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## Renormalized field theory of polymer solutions : extension to general polydispersity

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**Résumé.** — On étend la méthode du groupe de renormalisation à l'étude de solutions polymères de distributions de longueurs arbitraires (polydispersité). Dans la limite de volume exclu, la polydispersité ne peut être considérée ni comme pertinente, ni comme non pertinente, ni comme marginale. Les propriétés qualitatives (exposants critiques) ne sont pas influencées par la polydispersité. Les résultats quantitatifs (lois d'échelle) au contraire en dépendent et notre méthode permet de calculer ces effets. On établit facilement ces effets à l'ordre zéro (champ moyen) et ces derniers ont la forme que prévoient les théories classiques. De plus, notre formalisme fournit des relations générales entre la pression osmotique et ses dérivées thermodynamiques qui proviennent de la symétrie du groupe de symétrie. Une seule fonction universelle suffit à calculer les propriétés de toutes ces quantités.

**Abstract.** — We extend the renormalization group approach to polymer solutions of arbitrary chain length distribution (polydispersity). In the excluded volume limit polydispersity can be classified as neither relevant, irrelevant, nor marginal. The qualitative properties (the exponents) are not influenced by polydispersity. The quantitative results (scaling functions) are influenced, however, and our method allows for a calculation of these effects. Zero-order (*mean field theory*) results are easily established and show the structure expected from previous — non renormalization group — work. Further our formulation yields general relations among the osmotic pressure and its thermodynamic derivatives, which arise from the renormalization group symmetry. The overlap and polydispersity dependence of these quantities is governed by a single universal function.

**1. Introduction.** — A solution of randomly coiling long chain polymers possesses a type of scaling symmetry described [1] by the *renormalization group*. This renormalization symmetry dominates the behaviour of chains in a good solvent near the *critical point* where the mean length  $N$  approaches infinity and the chain concentration  $c_p$  tends to zero. Des Cloizeaux [2] has exploited this symmetry to show that near the critical point the osmotic pressure  $\Pi$  depends on  $N$  and  $c_p$  via

$$\frac{\Pi}{k_B T c_p} = 1 + \mathcal{F}(S_\kappa c_p N^{3\nu}) \quad (1.1)$$

where the exponent  $\nu$  and the scaling function  $\mathcal{F}$  are *universal*, i.e. independent of further properties of the system (temperature  $T$ , solvent density  $\rho_s$ , etc.). These properties influence only the nonuniversal

constant  $S_\kappa$ . Subsequently this approach has been used to discuss numerous properties of the polymer solutions [3-6]. In particular, in an earlier paper [7] (called SW in the following) we showed how renormalization symmetry could be used to give detailed information about the spatial correlations. The renormalization approach can be viewed as the microscopic theory underlying the more phenomenological approaches based on scaling hypotheses [8-11]. It allows one to verify these hypotheses and to calculate exponents and scaling functions.

A limitation of the renormalization approach to date has been the treatment of the chain length distribution (polydispersity). Most previous renormalization group theories contain a wide range of different chain lengths. Their distribution is governed by the requirement of monomer chemical equilibrium :

the monomers may attach themselves to and detach themselves from different chains. This equilibrium does not obtain in real polymer solutions; instead, each chain retains its original length. Thus to predict properties of the real solution one must transform the chemical equilibrium results to obtain those for the actual length distribution  $P(n)$ .

As Burch and Moore have shown [3, 4], this transformation process is easy for properties involving one or two chains; it is in principle straightforward for any finite number of chains. Still, this extra needed transformation is an awkward feature of the theory. In particular, it is hard to study general questions about the effect of polydispersity on scaling behaviour using these methods. Accordingly, we are led to incorporate the extra transformations into the basic theory itself so that it describes an arbitrary pre-specified chain length distribution  $P(n)$  from the outset.

In this generalized formalism we again can establish scaling laws. However, since now the dependence on a single variable, *viz.* the average chain length  $N$ , is substituted by the functional dependence on  $P(n)$ , neither the existence nor the form of the scaling laws is completely trivial. We find that the scaling laws adequately are expressed in terms of  $N$ ,  $c_p$ , and of the reduced chain length distribution  $p(x)$  defined as

$$P(n) = \frac{1}{N} p\left(\frac{n}{N}\right). \quad (1.2)$$

The function  $p(x)$  influences only the quantitative form of the scaling functions; the exponents and the qualitative form of the scaling laws are independent of polydispersity. For instance, the generalization of eq. (1.1) reads

$$\frac{\Pi}{k_B T c_p} = 1 + \mathcal{F}(S_\kappa c_p N^{3\nu}, [p(x)]) \quad (1.3)$$

where the function  $\mathcal{F}$  again is universal and can be calculated by field theoretic methods.

In establishing these results our tool is renormalized field theory together with De Gennes discovery [1] that the polymer system is related to a field theory of zero-component spins. We have attempted to exhibit the consequences of the field theory without presenting the derivation of the standard results <sup>(1)</sup>. Some special field theoretic features of the polymer system are discussed in Appendix B. The *zero-component* nature of the polymer field theory takes on a special importance when polydispersity questions are considered. The influence of polydispersity is not what one would expect by analogy with normal critical phenomena with other than zero-components. As we shall see below, the arbitrary polydispersity corresponds to a field theory with an infinity of zero-

component fields. Each field has its own correlation length which goes to infinity as the critical point  $N = \infty$ ,  $Nc_p = 0$  is approached. In ordinary critical phenomena one extra parameter suffices to describe the effect of the different correlation lengths. There is also an additional critical exponent associated with this parameter. In the polymer system, by contrast, the effects of polydispersity cannot be summarized in a single or a few parameters, and there is no new exponent needed. The reason for these differences is that the multiple-correlation length theory requires extra renormalization when there are more than zero-components, but no extra renormalizations are needed in the zero-component (polymer) system.

It is the main purpose of this paper to establish the generalization to arbitrary polydispersity, and this is the object of sections 2 and 3. In addition we discuss some simple consequences of our formalism. We derive the scaling law for the chemical potential and we show that all thermodynamic quantities can be simply expressed in terms of the scaling function  $\mathcal{F}(S_\kappa c_p N^{3\nu}, [p(x)])$  (section 4). Thus we obtain close relations between different thermodynamic measurements. We calculate  $\mathcal{F}$  in mean-field theory where it is independent of  $p(x)$  (section 5). This calculation is meant to illustrate our formalism and to provide a basis for more detailed calculations. Clearly the results of mean-field theory are not new (see, for instance, the monograph of Yamakawa [13]), except that renormalized field theory fixes the *effective coupling strength* — an undetermined parameter in previous mean-field theories — in the excluded volume limit. This was recently exploited [14] in a calculation of the *interpenetration function* for dilute solutions.

Our formalism is not restricted to thermodynamic quantities, and in section 6 we present general expressions and mean-field approximations for correlation functions. Section 7 contains our conclusions.

We repeat that our results are only valid for the excluded volume regime, where e.g. the chains are swollen by more than, say, a factor of three beyond their unperturbed dimensions. Thus our formulas do not describe the changes in the scaling functions as the temperature is reduced to the collapse temperature  $\theta$  for fixed average chain length.

**2. Unrenormalized formalism.** — We consider a solution containing chains of different lengths  $n$ . (In our theory the number of links  $n$  in a chain occurs only in combination with an arbitrary scale factor. We are thus free to define these links as we wish. For definiteness we will imagine a link to be a segment of the chain long enough to make an arbitrary angle with the next segment.) The partition function  $Z_p$  for  $m$  chains in solution relative to that of the pure solvent may be expressed in terms of some effective potential  $V_{\text{eff}} \{r_i(\lambda_i)\}$  depending explicitly on all the link coordinates  $r_i(\lambda_i)$ ,  $i = 1, \dots, m$ ;  $\lambda_i = 0, 1, \dots, n_i$ , and

<sup>(1)</sup> For a general reference we refer to the review article of Brézin *et al.* [12].

containing implicitly the influence of all the other degrees of freedom. Thus

$$Z_p(n_1, \dots, n_m) = Z(n_1, \dots, n_m; \mu_s, \Omega, T) / Z(\mu_s, \Omega, T) = \int_{\Omega} \prod_{i, \lambda_i} \left( \frac{d^d r_i(\lambda_i)}{(4\pi l^2)^{d/2}} \right) \exp \{ -V_{\text{eff}} \{ r_i(\lambda_i) \} \}. \quad (2.1)$$

Here  $d$  denotes the dimension of the space. The effective potential depends on the solvent chemical potential  $\mu_s$ , the temperature  $T$ , etc. The length  $l$  of a link has been introduced to make  $Z_p$  dimensionless, and each link coordinate is integrated over the volume  $\Omega$  of the system. Here — as in most equations — we have suppressed the factor  $(k_B T)^{-1}$ .

