

Short-distance monomer correlations in a self-repelling polymer chain

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(Received 31 July 1981; accepted 12 November 1981)

We calculate the amplitude of the large-wave vector scattering structure function $S(q)$ of a long random coil in a good solvent, using field theory renormalization and expanding to first order in $\epsilon \equiv 4 - (\text{dimension of space})$. This amplitude is some 35% smaller than that of a swollen Gaussian chain. This is consistent with nonrenormalization group theories and with experiment.

I. INTRODUCTION

Flexible linear polymers in a good solvent may be approximated as self-repelling chains. Such a chain is a critical object, having fluctuations similar to those encountered in phase transition phenomena.¹ In particular, the local density $\rho(r)$ of links (monomers) has power-law correlations over distances r much longer than a link, yet much shorter than the average size of the chain²⁻⁴

$$\langle \rho(r) \rho(0) \rangle \propto r^{1/\nu-3}, \quad (1)$$

where ν is the universal critical exponent relating the chain's radius of gyration R to its length n : $R \propto n^\nu$. These power-law correlations may be observed by light⁵ or neutron³ scattering, where they determine the structure function $S_n(q)$ at large wave vector q

$$S_n(q) = S_n(0) \zeta_\infty [qR/3^{1/2}]^{-1/\nu}. \quad (2)$$

The dimensionless coefficient ζ_∞ is a universal constant, independent of the polymer or solvent studied.⁶ Knowledge of ζ_∞ is important, since it governs the degree of physical or chemical interaction to be expected between nearby monomers. Although ζ_∞ is defined in the dilute solution limit, it also gives information about the semidilute regime, where the chains overlap strongly. In this regime, $S(q)$ for large q is independent of chain concentration—the correlations sufficiently deep within a chain are unaffected by the other chains.⁶ For similar reasons, $S(q)$ for large q is independent of the chain length distribution of the solution.⁷

In this note we calculate the universal coefficient ζ_∞ using a renormalization method^{8,6} like those used to describe phase transitions.⁹ It is similar in spirit to other renormalization treatments used to describe polymers.¹⁰⁻¹³ Our result is some 35% less than the simple "swollen Gaussian" approximation described below. Our result is consistent with the more realistic phenomenological calculations of McIntyre *et al.*⁵ Our calculation of ζ_∞ is based on expanding in $\epsilon \equiv 4$ minus the dimension d of space.

To calculate the coefficient ζ_∞ , we need the behavior of $S_n(q)$ at small and at large q . The behavior of $S_n(q)$

for small q has been calculated recently by Witten and Schäfer¹⁴ to first order in ϵ , using renormalization methods. We summarize their method in Sec. II below, and show how it may be extended to give the large q behavior in Sec. III. In Sec. IV we compare our result with previous calculations and with experiment.

II. RENORMALIZATION FORMALISM

The system is a grand canonical ensemble of single chains with all lengths n , with a monomer chemical potential s controlling the average length. (From this polydisperse ensemble we may readily extract the behavior of the monodisperse ensemble, with definite chain length n .) A chain may be represented as a sequence of points r_i , each at a fixed distance l from its predecessor. A short-ranged repulsive potential $v(r)$ acts between every pair of monomers at distance r in space. We may calculate $S(q)$ in terms of a certain constrained partition function $Y(x, s)$, defined by

$$Y(x, s) \equiv \sum_{\substack{\{r_i\} \\ (0, x)}} \exp(-sn/kT) \exp\left[-\sum_{i < j} v(r_i - r_j)/kT\right], \quad (3)$$

where T is the temperature. The primed sum is a sum over allowed configurations (assumed for convenience to be equally likely) of the chain without the repulsion, but constrained so that some point of the chain passes through the origin and some other point passes through the point x . Apart from a q -independent factor, the structure function $S(q, s)$ of this system is just the spatial Fourier transform of $Y(x, s)$. We denote this transform by $\bar{Y}(q, s)$. The desired asymptotic amplitude ζ_∞ of $S_n(q)$ is a simple multiple of the corresponding amplitude Z_∞ of $S(q, s)$.

