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Kinetics of Intermolecular Reactions in Dilute Polymer Solutions and Unentangled Melts

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ABSTRACT: Irreversible intermolecular reaction rates k in dilute polymer solutions and unentangled melts are studied as a function of time, molecular weight, and location of reactive groups along the polymer backbones. As for intramolecular reactions, the kinetics are determined by the reaction exponent $\theta \equiv (3 + g)/z$, where z and g are, respectively, the dynamical and excluded volume "correlation hole" exponents. Using scaling arguments, we show that k is *driven* to either mean-field (MF) or diffusion-controlled (DC) behavior, the short time rate $k(t)$ being driven by increasing time, the long time rate k_∞ by increasing chain length N. In parallel, detailed renormalization-group (RG) calculations of k are presented. The RG transformation drives the kinetics to either a DC or MF fixed point in correspondence to the scaling picture. In good solvents, dilute solutions ($\theta > 1$) exhibit intrinsically MF reaction kinetics, irrespective of group reactivity. k is so weakened by intercoil excluded volume repulsions that the DC limit does not exist. Thus $k \sim N^{-\nu g}$ (ν is the Flory exponent) scales as the equilibrium contact probability and for interior groups is related to the statistics of three-arm and four-arm star molecules. At small times $k(t)$ exhibits only a weak time dependence. In contrast, unentangled melts (Rouse dynamics) are intrinsically DC ($\theta < 1$) and $k(t) \sim t^{-1/4}$, $k_\infty \sim N^{-1/2}$ as derived by previous workers. We obtain crossover results describing the "trajectory" from MF to DC for moderately long chains. In Θ solvents ($\theta = 1$) kinetics are marginal and characterized by logarithmic dependencies $k(t) \sim 1/\ln t$ and $k_\infty \sim 1/\ln N$. For reacting polymers of very different lengths k is dominated by the smallest chain in all cases.

I. Introduction

The kinetics of reactions between macromolecules bearing reactive groups (see Figures 1 and 2) are unusual in many respects since the transport of one active group to another depends entirely on the statics and dynamics of the polymer chains to which they are attached. This paper deals with irreversible interpolymeric reactions in two extreme situations: dilute solutions and unentangled polymer melts.[1,2] In the former case the essential features governing the equilibrium and dynamical properties of the polymer chains are hydrodynamic interactions and (for good solvents) excluded volume repulsions, while in melts both types of interaction are screened out.[3,4] Correspondingly, we will see that reaction kinetics belong to different "universality classes" in each of these two situations: for long enough chains, the reaction rate "constant" k has quite different dependencies on degrees of polymerization N_1, N_2 (see Figure 2), on time t and on location (along the backbones of each chain) of the active groups. k is defined in terms of the second-order reaction kinetics which are assumed to govern the evolution of n_1 and n_2, the number densities of polymer chains of species 1 and 2, respectively

$$\dot{n}_1 = \dot{n}_2 = -k\, n_1 n_2 \qquad (1)$$

In the present study we treat reactions involving one active group per polymer; the three relevant classes of group location are illustrated in Figure 2, defined according to the number of groups which are at chain ends and the number which are interior. Now if the experimentalist "switches on" reactions at $t = 0$ (this might be, for example, the instant at which the sample is irradiated to produce reactive radical groups), then $k(t)$ will initially be *time-dependent*, settling down to its asymptotic value, which we will refer to as k_∞, after a transient.

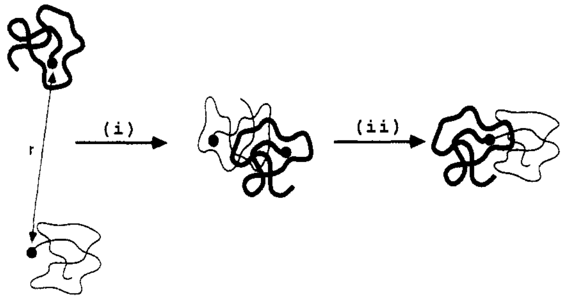

Figure 1. For times much greater than the coil relaxation time τ most of the pairs which have reacted were initially separated by much more than the coil size R, $r \gg R$. Reaction occurs if (i) center of gravity motion (Fickian diffusion) transports coils so they overlap, and then (ii) the small time scale motion can "collide" the reactive groups a sufficient number of times. For $t \ll \tau$ the only pairs which may react are those whose coils initially overlap (process ii).

The need to establish a basic theory of reactions between polymer chains arises from a number of diverse phenomena. The kinetics of interpolymeric reactions are of course fundamental to the evolution of various polymerization processes of industrial importance[5] (e.g. termination in free radical polymerizations[5-9]). Other "polymerizing" systems include solutions of elongated, wormlike, surfactant micelles ("living polymers") whose dynamics involve "reactions" between long flexible chains bearing "reactive" ends.[10,11] Meanwhile many experimental methods have been employed to measure irreversible interpolymeric reaction rates as a probe of fundamental polymer properties[12-15] including a number of fluorescence and phosphorescence studies;[13-16] of particular interest here are experimental measurements of rates of phosphores-

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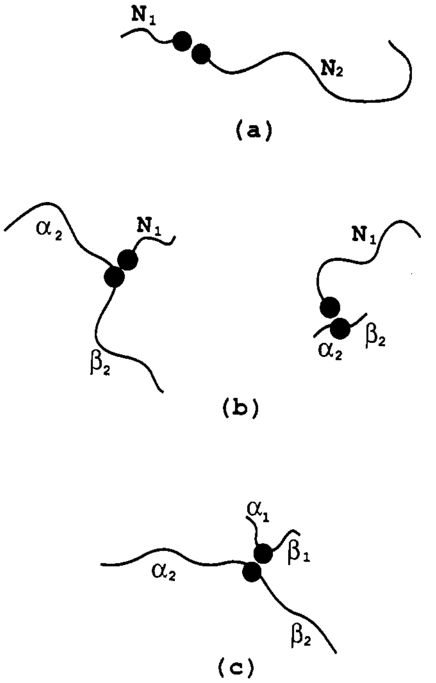

Figure 2. The form of k depends on whether: (a) both polymers bear reactive groups at chain ends; (b) one reactive group is at a chain end and one is internal; (c) both reactive groups are internal. The cases depicted are extreme examples, in which one chain is much longer than the other; k is dominated by the small chain. When one or more of the reactive groups are interior $k \propto \rho_{eq}$ is related to the statistics of three- and four-arm stars (b and c, respectively) through the equilibrium reactive group contact probability density ρ_{eq}.

cence quenching of end-labeled polymers[13,14] in dilute solutions.

In addition to dependencies of k on properties of the *polymer*, one expects the reactivity Q of the active groups themselves will play a role (where Q is the reaction rate per unit time given that a pair of reactive groups are within reacting range of one another). In practice, the magnitude of Q^{-1} spans a huge range, from $\sim 10^{-9}$ s (e.g., in radical polymerizations[5]) to seconds or longer. We will find that the extent to which reaction rates depend on the detailed chemistry of the reactive groups (as embodied by Q and the size of a single chain unit a) depends on chain length and, above all, on the "universality class" of the reaction kinetics. For sufficiently long chains in a melt the dependence on the local chemistry of the reactive groups disappears altogether; k depends, in a universal manner, on the size and relaxation time of the polymer alone. In dilute solution, by contrast, the specific properties of the reactive groups always matter, no matter how large N may be. That is, reaction kinetics in melts are characterized by a higher degree of universality.

Considerable theoretical progress has already been accomplished for the case of unentangled melts (N smaller than the entanglement threshold[17] N_e) whose dynamics are well-described by the Rouse model.[3,4] For reactions between Rouse chains bearing strongly reactive groups (very large Q)[1] Doi obtained $k_\infty \approx DR \approx R^3/\tau$, where D, R, and τ are, respectively, the center of gravity diffusivity, the root mean square (rms) size, and the longest relaxation time of a single polymer coil. The ideas of Doi were further clarified and developed by de Gennes[2,18] who studied interpolymeric reactions in both unentangled and entangled melts for large Q, finding $k_\infty \approx DR$ in both cases. In dilute solutions, however, the present understanding of reaction kinetics is confined to the case of very small Q ("chemically controlled"). Doi[1] showed that, quite generally, k_∞ obeys mean-field theory (MF) whenever Q is very small, i.e. $k \propto \rho_{eq}$, where ρ_{eq} is the equilibrium contact probability density for the reactive groups. Khokhlov[19] considered this limit in dilute solutions with good solvents, finding that $k \propto \rho_{eq}$ was determined by des Cloizeaux's three "correlation hole" exponents.[20]

From the present study we will see the emergence of a simple picture for reactions in dilute solutions. The main result for long chains in good solvents is that, no matter how large Q may be, reaction rates follow MF kinetics: $k = Q_{eff}V(a^3\rho_{eq})$ where Q_{eff} is an effective local reaction rate, dependent on Q (which will be described later), and V is the volume of the reaction vessel. In other words, mean field theory is obeyed even at large Q. That Khokhlov's results[19] should pertain for small Q is physically reasonable, the system remaining close to equilibrium. What is less intuitive is why this should remain true for large Q, in what has been called the "diffusion-controlled" (DC) case.[13,21] In fact "DC" is an inappropriate label; for large chain length N, we find that the system gets "driven" to MF behavior *independently* of the size of Q. The essential feature is that k always involves the small scales, the local properties of the active groups such as reactivity. At first sight this is somewhat counterintuitive; it is perhaps natural to expect that for sufficiently large local reactivity the rate-limiting step should become the transport through space of the chain units bearing the active groups, i.e. the polymer diffusion. This leads to the expectation that k should involve the *polymer* relaxation time τ and its size R. Indeed, this is precisely what happens for Rouse dynamics: from eq 1 the dimensions of k are volume divided by time so the large Q form $k_\infty \approx R^3/\tau$ fulfills these expectations. For Rouse dynamics the term "diffusion-controlled" makes sense, since this result can be thought of in terms of an *effective* capture radius and reactivity[22] equal to R and τ^{-1}, respectively; if ever the two coils of volume R^3 overlap for a time τ, reaction definitely occurs. Only the relatively "large" polymer scales are involved in k_∞. This logic breaks down for dilute polymers in good solvents because excluded volume repulsions strongly reduce the effective reactivity of the groups, the more so the larger N, since the groups are increasingly unlikely to be together. It happens that as N increases, the increase in τ is less rapid (i.e. a lower power of N) than the decrease in this effective reactivity. Therefore, even if Q is very large, the rate-limiting step for sufficiently large N is always the "local" reaction process. One never reaches the "DC" regime; we can say that reaction kinetics are dominated by the excluded volume correlation hole.[3,20]

It should be apparent from this discussion that for polymeric liquids the terms "DC" and "chemically-controlled" should not be used with reference to *local* properties of the reactive groups, in general. Rather, we should define different classes of polymer liquids as being characterized by reaction kinetics which are *intrinsically* DC or MF, in the sense that as $N \rightarrow \infty$ the kinetics will *always* be of that type regardless of the magnitude of Q. Thus we can say that Rouse dynamics are DC; dilute solutions are MF (good solvents). For example, reacting chains in an unentangled melt with weakly reactive groups will always follow DC kinetics provided the chains are sufficiently long. If Q is small, then shorter chains will exhibit MF kinetics, crossing over to DC kinetics at large N; in fact we will study the form of this crossover using renormalization group (RG) methods in section III. An obvious but essential point is that if Q is exceedingly small (as, for example, in many condensation polymerizations[5]), the chain length required to access the asymptotic regime will be unphysically large. In this case the observed kinetics will be MF and the fact that large enough N would give DC kinetics becomes physically irrelevant. The overall scheme we will establish, which is closely related to that for *intra*molecular reactions,[23] generalizes that of de Gennes[2] who classified reaction kinetics according as to whether the short time dynamics involve "compact" or "noncompact" exploration of space.

In the following section our general theoretical framework will be established. We develop two theoretical approaches in parallel; simple scaling arguments and rigorous "first principles" RG theory. The scaling arguments expose the physical meaning of the results in a very clear way, and we have structured the text such that the reader who wishes to avoid the technical details of the RG analysis (all of which are dealt with in appendices) may skip those parts without loss of continuity. Thus the basic forms are derived via scaling arguments which are self-contained, and in the main body of the text we present the RG results which are discussed and related to the scaling ideas. The role of the RG analysis is to justify and extend the scaling results and to identify a number of universal quantities which are experimentally measurable. In section III the theory is applied to the simplest case of unentangled melts (Rouse dynamics), which exemplify DC reaction kinetics. The results of Doi[1] and de Gennes[2] are extended in a number of ways via the RG: various universal observables are identified and the effects of reactive group location, of finite N (crossover), and of unequal chain lengths are examined. Dilute solutions, exhibiting MF kinetics, are considered in section IV and in section V we treat theta solvents. This last case, lacking the strong "correlation hole" effect, turns out to occupy the borderline between the DC and MF behaviors exhibited in melts and good solvents respectively; the kinetics are *marginal.* We conclude in section VI with a general discussion of our results.

