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Theory of polymer cyclization

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The simplest example of a reacting polymer system is studied, that of a single chain with reacting end groups. The long-time cyclization rate is calculated systematically using renormalization-group methods. Several types of single-chain dynamics are treated, with and without hydrodynamical and excluded-volume interactions. The hydrodynamical cases ("non-free-draining") describe cyclization in dilute polymer solutions. For free-draining polymers we find "diffusion-controlled" behavior for long chains: The ratio of the reaction rate to the longest relaxation rate of the unperturbed polymer is a universal constant independent of the chemistry of the reacting ends. For non-free-draining models the analogous ratio vanishes to order ϵ ($\epsilon=4-d$). In good solvents (hydrodynamics plus excluded volume) we predict that a "mass action" law holds asymptotically: The molecular weight dependence of the reaction rate is that of the probability that the chain ends are together in equilibrium. In all cases, the asymptotic behavior, either diffusion controlled or mass action, is determined by the class of dynamics and is independent of the reactivity of the end groups.

I. INTRODUCTION

The motivations for the study of intramolecular reactions in polymers fall into two broad categories. Firstly, such reactions occur in a wide variety of reacting polymer systems, for example, during the formation of networks[1-3] (gels, rubbers) and other polymerization processes.[4-6] Secondly, the experimental measurement of intramolecular reaction rates has provided a probe of the internal dynamics of a polymer molecule.[7,8]

In the present work we study the simplest reacting polymer system, namely, a single polymer chain with reacting groups attached to its ends (cyclization). This system has been previously considered in the works of Wilemski and Fixman,[9] and Doi.[10] The majority of the experiments probing polymer dynamics have involved cyclization in dilute solution;[11] the main results of this paper concern this case. In addition, results are presented for the "Rouse model"[12] which is relevant to polymer melts below the entanglement threshold.[13]

The first theoretical attempt to understand cyclization from first principles was (to our knowledge) that of Wilemski and Fixman[9] whose model is introduced in Sec. II. To extract the cyclization rate k they employed a closure approximation and deduced that for the Rouse model, k scales as the inverse of the longest relaxation time τ of the polymer. This model, within the closure approximation, was further investigated by Doi[10] who confirmed $k \sim \tau^{-1}$ with a prefactor independent of the capture radius (defined as the maximum separation at which the end groups may react). For θ solvents Doi incorporated preaveraged hydrodynamics and found logarithmic corrections involving the capture radius.

The prevailing view which has emerged from the above and other theoretical studies[14] and which has characterized the spirit in which experimental studies[15] have been performed is that $k \sim \tau^{-1}$ in the diffusion-controlled limit in which the reactive groups react on every encounter.

The purpose of this paper is to present a study of cyclization that is free of any *ad hoc* assumptions (a summary of our results has appeared elsewhere[16]), neither do we use the closure approximation nor do we preaverage hydrodynamic interactions. The latter are incorporated into our model, together with excluded-volume effects, in a systematic fashion for the first time. The essential point of our treatment is that by exploiting the fact that for $d > 4$ space is explored noncompactly[17] and reaction rates obey mean-field "laws of mass action," we are able to apply the renormalization group (and ϵ-expansion technique).

For the cases of the Rouse model and Rouse model plus excluded volume we will find $k \sim \tau^{-1}$ with a universal prefactor for long chains which is independent of the details of the reaction. Adding hydrodynamic interaction to the Rouse description we obtain a result qualitatively similar to Doi's: k scales as the inverse relaxation time with a logarithmic correction. Perhaps the most surprising result of the present work is for Rouse plus hydrodynamics plus excluded volume (describing chains in good solvents) for which we will find k does *not* scale as τ^{-1} but rather as the equilibrium probability that the ends are in contact (law of mass action). This implies a different molecular weight dependence of k than hitherto assumed and motivates further careful experiments.

The structure of this paper is as follows. Section II describes the models we use. Section III is a derivation of the bare perturbation theory for reaction rates. In Sec. IV we develop the renormalized perturbation theory and renormalization-group equations for reaction rates (Sec. IV A deals with the free draining case, Sec. IV B with the non-free-draining case). We present conclusions and a summary in Sec. V.

II. THE MODEL

We define the model of the cyclizing polymer in d dimensions by the following Fokker-Planck type equation for the probability $P(\{c\},t)$ of a configuration $\{c\}$ at time t:

$$\frac{\partial P}{\partial t}=FP+u_0\delta(c(N_0)-c(0))\,P\ . \tag{1}$$

The configuration $\{c\}\equiv c(\tau)$ is a vector valued function specifying the position of the τth element of the chain, $0\leq\tau\leq N_0$ where N_0 is the bare contour length. The sink term in Eq. (1) selects configurations whose ends are together (u_0 is the bare "reaction rate"). F is the diffusion operator[18] including the effect of hydrodynamics through the Oseen tensor $T_{\alpha\beta}$ and excluded volume through the Edwards Hamiltonian H. Explicitly,

$$F=\int_0^{N_0}d\tau\int_0^{N_0}d\tau'\sum_{\alpha\beta}\frac{\delta}{\delta c_\alpha(\tau)}\left[\frac{\delta_{\alpha\beta}}{\zeta_0}\delta(\tau-\tau')+T_{\alpha\beta}(c(\tau)-c(\tau'))\right]\left[\frac{\delta}{\delta c_\beta(\tau')}+\frac{\delta H}{8c_\beta(\tau')}\right]\ , \tag{2}$$

$$\begin{aligned}&T_{\alpha\beta}(x)=(2\pi)^{-d}\int d^dk\frac{1}{\eta k^2}\left[\delta_{\alpha\beta}-\frac{k_\alpha k_\beta}{k^2}\right]e^{ik\cdot x},\quad H=H_0+H_I,\quad H_0=\tfrac{1}{2}\int_0^{N_0}d\tau[\dot{c}(\tau)]^2\ ,\\&H_I=(\tilde{e}_0/2)\int_0^{N_0}d\tau\int_0^{N_0}d\tau'\delta(c(\tau)-c(\tau'))\ .\end{aligned} \tag{3}$$

Here ζ_0 and $\tilde{e}_0$ are the bare friction and excluded-volume coupling constants, respectively, and η is the fluid viscosity.

The model equation (1) is a particular realization of the class of models first introduced by Wilemski and Fixman[9] who considered a general sink term. We choose the δ function as the sink firstly because we believe it to be in the same universality class as other choices of sink and secondly for mathematical convenience in that it facilitates the use of field-theoretic methods. Note the parallel with the self-avoiding polymer problem: the Edwards Hamiltonian [see Eq. (3)], which involves δ-function interactions, is believed to belong to a large universality class of Hamiltonians involving other types of interactions (including hard core).

We now turn to a preliminary study of the dimensional analysis of the model. Assigning τ, the contour variable, a dimension l, and equating the dimensions of the terms in the Fokker-Planck equation we see that $u_0\zeta_0$ has the dimension $l^{d/2-2}$. We view (and this is borne out by subsequent calculation) $u_0\zeta_0$ as a natural coupling constant. We note that $u_0\zeta_0$ is dimensionless if $d=4$. Thus dimensional analysis suggests the efficacy of an expansion around four dimensions, i.e., the ϵ expansion where $\epsilon=4-d$.

