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The thermodynamic scaling function of a polymer solution

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Abstract. — We calculate the thermodynamic scaling function of a polymer solution in the good solvent regime. This function controls all thermodynamic properties, in particular the osmotic pressure. Our calculation uses a modification of the $\epsilon$-expansion, recently introduced by Schäfer and Horner to treat the Goldstone singularities of an isotropic magnet. This modified expansion concentrates on the vertex irreducible diagrams, and it gives a unified description of both the small overlap and the large overlap regime. We present a complete first order calculation, including also the effect of polydispersity. This effect is found to be small, influencing mainly the second virial coefficient. In the second order calculation we restrict ourselves to a polydisperse ensemble in which the chain length distribution is in chemical equilibrium, and we neglect some small contributions. The convergence is reasonable, and our results are in good agreement with experimental data.

1. Introduction. — Long polymer chains in a good solvent show scaling behaviour [1] which can be explained by the renormalization group. This approach can also be used to predict which aspects of the observed phenomena are universal, i.e. independent of variables like temperature $T$ or chemistry of the solution. Thus Des Cloizeaux has shown [2] that the osmotic pressure $\Pi$ of a dilute solution of long chains in the excluded volume limit obeys a scaling law

$$\frac{\Pi}{k_B T c_p} = 1 + \beta (B^d c_p N^{vd})$$

(1.1)

where $c_p$ and $N$ denote the concentration of chains and the (number-average) chain length, respectively, and $B$ is a non-universal length parameter. The exponent $\nu$ is universal, depending only on the space dimension $d$. Also the function $\beta$ is universal, it however will depend not only on $d$ but also on the chain length distribution (polydispersity) in the solution. As has been discussed previously [3], this dependence can be incorporated into the renormalization group approach, identifying $\beta$ as a universal functional of the chain length distribution. Furthermore it can be shown that $\beta$ determines not only the osmotic pressure but also other thermodynamic quantities of interest. For instance, the energy excess $\Delta u$ of the solution obeys the scaling law [3]

$$\Delta u = c_p [\alpha_1 N + \alpha_2 + \alpha_3 \beta (B^d c_p N^{vd})]$$

(1.2)
with non-universal constants $\alpha_i$ and similar results can be given for the entropy excess, the chemical potential, etc. Thus the functional $\mathcal{S}$ is the central thermodynamic quantity in the excluded volume limit.

When combined with the Feynman-graph methods of field theory the renormalization group approach allows for a calculation of the universal behaviour in an expansion in powers of $\varepsilon = 4 - d$, and this expansion has been used to get estimates for critical exponents (like $v$ in eq. (1.1)) and for some scaling functions. In this paper we use this method to calculate the thermodynamic scaling functional $\mathcal{S}$. In doing this we encounter two major complications. The first one is the polydispersity dependence mentioned above. A method to incorporate this dependence in an actual calculation was suggested in reference [3], and here for the first time this formalism is applied to a non-trivial example. The second complication concerns the treatment of the semi-dilute region where the chains overlap strongly. As is well known [2] (see also figure 5 of reference [4]) this region in the phase transition analogue of the excluded volume problem corresponds to the neighbourhood of the «coexistence» curve, where the «Goldstone» singularities occur. These singularities have an origin quite different from the «critical» power laws observed in dilute solutions. In the language of the polymer system they are collective effects due to monomer density fluctuations correlated over the volume occupied by a chain. Some years ago L. Schäfer and H. Horner [5] suggested a method to treat these Goldstone singularities on the same level as the critical singularities, and in the present paper we will rely heavily on their results. This enables us to calculate the functional $\mathcal{S}$ in the whole region ranging from vanishing to infinite overlap of the chains. We here restrict ourselves to the good solvent (excluded volume) limit. Similar results for a poor solvent have been presented by Des Cloizeaux [6].

The organization of this article is as follows:

In section 2 we calculate $\mathcal{S}$ to first order in $\varepsilon$ for a chain length distribution in chemical equilibrium, thereby explaining the salient features of our approach. In section 3 this calculation is modified so as to include polydispersity. In section 4 we directly use the results of reference [5] to get the functional $\mathcal{S}$ to second order for the equilibrium distribution, and section 5 contains a summary and a discussion of our results. Throughout the paper we use the conventions of reference [3].

This paper is certainly not self-contained in that we make extensive use of previous field theoretic work. It is our aim here to show how these field theoretic methods can be used to obtain detailed predictions taking into account the special features of the polymer problem. Furthermore a comparison of second order to first order results shall give us a feeling for the degree of accuracy that can be reached. A detailed comparison of our results to those of previous (non-renormalization group) theories goes beyond the frame of the present paper and will be published elsewhere.

2. Calculation of $\mathcal{S}$ in the equilibrium ensemble to first order. — 2.1 Definitions, and reduction to one-vertex irreducible diagrams. — The equilibrium ensemble is defined by a chemical potential $\mu(n)$ for chains of length $n$ which takes the form

$$\mu(n) = \mu_0 + \mu_1 n. \quad (2.1)$$

This chemical potential gives rise to a broad probability distribution $P(n)$ for chains of length $n$. In the dilute limit this distribution has the form [7]

$$P_\sigma(n) = \frac{\sigma}{NT(\sigma)} e^{-\frac{\sigma n}{N}} e^{-\frac{\sigma n}{N}} \quad (2.2)$$

where $\sigma$ is identical to the critical exponent $\gamma = 1.62$. The distribution changes with increasing overlap, and in the large overlap limit it again takes the form (2.2), but with $\sigma = 1$.

With the choice (2.1) of $\mu(n)$ polymer theory can be mapped [1, 2] onto a special Landau-Ginzburg-Wilson model of phase transitions. The osmotic pressure can be expressed as

$$\frac{\Pi}{k_B T} = 2 \gamma \rho \kappa \Gamma(t, M) \quad (2.3)$$

where $\Gamma(t, M)$ represents the renormalized dimensionless vertex function calculated from the set of all one-line irreducible diagrams with propagator $(q^2 + t)^{-1}$, four-point vertex $g$, and one-point vertices $M$, which are to be attached directly to four-point vertices (1). Closed propagator loops are forbidden in polymer theory, and the diagrams are subtracted at renormalization momentum $\kappa$ according to the massless renormalization scheme. This momentum scale $\kappa$ is also used to make all the quantities of the renormalized theory ($\Gamma$, $t$, $q$, etc.) dimensionless. The variables $t$ and $M$ are related to the concentrations of chains $c_p$ and of links $c_l = c_p$, $N$ by the equations

$$\kappa^{-d} c_p = \frac{1}{2} M \frac{\partial \Gamma}{\partial M} \equiv c_{p,R} \quad (2.4)$$

$$S_\kappa \kappa^{-d} c_l = \frac{\partial \Gamma}{\partial t} \equiv c_{l,R} \quad (2.5)$$

where

$$S_\kappa = A(\kappa l)^{1/v} \quad (2.6)$$

(1) For a definition of the field theoretic concepts used here we refer to the review article of Bézin et al. [8].
is a renormalization factor and $v = 0.588$ is the critical exponent in equation (1.1). The length $l$ is the average size of a link of the unrenormalized chain and thus it defines the microscopic length scale.

