FLUCTUATION EFFECTS IN MICROEMULSION REACTION MEDIA

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I. Introduction

The field of chemical engineering reactor design and kinetics, a traditional chemical engineering forté, has undergone a rapid transformation in the past two decades on both theoretical and practical fronts. On the theoretical front, the validity of classical theoretical ideas embodying *mean field* chemical rate expressions have been challenged, necessitating for resolution the injection of radically new ideas and concepts drawn from statistical mechanics and field theory [1–6]. These studies have led to a recognition of the

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importance of fluctuations and the role of spatial dimensionality in influencing chemical reaction kinetics. On the practical front, the focus is slowly moving away from classical reactors and catalysts and toward utilizing novel microstructured materials as catalysts and as reaction media for effecting reactions. For instance, nanoporous materials and self-assembled systems are presently being advanced as effective catalyst materials for their ability to provide compartmentalized spaces with a high surface-to-volume ratio [7]. It is therfore becoming imperative to gain a fundamental understanding of the reaction kinetics and mechanisms in such materials. However, most of the above-mentioned theoretical studies have so far dealt with the purported existence of a homogeneous continuum (which can be envisioned as the interior of a CSTR or a batch reactor), lacking the fine microscale structure characterizing these "novel" self-assembled materials. It is therefore of practical interest for chemical engineers to utilize the fundamental theoretical concepts developed so far to glean insights into the chemical kinetics of reactions effected in microstructured media. This article summarizes some of our own research focusing on this goal. While the example we have chosen is quite specific, the ideas embodied herein and the statistical mechanical tools and the issues thereby confronted possess a generic basis transcending the specificity of the scenario.

As previously mentioned, there has been a recent surge of interest in applications exploiting self-assembled systems such as micellar solutions, microemulsions, and lipid bilayers as reaction media [8, 9]. Among these systems, microemulsions have emerged as a popular choice for a number of diverse applications (cf., Refs. 10 and 11 and the references cited therein). Microemulsions represent thermodynamically stable dispersions of water in oil (or vice versa), owing their stability to the presence of an amphiphile at the interface between the constituents [12]. The phase behavior of these ternary mixtures has been extensively studied and can be considered well understood [12–15]. Thermodynamic studies have shown that, depending on the concentration of the different constituents, the structure of microemulsions can range from a dispersion of spherical droplets (at dilute concentrations of either oil or water) to complex interweaving bicontinuous networks of oil and water (at higher concentrations) [16]. The observed phase behavior of these microemulsions has presented interesting opportunities for the creation of novel materials by appropriate reactions within these media. A number of efforts are presently under way to "fix" these *nanoscale* structures of the microemulsion by reactions within the system. For instance, polymerization reactions have been carried out in microemulsions to produce the nanoscale analog of the latex particles conventionally produced by emulsion polymerization techniques [17]. Bicontinuous networks have also been fixed to create reticulated frameworks envisaging biomineralization applications [18]. Numerous other applications utilizing reactions in these microemulsion phases have also been suggested and implemented in contexts relating to catalysis, drug delivery, etc.

Considering the practical utility of such systems, the study of chemical reactivity in these systems is bound to possess important ramifications of relevance to the chemical engineering design of reactors envisioning the use of such media. In this context, it is pertinent to observe that most of the applications utilizing microemulsions as reaction media fall broadly into two generic classes: (i) those involving reactions within either or both (and possibly also at the interface) phases and (ii) those involving only reactions at the interface. It is to be noted here that there have been a few investigations on problems within the former category, focusing specifically on the effect of confining the reactants to "restricted" spaces [20–22]. In this work, we direct our considerations to the problems encompassed in the latter category. Within such a framework, we examine the effects (if any) of an oft-neglected issue in the consideration of reactions in these complex fluid systems, viz., the impact of thermal fluctuations upon the kinetics of interfacial reactions. Based on our (brief) description (in the preceding paragraph) of the different possible structures in these systems, it would be erroneous to conclude that the different phase structures observed in these systems are rigid and static. On the contrary, the surfactant interfaces that define the structure of the microemulsion possess bending moduli of the order of a few $k_\mathrm{b}T$ (where k_b represents the Boltzmann constant and T denotes the temperature), thereby making them highly susceptible to the influence of thermal fluctuations [23, 24]. Indeed, microemulsion phases owe their existence to the destruction of more ordered mesophases by thermal fluctuations. One may speculate that these fluctuations which dynamically modulate the interfaces might also influence the kinetics of reactions occurring on these "fluctuating" surfaces. It is to the examination of such effects that our analysis is directed in this two-part article. Our analysis is purely at the level of "transport processes"—"chemistry" issues relating to the possible change in mechanism of the reaction, etc., are completely ignored. Within a broader framework, our analysis identifies some important features in systems involving thermal fluctuations and diffusion limited reactions—a class of problems which, to our knowledge, has not been addressed heretofore in the literature. We also hope that this article will serve to highlight for the chemical engineering community some of the *nonclassical* issues encountered in reaction kinetics and the field-theoretic tools to resolve them.

In the following analysis, our primary interest centers on reactions of the type $A + B \rightarrow \emptyset$, wherein one of the reactants, say A, resides predominantly in the water phase, and the other reactant, B, resides in the oil phase. The product $\emptyset$ is assumed to be inert, chemically (i.e., does not react with A or B) and physicochemically (i.e., does not impede the transport of A or B or destabilize the microemulsion). In such a scenario, the reaction between A and B occurs predominantly at the oil–water interface. In this work, we also suppose that the reaction kinetics of such a reaction is of first order with respect to both the reactants, i.e., the rate of the reaction r is given by $-r = \lambda c_A c_B$, where λ denotes the second-order rate constant, and c_A and c_B denote the concentrations of A and B, respectively. Such an assumption is motivated purely by considerations of analytical tractability (in fact, we are forced to simplify this nonlinear kinetics even further in the second part of this work). Further, we focus specifically upon the bicontinuous and the droplet phases of the microemulsions (Fig. 1). As expounded in the Introduction both these structures have been utilized widely in applications, thereby rendering our analysis practically relevant. Moreover, the method of analysis employed for spherical microemulsions possesses a number of features generic to the comparable analysis of diffusion and reaction within ordered lyotropic phases. Thus, the qualitative features unearthed in the second part of this article (Section III) are expected to be equally valid for considerations pertaining to reactions carried out in lamellar phases, etc. Further, in both parts of the article (Sections II and III) we ignore the convective transport of the reactants (over and above that arising from pure molecular diffusion) arising as a consequence of the convective flow field generated due to fluctuations of the interface. While such effects are potentially interesting, they considerably complicate the analysis. The simplification arising from the neglect of convective transport can be construed as a low Péclet number limit of the physical situation. With such a scenario in mind, we henceforth focus on the purely diffusive transport of the solute species and their subsequent mutual anhiliation at the fluctuating interface.

