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Initial decay rate of the dynamical-scattering factor for dilute polymer solutions

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The initial decay rate of the dynamical-scattering factor for dilute polymer solutions is calculated with the aid of the renormalization-group theory, which has given reasonable results for transport coefficients. The fundamental kinetic equation for a polymer chain is reconsidered critically and the necessity of the ϵ expansion is explained.

I. INTRODUCTION

Dynamical light scattering experiments[1] in dilute polymer solutions give not only the translational diffusion constant, but also information on the internal chain motion. However, it is not easy to theoretically calculate the dynamical-scattering factor $I(\vec{k},t)$, where $I(\vec{k},t)$ is normalized so that $I(\vec{0},0)=1$. Akcasu[2] have shown that the initial decay rate

$$\Omega(\vec{k}) = -\left.\frac{d\ln I(\vec{k},t)}{dt}\right|_{t=0} \tag{1.1}$$

can be analytically calculated when excluded-volume effects are ignored. Even with excluded-volume interactions, $\Omega(\vec{k})$ can be obtained neatly with the aid of the thermal blob argument.[2(b)]

The dynamics of the chain are described by the following (so-called) full-diffusion equation:[3]

$$\frac{dP}{dt} = \mathscr{L}_F^* P , \tag{1.2}$$

where P is the distribution function for the conformation $\{\vec{c}(\tau),\ 0 \le \tau \le N_0\}$ with N_0 being the total contour length of the chain and $\vec{c}(\tau)$ is the position of the chain parametrized by the contour variable τ. The operator $\mathscr{L}_F^*$ is given by

$$\mathscr{L}_F^* = \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \frac{\delta}{\delta\vec{c}(\tau)} \left[\frac{k_B T}{\zeta_0}\delta(\tau-\tau')\overleftrightarrow{\mathbb{1}} + \frac{\rho^2 k_B T}{\eta_0}\overleftrightarrow{\mathrm{T}}(\vec{c}(\tau)-\vec{c}(\tau')) \right] \left[\frac{\delta}{\delta\vec{c}(\tau')} + \frac{\delta\mathscr{H}}{\delta\vec{c}(\tau')} \right] , \tag{1.3}$$

where ζ_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, ρ is the density of the solvent, $\overleftrightarrow{\mathrm{T}}$ is the Oseen tensor

$$\overleftrightarrow{\mathrm{T}}(\vec{r}-\vec{r}\,') = (2\pi)^{-d} \int d^d k \frac{1}{\eta_0 k^2} \left[\overleftrightarrow{\mathbb{1}} - \frac{\vec{k}\,\vec{k}}{k^2} \right] \times e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} , \tag{1.4}$$

and $\mathscr{H}$ is the Edwards Hamiltonian[4]

$$\mathscr{H} = \tfrac{1}{2} \int_0^{N_0} d\tau [\dot{\vec{c}}(\tau)]^2 d\tau + \frac{v_0}{2} \int_0^{N_0} d\tau \int_0^{N_0} d\sigma\, \delta(\vec{c}(\tau)-\vec{c}(\sigma)) \tag{1.5}$$

with v_0 being the (bare) excluded-volume parameter. It is understood that cutoffs must be imposed on the hydrodynamic and on the self-avoiding interactions to eliminate the unphysical self-interactions of chain units.

An important feature of Akcasu's theory is that the hydrodynamic interaction described by the Oseen tensor can be studied without any preaveraging approximation.[5] Thus, apparently, the hydrodynamic interaction can be exactly taken into account in the case of Ω. On the other hand, we know[6] that the hydrodynamic interaction described by the Oseen tensor must be renormalized. Unfortunately, we cannot exactly renormalize the Oseen tensor except for perturbatively. Therefore, there is an apparent conceptual contradiction.

The main purpose of the present paper is to resolve this contradiction and to give the calculation of $\Omega(\vec{k})$ using renormalization-group theory. We reconsider from the fundamental point of view the so-called full-diffusion equation (1.2), and show that it is justifiable only up to order ϵ ($=4-d$, d being the spatial dimensionality). Furthermore, the full-diffusion equation cannot be justified without the renormalization-group approach (ϵ-expansion method). This implies that the ϵ-expansion method is the only theoretically consistent method to study the full-diffusion equation. Of course, one might be able to treat the full-diffusion equation exactly, but there is no theoretical reason to believe the exact results are more accurate than the ϵ-expansion results; the ϵ expansion may give better results since the full-diffusion equation is a result correct up to order ϵ.

Even if we suppose that the full-diffision equation is exact, almost the only method to treat the excluded-volume effect without an arbitrary approximation is the ϵ-expansion method. We must therefore study the problem in $(4-\epsilon)$-space. Apparently, there are two possibilities; to use the hydrodynamic interaction of $(4-\epsilon)$-space, or to use the 3-space form of hydrodynamic interaction without any modification, as has been proposed by Adler and Freed.[7] However, one notes that the 3-space form of the hydrodynamic interaction is not renormalizable. More intuitively, this implies that we cannot properly extract macroscopic phenomenological laws insensitive to the microscopic details. Hence we have only one theoretical possibility; to calculate everything in $(4-\epsilon)$-space.

In Sec. II the formula for Ω based on the full-diffusion equation is briefly reviewed and conceptual problems are stated. In Sec. III, after introducing the kinetic-level description of the dilute-solution system, the full-diffusion equation is derived. The derivation clearly shows that the full-diffusion equation is not a reliable starting point. In Sec. IV the initial decay rate Ω is calculated in order ϵ in both the Gaussian and the self-avoiding-walk limits. In Sec. V our result is compared with experiments. Section VI is a summary.

II. FORMULA FOR THE INITIAL DECAY RATE OF THE DYNAMICAL-SCATTERING FACTOR

Let $\rho(\vec{r},t)$ be the (instantaneous) monomer density field at the space-time point $(\vec{r},t)$. In the continuum scheme we have

$$\rho(\vec{r},t)=\int_0^{N_0} d\tau\,\delta(\vec{r}-\vec{c}(\tau,t)) , \tag{2.1}$$

where $\{\vec{c}(\tau,t)\colon\ \tau\in[0,N_0]\}$ is the conformation of the chain at time t parametrized by the contour variable τ. The Fourier transform of (2.1) is given by

$$\tilde{\rho}(\vec{k},t)\equiv\int \rho(\vec{r},t)e^{i\vec{k}\cdot\vec{r}}\,d^dr=\int_0^{N_0} d\tau\, e^{i\vec{k}\cdot\vec{c}(\tau,t)} . \tag{2.2}$$

The (bare) dynamical-scattering factor $S_B(\vec{k},t)$ is defined by

$$S_B(\vec{k},t)\equiv\langle\tilde{\rho}(\vec{k},t)\tilde{\rho}(-\vec{k},0)\rangle , \tag{2.3}$$

where $\langle\ \rangle$ denotes the average with respect to P. Note that ρ is not directly observable, since we do not know anything about the unit of the chain. The unit need not be identical to the synthetic or structural unit. Hence S_B is not directly observable. However, the normalized scattering function I_B,

$$I_B\equiv S_B(\vec{k},t)/S_B(\vec{0},0) , \tag{2.4}$$

is directly observable.

The full-diffusion equation (1.2) which is supposed,[8] in general, to be a convenient starting point of almost all the theories of polymer dynamics, determines a Markov process whose generator $\mathscr{L}_F$ is the adjoint operator of $\mathscr{L}_F^*$ with respect to the following scalar product:

$$(f,g)=\int fg\mathscr{D}[\vec{c}\,] , \tag{2.5}$$

where f,g are functionals on the set of conformations. Thus we have

$$\mathscr{L}_F=\int_0^{N_0} d\tau\int_0^{N_0} d\sigma\left[-\frac{\delta\mathscr{H}}{\delta\vec{c}(\sigma)}+\frac{\delta}{\delta\vec{c}(\sigma)}\right]\overleftrightarrow{\mathrm{D}}\frac{\delta}{\delta\vec{c}(\tau)} , \tag{2.6}$$

where

$$\overleftrightarrow{\mathrm{D}}(\tau,\sigma)=\delta(\tau-\sigma)\frac{k_BT}{\zeta_0}+\frac{\rho^2k_BT}{\eta_0}\overleftrightarrow{\mathrm{T}}(\vec{c}(\tau)-\vec{c}(\sigma))$$

with T being the Oseen tensor defined by (1.4).