The $\varepsilon$-expansion proceeds by ordering the diagrams of $\Gamma(t, M)$ according to the number of integration loops. This yields a sensible theory in the dilute limit but breaks down as soon as Goldstone singularities become important. As Schäfer and Horner have shown one may construct a theory valid in all the range of interest by focussing attention on the one-vertex irreducible diagrams instead the one-line irreducible ones. (Recently Des Cloizeaux [6] has also given a theory of polymer solutions based on vertex irreducibility.) In addition a special choice of the renormalization momentum $\kappa$ is required as will be discussed in subsect. 2.3.

The analysis of $\Gamma(t, M)$ in terms of one-vertex irreducible parts $\mathcal{U}$ proceeds in close analogy to the topological analysis which establishes [9] the relation between Legendre transform and one-line irreducibility. We find

$$\Gamma(t, M) = \frac{1}{2} tM^2 + \frac{g}{24} M^4 - \frac{g}{6} c^2 - \mathcal{U} \quad (2.7)$$

where $\mathcal{U}$ denotes the sum of all one-vertex irreducible diagrams with propagators $(t+g/6 M^2 + g/3 c + q^2)^{-1}$ and $c$ represents the sum of all subdiagrams which can be attached to the diagrams by a single vertex. This partial summation can be interpreted formally as a Legendre transformation (see also reference [6]) with respect to $t$ of the non-trivial part

$$\Delta = \frac{1}{2} tM^2 + \frac{g}{24} M^4 - \Gamma,$$

and $c$ then is identified as

$$c = -\frac{\partial \Delta}{\partial t}. \quad (2.8)$$

Equation (2.5) immediately leads to a rigorous relation between $c$ and $c_{1R}$:

$$c_{1R} = \frac{1}{2} M^2 + c. \quad (2.9)$$

### 2.2 The One-Loop Approximation

In the equilibrium ensemble $\mathcal{U}$ and $c$ can be evaluated easily by introducing the notion of longitudinal and transverse propagators. Setting the basis for the treatment of general polydispersity we, however, prefer to construct $\mathcal{U}$ and $c$ by summing polymer diagrams. To one-loop order the diagrams are exhibited in figure 1. This yields for $\mathcal{U}$

$$\mathcal{U} = -\frac{1}{2} \frac{g}{3} M^2 \int_q \left[ \frac{1}{m_1^2 + q^2} - \frac{1}{q^2} + \frac{m_2^2}{q^2(q + \kappa'^{2})} \right] +$$

$$+ \frac{1}{2} \frac{1}{2} \left( \frac{g}{3} M^2 \right)^2 \int_q \left[ \frac{1}{(m_1^2 + q^2)^2} - \frac{1}{q^2(q + \kappa'^{2})} \right] - \frac{1}{2} \frac{1}{3} \left( \frac{g}{3} M^2 \right)^3 \int_q \left[ (m_1^2 + q^2)^{-3} + \frac{1}{2} \frac{1}{4} \left( \frac{g}{3} M^2 \right)^4 \right] \int_q \left[ (m_1^2 + q^2)^{-4} - ... \right] \quad (2.10)$$

$$= -\frac{1}{2} \int_q \left[ \ln \left( 1 + \frac{g}{3} M^2 (m_1^2 + q^2)^{-1} \right) - \frac{g}{3} M^2 q^{-2} + \frac{g}{3} M^2 \frac{m_1^2 + \frac{g}{6} M^2}{q^2(q + \kappa'^{2})} \right] \quad (2.11)$$

where we have explicitly given the first four terms of the series of one-loop diagrams including the counterterms. The unit vector $\kappa'$ fixes the direction of the renormalization momentum $\kappa$ and $m_1^2$ stands for

$$m_1^2 = t + \frac{g}{3} c_{1R}. \quad (2.12)$$

The symbol $\int_q$ represents $\int d^4 q/(2 \pi)^{-4}$. For $c$ we find in the same way

$$c = -\frac{g}{6} M^2 \int_q \left[ (q^2 + m_1^2)^{-1} (q^2 + m_2^2)^{-1} - q^{-2}(q + \kappa'^{2})^{-2} \right] \quad (2.13)$$

$$+ \ldots$$

$$+ \ldots$$

Fig. 1. — One-loop diagrams contributing to $\mathcal{U}$ (1a) or $c$ (1b). Full lines denote propagators and broken lines denote interaction vertices. The heavy dots stand for $M$-vertices.
where

\[ m_2^2 = m_1^2 + \frac{g}{3} M^2. \quad (2.14) \]

The integrals are easily evaluated to yield (compare Eq. (2.7))

\[ \Gamma(t, M) = \frac{1}{2} t M^2 + \frac{g}{24} M^4 - \frac{g}{6} c^2 + \frac{1}{2} (m_2^2 - m_1^2) s_4 J_3 + \frac{1}{4} (m_2^2 - m_1^2) s_4 J_4 \quad (2.15) \]

\[ c = \frac{1}{2} (m_2^2 - m_1^2) s_4 J_2 + \frac{1}{2} (m_2^2 - m_1^2) s_4 J_4 \quad (2.16) \]

where

\[ J_1 = \int_0^\infty dq q^{-3} (q + \kappa) = \frac{\pi T (2 - \varepsilon/2) T (1 - \varepsilon/2)}{2 (2 - \varepsilon)} \sin \pi \varepsilon/2 = \frac{1}{\varepsilon} + \frac{1}{2} + O(\varepsilon) \quad (2.17) \]

\[ J_2 = \int_0^\infty dq q^{-1} [q^2 + 1]^{-1} q^{-2} = - \frac{\pi}{2 \sin \pi \varepsilon/2} = - \frac{1}{\varepsilon} + O(\varepsilon) \quad (2.18) \]

\[ J_3 = \int_0^\infty dq q^{-1} \ln (1 + q^2) q^{-2} = - \frac{\pi}{d \sin \pi \varepsilon/2} = - \frac{1}{2 \varepsilon} - \frac{1}{8} + O(\varepsilon) \quad (2.19) \]

and

\[ s_4 = (2\pi)^{-4} \frac{2\pi^{3/2}}{\Gamma(2 - \varepsilon/2)}. \quad (2.20) \]

We shall need to consider a range of \( M \) such that \( M' \) is of order 1, whereas \( g \) is of order \( \varepsilon \). Indeed,

\[ g = \varepsilon^{-1} \, g^* \quad (2.21) \]

where the fixed-point coupling constant \( g^* \) takes the value \( g^* = 3\varepsilon/4 + O(\varepsilon^2) \). As an obvious check we thus might evaluate \( g \Gamma(t, M) \), equation (2.15), in the \( \varepsilon \)-expansion to first order, to recover the results of reference [8], equation (9.24). However, in a consistent treatment of the coexistence curve powers of the type \( m_1^2 \equiv m_1^{2-\varepsilon} \), or \( m_1^{2-\varepsilon} \equiv m_1^{2-\varepsilon} \), should not be \( \varepsilon \)-expanded since they hold the information on the Goldstone singularities. These singularities occur as \( m_1 \to 0 \), which in the present approximation describes the coexistence curve. (Powers \( m_2^2 \) should be \( \varepsilon \)-expanded, however, since they are not related to Goldstone modes; \( m_2 \to \text{const. as } m_1 \to 0 \).)