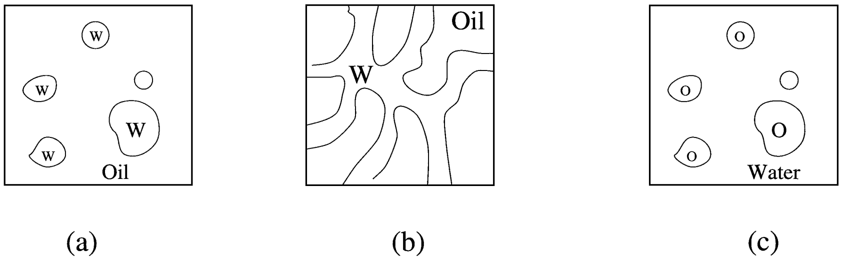

FIG. 1. The different microstructures of the microemulsion phase: (a) the water-in-oil droplet phase, (b) the bicontinuous phase, (c) the oil-in-water droplet phase.

In the following text we summarize the pertinent details of the analysis and the accompanying results. A reader who is interested in an elaboration of these details can refer to the detailed version of our previous article [25].

II. Reactions in the Bicontinuous Phase

A. DIFFUSION EQUATIONS

As expounded in Section I, we consider reactions of the type

$$A + B \to \emptyset, \qquad -r = \lambda c_A c_B, \tag{1}$$

where the reactants A and B possess contrasting affinities toward oil and water. Such an affinity is conveniently modeled within the framework of a diffusion equation by the inclusion of a biasing potential dependent upon the concentration of oil (or water). In the symmetric case involving equal oil and water concentrations (as we assume throughout this part of the article), the difference in the local concentrations of water and oil can instead be associated with an order parameter $\phi(\mathbf{x})$ [26], with the affinity of A and B then determined by the sign of $\phi(\mathbf{x})$. Without loss of generality, if we assume that reactant A has an affinity to water ($\phi > 0$) and B to oil ($\phi < 0$), we can formulate the transport and reaction of A and B in terms of a set of reaction–diffusion equations governing the concentrations c_A and c_B,

$$\frac{\partial c_A}{\partial t} = D_A \nabla^2 c_A - \lambda c_A c_B - \mu_A \nabla \cdot (c_A \nabla \phi), \tag{2}$$

$$\frac{\partial c_B}{\partial t} = D_B \nabla^2 c_A - \lambda c_A c_B + \mu_B \nabla \cdot (c_B \nabla \phi). \tag{3}$$

In the above equations D_A and D_B denote the diffusivities of A and B, respectively. The strengths of the affinities of the reactants A and B toward the solvents are quantified by μ_A and μ_B (each ≥ 0), respectively. While the above equation represents the most general structure for the diffusion equations appropriate for such a scenario, in an attempt to focus on the essential physics in the following analysis, we consider the symmetric case corresponding to $D_A = D_B = D$ and $\mu_A = \mu_B = \mu$.

To complete the description of the diffusion and reaction of solutes A and B in the fluctuating potential field $\phi(\mathbf{x}, t)$, we still need to specify the statistics of the fluctuations of $\phi(\mathbf{x}, t)$. To this purpose we conveniently adopt the "disordered fluid" model of the bicontinuous phase of the microemulsion [27] in conjunction with a conserved model for the dynamics of the fluctuations of potential field [28]. Within such a description, the *Gaussian* statistics of the potential field $\phi(\mathbf{x}, t)$ can be computed as[1]

$$\langle\phi(\mathbf{k}, \omega)\rangle = 0; \qquad \langle\phi(\mathbf{k}, \omega)\phi(\mathbf{k}', \omega')\rangle = \frac{\Delta^2 k^2 (2\pi)^d \delta^d(\mathbf{k} + \mathbf{k}')(2\pi)\delta(\omega + \omega')}{[\omega^2 + (uk^2 + vk^4 + wk^6)^2]}. \tag{4}$$

In the above equation Δ denotes a phenomenological constant specifying the strength of the fluctuations. Further, u, v, and w represent phenomenological parameters characterizing the equilibrium structure of the bicontinuous microemulsion. These parameters can be discerned experimentally by employing light-scattering techniques. In Eq. (4) we have displayed the results in terms of $\phi(\mathbf{k}, \omega)$, denoting the Fourier transform of $\phi(\mathbf{x}, t)$ and defined as

$$\phi(\mathbf{x}, t) = \int \frac{d^d\mathbf{k}}{(2\pi)^d} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\mathbf{k}\cdot\mathbf{x} - i\omega t} \phi(\mathbf{k}, \omega).$$

B. OBJECTIVES

The above set of equations, (1)–(4) (with $D_A = D_B = D$ and $\mu_A = \mu_B = \mu$), represents the field-theoretic formulation of the transport and reaction of solutes A and B in a bicontinuous phase of microemulsion. In view of the fact that the fluctuations corresponding to the order parameter ϕ possess a vanishing mean value, i.e., $\langle\phi\rangle = 0$, it is reasonable to query if one could, at sufficiently long length and time scales (to allow for the self-averaging of the fluctuating potential), infer that the effect of the fluctuations of the microemulsion proves irrelevant in impacting the transport and the reaction of solutes A and B. On the other hand, since the concentrations of the reactants are coupled to the fluctuations of the ϕ field, it also appears intuitive that the dynamic distribution of solutes A and B, and therefore the fluctuations of the microemulsion, should exert a discernible influence on the instantaneous reaction rate. In the former case, it should therefore be possible to quantify the decay rates of reactants A and B without any reference whatsoever to the fluctuating "potential" $\phi(\mathbf{x}, t)$. In the event that such a quantification is indeed possible, one could infer that the microscale fluctuations of the bicontinuous phase have no discernible effect on the overall transport and reaction processes. On the other hand, uncovering a nonclassical decay rate for the reactants would instead indicate a nontrivial behavior arising from the presence of fluctuations of the bicontinuous phase.

Mean-field scaling analysis provides a "quick and easy" way to discern the answers to the questions raised above. However, the results of such an

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[1] Note that a Gaussian field is uniquely specified by its first two moments.

analysis are not always accurate and would typically need to be corroborated by more rigorous analysis employing renormalization group theory (RG). Nevertheless, mean-field analysis enables one to glean physical insights into the results and also understand the regimes of their validity. In the following text, we elaborate the details of a self-consistent mean-field analysis which allows one to discern the asymptotic decay kinetics. Subsequently, we indicate the results of the RG calculations which confirm the results predicted by mean-field theory.

C. MEAN-FIELD ANALYSIS

At the outset we consider the case wherein $\phi(\mathbf{x}, t) = 0$ [29, 30] to elucidate the role of fluctuations and the (mean-field) manner in which they can be discerned. This also serves to illustrate the underlying basis for the *anomalous mean-field* (AMF) kinetics encountered in reaction-diffusion systems.[2] Subsequently, we extend the arguments to the case wherein the potential $\phi(\mathbf{x}, t)$ influences the dynamics.