Using the standard theory of Markov processes,[9] we know that this generator (of the Kolmogorov backward equation) governs the observables; that is, for the two time-dependent observables $A(t)$ and $B(t)$

$$\langle A(t)B(0)\rangle=\langle(e^{t\mathscr{L}_F}A)B\rangle .$$

Thus we have from (3)

$$S_B(k,t)=\langle\overline{\tilde{\rho}(k,0)}\,e^{t\mathscr{L}_F}\tilde{\rho}(\vec{k},0)\rangle \tag{2.7}$$

or

$$S_B(\vec{k},t)=\sum_{n=0}^{\infty}\langle\tilde{\rho}(\vec{k},0)\mathscr{L}_F^n\tilde{\rho}(\vec{k},0)\rangle t^n . \tag{2.8}$$

Since $S_B(\vec{k},0)$ is the static scattering factor $S_B(\vec{k})$,

$$S_B(\vec{k},0)=S_B(\vec{k}) . \tag{2.9}$$

From (2.9) we have

$$\ln\frac{S_B(\vec{k},t)}{S_B(\vec{k})}=\frac{\langle\overline{\tilde{\rho}(\vec{k},0)}\mathscr{L}_F\tilde{\rho}(\vec{k},0)\rangle}{S_B(\vec{k})}t+\cdots . \tag{2.10}$$

Thus from the definition (1.1)

$$\Omega_B(\vec{k})=-L_B(\vec{k})/S_B(\vec{k}) , \tag{2.11}$$

where

$$L_B(\vec{k})=\langle\overline{\tilde{\rho}(\vec{k})}\mathscr{L}_F\tilde{\rho}(\vec{k})\rangle_B . \tag{2.12}$$

In (2.12) $\tilde{\rho}(\vec{k},0)$ is denoted by $\tilde{\rho}(\vec{k})$. Thus Ω can be calculated with the knowledge of equilibrium statistics of the chain as has been first pointed out by Akcasu[2(a)] in the context of the polymer solution theory. As is mentioned by Akcasu the operator $\mathscr{L}_F$ need not be the one we have chosen but can be any time-dependent dynamical operator. This approach has been extended to various situations, e.g., branched polymers.[10]

We know $\tilde{\rho}(\vec{k})$:

$$\tilde{\rho}(\vec{k})=\int_0^{N_0} d\tau\, e^{i\vec{k}\cdot\vec{c}(\tau)} . \tag{2.13}$$

Thus at least for the Gaussian case (i.e., without the excluded-volume interaction) (2.12) can be analytically calculated in 3-space.[2]

In the calculation of transport properties such as the translational diffusion constant we know that, even in the Kirkwood-Riseman scheme,[11] the hydrodynamic effect can be systematically taken into account only by the perturbation approach.[12] Thus there is a question whether the straightforward calculation in 3-space is exact or not.

We wish to calculate $L_B(\vec{k})$ [or $\Omega(\vec{k})$ defined by (2.11)] with the definition of the Fokker-Planck operator given by (1.2). If the problem is merely computational, then the Akcasu calculation is exact and rigorously corect. However, we must consider the meaning of the full-diffusion equation, especially the Oseen tensor in this equation. Everyone knows that this description cannot be correct truly microscopically (cf. Ref. 8).

The reason why we can use such a model is because we are interested in the phenomenology of the solution. Many different models in a class (called the universality class) can give the same phenomenology. The phenomenology is extracted with the aid of the renormalization-group theory. The model described by the full-diffusion equation is (supposedly) in this universality class (see Ref. 13 for more details). Thus the model we are using presupposes some kind of renormalization procedure. Consequently, we must renormalize the hydrodynamic interaction. These considerations do not necessarily imply that we must use the ϵ expansion,[14] which is a method to implement the renormalization philosophy. Unfortunately, however, this is almost the only existing systematic analytical procedure applicable. Thus, at present, the only logically self-consistent analytical approach to $\Omega(\vec{k})$ is the ϵ-expansion method.

As we will see in Sec. III, the full-diffusion equation is not a fundamentally reliable starting point of the theory. This equation is justifiable only with the aid of the ϵ-expansion method from a logically sounder description of the dynamics of the polymer solution. Thus, *a fortiori,* we have to use the ϵ-expansion method to calculate $\Omega(\vec{k})$.

III. DERIVATION OF THE FULL-DIFFUSION EQUATION

In the full-diffusion equation the chain is described semimicroscopically; i.e., the description of the chain is at the kinetic level. The solvent is assumed to be a continuum and its description is at the hydrodynamic level. (For the levels of description, see, e.g., Ref. 15.) Thus there is an inconsistency. One might argue that a polymer chain is very long, so that in comparison to the chain the solvent molecules are sufficiently tiny. Then there would seem to be no inconsistency. This argument is, however, completely wrong.

We have not ignored the thermal fluctuation of the chain and so have the Fokker-Planck (or, more precisely, Smoluchowsky) type equation. The stochastic driving force acting on each chain unit is assumed to be statistically independent. Hence, even if the chain is very long, the size of the unit for its dynamical description has the same order of magnitude as that for the description of the solvent. However, we have ignored the solvent velocity field fluctuation. Hence, there is an inconsistency in the very description of the polymer solution by the full-diffusion equation. Nobody adopts such a starting point in the theory of critical dynamics;[15] it is well known that the fluctuation of the fluid velocity field is crucially important in the critical dynamics of binary mixtures.[16]

The correct consistent description of a polymer chain, which has been proposed in Ref. 17 by one of the present authors (Y.O.), and very recently extended to semidefinite solutions by Shiwa,[18] employs the kinetic-level description of both the chain and the solvent:

$$\frac{\partial}{\partial t}\vec{c}(\tau,t)=\vec{u}(\vec{c}(\tau,t),t)-\frac{1}{\zeta_0}\frac{\delta\mathscr{H}}{\delta\vec{c}(\tau,t)}+\vec{\theta}(\tau,t)\ , \tag{3.1}$$

$$\rho\frac{\partial}{\partial t}\vec{u}(\vec{r},t)=-\int_0^{N_0}d\tau\frac{\delta\mathscr{H}}{\delta\vec{c}(\tau,t)}\delta(\vec{r}-\vec{c}(\tau,t))+\eta_0\Delta\vec{u}(\vec{r},t)-\vec{\nabla}p(\vec{r},t)+\vec{f}(\vec{r},t)\ , \tag{3.2}$$

where $\vec{u}(\vec{r},t)$ is the solvent velocity field, ρ is the solvent density, p is the pressure, and $\vec{\theta},\vec{f}$ are independent Gaussian white noises with mean zero and

$$\langle\vec{\theta}(\tau,t)\vec{\theta}(\tau',t')\rangle=2\zeta_0^{-1}\delta(t-t')\delta(\tau-\tau')\overleftrightarrow{\mathbb{1}}\ , \tag{3.3}$$

$$\langle\vec{f}(\vec{r},t)\vec{f}(\vec{r}\,',t')\rangle=-2\eta_0\Delta\delta(t-t')\delta(\vec{r}-\vec{r}\,')\overleftrightarrow{\mathbb{1}}\ , \tag{3.4}$$

$\overleftrightarrow{\mathbb{1}}$ being the $d\times d$ unit tensor, and Δ the Laplacian. These noises satisfy the fluctuation-dissipation theorem. We have chosen the energy units so that $k_BT=1$. The simultaneous equations (3.1) and (3.2) are very similar to that for the binary fluid critical dynamics (e.g., Refs. 15, 16, and 18) (the so-called model H).

