

Renormalized field theory of polymer solutions. I. Scaling laws

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(Received 27 July 1976)

The large scale spatial correlations in a dilute solution of long chain molecules are dominated by excluded volume effects. We extend the field-theoretic methods of Des Cloizeaux and De Gennes to describe these correlations. We derive general scaling laws which the experimentally measured correlation functions must obey. The dependence on (scattering) wave number, concentration, and chain length is thereby reduced to a function of two variables. This function may moreover be calculated via well-studied approximations, leaving only an excluded volume parameter and a microscopic length parameter. Using the scaling law, we derive several experimentally observed power laws for parameters such as the radius of gyration, including limiting behavior for small overlap (independent chains), large overlap, and large wave vector.

I. INTRODUCTION

The properties of long-chain polymers in solution are often found experimentally to obey simple power laws as functions of chain length and concentration.^{1a} For instance, the radius of gyration R of an isolated chain appears to vary with the number of monomers N according to

$$R = KN^\nu, \quad (1)$$

where $\nu \approx 0.6$ and K is an arbitrary constant. The exponent ν is believed to take the same value independent of the nature of the chain or the solvent. The only requirements are that the chains not overlap, that the temperature be high enough to assure good solvation,^{1b} and that the number of monomers be sufficiently large. Behavior similar to this has also been observed in computer studies of the self-avoiding random walk.²

Usually the explanation of these phenomena follows ideas of Flory.³ Recently, however, DeGennes⁴ and Des Cloizeaux⁵ have proposed a new theory to explain these "excluded volume" effects. Their treatment shows that certain correlations in a solution of chains may be calculated using a classical field theory of the same type used to study phase-transition models like the Ising model. When applied to phase transitions, the field theory explains the origin of critical exponents and other critical phenomena.⁶ Applied to the polymer system, the field theory explains the occurrence of power laws like Eq. (1). In particular, the exponent ν defined above emerges as a critical exponent.

The work of Des Cloizeaux and of Emery⁷ makes it clear that the excluded volume problem is closely related to the random medium problem,⁸ the percolation problem,⁹ and the spin glass problem.^{10a}

In the present paper we extend the work of Des Cloizeaux and DeGennes. Their work shows how the field theory may be used to calculate the correlations between the end points of chains. Our work shows in addition how to calculate the correlations between arbitrary points of the chain(s). This is important because these latter correlations are the only type measurable

in current experiments. Further, there is currently some disagreement^{10b,11} over what form the experimental correlations should take. In the following section we define the correlations to be studied in terms of a suitable model of the polymer system due to Edwards.¹² Then we display the field theory and explain how it is used to calculate polymer correlations. We indicate how the field theory may be renormalized and how scaling laws for the correlations emerge from this renormalized field theory. Finally, we use standard field theoretic results to discuss the behavior of our scaling functions for small and large wave number and concentration. (We use the short-distance expansion of Wilson¹³ and Kadanoff¹⁴ to discuss the large wave number behavior.) The theory contains only two adjustable parameters, and it thus predicts strong interrelations among the results of different experiments.

The behavior observed experimentally¹¹ is consistent with these general predictions as far as the authors are aware. But more importantly, the machinery thus developed allows the exponent ν to be calculated approximately.¹⁵ Indeed, the same approximations may be used to calculate explicitly the correlations which are observed in scattering experiments. The most common approximation is the expansion in $(d-4)$, where d is the dimension of space, as developed by Wilson⁶ and Brezin *et al.*^{16,17} Our calculations using this approximation are in progress.

At present our theory (as well as that of Des Cloizeaux and DeGennes) has a shortcoming that should be noted. We assume that the monomers are in a chemical equilibrium characterized by a monomer chemical potential; this entails a broad (poly-disperse) distribution of chain lengths. By contrast, most experiments are performed on a sharply peaked length distribution. Thus, some of our more detailed predictions may not apply to these experiments.

II. POLYMER CORRELATIONS

In describing the large-scale properties of our polymer solution, we do not expect the chemical details of the chain structure or of the interaction between mono-

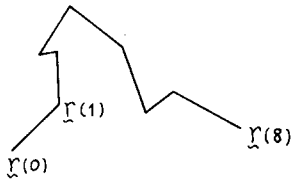


FIG. 1. A typical configuration of one chain with $N=8$.

mers to be important. Accordingly, we shall use a well-accepted model¹⁸ in which microscopic chemical features of the polymers are included in a schematic way. We consider a system of m polymers in solution in a volume Ω . Each chain i consists of N_i links of mean square length $2dl^2$, and its configuration is determined by fixing the endpoints of all links $\{\mathbf{r}_i(0), \mathbf{r}_i(1), \dots, \mathbf{r}_i(N_i)\}$ (Fig. 1). The cohesive energy associated with each chain ("Gaussian chains") is

$$H_0[N, \mathbf{r}(0), \dots, \mathbf{r}(N)] = \frac{1}{4l^2} \sum_{\lambda=1}^N [\mathbf{r}(\lambda) - \mathbf{r}(\lambda-1)]^2. \quad (2)$$

The interaction energy of the system is due to a repulsive,¹⁹ short-range potential $V(x)$ between any two points of chains:

$$H_I = \frac{1}{2} \sum_{i,i'=1}^m \sum_{\lambda=1}^{N_i} \sum_{\lambda'=1}^{N_{i'}} V[\mathbf{r}_i(\lambda) - \mathbf{r}_{i'}(\lambda')]. \quad (3)$$

The total energy H is thus

$$H = \sum_{i=1}^m H_0[N_i, \mathbf{r}_i(0), \dots, \mathbf{r}_i(N_i)] + H_I. \quad (4)$$

The partition function $Z(N_1, \dots, N_m)$ of the chains is defined by

$$Z(N_1, \dots, N_m) = \int_{\Omega} d^d \{[\mathbf{r}_i(\lambda)]\} e^{-H} \\ \equiv \int \prod_{\mu=1}^m (4l^2\pi)^{-N_{\mu}d/2} \prod_{\lambda_{\mu}=0}^{N_{\mu}} d^d \mathbf{r}_{\mu}(\lambda_{\mu}) e^{-H}, \quad (5)$$

where d denotes the dimension of space and the temperature has been set to unity.

In the sequel we shall be concerned with field-theoretic techniques for calculating the correlations in this system. In order to apply these techniques we must transform to the grand canonical ensemble. We allow all numbers m of chains but associate with each chain a weighting factor $l^2 h_0^2/2$. [This peculiar form of the weighting factor is motivated by the field theory. The chemical potential for chains is of course proportional to $-\log(l^2 h_0^2/2)$.] We allow all lengths of chains, but associate with each length N_i a weighting factor $e^{-\xi N_i}$. (It is at this point that we confine ourselves to an ensemble of chains with equilibrium chain-length distribution.) The partition function for the system now becomes

$$Z(\xi, h_0) = \sum_{m=0}^{\infty} \frac{(l^2 \frac{1}{2} h_0^2)^m}{m!} \sum_{N_1, \dots, N_m=1}^{\infty} e^{-\xi(N_1 + \dots + N_m)} Z(N_1, \dots, N_m). \quad (6)$$

As usual, we may recover the expectation value of m by differentiating $W \equiv [\log Z(\xi, h_0)]/\Omega$:

$$\frac{\langle m \rangle}{\Omega} = \frac{\partial W}{\partial \ln(l^2 h_0^2/2)} = \frac{1}{2} h_0 \frac{\partial W}{\partial h_0}. \quad (7)$$

We may find the expectation value of the total length of all the chains by differentiating W with respect to ξ :

$$\frac{1}{\Omega} \left\langle \sum_{i=1}^{\infty} N_i \right\rangle = - \frac{\partial W}{\partial \xi}. \quad (8)$$

The left-hand side of this equation is equal to C_l , the link concentration, while the quantity $\langle m \rangle/\Omega$ above is the concentration of chains C_p .

