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Nonlinear dynamics in micellar surfactant solutions. I. Kinetics

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This is the first of a pair of articles that present the theory of kinetic and transport phenomena in micelle-forming surfactant solutions in a form that facilitates discussion of large deviations from equilibrium. Our goal is to construct approximate but robust reduced models for both homogeneous and inhomogeneous systems as differential equations for unimer concentration c_1, micelle number concentration c_{m}, average micelle aggregation number q and (optionally) aggregation number variance σ_{m}^2. This first article discusses kinetics in homogeneous solutions. We focus particularly on developing models that can describe both weakly perturbed states and states in which c_1 is suppressed significantly below the critical micelle concentration, which leads to rapid shrinkage and dissociation of any remaining micelles. This focus is motivated by the strong local suppression of c_1 that is predicted to occur near interfaces during some adsorption processes that are considered in the second article. Toward this end, we develop a general nonlinear theory of fast stepwise processes for systems that may be subjected to large changes in q and c_1. This is combined with the existing nonlinear theory of slow association and dissociation processes to construct a general model for systems governed by stepwise reaction kinetics. We also consider situations in which the slow process of micelle creation and destruction instead occurs primarily by micelle fission and fusion, and analyze the dependencies of micelle lifetime and the slow relaxation time upon surfactant concentration in systems controlled by either association-dissociation or fission-fusion mechanisms.

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I. INTRODUCTION

In a micellar surfactant solution, surfactant clusters of varying aggregation number coexist with dissolved single molecules or “unimers.” The dynamical evolution of a homogeneous system is controlled by a set of reactions that redistribute molecules among clusters of different aggregation number and between clusters and a reservoir of unimers. Transport phenomena in inhomogeneous systems, such as diffusion to an interface, involve an interplay between these reactions and diffusion of both unimers and clusters. Reduced models that describe the evolution of a polydisperse system in terms a small set of statistical properties (e.g., average micelle aggregation number, micelle concentration, and unimer concentration) are useful both as a guide to qualitative understanding and as a potential basis for development of more efficient computational models of complex phenomena.

Early theoretical work on kinetics in surfactant solution, prior to approximately the year 2000, focused primarily on analysis of linearized models of small perturbations from equilibrium [1–4]. The resulting theories allow analysis of linear response experiments that track relaxation of small perturbations of homogeneous systems caused by sudden changes in temperature, pressure, or concentration [3,4]. Related work on linearized models of dynamics in weakly perturbed inhomogeneous systems has also allowed analysis of dynamic interfacial tension measurements in systems subject to small changes in interfacial area [5].

The present work is the first of a pair of articles that give a self-contained analysis of dynamical phenomena in micellar solutions in a form that facilitates analysis of strongly nonequilibrium states. This first article discusses reaction kinetics in spatially homogeneous systems. A second article discusses the combined effects of reaction and diffusion in inhomogeneous systems. The resulting analysis yields a set of reduced models that, in favorable cases, can describe the evolution of strongly nonequilibrium states as a closed set of differential equations for a small number of variables.

The analysis in these two papers was motivated in part by an interest in nonlinear dynamics of surfactant adsorption from a micellar solution to an initially bare or rapidly expanding interface. A simple example of this type of process is discussed in the accompanying paper. As shown there, such processes are characterized by strong depression of unimer concentration near the interface, which can lead to rapid local shrinkage and complete destruction of micelles in a nearby region. Previous work on nonlinear kinetics in homogeneous micellar surfactant solutions has focused primarily on situations that involve much smaller changes in average micelle aggregation number. Interest in transport phenomena thus motivated us, as a prerequisite, to develop a nonlinear theory for fast stepwise changes in average micelle aggregation number that allows for the possibility of large deviations from equilibrium.

The work presented here builds on a substantial body of prior work on nonlinear micelle kinetics in homogeneous

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micellar solutions. See Refs. [6,7] for reviews. The remainder of this section outlines key ideas from prior theoretical work and introduces some distinctive themes of the present work.

A. Equilibrium

Throughout this and the accompanying article, we consider dilute surfactant solutions containing clusters of all positive integer values of the cluster aggregation number n. Throughout, we refer to clusters of aggregation number n (i.e., clusters of n molecules) as n-mers, and to free surfactant molecules as unimers. Let c_n denote the number concentration of n-mers, so that c_1 is the unimer concentration. Let ρ denote the total surfactant concentration,

$$\rho \equiv \sum_{n=1}^{\infty} n c_n. \tag{1}$$

Let $c_{\rm m}$ denote the number concentration of micelles, defined as the total concentration of clusters with aggregation numbers greater than or equal to some cutoff value b. Let q denote the number average micelle aggregation number of these micellar clusters.

Let $W_n(c_1)$ denote the free energy to form an n-mer from unimers in a solution with a unimer concentration c_1. This is defined here as a difference

$$W_n(c_1) \equiv \mu_n^\circ - n\mu_1(c_1), \tag{2}$$

in which $\mu_n^\circ = \mu_n(c^\circ)$ is the standard chemical potential of n-mers in a hypothetical state in which c_n is equal to a standard concentration c°, and $\mu_1(c_1)$ is the chemical potential of unimers in a state with specified unimer concentration c_1.

Let $c_n^*(c_1)$ denote the value of c_n in an equilibrium state characterized by a unimer concentration c_1. We show in Sec. II that

$$c_n^*(c_1) = c^\circ \exp\left[-\beta W_n(c_1)\right], \tag{3}$$

where $\beta \equiv 1/(k_B T)$, k_B is Boltzmann's constant, and T is absolute temperature.

In a micelle-forming surfactant solution, the functions $W_n(c_1)$ and $c_n^*(c_1)$ exhibit qualitatively different dependences on n at values of c_1 above or below a characteristic value that we refer to as the critical dissociation concentration, denoted by $c_{\rm d}$. At concentrations $c_1 < c_{\rm d}$, $W_n(c_1)$ is a monotonically increasing function of n, so $c_n^*(c_1)$ is a monotonically decreasing function. At concentrations $c_1 > c_{\rm d}$, $W_n(c_1)$ exhibits a local maximum at a value denoted by $n_{\rm t}(c_1)$ and a local minimum at a value denoted by $n_{\rm e}(c_1)$. The quantity $n_{\rm e}(c_1)$ is the most probable micelle aggregation number in an equilibrated solution with unimer concentration c_1. The maximum in $W_n(c_1)$ at $n = n_{\rm t}(c_1)$ acts as a transition state for stepwise creation (association) or destruction (dissociation) of micelles.

The critical micelle concentration (CMC), denoted here by $c_{\rm c}$, is somewhat greater than $c_{\rm d}$. The CMC is, roughly speaking, the concentration above which a non-negligible concentration of micelles appear in an equilibrated solution, and above which the unimer concentration becomes nearly independent of total concentration. We use an operational definition of $c_{\rm c}$ as the value of c_1 in an equilibrated solution in which half of the total concentration ρ defined in Eq. (1) is in clusters with $n > n_{\rm t}(c_1)$.

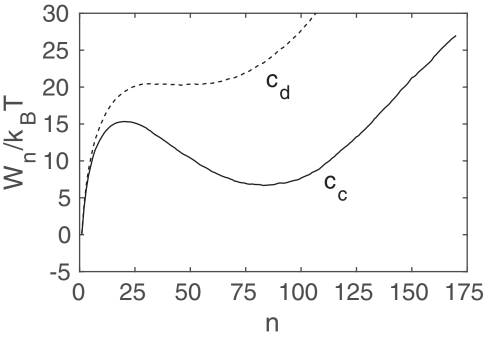

FIG. 1. Dependence of cluster formation free energy $W_n(c_1)$ vs aggregation number n as obtained in Ref. [8] for a bead-spring simulation model of a diblock copolymer surfactant, for the case $\alpha = 14$. The solid line shows results for $c_1 = c_{\rm c}$, and the dashed line shows $c_1 = c_{\rm d}$. Values of W_n shown here are defined using a standard concentration c° chosen to be equal to the critical micelle concentration $c_{\rm c}$.

As an example of the typical behavior of $W_n(c_1)$, Fig. 1 shows the measured dependence of $W_n(c_1)$ was obtained from simulations of a simple model of micelles formed by diblock copolymers in a polymeric solvent [8–11]. Results for W_n are shown here for $c_1 = c_{\rm c}$ (solid line) and $c_1 = c_{\rm d}$ (dashed line). These results were inferred from simulations of a bead spring model of AB diblock copolymer surfactants that each contain 28 beads of type A and four beads of type B that are dissolved in a liquid of A homopolymer solvent molecules that each contain 32 beads of type A. The dependence of free energy upon n has been measured using semigrand canonical Monte Carlo sampling [8]. The degree of segregation is controlled by the value of a parameter $\alpha = (\epsilon_{AB} - \alpha_{BB})/k_B T$, in which ϵ_{ij} is an energy that controls the strength of repulsive interactions between monomers of types i and j. The results shown here used $\alpha = 14$. For this particular model $c_{\rm d}/c_{\rm c} = 0.81$.

A variety of simplified molecular models and simulation models have been studied in order to characterize the behavior of $W_n(c_1)$ for a common surfactant system. Most phenomenological models of spherical micelles are variants of the droplet model introduced by Tanford [12–14]. Droplet models for a spherical micelle generally contain a cohesive contribution proportional to the core volume, an interfacial contribution, and an additional repulsive contribution that limits micelle growth. The repulsive contribution can be used to represent some combination of short-range head-group interactions, electrostatic double layer energy in ionic systems, and chain stretching [12,13,15–19]. Predictive models of cluster free energies for block copolymer surfactant micelles have also been obtained from numerical or approximate treatments of self-consistent field theory [20–24], and from recent coarse-grained molecular simulations [8,25].

Analyses of droplet models, self-consistent field theory and simulations have consistently predicted that experimentally studied systems (i.e., systems with non-negligible CMCs that equilibrate over experimentally accessible timescales) typically exhibit values of $c_{\rm d}$ and $c_{\rm c}$ that differ by only a few tens of percent. Note, for example, the value of $c_{\rm d}/c_{\rm c} = 0.81$ for the model shown in Fig. 1. This implies that suppression of c_1

below c_c by a rather modest amount can make micelles unstable with respect to rapid shrinkage and dissociation, even in systems in which micelles exhibit long equilibrium lifetimes in systems with $\rho > c_c$. This predicted fragility of micelles with respect to decreases in c_1 is relevant to experiments that subject a homogeneous solution to rapid dilution by a sufficiently large amount, and to dynamic adsorption phenomena in which c_1 is depressed near an interface.

Surfactants solutions can exhibit rodlike as well as spherical micelles. Shchekin, Kshevetskiy, Kuni and coworkers have extensively discussed dynamical properties of systems that can exhibit coexisting spherical and rodlike micelles [26–31]. Their work is based on a model for $W_n(c_1)$ that, at some concentrations, can exhibit two local minima corresponding to different types of micelles [26]. We focus throughout this work on systems that only form spherical micelles, for which $W_n(c_1)$ exhibits no more than one local minimum at $n > 1$.

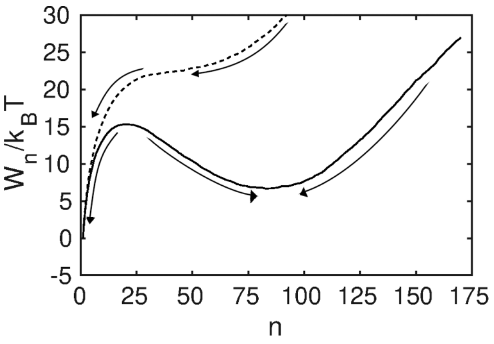

FIG. 2. Schematic of relationship between changes in average aggregation number $q(t)$ and the micelle formation free energy $W_n(c_1)$. Arrows show the direction of change of $q(t)$ in systems with $c_1 > c_d$ (solid line) and with $c_1 \leqslant c_d$ (dashed line) via stepwise processes. In both cases, $q(t)$ changes so as to cause a monotonic decrease in the value of $W_n(c_1)$ evaluated at $n = q(t)$.