Without loss of generality we may formulate our problem in the grand canonical ensemble, giving each species  $n$  a chemical potential  $\mu(n)$ . Thus for a monodisperse solution  $\exp \mu(n)$  would be zero except for  $n \equiv N$ , while in the equilibrium ensemble

$$\mu(n) = \mu_0 + n\mu_1. \quad (2.2)$$

The grand partition function depends on the infinite set of variables  $\mu(n)$ ,  $n = 1, 2, 3, \dots$

$$Z_p \{ \mu(n) \} = 1 + \sum_{m=1}^{\infty} \frac{1}{m!} \times \sum_{n_1 \dots n_m} \prod_{i=1}^m e^{\mu(n_i)} Z_p(n_1, \dots, n_m). \quad (2.3)$$

A Laplace transformation is used to eliminate the summation over the chain lengths  $n_i$  in favour of integrations over monomer fugacities  $\tau_i$ :

$$Z_p \{ \mu(n) \} = 1 + \sum_{m=1}^{\infty} \frac{1}{m!} \times \oint \prod_{j=1}^m \left( \frac{d\tau_j}{4\pi i} h_0^2(\tau_j) l^{d+2} \right) \tilde{Z}_p(\tau_1, \dots, \tau_m) \quad (2.4)$$

where

$$\frac{h_0^2(\tau)}{2} l^{d+2} = \sum_{n=1}^{\infty} e^{\mu(n)} \tau^{-n-1} \quad (2.5)$$

$$\tilde{Z}_p(\tau_1, \dots, \tau_m) =$$

$$= \sum_{n_1 \dots n_m=1}^{\infty} \prod_{i=1}^m \tau_i^{n_i} Z_p(n_1, \dots, n_m). \quad (2.6)$$

The integral over  $d\tau_i$  in eq. (2.4) is over a path in the complex  $\tau_i$  plane which encloses the singularities of  $\tau_i h_0^2(\tau_i)$  and excludes those of  $\tilde{Z}_p$  (see Fig. 1). The factors of  $l$ ,  $\pi$ , and 2 are introduced in such a way that this expression corresponds directly to the (equilibrium) partition function of our previous

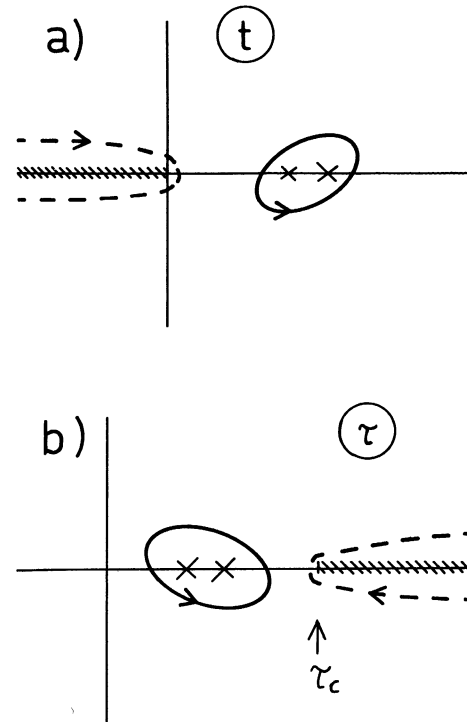


Fig. 1. — Structure of the complex  $t_i$ -plane (a) or  $\tau_i$ -plane (b). The full lines represent integration contours enclosing the singularities of  $h^2(t_i)$  or  $\tau_i h_0^2(\tau_i)$ , respectively. These singularities are represented by crosses. The broken lines represent integration contours around the cut of the vertex functions, which starts at  $t_i = 0$  or  $\tau_i = \tau_c$ , respectively.

paper <sup>(2)</sup> (SW) and of Des Cloizeaux [2]. We recover this earlier formalism by setting

$$h_0^2(\tau) = h_0^2 e^{\mu_1} (\tau - e^{\mu_1})^{-1} \tau^{-1}$$

and carrying through all integrations over the  $\tau_i$  variables.

To evaluate  $Z_p$  we first form the counterpart of the effective potential  $\Gamma_b(M_0)$  (SW, eq. (23)). This is the Legendre transform from  $h_0$  to  $M_0$  of  $\Omega^{-1} \ln Z_p$ . To be precise

$$\Gamma_b[M_0(\tau)] = -\frac{1}{\Omega} \ln Z_p[h_0(\tau)] + \int_{\tau} M_0(\tau) h_0(\tau) \quad (2.7)$$

where  $\int_{\tau}$  denotes  $\oint d\tau/2\pi i$ . According to the Legendre transform prescription, then

$$M_0(\tau) \equiv 2\pi i \delta \left( \frac{1}{\Omega} \ln Z_p \right) / \delta h_0(\tau). \quad (2.8)$$

<sup>(2)</sup> Since we have extracted all the dimensions in powers of  $l$  the factor  $l^2 h_0^2/2$  appearing in SW, eq. (6) *et seq.* is substituted by  $l^{d+2} h_0^2/2$ .

We may express measured quantities in terms of  $\Gamma_b[M_0]$ . Thus, the concentration  $c_p(n)$  of chains of length  $n$  is given by

$$c_p(n) = \partial \left( \frac{1}{\Omega} \ln Z_p \right) / \partial \mu(n) \quad (2.9)$$

or expressed in terms of  $h_0$  (eq. (2.5)) and  $M_0$  (eq. (2.8)),

$$c_p(n) = l^{-d-2} e^{\mu(n)} \int_0 \frac{d\tau}{2\pi i} \tau^{-n-1} \frac{M_0(\tau)}{h_0(\tau)}. \quad (2.10)$$

In eq. (2.10) the integration contour has to enclose the origin. This is indicated by the index 0.

The total polymer concentration has the simple form

$$c_p = \sum_n c_p(n) = \frac{1}{2} \int_{\tau} M_0(\tau) h_0(\tau). \quad (2.11)$$

The total link concentration  $c_l = N c_p$  is given by

$$c_l = \sum_n n c_p(n) = - \int_{\tau} M_0(\tau) \left( \frac{1}{2} + \tau \frac{\partial}{\partial \tau} \right) h_0(\tau). \quad (2.12)$$

By its definition (2.7) the effective potential  $\Gamma_b[M_0]$  is intimately related to the osmotic pressure  $\Pi$

$$\frac{\Pi}{k_B T} = \frac{1}{\Omega} \ln Z_p = 2 c_p - \Gamma_b[M_0]. \quad (2.13)$$

The results above hold for any  $V_{\text{eff}}$ , provided it gives a sensible thermodynamic limit. Following previous work on excluded volume properties we now approximate  $V_{\text{eff}}$  by a schematic form: the familiar Gaussian model [13]. In this model  $V_{\text{eff}}$  consists of a chain potential

$$H_0(i) = \frac{1}{4 l^2} \sum_{\lambda=1}^{n_i} (r_i(\lambda) - r_i(\lambda-1))^2 \quad (2.14)$$

describing the chemical bonds within each chain  $i$ . In addition, there is an excluded volume potential — a short-range interaction which on the average is repulsive and acts between all pairs of links:

$$H_1 = \frac{1}{2} \sum_{i,j} \sum_{\lambda_i, \lambda_j} v(r_i(\lambda_i) - r_j(\lambda_j)). \quad (2.15)$$

The range of  $v(r)$  is of the order of the distance  $l$ . With this form of  $V_{\text{eff}}$  we may conveniently calculate  $\Gamma_b[M_0]$  by a cluster expansion [13] of  $\exp(-V_{\text{eff}})$  in powers of  $\beta_e(r) = \exp(-v(r)) - 1$ . Being of short-range, the function  $\beta_e(r)$  is approximated by a  $d$ -dimensional  $\delta$ -function:  $\beta_e(r) = \beta_e \delta^d(r) l^d$ . We give the diagrammatic rules for the cluster expansion in Appendix A.

Our further discussion will proceed in terms of  $2m$ -point vertex functions  $\Gamma_b^{2m}(q_1, \dots, q_{2m}; \tau_1, \dots, \tau_m)$ . For vanishing momenta  $q_i$ ,  $i = 1, \dots, 2m$  these functions can be defined as coefficients in the functional power series of  $\Gamma_b[M_0]$ :

$$\Gamma_b[M_0] = \sum_{m=1}^{\infty} \frac{1}{m!} \times \int_{\tau_1, \dots, \tau_m} \prod_{i=1}^m \left( \frac{M_0^2(\tau_i)}{2} \right) \Gamma_b^{2m}(0, \dots, 0; \tau_1, \dots, \tau_m). \quad (2.16)$$

This will be sufficient for all thermodynamic quantities. For general momenta a simple diagrammatic definition can be given (see Appendix A). We later also need to consider vertex functions

$$\Gamma_b^{L, 2m}(q_1, \dots, q_L; p_1, \dots, p_{2m}; \tau_1, \dots, \tau_m)$$

with  $L$   $S^2$ -insertions of momenta  $q_1, \dots, q_L$ . We refer to Appendix A for the precise rules corresponding to such an insertion.

### 3. Renormalization and scaling laws. — 3.1

SOME RESULTS OF FIELD THEORY. — In the limit of long chains the cluster expansion diverges order by order. This is to be expected since the physical quantities themselves are divergent for  $N \rightarrow \infty$ . (We mention only the radius of gyration  $S$  of an isolated chain which for  $N \rightarrow \infty$  behaves as  $S \sim l N^{0.6}$ .) The process of renormalization yields a formalism in which the physical features of the  $N \rightarrow \infty$  limit may be obtained in spite of the divergences. The basic result of renormalization theory is contained in the following equations (3):

$$\Gamma_b^{L, 2m}(q_1, \dots, p_{2m}; \tau_1, \dots, \tau_m) = z^{-m} \times \left( \frac{z_2}{z} \right)^{-L} \chi^{d-m(d-2)-2L} \times \Gamma_b^{L, 2m} \left( \frac{q_1}{\chi}, \dots, \frac{p_{2m}}{\chi}; t_1, \dots, t_m \right) \{ 1 + \Delta^{L, 2m} \} \quad (3.1)$$

where

$$t_i = \left( 1 - \frac{\tau_i}{\tau_c} \right) S_{\chi}^{-1} \quad (3.2)$$

and

$$S_{\chi} = (\chi l)^2 \tau_c \frac{z_2}{z}. \quad (3.3)$$

The renormalized vertex functions  $\Gamma_b^{L, 2m}$  are calculated within the framework of renormalized field theory as defined in Appendix A. They are independent of  $l$  and  $\beta_e$  and therefore independent of the

(3) We use the massless renormalization scheme of Brézin *et al.* [12]. Deviating from the conventions of this reference we have made all quantities dimensionless by extracting powers of  $\chi$ .

microscopic structure, i.e. they are universal. The parameter  $\chi$  defines the momentum scale of the renormalized theory and can be chosen arbitrarily. This arbitrariness is compensated by the renormalization constants  $z, z_2$  which depend on  $l, \chi$  and  $\beta_c$ . The additive dimensionless constant  $\tau_c$  depends only on  $\beta_c$ . The correction terms  $\Delta^{L,2m}$  will be found to vanish in the critical limit. Substituting eq. (3.1) into the representation (2.16) of  $\Gamma_b[M_0]$  we get the renormalized functional  $\Gamma[M]$

$$\begin{aligned} \chi^{-d} \Gamma_b[M_0] &= \Gamma[M] = \\ &= \sum_{m=1}^{\infty} \frac{1}{m!} \oint \prod_j \left( \frac{dt_j}{4\pi i} M^2(t_j) \right) \\ &\times \Gamma^{2m}(0, \dots, 0; t_1, \dots, t_m) \{ 1 + \Delta\Gamma[M] \} \end{aligned} \quad (3.4)$$

where

$$M(t) = \chi^{1-d/2} \left( \frac{\tau_c S_\chi}{z} \right)^{1/2} M_0(\tau). \quad (3.5)$$