In order to define correlations, it is helpful to introduce the density functionals $\sigma_i(\mathbf{x})$ and $\rho_i(\mathbf{x})$. Thus, for example, the average density of endpoints of the first chain at location \mathbf{x} can be expressed as

$$\langle \sigma_1(\mathbf{x}) \rangle \equiv \frac{1}{Z} \sum_{m=0}^{\infty} \frac{(l^2 \frac{1}{2} h_0^2)^m}{m!} \sum_{N_1, \dots, N_m=1}^{\infty} e^{-\xi(N_1 + \dots + N_m)} \\ \times \int_{\Omega} d^d \{[\mathbf{r}_i(\lambda)]\} e^{-H} \sigma_1(\mathbf{x}), \quad (9)$$

where

$$\sigma_i(\mathbf{x}) \equiv \begin{cases} \delta[\mathbf{r}_i(0) - \mathbf{x}] + \delta[\mathbf{r}_i(N_i) - \mathbf{x}] & i \leq m \\ 0 & i > m \end{cases}.$$

Evidently, the total density of endpoints ($2C_p$) can be expressed as $\langle \sigma(\mathbf{x}) \rangle$, where

$$\sigma(\mathbf{x}) \equiv \sum_{i=1}^{\infty} \sigma_i(\mathbf{x}). \quad (10)$$

In similar fashion, we may define a functional $\rho_i(\mathbf{x})$, whose expectation value gives the density of any point along the i th chain at location \mathbf{x} :

$$\rho_i(\mathbf{x}) = \begin{cases} \sum_{\lambda=1}^{N_i} \delta[\mathbf{r}_i(\lambda) - \mathbf{x}] & i \leq m \\ 0 & i > m \end{cases}. \quad (11)$$

The total density of links C_l is then $\langle \rho(\mathbf{x}) \rangle$, where $\rho(\mathbf{x}) \equiv \sum \rho_i(\mathbf{x})$.

Now the quantities observed in scattering experiments are related to correlations of the density at different locations. In an experiment where every monomer scatters equally, the amount of scattering at wave vector k is proportional to $I_0(k)$, the Fourier transform of the cumulant $\langle \rho(\mathbf{x})\rho(0) \rangle - \langle \rho(0) \rangle^2$:

$$\delta(k+k') I_0(k) \equiv (2\pi)^{-2d} \int d^d x d^d x' e^{ikx} e^{ik'x'} \\ \times [\langle \rho(x')\rho(x) \rangle - \langle \rho(0) \rangle^2]. \quad (12)$$

Part of the intensity I_0 arises from correlations between different parts of the same chain. Defining i_a as the scattering due to one chain only, we find

$$\delta(k+k') i_a(k) \equiv \frac{1}{C_p} (2\pi)^{-2d} \int d^d x \int d^d x' e^{ikx} e^{ik'x'} \\ \times \left\langle \sum_{i=1}^{\infty} \rho_i(x)\rho_i(x') \right\rangle. \quad (13)$$

This "autocorrelation intensity" i_a can be measured by modifying the chains so that only a limiting small fraction of them cause scattering. In principle one may measure the correlations between the ends of chains by

using chains in which only the ends cause scattering. If all the ends scattered equally, the intensity would be proportional to I_e , defined like I_0 with ρ replaced by σ everywhere. The autocorrelation part of I_e is denoted by i_{ea} and is defined like i_a with ρ replaced by σ . In principle it too is measurable.

We note that the grand canonical ensemble can be readily extended to include solutions of several species of chains. In that case we would have a separate ζ and h_0 parameter for each species.

III. POLYMER FIELD THEORY

Des Cloizeaux⁵ and DeGennes⁴ have shown that the Edwards model for polymers described above is mathematically equivalent to a certain classical field theory. At every point in space a vector $\varphi_\alpha(x)$ is defined, where α labels the n vector components. The energy of a configuration is given by a Lagrangian of the form

$$L[\varphi] = \frac{1}{2} \int d^d x \sum_{\alpha=1}^n \{ \zeta/l^2 [\varphi_\alpha(x)]^2 + |\nabla \varphi_\alpha(x)|^2 \} + \frac{(2\pi)^d l^{-d}}{8} \int d^d x \int d^d x' \sum_{\alpha, \beta=1}^n \varphi_\alpha(x)^2 V(x-x') \times \varphi_\beta(x')^2 - \int d^d x h_0 \varphi_1(x). \quad (14)$$

The partition function $Z_n(\zeta, h_0)$ of the field theory is as usual the weighted sum over all configurations:

$$Z_n(\zeta, h_0) \equiv \int d[\varphi_1(x)] \cdots d[\varphi_n(x)] e^{-L[\varphi]}. \quad (15)$$

The configuration integral is a sum over all functions $\varphi_\alpha(x)$ within the volume Ω .

This field theory for $n=1, 2$, and 3 has been widely used to represent bulk matter near a second-order phase transition.^{6,16} For example, to represent an isotropic ferromagnet, one takes $d=n=3$. Then ζ represents the temperature and h_0 the magnetic field. Des Cloizeaux and DeGennes have shown that in the limit of long chains the polymer model corresponds to an $n \rightarrow 0$ limit of this field theory. Thus $W(\zeta, h_0)$ defined above Eq. (7) is given by

$$\Omega W(\zeta, h_0) \equiv \lim_{n \rightarrow 0} [\ln Z_n(\zeta, h_0)]. \quad (16)$$

The limit requires that we give a meaning to $Z_n(\zeta, h_0)$ even when n is not a natural number. This proves possible if we calculate Z by the usual Wick perturbation expansion (Feynman diagrams) in powers of $V(r)$.²⁰ In

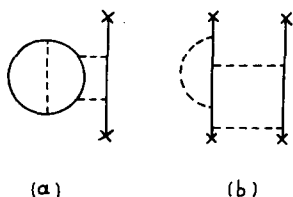


FIG. 2. Diagrams for $W_n(\zeta, h_0)$ (a) a diagram whose value is proportional to n ; (b) a diagram independent of n , which contributes to $W(\zeta, h_0)$ for $n=0$. Solid lines denote free propagators; broken lines denote factors of $-V(r'-r)/8$, where r' and r are the endpoints of the broken lines. Crosses, \times , denote factors of h_0 .

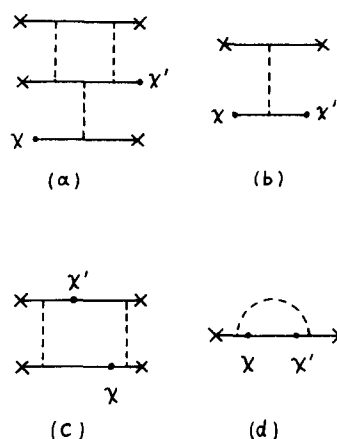


FIG. 3. Typical diagrams for various correlation functions. Diagrams a and b contribute to I_e ; diagram b also contributes to i_{ea} . Diagrams c and d contribute to I_0 ; diagram d also contributes to i_a .

that case each term in the expansion has an explicit polynomial dependence on n , and the meaning of the $n \rightarrow 0$ limit is unambiguous.²¹ The diagrammatic meaning of the $n \rightarrow 0$ limit is indicated in Fig. 2. Here we note that a general diagram contains loops of φ_α propagators, and after summing over the n possible values of α , each loop gives a contribution proportional to n . Thus the limit $n \rightarrow 0$ means precisely that all such loops are absent from the diagrams. The only propagator lines that remain are those which terminate at an h_0 vertex. It is suggestive to regard each diagram as a schematic picture of some of the configurations of the system. Each φ propagator line represents a polymer, and the dotted interaction lines represent the repulsion acting between arbitrary points of the various polymers. A detailed examination⁵ bears out this interpretation.

