditions on the composition of the solution are met precisely.

Just fitting to power laws one is restricted to the dilute or semidilute behavior in the scaling limits. Our method is not restricted to these limits, and we have presented some results from which the crossover can be extracted. A complete discussion of all observable quantities in all the available parameter regions can be found in ref 12. Our present quantitative results for the crossover functions are based on lowest order perturbation theory and therefore are not expected to be quantitatively correct. They, however, certainly reproduce the qualitative features of the crossover, and experience with binary solutions suggests that lowest order results of our scheme reproduce the experiments within 10% deviation. First-order results for the free energy and related quantities recently have been published in ref 18.

Our results show that the role of the χ_{12}-parameter is greatly overemphasized in the literature. This parameter is a nonuniversal quantity showing complicated crossover behavior. Its value, in general, gives no direct information on the compatibility of the system. Furthermore, focusing on χ_{12} we lose a lot of information contained in the data. This is particular obvious for unsymmetric solutions.

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