

Classification

Physics Abstracts

36.20 — 61.40K — 05.20 — 05.50

Scaling theory of star polymers and general polymer networks in bulk and semi-infinite good solvents

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(Reçu le 11 janvier 1988, accepté sous forme définitive le 1^{er} avril 1988)

Résumé. — Nous établissons une théorie d'échelle des réseaux généraux de polymères, dans de bons solvants, en volume et en milieu semi-infini, en utilisant l'équivalence entre la fonction génératrice du nombre total de configurations et la fonction de corrélation à plusieurs spins du modèle de Heisenberg classique à n composantes dans la limite $n \rightarrow 0$. Dans le cas de réseaux de polymères à topologie fixée \mathcal{G} , composés de f chaînes linéaires de longueur ℓ , le nombre total de configurations se comporte, pour ℓ grand, comme $\mathcal{N}_{\mathcal{G}}(\ell, \ell, \dots, \ell) \sim \ell^{\gamma_{\mathcal{G}}-1} \mu^{\ell f}$. L'exposant $\gamma_{\mathcal{G}}$ peut s'exprimer entièrement en terme des exposants $\gamma(f)$ et $\gamma_s(f)$ des polymères étoilés (libres et à centre fixé) à f branches. Quand les g des f branches du polymère étoilé sont attachés à une surface par leurs extrémités, les exposants $\gamma_{\mathcal{G}} \equiv \gamma_{11\dots 1}(f)$ sont donnés en terme de ceux des polymères étoilés à f branches et des exposants des chaînes linéaires $\gamma_{11\dots 1}(f) = \gamma(f) + \nu + g[\gamma_{11} - \gamma_1]$. De plus, l'exposant $\gamma_{\mathcal{G}}$ pour les polymères en forme de peigne (avec g unités trifonctionnelles) se réduit à une combinaison linéaire des polymères étoilés à 3 branches, $\gamma(3)$, et de l'exposant du nombre de configurations des chaînes linéaires, γ : $\gamma_{\text{comb}}(g) = \gamma + g[\gamma(3) - \gamma]$. Les exposants de polymères étoilés $\gamma(f)$, $\gamma_s(f)$ et $\gamma_{11\dots 1}(f)$ sont calculés dans la théorie du champ moyen et dans le développement en ε . Nos résultats pour $\gamma(f)$ et $\gamma_s(f)$ sont

$$\gamma(f) = 1 + (\gamma - 1) \left[f - \frac{f(f-1)}{2} \right] + f(f-1)(f-2)A(f),$$

$$\gamma_s(f) = 1 + (\gamma_1 - 1)f - (\gamma_{11} + \nu) \frac{f(f-1)}{2} + f(f-1)(f-2)B(f),$$

où $A(f)$ et $B(f)$ sont des fonctions régulières de f d'ordre ε^2 . Pour $A(f)$ nous trouvons $\varepsilon^2/64 + O(\varepsilon^3)$. Nos expressions de $\gamma_{\mathcal{G}}$ en fonction de $\gamma(f)$, $\gamma_s(f)$ sont en accord avec les résultats antérieurs de Duplantier. Toutefois notre première expression pour $\gamma(f)$ ne converge pas vers le résultat exact de Duplantier dans la limite de dimension 2. Nous obtenons la forme d'échelle de la fonction de distribution des extrémités d'un réseau de polymères de topologie générale \mathcal{G} : $p_{\mathcal{G}}(r) \sim r^{-d} \phi_{\mathcal{G}}(rL^{-\nu})$ où ν est l'exposant des chaînes linéaires et L la longueur totale des chaînes. En particulier la valeur moyenne carrée de la distance entre extrémités $\langle r^2 \rangle_{\mathcal{G}}$ se comporte en $L^{2\nu}$. Nous appliquons aussi les idées d'échelle à l'étude du cas où les réseaux de polymères sont faits de chaînes linéaires de différentes longueurs. Nous signalons aussi les relations avec la méthode directe.

Abstract. — A scaling theory of general polymer networks in bulk and semi-infinite good solvents is derived by using the equivalence between the generating function for the total number of configurations and the multi-spin correlation function of the classical n -component Heisenberg model in the limit $n \rightarrow 0$. For general polymer networks with fixed topology \mathcal{G} composed of f linear chains with the same length ℓ , the total number of configurations behaves for large ℓ as $\mathcal{N}_{\mathcal{G}}(\ell, \ell, \dots, \ell) \sim \ell^{\gamma_{\mathcal{G}}-1} \mu^{\ell f}$. The exponent $\gamma_{\mathcal{G}}$ is expressed exactly in terms of the corresponding exponents $\gamma(f)$ and $\gamma_s(f)$ of f -arm (free and center-adsorbed) star polymers. When g of the f arms of the star polymer are attached to the surface at their end points, the exponent $\gamma_{\mathcal{G}} \equiv \gamma_{11\dots 1}(f)$ is given in terms of that for f -arm star polymers $\gamma(f)$ and the exponents of linear chains as $\gamma_{11\dots 1}(f) = \gamma(f) + \nu + g[\gamma_{11} - \gamma_1]$. Also the exponent $\gamma_{\mathcal{G}}$ for comb polymers (with g 3-functional units) is reduced to a linear combination of the exponent of 3-arm star polymers, $\gamma(3)$, and the configuration number

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exponent of linear chains, γ , as $\gamma_{\text{comb}}(g) = \gamma + g[\gamma(3) - \gamma]$. The star-polymer exponents $\gamma(f)$, $\gamma_s(f)$ and $\gamma_{11\dots 1}(f)$ are evaluated by means of mean-field theory, ε expansion and some general considerations. Our results for $\gamma(f)$ and $\gamma_s(f)$ are

$$\begin{aligned}\gamma(f) &= 1 + (\gamma - 1) \left[f - \frac{f(f-1)}{2} \right] + f(f-1)(f-2)A(f), \\ \gamma_s(f) &= 1 + (\gamma_1 - 1) f - (\gamma_{11} + \nu) \frac{f(f-1)}{2} + f(f-1)(f-2)B(f),\end{aligned}$$

where $A(f)$ and $B(f)$ are regular functions of f and are of $O(\varepsilon^2)$. $A(f)$ is found to be $\varepsilon^2/64 + O(\varepsilon^3)$. Our first formula for $\gamma(f)$ is, however, inconsistent with Duplantier's exact result for the two-dimensional case, while our scaling relations for γ_g in terms of $\gamma(f)$, $\gamma_s(f)$ are consistent with his earlier results. The end-to-end distribution function $p_g(r)$ of a polymer network with general topology \mathcal{G} is found to have a scaling form $p_g(r) \sim r^{-d} \phi_g(rL^{-\nu})$ with the exponent ν of linear chains. Here L denotes the total length of chains. Thus the mean square end-to-end distance $\langle r^2 \rangle_g$ behaves like $L^{2\nu}$. Scaling ideas are also applied to study the case where linear chains with different lengths construct the polymer networks. Relations to the direct method are also pointed out.

1. Introduction.

The theory of linear polymers in a good solvent has been very successful as a result of the connection established by de Gennes [1, 2] and des Cloizeaux [3, 4] between the polymer statistics and the critical phenomena of the n -component classical Heisenberg model (we call this the n -vector model) in the $n \rightarrow 0$ limit. The effect of the walls or other confining geometries has also found considerable interest (see for example Ref. [5]) not only from the connection to surface critical phenomena (see Ref. [6] for a review) but also from the point of view of various applications [7, 8].

The more complicated statistics of general polymer networks has received a continuous attention over a long time [9]. Polymer gels [2] are huge networks of flexible chains with the general structure illustrated in figure 1.1. The statistics of such huge branched polymers are related to the configurations of lattice animals and standard percolation theory as was pointed out by Lubensky and Issacson [10]. In the dilute limit, the problem reduces to the study of a single polymer network in a good solvent. The simplest example of a polymer network is probably a single ring polymer [2], which has a behaviour quite different from that of the linear polymer. Certain more complicated networks like star polymers and comb polymers have only recently been studied

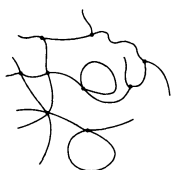


Fig. 1.1. — A general polymer network containing f -functional branch points, loops and loose chains with free ends (schematic).

intensively following experimental progress in the synthesis of such macromolecules [11]. Using the so-called *direct renormalization-group* (RG) *approach* associated with Edward's continuum model [12] up to the first order in $\varepsilon = 4 - d$ (d is the spatial dimension), Miyake and Freed [13, 14] studied star polymers, and Vlahos and Kosmas [15] studied comb polymers. Monte Carlo, molecular dynamics simulations and numerical series expansions were carried out by Wilkinson *et al.* [16], Barrett and Tremain [17], Lipson *et al.* [18], and Grest *et al.* [19] for the free star polymer, and by Colby *et al.* [20] for the surface-adsorbed star polymer. Moreover, Duplantier and Saleur [21-23] considered general polymer networks in bulk [21] and semi-infinite [22] two-dimensional geometry and obtained many exact results by invoking the conformal invariance. Reference [21] also treats the RG $\varepsilon = 4 - d$ expansion up to $O(\varepsilon)$, and reference [23] contains general scaling considerations.

The single polymer network in a good solvent in a semi-infinite geometry involves the statistics of the polymer network consisting of f linear chains each of which has length ℓ_i , $i = 1, \dots, f$. These chains are mutually connected at their ends, although some dangling ends are allowed. It is also possible to imagine that some of the ends or branch points are adsorbed on the surface plane. If there is no such adsorption, the network is called *free*. For each type of the polymer network \mathcal{G} , the structure of such connections is fixed topologically. With this fixed topology \mathcal{G} , chains move flexibly, but there exists a strong excluded volume effect between different chains forming the network as well as different points of the same chain in the network. One of the interesting statistical quantities is the total number of possible configurations $\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f)$. Particular attention will be paid to the case

$$\mathcal{N}_g(\ell, \ell, \dots, \ell), \quad (1.1a)$$

where all the chains have the same length ℓ , or alternatively to the case

$$\mathcal{N}_{\mathfrak{g}}(L) = \sum_{\ell_1=0}^{\infty} \sum_{\ell_2=0}^{\infty} \dots \sum_{\ell_f=0}^{\infty} \mathcal{N}_{\mathfrak{g}}(\ell_1, \ell_2, \dots, \ell_f) \times \delta_{\ell_1+\ell_2+\dots+\ell_f, L}, \quad (1.1b)$$

where the total chain length L is fixed. In (1.1b) we introduced Kronecker's δ as $\delta_{k,k} = 1$ and $\delta_{k,\ell} = 0$ for $k \neq \ell$. The quantities defined in (1.1a) and (1.1b) are expected to behave as (see Sect. 3)

$$\mathcal{N}_{\mathfrak{g}}(\ell, \ell, \dots, \ell) \sim \ell^{\gamma_{\mathfrak{g}}-1} \mu^{\ell f} \quad (1.2a)$$

and

$$\mathcal{N}_{\mathfrak{g}}(L) \sim L^{\hat{\gamma}_{\mathfrak{g}}-1} \mu^L, \quad (1.2b)$$

asymptotically for large ℓ and L . Here μ is a certain parameter associated with the critical temperature of the n -vector model in the limit $n \rightarrow 0$ (see (3.5)) and does not depend on the details of topology of the network. On the other hand, the exponents $\gamma_{\mathfrak{g}}$ and $\hat{\gamma}_{\mathfrak{g}}$ are universal quantities. They do not depend on the details of the underlying lattice but do depend on the spatial dimensionality d and the topology \mathfrak{g} .

The purpose of this paper is to give a unified scaling theory describing the statistics of general polymer networks in bulk and semi-infinite geometries. First of all, there is a relationship between the asymptotic behaviour of the polymer networks like (1.2) and the critical phenomena of the n -vector model in the limit $n \rightarrow 0$. We present a proof of this relationship in section 2 from the point of view of the high-temperature series expansion. Then, in section 3, the asymptotic behaviours of the number of configurations (1.2), the end-to-end distribution function and mean-square end-to-end distance are found to be related to critical phenomena of magnetic systems. In section 4, by developing a phenomenological scaling theory, we show that the exponent $\gamma_{\mathfrak{g}}$ of any general polymer network including polymer networks near walls in the dilute limit is related to the exponents of star polymers. Based on this, we will give an explicit calculation using mean-field theory (Sect. 5) and the RG $\epsilon = 4 - d$ expansion (Sect. 6) in order to derive the behaviour of free and adsorbed star polymers. A relation between the star polymer exponent $\gamma(f)$ and the contact exponent θ_i for a linear chain is also discussed in section 6. More general cases where the polymer network is constructed by linear chains with different lengths is dealt with in section 7. Finally, in section 8, we summarize our main results and give some discussions.

2. Equivalence between polymer networks and the n -vector model in the limit $n \rightarrow 0$.

The equivalence between the linear polymer chain and the n -vector model in the $n \rightarrow 0$ limit was first

pointed out by de Gennes [1]. This equivalence can be proven exactly by considering the high-temperature series expansion which is essentially a cluster expansion [24, 25]. Similar arguments are possible for more general cases of polymer networks.

The n -vector model is defined by the Hamiltonian

$$\mathcal{H} = -JH \quad (2.1)$$

$$H = \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2.2)$$

where the summation runs over all the nearest-neighbour pairs ij , and each spin at each lattice point, i , has n components

$$\mathbf{S}_i = (S_i^{(1)}, S_i^{(2)}, \dots, S_i^{(n)}) \quad (2.3)$$

and fixed length

$$|\mathbf{S}_i|^2 = n. \quad (2.4)$$

This Hamiltonian describes the Ising model, the Planar (XY) model and the classical Heisenberg model, respectively, for $n = 1, 2$ and 3.