III. DERIVATION OF BARE SERIES FOR REACTION RATES

The quantity of greatest experimental interest is the long-time reaction rate k, where $N(t)\sim e^{-kt}$ and $N(t)$ is the fraction of chains in the ensemble which have not reacted after time t.

The first step in calculating k is to derive the bare perturbation series in the coupling constant u_0. We introduce the Green's function $G(\{c'\},\{c\},t-t')$ for the polymer without a sink in terms of which the solution to Eq. (1) is

$$\begin{aligned}P(\{c\},t)=&P_{\rm eq}(\{c\})\\&+\int_0^t dt'\int d\{c'\}G(\{c'\},\{c\},t-t')\\&\times u_0\delta(c'(0)-c'(N_0))\\&\times P(\{c'\},t')\ .\end{aligned} \tag{4}$$

In the case where the initial distribution differs from the equilibrium one $P_{\rm eq}(\{c\})$, Eq. (4) is valid only for large t (which is our interest here). Integrating Eq. (1) over all configurations $\{c\}$ and noting that F conserves normalization, we have

$$\frac{dN}{dt}=u_0\int d\{c\}\delta(c(0)-c(N_0))P(\{c\},t)\ . \tag{5}$$

We remark at this stage that Wilemski and Fixman's closure approximation[9] amounted to approximating

$$\delta(c(0)-c(N_0))P\simeq\delta(c(0)-c(N_0))P_{\rm eq}\nu(t)\ ,$$

where the time-dependent factor $\nu(t)$ is determined self-consistently. Let us now introduce the transient part σ of the Green's function

$$G(\{c'\},\{c\},t)\equiv\sigma(\{c'\},\{c\},t)+P_{\rm eq}(\{c\})\ .$$

With the help of Eq. (5) we express Eq. (4) in terms of σ and find

$$\begin{aligned}P(\{c\},t)=&P_{\rm eq}(\{c\})N(t)\\&+u_0\int_0^t dt'\int d\{c'\}\sigma(\{c'\},\{c\},t-t')\\&\times\delta(c'(0)-c'(N_0))\\&\times P(\{c'\},t')\ .\end{aligned} \tag{6}$$

Solving the Laplace transform of Eq. (6) in terms of $P_p(\{c\})$, where the subscript p denotes the Laplace transform variable, and substituting the latter into the Laplace transform of Eq. (5) we obtain ($\mathcal{L}$ denotes Laplace transform)

$$\mathcal{L}\left[\frac{dN}{dt}\right]=z_pN_p \ , \tag{7a}$$

where

$$z_p=u_0\int d\{c\}\delta(c(0)-c(N_0)) \times[(I-u_0\hat{O}_p)^{-1}P_{\text{eq}}](\{c\}) \ , \tag{7b}$$

and

$$\hat{O}_p(\{c'\},\{c\})\equiv\delta(c'(0)-c'(N_0))\sigma_p(\{c'\},\{c\}) \ . \tag{7c}$$

We now assume that the long-time behavior is exponential: $N(t)\sim e^{-kt}$. It then follows that k is minus the smallest pole of N_p. From Eq. (7a) $N_p=1/(p-z_p)$, so k is the smallest root of the equation

$$k+z_{-k}=0 \ . \tag{8}$$

Expanding the operator $(I-u_0\hat{O}_p)^{-1}$ in Eq. (7b) yields a series for z_p. Inserting this into Eq. (8) and solving Eq. (8) for k in powers of u_0, we find to second order

$$-k=u_0\rho_{\text{eq}}+u_0^2\int_0^\infty dt\int d\{c\}d\{c'\}P_{\text{eq}}(\{c'\}) \times\delta(c'(0)-c'(N_0)) \times\sigma(\{c'\},\{c\},t) \times\delta(c(0)-c(N_0)) \ . \tag{9}$$

where ρ_{eq} is the probability to be looped in equilibrium.

Defining $R_t\equiv c(0,t)-c(N_0,t)$ to be the end-to-end vector at time t and using the definition of $\sigma\equiv G-P_{\text{eq}}$ we find that Eq. (9) can be rewritten:

$$-k=u_0\langle\delta(R)\rangle+u_0^2\int_0^\infty dt[\langle\delta(R_0)\delta(R_t)\rangle -\langle\delta(R)\rangle^2]+O(u_0^3) \ . \tag{10}$$

In Eq. (10) all averages refer to a polymer without a sink; the second order term is the finite part of the time integral of the "return probability" that an initially looped polymer is looped again at time t. To obtain k to second order in all coupling constants the average in the first term in Eq. (10) must be evaluated to first order in $\tilde{e}_0$ (statics being unaffected by hydrodynamics) while the average in the second term is that of the Rouse model [obtained by setting $\tilde{e}_0=T_{\alpha\beta}=0$ in Eqs. (2) and (3)].

Considering first the static quantity $\langle\delta(R)\rangle$ we have

$$\langle\delta(R)\rangle=\int d\{c\}e^{-H}\delta(c(0)-c(N_0))\Big/\int d\{c\}e^{-H} =\langle\delta(r)\rangle_0+\langle\delta(r)\rangle_0\langle H_I\rangle_0 -\langle H_I\delta(R)\rangle_0+O(\tilde{e}_0^2) \ , \tag{11}$$

where H_I is defined in Eq. (3), we have expanded to first order in $\tilde{e}_0$ and

$$\langle\cdots\rangle_0\equiv\int d\{c\}e^{-H_0}\{\cdots\}\Big/\int d\{c\}e^{-H_0} \ . \tag{12}$$

By use of the static Green's function for a Gaussian chain, it is straightforward to obtain

$$\langle H_I\rangle_0=\frac{\tilde{e}_0}{(2\pi)^{d/2}}\int_0^{N_0}\int_{\substack{0\\ \tau>\tau'}}^{N_0}d\tau\, d\tau'\frac{1}{|\tau-\tau'|^{d/2}} \ ,$$

$$\langle H_I\delta(r)\rangle_0=\frac{\tilde{e}_0}{(2\pi)^{d}}\int_0^{N_0}\int_{\substack{0\\ \tau>\tau'}}^{N_0}d\tau\, d\tau'\frac{1}{\{[N_0-(\tau-\tau')](\tau-\tau')\}^{d/2}} \ . \tag{13}$$

The integrals in Eq. (13) diverge like $1/\epsilon$ (where $\epsilon=4-d$) as d approaches 4. Noting that $\langle\delta(R)\rangle_0$ is simply the equilibrium loop probability for a Gaussian chain of length N_0, Eq. (13) in Eq. (11) yields to first order in $\tilde{e}_0$:

$$\langle\delta(R)\rangle=\frac{1}{(2\pi N_0)^{d/2}}-\frac{6\tilde{e}_0N_0^{2-d}}{(2\pi)^d}\frac{1}{\epsilon}+\mathcal{T}_{\text{ns}} \tag{14}$$

where $\mathcal{T}_{\text{ns}}$ denotes terms depending nonsingularly on dimension d.