Witten and Schäfer's calculation of \bar{Y} is based on a cluster expansion valid for weak repulsion $v(r)$. The cluster diagrams for the expansion represent the polymer chain with the constrained points 0 and x , and show the repulsion v acting between various parts of the chain. The diagrams up to first order in v are shown in Fig. 1. Each diagram represents a certain convolution of "free chain propagators" $G(p, t) \equiv 1/(p^2 + t)$, and $\bar{v}(p)$, the Fourier transform of $v(r)$. The variable t is a constant times s , shifted so that $\langle n \rangle \rightarrow \infty$ as $t \rightarrow 0$. Each segment of the solid line in the diagram corresponds to a G factor and each wavy line to a \bar{v} factor. Thus, the diagram g corresponds to the expression¹⁵

^{a)}Supported by U.S. National Science Foundation under DMR801-2867, Polymer Program.

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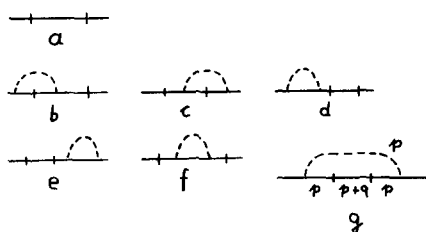


FIG. 1. The single zeroth order and $4!(2^2 1!)$ first-order diagrams for $\bar{Y}(q, t)$. Letters a-g label the diagrams. In diagram g the notations p , $p+q$ give the wave vectors of the corresponding propagator and interaction lines; p is an intermediate wave vector to be integrated.

$$G(0, t) \int d^d p G(p, t) \bar{v}(p) G(p+q, t) G(0, t). \quad (4)$$

The sum of the convolutions represented in Fig. 1 is equal to $\bar{Y}(q, t)$, expanded to first order in the interaction strength (up to an unimportant factor in l). We note the resemblance between these diagrams and those of Fig. III3 of Yamakawa's text.¹⁶ In order to be made useful, the expansion must be "renormalized"; that is, expressed in terms of quantities which will remain finite in the excluded volume limit $n \rightarrow \infty$. The present perturbation expansion may be renormalized by the same methods used for the field theory of critical phenomena. The prescription we use¹⁷ requires that we generalize the integrals to noninteger dimension d ; a standard and natural prescription¹⁸ is available for doing this for the type of integrals which appear in our theory. As mentioned above, the perturbation expansion develops divergences in the excluded volume limit. These same divergences also manifest themselves as divergences in the diagrams as d approaches four. However, the divergent pieces have a sufficiently simple form that they may be absorbed into factors z_i multiplying the pseudotemperature t , the repulsion strength \bar{v} , and \bar{Y} itself. Then the expansion for $\bar{Y}_R \equiv z_1 \bar{Y}$ is finite when expressed in terms of $t_R \equiv z_2 t$ and $\bar{v}_R \equiv z_3 \bar{v}$. This renormalized perturbation expansion has the same form as the original expansion, except that the singular (in $\epsilon \equiv 4 - d$) parts of all the subintegrations have been systematically subtracted away.^{19,20} The resulting expansion is well behaved in the limit $d \rightarrow 4$. Furthermore, the microscopic length l (the length of a link in our model) is absent from the renormalized theory. This amounts to a symmetry of the renormalized theory which puts certain constraints on its behavior. In order for the renormalized theory to be consistent with a physical microscopic theory (with, e.g., a noninfinite repulsion energy for two monomers), the dimensionless renormalized repulsion strength $\bar{v}_R t_R^{\epsilon/2}$ must approach a "fixed-point" value $g^* = -\epsilon/4 + O(\epsilon^2)$. This limit is independent of the repulsion strength v . Thus, v disappears from the renormalized theory in the limit of long chains. Remarkably, the dependence of Y_R on q and t_R becomes independent of the repulsion strength. Since the physical value of the coupling constant g^* is of order ϵ , one may consistently expand \bar{Y}_R or the exponents in ϵ using only a finite number of diagrams. To first order