Consider the system of f linear chains which do not have contacts with each other (see Fig. 2.1). We suppose that the i -th linear chain has length ℓ_i , starting from the point O_i and ending at the point P_i ($i = 1, \dots, f$), and that the numbers $\ell_1, \ell_2, \dots, \ell_f$ are all fixed and moreover that all the end points $O_1, P_1, O_2, P_2, \dots, O_f, P_f$ are fixed. This latter

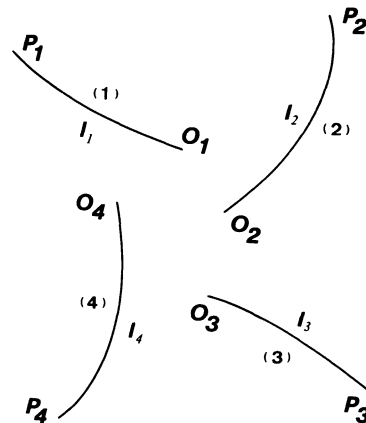


Fig. 2.1. — Many polymer system. Each chain i has length ℓ_i and carries the spin component (i) ; then this system maps onto the magnetic model in the $n \rightarrow 0$ limit.

condition will be removed later (Sect. 3) in discussing the total number of configurations $\mathcal{N}_{\mathfrak{g}}(\ell_1, \ell_2, \dots, \ell_f)$ introduced in paragraph 1. We write the number of configurations for this fixed topology \mathfrak{g} and for these fixed end-points as

$$\mathcal{N}_{\mathfrak{g}}(\ell_1, \ell_2, \dots, \ell_f) \quad (2.5)$$

(note that $\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f)$ in Sect. 1 is related to (2.5) by Eq. (3.6) in Sect. 3) and introduce its generating function as

$$Z_g(K) = \sum_{\ell_1=0}^{\infty} \sum_{\ell_2=0}^{\infty} \dots \sum_{\ell_f=0}^{\infty} N_g(\ell_1, \ell_2, \dots, \ell_f) \times K^{\ell_1+\ell_2+\dots+\ell_f}. \quad (2.6)$$

The aim of this section is to prove the equivalence between this generating function and the $2f$ -point correlation function

$$C_g(K) = \langle S_{O_1}^{(1)} S_{P_1}^{(1)} S_{O_2}^{(2)} S_{P_2}^{(2)} \dots S_{O_f}^{(f)} S_{P_f}^{(f)} \rangle \quad (2.7)$$

of the n -vector model in the limit $n \rightarrow 0$. For this identity, it is only necessary to assume the parameter relation

$$K = \frac{J}{k_B T} \quad (2.8)$$

as in the case of a linear chain. To construct the $2f$ -point correlation function (2.7), we introduce one spin for one end-point and assume that the two spins belonging to the same linear chain are of the same component, i.e., the two spins of the i -th chain are of the i -th component. Finally we take the thermal average of the product of these $2f$ spins to get (2.7).

The high-temperature series expansion is conveniently performed by introducing diagrams [24, 25]. We draw the nearest-neighbour spin pairs appearing in the Hamiltonian H [see (2.2)] with a straight line. On the other hand, we connect the two end-points O_i and P_i of the same chain by a wavy line for all $i = 1, \dots, f$. Then, for example, the spin trace which appears in the second order of the expansion

$$2! \text{Tr}_O \text{Tr}_P \text{Tr}_Q \left[S_{O_1}^{(1)} S_{P_1}^{(1)} \sum_{\alpha\beta} S_{O_2}^{(\alpha)} S_{Q_2}^{(\alpha)} S_{P_2}^{(\beta)} S_{Q_2}^{(\beta)} \right] = 2! \quad (2.9)$$

is diagrammatically represented by figure 2.2.

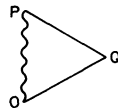


Fig. 2.2. — Diagram appearing in the second order. This diagram represents (2.9).

Now we discuss the property of the diagrammatic expansion in the limit $n \rightarrow 0$. We should first note that, in the limit $n \rightarrow 0$, we have the identity

$$\text{Tr} e^{KH} = 1 + \sum_{L=1}^{\infty} \frac{K^L}{L!} \text{Tr} H^L \sim 1, \quad (n \rightarrow 0) \quad (2.10)$$

because all the terms with $L \geq 1$ contain at least one loop and each loop carries a factor of n . Then we may expand the $2f$ -point correlation function in the power series of $K = J/k_B T$ like

$$C_g(K) \sim \text{Tr} [S_{O_1}^{(1)} S_{P_1}^{(1)} S_{O_2}^{(2)} S_{P_2}^{(2)} \dots S_{O_f}^{(f)} S_{P_f}^{(f)} e^{KH}] = \sum_{L=0}^{\infty} \frac{\alpha_L}{L!} K^L, \quad (2.11)$$

where we put

$$\alpha_L = \text{Tr} [S_{O_1}^{(1)} S_{P_1}^{(1)} S_{O_2}^{(2)} S_{P_2}^{(2)} \dots S_{O_f}^{(f)} S_{P_f}^{(f)} H^L] = \sum_{\mathcal{D}} \alpha_L(\mathcal{D}) \quad (2.12)$$

with $\alpha_L(\mathcal{D})$ as the contribution associated with the diagram \mathcal{D} .

From the symmetry of the Hamiltonian, it is obvious to see that a diagram \mathcal{D} with a vertex point at which odd numbers of (solid or wavy) lines meet does not contribute. Moreover, the diagram with a vertex point at which 4 or more (solid or wavy) lines meet does not contribute either, in the limit $n \rightarrow 0$, because the spin trace at this vertex carries at least a factor of n due to the normalization (2.4). This situation will be much more transparent, if we evaluate some examples of diagrams. Figure 2.3a represents a decorated loop diagram and figure 2.3b represents a two-loop diagram with one articulation point. The corresponding spin traces are $\alpha_L(\mathcal{D}) = (4!/2) n^2/(n+2)$ for figure 2.3a and $\alpha_L(\mathcal{D}) = n/(n+2)$ for figure 2.3b. These spin traces vanish in the limit $n \rightarrow 0$ because of the existence of the vertex point at which 4 solid lines meet. Each of these vertices carries a factor of n .

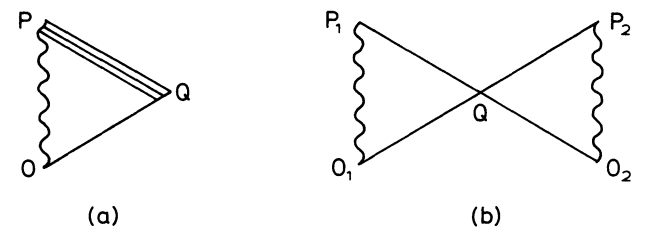


Fig. 2.3. — Examples of diagrams occurring in higher orders: (a) a triangular loop diagram with a decoration, and (b) a diagram with one articulation point. Both of these diagrams vanish in the $n \rightarrow 0$ limit.

In addition there is another property: if a diagram \mathcal{D} has a disconnected part involving no wavy line, this diagram does not contribute. This statement holds for general n , but, in the limit $n \rightarrow 0$, this is obviously understandable because the additional disconnected part carries a factor n due to a closed loop.

From these considerations, we are led to the conclusion : the $\alpha_L(\mathcal{D})$ is nonvanishing, if and only if the diagram \mathcal{D} is composed of f disconnected single loops each of which has one wavy line. For such a diagram with f single loops (an example of one single loop is given by Fig. 2.2 and Eq. (2.9)), we have

$$\alpha_L(\mathcal{D}) = L! \quad (2.13)$$

Thus, substituting this into (2.11), we have

$$C_g(K) \sim \sum_{L=0}^{\infty} N_g(L) K^L, \quad (n \rightarrow 0) \quad (2.14)$$

where $N_g(L)$ denotes the total number of lattice realizations of such diagrams, i.e., diagrams with f closed loops each of which contains one wavy line, consisting totally of L solid lines. Then, by using the number (2.5) of configurations, we may write

$$N_g(L) = \sum_{\ell_1=0}^{\infty} \sum_{\ell_2=0}^{\infty} \dots \sum_{\ell_f=0}^{\infty} N_g(\ell_1, \ell_2, \dots, \ell_f) \times \delta_{\ell_1+\ell_2+\dots+\ell_f, L} \quad (2.15)$$

which is comparable to (1.1b). Hence we are led to the desired identity

$$Z_g(K) = C_g(K) \quad (2.16)$$

in the limit $n \rightarrow 0$.

The physical polymer networks that we wish to describe do contain loops and branch points while the *networks* which are described so far by multi-spin correlation functions of the n -vector model are disconnected linear polymers. However, by requiring

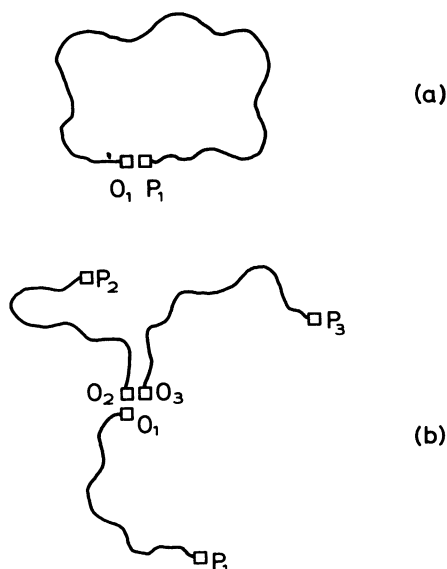


Fig. 2.4. — Construction of the polymer network. (a) loop geometry and (b) 3-arm star geometry are constructed by introducing proximity constraints for some of the end points.

that some of the end points of these linear polymers $\{O_1, P_1, \dots, O_f, P_f\}$ are in close proximity of each other, we in fact obtain the desired statistical properties of the considered network : e.g., properties of a closed loop are obtained requesting that the site P_1 is nearest neighbour of O_1 on the lattice ; a 3-arm star geometry is obtained if sites O_1, O_2, O_3 are nearest neighbours of each other (Fig. 2.4), while the sites of the points P_1, P_2, P_3 are not restricted, etc. In fact, using such a proximity constraint has the same physical effect as putting in suitable chemical crosslinks to form the network.

3. Relation to critical phenomena.

The equivalence between polymer networks and the n -vector model proved in the last section enables us to deduce several interesting quantities associated with polymer networks from the knowledge of the multi-spin correlation function of the magnetic system.

First of all, we consider the *whole* nonlinear susceptibility constructed from the multi-spin correlation function $C_g(K)$ which is associated with the topology g and given by (2.7) :

$$\chi_g(K) = \frac{1}{N_x} \sum_{\text{end- and branch-points}} C_g(K). \quad (3.1)$$

In (3.1), it is not necessary to assume that all the summations run over all space. For example, one can imagine a polymer adsorbed at a surface, where some of the summations run over sites on the surface plane only. Some suitable number of lattice points N_x is introduced in (3.1) in order to make $\chi_g(K)$ finite. For the semi-infinite solvents, N_x should be taken as

$$N_x = \begin{cases} N, & \text{for free polymers,} \\ N_s, & \text{for surface-adsorbed polymers,} \end{cases} \quad (3.2)$$

where N is the total number of lattice points and N_s , the number of surface lattice points. Near the critical point $K = K_c$, the nonlinear susceptibility (3.1) generally exhibits a singular behaviour like

$$\chi_g(K) \sim t^{-\gamma_g}. \quad (3.3)$$

Here t is the reduced temperature

$$t \sim 1 - \mu K, \quad (3.4)$$

$$\mu = \frac{k_B T_c}{J} = \frac{1}{K_c}. \quad (3.5)$$

The parameter μ is hence proportional to the critical temperature of the magnetic system.

Then we recall that $C_g(K)$ in (3.1) is identical to the generating function (2.6) for fixed topology and

for spatially fixed end points (the identity (2.16) between $Z_g(K)$ and $C_g(K)$). Substituting (2.6) in (3.1) (see (2.16)) and noticing the relation for the total number of configurations

$$\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f) = \frac{1}{N_x} \sum_{x \text{ end- and branch-points}} N_g(\ell_1, \ell_2, \dots, \ell_f), \quad (3.6)$$

we have

$$\chi_g(K) = \sum_{\ell_1=0}^{\infty} \sum_{\ell_2=0}^{\infty} \dots \sum_{\ell_f=0}^{\infty} \mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f) \times K^{\ell_1 + \ell_2 + \dots + \ell_f}. \quad (3.7)$$

Therefore introducing the total number of configurations with fixed total length L as defined in (1.1b), we obtain

$$\chi_g(K) = \sum_{L=0}^{\infty} \mathcal{N}_g(L) K^L. \quad (3.8)$$

If we replace this summation by an integration over L and introduce the reduced temperature t in a slightly different manner by

$$\mu K = e^{-t} \quad (3.9)$$

with μ given by (3.5) ($t=0$ corresponds to the critical point $K = K_c$ and Eq. (3.4) holds near the critical point), (3.8) becomes a form of Laplace-transformation :

$$\chi_g(K) \approx \int_0^{\infty} dL \left[\frac{\mathcal{N}_g(L)}{\mu^L} \right] e^{-tL}. \quad (3.10)$$

(Henceforth we use the symbol \approx for equalities valid only in the scaling limit.) Because the nonlinear susceptibility is expected to have a power-law singularity (3.3) near the critical temperature, an inverse Laplace-transformation of (3.10) with (3.3) gives

$$\mathcal{N}_g(L) \sim L^{\hat{\gamma}_g - 1} \mu^L \quad (3.11)$$

which is identical to (1.2b). Thus the exponent $\hat{\gamma}_g$ for the total number of configurations of networks with total length L is found to be identical to the exponent of the nonlinear susceptibility (3.1). In enumerations of self-avoiding walk models of polymers on lattices, the constant μ , which is given by equation (3.5), is sometimes called the *effective coordination number*. This mapping shows that μ is independent of the topology of the polymer network, in agreement with conclusions of reference [16].

