

Concentration dependence of the initial decay rate of the polymer dynamical scattering factor: A renormalization-group study

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(Received 8 July 1985)

The initial decay rate of the dynamical scattering function for semidilute polymer solutions is calculated as a function of solvent quality with the aid of the ϵ -expansion method, which has been semiquantitatively reliable for various properties of polymer systems. In the present calculation, the hydrodynamic screening effect, which presumably is relevant for larger wave numbers, is not taken into account. Comparison of the results given here and experimental results should reveal the significance of the screening effect. Computational tools for semidilute solutions are streamlined and systematized in the appendixes, and the static scattering function is also given as a function of the solvent quality.

I. INTRODUCTION

The initial decay rate of the dynamical scattering factor for dilute polymer solutions has been calculated with the aid of the renormalization-group (RG) theory,¹ giving semiquantitative agreement with experiments. The purpose of this paper is to extend this calculation to the semidilute regime of polymer solutions.

So far many static and dynamical quantities have been calculated using RG theory.² For dilute solutions, results have been provided for not only static quantities,³ but also transport properties.⁴ Even explicitly time-dependent quantities such as correlation functions⁵ and the frequency-dependent intrinsic viscosity⁶ have been obtained recently. For semidilute solutions, RG approaches have supplied theoretical curves for static quantities,⁷ which agree with experiments without any adjustable parameters.

In this paper, the initial decay rate of the dynamical scattering function for the semidilute solution is calculated⁸ without taking account of the so-called hydrodynamic screening effect. Although this effect should not exist for smaller wave numbers k , for larger k the effect is expected to be relevant. The comparison of the present calculation (without incorporating the hydrodynamic screening effect) and corresponding experimental results should reveal how significant the effect is. We might reemphasize that our calculation is interesting and meaningful, whether the screening is important or not. In any case, accurate quantitative experimental results on the initial decay rate are sorely needed.

The paper is organized as follows. Section II introduces our dynamical model for the polymer semidilute solution system. This minimal model describes the chain connectivity, the excluded volume, and hydrodynamic interactions in a simple way. The initial decay rate is completed in Sec. III. Section IV checks the consistency of the variables employed using a renormalization-group argument, and Sec. V is a summary of the results. Those who are only interested in the experimentally observable

results should go to Sec. V directly. Appendixes C and D discuss calculational tools for evaluating density correlation functions.

As we frequently reference two previous works [Lee, Baldwin, and Oono, Ref. 1 (1984)] and [Nakanishi and Ohta, Ref. 3 (1985)], we refer to them as LBO and NO, respectively.

II. DYNAMICS OF SEMIDILUTE SOLUTIONS

To arrive at a formula for the initial decay rate, we proceed in a fashion which is similar to LBO and was first employed by Ackasu.⁹ More details may be found there, but we sketch the entire argument here for a self-contained reading.

We define the initial decay rate as

$$\Omega(\mathbf{k}) = - \frac{d}{dt} \ln S(\mathbf{k}, t) \big|_{t=0}, \quad (2.1)$$

where $S(\mathbf{k}, t)$ is a density correlation function for the polymer solution and is defined by

$$S(\mathbf{k}, t) = \langle \rho(-\mathbf{k}, 0) \rho(\mathbf{k}, t) \rangle, \quad (2.2)$$

where $\rho(\mathbf{k}, t)$ is the Fourier transform of the monomer density at time t [see (3.1)] and $\langle \rangle$ is an equilibrium average over the chain conformation variables. If we formally write

$$\rho(\mathbf{k}, t) = e^{t\mathcal{L}_F} \rho(\mathbf{k}, 0), \quad (2.3)$$

then we can easily evaluate Eq. (2.1) as

$$\Omega(\mathbf{k}) = -L(\mathbf{k})/S(\mathbf{k}) = -L(\mathbf{k})/N_0^2 I(\mathbf{k}), \quad (2.4)$$

where N_0 is the contour length of the chain,

$$L(\mathbf{k}) = \langle \overline{\rho(\mathbf{k})} \mathcal{L}_F \rho(\mathbf{k}) \rangle, \quad (2.5)$$

and

$$I(\mathbf{k}) = \langle \overline{\rho(\mathbf{k})} \rho(\mathbf{k}) \rangle / N_0^2. \quad (2.6)$$

The operator \mathcal{L}_F which we have introduced is precise-

ly the generator of the Markov process.¹⁰ To find \mathcal{L}_F , we let the dynamics of the conformation of the chain be governed by the probability distribution function $P\{\mathbf{c}^\alpha, t\}$ and write the corresponding diffusion equation¹¹

$$\frac{\partial}{\partial t} P\{\mathbf{c}^\alpha(\tau), t\} = \mathcal{L}_F^* P\{\mathbf{c}^\alpha(\tau), t\}. \quad (2.7)$$

Here $\mathbf{c}^\alpha(\tau)$ denotes the position of the τ th monomer of the α th chain.

The operator \mathcal{L}_F can be determined by writing down the differential equations for the system of chain and solvent. We start with Shiwa's¹² Langevin equations for polymer solution, which describe the time evolution of both solvent and chain

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{c}^\alpha(\tau, t) &= \mathbf{u}(\mathbf{c}^\alpha(\tau, t), t) + \frac{1}{\xi_0} \frac{\delta \mathcal{H}}{\delta \mathbf{c}^\alpha(\tau, t)} + \boldsymbol{\Theta}^\alpha(\tau, t), \\ \rho \frac{\partial}{\partial t} \mathbf{u}(\mathbf{r}, t) &= - \sum_{\alpha} \int_0^{N_0} d\tau \frac{\delta \mathcal{H}}{\delta \mathbf{c}^\alpha(\tau, t)} \delta(\mathbf{r} - \mathbf{c}^\alpha(\tau, t)) \\ &\quad + \eta_0 \Delta \mathbf{u}(\mathbf{r}, t) - \nabla p(\mathbf{r}, t) + \mathbf{f}(\mathbf{r}, t), \end{aligned} \quad (2.8)$$

$$\nabla \cdot \mathbf{u} = 0,$$

where $\mathbf{u}(\mathbf{r}, t)$ is the solvent velocity field, ρ is the solvent density, p is the pressure, ξ_0 is the bare friction coefficient of the chain unit, η_0 is the viscosity of the solvent, $k_B T$ is the absolute temperature in energy units, and $\boldsymbol{\Theta}, \mathbf{f}$ are independent Gaussian white noises with mean zero and

$$\langle \boldsymbol{\Theta}_\alpha(\tau, t) \boldsymbol{\Theta}_\beta(\tau', t') \rangle = 2\xi_0^{-1} \delta(t - t') \delta(\tau - \tau') \vec{\mathbf{I}}_{\alpha\beta}, \quad (2.9)$$

$$\langle \mathbf{f}(\mathbf{r}, t) \mathbf{f}(\mathbf{r}', t') \rangle = -2\eta_0 \Delta \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') \vec{\mathbf{I}}, \quad (2.10)$$

$\vec{\mathbf{I}}$ being the $d \times d$ unit tensor. These noises satisfy the fluctuation-dissipation theorem. We have chosen the energy unit so that $k_B T = 1$. Also, in (2.8) $\delta \mathcal{H} / \delta \mathbf{c}^\alpha(\tau, t)$ is a force term derived from the Edwards Hamiltonian¹³

$$\begin{aligned} \mathcal{H} &= \frac{1}{2} \int_0^{N_0} d\tau \dot{\mathbf{c}}^2(\tau) \\ &\quad + \frac{u}{2} \sum_{\alpha=1}^n \sum_{\beta=1}^n \int_0^{N_0^\alpha} d\tau \int_{|\tau-\sigma|>a}^{N_0^\beta} d\sigma \delta(\mathbf{c}^\alpha(\tau) - \mathbf{c}^\beta(\sigma)). \end{aligned} \quad (2.11)$$