in ϵ , we obtain¹⁵ [Eq. (14) of Ref. 14]

$$\bar{Y}_R(q, t_R) = t_R^{-3} (1 + \hat{q}^2)^{-1} \left(1 - \epsilon/4 \left\{ -1 - \int_0^1 dx \ln[1 + x(1-x)\hat{q}^2] + \frac{1}{4}(1 + \hat{q}^2) \int_0^1 dx [1 + x(1-x)\hat{q}^2]^{-1} \right\} + O(\epsilon^2) \right), \quad (5)$$

where $\hat{q}^2 \equiv q^2/t_R$, and χ^2 has been set equal to t_R . The integrals may be performed to yield for the coefficient of $-\epsilon/4$

$$1 + B \ln \left[\frac{B+1}{B-1} \right] \left(-1 + \frac{1 + \hat{q}^2}{2B^2} \right), \quad (6)$$

where $B \equiv (1 + 4\hat{q}^2)^{1/2}$.

III. EXTRACTING ASYMPTOTIC BEHAVIOR

To obtain the large- q limit of $S(q)$, we start from this ϵ -expanded formula for $\bar{Y}_R(q, t_R)$. The naive approach here is to use the coefficient of the asymptotic q power of this formula. This approach is unsettling, since $Y(q)$ is ill-behaved for large q ; the ϵ expansion breaks down in this limit because of $\epsilon q^{-2} \ln q$ terms which dominate the $\epsilon^0 q^{-2}$ behavior. To remedy this convergence problem, one may extract from the raw ϵ -expanded quantity something which is known to vary uniformly in ϵ and q . The methods used to obtain large- q information in phase transition problems^{21,22} are not applicable. In these latter problems, the large q behavior may be obtained via scaling from the small- q behavior at the critical point. The analogous argument fails for polymers, because the required limit lies at an "exceptional momentum" (see Ref. 6) point—not given by scaling—of the field theory.

Our method is based on the idea of an effective exponent $D(q)$ describing the q dependence of $S(q, s)$. Effective exponent techniques have been used to calculate the thermodynamic quantities²³⁻²⁵ but, not to our knowledge, for correlation functions.

We define the effective exponent $D(q)$ for $1/S(q, s)$ as

$$D(q) \equiv \frac{\partial \ln[S^{-1}(q, s) - S^{-1}(0, s)]}{\partial \ln(q)}, \quad (7)$$

since $S^{-1}(q, s)$ goes as a constant $+ O(q^2)$ at small q , and as $q^{1/\nu}$ at large q , the effective exponent $D(q)$ should vary smoothly from 2 to $1/\nu$. Since ν can be expanded in powers of ϵ , we anticipate that $D(q)$ is uniformly²⁶ expandable in ϵ , unlike $S(q, s)$. Furthermore, the ϵ expansion for $D(q)$ may be readily obtained from the ϵ expansion for $\bar{Y}_R(q, s)$. One may then reintegrate the definition of D to obtain the asymptotic amplitude Z_∞ of $S(q, s)$. This D could also be used to obtain the entire q dependence of $S(q, s)$; this representation of S automatically has reasonable behavior at small and large q . The same technique could be used to represent $S_n(q)$.

We find that to first order in ϵ $D(q)$ is well behaved as anticipated. To calculate $D(q)$, we note that $S^{-1}(q, s)$ may be simplified using the scaling form^{6,14}

$$S^{-1}(q, s) = S^{-1}(0, s) f(q\xi), \quad (8)$$

where the correlation length $\xi \equiv \langle R \rangle / d^{1/2}$ is defined to

make $f(x) = 1 + x^2 + O(x^4)$. The asymptotic amplitude Z_∞ is defined by

$$S(q, s) \xrightarrow{q \rightarrow \infty} S(0, s) Z_\infty (q\xi)^{-1/\nu}. \quad (9)$$