Now we want to know the behaviour of $\mathcal{N}_g(\ell, \ell, \dots, \ell)$, where each single chain has the same fixed length ℓ . To this end, we assume that if all chain lengths $\ell_1, \ell_2, \dots, \ell_f$ are of the same order, then $\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f)$ behaves like

$$\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f) \sim (\ell_1 + \ell_2 + \dots + \ell_f)^{\gamma_g - 1} \times \mu^{\ell_1 + \ell_2 + \dots + \ell_f} \quad (3.12)$$

which should be compared with (1.2a). If such a region dominates in the summation of (1.1b), we may substitute (3.12) in (1.1b) to obtain

$$\mathcal{N}_g(L) \sim L^{\gamma_g - 1} \mu^L \times \sum_{\ell_1=0}^{\infty} \sum_{\ell_2=0}^{\infty} \dots \sum_{\ell_f=0}^{\infty} \delta_{\ell_1 + \ell_2 + \dots + \ell_f, L} \sim L^{\gamma_g + f - 2} \mu^L. \quad (3.13)$$

Then the comparison between (3.11) and (3.13) yields

$$\gamma_g = \hat{\gamma}_g + 1 - f. \quad (3.14)$$

At this point we should give some comments on (3.13) and (3.14). The nonlinear susceptibility $\chi_g(K)$ can be calculated with the help of renormalization group (RG) theory as is done in later sections. It is known [26], however, that the function (3.1) which is given as thermal average of the product of composite operators (explicit forms are presented in (4.1)-(4.4) in the next section) becomes, after renormalization, a linear combination of the original function and other functions which have the same or lower canonical dimensions. What we call *other functions* here are susceptibilities related to other topologies which can be deduced from the original topology \mathcal{G} by shrinking some arms (linear chains) which form the network (in our problem, all the external momenta are zero and the terms with external momenta as a factor are unimportant). Because we are interested in the configurations of networks with the same chain length ℓ , we should discard all these terms which occur due to additive renormalization. Thus it is only necessary to identify the renormalization factor associated with the topology \mathcal{G} itself. We will call this part of the renormalized nonlinear susceptibility the *essential* part. Equations (3.13) and (3.14) are basically true for the essential part. The scaling theory which will be developed in next section is based on this idea and valid in discussing the case where each chain has the same length ℓ . On the other hand, if we are interested in the configurations of networks with total length L , then we should identify the most singular term among the linear combination obtained by the additive renormalization. This procedure is equivalent to searching the most dominant part of the partial summations in the summation (1.1b). In later sections, we evaluate the number of configuration exponent γ_g from the essential part of the nonlinear susceptibility.

Next, we introduce the *local* nonlinear susceptibility in order to discuss the end-to-end distribution of the polymer network :

$$\chi_{\mathfrak{g}}(O_i, P_j; K) = \sum_{\text{end- and branch-points except } O_i \text{ and } P_j} C_{\mathfrak{g}}(K). \quad (3.15)$$

Note that the summations with respect to two end points O_i and P_j are omitted in the right hand side, so that this function depends explicitly on these sites O_i and P_j . Now we use the identity (2.16) in (3.15). After the substitution, we have

$$\chi_{\mathfrak{g}}(O_i, P_j; K) = \sum_{L=0}^{\infty} \mathcal{N}_{\mathfrak{g}}(O_i, P_j; L) K^L, \quad (3.16)$$

where we have introduced the number of configurations with fixed total length L and with two fixed end points O_i and P_j :

$$\mathcal{N}_{\mathfrak{g}}(O_i, P_j; L) = \sum_{\text{end- and branch-points except } O_i \text{ and } P_j} N_{\mathfrak{g}}(L) \quad (3.17)$$

(for $N_{\mathfrak{g}}(L)$ see (2.15)). Then introducing the reduced temperature as (3.9), we are led to the Laplace-transformation

$$\chi_{\mathfrak{g}}(O_i, P_j; K) \approx \int_0^{\infty} dL \left[\frac{\mathcal{N}_{\mathfrak{g}}(O_i, P_j; L)}{\mu^L} \right] e^{-tL}. \quad (3.18)$$

In the case of free polymer networks, $\chi_{\mathfrak{g}}(O_i, P_j; K)$ has the scaling form

$$\chi_{\mathfrak{g}}(O_i, P_j; K) \approx \frac{1}{r_{ij}^{d-2+\eta_{\mathfrak{g}}}} \theta_{\mathfrak{g}} \left(\frac{r_{ij}}{t^{-\nu}} \right), \quad (3.19)$$

where ν is the correlation length exponent and $\eta_{\mathfrak{g}}$ is related to $\hat{\gamma}_{\mathfrak{g}}$ by $\hat{\gamma}_{\mathfrak{g}} = \nu(2 - \eta_{\mathfrak{g}})$; r_{ij} denotes the distance between O_i and P_j . Inverse-Laplace-transformation of (3.18) with (3.19) gives

$$\mathcal{N}_{\mathfrak{g}}(O_i, P_j; L) \approx \frac{\mu^L}{L r_{ij}^{d-2+\eta_{\mathfrak{g}}}} \tilde{\theta}_{\mathfrak{g}}(r_{ij} L^{-\nu}). \quad (3.20)$$

Finally, dividing this by the total number of configurations, we obtain the distribution function for general polymer networks with fixed total length L as

$$\begin{aligned} p_{\mathfrak{g}}(r_{ij}) &= \frac{\mathcal{N}_{\mathfrak{g}}(O_i, P_j; L)}{\mathcal{N}_{\mathfrak{g}}(L)} \approx \frac{1}{L^{\hat{\gamma}_{\mathfrak{g}}} r_{ij}^{d-2+\eta_{\mathfrak{g}}}} \hat{\theta}_{\mathfrak{g}}(r_{ij} L^{-\nu}) \\ &= \frac{1}{r_{ij}^d} \phi_{\mathfrak{g}}(r_{ij} L^{-\nu}) \end{aligned} \quad (3.21)$$

which takes exactly the same form as the distribution function for the single chain problem (see for example Ref. [2]). It is easy to see that the distribution function for general polymer networks where all chains have the same length ℓ also has the same form as (3.21). Thus we get to the mean square end-to-end distance

$$\langle r_{ij}^2 \rangle_{\mathfrak{g}} = \frac{\int dr r^2 p_{\mathfrak{g}}(r)}{\int dr p_{\mathfrak{g}}(r)} \sim L^{2\nu} \quad (3.22)$$

which behaves like a single polymer chain. While the exponent describing the end-to-end distance does not depend on the topology \mathfrak{G} of the network, the proportionality constant in the relation (3.22) surely does. E.g., for star polymers with f arms it is interesting to consider how this prefactor depends on f [13-18]. This question cannot be answered by us using only scaling consideration.

4. Phenomenological scaling theory of general polymer networks.

Arbitrary polymer networks with fixed topology and fixed total length L may be discussed in a rigorous manner by invoking the magnetic analogy given in sections 2 and 3. However, the scaling theory that will be developed in this section is rather closely related to the case where each linear chain has the same fixed length ℓ , because the following scaling assumption is valid only for the essential part of the nonlinear susceptibility discussed in section 3.

Our discussion is in principle applicable to any geometry of the container for the solvents. To assume some geometry of the container corresponds to assume the same geometry of the lattice model. Typically, we deal with a semi-infinite geometry of the container and discuss surface-adsorbed polymer networks as well as free polymer networks. However, in the case of the surface problem we do not consider any forces between the wall and the monomers which form the polymer, rather we assume as a geometrical constraint that some end points or branch points of the networks are attached to the surface.

Consider the polymer network \mathfrak{G} composed of f mutually connected linear chains. In the following scaling theory of general polymer networks, the nature of the g -functional unit (the g -fold branch point) plays a central role. The g -functional unit around point P consists of g neighbouring points P_1, P_2, \dots, P_g , at which each linear chain starts. See figure 4.1 for example. Then introduce the g -th order composite operator

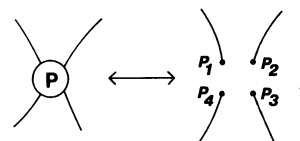


Fig. 4.1. — g -functional unit at point P . A Branch point is composed of several neighbouring sites P_1, P_2, \dots, P_g at which each polymer chain is starting.

$$\Psi_g^{(m_1, m_2, \dots, m_g)} = \sum_P S_{P_1}^{(m_1)} S_{P_2}^{(m_2)} \dots S_{P_g}^{(m_g)} \quad (4.1)$$

for each g -functional unit. In this summation over all points P , one should fix the vertex structure, because the neighbouring points P_1, P_2, \dots, P_g do not change their configuration around the point P . One can also consider the g -th order composite operator at the surface as

$$\Psi_g^{(m_1, m_2, \dots, m_g)} = \sum_{P \in \text{surface}} S_{P_1}^{(m_1)} S_{P_2}^{(m_2)} \dots S_{P_g}^{(m_g)}. \quad (4.2)$$

Then, from the equivalence between polymer networks and the n -vector model discussed in sections 2 and 3, the generating function for the number of configurations of this polymer network \mathcal{G} is given by the $n \rightarrow 0$ limit of the nonlinear susceptibility

$$\chi_{\mathcal{G}}(K) = \frac{1}{N_x} \left\langle \prod_g [\Psi_g^{(\dots)} \Psi_g^{(\dots)} \dots \Psi_g^{(\dots)}] \right\rangle, \quad (4.3)$$

where some of the Ψ_g may be replaced by the surface operator Ψ'_g , and N_x is taken as (3.2). One should recall that the i -th chain carries the i -th spin component, so that the same component appears just twice in the brackets of (4.3). An example of the polymer network \mathcal{G} is given by figure 4.2. For this network, we have

$$\frac{1}{N_x} \langle \Psi_1^{(1)} \Psi_1^{(2)} \Psi_1^{(5)} \Psi_3^{(3,4,5)} \Psi_4^{(1,2,3,4)} \rangle. \quad (4.4)$$

Note that the first order composite operator is identical to the summation of the single spin variable over all space

$$\Psi_1^{(m)} = \sum_P S_P^{(m)}. \quad (4.5)$$

In order to develop the phenomenological scaling theory, we introduce the n -vector model

$$\frac{\mathcal{H}}{k_B T} = -KH - \mathcal{H}_{cf} - \mathcal{H}'_{cf} \quad (4.6)$$

with composite fields,

$$\begin{aligned} \mathcal{H}_{cf} = & \sum_{m=1}^n h_1^{(m)} \Psi_1^{(m)} + \sum_{m=1}^n \sum_{\ell=1}^n h_2^{(m,\ell)} \Psi_2^{(m,\ell)} + \\ & + \sum_{m=1}^n \sum_{\ell=1}^n \sum_{k=1}^n h_3^{(m,\ell,k)} \Psi_3^{(m,\ell,k)} + \dots \end{aligned} \quad (4.7a)$$

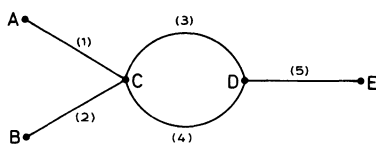


Fig. 4.2. — An example of polymer networks. This network is related to the correlation function given by (4.4).

and

$$\begin{aligned} \mathcal{H}'_{cf} = & \sum_{m=1}^n h_1^{(m)} \Psi_1^{(m)} + \sum_{m=1}^n \sum_{\ell=1}^n h_2^{(m,\ell)} \Psi_2^{(m,\ell)} + \\ & + \sum_{m=1}^n \sum_{\ell=1}^n \sum_{k=1}^n h_3^{(m,\ell,k)} \Psi_3^{(m,\ell,k)} + \dots \end{aligned} \quad (4.7b)$$

(H is given by (2.2)). Then the generating function (4.3) is evaluated by differentiating the free energy

$$F = -k_B T \log [\text{Tr } e^{-\mathcal{H}/k_B T}] \quad (4.8)$$

constructed from the above Hamiltonian with respect to fields :

$$\chi_{\mathcal{G}}(K) = -\frac{1}{N_x} \left[\prod_g \frac{\partial}{\partial h_g^{(\dots)}} \frac{\partial}{\partial h_g^{(\dots)}} \dots \frac{\partial}{\partial h_g^{(\dots)}} \right] F \Big|_{h=0}. \quad (4.9)$$

Here h_g may be either the bulk field or the surface field. In this way, (4.4) is rederived by

$$-\frac{1}{N_x} \left[\frac{\partial}{\partial h_1^{(1)}} \frac{\partial}{\partial h_1^{(2)}} \frac{\partial}{\partial h_1^{(5)}} \frac{\partial}{\partial h_3^{(3,4,5)}} \frac{\partial}{\partial h_4^{(1,2,3,4)}} \right] F \Big|_{h=0}. \quad (4.10)$$

Now, it is natural to suppose that the g -th order composite fields h_g and h'_g scale, respectively, as t^{d_g} and $t^{d'_g}$, independent of their components. That is, the free energy (4.7) of the system with Hamiltonian (4.6) is assumed to have the scaling form

$$F \sim NF_b + N_s F_s \quad (4.11)$$

$$F_b = t^{2-\alpha} \Phi_b \left(\frac{h_1}{t^{d_1}}, \frac{h_2}{t^{d_2}}, \dots \right) \quad (4.12)$$

$$F_s = t^{2-\alpha-\nu} \Phi_s \left(\frac{h_1}{t^{d_1}}, \frac{h_2}{t^{d_2}}, \dots, \frac{h'_1}{t^{d'_1}}, \frac{h'_2}{t^{d'_2}}, \dots \right). \quad (4.13)$$

Here α is the specific-heat exponent and given by the hyperscaling relation

$$\alpha = 2 - \nu d. \quad (4.14)$$

Note that the additional factor $t^{-\nu}$ which appears in the surface free energy (4.13) is due to the integration of the free energy density over the distance $\xi \sim t^{-\nu}$ from the surface (for further details the reader may refer to Ref. [6]) ; ν is the correlation length exponent for the single chain problem. This scaling assumption of the composite fields is a plausible one, but, as was discussed in section 3, one should note that the multi-spin correlation function with composite operators is often not multiplicatively renormalizable but mixed with other functions which have same or lower canonical dimension [26]. This is related to the fact that, in the configurations of the network \mathcal{G} with fixed total length L , there appear simpler networks which can be obtained from \mathcal{G} by

shrinking some of the linear chains. In order to discuss the configurations with all chain lengths being the same, we should discard all such terms and preserve only the singularity associated with the topology \mathcal{G} (essential part). The corresponding exponent $\gamma_{\mathcal{G}}$ is obtained from the exponent $\hat{\gamma}_{\mathcal{G}}$ of the essential part associated with the topology \mathcal{G} of the nonlinear susceptibility *via* equation (3.14).