As has been discussed in detail in reference [5] with the correct choice of \( K \) we may set up the theory as a double expansion in the two parameters \( \varepsilon \) and \( m_1^2 (m_1^{2-\varepsilon} - 1) \), and the one-loop approximation to one-vertex irreducible parts as discussed here is correct to first order in both parameters. (Note that in this expansion a term of the type \( \varepsilon_m^2 (m_1^{2-\varepsilon} - 1) \) is taken to be of second order.) From equations (2.16) to (2.18) the term \( g . c \) is found to be of first order:

\[ \frac{g}{3} c = \frac{\varepsilon}{8} m_2^2 \ln m_2 + \frac{\varepsilon}{16} (m_2^2 - m_1^2) + \frac{1}{8} m_2^2 (m_1^{2-\varepsilon} - 1). \quad (2.22) \]

Thus terms of order \( (g . c)^2 \) or \( g^* (g . c) \) will be neglected in the following.

The generalization of our method to arbitrary polydispersity is easier if we express all results in terms of polymer variables. A rigorous expression for \( c_{1,R} \) is given by equation (2.9), and a simple calculation based on equations (2.4), (2.12), (2.14), (2.15) yields to first order

\[ g c_{p,R} = \frac{1}{2} g M^2 \left[ m_2^2 + g^* (m_1^{2-\varepsilon} J_2 + m_2 J_1) \right] = \frac{1}{2} g M^2 \left[ m_2^2 + g^* m_2^2 + g^* m_2^2 \ln m_2 + O(\varepsilon^2) \right]. \quad (2.23) \]

We use these relations to eliminate \( t \) and \( M^2 \) in equation (2.15)

\[ \frac{g}{3} \Gamma = \frac{g}{3} c_{p,R} - \frac{1}{2} \left( \frac{g}{3} c_{1,R} \right)^2 \left[ 1 + \frac{2}{3} g^* J_1 \right] \quad (2.24) \]

\[ \frac{g}{3} c_{p,R} = \frac{g}{3} c_{1,R} m_1^2 g^* \left[ J_1 - \frac{1}{2} - \ln m_2 \right] - \frac{g}{3} c m_2^2 g^* J_1 + \frac{g^*}{6} J_3 (m_2^2 - m_1^2). \quad (2.24) \]
Though the integrals $J_1$ and $J_3$ diverge as $1/e$, $\Gamma$ must have no such divergence. Indeed, we may rewrite the last term on the r.h.s. using $m_2^2 = m_1^2 + g/3 \, M^2$ and $1/2 \, M^2 = c_{1,R} - c$:

$$m_2^2 - m_1^2 = 4 \, m_2^3 \frac{g}{3} (c_{1,R} - c) - 4 \left( \frac{g}{3} c_{1,R} \right)^2 + 8 \frac{g}{3} c_{1,R} \frac{g}{3} c - \varepsilon m_2^2 \ln m_2 - m_1^2 (m_1^{*2} - 1) .$$

(2.25)

To first order this yields

$$\frac{g}{3} \Gamma = \frac{g}{3} c_{1,R} - \frac{1}{2} \left( \frac{g}{3} c_{1,R} \right)^2 \left( 1 + \frac{e}{8} \right) - \frac{g}{3} c_{1,R} m_2^2 \frac{e}{16} +$$

$$+ \frac{m_1^4}{16} (m_1^{*2} - 1) + m_2^2 \ln m_2 \cdot \frac{e}{4} \left( \frac{m_2^2}{4} - \frac{g}{3} c_{1,R} \right) .$$

(2.26)

Equations (2.14), (2.9) and (2.23) yield to lowest order

$$m_1^2 = \frac{c_{1,R}}{c_{1,R}}$$

(2.27)

$$m_2^2 = \frac{c_{1,R}}{c_{1,R}} + \frac{g}{3} c_{1,R}$$

(2.28)

and equations (2.26) to (2.28) constitute the representation of $\Gamma$ in terms of polymer variables.

2.3 THE CHOICE OF THE RENORMALIZATION MOMENTUM. — As explained in detail in reference [5] the present problem possesses two length scales given by $m_1^{-1}$ and $m_2^{-1}$. The length $m_1^{-1}$ approximates the end-to-end distance of a single chain in the solution (transverse correlation length). It diverges in the limit $N \to \infty$.

In the dilute limit $m_2 \sim m_1 \to 0$ as $N \to \infty$. In the semi-dilute limit, however, $m_2$ stays finite as $m_1 \to 0$, $N \to \infty$; its order of magnitude in this region is given by $c_{1,R}$ (compare Eq. (2.28)). As shown in reference [5] the renormalization point is determined by the shorter correlation length, and we therefore fix $\kappa$ by choosing $m_2^2 = 1 + ae$. (Note that $m_2$ is dimensionless, the scale being given by $\kappa$.) Equations (2.14), (2.9), (2.23) then yield to first order

$$1 + ae = m_1^2 + \frac{2}{3} g(c_{1,R} - c) = \frac{c_{1,R}}{c_{1,R}} + \frac{2}{3} g(c_{1,R} - c) - \frac{g^*}{6}$$

(2.29)

and we choose $a$ such as to cancel the term $-g^*/6$ on the r.h.s. Introducing the notation

$$N_R = AN = Ac_{1,R}$$

(2.30)

and using equations (2.4)-(2.6) we find

$$1 = (N_R^{(\kappa l)^{1/v}})^{-1} \left[ 1 + \frac{gc}{g t^d \, c_p \, N_R^{(\kappa l)^{1/v}}} \right] + 2 \frac{g}{3} c_p \, N_R (\kappa l)^{1/d} - \frac{2}{3} gc ,$$

(2.31)

an equation which defines the renormalization point $\kappa$ implicitly as function of $c_p$ and $N_R$.

Equations (2.22), (2.27) yield

$$\frac{g}{3} c = \frac{e}{16} (1 - (\kappa l)^{-1/v} \, N_R^{-1}) + \frac{1}{8} (\kappa l)^{-1/v} \, N_R^{-1} \, [(N_R^{(\kappa l)^{1/v}})^{2/3} - 1] .$$

(2.32)

To eliminate $N_R$ we define a parameter $w$ by

$$\kappa l = (N_R \, w^{-v})^{-1}$$

(2.33)

thus reducing equations (2.31) and (2.32) to the form

$$w^{-1} = 1 + \frac{gc}{g s_R} w^{1-d} + \frac{2}{3} g s_R \, w^{d-2} - \frac{2}{3} gc w^{-1}$$

(2.34i)

$$\frac{g}{3} c = \frac{e}{16} (1 - w) + \frac{1}{8} w(w^{-d/2} - 1)$$

(2.34ii)

where the « overlap » $s_R$ is defined as

$$s_R = t^d \, c_p \, N_R^{d-2} \equiv B^d \, c_p \, N^{d-2} .$$

(2.35)
Solving equation (2.34i) for the overlap $s_R$ we find to first order

$$\frac{2}{3} g s_R = w^{1-vd} \left\{ 1 - w + \frac{2}{3} g c \left( 1 - \frac{w}{1-w} \right) \right\}. \quad (2.36)$$

We note the occurrence of the typical Goldstone mode term $w(w^{-v/2} - 1)$ contained in $c$ (Eq. (2.34ii)).