Due to the arbitrariness of  $\chi$  renormalized vertex functions obey a scaling law

$$\begin{aligned} \Gamma^{L,2m} \left( \frac{q_1}{\chi}, \dots, \frac{p_{2m}}{\chi}; t_1, \dots, t_m \right) &= \\ &= \lambda^{L+2m\beta-\nu d} \Gamma^{L,2m} \left( \frac{q_1}{\chi} \lambda^\nu, \dots, \frac{p_{2m}}{\chi} \lambda^\nu; t_1 \lambda, \dots, t_m \lambda \right). \end{aligned} \quad (3.6)$$

Here  $\lambda$  is an arbitrary scale parameter and  $\nu, \beta$  are universal numbers (critical exponents) defined by logarithmic derivatives of the renormalization factors  $z$  and  $z_2$  with respect to  $\chi$ . The leading correction term  $\Delta^{L,2m}$  also obeys a scaling law of the type (3.6), but with the factor  $\lambda^{L+2m\beta-\nu d}$  substituted by  $\lambda^{-\nu\omega}$  where  $\nu\omega > 0$ . We now substitute the scaling law

(3.6) into the power series (3.4). This yields the corresponding scaling law for  $\Gamma[M]$ . Neglecting the correction term  $\Delta\Gamma[M]$  we find

$$\Gamma[M] = \lambda^{-\nu d} \Gamma[M_\lambda] \quad (3.7)$$

$$M_\lambda(t) = \lambda^{\beta-1/2} M(t/\lambda). \quad (3.8)$$

Eqs. (3.1) to (3.8) constitute the basic results which allow us to generalize the results obtained previously for chemical equilibrium  $\mu(n) = \mu_0 + n\mu_1$  to arbitrary polydispersity. They are standard results only for a system with a single variable  $t \equiv t_i$ . The extension to the case of several variables  $t_i$  is not completely trivial. In fact, as explained in Appendix B, the simple form of eq. (3.1) is a special property of the polymer system. For other systems with several variables <sup>(4)</sup>  $t_i$  several renormalization factors have to be introduced and as a consequence the critical properties for  $t_i \neq t_j$  are different from those for  $t_i = t_j = t$ . It is the absence of these additional renormalizations which allows us to give a general theory of the excluded volume problem in which polydispersity is included as a physical variable.

**3.2 ANALYTIC STRUCTURE IN THE  $t_i$ -SPACE AND CRITICAL REGION FOR THE POLYMER SYSTEM.** — The scaling laws emerge if we can neglect the correction terms  $\Delta^{L,2m}$  or  $\Delta\Gamma[M]$ . This neglect can be justified if the leading contributions to all quantities are due to a range of the variables  $t_i$  which shrinks to  $t_i = 0$  in the critical limit  $N \rightarrow \infty, c_1 \rightarrow 0$ . To make this clear we consider the behaviour of the bare vertex function  $\Gamma_b^{L,2m}$  (eq. (3.1)), suppressing all unnecessary constants, indices, and variables. In view of the scaling behaviour of the renormalized  $\Gamma$ 's and the  $\Delta$ 's we find

$$\Gamma_b(\tau_1, \dots, \tau_m) = \lambda^{\text{power}} \Gamma(\lambda t_1, \dots, \lambda t_m) \{ 1 + \lambda^{-\omega\nu} \Delta(\lambda t_1, \dots, \lambda t_m) \}. \quad (3.9)$$

We have kept the leading correction term. The correction can be neglected provided that only the range  $|t_i| < t(N), i = 1, 2, 3, \dots$ , contributes, where  $t(N) \rightarrow 0$  for  $N \rightarrow \infty$ . In that case setting  $\lambda = t(1)/t(N)$  we find

$$\Gamma_b(\tau_1, \dots, \tau_m) = \lambda^{\text{power}} \Gamma \left( t(1) \frac{t_1}{t(N)}, \dots, t(1) \frac{t_m}{t(N)} \right) \left\{ 1 + \left( \frac{t(N)}{t(1)} \right)^{\omega\nu} \Delta \left( t(1) \frac{t_1}{t(N)}, \dots, t(1) \frac{t_m}{t(N)} \right) \right\} \quad (3.10)$$

and the correction term vanishes for  $N \rightarrow \infty$ .

We now verify that the important range of  $t_i$  does indeed shrink to zero as assumed above. The range of integration over the variables  $t_i$  is determined by the singularities of  $h_0^2(\tau_i)$  and of  $\Gamma_b^{L,2m}$ . Perturbation theory indicates that the singularities of the  $\Gamma^{L,2m}$  take the form of cuts which occur if (at least) one of the  $t_i$  becomes negative (see Fig. 1a). This implies that the singularities of the unrenormalized

functions  $\tilde{Z}(\tau_1, \dots, \tau_m)$  occur for  $\tau_i \geq \tau_c$  (see Fig. 1b). For our formalism to make sense the singularities

<sup>(4)</sup> In the theory of phase transitions the variable  $t$  represents the deviation from the critical temperature. Thus our theory can be said to involve an infinity of (complex) temperatures. Note, however, that here the variables  $t_i$  correspond to the fugacities and not to the physical temperature  $T$ .

of  $h_0^2(\tau)$  have to occur inside the circle  $|\tau| < |\tau_c|$ , and by construction the contour of the  $\tau_i$ -integration has to enclose all singularities of  $\tau_i h_0^2(\tau_i)$ . Obviously the correction can be neglected if the whole integration contour approaches  $\tau_i = \tau_c$  (or  $t_i = 0$ , equivalently). For instance, for the equilibrium ensemble  $\tau h_0^2(\tau)$  has a simple pole at  $\tau_0 = \exp(\mu_1)$ , which may be brought arbitrarily close to  $\tau_c$  by making  $N$  large and  $c_1$  small. With the so-called Schultz-distributions the situation is similar, as we discuss in sect. 5. However, this simple argument does not work for all distributions of interest. The most prominent counterexample is the monodisperse distribution, where  $\tau h_0^2(\tau) \sim \tau^{-N}$ . Here the integration contour always encircles the zero of the  $\tau$ -plane and never approaches  $\tau_c$ . A similar case happens in eq. (2.10) relating  $c_p(n)$  to  $\mu(n)$ . To deal with these cases we have to resort to a second, more general, argument.

We now assume that we can transform the integration contour in the  $\tau_i$ -plane such that it surrounds the singularities of  $\tilde{Z}(\tau_1, \dots, \tau_m)$  or of the vertex functions, equivalently. This transformation is possible provided  $\tau_i h_0^2(\tau_i) \tilde{Z}$  tends to zero as  $|\tau_i| \rightarrow \infty$ , a condition which is met for reasonable distributions  $h_0^2(\tau_i)$ . We then have to assume that in the critical limit  $h_0^2(\tau_i)$  decreases rapidly enough to suppress contributions from outside the critical region. This obviously is fulfilled for the monodisperse ensemble where  $h_0^2(\tau) \sim \tau^{-N-1}$  and  $N \rightarrow \infty$  in the limit of interest.

All this discussion shows that it is the form of  $h_0^2(\tau)$  and thus of  $P(n)$  which decides whether we are in the scaling regime or not. In the critical limit we reach the scaling regime for a large set of distributions ranging from the broad equilibrium distribution to the monodisperse ensemble. In the sequel we will restrict ourselves to distributions for which the neglect of  $\Delta^{L,2m}$ ,  $\Delta\Gamma$  is justified. We furthermore assume that we can transform all the integration contours around singularities of  $\tau h_0^2(\tau)$  or around  $\tau = 0$  in accordance with our second argument. Thus henceforth all integrals are to be interpreted as integrations around the singularities of the vertex functions.

**3.3 SCALING LAWS FOR THE POLYMER SYSTEM.** — With the insight gained by the above discussion we now formulate the scaling laws in terms of the measured quantities like  $c_p(n)$ . We first introduce the renormalized fugacity

$$h(t) = 2\pi i \frac{\delta\Gamma}{\delta M(t)} = \chi^{-\frac{d}{2}-1} (\tau_c z S_\chi)^{1/2} h_0(\tau) \quad (3.11)$$

$h(t)$  can be considered as a functional of  $M$  which in virtue of its definition obeys a scaling law involving  $M_\lambda$  (cf. eqs. (3.8), (3.7))

$$h(t, [M]) = \lambda^{1/2+\beta-\nu d} h(t\lambda, [M_\lambda]). \quad (3.12)$$

We next define the renormalized concentration  $c_{pR}(n_R)$ :

$$c_{pR}(n_R) = S_\chi^{-1} \chi^{-d} c_p(n) \quad (3.13)$$

where

$$n_R = S_\chi n \quad (3.14)$$

is the renormalized chain length. We stress again that the factor  $S_\chi$  is independent of  $c_p(n)$ . Renormalizing the relation between  $c_p(n)$  and  $h_0$ ,  $M_0$  (see eqs. (2.10), (2.5)) we find

$$c_{pR}(n_R) = \int \frac{dt}{2\pi i} e^{n_R t} \frac{M(t)}{h(t)} \int \frac{dt'}{4\pi i} e^{-n_R t'} h^2(t') \quad (3.15)$$

where we have neglected terms of order  $1/n$  and we have used  $\tau^n \sim \tau_c^n \exp(-n S_\chi t)$ .