Turning to the second term in Eq. (11) we find

$$\langle\delta(R_0)\delta(R_t)\rangle_0=\frac{1}{(2\pi)^{2d}}\int d^dk\, d^dl\, e^{-g(k,l)} \ ,$$

where

$$g(k,l)=(1/2d)[(k^2+l^2)\langle R^2\rangle_0+2(k\cdot l)\langle R_0\cdot R_t\rangle_0] \ . \tag{15}$$

To obtain Eq. (15) the δ functions were expressed in integral form and we have used the fact that under the averaging defined by Eq. (12) R_t is a Gaussian variable. The integral in Eq. 15 can be obtained from the general result (valid when $a_{ij}=a_{ji}$):

$$\int\prod_{i=1}^n d^dx_i\exp\left[-\sum_{i,j=1}^n a_{ij}x_ix_j\right]=\frac{\pi^{nd/2}}{(\det\{a_{ij}\})^{d/2}} \ , \tag{16}$$

by setting $n=2$ $a_{11}=a_{22}=\langle R^2\rangle_0/2d$, and $a_{12}=a_{21}=\langle R^2\rangle_0\tilde{f}(t)/2d$. Here $\tilde{f}(t)$ is the dimensionless correlation function for Rouse dynamics:[19]

$$\tilde{f}(t)\equiv\frac{\langle R_0\cdot R_t\rangle}{\langle R^2\rangle}=\frac{8}{\pi^2}\sum_{\text{odd }p}\frac{e^{-\pi^2p^2t/\zeta_0N_0^2}}{p^2} \ . \tag{17}$$

Thus we find

$$\int_0^\infty dt[\langle \delta(R_0)\delta(R_t)\rangle_0-\langle\delta(R)\rangle_0^2]$$
$$=\frac{1}{(2\pi N_0)^d}\frac{\zeta_0 N_0^2}{\pi^2}\int_0^\infty dt\left[\frac{1}{[1-f^2(t)]^{d/2}}-1\right], \tag{18}$$

where we define $f(\pi^2 t/\zeta_0 N_0^2)\equiv\tilde{f}(t)$. From Eq. (17) we find the small-time behavior of $f(t)$ is given by

$$f(t)\sim 1-\frac{4t^{1/2}}{\pi^{3/2}}\ . \tag{19}$$

Using this result in Eq. (18) enables us to determine the singular (at $d=4$) part of the expression in Eq. (18) which again diverges like $1/\epsilon$:

$$\int_0^\infty dt[\langle \delta(R_0)\delta(R_t)\rangle_0-\langle\delta(R)\rangle_0^2]$$
$$=\zeta_0 N_0^{2-d}\pi^{-2-d/4}2^{-(5d/2)+2}1/\epsilon+\mathcal{T}_{\rm ns}\ . \tag{20}$$

Defining dimensionless coupling constants $w_0\equiv u_0L^{\epsilon/2}\zeta_0$, and $e_0\equiv\tilde{e}_0L^{\epsilon/2}$, and substituting Eqs. (14) and (20) into Eq. (10) we obtain finally for the bare series

$$-kN_0^2=A\frac{w_0}{\zeta_0}\left[\frac{N_0}{L}\right]^{\epsilon/2}+\frac{w_0^2}{\zeta_0}\left[\frac{N_0}{L}\right]^{\epsilon}\left[\frac{B}{\epsilon}+C\right]$$
$$+\frac{w_0e_0}{\zeta_0}\left[\frac{N_0}{L}\right]^{\epsilon}\left[\frac{D}{\epsilon}+E\right],$$

where

$$A=(2\pi)^{(\epsilon/2)-2}\ ,$$
$$B=4^{(5\epsilon/4)-4}\pi^{(\epsilon/4)-3}\ , \tag{21}$$
$$D=6(2\pi)^{\epsilon-4}\ ,$$

and C and E are dimensionless and depend nonsingularly on spatial dimension. L is a phenomenological length scale.[18]

We remark that $-k$ is synonymous with the ground-state eigenvalue (which of course vanished in the sink-free case), and we have also obtained the series to second order, Eq. (21), by using the methods of standard quantum-mechanical perturbation theory.[20,21]

IV. RENORMALIZED PERTURBATION THEORY FOR REACTION RATES

In this section we proceed to renormalize the bare series for the reaction rate k [Eq. (21)], to derive the renormalization-group equations for k and to obtain the solutions of the latter. In IV A we consider cases with no hydrodynamic interaction [$T_{\alpha\beta}=0$ in Eq. (2)], termed "free-draining" cases in the polymer literature. There are two such cases; Rouse model plus sink and Rouse model plus excluded volume plus sink. In Sec. IV B we consider the so-called non-free-draining cases (hydrodynamic interaction included), namely, the "Zimm" model[19] plus sink [$\tilde{e}_0=0$ in Eq. (3)] and the Zimm model plus excluded volume plus sink.

In the following subsections we shall make a number of renormalization assumptions. These assumptions are of two types. The first type of assumption is whether a particular model is renormalizable. Physically, what we are assuming by renormalizability is that the model [Eqs. (1), (2), and (3)] is a good coarse-grain description of cyclization. The detailed calculations in the following are at least consistent with this assumption. We should stress that such an assumption is almost universal in renormalization group calculations, except for the small class of models in which perturbative renormalizability may actually be proven.

The second type of assumption concerns the manner in which the renormalization is done. Here the main assumption is that the sink does not change the renormalization of any parameter present in the sink-free case (for example N_0 is renormalized exactly in the same way as in the sink-free case). We view this assumption as being reasonable also. This assumption is verified to the order to which we calculate. More generally, we find it difficult to see how a perturbation restricted to the chain ends (i.e., the sink is at the end of the chain) should change the renormalization of sink-free parameters.

The calculations in the following sections are essentially straightforward application of direct renormalization methods for polymers;[18] we have chosen to make all assumptions we have made explicit for the sake of completeness.

A. Free-draining models

We first consider the Rouse model plus sink case for which the bare perturbation series [$\tilde{e}_0=0$ in Eq. (21)] reads

$$-kN_0^2=A\frac{w_0}{\zeta_0}\left[\frac{N_0}{L}\right]^{\epsilon/2}+\frac{w_0^2}{\zeta_0}\left[\frac{N_0}{L}\right]^{\epsilon}\left[\frac{B}{\epsilon}+C\right]. \tag{22}$$

We now renormalize the theory in the standard way, replacing bare quantities by renormalized quantities which are chosen to eliminate the singularities order by order in the bare perturbation series. In principle, there are four candidates for renormalization: k, N_0, ζ_0, and w_0. However, we can immediately deduce that k is not renormalized, since the reaction rate is a directly observable experimental quantity.[18] In fact, it transpires that to first order in w_0 neither N_0 nor ζ_0 are renormalized (i.e., $N_0=N$, $\zeta_0=\zeta$) as can be seen from the following argument. Since the sink introduces no external forces the diffusion coefficient D is equal to the value for the Rouse model without sink, namely[19] $D=1/\zeta_0N_0$. Since $(\zeta_0N_0)^{-1}=(\zeta Z_\zeta N Z_N)^{-1}$, where $\zeta_0=\zeta Z_\zeta$ and $N_0=NZ_N$, and there are no singularities in D to be absorbed, it follows that $Z_N Z_\zeta$ must contain no singularities. However, we are employing a minimal subtraction scheme and hence $Z_\zeta Z_N=1$.