We can derive from this a Fokker-Planck-type full-diffusion equation¹¹

$$\frac{\partial}{\partial t} P(\mathbf{u}, \mathbf{c}^\alpha, t) = \mathcal{L} P(\mathbf{u}, \mathbf{c}^\alpha, t), \quad (2.12)$$

where

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_{\text{int}}, \quad (2.13)$$

with

$$\begin{aligned} \mathcal{L}_0 &= \sum_{\alpha} \int d\tau \frac{\delta}{\delta \mathbf{c}^\alpha(\tau)} \frac{1}{\xi_0} \left[\frac{\delta}{\delta \mathbf{c}^\alpha(\tau)} + \frac{\delta \mathcal{H}}{\delta \mathbf{c}^\alpha(\tau)} \right] \\ &\quad + \int \mathbf{k} \frac{\delta}{\delta \mathbf{u}_{\mathbf{k}}} (\vec{\mathbf{I}} k^2 - \mathbf{k} \mathbf{k}) \left[\frac{\delta}{\delta \mathbf{u}_{-\mathbf{k}}} + \mathbf{u}_{\mathbf{k}} \right], \end{aligned} \quad (2.14)$$

$$\begin{aligned} \mathcal{L}_{\text{int}} &= \sum_{\alpha} \left[-\rho_0 \int_{\mathbf{k}} \int d\tau \frac{\delta}{\delta \mathbf{c}^\alpha(\tau)} \mathbf{u}_{\mathbf{k}} \exp[-i\mathbf{k} \cdot \mathbf{c}^\alpha(\tau)] \right. \\ &\quad \left. + \rho_0 \int_{\mathbf{k}} \int d\tau \frac{\delta}{\delta \mathbf{u}_{\mathbf{k}}} \frac{\delta \mathcal{H}}{\delta \mathbf{c}^\alpha(\tau)} e^{i\mathbf{k} \cdot \mathbf{c}^\alpha(\tau)} \right], \end{aligned} \quad (2.15)$$

$$\int_{\mathbf{k}} = \int \frac{d^d k}{(2\pi)^d}.$$

The problem is to integrate out the solvent velocity field variables and thus transform (2.12) to (2.7). This procedure may be carried out to order ϵ and is explained in Appendix A of LBO. The same method was applied by Onuki and Kawasaki to the binary critical fluid.¹⁴ The result is

$$\begin{aligned} \mathcal{L}_F &= \sum_{\alpha=1}^n \sum_{\beta=1}^n \int_0^{N_0} d\tau' \int_0^{N_0} d\sigma' e^{\mathcal{H}} \frac{\delta}{\delta \mathbf{c}_\beta(\sigma')} \\ &\quad \times e^{-\mathcal{H}} \vec{\mathbf{D}}^{\beta\alpha}(\tau', \sigma') \frac{\delta}{\delta \mathbf{c}_\alpha(\tau')}, \end{aligned} \quad (2.16)$$

$$\begin{aligned} \frac{1}{k_B T} \vec{\mathbf{D}}^{\beta\alpha}(\tau', \sigma') &= \delta(\tau' - \sigma') \delta_{\alpha\beta} \frac{1}{\xi_0} \mathbf{1} \\ &\quad + \frac{1}{\eta_0} \vec{\mathbf{T}}(\mathbf{c}^\beta(\tau') - \mathbf{c}^\alpha(\sigma')), \end{aligned} \quad (2.17)$$

where

$$\vec{\mathbf{T}}(\mathbf{r}) = \int_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{r}} \left[\vec{\mathbf{I}} - \frac{\mathbf{k} \mathbf{k}}{k^2} \right] \frac{1}{k^2}. \quad (2.18)$$

The derivation of Eq. (2.16) makes use of one important approximation. We assume that the relaxation time of the solvent field is much smaller than that of the conformation, so that the solvent instantaneously follows the chain. This physical consideration enters in two places in the derivation. If we denote p a projection operation which integrates out the solvent velocity field variables and denote q by $q = 1 - p$, then we claim $(\partial/\partial t)_q \times P(\{\mathbf{u}\}, \{\mathbf{c}^\alpha\}, t) = 0$. [Essentially that $P(\{\mathbf{u}\}, \{\mathbf{c}^\alpha\}, t) = P(\{\mathbf{u}\}, \{\mathbf{c}^\alpha(t)\})$.] The same reasoning implies

$$\int_0^\infty dt e^{t(\mathcal{L}_c + \mathcal{L}_u)} \cong \int_0^\infty dt e^{t\mathcal{L}_u}$$

where \mathcal{L}_c governs $\{\mathbf{c}\}$ and \mathcal{L}_u governs $\{\mathbf{u}\}$ in the case where we do not consider the interactions between the two fields.

Equivalent to this projection-operator method, we could have merely written $\partial \mathbf{u} / \partial t = 0$ in (2.8), solved for $\mathbf{u}(\mathbf{r})$, and finally solved for \mathcal{L}_F directly from the resulting equation for $\mathbf{u}(\mathbf{r})$ in (2.8). Thus our procedure is precisely the Kirkwood approximation, although the projection-operator argument is more formal and shows more explicitly the physical assumptions being made and their regimes of validity [for example, (2.16) is correct only to order ϵ]. Fortunately the Kirkwood approximation has already been shown to give semiquantitative results for transport properties in OBO (Ref. 4). There it was argued that the Kirkwood approximation was correct for long wavelengths although not necessarily for shorter ones in

the semidilute regime. This approximation, however, may not be reliable for shorter wavelengths due to the possible effects of hydrodynamic screening.

III. CALCULATION OF INITIAL DECAY RATE

A. Equation for $L(k)$

We may now return to the calculation of (2.4). We may write the polymer density in the continuum scheme as

$$\rho(k) = \sum_{\alpha=1}^n \int_0^{N_0} d\tau e^{i\mathbf{k} \cdot \mathbf{c}_\alpha(\tau)}. \quad (3.1)$$

Then (2.4) becomes

$$L(k) = ck_B T \left[\frac{N_0 k^2}{\xi_0} + \frac{1}{\eta_0 c} \int^q \frac{k^2 q^2 - (\mathbf{k} \cdot \mathbf{q})^2}{q^4} S_0(\mathbf{k} + \mathbf{q}) \right] \quad (3.2)$$

to $O(\epsilon)$. Here S_0 is the $\epsilon=0$ result for the scattering function²

$$S_0(1) = \frac{1}{V} \langle \overline{\rho(-1)} \rho(1) \rangle_0 = 2cN_0^2 \frac{g_0(1)}{1 + 2X_0 g_0(1)}, \quad (3.3)$$

where $g_0(1)$ is the Debye scattering function and $X_0 = cuN^2$, u is the excluded-volume parameter defined in Eq. (2.11).

Power counting shows quickly that the integral in (3.2) is divergent. However we can implement a cutoff renormalization, $q_{\max} = 1/\sqrt{a}$. Reparametrizing the integral by $q = \sqrt{2/N} Q$ and letting

$$\mathbf{k} = \sqrt{2/N} \mathbf{K}, \quad 1/\sqrt{a} = \sqrt{2/N} \Lambda, \quad (3.4)$$

we find

$$L(\mathbf{k}) = \frac{cN_0 k^2}{\xi_0} k_B T \left[1 + 4 \frac{\xi_0}{\eta_0} I_1(k) \right], \quad (3.5)$$

where

$$I_1(\mathbf{k}) = \frac{1}{2K^2} \int_Q^\Lambda \frac{Q^2 K^2 - (\mathbf{K} \cdot \mathbf{Q})^2}{Q^4} \frac{J_2((\mathbf{K} + \mathbf{Q})^2)}{1 + X_0 J_2((\mathbf{K} + \mathbf{Q})^2)}, \quad (3.6)$$

$$J_2(x) = \frac{2}{x^2} (e^{-x} - 1 + x).$$

The exact value of the integral is given in Appendix B. A very good approximate form is

$$I_1(k) = \frac{3}{64\pi^2} \left[\ln \left[\frac{\Lambda^2}{K^2} \right] - \ln F^2 + \frac{1}{3F^2 - 1} \right], \quad (3.7)$$

where

$$F^2 = \frac{K^2 + 2(1 + X)}{K^2} \quad (> 1). \quad (3.8)$$

We can exponentiate the divergent term to get for $L(k)$ (write $K^2 = \theta_0$ for clarity)

$$L(k) = \frac{ck_B T}{\xi_0} N_0 k^2 \left[\frac{\Lambda^2}{\theta_0} \right]^{(3/16)\eta^2(\xi_0/\eta_0)} \times \exp \left[\frac{3}{16\pi^2} \frac{\xi_0}{\eta_0} \left[\frac{1}{3F^2 - 1} - \ln F^2 \right] \right]. \quad (3.9)$$

We know from LBO that $L(k)/N_0^2$ is observable, and needs no renormalization factor. We use the renormalization scheme discussed there¹⁵ and find

$$\frac{\eta_0}{\xi_0} = \frac{1}{\xi_0} L^{-\epsilon/2} \quad \text{and} \quad (3.10)$$

$$\frac{1}{N_0 \xi_0} = \frac{1}{N \xi} Z_N Z_\xi = \frac{1}{N \xi} \left[1 - \frac{3}{16\pi^2} \ln \frac{L}{a} \right].$$

Here L is the phenomenological length scale which appears later in the RG equation (see Sec. IV). We use the definition of variables described in Ref. 16 to find

$$\begin{aligned} \frac{\eta_0 L_B(k)}{cN_0^2 k^d (k_B T)} &= \frac{1}{\xi^*} \left[\frac{\xi^*}{\xi} \right]_{\epsilon=0} (2\pi)^{-(3\epsilon/8)(\xi/\xi^*) + \epsilon/2} \\ &\times (2\theta)^{-1 + \epsilon/2 - (3\epsilon/8)(\xi/\xi^*)} \\ &\times \exp \left[\frac{3\xi}{16\pi^2} \left[\frac{1}{3F^2 - 1} - \ln F^2 \right] \right], \end{aligned} \quad (3.11)$$

where we have written

$$\begin{aligned} \theta &= \theta_0 = \left[\frac{2\pi N}{L} \right]^{(\epsilon/8)(u/u^*)}, \\ X &= X_0 = \left[\frac{2\pi N}{L} \right]^{-(\epsilon/4)(u/u^*)}. \end{aligned} \quad (3.12)$$