The two-point correlation of φ is found to be proportional to the intensity function I_e ; indeed,

$$\langle \sigma(x)\sigma(x') \rangle - \langle \sigma(0) \rangle^2 = h_0^2 \lim_{n \rightarrow 0} [\langle \varphi_1(x)\varphi_1(x') \rangle_n - \langle \varphi_1(0) \rangle_n^2], \quad (17)$$

where again the limit $n \rightarrow 0$ is taken after the correlations have been computed from diagrams valid for general n . The diagrammatic representations of the φ - φ correlations are illustrated in Fig. 3. In calculating the autocorrelation function we must guarantee that it is the ends of the same chain that scatter. Des Cloizeaux has shown that this can easily be done by asking for the correlations between field components $\varphi_\alpha(x)$ which do not couple to the field h_0 [$\varphi_2(x)$, for instance]. Properly normalized his result reads

$$\left\langle \sum_{i=1}^{\infty} \sigma_i(x)\sigma_i(x') \right\rangle = h_0^2 \lim_{n \rightarrow 0} \langle \varphi_2(x)\varphi_2(x') \rangle_n. \quad (18)$$

Diagrammatically, one simply sums that subset of $\langle \varphi(x)\varphi(x') \rangle$ diagrams which have the two external endpoints $\varphi(x)$ and $\varphi(x')$ on the same line. On the other hand, in normal field theories with $n=2, 3, \dots$ the φ_2 - φ_2 correlation is the *transverse* correlation.

We may now extend Des Cloizeaux's field theory to treat the experimentally observed intensities I_0 and i_a . To compute I_0 we require the Fourier transform of $\langle \rho(x)\rho(x') \rangle - \langle \rho \rangle^2$. This correlation is the (suitably normalized) sum over all configurations with the constraint that some point of a chain pass through x and some point

pass through x' . To find the field theory analog of such a sum, it is suggestive to include just those Feynman diagrams for which some propagator (polymer) line passes through x and some line passes through x' (Fig. 3). This is just the structure found in diagrams for $\langle \varphi^2(x)\varphi^2(x') \rangle$. The exact statement proves to be

$$\langle \rho(x)\rho(x') \rangle - \langle \rho(0) \rangle^2 = l^{-4} \lim_{n \rightarrow 0} [\langle \frac{1}{2} |\varphi(x)|^2 \frac{1}{2} |\varphi(x')|^2 \rangle_n - \langle \frac{1}{2} |\varphi|^2 \rangle_n^2], \quad (19)$$

where $|\varphi|^2$ denotes $\sum_{\alpha} \varphi_{\alpha}^2$. The autocorrelation part $\langle \sum_i \rho_i(x)\rho_i(x') \rangle$ is given by that subset of diagrams for $\langle \frac{1}{2} |\varphi(x)|^2 \frac{1}{2} |\varphi(x')|^2 \rangle$ in which both φ^2 insertions occur on the same polymer line. We can find a closed-form expression for the autocorrelation by copying the procedure used experimentally. We introduce a second field $\varphi'(x)$ into the Lagrangian to represent a second species of chain, whose concentration is taken to be very small. Then the autocorrelation of our original system can be expressed as $\langle \frac{1}{2} |\varphi'(x)|^2 \frac{1}{2} |\varphi'(x')|^2 \rangle$. We explain this more fully in Appendix A.

Equation (19) may be established rigorously by allowing the chemical potential ζ to depend on position x . We specify how this is done in Appendix A. Then since $\zeta(x)$ is conjugate to $\rho(x)$, we have

$$\langle \rho(x)\rho(0) \rangle - \langle \rho(0) \rangle^2 = \frac{\delta \Omega W}{\delta \zeta(x) \delta \zeta(0)}. \quad (20)$$

However, the same derivative is defined in the field theory:

$$\frac{\delta \Omega W_n}{\delta \zeta(x) \delta \zeta(0)} = l^{-4} [\langle \frac{1}{2} |\varphi(x)|^2 \frac{1}{2} |\varphi(0)|^2 \rangle_n - \langle \frac{1}{2} |\varphi|^2 \rangle_n^2]. \quad (21)$$

Now taking the limit $n \rightarrow 0$, we obtain Eq. (19).²²

In diagrams for W and the correlation functions I , certain basic pieces appear repeatedly; these special pieces are given the name "vertex functions." The vertex functions contain all the essential physics of the renormalization symmetry, and they are more manageable than the W and I functions themselves. A typical vertex function is the "four-point function" or "effective four-point coupling" $\Gamma^{(0,4)}(p_1, p_2, p_3, p_4; \zeta)$. It is defined as the sum of all "irreducible" pieces of Feynman diagrams at chemical potential ζ having four vertices where propagator legs may be attached. Irreducible pieces are those which cannot be separated into disconnected parts by cutting a single propagator line. The wave numbers $p_1 \dots p_4$ are conjugate to the positions of the four vertices. For our discussion we must consider the general $\Gamma^{(L,N')}(q_1 \dots q_L; p_1 \dots p_{N'}, \zeta)$, which has L φ^2 vertices as well as N' places where propagator (polymer) lines may be attached. [The two-point vertex $\Gamma^{(0,2)}(p_1 - p, \zeta)$ contains an added noninteracting term $p^2 + \zeta/l^2$.] Vertex functions are discussed in detail, for example, in Ref. 23.

We may construct $W(\zeta, h_0)$ and the intensity functions I directly from algebraic combinations of the vertex functions. We introduce a parameter $M_0 = \partial W(\zeta, h_0) / \partial h_0$ and we define M_0 -dependent vertex functions as generating functions for our original Γ 's:

$$\Gamma_b^{(L,N')}(\{q_i\}, \{p_j\}, \zeta, M_0) = \sum_{\nu=0}^{\infty} \frac{M_0^{\nu}}{\nu!} \Gamma_b^{(L,N'+\nu)}(q_1 \dots q_L; p_1 \dots p_{N'}, 0, \dots, 0, \zeta). \quad (22)$$

Next we define the autocorrelation part $\Gamma_{ba}^{(L,N')}(\{q_i\}; \{p_j\}, \zeta, M_0)$ as that subset of the diagrams for $\Gamma_b^{(L,N')}(\dots, M_0)$ for which all the $L+N'$ external vertices occur on the same polymer line.

Now the connection of the $\Gamma_b^{(L,N')}$ to physical quantities is as follows. First the function W is the Legendre transform of $\Gamma_b^{(0,0)}$ as derived in Ref. 23:

$$W(\zeta, h_0) + \Gamma_b^{(0,0)}(\zeta, M_0) = M_0 h_0. \quad (23)$$

Using the properties of Legendre transformation we may re-express C_p and C_l in terms of derivatives of $\Gamma^{(0,0)}$. For example, C_p is proportional to $\Gamma^{(0,1)}$ at zero momentum:

$$C_p \left(= \frac{h_0}{2} \frac{\partial W}{\partial h_0} \right) = \frac{M_0}{2} \Gamma_b^{(0,1)}(\zeta, M_0) = \frac{h_0 M_0}{2}. \quad (24)$$

Similarly,

$$C_l = l^{-2} \Gamma_b^{(1,0)}(q=0, \zeta, M_0). \quad (24')$$

The end-point correlations can be shown to be inversely proportional to the two point function:

$$I_e(p) = 2C_p^2 \left[\frac{M_0^2}{2} \Gamma_b^{(0,2)}(p, -p, \zeta, M_0) \right]^{-1}, \quad (24'')$$

$$i_{ea}(p) = 2C_p \left[\frac{M_0^2}{2} \Gamma_{ba}^{(0,2)}(p, -p, \zeta, M_0) \right]^{-1}. \quad (24''')$$

The full density correlations are more complicated:

$$I_0(p) = l^{-4} \left\{ -\Gamma_b^{(2,0)}(p, -p, \zeta, M_0) + \frac{[\Gamma_b^{(1,1)}(p, -p, \zeta, M_0)]^2}{\Gamma_b^{(0,2)}(p, -p, \zeta, M_0)} \right\},$$

$$i_a(p) = \frac{1}{C_p l^4} \left\{ -\Gamma_{ba}^{(2,0)}(p, -p, \zeta, M_0) + \frac{[\Gamma_{ba}^{(1,1)}(p, -p, \zeta, M_0)]^2}{\Gamma_{ba}^{(0,2)}(p, -p, \zeta, M_0)} \right\}. \quad (25)$$

We illustrate the meaning of one of these expressions by the use of skeleton diagrams in Fig. 4.