1. $\phi(\boldsymbol{x}, \mathrm{t}) = 0$ *(AMF Kinetics)*

At $t = 0$, the mean densities n_{0A} and n_{0B} of reactants A and B are identical (denoted n_0) and spatially homogeneous. However, the randomness embodied in the distribution of A and B allows for fluctuations in the number of particles within a volume V to an order $(n_0V)^{1/2}$. After a time t, the particles have had a chance to diffuse and mutually anhiliate other particles within a volume $(Dt)^{d/2}$ around themselves. Therefore, after the elapse of the time t, the volume $(Dt)^{d/2}$ retains only the initial imbalance resulting from fluctuations. This corresponds to the presence of $[n_0(Dt)^{d/2}]^{1/2}$ particles in the volume $(Dt)^{d/2}$, and therefore a density $[n_0/(Dt)^{d/2}]^{1/2}$, yielding $n(t) \approx n_0^{1/2}(Dt)^{-d/4}$.

2. *In the Presence of the Potential* $\phi(\boldsymbol{x}, \mathrm{t})$

It is evident from the above argument that the temporal variation of the mean-squared displacement of the reactants determines the asymptotic decay rates. For instance, if $\langle\langle r^2\rangle\rangle \sim t^\delta$ (where the notation $\langle\langle\cdots\rangle\rangle$ is used to denote ensemble averages over the different particles of a reactant species), then the concentrations decay as $n_0^{1/2}t^{-d\delta/4}$. Therefore it behooves us to determine the exponent δ for diffusion in the fluctuating potential field.

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[2] This is in contrast to the classical kinetics, which, for a second-order reaction of the type considered in this article, would predict $c_A(t), c_B(t) \sim t^{-1}$ when $c_A(t = 0) = c_B(t = 0)$.

In the following we outline a self-consistent Flory-type argument to enable the computation of δ. This type of argument has also been used in contexts relating to the wandering exponent of polymers [31] and diffusion in turbulent velocity fields [32] and has provided results reasonably in accord with more rigorous calculations.

The starting point for this analysis is the Langevin equation for the motion of a particle in the potential field ϕ (in the absence of inertial terms)

$$\frac{d\mathbf{r}}{dt} = -\nabla\phi + \boldsymbol{\xi}(t). \tag{5}$$

$\boldsymbol{\xi}$ represents a random thermal noise with statistics,

$$\langle\boldsymbol{\xi}(t)\rangle = 0; \qquad \langle\boldsymbol{\xi}(t)\boldsymbol{\xi}(t')\rangle = 2D\mathbf{I}\delta(t-t'), \tag{6}$$

where D represents the diffusivity of the particle and $\mathbf{I}$ denotes the idemfactor (or unit tensor). The above Langevin equation in conjunction with the noise statistics (6) is formally equivalent to the diffusion equation (2) [or (3)] in the absence of reaction terms ($\lambda = 0$).

We commence our analysis by considering the motion of the particle in the fluctuating potential ϕ and in the absence of the thermal noise ξ. In such a case, the mean-squared displacement of the particle, denoted $\sigma^2(t)$, can be expressed in terms of a heuristic generalization of the Kubo formula[3]

$$\sigma^2(t) \sim t\int_0^t d\tau\langle\langle\nabla\phi(\mathbf{r}(\tau),\tau)\cdot\nabla\phi(\mathbf{r}(0),0)\rangle_\phi\rangle_{\mathbf{r}}. \tag{7}$$

(In the following our interest centers on scaling laws, and therefore we omit the numerical prefactors that accompany the expressions.) In the above equation, we use the notation $\langle\cdots\rangle_\phi$ to denote an average over the statistics of the fluctuating field ϕ and $\langle\cdots\rangle_{\mathbf{r}}$ to denote a comparable average over an ensemble of particle displacements.

The results utilized so far to describe the dynamics of the particle are accurate and involve no assumptions [except insofar as the validity of Eq. (7), which posits that sufficient time has elapsed to assure stationarity properties]. However, to evaluate the averages embodied in Eq. (7) we require the statistics of the paths of the particle—which is unknown. Consequently, we invoke the assumption that the statistics of the particle paths are Gaussian with a variance $\sigma^2(t)$ to be determined *self-consistently* from Eq. (7). This assumption is equivalent to the claim that the statistics of the particle trajectories can be determined from the knowledge of the first two moments

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[3] Since $\langle\phi\rangle = 0$, there is no net drift of the particle.

of the trajectory. Within such an assumption, the probability distribution $P[\mathbf{r}(t)]$ for the displacement of the particle $\mathbf{r}(t)$ can be written

$$P[\mathbf{r}(t)] = \frac{1}{[2\pi\sigma^2(t)]^{d/2}} \exp\left[-\frac{\mathbf{r}^2(t)}{2\sigma^2(t)}\right]. \tag{8}$$

Utilizing the above assumption and Eq. (4) we obtain

$$\begin{aligned} &\langle\langle\nabla\phi(\mathbf{r}(\tau),\tau)\cdot\nabla\phi(\mathbf{r}(0),0)\rangle_\phi\rangle_\mathbf{r} \\ &\quad\sim \int d^d\mathbf{r}\, P[\mathbf{r}(t)] \int \frac{d^d\mathbf{k}}{(2\pi)^d} \frac{k^2 e^{-i\mathbf{k}\cdot\mathbf{r}} e^{-k^2(u+vk^2+wk^4)t}}{u+vk^2+wk^4}, \end{aligned} \tag{9}$$

The quadratures involving $\mathbf{r}$ in the above equation can be explicitly evaluated to yield

$$\langle\langle\nabla\phi(\mathbf{r}(\tau),\tau)\cdot\nabla\phi(\mathbf{r}(0),0)\rangle_\phi\rangle_\mathbf{r} \sim \int k^{d+1} dk \frac{e^{-k^2(u+vk^2+wk^4)t-k^2\sigma^2/2}}{u+vk^2+wk^4}. \tag{10}$$

The above expression can be evaluated asymptotically for $t \to \infty$ by Laplace's method to yield

$$\langle\langle\nabla\phi(\mathbf{r}(\tau),\tau)\cdot\nabla\phi(\mathbf{r}(0),0)\rangle_\phi\rangle_\mathbf{r} \sim \left(\frac{\sigma^2}{2}+ut\right)^{-(d+2)/2}. \tag{11}$$

Using Eq. (7) in conjunction with the above result we obtain,

$$\frac{d}{dt}\left(\frac{\sigma^2}{t}\right) \sim \left(\frac{\sigma^2}{2}+ut\right)^{-(d+2)/2}. \tag{12}$$

If $\sigma^2/t \gg u$ as $t \to \infty$ (to be verified *a posteriorily*), then

$$\frac{d}{dt}\left(\frac{\sigma^2}{t}\right) \sim t^{-(d+2)/2}\left(\frac{\sigma^2}{t}\right)^{-(d+2)/2}, \tag{13}$$

i.e.,

$$\sigma^2 \sim t^{4/(d+4)}. \tag{14}$$

However, this result is not consistent with the assumption employed in reducing the differential equation (12) to Eq. (13). Therefore we set $\sigma^2/t \ll u$ as $t \to \infty$ to obtain

$$\frac{d}{dt}\left(\frac{\sigma^2}{t}\right) \sim t^{-(d+2)/2}, \tag{15}$$

i.e.,

$$\sigma^2 \sim t^{(2-d)/2}. \tag{16}$$

The above self-consistent analysis suggests that the asymptotic dynamics of a particle in the fluctuating potential field satisfies $\sigma^2(t) \sim t^{(2-d)/2}$. Note that the above analysis has neglected the thermal noise $\boldsymbol{\xi}(t)$. If we append the thermal noise to the above dynamics, we obtain $\sigma^2(t) \sim t^{(2-d)/2} + t \sim t$ as $t \to \infty$ ($\forall d > 0$). Therefore, we obtain the surprising result that the thermal noise dominates the diffusion dynamics of the particle in the potential field. Thus, the mean-squared displacement of the particle is expected to be identical to that in the absence of the potential ϕ, and therefore the reaction kinetics is expected to be unmodified from its value in the absence of the potential, viz., $c(t) \sim t^{-d/4}$.