II. Theoretical Framework

Each polymer chain of N units bears one reactive group, illustrated in Figure 3 for the particular case of an end group. The chain units are of size a and relaxation time t_a and the reaction probability profile is assumed short-ranged such that after coarse-graining (the chain units already contain several monomers) one can identify just one of the units as "reactive" and correspondingly assign it a reaction rate Q. The interpretation of Q is then (roughly) the reaction probability per unit time given that the reactive units of two chains overlap.

Suppose that at time t there remain $\mathcal{M}_1(t),\mathcal{M}_2(t)$ unreacted polymers of species 1 and 2, respectively, in the reaction vessel of volume V, reactions having begun at $t = 0$. Defining Γ_t to be the pair survival probability, and $n_i \equiv \mathcal{M}_i/V$ the chain number density of species i ($i = 1, 2$), since there are $\approx\mathcal{M}_1\mathcal{M}_2$ pairs for large $\mathcal{M}_i$ one has $\dot{\mathcal{M}}_i(t) = \dot{\Gamma}_t\mathcal{M}_1\mathcal{M}_2$, implying $\dot{n}_i = -kn_1n_2$ with rate "constant" $k(t)$ given by

$$k(t) = -V\dot{\Gamma}_t \tag{2}$$

We remark that implicit in deriving eqs 1 and 2 is the assumption that density fluctuations on scales much greater than the polymer size can be ignored. There is considerable evidence that for spatial dimensions $d > 2$ this is justified.[2,24] The polymer scale fluctuations, however, are crucial and determine the structure of k.

Our scaling arguments which follow will treat the simplest case of identical chains and reactive groups i.e. $N_1 = N_2 \equiv N$. Now at $t = 0$ the coils of rms size $R \equiv aN^{\nu}$ and longest relaxation time $\tau \equiv t_aN^{\nu z}$ are in equilibrium, where ν and z are respectively the (static) Flory and dynamical exponents.[3] Consider one pair of chains, whose reactive groups are separated by r (see Figure 1). Let $P_{\text{eq}}(r<x)$ be the equilibrium probability that $r < x$ and $P_{\text{eq}}(r<x_1|r<x_2)$ the conditional probability that $r < x_1$ *given* $r < x_2$. To estimate the fraction of chains which have reacted, we note that a prerequisite for a pair to have reacted by the time t is that their initial separation be less than the distance which diffusion can transport an active group in the time t, namely the rms displacement of each group which we name x_t. Whenever diffusion brings the groups to within a distance a of one another, reaction is a possibility: each such event, of duration t_a, is called a "collision". Each time the groups "collide" they react with probability $\approx Qt_a$. Thus for small times, $t \ll \tau$, the reacted fraction is approximately given by

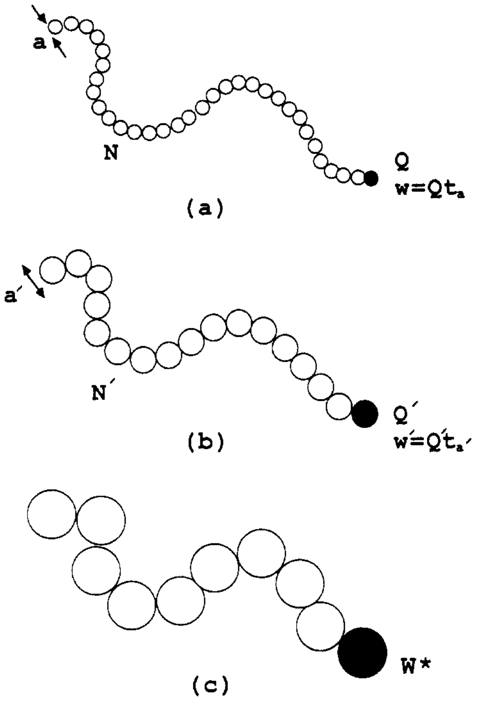

Figure 3. Representation of a polymer bearing a reactive end group, and its evolution under the coarse-graining (RG) transformation. (a) The polymer comprises N units of size a, with end unit of reactivity Q or dimensionless reactivity $w \equiv Qt_a$. (b) Under coarse-graining the number of units decreases: $N \rightarrow N'$. Each of the N' "blobs" is of size $a' > a$. The end blob is reactive, with "renormalized" reaction rate Q' or equivalently w'. (c) After many coarse-graining steps w approaches a fixed point value w^*.

$$1 - \Gamma_t \approx P_{\text{eq}}(r<x_t)\, f[\mathcal{N}(t)],$$
$$\mathcal{N}(t) \equiv QtP_{\text{eq}}(r<a|r<x_t), \qquad t \ll \tau \tag{3}$$

The $P_{\text{eq}}(r<x_t)$ factor in eq 3 is the fraction of pairs initially close enough such that after t the groups may have "collided", while $\mathcal{N}(t)$ is the average number of "reactions" between a pair initially within range (during each of the $(t/t_a)P_{\text{eq}}(r<a|r<x_t)$ "collisions" the reaction probability is Qt_a). In reality, of course, only one reaction can happen: The function f is defined in such a way that $f[\mathcal{N}]$ is the true reaction probability (i.e. the probability of one or more "reactions"). If, for example, each collision were independent, then $f(u) = 1 - e^{-u}$ would have Poissonian form; generally the important features are

$$f(u \ll 1) \sim u, \qquad f(u \gg 1) \rightarrow 1 \tag{4}$$

Note that in general $f[\mathcal{N}(t)]$ may either increase or *decrease* in time since at each instant it represents an average over a different ensemble of reaction pairs (namely, those which were initially within a distance x_t of one another). At long times, $t \gg \tau$ ($x_t \gg R$), one can view reaction as a two-step process: center of gravity diffusion must firstly overlap the coils (Figure 1, process i) before the short time motion may facilitate reaction (Figure 1, process ii). Thus

$$1-\Gamma_t \approx P_{\text{eq}}(r<x_t)\, f[\mathcal{N}(t)],$$
$$\mathcal{N}(t) \equiv \frac{t}{\tau} P_{\text{eq}}(r<R|r<x_t)\, f[\mathcal{N}(\tau)], \qquad t \gg \tau \quad (5)$$

Here $\mathcal{N}(t)$ is the product of (i) the number of distinct times two coils overlap during the time t given they were initially in range, namely $(t/\tau)P_{\text{eq}}(r<R|r<x_t)$, with (ii) the reaction probability during each overlap period of duration τ, namely $f[\mathcal{N}(\tau)]$. But for scales r much larger than the coil size R equilibrium correlations are ideal,[25] i.e. $P_{\text{eq}}(r<R|r<x_t) \approx (R/x_t)^d$ in d-dimensional space. Correspondingly, on time scales much greater than τ the dynamics are simple center of gravity diffusion, $x_t \approx R(t/\tau)^{1/2}$. Hence $(t/\tau)P_{\text{eq}}(r<R|r<x_t) \approx (t/\tau)^{1-d/2}$ which is much smaller than unity for large t/τ provided $d > 2$. But since $f[\mathcal{N}(\tau)]$ is bounded by unity, it follows that $\mathcal{N}(t)$ in eq 5 is itself much less than unity, whence $f[\mathcal{N}(t)] \approx \mathcal{N}(t)$. Thus for the usual case of $d = 3$ we have

$$1-\Gamma_t \approx \frac{t}{\tau} P_{\text{eq}}(r<R) f[\mathcal{N}(\tau)], \qquad t \gg \tau \qquad (6)$$

We note the significance of $d = 2$ as[2] the compact → noncompact crossover dimension for simple Fickian diffusion. Had we aimed to derive eq 6 for low dimensions $d < 2$ the step $f[\mathcal{N}(t)] \approx \mathcal{N}(t)$ would not have been valid (instead $f[\mathcal{N}(t)] \approx 1$ in that case). Indeed, de Gennes[2] has discussed in detail the fundamentally different nature of reaction kinetics above and below two spatial dimensions.

Equations 3 and 6 are our basic scaling results which allow one to obtain k for short and long times, respectively, with the help of eq 2. In subsequent sections these equations will be specialized to melts and dilute solutions. However, we need a more precise theoretical approach for the purpose of justifying the assumptions implicit in the above arguments and in order to make certain detailed experimental predictions. The natural systematic framework is a Fokker–Planck equation[26,27] describing the evolution of $P([\mathbf{r}_1],[\mathbf{r}_2],t)$, namely the joint probability density that the reacting chains 1 and 2 have configurations $[\mathbf{r}_1(n)]_{n=0}^{n=N_1}$ and $[\mathbf{r}_2(n)]_{n=0}^{n=N_2}$ respectively at time t

$$\partial P/\partial t = F_{12}P + u_0\delta(\mathbf{r})\, P, \qquad \mathbf{r} \equiv \mathbf{r}_1(\alpha_1) - \mathbf{r}_2(\alpha_2) \quad (7)$$

where the chains are of N_1 and N_2 units respectively and the ith chain bears a reactive group on its α_ith unit. Let us also define $\beta_i \equiv N_i - \alpha_i$, as illustrated in Figure 2. The operator F_{12} (see Appendix A) would describe two-chain dynamics in the absence of reactive groups. It includes all relevant interchain and intrachain interactions (which depend upon the regime under consideration of course). The last term is a sink which reacts chains, if ever the positions of the reactive groups coincide (i.e. $\mathbf{r} = 0$), with local reaction rate u_0 (which may be thought of as a^dQ in d dimensions). Equation 7 describes a somewhat coarse-grained model. No matter what the chemical details of the actual reactive groups may be, the delta function is believed to be the appropriate coarse-grained sink function (provided the original reaction profile is short-ranged). This point has been discussed elsewhere in the context of intrapolymeric reactions.[28]

Solving perturbatively for k in powers of the coupling constant from eq 7 leads to a bare series whose structure to second order closely resembles that for the case of *intra*molecular reactions[28–30]

$$-\frac{k(t)}{V} = u_0\rho^\circ_{\text{eq}} + u_0^2{\rho^\circ_{\text{eq}}}^2\int_0^t \mathrm{d}t'\, S(t') + O(u_0^3) \qquad (8)$$

where $\rho^\circ_{\text{eq}} \equiv \langle\delta(\mathbf{r})\rangle$ is the equilibrium reactive group contact probability density and $S(t)$ the dimensionless return probability in the absence of reactions,[2] proportional to the contact probability at time t given initial contact:

$$S(t) \equiv \frac{\langle\delta(\mathbf{r}_t)\delta(\mathbf{r}_0)\rangle}{\langle\delta(\mathbf{r})\rangle^2} = \frac{V}{(2\pi)^{d/2}}\left(\frac{d}{{x_{1t}}^2 + {x_{2t}}^2}\right)^{d/2} \qquad (9)$$

Here $\mathbf{r}_t$ is the group separation at time t and x_{it} the rms displacement of the reactive group on chain i. Equations 8 and 9 are derived in Appendix B. The form of $S(t)$ above is correct to zeroth order in all coupling constants (i.e. Rouse dynamics), as appropriate to our overall second order requirements in eq 8. Thus x_{it} is the Rouse dynamics result[4] which we express below in terms of the dimensionless function h_i

$$x_{it}^2 = R_i^2 h_i(t/\tau_i, \alpha_i/N_i) \qquad h_i(u \ll 1, x) = \theta_i u^{1/2} + \ldots, \qquad h_i(u \gg 1, x) \sim u$$

$$\theta_i = \begin{cases} 4/\pi^{3/2} & \text{(end group)} \\ 2/\pi^{3/2} & \text{(interior group)} \end{cases} \qquad (10)$$

For the RG analysis it is convenient to choose units (see Appendix A) such that $a^2/d = k_{\mathrm{B}}T = 1$. Then $R_i^2 = dN_i$ in eq 10 is the ideal coil size in d-dimensional space and $\tau_i \propto \zeta_0 N_i^2/\pi^2$ the longest Rouse relaxation time where ζ_0 is the local Rouse friction coefficient ($\zeta_0 = t_a$ in these units). The prefactor to the well-known Rouse short time behavior, $x_{it}^2 \sim t^{1/2}$, depends only on whether the group occupies an end or an interior position. Note that only for $d > 2$ does the long time behavior $x_{it}^2 \sim t$ guarantee the convergence as $t \to \infty$ of the time integral of $S(t)$ in eq 8 and hence the existence (perturbatively) of k_∞ as discussed by de Gennes.[2] This is just a rephrasing of our previous observation that only for $d > 2$ does $\dot{\Gamma}_t$ approach a constant for large t (eq 6). We remark that the choice of N_i (rather than say α_i or β_i) as the "dimension" with which to scale chain lengths, leading to the dependence of h_i on t/τ_i, α_i/N_i is arbitrary. Note that in the following we will drop explicit reference of the α_i/N_i argument in order to ease notation.