B. Scattering function

From NO it is easy to find the form of $I(k)$ away from the fixed points

$$\begin{aligned} I(k) &= \frac{S(k)}{cN^2} \\ &= \frac{J_2(\theta)}{1 + XJ_2(\theta)} \exp \left[\epsilon \frac{u}{u^*} \frac{2N(\sqrt{\theta}, X)}{[1 + XJ_2(\theta)]J_2(\theta)} \right]. \end{aligned} \quad (3.13)$$

Here

$$N(Q, X) = \frac{1}{2\pi} \int_0^\infty P^3 dP \int_0^\pi d\theta \sin^2 \varphi \left[\left[\frac{-\hat{F}^{(4)}(Q, P)}{1 + XJ_2(P^2)} - Q^2 J_2'(Q^2) \frac{2 \cos^2 \varphi}{P^4 + 1} \right] + 9X \left[\frac{[F^{(3)}(Q, P)]^2}{[1 + XJ_2(P^2)][1 + XJ_2((P + Q)^2)]} - \frac{J_2^2(Q^2)/9}{P^4 + 1} \right] \right]. \quad (3.14)$$

The functions $\hat{F}^{(4)}$ and $F^{(3)}$ are given in Appendix C.

C. Initial decay rate

Dividing (3.11) by (3.13) gives us a formula for the initial decay rate

$$\frac{\eta_0 \Omega(k)}{k_B T k^d} = \left[\frac{1 + XJ_2(\theta)}{J_2(\theta)} \right] \exp \left[-2\epsilon \frac{u}{u^*} \frac{N(\sqrt{\theta}, X)}{J_2(\theta)[1 + XJ_2(\theta)]} \right] \frac{1}{\xi^*} \left[\frac{\xi^*}{\xi} \right]_{\epsilon=0} \times (2\pi)^{\epsilon/2 - (3\epsilon/8)(\xi/\xi^*)} (2\theta)^{-1 + \epsilon/2 - (3\epsilon/8)(\xi/\xi^*)} \exp \left[\frac{3\epsilon}{8} \frac{\xi}{\xi^*} \left[\frac{1}{3F^2 - 1} - \ln F^2 + \Delta \right] \right]. \quad (3.15)$$

In the calculation presented Δ is zero. However, a slightly more difficult dimensional regularization approach gives

$$\Delta = 2.802 = 2 \left[\ln(2\pi) - \frac{1}{S_2} \frac{\partial S_d}{\partial d} \right]_{d=3} - \frac{\partial}{\partial d} \left[\ln \int_0^{\pi/2} d\theta \cos^d \theta \right]_{d=4}, \quad (3.16)$$

where S_{d-1} is the area of a d -dimensional unit ball. In our graphs we include this constant as agreement with experiment is more accurate (see Appendix A).

It is not very easy to garner the concentration dependence from Eq. (3.15). If we proceed in our calculation slightly differently by writing from Eq. (3.6)

$$I_1(k, X) = I_1(k, 0) + \Delta I(k, X), \quad (3.17)$$

we easily find

$$\frac{\Omega(k, X)}{\Omega(k, 0)} = [1 + XJ_2(\theta)] \exp \left[-2\epsilon \frac{u}{u^*} \left[\frac{N(k, X)}{J_2(\theta)[1 + XJ_2(\theta)]} - \frac{N(k, 0)}{J_2(\theta)} \right] \right] \times \left[1 + \frac{2X}{2 + \theta} \right]^{-(3\epsilon/8)(\xi/\xi^*)} \exp \left[-\frac{3\epsilon}{8} \frac{\xi}{\xi^*} \frac{3\theta X}{2} \frac{1}{(3 + \theta)[\theta + 3(1 + X)]} \right]. \quad (3.18)$$

If we recall that $J_2(\theta) \rightarrow 2/\theta$ and that $N(k, X) \rightarrow N(k, 0)$ for large k we see that the asymptotic value is unchanged by the concentration dependence. This is verified in the graphs, and is consistent with the concept that at large frequencies or over small distances we should be unaware of the total concentration dependence.

We also find

$$\frac{\Omega(k, X)}{k^2 D_0(X)} = \frac{1 + XJ_2(\theta)}{(1 + X)J_2(\theta)} \left[\frac{2(1 + X)}{\theta + 2(1 + X)} \right]^{(3\epsilon/8)(\xi/\xi^*)} \exp \left[\frac{3\epsilon}{8} \frac{\xi}{\xi^*} \frac{1}{3F^2 - 1} \right] \times \exp \left[-\epsilon \frac{u}{u^*} \left[\frac{2N(k, X)}{J_2(\theta)[1 + XJ_2(\theta)]} - \frac{2N(0, X)}{1 + X} \right] \right]. \quad (3.19)$$

Equation (3.18) also gives a relation for the instantaneous diffusion coefficients

$$D_0 = \lim_{k \rightarrow 0} \frac{\Omega}{k^2}. \quad (3.20)$$

From (3.18) then we derive

$$\frac{D_0(X)}{D_0(X=0)} = \lim_{k \rightarrow 0} \frac{\Omega(k, X)}{\Omega(k, 0)} = (1 + X)^{1 - (3\epsilon/8)(\xi/\xi^*)} \exp \left[-2\epsilon \frac{u}{u^*} \frac{N(0, X)}{1 + X} \right]. \quad (3.21)$$

This is essentially the result of OBO, the discrepancy being of order ϵ^2 .

IV. RENORMALIZATION-GROUP EQUATION FOR $\Omega(k, c)$

We have worked with hindsight in Sec. III, where we chose to rewrite the equations in terms of variables which made the formulas convenient and which also canceled unwanted cutoff-dependent terms arising in the scattering function $S(k)$. In this section we write down a renormalization-group equation for Ω and use dimensional analysis to justify that the variables we have employed are exactly the scaling variables.

We proceed as in Ref. 16. The function

$$\frac{\eta_0 \Omega}{k_B T k^d} = H(L, N, u, \xi, c, \mathbf{k}) \quad (4.1)$$

satisfies the RG equation

$$\left[L \frac{\partial}{\partial L} + \beta_u \frac{\partial}{\partial u} + \beta_\xi \frac{\partial}{\partial \xi} + \gamma_N \frac{\partial}{\partial N} \right] H = 0. \quad (4.2)$$

Equation (4.2) means that our function H is independent of the phenomenological length scale L . Our β functions are as usual¹⁶

$$\begin{aligned} \beta_u(u) &= L \frac{\partial u}{\partial L} \Big|_{\text{bare}} = \frac{u\epsilon}{2} [(u^* - u)/u^*], \\ \beta_\xi(\xi, u) &= L \frac{\partial \xi}{\partial L} \Big|_{\text{bare}} \\ &= \frac{\xi\epsilon}{2} \left[\frac{3}{4}(\xi^* - \xi)/\xi^* + \frac{1}{4}(u^* - u)/u^* \right], \end{aligned} \quad (4.3)$$

$$\gamma_N(u) = L \frac{\partial \log Z_N}{\partial L} \Big|_{\text{bare}} = \frac{\epsilon}{8} \frac{u}{u^*},$$

where $u^* = \pi^2 \epsilon / 2$ and $\xi^* = 2\pi^2 \epsilon$. The derivatives in Eq. (4.3) are taken when the quantities u , ξ , and Z_N are written in terms of the bare (unrenormalized) parameters u_0 and ξ_0 , which in turn are dependent on the length scale L . Using the same scaling variables as in Ref. 16 we find

$$H = G(Lw^{-2/\epsilon}, N(1+w)^{-1/4}, (1+w)^{3/4}(1-\hat{z})/\hat{z}, c, \mathbf{k}). \quad (4.4)$$

Referring to LBO, the following dimensional analysis shows that if

$$[\tau] = C, \quad (4.5)$$

then

$$\begin{aligned} [N] &= [L] = [p] = C, \quad [S/cN^2] = 1, \quad [c] = C^{-d/2}, \quad [X] = C^{\epsilon/2}, \\ [\mathbf{k}] &= C^{-1/2}, \quad [L/cN^2] = [\mathcal{L}_F] = C^{-d/2}, \quad [\Omega/k^d] = 1. \end{aligned} \quad (4.6)$$