Note, however, that the conclusions drawn are valid only in the asymptotic long-time limit ($t \to \infty$). At short time scales, the particle can be envisioned to execute a random walk in a potential field wherein the term corresponding to $w\nabla^6\phi$ dominates the dynamics of the fluctuations of the potential field. In such a case, one can repeat the above analysis by utilizing the following functional form for the correlations of ϕ

$$\langle \phi(\mathbf{k}, \omega)\phi(\mathbf{k}', \omega')\rangle = \frac{\Delta^2 k^2 (2\pi)^d \delta^d(\mathbf{k} + \mathbf{k}')(2\pi)\delta(\omega + \omega')}{\omega^2 + w^2 k^{12}}. \tag{17}$$

Such an exercise yields $\sigma^2(t) \sim t^{(4-d)/2}$ and therefore $c(t) \sim t^{-d(4-d)/8}$. However, this result is valid only for times t such that $\sigma^2(t) > Dt$ (to dominate thermal diffusion) and $\sigma^2(t) < 1/q_m^2$, where q_m denotes the wavelength at the which the dynamics of the fluctuations of ϕ crosses over to the hydrodynamic form. In situations encountered in practice, this crossover length is of the order of few hundred angstroms,[4] indicating therefore that this regime might be practically unobservable.[5] Thus, mean-field arguments suggest that $c_A, c_B \sim n_0^{1/2} t^{-d/4}$, for $t \to \infty$.

D. RENORMALIZATION GROUP THEORY

Renormalization group theory (RG) provides a natural framework for identifying the behavior of a system at the longest length and time scales [33]. RG enables one to relate the corresponding changes in the magnitudes of the parameters of a model to a change in the length scale of observation. The results of a RG analysis are typically expressed in the form of a flow equation yielding $\psi(l)$, where ψ represents the parameter and l the (variable) length scale of the observation. Synchronous with a rescaling of the length

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[4] Scattering experiments on bicontinuous microemulsions indicate a peak at a wavelength $q = q^* \sim 10^{-2}$ Å^{-1} [15, 27]. The regime in which the above functional form for the potential is valid corresponds to $q \gg q^*$.

[5] Other factors might also preclude the existence of this regime, for instance, the validity of the Kubo formula for such short time scales.

by a factor b, the time also gets rescaled as $t \to tb^z$, where z is termed the dynamical exponent. The dynamical exponent z embodies the interplay among diffusion, the fluctuations of the potential, and possibly also the reaction. It is evident from straightforward dimensional analysis that the exponent δ in the preceding section is related to z by

$$\delta = \frac{2}{z}. \tag{18}$$

The accompanying discussion in the preceding section then suggests that the asymptotic decay kinetics is of the form $c_A, c_B(t) \sim t^{-d/2z}$.[6] Thus, determining the dynamical exponent z also determines the functional form of the asymptotic decay kinetics. This is the philosophy underlying the analysis we effected. However, in the following we eschew the details of the RG calculations, confining ourselves to a discussion of the resulting flow equations and the manner in which they tie into the mean-field analysis presented. A reader who is interested in the details of the RG calculations is advised to refer to our article [25].

To implement a RG analysis, we need to reformulate the diffusion equations (2) and (3) as a path integral. Such an objective is realized using the generating functional formalism of Martin, Siggia, and Rose (MSR) [34]. In this framework, the field theory corresponding to the above diffusion equations is reexpressed in terms of a generating functional $\mathcal{Z}$. Subsequently, a diagrammatic expansion of the generating functional is employed to discern the functional forms of the renormalized parameters. We employ the (by now) standard momentum space renormalization procedure of Wilson [33, 39]. Subsequently, the length and time scales within the generating functional are rescaled so as to regenerate an action identical in form to the original, with, however, the renormalized parameters replacing the bare (or unrenormalized) parameters. Carrying out this procedure for an infinitesimal rescaling of length enables one to generate (differential) flow equations relating the renormalization of parameters to the renormalization of length.

As indicated at the outset of the RG analysis, our primary interest centers upon the dynamical exponent z. The relevance or irrelevance of the fluctuations of the potential $\phi(\mathbf{x}, t)$ is circumscribed by the explicit value of the dynamical exponent z. If the fluctuations of the potential have no effect on the transport and reaction kinetics of the solute, then the parameter μ in the above equations will flow successively toward smaller values on rescaling, eventually vanishing at the longest length scales ($l \to \infty$). In such a case, we can set $z = 2$, thereby leaving D and u invariant upon rescaling. This would then preserve the kinetics as obtained in the absence of the potential $\phi(\mathbf{x}, t) = 0$. In the following (refer to Ref. 25 for details) we discuss the flow

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[6] In the case of diffusion in the absence of the potential and reactions, we have $z = 2$, thereby yielding the results in Refs. 29 and 30.

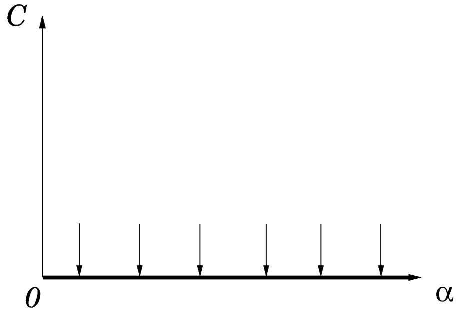

FIG. 2. The phase-space flow diagram corresponding to Eqs. (20) and (21).

equations for n_0, $\alpha = u/D$, and $C = \mu^2\Delta^2/D^3d$, where d denotes the spatial dimensionality of the reaction media

$$\frac{\partial \ln n_0}{\partial l} = d, \tag{19}$$

$$\frac{\partial \ln C}{\partial l} = -d - C\frac{7-3\alpha}{2\alpha(1+\alpha)^2}, \tag{20}$$

$$\frac{\partial \ln \alpha}{\partial l} = -C\frac{3}{4(1+\alpha)^2}. \tag{21}$$

The above set of flow equations possesses a line of stable fixed points at $C = 0$ (cf. Fig. 2), implying that at the longest length scales the renormalized system flows toward one wherein C vanishes. This result indicates that the coupling strength β vanishes upon renormalizing, thereby suggesting that the fluctuations of the microemulsion are indeed *irrelevant* in impacting the long-time kinetics of the reaction.