Thus, Z_∞ can be expressed in terms of $f(x)$

$$f(x) \xrightarrow{x \rightarrow \infty} (Z_\infty)^{-1} x^{1/\nu}. \quad (10)$$

In turn, $f(x)$ can be expressed in terms of $D(q)$

$$\ln[f(x) - 1] - \ln[f(x_0) - 1] = \int_{x_0}^x D(q) \frac{d(q\xi)}{q\xi}. \quad (11)$$

The limiting coefficient may be extracted by subtracting a suitable term from the integrand, then sending x to infinity and x_0 to zero.

$$\ln Z_\infty = - \int_0^\infty \frac{dx}{x} \left[D(x/\xi) - 2 - \frac{(1/\nu - 2)x^2}{(1+x^2)} \right]. \quad (12)$$

The right-hand side is readily expandable in ϵ to give an approximate value for Z_∞ .

To first order in ϵ $1/\nu - 2 = -\epsilon/4$ and $D(q)$ may be expressed as $D(q) = 2[1 + \epsilon/4 D^{(1)}(q)]$, where $D^{(1)}$ is the non-trivial contribution arising from the diagrams. It may be calculated from $Y_R(q, t) = \text{constant } S(q, t)$ terms of $r \equiv (\hat{q})^{-2}$ and $B \equiv (1+4r)^{1/2}$

$$D^{(1)}(q) = -1 - \frac{11}{4} r + \frac{(1+2r+r^2)}{2(1+4r)} + \frac{1}{2B} \ln \left[\frac{B+1}{B-1} \right] \left[1 + 6r + 11r^2 - (1+r)^2 \frac{1+2r}{1+4r} \right]. \quad (13)$$

This function passes smoothly and nearly monotonically from 0 to $-1/2$ as q goes from 0 to infinity, despite the divergences in individual terms. Given this expression, one may readily perform the integration in Eq. (12) numerically. The integrand has a single maximum of about 0.7 at $\hat{q} \approx 1.6$. The result of the integration is $\ln Z_\infty = -0.4268\epsilon$. A naive ϵ expansion²⁷ of

$$Z_\infty = \left(\frac{\partial \ln Y_R}{\partial q^2} \right)^{1/(2\nu)} \lim_{q \rightarrow \infty} \left[\frac{Y_R(q) q^{1/\nu}}{Y_R(0)} \right]$$

confirms this result and makes it precise

$$\ln Z_\infty = -41/96\epsilon = -0.4271\epsilon. \quad (14)$$

These results describe the asymptotic behavior of the constrained partition function $\bar{Y}(q, s)$. We may now transform to obtain the analogous result for $S_n(q)$ for a monodisperse ensemble with chains of length n . We first note that $S_n(q)$ is equal up to a q -independent factor to $Y_n(q)$, the inverse Laplace transform of $\bar{Y}(q, s)$

$$\bar{Y}(q, s) = \sum_n \exp(-sn) Y_n(q). \quad (15)$$

Furthermore, $\bar{Y}(q, s)$ obeys a scaling law⁸ in q and s

$$\bar{Y}(q, s) = t^{-\gamma-2} f_1(q t^\nu), \quad (16)$$

where t is linearly related to s via two unimportant constants c_1 and s_c : $t = c_1(s - s_c)$. The critical exponent γ relates the chain's partition function to its length n .²⁸ Since $\bar{Y}(q, s)$ has the form $a_0 t^{-\gamma-2} q^0 + a_2 t^{-\gamma-2-2\nu} q^2 + O(q^4)$ at small q and $a_\infty t^{-\gamma-1} q^{-1/\nu}$ for large q , it follows that for large n , $Y_n(q)$ has the form

$$\alpha_0(n) q^0 + \alpha_2(n) q^2 + O(q^4)$$

for small q and $\alpha_\infty(n) q^{-1/\nu}$ for large q . These α coefficients are proportional to the a coefficients

$$\alpha_0 = \frac{\exp(ns_c) c_1^{-\gamma-2} n^{\gamma+1}}{\Gamma(\gamma+2)} a_0, \quad (17)$$