Now in fact careful scrutiny of higher orders in the series for k, eq 8, exposes it to be a sum of powers of $u_0\zeta_0N^{\epsilon/2}$ where $\epsilon = 4 - d$. Thus it is conveniently reexpressed in terms of a dimensionless coupling constant $w_0 \equiv u_0\zeta_0L^{\epsilon/2}$ where we introduce the arbitrary polymer backbone scale L which later will represent the coarse-graining scale in the RG transformation[31] (see Figure 3). Noting that to leading order $\rho^\circ_{\text{eq}} = 1/V$ (see Appendix D), one obtains to second order

$$-k(t)\zeta_0L^{\epsilon/2} = w_0V\rho^\circ_{\text{eq}} + w_0^2\left(\frac{N_1}{L}\right)^{\epsilon/2}\frac{1}{(2\pi)^{d/2}\pi^2}\int_0^{t/\tau_1}\frac{\mathrm{d}u}{\{h_1(u) + (1/\lambda)\,h_2(\lambda^2u)\}^{d/2}}$$
$$\lambda \equiv N_1/N_2 \qquad (11)$$

Our final form for the bare perturbation series is expressed in terms of the important parameter λ, the ratio of molecular weights. The dependencies on dimensionless reactive group locations α_1/N_1 and α_2/N_2 are implicit in h_1 and h_2, respectively.

We have seen above the particular significance of $d = 2$, separating one type of behavior from another. It is easy to see that $d = 4$, that is $\epsilon = 0$, also plays a special role by examining the reaction probability when two coils overlap, $f[\mathcal{N}(\tau)]$, in the Rouse model. In this case statics are ideal ($\nu = 1/2$) and $R \sim \tau^{1/4}$ ($z = 4$) whence $P_{\text{eq}}(r<a|r<R) =$

$(a/R)^d = (\tau/t_a)^{-d/4}$ in eq 3 which leads to

$$\mathcal{N}(\tau) = Qt_a\left(\frac{\tau}{t_a}\right)^{\epsilon/4}, \qquad \text{Rouse} \tag{12}$$

For $d < 4$, $\epsilon > 0$ the reaction probability is virtually unity if ever the two coils overlap (provided N is large so τ/t_a is sufficiently large). This is DC behavior. On the other hand for $d > 4$, $\epsilon < 0$ reaction is very unlikely even when the coils meet; this leads to MF kinetics (see later). Thus *$d = 4$ is the DC → MF crossover dimension*. In fact this dimension is always significant since, even when excluded volume and hydrodynamical interactions feature, ideal statics and (Rouse) dynamics are obeyed[32,3] above $d = 4$; thus the kinetics are always "simple" (in that mean field theory works) for such dimensions. This fact will be exploited (as for intramolecular reactions[29,33,23]) in the RG analysis by evaluating k close to the "simple" dimensions; k is expanded in powers of ϵ.

The above discussion suggests something special should happen to the perturbation series eq 11 at $d = 4$. Indeed, for dimensions greater than 4 the series does not exist: as $d = 4$ is approached from below the time integral diverges as $1/\epsilon$ due to the small time behavior. Explicitly, from eq 10 one finds

$$\int_0^{t/\tau_1} \frac{\mathrm{d}u}{\{h_1(u) + (1/\lambda)\, h_2(\lambda^2 u)\}^{d/2}} \approx \frac{1}{(\theta_1 + \theta_2)^{d/2}} \frac{4}{\epsilon}\left(\frac{t}{\tau_1}\right)^{\epsilon/4}, \qquad \frac{t}{\tau_1} \ll 1 \tag{13}$$

Note that the divergence depends on the locations (end or interior) of the two reactive groups involved in the reaction via θ_1 and θ_2. In the following sections this divergence (and others) in the "bare" series eq 11 will be renormalized to produce the renormalized series for k.

To conclude this section let us briefly discuss the role of the RG calculations, which are important in two respects. In many cases they can furnish a level of detail to experimental predictions which is unavailable from the nonetheless more transparent scaling arguments. But another important role is to justify the approximations used in all previous theoretical analyses of polymer reactions[2,27,34-36] *and indeed used in our scaling arguments*. As will become clear in what follows the scaling arguments make the implicit assumption that the configurations of the unreacted polymers are unchanged from equilibrium. We find in the present work, as in the case of intramolecular reactions,[29,33,23] that after making a corresponding assumption in the RG analysis (namely, that nonsink static and dynamic properties are renormalized as they are in the absence of the sink) the theory can be consistently developed (i.e. it is renormalizable) which though not a proof (in practice we can only achieve this to lowest orders) is strongly suggestive of the validity of the general procedure.

III. Unentangled Melts (Rouse Dynamics): DC Kinetics

That Rouse dynamics, describing $N < N_e$ melts, exhibit intrinsically DC kinetics is most clear from the reaction probability in $d = 3$ during the period when two coils overlap. From eq 12 in the $d = 3$ case one has

$$f[\mathcal{N}(\tau)] = f\left[Qt_a\left(\frac{\tau}{t_a}\right)^{1/4}\right] \approx 1 \tag{14}$$

for very large N, i.e. very large τ/t_a. From eqs 6 and 2 one immediately obtains

$$k_\infty \approx \frac{R^3}{\tau} \sim N^{-1/2} \tag{15}$$

since $P_{\text{eq}}(r{<}R) \approx R^3/V$ (ideal statistics).

In developing our scaling results, it is conceptually helpful to phrase the arguments in terms of general spatial dimension d, specializing to $d = 3$ at the end. Now in de Gennes' language,[2] the essence of short time Rouse dynamics here is the "compactness" (for $d < 4$) of the trajectory followed by a chain unit, i.e. the fact that the volume explored grows less rapidly than t: $x_t^d \approx a^d(t/t_a)^{d/4}$. Thus for short times $t \ll \tau$ one has from eq 3 $\mathcal{N}(t) \approx Qt(a/x_t)^d \approx Qt_a(t/t_a)^{1-d/4} \gg 1$ for large t/t_a and $d < 4$, i.e. $f[\mathcal{N}(t{\gg}t_a)] \approx 1$ in three-dimensional space. Then using eqs 3 and 2 the small time rate is

$$k(t{\ll}\tau) \approx \frac{\mathrm{d}}{\mathrm{d}t}x_t^{\,3} \approx \frac{a^3}{t_a}\left(\frac{t}{t_a}\right)^{-1/4} \tag{16}$$

The results of eqs 15 and 16 were first obtained by Doi[1] and de Gennes,[2] respectively. The time-dependent rate $k(t)$ at short times is (to within constant prefactors) the rate at which volume is explored. This is DC kinetics; the conditional reaction probability after time t, $f[\mathcal{N}(t)]$, is essentially unity for large t/t_a, i.e. two reactive groups will definitely react if they have a chance to meet, so the amount reacted is proportional to the volume swept out by a reactive group, x_t^3. Now if the groups are very weakly reactive, $Qt_a \ll 1$, then $f[\mathcal{N}(t)] = f[Qt_a(t/t_a)^{1/4}]$ will be small at smaller times. Small reaction probability implies MF kinetics since the polymers are close to equilibrium and k will then be proportional to the equilibrium contact probability (see next section). However the probability inevitably grows and approaches unity at large enough times, corresponding to a *crossover* from MF to DC behavior. We can say the kinetics are *driven* to DC behavior as time grows. Similarly, the long time result is of DC type; if two coils overlap, reaction definitely happens ($f[\mathcal{N}(\tau)] = 1$). The mean distance each active group belonging to two overlapping coils must traverse in order to meet is of order R, the mean time taken of order τ whence $k_\infty \approx R^3/\tau$. Again, for small Qt_a it may be that $f[\mathcal{N}(\tau)]$ (see eq 14) is small, but for longer and longer chains (increasing τ) it approaches unity. Increasing N *drives* the kinetics to DC. It is in this sense that reaction kinetics under Rouse dynamics are *intrinsically* DC.

Clearly, the smaller Qt_a the greater t or N must be in order that the asymptotic behavior be realized. Thus both the MF regime and the crossover to DC behavior as, say, N increases should be Q-dependent. Once the asymptotic regime is realized, however, $k(t)$ (see eqs 15 and 16) is independent of Q. Indeed the RG analysis, whose results are presented below, is able to demonstrate that even the prefactors in eqs 15 and 16 are *universal* constants. Thus k is the same for all polymer-reactive group species when expressed in terms of (say) R and τ. The chemical details of the reactive groups are completely irrelevant. In Appendix C the RG analysis for the Rouse case is presented, and for short times we find

$$k(t{\ll}\tau_i) = \frac{\pi^4(\theta_1+\theta_2)^2}{1+X_t}\frac{1}{\zeta_0}\left(\frac{t}{\zeta_0}\right)^{-1/4} = \frac{\pi^2(\theta_1+\theta_2)^2}{16}\frac{1}{1+X_t}\frac{R_i^{\,3}}{\tau_i}\left(\frac{t}{\tau_i}\right)^{-1/4}$$

$$X_t \equiv \left(\frac{t}{t_{\mathrm{L}}}\right)^{-1/4} \frac{w^* - w}{w} \qquad (17)$$

We remind the reader that for convenience our RG calculations use dimensions such that the size of a chain unit is dimensionless ($a^2 = 3$) and ζ_0 is a time scale. In the above $w^* \equiv -\pi^4(\theta_1 + \theta_2)^2$, $t_{\mathrm{L}} \equiv \zeta_0 L^2/\pi^2$ is the Rouse time for the coarse-graining scale L, and w is the dimensionless reactivity of the active groups (one may think of w as Qt_a in the scaling argument language). This result nicely reflects the features which emerged from the scaling analysis. No matter how small the magnitude of w, increasing t eventually *drives* $k(t)$ to the anticipated DC form, $k(t) \sim t^{-1/4}$ (as in eq 16) because the crossover parameter X_t becomes very small for large t. For a given reactivity w, however, at small enough times X_t becomes sufficiently large to cancel the $t^{1/4}$ factor. For such small t, therefore, $k(t)$ is a nonuniversal (i.e. involving w) constant. This is MF kientics, k proportional to the equilibrium group contact probability which is independent of molecular weight in melts (statistics being ideal). Evidently then X_t interpolates between MF and DC kinetics. Of course, if w is so small that the crossover time exceeds the $\{\tau_i\}_{i=1}{}^2$, i.e. is beyond the time domain of the above result, then MF kinetics will prevail at all times.

Note the universality of $k(t)$ in the DC limit, $X_t \gg 1$; all characteristics of the reactive groups drop out, leaving a universal prefactor depending only on group positioning via θ_1 and θ_2 (see eq 10). That is, the prefactor depends only upon which of the three types of situation depicted in Figure 2 pertains. Even though eq 17 describes chains of arbitrary lengths N_1, N_2 (and arbitrary $\{\alpha_i,\beta_i\}$), the result is *independent* of these lengths which is physically sensible since at these short times the groups do not "know" the lengths of the chains to which they are attached. Though $k(t)$ has been expressed in terms of the measurable properties R_i and τ_i to render it directly comparable with experiment, observe that the powers of N_i cancel. (To be more precise about our definition of "short" times here, we mean $t \ll \{\tau_i\}$ for end groups and $t \ll \{\tau_{\alpha_i},\tau_{\beta_i}\}$ for interior groups where $\tau_{\alpha_i} \equiv \alpha_i^2\zeta_0/\pi^2$ is the Rouse relaxation time for the chain segment of length α_i and similarly for τ_{β_i}.)

Figure 3 illustrates the nature of the coarse-graining transformation used to obtain the above and subsequent RG results. The effect on one chain with a reactive end group is shown. The original chain is coarse-grained into $N' < N$ units of increased size $a' > a$ (Figure 3b). The new end unit is still the only reactive one, but its dimensionless reactivity must be updated $w \rightarrow w'$. For Rouse dynamics, after many coarse-graining steps w ceases to change, approaching a finite value w^* (the fixed point value of the transformation). The existence of a finite w^* corresponds to DC behavior as can be seen directly from eq 17 where X_t vanishes if one sets $w = w^*$. That is, the DC behavior is realized either at large t or at $w = w^*$.