E. DISCUSSION

In this section, we summarize our results and discuss their physical implications on the reaction kinetics in the bicontinuous phases. *The RG analysis confirmed our mean-field arguments and thereby predicts that the dynamic fluctuations of the microemulsion will be irrelevant in impacting the hydrodynamic behavior (long length and time scale) of the system. Thus, the kinetics of the reaction* $A + B \rightarrow 0$ *is expected to follow the anomalous mean-field regime (AMF), one wherein concentrations decay as* $c_A, c_B \sim (n_0)^{1/2}(Dt)^{-d/4}$ *at long times*. This constitutes the central result of this part of the article.

While this result conforms to our scaling analysis, it nevertheless runs counterintuitive to our physical expectations. For instance, in the extreme limit wherein reactants A and B exhibit a "strong coupling" to the solvents, one might expect the solutes to be confined to the respective phases. In such a scenario, the reaction would occur exclusively at the fluctuating interface. This leads one to expect that confinement of the reaction to a fractal manifold, and the accompanying fluctuations of the interfacial area, would nontrivially impact on the kinetics of the reaction. However, our results in the previous section seem to nullify such an expectation. Some features of our analysis can be identified *a posteriorily* as possibly responsible for this (surprising) result.

(i) The model employed for the reaction and diffusion utilizes a potential field to model the background fluctuations. Our self-consistent mean-field arguments showed that diffusion of the solutes in this "short-ranged" fluctuating potential field is irrelevant compared to random thermal Brownian motion. Indeed, for cases involving long-ranged potentials whose fluctuation statistics exhibit correlations which diverge with the system length, the diffusion of the reactant species exhibits anomalous dynamics, thereby leading to nontrivial reaction kinetics. For instance, reactions effected in a critical fluid can therefore be expected to possess nontrivial decay dynamics.

(ii) Our RG analysis was restricted to the long-time limit. It might, however, be that the fluctuations of the microemulsion do impact on the kinetics at shorter times. Indeed, as demonstrated in Section II.C, such short time regimes do exist but are not discernible by the asymptotic analysis carried out in the present study.

F. SUMMARY

In this part of the article we have considered the effect of the thermal fluctuations of the bicontinuous phase on the reaction kinetics in such phases. We employed a field theoretical ("disordered fluid") model to quantify the structure and the fluctuations of the microemulsion. Subsequently, we analyzed the diffusion and anhiliation of a pair of species, A and B, that are preferentially attracted to oil and water. The analysis indicated that, unexpectedly, the fluctuations of the potential are irrelevant in impacting the kinetics in the hydrodynamic limit. This result is counterintuitive to the expectations derived both on physical grounds and based on analogies to other, comparable studies. Subsequently, we also identified some physical reasons possibly responsible for this surprising result. These arguments suggest the imperativeness of treating the "strong-coupling" case, at least within some limits, to discern more carefully the effect of the fluctuating interfaces.

Furthermore, an analysis encompassing the intermediate time scales in addition to the long-time asymptotics would be of value in identifying effects of relevance to practical applications. In Section III, we consider another limiting case of reactions in microemulsions, namely, that involving the droplet phase of the microemulsion. In this case, because of the geometrical simplifications, we are able to account for the entire range possible for the time scales and, also, analyze the strong-coupling limit of the system.

III. Reactions in the Droplet Phase

A. Outline

In this section we provide a brief outline of this part of the article, simultaneously highlighting the assumptions invoked in the subsequent analysis.

As stated earlier, our interest centers on bimolecular reactions of the type $A + B \to \emptyset$, wherein the solute A resides in water and B in oil—necessitating that the anhiliation occurs exclusively at the fluctuating surfaces of the droplets. However, in contrast to the analysis detailed in Section II, it does not appear possible simultaneously to render an exact analytical treatment of this problem and to realize the objectives stated above. Therefore, to focus on the elusive issues pertaining to the effect of fluctuations, we restrict our considerations to a simplified scenario wherein the reaction proceeds at an infinitely fast rate, thereby enabling the droplets to serve as a *perfect* sink (albeit one which is fluctuating). In such a case, it suffices to focus on the reaction $A \to \emptyset$ occurring on the surface of the fluctuating droplets. In addition, a boundary condition requiring the concentration of A to vanish at the surface of the fluctuating droplets imposes the "perfect-sink" nature of the fluctuating interfaces. Within this framework, we analyze the diffusion-limited reactive transport processes of solute A.

We initiate our analysis in Section III.B by providing a brief overview of the dynamical aspects of fluctuations of the droplets of the microemulsion. These features have been analyzed in seminal studies by Safran and Milner [23, 24], allowing us thereby to extract the requisite results. Section III.C commences our analysis by considering the case wherein the concentration of droplets can be termed dilute, thereby enabling us to restrict our considerations to the transport and reaction on a *single* fluctuating sink. In relation to the scenario encountered in practice, such an assumption can be deemed reasonable since the droplet phase of the microemulsion occurs only at very low concentrations of oil (or water) [12]. The ensuing "single-sink" analysis can be construed as a generalization of the Smoluchowski's problem of reaction and diffusion on a sink [36] to one wherein the sinks are allowed to fluctuate. However, even within this simplified case, an exact analytical solution proves elusive, and so we are forced to restrict our analysis to the case wherein the fluctuation amplitudes are small in relation to the mean radius of the droplet. In such a scenario, we can employ (boundary) perturbation techniques [37] to effect the solution of the corresponding equations. The explicit results of such an analysis constitute the main feature of this part of the article. Based on these results, we identify different regimes corresponding to intermediate and long time scales and thereby answer some of the questions left unattended in Section II. In closing, we also briefly highlight the manner in which some of the assumption invoked in this article can be relaxed.

Consistent with the philosophy adopted in II, we eschew elaborating the manifold algebraic details. A reader who is interested in the details of the solution may want to refer to our previous article [25].

B. Fluctuations of the Droplet Phase

In this section, we briefly outline the model adopted for quantifying the fluctuations of the microemulsion droplets. The statistics of these dynamical fluctuations have been studied by Milner and Safran [24] (cf. Safran [23] for an exposition of the equilibrium aspects) in the dilute limit. They addressed the linearized hydrodynamics of the fluctuations of the droplets in the creeping flow limit assuming that the fluids internal and external to the droplets possess identical viscosities. The fluctuations of the microemulsions droplets arise from the presence of an excess area over and above that of a sphere of equivalent volume. In the case wherein one considers an isolated droplet in solution (i.e., at dilute concentrations and for time scales during which the collisions and exchange of material between the droplets can be ignored), this excess area ΔA remains a specified constant during the fluctuations of the droplet. However, imposing this constraint on the excess areas within a dynamical formulation proves cumbersome, and *so a Lagrange multiplier γ is invoked to account for this constraint*. Further, in the case of microemulsion droplets the statistics of the excess areas possessed by a droplet abstracted from the equilibrium solution (of droplets) can be discerned based on equilibrium energetic considerations [24]. Thus, one can identify the (constant) excess area possessed by our fluctuating droplet with mean excess area $\langle \Delta A \rangle$ possessed by a droplet in the microemulsion solution. This enables one to determine the explicit value of this Lagrange multiplier γ based upon the equilibrium statistics of the fluctuations. Such an exercise has been effected in Ref. 24, to which we refer the reader interested in the pertinent details.