$$\alpha_2 = \frac{\exp(ns_c) c_1^{-\gamma-2-2\nu} n^{\gamma+1+2\nu}}{\Gamma(\gamma+2+2\nu)} a_2,$$

$$\alpha_\infty = \frac{\exp(ns_c) c_1^{-\gamma-1} n^\gamma}{\Gamma(\gamma+1)} a_\infty,$$

where Γ denotes Euler's gamma function. The desired ratio ζ_∞ is a combination of α_0 , α_2 , and α_∞

$$\zeta_\infty = \frac{\alpha_\infty}{\alpha_0} \left(\frac{\alpha_2}{\alpha_0} \right)^{1/2\nu}, \quad (18)$$

or in terms of the grand canonical coefficients a_i

$$\zeta_\infty = (\gamma+1) \left[\frac{\Gamma(\gamma+2)}{\Gamma(\gamma+2\nu+2)} \right]^{1/(2\nu)} \frac{a_\infty}{a_0} \left(\frac{a_2}{a_0} \right)^{1/(2\nu)}. \quad (19)$$

The combination of a coefficients is just Z_∞ . Thus, ζ_∞ for a monodisperse ensemble is a known factor times its grand canonical counterpart Z_∞ . Using the accepted²⁹ values for γ , 1.162, and for ν , 0.588, and our $O(\epsilon)$ result for $\ln Z_\infty$ (Eq. 14), we find

$$\zeta_\infty = 0.4348 + O(\epsilon^2). \quad (20)$$

This is roughly a third smaller than the ideal chain value of $2/3$.

IV. DISCUSSION

Our result for ζ_∞ may also be compared with the "swollen Gaussian" (SG) model of Ptitsyn.³⁰ In this model, any pair of links i and $i+k$ is assumed distributed in space as in an ideal chain, but with an average separation varying as k^ν instead of $k^{1/2}$. This simple model already gives the correct asymptotic behavior $S(q) \sim q^{-1/\nu}$, and thus it gives a value for ζ_∞ which can be compared with experiment

$$\zeta_{\infty, \text{SG}} = \left[\frac{2}{(2\nu+1)(2\nu+2)} \right]^{1/2\nu} \frac{\Gamma[1/(2\nu)]}{\nu}, \quad (21)$$

which with the accepted value of ν yields $\zeta_\infty = 0.6589$ —nearly the ideal chain value.

The Ptitsyn model has been refined by McIntyre, Mazur, and Wims⁵ by using more realistic pair distribution functions. They found a value for ζ_∞ some 15% smaller than the swollen Gaussian model. Recent work on the pair distribution function⁴ suggests revised values for the McIntyre–Mazur–Wims parameters. Their exponent α describing the short distance behavior of the pair distribution function is believed to have a value near 2.71 ($2 + \theta_2$ of Ref. 4). Their exponent t describing the long-distance fall-off is expected^{1,31,8} to be $(1-\nu)^{-1}$. Their exponent ϵ is³² our $2\nu - 1$. For the general McIntyre–Mazur–Wims theory, we find

$$\frac{\zeta_\infty}{\zeta_{\infty, \text{SG}}} = \frac{\Gamma[(\alpha - 1/\nu + 1)/t]}{\Gamma[(3 - 1/\nu)/2]} \frac{\Gamma(3/2)}{\Gamma[(\alpha + 1)/t]} \left[\frac{2\Gamma[(\alpha + 3)/t]}{3\Gamma[(\alpha + 1)/t]} \right]^{1/(2\nu)}. \quad (22)$$

Using the values above for α , t , and ν yields a ζ_∞ some 25% smaller than the swollen Gaussian model value $\zeta_{\infty, \text{SG}}$.