B. Fast vs slow processes

Experimental studies of the relaxation dynamics of weakly perturbed micellar solutions [32–39] and ultrasonic spectroscopy [39–42] long ago established the existence of "fast" and "slow" relaxation processes with widely disparate relaxation times. The "fast" process, with a relaxation time denoted here by τ_1, involves repartitioning of surfactant between micelles and a reservoir of free unimers by insertion and expulsion of individual unimers, with negligible change in the total number of micelles. This process leads to a change in both average micelle aggregation number and umimer concentration. The fast process ends when the system reaches a state of partial or quasi-equilibrium in which the free energy has reached a minimum subject to a constraint on the number of micelles. The "slow" process, with relaxation time τ_2, involves a change in the total number of micelles by rare processes that create or destroy entire micelles.

The stepwise reaction model introduced by Aniansson and Wall [1,2] assumes that both the fast and slow processes occur solely via stepwise elementary reactions in which individual surfactant molecules are inserted into or expelled from a surfactant cluster [1–4,6,43–47]. The fast process observed in experiments is assumed to occur via expulsion and insertion of a few molecules per micelle with negligible change in the number of micelles. The slow process is assumed to occur via rare events that lead to formation of a new micelle by stepwise association of unimers or destruction of an existing micelle by stepwise dissociation.

In systems with $c_1 > c_d$, the existence of a maximum in $W_n(c_1)$ creates barriers to stepwise association and dissociation. When these barriers are much greater than k_BT, micelle association and dissociation become very rare thermally activated events, creating a separation of timescales between fast and slow processes. This separation of timescales thus exists, however, only in systems with $c_1 > c_d$ and substantial barriers to both processes.

Consider the predictions of the stepwise reaction model for the evolution of a strongly perturbed homogeneous system. Assume an initial condition at $t = 0$ in which the system contains a bimodal distribution of clusters that is dominated by unimers and micelles, for which c_n contains a micellar peak with values of n clustered around an average value $q(t = 0)$. The subsequent time dependence of $q(t)$ can exhibit two qualitatively different trajectories, depending on the nature of the initial values of c_1 and q. These two possibilities are shown schematically in Fig. 2.

Micellar systems with initial values $c_1 > c_d$ and $q > n_t(c_1)$ typically exhibit a two-stage relaxation similar to that observed in experiments on weakly perturbed micellar solutions. During the initial fast process, $q(t)$ migrates towards the local minimum of $W_n(c_1(t))$ at $n = n_e(c_1(t))$, as indicated by arrows on the solid line in Fig. 2. The variables $c_1(t)$ and $n_e(c_1(t))$ also change, but $c_m(t)$ remains nearly constant during this process. During the subsequent slow process, $c_m(t)$ relaxes more slowly by rare dissociation and association events, while $q(t)$ remains nearly equal to $n_e(c_1(t))$ throughout this process. For a system that starts in a state with micelles and relaxes to a final equilibrium unimer concentration $c_1 \in [c_d, c_c]$ (e.g., due to sudden dilution to a concentration $\rho < c_c$), this can lead to slow destruction of essentially all micelles with almost no change in the average aggregation number $q(t)$ of remaining micelles.

A different scenario is expected either in a system with an initial value $c_1 < c_d$, or one with $c_1 > c_d$ but $q < n_t(c_1)$. In both of these cases, there is no local maximum of $W_n(c_1)$ in the range $[0, q]$ at time $t = 0$, and thus no barrier to rapid stepwise dissociation. These situations are expected to yield a fast single-stage relaxation in which the average aggregation number $q(t)$ steadily shrinks by unimer expulsion until micelles finish dissociating into unimers when $q(t)$ approaches zero. During the early stages of this process, expulsion of individual unimers has little effect on $c_m(t)$, which remains nearly constant until near the end of the process. Micelles can thus be destroyed by either of two distinct processes that occur under different conditions.

Physical processes during the single-stage shrinkage of unstable micelles in the second scenario are very similar to those which occur in the initial fast relaxation of a two-stage relaxation. In what follows, we thus refer to both of these processes as examples of "fast" stepwise processes and consider them together.

C. Fast processes

Fast processes in micellar solutions are characterized by comparatively rapid changes in q and c_1 with negligible change in the micelle number concentration $c_{\rm m}$. We assume here that such processes are adequately described by a stepwise reaction model.

The seminal theoretical work of Aniansson and Wall considered predictions of a stepwise reaction model for both fast and slow relaxation rates [1–3] for systems subjected to infinitesimal perturbations from equilibrium. Their analysis of fast processes used a linearized dynamical model with a constant micelle number concentration $c_{\rm m}$ that they further simplified by introducing the following physically motivated approximations:

(a) The cluster free energy W_n in the final equilibrium state was approximated by a quadratic function of n, yielding a Gaussian equilibrium distribution.

(b) The expulsion rate constant was taken to be independent of n.

(c) A continuum diffusion approximation was introduced in which n is treated as a continuous variable, and the discrete reaction equations were approximated by a continuum diffusion equation.

This set of approximations allows the discrete stepwise reaction model for fast processes to be mapped onto a model of one-dimensional diffusion with constant diffusivity in a harmonic effective potential. This simplified model was solved by Aniansson and Wall [1,2] by introducing a basis of Hermite polynomial eigenfunctions of the associated Fokker-Planck operator.

An alternative method of characterizing fast processes is to analyze the time dependence of moments of the size distribution [29,48,49]. The average micelle aggregation number q and the aggregation number variance $\sigma^2_{\rm m}$ are the first moment and the second central moment of n for proper micelles, respectively. Time derivatives of these and other moments can be expressed as sums over n in which the summands depend on cluster free energies, reaction rate constants and c_n, as shown here in Sec. III A. To obtain a closed set of approximate differential equations (ODEs) for a small set of moments, however, one generally must introduce approximations that approximate these sums as functions of the chosen set of moments.

Compact expressions for $dq(t)/dt$ and $d\sigma^2_{\rm m}(t)/dt$ were first derived by Danov *et al.* [48,49]. These authors used these exact expressions to derive a close system of ODEs for the evolution of $q(t)$ and $\sigma^2_{\rm m}(t)$ during a fast process by considering only infinitesimal perturbations, approximating $c_n(t)$ by a Gaussian function of n, and assuming a constant expulsion rate constant (approximation b). Unlike Aniansson and Wall, however, these authors analyzed the underlying discrete rate equations rather than introducing a continuum diffusion approximation.

Kshevetskiy and Shchekin [29] have derived equations for moments of the micelle size distribution in a model that allowed for the coexistence of spherical and longer rodlike micelles, using an analysis that did not linearize the governing equations. For simplicity, these authors assumed a quadratic dependence of $W_n(c_1)$ on n for the spherical micelle population, and a linear dependence on n for rodlike micelles. These authors also retained approximations (b) and (c) of the work of Aniansson and Wall. The use of simple approximations for the formation free energies and rate constants for both types of micelle allowed analytic results to be obtained for all of the integrals with respect to aggregation number that appear in expressions for the time derivatives of arbitrary moments. In the cases of rodlike micelles and of coexisting spherical and rodlike micelles, this approach was found to yield nonlinear ODEs that predict nonexponential time dependence. In the case of spherical micelles that we consider here, however, this combination of approximations was found to yield linear ODEs for $q(t)$ and $\sigma^2_{\rm m}(t)$ similar to those obtained in earlier studies of linearized models. The similarity in results was primarily the result of continued use of a quadratic approximation for W_n for spherical micelles, which also limits the range of validity of this analysis to phenomena involving relatively small changes in q.

The analysis of fast processes given in this article is designed to avoid several of the limitations of previous work, and to allow analysis of processes involving large changes in q and c_1. Our analysis starts from the exact expressions for dq/dt and $d\sigma^2_{\rm m}/dt$ obtained by Danov *et al.* [48,49] from the discrete stepwise reaction equations. A closed set of ODEs is obtained here by introducing local (rather than global) Taylor expansions for the dependence of $W_n(c_1(t))$ and the expulsion rate constant on n in a small range of values of n near the instantaneous average value $q(t)$. This approach is based on an underlying assumption that $c_n(t)$ always exhibits a bimodal dependence on n for which the total surfactant concentration is dominated by unimers and by micelles with a relatively narrow range of aggregation numbers clustered around $q(t)$. It does not, however, restrict either the allowed range of values of $q(t)$ or the allowed functional form of the dependence of W_n on n. The resulting approximation yields predictions that correctly describe behavior both near a micellar equilibrium state and under circumstances in which micelles are unstable to steady shrinkage.

D. Slow processes

Slow processes are characterized by changes $c_{\rm m}(t)$ in systems with $c_1 > c_{\rm d}$ caused by rare events that create or destroy micelles. The stepwise reaction model posits that this change occurs via stepwise association and dissociation. It has long been recognized, however, that the slow process could instead occur in some systems by fission and fusion of micelles [50–54]. Early analyses of both association-dissociation and fission-fusion mechanisms relied on linear dynamical models of weak perturbations [1–4,54]. Substantial progress has since been made on analyzing relaxation of large perturbations, particularly for stepwise association and dissociation.

1. Association and dissociation

A fully nonlinear theory of stepwise association and dissociation in systems with $c_1 > c_{\rm d}$ was developed by Grinin, Kuni, Rusanov, and Shchekin (GKRS) [43–47] in 1999–2001, 25 years after the work of Aniansson and Wall [1–3]. The stepwise reaction model underlying the GKRS theory is closely analogous to the Becker-Döring model of stepwise nucleation of liquid from a supersaturated vapor. Like the theory of nucleation, it yields an expression for the rate of association that decreases exponentially with increases in the magnitude of the local maximum in $W_n(c_1)$ at $n = n_t(c_1)$. The corresponding rate of micelle dissociation instead depends exponentially on the difference between this local maximum and the local minimum at $n = n_e(c_1)$. The GKRS theory is applicable only for systems with $c_1 > c_d$ for which barriers to both processes remain much greater than k_BT. Comparison of the GKRS theory to numerical simulations of the stepwise reaction model for strongly perturbed systems have confirmed the accuracy of the theory [55]. A great deal of subsequent work on nonlinear dynamics has been presented by GKRS, their coworkers, and others on further analysis of the original theory [56–58], extensions to situations involving rodlike micelles and/or fission and fusion processes [26,27,30] and numerical studies of both the stepwise reaction model [31,55,59] and of a generalized Smoluchowski model that allows for fission and fusion [60–62].

The association and dissociation rates predicted by the GKRS theory exhibit a strongly nonlinear dependence on instantaneous unimer concentration c_1, as a result of a sensitive dependence of the values of the extrema of $W_n(c_1)$ on c_1. Consequently, the linearized theory of Aniansson and Wall has been shown to be valid only for very weak deviations from equilibrium, corresponding to very small initial perturbations or very late stages of relaxation from a large perturbation [46]. For larger perturbations, there has been shown to exist an intermediate regime during which the net rate of change of $c_m(t)$ is dominated by either association or dissociation, depending on the sign of the initial perturbation, and during which the deviation of c_1 from its final value was shown to exhibit a power-law dependence on time [46,57].

2. Fission and fusion

Like association and dissociation events, micelle fission and fusion events each increase (for fission) or decrease (for fusion) the number of micelles in a system by one micelle. Kahlweit and coworkers presented evidence that, in ionic surfactant systems, association and dissociation dominate at low surfactant and salt concentrations but that fission and fusion dominate at higher concentrations [4,50–53]. This conclusion was based on an analysis of the concentration dependence of the slow relaxation rate τ_2^{-1}, for which the stepwise reaction model predicts a decrease with increasing concentration. In ionic systems, upon increasing concentration, τ_2^{-1} is found to decrease at low concentrations, reach a minimum, and then increase at higher concentration. Kahlweit and coworkers argued that this reversal in behavior indicates a change in mechanism. They hypothesized that fusion is suppressed in systems of low ionic strength by electrostatic repulsion between micelles but that fission and fusion dominate at higher ionic strengths. Herrmann and Kahlweit also found that τ_2^{-1} increases with concentration at all concentrations in solutions of Triton X-100 nonionic surfactant [63], suggesting a fission-fusion mechanism in this case. Recent molecular simulations of nonionic block copolymer surfactants with an adjustable parameter that controls surfactant solubility indicate that the mechanism of slow relaxation changes from an association-dissociation mechanism to a fission-fusion mechanism with decreasing surfactant solubility, or decreasing CMC [8,9,11].