Incorporating the scaling of  $M/h$  and  $h^2$  we obtain the scaling properties of  $c_{pR}$

$$c_{pR}(n_R, [M]) = \lambda^{-\nu d-1} c_{pR}(n_R/\lambda, [M_\lambda]). \quad (3.16)$$

Now the relation between  $c_{pR}(n)$  and  $M(t)$  can be inverted:

$$M(t) = M(t, [c_{pR}]), \quad (3.17)$$

for some functional  $M$ . Eq. (3.16) yields then

$$M_\lambda(t) = M(t, [c_{pR,\lambda}]) \quad (3.18)$$

where  $c_{pR,\lambda}$  is defined as

$$c_{pR,\lambda}(n_R) = \lambda^{\nu d+1} c_{pR}(n_R, \lambda). \quad (3.19)$$

Eqs. (3.7), (3.17), and (3.18) yield the scaling law for  $\Gamma$ , expressed by polymer variables:

$$\Gamma[c_{pR}] = \lambda^{-\nu d} \Gamma[c_{pR,\lambda}]. \quad (3.20)$$

We now consider a set of functions  $c_{pR}(n_R)$  expressed in terms of a reduced distribution function  $p(x)$ :

$$c_{pR}(n_R) = \chi^{-d} c_p N_R^{-1} p(n_R/N_R) \quad (3.21)$$

where by definition

$$\frac{1}{N_R} \sum_{n_R} p(n_R/N_R) = 1 \quad (3.22i)$$

$$\frac{1}{N_R} \sum_{n_R} \frac{n_R}{N_R} p(n_R/N_R) = 1. \quad (3.22ii)$$

The set (3.21) depends parametrically on the average renormalized chain length. In eq. (3.20) we choose  $\lambda = N_R/N_0$ , where  $N_0$  is some fixed reference value of the average chain length. We find

$$\begin{aligned} \Gamma[N_R^{-1} \chi^{-d} c_p p(n_R/N_R)] &= \\ &= \left(\frac{N_0}{N_R}\right)^{\nu d} \Gamma\left[\left(\frac{N_R}{N_0}\right)^{\nu d} N_0^{-1} \chi^{-d} c_p p\left(\frac{n_R}{N_0}\right)\right] \end{aligned} \quad (3.23)$$

or

$$\Gamma[c_{\text{PR}}(n_{\text{R}})] = N_{\text{R}}^{-\nu d} F^{00}(N_{\text{R}}^{\nu d} c_{\text{p}} \chi^{-d}, [p]) \quad (3.24)$$

where the scaling functional  $F^{00}$  is defined by the reference state. Eq. (3.24) is the desired generalization of the results of Des Cloizeaux [2]. It shows that  $\Gamma(c_{\text{p}}, N_{\text{R}}, [p])$  depends nontrivially only on the overlap

$$s_{\text{R}} \equiv N_{\text{R}}^{\nu d} c_{\text{p}} \chi^{-d} \quad (3.25)$$

and on the reduced chain length distribution. This result immediately yields a scaling law for the osmotic pressure  $\Pi$  which according to eq. (2.13) is directly related to  $\Gamma$  :

$$\frac{\Pi}{k_{\text{B}} T} = c_{\text{p}} [1 + \mathcal{F}(s_{\text{R}}, [p])] \quad (3.26)$$

Being constructed within the renormalized formalism the scaling functions  $F^{00}$  and  $\mathcal{F}$  are universal. Details of the chemistry of the system and of other irrelevant degrees of freedom influence the scale of  $s_{\text{R}}$ , only. Using eq. (3.14) we can express  $s_{\text{R}}$  by unrenormalized quantities :

$$s_{\text{R}} = \left( \frac{S_{\chi}^{\nu}}{\chi} \right)^d N^{\nu d} c_{\text{p}} = B^d N^{\nu d} c_{\text{p}} \quad (3.27)$$

The system-dependent parameter  $B = S_{\chi}^{\nu}/\chi$  has dimensions of a length.  $B^d$  can be interpreted as a measure of the *excluded volume* per monomer.

To formulate the scaling law for the chemical potential we eliminate in the scaling law (3.12) for  $h$  the variables  $M$  and  $M_{\lambda}$  in favour of  $c_{\text{PR}}$  and  $c_{\text{PR},\lambda}$ . Eqs. (3.17) and (3.18) yield

$$h(t, [c_{\text{PR}}]) = \lambda^{1/2 + \beta - \nu d} h(t\lambda, [c_{\text{PR},\lambda}]) \quad (3.28)$$

We then invert eq. (2.5) which defines  $h_0$  in terms of  $\mu(n)$  and we express  $h_0$  by  $h$  (eq. (3.11)). We find

$$e^{\mu(n)} = \frac{1}{2} (\chi l)^{d+2} \tau_{\text{c}}^n z^{-1} \oint \frac{dt}{2\pi i} e^{-n\tau_{\text{c}} t} h^2(t, [c_{\text{PR}}]) \quad (3.29)$$

The scaling law for  $\mu(n)$  follows :

$$\mu(n, [c_{\text{PR}}]) - n \ln \tau_{\text{c}} = 2(\beta - \nu d) \ln \lambda + \mu\left(\frac{n}{\lambda}, [c_{\text{PR},\lambda}]\right) - \frac{n}{\lambda} \ln \tau_{\text{c}} \quad (3.30)$$

A direct consequence is the scaling law for the average chemical potential  $\langle \mu \rangle$  defined as

$$\langle \mu \rangle = \sum_n P(n) \mu(n) \quad (3.31)$$

We recall the definition  $P(n) = c_{\text{p}}(n)/c_{\text{p}}$ . We find

that  $\langle \mu \rangle$  may be expressed explicitly, apart from an arbitrary function  $F_{\mu}$  of the overlap

$$\langle \mu \rangle - N \ln \tau_{\text{c}} = 2(\beta - \nu d) \ln N_{\text{R}} + F_{\mu}(s_{\text{R}}, [p]) + \text{constant} \quad (3.32)$$

Eq. (3.29) shows that all terms on the r.h.s., except for the constant, are universal.

#### 4. The role of the thermodynamic scaling function.

— 4.1 A RELATION FOR THE CHEMICAL POTENTIAL. — The overlap dependence of the scaling functional introduced in the scaling law (3.32) for  $\langle \mu \rangle$  can be expressed in terms of  $\mathcal{F}(s_{\text{R}}, [p])$  by virtue of the thermodynamic connection between pressure and chemical potential. We differentiate  $\langle \mu \rangle$  with respect to  $c_{\text{p}}$ , keeping  $P(n)$ ,  $T$ , and  $\mu_{\text{s}}$  of the solvent fixed

$$\frac{d\langle \mu \rangle}{dc_{\text{p}}} = \sum_n P(n) \frac{d\mu(n)}{dc_{\text{p}}} \quad (4.1)$$

A Gibbs-Duhem relation relates this derivative to a derivative of the osmotic pressure :

$$c_{\text{p}} \sum_n P(n) \frac{d\mu(n)}{dc_{\text{p}}} - \frac{1}{k_{\text{B}} T} \frac{d\Pi}{dc_{\text{p}}} = 0 \quad (4.2)$$

In view of the scaling law (3.26) for  $\Pi/k_{\text{B}} T$  this yields

$$\frac{d}{dc_{\text{p}}} (\langle \mu \rangle - \mathcal{F}(s_{\text{R}}, [p])) = \frac{1}{c_{\text{p}}} + \frac{\mathcal{F}(s_{\text{R}}, [p])}{c_{\text{p}}} \quad (4.3)$$

Integrating this equation we find an expression for  $\langle \mu \rangle$  which is to be compared to the scaling law (3.32).

Our result for  $\langle \mu \rangle$  follows :

$$\langle \mu \rangle - N \ln \tau_{\text{c}} = -\gamma \ln N + \ln c_{\text{p}} + F_0[p] + \mathcal{F}(s_{\text{R}}, [p]) + \int_0^{s_{\text{R}}} \frac{dy}{y} \mathcal{F}(y, [p]) + \text{constant} \quad (4.4)$$

The constant  $\gamma$  is defined as  $\gamma = \nu d - 2\beta$ . The overlap independent functional  $F_0$  can be calculated exactly by evaluating  $\langle \mu \rangle$  in the zero-overlap limit. We use the fact that each chain of length  $n$  has a partition function of the form [16]  $n^{\gamma-1}(\text{const.})^n$

$$F_0[p] = \int_0^{\infty} dx p(x) \ln(x^{1-\gamma} p(x)) \quad (4.5)$$

Thus  $\langle \mu \rangle$  is known, once the thermodynamic scaling function  $\mathcal{F}$  has been calculated.



4.2 THE ENERGY EXCESS, AND OTHER THERMODYNAMIC QUANTITIES. — The excess of the internal energy is defined as

$$\frac{u_p}{k_B T} = \frac{1}{\Omega} T \frac{\partial}{\partial T} \ln Z_p \quad (4.6)$$

where the derivative is taken with fixed fugacities

$h_0^2(\tau)$ ,  $\exp(\mu_s/k_B T)$ . Now  $u_p$  contains a non-critical contribution proportional to  $c_1$  which is the energy of solvation of the chain molecules. This contribution has to be extracted exactly before we can use the Gaussian model. We thus go back to eqs. (2.7), (2.8), and we take eq. (2.16) to be the definition of  $\Gamma_b^{2m}$  for general  $V_{\text{eff}}$ . The properties of the Legendre transform yield

$$\frac{u_p}{k_B T} = \sum_{m=1}^{\infty} \frac{1}{m!} \int_{\tau_1, \dots, \tau_m} \prod_i \left( \frac{M_0^2(\tau_i)}{2} \right) \left( -T \frac{\partial}{\partial T} \right)_{\tau_i, \mu_s/k_B T} \Gamma_b^{2m}(0, \dots, 0; \tau_1, \dots, \tau_m). \quad (4.7)$$

With the definition (3.2) of the variables  $t_i$  we write

$$-T \frac{\partial}{\partial T} \Big|_{\tau_i, \mu_s/k_B T} = -T \frac{\partial}{\partial T} \Big|_{t_i, \mu_s/k_B T} + \left( T \frac{\partial}{\partial T} \Big|_{\mu_s/k_B T} \ln S_x \right) \sum_{i=1}^m t_i \frac{\partial}{\partial t_i} + \left( T \frac{\partial}{\partial T} \ln \tau_c \Big|_{\mu_s/k_B T} \right) \sum_{i=1}^m \tau_i \frac{\partial}{\partial \tau_i}. \quad (4.8)$$

In all the differentiations with respect to  $t_i$  or  $\tau_i$ ,  $S_x$  and  $\tau_c$  have to be held fixed. The contribution proportional to  $\partial \ln \tau_c / \partial T$  can be evaluated exactly :

$$\sum_m \frac{1}{m!} \int_{\tau_1, \dots, \tau_m} \prod_i \left( \frac{M_0^2(\tau_i)}{2} \right) \sum_{j=1}^m \tau_j \frac{\partial}{\partial \tau_j} \Gamma_b^{2m}(0, \dots, 0; \tau_1, \dots, \tau_m) = \int d\tau \frac{M_0^2(\tau)}{2} \tau \frac{\partial}{\partial \tau} \left( \frac{1}{M_0(\tau)} \frac{\delta \Gamma_b[M_0]}{\delta M_0(\tau)} \right) = -c_1. \quad (4.9)$$

We have used the representation (2.12) of  $c_1$  together with the relation  $h_0 = 2 \pi i \delta \Gamma_b / \delta M_0$  which both hold for general  $V_{\text{eff}}$ .