Let us now examine the long time RG result, derived in Appendix C. For two chains of equal molecular weight $N_1 = N_2$ we find ($R \equiv R_i$, $\tau \equiv \tau_i$)

$$k_\infty = \frac{1}{1+X}\,\frac{\pi^2(\theta_1+\theta_2)^2}{16}\,\frac{R^3}{\tau}, \qquad X \equiv \left(\frac{N}{L}\right)^{-1/2} \frac{w^* - w}{w} \qquad (18)$$

As expected from our scaling discussions the value of the crossover parameter X is now determined by *chain length*: for very large N ($X \ll 1$) k_∞ is *driven* to DC form, eq 16, no matter how small w. At the DC fixed point the universal prefactor is unchanged from the short time result. For small chains, or small w, one has $X \gg 1$ and the powers of N cancel leading to constant k_∞ (MF). It is important to note that if w is so small that the "very large N" value required for the DC law to be applicable turns out to exceed the entanglement threshold N_e, then of course in practice this asymptotic Rouse behavior will not be realized. Reaction rates are then strongly modified by entanglements.[18]

As one would expect, the crossover factors are related to the *reaction probabilities* ($f[\mathcal{N}]$) which in our scaling picture determined the MF → DC transition. Thus, the factor $1/(1 + X_t)$ is analogous to the reaction probability after time t, $f[\mathcal{N}(t)]$; for small times $f[\mathcal{N}(t)] \sim \mathcal{N}(t) \sim t^{1/4}$ and $1/(1 + X_t) \sim t^{1/4}$ while at large times $f[\mathcal{N}(t)] = 1/(1 + X_t) \approx 1$. In a similar way $1/(1 + X)$ is analogous to the reaction probability during a coil–coil "collision", namely $f[\mathcal{N}(\tau)]$; for small N one has $f[\mathcal{N}(\tau)] \approx \mathcal{N}(\tau) \sim \tau^{1/4} \sim N^{1/2}$ from eq 14 while $1/(1+X) \sim N^{1/2}$, and at large N one has $f[\mathcal{N}(\tau)] = 1/(1 + X) \approx 1$.

What happens to k_∞ for chains of different lengths? In particular, in Appendix C we study k_∞ for the case when one chain is much longer than the other. The conclusion is that the reaction kinetics are dominated by the *small* chain

$$k_\infty \approx H\left(X, \frac{\alpha_1}{N_1}\right)\frac{R_1^{\,3}}{\tau_1}, \qquad N_1 \ll N_2 \qquad (19)$$

where X is as defined in eq 18 but with N replaced by N_1, and $H(X,\alpha_1/N_1)$ is a universal function of X and the dimensionless group positioning on the small chain only (H depends on the long chain only via θ_2). The corrections to the above result are of order $(N_1/N_2)^2$. Thus for long chains $k_\infty \propto N_1^{-1/2}$ at fixed α_1/N_1 scales with a power of the small chain. In the MF limit, $X \gg 1$, H has the behavior $H(X,\alpha_1/N_1) =$ constant $1/X$. Note that N_1 also determines X; thus, for example, reaction kinetics are predicted to be MF if N_1 is small enough to be "in" the MF regime even if N_2 is long enough to be "in" the DC regime. This has interesting consequences on the limiting situation of this type, reaction between a macromolecule and a small molecule.[37,14]

IV. Dilute Solutions, Good Solvents: MF Kinetics

For good solvents, the situation in dilute solutions is the "opposite" of that in melts. The origin is the "correlation hole",[3,20,25] that is the strongly diminished probability (relative to ideal statistics) that two reactive groups encounter one another when their respective host coils overlap

$$P_{\mathrm{eq}}(r<x) \approx \frac{x^d}{V}\left(\frac{x}{R}\right)^g, \qquad x \ll R$$

$$P_{\mathrm{eq}}(r<x) \approx \frac{x^d}{V}, \qquad x \gg R$$

$$P_{\mathrm{eq}}(r<a|r<R) \approx \left(\frac{a}{R}\right)^{d+g} = N^{-\nu(d+g)} \qquad (20)$$

Comparing to the ideal result (pertaining to melts), $P_{\mathrm{eq}}(r<a|r<R) \approx (a/R)^d$, one sees that the reduction in contact probability varies as $N^{-\nu g}$ where g is the correlation hole exponent[20,25,38] and $\nu \approx 3/5$ is the Flory exponent.[3] The value of the exponent g depends on positioning of the reactive groups on the polymer backbones: for $d = 3$, $g = g_1 \approx 0.27$ for end groups on both chains (see Figure 2a), $g = g_2 \approx 0.46$ for one end group plus one internal (Figure 2b) and $g = g_3 \approx 0.71$ when both groups are internal (Figure 2c). Now the key point is that the total reaction probability $f[\mathcal{N}(\tau)]$ during the period τ for which two coils remain overlapped (should they happen to "collide") becomes very small for large N as a result of this diminished contact probability. From eqs 3 and 20 we have ($x_\tau \equiv R$)

$$f[\mathcal{N}(\tau)] \approx \mathcal{N}(\tau) = Qt_a\left(\frac{\tau}{t_a}\right)^{1-\theta} \ll 1$$

$$\theta \equiv \frac{d+g}{z} > 1 \tag{21}$$

where[23] the "reaction exponent" θ is greater than unity in all spatial dimensions below 4 since for dilute solutions[3] $z = d$; i.e. $\tau \propto R^d$ and $x_t \propto t^{1/d}$. Then using eq 3 to rewrite $\mathcal{N}(\tau) = Q\tau P_{\mathrm{eq}}(r{<}a|r{<}R)$ one has from eq 6 $1 - \Gamma_t \approx QtP_{\mathrm{eq}}(r{<}a) \equiv Qta^d\rho_{\mathrm{eq}}$, where $\rho_{\mathrm{eq}} \equiv a^{-d}P_{\mathrm{eq}}(r{<}a)$ is the group contact probability density. Thus, from eq 2, k_∞ has MF form ($d = 3$)

$$k_\infty = Qa^3V\rho_{\mathrm{eq}} \approx Qa^3N^{-\nu g} \tag{22}$$

In fact from eq 3 the conditional reaction probability for times less than τ is also small provided t is large compared to t_a

$$f[\mathcal{N}(t)] \approx \mathcal{N}(t) \approx Qt_a\left(\frac{t}{t_a}\right)^{1-\theta} \ll 1$$

$$t_a \ll t \ll \tau \tag{23}$$

This leads to (see eqs 3 and 2)

$$k(t \ll \tau) = k_\infty \approx (Qa^3)N^{-\nu g} \tag{24}$$

Our conclusion is that $k \propto \rho_{\mathrm{eq}}$ obeys MF kinetics both for short and long times with at most a weak time dependence. Large t ($f[\mathcal{N}(t)]$) and large N ($f[\mathcal{N}(\tau)]$) *drive* the kinetics to MF form (i.e. in the opposite direction to that for Rouse dynamics) *even for large Q*. The prediction then is that (as for small[19] Q) $k \propto N^{-\nu g}$ i.e. $k \propto N^{-0.16}$, $N^{-0.27}$, $N^{-0.43}$ according to group location. Note that *nonuniversal* reaction group characteristics (i.e. Qa^3) appear as prefactors in k, in contrast to the Rouse case where all such quantities dropped out at large t or N.

Let us see how the RG results reflect this picture. For short times (see Appendix E, eq E6) our result involves the expected exponent $\theta - 1 = g/3$ (in $d = 3$):

$$k(t \ll \{\tau_{\alpha_i}, \tau_{\beta_i}\}) = \mathrm{const}\frac{kT}{\eta}\frac{w^*}{X_t - 1}\left(\frac{t}{\tilde{\tau}}\right)^{\theta-1}$$

$$X_t \equiv \left(\frac{t}{t_{\mathrm{L}}}\right)^{\theta-1}\frac{w - w^*}{w}, \qquad \frac{\tilde{\tau}}{t_{\mathrm{L}}} = \left(\frac{\tilde{N}}{L}\right)^{3\nu} \tag{25}$$

where $\tilde{N}$ is a characteristic chain length determined by the formulas (see Figure 2)

$$\frac{1}{\tilde{N}} = \begin{cases} \dfrac{1}{N_1} + \dfrac{1}{N_2} & \text{2 end groups} \\ \left(\dfrac{1}{N_1} + \dfrac{1}{\alpha_2}\right)^{1/2}\left(\dfrac{1}{N_1} + \dfrac{1}{\beta_2}\right)^{1/2} & \text{1 end, 1 interior} \\ \left(\dfrac{1}{\alpha_1} + \dfrac{1}{\alpha_2}\right)^{1/4}\left(\dfrac{1}{\beta_1} + \dfrac{1}{\beta_2}\right)^{1/4}\left(\dfrac{1}{\alpha_1} + \dfrac{1}{\beta_2}\right)^{1/4}\left(\dfrac{1}{\beta_1} + \dfrac{1}{\alpha_2}\right)^{1/4} & \text{2 interior} \end{cases} \tag{26}$$

Here $\tau_{\alpha_i} \propto \alpha_i^{3\nu}$ is the relaxation time of the chain length α_i (and similarly for other lengths), t_{L} is a local relaxation time, and w^* is a positive constant of order unity and we have reintroduced the thermal energy factor kT.[4] The factor kT/η can be interpreted as a^3/t_a. Now since this result is only valid for large t/t_{L}, X_t is never small so eq 25 describes a weak time dependence only. This transient, though weak, is bizarre in that $k(t)$ is actually an *increasing* function of time in the initial stages. After a short period the increase saturates as X_t becomes large ($\theta > 1$) and cancels the $t^{\theta-1}$ factor. The value at which k saturates, not surprisingly, is the same as the long time value, k_∞ (i.e. k ceases to change after that point). We demonstrate this in Appendix E. From eq 25 we have

$$k(t \gg t_{\mathrm{L}}) = \mathrm{const}\frac{kT}{\eta}\frac{ww^*}{w - w^*}\left(\frac{\tilde{N}}{L}\right)^{-\nu g} \propto \rho_{\mathrm{eq}} \tag{27}$$

which again involves ρ_{eq}, the equilibrium contact probability density. This is of MF form. The important feature of the characteristic chain length $\tilde{N}$ is that the small lengths dominate. Note that the expected nonuniversal sink prefactor, $(kT/\eta)ww^*/(w - w^*)$, is very small for small $|w|$ but saturates at approximately a^3/t_a as the magnitude of w becomes large. This makes physical sense since the local reaction time cannot possibly be less than the diffusion time t_a to bring the groups together.

Clearly the factor in eq 25 involving the crossover parameter X_t, namely $1/(X_t - 1) \sim 1/(\mathrm{constant}\ t^{\theta-1} - 1)$ is analogous to $f[\mathcal{N}(t)]$ (see eq 23). With increasing t this factor becomes smaller and smaller and the result is driven to MF form. Similarly (see Appendix E) for large times the relevant crossover parameter (see eq E7) $X \propto N^{-\nu g} \propto \tau^{1-\theta}$ is analogous to $f[\mathcal{N}(\tau)]$ of eq 21. In contrast to the Rouse case, under the coarse-graining transformation (Figure 3) the fixed point value of the dimensionless reaction rate w *vanishes*. Increasing N or t drives w toward zero, i.e. toward weak MF behavior.