Thus $H \propto \Omega/k^d$ is unchanged by a reparametrization of the model. So

$$H = H^{(0)}(CLw^{-2/\epsilon}, CN(1+w)^{-1/4}, (1+w)^{3/4}(1-\hat{z})/\hat{z}, cC^{-d/2}, \mathbf{k}C^{-1/2}). \quad (4.7)$$

If we choose

$$CN(1+w)^{-1/4} = 1, \quad (4.8)$$

a little bit of algebra (see Ref. 16) shows we can write

$$\frac{\eta_0 \Omega}{k_B T k^d} = H^{(1)}(\xi, \delta, X_0(2\pi N/L)^{-(\epsilon/4)(u/u^*)}, \theta_0(2\pi N/L)^{(\epsilon/8)(u/u^*)}). \quad (4.9)$$

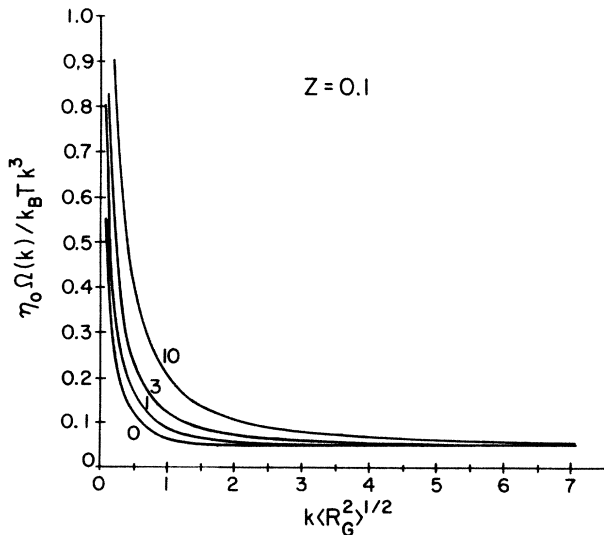


FIG. 1. Plots of $\eta_0 \Omega(k, X, Z)/k_B T k^3$ vs kR_G for various values of X in the Gaussian limit ($Z = 0.1$ small corresponding to poor solvents).

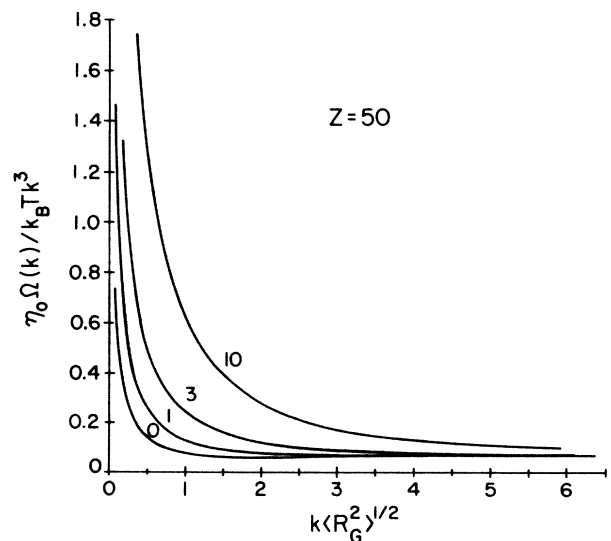


FIG. 2. Curves similar to Fig. 1 except here the Z parameter is large, corresponding to the self-avoiding limit. This good solvent limit shows much more pronounced concentration dependence.

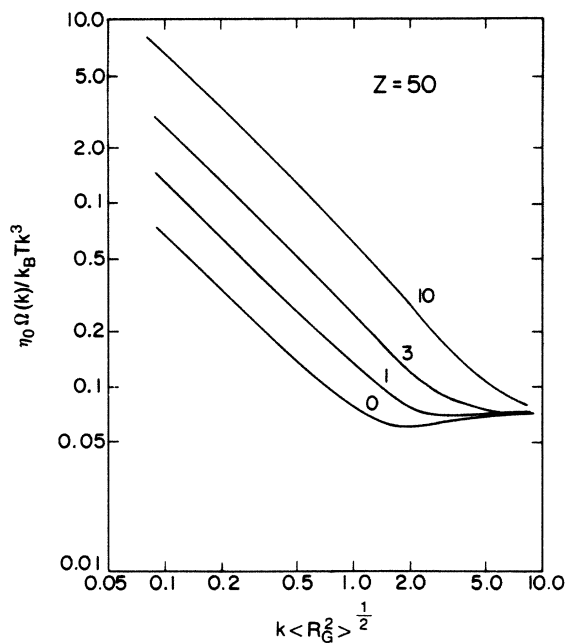


FIG. 3. Same as Fig. 2 with log-log axes.

Comparing then (4.9) and (3.12) we have shown that we have exactly chosen the variables required by the scaling hypothesis.

V. COMPARISON WITH EXPERIMENTS AND SUMMARY

From Eqs. (3.15) and (3.19) we can make graphs of $\eta_0 \Omega / k_B T k^3$ and $\Omega / k^2 D_0$ as a function of θ . However, θ

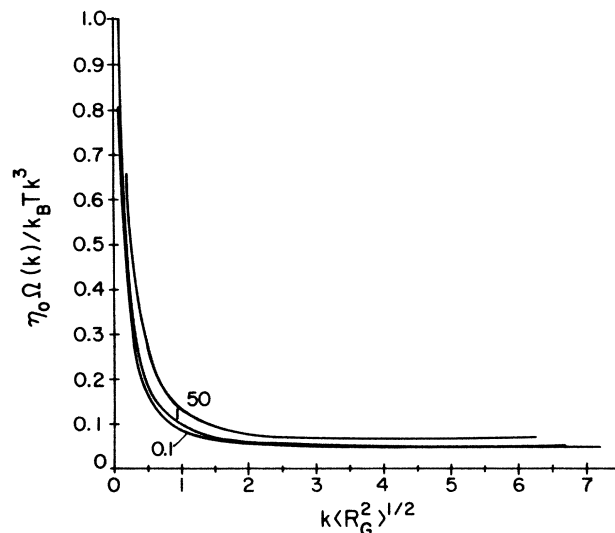


FIG. 4. This graph shows the solvent effects on $\eta_0 \Omega(k, X, Z) / k_B T k^3$ vs $k R_G$. The monotonicity of Ω in Z is made clear. Here $X=1$.

is closely related to $k R_G$ which has already been calculated in the semidilute regime.^{3(b)} The formula relating $k R_G$ and θ is

$$k^2 R_G^2 = \theta \exp \left[\frac{\epsilon}{4} \left(\frac{u}{u^*} \right) \right] \int_0^\infty dy \left[y^5 V(y) \frac{1}{1 + X J_2(y^2)} - \frac{y^3}{y^4 + 1} \right] \left| \frac{4}{3} e^{-\epsilon/4} \right. \quad (5.1)$$

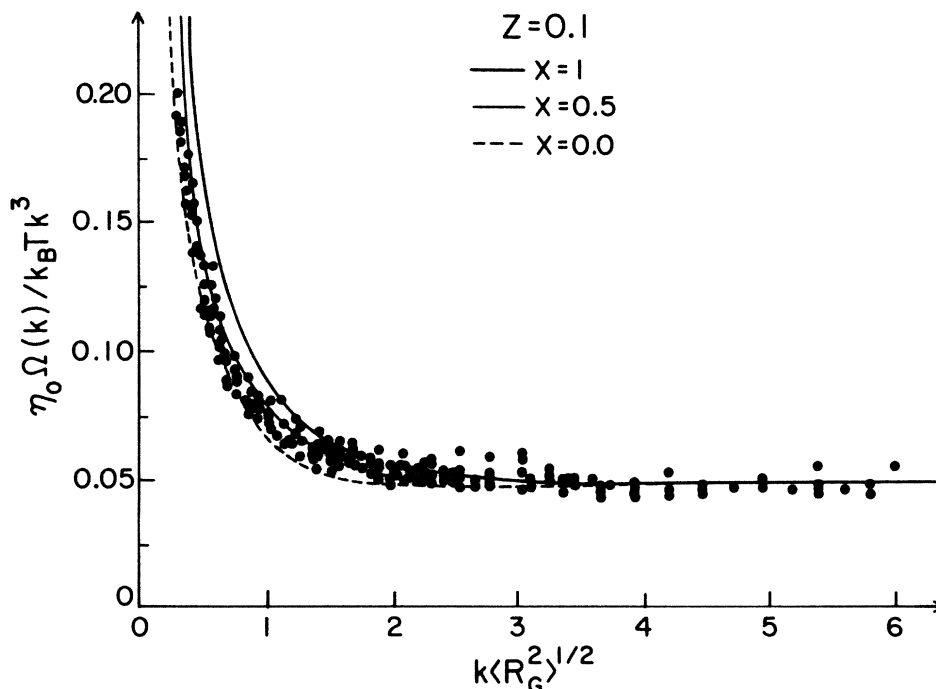


FIG. 5. Plots of $\eta_0 \Omega(k) / k_B T k^3$ vs $k R_G$ in the poor solvent limit (small Z) for small values of X . An X value of $X=0.5$ gives nearly perfect agreement with the experimental results taken from Han and Ackasu (Ref. 17).