Equations (1.1), (2.3), (2.4) identify the thermodynamic scaling function as

$$f[s_R] = 1 - \frac{g f}{g c_{p,R}}$$

$$= \frac{1}{2} \frac{c_{l,R}}{c_{p,R}} \left( 1 + \frac{e}{8} \right) + \frac{e}{16} \frac{c_{l,R}}{c_{p,R}} - \frac{3}{16} \frac{c_{p,R}}{g c_{l,R}} \left( \frac{c_{p,R}}{c_{l,R}} \right)^{-v/2} - 1). \quad (2.38)$$

Equations (2.4) to (2.6) and (2.33) yield rigorously

$$\frac{c_{l,R}}{c_{p,R}} = w^{-1} \quad (2.39i)$$

$$\frac{c_{l,R}^2}{c_{p,R}} = s_R w^{v-2} \quad (2.39ii)$$

and we thus find

$$f(s_R) = \frac{1}{4} \left( \frac{2}{3} g s_R \right) w^{v-2} \left( 1 + \frac{e}{8} \right) + \frac{e}{16} w^{-1} - \frac{w}{8} w^{-v/2} - 1 \quad (2.40)$$

Equations (2.34ii), (2.36), (2.40) constitute a parameter representation of $f(s_R)$. We postpone its discussion to the next section where we derive the result for arbitrary polydispersity. We here only note that the parameter $w$ can be given a physical meaning in the context of scaling considerations. It is easily found to be proportional to the fraction of a chain occupying a «blob», where a blob is defined as a part of a chain not interpenetrated by another chain. (The concept of «blobs» is discussed in detail in chapter III, 2 of reference [1]). As a consequence the correlation length $m_2^{-1}$ can be interpreted as the size of a «blob».

3. The thermodynamic scaling function for arbitrary polydispersity. — 3.1 ONE-LOOP CALCULATION. —
A formulation for arbitrary polydispersity has been presented in reference [3], which in this section will be referred to as I, with the corresponding number of equations in brackets, if necessary. The formulation of I introduces a different variable $t_i$ for each polymer chain. A separate weight factor $M^2(t_i)$ regulates the number of chains with $t = t_i$, and the effective potential $\Gamma$ is a functional of $M^2(t_i)$. The integrations over $t_i$ appearing in this functional are taken along a contour $\Gamma$ enclosing the singularities of the vertex functions in the $t_i$. The generalizations of equations (2.4) and (2.5) defining $c_p$ and $c_l$ are given in equations (I 5.7, 5.8), respectively :

$$c_{p,R} = \frac{1}{2} \int_0^\infty \frac{dt}{\pi t} M(t) H(t)$$

$$c_{l,R} = \frac{1}{2} \int_0^\infty \frac{dt}{\pi t} M(t) \frac{dH(t)}{dt}. \quad (3.2)$$

The function

$$H(t) = \frac{\delta \Gamma}{\delta M(t)}$$

in mean field order is related to the chain length distribution $P(n) = 1/N \ p(n/N)$ by equations (I 6.17, 5.5) :

$$H^2(t) = 2 c_{p,R} \int_0^\infty dy \ p(y) \ exp \left[ \left( t + \frac{1}{3} X + \frac{g}{3} c \right) S_{x,y} \right] \quad (3.4)$$

$$X = \frac{\theta}{2} \int_0^\infty \frac{dt}{\pi t} M^2(t). \quad (3.5)$$

We here have modified equation (I 5.5) by the additional shift of $t$ due to the $c$-insertions.
Our first task consists in the calculation of the diagrams of figure 1. The basic piece is presented in figure 2a. It yields the contribution (compare I 6.18-6.20)

\[ R(q) = \int \frac{dt}{2 \pi i} M^2(t) \left[ t + \frac{1}{3} X + \frac{q}{3} c + q^2 \right]^{-1} = 2 c_{p,R}(S_X N)^2 Q^{-4} \left[ \tilde{p}(Q^2) - 1 + Q^2 \right] \]  

where (Eq. I 6.21)

\[ Q^2 = S_X N q^2 \]  

and \( \tilde{p}(Q^2) \) is the Laplace transform of \( p(y) \). We note that \( p(y) \) is normalized such that (I 3.22)

\[ \tilde{p}(0) = 1 \]  

\[ \frac{\partial}{\partial X} \tilde{p}(X) \bigg|_{X=0} = 1 . \]  

In the diagrams for \( c \) there occurs a second basic piece shown in figure 2b. This yields

\[ R_c(q) = \int \frac{dt}{2 \pi i} M^2(t) \left[ t + \frac{1}{3} X + \frac{q}{3} c + q^2 \right]^{-2} = - \frac{\partial}{\partial q^2} R(q) . \]  

With the expressions for the basic diagrammatic structures at hand the calculation of the one-loop contributions proceeds as in the previous section. The subtraction scheme remains unchanged and we find

\[ \Gamma = \frac{1}{2} \int \frac{dt}{2 \pi i} t M^2(t) + \frac{X^2}{6 g} - \frac{q}{6} c^2 + \frac{1}{2} \int \left( \ln \left( 1 + \frac{q}{3} R(q) \right) - \frac{2 X}{3 q^2} \right) + + \frac{q}{6} \int \frac{dt}{2 \pi i} M^2(t) \left( t + \frac{q}{3} c + \frac{X}{3} \right) S_q J_1 + \left( \frac{X}{3} \right)^2 S_q J_1 \]  

\[ c = \frac{X}{3} S_q J_1 - \frac{q}{6} \int \frac{R_c(q)}{1 + g/3 R(q)} . \]  

Following the procedure of section 2 we eliminate \( \int M^2(t) t \) and \( X = \int M^2(t) g/2 \) in favour of \( c_{p,R} \) and \( c_{1,R} \):

\[ c_{p,R} = \frac{1}{2} \int \frac{dt}{2 \pi i} M^2(t) t + \frac{1}{3} \left[ \frac{R(q)}{1 + g/3 R(q)} - \frac{2 X}{g q^2} \right] + + \left[ \frac{q}{6} \int \frac{dt}{2 \pi i} M^2(t) t + \frac{X}{3} \left( \frac{X}{3} + \frac{q}{3} c \right) + 2 \left( \frac{X}{3} \right)^2 \right] S_q J_1 \]  

\[ c_{1,R} = \frac{X}{g} + c . \]  