We are interested in the low-frequency behavior of the system, so we may ignore the longitudinal velocity component and assume that the solvent is incompressible. As is well known, we can eliminate the pressure. Then (3.2) can be rewritten as[19,20]

$$\rho\frac{\partial}{\partial t}\vec{u}(\vec{r},t)=\left[-\int_0^{N_0}d\tau\frac{\delta\mathscr{H}}{\delta\vec{c}(\tau,t)}\delta(\vec{r}-\vec{c}(\tau,t))+\eta_0\Delta\vec{u}+\vec{f}\right]_{\perp}\ , \tag{3.2$'$}$$

where $\perp$ is the result obtained by operating in the large parenthesis with a projection operator which selects the transversal components. It is more convenient to rewrite (3.2′) in terms of the Fourier transform of $\vec{u}$ defined by

$$\vec{u}_{\vec{k}}(t)=\int\vec{u}(\vec{r},t)e^{i\vec{k}\cdot\vec{r}}d^dr\ . \tag{3.5}$$

We have

$$\rho\frac{\partial}{\partial t}\vec{u}_{\vec{k}}(t)=\left[\overleftrightarrow{\mathbb{1}}-\frac{\vec{k}\vec{k}}{k^2}\right]\cdot\left[-\int_0^{N_0}d\tau\frac{\delta\mathscr{H}}{\delta\vec{c}(\tau,t)}e^{i\vec{k}\cdot\vec{c}(\tau,t)}-\eta_0k^2\vec{u}_{\vec{k}}\right]+\vec{f}^{\,\perp}_{\vec{k}}(t)\ , \tag{3.6}$$

where

$$\langle\vec{f}^{\,\perp}_{\vec{k}}(t)\vec{f}^{\,\perp}_{\vec{k}'}(t')\rangle=k^2\eta_0\left[\overleftrightarrow{\mathbb{1}}-\frac{\vec{k}\vec{k}\,'}{k^2}\right]\delta(\vec{k}+\vec{k}\,')\delta(t-t')\ . \tag{3.7}$$

The corresponding Fokker-Planck equation is given by

$$\frac{d}{dt}P=\mathscr{L}P\ , \tag{3.8}$$

where P is the simultaneous distribution function of $\vec{c}$ and $\vec{u}$. The operators are defined as

$$\mathscr{L}=\mathscr{L}_0+\mathscr{L}_{\rm int}\ ,$$

$$\begin{aligned}\mathscr{L}_0=&\int d\tau\frac{\delta}{\delta\vec{c}(\tau)}\frac{1}{\zeta_0}\left[\frac{\delta}{\delta\vec{c}(\tau)}+\frac{\delta\mathscr{H}}{\delta\vec{c}(\tau)}\right]\\&+\int_{\vec{k}}\frac{\delta}{\delta\vec{u}_{\vec{k}}}(k^2\overleftrightarrow{1}-\vec{k}\,\vec{k})\left[\frac{\delta}{\delta\vec{u}_{-\vec{k}}}+\vec{u}_{\vec{k}}\right]\ ,\end{aligned} \tag{3.9}$$

$$\begin{aligned}\mathscr{L}_{\rm int}=&-p_0\lambda_0\int_{\vec{k}}\int d\tau\frac{\delta}{\delta\vec{c}(\tau)}\vec{u}_{\vec{k}}e^{-i\vec{k}\cdot\vec{c}(\tau)}\\&+p_0\lambda_0\int_{\vec{k}}\int d\tau\frac{\delta}{\delta\vec{u}_{\vec{k}}}\frac{\delta\mathscr{H}}{\delta\vec{c}(\tau)}e^{i\vec{k}\cdot\vec{c}(\tau)}\ ,\end{aligned}$$

where

$$\int_{\vec{k}}=(2\pi)^{-d}\int d^dk$$

and the mode-coupling constant λ_0 is added for the sake of "tracing the order." After renormalization in $(4-\epsilon)$-space λ_0 becomes of order $\epsilon^{1/2}$.[19]

What we want to do is to eliminate the variable $\vec{u}$ from (3.8) in order to write down an effective Fokker-Planck equation for the conformation. There is a standard way to do this with the aid of the projection operator.[19] The details are explained in Appendix A. The essence of the argument is that to order ϵ we have only to take into account the mode-coupling terms to the lowest nontrivial order; the result is the description of the fluid by the Oseen tensor, i.e., the full-diffusion equation. This is well known in critical dynamics as was demonstrated by Kawasaki long ago.[21] If we insist on having terms to higher order in ϵ, the equation is very complicated, and does not look tractable. In any case, if we take into account $O(\epsilon^2)$ terms, then we must abandon the full-diffusion equation. The effect of $O(\epsilon^2)$ terms is more drastic if there is a macroscopic flow field; we cannot even use the Markovian approximation as is pointed out in Ref. 19.

IV. THE ϵ-EXPANSION CALCULATION OF THE INITIAL DECAY RATE

As has been discussed in Sec. II, if we want to be logically self-consistent, it is almost mandatory to use the renormalization-group theories. Then, if we want to study the universal functions, we are forced to use the ϵ-expansion method. In our present problem of calculating the initial decay rate of the structure factor, the equation which we start from is correct only up to $O(\epsilon)$ as we have seen in Sec. II. Hence the ϵ-expansion method is, at present, the only consistent way to study the problem.

A. Bare perturbation calculation

First, we evaluate $L_B(\vec{k})$ defined by (2.12). Using (2.13) we rewrite it as

$$\begin{aligned}L_B(\vec{k})=&\int_0^{N_0}d\tau\int_0^{N_0}d\sigma\langle e^{-i\vec{k}\cdot\vec{c}(\sigma)}\mathscr{L}_Fe^{i\vec{k}\cdot\vec{c}(\tau)}\rangle\\=&\,\vec{k}\,\vec{k}:\int_0^{N_0}d\tau\int_0^{N_0}d\sigma\langle\overleftrightarrow{D}(\tau,\sigma)e^{i\vec{k}\cdot[\vec{c}(\tau)-\vec{c}(\sigma)]}\rangle\ .\end{aligned} \tag{4.1}$$

Explicitly writing D given in (2.6), we get

$$\zeta_0L_B(\vec{k})=\vec{k}\,\vec{k}:\int_0^{N_0}d\tau\int_0^{N_0}d\sigma\left\langle\left[kT\delta(\tau-\sigma)\overleftrightarrow{1}+\frac{\zeta_0}{\eta_0}\overleftrightarrow{T}(\vec{c}(\tau)-\vec{c}(\sigma))\right]e^{i\vec{k}\cdot[\vec{c}(\tau)-\vec{c}(\sigma)]}\right\rangle\ . \tag{4.2}$$

The rest of the calculation of order ϵ is performed in 4-space with an explicit cutoff or in $(4-\epsilon)$-space without any cutoff depending on the renormalization-group schemes. Here we will use the former scheme, as in Ref. 22.

We find (Appendix B)

$$\begin{aligned}(k_BT)^{-1}\zeta_0\vec{k}\,\vec{k}:&\langle\overleftrightarrow{D}(\tau,\sigma)e^{i\vec{k}\cdot[\vec{c}(\tau)-\vec{c}(\sigma)]}\rangle\\&=k^2\delta(\tau-\sigma)+\frac{k^2\rho^2\zeta_0^2}{(2\pi)^4\eta_0}I(\tau-\sigma)\ ,\end{aligned} \tag{4.3}$$

where

$$I(y)=\frac{3\pi^2}{2y}\left[2\left[\frac{1-e^{k^2y/2}}{k^2y/2}\right]-\left[\frac{e^{-k^2y/2}-1+k^2y/2}{y^2k^4/8}\right]\right]\ . \tag{4.4}$$

In the small-y limit we can see in (4.4) that both terms in parenthesis and hence the term in square brackets tend toward 1, showing that $I(y)$ goes as $3\pi^2/2y$ for y small.