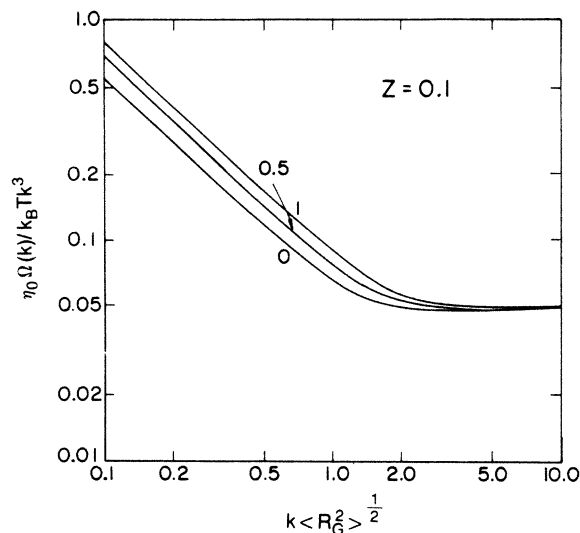


FIG. 6. Same as Fig. 5 with log-log axes.

where

$$V(y) = -\frac{1}{24}J_6(y^2) + \frac{1}{5}J_5(y^2) - \frac{1}{4}J_4(y^2) + \frac{1}{8}J_2(y^2). \quad (5.2)$$

Equation (3.15) is plotted against kR_G from Eq. (5.1) in Figs. 1–8, and Eq. (3.19) against Eq. (5.1) in Figs. 9–11. We may also plot (3.19) against $I(k, X) = S(k, X)/cN^2$ as shown in Fig. 12. This is a truly universal curve—note that kR_G depends on the specific polymer.

The graphs are labeled by two parameters X and Z . The parameter Z is related to the variables already discussed by the relations (see Ref. 16)

$$(u/u^*)_{\epsilon=0} = Z/(1+Z), \quad (5.3)$$

$$(\xi/\xi^*)_{\epsilon=0} = (u/u^*)_{\epsilon=0}/[1 - (1+Z)^{-3/4}].$$

The following features of the graphs are readily noted.

(i) $\Omega(k, X, Z)$ is a monotone increasing function in both X and Z .

(ii) $\Omega(k, X, Z)/k^d$ approaches $\Omega(k, 0, Z)/k^d$ asymptotically in the $k \rightarrow \infty$ limit. That is, the X dependence of Ω becomes irrelevant in the large- k limit. Recall the discussion following Eq. (3.18).

(iii) In the large- k limit, the ratio between the slopes of $\Omega(k)/k^2 D_0$ at X and $X=0$ is just $D(X=0)/D(X)$, which can be found from Eq. (3.22).

Agreement with available experimental evidence is very good. We must add, however, that the Z dependence demonstrated in the graphs should not be taken very seriously, since there is no reliable semidilute solution theory which can describe the crossover from the high-temperature regime to the theta regime.

Again we emphasize that our model does not incorporate the hydrodynamic screening effects, nor the effect of entanglements between polymer chains. Although this latter effect may be negligible for not too large values of concentration, we cannot reasonably put any constraints on the effect of hydrodynamic screening. We know that the long-wavelength regime and the low-concentration regime are adequately described by our model, but we must await further experimental results to ascertain the reliability of our model for moderate values of concentration in the short-wavelength regime. This in turn will reflect the importance of the hydrodynamic screening effect.

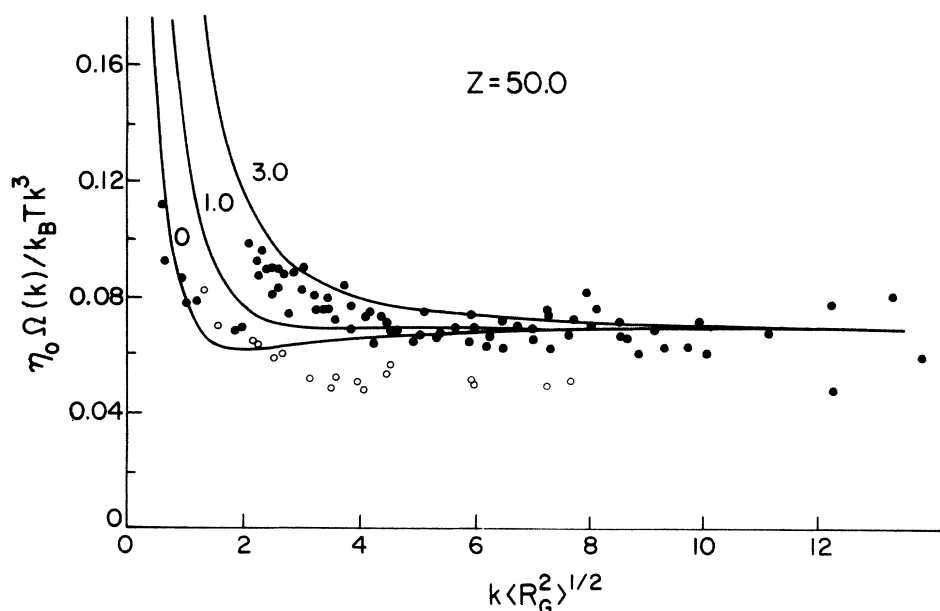


FIG. 7. Plots of $\eta_0\Omega(k)/k_B T k^3$ vs kR_G in the self-avoiding limit for a few values of X . Experimental points are ●, Han and Ackasu (Ref. 17); ○, Kurata *et al.* (Ref. 18).

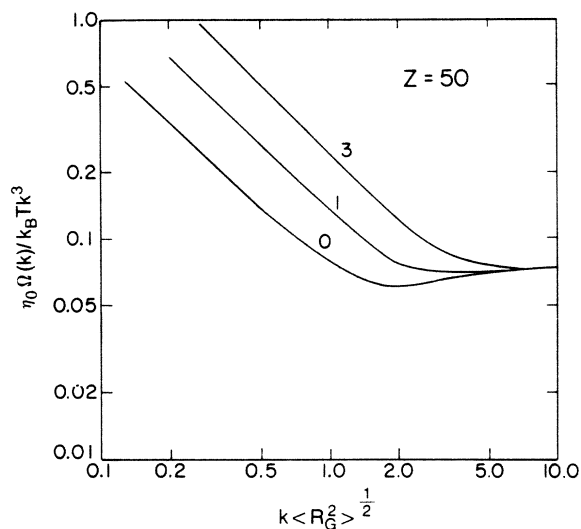
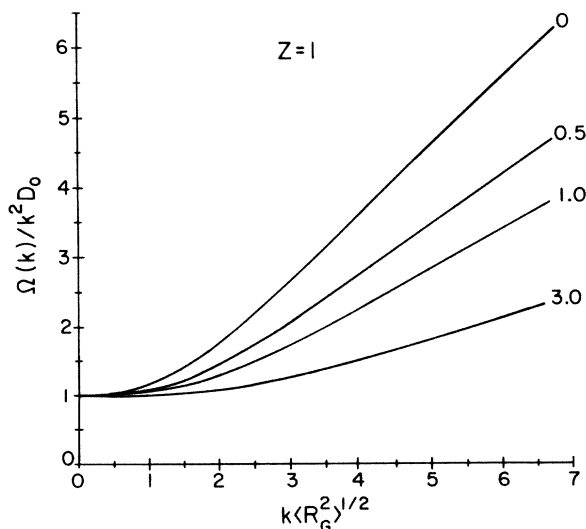
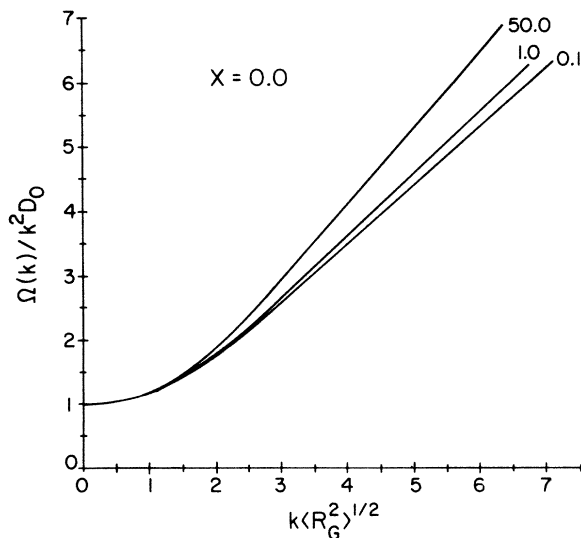


FIG. 8. Same as Fig. 7 with log-log axes.