This yields for the scaling function \( \mathcal{F}(s_X) \) defined as in equation (2.37)

\[ \mathcal{F}(s_X) = \frac{g c_{1,R}^2}{6 c_{p,R}} \left[ 1 + \frac{2}{3} g^* J_1 \right] + \frac{g}{2} (g c_{p,R})^{-1} \int \left[ \frac{g/3 R(q)}{1 + g/3 R(q)} - \ln \left( 1 + g/3 R(q) \right) \right] \]  

a formula which generalizes equation (2.38). Introducing the function

\[ \hat{R}(Q) = \frac{2}{3} g c_{1,R}^2 Q^{-4} \left[ \tilde{p}(Q^2) - 1 + Q^2 \right] \]
we rewrite this result in the form

\[ \tilde{\beta}(s_R) = \frac{g c_{1,R}}{6 c_{p,R}} \left( 1 + \frac{2}{3} g^* J_1 \right) + \frac{g^*}{2} \frac{1}{g c_{p,R}} (S_x N)^{-d/2} K_1 \]  

(3.16)

where \( K_1 \) stands for the integral

\[ K_1 = S_{\delta}^{-1} \int_0^1 \left[ \frac{\tilde{R}(Q)}{1 + \tilde{R}(Q)} - \ln(1 + \tilde{R}(Q)) \right] . \]  

(3.17)

The renormalization momentum \( \kappa \) is chosen as in the previous section (Eqs. (2.29) or (2.31)); only the expression for \( c \) changes. Equation (3.11) yields

\[ c = \frac{g^*}{3} J_1 c_{1,R} + \frac{1}{2} (S_x N)^{-d/2} S_{\delta} K_2 \]  

(3.18)

where

\[ K_2 = S_{\delta}^{-1} \int_0^1 \frac{\partial}{\partial Q^2} \tilde{R}(Q) \frac{1 + \tilde{R}(Q)}{1 + \tilde{R}(Q)}. \]  

(3.19)

The rigorous relations (2.39) for \( c_{1,R}, c_{p,R} \) hold also in the present case. We thus find

\[ c_{1,R} = s_R w^{d-1} \]  

(3.20i)

\[ S_x N = \frac{c_{1,R}}{c_{p,R}} = w^{-1}. \]  

(3.20ii)

Equations (2.36), (3.18), and (3.20) yield the equation for \( s_R \)

\[ \frac{2}{3} g s_R = w^{1-vd} \left\{ 1 - w + \frac{g^*}{3} J_1 (1 - 2 w) + \frac{g^*}{3} w^{d/2-1} K_2 \frac{1 - 2 w}{1 - w} \right\}. \]  

(3.21)

\( \tilde{\beta}(s_R) \) is given by equations (3.16) and (3.20)

\[ \tilde{\beta}(s_R) = \frac{g}{6 s_R} w^{d-2} \left( 1 + \frac{2}{3} g^* J_1 \right) + \frac{g^*}{3} w^{d/2-1} K_1. \]  

(3.22)

Equations (3.21) and (3.22) give the parameter representation for general polydispersity to first order. The \( 1/\epsilon \) contributions in \( J_1 \) are cancelled by parts of the integrals \( K_1, K_2 \), respectively. The results of the previous section can easily be recovered by evaluating \( K_1, K_2 \) with \( \tilde{R}(Q) = (1/w - 1) (1 + Q^2)^{-1} \), the correct choice for the equilibrium ensemble \( \langle \hat{p}(x) \rangle = (1 + x)^{-1} \) to leading order in \( \epsilon \). All the polydispersity dependence is contained in the function \( \tilde{R}(Q) \) and thus in \( K_1, K_2 \). The Goldstone mode contributions are contained in \( K_1, K_2 \), and in the explicit factors \( w^{d/2-1} \).

We note that this derivation of \( \tilde{\beta}(s_R) \) has some features in common with the work of Des Cloizeaux [6] which applies to poor solvents. The crucial new feature in the theory of a good solvent as presented here is the use of the appropriately chosen running renormalization point as specified by \( \kappa \).

3.2 Lowest order results. — In lowest order our parameter representation reads

\[ \tilde{\beta}(s_R) = \frac{1}{4} w^{-1} (1 - w) \]  

(3.23i)

\[ \frac{2}{3} g s_R = w^{1-vd} (1 - w). \]  

(3.23ii)

This result is a remarkable improvement over the simple mean-field result \( \tilde{\beta}(s_R) = g/6 s_R \) given in (15.10). It reduces to this result for \( vd = 2 \). Both results are based only on tree-diagrams and respect the scaling laws, but equations (3.23) in addition show the correct asymptotic behaviour

\[ \tilde{\beta}(s_R) \sim \frac{1}{4} \left( \frac{2}{3} g s_R \right)^{1/vd-1}. \]  

(3.24)
(This asymptotic behaviour is an immediate result of the general structure of our equations (3.21, 3.22). To our knowledge it is proved here — and not postulated — for the first time). Furthermore we will find below that the higher order approximations do not change the lowest order result drastically and that even the lowest order result fits the data reasonably well. Thus this result in many aspects is analogous to the empirically established parameter representation of the equation of state [10]. We note that the result (3.23) is independent of polydispersity.

3.3 THE REGION OF LARGE OVERLAP. — In the limit of large overlap the thermodynamic scaling function is expected to be independent of polydispersity. Our result agrees with this expectation since as $s_R \to \infty$ the integrals $K_1, K_2$ are dominated by the integration over large momenta $q$ where $\tilde{R}(q) \to 2/3 g^* c_2^{1/2} R/c_p, R q^{-2}$ independent of polydispersity (2). An asymptotic analysis of the integrals yields

\[
K_1 = \left[ \frac{2}{3} g s_R w^{d-2} \right]^{d/2 - 1} (J_2 - J_1) + \left[ \frac{2}{3} g s_R w^{d-2} \right]^{d/2 - 1} \frac{\varepsilon}{4} \frac{\pi}{\sin \pi \varepsilon/2} + \text{const.} \tag{3.25i}
\]

\[
K_2 = \left[ \frac{2}{3} g s_R w^{d-2} \right]^{d/2 - 1} J_2 + \text{const.} \tag{3.25ii}
\]

where the leading polydispersity dependence of $K_1, K_2$ is in the unspecified constants. Substituting these results into the parameter representation we find

\[
\beta(s_R) \xrightarrow{s_R \to \infty} \frac{1}{4} \left( 1 + \frac{3}{8} \varepsilon \right) \left( \frac{2}{3} g s_R \right)^{d-1} + \frac{\varepsilon}{16} + O(\epsilon^3) \left( \frac{1}{s_R} \right)^{d-1}. \tag{3.26}
\]

We note that to order $\varepsilon$ not only the leading term $\sim \frac{1}{s_R} \varepsilon^{d-1}$ but also the next to leading term $\sim \frac{s_R^0}{\varepsilon}$ is independent of polydispersity. The leading polydispersity dependence is of order $s_R^{-d-1}$.