As a result, the scaling form of $\chi_{\mathcal{G}}(K)$ depends only on the number of g -functional free units n_g and the number of g -functional surface units n'_g . This scaling theory concerns only the mutually connected polymer networks. One should not worry about the polymer networks composed of several disconnected parts because each disconnection brings the additional factor $t^{2-\alpha}$ in $\chi_{\mathcal{G}}(K)$ (hence the additional factor $L^{\alpha-1}$ in $\mathcal{N}_{\mathcal{G}}(L)$) and makes their contribution less singular. (Note that $\alpha \cong 0.23$ for $d = 3$ and $\alpha = 1/2$ for $d = 2$ using the hyperscaling relation $d\nu = 2 - \alpha$ and the known exponent of ν .) If we consider the bulk problem, we have the essential part of the nonlinear susceptibility

$$\chi_{\mathcal{G}}(K) \sim -\frac{1}{N} \left[\prod_g \frac{\partial^{n_g}}{\partial h_g^{n_g}} \right] F \Big|_{h=0} \sim t^{-\hat{\gamma}_{\mathcal{G}}}$$

with

$$\hat{\gamma}_{\mathcal{G}} = \alpha - 2 + \sum_{g=1}^{\infty} n_g \Delta_g.$$

Then using the relation (3.14), the exponent for the total number of configurations $\gamma_{\mathcal{G}}$ is given by

$$\gamma_{\mathcal{G}} = \alpha - 1 - f + \sum_{g=1}^{\infty} n_g \Delta_g. \quad (4.15)$$

An expression equivalent to equation (4.15) was obtained by Duplantier [21] by a somewhat different approach. On the other hand, if we consider the surface-adsorbed problem, we have

$$\chi_{\mathcal{G}}(K) \sim -\frac{1}{N} \left[\prod_g \frac{\partial^{n_g}}{\partial h_g^{n_g}} \frac{\partial^{n'_g}}{\partial h'_g{}^{n'_g}} \right] F \Big|_{h=0} \sim t^{-\hat{\gamma}_{\mathcal{G}}}$$

with

$$\hat{\gamma}_{\mathcal{G}} = \alpha - 2 + \nu + \sum_{g=1}^{\infty} [n_g \Delta_g + n'_g \Delta'_g]$$

and, in turn,

$$\gamma_{\mathcal{G}} = \alpha - 1 - f + \nu + \sum_{g=1}^{\infty} [n_g \Delta_g + n'_g \Delta'_g]. \quad (4.16)$$

For the simplest cases of linear chains shown in figures 4.3a-e, we should regain the known exponents. The exponents γ_1 and γ_{11} describe the asymptotic behaviour of linear chains with one end or both ends attached to the surface. In the magnetic

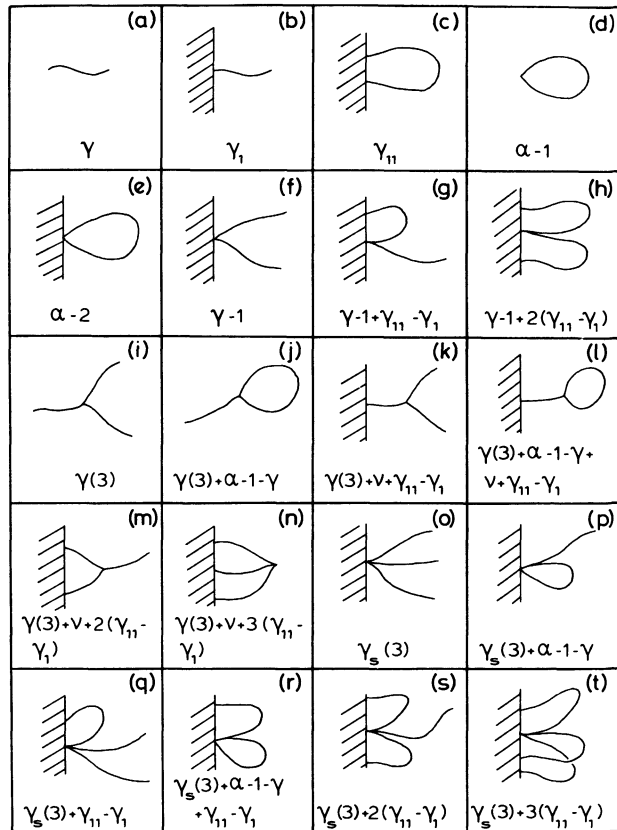


Fig. 4.3. — Exponent $\gamma_{\mathcal{G}}$ for polymer networks expected from the present scaling theory. Only simple networks with 1-, 2- and 3-functional units are presented here. Similar expressions are obtained for more complicated networks also by (4.15), (4.16), (4.19) and (4.20).

problem, γ_1 and γ_{11} are the surface exponents for the layer- and the local-susceptibilities, respectively [5, 6]. Therefore, for the first three topologies we have

$$\text{figure 4.3a : } \alpha - 2 + 2 \Delta_1 = \gamma; \quad (4.17a)$$

$$\text{figure 4.3b : } \alpha - 2 + \nu + \Delta_1 + \Delta'_1 = \gamma_1; \quad (4.17b)$$

$$\text{figure 4.3c : } \alpha - 2 + \nu + 2 \Delta'_1 = \gamma_{11}. \quad (4.17c)$$

To avoid confusion, it should be noted here that in the standard literature (e.g. Ref. [6]) the present Δ_1 is denoted as Δ_b , and Δ'_1 is denoted as Δ_1 . The next two topologies (Figs. 4.3d and e) are associated with single loop polymers whose exponent is given by that for the energy density, i.e., $\langle S_{O_1}^{(i)} S_{O_2}^{(i)} \rangle$ for neighbouring sites O_1 and O_2 [2]. Because the bulk energy density behaves as $t^{1-\alpha}$ and the surface energy density behaves as $t^{2-\alpha}$ [27], we obtain $\gamma_{\mathcal{G}} = \alpha - 1$ and $\alpha - 2$, respectively, for figures 4.3d and 4.3e. Therefore we identify

$$\text{figure 4.3d : } \Delta_2 = 1, \quad (4.17d)$$

$$\text{figure 4.3e : } \Delta'_2 = -\nu. \quad (4.17e)$$

Thus we can express the exponents Δ_1 , Δ'_1 , Δ_2 and

Δ'_2 by means of known exponents. From (4.17a)-(4.17c), we have the well-known surface scaling relation [6]

$$2 \gamma_1 - \gamma_{11} = \gamma + \nu. \quad (4.18)$$

We consider next the simple case of star polymers (Fig. 4.3i and o). A star polymer is a simple polymer network which has many arms (linear chains) starting from the center (see Fig. 4.4). If we put $\gamma_g = \gamma(f)$ for the free star polymer with f arms (Fig. 4.4a), it is given by

$$\gamma(f) = \alpha - 1 + \frac{f}{2} (\gamma - \alpha) + \Delta_f. \quad (4.19)$$

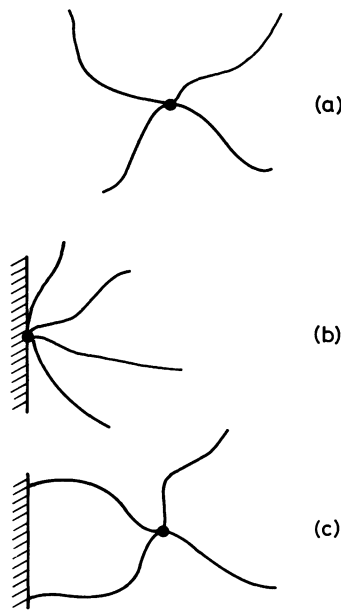


Fig. 4.4. — Three topologies of star polymers : (a) the free star, (b) the center-adsorbed star and (c) the arm-adsorbed star.

On the other hand, if we consider the star polymer with f arms whose center is adsorbed at the surface (see Fig. 4.4b) and write its exponent as $\gamma_g = \gamma_s(f)$, then we obtain

$$\gamma_s(f) = \alpha - 1 + \nu + \frac{f}{2} (\gamma - \alpha) + \Delta'_f. \quad (4.20)$$

Now the exponent γ_g for an arbitrary polymer network in the bulk or semi-infinite geometry is expressed by means of the well known exponents γ , ν , α , γ_1 and γ_{11} (note that these are not mutually independent because of (4.14) and (4.18)) and the star polymer exponents $\gamma(f)$ and $\gamma_s(f)$, because (4.15) and (4.16) can be rewritten by means of these exponents. The values of γ_g for several simple examples are listed in figure 4.3. E.g. one may consider the case where due to the chemistry the

branch point is attached to the surface (Fig. 4.3e, f, o and p) ; or, alternatively, the different chemical nature of end groups leads to binding of these groups to the wall (Fig. 4.3b, c, k, l, m and n) ; or both the branch point and the end groups may sit on the wall (Fig. 4.3g, h, q, r, s and t).

The exponent γ_g for star polymers where some of the arm-end points are adsorbed at the surface is, thus, not an independent exponent. If g of f arm-end points are adsorbed on the surface (Fig. 4.4c), and if we write its γ_g as $\gamma_{11\dots 1}(f)$ with g subscripts 1, we have the relation

$$\gamma_{11\dots 1}(f) = \gamma(f) + \nu + g(\gamma_{11} - \gamma_1). \quad (4.21)$$

Also interesting is the case of comb polymers [15]. If we consider comb polymers with $g = (f - 1)/2$ 3-functional units and $g + 2$ dangling ends (Fig. 4.5), we have the exponent

$$\gamma_{\text{comb}}(g) = \gamma + g[\gamma(3) - \gamma]. \quad (4.22)$$

It is left as a simple exercise to the reader to work out the exponent for a comb polymer adsorbed on the surface with all its trifunctional units or with all its dangling ends, respectively.



Fig. 4.5. — The topology of comb polymers. There are g branch points and $g + 2$ linear chains.

Since the exponents γ_g for all topologies of branched polymer networks can always thus be expressed as linear combinations of the exponents $\gamma(f)$ and $\gamma_s(f)$ of f -arm star polymers and the exponents describing linear polymers, it remains to calculate $\gamma(f)$ and $\gamma_s(f)$ explicitly. This problem is addressed in the next section (in order to check the scaling relation (4.21), we calculate $\gamma_{11\dots 1}(f)$ as well).

5. Mean-field theory of star polymers in the semi-infinite space.

The simplest topologies of a star polymer in semi-infinite space are shown in figure 4.4 : (a) is the free star polymer, (b) gives the center-adsorbed case and (c), the arm-adsorbed case. This section deals with mean-field theory for these star polymers and the next section is devoted to an ϵ expansion.

Consider first the n -vector model (2.1) with (2.2) in semi-infinite space. Taking the continuous limit of this lattice Hamiltonian and neglecting the irrelevant

higher powers of the spins, we are led to the S^4 model in semi-infinite space :

$$\mathcal{H} = \int_{z>0} d\mathbf{r} \left\{ \frac{1}{2} \sum_{m=1}^n [(t + c\delta(z)) S_r^{(m)} + (\nabla S_r^{(m)})^2] + \frac{u}{4!} \left(\sum_{m=1}^n S_r^{(m)} \right)^2 \right\}. \quad (5.1)$$

Here the surface lies at $z = 0$ and the space coordinate \mathbf{r} means $\mathbf{r} = (\mathbf{x}, z)$ with z as the distance from the surface and with \mathbf{x} as the $(d - 1)$ -dimensional coordinate parallel to the surface. Note that the parameter $t (> 0)$ plays the role of the reduced temperature (3.4) and the effect of the repulsive surface is simulated by the surface potential $c\delta(z)$ with $c \rightarrow \infty$. The condition $c \rightarrow \infty$ corresponds to the ordinary transition of the magnetic problem [6].

In the last two sections, we discussed the problem of the essential part of the nonlinear susceptibility in relation to the RG theory. In the case of star polymers (or generally for any *tree* polymers including no loops), however, it is not necessary to worry about this problem at least in discussing low orders of the ϵ expansion, because the essential part of the nonlinear susceptibility shows the most singular behaviour.

5.1 THE MAGNETIC PROBLEM [6]. — In mean-field theory ($u = 0$), the 2-point correlation function

$$C(\mathbf{r}, \mathbf{r}') = C_\rho(z, z') = \langle S_r^{(i)} S_{r'}^{(i)} \rangle \quad (5.2)$$

($\rho = |\mathbf{x} - \mathbf{x}'|$ means the projected distance parallel to the surface) obeys the differential equation

$$[t - \nabla_r^2] C(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (5.3)$$

with the boundary condition

$$C_\rho(0, z) = C_\rho(z, 0) = 0. \quad (5.4)$$

The solution of (5.3) satisfying (5.4) is obtained by transforming it from real space (\mathbf{x}, z) to $(d - 1)$ -dimensional Fourier space (\mathbf{q}, z) :

$$\tilde{C}_q(z, z') = \frac{1}{2\sqrt{t + q^2}} [e^{-\sqrt{t + q^2}|z - z'|} - e^{-\sqrt{t + q^2}(z + z')}] \quad (5.5)$$

The symbol \sim denotes Fourier-transformed functions. The real space function is, then, by transforming (5.5) inversely and using the integral given in reference [28] (p. 706, No. (6, 596, 7)),

$$\begin{aligned} C_\rho(z, z') &= \frac{1}{(2\pi)^{(d-1)/2}} \frac{1}{\rho^{(d-3)/2}} \int_0^\infty dq q^{(d-1)/2} J_{(d-3)/2}(q\rho) \tilde{C}_q(z, z') \\ &= \frac{2}{(2\pi)^{d/2}} \frac{1}{\rho^{(d-3)/2}} \int_0^\infty \frac{dq q^{(d-1)/2}}{[t + q^2]^{1/4}} J_{(d-3)/2}(q\rho) \times \\ &\times [|z - z'|^{1/2} K_{1/2}(\sqrt{t + q^2}|z - z'|) - (z + z')^{1/2} K_{1/2}(\sqrt{t + q^2}(z + z'))] \\ &= \frac{2}{(2\pi)^{d/2}} t^{(d-2)/4} \left[\frac{K_{(d-2)/2}(\sqrt{t} s)}{s^{(d-2)/2}} - \frac{K_{(d-2)/2}(\sqrt{t} \bar{s})}{\bar{s}^{(d-2)/2}} \right], \end{aligned} \quad (5.6)$$

where $J_\nu(\xi)$ and $K_\nu(\xi)$ are the Bessel and the modified Bessel functions [28] ; s denotes the real distance

$$s = \sqrt{\rho^2 + (z - z')^2} = |\mathbf{r} - \mathbf{r}'| \quad (5.7a)$$

and \bar{s} denotes the image distance

$$\bar{s} = \sqrt{\rho^2 + (z + z')^2}. \quad (5.7b)$$

The linear susceptibility at a distance z from the surface is found by elementary integration :

$$\chi_{MF}(z, t) = \lim_{q \rightarrow 0} \int_0^\infty \tilde{C}_q(z, z') dz' = \frac{1}{t} [1 - e^{-\sqrt{t}z}] \quad (5.8)$$

which behaves like

$$\chi_{MF}(z, t) \sim \frac{1}{t} \quad (5.9a)$$

(Curie-Weiss' law) for large z and

$$\chi_{MF}(z, t) \sim \frac{z}{\sqrt{t}} \quad (5.9b)$$

for small z . From these expressions, two exponents $\gamma = 1$ and $\gamma_1 = 1/2$ are identified within mean-field theory.