To evaluate the other contributions we use the Gaussian model. Taking the  $\lambda$ -derivative at  $\lambda = 1$  of the scaling law (3.6) for  $\Gamma^{L, 2m}$  we find

$$\sum_i t_i \frac{\partial}{\partial t_i} \Gamma^{2m}(0, \dots, 0; t_1, \dots, t_m) = (vd - 2m\beta) \Gamma^{2m}(0, \dots, 0; t_1, \dots, t_m). \quad (4.10)$$

Eq. (3.1) yields

$$-T \frac{\partial}{\partial T} \Big|_{t_i, \mu_s/k_B T} \Gamma_b^{2m}(0, \dots, 0; \tau_1, \dots, \tau_m) = T \frac{\partial \ln z}{\partial T} \Big|_{\mu_s/k_B T} m \Gamma_b^{2m}(0, \dots, 0; \tau_1, \dots, \tau_m). \quad (4.11)$$

Combining these results we find the expression for  $u_p$  in terms of  $\mathcal{F}$  :

$$\frac{u_p}{k_B T} = -\frac{\partial \ln \tau_c}{\partial \ln T} c_1 + \frac{\partial \ln [(S_x)^y \cdot z]}{\partial \ln T} c_p - c_p v d \frac{\partial \ln S_x}{\partial \ln T} \mathcal{F}(s_R, [p]). \quad (4.12)$$

The derivatives have to be taken with fixed  $\mu_s/k_B T$ .

This relation is the generalization to arbitrary polydispersity of the results obtained previously [15] for the equilibrium ensemble. We here have omitted the corrections to scaling, which have been discussed for the equilibrium ensemble in ref. [15]. In the single chain limit the contribution proportional to  $\mathcal{F}$  vanishes, and a critical examination of the single chain results for  $u_p$  and other thermodynamic quantities in relation to Flory theory has been given by Des Cloizeaux [16].

The argument of this section can be repeated for other thermodynamic quantities, such as, the change  $\Delta \rho_s$  in solvent density

$$\Delta \rho_s = \frac{k_B T}{\Omega} \frac{\partial \ln Z_p}{\partial \mu_s} \Big|_{T, h_0^2(\tau)}. \quad (4.13)$$

The result obviously is of the form (4.12) with

—  $k_B T \partial/\partial \ln T$  substituted by  $k_B T \partial/\partial \mu_s$ . Then using the general thermodynamic relation

$$\Pi = k_B T s_p - u_p + \mu_s \Delta \rho_s + k_B T c_p \langle \mu \rangle \quad (4.14)$$

we find the excess entropy density  $s_p$ . Thus the overlap- and polydispersity-dependence of all natural thermodynamic quantities is known, once it is known for the osmotic pressure.

**5. Mean-field theory.** — The well-known mean-field approximation [19-21] is the starting point for the  $|4-d|$  expansion of the field theory. This expansion [12] is used to obtain concrete predictions. In this section we check that our formalism works smoothly in this important limit. In the mean-field limit the exponents are simple,  $\nu = \frac{1}{2}$ ,  $\gamma = 1$ ; and the form of the results (cf. eqs. (5.10) and (6.27)-(6.30)) is well-known. The present renormalized formulation recovers these results; in addition, it fixes the effective interaction strength, which remained undetermined in previous work. An application of this appears in ref. [14].

In the mean-field (or *tree*) approximation only those diagrams without an internal  $q$ -integration are taken into account. All vertex functions  $\Gamma^{0,2m}$ ,  $m > 2$ ;  $\Gamma^{1,2m}$ ,  $m > 1$ ;  $\Gamma^{2,2m}$ ,  $m \geq 0$  vanish identically. The only  $q$ -dependence is found in  $\Gamma^{0,2}$ :

$$\Gamma^{0,2}(q/\chi, -q/\chi; t) = (q/\chi)^2 + t \quad (5.1)$$

whereas  $\Gamma^{0,4}$  and  $\Gamma^{1,2}$  are independent of the momenta:

$$\Gamma^{0,4}(q_1, q_2, q_3, -q_1 - q_2 - q_3; t_1, t_2) = g^*/3 \quad (5.2)$$

$$\Gamma^{1,2}(q_1; q_2, -q_1 - q_2; t) = 1. \quad (5.3)$$

Here  $g^*$  is the fixed point value of the renormalized coupling constant [12].

$$g^* = (4\pi)^{d/2} \Gamma(d/2) 3/8(4-d) [1 + O(4-d)].$$

**5.1 THE THERMODYNAMIC SCALING FUNCTIONAL.** — As shown in section 4 the scaling functional  $\mathcal{F}(s_R, [p])$  is the central thermodynamic quantity. We may easily calculate this quantity in the mean-field approximation. Using eqs. (5.1) and (5.2) we can evaluate the definition (3.4) of  $\Gamma[M]$ :

$$\Gamma[M] = \frac{1}{2} \int \frac{dt}{2\pi i} t M^2(t) + \frac{1}{6 g^*} X^2 \quad (5.4)$$

where

$$X = \frac{g^*}{2} \int \frac{dt}{2\pi i} M^2(t). \quad (5.5)$$

Eq. (3.11) yields  $h(t)$ :

$$h(t) = M(t) (t + \frac{1}{3} X) \quad (5.6)$$

whereas  $c_p$  is found as

$$\begin{aligned} \chi^{-d} c_p &= \frac{1}{2} \int \frac{dt}{2\pi i} h(t) M(t) \\ &= \frac{1}{2} \int \frac{dt}{2\pi i} t M^2(t) + \frac{1}{3 g^*} X^2. \end{aligned} \quad (5.7)$$

The expression for  $c_1$  in terms of renormalized quantities is found by transforming the definition (2.12). Neglecting terms of order  $1/N$  we find

$$\chi^{-d} c_1 = S_\chi^{-1} \int \frac{dt}{2\pi i} M(t) \frac{\partial h}{\partial t}. \quad (5.8)$$

With  $h(t)$  given by eq. (5.6) this expression can be related to  $X$ :

$$X = g^* \chi^{-d} S_\chi c_1. \quad (5.9)$$

Combining all these results we find

$$\mathcal{F}(s_R, [p]) = \frac{1}{6} g^* s_R. \quad (5.10)$$

It is interesting to note that  $\mathcal{F}(s_R, [p])$  in the mean field approximation is independent of  $p(x)$ . This suggests that the exact functional  $\mathcal{F}$  is not very sensitive to polydispersity. This statement is also supported by the results reported in ref. [13], section 27d (ii).

**5.2 CHEMICAL POTENTIAL AND CHAIN LENGTH DISTRIBUTION.** — The chain length distribution

$$P(n) = c_p(n)/c_p$$

is related to the chemical potential  $\mu(n)$  through eq. (2.10):

$$c_p(n) = \chi^{-2} S_\chi z l^{-d-2} \tau_c^{-n} e^{\mu(n)} \int \frac{dt}{2\pi i} e^{n S_\chi t} \frac{M(t)}{h(t)} \quad (5.11)$$

where we have used the renormalized  $M$  and  $h$ . In the mean field approximation,  $h(t)$  is given by eq. (5.6) and thus

$$\int \frac{dt}{2\pi i} e^{(n S_\chi t)} \frac{M(t)}{h(t)} = e^{-[n S_\chi X/3]} \quad (5.12)$$

$$e^{\mu(n)} \tau_c^{-n} = \text{constant} \exp\left(\frac{g^*}{3} s_R \frac{n}{N}\right) c_p(n). \quad (5.13)$$

The average chemical potential is then

$$\begin{aligned} \langle \mu \rangle - N \ln \tau_c &= \frac{g^*}{3} s_R - \ln N + \ln c_p + \\ &+ \int_0^\infty dx p(x) \ln p(x) + \text{constant}. \end{aligned} \quad (5.14)$$

Since in mean-field approximation  $\gamma = 1$  and  $\mathcal{F}$  is given by eq. (5.10) this result is in agreement with the general expressions (4.4), (4.5).