Given ζ_∞ , one may predict the asymptotic scattering intensity in a solution with overlapping chains of different lengths. For large wave vector q , each short segment of chain of size of order $1/q$ scatters independently. The intensity is then proportional to the number of such segments.^{6,7} Thus, if the number-averaged chain length is $\langle n \rangle$ and the polymer concentration is C_p

$$S(q) \xrightarrow{q \rightarrow \infty} b_\infty \langle n \rangle C_p q^{-1/\nu}, \quad (23)$$

where the constant b_∞ is independent of n , C_p , and q . On the other hand, in the dilute, monodisperse limit, the scaling law of Eq. (2) holds

$$S_n(q) = n^2 C_p f(qR/d^{1/2}), \quad (24)$$

where $f(x) \rightarrow \zeta_\infty x^{-1/\nu}$ for large x . Comparing these two expressions for $S(q)$, we conclude

$$b_\infty = \zeta_\infty [n(R/d^{1/2})^{-1/\nu}]. \quad (25)$$

The coefficient in [] depends on the type of polymer and solvent, but not on n or C_p .³³ In a system where this coefficient is known, ζ_∞ can be measured even in a semi-dilute, polydisperse solution by measuring b_∞ . Once an accurate value of ζ_∞ has been established, the value of b_∞ will be known for any polymer-solvent with known $nR^{1/\nu}$.

Some experimental information on ζ_∞ is available in published light^{5,2,34,35} and neutron³ scattering data. Two conditions must be met to attain the asymptotic regime of our theory. First, the wave vector q must be large compared to the inverse chain size $qR \gg 1$. Second, segments of the polymer of size $\sim 1/q$ must be large enough to be considered as excluded-volume chains themselves; i. e., the number of links $n(q)$ in such a segment should obey $1/q \sim n(q)^\nu$. Flory theory²¹ and lattice studies³⁶ suggest that the excluded volume behavior is largely attained when the linear swelling factor α_q of the segment is larger than ~ 1.3 . Since the linear swelling factor of a chain or segment goes as its size $1/q$ to the $\sim 1/6$ power, we require a global swelling factor α satisfying $\alpha(qR)^{-1/6} \gtrsim 1.3$. For wave vectors q too large to satisfy this condition, the asymptotic scattering becomes that of ideal segments³⁷ or of individual links.

The experiment of Slagowski³⁸ discussed by Mazur and McIntyre² appears to come closest to satisfying these conditions. By using polystyrene of molecular weight exceeding 40 million in benzene, he attained values of $qR \approx 20$ and $\alpha(qR)^{-1/6} \approx 1.5$. Values of ζ_∞ from these data decrease with improving solvent and attain a value of 0.585 in the best solvent. To obtain this value, we applied a 16% polydispersity correction, which assures that the asymptotic scattering observed in a θ solvent has the Debye value $\zeta_\infty = 2/3$. The measured ζ_∞ lies below the swollen Gaussian prediction in accord with our result and with the refined Ptitsyn theories (Eq. 22). As the experiments come closer to the asymptotic regime, the measured ζ_∞ appears to be approaching the predicted values.

Neutron scattering data³ on the asymptotic $S(q)$ report the $q^{-5/3}$ behavior we expect. However, in these data, the wave vectors q are too large to satisfy our second

condition: segments of size $\sim 1/q \approx 10 \text{ \AA}$ are not much longer than the statistical segment length, and thus may not show the asymptotic excluded volume effects.

V. CONCLUSION

This study shows that the amplitude of the asymptotic structure function for a self-repelling chain can be calculated directly by renormalized field theory method using the ϵ expansion. The $O(\epsilon)$ result presented here shows that the reduced amplitude ζ_∞ should depend strongly on the dimension of space. This first approximation is consistent with experiment and with previous empirical theories. Our work indicates a stronger departure from swollen Gaussian behavior than do these theories. Our method requires no explicit assumptions about the pair distribution function. And our result can be systematically improved by calculating to higher orders in ϵ and applying recent resummation methods.³⁹

I am grateful to Professor L. Schäfer for his indispensable role in the early formulation of this problem. R. Ullman made useful comments on the manuscript. I thank the Center for Polymer Studies at Boston University for hospitality during an early stage of this work.

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