We next consider the perturbation of certain faster relaxation rates by the sink. Let $\lambda_{1p\alpha}$ denote the eigenvalue of the eigenfunction in which the (p,α)th Rouse model is in the first excited state and all other modes are in the ground state.[21] A straightforward calculation shows that to first order in w_0 the perturbation by the sink of $\lambda_{1p\alpha}$ is nonsingular. Since[21]

$$\lambda_{1p\alpha}=\pi^2 p^2/(\zeta_0 N_0^2)\ ,$$

on replacing $\zeta_0 N_0$ by ζN we find that N_0 is not renormalized to first order in w_0. Consequently to first order in w_0 neither N_0 nor ζ_0 are renormalized.

To determine the renormalization of w_0 to lowest nontrivial order we return to the expression Eq. (22) for the reaction rate. Assuming $w_0=w+A_1 w^2+\mathcal{T}_{\text{HO}}$, where $\mathcal{T}_{\text{HO}}$ denotes higher-order terms, we substitute this expression in (22) to determine the coefficient A_1. To eliminate the singularity in the reaction rate requires

$$\frac{A_1 w^2}{\zeta N^2}A+\frac{w^2 B}{\zeta N^2}\frac{1}{\epsilon}=0\ , \tag{23}$$

whence $A_1=-(B/A)(1/\epsilon)$ (where A and B are evaluated at $d=4$). The explicit value of B/A is $1/64\pi$, so

$$w_0=w-\frac{1}{64\pi}w^2\frac{1}{\epsilon}+\mathcal{T}_{\text{HO}}\ . \tag{24}$$

Having determined the renormalization constants for the Rouse plus sink model to lowest order we proceed to explore the consequences of renormalizability. Assuming the nonrenormalization of ζ_0 and N_0 to all orders ($\zeta_0=\zeta$, $N_0=N$) we obtain the following renormalization-group equation by following the standard procedure:[18]

$$L\frac{\partial k}{\partial L}+\beta(w)\frac{\partial k}{\partial w}=0\ , \tag{25}$$

where $\beta(w)\equiv L(\partial w/\partial L)_{\tilde{w}_0,\zeta_0,N_0}$ and $\tilde{w}_0=w_0 L^{-\epsilon/2}$. Recall that the physical meaning of the renormalization-group equation is an assertion of the existence of macroscopic relationships which are independent of microscopic details.

To investigate the large-N behavior of the model we study (25) at the fixed-point value[18] of $w\equiv w^*$ [i.e., w such that $\beta(w)=0$]. At the fixed point $L(\partial k/\partial L)=0$, so k is independent of L, i.e., we may write $k=f(N,\zeta)$. A standard argument then yields that k has a $1/N^2$ dependence on N. For completeness we recall this argument. From our initial Fokker-Planck equation [Eqs. (1) and (2)] we see there are two dimensions in the problem, namely a contour "length" scale $[\tau]\equiv l$ ([ ] means dimension) and a time scale $[t]\equiv t$. It then follows that $[\zeta]=t/l^2$ and $[k]=1/t$. Let us now rescale t by C_1 so $k=C_1 f(N,C_1\zeta)$, and then l by C_2 so $k=C_1 f[C_2 N, (C_1/C_2^2)\zeta]$. By choosing $C_2=1/N$ and $C_1=1/\zeta N^2$ we see $k=(1/\zeta N^2)f(1,1)$. That is, the existence of a fixed point plus no renormalization of N and ζ implies k scales like $1/N^2$. Moreover, the above argument shows that the ratio of k to the longest relaxation rate for the unperturbed Rouse chain ($\pi^2/\zeta N^2$) is a universal ratio for very long chains under the same assumptions since f is a universal function. Doi[10] had previously derived that k scales like $1/N^2$ with the prefactor independent of the size of the reaction region (for very long chains) within the closure approximation of Wilemski and Fixman.

It is important to note that we have thus far only verified the nonrenormalization of ζ_0 and N_0 to first order in w_0. We believe, however, this result result holds to all orders in w_0. Indeed, we have explicitly calculated k to order w_0^3 (details are planned to be presented elsewhere[22]) and find the theory is only renormalizable to this order provided ζ_0 and N_0 are not renormalized to second order in w_0. Note that if one of N_0,ζ_0 is not renormalized the other is not renormalized since the combination $1/\zeta_0 N_0$ is not renormalized. We now use the relationship between w and w_0 to calculate w^* to first order in ϵ. We use the chain rule to calculate[18] $\beta(w)$ and find to second order in w $\beta(w)=(w/128\pi)(w-w^*)$ where $w^*=-64\pi\epsilon$. Thus $\beta(w)$ has two zeros, $w_t^*=0$ and $w^*=-64\pi\epsilon$. From a crossover result we will present shortly, we will see that $w^*=-64\pi\epsilon$ is the stable zero, namely, no matter which (negative) value of w we "start" with, for a sufficiently long chain we are driven to an "effective" theory with $w^*=-64\pi\epsilon$. Substituting this fixed-point value into the renormalized series for k [i.e., Eq. (22) with w substituted for w_0 according to Eq. (24)] yields the reaction rate to $O(\epsilon)$ for $N\rightarrow\infty$:

$$k=16\epsilon/\pi\zeta N^2\ . \tag{26}$$

From Eq. (26) we see that to order ϵ the ratio of k to the longest relaxation rate for the unperturbed Rouse chain is $16\epsilon/\pi^3$. At $\epsilon=1$, this ratio equals approximately 0.52. Wilemski and Fixman have numerically evaluated this ratio to be ≈ 0.46 in the closure approximation for the choice of the sink function S where immediate reaction occurs when the reacting groups are closer than some distance b. To our knowledge, no systematic experimental study of the dependence of k on molecular weight has been performed yet in melts and since our theory is applicable only to long chains, it seems unlikely to be directly applicable due to the neglect of entanglements. However, Sakata and Doi[23] have performed numerical simulations of Rouse chains with reacting groups on the ends. These results suggest that k goes as $1/N^2$; however, the chains in the simulation were apparently too short to test the value and universality of the above-mentioned ratio.

Finally, we present a crossover result (in the molecular weight) for the reaction rate k. By solving the renormalization-group equation [Eq. (25)] for finite chains (that is, $w\neq w^*$) and manipulating the perturbation series for k in the standard way[18] (see Appendix A for a similar calculation) we obtain the following crossover result to order ϵ:

$$k=\frac{X}{1+X}\frac{16}{\pi}\frac{\epsilon}{N^2\zeta}\ , \tag{27}$$

where

$$X=\left[\frac{N}{L}\right]^{\epsilon/2}\frac{w}{w^*-w}\ .$$

This result interpolates between the weak-sink small molecular weight limit ($X\ll 1$) and the strong-sink high molecular weight limit ($X\gg 1$). In the former limit the $N^{-d/2}$ dependence is that of first-order perturbation theory in which the rate is proportional to the equilibrium probability of the ends being together $\rho_{\rm eq}$. The $X \gg 1$ limit is our asymptotic result [Eq. (26)]. Note that Eq. (27) is valid only for $w^* < w < 0$.