The general form of the reaction equations for a system in which micelles undergo fission and fusion is determined by the requirement of detailed balance, and is well understood [30,54]. Early analyses by Kahlweit [53] and Waton [54] introduced a partial or "quasi"-equilibrium hypothesis, which assumes full relaxation of the fast process, to obtain expressions that relate the slow time τ_2 observed in linear relaxation experiments to the equilibrium fission lifetime. Shchekin, Kshevetskiy, and Pelevina formulated a very general set of nonlinear equations to describe slow relaxation in systems that can contain both spherical and cylindrical micelles, in which the concentrations of both types of micelle can change via either stepwise or fission-fusion processes [30], while assuming partial equilibrium conditions for both species of micelle.

Several studies have presented numerical simulations of the evolution of $c_n(t)$ after both small and large perturbations of systems in which micelles can undergo fission and fusion involving clusters of arbitrary size [60–62]. These simulations have thus far relied on variants of a generalized Smoluchowski equation in which fusion is either taken to be diffusion controlled or in which fusion rates are suppressed relative to diffusion controlled rates by factors that depend on an empirical parameter. Theoretical progress on clarifying the importance of fission and fusion has been limited in part by a lack of reliable information about the magnitude of barriers to fusion, and thus about the magnitude of the relevant rate constants.

Early discussions by Kahlweit and coworkers about the possible relevance of fission and fusion to results of linear relaxation experiments postulated a mechanism involving fusion of submicellar aggregates, with $n < n_t$, to create clusters with $n \in [n_t, 2n_t]$. Griffiths *et al.* [60] distinguished between this and another possible mechanism in which clusters with $n \in [n_e/2, n_e]$ fuse to create rare "super-micelles" with $n \in [n_e, 2n_e]$. Griffiths *et al.* used numerical simulations of a generalized Smoluchowski equation to study the effectiveness of both hypothesized mechanisms in speeding relaxation after rapid dilution of a micellar solution to a final concentration that remains above the CMC. Their simulations used a free energy model with a rather large dissociation barrier ($\Delta W_a \simeq 14k_BT$) that was designed to describe the sparingly soluble nonionic polyoxyethylene glycol alkyl surfactant $C_{10}E_8$. Griffiths *et al.* found that, for this model, the mechanism proposed by Kahlweit had a negligible effect on the relaxation rate of the slow process, but that the mechanism that involves creation and fission of super-micelles dominated the predicted slow relaxation rate over a wide range of assumed values of fusion rate constant. These conclusions are consistent with results of more recent MD simulations [8,9,11] that showed that fission and fusion can dominate the slow process in solutions of sufficiently sparingly soluble surfactants, as the result of the appearance of a large barrier to the competing association-dissociation mechanism, and that the dominant relaxation mechanism in such systems involves fission and formation of super-micelles.

As emphasized by Kahlweit and coworkers, the concentration dependence of the slow relaxation time provides important experimental clues about the mechanism of the slow relaxation. Sections VI and VII present an analysis of the predicted concentration dependence for both association-dissociation and fission-fusion mechanisms in nonionic systems, in a form that takes into account our current understanding of the relevant fission-fusion mechanism.

E. Overview

The contents of the remainder of this article are as follows: Sec. II discusses equilibrium statistical mechanics. Section III reviews governing equations for the stepwise reaction theory. Section IV and the three Appendixes present a nonlinear model of fast stepwise process. Section V discusses the partial equilibrium state that is reached after completion of a fast relaxation process. Section VI reviews the GKRS nonlinear theory of slow stepwise processes. Section VII discusses slow processes for systems in which micelle creation and destruction occur primarily by fission and fusion. Section VIII discusses the construction of nonlinear reduced models that allow for both fast and slow processes and that correctly describe behavior for both $c_1 > c_{\rm d}$ and $c_1 < c_{\rm d}$. Section IX summarizes conclusions.

II. EQUILIBRIUM

The chemical potential of n-mers, denoted by μ_n, is given in any dilute solution by

$$\mu_n(c_n) = \mu_n^\circ + k_BT \ln\left(\frac{c_n}{c^\circ}\right). \tag{4}$$

Here μ_n° is a standard state chemical potential for n-mers and c° is a standard number concentration. By convention, we use the same standard concentration for all species.

A. Equilibrium distribution

Let $c_n^*(c_1)$ denote the equilibrium concentration of n-mers in an equilibrium state with a unimer concentration c_1. A polydisperse solution is in equilibrium when the equilibrium condition

$$\mu_n = n\mu_1 \tag{5}$$

is satisfied for all $n > 1$. Equation (3) for $c_n^*(c_1)$ may be obtained by using Eq. (4) for both μ_n and μ_1 in Eq. (5) and solving for c_n as a function of c_1.

Using Eq. (4) for $\mu_1(c_1)$, we may write Eq. (2) for $W_n(c_1)$ more explicitly as a difference

$$W_n(c_1) = W_n^\circ - nk_BT \ln\left(\frac{c_1}{c^\circ}\right) \tag{6}$$

in which

$$W_n^\circ \equiv W_n(c^\circ) = \mu_n^\circ - n\mu_1^\circ \tag{7}$$

is the standard Gibbs free energy of formation of an n-mer from unimers, in which $\mu_n^\circ = \mu_n(c^\circ)$ and $\mu_1^\circ = \mu_1(c^\circ)$ are both evaluated at the standard concentration. Substituting Eq. (6) for $W_n(c_1)$ into Eq. (3) for $c_n^*(c_1)$ yields an alternate expression

$$c_n^*(c_1) = K_n c_1^n, \quad K_n = e^{-\beta W_n^\circ}/(c^\circ)^{n-1} \tag{8}$$

of the form required by the mass-action law.

Some previous studies have defined a "work of aggregation" [43–47]) that is similar but not completely equivalent to the quantity $W_n(c_1)$ defined here. This work of aggregation is given by the value of $W_n(c_1)$, as defined in Eq. (2), evaluated with the standard n-mer concentration c° set equal to the unimer concentration c_1. Throughout this work, we instead leave c° unspecified and treat it as a constant that is independent of c_1.

1. Critical dissociation concentration

Consider the mathematical criteria for identifying the critical dissociation concentration $c_{\rm d}$ above which $W_n(c_1)$ exhibits a local maximum and local minimum. For this purpose, it is convenient to treat W as a continuous function of both n and c_1, denoted by $W(n, c_1)$. For $c_1 < c_{\rm d}$, $\partial W(n, c_1)/\partial n > 0$ for all n. At exactly $c_1 = c_{\rm d}$, there exists a unique value of n, denoted by $n_{\rm d}$, at which

$$0 = \left.\frac{\partial W}{\partial n}\right|_{n=n_d} = \left.\frac{\partial^2 W}{\partial n^2}\right|_{n=n_d}, \tag{9}$$

while $\partial W/\partial n > 0$ for all $n \neq n_{\rm d}$. For $c_1 > c_{\rm d}$, $W(n, c_1)$ develops a local maximum and a local minimum with respect to n.

In Eq. (6) for W, the only term on the right-hand side (r.h.s.) that depends on c_1 is also linear in n. This implies that $\partial^2W/\partial n^2$ is independent of c_1. We may thus identify $n_{\rm d}$ as the value of n at which $\partial^2W/\partial n^2 = 0$, which is independent of c_1.

Using Eq. (6), one may show that the value $c_1 = c_{\rm d}$ at which $\partial W/\partial n = 0$ at $n = n_{\rm d}$ must satisfy

$$\ln\left(\frac{c_{\rm d}}{c_{\rm c}}\right) = \frac{1}{k_BT}\left.\frac{\partial W}{\partial n}\right|_{c_1=c_{\rm c}, n=n_{\rm d}}. \tag{10}$$

Typical molecular models with $n_{\rm e} \sim 50$–100, $n_{\rm t}/n_{\rm e} \sim 0.2$–$0.3$, and modest dissociation barriers of less than $20k_BT$ at $c_1 = c_{\rm c}$ normally lead to values of $c_{\rm d}/c_{\rm c} > 2/3$ [18].

2. Extrema and barriers

For $c_1 > c_{\rm d}$, $W(n, c_1)$ exhibits a local maximum at $n = n_{\rm t}(c_1)$ and a local minimum at $n = n_{\rm e}(c_1)$. Let

$$W_{\rm t}(c_1) \equiv W_{n_{\rm t}(c_1)}(c_1), \quad W_{\rm e}(c_1) \equiv W_{n_{\rm e}(c_1)}(c_1) \tag{11}$$

denote the values of $W_n(c_1)$ at these two extrema. The barrier to micelle formation by stepwise association in such a system, denoted by $\Delta W_{\rm a}(c_1)$, is given by the difference

$$\Delta W_{\rm a}(c_1) \equiv W_{\rm t}(c_1) - W_1(c_1). \tag{12}$$

The corresponding barrier to micelle destruction by stepwise dissociation, denoted by $\Delta W_{\rm d}(c_1)$, is given by the difference

$$\Delta W_{\rm d}(c_1) \equiv W_{\rm t}(c_1) - W_{\rm e}(c_1) \tag{13}$$

between the local maximum and local minimum values.

Upon increasing c_1, $\Delta W_{\rm a}(c_1)$ decreases while $\Delta W_{\rm d}(c_1)$ increases, as illustrated in Fig. 1. Using Eq. (6), it is straightforward to show that

$$\frac{1}{k_BT}\frac{d\Delta W_{\rm a}(c_1)}{d\ln c_1} = -(n_{\rm t} - 1), \tag{14}$$

$$\frac{1}{k_BT}\frac{d\ \Delta W_{\rm d}(c_1)}{d\ln c_1} = n_{\rm e} - n_{\rm t}. \tag{15}$$

B. Micelle statistical properties

To define micelle statistical properties, we classify all clusters of aggregation number n greater than or equal to a cutoff value b as "proper" micelles. The total number concentration $c_{\rm m}$ of such micelles is given by a sum

$$c_{\rm m} \equiv \sum_{n=b}^{\infty} c_n. \tag{16}$$

Let $\rho_{\rm m}$ denote the corresponding concentration of surfactant in proper micelles, given by

$$\rho_{\rm m} = \sum_{n=b}^{\infty} n c_n. \tag{17}$$

Let $\langle B\rangle_{\rm m}$ denote the number average of some property B_n of n-mers, defined as an average over the proper micelle range,

$$\langle B\rangle_{\rm m} \equiv \frac{1}{c_{\rm m}} \sum_{n=b}^{\infty} B_n c_n. \tag{18}$$

The number average micelle aggregation number, denoted by q, is given by the ratio

$$q \equiv \langle n\rangle_{\rm m} = \frac{\rho_{\rm m}}{c_{\rm m}}. \tag{19}$$

The variance of the micelle aggregation number, denoted by $\sigma_{\rm m}^2$, is given by the mean-squared deviation

$$\sigma_{\rm m}^2 = \langle (n-q)^2\rangle_{\rm m}, \tag{20}$$

or, equivalently, $\sigma_{\rm m}^2 = \langle n^2\rangle_{\rm m} - q^2$.

In what follows, we will often assume for simplicity that the total surfactant concentration ρ is dominated by the contributions of unimers ($n = 1$) and proper micelles, giving

$$\rho \simeq c_1 + \rho_{\rm m}, \tag{21}$$

thus assuming negligible concentrations for clusters with $1 < n < b$.

Let $\rho^*(c_1)$, $c_{\rm m}^*(c_1)$, $\rho_{\rm m}^*(c_1)$, $q^*(c_1)$, and $\sigma_{\rm m}^*(c_1)$ denote equilibrium values of ρ, $c_{\rm m}$, $\rho_{\rm m}$, q, and $\sigma_{\rm m}$, respectively, in an equilibrium state with a unimer concentration c_1. These quantities are all defined by replacing c_n by $c_n^*(c_1)$ in all of the sums that appear in Eqs. (1)–(19).

Consider how equilibrium micelle properties vary with changes in c_1. Differentiating Eq. (8) for $c_n^*(c_1)$ with respect to c_1 yields

$$\frac{dc_n^*(c_1)}{dc_1} = \frac{nc_n^*(c_1)}{c_1} \tag{22}$$

for all $n \geqslant 1$. Using this to evaluate the derivatives of Eq. (16) for $c_{\rm m}$ and Eq. (17) for $\rho_{\rm m}$ yields

$$\frac{dc_{\rm m}^*(c_1)}{dc_1} = \frac{c_{\rm m}^* q^*}{c_1}, \tag{23}$$

$$\frac{d\rho_{\rm m}^*(c_1)}{dc_1} = \frac{c_{\rm m}^* \langle n^2\rangle_{\rm m}^*}{c_1}. \tag{24}$$

The corresponding derivative of $q^* = \rho_{\rm m}^*/c_{\rm m}^*$ is given by

$$\frac{dq^*(c_1)}{dc_1} = \frac{(\sigma_{\rm m}^*)^2}{c_1}, \tag{25}$$

where $(\sigma_{\rm m}^*)^2 = \langle n^2\rangle_{\rm m}^* - (q^*)^2$.