In the following, we quote the results derived in Ref. 24 for the statistics of the fluctuations of the droplets.

In this and the following analysis, we assume that the microemulsion droplets possess a mean radius R. However, this mean radius can in general be different from the spontaneous radius of these droplets R_s. The instantaneous shape of the droplet can be parametrized as $r = R'(\theta, \phi, t)$, with R' expressed in terms of an expansion in spherical harmonics as

$$R'(\theta, \phi, t) = R\left[1 + \sum_{l>1,m} \hat{a}_{lm}(t) Y_{lm}(\theta, \phi)\right], \tag{22}$$

with $\hat{a}_{lm}(t)$ representing the amplitudes of the different modes of fluctuation. The fluctuation mode corresponding to $l = 0$ is restrained by the conservation requirement imposed upon the volume of the droplets and, so, is not included in the above expression [24]. Further, the mode corresponding to $l = 1$ signifies spatial translations of the center of the droplet and is, therefore, irrelevant for considerations pertaining to the fluctuations of a single sphere. For concisencess, we henceforth resort to the notation $\sum_{lm}$ to denote $\sum_{l>1,m}$. In the above expression, Y_{lm} denotes the spherical harmonic function [38] of order l,m, which is assumed in this work to be appropriately normalized such that

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta Y_{lm}(\theta, \phi) Y_{pq}(\theta, \phi) = \delta_{lp}\delta_{mq},$$

to obviate bookkeeping cumbersome algebraic factors.

Within the framework of the above parameterization, the statistics of the fluctuation amplitudes $\hat{a}_{lm}(t)$ was determined in Ref. 24 as

$$\langle \hat{a}_{lm}(t)\rangle = 0; \qquad \langle \hat{a}_{lm}(t)\hat{a}_{l'm'}(0)\rangle = \delta_{ll'}\delta_{mm'} \exp(-\omega_{lm} t) M_{lm}, \tag{23}$$

where the static mean-squared fluctuation amplitude, denoted M_{lm}, is of the functional form,

$$M_{lm} = \frac{k_B T}{\kappa} = \{(l+2)(l-1)[l(l+1) - 4u + 2u^2 - \gamma]\}^{-1} \tag{24}$$

with κ representing the bending moduli of the surfactant interfaces and u denoting the ratio R/R_s. The term γ in the above expression denotes the Lagrange multiplier discussed in the preceding paragraph. The corresponding frequencies of fluctuations of the different modes ω_{lm} have been determined as

$$\omega_{lm} = \frac{\kappa}{\eta R^3} \frac{[l(l+1) - \gamma - 4u + 2u^2][l(l+1)(l+2)(l-1)]}{(2l+1)(2l^2+2l-1)} \tag{25}$$

where η denotes the viscosity of the surrounding medium.

C. DIFFUSION EQUATION AND PERTURBATION EXPANSION

In this section we commence our analysis of the diffusion-limited reaction of solute A. As expounded in Section III.A, we initially restrict our considerations to the scenario wherein the concentration of the droplets can be construed as dilute. In such a case, it suffices to focus on the diffusion and reaction of A in the presence of a single fluctuating sink. In view of the spherical symmetry exhibited by the problem, we formulate the transport and reaction of A in terms of a diffusion equation expressed in spherical coordinates (r, θ, ϕ)

$$\frac{\partial c}{\partial t} = D\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial c}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 c}{\partial \phi^2}\right], \quad (26)$$

In the above equation we use the symbols c and D to denote, respectively, the concentration and the diffusivity of A. The above conservation equation is to be supplemented by the boundary condition embodying the "perfect-sink" nature of the fluctuating surfaces [cf. Eq. (22)]:

$$c = 0 \qquad \text{on} \qquad r = R[1 + \sum_{lm} \hat{a}_{lm}(t) Y_{lm}(\theta,\ \phi)], \quad (27)$$

Further, for convenience, we consider the scenario wherein we maintain a fixed source of the solute A at $r = \infty$, i.e.,

$$c(r,\ \theta,\ \phi) = \bar{c} \qquad \text{as} \qquad r \to \infty \quad (28)$$

and

$$c(r,\ \theta,\ \phi,\ t = 0) = \bar{c}. \quad (29)$$

The conservation equation (26) supplemented by the boundary conditions (27) and (28) represents the mathematical formulation of the diffusion and reaction of solute A in the presence of fluctuating microemulsion droplets in the limit of dilute concentration of these droplets.

An exact analytical solution of the above equations does not appear possible due to the complicated boundary condition (27). However, in the limit wherein the fluctuation amplitudes are low in relation to the radii of the droplets, i.e.,

$$\sqrt{\frac{k_{\mathrm{b}}T}{\kappa}} \equiv \epsilon \ll 1, \quad (30)$$

we can obtain an explicit solution for the solute concentration c quantified in the form of a perturbation series with fluctuation amplitudes ϵ serving as the perturbation parameter. Effecting a transformation of the variables

$\hat{a}_{lm} = a_{lm}\epsilon$ to render the magnitudes of the fluctuation amplitudes explicit enables us to look for a solution of the form

$$c(r, \theta, \phi, t) - \bar{c} = \sum_{i=0}^{\infty} \epsilon^i c_i(r, \theta, \phi, t), \tag{31}$$

The diffusion equations and the corresponding boundary conditions satisfied at each order of perturbation by the different c_i's can be obtained by substituting the above expansion (31) into Eqs. (26)–(28). Subsequently, the solution at each order of the series can be determined sequentially based on the solutions at the preceding orders.

In lieu of the detailed spatial and temporal information embodied within the concentration field $c(r, \theta, \phi, t)$, it is of interest to compute a global temporal measure of the reaction kinetics so as to discern the explicit effect of the fluctuations. Consequently, in addition to the concentration field c, we also compute the averaged time-dependent consumption rate of A, denoted $J(t)$ and defined as

$$J(t) = \frac{d}{dt}\left\langle \int_V d^3\mathbf{r}c(r, \theta, \phi, t) \right\rangle, \tag{32}$$

In the above equation, V denotes the exterior volume enclosed between the surface of the fluctuating droplet and $r = \infty$. In contrast to the explicit spatial dependence embodied in the concentration field c, $J(t)$ embodies a purely temporal characteristic that manifests the spatial features of the concentration field in an averaged manner. Thereby, a comparison of the values of $J(t)$ provides a convenient measure for quantifying the explicit dynamical effects of the fluctuations of the sinks. One can transform the above expression by expanding the above integral and the concentration field c as a power series in ϵ, thereby enabling us to utilize the solutions of the diffusion equation at each order.