We now consider the addition of excluded volume, i.e., the case of Rouse plus excluded volume plus sink. This case is conceptually similar to the previous case, Rouse plus sink.

The bare perturbation theory for k (to second order) is the full expression, Eq. (21). There are again potentially three quantities to renormalize: N_0, ζ_0, and w_0. To first order we can show that the renormalization of N_0 and ζ_0 is the same as for the dynamics of a sink-free Rouse chain with excluded volume, that is,

$$\begin{aligned} N_0 &= N\left[1-\frac{e}{2\pi^2\epsilon}+\mathcal{T}_{\rm HO}\right] \equiv NZ_N \ , \\ \zeta_0 &= \zeta\left[1+\frac{e}{2\pi^2\epsilon}+\mathcal{T}_{\rm HO}\right) \equiv \zeta Z_\zeta \ . \end{aligned} \tag{28}$$

We show this by noting first that the diffusion constant D equals $1/\zeta_0 N_0$ (internal forces "added" by excluded volume do not affect the motion of the center of mass) so D is not renormalized and $Z_\zeta Z_N = 1$. As before, $\lambda_{1p\alpha}$ does not pick up any singularities from the sink term to first order so Z_N is determined by the perturbation of $\lambda_{1p\alpha}$ due to excluded volume only. We thus conclude Z_N and Z_ζ are the same as the no sink case to lowest nontrivial order. Substituting into Eq. (20) $N_0 = Z_N N$, $\zeta_0 = Z_\zeta \zeta$, and $e_0 = e$ where e is the renormalized excluded-volume parameter [since e_0 appears only in the factor $e_0 w_0$ we only need $e_0(e)$ to lowest order] we determine

$$w_0 = w\left[1+\left[\frac{1}{\pi^2\epsilon}\right]e-\left[\frac{1}{64}\frac{1}{\pi\epsilon}\right]w+\mathcal{T}_{HO}\right] \ . \tag{29}$$

Assuming renormalizability we now write down a renormalization-group equation for k (derived in the standard way:[18]

$$\left[L\frac{\partial}{\partial L}+\beta_e(e)\frac{\partial}{\partial e}+\beta_w(e,w)\frac{\partial}{\partial w} +\gamma_N(e)N\frac{\partial}{\partial N}+\gamma_\zeta(e)\zeta\frac{\partial}{\partial \zeta}\right]k = 0 \ , \tag{30}$$

where

$$\beta_e(e) = L\left[\frac{\partial e}{\partial L}\right]_{\tilde{e}_0,\tilde{w}_0,N_0,\zeta_0} \ ,$$

$$\beta_w(e,w) = L\left[\frac{\partial w}{\partial L}\right]_{\tilde{e}_0,\tilde{w}_0,N_0,\zeta_0} \ ,$$

$$\gamma_N(e) = L\left[\frac{\partial \ln Z_N}{\partial L}\right]_{\tilde{e}_0,\tilde{w}_0,N_0,\zeta_0} \ ,$$

and

$$\gamma_\zeta(e) = L\left[\frac{\partial \ln Z_\zeta}{\partial L}\right]_{\tilde{e}_0,\tilde{w}_0,N_0,\zeta_0} \ .$$

Note that $\tilde{w}_0 = u_0\zeta_0$. We have assumed β_e, γ_N, and γ_ζ are independent of w (see below).

For simplicity, we will only consider the solutions of this equation in the limit of strong excluded volume, namely, $e = e^*$ where $\beta_e(e^*) = 0$. Furthermore, we shall assume that e_0 is renormalized in exactly the same way as in the sink-free case; in particular, e^* equals its static fixed point value. In the limit of very long chains ($e = e^*$, $w = w^*$) Eq. (30) simplifies to

$$\left[L\frac{\partial}{\partial L}+\gamma_N(e^*)N\frac{\partial}{\partial N}+\gamma_\zeta(e^*)\zeta\frac{\partial}{\partial \zeta}\right]k = 0 \ . \tag{31}$$

We showed above that N_0 and ζ_0 are renormalized exactly as for the problem without sink, i.e., Rouse model plus excluded volume, to first order. If we assume this is true to all orders Eq. (31) plus ordinary dimensional analysis then implies that

$$k = N^{-1-2\nu}\zeta^{-1}L^{-1}L^{2\nu}g(1,1) \ , \tag{32}$$

where ν is the static exponent (i.e., $\langle R^2\rangle \sim N^{2\nu}$) and $g(\zeta,N)$ is a universal function. For a derivation of Eq. (32) see Appendix A where Eq. (30) is also solved for general $w \neq w^*$. Under the above assumptions the ratio of k to the slowest nonsink relaxation rate τ^{-1} (where[24] $\tau \sim N^{\nu Z}$, $z = 2 + 1/\nu$) is again universal. This ratio should be accessible to computer simulations, though probably not to experiment.

We now turn to the determination of w^* to order ϵ for which we must calculate $\beta_w(e^*, w)$. It is straightforward (see Oono[18] for analogous computations) to show from Eq. (29) that

$$\beta_w(e,w) = (e/2)w\left[1+\left[\frac{1}{64\pi}\right]\frac{1}{\epsilon}w-\left[\frac{1}{\pi^2\epsilon}\right]e+\mathcal{T}_{\rm HO}\right] \ . \tag{33}$$

Substituting[18] $e^* = \pi^2\epsilon/2$ determines the two fixed points $w^* = -32\pi\epsilon$ and $w_t^* = 0$. A crossover analysis similar to that for the Rouse plus sink case shows w^* is the stable fixed point (see Appendix A). Substituting for $e_0(e)$ and $w_0(w)$ into Eq. (21) yields the renormalized series for k. Setting $e = e^*$ we obtain

$$k = \frac{w}{(2\pi)^2}\frac{1}{\zeta N^2}+\mathcal{T}_{\rm HO} \ . \tag{34a}$$

Using the fixed-point value $w = w^*$ gives the asymptotic ($N \to \infty$) value of k to $O(\epsilon)$:

$$k = 8\epsilon/(\pi\zeta N^2) \ . \tag{34b}$$

Since to zeroth order in ϵ the relaxation rate equals the Rouse value of $\pi^2/\zeta N^2$, Eq. 34b implies the ratio of k to the longest relaxation rate without sink equals $8\epsilon/\pi^3$ to order ϵ.