3.4 THE SECOND VIRIAL COEFFICIENT. — In the present context it is natural to define the second virial coefficient $A_2$ by the relation

\[
\beta(s_R) = \frac{2}{3} g s_R A_2 + O\left( \frac{2}{3} g s_R \right)^2. \tag{3.27}
\]

Since $vd - 2 = O(\epsilon)$ the expression (3.22) for $\beta(s_R)$ shows that for a calculation of $A_2$ to order $\epsilon$ it is sufficient to know the function $w(s_R)$ to order $\epsilon^2$, only. A simple calculation yields

\[
A_2 = \frac{1}{4} \left( 1 + \frac{\varepsilon}{2} (J_1 + 2 k_2) + O(\epsilon^3) \right) \tag{3.28}
\]

where $k_2$ is the first non-vanishing virial coefficient of $K_1$:

\[
K_1 = k_2 \left( \frac{2}{3} g s_R \right)^2 + O\left( \frac{2}{3} g s_R \right)^3 \tag{3.29}
\]

\[
k_2 = - \frac{1}{2} \int dq q^{-d-1} \{ q^{-4} (\tilde{R}(q^2) - 1 + q^2) \}. \tag{3.30}
\]

Evaluating this coefficient we find

\[
A_2 = \int dy dy' p(y) p(y') a_2(y, y') \tag{3.31}
\]

\[
a_2(y, y') = A_0 \left[ yy' + \frac{\varepsilon}{8} ((y + y')^2 \ln (y + y') - y^2 \ln y - y'^2 \ln y' - 2 yy' \ln (yy')) \right] + O(\varepsilon^2). \tag{3.32}
\]

\[
A_0 = \frac{1}{4} \left( 1 + \frac{\varepsilon}{8} (3 - 2 \tilde{v}_{ii}) \right). \tag{3.33}
\]

(2) See also the second paper of reference [6].
where $y_{Eu} = 0.577...$ is Euler's number. For the monodisperse ensemble $p(y) = \delta(y - 1)$ we immediately find

$$A_2^{(m)} = A_0 \left( 1 + \frac{e}{2} \ln 2 \right)$$

$$= \frac{1}{4} \left( 1 + \frac{e}{8} (3 - 2 y_{Eu} + 4 \ln 2) \right) + O(e^2). \quad (3.34i)$$

For the exponential distribution $p(y) = e^{-y}$ the value

$$A_2^{(e)} = \frac{1}{4} \left( 1 + \frac{e}{2} \right) + O(e^2). \quad (3.34ii)$$

results. Since the scale of $s_R$ is not universal, these $\epsilon$-expansions have no scale-independent meaning. We can, however, form a universal ratio measuring the polydispersity dependence of the second virial coefficient:

$$\frac{A_2^{(e)}}{A_2^{(m)}} = 1 + \frac{e}{8} (1 - 4 \ln 2 + 2 y_{Eu}) + O(e^2). \quad (3.35)$$

The $\epsilon$-expansion (3.32) of $a_2(y, y')$ does not fully exploit the scaling information. From $s/c_p \sim N^{vd} + O(c_p)$ it follows that $a_2(y, y')$ obeys the homogeneity law $a_2(\lambda y, \lambda y') = \lambda^{vd} a_2(y, y')$. This law is consistent with the $\epsilon$-expansion, and it suggests a way to interpret the logarithms in equation (3.32). Thus one form equivalent to (3.32) in $O(\epsilon)$ is

$$a_2(y, y') = \frac{1}{2} A_0 \left[ 4(y y')^{vd/2} + y^{vd} + y'^{vd} - (y + y')^{vd} \right]. \quad (3.36)$$

We stress that this is just a convenient guess; to construct the functional form of $a_2(y, y')$ uniquely we need additional information beyond scaling and the $\epsilon$-expansion. Note, however, that the $\epsilon$-expansion is not compatible with the form [11] $a_2(y, y') \sim (y^2 + y'^2)$ which treats the interacting polymers as hard spheres.

Using the form (3.36) we have evaluated $A_2$ for the Schultz-distributions (2.2). This yields

$$A_2(\sigma) = \frac{A_0}{2 \sigma^{vd}} \left\{ 4 \left( \frac{\Gamma(\sigma + vd)}{\Gamma(\sigma)} \right)^2 + 2 \frac{\Gamma(\sigma + vd)}{\Gamma(\sigma)} - \frac{\Gamma(2 \sigma + vd)}{\Gamma(2 \sigma)} \right\}. \quad (3.37)$$

As function of the ratio of the weight average to the number average molecular weight $M_w/M_n = 1 + 1/\sigma$, $A_2(\sigma)$ interpolates essentially linearly between the values $A_2(\infty) = 1.30 A_0$ for the monodisperse ensemble and $A_2(1) = 1.20 A_0$ for the exponential distribution. The deviation of $A_2(\sigma)$ from a linear decrease is less then 4%.

Obviously the influence of polydispersity on $A_2$ is not very strong. Whereas the absolute numbers for $A_2(\sigma)$ are subject to the uncertainties of the $\epsilon$-expansion the relative trend stays the same. For instance, based on equation (3.32) $A_2(\sigma)$ changes from 1.35 $A_0$ for monodisperse to 1.27 $A_0$ for $\sigma = 1$.

3.5 NUMERICAL EVALUATION. — We have evaluated $\delta(s_R)$ numerically for $d = 3$ for the monodisperse and the exponential ensemble. In figure 3 we plot our results for $\delta(s_R)/s_R$. As expected from our previous discussion the polydispersity dependence of $\delta$ is weak. It is largest for small overlap. In the same plot we have given the asymptotic behaviour $\delta \sim s^{1/(vd-1)}$ to show that the calculated curve gives a smooth interpolation between large and small overlap limits.

Fig. 3. — First order results for $\delta(s_R)/s_R$ as function of $s_R$. Results are given for the monodisperse ensemble (full line) and the exponential distribution (dotted line). Also indicated is the asymptotic behaviour (broken line).
4. Second order calculation for the equilibrium ensemble. — The equation of state of a $n$-component Landau-Ginzburg model connects the magnetization $M$ to the magnetic field $H$ and the temperature $t$. The renormalization group predicts the scaling form

$$g^{1/2} H (g^{1/2} M)^{-\delta} = f(t(g^{1/2} M)^{-1/\beta})$$

where $t, M, H$ are renormalized quantities measured in units of some fixed momentum $k$ and $t = 0$ is the critical temperature. The $\varepsilon$-expansion of $f(x)$ has been calculated to second order [12]. In reference [5] a parameter-representation of the equation of state has been derived which included the influence of the Goldstone modes:

$$ag^{1/2} H (g^{1/2} M)^{-\delta} = w(1 - w)^{1/2}$$

$$x = t(g^{1/2} M)^{-1/\beta} = h(w)$$

$$h(w) = (1 - w)^{-1/2} \left[ -1 + c_1 w + c_2 w^2 + G(c_3 + c_4 w) + G^2 c_5 + \varepsilon^2 w^3 D(w) \right]$$

Here $G$ is the Goldstone-mode term

$$G = w(w^{-1/2} - 1).$$

The calculation of reference [5] is of second order in the Goldstone-mode terms, but it omits $D(w)$ and the $O(\varepsilon^3)$ contributions to $c_1, c_2$. Comparing the $\varepsilon$-expansion of the parameter representation to the $O(\varepsilon^2)$ results for $f(x)$ we have been able to determine $D(w)$ and the $O(\varepsilon^2)$ contribution to $c_2$. A $O(\varepsilon^2)$ change of $c_1$ can be absorbed into the scale parameter $\alpha$ (Eq. (4.2)), and therefore this coefficient cannot be determined unambiguously in a second order calculation. Our results for $D(w)$ and the $c_i$ are presented in the appendix.