5.2 BULK AND CENTER-ADSORBED STAR POLYMERS. — Within mean-field theory, the $2f$ -point correlation function $C_g(K)$ given by (2.7) decouples into the f multiples of the 2-point correlation function as

$$C_g(K) \cong \langle S_O^{(1)} S_{P_1}^{(1)} \rangle \langle S_O^{(2)} S_{P_1}^{(2)} \rangle \dots \langle S_O^{(f)} S_{P_1}^{(f)} \rangle, \quad (5.10)$$

where the point O denotes the center of the star and the points P_1, \dots, P_f denote the ends of the arms. This decoupling is graphically represented by fig-

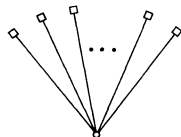


Fig. 5.1. — Diagrammatic representation of the mean-field nonlinear susceptibility $\chi_{MF}(z, t)$ for star polymers. Solid lines represent arms, (O) denotes the center and (□) indicates the full spatial integral. This diagram corresponds to equation (5.10).

ure 5.1, if we draw the two point correlation function starting at the center O and ending at P_i as a solid line. In this subsection, we deal with a star polymer whose arms do not touch the surface (Fig. 5.2). If we fix the location of the center of the star, O, and evaluate the related nonlinear susceptibility in order to count the number of possible configurations, then the result will in general depend on z , the distance between the center O and the surface (see Fig. 5.2).

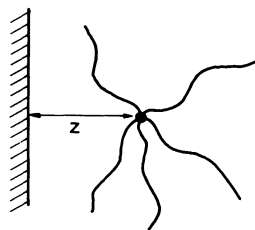


Fig. 5.2. — Star polymers with fixed center point. The center is fixed at a distance z from the surface. Free and center-adsorbed star polymers are obtained, respectively, for $z \rightarrow \infty$ and $z \rightarrow 0$.

The two cases illustrated in figure 4.4a (free star polymer) and figure 4.4b (center-adsorbed star polymer) correspond, respectively, to the large and small z limits. The generating function for the number of configurations which is identical to the nonlinear susceptibility reduces in the approximation (5.10) to

$$\chi_g(K) \cong \left(\sum_P \langle S_O^{(i)} S_P^{(i)} \rangle \right)^f = [\chi_{MF}(z, t)]^f, \quad (5.11)$$

where $\chi_{MF}(z, t)$ denotes the mean-field linear susceptibility of the semi-infinite system which behaves like (5.9). Then the two limiting cases are obtained as

$$\chi_g(K) \sim \begin{cases} t^{-f}, & z \rightarrow \infty; \\ z^f t^{-f/2}, & z \rightarrow 0. \end{cases} \quad (5.12)$$

Hence, for the free star polymer, $\hat{\gamma}_g = f$ and, in turn the relation (3.14) yields $\gamma(f) = 1$. On the other hand, for the center-adsorbed star polymer, we have $\hat{\gamma}_g = f/2$ and then $\gamma_s(f) = 1 - f/2$.

5.3 ARM-ADSORBED STAR POLYMER. — Next we consider the star polymer some of whose arm ends are attached to the surface as is shown in figure 4.4c. Suppose that the total number of arms is f , the number of surface-adsorbed arms is $g (\geq 1)$ and $h = f - g$. We first treat the more general case where these g end points are attached to a plane parallel to the surface at a distance z apart from the surface, while the center of the star lies at a distance z' from the surface (see Fig. 5.3). The result should

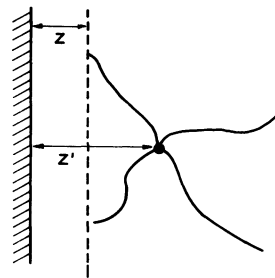


Fig. 5.3. — Star polymers with fixed center and fixed ends. Some of the ends of the arms are fixed at a distance z and the center is fixed at a distance z' , respectively, from the surface. The distance z' should be integrated over to get arbitrary configurations of arm-adsorbed star polymers.

be integrated over z' . The nonlinear susceptibility depends on z and is given by, in the mean-field approximation,

$$\begin{aligned} \chi_g(K) &\cong \int_0^\infty [\chi_{MF}(z, t)]^h [\tilde{C}_g(z, z')]^g dz' \\ &= \frac{1}{t^h (2\sqrt{t})^g} \int_0^\infty [1 - e^{-\sqrt{t}z'}]^h \times \\ &\quad \times [e^{-\sqrt{t}|z-z'|} - e^{-\sqrt{t}(z+z')}]^g dz' \\ &= \frac{1}{t^h (2\sqrt{t})^g} \sum_{\ell=0}^h \binom{h}{\ell} (-)^\ell \sum_{m=0}^g \binom{g}{m} (-)^m I_{\ell, m} \end{aligned} \quad (5.13)$$

with

$$\begin{aligned} I_{\ell, m} &= \int_0^\infty \exp[-\sqrt{t} \{ \ell z' + (g-m)|z-z'| + \\ &\quad + m(z+z') \}] dz' \\ &= \frac{e^{-g\sqrt{t}z} - e^{-(\ell+2m)\sqrt{t}z}}{(\ell+2m-g)\sqrt{t}} - \frac{e^{-(\ell+2m)\sqrt{t}z}}{(\ell+g)\sqrt{t}}. \end{aligned} \quad (5.14)$$

From some detailed calculations, we find that the most singular behaviour for small $\sqrt{t}z$ appears from the highest power of m in each order of the expansion with respect to small $\sqrt{t}z$ and hence from the last term of (5.14); and it is enough to replace $I_{\ell, m}$ by

$$I_{\ell, m} \sim \frac{e^{-2m\sqrt{t}z}}{(\ell+g)\sqrt{t}}. \quad (5.15)$$

Finally, equation (5.13) is evaluated as follows :

$$\begin{aligned} \chi_g(K) &\sim \frac{1}{t^h(2\sqrt{t})^g \sqrt{t}} \sum_{l=0}^h \binom{g}{m} \frac{(-)^l}{l+g} \times \\ &\times \sum_{m=0}^g \binom{g}{m} (-)^m e^{-2m\sqrt{t}z} \\ &= \frac{B(g, h+1)}{t^h(2\sqrt{t})^g \sqrt{t}} [1 - e^{2\sqrt{t}z}]^g \sim \frac{B(g, h+1)}{t^{1/2+h}} z^g, \\ &\quad (z \rightarrow 0). \end{aligned} \quad (5.16)$$

Here $B(\alpha, \beta)$ is the Beta function [28]. Comparing (5.16) with (3.3), we get $\hat{\gamma}_g = 1/2 + h = 1/2 + f - g$. If we write the corresponding exponent γ_g as $\gamma_{11\dots 1}(f)$ with g subscripts 1, then, *via* the relation (3.14), we obtain $\gamma_{11\dots 1}(f) \cong 3/2 - g$. The exponents Δ_f and Δ'_f , which according to equations (4.15) and (4.16) allow to express γ_g for arbitrary polymer networks (remember $\alpha = 0, \nu = 1/2$ in mean field theory), become $\Delta_f = 2 - f/2$ and $\Delta'_f = 3/2 - f$.

6. ϵ expansion for star polymers in semi-infinite space.

In order to go beyond mean-field theory, one may construct a systematic expansion by regarding the S^4 interaction as a small perturbation and applying the renormalization-group (RG) $\epsilon = 4 - d$ expansion scheme. The S^4 coupling corresponds to the excluded volume interaction in the problem of polymer networks. Drawing the mean-field 2-point correlation function with a solid line and the S^4 interaction with a dotted line, the first order correction to mean-field theory is given graphically by figure 6.1a and b. (The zeroth order graph is shown in Fig. 5.1, which corresponds to Eq. (5.10).)

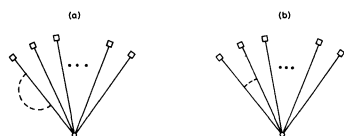


Fig. 6.1. — The diagrams appearing in the 1st order in $\epsilon = 4 - d$. (a) is the case of intra-arm interaction and (b) is the case of inter-arm interaction.

There are f ways of drawing the single intra-arm interaction like figure 6.1a, because there are f arms, i.e., f solid lines. Hence the contribution from figure 6.1a is proportional to f . On the other hand, there are $f(f - 1)/2$ ways of drawing the single inter-arm interaction like figure 6.1b, so that figure 6.1b contributes with a factor $f(f - 1)/2$. The result for the free star polymer is given by

$$\gamma(f) = 1 + \frac{\epsilon}{8} \left[f - \frac{f(f-1)}{2} \right] + O(\epsilon^2). \quad (6.1)$$

This result is the same as that of Miyake and Freed [13, 14], who used the direct RG approach. In the following two subsections, the first order correction to the mean-field values of $\gamma_s(f)$ and $\gamma_{11\dots 1}(f)$ is evaluated explicitly by using the magnetic analogy. In the last subsection, $\gamma(f)$ for free star polymers and $\gamma_s(f)$ for center-adsorbed star polymers are considered in more detail.

6.1 CENTER-ADSORBED STAR POLYMER. — The first problem is a star polymer in semi-infinite space whose arms do not touch the surface (see Fig. 5.2). The center of the star has a fixed distance z from the surface. The diagrams to be evaluated are shown in figures 6.1a and b. Just the solid lines connected by the dotted line are important, because all the other solid lines are non-interacting and only contribute to the mean-field susceptibility, $\chi_{MF}(z, t)$, as a factor. The interacting part is shown in figures 6.2a and b. In these figures, a square (\square) indicates the full spatial integral of that point and a circle (\circ) indicates the center of the star which is fixed at a distance z from the surface. Interactions are assumed to occur at a distance z' from the surface. Then the solid line whose one end has the square (\square) and another end lies at z' means the mean-field layer-susceptibility $\chi_{MF}(z', t)$. The distance z' should be integrated out to yield the final result depending only on z .

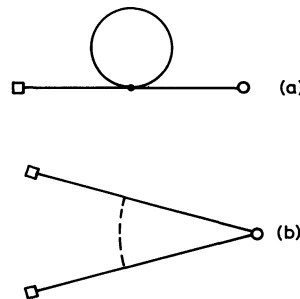


Fig. 6.2. — Interacting part of the first order diagram, figure 6.1. The diagram (a) represents the intra-arm interaction. This diagram is identical to that of the 1st order correction to the mean-field layer susceptibility $\chi_{MF}(z, t)$. The diagram (b) represents the inter-arm interacting part.

Figure 6.2a gives the one loop correction to the mean-field layer-susceptibility $\chi_{MF}(z, t)$, which was evaluated in the earlier paper of Reeve and Guttman [29]. Here we will rederive the same result by using the z -representation in place of their Fourier-sine representation :

$$\begin{aligned} \chi^{(a)}(z, t) &= -\frac{n+2}{6} u \int_0^\infty \chi_{MF}(z', t) \times \\ &\times \Sigma(z', t) \tilde{C}_{q=0}(z, z') dz'. \end{aligned} \quad (6.2)$$

In (6.2), the self-energy

$$\Sigma(z', t) = C_{\rho=0}(z', z') - C_{\rho=0}(\infty, \infty)|_{t=0} \quad (6.3)$$

is evaluated, by using (5.6), taking account of [28]

$$K_1(\xi) = \frac{1}{\xi} + \frac{\xi}{2} \left(\gamma_E - \frac{1}{2} + \log \xi \right) + O(\xi^3) \quad (6.4)$$

(γ_E denotes Euler's constant) and introducing a suitable momentum cutoff Λ , as

$$\Sigma(z', t) \sim \frac{1}{2(2\pi)^2} \times \left[t \log \sqrt{t} \Lambda^{-1} - \frac{\sqrt{t} K_1(2\sqrt{t} z')}{z'} \right] \quad (6.5)$$

at $d = 4$. Using this together with χ_{MF} of (5.8) and C of (5.5) yields the relevant logarithmic behaviour

$$\chi^{(a)}(z, t) \sim -\frac{n+2}{6} \frac{u}{(4\pi)^2} \frac{z}{\sqrt{t}} \times [\log \sqrt{t} \Lambda^{-1} + \log \sqrt{t} z]. \quad (6.6)$$

If this logarithmic behaviour is exponentiated together will the zeroth order term $\chi_{MF}(z, t)$, and using the well-known fixed-point value [26]

$$\frac{2}{(4\pi)^2} u^* = \frac{6}{n+8} \varepsilon + O(\varepsilon^2), \quad (6.7)$$

then the layer susceptibility exponent is found to be $\gamma_1 = 1/2 + (n+2)\varepsilon/2(n+8) + O(\varepsilon^2)$ [5, 6, 29].