IV. SCALING LAWS

The renormalization symmetry of the vertex functions arises in the regime where the length scales of interest

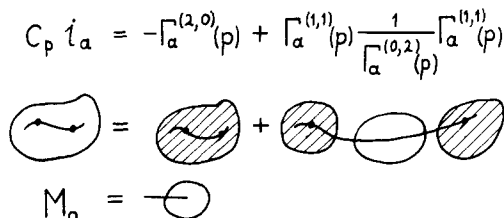


FIG. 4. Skeleton diagrams for $C_p i_a(p)$. Each φ^2 insertion and each external line is at wave number p . Open circles denote all diagrams with the indicated structure (with weighting factor h_0 at the end of each polymer line). Shaded circles denote irreducible diagrams (with weighting factor M_0 at the end of each polymer line). A diagrammatic representation for M_0 ($= \partial W / \partial h_0$) is also shown. One readily verifies that a diagram belonging to the set on the left side must have the form of either the first or the second term on the right side.

are much longer than both the length l of a link and the range of $V(x)$. The physical phenomena of interest are not spoiled by taking $V(x)$ to be zero range:

$$V(x) = \frac{g_0}{3(2\pi)^d} (l\Lambda)^\epsilon l^d \delta^d(x) \quad \epsilon \equiv 4 - d, \quad (26)$$

where the wave number Λ is defined below, and g_0 is a dimensionless coupling constant. This choice creates unphysical singularities due to integrations over large intermediate wave vectors (small distances) in the diagrams, which are regularized by introducing a cutoff wave vector Λ as an upper bound in momentum (wave vector) integrations. There exist methods to subtract the singular parts of the diagrams in such a way that firstly the long-range behavior of interest remains unchanged, and secondly, the limit $\Lambda \rightarrow \infty$ can be taken in the subtracted theory. There exists a continuum of these "renormalization" methods, characterized by an arbitrary parameter μ with dimensions of a wave number. One then finds that the bare vertex functions are proportional to the renormalized ones, through two dimensionless factors z and z_2 , which depend only on g_0 and μ/Λ ²⁴:

$$\begin{aligned} \Gamma_b^{(L, N')} &(q_1 \cdots p_{N'}; \zeta, M_0, g_0, \Lambda) \\ &= (z_2/z)^{-L} z^{-N'/2} \Gamma_R^{(L, N')} (q_1, \cdots, p_{N'}; t, M, g^*, \mu) \\ &\quad \times [1 + (\text{corrections})]. \end{aligned} \quad (27)$$

The Γ_R 's can be calculated by a diagrammatic procedure similar to that for the Γ_b 's, except that one replaces M_0 , ζ , and g_0 by M , t , and g^* . The M and t prove to be linearly related to their bare counterparts:

$$M = M_0 z^{-1/2}, \quad t = (\zeta - \zeta_c) / l^2 (z_2/z)^{-1}. \quad (27')$$

The effective coupling constant g^* is independent of g_0 . It depends only on the structure of the diagrams and the dimension of space. Thus in the n -component field theory,¹⁶

$$g^* = \frac{(2\pi)^d \Gamma(d/2)}{2\pi^{d/2}} \frac{6}{n+8} \epsilon \left[1 + \left(\frac{3(n+14)}{(n+8)^2} - \frac{1}{2} \right) \epsilon + \mathcal{O}(\epsilon^2) \right], \quad (27'')$$

and for the polymer field theory we set $n=0$. The "corrections" in Eq. (27) vanish in the limit t/Λ^2 , μ/Λ , $M/\Lambda^{1-\epsilon/2} \rightarrow 0$, and we shall ignore them for the moment. The "critical chemical potential" ζ_c depends only on g_0 . The renormalization of the autocorrelation parts $\Gamma_b^{(L, N')}$ follows the same law with the same renormalization constants as does the full $\Gamma_b^{(L, N')}$.

Equation (27) implies that a change in μ can be compensated by a change of the scale factors z_2/z and z , since the left side cannot depend on the renormalization parameter μ . We may use the relation between μ and the z 's to make explicit the dependence of the Γ_R on one of its arguments. We can eliminate a second argument from the Γ_R by using dimensional analysis. As a result, we can express $\Gamma_R^{(L, N')}$ in terms of a function $F^{(L, N')}$ having two fewer arguments:

$$\begin{aligned} \Gamma_R^{(L, N')} &(\{q_i\}; \{p_j\}, t, M, \mu) \\ &= \mu^{d - (N'/2)(d-2) - 2L} (g^*)^{N'/2 - 1} w^{N'\beta - \nu d + L} F^{(L, N')}(\{Q_i\}; \{P_j\}; y), \end{aligned} \quad (28)$$

where w and y are dimensionless parameters defined by

$$w \equiv \left[g^* \frac{M^2}{\mu^{2-\epsilon}} \right]^{-1/2\beta}, \quad y \equiv t w / \mu^2, \quad (28')$$

and Q_i and P_j are rescaled wave vectors:

$$Q_i \equiv \frac{q_i}{\mu} w^\nu, \quad P_j \equiv \frac{p_j}{\mu} w^\nu, \quad (28'')$$

The exponents ν and β are critical exponents to be calculated from the renormalization factors. For example,

$$\begin{aligned} \bar{\nu} &\equiv \lim_{\Lambda \rightarrow \infty} \mu \frac{\partial}{\partial \mu} \Big|_{g_0, \Lambda \text{ fixed}} \ln \frac{z_2}{z} (g_0, \mu/\Lambda), \\ \nu &\equiv (\bar{\nu} + 2)^{-1}. \end{aligned} \quad (29)$$

The quantities ν and $\bar{\nu}$ are independent of g_0 , since otherwise the Γ_R 's would depend on g_0 .

The scaling law of Eq. (28) expresses the renormalization symmetry in a concrete way. Only its structure arises from the symmetry; the symmetry says nothing about the "scaling functions" $F^{(L, N')}$ or about the values of the exponents ν and β . To determine these one must study the renormalized field theory in more detail. We merely note here that the same well-studied techniques used to estimate these objects in phase-transition problems can be applied directly to the polymer problem. Indeed, DeGennes⁴ has already estimated $\nu \approx 0.597$ using the technique of expanding in $(4-d)$. Since the exponents and scaling functions are purely properties of the renormalized theory, they are not affected by the chemical details of the polymer system: they are "universal." In the present work we shall limit ourselves to general consequences of the scaling law. We now deduce the scaling laws obeyed by the polymer variables as a consequence of Eq. (28).

We could carry through the transformation to polymer variables directly in the renormalized formalism. We prefer however to transform back to the bare vertex functions in order to eliminate the unphysical parameter μ . For this purpose we have to know the dependence of the renormalization factors on μ/Λ . The method, which essentially consists in integrating relations like Eq. (29), is described in Ref. 25. The result for $z(g_0, \mu/\Lambda)$ derived there reads in our case

$$z(g_0, \mu/\Lambda) \rightarrow A_1(g_0) (\mu/\Lambda)^{2-d+2\beta/\nu} \quad \Lambda \gg \mu, \quad (30)$$

where A_1 is a dimensionless constant of integration which may depend on g_0 . The method can easily be modified to yield

$$\frac{z_2}{z} (g_0, \mu/\Lambda) \rightarrow A_2(g_0) (\mu/\Lambda)^{1/\nu-2} \quad \Lambda \gg \mu. \quad (31)$$