To understand the above results for the two free-draining cases note for free-draining models the dynamical exponent is[24] $z = 2 + 1/\nu$. When[18] $d > 4$, $\nu = 1/2$ so that the volume explored after time t, $\simeq t^{d/z}$, increases more rapidly than t; this is noncompact exploration[17] and we expect that the sink is a weak perturbation and k obeys a mean field "law of mass action" (LMA), i.e., is proportional to the equilibrium probability that the reactive groups are together, namely, ρ_{eq} of Eq. (9). Correspondingly $w^*=0$ is stable for $d>4$. When $d<4$ an argument based on hyperscaling (presented below) shows that $d/z<1$ and the exploration is compact. The sink is now a relevant perturbation and the nonzero fixed point becomes stable. From the results presented above the corresponding behavior is diffusion-controlled (DC) in that k scales as the longest relaxation rate. To show that $d/z<1$ for $d<4$ in free-draining cases, first note that the hyperscaling relation[12] implies $\nu=(2-\alpha)/d$ where ν is defined as before and α in the case of critical phenomena is the specific heat exponent. For polymers,[25] $\alpha>0$ for $d\leq 4$ so this means $\nu\leq 2/d$. Secondly, we note that $2-4/d\leq 1$ for $0\leq d\leq 4$, so $(2/d)(d-2)\leq 1$. It follows that $\nu(d-2)\leq 1$, i.e., $d\leq 1/\nu+2$ which translates to $d\leq z$.

B. Non-free-draining models

In this section the two non-free-draining cases will be treated: The Zimm model plus sink (the Zimm model[19] is defined to be the Rouse model plus hydrodynamics) and the Zimm model plus excluded volume plus sink. These models describe dilute chains in θ solvents and good solvents respectively. Up to the point where we determine the fixed points we will handle these cases simultaneously. The starting point is the expression for the bare reaction rate Eq. (21). Note that the bare reaction rate (to second order) is the same for the free-draining and the non-free-draining cases; differences arise only through renormalization. Defining $\xi_0\equiv(\zeta_0/\eta_0)L^{\epsilon/2}$, Eq. (21) is rewritten:

$$\begin{aligned}-kN_0^2=w_0AN_0^{\epsilon/2}/(\xi_0\eta_0)&\\+(w_0^2L^{-\epsilon/2}N_0^{\epsilon}/\xi_0\eta_0)(B/\epsilon+C)&\\+(w_0e_0L^{-\epsilon/2}N_0^{\epsilon}/\xi_0\eta_0)(D/\epsilon+E)\ ,&\qquad(35)\end{aligned}$$

where A, B, C, D, and E are defined as before [see Eq. (21)]. ξ_0 is a dimensionless coupling constant which measures the strength of hydrodynamic interaction.

Before proceeding to renormalize Eq. (35), let us pause to anticipate results for the non-free-draining cases. For $d>4$ the picture is as before: space is explored noncompactly since[18] $z=4$ and we will find that $w^*=0$ is stable as expected. But for $d<4$ since[24] $z=d$, we see that the exploration is marginal; one cannot *a priori* determine which of the two fixed points, LMA or DC will be stable. This geometric aspect is reflected by the fact that the coupling constant u_0 is now dimensionless independent of spatial dimension [as is seen by dimensionally analyzing Eq. (2) for $T_{\alpha\beta}\neq 0$]. Consequently, there is an arbitrariness in the choice of the coupling constant corresponding to the sink; we are guided to the choice $w_0=\zeta_0u_0L^{\epsilon/2}$ by the free-draining calculation and by the expectation that a term $1/\xi_0$ should naturally factor out of the bare longest relaxation rate as it does in ordinary polymer hydrodynamics.[18]

We now turn to the renormalization of the model. Since η_0 is not renormalized in polymer hydrodynamics[18] there are four candidates for renormalization: w_0, e_0, ξ_0, and N_0. We shall assume the renormalization of static quantities is not affected by the sink. Thus[18]

$$\begin{aligned}&e_0=e\left[1+\left[\frac{2}{\epsilon\pi^2}\right]e+\mathcal{T}_{\mathrm{HO}}\right]\ ,\\&N_0=NZ_N,\quad Z_N=1-\frac{e}{2\pi^2\epsilon}+\mathcal{T}_{\mathrm{HO}}\ .\end{aligned}\qquad(36)$$

Under these assumptions one can show that the renormalization of ξ_0 is not affected by the sink to second order in the coupling constants, that is,[18]

$$\xi_0=\xi\left[1+\frac{3}{(8\pi^2\epsilon)}\xi+\frac{1}{(2\pi^2\epsilon)}e+\mathcal{T}_{\mathrm{HO}}\right]\ .\qquad(37)$$

To show this, we have examined the perturbation to first order of $\lambda_{1p\alpha}$ by the sink, which we find to be nonsingular. Hence the renormalization of ξ_0 is determined by the singularities arising from hydrodynamics and excluded volume (to this order) and thus is left unchanged from the sink-free value. (Note that the first-order calculation for $\lambda_{1p\alpha}$ determines the renormalization of ξ_0 to second order, just as it does in ordinary polymer hydrodynamics.[18]) We thus need only determine the renormalization of w_0. Substituting the form $w_0=w(1+C_1w+C_2e+C_3\xi+\mathcal{T}_{\mathrm{HO}})$ into Eq. (35) [along with the expressions for e_0, N_0, and ξ_0 in terms of renormalized quantities, see Eqs. (36) and (37)] and choosing C_1, C_2, and C_3 to eliminate the poles in ϵ, we find $C_1=-1/(64\pi\epsilon)$, $C_2=1/(\pi^2\epsilon)$, and $C_3=3/(8\pi^2\epsilon)$.

Assuming the renormalizability of the model we write down the following renormalization-group equation (derived in the standard way):

$$\left[L\frac{\partial}{\partial L}+\beta_e(e)\frac{\partial}{\partial e}+\beta_w(e,w,\xi)\frac{\partial}{\partial w}+\beta_\xi(e,\xi)\frac{\partial}{\partial\xi}+\gamma_N(e)\frac{\partial}{\partial N}\right]k=0\ ,\qquad(38)$$

where $\beta_e(e)\equiv L(\partial e/\partial L)_{\tilde{e}_0}$, $\beta_\xi(e,\xi)\equiv L(\partial\xi/\partial L)_{\tilde{e}_0,\zeta_0}$, and $\gamma_N(e)\equiv L(\partial\ln Z_N/\partial L)_{\tilde{e}_0}$ are the same as in ordinary polymer hydrodynamics[18] and

$$\beta_w(e,w,\xi)\equiv L(\partial w/\partial L)_{\tilde{e}_0,\tilde{w}_0,\zeta_0}$$

(we have used an abbreviated notation for the quantities which are fixed during differentiation).