In the following we do not elaborate the details of the solution procedure but, instead, quote our final results [up to $\mathcal{O}(\epsilon^2)$] for the quantity $J(t)$:

$$J(t) = J_0(t) + \epsilon J_1(t) + \epsilon^2 J_2(t) + \mathcal{O}(\epsilon^3), \tag{33}$$

where

$$J_0(t) = 4\pi DR\bar{c}\left(1 + \frac{R}{\sqrt{\pi Dt}}\right). \tag{34}$$

$$J_1(t) = 0, \tag{35}$$

and

$$J_2(s) = \bar{c}RDg(R,\, s) - \frac{3\chi\bar{c}R^3}{2} + \bar{c}R\sqrt{\frac{s}{D}}\left[Rg(R,\, s)D - \frac{\chi R^3}{2}\right], \tag{36}$$

where

$$g(R,\, s) = \frac{1}{2}\left\{\left(\frac{1}{s} + \frac{R}{\sqrt{sD}}\right)\left(\chi + \sum_{lm} M_{lm}\, p(s)\frac{K_{l+3/2}[p(s)] + K_{l-1/2}[p(s)]}{K_{l+1/2}[p(s)]}\right)\right.$$
$$\left. - \chi\left(\frac{2}{s} + \frac{2R}{\sqrt{sD}} + \frac{R^2}{D}\right)\right\} \tag{37}$$

and $J_2(s)$ represents the Laplace transform of $J_2(t)$.

Two important features can be discerned from the above expressions.

1. In the limit $t \to \infty$, the expression for $J_0(t)$ corresponds to the classical Smoluchowski expression for the (diffusion-limited) reaction rate expression in the presence of a dilute concentration of rigid spherical sinks [36]. It is therefore evident that the steady-state limit of the higher-order terms in the expansion to (33) provides the corrections to the reaction rate arising from the dynamic fluctuations of the sink.
2. The main feature of the above expression (37) is the absence of secular (or diverging) temporal corrections to the zeroth-order field. The fastest-diverging term in the above expression for $s \to 0$ evolves as $1/s$, indicating that the presence of the dynamic fluctuations influences the zeroth-order field only in a perturbative manner at the longest time scales. This result is consistent with the prediction outlined in Section II, wherein we claimed that in the hydrodynamic regime (long times) the dynamics (quantified in terms of the decay exponent of the reactants) is unmodified by the presence of the dynamic fluctuations. However, the fact that we have an exact expression (albeit in a perturbative sense) for the concentration field, supposedly valid at all times, enables us to discern the explicit effect of the fluctuations at intermediate time scales. Such effects might prove of relevance to applications wherein the "long-time" limit might in fact prove unachievable in practice. In the next section, we explicitly analyze the behavior of the consumption field $J(t)$ in different temporal regimes to discern the specific effect of the dynamic fluctuations of the microemulsion droplet.

D. Consideration of Temporal Regimes

As argued earlier in the text, $J_2(t)$ serves as an appropriate spatially independent measure of the impact of the dynamical fluctuations on the kinetics of the reaction. The absence of secular terms in $J_2(t)$ [cf. Eq. (36)] enables us to treat it as a purely perturbative correction to $J_0(t)$. In such a case, we can discern the impact of the dynamical fluctuations by analyzing the temporal features of $J_2(t)$, with the implicit specification that ϵ is small enough to maintain the perturbative nature of the corrections.[7] The following discussion is devoted to effecting such an analysis, deferring a discussion of the implications to the next section.

To focus on the main dynamical features, in the following analysis we concentrate on the mode $l = 2$ and ignore considerations arising from the presence of other modes $l \neq 2$. This assumption does not modify the qualitative features of the results subsequently unearthed. Further, our assumption is physically justified based on the results of Safran [23], who showed that the fluctuations of the mode $l = 2$ possesses the maximal amplitude (represented by M_{lm}). In this limit we can set $\sum_m M_{2m} = \chi$ and further use the unadorned notation ω to denote ω_{2m}. Furthermore, within the same approximation, $\epsilon^2\chi = \langle\Delta A\rangle/R^2$, where $\langle\Delta A\rangle$ represents the mean excess area (in an ensemble of microemulsion droplets) over and above a perfect sphere of radius R.

1. Steady State

The steady-state limit of expression (36) can be obtained by adopting the dual limit $s \ll \omega$ and $s \ll D/R^2$. Then

$$p(s) = R\sqrt{\frac{\omega}{D}} \tag{38}$$

whose explicit magnitude is $\ll 1$ in view of our assumption of small Péclet numbers (refer to Section I). Simplifying the resulting expression for $J_2(t)$, we obtain

$$J_2(s) \longrightarrow \frac{2\bar{c}RD\chi}{s}, \tag{39}$$

As indicated in Section III.C, the steady-state value of $J(t)$ embodies the (Smoluchowski's) diffusion-limited reaction rate. On appending the above contribution to (34), we obtain the leading order corrections to the diffusion-limited reaction rate arising from the dynamical fluctuations of the spherical sinks

$$\begin{aligned} J(t \to \infty) &= 4\pi DR\hat{c}\left(1 + \epsilon^2\frac{\chi}{2\pi}\right) \\ &= 4\pi DR\bar{c}\left(1 + \frac{\langle\Delta A\rangle}{2\pi R^2}\right), \end{aligned} \tag{40}$$

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[7] If $J_2(t)$ had, in contrast, possessed secular terms, then as $t \to \infty$ it would be impossible to choose an ϵ small enough to maintain the perturbative nature of the correction—necessitating a renormalization procedure.

We conclude from the above expression that the dynamical fluctuations always *enhances* the reaction rate by a magnitude proportional to the excess area contained in the droplets. While this result may seem logical in view of the enhanced flux resulting from the excess area, it is to be noted here that in deriving the result we employed the assumption $R\sqrt{\omega/D} \ll 1$. In fact, in the next section, we consider the opposite limit corresponding to $R\sqrt{\omega/D} \gg 1$, wherein the steady-state correction embodies nontrivial contributions dependent on $R\sqrt{\omega/D}$.

E. INTERMEDIATE TIMES

In view of the assumption we have invoked regarding the magnitude of the Péclet number (requiring $\omega R^2/D \ll 1$), the intermediate time regime corresponds to times much longer than the diffusive time scale of the solute species but still short compared to the time scales corresponding to the fluctuations of the droplets, i.e., $\omega \ll s \ll D/R^2$. In such a case,

$$p(s) = R\sqrt{\frac{s}{D}} \ll 1. \tag{41}$$

Simplifying the resulting expression for $J_2(t)$, we obtain

$$J_2(s) \longrightarrow \frac{2\bar{c}RD\chi}{s}. \tag{42}$$

The above expression is identical to that obtained in the steady-state limit (39). This indicates that the diffusion-limited reaction processes reaches a steady state in the time scale comparable to the diffusion of the solute, despite the fact that the fluctuations of the sink have not relaxed within such times.