Finally, we can evaluate (4.1) as follows:

$$\begin{aligned}(k_BT)^{-1}L_B(\vec{k})=&\int_0^{N_0}d\tau\int_0^{N_0}d\sigma f(|\tau-\sigma|)\\=&\,2\int_0^{N_0}dy(N_0-y)f(y)\ ,\end{aligned} \tag{4.5}$$

where f is given by (4.3). The small-y behavior of $I(y)$ shows that the last integral has a logarithmic divergence, and so we must impose a cutoff a where necessary so that $y=|\tau-\sigma|>a$.

We write $\theta_0=\frac{1}{2}k^2N_0$ and find (Appendix C)

$$L_B(k)=\frac{2k_BT}{\zeta_0}\theta_0\left[1-\frac{3}{16\pi^2}\frac{\zeta_0}{\eta_0}\ln\left[\frac{a}{N}\right]+\frac{3}{8\pi^2}\frac{\zeta_0}{\eta_0}V(\theta_0)\right]\ , \tag{4.6}$$

where

$$V(\theta_0)=-\tfrac{1}{2}-\tfrac{1}{6}\theta_0\Psi_3(\theta_0) \tag{4.7}$$

and

$$\Psi_3(\theta_0)=\int_0^1 dz\frac{1-\theta_0 z+(\theta_0 z)^2/2-e^{-\theta_0 z}}{(\theta_0 z)^3/6}$$

$$=-\frac{6}{\theta_0}\left\{\tfrac{1}{2}-\tfrac{1}{2}\ln\theta_0+\left[\frac{1}{4}-\frac{\hat{\gamma}}{2}\right]-\frac{1}{\theta_0}+\frac{1}{2\theta_0^2}+\tfrac{1}{2}e^{-\theta_0}\left[\frac{1}{\theta_0}-\frac{1}{\theta_0^2}-\int_0^\infty dz\,e^{-z}\ln\left[1+\frac{z}{\theta_0}\right]\right]\right\}. \tag{4.8}$$

Equation (4.7) shows the small- and large-θ_0 behavior of $V(\theta_0)$ clearly. Note that $\Psi_3(\theta_0)\rightarrow 1$ as $\theta_0\rightarrow 0$.

Next we calculate $S_B(\vec{\mathrm{k}})$. The following quantity has been given in a previous paper as[27]

$$\int\mathscr{D}[\vec{\mathrm{c}}]\int_0^{N_0}d\tau\int_0^{N_0}d\sigma\, e^{i\vec{\mathrm{k}}\cdot[\vec{\mathrm{c}}(\tau)-\vec{\mathrm{c}}(\sigma)]}e^{-\mathscr{H}}$$

$$=N_0^2\left[\frac{1}{\theta_0}-\frac{1}{\theta_0^2}+\frac{e^{-\theta_0}}{\theta_0^2}\right]-\frac{u_0}{4\pi^2}N_0^2\bigg[\frac{1}{\theta_0}\left[\frac{N_0}{a}\right]\bigg]\bigg[1-\frac{1}{\theta_0}-\frac{e^{-\theta_0}}{\theta_0}\bigg]$$

$$+\left[\frac{e^{-\theta_0}}{\theta_0}+\frac{e^{-\theta_0}}{\theta_0^2}-\frac{1}{\theta_0^2}\right]\ln\left[\frac{N_0}{a}\right]\bigg]\bigg]-\frac{u_0}{4\pi^2}g(\theta_0)N_0^2+\cdots. \tag{4.9}$$

We know

$$\int\mathscr{D}[\vec{\mathrm{c}}]e^{-\mathscr{H}}=1-\frac{u_0}{4\pi^2}\left[\left[\frac{N_0}{a}-1\right]-\ln\left[\frac{N_0}{a}\right]\right]+\cdots. \tag{4.10}$$

Then, dividing (4.9) by (4.10), we obtain

$$S_B(\vec{\mathrm{k}})=N_0^2 f(\theta_0)\left[1-\frac{u_0}{4\pi^2}\right]+\frac{N_0^2u_0}{4\pi^2}\theta_0\frac{\partial f(\theta_0)}{\partial\theta_0}\ln\frac{N_0}{a}$$

$$-\frac{u_0}{4\pi^2}g(\theta_0)N_0^2+\cdots, \tag{4.11}$$

where

$$f(\theta_0)=\frac{1}{\theta_0}-\frac{1}{\theta_0^2}+\frac{e^{-\theta_0}}{\theta_0^2}, \tag{4.12}$$

the Debye function. Thus the bare perturbation result is given by the ratio of (4.6) and (4.11). We see the result depends on the cutoff $\underline{a}$, which has to be absorbed into the renormalization constants to extract phenomenological consequences.

B. Renormalization

We introduce the phenomenological length scale L and rewrite

$$\ln(N_0/a)=\ln(N_0/L)-\ln(a/L). \tag{4.13}$$

Next let us introduce the renormalization constants

$$N=Z_N N_0,$$
$$\xi=Z_\xi\xi_0, \tag{4.14}$$
$$u=Z_u u_0,$$

where $u_0=v_0L^{\epsilon/2}$, $\xi_0=(\zeta_0/n_0)L^{\epsilon/2}$ and N,ξ,u are phenomenological counterparts of N_0,ξ_0,u_0, respectively.

Since the decay rate Ω is a directly observable quantity, so $\Omega=\Omega_B$. From the calculation in Ref. 17, we know

$$Z_u=1-\frac{u}{\pi^2}\ln\left[\frac{L}{a}\right]+\cdots, \tag{4.15}$$

$$Z_N=1+\frac{u}{4\pi^2}\ln\left[\frac{L}{a}\right]+\cdots \tag{4.16}$$

Using these constants, we find that the choice

$$Z_\xi=1-\frac{u}{4\pi^2}\ln\left[\frac{L}{a}\right]-\frac{3}{16\pi^2}\xi\ln\left[\frac{L}{a}\right]+\cdots \tag{4.17}$$

eliminates a completely from the bare perturbation result:

$$\Omega(\vec{\mathrm{k}})=\frac{k_BTk^2}{\zeta N}\left[1+\frac{u}{4\pi^2}\right]\frac{1}{f(\hat{\theta})}\left[\frac{N}{L}\right]^{3\xi/16\pi^2}$$

$$\times\exp\left[\frac{3}{8\pi^2}\xi V(\hat{\theta})+\frac{u}{4\pi^2}\frac{g(\hat{\theta})}{f(\hat{\theta})}\right], \tag{4.18}$$

where $\hat{\theta}=Nk^2(N/L)^{u/4\pi^2}/2$ and we have already exponentiated the $O(\epsilon)$ terms.

C. Renormalization-group equation and universal form for Ω

The renormalization-group equation for Ω can be obtained in a quite standard way as

$$\left[L\frac{\partial}{\partial L}+\beta_u\frac{\partial}{\partial u}+\beta_\xi\frac{\partial}{\partial\xi}+\gamma N\frac{\partial}{\partial N}\right]\Omega(\vec{\mathrm{k}})=0, \tag{4.19}$$

where

$$\beta_u(u)=\frac{\epsilon}{2}u-\frac{u^2}{\pi^2}+\cdots, \tag{4.20}$$

$$\beta_\xi(u,\xi)=\xi\left[\frac{\epsilon}{2}-\frac{3}{16\pi^2}\xi-\frac{1}{4\pi^2}u\right]+\cdots, \tag{4.21}$$

$$\gamma(u)=\frac{u}{(2\pi)^2}+\cdots \ . \tag{4.22}$$

The fixed-point parameters can be obtained from $\beta_u=\beta_\xi=0$. We have four fixed points, they are

(a) $u^*=0, \xi^*=0$;
(b) $u^*=\pi^2\epsilon/2, \xi^*=0$;
(c) $u^*=0, \xi^*=8\pi^2\epsilon/3$;
(d) $u^*=\pi^2\epsilon/2, \xi^*=2\pi^2\epsilon$.