We will not discuss the consequences of the existence of a nontrivial fixed point and our renormalization procedure since the existence of a physical nontrivial fixed point is *a priori* unclear. (The sink for $d\leq 4$ is always a "marginal" perturbation.) We turn then to a determination of the fixed points to lowest nontrivial order. From the definition of β_w we find (for an analogous calculation see Ref. 18)

$$\beta_w = (\epsilon/2) w (1 - C_1 w - C_2 e - C_3 \xi) \ , \qquad (39)$$

with C_1, C_2, and C_3 defined as before. Considering firstly the Zimm case we find at the nondraining, Gaussian fixed point[18] ($e^* = 0$ $\xi^* = 8\pi^2\epsilon/3$) that $\beta_w = w^2/(128\pi)$. That is, to order ϵ, there is a double zero at $w_t^* = 0$ (the β function has no nontrivial fixed point). In the second case, Zimm plus excluded volume, we find at the nondraining self-avoiding fixed point[18] ($e^* = \pi^2\epsilon/2$, $\xi^* = 2\pi^2\epsilon$) that

$$\beta(w) = \frac{-w}{128\pi}(w^* - w) \ , \qquad (39a)$$

where $w^* = 16\pi\epsilon$. Here the β function has a nontrivial zero but this zero is positive (corresponding to creation of probability) and thus unphysical. The physical fixed point again vanishes: $w_t^* = 0$. Therefore to understand the large N behavior of k we must study crossover behavior describing the approach of w to $w_t^* = 0$.

In the Zimm case, solving the renormalization-group equation for finite w (of order ϵ) and manipulating[18] the perturbation series for k we obtain (see Appendix B)

$$k = -\left[\frac{12}{\pi^3 \eta N^{d/2} \epsilon}\right] \frac{1}{X} \ , \qquad (40)$$

where $X = 128\pi/w + \ln(L/N)$.

Although w, X, and N are not universal parameters, the functional relationship given above is universal. If we assume that w is only weakly dependent on N (we expect a leading N-independent term but we stress that this is an assumption concerning a nonuniversal quantity), then one has $k \sim N^{-d/2}/\ln(N/L)$ as $N \to \infty$. Note this is qualitatively similar to Doi's result.[10] We can explain experimental results in θ solvents by assuming w is small and N is relatively small (but large enough so the model makes sense). In this case (in three dimensions) according to Eq. (40) k scales as $N^{-3/2}$ with a prefactor strongly dependent on the reactive end groups. This appears to be what is observed experimentally.[15]

In the good solvent case, solving the renormalization-group equation for finite w and manipulating the perturbation series for k we find (see Appendix C)

$$k = (2/\pi^3\eta)(L/N)^{\nu d} L^{-d/2}[1/(X-1)] \ , \qquad (41)$$

where

$$X = \left[\frac{N}{L}\right]^{\epsilon\nu/4} \left[\frac{w - w^*}{w}\right], \quad w^* = 16\pi\epsilon \ .$$

Equation (41) implies $k \sim N^{-\nu(d+\epsilon/4)}$ for large N, with a nonuniversal prefactor. Since[18] $\nu = \frac{1}{2}(1 + \epsilon/8 + \cdots)$ we see that to order ϵ this is $k \sim \tilde{\rho}_{\mathrm{eq}}$ where $\tilde{\rho}_{\mathrm{eq}}$ is the renormalized equilibrium loop probability[12] $\tilde{\rho}_{\mathrm{eq}} \sim N^{-\nu(d+g)}$ and $g = \epsilon/4 + \cdots$ the exponent describing the correlation hole.[12,18,26] Thus k has the law of mass action form as expected from the stability of the fixed point $w^* = 0$. The present experimental data cannot quite distinguish between this result and the diffusion controlled prediction that k should scale as the inverse relaxation time, $k \sim N^{-\nu d}$.

To close this section we make the final obvious (at this point) though important comment that in non-free-draining cases the ratio of the unperturbed slowest relaxation rate to the reaction rate is, to order ϵ, 0. We conjecture the preceding statement to be true to every order in ϵ (within the Oseen tensor description of hydrodynamics.)

V. CONCLUSIONS

We have developed a direct renormalization scheme to calculate polymer cyclization rates k. For free-draining models we find that the ratio of k to the unperturbed relaxation rate for long chains in universal for $d < 4$: Under the renormalization group, the models are driven to diffusion-controlled behavior in a universal manner independently of the chemistry of the reacting ends (in particular, this universality is *not* restricted to the case where reaction occurs on every encounter of the end groups). When hydrodynamics is included we find that for $d < 4$ the stable fixed-point value of the sink coupling constant vanishes to order ϵ. Intuitively, we expect that this is true to all orders. In consequence, the large-N behavior of k is that predicted by mean-field theory with logarithmic corrections in the case of θ solvents.

Perhaps the most surprising and significant outcome of this work is the prediction that for dilute polymers in good solvents the cyclization rate will *not* scale as the inverse relaxation time of the unperturbed chain (i.e., without reactive end groups). Rather, k is predicted to scale as the equilibrium probability that the end groups are in contact (the mean-field result). The physical origin of this result lies in the existence of the "correlation hole",[12,26] namely, the reduced probability of chain end contact when excluded-volume interactions are important (as in good solvents). As discussed in the text, for good solvents the exploration is marginal for $d < 4$; the effect of the correlation hole is to "tip the balance" in the noncompact mean-field direction. To appreciate why this happens, consider the number of "collisions" between two chain ends in one polymer relaxation time τ, which we name Z. We imagine that all reactions are "switched off" and we define the chain "ends" to be the terminal "blobs" containing L units with blob relaxation time t_L. For a chain of N units, we have

$$Z \approx (\tau/t_L)(N/L)^{-\nu(d+g)} \ ,$$

which is the product of the number of "steps" in one relaxation time τ (each step lasting t_L) with the fraction of these steps for which the end blobs are in contact. Ergodicity of the dynamics ensures that this latter fraction is determined by the correlation hole exponent g describing the equilibrium statistics of the chain of N/L blobs. Thus $Z \approx (N/L)^{\nu(z-d-g)}$. Switching on the reactivity of the end blobs once again, this leads to a mean-field estimate of the reaction rate as $k \approx q_L(t_L/\tau)Z$ where q_L is the probability per unit time of reaction when the blobs overlap. This estimate is only sensible if the total probability of reaction in the time τ is small, i.e., if $Zq_L t_L = k\tau$ is much less than unity. For large N this clearly depends on the exponent $z-d-g$. For good solvents $z=d$, and since g is positive $Z \sim N^{-\nu g}$ is arbitrarily small for large enough N; the mean-field result is asymptotically valid and $k \sim Z/\tau$ scales as the equilibrium loop probability. For the Rouse model, on the other hand, $z=4$ and $g=0$ whence $Z \sim N^{\nu\epsilon}$. Thus for $d<4$ Z becomes very large for large N, i.e., the number of collisions in τ becomes very large. Hence in the time τ reaction is almost certain and "diffusion-controlled" behavior is recovered, i.e., $k \sim \tau^{-1}$. From this discussion it is clear that the criterion governing the asymptotic form of k involves more than the compactness or otherwise of the exploration. The relevant criterion is the parameter Z. Depending on the N dependence of Z, k is driven to a diffusion-controlled or mean-field asymptotic form (regardless of the reactivity of the end groups).