Using the known scaling behaviour of $\Gamma(t, M)$ we can define a scaling function $\psi(w)$ as

$$\psi(w) = (g^{1/2} M)^{-\varepsilon/\beta} g \Gamma(t, M).$$

The relation $H = \partial \Gamma/\partial M$ implies a differential equation relating $h(w)$ to $\psi(w)$

$$v a \psi(w) - \frac{h(w)}{h'(w)} \psi(w) = \frac{\beta}{\alpha} w(1 - w)^{1/2}$$

with the formal solution

$$\psi(w) = -h(w) \int dw' h'(w') \frac{\beta}{\alpha} w'(1 - w')^{1/2} (h(w'))^{1 - \varepsilon v}.$$  

The evaluation of this integral is not trivial since $h(w)$ vanishes along the line $t = 0, M \neq 0$ (compare Eq. (4.3)) corresponding to $w = w_0$. The absence of a singularity in $\psi(w)$ at $w = w_0$ serves as a boundary condition in the integration. A somewhat lengthy and tedious calculation reveals that $\psi(w)$ has a form quite similar to $h(w)$. We find

$$\psi(w) = \frac{1}{a} \frac{\beta}{\varepsilon v} (1 - w)^{1/2} \left[ b_0 + b_1 w + b_2 w^2 + G(b_3 + b_4 w) + G^2 b_5 + \varepsilon^2 w^3 R(w) \right].$$

The coefficients $b_i$ and the function $R(w)$ are again given in the appendix. $R(w)$ has no simple explicit form, but we can give an adequate and simple approximate parametrization.

The concentration $c_p$ in the present formulation is determined from equations (2.4) and (4.2)

$$a g c_p R = \frac{1}{2} w(1 - w)^{1/2} (g^{1/2} M)^{-\varepsilon/\beta}.$$  

The monomer concentration $c_1$ is given by equations (2.5), (4.3), (4.6)

$$ag c_{1, R} = \frac{\psi(w)}{h'(w)} (g^{1/2} M)^{(\varepsilon - 1)/\beta} = (g^{1/2} M)^{(\varepsilon - 1)/\beta} \left[ v a \frac{\psi(w)}{h'(w)} - \frac{\beta}{\alpha} w(1 - w)^{1/2} \right].$$  

From these equations the overlap is easily found as

$$\text{const. } s = \frac{\psi(w)}{1 - w} \left[ \frac{\psi(w)}{1 - w} - w \right]^{\varepsilon v (1 - w)}.$$
where we have introduced the functions $h$, $\psi$ to denote the parts in square brackets in equations (4.4), (4.9), respectively. Equations (4.11) and (4.10) yield the thermodynamic scaling function as

$$\beta(s_k) = 1 - \frac{2 \beta \psi(w)}{v_d w(1 - w)}. \quad (4.13)$$

The following parameter representation of $\beta(s_k)$ results

$$\beta^d s_k = w^1 v_d(1 - w) \left( 1 - \frac{5}{64} \varepsilon^2 w - \frac{27}{256} + \frac{\pi^2}{128} \varepsilon^3 w^2 + \left( \frac{3}{16} + \frac{\pi^2}{64} \right) \varepsilon^2 \frac{w^3}{3w - 1} + \frac{1}{4} \frac{G}{1 - w} \left( 1 - \frac{37}{32} \varepsilon - \frac{9}{16} \varepsilon w \right) + \frac{15}{16} - \frac{5w}{16} \right) + \frac{3}{32} \frac{G^2}{1 - w} \left[ 1 - \left( \frac{6 - 256}{3} b'' - 2 w \right) \frac{w}{3w - 1} \right] \right)^{1d}. \quad (4.14)$$

$$\beta(s_k) = \frac{1}{4w} \left( 1 - \frac{3}{8} \varepsilon + \left( \frac{\pi^2}{192} - \frac{23}{256} \right) \varepsilon^2 \frac{w^2}{3w - 1} \right) + \frac{1}{2} G - \frac{29}{32} \frac{w}{1 - w} \left[ 1 + \frac{11}{4} \varepsilon \right] + \frac{13}{16} \frac{w^2}{1 - w} \right) + \left( \frac{G}{1 - w} \frac{1}{4 - 8b''w} \right). \quad (4.15)$$

The constant $b''$ is a parameter introduced in the approximate representation of $R(w)$; it is determined such that the $O(\varepsilon^2)$ contribution in equation (4.14) is analytic at $w_0 = 1/3$. For $\varepsilon = 1$ the value $b'' = -0.0554$ results.

We have evaluated this parameter representation for $\varepsilon = 1$ using the best known value for $v_d$ : $v_d = 1.77$. Our formulae allow for three successive stages of approximation. We always keep the exact value of $v_d$, but in zero order we neglect all terms of order $\varepsilon$ or $G$. In first order we include the terms linear in these parameters and in second order we keep the full equations. The results are plotted in figure 4. The first order correction is found to have a large effect whereas the second order correction changes the curve only slightly. However, even the zero order curve has the right qualitative character, the large first order effect can be almost entirely compensated by a change of the scale $B$ of $s_k$. This is obvious from the expansion of the critical ratio connecting the large overlap behaviour to the second virial coefficient. This universal number can be defined as

$$R = \left[ \lim_{s_k \to \infty} \beta(s_k) s_k^{-1} \right]^{1 - v_d} \lim_{s_k \to 0} \beta(s_k) s_k^{-1}. \quad (4.16)$$

Evaluating this ratio in a strict $\varepsilon$-expansion, also taking into account the expansion of $v_d$, we find

$$R = 1 + 0.222 \varepsilon + 0.058 \varepsilon^2 + O(\varepsilon^3). \quad (4.17)$$

If we therefore normalize the asymptotic behaviour of $\beta(s_k)$ then the combined effect of the first and second order corrections, which is largest for small overlap, amounts to less then a 30% change.

In closing this section we want to point out again that our second order correction suffers from some uncertainties. Firstly we have not taken into account certain integrals exactly. This approximation can be checked, and we find an error less then 10% of the already very small $O(\varepsilon^3)$ correction. The uncertainty of the $O(\varepsilon^3)$ contribution to $c_1$ may be more serious. However, this uncertainty does not influence the strict $\varepsilon$-expansion to $O(\varepsilon^3)$ and being multiplied by $w$ the coefficient $c_1$ (Eq. (4.4)) also does not influence the large overlap limit. Thus we feel that our evaluation of the $O(\varepsilon^3)$ contribution is adequate.
5. Conclusions. — This work has demonstrated that renormalized field theory allows for detailed calculations of polymer scaling functions, even including the effect of polydispersity and the cross-over to the semi-dilute (large overlap) region. The Goldstone singularities are present in this calculation, but they only give small corrections. To make sure that we do not ignore subtle instabilities of our ensemble which might be related to the «negative susceptibility» discussed in reference [13], in the equilibrium ensemble we have calculated the derivative matrix of the chemical potentials with respect to the concentrations. The positiveness of this matrix ensures that our ensemble is stable. Thus, at least for thermodynamic quantities the field theory is perfectly meaningful also in the semi-dilute region.