We now are in a position to describe the transformation⁵ from the renormalized variables y , w to the (bare) polymer variables C_i , C_p (or C_i , N). Equation (27) yields

$$\Gamma_b^{(0,0)}(\zeta, M_0) = \Gamma_R^{(0,0)}(t, M). \quad (32)$$

Using this, C_i can be written in terms of the scaling function $F^{(0,0)}(y)$:

$$C_l = \frac{\partial}{\partial \zeta} \Gamma_b^{(0,0)} = \frac{\partial t}{\partial \zeta} \mu^{-2} w \frac{\partial \Gamma_R^{(0,0)}}{\partial y} \\ = S_2^{-1} \mu^d (\mu l)^{-1/\nu} w^{1-\nu d} (g^*)^{-1} \frac{\partial F^{(0,0)}}{\partial y}, \quad (33)$$

where

$$S_2 \equiv A_2 (g_0) (l\Lambda)^{2-1/\nu}. \quad (34)$$

The concentration C_p can also be written in terms of $F^{(0,0)}$:

$$C_p = \frac{M_0}{2} \frac{\partial}{\partial M_0} \Gamma_b^{(0,0)} = \frac{M}{2} \frac{\partial}{\partial M} \Gamma_R^{(0,0)} = \frac{\mu^d}{2g^*} w^{-\nu d} f(y), \quad (35)$$

where

$$f(y) = \frac{1}{\beta} \left(\nu d - y \frac{\partial}{\partial y} \right) F^{(0,0)}(y). \quad (36)$$

We introduce the "overlap" variable s - a combination of C_p and N which depends only on the scaling variable y :

$$s \equiv \frac{1}{2} f(y)^{1-\nu d} \left(2 \frac{\partial F^{(0,0)}}{\partial y} \right)^{\nu d} = l^d g^* C_p (S_2 N)^{\nu d}. \quad (37)$$

By inverting this relation, one may obtain y as a function of the overlap s . The variable w and the momentum variables Q can be expressed by

$$w = NS_2 (l\mu)^{1/\nu} \frac{f(y)}{2(\partial F^{(0,0)}/\partial y)}, \quad (38)$$

$$Q = ql(NS_2)^{\nu} \left(\frac{f(y)}{2(\partial F^{(0,0)}/\partial y)} \right)^{\nu}. \quad (39)$$

None of these equations involves the scale A_1 . We will find below that the absence of A_1 is a general feature of our expressions.

In computing bare quantities the factors μ obviously have to cancel, and Λ occurs only as a factor in S_2 . Thus our theory involves only the excluded volume parameters S_2 and the microscopic length l , as does Flory's theory of excluded volume effects.^{26a} (Further, as in Flory's theory, l should vary only gradually with temperature.)

For readers familiar with the theory of magnetic phase transitions we include a plot showing the relation between the "magnetic" variables (M, t) and the polymer variables (C_l, N) using the mean-field ($d=4$) values $f(y) = y + 1/6$; $\partial F^{(0,0)}/\partial y = 1/2$ (Fig. 5).

We can now write the scaling laws for the scattering functions I . We start by expressing each I function in terms of the bare vertex functions as in Eq. (25). Then we express each of the vertex functions in scaling form, using the scaling law Eq. (28) and the necessary factors to convert from Γ_R 's to Γ_b 's as in Eq. (27). The I functions can then be simplified by combining some prefactors in w, S_2 , etc. Finally, we eliminate w and y in favor of N and the overlap s , using the implicit relations (37) and (38). The result is a scaling formula for each scattering function I in which (for fixed overlap s) all the N dependence has been made explicit. The dependence on q, C_p , and N has been reduced to a scaling function \mathcal{I} with two variables only:

$$I_0(q, C_p, N) = l^{-d} S_2^{-\nu d} (g^*)^{-1} N^{2-\nu d} \mathcal{I}_0(Q, s), \quad (40)$$

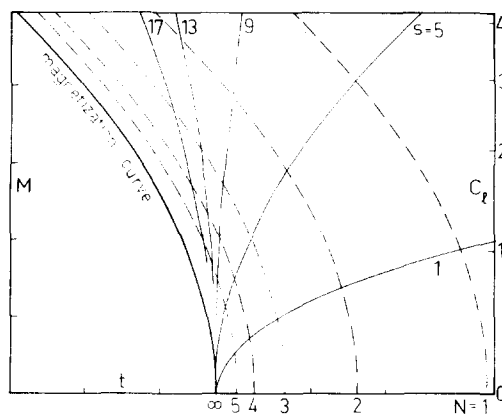


FIG. 5. Polymer variables N, C_l , and s plotted against the magnetic variables M and t , using the mean field approximation.

$$C_p \mathcal{I}_a(q, C_p, N) = l^{-d} S_2^{-\nu d} (g^*)^{-1} N^{2-\nu d} \mathcal{I}_a(Q, s), \quad (41)$$

$$\mathcal{I}_0(Q, s) \equiv \left(\frac{f(y)}{2(\partial F^{(0,0)}/\partial y)} \right)^{2-\nu d} \\ \times \left[\frac{[F_{(a)}^{(1,1)}(Q, -Q, y)]^2}{F_{(a)}^{(0,2)}(Q, -Q, y)} - F_{(a)}^{(2,0)}(Q, -Q, y) \right], \quad (42)$$

where $y(s)$ is defined implicitly by Eq. (37). The end-point scattering functions obey

$$I_e(q, C_p, N) = 4C_p^2 l^d (S_2 N)^{\nu d} g^* \mathcal{I}_e(Q, s), \quad (43)$$

$$I_{ea}(q, C_p, N) = 4C_p l^d (S_2 N)^{\nu d} g^* \mathcal{I}_{ea}(Q, s), \quad (44)$$

$$\mathcal{I}_{e(a)}(Q, s) \equiv \left(\frac{f(y)}{2(\partial F^{(0,0)}/\partial y)} \right)^{\nu d} [F_{(a)}^{(0,2)}(Q, -Q, y)]^{-1}. \quad (45)$$

These scaling laws for the I functions are the central result of this work. Again, the renormalization symmetry is expressed in the structure of Eqs. (40), (41), (43), and (44). The explicit form of the scaling functions \mathcal{I} and the value of the exponent ν are more detailed properties of the renormalized field theory. These are universal and are uniquely (if implicitly) defined by the field theory, independently of details of the system, and they can be computed approximately. Thus, for example, in mean field theory

$$\mathcal{I}_0(Q, s) = \frac{1}{Q^2 + 1/(2s) + \frac{1}{3}}, \quad \mathcal{I}_a(Q, s) = \frac{1}{Q^2 + 1/(2s)}. \quad (45')$$

The details of the system enter only in the scale factors l and S_2 .

We want to add some remarks on the range of validity of these equations. Above, we have stressed that we are concerned with length scales large compared to l and Λ^{-1} . If the average distance between different links is to fulfill this condition we have to restrict ourselves to dilute solutions of very long chains. We therefore expect these results to be correct in the limit $N \gg 1$; $C_l \ll l^{-d}, \Lambda^d$; and $q \ll l^{-1}, \Lambda$ [which corresponds to the critical region $t \approx 0, M \approx 0$ (Fig. 5)].^{26b} Experimentally it is found²⁷ that in good solvents universal power laws hold for $N \gtrsim 100$ monomers and almost all concentrations.

The general laws have not yet been tested experimentally. Rather, experiments concentrate on certain lim-

iting regions. In the next section we evaluate the general laws in some limits of interest. This can be done with the help of further information.