Next, we turn our attention to figure 6.2b. It is expressed by the integral

$$\chi^{(b)}(z, t) = -\frac{u}{4!} 8 \times \int_0^\infty [\chi_{MF}(z', t)]^2 \tilde{\Pi}_{q=0}(z, z') dz', \quad (6.8)$$

where $\tilde{\Pi}_q(z, z')$ is the Fourier-transform of the single bubble

$$\Pi_\rho(z, z') = [C_\rho(z, z')]^2. \quad (6.9)$$

The $q = 0$ component of $\tilde{\Pi}_q$ is evaluated for small z at $d = 4$ as

$$\tilde{\Pi}_{q=0}(z, z') = \frac{2}{(2\pi)^2} \int_0^\infty dq q^2 [\tilde{C}_q(z, z')]^2 \sim \frac{1}{(2\pi)^2} \frac{tz^2}{z'} K_2(2\sqrt{t} z') \quad (6.10)$$

by using the integral formula listed in reference [30] : p. 27, No. (I, 3.12). Then, substituting (6.10) into (6.8) gives for small z

$$\chi^{(b)}(z, t) \sim -\frac{1}{3} \frac{u}{(2\pi)^2} \frac{z^2}{t} \times \int_0^\infty [1 - e^{-\sqrt{t} z'}]^2 \frac{K_2(2\sqrt{t} z')}{z'} dz' \sim -\frac{1}{3} \frac{u}{(2\pi)^2} \frac{z^2}{t} \left(-\frac{1}{2} \log \sqrt{t} z \right) \quad (6.11)$$

which yields the relevant logarithmic correction to mean-field behaviour. Together with the former result of figure 6.2a (Eq. (6.6)), the nonlinear susceptibility up to first order is evaluated for small z as

$$\chi_g(K) = [\chi_{MF}(z, t)]^f + f[\chi_{MF}(z, t)]^{f-1} \chi^{(a)}(z, t) + \frac{f(f-1)}{2} [\chi_{MF}(z, t)]^{f-2} \chi^{(b)}(z, t) + O(u^2) \sim \left(\frac{z}{\sqrt{t}} \right)^f \left\{ 1 - \frac{1}{6} \frac{u}{(4\pi)^2} [(n+2)f - f(f-1)] \log t + \dots \right\}. \quad (6.12)$$

Exponentiating this with the fixed-point value (6.7), the exponent $\hat{\gamma}_g$ is found to be

$$\hat{\gamma}_g = \lim_{n \rightarrow 0} \left\{ \frac{f}{2} + \frac{1}{6} \frac{u^*}{(4\pi)^2} [(n+2)f - f(f-1)] + O(u^2) \right\} = \frac{f}{2} + \frac{\varepsilon}{8} \left[f - \frac{f(f-1)}{2} \right] + O(\varepsilon^2). \quad (6.13)$$

Hence through the relation (3.14) we have the final result

$$\gamma_s(f) = 1 - \frac{f}{2} + \frac{\varepsilon}{8} \left[f - \frac{f(f-1)}{2} \right] + O(\varepsilon^2) \quad (6.14)$$

for the configuration-number exponent of a center-

adsorbed star polymer. If we put $f = 1$ and $f = 2$ in (6.14), we retrieve the expected results $\gamma_1 = 1/2 + \varepsilon/8 + O(\varepsilon^2)$ and $\gamma - 1 = \varepsilon/8 + O(\varepsilon^2)$, respectively. All of these calculations become much simpler when we take the opposite limit $z \rightarrow \infty$; in this case we retrieve the exponent $\gamma(f)$ for a free star polymer (6.1). We do not enter into details of this calculation.

6.2 ARM-ADSORBED STAR POLYMER. — The second problem is a star polymer in semi-infinite space some of whose arms touch the surface (see Fig. 5.3). The touching is conveniently expressed by the limit $z \rightarrow 0$, where the ends of g arms are all assumed to be fixed at a distance z from the surface. The relevant diagrams up to first order in ε are shown in figures 6.3a-e. We first note that, for small z , the mean-field correlation function with $q = 0$ behaves as

$$\tilde{C}_{q=0}(z, z') \sim z e^{-\sqrt{t}z'}, \quad (z \rightarrow 0). \quad (6.15)$$

We also note that the mean-field susceptibility function $\chi_{MF}(z', t)$ is given by (5.8) with z replaced by z' . Then the diagrams figures 6.3a-c are evaluated using the integral

$$L_{\ell, m} = \int_0^\infty dz_1 e^{-\ell \sqrt{t}z_1} \int_0^\infty dz_2 e^{-m \sqrt{t}z_2} \tilde{\Pi}_{q=0}(z_1, z_2) \sim \frac{2}{(4\pi)^2} \frac{1}{4(\ell+m)\sqrt{t}} \log \frac{\sqrt{t}}{2\Lambda} \quad (6.16)$$

as

$$\chi^{(a)} = -\frac{h(h-1)}{2} 8 \frac{u}{4!} \frac{z^g}{t^h} \sum_{\ell=0}^2 \binom{2}{\ell} (-)^{\ell} \times \sum_{m=0}^{h-2} \binom{h-2}{m} (-)^m L_{\ell, m+g}, \quad (6.17a)$$

$$\chi^{(b)} = -hg \cdot 8 \frac{u}{4!} \frac{z^g}{t^h} \sum_{\ell=0}^1 (-)^{\ell} \times \sum_{m=0}^{h-1} \binom{h-1}{m} (-)^m L_{\ell+1, m+g-1} \quad (6.17b)$$

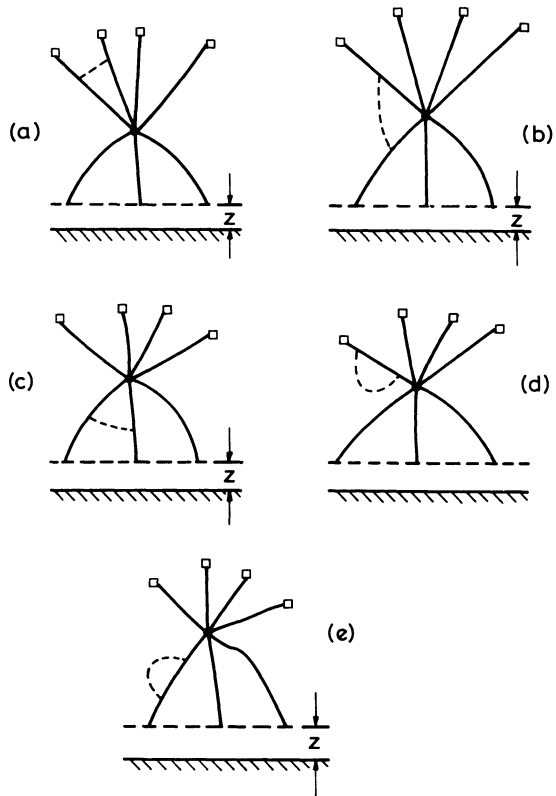


Fig. 6.3. — The diagrams which appear in the calculation in the 1st order in $\varepsilon = 4 - d$ for the star polymer which has some of its ends at a (close) distance z from the surface.

and

$$\chi^{(c)} = -\frac{g(g-1)}{2} 8 \frac{u}{4!} \frac{z^g}{t^h} \sum_{m=0}^h \binom{h}{m} (-)^m L_{2, m+g-2} \quad (6.17c)$$

for small z . On the other hand, the diagrams figures 6.3d and e are evaluated using the integral

$$M_{\ell, m} = \int_0^\infty dz_1 e^{-\ell \sqrt{t}z_1} \int_0^\infty dz_2 e^{-m \sqrt{t}z_2} \Sigma(z_1, t) \tilde{C}_{q=0}(z_1, z_2) \sim \frac{2}{(2\pi)^2} \left\{ \frac{1}{4(\ell+1)(m+1)(\ell+m)} + \frac{1}{8(m+1)} \right\} \frac{1}{\sqrt{t}} \log \frac{\sqrt{t}}{2\Lambda} \quad (6.18)$$

as

$$\chi^{(d)} = -h \cdot 4(n+2) \frac{u}{4!} \frac{z^g}{t^h} \sum_{\ell=0}^1 (-)^{\ell} \sum_{m=0}^{h-1} \binom{h-1}{m} (-)^m M_{\ell, m+g}, \quad (6.19a)$$

and

$$\chi^{(e)} = -g \cdot 4(n+2) \frac{u}{4!} \frac{z^g}{t^h} \sum_{m=0}^h \binom{h}{m} (-)^m M_{1, m+g-1}, \quad (6.19b)$$

for small z . If the explicit forms of $L_{\ell, m}$ and $M_{\ell, m}$ are inserted into $\chi^{(a)}$, $\chi^{(b)}$, ..., and $\chi^{(e)}$, the summations appearing in these expressions become

$$\sum_{\ell=0}^k \binom{k}{\ell} (-)^{\ell} \sum_{m=0}^{h-k} \binom{h-k}{m} \frac{(-)^m}{\ell+m+g} = B(g, h+1) \quad (k = 0, 1 \text{ and } 2), \quad (6.20a)$$

$$\sum_{\ell=0}^1 (-)^\ell \sum_{m=0}^{h-1} \binom{h-1}{m} (-)^m \left\{ \frac{2}{(\ell+1)(m+1)(\ell+m)} + \frac{1}{m+g+1} \right\} =$$

$$= B(g, h+1) \left\{ 2 + \frac{g}{h} [\psi(g+1) - \psi(g+h+1)] \right\}, \quad (6.20b)$$

$$\sum_{m=0}^h \binom{h}{m} (-)^m \left\{ \frac{1}{m+g} + \frac{1}{(m+g)^2} \right\} = B(g, h+1) \{1 - [\psi(g) - \psi(g+h+1)]\}, \quad (6.20c)$$

where $\psi(x+1) = \psi(x) + 1/x$ is the psi (poly-Gamma) function [28]. Combining these results, we obtain

$$\chi^{(a)} + \chi^{(b)} + \chi^{(c)} = \left[\frac{h(h-1)}{2} + hg + \frac{g(g-1)}{2} \right] 8 \frac{u}{4!} \frac{2}{(2\pi)^2} \frac{B(g, h+1)}{4} \frac{z^g}{t^{1/2+h}} \log \frac{\sqrt{t}}{2\Lambda}$$

$$= \frac{f(f-1)}{2} 8 \frac{u}{4!} \frac{2}{(2\pi)^2} \frac{B(g, h+1)}{4} \frac{z^g}{t^{1/2+h}} \log \frac{\sqrt{t}}{2\Lambda} \quad (6.21)$$

and

$$\chi^{(d)} + \chi^{(e)} = - \left[f - \frac{g-1}{2} \right] 4(n+2) \frac{u}{4!} \frac{2}{(2\pi)^2} \frac{B(g, h+1)}{4} \frac{z^g}{t^{1/2+h}} \log \frac{\sqrt{t}}{2\Lambda}. \quad (6.22)$$

Then comparing these logarithmic factors with the mean-field value (5.16) and using the fixed point value u^* given by (6.7) yields

$$\hat{\gamma}_g = \lim_{n \rightarrow 0} \left\{ \frac{1}{2} + h + \frac{1}{6} \frac{u^*}{(4\pi)^2} \left[(n+2) \left(f - \frac{g-1}{2} \right) - f(f-1) \right] + O(u^2) \right\}$$

$$= \frac{1}{2} + h + \frac{\varepsilon}{8} \left\{ f - \frac{f(f-1)}{2} - \frac{g-1}{2} \right\} + O(\varepsilon^2) \quad (6.23)$$

and through the relation (3.14)

$$\gamma_{11\dots 1}(f) = \frac{3}{2} - g +$$

$$+ \frac{\varepsilon}{8} \left\{ \left[f - \frac{f(f-1)}{2} \right] - \frac{g-1}{2} \right\} + O(\varepsilon^2). \quad (6.24)$$

This is our final result for the configuration-number exponent for an arm-adsorbed star polymer. Using (6.1) for $\gamma(f)$ and using $\nu = 1/2 + \varepsilon/16 + O(\varepsilon^2)$ [26] and $\gamma_1 - \gamma_{11} = \gamma + \nu - \gamma_1 = 1 + \varepsilon/16 + O(\varepsilon^2)$, we find

$$\gamma(f) + \nu + g(\gamma_{11} - \gamma_1) = \frac{3}{2} +$$

$$+ \frac{\varepsilon}{8} \left[f - \frac{f(f-1)}{2} \right] + \frac{\varepsilon}{16} - \left(1 + \frac{\varepsilon}{16} \right) g + O(\varepsilon^2) \quad (6.25)$$

and hence our result (6.24) is certainly consistent with the scaling relation (4.21). Moreover, as is expected, (6.24) reduces to γ_1 when $g=1$ and $f=1$ or 2, and reduces to γ_{11} when $g=f=2$.

6.3 FURTHER CONSIDERATIONS. — We now consider the properties of the exponent γ_g for star polymers in more detail. If we write the nonlinear susceptibility associated with a *free* star polymer as

$$\chi(f; K) = t^{-f} \left\{ 1 + ft \Theta_1(t) + \frac{f(f-1)}{2} t^2 \Theta_2(t) + \frac{f(f-1)(f-2)}{3!} t^3 \Theta_3(t) + \dots \right\}, \quad (6.26)$$

we can identify the first two terms very easily from the ε expansion without any explicit calculation. First of all, it is obvious to see that the term proportional to f is related to the usual linear susceptibility as

$$\Theta_1(t) = \chi(1; t) - \frac{1}{t}, \quad (6.27)$$

where $1/t$ means its mean-field value (see (5.9a)). Next, we operate with $-\partial/\partial t$ on this function. A solid line in the diagrammatic representation of the ε expansion is given by the mean-field 2-point correlation function

$$\tilde{C}(q) = \frac{1}{t + q^2} \quad (6.28)$$

in d -dimensional Fourier-space. Note the relation

$$-\frac{\partial}{\partial t} \tilde{C}(q) = [\tilde{C}(q)]^2, \quad (6.29)$$

which corresponds diagrammatically to an insertion of the circle (O) in the solid line. Hence, the

derivative $-(\partial/\partial t) \Theta_1(t)$ yields the summation of all possible insertions of one circle (O) into the diagrams for $\Theta_1(t)$. If we regard this circle as the center of the star, then we have automatically all possible interactions between two arms. Thus we have the identity

$$-\frac{\partial}{\partial t} \Theta_1(t) = \frac{2}{t} \Theta_1(t) + \Theta_2(t). \quad (6.30)$$

Therefore, putting $\chi(1; t) \sim \Gamma t^{-\gamma}$, we have

$$\chi(f; K) \sim t^{-f} \left\{ 1 + f[\Gamma t^{1-\gamma} - 1] + \frac{f(f-1)}{2} \times \right. \\ \left. \times [(2-\gamma)\Gamma t^{1-\gamma} - 1] + \frac{f(f-1)(f-2)}{3!} t^3 \Theta_3(t) + \dots \right\}. \quad (6.31)$$

After some calculation, we find that this expression can be exponentiated to give

$$\chi(f; K) \sim \hat{\Gamma}(f) t^{-\hat{\gamma}(f)} \quad (6.32)$$

with

$$\hat{\Gamma}(f) = 1 + f[\Gamma - 1] - \frac{f(f-1)}{2} [(2-\gamma)\Gamma - 1] + O[f(f-1)(f-2)] \quad (6.33)$$

and

$$\hat{\gamma}(f) = f + (\gamma - 1) \left[f - \frac{f(f-1)}{2} \right] + O[f(f-1)(f-2)]. \quad (6.34)$$

Here $O[f(f-1)(f-2)]$ denotes a term which vanishes for $f = 0, 1$ and 2 . Finally using the relation (3.14) yields a result valid to all orders in ϵ

$$\gamma(f) = 1 + (\gamma - 1) \left[f - \frac{f(f-1)}{2} \right] + f(f-1)(f-2) A(f). \quad (6.35)$$

We have introduced the function $A(f)$ which is a regular function of f (finite for $f = 0, 1$ and 2) and of $O(\epsilon^2)$.