We next use these results to examine the relation among  $c_p(n)$  and the singularities of  $\tau h_0^2(\tau)$ . This is meant to provide a more concrete background for some parts of the general discussion of section 3.2. Using the definition (2.5) together with the result (5.13) we find  $h_0^2(\tau)$  as a linear transform of the chain length distribution

$$\tau h_0^2(\tau) = \text{constant} \sum_{n=1}^{\infty} \left( \frac{\tau_c}{\tau} \right)^n \exp \left( \left[ \frac{g^*}{3} s_R \frac{n}{N} \right] \right) c_p P(n) \quad (5.15)$$

$$= \text{constant} c_p \sum_{n=1}^{\infty} P(n) \left( \frac{\tau_c}{\tau} e^{g^* s_R / 3N} \right)^n. \quad (5.16)$$

We note here that the concentration dependence of  $\tau h_0^2(\tau)$  is equivalent to a mere change of  $\tau_c$ . For our discussion we use a Schultz-distribution for  $P(n)$

$$P(n) = \frac{\sigma}{N\Gamma(\sigma)} \left( \frac{\sigma n}{N} \right)^{\sigma-1} \exp \left( -\sigma \frac{n}{N} \right). \quad (5.17)$$

Here  $\sigma$  is a parameter governing the sharpness of the distribution and  $\Gamma(\sigma)$  denotes Euler's  $\Gamma$ -function. Choosing  $\sigma = 1, 2, \dots$ , we can evaluate the sum in eq. (5.16) without any approximations

$$\begin{aligned} \tau h_0^2(\tau) &= \text{constant} c_p N^{-\sigma} \frac{(\sigma)^\sigma}{\Gamma(\sigma)} \frac{\partial^{\sigma-1}}{\partial z^{\sigma-1}} \times \\ &\times \left( \frac{\tau}{\tau_c} e^{-z} - 1 \right)^{-1} \Big|_{z = \frac{1}{N} \left( \frac{g^*}{3} s_R - \sigma \right)}. \end{aligned} \quad (5.18)$$

Thus the singularities of  $\tau h_0^2(\tau)$  take the form of a

superposition of poles of different order, all situated at

$$\tau_0 = \tau_c \exp \left[ - \left( \sigma - \frac{g^*}{3} s_R \right) / N \right], \quad (5.19)$$

and  $\tau_0$  tends to  $\tau_c$  in the critical limit  $N \rightarrow \infty$ ,  $c_1 \rightarrow 0$ . Thus for this discrete set of chain length distributions the approach to the critical point is adequately treated by the first argument of section 3.2 : All singularities of  $\tau h_0^2(\tau)$  — and thus the whole integration contour — approach  $\tau_c$ .

Eq. (5.19) shows that for large overlap  $s_R$  the singularities may occur for  $t < 0$  (or  $\tau > \tau_c$  equivalently), thus raising the danger of a confluence of singularities of  $h^2(t)$  and  $\Gamma^{L,2m}$ . This is due to the fact that we here have abandoned the proper perturbation expansion in powers of  $g^*$  in favour of the *loop expansion*, where  $g^* M^2(t)$ , and thus  $g^* s_R$  is taken to be  $0(1)$  instead of  $0(g^*)$ . Now the same partial summation changes the unperturbed propagator from  $(t + q^2)^{-1}$  to  $(t + q^2 + g^* s_R / (3 N_R))^{-1}$  (see section 6.2), and this guarantees that the singularities of  $h^2(t)$  and of the appropriately resummed vertex functions are kept distinct.

**6. Correlation functions.** — **6.1 GENERAL EXPRESSIONS.** — For the equilibrium chain length distribution the correlation functions (scattering form factors) have been discussed in SW and in ref. [2]. This discussion can easily be generalized to arbitrary polydispersity. The topology of the contributing diagrams remains unchanged, and the only difference is in the occurrence of integrals over the fugacities  $\tau_i$  (or  $t_i$ ). We therefore here give the results without the details of the derivation, and we always quote the number of the equation of SW to which the result given is a simple generalization.

We define  $M_0(\tau)$ -dependent vertex functions as

$$\begin{aligned} \Gamma_b^{L,m}(q_1, \dots, q_L; p_1, \dots, p_{2m}; \tau_1, \dots, \tau_m; [M_0]) &= \\ &= \sum_{k=0}^{\infty} \frac{1}{k!} \int_{\tau'_1, \dots, \tau'_k} \prod_{i=1}^k \left( \frac{M_0^2(\tau'_i)}{2} \right) \Gamma_b^{L,2(m+k)}(q_1, \dots, q_L; p_1, \dots, p_{2m}, 0, \dots; \tau_1, \dots, \tau_m, \tau'_1, \dots, \tau'_k) \end{aligned} \quad (6.1)$$

and we introduce the autocorrelation propagator

$$G_{b,a}(q, \tau) = [\Gamma_b^{0,2}(q, -q; \tau, [M_0])]^{-1}. \quad (6.2)$$

Then the average endpoint autocorrelation function is simply the  $h_0^2(\tau)$ -weighted average of the  $G_{b,a}(q, \tau)$  functions. Following SW, eq. (24'''), we denote this average by  $i_{ea}(q)$ ; thus,

$$i_{ea}(q) = \frac{1}{c_p} \int_{\tau} h_0^2(\tau) G_{b,a}(q, \tau). \quad (6.3)$$

The correlations between arbitrary endpoints have a more complicated structure. One needs the correlations between the endpoint density of the  $\tau$  component and that of the  $\tau'$  component of the solution — for general  $\tau$  and  $\tau'$ . We denote this as  $G_b(q, \tau, \tau')$  without the subscript  $a$ . Expressed in terms of the cluster expansion it is the sum of all connected diagrams with a free end on one line of link fugacity  $\tau$  and another on a line of link fugacity  $\tau'$ . This set cannot be expressed as the inverse of a vertex function. Instead, one must include an arbitrary string of

irreducible pieces, each connected by a  $G_{b,a}(q, \tau'')$  correlation line with arbitrary  $\tau''$ . These diagrams can be represented as an integral equation for  $G_b(q, \tau, \tau')$ , shown in schematic form in figure 2

$$G_b(q, \tau, \tau') = G_{b,a}(q, \tau) \left[ 2 \pi i \delta(\tau - \tau') - M_0(\tau) \times \int_{\tau''} M_0(\tau'') \Gamma_b^{0,4}(q, 0, -q, 0; \tau, \tau'', [M_0]) G_b(q, \tau'', \tau') \right]. \quad (6.4)$$

Eq. (6.4) is to be interpreted once the integration contour for all the  $\tau$  integrations has been fixed, and is valid for  $\tau$  and  $\tau'$  on that contour. The full endpoint density correlation function  $I_e(q)$  is then the weighted average of  $G_b$  [SW, eq. (24'')]:

$$I_e(q) = \int_{\tau\tau'} h_0(\tau) h_0(\tau') G_b(q, \tau, \tau'). \quad (6.5)$$

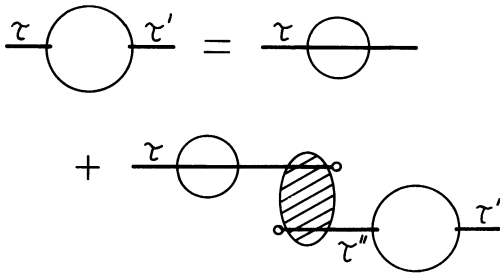


Fig. 2. — Diagrammatic representation of the integral equation for  $G_b$ . The empty blobs represent correlation functions and the shaded blob represents the vertex function.

The expression of these correlation functions in renormalized form is the same apart from scale factors and the replacement of the  $\tau$  integrals by the corresponding  $t$  integrals. (Cf. the renormalized equation for  $\Gamma[M]$  eq. (3.4).) Thus, for  $i_{ea}$  and  $I_e$  we have

$$i_{ea}(q) = \frac{\chi^d}{c_p} \int \frac{dt}{2 \pi i} h^2(t) G_a(\bar{q}, t) \quad (6.6)$$

$$I_e(q) = \chi^d \int \frac{dt}{2 \pi i} \int \frac{dt'}{2 \pi i} h(t) h(t') G(\bar{q}, t, t') \quad (6.7)$$

where  $G(\bar{q}, t, t')$  and  $G_a(\bar{q}, t)$  are defined like  $G_b$ ,  $G_{b,a}$  (eqs. (6.4), (6.2)) with all  $\Gamma_b$ ,  $M_0$ ,  $h_0$ ,  $\tau$  replaced by  $\Gamma$ ,  $M$ ,  $h$ ,  $t$ , respectively.  $\bar{q} = q/\chi$  is the dimensionless momentum.

In this same spirit we can derive expressions for the correlation functions of the link (or monomer) density  $\rho$ . Thus, the renormalized expression for the autocorrelation function  $i_a(q)$  (both correlated points

lie on the same chain) again has the same form as in SW, eq. (25), (cf. Fig. 3a)

$$i_a(q) = \chi^d c_p^{-1} S_\chi^{-2} \left[ -\Gamma_a^{2,0}(\bar{q}, -\bar{q}, [M]) + \int \frac{dt}{2 \pi i} (M(t) \Gamma_a^{1,2}(\bar{q}; -\bar{q}, 0; t, [M]))^2 G_a(\bar{q}, t) \right]. \quad (6.8)$$

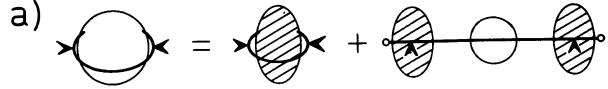


Fig. 3. — a) Diagrammatic analysis of  $i_a(q)$ . Shaded blobs represent vertex functions.

In  $\Gamma_a^{2,0}$  the two  $S^2$ -insertions have to occur in the same polymer line and in  $\Gamma_a^{1,2}$  the subscript «a» means that only diagrams with the  $S^2$ -insertion and the two external legs on the same polymer line are to be included.

In order to express the full correlation function for the link density,  $I_0(q)$ , one needs a more complicated formula than in SW, eq. (25), (cf. Fig. 3b)

$$I_0(q) = \chi^d S_\chi^{-2} \left[ -\Gamma^{2,0}(\bar{q}, -\bar{q}, [M]) + \int \frac{dt}{2 \pi i} \int \frac{dt'}{2 \pi i} M(t) \Gamma^{1,2}(\bar{q}; -\bar{q}, 0; t, [M]) \times G(\bar{q}; t, t') \Gamma^{1,2}(q; -q, 0; t', [M]) M(t') \right]. \quad (6.9)$$

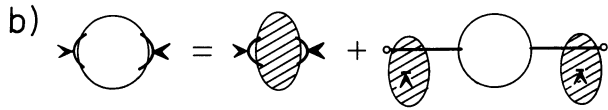


Fig. 3. — b) Diagrammatic analysis of  $I_0(q)$ . It differs from a) in that the insertions are not bound to occur in the same polymer line.