V. SPECIAL LIMITS

A. Single chain limit

To obtain this limit we assume the existence of a virial expansion, i. e., of an expansion for the free energy and expectation values in powers of C_p for finite fixed N . From Eqs. (33), (35), and (22) we find for small M_0^2 and fixed ξ that $C_p \sim C_l \sim M_0^2$. Therefore the existence of the virial expansion is equivalent to the analyticity in M_0^2 of the vertex functions for $t > 0$ (Griffiths analyticity). Obviously for $C_p \rightarrow 0$ the correlation functions tend to their autocorrelation parts and, starting with M_0^2 terms, both I_0 and I_e are proportional to C_p in that limit. We find

$$\lim_{C_p \rightarrow 0} \frac{1}{C_p} I_0(q, C_p, N) = l^{-d} S_2^{-\nu d} (g^*)^{-1} N^{2-\nu d} \times (l^d g^* S_2^{\nu d} N^{\nu d}) \lim_{s \rightarrow 0} \frac{1}{s} g_0(Q, s) \equiv N^2 \hat{g}_0[q l (N S_2)^\nu]. \quad (46)$$

Performing the same steps on I_e , we recover a single-chain limit without a prefactor in N :

$$\lim_{C_p \rightarrow 0} \frac{1}{C_p} I_e(q, C_p, N) = 4 \hat{g}_e[q l (N S_2)^\nu]. \quad (47)$$

Defining the radius of gyration as the negative Laplacian of the logarithm of I_a , $R^2 = -\Delta_q \ln I_a(q, C_p, N)|_{q=0}$, we immediately find

$$R^2(C_p = 0) = l^2 (N S_2)^{2\nu} [-\Delta_q \ln \hat{g}_0(Q)]_{Q=0}, \quad (48)$$

which matches the empirical scaling law mentioned in the introduction. In the next order of the virial expansion, we find scaling laws for the second virial coefficients; for instance, we may obtain the compressibility $I_0(q=0)$:

$$I_0(0, C_p, N) = C_p N^2 [g_0^{(1)} + \frac{1}{2} C_p l^d g^* (S_2 N)^{\nu d} g_0^{(2)} + \mathcal{O}(C_p^2)], \quad (49)$$

where the universal numbers $g_0^{(1)}$, $g_0^{(2)}$ are derivable from $g_0(Q, s)$ [Eq. (42)]. Similarly, the correlation length ξ of the full scattering function I_0 can be written

$$\xi \equiv [-\Delta_q \ln I_0(q, C_p, N)|_{q=0}]^{1/2} = l (N S_2)^\nu [\xi^{(1)} + \frac{1}{2} C_p l^d g^* (S_2 N)^{\nu d} \xi^{(2)} + \mathcal{O}(C_p^2)], \quad (50)$$

where $\xi^{(1)}$, $\xi^{(2)}$ are also obtained from $g_0(Q, s)$, together with the definition of Q [Eq. (39)]. The quantity $\frac{1}{2} N^2 g_0^{(1)}$ represents the second moment $\langle N^2 \rangle$ of the length distribution in our ensemble, as is easily seen from the definition of I_a . Using Eqs. (49) and (50) and similar relations for other quantities, we can define a number of experimentally accessible universal ratios. By way of example we mention one expression²⁸ which can be determined from $I_0(q, C_p, N)$ alone:

$$\xi^{-d} (C_p = 0) \left[\frac{(\partial^2 / \partial C_p^2) I_0}{(\partial I_0 / \partial C_p)} \right]_{q=C_p=0} = (\xi^{(1)})^{-d} \frac{g^* g_0^{(2)}}{g_0^{(1)}}. \quad (51)$$

In the $(4-d) (\equiv \epsilon)$ expansion this has the value $-\epsilon \pi^2/8$

+ $\mathcal{O}(\epsilon^2)$, as can be deduced from Eqs. (27''), (40), and (45a).

B. Limit of large s

We may realize the limit of large s by letting $N \rightarrow \infty$ as C_l remains constant, thereby preserving the condition that $C_l^{-d} \gg l$. This is known as the semidilute regime. A general statement of the behavior of the correlation function for the $n=0$ model has not yet been found. In the limit $N \rightarrow \infty$ we approach the magnetization curve (see Fig. 5) where for $n \geq 2$ new (Goldstone) singularities are found. With convincing argument missing, we make the simplest possible hypothesis. We assume that no new dominant singularity appears at the magnetization curve, and that the leading power of N in the limit $N \rightarrow \infty$, $C_l \neq 0$, fixed, is given by mean field theory, Eq. (45').²⁹ This implies for instance that $I_0(q, C_p, N)$ tends to some finite value

$$I_0(q, C_p, N) \rightarrow C_l S_2^{-1} (C_l S_2 l^d g^*)^{1/(1-\nu d)} g_\infty[q l (C_l S_2 l^d g^*)^{\nu/(1-\nu d)}], \quad (52)$$

where

$$g_\infty[q l (C_l S_2 l^d g^*)^{\nu/(1-\nu d)}] = \lim_{\substack{N \rightarrow \infty \\ C_l \text{ fixed}}} (s)^{(2-\nu d)/(\nu d-1)} g_0(Q, s). \quad (53)$$

Thus

$$I_0(0, C_p, N) \rightarrow C_l S_2^{-1} (C_l S_2 l^d g^*)^{1/(1-\nu d)} g_\infty(0) \quad (53')$$

and

$$\xi \rightarrow l (C_l S_2 l^d g^*)^{\nu/(1-\nu d)} [-\Delta_k \ln g_\infty(k)|_{k=0}]^{1/2}. \quad (54)$$

The power laws for $I_0(0, C_p, N)$ and ξ have first been given by Daoud *et al.*¹⁴ They are supported by experiment. Again we can construct universal ratios like

$$\frac{\xi^{-d} I_0(0, C_p, N)}{C_l^2} \rightarrow g^* g_\infty(0) [-\Delta_k \ln g_\infty(k)|_0]^{-d/2} - \frac{1}{8} \pi^2 \epsilon + \mathcal{O}(\epsilon^2). \quad (55)$$

Results for the other scattering functions can be derived in a corresponding fashion.

C. Behavior for large momentum transfer

For momenta in the range $\xi^{-1} \ll q \ll \Lambda$ the behavior of the scattering functions can be studied by field-theoretic methods. We use Weinberg's theorem³⁰ on the large-momentum behavior of Feynman diagrams to identify those diagrams which contribute to the leading term. We prove in Appendix B. I that the leading diagrams in $I_0(q, C_p, N)$ are of the type of autocorrelation diagrams. We therefore conclude that I_0 and $C_p i_a$ become equal in this limit:

$$I_0(q, C_p, N) = C_p i_a(q, C_p, N) \left[1 + \mathcal{O}\left(\frac{q}{\Lambda}, \frac{1}{q\xi}\right) \right]. \quad (56)$$

The interpretation of this result is obvious. It implies that in a semidilute solution there exists a range of distances large compared to the scale of the microscopic structure, where still the probability of finding two monomers on the same chain dominates that for finding two monomers on different chains.

The asymptotic behavior of $I_0(q, C_p, N)$ can be worked out with the help of the short-distance expansion.³¹ This method assumes that a product of two operators local-

ized at neighboring points in space can be expanded in a sum of local operators. We give an example:

$$\varphi^2(r-x/2)\varphi^2(r+x/2) = c_1(x)\varphi^2(r) + c_2(x)\varphi^4(r) + \dots \quad (57)$$

The coefficients $c_i(x)$ are number-valued functions. In Appendix B.II we use this method to find the asymptotic behavior of $I_0(q, C_p, N)$:

$$I_0(q, C_p, N) \sim a_1 S_2^{-1} C_1(lq)^{-1/\nu} + a_2 \left[\left(\frac{\partial F^{(0,0)}}{\partial y} \right)^{-1} C_1 l^d g^* S_2 \right]^{2\beta/(\nu d-1)} (ql)^{(\nu-2)/\nu}, \quad (58)$$

where a_1 and a_2 are undetermined numerical coefficients, and $\gamma \equiv \nu d - 2\beta$. The exponents of both terms are approximately equal, the next corrections being about a factor of q^{-2} smaller. The coefficients a_1 and a_2 can be calculated from renormalized perturbation theory, where a_2 is found to vanish in lowest order.