The dimensionless derivative $d\rho_{\rm m}^*/dc_1$ will appear frequently in subsequent discussions and will hereafter be denoted by the symbol

$$\kappa_{\rm e}(c_1) \equiv \frac{d\rho_{\rm m}^*(c_1)}{dc_1}. \tag{26}$$

To describe changes in $\rho_{\rm m} = c_{\rm m} q$ in systems with $q = q^*$ that arise from changes in q^* at fixed $c_{\rm m}$, we also introduce a related definition

$$\kappa_{\rm p}(c_1, c_{\rm m}) \equiv c_{\rm m}\frac{dq^*(c_1)}{dc_1} = \frac{c_{\rm m}(\sigma_{\rm m}^*)^2}{c_1}. \tag{27}$$

Typical micellar solutions with $\rho > c_{\rm c}$ and $c_1 \simeq c_{\rm c}$ have $q \sim \sigma_{\rm m}^2 \sim 10^2$, giving $\sigma_{\rm m}^2 \ll q^2$ and $\langle n^2\rangle_{\rm m} \simeq q^2$. In such solutions, $\kappa_{\rm e} \simeq (\rho_{\rm m}/c_{\rm c})q$ and $\kappa_{\rm p} \simeq (\rho_{\rm m}/c_{\rm c})((\sigma_{\rm m}^*)^2/q)$. In such solutions, $\kappa_{\rm e} \gg 1$ for $(\rho - c_{\rm c})/c_{\rm c} \gg q^{-1}$, giving $\kappa_{\rm e} \gg 1$ whenever ρ exceeds $c_{\rm c}$ by more than a few percent.

Consider the relationship between total surfactant concentration ρ and unimer concentration c_1 in a system with $c_1 > c_{\rm d}$ in which we assume that $\rho = c_1 + \rho_{\rm m}$. Differentiating ρ with respect to c_1 yields $d\rho/dc_1 = 1 + \kappa_{\rm e}$ or, equivalently,

$$\frac{dc_1}{d\rho} = \frac{1}{1+\kappa_{\rm e}}. \tag{28}$$

States with $\rho < c_{\rm c}$ in which $\rho_{\rm m}$ is negligible have $\rho \simeq c_1$, $dc_1/d\rho \simeq 1$, and $\kappa_{\rm e} \ll 1$. Well-developed micellar states in which ρ exceeds $c_{\rm c}$ by more than a few percent are characterized by values of $\kappa_{\rm e} \gg 1$, giving $dc_1/d\rho \ll 1$, so that c_1 remains near $c_{\rm c}$ and depends only weakly on ρ. For large micelles, with $q^*(c_{\rm c}) \gg 1$, the crossover from $\kappa_{\rm e} \ll 1$ to $\kappa_{\rm e} \gg 1$ occurs over a very narrow range of values of ρ near $c_{\rm c}$.

III. STEPWISE REACTION MODEL

The stepwise reaction model assumes that the only relevant elementary processes in a surfactant solution are unimer insertion and expulsion. The rate of insertion of free unimers into n-mers (events per volume per time), denoted by r_n^+, is given by

$$r_n^+ = k_n^+ c_1 c_n, \tag{29}$$

where k_n^+ is the associated insertion rate constant. The corresponding rate for the reverse reaction, expulsion of unimers from $(n+1)$-mers, is given by

$$r_n^- = k_n^- c_{n+1}, \tag{30}$$

where k_n^- is the expulsion rate constant. Let

$$I_n = r_n^+ - r_n^- \tag{31}$$

denote the net rate of conversion of n-mers into $(n+1)$-mers, for any $n \geqslant 1$.

Let G_n denote the net rate of creation of n-mers, such that

$$\frac{dc_n(t)}{dt} = G_n(t) \tag{32}$$

in a homogeneous system. This net creation rate is given by the difference

$$G_n = I_{n-1} - I_n, \tag{33}$$

for all $n > 1$, and by a sum

$$G_1 = -2I_1 - \sum_{n=2}^{\infty} I_n, \tag{34}$$

for the special case $n = 1$.

The principle of detailed balance requires that $r_n^+ = r_n^-$ or (equivalently) $I_n = 0$ for all $n \geqslant 1$ in any equilibrium state. Let $r_n^*(c_1)$ denote the value of r_n^+ or r_n^- in an equilibrium state with a unimer concentration c_1, given by

$$r_n^*(c_1) = k_n^+ c_1 c_n^*(c_1) = k_n^- c_{n+1}^*(c_1). \tag{35}$$

By combining this with Eq. (3) for $c_n^*(c_1)$, we find that k_n^+ and k_n^- must satisfy

$$k_n^+ c_1 = k_n^- e^{-\beta \Delta W_n(c_1)}, \tag{36}$$

where $\beta \equiv 1/k_B T$ and where

$$\Delta W_n(c_1) \equiv W_{n+1}(c_1) - W_n(c_1). \tag{37}$$

Using Eq. (6) for $W_n(c_1)$ yields

$$\Delta W_n = \Delta W_n^\circ - k_B T \ln\left(\frac{c_1}{c^\circ}\right), \tag{38}$$

where $\Delta W_n^\circ \equiv W_{n+1}^\circ - W_n^\circ$. Note that Eq. (36) is actually valid for any value of c_1. This is possible because Eq. (38) yields $e^{-\beta \Delta W_n(c_1)} \propto c_1$, giving an equation in which both sides of the equation are proportional to c_1.

Using Eq. (36), we may express Eq. (31) for I_n as a sum

$$I_n = k_n^-(c_n e^{-\beta \Delta W_n(c_1)} - c_{n+1}) \tag{39}$$

or, equivalently,

$$I_n = k_n^- c_n (e^{-\beta \Delta W_n(c_1)} - 1) - k_n^-(c_{n+1} - c_n), \tag{40}$$

for all $n \geqslant 1$. In Eq. (40), the first term on the r.h.s. is a flux that is driven by the difference ΔW_n, and that vanishes when $\Delta W_n = 0$. The second term instead arises from "diffusion" of n, with an effective diffusivity k_n^-.

A. Evolution of statistical properties

We next consider predictions of the stepwise reaction model for the time dependence of the micelle properties $c_{\rm m}(t)$, $\rho_{\rm m}(t)$, $q(t)$, and $\sigma_{\rm m}^2(t)$. Time derivatives of $c_{\rm m}(t)$ and $\rho_{\rm m}(t)$ can be obtained by combining their definitions, given in Eqs. (16) and (17), with Eq. (33) for $dc_n/dt = G_n$. This immediately yields

$$\frac{dc_{\rm m}}{dt} = \sum_{n=b}^{\infty} G_n = \sum_{n=b}^{\infty} (I_{n-1} - I_n)\,, \tag{41}$$

$$\frac{d\rho_{\rm m}}{dt} = \sum_{n=b}^{\infty} nG_n = \sum_{n=b}^{\infty} n(I_{n-1} - I_n). \tag{42}$$

The sum of differences in Eq. (41) may be evaluated immediately if we assume that $I_n \to 0$ as $n \to \infty$. This yields

$$\frac{dc_{\rm m}}{dt} = I_{b-1}. \tag{43}$$

The current I_{b-1} is simply the net rate at which aggregates with $n < b$ grow to the cutoff value b beyond which they are counted as proper micelles. The sum in Eq. (42) may be simplified by summation by parts, which yields

$$\frac{d\rho_{\rm m}}{dt} = \sum_{n=b}^{\infty} I_n + bI_{b-1}. \tag{44}$$

Equations (43) and (44) may then be combined to compute the time derivative of $q(t) = \rho_{\rm m}(t)/c_{\rm m}(t)$. A straightforward calculation yields

$$\frac{dq(t)}{dt} = \frac{1}{c_{\rm m}}\left[\sum_{n=b}^{\infty} I_n + (b-q)I_{b-1}\right]. \tag{45}$$

The term proportional to I_{b-1} in Eq. (45) may be ignored when considering fast processes, for which we assume that $dc_{\rm m}/dt = I_{n-1} \simeq 0$.

The quantities $c_{\rm m}(t)$ and $\rho_{\rm m}(t)$ are the zeroth and first moments of the cluster concentration $c_n(t)$ in the proper micelle range, respectively. We extend the above analysis in Appendix A by considering the time derivative of the corresponding second moment, which we use to compute the time derivative of the variance $\sigma_{\rm m}^2$. The analysis given there yields

$$\frac{d\sigma_{\rm m}^2(t)}{dt} = \frac{1}{c_{\rm m}} \sum_{n=b}^{\infty} (2n+1-q)I_n + \frac{1}{c_{\rm m}}\left[(q-b)^2 - \sigma_{\rm m}^2\right] I_{b-1}. \tag{46}$$

Equations (45) and (46) are both exact expressions that have been given previously by Danov *et al.* [48].

B. Continuum diffusion approximation

Many previous analyses of the stepwise reaction model have introduced a continuum approximation in which the discrete model is approximated by a continuous model of diffusion of n. In this approximation, we treat n as a continuous variable, and treat c_n, $W_n(c_1)$, k_n^-, and I_n as differentiable functions of n, denoted by $c(n,t)$, $W(n,t)$ $k^-(n)$, and $I(n,t)$. We also assume that differences between values of functions of n at neighboring integers are small, and approximate finite differences such as ΔW_n by derivatives with respect to n.

The stepwise reaction model reduces in this approximation to a one-dimensional diffusion model in which

$$\frac{\partial c(n,t)}{\partial t} = -\frac{\partial I(n,t)}{\partial n} \tag{47}$$

with a current

$$I = -k^-\left(c\frac{\partial(\beta W)}{\partial n} + \frac{\partial c}{\partial n}\right). \tag{48}$$

Equations (47) and (48) are valid if and only if: (a) c_n, W_n and k_n^- are smoothly varying functions of n, with very small second derivatives, and (b) $\beta\Delta|W_n| \ll 1$ for all relevant values of n. Observe that assumption (b) is necessary in order to justify Eq. (48) for I as a valid approximation to Eq. (40), because this assumption allows us to approximate the difference $(e^{-\beta\Delta W_n} - 1)$ that appears in Eq. (40) by the derivative $-\partial(\beta W)/\partial n$ that appears in Eq. (48).

This continuum approximation is approximately valid for weakly perturbed micellar systems for which $q \gg 1$ and

$\sigma_{\rm m} \gg 1$ in equilibrium, which have been the primary focus of most previous work on fast processes. This approximation is actually never valid, however, in the limit of low unimer concentration, $c_1 \rightarrow 0$. To show this, we note that Eq. (38) implies that $\Delta W_n \rightarrow \infty$ in the limit $c_1 \rightarrow 0$, violating the necessary requirement that $\beta|\Delta W_n| \ll 1$. The correct limiting value of I_n in the limit $c_1 \rightarrow 0$, can instead be obtained by simply suppressing the contribution to I_n arising from insertion, leaving only the expulsion contribution to obtain $I_n = -k_n^- c_{n+1}$. This limiting behavior is correctly recovered by the discrete expression given in Eq. (39), because $e^{-\beta\Delta W_n(c_1)} \rightarrow 0$ as $c_1 \rightarrow 0$, but is not recovered from Eq. (48). Models of phenomena that may involve large changes in c_1 must thus avoid relying on this form of continuum approximation.

C. Diffusion-controlled insertion

Several prior treatments of the stepwise reaction model have considered simplified models in which either the expulsion or insertion rate constants are taken to be independent of n. To improve on this, it is useful to consider a physically motivated approximation for how these quantities actually depend on n.