F. SHORT TIME REGIME

For times s such that $s \gg D/R^2$ and $s \gg \omega$, neither the diffusion of the solute nor the fluctuations of the sink have relaxed. In such a case, the leading order contribution to J_2 can be obtained by imposing this dual limit on Eq. (36). This yields

$$J_2(s) \longrightarrow -\chi R^4\bar{c}\sqrt{\frac{s}{D}}. \tag{43}$$

Thus we have,

$$J(s) \sim 4\pi DR\bar{c}\frac{R}{\sqrt{sD}} - \langle\Delta A\rangle R^2\bar{c}\sqrt{\frac{s}{D}}. \tag{44}$$

The above result suggests that the dynamical fluctuations possess a nontrivial effect on the kinetics of consumption of solute A in the initial time regime. Explicitly, the perturbative correction to the consumption rate J evolves as $1/t^{3/2}$, in contrast to the $1/t^{1/2}$ behavior embodied in $J_0(t)$ [cf. Eq. (34)]. However, it is to be noted that to maintain the perturbative nature of the correction, ϵ should be small enough. In other words, the above result is valid only for times $t > t^*$, where

$$t^* \sim \frac{\langle \Delta A \rangle}{D}. \tag{45}$$

G. Effect of the Péclet Number

So far, the entirety of our analysis has invoked the assumption corresponding to small Péclet numbers wherein it is justified to ignore the effect of the convective transport altogether. Quantitatively this assumption required that the time scales of fluctuation and diffusion satisfy the following criterion: $\omega R^2/D \ll 1$. However, practically encountered situations might not strictly satisfy this assumption.[8] It is therefore of interest to discern the explicit effect of the fluctuations in the opposite limit, wherein $\omega R^2/D \gg 1$. In this case, if instead of solving the convective-diffusion equation (as necessitated by the magnitude of the Péclet number and the fact that the problem becomes one involving singular perturbation in the Péclet number), we assume that the above expressions (36) are still applicable, then we can repeat the analysis outlined in the preceding section under limits consistent with the limit $\omega R^2/D \gg 1$. However, such an analysis is not rigorously valid and hence the results so obtained must be interpreted with caution and at a qualitative level only. The results of such an analysis indicate the following.

(i) The steady-state dynamics embodied in (39) is unchanged qualitatively. However, the explicit correction to the steady-state reaction rate now scales as $\langle \Delta A \rangle \sqrt{\omega / R^2 D}$. Therefore, it can be inferred that while the correction is proportional to the excess area (as is intuitive), it also embodies nontrivial contributions arising from the ratio of the time scales for diffusion and fluctuation.

(ii) The intermediate time regime in the limit $s \ll \omega$ and $s \gg D/R^2$ (times much before the equilibration of the diffusive transport) contrasts with the dynamics in the above-outlined intermediate time regime. The explicit functional form of the kinetics is a bit more

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[8] An order-of-magnitude estimate suggests that the Péclet number is $\mathcal{O}$ (1) for realistic situations.

complicated and depends on the magnitudes of the ratios ω/s and $\omega R^2/D$. In the case where the former ratio is of a greater magnitude (shorter times), then the consumption rate exhibits anomalous kinetics similar to that unearthed in the short time regime of the preceding section. In the opposite limit, wherein $\omega R^2/D \gg \omega/s$, the perturbative correction matches the functional form of $J_0(t)$ and exhibits a $1/t^{1/2}$ behavior.

(iii) The short-time behavior ($s \gg \omega, D/R^2$) matches qualitatively and quantitatively the expressions obtained in the previous section [cf. Eq. (44)].

H. Discussion

The preceding sections have outlined the analysis of the transport and reaction of the solute in the presence of fluctuating spherical sinks (representing the droplets of microemulsion). In the following, we summarize the main results and discuss their implications in the context of Section II. The analysis of the leading order corrections [$\mathcal{O}(\epsilon^2)$] to the concentration field and the consumption rates leads to the following conclusions.

1. *The long-time dynamical evolution of the consumption rate is unaffected by the presence of the dynamical fluctuations of the sink. However, the explicit magnitude of the reaction rate is enhanced by the fluctuations.* This result is consistent with our prediction in Section II that the dynamics (or decay exponent) of the reaction is unaffected by the fluctuations of the interfaces. However, the correction to the reaction rate was shown to embody nontrivial corrections arising from the fluctuations of the droplets. The occurrence of a steady state and the dynamical features embodied in the intermediate and short time scales (see below) suggest that the exponentially decaying (in time) correlation structure possessed by the fluctuations of the microemulsion media is possibly responsible for this result. This leads us to speculate that if the correlation structure of the fluctuation amplitudes possesses no intrinsic time scale (i.e., exhibits a power-law correlation behavior), then the long-time kinetics of the microemulsion will possess a nontrivial secular structure manifesting the fluctuation dynamics.
2. *The steady state was reached in a time scale set by the diffusion of the solute species.* This result was a manifestation of the low Péclet number limit assumed to be applicable in our physical situation. As indicated in the previous section, the opposite limit ($\omega R^2/D \gg 1$) involves a different dynamical evolution in the intermediate time regime.

3. *The correction to the consumption rate in the short time regime (corresponding to $t \ll R^2/D$) embodies an anomalous kinetic behavior*. This result is again consistent with our original hypothesis that the short-time dynamics might manifest a profound influence arising from the fluctuations of the interface. In fact, this result might prove of significance to practical applications wherein the steady-state or the long-time limits prove "too long" to realize.

I. OTHER EFFECTS

The above discussion summarizes the main results obtained in the previous sections, emphasizing their relationship to the results of the preceding article which motivated this analysis. However, as motivated in the text, study of reactions in the droplet and other ordered lyotropic phases possesses enough practical applications to justify an independent study, and therefore we indicate briefly some effects which need to be accounted for in future work to impact on such applications.

1. The main assumption involved in the preceding analysis involves envisioning the droplet phase as dilute and, therefore, eschews considerations such as collisions and the exchange of material arising between droplets.
2. Competition effects between the sinks might manifest even in the absence of a translational mobility.
3. At higher concentrations of sinks, one might also expect shape transitions to ordered surfactant phases of microemulsion.
4. Finally, our analysis was restricted to the case wherein the amplitudes of fluctuation were low.

In all of the preceding contexts, it might prove expedient to employ a different solution technique to the analysis of the situation. The path integral technique of Kardar and co-workers appear promising in this regard [39].

J. SUMMARY

In Section III, we have analyzed a simple model for discerning the impact of the fluctuations of the droplet phase of the microemulsion on the reaction kinetics in such media. The results of this analysis are consistent with those outlined in Section II. We have delineated the different temporal regimes to identify the explicit effect of the dynamical fluctuations of the sink. Finally, we have also elucidated some possible directions for future study and our own preliminary results in that context.

Our analyses in Sections II and III highlight some of the novel issues arising from the interplay between thermal fluctuations and diffusion-limited reactions in complex fluid media—an issue unaddressed heretofore in the literature. Most of the results unearthed herein lend themselves to experimental verification. For future work, it will be of interest to study the effects arising from relaxing the assumptions invoked in this study (see the preceding section).

This article was meant to highlight for the chemical engineering community the "nonclassical" issues pertaining to reaction kinetics and some of the statistical mechanical tools employed to resolve them. To maintain brevity we eschewed detailing the intermediate steps of the analysis. A reader who is interested in the accompanying details is advised to refer to Ref. 25.

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