The large momentum behavior of the end-point correlation functions is well known.³² We here recall the result, expressed in polymer variables:

$$C_p i_{ea}(q, C_p, N) \sim I_e(q, C_p, N) \sim 4 C_p^2 l^d g^* \left(N S_2 \frac{f(y)}{2(\partial F^{(0,0)}/\partial y)} \right)^{2\beta} a_3 (ql)^{-\gamma/\nu}. \quad (59)$$

VI. CONCLUSION

We have extended the renormalized theory of a polymer solution to include the experimentally measured

scattering functions. The theory predicts the scaling laws of Eqs. (40), (41), (43), and (44), which constrain the dependence of the scattering on q , C_p , and N . The field theory also allows us to infer the behavior of the scaling functions $\mathcal{g}(Q, s)$ for large or small Q and for small overlap s . We have also suggested a plausible behavior for large s . Using these results we obtained the power laws of Eqs. (48)–(50) for the compressibilities and correlation lengths for small overlap. At large overlap these quantities are given by Eqs. (53') and (54). The leading power behavior for all these equations has been verified experimentally.¹¹ The dominant behavior at high q is predicted in Eq. (58). This is also consistent with experiments.²⁷ Reference 10b even hints that the second term in Eq. (58) may be visible. Beyond these leading power laws, the field theory can predict the functional form of the scaling functions \mathcal{g} . Once the \mathcal{g} are calculated, they can be compared with experiment by measuring dimensionless ratios such as Eqs. (51) and (55). Our calculation of the \mathcal{g} functions is in progress.

ACKNOWLEDGMENTS

The authors owe a great debt to E. Brézin and the Service de Physique Théorique at Saclay for hospitality, guidance, and support (of T.W.). L.S. wants to thank the Deutsche Forschungsgemeinschaft for a fellowship. We benefited from discussions with M. Mirkovitch, G. Jannink, M. Daoud, J. Des Cloizeaux, and Royce K. P. Zia.

APPENDIX A: FIELD-THEORETIC REPRESENTATION OF THE SCATTERING FUNCTIONS

We prove that with the definitions [cf. Eqs. (4) and (14)]

$$H = H_0 + H_I + \int d^d x \xi(x) \rho(x), \quad (A1)$$

$$\mathcal{L}[\varphi, \xi] = L[\varphi] + \frac{1}{2l^2} \int d^d x \xi(x) \varphi^2(x),$$

we have

$$Z[H] = \lim_{n \rightarrow 0} \int \prod_{\alpha=1}^n d[\varphi_\alpha(x)] e^{-\mathcal{L}[\varphi, \xi]}. \quad (A2)$$

The basic tool is the following lemma.⁵ We define

$$s(N; q_0, \dots, q_r; j_1, \dots, j_{r-1}) = (4l^2\pi)^{-N(d/2)} \int d^d x_0 \dots d^d x_N \exp\left(-i \sum_{\rho=0}^r q_\rho x_{j_\rho} - \frac{1}{4l^2} \sum_{\eta=1}^N (x_\eta - x_{\eta-1})^2\right), \quad (A3)$$

$$0 = j_0 < j_1 \leq \dots \leq j_{r-1} \leq j_r = N.$$

It is found by Gaussian integration that

$$s(N; q_0, \dots, j_{r-1}) = (2\pi)^d \delta^d\left(\sum_{\rho=0}^r q_\rho\right) \exp\left[-l^2 \sum_{\rho=0}^{r-1} \left(\sum_{\sigma=0}^{\rho} q_\sigma\right)^2 (j_{\rho+1} - j_\rho)\right].$$

We now sketch the proof of Eq. (A2), using the one-chain contribution,

$$A \equiv \frac{\partial Z[H]}{\partial l^2 h_0^2/2} \Big|_{h_0=0}, \quad (A4)$$

as an example:

$$A = l^{-d} \sum_{N=1}^{\infty} e^{-\tau N} \int d^d x_0 \dots d^d x_N \exp\left(-\frac{1}{4l^2} \sum_{\eta=1}^N (x_\eta - x_{\eta-1})^2 - \frac{1}{2} \sum_{j, j'=1}^N V(x_j - x_{j'}) - \sum_{\lambda=1}^N \xi(x_\lambda)\right) (4l^2\pi)^{-N(d/2)}. \quad (A5)$$

We write

$$V(x) = \int d^d q \tilde{V}(q) e^{-iqx}, \quad \zeta(x) = \int d^d q \tilde{\zeta}(x) e^{-iqx}, \tag{A6}$$

and we expand in powers of \tilde{V} and $\tilde{\zeta}$:

$$A = l^{-d} \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} \frac{(-)^{\alpha+\beta}}{\alpha! \beta! 2^\alpha} \int d^d q_1 \cdots d^d q_{2\alpha+\beta} \prod_{\gamma=1}^{\alpha} \tilde{V}(q_\gamma) \delta^d(q_\gamma + q_{\alpha+\gamma}) \prod_{\delta=1}^{\beta} \tilde{\zeta}(q_{2\alpha+\delta}) \hat{g}(\zeta, q_1 \cdots q_{2\alpha+\beta}), \tag{A7}$$

where

$$\hat{g}(\zeta, q_1, \dots, q_{2\alpha+\beta}) \equiv \sum_{N=1}^{\infty} e^{-\zeta N} \sum_{j_1 \cdots j_{2\alpha+\beta}=1}^N \int d^d x_0 \cdots d^d x_N (4l^2\pi)^{-N(d/2)} \exp\left(-\frac{1}{4l^2} \sum_{\rho=1}^N (x_\rho - x_{\rho-1})^2 - i \sum_{\rho=1}^{2\alpha+\beta} q_\rho x_{j_\rho}\right). \tag{A8}$$

Ordering the j 's and applying the lemma with $q_0 = q_r = 0$, we find

$$\hat{g}(\zeta; q_1 \cdots q_{2\alpha+\beta}) = \sum_P \sum_{N=0}^{\infty} \sum_{0 < j_1 \leq \dots \leq j_{2\alpha+\beta} \leq N} (2\pi)^d \delta^d\left(\sum q_\rho\right) \exp\left\{-\sum_{\rho=0}^{2\alpha+\beta} \left[\zeta + l^2 \left(\sum_{\sigma=0}^{\rho} q_{P(\sigma)}\right)^2\right] (j_{\rho+1} - j_\rho)\right\}, \tag{A9}$$

where the first sum ranges over all permutations P of $\{1, 2, \dots, (2\alpha + \beta)\}$. Next we transform the summations into integrals, assuming that both ζ and $l^2 q_\sigma^2$ are small. This yields

$$\hat{g}(\zeta, q_1 \cdots q_{2\alpha+\beta}) = (2\pi)^d \delta^d\left(\sum q_\rho\right) \sum_P \prod_{\rho=0}^{2\alpha+\beta} \left[\zeta + l^2 \left(\sum_{\sigma=0}^{\rho} q_{P(\sigma)}\right)^2\right]^{-1}, \tag{A10}$$

or

$$A = l^{-d} (2\pi)^d \sum_{\alpha, \beta} \frac{(-)^{\alpha+\beta}}{2^\alpha \alpha! \beta!} \sum_{P(2\alpha+\beta)} \int d^d q_0 \cdots d^d q_{2\alpha+\beta} \delta^d\left(\sum_{\rho=0}^{2\alpha+\beta} q_\rho\right) \delta^d(q_0) \prod_{\gamma=1}^{\alpha} \left(\frac{1}{l^4} \tilde{V}(q_{P(\gamma)}) \delta^d(q_{P(\gamma)} + q_{P(\alpha+\gamma)})\right) \times \prod_{\delta=1}^{\beta} \left(\frac{1}{l^2} \tilde{\zeta}(q_{P(2\alpha+\delta)})\right) \prod_{\rho=0}^{2\alpha+\beta} \left[\zeta + l^2 \left(\sum_{\sigma=0}^{\rho} q_\sigma\right)^2\right]^{-1}. \tag{A11}$$

This expression can be represented by the sum of all Feynman diagrams with one polymer line, propagators $[(\zeta)/l^2 + q^2]^{-1}$, four-point vertices of the type $l^{-4} \tilde{V}(q)$, and a two-point vertex $\zeta(q)l^{-2}$. This concludes our sketch of the proof of Eq. (A2).