In our treatment we have included the second order corrections in order to get a feeling for the quality of our expansion. The outcome is encouraging. The second order contribution is almost negligible. Furthermore our result compares well with experiment. In figure 4 we have given a typical set of data taken from reference [14]; the non-universal scale of the overlap has been fitted such that the large overlap limit of the data falls upon the second order curve. Obviously the over-all agreement between experiment and theory is quite good. This is in accord with the general observation that $\Theta(\epsilon)$ or $\Theta(\epsilon^2)$ results fit experimental data very well. In view of the smallness of the second order correction it suggests that a one-loop calculation of polymer scaling functions should give reasonable results. A more extensive comparison of our results to previous theories and to experimental data will be published elsewhere.

The polydispersity dependence of the thermodynamic scaling function is found to be small. This was to be expected since the mean-field approximation and the large overlap behaviour are both independent of polydispersity. We find that the second virial coefficient decreases with increasing width of the chain-length distribution. Surprisingly this contradicts earlier theories [11], and we hope to elucidate this point in a subsequent publication.

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APPENDIX

Numerical values of the coefficients in $h(w)$ and $\psi(w)$. — The coefficients $c_3$, $c_4$, $c_5$ of $h(w)$ can be taken from reference [5]:

$$c_3 = \frac{n - 1}{n + 8} + \frac{n - 1}{(n + 8)^2} \left( n + 30 - \frac{60}{n + 8} \right) \epsilon$$  \hspace{1cm} (A.1)

$$c_4 = -9 \frac{n - 1}{(n + 8)^2} \epsilon$$ \hspace{1cm} (A'.2)

$$c_5 = 6 \frac{n - 1}{(n + 8)^2}$$  \hspace{1cm} (A.3)

where $n$ denotes the number of spin components of the order parameter field. Since $G = w^{\nu/2} - 1$ is formally of order $\epsilon$, the coefficients as given here are sufficient for an $\Theta(\epsilon^2)$ calculation. Other terms of order $\epsilon^2$ are determined by fitting the parameter representation to the $\epsilon$-expansion of reference [12]:

$$c_2 = \frac{n - 1}{2(n + 8)^2} \left( \frac{\pi^2}{2} - 33 \frac{\epsilon}{\epsilon^2} \right)$$ \hspace{1cm} (A.4)

$$D(w) = \frac{n - 1}{2(n + 8)^2} \left\{ \frac{15}{2} - \pi^2 / 5 \ln w - 3 \ln^2 w + (3 - w) \frac{\hat{I}_1(w)}{w^3} - (1 - w) \frac{\hat{I}_2(w)}{w^3} \right\}.$$ \hspace{1cm} (A.5)

Here the functions $\hat{I}_k(w)$ are defined in terms of the functions $I_k(\rho)$, $\rho = \frac{1}{4} \left( 1 + \frac{2}{w} \right)$ of reference [12] by extracting the asymptotic behaviour as $\rho \to \infty$ so that $\hat{I}_k(w)/w^3$ stays finite as $w \to 0$:

$$\hat{I}_1(w) = \int_0^\rho \frac{du}{u} \ln u \left[ \left( 1 - \frac{u}{\rho} \right)^{1/2} - 1 \right] - \int_\rho^\infty \frac{du}{u} \ln u \left[ \frac{1}{4 \rho} \ln^2 4 \rho + 2 \ln 4 \rho + 2 + \frac{\pi^2}{3} \right] - \frac{1}{4 \rho^2} \left[ \ln^2 4 \rho - \ln 4 \rho - \frac{7}{2} + \frac{\pi^2}{3} \right]$$ \hspace{1cm} (A.6)
As mentioned in the text the \(O(\varepsilon^2)\) contribution of \(c_1\), cannot be determined uniquely by the matching procedure. We only get a relation for the \(O(\varepsilon^2)\) contribution of \(a + c_1\). This relation suggests as a plausible choice

\[
c_1 = 3 + \varepsilon + \frac{1}{(n + 8)^2} \left( 6n + 21 + \frac{2}{3}\pi^2(n - 1) \right) \varepsilon^2.
\]  

Our results for the coefficients \(b_i\) of \(\psi(w)\) read

\[
b_0 = \frac{2}{n - 4} - \frac{n + 2}{(n + 8)(n - 4)} \varepsilon + \frac{17 - \pi^2}{512 - 384} \varepsilon^2
\]  

\[
b_1 = - \frac{12}{n - 4} - \frac{1}{n - 4} \varepsilon + \frac{1}{128} + \frac{\pi^2}{192} \varepsilon^2
\]  

\[
b_2 = 2 \frac{n + 5}{n - 4} + \frac{n^2 + 16n + 10}{(n + 8)(n - 4)} \varepsilon - \left( \frac{21}{512} + \frac{\pi^2}{384} \right) \varepsilon^2
\]  

\[
b_3 = - 8 \frac{n - 1}{(n + 8)(n - 4)} \left[ 1 + \frac{1}{4(n + 8)} \left( n + 52 - \frac{120}{n + 8} \right) \varepsilon \right]
\]  

\[
b_4 = 2 \frac{n - 1}{n - 4} \left[ 1 + \frac{1}{2(n + 8)} \left( n + 32 + 6 \frac{n - 8}{n + 8} \right) \varepsilon \right]
\]  

\[
b_5 = 8 \frac{n - 1}{(n + 8)^2}.
\]

The underlined terms have been determined only for the polymer case \(n = 0\). The function \(R(w)\) is given by a complicated integral over \(D(w)\) and can be evaluated only numerically. It is found to yield a maximum contribution of order \(0.02 \varepsilon^2\). This being a small effect a rough representation of \(R(w)\) is sufficient. \(R(w)\) mainly is needed to fulfill certain boundary conditions. As is found from the differential equation (4.7) the function \(\psi(w)\) obeys the boundary condition

\[
\lim_{w \to 1} \frac{\psi(w)}{1 - w} = \frac{vd}{2\beta},
\]

a relation which guarantees that \(\beta(s_R) \to 0\) as \(s_R \to 0\) (compare Eq. (4.13)). Furthermore \((\psi(w)/(1 - w) - w h^{-1}(w)\) is regular at the zero of \(h(w)\) (compare Eq. (4.12)). Both these conditions can be fulfilled with the ansatz

\[
R(w) = - b' \frac{2}{\varepsilon} (w^{-\varepsilon^2} - 1) + b'' \frac{4}{\varepsilon^2} (w^{-\varepsilon^2} - 1)^2.
\]

Condition (A.15) determines \(b'\) as \(b' = 13/128\), and the second condition for \(\varepsilon = 1\) is fulfilled with the choice

\[
b'' = \frac{1}{16} - \frac{5}{192(\sqrt{3} - 1)} - \frac{1 + \pi^2/24}{32(\sqrt{3} - 1)^2} \sim - 0.0554.
\]

It turns out that this simple ansatz takes care of at least 80\% of the contribution of \(w^3 R(w)\).
References