In Figure 2 several extreme situations are shown in which one of the two reacting chains is much shorter than the other. Generally, the expressions for $\tilde{N}$ in eq 26 are related to the statistics of three- and four-arm stars for the interior group cases.[25,38] Now the expressions for $\tilde{N}$ tell us to (i) compare all segment pairs *between* 2 chains, (ii) choose the smallest (when one is much smaller than the other), (iii) form the product of every "winner" of each comparison, and (iv) take the logarithmic mean to get the right dimensions. Thus for the situation of Figure 2a (end groups with $N_1 \ll N_2$) one has $k \propto N_1^{-\nu g} \approx N_1^{-0.16}$ (as derived for small Q by Khokhlov[19]), while for the situations of Figure 2b we have using eqs 25 and 26

$$k \propto N_1^{-\nu g_2} \approx N_1^{-0.27}, \qquad N_1 \ll \alpha_2,\beta_2$$

$$k \propto ((\alpha_2\beta_2)^{1/2})^{-\nu g_2}, \qquad N_1 \gg \alpha_2,\beta_2$$

$$\text{1 end, 1 interior} \tag{28}$$

Thus in the second case of eq 28, $k \propto N_2^{-\nu g_2}$ at fixed dimensionless group location on the small chain, α_2/β_2. For the situation of Figure 2c one has $k \propto ((\alpha_1\beta_1)^{1/2})^{-\nu g_3}$ i.e.

$$k \propto N_1^{-\nu g_3} \approx N_1^{-0.43}, \qquad N_1 \ll N_2, \qquad \text{fixed } \alpha_1/\beta_1$$

$$\text{(2 end groups)} \tag{29}$$

Now since k is essentially equal to ρ_{eq} (see eq 27), or more accurately k is proportional to ρ_{eq} averaged over a small length scale near the origin (corresponding in the expressions for $\tilde{N}$ to a polymer backbone scale L), we expect k to exhibit certain "crossover" properties. Indeed, an interesting property of the expression for $\tilde{N}$ in eq 26 is that in the limit of very small (i.e. of order L) values of any of the chain segments, the expressions for k (provided they are appropriately interpreted) do interpolate between one class of group locations and another. For example, consider the case of 1 end and 1 interior group when α_2 is much smaller than both N_1 and β_2, i.e. when the reactive groups are in contact α_2 is like a small "dangling end".

Then from eqs 27 and 26 one has

$$k \approx \text{const}\left(\frac{L}{\alpha_2}\right)^{\nu g_2/2}\left(\frac{L}{\beta_2}+\frac{L}{N_1}\right)^{\nu g_2/2} \propto \left(\frac{L}{\alpha_2}\right)^{\nu g_2}\left(\frac{\alpha_2}{\beta_2}+\frac{\alpha_2}{N_1}\right)^{\nu g_2/2} \rightarrow \left(\frac{L}{\alpha_2}\right)^{\nu g_2}\left(\frac{\alpha_2}{\beta_2}+\frac{\alpha_2}{N_1}\right)^{\nu g_1} \quad (30)$$

where we have interpreted $g_2/2$ as g_1 (which is true to first order in ϵ). The motivation for this interpretation is that if one "reblobs" all chain segments into blobs containing chain of length α_2, then the situation here is one of two reactive *end*-blobs on two chains containing respectively β_2/α_2 and N_1/α_2 blobs. k in eq 30 is equal to the group contact probability for such a situation (it involves g_1), multiplied by the factor $(L/\alpha_2)^{\nu g_2}$ which is the appropriate weighting for the small blob, which contains polymer of length α_2, and which is an "interior-end" group situation (thus involving g_2). Note that if one could calculate the exact expression for $\tilde{N}$ (i.e. to all orders in ϵ), this property must, on physical grounds, be robust. That is, the "logarithmic averaging" rule, whatever its exact structure may be, must be such as to transform one g value into another in the limit of small chain segments. This implies that the structure of $\tilde{N}$ displayed in eq 26 for the two cases involving interior groups is not exact to all orders since $g_3 = 2g_2 = 2g_1$ is not true to all orders. We expect then that eq 27 is an exact statement, but eq 26 is not; however, its most important feature ("small wins") *is* indeed expected to be true to all orders.

In conclusion of this section, the general picture (as for melts) is that reaction kinetics are dominated by the smallest chain lengths. We can summarize all the long time good solvent results in the following way:

$$k = Q_{\text{eff}}a^3\tilde{N}^{-\nu g} \quad (31)$$

where Q_{eff} is an effective local reaction rate which saturates at about $1/t_a$.

V. Dilute Solutions, Θ Solvents: Marginal Kinetics

In Θ solvents the correlation hole effect, predominant in good solvents, is screened away i.e. $g = 0$. Now the dynamical exponent[3] is unchanged ($z = d$) and the net effect is that kinetics are *marginal*. This is easily seen from the expression for $\mathcal{N}(\tau) = Q\tau(a/R)^d = Qt_a$ (see eq 3, with $R \sim \tau^{1/d}$) or indeed from $\mathcal{N}(t) \approx Qt_a$ in general. Thus we have

$$\mathcal{N}(\tau) \sim \tau^0, \qquad \mathcal{N}(t) \sim t^0 \quad (32)$$

Neither increasing N nor increasing t seems to drive the kinetics toward either MF or DC form. The DC "result" ($k \sim R^d/\tau \sim N^0$) and the MF "result" ($k \sim \rho_{\text{eq}} \sim N^0$) coincide since[3] $R \sim N^{1/2}$ (Gaussian statistics) and $\tau \sim R^d$ (hydrodynamics). Reaction kinetics are apparently borderline, between MF and DC behaviors, which in analogy with other marginal statistical mechanical systems[39] leads one *to anticipate logarithmic forms* $k(t) \sim (1/\ln t)^{\omega_1}$ and $k_\infty \sim (1/\ln N)^{\omega_2}$ where ω_1, ω_2 are simple powers. Scaling cannot find logarithms, so we consult the RG. In Appendix F we show that the initial behavior is indeed logarithmic in time:

$$k(t \ll \{\tau_{\alpha_i},\tau_{\beta_i}\}) \approx \left[\frac{3kT\,\pi^2(\theta_1+\theta_2)^2}{2\eta}\right]\frac{1}{\ln(t/t_0)} = C\,(\theta_1+\theta_2)^2\frac{R^3}{\tau}\frac{1}{\ln(t/t_0)} \quad (33)$$

where t_0 is a nonuniversal local time scale and the result is valid for $t \gg t_0$. As for good solvents, we have explicitly reintroduced the kT factor. R and τ are the coil size and relaxation time of either of the two chains (the powers of N_i cancel) and C is a universal constant. The result has been expressed in terms of R and τ to indicate that the prefactor is composed from measurable quantities and is of universal form. Thus the prediction is, for example, that the ratio of $k(t)$ (at short times) for two end groups (Figure 2a) to that for two interior groups (Figure 2c) is a universal constant which we estimate (to leading order) to be 4 (see eq 10).

At long times for identical chains we show (Appendix F)

$$k_\infty = \left[\frac{3kT\pi^2(\theta_1+\theta_2)^2}{4\eta}\right]\frac{1}{\ln N/N_0} = \frac{C}{2}(\theta_1+\theta_2)^2\frac{R^3}{\tau}\frac{1}{\ln(N/N_0)}$$

$$N_1 = N_2 \equiv N \quad (34)$$

which is valid for $N \gg N_0$, N_0 being a nonuniversal local chain length. The constant C is the same as that in eq 33 and similar comments as for short times apply. Thus $k \propto 1/\ln t$ and $1/\ln N$ at short and long times, respectively, with universal prefactors. The crossover parameters in the RG analysis (X_t and X) no longer grow algebraically but now depend logarithmically on t and N (see eqs F1 and F3, respectively). In fact increasing t and N drives the kinetics to a weak sink limit (the fixed point value of the dimensionless reaction rate w under the coarse-graining transformation vanishes) albeit in a slow logarithmic manner.

Finally, when one chain is much shorter than the other, it is again the short chain which governs the reaction rate: for sufficiently long chains k_∞ is given by the same expression as in eq 34 but with $N \rightarrow N_1$. For moderately long chains the expression picks up a prefactor which depends also on the dimensionless group location on the short chain, i.e. on α_1/N_1; this dependence decays only slowly with large N_1, being of order $1/\ln N_1$ (see eq F5).

VI. Discussion

Reaction kinetics in dilute solutions with good solvents are dominated by excluded volume effects; for large N the reactive groups constitute a weak perturbation even when their reactivity Q is large, and k obeys a MF (mean field theory): k involves local time and length scales, is only weakly time-dependent, and $k \sim N^{-0.16}$, $N^{-0.27}$, and $N^{-0.43}$ for the three cases of Figure 2. Thus the N dependence at large Q is the same as that obtained by Khokhlov[19] for small Q. The underlying reason is that while the time for which two coils remain overlapped increases as $N^{3\nu}$, the fraction of this time during which the reactive groups are in contact decreases as $N^{-(3\nu+\nu g)}$ on account of the *correlation hole*; thus the mean number of "collisions" decreases as $N^{-\nu g}$. In consequence, the reaction probability when two coils encounter (namely $f[\mathcal{N}(\tau)]$) becomes tiny for large enough N. Rouse dynamics (unentangled melts) exhibit, on the other hand, intrinsically DC behavior since the overlap time and contact probability vary respectively as N^2 and $N^{-3/2}$; thus the number of "collisions" increases as $N^{1/2}$ and for large enough N reaction is inevitable should the two coils encounter, even when Q is small. The correspondence to these two types of behavior in the RG trajectories of the reaction coupling w is very clear. For good solvents the coarse-graining transformation drives w to the trivial stable fixed point $w^* = 0$ even if the "initial" value is large, while for Rouse dynamics even a small initial value is driven to the nontrivial finite fixed point $w^* < 0$. This trajectory, to one or the other of the fixed points, is governed by a crossover parameter which either grows or decays with increasing N or equivalently increasing coarse-graining scale along the polymer backbone. Reaction rates for intermediately long chains can be expressed as functions of the crossover parameter; i.e. one can derive crossover expressions for k whose form lies somewhere between the MF and DC limits.

Similar issues govern the short time behavior of k. Consider a pair of reactive groups, belonging to two initially interpenetrating coils, which are close enough such that they *may* have reacted by the time t. Take the case of dilute solution with good solvent. A pair of reactive groups which *may* have met must initially have been separated by a distance less than $x_t \sim t^{1/3}$, i.e. the pair must initially have been contained within a volume less than or of the order of the exploration volume $\sim t$. The relevant question is: among these particular pairs, what fraction have reacted? To answer this, we need the fraction of time for which a typical such pair was "in collision" during the period t, namely $P_{\mathrm{eq}}(r<a|r<x_t)$ (initial conditions are equilibrium) which scales as $x_t^{-(3+g)} \sim t^{-(1+g/3)}$ (see eq 20). Thus it follows that the average number of "collisions" between pairs initially within range varies as $t^{-g/3}$. As time progresses, therefore, the probability that a given pair initially within range has reacted becomes very small, i.e. one has MF kinetics at short times (other than a weak initial transient). For Rouse dynamics meanwhile the fraction of time "in collision" decays only as $t^{-3/4}$ so the mean number of "collisions" grows as $t^{1/4}$ and for large enough t reaction is certain for all those pairs initially within range—this is the definition of DC reaction kinetics and implies that the reaction rate is proportional to the rate of increase of volume explored. For short times it is time t, through a time-dependent crossover parameter, which drives the RG trajectories to either the MF or the DC fixed points.

Generally, the universality class to which the reaction kinetics belongs is determined by the characteristic "reaction exponent" $\theta \equiv (d + g)/z$ for general spatial dimension d. $\theta > 1$ implies MF kinetics, $\theta < 1$ implies DC kinetics. The good solvent expressions, eqs 21 and 23, for the number of "collisions" $\mathcal{N}$ (which is the determinant of reaction probabilities) are in fact quite general

$$\mathcal{N}(\tau) \sim \tau^{1-\theta} \sim N^{\nu z(1-\theta)}, \qquad \mathcal{N}(t) \sim t^{1-\theta}$$

$$\theta = \begin{cases} 3/4, & \text{Rouse} \\ 1 + g/3, & \text{good solvents} \\ 1, & \text{theta solvents} \end{cases} \tag{35}$$

These values of θ follow because for Rouse dynamics $z = 4$, $g = 0$ while in theta solvents $z = 3$, $g = 0$. The general picture is very similar to that for intramolecular reactions[30,28] where the theta solvent case was found to be marginal. The same is true here; the reaction exponent $\theta = 1$ is borderline for Θ solvents and k exhibits the logarithms characteristic of marginality: $k \sim 1/\ln t$ and $k \sim 1/\ln N$ at short and long times, respectively.

The above scheme is a generalization of de Gennes' classification of reaction kinetics[2] according as to whether space is explored "compactly" or "noncompactly". The generalization is necessary to deal with correlations between the reactive groups. Switching off such correlations, i.e. setting $g = 0$, θ reduces to d/z and the criterion on θ becomes equivalent to asking if x_t^d varies with a power of t which is greater than or less than unity, i.e. the compact vs noncompact criterion.