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APPENDIX A

In this appendix we derive the solution to the renormalization-group equation for Rouse plus excluded volume plus sink, at the excluded volume fixed point. At the fixed point $e=e^*$ Eq. (30) has the form

$$L\frac{\partial k}{\partial L}+\beta_w(w)\frac{\partial k}{\partial w}+\gamma_N^* N\frac{\partial k}{\partial N}+\gamma_\zeta^*\zeta\frac{\partial k}{\partial \zeta}=0\ , \tag{A1}$$

where we write $\beta_w(w)\equiv\beta_w(e^*,w)$, $\gamma_N^*\equiv\gamma_N(e^*)$, and $\gamma_\zeta^*\equiv\gamma_\zeta(e^*)$. However, since $Z_N Z_\zeta=1$ then $\gamma_\zeta^*=-\gamma_N^*$ and we call $\gamma_N^*=\gamma^*$. Equation (A1) has the solution

$$k=f\left[LN^{-1/\gamma^*},L\zeta^{1/\gamma^*},L\exp\left[-\int_{w_1}^{w}\frac{ds}{\beta_w(s)}\right]\right] \tag{A2}$$

where f is an arbitrary well-behaved function. From Eq. (33) with $e=e^*$ it follows that

$$\beta_w(e^*,w)\equiv\beta_w(w)=[w/(128\pi)](w-w^*)$$

with $w^*=-32\pi\epsilon$.

Consequently, we find the last argument in (A2) equals $L[(w^*-w)/w]^{4/\epsilon}$. We next apply dimensional analysis to the solution, rescaling the time dimension t by $C_1=(L^2\zeta)^{-1}(N/L)^{-2\nu(2-\gamma^*)}$, where $2\nu=(1-\gamma_N^*)^{-1}$, and the contour dimension l by $C_2=L^{-1+2\nu}N^{-2\nu}$. It follows that k has the form

$$k=C_1 f\{1,1,(N/L)^{-2\nu}[(w^*-w)/w]^{4/\epsilon}\}\ . \tag{A3}$$

Thus a good variable for the solution is $Q\equiv(L/N)^{\nu\epsilon/2}[(w^*-w)/w]$.

Now we manipulate our first-order result for the reaction rate, Eq. (34a), into the form (A3) assuming $w^*\le w\le 0$. To order ϵ,

$$w=w^*(1+Q)^{-1}\ . \tag{A4}$$

Substituting (A4) in Eq. (34a) we conclude

$$k=-w^*(1+Q)^{-1}(2\pi)^{-2}(L^2\zeta)^{-1}(N/L)^{-2\nu-1} \tag{A5}$$

Note that Eq. (A5) is consistent with the form [Eq. (A3)] dictated by the renormalization-group equation. In the small-Q limit this has the form of Eq. (32) and is equivalent to (to within terms of order ϵ^2) Eq. (34A). In the large-Q limit, assuming that w does not depend strongly on molecular weight, we find $k \sim N^{-\nu(d+g)}$ where g agrees to order ϵ with the exponent describing the correlation hole (of course, the natural conjecture is that g is the correlation hole exponent and consequently k scales as the probability in equilibrium that the ends are together).

APPENDIX B

In this appendix we solve the renormalization-group equation for the reaction rate in the case Zimm plus sink, which reads [Eq. (38)]

$$L\frac{\partial k}{\partial L}+\beta_w(w,\xi^*)\frac{\partial k}{\partial w}=0\ , \tag{B1}$$

in the Gaussian non-free-draining limit [here $\xi^*=8\pi^2\epsilon/3$, $\beta_w(w,\xi^*)\equiv\beta w(e^*=0,w,\xi=\xi^*)$]. Equation (B1) has the solution

$$k=F\left[L\exp-\int_{w_1}^{w}\frac{ds}{\beta(s)}\right]\ , \tag{B2}$$

where F is an arbitrary well-behaved function. Recalling that, to $O(\epsilon)$, $\beta(s)=s^2/128\pi$ we have

$$L\exp\left[-\int_{w_1}^{w}\frac{ds}{\beta(s)}\right]=L\exp(128\pi/w)\ . \tag{B3}$$

Rescaling L by $C_1=1/N$, (and since $[k]=[L]^{-d/2}$ it follows that the solution has the form (we work in units where $\eta_0=1$)

$$k=(1/N^{d/2})F((L/N)\exp(128\pi/w))\ . \tag{B4}$$

Hence a good variable for the solution is $X=\ln(L/N)+128\pi/w$. w is then given by

$$w=128\pi[X-\ln(L/N)]^{-1}\ . \tag{B5}$$

Substituting (B5) into the lowest-order renormalized perturbation-theory result [which is identical to Eq. (34a)], we see on substituting the value of ξ^* that

$$k=12[\epsilon\pi^3N^{d/2}(X-\ln L/N)]^{-1}\ . \tag{B6}$$

Since we are free to add and subtract higher-order terms we manipulate Eq. (B6) into

$$k=12(\epsilon\pi^3N^{d/2}X)^{-1}\ , \tag{B7}$$

consistent with Eq. (B4). (Note in doing this we have assumed w is of order ϵ.)

APPENDIX C

In this appendix we derive the solution for Eq. (38) at the excluded volume, nondraining fixed point. In this case the renormalization-group equation is

$$L\frac{\partial k}{\partial L}+\beta_w(e^*,w,\xi^*)\frac{\partial k}{\partial w}+\gamma_N(e^*)N\frac{\partial k}{\partial N}=0\ , \tag{C1}$$

where $e^*=\pi^2\epsilon/2$, $\xi^*=2\pi^2\epsilon$.

The solution to (C1) is

$$k=f\left[LN^{-1/\gamma_N^*},L\exp\left[-\int_{w_1}^{w}\frac{ds}{\beta(s)}\right]\right], \tag{C2}$$

where $\gamma_N^*\equiv\gamma_N(e^*)$. Using the expression for $\beta(s)$ [Eq. (39a)] we find

$$k=f\left[LN^{-1/\gamma_N^*},L\left[\frac{w-w^*}{w}\right]^{-8/\epsilon}\right]. \tag{C3}$$

Applying dimensional analysis to Eq. (C3), by rescaling the dimension of the contour variable by

$$C=L^{\gamma_N^*(1-\gamma_N^*)^{-1}}N^{(-1+\gamma_N^*)^{-1}}\ , \tag{C4}$$

we conclude the solution has the form

$$k=L^{-(d/2)+\nu d}N^{-\nu d}f((N/L)^{-2\nu}[(w-w^*)/w]^{-8/\epsilon})\ , \tag{C5}$$

where $w^*=16\pi\epsilon$. Thus a good variable for the solution is

$$X=(N/L)^{\epsilon\nu/4}(w-w^*)/w\ . \tag{C6}$$

To order ϵ (C6) implies

$$w=-w^*(-1+X)^{-1}\ . \tag{C7}$$

Substituting (C7) into the lowest-order renormalized perturbation theory result for k (which is identical to Eq. (34a) since we are working to lowest order) yields

$$\begin{aligned}k&=-w^*(-1+X)^{-1}L^{(-d/2)+\nu d}N^{-\nu d}\xi^{*-1}(2\pi)^{-2}\\&=2\pi^{-3}(L/N)^{-\nu d}L^{-d/2}(X-1)^{-1}\ .\end{aligned} \tag{C8}$$

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