The fixed points (a) and (b) represent the free-draining cases and (c) and (d) the nondraining cases. The fixed points with $u^*=0$ correspond approximately to the theta state, and those with $u^*=\pi^2\epsilon/2$ to the self-avoiding limit. Since the free-draining cases are meaningless for solution theories, we consider only (c) and (d).

At the fixed points β and β_ξ vanish, so that (4.19) becomes

$$\left[L\frac{\partial}{\partial L}+\gamma^* N\frac{\partial}{\partial N}\right]\Omega(\vec{\mathrm{k}})=0 \ , \tag{4.23}$$

where $\gamma^*=\gamma(u^*)$. The general solution to this is

$$\Omega=f(LN^{-1/\gamma^*},\vec{\mathrm{k}}) \ , \tag{4.24}$$

where f is a well behaved but as yet unspecified function.

Let us find the reparametrization symmetry of our model. The Edwards Hamiltonian (1.5) is invariant under the reparametrization derived from the following dimensional analysis:

$$[\vec{\mathrm{c}}]=C^{1/2}, \ \ [N]=[\tau]=C, \ \ [v_0]=C^{-\epsilon/2} \ . \tag{4.25}$$

$[\vec{\mathrm{k}}\cdot\vec{\mathrm{c}}]=1$ implies $[\vec{\mathrm{k}}]=C^{-1/2}$, so that the Oseen tensor (1.5) has $[\vec{\mathrm{T}}]=[\vec{\mathrm{k}}]^{d-2}=C^{(2-d)/2}$. From (2.6) we get $[\delta/\xi]=[T]$ or $[\zeta]=C^{-\epsilon/2}$ (this is the reason why the ϵ-expansion method works for the hydrodynamic interaction as well). Since $[\delta/\delta\vec{\mathrm{c}}(\tau)]=C^{-3/2}$, the dimension of the operator $\mathscr{L}_F$ is $[\mathscr{L}_F]=[\tau]^2[\delta/\ \delta\vec{\mathrm{c}}\,]^2[\delta/\zeta]=C^{-d/2}$. Hence the time scale T_0 of the system behaves like $[T_0]=C^{d/2}$. This implies that the decay rate Ω must behave as $[\Omega]=C^{-d/2}$. Any observable quantity must be invariant under the reparametrization of the model, so we must have

$$f(S^{1-1/\gamma^*}LN^{-1/\gamma^*},S^{-1/2}\vec{\mathrm{k}})=S^{-d/2}f(LN^{-1/\gamma^*},\vec{\mathrm{k}}) \ . \tag{4.26}$$

If S is chosen so that

$$S^{1-1/\gamma^*}LN^{-1/\gamma^*}=1 \ , \tag{4.27}$$

then we get

$$\Omega(\vec{\mathrm{k}})=(LN^{-1/\gamma^*})^{(2-\epsilon/2)\gamma^*/(1-\gamma^*)} \times f((LN^{-1/\gamma^*})^{\gamma^*/2(\gamma^*-1)}\vec{\mathrm{k}}) \ . \tag{4.28}$$

Since $\gamma^*=1-1/2\nu$,[22] absorbing L into the definition of f, we get

$$\Omega(\vec{\mathrm{k}})=N^{-(4-\epsilon)\nu}f(N^{\nu}\vec{\mathrm{k}}) \ . \tag{4.29}$$

This implies that the dynamical exponent $z=d$. Equation (4.29) tells us that a natural variable is proportional to $N^{2\nu}k^2$.

Equation (4.18) yields

$$\frac{\eta_0\Omega(\vec{\mathrm{k}})}{k_BT}=\frac{2\hat{\theta}}{\xi^*N^{(4-\epsilon)\nu}}e^{u^*/4\pi^2}L^{d\nu-2+\epsilon/2} \times\frac{1}{F(\hat{\theta})}\exp\left[\frac{3}{8\pi^2}\xi^*V(\hat{\theta})+\frac{u^*}{4\pi^2}\frac{g(\hat{\theta})}{f(\hat{\theta})}\right] . \tag{4.30}$$

Simple algebra shows that we may also write this as

$$\frac{\eta_0\Omega(\vec{\mathrm{k}})}{k_BT}=\left[N\left[\frac{N}{L}\right]^{2(\nu-1/2)}\right]^{-d/2}\frac{2\hat{\theta}}{\xi^*f(\hat{\theta})}e^{u^*/4\pi^2} \times\exp\left[\frac{3}{8\pi^2}\xi^*V(\hat{\theta})+\frac{u^*}{4\pi^2}\frac{g(\hat{\theta})}{f(\hat{\theta})}\right] , \tag{4.31}$$

where $\nu=\frac{1}{2}$ at (c) and $\nu=\frac{1}{2}(1+\epsilon/8)$ at (d).

V. COMPARISON WITH EXPERIMENTS

We would like to obtain from Eq. (4.31) dimensionless functions which may be directly compared with experimental results. Thus we calculate $\eta_0\Omega/k^dk_BT$ and Ω/k^2D_0 as functions of kR_G. Here $R_G=(\langle R_G^2\rangle)^{1/2}$ is the mean-square radius of gyration of the polymer and D_0 is a constant such that $\Omega(k)/k^2D_0\to 1$ as $kR_G\to 0$. These functional relations are universal; i.e., free from chemical details of the system.

We have the following results. In the Gaussian limit (c),

$$\frac{\eta_0\Omega(\vec{\mathrm{k}})}{k_BTk^d}=\frac{3\sqrt{2}}{16\pi^2}y^{-1/2}\frac{1}{f(y)}\exp\left[V(y)-\frac{1}{4}-\frac{1}{4}y\frac{f'(y)}{f(y)}\right] , \tag{5.1}$$

$$\frac{\Omega(k)}{k^2D_0}=\frac{1}{2f(y)}\exp\left[V(y)+\frac{1}{2}-\frac{1}{4}y\frac{f'(y)}{f(y)}\right] . \tag{5.2}$$

In the self-avoiding limit (d) we have

$$\frac{\eta_0\Omega(\vec{\mathrm{k}})}{k_BTk^d}=\frac{\sqrt{2}}{4\pi^2}y^{-1/2}\frac{1}{f(y)}\exp\left[\frac{3}{4}V(y)+\frac{1}{8}\left[1+\frac{g(y)}{f(y)}\right] -n\left[1+y\frac{f'(y)}{f(y)}\right]\right] , \tag{5.3}$$

$$\frac{\Omega(\vec{\mathrm{k}})}{k^2D_0}=\frac{1}{2f(y)}\exp\left[\frac{3}{4}\left[\frac{1}{2}+V(y)\right]+\frac{1}{8}\left[1+\frac{g(y)}{f(y)}\right] -ny\frac{f'(y)}{f(y)}\right] . \tag{5.4}$$

In the above $y=\frac{3}{4}k^2R_G^2$, $d=3$, and $n=0.156$.

It is unfortunate that there is little experimental data with which we can compare our results. In Figs. 1–3 we

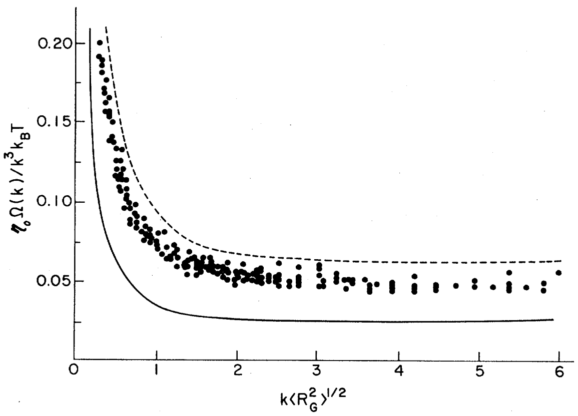

FIG. 1. Universal plot $\eta_0\Omega(\vec{k})/k_BTk^3$ vs $k\langle R_G^2\rangle^{1/2}$ in the Gaussian limit [Eq. (5.1)]. Solid curve is our result to order ϵ ($\epsilon=1$), and dashed curve is the result of Akcasu and Gurol [Ref. 2(a)]. Experimental points are taken from Akcasu and Han (Ref. 23).