ACKNOWLEDGMENTS

The author is deeply indebted by Y. Oono for his advice and general contributions to this problem. The author would also like to thank T. Ohta and A. Nakanishi, whose works provide the basis and much of the formulation of Appendix C, as well as Andre Lee, for early collaboration on the problem and for helping with the figures. This work is, in part, supported by the National Science Foundation under Materials Research Laboratories Program (MRL) Grant Nos. DMR-83-16981 and DMR-84-05355 (polymers program).

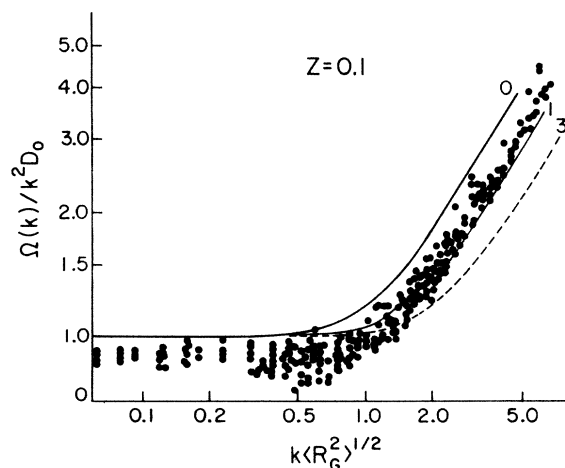
FIG. 9. Plots of $\Omega(k)/k^2 D_0$ for various values of X . We have chosen an intermediate solvent quality variable $Z = 1$.FIG. 10. Solvent quality effects are demonstrated in the curve of $\Omega(k)/k^2 D_0$ in the dilute limit.APPENDIX A: A TECHNICAL COMMENT
ON THE SOLUTION TO UNNORMALIZED
FUNCTIONS IN ϵ EXPANSION CALCULATIONS

Consider the function

$$F(x) = x \exp \left[-\epsilon \int_0^x \left(\frac{1-e^{-t}}{t} \right) dt \right]. \quad (\text{A1})$$

We know that $\lim_{x \rightarrow \infty} F(x) = F_\infty$ is finite at $\epsilon = 1$. Suppose now we write $x = yK^\epsilon$. Then to $O(\epsilon)$,

$$\lim_{x \rightarrow \infty} F(x) = \lim_{y \rightarrow \infty} yK^\epsilon \exp \left[-\epsilon \int_0^y \left(\frac{1-e^{-t}}{t} \right) dt \right]. \quad (\text{A2})$$

FIG. 11. Comparison of theoretical plots for $\Omega(k)/k^2 D_0$ vs kR_G for several values of X with experimental results from Han and Ackasu (Ref. 17). The curve for $X = 0$ (the dilute limit) is in good agreement with experimental data when the latter is normalized properly.

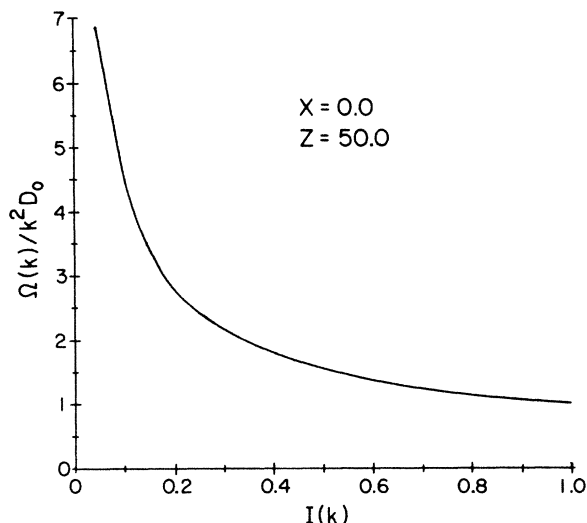


FIG. 12. Plot of $\Omega(k)/k^2 D_0$ vs $I(k)$, the normalized scattering function, in the good solvent and dilute limit. This is a truly universal curve and does not depend on any innate property of the polymer.

Unfortunately, this type of situation occurs in our renormalization-group calculations. Typically K might be a constant such as 2π which is absorbed into a redefinition of one of the variables. This suggests that generally only results that have been somehow normalized will give quantitative agreement with reality. However, the renormalization-group calculation will, more importantly, preserve the functional form. For this reason we justify our steps taken in Sec. III C. We must add, however, that this seemingly arbitrary analytical procedure will never affect properly normalized functions such as $\Omega(k)/k^2 D_0$.

APPENDIX B: EXACT VALUE OF INTEGRAL IN (3.7)

We can evaluate the integral in Eq. (3.6) by replacing J_2 by \tilde{J}_2 , since there are no large cancellations as we have explained in Appendix D. Using this approximation we find

$$I_1(k) = \frac{3}{64\pi^2} \left[\ln \left[\frac{\Lambda^2}{K^2} \right] - \ln F^2 + \left(\frac{1}{3} F^2 \right) S \left[\frac{1}{F^2} \right] \right], \quad (\text{B1})$$

where

$$S(x) = \frac{6}{x^3} \left[\frac{3x^2}{4} - \frac{x}{2} - \frac{(1-x)^2}{2} \ln(1-x) \right]. \quad (\text{B2})$$

Now $F^2 \in [1, \infty)$ so $1/F^2 \in [0, 1]$. In this regime we can closely approximate $S(x)$ by $3/(3-x)$. Equation (3.7) then follows.

APPENDIX C: CALCULATION OF DENSITY CORRELATION FUNCTIONS FOR POLYMER SOLUTIONS

In this appendix we present techniques for calculating semidilute solution static correlation functions. In the course of the discussion we explicate the loop expansion, which involves a diagrammatic technique where there exist vertex functions to all orders. Our formulation follows in a general way that given in Ref. 3(c).

The semidilute Edwards Hamiltonian [Eq. (2.11)] may be written

$$\mathcal{H}\{\mathbf{c}\} = \frac{1}{2} \sum_{i=1}^n \int_0^N d\tau \left[\frac{d\mathbf{c}_i}{d\tau} \right]^2 + \frac{1}{2} \int_q P_q P_{-q}, \quad (\text{C1})$$

where

$$P_q = u^{1/2} \int_0^N d\tau \sum_{i=1}^n e^{iq \cdot \mathbf{c}_i(\tau)} = \left[\frac{X}{c} \right]^{1/2} \int_0^1 d\tau \sum_{i=1}^n \exp[i\mathbf{Q} \cdot \mathbf{C}_i(Nt)\sqrt{2/N}], \quad (\text{C2})$$

and

$$\int_q = \int \frac{d^d q}{(2\pi)^d}. \quad (\text{C3})$$

(As in the main text, a capitalized momentum vector is related to an uncapitalized momentum vector by the relation $\mathbf{q} = \sqrt{2/N} \mathbf{Q}$.) The partition function is given by

$$Z = \int \mathcal{D}\{\mathbf{c}\} e^{-\mathcal{H}\{\mathbf{c}\}}. \quad (\text{C4})$$

We would like to introduce a transform variable to decouple the chains. This is done by writing

$$\begin{aligned} & \exp \left[-\frac{1}{2} \int_q P_q P_{-q} \right] \\ & \propto \left[\int \mathcal{D}\{\psi\} \exp \left[-\frac{1}{2} \int_q (\psi_{-q} - iP_q)(\psi_q - iP_{-q}) \right] \right] \\ & \quad \times \exp \left[-\frac{1}{2} \int_q P_q P_{-q} \right]. \end{aligned} \quad (\text{C5})$$

This transforms Eq. (4) to

$$Z = \int \mathcal{D}\{\psi\} \exp \left[-\frac{1}{2} \int_q \psi_q \psi_{-q} \right] \int \mathcal{D}\{\mathbf{c}\} e^{-\mathcal{H}_0\{\mathbf{c}\}} \exp \left[i \int_q \psi_q P_{-q} \right] \quad (\text{C6})$$

$$= V^n \int \mathcal{D}\{\psi\} \exp \left[-\frac{1}{2} \int_q \psi_q \psi_{-q} \right] [G(\psi)]^n. \quad (\text{C7})$$

If we write

$$\psi_q = \varphi_q + \psi_0 \delta_{q,0} \quad (\text{C8})$$

$$= \varphi_q + \psi_0 \frac{(2\pi)^d \delta^d(q)}{V}, \quad (\text{C9})$$

(where $\varphi_0=0$), we can integrate out the ψ_0 field to find

$$Z = V^n e^{-(1/2)VcX} Z_1, \quad (\text{C10})$$

where

$$Z_1 = \int \mathcal{D}\varphi \exp \left[-\frac{1}{2} \int^q \varphi_q \varphi_q \right] [G(\varphi)]^n, \quad (\text{C11})$$

$$G(\varphi) = \frac{1}{V} \int \mathcal{D}\{\mathbf{c}\} \exp \left[-\frac{1}{2} \int_0^{N_0} d\tau \left[\frac{d\mathbf{c}_i}{d\tau} \right]^2 + i \int_q \varphi_q P_{-q}^{n=1} \right] \quad (\text{C12})$$

$$= \left\langle \exp \left[i \left[\frac{X}{c} \right]^{1/2} \int_q \int_0^1 d\tau \exp[i\mathbf{Q} \cdot \mathbf{c}(Nt) \sqrt{2/N}] \varphi_q \right] \right\rangle. \quad (\text{C13})$$