Analyses of experiments on small molecule surfactants and simulations of moderately soluble block copolymer surfactants [9] suggest that insertion of individual molecules into a micelle is generally diffusion controlled. A diffusion-controlled model for insertion yields an insertion rate constant

$$k^+(n) = 4\pi D_1 R_+(n), \tag{49}$$

in which R_+ is an effective capture radius that is generally comparable to the micelle core radius, and in which we have used a continuum notation for the dependence of k^+ and R_+ on n

Spherical micelles contain a spherical core of solventphobic material with a core radius $R_{\rm core}$ that increases with aggregation number as approximately $R_{\rm core} \propto n^{1/3}$. An assumption that R_+ is equal or proportional to this core radius thus yields $R_+ \propto n^{1/3}$. Because R_+ is the only factor on the r.h.s. of Eq. (49) that depends on n, this assumption yields an expression for the derivative of $\ln k_n^+$ as

$$\frac{d\ln k^+}{dn} = \frac{d\ln R_+}{dn} \simeq \frac{1}{3n}. \tag{50}$$

The expulsion rate constant k^- is related to the insertion constant by the detailed balance condition $k_n^- = c_1 k_n^+ e^{\beta\Delta W_n}$ of Eq. (36). The assumption that $R_+ \propto n^{1/3}$ thus yields giving a corresponding expression for the derivative of $\ln k^-$ as

$$\frac{d\ln k^-}{dn} \simeq \frac{1}{3n} + \frac{W''}{k_B T}, \tag{51}$$

where $W'' = \partial^2 W(n, c_1)/\partial n^2$.

In an equilibrium state, $(\sigma_{\rm m}^*)^2 \simeq k_B T/W''$, and so the second term on the r.h.s. of Eq. (51) is approximately equal to $1/(\sigma_{\rm m}^*)^2$. Typical micellar aggregates have $n \sim \sigma_{\rm m}^2 \sim 10^2$. This implies that each of the two terms on the r.h.s. of Eq. (51) and the resulting expressions for $d\ln k^-/dn$ are all typically of order 10^{-2}.

In what follows, we obtain some small corrections to expressions obtained in some earlier treatments that are proportional to either $d\ln k^-/dn$ or $\beta W''$. Corrections of this form arise either from use of a model in which k_n^- depends on n or from our avoidance of the continuum diffusion approximation. When computing such corrections, we assume that the dimensionless quantities $d\ln k^-/dn$ and $\beta W''$ are small parameters, and expand our results only to first order in these parameters.

IV. FAST STEPWISE PROCESSES

Fast processes in micellar systems are characterized by relatively rapid changes in $c_1(t)$, $q(t)$, and $\sigma_{\rm m}^2(t)$ with negligible change in $c_{\rm m}(t)$ over the relevant time range. In this section, we thus develop explicit approximate expressions for $dq(t)/dt$ and $d\sigma_{\rm m}^2(t)/dt$ for processes during which $c_{\rm m}$ remains approximately constant. Details of the calculation of $dq(t)/dt$ are given in the body of the paper, while corresponding details of the calculation of $d\sigma_{\rm m}^2(t)/dt$ are relegated to Appendix A.

A. Evolution of $q(t)$

Consider predictions of the stepwise reaction model for $dq(t)/dt$ under conditions for which $dc_{\rm m}/dt \simeq 0$. By Eq. (43), the assumption that $dc_{\rm m}/dt \simeq 0$ implies that $I_{b-1} \simeq 0$, allowing us to ignore the boundary term proportional to I_{b-1} in Eq. (45) for dq/dt. In this limit, we thus obtain

$$\frac{dq}{dt} \simeq \frac{1}{c_{\rm m}} \sum_{n=b}^{\infty} I_n. \tag{52}$$

The fast process drives the system towards a partial equilibrium state in which $I_n = 0$ throughout the proper micelle range, in which the r.h.s. of Eq. (52) vanishes.

1. Aggregation number velocity

By using Eqs. (29)–(31) for I_n, Eq. (52) may be rewritten as a micelle number average

$$\frac{dq(t)}{dt} = \frac{1}{c_{\rm m}} \sum_{n=b}^{\infty} c_n V_n = \langle V \rangle_{\rm m} \tag{53}$$

of a quantity

$$V_n \equiv k_n^+ c_1 - k_{n-1}^-, \tag{54}$$

which we refer to as the aggregation number velocity. Observe that V_n is simply the difference between the rate $k_n^+ c_1$ per cluster of insertion of unimers into n-mers and the corresponding rate k_{n-1}^- of expulsion from n-mers. The velocity V_n thus gives dq/dt for a hypothetical monodisperse distribution.

By using detailed balance, we may express V_n as a function of only k_n^- and W_n, giving

$$V_n \equiv k_n^- e^{-\beta\Delta W_n} - k_{n-1}^-, \tag{55}$$

or, equivalently,

$$V_n \equiv k_n^-(e^{-\beta\Delta W_n} - 1) + \Delta k_{n-1}^-, \tag{56}$$

where $\Delta k_{n-1}^- = k_n^- - k_{n-1}^-$.

In what follows, we will consider approximations for k_n^-, W_n and V_n that require that we treat these quantities as continuous functions of n. For this purpose, we adopt a continuous notation in which $V(n) \equiv V_n$, $W(n) \equiv W_n$, and $k(n) \equiv k_n^-$, and in which we use primes to indicate differentiation with respect to n, giving, e.g., $k'(n) = dk(n)/dn$. Note that we use k, with no $-$ or $+$ superscript, to denote the expulsion constant k_n^-. It is possible to suppress the $-$ superscript without ambiguity because we use expressions in which the detailed balance condition is used to consistently rewrite k_n^+ in terms k_n^-, giving expressions that involve only k_n^- and W_n.

To compute dq/dt, we must evaluate the average $\langle V\rangle_{\mathrm{m}}$ given in Eq. (53). It is not possible to give an exact analytic expression for such an average value for a model in which W_n and k_n^- can have an arbitrary dependence on n. To construct useful approximations, we assume in what follows that, at any time t, number averages such as $\langle V\rangle_{\mathrm{m}}$ are dominated by the contributions of a relatively narrow range of values of n close to the current average value $q(t)$. We then assume that, as a result, quantities other than $c(n,t)$ that appear within the sum that defines such an average can be adequately approximated within this limited range by a low order Taylor expansion around their values at $n = q(t)$.

In the stepwise reaction model, all quantities of interest can be expressed as functions of $W(n, c_1)$ and $k(n)$. We thus begin by introducing physically motivated assumptions about the behavior of these two input quantities. Throughout our analysis, we assume the following:

(i) The function $W(n, c_1)$ can be adequately approximated over the width of the micellar peak in $c(n,t)$ by a second-order Taylor expansion about its value at $q(t)$, with a second derivative $|W''| \ll k_BT$.

(ii) The expulsion rate constant $k(n)$ is adequately approximated over this range by a linear Taylor expansion, with a first derivative $|k'| \ll k$.

The assumptions that $|k'| \ll k$ and $|W''| \ll k_BT$ are used in what follow to systematically categorize contributions to $V(n)$ and $\langle V\rangle_{\mathrm{m}}$ in powers of the dimensionless quantities k'/k and $\beta W''$.

In continuous notation, in a system in which $k(n)$ is a locally linear function of n, Eq. (56) becomes

$$V(n) = k(n)(e^{-\beta\Delta W(n)} - 1) + k', \tag{57}$$

where $\Delta W(n) \equiv W(n+1) - W(n)$ and k' is a constant. Using the fact that $\Delta W(n) = W'(n) + W''/2$ whenever $W(n)$ is quadratic, and the assumption that $\beta|W''| \ll 1$, we may expand the exponential as

$$e^{-\beta\Delta W(n)} \simeq e^{-\beta W'(n)}(\,1 - \beta W''/2\,). \tag{58}$$

This yields an approximate expression for $V(n)$ as

$$\begin{aligned} V \simeq{}& k(e^{-\beta W'} - 1) \\ &+ k' - \tfrac{1}{2}k\beta W'' e^{-\beta W'}. \end{aligned} \tag{59}$$

The dominant contribution to the r.h.s. of Eq. (59) is given by the first line. The largest subdominant contributions are given in the second line, which are suppressed relative to the dominant contribution by prefactors of k'/k and $\beta W'$. Higher order corrections have been neglected.

We will need a corresponding expression for the second derivative $V''(n)$ in what follows. Straightforward differentiation of the r.h.s. of Eq. (59), in which we take $k(n)$ and $\Delta W(n)$ to be linear functions of n, yields a dominant contribution

$$V'' \simeq -(2k' - k\beta W'')\beta W'' e^{-\beta W'}, \tag{60}$$

in which we have dropped contributions of higher than linear order in $\beta W''$ and k'/k.

Note that our analysis assumes that second derivative of βW is small (i.e., that $|\beta W''| \ll 1$), but does *not* assume that the first derivative $\beta W'$ is small. We must allow for potentially large values of $\beta W'$ in order to correctly treat large changes in unimer concentrations, because $W'(n) = dW^\circ/dn - k_BT\ln(c_1/c^\circ)$ contains a contribution $-k_BT\ln(c_1/c^\circ)$ that diverges in the limits $c_1 \to 0$ or $c \to \infty$. However, because this contribution to $W'(n)$ is independent of n, $W''(n)$ is independent of c_1, allowing us to assume that $\beta|W''(n)| \ll 1$ at any value of c_1 without contradiction.

To compute $\langle V\rangle_{\mathrm{m}}$, we approximate $V(n)$ within the sum that defines the number average by a Taylor expansion about its value at $n = q(t)$. We show in what follows that use of a Taylor expansion leads naturally to approximations in which the average is expressed as a sum of moments of the size distribution. Different low-order expansions lead to different possible approximations.

An exact treatment of an equilibrium in a system of constant c_{m} must yield $dq/dt = 0$. To test whether this criterion is satisfied by any proposed approximation, it is useful to consider an equilibrium state of a model in which $W(n, c_1)$ is a locally quadratic function of n, as assumed throughout our analysis. A quadratic model for $W(n)$ yields a Gaussian distribution for $c_n^*(c_1)$, for which $q^* = n_{\mathrm{e}}(c_1)$ and $(\sigma_{\mathrm{m}}^*)^2 = k_BT/W''$. Because $W'(n_{\mathrm{e}}) = 0$ and $q^* = n_{\mathrm{e}}$, $W'(q^*) = 0$ in any such state. A model with a locally quadratic free energy should thus yield $dq/dt = \langle V\rangle = 0$ when $W'(q) = 0$ and $\beta W''\sigma_m^2 = 1$.

2. *Local linear approximation for* $V(n)$

We first consider an approximation that is based on a linear Taylor approximation for $V(n)$, as a sum

$$V(n) = V(q) + V'(q)\delta n, \tag{61}$$

where $\delta n = n - q$ and $q = \langle n\rangle_{\mathrm{m}}$. By using this approximation to evaluate the average $\langle V\rangle_{\mathrm{m}}$, while noting that $\langle \delta q\rangle_{\mathrm{m}} = 0$, we obtain

$$\frac{dq}{dt} = \langle V\rangle_{\mathrm{m}} = V(q), \tag{62}$$

where $V(n)$ is given by Eq. (59). Note that, in a model with known input parameters, this gives an approximation for dq/dt as a function of q and c_1 alone, with no dependence on σ_{m}^2 or any higher moment.

Note that Eq. (59) yields a nonzero value of $V(q)$ in states with $W'(q) = 0$, because the subdominant contribution in the second line of Eq. (59) do not vanish in this limit. Equation (62) for $dq(t)/dt$ thus does not satisfy our criterion for consistent treatment of Gaussian equilibrium states.

3. Local quadratic approximation for $V(n)$

We next consider a local quadratic approximation for $V(n)$, as a Taylor expansion

$$V(n) = V(q) + V'(q)\delta n + \tfrac{1}{2}V''(q)(\delta n)^2. \tag{63}$$

Using this to evaluate the average $\langle V\rangle_{\rm m}$ yields

$$\langle V\rangle_{\rm m} = V(q) + \tfrac{1}{2}V''(q)\sigma_{\rm m}^2, \tag{64}$$

where we have used the fact that $\langle \delta n\rangle_{\rm m} = 0$ and the definition $\sigma_{\rm m}^2 = \langle(\delta n)^2\rangle_{\rm m}$.

Using Eq. (59) for $V(q)$ and Eq. (60) for $V''(q)$ then yields a final expression

$$\begin{aligned}\frac{dq}{dt} &\simeq k(e^{-\beta W'} - 1)\\ &\quad -\frac{1}{2}k\beta W''\big(1 - \beta W''\sigma_{\rm m}^2\big)e^{-\beta W'}\\ &\quad + k'\big(1 - \beta W''\sigma_{\rm m}^2 e^{-\beta W'}\big),\end{aligned} \tag{65}$$

in which all quantities on the r.h.s. are evaluated at $n = q(t)$ and $c_1 = c_1(t)$.