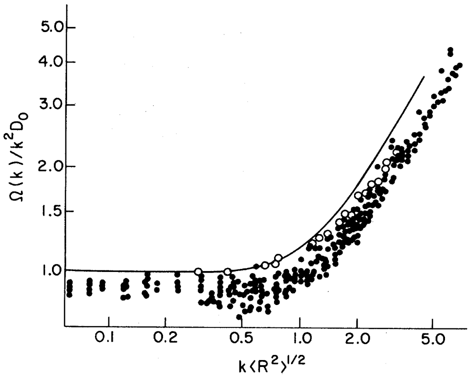

FIG. 3. Universal plot $\Omega(\vec{k})/k^2D_0$ vs $k\langle R_G^2\rangle^{1/2}$ in the Gaussian limit [Eq. (5.2)]. Solid curve is our result to order ϵ ($\epsilon=1$). By definition $\Omega(\vec{k})/k^2D_0$ must be unity in the small $k\langle R_G^2\rangle^{1/2}$ limit. If we properly normalize the experimental data (○) taken from Akcasu and Han (Ref. 23), the agreement of our result with experiments is satisfactory. However, we have a discrepancy with the data (●) taken from Tsunashima *et al.* [Ref. 24(a)].

have superimposed our curves [Eqs. (5.1)–(5.3)] on data from a paper by Akcasu and Han[23] and from Tsunashima *et al.*[24] Although our curves for $\eta_0\Omega/k_BTk^d$ lie below the data, we observe that at the θ point the curve matches the data extremely well if the curves are scaled (as has been suggested in Akcasu and Han[23]). In the good solvent limit, our asymptotic estimate of $\eta_0\Omega/k_BTk^d$ seems to agree with the result of Tsunashima *et al.*[24] Moreover, the graph of Ω/k^2D_0 versus kR_G (Fig. 3) shows excellent agreement with experiment, especially since Akcasu and Han have not used a D_0 such that $\Omega/k^2D_0\to 1$ as $k\to 0$. If they had done so, their data would be shifted slightly upwards, precisely overlapping our curve.

By noting the value of kR_G at which our curves have the sharpest change in slope one may also remark that the data points in all three of the graphs (Figs. 1–3) are shifted to the right slightly in comparison to our theoretical calculations. Yet this is consistent with the tendency that experimental values of kR_G are overestimated in comparison to their true physical values.

As a final comment concerning Fig. 3 (Ω/k^2D_0 versus kR_G) we mention that the Akcasu and Han calculation for large kR_G yields $\Omega/k^2D_0\sim\frac{3}{8}\sqrt{\pi}kR_G$. This curve, if plotted, would lie parallel to, although well below the data, making our theoretical calculation a more reliable one.

Since, generally, the radius of gyration is obtained from the static scattering function $S(\vec{k})$ as

$$I(\vec{k})=\frac{S(\vec{k})}{S(\vec{0})}=1+\frac{N^2}{2d}\langle R_G^2\rangle k^2+\cdots ,$$

i.e., from the $k\to 0$ limit behavior of $S(k)$. This extrapolation is technically not very easy. For example, there is a tendency for R_G to be estimated too large. Since $S(\vec{k})$ or

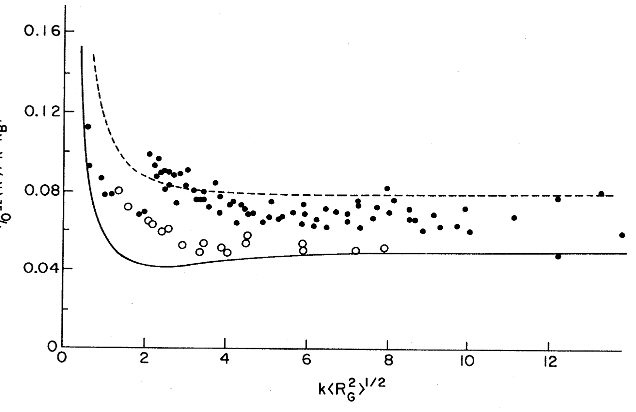

FIG. 2. Universal plot $\eta_0\Omega(\vec{k})/k_BTk^3$ vs $k\langle R_G^2\rangle^{1/2}$ in the self-avoiding limit [Eq. (5.3)]. Solid curve is our result to order ϵ ($\epsilon=1$), and the broken curve is the result of Akcasu and Benmouna [Ref. 2(b)]. Experimental points are ○, Akcasu and Han (Ref. 23); ● Nemato *et al.* [Ref. 24(b)]. Solid curve exhibits a minimum, but this may be due to our approximation.

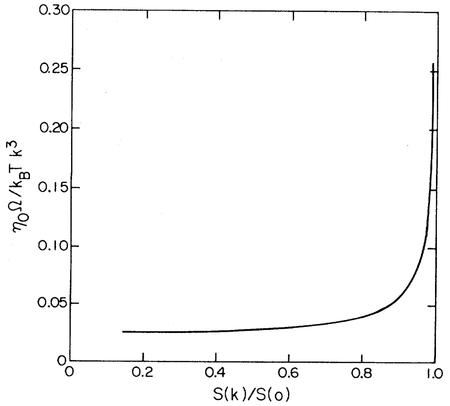

FIG. 4. Universal plot $\eta_0\Omega/k_BTk^3$ vs $S(\vec{k})/S(\vec{0})$ in the Gaussian limit. Theoretical curve is given. This does not require the determination of the radius of gyration, which may cause an extra experimental error. However, the estimate of $S(k)/S(0)$ is not very satisfactory, so that curves given in Figs. 4–7 exhibit only qualitative features.

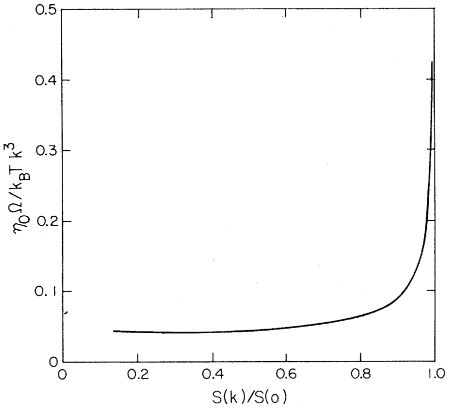

FIG. 5. Universal plot $\eta_0\Omega/k_BTk^3$ vs $S(\vec{k})/S(\vec{0})$ in the self-avoiding limit. Theoretical curve is given.

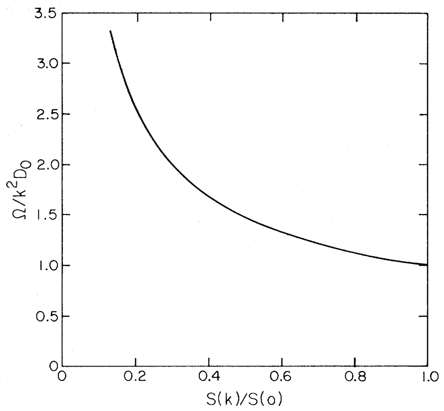

FIG. 7. Universal plot Ω/k^2D_0 vs $S(\vec{k})/S(\vec{0})$ in the self-avoiding limit. Theoretical curve is given.

$I(\vec{k})$ is a monotonically decreasing function of kR_G, we can replace kR_G with $I(\vec{k})$ to have universal curves more directly accessible experimentally. $I(\vec{k})$ is given as follows:

$$I(\vec{k},N)=2f(y)\exp\left[\frac{1}{4}y\frac{f'(y)}{f(y)}\right] \tag{5.5}$$

is the Gaussian form, and

$$I(\vec{k},N)=2f(y)\exp\left[-\frac{1}{8}\left[1+\frac{g(y)}{f(y)}\right]+\frac{37}{96}y\frac{f'(y)}{f(y)}\right] \tag{5.6}$$

the SAW, where again $y=3k^3R_G^2/4$.