Here the average $\langle \rangle_0$ is performed with respect to the $u=0$ Edwards Hamiltonian, \mathcal{H}_0 , where we consider the system to be large enough so that we may ignore boundary conditions. To evaluate (C13), we expand the exponential, perform the average $\langle \rangle_0$ and then carry out the t integration. We start by writing

$$G(\varphi) = \sum_{m=0}^{\infty} \frac{1}{m!} (i)^m \left[\frac{X}{c} \right]^{m/2} \prod_{j=1}^m \int_{q_j} \varphi_{q_j} \int_0^1 dt_j \left\langle \exp \left[i \sum_j \mathbf{Q}_j \cdot \mathbf{c}(Nt) \sqrt{2/N_0} \right] \right\rangle \quad (\text{C14})$$

$$= \sum_{m=0}^{\infty} \frac{1}{m!} (i)^m \left[\frac{X}{c} \right]^{m/2} \prod_{j=1}^m \int_{q_j} \varphi_{q_j} \int_0^1 dt_j \exp \left[- \sum_{i,j} \mathbf{Q}_i \cdot \mathbf{Q}_j \chi_{ij} \right], \quad (\text{C15})$$

with

$$\chi_{ij} = -\frac{1}{2N} \langle [c^a(Nt_i) - c^a(Nt_j)]^2 \rangle_0 \quad (\text{C16})$$

$$= -\frac{1}{2} |t_i - t_j|. \quad (\text{C17})$$

We may pick a particular ordering for the magnitude of the t 's as long as we shuffle the indices of Q_i 's. Thus

$$G(\varphi) = \sum_{m=0}^{\infty} \frac{(i)^m}{m!} \left[\frac{X}{c} \right]^{m/2} \int_{q_1, \dots, q_m} \varphi_{q_1} \cdots \varphi_{q_m} \int_{t_1 > \dots > t_m}^1 dt_1 \cdots dt_m \sum_{p_m(\sigma)} \exp \left[\frac{1}{2} \sum_{i,j} |t_i - t_j| \mathbf{Q}_{\sigma_i} \cdot \mathbf{Q}_{\sigma_j} \right], \quad (\text{C18})$$

where $\sum_{p_m(\sigma_i)}$ is the sum over the possible permutations of the first m integers. The sum of the q_i 's (respectively Q_i 's) is required to be zero due to the translational symmetry. We may enter this condition by inserting the function $[(2\pi)^d/V] \delta(\sum q_i)$. This implies

$$\frac{1}{2} \sum_{i,j} |t_i - t_j| \mathbf{Q}_{\sigma_i} \cdot \mathbf{Q}_{\sigma_j} = - \sum_{s=1}^m \Delta_s \left[\sum_{a=1}^s \mathbf{Q}_{\sigma_a} \right]^2, \quad (\text{C19})$$

where

$$\Delta_s = t_s - t_{s+1} > 0 \quad (1 \leq s \leq m-1), \quad (\text{C20})$$

$$\Delta_m = t_m.$$

In Eq. (18) we also note that due to the symmetry in the φ_q 's, we may actually pick an ordering for $p_m\{\sigma_i\}$ and gain a factor of $m!$ (In practice, desymmetrizing the vertex makes calculations easier.) We find

$$\int_{t_1 > \dots > t_m}^1 dt_1 \cdots dt_m \exp \left[- \sum_{s=1}^m \Delta_s P_s^2 \right] = \int^{\Delta_1 + \dots + \Delta_m \leq 1} d\Delta_1 \cdots d\Delta_m \exp \left[- \sum_{s=1}^m \Delta_s P_s^2 \right] \quad (\text{C21})$$

$$= (-1)^{m+1} \sum_{i=1}^m \frac{J_1(P_i^2)}{\prod_{j \neq i} (P_i^2 - P_j^2)}, \quad (\text{C22})$$

where

$$J_m(x) = \sum_{n=0}^{\infty} (-x)^n \frac{m!}{(n+m)!} \quad (C23)$$

$$= \left[\frac{(-x)^n}{n!} \right]^{-1} \left[e^{-x} - 1 + x - \cdots - (-1)^{n-1} \frac{x^{n-1}}{(n-1)!} \right]. \quad (C24)$$

Using Eqs. (C18)–(C24), we find

$$G(\varphi) = 1 + \sum_{m=2}^{\infty} i^m \left[\frac{X}{c} \right]^{m/2} \left[\frac{1}{V} \right] \int_{q_1, \dots, q_{m-1}} \varphi_{q_1} \varphi_{q_2-q_1} \cdots \varphi_{-q_{m-1}} H^{(m)}(Q_1, \dots, Q_{m-1}), \quad (C25)$$

where

$$H^{(m)}(P_1, \dots, P_{m-1}) = \frac{1}{2} (-1)^m \sum_{i=1}^{m-1} \frac{J_2(P_i^2)}{\prod_{j=1}^{m-1} (P_i^2 - P_j^2)} \quad (C26)$$

is the integral evaluated in (C23) with $P_m = 0$.

We return to the calculation of Z_1 . Using Eqs. (C11), (C12), (C25), and (C26) we can write

$$Z_1 = \int \mathcal{D}\{\varphi\} \exp \left[-\frac{1}{2} \int_q \varphi_q \varphi_{-q} [1 + X J_2(Q^2)] \right] \times \left[\exp \left[c \sum_{m=3}^{\infty} (i)^m \left[\frac{X}{c} \right]^{m/2} \int_{q_1}^{q_{m-1}} \varphi_{q_1} \varphi_{q_2-q_1} \cdots \varphi_{-q_{m-1}} F^{(m)}(Q_1, \dots, Q_{m-1}) \right] \right]. \quad (C27)$$

The functions $F^{(m)}$ are formed from the $H^{(m)}$ and products of δ functions. To find the relationship, we must evaluate the b_i 's in terms of the a_j 's in the following expression:

$$\sum_{i=2}^{\infty} b_i x^i = \ln \left[1 + \sum_{j=2}^{\infty} a_j x^j \right]. \quad (C28)$$

The solution is

$$b_r = \sum_{j=1}^{[r/2]} \frac{(-1)^{j+1}}{j} \sum_{m_1=0}^{r-2j} \cdots \sum_{m_j=0}^{r-2j} a_{m_1+2} \cdots a_{m_j+2} \times \delta \left[2j + \sum_{s=1}^j m_s - r \right]. \quad (C29)$$

We list the lower-order expressions:


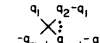

$$\begin{aligned} b_2 &= a_2, \\ b_3 &= a_3, \\ b_4 &= a_4 - \frac{1}{2} a_2^2, \\ b_5 &= a_5 - a_3 a_2, \\ b_6 &= a_6 - a_4 a_2 - \frac{1}{2} a_3^2 + \frac{1}{3} a_2^3. \end{aligned} \quad (C30)$$

It is easy now to construct the F 's from the H 's. For example,

$$\begin{aligned} F^{(4)}(Q_1, Q_2, Q_3) &= H^{(4)}(Q_1, Q_2, Q_3) \\ &\quad - \frac{1}{2V} (2\pi)^d \delta(q_2) H^{(2)}(Q_1) H^{(2)}(Q_3). \end{aligned} \quad (C31)$$

A. Diagrammatics and perturbation theory

The partition function in (C27) gives rise to the following diagrammar for calculating correlation functions:

internal (external) line		$\frac{1}{1 + X J_2(Q^2)}$
vertex with m legs ($m \geq 3$)		$c (X/c)^{m/2} (i)^m F^{(m)}(Q_1 \cdots Q_{m-1})$
loop		$(2/N)^{d/2} \int_Q$

a symmetry factor of $1/j!$ for j identical vertices, and an overall factor of V . (C32)

It is easy to see that perturbative calculations of correlation functions may be done by a loop expansion. Checking only factors of c , u , and N we see that a general graph has the contribution

$$\left[\frac{X}{c} \right]^{\mathcal{E}} N^{-(d/2)L} c^v, \quad (C33)$$

where I is the number of internal lines, v_j the number of vertices with j legs, E the number of external lines, L the number of lines, v the total number of vertices $\sum_{j=3}^{\infty} v_j$, and \mathcal{E} is shorthand for $\frac{1}{2} \sum_{j=3}^{\infty} j v_j$. There are two constraint equations for graphs

$$\sum_{j=3}^{\infty} j v_j = 2I + E, \quad (C34)$$

$$L = 1 + I - v, \quad (C35)$$

or combining the last two equations

$$E - 2 + 2L = \sum_{j=3}^{\infty} j v_j - 2v. \quad (C36)$$

If we use Eqs. (C33) and (C36) in four-dimensional space we find the contribution for a general graph to be

$$u^L X^v \left(\frac{X}{c} \right)^{(E-2)/2}. \quad (\text{C37})$$

The factor u appears with a power of L . Since u becomes of order ϵ after renormalization, the loop expansion is a systematic way to calculate correlation functions.