Repeating the arguments of section (3.3) which led to the scaling law for  $\Gamma[M]$  we can construct the scaling laws for the scattering form factors. We find

$$I_e(q) = N^{-vd} B^{-d} J_e(Q, s_R, [p]) \quad (6.10)$$

$$i_{ea}(q) = J_{ea}(Q, s_R, [p]) \quad (6.11)$$

$$I_0(q) = N^{2-vd} B^{-d} J_0(Q, s_R, [p]) \quad (6.12)$$

$$i_a(q) = N^2 J_a(Q, s_R, [p]). \quad (6.13)$$

We have introduced the scaling variables for the momentum <sup>(5)</sup>

$$Q = qBN^v. \quad (6.14)$$

All the scaling functionals  $J$  are universal.

**6.2 MEAN-FIELD RESULTS.** — In mean-field theory the spatial correlations become essentially the same as for free chains. The mean-field result for the autocorrelation propagator can be read off using its definition (eqs. (6.2), (6.1)) together with the results (5.1), (5.2)

$$G_a(\bar{q}, t) = (t + \bar{q}^2 + \frac{1}{3}X)^{-1}. \quad (6.15)$$

For the autocorrelation function  $i_{ea}$  one has only to evaluate the renormalized  $h^2(t)$  function at the pole of  $G_a$ , i.e.

$$\begin{aligned} \chi^{-d} c_p i_{ea}(q) &= \int \frac{dt}{2\pi i} h^2(t) G_a(\bar{q}, t) = \\ &= -h^2(-\bar{q}^2 - \frac{1}{3}X) \end{aligned} \quad (6.16)$$

where  $h^2(t)$  is given essentially by eq. (5.16).

$$-h^2(t) = 2\chi^{-d} c_p \int_0^\infty dy \exp[(t + \frac{1}{3}X) S_x N y] p(y). \quad (6.17)$$

Evaluating at  $t = -\bar{q}^2 - \frac{1}{3}X$  one recovers the result expected for  $i_{ea}$ : a superposition of Gaussian correlation functions independent of the overlap.

To obtain the link density autocorrelation  $i_a$  defined in eq. (6.8) we note that  $\Gamma^{2,0} = 0$  and  $\Gamma^{1,2} = 1$ . Then

$$S_x^2 \chi^{-d} c_p i_a(q) = R(q) = \int \frac{dt}{2\pi i} M^2(t) G_a(\bar{q}, t). \quad (6.18)$$

Expressed in terms of  $h^2(t)$ , via  $h(t) = M(t) (t + \frac{1}{3}X)$

$$\begin{aligned} R(q) &= \int \frac{dt}{2\pi i} \left(t + \frac{1}{3}X\right)^{-2} \times \\ &\times \left(t + \bar{q}^2 + \frac{1}{3}X\right)^{-1} h^2(t) \\ &= -\chi^{-d} 2 c_p \int_0^\infty dy p(y) \times \\ &\times \int \frac{dt}{2\pi i} e^{t S_x N y} t^{-2} (t + \bar{q}^2)^{-1} \end{aligned} \quad (6.19)$$

where we have shifted the integration to eliminate  $X$ . Evaluating the  $t$  integral, one obtains a superposition of Debye scattering functions [17, 18]

$$R(q) = 2 s_R \int_0^\infty dy p(y) Q^{-4} [e^{-y Q^2} - 1 + y Q^2] \quad (6.20)$$

where

$$Q = (S_x N \bar{q}^2)^{1/2} \quad (6.21)$$

is the mean-field expression for the variable  $Q$  (eq. (6.14)).

We next calculate the full correlation function for the endpoint density,  $I_e(q)$ . For this we need the full propagator  $G(q)$  as defined by the integral eq. (6.4). The equation becomes separable in mean-field theory ( $\Gamma^{0,4}$  is independent of  $t$ ), and the solution is

$$\begin{aligned} G(\bar{q}, t_1, t_2) &= G_a(\bar{q}, t_1) 2\pi i \delta(t_1 - t_2) - \\ &- \frac{g^*}{3} G_a(\bar{q}, t_1) \frac{M(t_1) M(t_2)}{1 + \frac{g^*}{3} R(q)} G_a(\bar{q}, t_2). \end{aligned} \quad (6.22)$$

Averaging over  $t_1$  and  $t_2$  (eq. (6.7)) one obtains  $I_e(q)$

$$\begin{aligned} \chi^{-d} I_e(q) &= -h^2\left(-\bar{q}^2 - \frac{1}{3}X\right) - \\ &- \frac{g^*}{3} \frac{\left[\frac{2}{g^*} X - \bar{q}^2 R(q)\right]^2}{1 + \frac{g^*}{3} R(q)}. \end{aligned} \quad (6.23)$$

The full density correlation function can also be obtained from  $G$ :

$$\begin{aligned} \chi^{-d} S_x^{+2} I_0(q) &= \\ &= \int \frac{dt}{2\pi i} \int \frac{dt'}{2\pi i} M(t) M(t') G(\bar{q}, t, t'). \end{aligned} \quad (6.24)$$

To summarize, we re-arrange the above expressions to obtain the scaling functions  $J$  defined above, thus verifying that our results are consistent with the scaling laws. We define  $\tilde{p}(Q^2)$  as the superposition of Gaussian functions found above:

$$\tilde{p}(Q^2) = \int_0^\infty dy p(y) e^{-Q^2 y} \quad (6.25)$$

and note that  $R(q)$  can be written

$$R(q) = 2 Q^{-4} s_R (\tilde{p}(Q^2) - 1 + Q^2). \quad (6.26)$$

<sup>(5)</sup> The difference between  $Q$  as introduced here and  $Q$  as defined in SW, eq. (39), is absorbed in the scaling functionals. The same holds for some factors.

Then

$$J_{ea}(Q, s_R) = 2 \tilde{p}(Q^2) \quad (6.27)$$

$$J_e(Q, s_R) = 2 s_R \tilde{p}(Q^2) - \frac{g^*}{3} s_R^2 \frac{\left(2 - \frac{Q^2}{s_R} R(q)\right)^2}{1 + \frac{g^*}{3} R(q)} \quad (6.28)$$

$$J_a(Q, s_R) = R(q) s_R^{-1} \quad (6.29)$$

$$J_0(Q, s_R) = \frac{R(q)}{1 + \frac{g^*}{3} R(q)} \quad (6.30)$$

**7. Conclusion.** — Three noteworthy features have emerged from this work.

Firstly, the renormalization group approach can deal with arbitrary polydispersity of polymer solutions. We have found that polydispersity is a relevant degree of freedom, in the sense that it influences the results also in the critical limit  $N \rightarrow \infty$ ,  $c_1 \rightarrow 0$ . This influence, however, is restricted to the quantitative form of the scaling functions and leaves the qualitative structure of the scaling laws and the numerical values of the exponents unchanged.

Secondly, our generalized formalism can be used for the evaluation of the scaling functionals. We have verified that the formalism works naturally and correctly in the mean field limit; it reproduced some

well-known results for the correlation functions. In a recent paper [14] we applied our mean-field theory to include polydispersity effects in a calculation of a critical ratio and found good agreement with experiment. Our mean-field theory may be used as the starting point for systematic expansions (e.g. in  $d - 4$ ) to improve the accuracy of the predictions. Thus the effects of polydispersity in the excluded volume limit can be explored in a systematic way. Such a study, for the thermodynamic scaling function  $\mathcal{F}$ , is in progress.

Thirdly, certain rigorous interrelations among thermodynamic quantities apply to polymer solutions. We have found (section 4) that the usual thermodynamic quantities can be expressed by the single scaling functions  $\mathcal{F}(s_R, [p])$  in a simple way. These results may be useful as a check for more heuristic approaches like the Flory Huggins theory, which are meant to hold both inside and outside the critical region.

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**Appendix.** — A) PERTURBATION THEORY. — Our problem in general terms is to compute thermodynamic averages of the form

$$Z_p = \sum_{\substack{\text{number of} \\ \text{polymers } m}} \sum_{\substack{\text{length of} \\ \text{each polymer}}} \dots \sum \text{weighting factors} \times \sum_{\substack{\text{configurations} \\ \text{of polymers}}} e^{-V_{\text{eff}}} \quad (\text{A.1})$$

in the case where  $V_{\text{eff}}$  consists of a simple (harmonic) attraction binding each link  $r_i$  to its successor along the chain, plus an excluded volume repulsion between all pairs of coordinates. The diagrammatic perturbation theory provides a systematic way to calculate  $\log Z_p$  or correlation functions as an expansion in the strength of the excluded volume repulsion. Each term in this expansion is a sum of certain convolutions of free-chain correlation functions (no excluded volume)  $G_0$ , with the weighting factors. Each of these convolutions can be conveniently represented by a geometric figure, and the proper sum of convolutions for each order can be found by i) drawing all possible diagrams which satisfy a specific set of geometric rules, and ii) adding the specific convolutions to which these correspond. We now state these rules for our renormalized theory.

The basic pieces of the diagrams are displayed in figure 4. A connected correlation function (cumulant)  $G^{L,2m}$  is given by the sum of all connected diagrams which can be constructed out of the free propagator (4a), the 4-point vertex (4b) and the  $h$ -

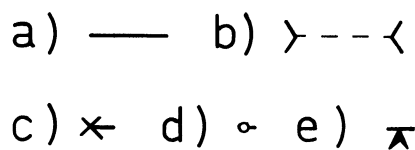


Fig. 4. — Diagrammatic symbols. a) Unperturbed propagator; b) Four-point vertex; c)  $h$ -vertex; d)  $M$ -vertex; e)  $S^2$ -insertion.

vertex (4c). Each diagram has  $L$  density insertions (4e) ( $S^2$ -vertices) and  $2m$  open ends. A connected sequence of propagators makes up one polymer line, and closed loops of polymer lines are forbidden ( $n = 0$  theory). Each end of a polymer line may either be open or attached to an  $h$ -vertex. Some diagrams for  $G^{0,0} = \frac{1}{\Omega} \ln Z_p$  and for  $G^{1,2}$  are given in figure 5.