In addition to the general dependence of k on concentration regime and solvent quality, we have studied its dependence on reactive group backbone location and on chain lengths when two polymers of different molecular weights are involved. In the case of good solvents (MF kinetics) this has involved, in effect, calculating the equilibrium contact probability between a pair of chain units belonging to two interpenetrating polymer coils, and for internally positioned groups our results are related to the entropy of three-arm and four-arm star molecules[25,38] as is apparent from parts b and c of Figure 2. When one chain is much smaller than the other, the general rule to emerge for this case and for melts and theta solvents is that k is determined by the *small* chain length.

How do these results compare with experiment? Our prediction for end groups is that k should scale with N with a power of about -0.16 for "very long" chains, where "very long" means long enough that excluded volume statistics apply. For shorter chains we predict nonpower law behavior, i.e. changing slope whose magnitude approaches about 0.16 for very big N. A clear experimental picture has not yet emerged, though a number of interesting and illuminating studies exist. On the basis of phosphorescence quenching (large Q) measurements on end-labeled polystyrene[13] in good solvents, Horie and Mita report $k \sim N^{-\beta}$ with $\beta \approx 0.30$, larger than our prediction of about 0.16. A similar power is reported from triplet–triplet annihilation studies on polystyrene.[40] Since these slopes refer to degrees of polymerization N ranging from a few units up to about 4000, i.e. the smaller chains are almost certainly too short to be in the asymptotic regime, the data are at least consistent with our picture. Indeed, measured[41] combination rates of radical groups positioned at poly(oxyethylene) chain ends in dilute solution exhibit a k_∞ vs N relation whose slope is ever-decreasing as N increases; at the largest N values of a few thousand the local slope is well below 0.3 and very close to the theoretical value (of course since this measured value is based on only these last few data points, it is far from conclusive). Meanwhile, interpretation of free radical (large Q) polymerization data[8] suggests a value of β in good solvents lying in the range 0.075 to 0.13 and a very weak power in poorer solvents (consistent with the logarithmic behavior predicted here). These latter results are very difficult to interpret, being arrived at through a detailed model of the polymerization process in the dilute regime. Rates in poorer solvents were also measured by Horie and Mita[13] using phosphorescence quenching; neither power law or logarithmic behavior is obeyed. In summary, there is a need for further measurements of k_∞ in good solvents on chains long enough to unambiguously obey "self-avoiding" statistics in order to conclusively test for the existence of an asymptotic power and its value.

Further computer simulation[42,43] of reaction rates would also provide important tests of theory. Very few such studies (involving long flexible chains) exist and indeed none exist (to our knowledge) which probe intermolecular reactions. In this context it is worth mentioning that the physically unrealizable case of "Rouse plus excluded volume" dynamics (no hydrodynamic interactions) provides an interesting test of the ideas presented here and in the present authors' study of intramolecular reactions.[28] For these dynamics, which are relatively easy to simulate numerically, the prediction is[28] that the universality class itself is dependent on group location: $\theta - 1$ is positive (MF) when both groups are internal but negative (DC) for one end and one interior or two end groups. This switch in reaction kinetics as groups are moved to internal positions is predicted both for intramolecular and intermolecular reactions since the expressions for θ are the same in each case.

In conclusion, the terms "diffusion-controlled" and "chemically-controlled" must be used with care. For interpolymeric reactions a simple comparison of the magnitudes of τ (the relaxation time of the polymer) and Q^{-1} (the time for reaction to happen should the reactive groups collide) is inadequate. The logic would be that if, say, Q^{-1} is much smaller than τ, then the characteristic time-scale featuring in k should be τ since diffusive transport through space must surely be the rate-limiting step. However Q^{-1} is not the appropriate measure of "reaction time". The appropriate time scale with which to compare τ is not Q^{-1} but rather the mean reaction time τ^{react} (given that the two reacting coils overlap) based on the assumption that equilibrium is undisturbed, i.e. $\tau^{\text{react}} \approx Q^{-1}/P_{\text{eq}}(r<a|r<R)$ which is a much larger time: $\tau^{\text{react}} \approx Q^{-1}(\tau/t_a)^{\theta}$. If $\tau^{\text{react}} \gg \tau$, i.e. $Qt_a(\tau/t_a)^{1-\theta} \ll 1$ (which for large τ is inevitable if $\theta > 1$), then equilibrium is undisturbed (i.e. the system can easily equilibrate in the time for reaction to occur) and reaction kinetics are "reaction-controlled". But when $\tau^{\text{react}} \ll \tau$ (i.e. $\theta < 1$), pairs are reacting far more rapidly than the rate ($1/\tau$) at which diffusion is able to restore equilibrium, so the distribution of pair separations becomes depleted (relative to the equilibrium $P_{\text{eq}}(r)$). Under these circumstances the rate-limiting step is the diffusion process bringing the unreacted pairs together and tending to restore the depletion. This is diffusion control. Evidently, then, the comparison of τ^{react} with τ is precisely the criterion on θ which we have developed in this paper.

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Appendix A. The Operator F_{12}

F_{12} describes two-chain dynamics in the absence of reactions:

$$F_{12} = \sum_{i=1}^{2}\sum_{j=1}^{2}\int_0^{N_i^0} \mathrm{d}n \int_0^{N_j^0} \mathrm{d}n' \sum_{\alpha\beta} \frac{\delta}{\delta \mathbf{r}_{i\alpha}(n)} \times \left[\frac{\delta_{\alpha\beta}\,\delta_{ij}}{\zeta_0}\delta(n-n') + T_{\alpha\beta}(\mathbf{r}_i(n) - \mathbf{r}_j(n'))\right] \times \left[\frac{\delta}{\delta \mathbf{r}_{j\beta}(n')} + \frac{\delta H}{\delta \mathbf{r}_{j\beta}(n')}\right]$$

where

$$T_{\alpha\beta}(x) = \frac{1}{(2\pi)^d}\int \frac{d^dk}{\eta k^2}\left[\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right] e^{ikx},$$
$$H = H_0 + H_{\mathrm{I}}$$
$$H_0 = \frac{1}{2}\sum_{i=1}^{2}\int_0^{N_i^0}\left(\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}n}\right)^2,$$
$$H_{\mathrm{I}} = \sum_{i=1}^{2}\sum_{j=1}^{2}\frac{v_0}{2}\int_0^{N_i^0} dn \int_0^{N_j^0} \mathrm{d}n'\, \delta(\mathbf{r}_i(n) - \mathbf{r}_j(n')) \tag{A1}$$

Note that α,β label Cartesian coordinates while i, j identify the chain (1 or 2). In the appendices, where all detailed RG calculations are performed, our notation will always distinguish between bare (superscript zero) and renormalized (no superscript) quantities in the standard way. Thus, for example N_i^0 appears in eq A1 and the reactive group locations are determined by the bare segment lengths $\{\alpha_i^0,\beta_i^0\}$. In the main body of the text, however, all such variables are always unsuperscripted to help unify the presentation of scaling ideas and detailed RG calculations.

F_{12} above is of similar form to the operator F in ref 44 (see Appendix A therein) which describes interactions within a single chain. F_{12} is the two-chain generalization of F which is itself of standard form;[31] thus excluded volume and hydrodynamical interactions within and between chains are described by the Edwards Hamiltonian H and the Oseen tensor T. All coupling constants are as in that reference: ζ_0 and v_0 are the bare friction and excluded volume couplings, respectively, and η is the solvent viscosity. The reader is referred to ref 44 for further details.

Appendix B. Derivation of Bare Series

The derivation of the bare series from eq 7 is very similar to that in the intramolecular case.[28] The solution to eq 7 is expressed self-consistently in terms of Green's function G_{12}

$$P([\mathbf{r}_1,\mathbf{r}_2],t) = P_{\text{eq}}([\mathbf{r}_1,\mathbf{r}_2]) + u_0\int_0^t \mathrm{d}t' \int \mathrm{d}[\mathbf{r}_1']\mathrm{d}[\mathbf{r}_2'] \times G_{12}([\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1',\mathbf{r}_2'], t-t')\,\delta(\mathbf{r}')\,P([\mathbf{r}_1',\mathbf{r}_2'],t') \tag{B1}$$

where the initial condition is P_{eq}, the equilibrium distribution, and $\mathbf{r}' \equiv \mathbf{r}_1'(\alpha_1^0) - \mathbf{r}_2'(\alpha_2^0)$ is the location of one reactive group relative to the other. We want the pair survival probability Γ, i.e. the normalization of P. Iterating twice to obtain P to order u_0^2 from eq B1, integrating over all $[\mathbf{r}_1,\mathbf{r}_2]$ and differentiating with respect to time one obtains

$$\dot{\Gamma}_t = u_0\int \mathrm{d}[\mathbf{r}_1']\mathrm{d}[\mathbf{r}_2']\,P_{\text{eq}}([\mathbf{r}_1',\mathbf{r}_2'])\,\delta(\mathbf{r}') + u_0^2\int_0^t \mathrm{d}t' \int \mathrm{d}[\mathbf{r}_1]\mathrm{d}[\mathbf{r}_2]\mathrm{d}[\mathbf{r}_1']\mathrm{d}[\mathbf{r}_2']\delta(\mathbf{r}) \times G_{12}([\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1',\mathbf{r}_2'], t-t')\,\delta(\mathbf{r}')\,P_{\text{eq}}([\mathbf{r}_1',\mathbf{r}_2']) \tag{B2}$$

where we have used the fact that G_{12} is normalized to unity. Since $\dot{\Gamma}_t = -k/V$, the above expression is equivalent to eq 8 in the main text.

When v_0 and T are deleted, F_{12} describes Rouse dynamics. To obtain the explicit form of the return probability $S(t)$ under Rouse dynamics, we consider the probability density that the group separation $\mathbf{r}_t$ equals zero, given it was initially zero

$$\frac{\langle\delta(\mathbf{r}_t)\delta(\mathbf{r}_0)\rangle}{\langle\delta(\mathbf{r}_0)\rangle} = \langle\delta(\mathbf{r}_t)\rangle_{|\mathbf{r}_0=0} = \left(\frac{1}{2\pi}\right)^d \int \mathrm{d}^d\mathbf{k}\,\langle\exp\{i\mathbf{k}\cdot\mathbf{r}_t\}\rangle_{|\mathbf{r}_0=0} = \left(\frac{d}{2\pi\langle\mathbf{r}_t^2\rangle}\right)^{d/2}_{|\mathbf{r}_0=0} \tag{B3}$$

We used the fact that $\mathbf{r}_t$ is Gaussian since Rouse dynamics are linear and forced by Gaussian noise. But $\langle\mathbf{r}_t^2\rangle|_{\mathbf{r}_0=0} = \langle x_{1t}^2 + x_{2t}^2\rangle - 2\langle x_{1t}\rangle\langle x_{2t}\rangle = \langle x_{1t}^2 + x_{2t}^2\rangle$ where x_{it} is the displacement of the reactive group on the ith chain. Substituted into eq B3 and noting that $\langle\delta(\mathbf{r})\rangle = 1/V$ to leading order, this yields eq 9.

Appendix C. RG Analysis for Rouse Dynamics

The starting point is eq 11 with $\rho_{\text{eq}}^0 = 1/V$ (ideal statistics). In the following certain details will be omitted; we refer readers to refs 33 and 23 for similar calculations (which are for the *intra*molecular case). Generally $k(\zeta,\{\alpha_i,\beta_i\}_{i=1}^{i=2}, w, L, t)$ depends on all renormalized quantities (superscript or subscript zero dropped) and the polymer contour scale L. For Rouse dynamics[29,33] only w_0 is renormalized. Using the short time form of the bare series (i.e. using the result eq 13) and choosing w to (minimally[31]) absorb the divergences (see eq 13) leads to the following renormalized series at short times to order ϵ

$$-k(t\ll\tau_{\rm i})\,\zeta L^{\epsilon/2} = w\left[1-\frac{w}{w^*}\frac{\epsilon}{4}\left\{\ln\frac{t}{\tau_1}+2\ln\frac{N_1}{L}\right\}\right] + O_{\rm c}(\epsilon^2)+O(\epsilon^3) \quad ({\rm C1})$$

where $w^* \equiv -\epsilon\pi^4(\theta_1+\theta_2)^2$ is the stable fixed point of the beta function $\beta_w = (\epsilon w/2w^*)(w^*-w)$, and we use the symbol $O_{\rm c}(\epsilon^n)$ throughout this study to denote terms of order ϵ^n which are pure constants (i.e. are independent of $\{\alpha_{\rm i},\beta_{\rm i},N_{\rm i}\},L,t$). Solving the RG equation (RGE) $\partial k/\partial L = 0$ determines the general structure of k

$$k = \frac{1}{\zeta}\left(\frac{t}{\zeta}\right)^{-\epsilon/4} h(X_t,\{t/\tau_{\alpha_{\rm i}},t/\tau_{\beta_{\rm i}}\})$$

$$X_t \equiv \left(\frac{t}{t_{\rm L}}\right)^{-\epsilon/4}\frac{w^*-w}{w} \quad ({\rm C2})$$

where h is a universal function and $\tau_{\alpha_{\rm i}},\tau_{\beta_{\rm i}},t_{\rm L}$ are defined in section III. To derive eq C2 we have exploited the dimensional analysis of ζ and k. All dimensional analysis is as for intramolecular reactions[33] with one important difference: now $[k] = [r]^d/[t] = [L]^{d/2}/[t]$ which can be seen from eq 2. Expressing w in terms of X_t to order ϵ we rewrite the renormalized series in terms of X_t and exponentiate to render k consistent with the RGE solution. This leads to the final short time result:

$$-k(t\ll\tau_i) = \frac{\epsilon\pi^4(\theta_1+\theta_2)^2}{1+X_t}\frac{1}{\zeta}\left(\frac{t}{\zeta}\right)^{-\epsilon/4} \quad ({\rm C3})$$

The factor $\epsilon\pi^4(\theta_1+\theta_2)^2/(1+X_{\rm t})$ is thus interpreted as $h(X_{\rm t},\{0,0\})$ calculated to $O(\epsilon)$.