Now we consider some special properties of $\gamma(f)$. If we take the limit $f \rightarrow 0$, we should have $\hat{\gamma}(f) = 0$ or identically

$$\gamma(0) = 1 \quad (6.36)$$

because we expect

$$\lim_{f \rightarrow 0} \sum_{P_1} \sum_{P_2} \dots \sum_{P_f} \times \langle S_{O_1}^{(1)} S_{P_1}^{(1)} S_{O_2}^{(2)} S_{P_2}^{(2)} \dots S_{O_f}^{(f)} S_{P_f}^{(f)} \rangle = 1 = t^0. \quad (6.37)$$

Moreover, we should have

$$\gamma(1) = \gamma(2) = \gamma \quad (6.38)$$

because a star polymer with one or two arms is identical to a linear chain. One can easily see that the general form (6.35) certainly satisfies these special properties. It is interesting, however, to note that the result for a two-dimensional star polymer due to Duplantier [21], namely

$$\gamma(f) = \frac{17}{16} - \frac{9}{32} \left[f - \frac{f(f-1)}{2} \right] \quad (6.39)$$

does not satisfy our simple expectation (6.35) which implies $\gamma(0) = 1$ in contrast to $\gamma(0) = 17/16$. Perhaps this discrepancy occurs because two dimensions for random walk problems is very special ($d = 2$ is the same as the *fractal dimension* of simple random walks). Since equation (6.39) is thought [21] to be exact, the implication is that the ϵ expansion breaks down in $d = 2$.

The function $A(f)$ in (6.35) has been calculated within the framework of an ϵ expansion up to second order in $\epsilon = 4 - d$. Details of this calculation will be published elsewhere [31]. Here we only mention the final result

$$A(f) = \frac{\epsilon^2}{64} + O(\epsilon^3). \quad (6.40)$$

Now we discuss additional scaling relations which relate the exponents $\gamma(3), \gamma(4)$ for star polymers with three and four arms to the exponents θ_1, θ_2 describing the short distance behaviour of the distribution functions $p(\mathbf{r}_1), p(\mathbf{r}_2)$ between an end point of a linear chain and a point in its interior (Fig. 6.4b) or two interior points of a chain (Fig. 6.4c). These distribution functions have been considered by des Cloizeaux [32] who also obtained the exponents θ_1, θ_2 by ϵ expansion up to order ϵ^2 , as well as the exponent θ_0 describing the short distance behaviour of the end-to-end distance distribution $p(\mathbf{r}_0)$ of a polymer chain (Fig. 6.4a)

$$p(\mathbf{r}_0) = \frac{1}{r_0^d} \phi_0(r_0 \ell^{-\nu}) \sim \ell^{-d\nu - \nu\theta_0} r_0^{\theta_0}, \quad (r_0 \rightarrow 0) \quad (6.41a)$$

$$p(\mathbf{r}_1) = \frac{1}{r_1^d} \phi_1(r_1 \ell^{-\nu}) \sim \ell^{-d\nu - \nu\theta_1} r_1^{\theta_1}, \quad (r_1 \rightarrow 0) \quad (6.41b)$$

$$p(\mathbf{r}_2) = \frac{1}{r_2^d} \phi_2(r_2 \ell^{-\nu}) \sim \ell^{-d\nu - \nu\theta_2} r_2^{\theta_2}, \quad (r_2 \rightarrow 0) \quad (6.41c)$$

where the exponents θ_0, θ_1 and θ_2 are [32]

$$\theta_0 = \frac{\epsilon}{4} + \frac{9}{128} \epsilon^2 + O(\epsilon^3), \quad (6.42a)$$

$$\theta_1 = \frac{\epsilon}{2} - \frac{3}{64} \epsilon^2 + O(\epsilon^3), \quad (6.42b)$$

$$\theta_2 = \epsilon - \frac{15}{32} \epsilon^2 + O(\epsilon^3). \quad (6.42c)$$

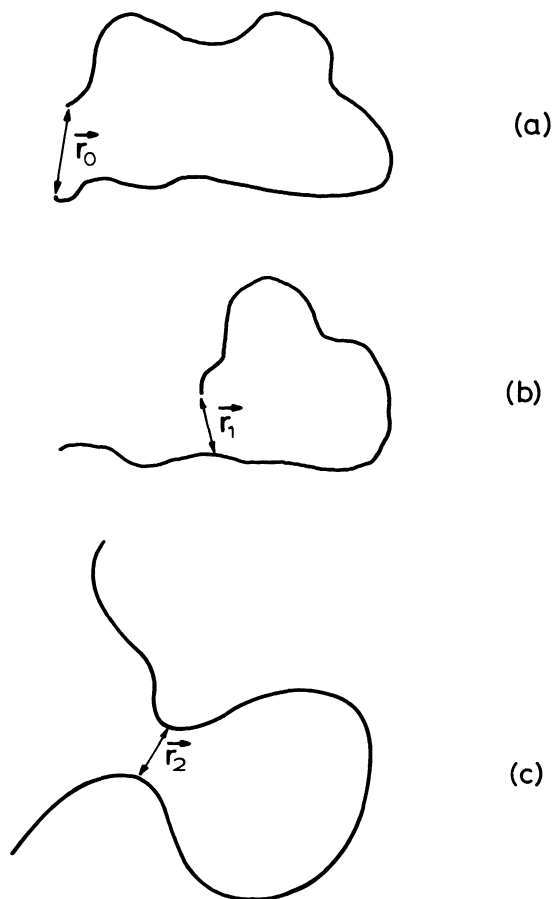


Fig. 6.4. — Distribution function for the distances r_0 , r_1 , r_2 between pairs of points in a linear chain : case (a) refers to both points being end points, case (b) refers to the case where one point is an end point and the other point is in the interior of the chain, while case (c) refers to the case where both points are interior points of the chain.

Putting now r_0 , r_1 and r_2 equal to a nearest neighbour distance and multiplying these probabilities $p(r_0)$, $p(r_1)$, $p(r_2)$ with the total number of configurations for the linear chain without any constraint, $\mathcal{N}(\ell) \sim \ell^{\gamma-1} \mu^\ell$, yields the total number of configurations for the polymer networks with the topologies shown in figures 4.3d, j, and 6.5a, respectively. Therefore, we obtain the scaling relations (remember that in figures 4.3 and 6.5a the exponent γ_g rather than $\gamma_g - 1$ is shown)

$$\gamma - \nu d - \nu \theta_0 = \alpha - 1, \quad \theta_0 = (\gamma - 1)/\nu, \tag{6.43a}$$

$$\begin{aligned} \gamma - \nu d - \nu \theta_1 &= \gamma(3) + \alpha - 1 - \gamma, \\ \gamma(3) &= 2\gamma - 1 - \nu \theta_1, \end{aligned} \tag{6.43b}$$

$$\begin{aligned} \gamma - \nu d - \nu \theta_2 &= \gamma(4) + \alpha - 1 - \gamma, \\ \gamma(4) &= 2\gamma - 1 - \nu \theta_2. \end{aligned} \tag{6.43c}$$

This type of reasoning has first been proposed by Duplantier [23]. In fact, this type of scaling consideration can be generalized to star polymers with a

general number f of arms : e.g., the probability distribution that both two interior points and one end point of a linear chain come into close proximity (distances r much smaller than the radius ℓ^ν of the loops involved in this configuration), see figure 6.5b, would be analogously related to a branched polymer with a five-fold branch point and the topology shown in figure 6.5c, which has the exponent $\gamma(5) - 2\gamma + 2\alpha - 2$. However, the corresponding exponent θ_i for configurations as shown in figure 6.5b or configurations involving the close proximity of even more points of a linear chain have not been calculated yet.

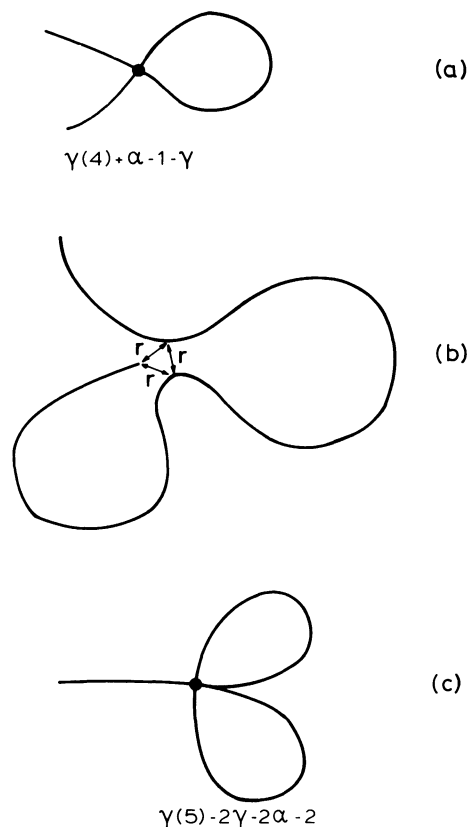


Fig. 6.5. — Polymer network with one 4-fold branch point and two free ends (a) which corresponds to the configuration of one linear chain as shown in figure 6.4c, and a linear chain with two interior points as well as an end point in close proximity (b) compared to the corresponding network with a five-fold branch point (c). Exponents γ_g for the networks are quoted in the figure.

Using equations (6.43a-c), (6.42a-c), (6.35) and (6.40) and the ϵ expansion for the bulk exponents [26]

$$\gamma = 1 + \frac{\epsilon}{4} + \frac{13}{256} \epsilon^2 + O(\epsilon^3), \tag{6.44a}$$

$$\nu = \frac{1}{2} + \frac{\epsilon}{16} + \frac{15}{512} \epsilon^2 + O(\epsilon^3), \tag{6.44b}$$

it is a matter of simple algebra to verify that equations (6.43a-c) are satisfied to order ϵ^2 . Thus we could check our scaling relation for these special cases up to $O(\epsilon^2)$.

Before ending this section, we also give a general form of the exponent $\gamma_s(f)$ for center-adsorbed star polymers with f arms. Since we should have $\gamma_s(1) = \gamma_1$ and $\gamma_s(2) = \gamma - 1$, we can expect that $\gamma_s(f)$ has the form

$$\gamma_s(f) = 1 + (\gamma_1 - 1)f - (\gamma_{11} + \nu) \frac{f(f-1)}{2} + f(f-1)(f-2)B(f). \quad (6.45)$$

Here we used the surface scaling relation (4.18); $B(f)$ is a regular function of f and is of $O(\epsilon^2)$. The evaluation of $B(f)$ up to second order in ϵ is left to a future study. The expression (6.45) is consistent with Duplantier and Saleur's result [22] for the two-dimensional center-adsorbed star polymers.

7. Polymers with different length.

* SCALING AND CONNECTION TO DIRECT METHOD. Scaling ideas can also be applied to study precisely the case where the polymer network is composed of linear chains with different lengths. Note that the equivalence proved in section 2 becomes somewhat useless in its original form for this purpose, because it deals with polymer networks with fixed total chain length or with all chains having the same fixed chain length. In order to formulate the polymer networks composed of many linear chains with different fixed lengths, we should introduce the anisotropic n -vector model, where different spin components have different coupling constants :

$$\mathcal{H}/k_B T = - \sum_{m=1}^n K^{(m)} \sum_{\langle ij \rangle} S_i^{(m)} S_j^{(m)}. \quad (7.1)$$

The consideration in section 2 can be extended straightforwardly to this more general case. Along the same lines as in section 2, one finds that the generating function with f variables

$$Z_g(\{K^{(m)}\}) = \sum_{\ell_1=0}^{\infty} \sum_{\ell_2=0}^{\infty} \dots \sum_{\ell_f=0}^{\infty} \times \mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f) \prod_{m=1}^f [K^{(m)}]^{\ell_m} \quad (7.2)$$

for the number of configurations of the polymer network with fixed topology \mathcal{G} and with fixed end- and branch-points is identical to the $2f$ -point correlation function

$$C_g(\{K^{(m)}\}) = \langle S_{O_1}^{(1)} S_{P_1}^{(1)} S_{O_2}^{(2)} S_{P_2}^{(2)} \dots S_{O_f}^{(f)} S_{P_f}^{(f)} \rangle \quad (7.3)$$

for the anisotropic n -vector model in the $n \rightarrow 0$ limit. Then, as was discussed in section 3, if we remove the

constraint of fixed end- and branch-points, the generating function for $\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f)$ becomes equivalent to the nonlinear susceptibility associated with the same topology \mathcal{G}

$$\chi_g(\{K^{(m)}\}) = \frac{1}{N_x} \sum_{\text{end- and branch-points}} C_g(\{K^{(m)}\}). \quad (7.4)$$

Here N_x is given by (3.2) and the summations run over all the end- and branch-points. We should first note that, in the limit $n \rightarrow 0$, if at least one of $K^{(m)}$ s approaches the critical value K_c of the isotropic model, then the corresponding spin component becomes critical. Thus we introduce the reduced temperatures *via* the relations

$$\mu K^{(m)} = e^{-t_m} \quad (7.5)$$

with the same μ as the isotropic case (see (3.5) and (3.9)). The nonlinear susceptibility of this anisotropic model as a scaling form

$$\chi_g(\{K^{(m)}\}) \sim t_1^{-\hat{\gamma}_g} \tilde{Y}_g\left(\frac{t_2}{t_1}, \frac{t_3}{t_1}, \dots, \frac{t_f}{t_1}\right), \quad (7.6)$$

where $\hat{\gamma}_g$ is the exponent for the isotropic case (note that we may not use the form of (7.6) for the usual system with magnetic anisotropies, if the limit $n \rightarrow 0$ is not taken for granted [33]). The scaling function \tilde{Y}_g becomes constant when all the arguments become unity. By using (7.5) and replacing summations over the chain lengths by means of integrals, the generating function (7.2) is expressed as multiple inverse-Laplace-transformations :

$$\chi_g(\{K^{(m)}\}) \approx \int_0^\infty d\ell_1 \int_0^\infty d\ell_2 \dots \int_0^\infty \times d\ell_f \left[\frac{\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f)}{\mu^{\ell_1 + \ell_2 + \dots + \ell_f}} \right] e^{-\sum_{i=1}^f t_i \ell_i}. \quad (7.7)$$

Therefore, putting (7.6) in this formula, we obtain the scaling form for the total number of configurations

$$\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f) \sim \ell_1^{\gamma_g - 1} Y_g\left(\frac{\ell_2}{\ell_1}, \frac{\ell_3}{\ell_1}, \dots, \frac{\ell_f}{\ell_1}\right) \times \mu^{\ell_1 + \ell_2 + \dots + \ell_f}. \quad (7.8)$$

Here we used the relation $\gamma_g = \hat{\gamma}_g + 1 - f$ (see (3.14)). Also note that the scaling function Y_g becomes constant when all the arguments become unity.