In the perturbation expansion for a vertex function there contribute only diagrams which cannot be separated by cutting one propagator.  $h$ -vertices are eliminated in favour of  $M$ -vertices (Fig. 4d) which are directly attached to a four-point vertex. The vertex

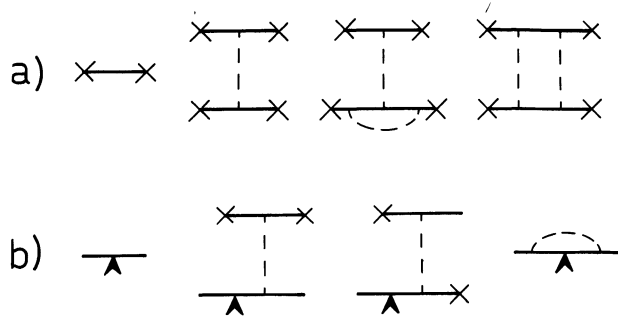


Fig. 5. — a) Some diagrams contributing to  $1/\Omega \ln Z_p$ . b) Some diagrams contributing to  $G^{1,2}$ .

function is connected to its external points by legs which do not contribute a free propagator. Figure 6 shows some diagrams contributing to  $\Gamma^{0,4}(\bar{q}_1, \dots, \bar{q}_4; \tau_1, \tau_2, [M])$ . This figure also clarifies our conventions concerning the ordering of the variables.

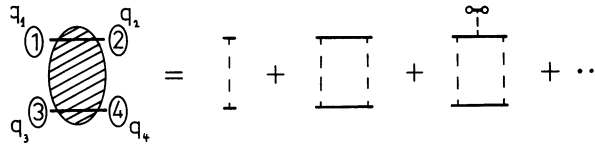


Fig. 6. — Schematic representation, and some diagrams, for the vertex function  $\Gamma^{0,4}(q_1, q_2, q_3, q_4; \tau_1, \tau_2, [M])$ .

In renormalized perturbation theory the diagrams are evaluated according to the following rules : A propagator of (dimensionless) momentum  $\bar{q}$ , which is part of the  $i$ th polymer line, contributes a factor  $(t_i + \bar{q}^2)^{-1}$ . The temperature  $t_i$  is characteristic of the  $i$ th polymer line. A four point vertex yields a factor  $-g^*/3$  and an  $S^2$ -vertex (of external momentum  $\bar{q}$ ) yields a factor  $(-1)$ . An  $h$ -vertex ( $M$ -vertex) in the  $i$ th line yields a factor  $h(t_i)$  ( $M(t_i)$ ). The momentum is conserved at each vertex, which means that the sum of external and internal momenta flowing into any vertex has to vanish. All internal momenta have to be integrated over the whole momentum space. In addition we have to carry through the  $t_i$ -integrations for those polymer lines which are closed at both ends by either  $h$ - or  $M$ -vertices. Symmetry factors are to be calculated by the usual rules and the theory is to be subtracted in accordance with the massless (i.e.  $t_i = 0$  for all  $i$ ) renormalization scheme (see ref. [12]). We have identified the coupling constant  $g$  with its fixed point value  $g^*$  which is appropriate in the critical region. This prescription for  $\Gamma^{L,2m}$  given here is nearly in all respects the one given in ref. [12] except that there is a separate temperature for each pair of external legs. The only difference is that closed propagator loops are allowed in these diagrams and forbidden in ours.

The rules of unrenormalized perturbation theory are of no importance here, except for two remarks.

We have evaluated the partition function for discrete chains of Gaussian elements of mean length  $l$  in a straightforward cluster expansion. This yields an unperturbed propagator  $G_0$  of the form

$$(1 - \tau_i e^{-l^2 q^2})^{-1}.$$

In order to find the renormalized propagator we have to expand this expression around  $\tau = \tau_c$ ,  $q = 0$  and this yields the relation (3.2) between  $t_i$  and  $\tau_i$ . A factor of  $\tau_i^{-1}$  which occurs in this calculation, is combined with similar factors from other sources and absorbed in the coupling constant. An  $S^2$ -insertion introduces an additional propagator, and the corresponding factor  $\tau^{-1}$  cannot be absorbed into a coupling constant. This is the origin of the factors  $\tau_c^2$  which are combined with the renormalization factors  $z_2/z$  to yield the powers of  $S_x$  occurring in eqs. (6.8) and (6.9). (Note that in the critical region  $\tau = \tau_c + O(1/N, c_l)$ .)

#### B) RENORMALIZATION OF THE MULTIPLE- $t_i$ THEORY.

— We have noted above that the partition function for our polymer system has a structure virtually identical to that of an extended system near a phase transition : *viz*, a system with many order parameters  $S_i$  each at a different distance  $t_i$  from the critical temperature. The following is a discussion of the renormalization of the present theory as contrasted with a theory in which propagator loops are allowed.

The renormalization of the temperature  $t_i$  has to eliminate the primitive divergencies of diagrams of the type  $\Gamma^{1,2}$ . For the polymer system  $\Gamma^{1,2}$  contains only a *single polymer line*, whereas in general  $\Gamma^{1,2}$  may contain an *arbitrary number of closed loops* of propagators. Thus in the general case an insertion of  $S_i^2$  in a loop of propagators of the field  $S_i$  may be coupled to a line of propagators of the field  $S_j$ ,  $j \neq i$ , thus effecting an  $S_i^2$ -insertion in line  $j$  (Fig. 7). The renormalization of these diagrams couples the temperatures  $t_i$  and  $t_j$  and this coupling creates a qualitative difference of the case  $t_i = t_j$  as compared to  $t_i \neq t_j$ . In the former case the system is governed by the isotropic fixed point ( $t_i = t$  for all  $i$ ), whereas in the latter case the anisotropic fixed point determines the behaviour in the critical region. At the isotropic fixed point the anisotropy  $g_a = (t_i - t_j)$  is a relevant variable which scales differently from the temperature :  $g_a \rightarrow \lambda^\varphi g_a$ ,  $\varphi \neq 1$ . Exponents and scaling functions are unstable against anisotropy.

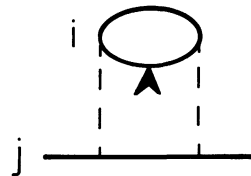


Fig. 7. — A diagram which contributes to the coupling of  $t_i$  to  $t_j$  in the general case.

On the other hand for the polymer system the singular coupling of  $S_i^2$  to  $S_j^2$  is absent and as a consequence  $g_a$  is not an essentially new variable since it scales like a temperature,  $\varphi = 1$ . The renormalization group equations (R.G.E.) for the different temperatures are decoupled since only diagrams with a single polymer line contribute. Furthermore, all these R.G.E. are identical to the equation for the isotropic case. Thus for the multiple-temperature polymer theory the isotropic fixed point still governs the critical region. We can think of the isotropic fixed point as being imbedded in a multiple temperature space. Each temperature coordinate is relevant, but transforms under the R.G. independently from all others. Clearly these considerations are not new, but are implicit in former work [3, 4, 6].

Since we can identify the polymer lines by their endpoints, we can represent a vertex function  $\Gamma^{L,2m}$  by a simultaneous power series in all  $m$  variables  $t_i$ . The coefficients in this power series are vertex func-

tions with a well defined number of  $S_i^2$ -insertions for each line  $i$ , evaluated at  $t_i = 0$ ,  $i = 1, \dots, m$ . Each of these insertions is renormalized by the same renormalization factor  $z_2/z$ , and we thus can repeat for this more complicated case the argument of Brézin *et al.* [12], section 6.3. The result (3.1) follows.

Whether the integrations over the variables  $t_i$ , which occur in our formalism, are well behaved, is just a question of the form of the functions  $h^2(t_i)$ . They certainly are well behaved if the integration contour is a closed finite line in the complex  $t_i$ -plane, encircling the singularities of  $h^2(t_i)$ , but excluding the singularities of the vertex functions. We have shown that this holds for the set of Schultz distributions (and clearly we can find an infinite set of other distributions with this property).

Therefore for reasonable distributions we do not expect any divergencies from the  $t_i$ -integrals. The results of the mean-field calculation obviously support this view.

### References

- [1] DE GENNES, P. G., *Phys. Lett. A* **38** (1972) 339.
- [2] DES CLOIZEAUX, J., *J. Physique* **36** (1975) 281.
- [3] BURCH, D. and MOORE, M. A., *J. Phys. A* **9** (1976) 435.
- [4] BURCH, D. and MOORE, M. A., *J. Phys. A* **9** (1976) 451.
- [5] LUBENSKY, T. C. and ISAACSON, J., *Phys. Rev. Lett.* **41** (1978) 829.
- [6] DES CLOIZEAUX, J., *J. Physique*, to be published.
- [7] SCHÄFER, L. and WITTEN, T. A., *J. Chem. Phys.* **66** (1977) 2121.
- [8] DAOUD, M. *et al.*, *Macromolecules* **8** (1975) 804.
- [9] DAOUD, M. and DE GENNES, P. G., *J. Physique* **38** (1977) 85.
- [10] KOSMAS, M. K. and FREED, K. F., *J. Chem. Phys.* **69** (1978) 3647.
- [11] DAOUD, M. and JANNINK, G., *J. Physique* **36** (1975) 281.
- [12] BRÉZIN, E., LE GUILLOU, J. C. and ZINN-JUSTIN, J., in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York) 1976, Vol. VI.
- [13] YAMAKAWA, H., *Modern Theory of Polymer Solutions* (New York, Harper and Row) 1971.
- [14] WITTEN, T. A. and SCHÄFER, L., *J. Phys. A* **11** (1978) 1843.
- [15] SCHÄFER, L., *J. Phys. A* **9** (1976) L71.
- [16] DES CLOIZEAUX, J., *J. Physique* **37** (1976) 431.
- [17] DEBYE, P., *J. Phys. Colloid Chem.* **51** (1947) 18.
- [18] ZIMM, B. H., *J. Chem. Phys.* **16** (1948) 1093.
- [19] EDWARDS, S. F., *Proc. Phys. Soc. London* **88** (1966) 265.
- [20] MOORE, M. A., *J. Physique* **38** (1977) 265.
- [21] JANNINK, G. and DE GENNES, P. G., *J. Chem. Phys.* **48** (1968) 2260.