Note that Eq. (65) yields an expression for dq/dt that depends on the instantaneous value of $\sigma_{\rm m}^2(t)$ as well as $c_1(t)$ and $q(t)$. Equation (65) can thus be used to construct a model for fast processes as a closed set of differential equations for c_1, q and $\sigma_{\rm m}^2$, but cannot be used to construct a simpler model that does not track $\sigma_{\rm m}^2$.

Observe that Eq. (65) yields $dq/dt = 0$ in any equilibrium state with $W'(q) = 0$ and $\beta W''(q)\sigma_{\rm m}^2 = 1$. This approximation thus satisfies our consistency criterion for Gaussian equilibrium states.

4. Simplified form

For some purposes, it is useful to consider a simplified approximation for dq/dt as a function of c_1 and q, with no explicit dependence on $\sigma_{\rm m}^2$. In Eq. (65) the dependence of dq/dt on $\sigma_{\rm m}^2$ arises from the second and third lines of the r.h.s., which both yield subdominant terms proportional to the deviation of $\sigma_{\rm m}^2$ from its equilibrium value. The simplest thermodynamically consistent approximation for $dq(t)/dt$ that does not depend on $\sigma_{\rm m}^2$ is obtained by simply neglecting all of the subdominant terms proportional to k' and $k\beta W''$ in Eq. (65), leaving only the dominant contribution

$$\frac{dq(t)}{dt} \simeq k(q)(e^{-\beta W'(q)} - 1). \tag{66}$$

Use of Eq. (66) is preferable to use of the approximation $dq/dt = V(q)$ given in Eq. (62) because Eq. (66) correctly yields $dq/dt = 0$ when $W'(q) = 0$, and thus yields dynamics in which $q(t)$ relaxes to the correct equilibrium value.

Equation (66) yields an expression for $dq(t)/dt$ that is always of the same sign as $-W'(q)$. It thus yields gradient-search dynamics in which $q(t)$ always migrates in the direction of locally decreasing $W(n)$, as assumed without proof throughout the qualitative discussion of fast processes given in Sec. I B. Equation (66) is also designed to yield the correct limiting behavior in the limit $c_1 \rightarrow 0$ in which the insertion rate becomes negligible.

We have shown the quantities k'/k and $\beta W''$ are both typically of order 10^{-2} in micellar systems. Neglect of subdominant contributions in which these quantities appear as prefactors is thus expected to cause no qualitative change and very small quantitative changes in resulting predictions for $q(t)$.

A simple nonlinear model of fast processes in situations in which $c_{\rm m}$ remains constant can be constructed by using Eq. (66) for dq/dt while using the constraint of constant total concentration $\rho_{\rm m}(t) = c_1(t) + c_{\rm m}q(t)$ to determine $c_1(t)$.

B. Evolution of $\sigma_{\rm m}^2(t)$

It is straightforward to compute $d\sigma_{\rm m}^2(t)/dt$ by methods analogous to those used above to compute $dq(t)/dt$. The required calculation is presented in Appendix A, where we obtain the expression

$$\begin{aligned}\frac{d\sigma_{\rm m}^2(t)}{dt} &\simeq 2k\big(1 - \beta W''\sigma_{\rm m}^2 e^{-\beta W'}\big)\\ &\quad + k(e^{-\beta W'} - 1)\\ &\quad + k'(e^{-\beta W'} - 1)\sigma_{\rm m}^2.\end{aligned} \tag{67}$$

Here all functions on the r.h.s. are evaluated at $n = q(t)$ and $c_1 = c_1(t)$. Note that $d\sigma_{\rm m}^2/dt$ vanishes in an equilibrium state in which $\beta W''(q)\sigma_{\rm m}^2 = 1$ and $W'(q) = 0$, as required for consistency with equilibrium statistical mechanics.

A nonlinear model for the coupled evolution of q and $\sigma_{\rm m}^2$ during a fast process can be constructed by combining Eq. (65) for $dq(t)/dt$ with Eq. (67) for $d\sigma_{\rm m}^2(t)/dt$, while assuming constant $c_{\rm m}$ and using the conservation of surfactant to compute $c_1(t)$.

C. Linearized models

Linearized dynamical models of the relaxation of small perturbations can be obtained either by linearizing either: (a) the simplified expression for dq/dt given in Eq. (66) or (b) the coupled equations for dq/dt and $d\sigma_{\rm m}^2/dt$ given by Eqs. (65) and (67). Both analyses are shown to recover previously published results. Details of the linearization procedure are given in Appendix B, and results presented below.

We consider relaxation of infinitesimal perturbations from an equilibrium state characterized by a unimer concentration $\overline{c}_1$. Deviations of q and $\sigma_{\rm m}^2$ from equilibrium values are denoted by δq and $\delta\sigma_{\rm m}^2$, respectively. All relevant relaxation times are all proportional to a timescale

$$\tau_\sigma \equiv \frac{(\sigma_{\rm m}^*)^2}{k^-}, \tag{68}$$

in which $(\sigma_{\rm m}^*)^2$ is evaluated in the reference equilibrium state and k^- is evaluated at the most probable value $n_{\rm e}(\overline{c}_1)$. Time τ_σ is the autocorrelation time for fast dynamical fluctuations in the aggregation number of individual micelles in an equilibrated solution.

Simplified model: Linearization of the simplified expression for dq/dt given in Eq. (66) is found to yield the linear ordinary differential equation (ODE)

$$\frac{d(\delta q)}{dt} \simeq -\frac{1}{\tau_1}\delta q, \tag{69}$$

where τ_1 is the fast relaxation time predicted by Aniansson and Wall, given by

$$\frac{1}{\tau_1} = (1 + \kappa_{\rm p})\frac{1}{\tau_\sigma}. \tag{70}$$

Here $\kappa_{\rm p} = c_{\rm m} dq^*(c_1)/dc_1 = c_{\rm m}\sigma_{\rm m}^2/c_1$ is the quantity defined in Eq. (27), evaluated in the equilibrium state. This approximation simply recovers the prediction of Aniansson and Wall [1,2].

Full model: Linearization of Eqs. (65) and Eq. (67) yields

$$\frac{d(\delta q)}{dt} = -\frac{1}{\tau_1}\delta q - \frac{F}{\tau_\sigma}\delta\sigma_{\rm m}^2\,, \tag{71}$$

$$\frac{d(\delta\sigma_{\rm m}^2)}{dt} = -\frac{G}{\tau_1}\delta q - \frac{2}{\tau_\sigma}\delta\sigma_{\rm m}^2, \tag{72}$$

in which

$$F = \frac{k'}{k} - \frac{\beta W''}{2}, \quad G = 1 + \frac{k'}{\beta W''} \tag{73}$$

are dimensionless parameters. Note that F is a small parameter, of order 10^{-2}, but that G is order unity.

Equations (71)–(73) are a slight generalization of the linearized dynamical equations obtained previously by Danov *et al.* [48]. Danov *et al.* [48] considered a model with an n-independent value of the expulsion rate constant k, for which $k' = 0$, but used discrete reaction kinetics rather than relying on a continuum diffusion approximation. We have confirmed that the linearized equations obtained by Danov *et al.* are equivalent to Eqs. (71) and (72) with k' set to zero.

The only difference between Eqs. (71) and (69) for $dq(t)/dt$ is the presence of the subdominant term $F\delta\sigma_{\rm m}^2/\tau_\sigma$ on the r.h.s. of Eq. (71). Because the dimensionless parameter F is expected to be quite small, of order 10^{-2}, deviations from the predictions of Aniansson and Wall for $q(t)$ are also expected to be small [48] and may be experimentally undetectable.

D. Continuum vs discrete models

Several previous studies of the dynamics of the fast relaxation process have relied on a continuum diffusion approximation for micelle dynamics [1,2,29]. To facilitate understanding of the consequences of different possible mathematical approximations, we have derived nonlinear expressions for dq/dt and $d\sigma_{\rm m}^2/dt$ by a method that relies on the continuum approximation for $\partial c(n,t)/\partial t$ given in Eqs. (47) and (48), but that is otherwise very closely analogous to the analysis given above. As in the above analysis, the dependences of $W(n,c_1)$ and $k'(n)$ on n are approximated by local Taylor expansions about $n = q(t)$ to obtain expressions that depend on the derivatives of $W(n,c_1)$ at $n = q(t)$. The main differences between our treatments of discrete and continuum models are simply the replacement of sums by integrals and replacement of a discrete model for I_n by the continuum expression given in Eq. (48).

Details of the required continuum analysis are given in Appendix C. That analysis yields nonlinear differential equations

$$\frac{dq}{dt} \simeq -k\beta W' + k'\big(1 - \beta W''\sigma_{\rm m}^2\big), \tag{74}$$

$$\frac{d\sigma_{\rm m}^2}{dt} \simeq 2k\big(1 - \beta W''\sigma_{\rm m}^2\big) - k'\beta W'\sigma_{\rm m}^2, \tag{75}$$

in which all the functions W', W'' and k are evaluated at $n = q(t)$ and $c_1 = c_1(t)$.

To facilitate comparison to earlier studies of linearized models, Eqs. (74) and (75) can be linearized by repeating the reasoning used to obtain Eqs. (71) and (72). This analysis yields a pair of linear ODEs of the same form as those given in Eqs. (71) and (72), except for the appearance of modified values for the coefficients F and G, for which the continuum analysis yields

$$F = \frac{k'}{k} \quad G = \frac{k'}{\beta W''}. \tag{76}$$

Note that Eq. (76) gives expressions for both coefficients that are both proportional to k', and that are identical to the terms proportional to k' in Eq. (73) for F and G.

The coefficients F and G are prefactors of the "off-diagonal" terms that couple relaxation of δq and $\delta\sigma_{\rm m}^2$ in Eqs. (71) and (72). In the continuum model, these coefficients vanish when $k' = 0$. A linearized continuum approximation for a model with $k' = 0$ thus yields uncoupled relaxation of $\delta q(t)$ and $\delta\sigma_{\rm m}^2(t)$ with relaxation times τ_1 and $\tau_\sigma/2$, respectively, as originally predicted by Aniansson and Wall. The linearized continuum ODEs obtained here are thus a generalization of those obtained by Aniansson and Wall to models in which k varies with n.

Nonlinear Eqs. (74) and (75) are the continuum analogs of Eqs. (65) and (67). Two differences are particularly apparent upon comparison of the r.h.s. of these pairs of equations, which we refer to here as "continuum" and "discrete" equations.

One obvious difference is the replacement of the continuum drift velocity $-k\beta W'$ that appears in two places in the continuum equations by corresponding factors of $k(e^{-\beta W'} - 1)$ in the analogous discrete equations. This replacement is a straightforward result of the use of a discrete rather than continuum expression for the current I.

A second notable difference is the existence of two terms in the discrete equations for which there are no analogous terms in the continuum equations. Specifically, the continuum equations do not contain any terms analogous to the following:

(i) The contribution $-\frac{1}{2}k\beta W''(1 - \beta W''\sigma_{\rm m}^2)$ in the second line of Eq. (65) for dq/dt or

(ii) The contribution $k(e^{-\beta W'} - 1)$ in the second line of Eq. (67) for $d\sigma_{\rm m}^2/dt$.

Both of these are cross-coupling contributions that make the relaxation of one of the variables $q(t)$ or $\sigma_{\rm m}^2(t)$ depend on the other. The contributions of these two terms to the corresponding linearized equations give rise to the terms in Eq. (73) for the coefficients F and G that are absent in the corresponding continuum expressions of Eq. (76). These two terms in the linearized equations are the only cross-coupling terms that are independent of k', and have both been previously identified in the linearized analysis of a discrete model with $k' = 0$ by Danov *et al.* [48]. The fact that no analogous contributions appear in the ODEs obtained from a continuum model shows that the existence of these terms is a direct result of the use of a discrete model for reaction rates.

V. PARTIAL EQUILIBRIUM

In systems with $c_1 > c_{\rm d}$ and widely disparate fast and slow relaxation times, the fast process allows redistribution of material between micelles of different sizes and between unimer and micelles, but preserves the total number of micelles. After completion of the fast process, such a system is thus left in a state of partial equilibrium in which the free energy is minimized subject to a constraint on the number of proper micelles.