The four plots are given in Figs. 4—7. Again it should be emphasized that these plots for polymer solution depend only on the quality of solvent. We do not have experimental data with which to compare these plots.[25]

Specifically, the two plots $\eta_0\Omega/k_BTk^3$ versus I are equivalent if we scale the figures by an appropriate amount. This indicates that at any strength of excluded-volume parameter we have the relation

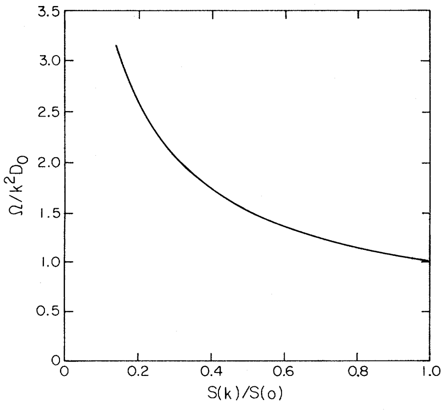

FIG. 6. Universal plot Ω/k^2D_0 vs $S(\vec{k})/S(\vec{0})$ in the Gaussian limit. Theoretical curve is given.

$$\frac{\eta_0\Omega}{k_BTk^d}\simeq\left[\frac{\eta_0\Omega}{k_BTk^d}\right]_{\text{Gaussian}}f(Z)\,, \tag{5.7}$$

where f is a monotonic increasing function of Z, the parameter proportional to $uN^{1/2}$ appearing in the study of crossover behaviors.[13] The relative scaling of the curve can then be used to isolate solvent effects. The temperature dependence will be published elsewhere.[26]

One also notices that the two plots of Ω/k^2D_0 versus I are virtually indistinguishable. This interesting result indicates that such a curve should be a universal one for long unbranched polymers in dilute solutions.

VI. SUMMARY

We can summarize the contents of the paper as follows.

(1) The full-diffusion equation, which is supposed to be the convenient starting point of the polymer dynamics, is justifiable only to order ϵ $(=4-d)$ from a more fundamental kinetic description of the polymer solution. The latter is quite analogous to the description accepted with theory of dynamical critical phenomena.

(2) Thus the results derived from the full-diffusion equation is reliable up to order ϵ; the ϵ expansion is the only way to study the full-diffusion equation in a way that is consistent with the foundation of this equation.

(3) We have performed an ϵ-expansion calculation of the initial decay rate $\Omega(\vec{k})$ of the dynamical scattering factor. Our calculation of $\Omega(\vec{k})/k^2D_0$, where $D_0=\lim_{k\to 0}\Omega(k)/k^2$ in kR_G appears to be in satisfactory agreement with experiments. About the universal ratio $\lim_{k\to\infty}\Omega\eta_0/k_BTk^d$ there seem to be discrepancies between our results and experimental results. We do not claim that our theory is quantitatively highly reliable, but we must point out the overall semiquantitative success of the renormalization-group theory in previous publications of our[12,13,27] and other groups.[28]

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF THE FULL-DIFFUSION EQUATION

This appendix describes how to derive an effective operator $\mathscr{L}_{\text{eff}}$ for the Fokker-Planck equation, where the effects of the solvent velocity field have been averaged out. We write

$$\mathscr{L}=\mathscr{L}_0+\mathscr{L}_{\text{int}} \tag{A1}$$

as in (3.8) and (3.9). We denote the normalized equilibrium distribution function by $W(\{\vec{c}\},\{\vec{u}\})$, which satisfies

$$\mathscr{L}W(\{\vec{c}\},\{u\})=0\ . \tag{A2}$$

If there is no systematic macroscopic flow, we may factor W as

$$W(\{\vec{c}\},\{u\})=W_c(\{\vec{c}\})W_u(\{\vec{u}\})\ . \tag{A3}$$

By examining (3.8) we see then that

$$\mathscr{L}_0W=0\ , \tag{A4}$$

which implies

$$\mathscr{L}_{\text{int}}W=0\ . \tag{A5}$$

Here we introduce the projection operator $\mathscr{P}$ by

$$\mathscr{P}=W_u\{u\}\int_{\vec{u}}\ , \tag{A6}$$

where $\int_v=\int d\{\vec{u}\}$ is a functional integral over the velocity field. Following a derivation very similar to that in Onuki and Kawasaki[19] we find that

$$P(\{\vec{c}\},t)=\int_{\vec{u}}p(\{\vec{c}\},\{\vec{u}\},t) \tag{A7}$$

obeys the equation

$$\frac{dP(\{\vec{c}\},t)}{dt}=\mathscr{L}_{\text{eff}}p(\{\vec{c}\},t) \tag{A8}$$

with

$$\mathscr{L}_{\text{eff}}=\langle\mathscr{L}\rangle_{\vec{u}}+\langle\mathscr{L}(1-\mathscr{P})(\delta-\mathscr{L})^{-1}(1-\mathscr{P})\mathscr{L}\rangle_{\vec{u}}\ , \tag{A9}$$

where δ is a positive infinitesimal number and

$$\langle Q\rangle_u=\int_{\vec{u}}QW_u(\{\vec{u}\})\ . \tag{A10}$$

We wish to evaluate $\mathscr{L}_{\text{eff}}$ to order ϵ. The first term of (A9) is

$$\langle\mathscr{L}\rangle_{\vec{u}}=\int d\tau\frac{\delta}{\delta\vec{c}(\tau)}\frac{1}{\zeta_0}\left[\frac{\delta}{\delta\vec{c}(\tau)}+\frac{\delta\mathscr{H}_E}{\delta\vec{c}(\tau)}\right]\ . \tag{A11}$$

Since W_u decays rapidly as $u\to\infty$, and $\langle\vec{u}_{\vec{k}}\rangle=0$.

The second term of (A9) may be simplified as follows.

(i) We first note that

$$\int_{\vec{u}}\mathscr{L}(1-\mathscr{P})=\int_{\vec{u}}\mathscr{L}_{\text{int}}(1-\mathscr{P})\ . \tag{A12}$$

Then the second term in (A9) becomes

$$\langle\mathscr{L}_{\text{int}}(1-\mathscr{P})(\delta-\mathscr{L})^{-1}(1-\mathscr{P})\mathscr{L}_{\text{int}}\rangle_{\vec{u}}\ . \tag{A13}$$

(ii) As will be justified later, $\mathscr{L}_{\text{int}}$ is of order $\epsilon^{1/2}$. So in our order-ϵ calculation we may replace $\mathscr{L}$ by $\mathscr{L}_0$ in (A13).