For long times $t/\tau_1^0 \to \infty$ the time integral in the bare series eq 11 gives a constant when $\lambda = 1$ ($N_1 = N_2$), and the renormalized series is in consequence identical to eq C1 other than for the absence of the $\ln t/\tau_1$ term. We use an equivalent solution of the RGE ($\tilde{h}$ is another universal function)

$$k = \frac{R_1^{\,d}}{\tau_1}\tilde{h}\,(X,\{\alpha_i/N_i\},t/\tau_1)$$

$$X \equiv \left(\frac{N_1}{L}\right)^{-\epsilon/2}\frac{w^*-w}{w} \quad ({\rm C4})$$

which is helpful for large times. Expressing the renormalized series in terms of X and exponentiating (guided by the RGE solution eq C4 in which a prefactor $\propto N_1^{-\epsilon/2}$ appears) one obtains

$$k_\infty = \frac{\epsilon\pi^2(\theta_1+\theta_2)^2}{16}\frac{R_1^{\,d}}{\tau}\frac{1}{1+X}$$

$$N_1 = N_2 = N \quad ({\rm C5})$$

Consider now the case of general $\{N_i,\alpha_i\}$ when the structure of k is given by eq C4. Now when one chain is much smaller than the other, $N_1/N_2 \equiv \lambda \ll 1$, eq 10 implies that $(1/\lambda)g_2(u\lambda^2) \approx \theta_2 u^{1/2}$ provided $u \le 1/\lambda^2$. Thus the time integral in eq 11 simplifies somewhat

$$\int_0^\infty {\rm d}u\left(\frac{1}{g_1(u)+\lambda^{-1}g_2(u\lambda^2)}\right)^{d/2} \approx \int_0^\infty {\rm d}u\left(\frac{1}{g_1(u)+\theta_2 u^{1/2}}\right)^{d/2} \equiv I\left(\frac{\alpha_1}{N_1}\right) \quad ({\rm C6})$$

with correction terms of order $\int_{1/\lambda^2}^\infty {\rm d}u\, u^{-d/2} \sim \lambda^{2-\epsilon}$ since $g_1 \sim g_2 \sim u$ for large u. The function I depends on α_1/N_1 through the implicit dependence of g_1 on that variable. The α_2/N_2 dependence drops out in this limit. Now since I has unchanged divergence structure, the resultant renormalized series matches eq C1 except that the $\{...\}$ term lacks $\ln t/\tau_1$ and gains the nonsingular part of I plus corrections of order λ^2. Thus we find to leading orders in ϵ

$$k_\infty = H\left(X,\frac{\alpha_1}{N_1}\right)\frac{R_1^{\,d}}{\tau_1}[1+O(\lambda)^2]$$

$$N_1 \ll N_2 \quad ({\rm C7})$$

where $X \equiv (N_1/L)^{-\epsilon/2}(w^*-w)/w$ is governed by N_1. $H(X,\alpha_1/N_1)$ is a universal function of dimensionless reactive group location on the small chain and is equal to $(1+X)^{-1}(\epsilon\pi^2/16)(\theta_1+\theta_2)^2$ to $O(\epsilon)$. For $X \gg 1$, $H(X,\alpha_1/N_1) \approx$ constant $1/X$.

Appendix D. Calculation of $\rho^0{}_{\rm eq}$

To complete the bare series eq 11 to second order we need $\rho^0{}_{\rm eq}$ to first order in υ_0

$$\rho^0{}_{\rm eq} = \langle\delta(\mathbf{r})\rangle \equiv \mathcal{N}^{-1}\int {\rm d}[\mathbf{r}_1]\,{\rm d}[\mathbf{r}_2]\exp\{-H_0[\mathbf{r}_1,\mathbf{r}_2] - H_{\rm I}[\mathbf{r}_1,\mathbf{r}_2]\}\,\delta(\mathbf{r}) \quad ({\rm D1})$$

where $\mathcal{N}$ is the normalization (i.e. the numerator without the $\delta(\mathbf{r})$ factor) and H_0 and $H_{\rm I}$ are given in eq A1. Expanding in powers of υ_0 (noting $H_{\rm I} \propto \upsilon_0$) one finds (see ref 44 for a similar calculation where the diagram rules etc. are described in detail)

$$\langle\delta(\mathbf{r})\rangle = \langle\delta\rangle_0 - \langle H_{\rm I}\delta\rangle_0 + \langle\delta\rangle_0\langle H_{\rm I}\rangle_0 + O(\upsilon_0^{\,2}) \quad ({\rm D2})$$

where $\langle...\rangle_0 \equiv \mathcal{N}_0^{-1}\int {\rm d}[\mathbf{r}_1]\,{\rm d}[\mathbf{r}_2]\exp\{-H_0\}\{...\}$ and $\mathcal{N}_0$ is the noninteracting normalization. Now clearly $\langle\delta\rangle_0 = 1/V$ since $\langle...\rangle_0$ refers to Gaussian (ideal) chains. From the expression for $H_{\rm I}$ in eq A1 we have

$$\langle H_{\rm I}\rangle_0 = \frac{\upsilon_0}{2}(D_2(N_1^{\,0}) + D_2(N_2^{\,0})) + O\left(\frac{\upsilon_0}{V}\right)$$

$$D_2(N^0) \equiv \int_0^{N^0}{\rm d}n\int_0^{N^0}{\rm d}n'\,\langle\delta(\mathbf{r}(n)-\mathbf{r}(n'))\rangle_0 = \frac{2}{(2\pi)^{d/2}}(N_1^{\,0})^{\epsilon/2}\left[-\frac{2}{\epsilon}+O_{\rm c}(\epsilon^0)\right] = -\frac{1}{\epsilon\pi^2}-\frac{1}{2\pi^2}\ln N_1^{\,0} + O_{\rm c}(\epsilon^0) \quad ({\rm D3})$$

where $D_2(N^0)$ is the diagram in Figure 4a. The $O(1/V)$ correction is the contribution of the diagram of Figure 4b, namely $(\upsilon_0/2)\int_0^{N_1^0}{\rm d}n\int_0^{N_1^0}{\rm d}n'\,\langle\delta(\mathbf{r}(n)-\mathbf{r}(n'))\rangle_0 = (\upsilon_0/2)N_1^{\,0}N_2^{\,0}/V$. Note the anticipated $1/\epsilon$ poles in D_2 and note also that we want to retain all $\{\alpha_i,\beta_i,N_i\}$-dependent terms up to $O(\epsilon^0)$.

For the $\langle H_{\rm I}\delta\rangle_0$ term in eq D2 we will need another diagram

$$\tilde{D}(\alpha^0,\beta^0) \equiv 2\int_0^{\alpha^0}{\rm d}n_1\int_{\alpha^0}^{\alpha^0+\beta^0}{\rm d}n_2\,\langle\delta(\mathbf{r}(n_1)-\mathbf{r}(n_2))\rangle_0 \quad ({\rm D4})$$

which is defined (see Figure 4c) such that the two ends of the dotted interaction lines can be anywhere provided they lie on opposite sides of the black dot. Thus $\tilde{D}$ sums interactions between points belonging to different subsegments of a segment of Gaussian chain, whereas D_2 includes also pairs belonging to the same subsegment. Thus

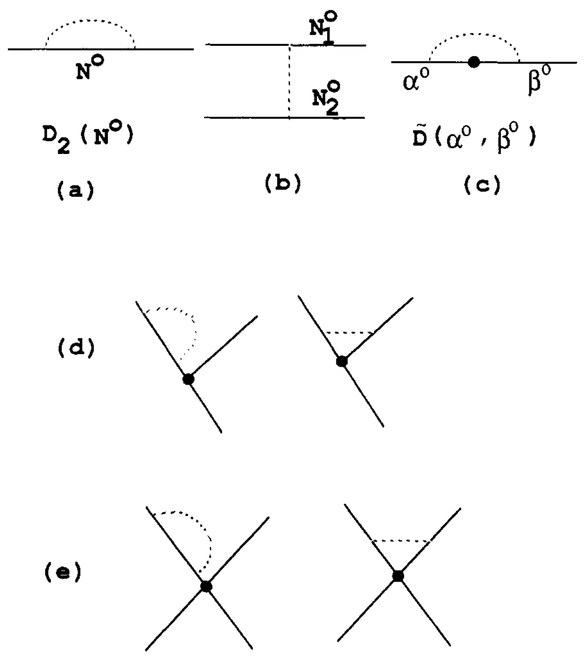

Figure 4. Diagrams used to calculate $\rho^0{}_{\rm eq}$.

$$\tilde{D}(\alpha^0,\beta^0) = D_2(\alpha^0+\beta^0) - D_2(\alpha^0) - D_2(\beta^0) = \frac{1}{\pi^2\epsilon} + \frac{1}{2\pi^2}\ln\frac{\alpha^0\beta^0}{\alpha^0+\beta^0} + O_{\rm c}(\epsilon^0) \quad \text{(D5)}$$

We can now evaluate $\langle H_{\rm I}\delta\rangle_0$. This is simplest for two end groups (Figure 2a)

$$V\langle H_{\rm I}\delta\rangle_0 = \frac{\upsilon_0}{2}D_2({N_1}^0+{N_2}^0) = \frac{\upsilon_0}{2}\left\{-\frac{1}{\epsilon\pi^2} - \frac{1}{2\pi^2}\ln({N_1}^0 + {N_2}^0)\right\} + O_{\rm c}(\epsilon^0), \qquad \text{2 end} \quad \text{(D6)}$$

For one end and one interior all diagrams of the type illustrated in Figure 4d must be summed, where the three arms are of lengths $N_1{}^0$, $\alpha_2{}^0$, $\beta_2{}^0$ (see Figure 2b). Whenever the interaction line straddles the dot, the same rules as for $\tilde{D}$ apply. Thus

$$V\langle H_{\rm I}\delta\rangle_0 = D_2({N_1}^0) + D_2({\alpha_2}^0) + D_2({\beta_2}^0) + \tilde{D}({\alpha_2}^0,{\beta_2}^0) + \tilde{D}({\alpha_2}^0,{N_1}^0) + \tilde{D}({\beta_2}^0,{N_1}^0)$$
$$= \frac{\upsilon_0}{2}\frac{1}{2\pi^2}\ln\left\{\frac{{\alpha_2}^0{\beta_2}^0{N_1}^0}{({\alpha_2}^0+{\beta_2}^0)({\alpha_2}^0+{N_1}^0)({\beta_2}^0+{N_1}^0)}\right\} + O_{\rm c}(\epsilon^0), \qquad \text{1 end, 1 interior} \quad \text{(D7)}$$

Note that the $1/\epsilon$ poles cancel. Turning now to the case of two interior groups, in Figure 4e the relevant classes of diagrams are shown where the four arms are of lengths $\{\alpha_i{}^0,\beta_i{}^0\}$. Summing over all such diagrams one obtains

$$V\langle H_{\rm I}\delta\rangle_0 = \sum_{i=1}^{2}(D_2({\alpha_i}^0) + D_2({\beta_i}^0)) + \sum_{ij=1}^{2}\tilde{D}({\alpha_i}^0,{\beta_j}^0) + D_2({\alpha_1}^0,{\alpha_2}^0) + D_2({\beta_1}^0,{\beta_2}^0)$$
$$= \frac{\upsilon_0}{2}\left[\frac{2}{\epsilon\pi^2} + \frac{1}{2\pi^2}\ln\left\{\frac{(\alpha_1^0\alpha_2^0\beta_1^0\beta_2^0)^2}{({\alpha_1}^0+{\alpha_2}^0)({\beta_1}^0+{\beta_2}^0)\,\Pi_{ij}({\alpha_i}^0+{\beta_j}^0)}\right\}\right], \qquad \text{2 interior} \quad \text{(D8)}$$