A. Definition

The reaction equilibrium criterion for a reaction involving insertion of a single unimer into an n-mer is

$$\mu_{n+1} = \mu_n + \mu_1. \tag{77}$$

In a partial equilibrium state, this criterion is satisfied for all stepwise reactions involving the numerous proper micelles, with $n \geqslant b$, but is generally not satisfied for rare aggregates with $1 < n < b$. Equation (77) is satisfied for all $n \geqslant b$ if and only if

$$\mu_n = n\mu_1 + \lambda \tag{78}$$

for all $n \geqslant b$, where λ is a chemical potential difference that is independent of n. The condition for full equilibrium instead requires that $\mu_n = n\mu_1$, corresponding to $\lambda = 0$.

An expression for the number concentration c_n of proper micelles in a partial equilibrium state may be obtained by substituting Eq. (4) for μ_n and μ_1 into Eq. (78). Solving the resulting equation for c_n yields a distribution

$$c_n = Y c_n^*(c_1) \tag{79}$$

for all $n \geqslant b$, where $Y \equiv e^{\lambda/k_BT}$ is a related dimensionless, n-independent number. Full equilibrium, with $c_n = c_n^*(c_1)$, is recovered in the special case $Y = 1$ or $\lambda = 0$.

In such a partial equilibrium state, it follows from Eq. (79) and the definitions of $c_{\rm m}$ and $\rho_{\rm m}$ that

$$c_{\rm m} = Y c_{\rm m}^*(c_1), \quad \rho_{\rm m} = Y\rho_{\rm m}^*(c_1). \tag{80}$$

It also follows that the average aggregation number $q \equiv \rho_{\rm m}/c_{\rm m}$ is equal to the equilibrium value at the relevant unimer concentration,

$$q = q^*(c_1), \tag{81}$$

independent of Y.

B. Quasistatic evolution

After completion of the fast process, a disturbed system remains in a slowly evolving partial equilibrium state throughout the slow process. In a system of fixed temperature and pressure, a partial equilibrium state can be uniquely specified by specifying values for two independent variables. These can be chosen to be either c_1 and Y or c_1 and $c_{\rm m}$, where $c_{\rm m}(Y, c_1) = Y c_{\rm m}^*(c_1)$. During a slow process, a system thus evolves along a path within a two-dimensional space of possible partial equilibrium states. The requirement that total surfactant concentration ρ remains constant is thus sufficient to define a unique one-dimensional path for evolution of a system with a specified total concentration ρ.

To analyze processes that occur at fixed total concentration ρ, we assume that ρ is dominated by contributions of unimers and proper micelles, as in Eq. (21). When applied to a partial equilibrium state, in which $q = q^*(c_1)$, Eq. (21) implies that

$$\rho(c_1, c_{\rm m}) = c_1 + c_{\rm m} q^*(c_1), \tag{82}$$

or, equivalently, that

$$\rho(c_1, Y) = c_1 + Y\rho_{\rm m}^*(c_1)\,. \tag{83}$$

By requiring that $d\rho = 0$ during an infinitesimal change of state, while using state variables c_1 and Y and starting from Eq. (83) for ρ, we obtain a differential constraint

$$0 = d\rho = (1 + Y\kappa_{\rm e})dc_1 + \rho_{\rm m}^* dY. \tag{84}$$

By instead using c_1 and $c_{\rm m}$ as state variables and starting from Eq. (82), we obtain an equivalent constraint

$$0 = d\rho = (1 + \kappa_{\rm p})dc_1 + q^* dc_{\rm m}, \tag{85}$$

in which $\kappa_{\rm p} = c_{\rm m} dq^*(c_1)/dc_1$ is defined in Eq. (27).

By combining Eqs. (85) and (84), we find that

$$\frac{dY}{dc_{\rm m}} = \frac{1 + Y\kappa_{\rm e}(c_1)}{1 + \kappa_{\rm p}(c_1, c_{\rm m})}\frac{1}{c_{\rm m}^*(c_1)}. \tag{86}$$

Equation (86) applies along any path of constant ρ through the space of partial equilibrium states, independent of any assumptions regarding the mechanism of the change in $c_{\rm m}$. Specifically, it applies equally well whether $c_{\rm m}$ changes primarily by stepwise association and dissociation or primarily by fission and fusion.

VI. SLOW STEPWISE PROCESSES

During the so-called slow relaxation process of a system of metastable micelles, $c_{\rm m}(t)$ changes via rare events that create and destroy micelles while the system remains in partial equilibrium. The stepwise reaction model assumes that this occurs via rare association and dissociation events. This section briefly reviews the nonlinear theory of stepwise association and dissociation [43–47] developed by Grinin, Kuni, Rusanov, and Shchekin (GKRS), using results from Sec. V to simplify some aspects of the analysis.

In this context, it is convenient to define a relative concentration

$$y_n \equiv \frac{c_n}{c_n^*(c_1)} \tag{87}$$

for all $n \geqslant 1$, in which c_n and c_1 denote the actual n-mer and unimer concentrations. By definition, $y_1 = 1$. A partial equilibrium state is one in which y_n is independent of n in the proper micelle range $n > b$, within which $y_n = Y$. It is straightforward to show that, in the stepwise reaction model,

$$r_n^+ = y_n r_n^*(c_1), \quad r_n^- = y_{n+1} r_n^*(c_1), \tag{88}$$

for all $n \geqslant 1$, where $r_n^*(c_1)$ is the equilibrium rate of either reaction. It follows immediately that

$$I_n = -r_n^*(c_1)(y_{n+1} - y_n) \tag{89}$$

for all $n \geqslant 1$.

A. Association-dissociation kinetics

Consider the calculation of $dc_{\rm m}(t)/dt$ for a system that remains in partial equilibrium throughout the proper micelle range and in which $c_1 > c_\mathrm{d}$ and $\Delta W_\mathrm{d} \gg k_BT$. We assume that the total surfactant concentration ρ is dominated by unimers and proper micelles, as indicated by Eq. (21). The assumption of negligible concentrations $c_n(t) \simeq 0$ in the rare cluster range $n \in [2, b-1]$ also implies that $0 = dc_n(t)/dt = I_{n-1} - I_n$ in this range. This, in turn, implies the existence of quasistationary current

$$I_1 = I_2 = \cdots = I_{b-1} = I \tag{90}$$

throughout the rare cluster range. Equation (43) implies that $I = I_{b-1} = dc_\mathrm{m}/dt$ is the net rate of micelle creation.

The value of the flux $I(t)$ through the rare cluster range may be computed by a method analogous to that used to compute the electrical current through resistors in series: Rewriting Eq. (89) in the form $y_{n+1} - y_n = -I/r_n^*(c_1)$ we treat I as the analog to an electrical current through resistors in series, and treat $1/r_n^*(c_1)$ as a resistance between nodes n and $n+1$. We assume partial equilibrium for $n \geqslant b$, implying that $y_b = Y$. Summing differences in neighboring values of y_n over the range $[1, b]$, noting that $y_1 = 1$, we obtain

$$\frac{dc_\mathrm{m}}{dt} = I = \frac{-1}{R(c_1)}(Y-1), \tag{91}$$

where

$$R(c_1) \equiv \sum_{n=1}^{b-1} \frac{1}{r_n^*(c_1)} \tag{92}$$

denotes the total resistance.

Using the relation $Y = c_\mathrm{m}/c_\mathrm{m}^*(c_1)$, we may rewrite Eqs. (91) as a differential equation for $c_\mathrm{m}(t)$, of the form

$$\frac{dc_\mathrm{m}(t)}{dt} = k_a(c_1) - k_d(c_1)c_\mathrm{m}, \tag{93}$$

in which

$$k_a(c_1) = \frac{1}{R(c_1)} \tag{94}$$

is the rate of micelle creation by stepwise association, while $k_d(c_1)c_m$ is the corresponding rate of micelle dissociation, with a rate constant

$$k_d(c_1) = \frac{1}{R(c_1)c_\mathrm{m}^*(c_1)}. \tag{95}$$

The inverse of $k_d(c_1)$ is a characteristic micelle dissociation lifetime, denoted here by

$$\tau_\mathrm{d}(c_1) \equiv 1/k_d(c_1). \tag{96}$$

The time $\tau_\mathrm{d}(c_1)$ is equal to the average time for a micelle chosen at random from an equilibrated solution to be destroyed by stepwise dissociation [9,45].

Equation (94) for $k_a(c_1)$ and Eq. (95) for $k_d(c_1)$ can be further simplified for systems in which $\Delta W_\mathrm{a} \gg k_BT$ and $\Delta W_\mathrm{d} \gg k_BT$ by approximating sums over n by Gaussian integrals [44]. A straightforward analysis of Eq. (92) for $R(c_1)$, using a Gaussian approximation for $1/c_n^*(c_1)$ for $n \sim n_\mathrm{t}(c_1)$, yields

$$k_a(c_1) \simeq \frac{k_\mathrm{t}^-}{\sqrt{2\pi}\sigma_\mathrm{t}} c_1 e^{-\beta\Delta W_\mathrm{a}(c_1)}, \tag{97}$$

in which $k_\mathrm{t}^- = k_{n_\mathrm{t}}^-$ is the expulsion constant at the transition state and $\sigma_\mathrm{t}(c_1)$ denotes the width (or standard deviation) of the Gaussian peak in $1/c_n^*(c_1)$. Using Eq. (95) for k_d and a corresponding Gaussian approximation for $c_\mathrm{m}^*(c_1)$ then yields

$$k_d(c_1) \simeq \frac{k_\mathrm{t}^-}{2\pi\sigma_\mathrm{t}\sigma_\mathrm{m}^*} e^{-\beta\Delta W_\mathrm{d}(c_1)}, \tag{98}$$

where $\sigma_\mathrm{m}^*(c_1)$ is the equilibrium standard deviation of the Gaussian peak in $c_\mathrm{m}^*(c_1)$ for $n \sim n_\mathrm{e}(c_1)$.

B. Evolution of $c_\mathrm{m}(t)$

Analysis of the slow process in a closed system is complicated by the fact that the unimer concentration c_1 changes as micelles are created and destroyed, causing c_m^*, k_a and k_d to change as well as c_m. Analysis of this coupled evolution may be simplified by invoking the analysis of quasistatic evolution of systems that remain in partial equilibrium given in Sec. V B.

It is convenient to consider the evolution of the ratio $Y(t) = c_\mathrm{m}(t)/c_\mathrm{m}^*(t)$, which approaches $Y = 1$ in equilibrium. Using the chain rule to compute the derivative $dY(t)/dt$ from knowledge of Eq. (91) for dc_m/dt and Eq. (86) for dY/dc_m for a system that remains in partial equilibrium, we obtain

$$\frac{dY}{dt} = \frac{dY}{dc_\mathrm{m}}\frac{dc_\mathrm{m}}{dt} = \frac{1 + Y\kappa_\mathrm{e}(c_1)}{1 + \kappa_\mathrm{p}(c_1, c_\mathrm{m})}\frac{1}{\tau_d(c_1)}(Y-1). \tag{99}$$

In Eq. (99) the unimer concentration $c_1 = c_1(t)$ is an implicit function of $Y(t)$ and total surfactant concentration ρ, given by the requirement that $\rho = c_1 + Y\rho_\mathrm{m}^*(c_1)$. Equation (99) thus yields a single nonlinear ODE for $Y(t)$ in a homogeneous system.

The Aniansson-Wall linearized model of infinitesimal perturbations can be easily recovered by linearizing Eq. (99) around $Y = 1$. Expanding the r.h.s. of Eq. (99) to linear order in a deviation $\delta Y = Y - 1$ yields a linear differential equation

$$\frac{dY}{dt} \simeq -\frac{1}{\tau_2}(Y-1), \tag{100}$$

in which

$$\frac{1}{\tau_2} \equiv \frac{1+\kappa_\mathrm{e}}{1+\kappa_\mathrm{p}}\frac{1}{\tau_d} \tag{101}$$

is the slow relaxation time obtained by Aniansson and Wall [1,2]. Here κ_e, κ_p, and τ_d are all constants that are evaluated in the final equilibrium state.