(iii) We now break $\mathscr{L}_{\text{int}}$ into two parts:

$$\mathscr{L}_{\text{int}}=\mathscr{L}_1+\mathscr{L}_2\ , \tag{A14}$$

$$\mathscr{L}_1=-\lambda_0\int_{\vec{k}}\int d\tau\frac{\delta}{\delta\vec{c}(\tau)}\vec{u}_{\vec{k}}e^{-i\vec{c}(\tau)\cdot\vec{k}}\ , \tag{A15}$$

$$\mathscr{L}_2=\lambda_0\int_{\vec{k}}\int d\tau\frac{\delta}{\delta\vec{u}_{\vec{k}}}\left[\frac{\delta\mathscr{H}_E}{\delta\vec{c}(\tau)}\right]_{\perp}e^{i\vec{k}\cdot\vec{c}(\tau)}\ . \tag{A16}$$

However, integration by parts shows that if we replace the first $\mathscr{L}_{\text{int}}$ in Eq. (A13) by $\mathscr{L}_2$ we get zero. Thus using (ii) and (iii) Eq. (A13) becomes

$$\begin{aligned}&\langle\mathscr{L}_1(1-\mathscr{P})(\delta-\mathscr{L}_0)^{-1}(1-\mathscr{P})\mathscr{L}_1\rangle\\&\quad+\langle\mathscr{L}_1(1-\mathscr{P})(\delta-\mathscr{L}_0)^{-1}(1-\mathscr{P})\mathscr{L}_2\rangle\ .\end{aligned} \tag{A17}$$

To proceed further we note that the correlation time of the velocity field is much smaller than that for the conformation, so that

$$(\delta-\mathscr{L}_0)^{-1}=\int_0^\infty dt\,e^{t\mathscr{L}_0}\simeq\int_0^\infty dt\,e^{t\mathscr{L}_u}\ , \tag{A18}$$

where $\mathscr{L}_u$ is the second term of $\mathscr{L}_0$. Since

$$\langle\vec{u}_{\vec{k}}e^{t\mathscr{L}_0}\vec{u}_{\vec{k}'}\rangle=\langle\vec{u}_{\vec{k}}(t)\vec{u}_{\vec{k}'}(0)\rangle \tag{A19}$$

and

$$\int_0^\infty dt\langle\vec{u}_{\vec{k}}(t)\vec{u}_{\vec{k}'}(0)\rangle=\delta(\vec{k}+\vec{k}')\overleftrightarrow{T}_{\vec{k}}\ , \tag{A20}$$

where $\overleftrightarrow{T}_{\vec{k}}$ is the Fourier transform of the Oseen tensor, we find that the first term of (A17) becomes

$$\lambda_0^2\int d\tau\int d\tau'\frac{\delta}{\delta\vec{c}(\tau)}\overleftrightarrow{T}(\tau,\tau')\frac{\delta}{\delta\vec{c}(\tau')}\ , \tag{A21}$$

and the second term of (A17)

$$\lambda_0^2\int d\tau\int d\tau'\frac{\delta}{\delta\vec{c}(\tau)}\overleftrightarrow{T}(\tau,\tau')\frac{\delta\mathscr{H}_E}{\delta\vec{c}(\tau')}\ . \tag{A22}$$

We now add (A11), (A21), and (A22) together to obtain the order-ϵ result for $\mathscr{L}_{\text{eff}}$ in Eq. (A9):

$$\mathscr{L}_{\text{eff}}=\int d\tau\int d\tau'\frac{\delta}{\delta\vec{c}(\tau)}\overleftrightarrow{D}(\tau,\tau')\left[\frac{\delta}{\delta\vec{c}(\tau')}+\frac{\delta\mathscr{H}_E}{\delta\vec{c}(\tau')}\right]\ , \tag{A23}$$

where D is given in (2.6). Equation (4.1) then follows immediately from (A23). Again, however, we stress that (A23) is correct only to order ϵ.

APPENDIX B: DERIVATION OF EQS. (4.3) AND (4.4)

We will need

$$\int d^3\vec{l}\, e^{-al^2}=(\pi/a)^{3/2} \tag{B1}$$

and

$$\int dv\, e^{-(av^2+2bv+c)}=(\pi/a)^{1/2}e^{-(c-b^2/a)} . \tag{B2}$$

The left-hand side of (4.3) is quickly seen to be

$$\frac{k^2}{\zeta_0}\delta(y)+\frac{1}{(2\pi)^4\eta_0}\int d^4\vec{q}\,\frac{1}{q^2}\left[k^2-\frac{(\vec{q}\cdot\vec{k})^2}{q^2}\right] \times\exp[-\tfrac{1}{2}(\vec{k}+\vec{q})^2y] , \tag{B3}$$

where we have performed the Gaussian average over chain conformations. Let $\vec{q}=(\vec{l},r)$ where $\vec{l}$ is a three-vector and $(\vec{l},0)\cdot\vec{k}=0$. By comparing (B3) and (4.3) we get

$$I(y)=\int d^3\vec{l}\,dr\frac{l^2}{(l^2+r^2)^2}\exp\{-\tfrac{1}{2}[l^2+(\vec{r}+\vec{k})^2]y\} \tag{B4}$$

$$=k^2\int d^3\vec{u}\,dv\frac{u^2}{(u^2+v^2)^2}\exp\{-K[u^2+(v+1)^2]\} , \tag{B5}$$

where $K=\frac{1}{2}k^2y$.

$$I(y)=k^2\left[-\frac{d}{dx}\bigg|_{x=1}\right]\int d^3u\,dv\frac{1}{xu^2+v^2}\exp\{-K[u^2+(v+1)^2]\} \tag{B6}$$

$$=Kk^2\left[-\frac{d}{dx}\bigg|_{x=1}\right]\int d^3u\,dv\int_0^{\infty}d\alpha\exp\{-\alpha K(xu^2+v^2)-K[u^2+(v+1)^2]\} . \tag{B7}$$

Now we can use (B1) and (B2) to get

$$I(y)=\tfrac{3}{2}Kk^2\left[\frac{\pi}{K}\right]^2 \times\int_0^{\infty}d\alpha\,\alpha\left[\frac{1}{1+\alpha}\right]^3 \times\exp\left[-K\left[1-\frac{1}{1+\alpha}\right]\right] . \tag{B8}$$

Now let $\beta=1-1/(1+\alpha)$, and

$$I(y)=\frac{3\pi^2}{2y}\int_0^1 d\beta(2\beta e^{-K\beta}) , \tag{B9}$$

from which (4.4) follows immediately using $K=\frac{1}{2}k^2y$.

APPENDIX C: DERIVATION OF EQS. (4.7) AND (4.8)

From (4.3)—(4.5) we have

$$\frac{L(\vec{k})}{k_BT}=\frac{N_0k^2}{\zeta_0}+\frac{2k^2}{(2\pi)^4\eta_0}\int_0^{N_0}dy(N_0-y)I(y) . \tag{C1}$$

We can rewrite (C1) using (B12) as

$$\frac{L(\vec{k})}{k_BT}=\frac{N_0k^2}{\zeta_0}+\frac{2k^2}{(2\pi)^4\eta_0}\int_0^{N_0}dy(N_0-y)\left[\frac{3\pi^2}{2y}\right] \times\int_0^1 d\beta\,2\beta e^{-k^2y\beta/2} . \tag{C2}$$

Let $y=N_0Z$ and $\theta=k^2N_0/2$. Then we obtain

$$\frac{L(\vec{k})}{k_BT}=\frac{2\theta}{\zeta_0}+\frac{3\theta}{8\pi^2\eta_0}\int_{a/N_0}^{1}dz\left[\frac{1}{z}-1\right] \times\int_0^1 d\beta\,2\beta\exp(-\beta\theta z) . \tag{C3}$$

We can subtract off the divergent part and then set $a=0$,

$$\frac{L(\vec{k})}{k_BT}=\frac{2\theta}{\zeta_0}+\frac{3\theta}{8\pi^2\eta_0}\left[-\ln\frac{a}{N_0}-1+\int_0^1\left[\frac{1}{z}-1\right]\left[\int_0^1 d\beta\,2\beta e^{-\beta\theta z}-1\right]\right] . \tag{C4}$$

If we rearrange terms, we find

$$L(\vec{k})=2k_BT\frac{\theta}{\zeta_0}\left\{1-\frac{3\zeta_0}{16\pi^2\eta_0}\ln\frac{a}{N_0}+\frac{3}{8\pi^2}\frac{\zeta_0}{\eta_0}\left[-\frac{1}{2}-\frac{\theta}{\gamma}\int_0^1 dz\,3\left[\frac{1}{z}-1\right]\left[\frac{1-\int_0^1 d\beta\,2\beta e^{-\theta\beta z}}{\theta}\right]\right]\right\} . \tag{C5}$$

This is exactly (4.7), where the last integral in (C5) is easily evaluated to yield $\Psi_3(\theta)$ as given in Eq. (4.8).

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