Using all of these results in eq D2 we have to $O(\upsilon_0)$

$$V\rho^0_{\rm eq} \equiv V\langle\delta\rangle_0 = 1 + \frac{\upsilon_0}{2\pi^2}\left\{\frac{-1/-2/-4}{\epsilon} + \frac{1}{2}\ln Y\right\}$$
$$Y \equiv \left\{\left(\frac{{N_1}^0+{N_2}^0}{{N_1}^0{N_2}^0}\right)\Big/\left(\frac{({\alpha_2}^0+{N_1}^0)({\beta_2}^0+{N_1}^0)}{({\alpha_2}^0{\beta_2}^0{N_1}^0)^2}\right)\Big/\left(\frac{({\alpha_1}^0+{\alpha_2}^0)({\beta_1}^0+{\beta_2}^0)({\alpha_1}^0+{\beta_2}^0)({\beta_1}^0+{\alpha_2}^0)}{({\alpha_1}^0{\alpha_2}^0{\beta_1}^0{\beta_2}^0)^2}\right)\right\},$$
$$\text{2 end/1 end, 1 interior/2 interior} \quad \text{(D9)}$$

Appendix E. RG Analysis for Good Solvents

With $V\rho^0{}_{\rm eq}$ given in eq D9 the bare series eq 11 acquires an extra w_0e_0 term where $e_0 \equiv \upsilon_0L^{\epsilon/2}$ is a dimensionless excluded volume coupling. To order ϵ^2

$$-k\xi_0\eta = w_0 + w_0e_0L^{-\epsilon/2}\frac{1}{2\pi^2}\left\{\frac{-(1/2/4)}{\epsilon} + \frac{1}{2}\ln(...)/(...)/(...)\right\} + w_0^2L^{-\epsilon/2}\int_0^t {\rm d}t'\,\frac{S(t')}{\zeta_0V} \quad \text{(E1)}$$

where ln(...)/(...)/(...) denotes the logarithm factor in eq D9 and our convention hereafter is that (...)/(...)/(...) refers to (2 end groups)/(one end, one interior)/(2 interior) respectively. $\xi_0 \equiv \zeta_0L^{\epsilon/2}/\eta$ is the dimensionless hydrodynamical coupling constant (from the definition of F_{12} in eq A1 the relevant dimensional relationships are $[r^2] = [N^0]$,$[t] = [N^0]^{d/2}$, and $[\zeta_0] = [t]/[N^0]^2$). We assume the relations between bare and renormalized quantities are as for intramolecular reactions:[33] $\xi_0{}^{-1} = \xi^{-1}(1-3\xi/8\pi^2\epsilon - e/2\pi^2\epsilon)$ and $e_0 = e$ (this last relation is only needed to first order). That is, we assume e_0 and ξ_0 are renormalized as for no sink.[31] For intramolecular reactions,[29,33,23] this has always produced consistently renormalizable expressions (to the orders dealt with) and it seems to be a reasonable assumption that this remains true for the intermolecular case.

Renormalizing ξ_0 and w_0 (which now depends on w, e, and ξ) one finds the $\rho^0{}_{\rm eq}$ and $w_0{}^2$ divergences are absorbed by the $\xi_0{}^{-1}$ w_0 term if w_0 is defined appropriately. Since all terms involving chain lengths possess second order prefactors, the renormalization to this order is trivial: $\{\alpha_i{}^0,\beta_i{}^0,N_i{}^0\} \rightarrow \{\alpha_i,\beta_i,N_i\}$. Noting that the $w_0{}^2$ term in eq E1 is unchanged from Rouse dynamics so we can use eq 13 for its short time form, and taking the excluded volume and hydrodynamical fixed points[31] $e \rightarrow e^* = \pi^2\epsilon/2$, $\xi \rightarrow \xi^* = 2\pi^2\epsilon$ the renormalized short time series reads

$$k(t \ll \tau_i)\,\xi^*\,\eta = -w\left[1 + \frac{\epsilon}{8}\ln(...)/(...)/(...) + \frac{\epsilon}{8}(1/2/4)\ln L + \frac{\epsilon w}{16w^*}(1/2/4)\ln\frac{t}{t_{\rm L}}\right] \quad \text{(E2)}$$

Here $t_{\rm L} = \zeta L^{d/2}$ and $w^* = (\epsilon\pi^4/4)(\theta_1+\theta_2)^2[1/2/4]$ is the positive unstable fixed point of the beta function $\beta_{\rm w} = w(w-w^*)/[2\pi^4(\theta_1+\theta_2)^2]$ whose stable fixed point *vanishes*.

The RGE is very similar to that for intramolecular reactions,[44] as is the dimensional analysis with the important difference that, since $[t] = [r]^d$, it follows from eq 2 that k is now dimensionless. To describe the short time behavior, we choose a rescaling factor which eliminates the time argument in the general solution to the RGE. Thus one obtains

$$k = G(\{t/\tau_{0_i},t/\tau_{\beta_i}\}, X_t)$$

$$X_t \equiv \left(\frac{t}{t_{\mathrm{L}}}\right)^{\theta-1}\frac{w-w^*}{w}, \qquad \theta - 1 = \frac{g}{d},$$
$$\frac{\tau_{0_{\mathrm{i}}}}{t_{\mathrm{L}}} = \mathrm{const}\left(\frac{\alpha_i}{L}\right)^{\nu d} \quad \text{(E3)}$$

where $g = (\epsilon/4)/(\epsilon/2)/\epsilon$ is identified as the correlation hole exponent of des Cloizeaux,[20] correct to order ϵ. $\tau_{\alpha_{\mathrm{i}}}$ is the relaxation time[31] of the segment of length α_i and $\theta \equiv (d + g)/z = 1 + g/d$ is the reaction exponent introduced in the main body of the text. Next we express w in terms of X_{t} and we note that the $\ln L$ terms in eq E2 exactly convert the $\{\alpha_i,\beta_i,N_i\}$ variables in the logarithm to $\{\alpha_i/L,\beta_i/L,N_i/L\}$. One obtains

$$k\xi^*\eta = \frac{w^*}{X_t - 1}\left\{1 + \frac{\epsilon}{8}\ln(...)/(...)/(...) + \frac{g}{4}\ln\frac{t}{t_{\mathrm{L}}}\right\}$$
$$= \frac{w^*}{X_t - 1}\left\{1 + \frac{g}{d}\ln(...)^{\nu d}/(...)^{\nu d/2}/(...)^{\nu d/4} + \frac{g}{d}\ln\frac{t}{t_{\mathrm{L}}}\right\} \quad \text{(E4)}$$

where the interpretations $\epsilon/8 = (g\nu)/(g\nu/2)/(g\nu/4)$ and $g/4 = g/d$, consistent to the orders we retain, are made under guidance of the RGE solution eq E3. Exponentiating (one is forced into some kind of exponentiation to avoid negative k at large $\{N_i,\alpha_i,\beta_i\}$) we have

$$k\xi^*\eta = \frac{w^*}{X_t - 1}\left(\frac{t}{\tilde{\tau}}\right)^{g/d}, \quad \frac{\tilde{\tau}}{t_{\mathrm{L}}} \equiv \left(\frac{\tilde{N}}{L}\right)^{\nu d}, \quad t \ll \{\tau_{\alpha_{\mathrm{i}}},\tau_{\beta_{\mathrm{i}}}\} \quad \text{(E5)}$$

where $\tilde{N}$ is defined in the main text in eq 26. For $t \gg t_{\mathrm{L}}$ since $X_t \gg 1$ the time-dependence drops out

$$k(t_{\mathrm{L}} \ll t \ll \{\tau_{\alpha_{\mathrm{i}}},\tau_{\beta_{\mathrm{i}}}\})\xi^*\eta \approx \frac{w^* w}{w - w^*}\left(\frac{\tilde{N}}{L}\right)^{-\nu g} \quad \text{(E6)}$$

For long times the analysis is very similar. Choosing to scale all lengths with N_1 leads to a RGE solution of the form

$$k = \tilde{G}(\{\alpha_i/N_1,\beta_i/N_1\},X,t/\tau_1), \qquad X \equiv \left(\frac{N_1}{L}\right)^{-\nu g}\frac{w}{w - w^*} \quad \text{(E7)}$$

The change in the bare series relative to short times is a more complex $w_0{}^2$ term involving the time integral of $S(t)$. Renormalization is unchanged and when expressed in terms of X the renormalized series for N_1 large ($X \ll 1$) gives the identical result to the intermediate time result of eq E6. In this limit the complex time integral of $S(t)$ is $O(X^2)$ and so may be dropped.

Appendix F. RG Analysis for Θ Solvents

To the orders at which we work the renormalized series is the same as that for Rouse dynamics, eq C1, since the bare series are identical. The difference is that ξ_0 is renormalized, leading to a different beta function at the hydrodynamic and Gaussian fixed point[31] $\xi = \xi^* = 8\pi^2\epsilon/3$. We find $\beta_{\mathrm{w}} = w^2/[2\pi^4(\theta_1 + \theta_2)^2]$ has a double zero, indicating logarithmic behavior. The RGE is, as for the Rouse and good solvent cases, very similar to the intramolecular case and dimensional analysis is unchanged from that described in Appendix E for good solvents. Solving the RGE and scaling out the t argument we find

$$k = G\left(X_t, \left\{\frac{t}{\tau_{\alpha_{\mathrm{i}}}}, \frac{t}{\tau_{\beta_{\mathrm{i}}}}\right\}\right), \qquad X_t \equiv 1/[\ln(t/t_{\mathrm{L}}) - 4\pi^4(\theta_1 + \theta_2)^2/w] \quad \text{(F1)}$$

where $\tau_{\alpha i} \propto \alpha_i{}^{d/2}$ ($\nu = 1/2$). Rephrasing the short time renormalized series in terms of X_t leads to

$$k = \frac{3\pi^2(\theta_1 + \theta_2)^2 X_t}{2\epsilon\eta}, \qquad t \ll \{\tau_{\alpha_{\mathrm{i}}},\tau_{\beta_{\mathrm{i}}}\} \quad \text{(F2)}$$

At large times relative to t_{L} (but still short compared to $\{\tau_{\alpha_{\mathrm{i}}},\tau_{\beta_{\mathrm{i}}}\}$) this implies $k \propto 1/\ln(t/t_{\mathrm{L}})$.

At long times it helps to scale the RGE solution differently, such that chain lengths are measured in units of N_1. We find

$$k = \tilde{G}\left(X, \left\{\frac{\alpha_i}{N_1}\right\}, \frac{t}{\tau_{N_1}}\right), \qquad X \equiv 1/[\ln(N_1/L) - 2\pi^4(\theta_1 + \theta_2)^2/w] \quad \text{(F3)}$$

When $N_1 = N_2$ the renormalized series at long times is, as for the Rouse case, given by eq (C1) without the $\ln t/\tau_1{}^0$ term. In terms of X, we find

$$k_\infty = \frac{3\pi^2(\theta_1 + \theta_2)^2}{4\epsilon\eta}X \rightarrow \frac{3\pi^2(\theta_1 + \theta_2)^2}{4\epsilon\eta}\frac{1}{\ln N/L}, \quad \frac{N}{L} \gg 1, \quad N_1 = N_2 \equiv N \quad \text{(F4)}$$

Consider $N_1 \neq N_2$ in the special case of $N_1 \ll N_2$. As discussed in Appendix C in this case the w^2 term in the renormalized series now picks up a dependence on α_1/N_1 but not on α_2/N_2, i.e. only the small chain group positioning is involved. This leads to

$$k_\infty = \frac{3\pi^2(\theta_1 + \theta_2)^2}{4\epsilon\eta}X\left\{1 + \mathrm{const}\, X\left[F\left(\frac{\alpha_1}{N_1}\right) + \mathrm{O}\left(\frac{N_1}{N_2}\right)^2\right]\right\} + O_{\mathrm{c}}(\epsilon^2) + O(\epsilon^3) \quad \text{(F5)}$$

where F is a universal function.

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