We now pose the question: What L -loop graphs need be included in the calculation of an E -point correlation function? The answer to this question is not at all obvious as E and or L become large. Rewriting Eq. (C36) provides the solution, however:

$$\sum_{j=3}^{\infty} (j-2)v_j = E - 2 + 2L. \quad (\text{C36})$$

Thus to find all the types of two loop graphs for the two point function we find

$$4 = \sum_{j=1}^{\infty} (v_{j+2})(j). \quad (\text{C38})$$

The problem thus reduces to finding integral partitions of 4. For example,

$$4 = 1 + 1 + 1 + 1 = 2 + 1 + 1 = 2 + 2 = 3 + 1 = 4. \quad (\text{C39})$$

Thus we can construct two-point graphs with two loops, from four three-point functions; or two three-point and one four-point function; or two four-point functions; or a five-point and a three-point function; or a six-point function. Next we must connect the vertices up in all possible ways to give the proper contributions to the two-point function.

B. $S(\mathbf{k})$ to $o(\epsilon)$

The scattering function is given by

$$S(\mathbf{q}) = \frac{1}{V} \langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}} \rangle = \frac{1}{u} \left[1 - \frac{1}{V} \langle \varphi_{\mathbf{q}} \varphi_{-\mathbf{q}} \rangle \right], \quad (\text{C40})$$

To order ϵ , we must then find the one-loop contributions to the two-point function. Now $E - 2 + 2L = 2 = 1 + 1$. Thus we get contributions from two three-point functions and a four-point function. The topological diagrams are

$$\text{---} = \text{---} + \text{---} \circ \text{---} + \text{---} \bigcirc \text{---}, \quad (\text{C41})$$

but recall that the vertex functions are not symmetric so that we must carefully consider the different ways to connect vertices.

Using our diagrammatic rules (C32) and carefully considering symmetry factors, we find to order ϵ

$$\begin{aligned} \langle \varphi_{\mathbf{q}} \varphi_{-\mathbf{q}} \rangle = & \frac{V}{1 + XJ_2(Q^2)} \left[1 - \frac{72uX^2}{1 + XJ_2(Q^2)} \int^P \frac{[F^{(3)}(Q, P)]^2}{[1 + XJ_2(P^2)] \{1 + XJ_2[(P + Q)^2]\}} \right. \\ & \left. + \frac{8uX}{1 + XJ_2(Q^2)} \int^P \frac{\hat{F}^{(4)}(Q, P)}{[1 + XJ_2(P^2)]} \right], \end{aligned} \quad (\text{C42})$$

where as usual

$$\int^Q = \int \frac{d^d Q}{(2\pi)^d}. \quad (\text{C43})$$

Also $\hat{F}^{(4)}$ is given by

$$\hat{F}^{(4)}(Q, P) = 2F^{(4)}(Q, 0, P) + 2F^{(4)}(Q, Q + P, P) + F^{(4)}(Q, P + Q, Q) + F^{(4)}(P, P + Q, P). \quad (\text{C44})$$

Here $F^{(4)} = H^{(4)}$ except

$$F^{(4)}(Q, 0, P) = H^{(4)}(Q, 0, P) - \frac{1}{2} H^{(2)}(Q) H^{(2)}(P), \quad (\text{C45})$$

as seen from Eq. (C31). Most explicitly the expressions for $F^{(3)}(Q, P)$ and $\hat{F}^{(4)}(Q, P)$ become

$$F^{(3)}(Q, P) = -\frac{1}{6} \left[\frac{J_2(S^2) - J_2(Q^2)}{S^2 - Q^2} + \frac{J_2(Q^2) - J_2(P^2)}{Q^2 - P^2} + \frac{J_2(P^2) - J_2(S^2)}{P^2 - S^2} \right], \quad (\text{C46})$$

$$\begin{aligned} \hat{F}^{(4)}(P, Q) = & -\frac{1}{3} \frac{J_3(P^2) - J_3(Q^2)}{P^2 - Q^2} - \frac{1}{Q^2 - S^2} \left[\frac{J_2(S^2) - J_2(P^2)}{S^2 - P^2} - \frac{J_2(Q^2) - J_2(P^2)}{Q^2 - P^2} \right] \\ & + \frac{1}{2(S^2 - Q^2)^2} [J_2(S^2) - J_2(Q^2) - (S^2 - Q^2)J_2'(Q^2)] \\ & + \frac{1}{2(S^2 - P^2)^2} [J_2(S^2) - J_2(P^2) - (S^2 - P^2)J_2'(P^2)] - \frac{1}{4} J_2(Q^2) J_2(P^2). \end{aligned} \quad (\text{C47})$$

We note that Eq. (C42) must still be renormalized as is shown in the text and done explicitly in NO.

APPENDIX D: PROPERTIES OF THE FUNCTIONS J_i AND THEIR APPROXIMANTS

We now discuss the functions J_m and introduce convenient forms for approximating them. From Eq. (C24) we can write out explicitly some J_m for small values of m ($m > 1$)

$$\begin{aligned} J_0(x) &= e^{-x}, \\ J_1(x) &= (1 - e^{-x})/x, \\ J_2(x) &= (e^{-x} - 1 + x)/(1/2x^2). \end{aligned} \quad (D1)$$

We immediately note three properties of the J_m ($m > 0$):

- (a) $J_m(x) \rightarrow 1$ as $x \rightarrow 0$,
- (b) $J_m(x) \rightarrow m/x$ as $x \rightarrow \infty$,
- (c) J_m 's monotone decreasing analytic functions in x with range (0,1) for positive x , and
- (d) $J_{m+1}/m + 1 < J_m/m < J_{m+1}/m$.

Indeed, if we write

$$J_m(x) = (K/x^m)[e^{-x} - q(x)], \quad (D2)$$

where K is a constant and $q(x)$ a polynomial then conditions (a) and (b) uniquely determine $K, q(x)$. The J_m 's have also the following properties.

Recursion relations. The J_m 's have the recursion relations

$$xJ_{m+1}(x) = (m+1)[1 - J_m(x)]. \quad (D3)$$

Derivatives. The J_m 's have the derivatives

$$\frac{dJ_m}{dx} = \frac{m}{m+1} J_{m+1} - J_m, \quad (D4)$$

or writing $S_m = J_m/m$ we find

$$\frac{dS_m}{dx} = S_{m+1} - S_m, \quad (D5)$$

and

$$D^k S_m = \sum_{j=0}^k (-1)^j \begin{bmatrix} k \\ j \end{bmatrix} S_{m+k-j}, \quad (D6)$$

which is an easy formula to remember.

Integrals. The J_m 's have the integrals

$$\int_0^x \frac{J_{m+1}(y)dy}{m+1} = \int_0^x J_1(y)dy - \sum_{n=1}^m \frac{1 - J_n(x)}{n}. \quad (D7)$$

Formulas (D3)–(D7) are very useful in calculating the mean square radius of gyration.

Approximate formulas for the J 's. Properties (a)–(c) suggest the following formula for the J_m 's ($m > 0$):

$$J_m(x) \cong \tilde{J}_m(x) = \frac{m}{m+x}. \quad (D8)$$

This formula is found to be quite accurate at all values of x and increasingly so as we proceed to larger m . For $m=4$,

$$\frac{J_4 - \tilde{J}_4}{J_4} < 6\%. \quad (D9)$$

If we use this approximation procedure we find that

$$\begin{aligned} H^{(m)}(Q_1, \dots, Q_{m-1}) &\cong \tilde{H}^{(m)}(Q_1, \dots, Q_{m-1}) \\ &= \left(\frac{1}{2}\right)^{m-1} \prod_{i=1}^{m-1} \tilde{J}_2(Q_i^2). \end{aligned} \quad (D10)$$

This formula is not accurate when the values of Q 's are close together and small, since we know, for example, that

$$H^{(m)}(0, \dots) = \frac{1}{m!} \neq \frac{1}{2^{m-1}} = \tilde{H}^{(m)}(0, \dots). \quad (D11)$$

However, we argue that this error most likely is not critical in the calculation of the scattering function, where the high- Q regime is the crucial one, where, for example, the divergences take place.

In Appendixes C and D we have presented analytical techniques for calculating the static scattering function. The scattering function to one-loop order has been evaluated, and using the approximation procedure in Appendix D [explicitly Eq. (D10)] and the diagrammatic technique discussed in Appendix C, it becomes straightforward to calculate the scattering function to two-loop order as well.

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