In mean-field approximation, the multi-spin correlation function (7.3) decouples into f multiples of the 2-point correlation functions, as was discussed in section 5. The 2-point correlation function for the i -th linear chain in the free network is given by

$$\tilde{C}^{(i)}(q) = \frac{1}{t_i + q^2} \tag{7.9}$$

in d -dimensional Fourier space. In order to discuss the number of configurations, one should consider inverse-Laplace-transformations. The inverse-Laplace-transform of $\tilde{C}^{(i)}(q)$ is introduced *via*

$$\int_0^\infty e^{-t_i \ell_i} \tilde{G}^{(i)}(q) d\ell_i = \tilde{C}^{(i)}(q), \tag{7.10}$$

from which one obtains

$$\tilde{G}^{(i)}(q) = e^{-q^2 \ell_i}. \tag{7.11}$$

Next, we transform this into real space. The real-space propagator is given by the d -dimensional inverse-Fourier-transformation as

$$\begin{aligned} G^{(i)}(r) &= \frac{1}{(2\pi)^{d/2}} \frac{1}{r^{(d-2)/2}} \times \\ &\times \int_0^\infty dq q^{d/2} J_{(d-2)/2}(qr) \tilde{G}^{(i)}(q) \\ &= \frac{1}{(2\pi)^{d/2}} \frac{1}{(2\ell_i)^{d/2}} \exp\left(-\frac{r^2}{4\ell_i}\right). \end{aligned} \tag{7.12}$$

This is obviously the propagator in the direct problem [12]. In such a way, our magnetic approach is surely consistent with the direct approach.

We also make a comment on the value of exponents γ_g of arbitrary free networks within mean-field theory. The value of the exponent γ_g for an arbitrary free polymer network \mathfrak{G} is expressed by (4.15). Within mean-field theory, Δ_g is given by

$$\Delta_g = 2 - \frac{g}{2} \tag{7.13}$$

(for surface-adsorbed problem, $\Delta'_g = 3/2 - g$). Using $\alpha = 0$ together with the topological relations for the number of linear chains f and for the number of loops n_{loop}

$$f = \frac{1}{2} \sum_{g=1}^\infty g n_g, \tag{7.14}$$

$$n_{\text{loop}} = 1 + \frac{1}{2} \sum_{g=1}^\infty (g-2) n_g, \tag{7.15}$$

we identify the mean-field exponent

$$\gamma_g = 1 - 2 n_{\text{loop}} \tag{7.16}$$

for arbitrary free networks.

Now we give two examples of the scaling function Y_g within mean-field theory. First of all, we have $Y_g = 1$ and $\gamma_g = 1$ for any free *tree* networks including no loops. A nontrivial ℓ -dependence appears in general networks with at least one loop. To see this, we consider *watermelon* [21] networks

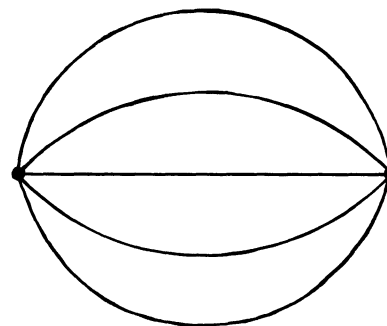


Fig. 7.1. — Watermelon networks. For this network, the number of configurations is given by (7.18) within mean-field theory.

shown in figure 7.1. The total number of configurations of this network is calculated as

$$\begin{aligned} \mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f) &\equiv \int dr \prod_{i=1}^f G^{(i)}(r) = \\ &= \frac{\mu^{\sum_i \ell_i}}{\prod_i (2\ell_i)^{d/2}} \int dr \exp\left[-\frac{1}{4} \left(\sum_i \frac{1}{\ell_i}\right) r^2\right] \\ &\sim \frac{\mu^{\sum_i \ell_i}}{\prod_i (2\ell_i)^{d/2}} \frac{1}{\left[\sum_i \frac{1}{\ell_i}\right]^{d/2}} \end{aligned} \tag{7.17}$$

and hence at $d = 4$ where mean-field theory should apply, we have

$$\mathcal{N}_g(\ell_1, \ell_2, \dots, \ell_f) \sim \frac{\mu^{\sum_i \ell_i}}{\prod_i (2\ell_i)^2 \left[\sum_i \frac{1}{\ell_i}\right]^2}. \tag{7.18}$$

For comb polymers as shown in figure 4.5, one such scaling function was calculated by Vlahos and Kosmas [15] up to first order in $\varepsilon = 4 - d$.

We end this section by pointing out specific applications of equation (7.8) which arise when some of the chain lengths ℓ_i involved in the network become very small. Then it may happen that branch points which previously were separated by a chain of length ℓ_i merge and hence form a higher-order branch point. In this limit of small ℓ_i , the dependence of the scaling function Y_g on ℓ_i must become a simple power-law. As an example, let us consider a comb polymer as shown in figure 4.5, assuming that there are $g = 2$ branch points of functionality $f = 3$ connected by a chain of length ℓ' while all other chains in the comb polymer are assumed to have the same length ℓ . Then equation (7.8) reduces to

$$\mathcal{N}_g(\ell, \ell') \sim \ell^{\gamma_g - 1} Y_g\left(\frac{\ell'}{\ell}\right) \mu^{4\ell + \ell'}, \tag{7.19}$$

where $\gamma_g = \alpha - 6 + 4 \Delta_1 + 2 \Delta_3$ and $Y_g(1) = 1$. On the other hand, if $l' \rightarrow 0$ the comb polymer reduces to a star polymer with four arms, and we then have $\mathcal{N}_g(l, l' \rightarrow 0) \sim l^{\gamma(4)-1} \mu^{4l}$ (with $\gamma(4) = \alpha - 5 + 4 \Delta_1 + \Delta_4$). This implies that $Y_g(z \rightarrow 0) \sim z^{\gamma_1}$ with $\gamma_1 = -1 + 2 \Delta_3 - \Delta_4$, and hence

$$\mathcal{N}_g(l, l' \ll l) \sim l^{\gamma(4)-1} (l')^{-1+2\Delta_3-\Delta_4} \mu^{4l+l'} \tag{7.20}$$

Similarly, if $l' \rightarrow \infty$, we obtain essentially a linear polymer decorated at its ends with two short linear chains of length l each; since $\mathcal{N}_g(l, l' \rightarrow \infty) \sim (l')^{\gamma-1} \mu^{l'}$ we can conclude $Y_g(z \rightarrow \infty) \sim z^{\gamma-1}$ and hence

$$\mathcal{N}_g(l, l' \gg l) \sim (l')^{\gamma-1} l^{-4+2\Delta_1+2\Delta_3} \mu^{4l+l'} \tag{7.21}$$

It is straightforward to carry out similar considerations for more complicated topologies as well.

8. Summary and discussion.

First we summarize the main results of this paper. The generating function of the number of configurations, $Z_g(K)$ introduced in (2.6), was shown to be identical to the $2f$ -point correlation functions, associated with the same geometry \mathcal{G} , of the n -vector model in the limit $n \rightarrow 0$ (see Sect. 2 for further details). It was found that the exponent γ_g for the number of configurations with all chain lengths being the same is related by equation (3.14) to the critical exponent of the essential part (Sects. 3 and 4) of the nonlinear susceptibility associated with the $2f$ -point correlation function. Therefore it becomes possible to evaluate γ_g more easily from the many-point correlation function of magnetic system than by other methods. New results for γ_g for the surface-adsorbed star polymers were derived by mean-field theory (Sect. 5) and by an ϵ expansion (Sect. 6). When the center of the star is adsorbed at the surface, our result for the exponent γ_g is

$$\gamma_s(f) = 1 - \frac{f}{2} + \frac{\epsilon}{8} \left[f - \frac{f(f-1)}{2} \right] + O(\epsilon^2) \tag{8.1}$$

for the f -arm star polymer. When g ends of arms are adsorbed on the surface, our result is

$$\gamma_{11\dots 1}(f) = \frac{3}{2} - g + \frac{\epsilon}{8} \left\{ \left[f - \frac{f(f-1)}{2} \right] - \frac{g-1}{2} \right\} + O(\epsilon^2), \tag{8.2}$$

where, needless to say, there are g subscripts 1 in this notation. From further calculations, one can

identify the dependence of $\gamma(f)$ and $\gamma_s(f)$ on f and $\epsilon = 4 - d$. Our final results are given by (6.35) with (6.40), and (6.45). Especially, $\gamma(f)$ was obtained accurately up to $O(\epsilon^2)$, while all previous work was restricted to $O(\epsilon)$. Our formula (6.35) for $\gamma(f)$ is valid to all orders in ϵ , but inconsistent with Duplantier's [21] two dimensional exact result (6.39).

In section 4, we presented a phenomenological scaling theory for general polymer networks in semi-infinite solvents from the point of view of the mapping to the magnetic problem. Using this scaling approach, we argued that γ_g for any general polymer networks can be expressed in terms of well-known exponents like $\gamma, \nu, \alpha, \gamma_1$ and γ_{11} , and the exponents $\gamma(f)$ and $\gamma_s(f)$ for free and center-adsorbed star polymers. If the polymer network \mathcal{G} has n_g free g -functional units and no surface-adsorbed points, then γ_g is expressed by (Eq. (4.15))

$$\gamma_g = \alpha - 1 - f + \sum_{g=1}^{\infty} n_g \Delta_g \tag{8.3a}$$

On the other hand, if there are also n'_g surface-adsorbed g -functional units, then γ_g is given by (Eq. (4.16))

$$\gamma_g = \alpha - 1 - f + \nu + \sum_{g=1}^{\infty} [n_g \Delta_g + n'_g \Delta'_g] \tag{8.3b}$$

Here the quantities Δ_g and Δ'_g are related to the exponent for star polymers as follows :

$$\Delta_g = \gamma(g) + 1 - \alpha + \frac{g}{2} (\alpha - \gamma) \tag{8.4a}$$

$$\Delta'_g = \gamma_s(g) + 1 - \alpha + \nu + \frac{g}{2} (\alpha - \gamma) \tag{8.4b}$$

(see (4.19) and (4.20)). In particular, a comb polymer containing g 3-functional units can be described by an exponent $\gamma_{\text{comb}}(g) = \gamma + [\gamma(3) - \gamma]$, and hence does not involve any new exponents. The relations (8.3a) and (8.4a) are the same as those of Duplantier [21]. Surface-adsorbed polymer networks have previously been considered in two dimensions only [22]; our equations (8.3b) agrees with the corresponding scaling relation of Duplantier and Saleur [22] in this special case.

In section 6, the scaling relation between the configuration number exponents $\gamma(f)$ for star polymers and the contact exponents θ_i for linear chains was discussed and checked up to $O(\epsilon^2)$ by using des Cloizeaux's result [32] for contact exponents. Moreover, we discussed, in section 3, the end-to-end distribution function $p_g(r)$ of the polymer-network \mathcal{G} . The exact scaling form of $p_g(r)$ was found to be linear-chain-like, that is,

$$p_g(r) = \frac{1}{r^d} \phi_g(rL^{-\nu}), \tag{8.5}$$

where $L = \ell_1 + \ell_2 + \dots + \ell_f$. From (8.5), the mean square end-to-end distance behaves as

$$\langle r^2 \rangle_{\mathcal{G}} \sim L^{2\nu} \quad (8.6)$$

which has the same form as for a linear chain. Different topologies \mathcal{G} of the polymer network show up only in the prefactor in equation (8.6).

Another interesting feature of this paper is that our Hamiltonian (4.6) with composite fields (4.7) has a structure quite similar to that obtained earlier by Lubensky and Issacson [10], who dealt with the problem of lattice animals. Our derivation of (4.7) offers a good basis of discussing such a problem. A somewhat related approach has been presented also by Gonzales [34]. However, in dealing with general branched polymer networks one must keep in mind that our treatment refers to networks with a fixed topology \mathcal{G} (containing a finite number of loops and branch points), in the limit where all polymer chains in the loops or in between the branch points (as well as the dangling chains with the loose ends) have about the same length ℓ , and the scaling limit $\ell \rightarrow \infty$ is considered.

When some of the linear chains forming the network become relatively longer or shorter than the others, there occurs another power-law dependence in the number of configurations. This behaviour was discussed briefly in the last part of section 7.

Next we should mention some future problems. The polymer networks in solvents at the θ temperature are expected to behave in a somewhat different manner [35-37], although that has not been dealt with in this paper. Such an extension will be left for a future study. One further problem is to carry out the ε expansion for $\gamma(f)$ and $\gamma_s(f)$ for star polymers to

higher order. From the present analysis (Sect. 6.3), it becomes obvious that, if we consider the large order behaviour, higher powers of f appear in the result of $\gamma(f)$ and $\gamma_s(f)$. Therefore, in order to discuss star polymers with a large number of arms f , it is necessary to incorporate higher-order terms of the ε expansion. To this end, we have recently considered the most important behaviour for large f in each order of the expansion for $\gamma(f)$, and attempted to make a resummation of all these dominant terms. This work will appear elsewhere together with the calculational details for the present second-order result [31].

Another interesting topic is the density profile of star polymers for which scaling ideas have so far been proposed on the basis of the phenomenological *blob picture* [38]. It would be interesting to check these ideas from a study of distribution functions for internal distances in star polymers based on the present mapping to the magnetic $n \rightarrow 0$ problem, which is then related to a semi-dilute polymer solution just as for linear polymers [2, 3]. From that we can immediately conclude that the screening length $\xi(c)$ for solutions of branched polymers (e.g., stars) at concentration c scales with c in the same way as for solutions of linear polymers. For star polymers this result was anticipated by Daoud and Cotton [38].

Acknowledgments.

One of us (K. O.) thanks the Alexander-von-Humboldt foundation for their support. We are grateful to K. Kremer, H. W. Diehl, E. Eisenriegler, I. Batoulis and H. Müller-Krumbhaar for useful discussions.

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