To include autocorrelations, we introduce a second n -component field φ' into the Lagrangian, with its own h'_0 and $\zeta'(x)$ parameters. The φ' field interacts exactly like the original φ field; thus the Lagrangian $\tilde{\mathcal{L}}$ for the whole system becomes

$$\tilde{\mathcal{L}} = L[\varphi, \zeta, h_0] + L[\varphi', \zeta', h'_0] + (2\pi)^d l^{-4} \int d^d x \int d^d x' |\varphi'(x)|^2 V(x-x') |\varphi(x')|^2. \tag{A12}$$

The autocorrelation $\langle \sum_i \rho_i(x) \rho_i(x') \rangle$ can then be expressed as

$$\lim_{h'_0 \rightarrow 0} \lim_{n \rightarrow 0} \left[\frac{h_0^2}{h_0^2} \frac{\delta \Omega W_n[\tilde{\mathcal{L}}]}{\delta \zeta'(x) \delta \zeta'(x')} \right]. \tag{A13}$$

APPENDIX B: CORRELATION FUNCTIONS FOR LARGE MOMENTUM

I. Proof of Eq. (56)

The proof is based on Weinberg's theorem.³⁰ The asymptotic behavior of a diagram $D(q)$ up to $\log(q)$ factors is given by $D(q) \sim q^{\Sigma(w)}$, where $\Sigma(w) \equiv \sup_{s \in D} w(s)$ and $w(s) \equiv dL(s) - 2l(s)$. Here $L(s)$ and $l(s)$ are the number of loops and the number of internal lines of the subdiagram s . The symbol s represents any connected subdiagram of D which contains all external vertices with nonvanishing momentum (essential subdiagrams).

Let $\mathfrak{D}_a[\mathfrak{D}]$ denote the set of all diagrams contributing to $\Gamma_a^{(2,0)}$ [$\Gamma^{(2,0)}$]: $\mathfrak{D} = \mathfrak{D}_a \cup (\mathfrak{D} - \mathfrak{D}_a)$. An essential subdiagram contains both φ^2 insertions and has E external legs. Using well-known topological relations we find

$$-w(s) = E(s) + (4-d)L(s). \tag{B1}$$

The leading contribution to \mathfrak{D}_a arises from $E=2$. All essential subdiagrams of D in $(\mathfrak{D} - \mathfrak{D}_a)$ have $E=4$. Therefore the large $-q$ contribution from $\mathfrak{D} - \mathfrak{D}_a$ is dominated by that of \mathfrak{D}_a . As usual, the argument holds order for order in the loop expansion. This proves our statement for the irreducible part. The reducible part can be treated in the same way.

II. The large-momentum behavior of $l_0(q, C_\rho, N)$

Treating $\Gamma_R^{(1,1)}(q, -q, t, M)$ first, we apply the operator product expansion in the form

$$\varphi_\alpha(q) |\varphi|^2(-q) = c_1(q, \mu) \varphi_\alpha(0) + c_3(q, \mu) \varphi_\alpha(0) |\varphi(0)|^2. \tag{B2}$$

Substituting this ansatz into $\Gamma_R^{(L, N')}(q, 0, \dots, 0; -q, 0, \dots, 0; t)$ we find

$$\Gamma_R^{(L, N')}(q, 0 \cdots 0; -q, 0 \cdots 0; t) = c_1(q, \mu) \Gamma_R^{(L-1, N')}(0 \cdots 0; t) + c_3(q, \mu) \Gamma_{\varphi^3, R}^{(L-1, N'-1)}(0 \cdots 0; t). \tag{B3}$$

The equations of motion¹⁷ for a φ^4 theory show that $\Gamma_{\varphi^3, R}^{(L-1, N'-1)}(0 \dots 0; t)$ is proportional to $\Gamma_R^{(L-1, N')}(0 \dots 0; t)$, and we therefore find

$$\Gamma^{(L, N')}(q, 0 \dots 0; -q, 0 \dots 0; t) = c(q, \mu) \Gamma^{(L-1, N')}(0 \dots 0; t). \quad (\text{B4})$$

Use of the scaling laws for $M=0$ yields

$$\mu^2 \left(\frac{t}{\mu^2}\right)^{-1} \hat{F}^{(L, N')} \left[\frac{q}{\mu} \left(\frac{t}{\mu^2}\right)^{-\nu} \right] = c(q, \mu) \hat{F}^{(L-1, N')}(0), \quad (\text{B5})$$

or

$$c(q, \mu) = a \mu^{-2} \left(\frac{q}{\mu}\right)^{-1/\nu}. \quad (\text{B6})$$

Equations (B3) and (B4) hold only if primitively divergent vertex functions do not appear on the right-hand side; this excludes $N'=4$, $L \leq 1$ and $N'=2$, $L \leq 2$. To evaluate $\Gamma^{(1,4)}$ and $\Gamma^{(1,2)}$ we increase L by differentiating with respect to t , apply Eqs. (B5) and (B6), and integrate back. The integration constants give rise to additional terms, which have to be analyzed with the help of the scaling laws. We find

$$\Gamma_R^{(1,4)}(q; -q, 0, 0, 0; t) = c(q, \mu) \Gamma_R^{(0,4)}(0 \dots 0; t) + \mu^{2-4} a_1 \left(\frac{q}{\mu}\right)^{(1/\nu)(2\gamma-\nu d-1)}, \quad (\text{B7})$$

$$\Gamma_R^{(1,2)}(q; -q, 0; t) = c(q, \mu) \Gamma_R^{(0,2)}(0, 0; t) + a_2 \left(\frac{q}{\mu}\right)^{(\gamma-1)/\nu} + a_3 \left(\frac{q}{\mu}\right)^{(\gamma-2)/\nu}. \quad (\text{B8})$$

Substituting these results into Eq. (22), we find after some straightforward manipulations

$$F^{(1,1)}(Q, -Q, y) = a_1^{(1,1)} Q^{(\gamma-1)/\nu} + a_2^{(1,1)} f(y) Q^{-1/\nu} + a_3^{(1,1)} Q^{(1/\nu)(2\gamma-\nu d-1)} + a_4^{(1,1)} y Q^{(\gamma-2)/\nu}. \quad (\text{B9})$$

The asymptotic behavior of $\Gamma_R^{(0,2)}$ can be taken from the literature.³² For the discussion of $\Gamma_R^{(2,0)}$ we use the relation

$$\varphi^2(q) \varphi^2(-q) - C_2(q, \mu) \varphi^2(0). \quad (\text{B10})$$

Proceeding in the same way as above, we find

$$F^{(2,0)}(Q, -Q, y) = a_1^{(2,0)} \frac{\partial F^{(0,0)}}{\partial y} Q^{-1/\nu} + a_2^{(2,0)} Q^{(\gamma-2)/\nu} + n a_3^{(2,0)} y Q^{(1/\nu)(\nu d-3)} + n a_4^{(2,0)} Q^{(1/\nu)(\nu d-2)}. \quad (\text{B11})$$

The last two terms vanish in the limit $n \rightarrow 0$. Note that these results can also be derived with the help of the Callan-Symanzik equations for a massive theory.

¹(a) See, for example, H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1970); (b) Thus we do not consider here the observed variations in ν near the collapse temperature θ .

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¹⁸For similar models, see Ref. 11 and K. F. Freed, *Adv. Chem. Phys.* **22**, 1 (1972).

¹⁹The potential may have attractive parts as well, provided they are sufficiently weak. The attraction between links in real polymers is believed to be "sufficiently weak" provided the temperature is above the collapse temperature θ . See P. G. DeGennes, *J. Phys. (Paris) Lett.* **36**, L55 (1975).

²⁰See, for example, C. Bloch, *Stud. Stat. Mech.* **3**, 1 (1965).

²¹The resulting diagrammatic structure is discussed, for example, in Freed, Ref. 18, p. 74.

²²The interchange of this limit with the differentiation is justified to any order in perturbation theory, since any diagram has the form (polynomial in n) times a well-behaved function of ζ .

²³See Ref. 17. See also C. De Dominicis, *J. Math. Phys.* **4**, 225 (1963); C. De Dominicis and P. C. Martin, *J. Math. Phys.* **5**, 14, 31 (1964); G. Jona-Lasinio, *Nuovo Cimento* **34**, 1790 (1964).

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³³The derivation is easily modified for ζ not small.