C. Relaxation rate vs concentration

The dependence of τ_d and τ_2 on total concentration has been analyzed by Aniansson *et al.* [3] and by Kahlweit and Teubner [4]. Their conclusions may be recovered as follows: Starting from Eq. (98) for τ_d, we assume that the dependence of $\ln\tau_\mathrm{d}$ on $\ln c_1$ is dominated by the contribution of the barrier $-\beta\Delta W_\mathrm{d}$, and thus that

$$\frac{d\ln\tau_\mathrm{d}^{-1}}{d\ln c_1} \simeq \frac{-1}{k_BT}\frac{d\Delta W_\mathrm{d}}{d\ln c_1} \simeq -(n_\mathrm{e} - n_\mathrm{t}), \tag{102}$$

where we have used Eq. (15) for $d\Delta W_\mathrm{d}/d\ln c_1$. We then compute $d\ln\tau_\mathrm{d}^{-1}/d\ln\rho_\mathrm{m}$ by dividing the above by $d\ln\rho_\mathrm{m}/d\ln c_1 = c_1\kappa_\mathrm{e}/\rho_\mathrm{m}$. Approximating $\kappa_\mathrm{e} \simeq \rho_\mathrm{m}q/c_1$ and

$q \simeq n_{\rm e}$ yields

$$\frac{d \ln \tau_{\rm d}^{-1}}{d \ln \rho_{\rm m}} \simeq -\left(1 - \frac{n_{\rm t}}{n_{\rm e}}\right). \tag{103}$$

Let X denote the dimensionless concentration

$$X = \frac{\rho_{\rm m}}{c_1} \simeq \frac{\rho - c_{\rm c}}{c_{\rm c}}. \tag{104}$$

By assuming that $n_{\rm t}$ and $n_{\rm e}$ are nearly independent of $\rho_{\rm m}$, we obtain

$$\tau_{\rm d}^{-1} \propto X^{\alpha_d} \tag{105}$$

with an effective exponent

$$\alpha_d = \frac{n_{\rm t}}{n_{\rm e}} - 1. \tag{106}$$

Because $0 < n_{\rm t}/n_{\rm e} < 1$, this yields a negative exponent $-1 < \alpha_d < 0$, giving a rate $\tau_{\rm d}^{-1}$ that decreases with increasing concentration. For the polymer models studied in Refs. [8,9], $n_{\rm t}/n_{\rm e} \simeq 0.2$–$0.3$, giving $|\alpha_d| \simeq 0.7$–0.8.

By substituting Eq. (105) for $\tau_{\rm d}^{-1}$ into Eq. (101) for τ_2, while assuming $\kappa_{\rm e} \gg 1$ and $\kappa_{\rm e} \propto X$, we obtain an inverse slow relaxation time

$$\frac{1}{\tau_2} \propto \frac{X^{n_{\rm t}/n_{\rm e}}}{1 + (\sigma_{\rm m}^2/q)X}, \tag{107}$$

consistent with Eq. (VI.31) of Ref. [4].

VII. SLOW FISSION-FUSION PROCESSES

We now consider the rate of the slow process for systems in which micelle birth and death occur predominantly by fission and fusion. Fission and fusion are rare events that can produce clusters with aggregation numbers that would be quite rare in a partial equilibrium state. We assume, however, that products of fission and fusion experience a sequence of a comparatively rapid sequence of stepwise processes by which reaction products rapidly revert to a partial equilibrium distribution of aggregation numbers. Following Waton [54] and Shchekin *et al.* [30], we thus assume here that partial equilibrium is maintained throughout the slow process when this process occurs by fission and fusion, as well as when it occurs by association and dissociation.

A. Fission-fusion kinetics

The rate equations for a model that includes fission and fusion of clusters of arbitrary aggregation number are a straightforward generalization of those used in the stepwise reaction model. Let $r^+_{n,n'}$ denote the rate (events per unit volume and time) of fusion of clusters of aggregation numbers n and n', with $n \geqslant n'$, given by

$$r^+_{n,n'} = k^+_{n,n'} c_n c_{n'}, \tag{108}$$

where $k^+_{n,n'}$ is a fusion rate constant. Let $r^-_{n,n'}$ denote the rate of fission events in which of clusters of aggregation number $n + n'$ fission into products of aggregation numbers n and n' with $n \geqslant n'$, given by

$$r^-_{n,n'} = k^-_{n,n'} c_{n+n'}, \tag{109}$$

where $k^-_{n,n'}$ is a fission rate constant. The principle of detailed balance implies that $r^+_{n,n'} = r^-_{n,n'}$ in any equilibrium state. Let

$$r^*_{n,n'}(c_1) = k^+_{n,n'} c^*_n c^*_{n'} = k^-_{n,n'} c^*_{n+n'} \tag{110}$$

denote the rate of either such reaction in an equilibrium state characterized by a unimer concentration c_1, in which $c^*_n = c^*_n(c_1)$.

Let $r_{\rm fus}$ and $r_{\rm fis}$ denote the overall rates of fusion and fission events involving proper micelles, respectively, given by

$$r_{\rm fus} = \sum_{n=n'}^{\infty} \sum_{n'=b}^{\infty} k^+_{n,n'} c_n c_{n'}, \tag{111}$$

$$r_{\rm fis} = \sum_{n=n'}^{\infty} \sum_{n'=b}^{\infty} k^-_{n,n'} c_{n+n'}. \tag{112}$$

These quantities must be equal in equilibrium.

Let $r^*_{\rm f}(c_1)$ denote the overall rate of micelle fission or fusion reactions in equilibrium, as given by the sum

$$r^*_{\rm f}(c_1) = \sum_{n=n'}^{\infty} \sum_{n'=b}^{\infty} r^*_{n,n'}(c_1). \tag{113}$$

Let $\tau_{\rm f}$ denote the equilibrium fission lifetime, which is defined by the expression

$$\frac{1}{\tau_{\rm f}(c_1)} \equiv \frac{r^*_{\rm f}(c_1)}{c^*_{\rm m}(c_1)}, \tag{114}$$

in which the r.h.s. is the frequency of fission events per proper micelle.

In equilibrium, the micelles that undergo fission typically have aggregation numbers greater than the average q, because the fission rate constant increases with increasing aggregation number. Let $n_{\rm f}$ denote the average aggregation number of micelles that undergo fission. This quantity is given by the weighted average

$$n_{\rm f}(c_1) \equiv \frac{1}{r^*_{\rm f}(c_1)} \sum_{n=n'}^{\infty} \sum_{n'=b}^{\infty} (n + n') r^*_{n,n'}(c_1). \tag{115}$$

Analysis of a simple simulation model of block copolymer micelles by Mysona *et al.* [8,9,11] indicates a value of $n_{\rm f} \sim 1.4 n_{\rm e}$ in systems in which the slow process is dominated by fission and fusion. Because fission was found to usually yield two child clusters of comparable aggregation number [9], this yields typical fission products with aggregation numbers roughly 30% less than q.

We may characterize the dependence of $r^*_{\rm f}(c_1)$ on c_1 by computing the logarithmic derivative $d \ln r^*_{\rm f}(c_1)/d \ln c_1$. A straightforward calculation, based on Eqs. (110) and (113) for $r^*_{\rm f}$ and Eq. (22) for $dc^*_n(c_1)/dc_1$, yields

$$\frac{d \ln r^*_{\rm f}(c_1)}{d \ln c_1} = n_{\rm f}(c_1). \tag{116}$$

The dependence of the equilibrium reaction rate on c_1 is thus controlled by the average aggregation number of a fusion product, or of a fission reactant.

To describe the slow process for a system that remains in partial equilibrium, we assume that $c_n = Y c^*_n(c_1)$ throughout the proper micelle range $n \geqslant b$, where Y is independent of n.

Using this in Eq. (112) yields an overall fission rate

$$r_{\rm fis} = Y r_{\rm f}^{*}(c_1), \tag{117}$$

which is linear in Y at fixed c_1 because fission is a first-order reaction, Similar reasoning yields an overall fusion rate

$$r_{\rm fus} = Y^2 r_{\rm f}^{*}(c_1), \tag{118}$$

which is quadratic in Y because fusion is a second-order reaction. These simple expressions for the dependence of reaction rates on Y in a partial equilibrium state were clearly implicit in the approach of Shchekin, Kshevetskiy, and Pelevina [30], but do not seem to have been made explicit.

B. Evolution of $c_{\rm m}(t)$

Combining these expressions for fission and fusion rates, and noting that fission creates one new micelle and fusion destroys one, yields a rate law

$$\frac{dc_{\rm m}}{dt} = -(Y^2 - Y) r_{\rm f}^{*}(c_1). \tag{119}$$

Repeating the reasoning used for the stepwise model, we then use the assumption of partial equilibrium and Eq. (86) for $dY/dc_{\rm m}$ to show that $Y(t)$ thus obeys the differential equation

$$\begin{aligned}\frac{dY}{dt} &= \frac{dY}{dc_{\rm m}}\frac{dc_{\rm m}}{dt}\\ &= -\frac{1+Y\kappa_{\rm e}}{1+\kappa_{\rm p}}\frac{1}{\tau_{\rm f}(c_1)}Y(Y-1).\end{aligned} \tag{120}$$

The timescale $\tau_{\rm f}(c_1)$, as defined in Eq. (114), is the fission lifetime in a hypothetical equilibrated system with a unimer concentration equal to the actual instantaneous unimer concentration. As in systems in which the slow process occurs by stepwise processes, the unimer concentration $c_1(t)$ in a closed system is implicitly determined as a function of Y by the requirement that $\rho = c_1 + Y\rho_{\rm m}^{*}(c_1)$ remain independent of time.

The case of small deviation from equilibrium can be treated by linearizing Eq. (120). This yields the linear differential equation

$$\frac{dY}{dt} \simeq -\frac{1}{\tau_2}(Y-1) \tag{121}$$

with a slow relaxation time given by

$$\frac{1}{\tau_2} = \frac{1+\kappa_{\rm e}}{1+\kappa_{\rm p}}\frac{1}{\tau_{\rm f}}, \tag{122}$$

where $\tau_{\rm f}$ is the fission lifetime in the final equilibrium state. Equation (122) for the slow time was originally given in slightly simplified form by Kahlweit [53] and in a form equivalent to that given here by Waton [54].

Equations (122) and (101) give analogous expressions for the slow time τ_2 in systems in which the slow process occurs primarily by fission and fusion and by stepwise processes, respectively. Note that the only difference between these two equations is the replacement of the equilibrium dissociation lifetime $\tau_{\rm d}(c_1)$ that appears in Eq. (101) by the fission lifetime $\tau_{\rm f}(c_1)$ in Eq. (122). The relationship between the equilibrium micelle lifetime and the relaxation time τ_2 observed in a macroscopic relaxation experiment is thus independent of the mechanism of micelle creation and destruction, and is instead a more general consequence of the partial equilibrium condition.

C. Relaxation rate vs concentration

We now consider the dependence of $\tau_{\rm f}$ and τ_2 on surfactant concentration. To begin, we consider the dependence of $\tau_{\rm f}$ on c_1. Using Eq. (114) for $\tau_{\rm f}$, we find

$$\frac{d\ln\tau_{\rm f}^{-1}(c_1)}{d\ln c_1} = \frac{d\ln r_{\rm f}^{*}(c_1)}{d\ln c_1} - \frac{d\ln c_{\rm m}^{*}(c_1)}{d\ln c_1}. \tag{123}$$

Using Eq. (116) for $d\ln r_{\rm f}^{*}/d\ln c_1$ and Eq. (23) for $dc_m^{*}(c_1)/dc_1$ then yields

$$\frac{d\ln\tau_{\rm f}^{-1}}{d\ln c_1} = n_{\rm f} - q, \tag{124}$$

where $n_{\rm f}$ is the number average aggregation number of micelles that undergo fission, as defined in Eq. (115). The corresponding derivative with respect to $\ln\rho_{\rm m}$ is then obtained by dividing by $d\ln\rho_{\rm m}/d\ln c_1 = c_1\kappa_{\rm e}/\rho_{\rm m}$. By assuming $\kappa_{\rm e} \simeq (\rho_{\rm m}/c_1)q$ and $q \simeq n_{\rm e}$, we find that

$$\frac{d\ln\tau_{\rm f}^{-1}}{d\ln\rho_{\rm m}} \simeq \frac{n_{\rm f}}{n_{\rm e}} - 1. \tag{125}$$

Assuming that $n_{\rm f}$ and $n_{\rm e}$ are almost independent of ρ, we obtain a power-law relationship

$$\tau_{\rm f}^{-1} \propto X^{\alpha_f} \tag{126}$$

with an effective exponent

$$\alpha_f = \frac{n_{\rm f}}{n_{\rm e}} - 1. \tag{127}$$

For the expected case $n_{\rm e} < n_{\rm f} < 2n_{\rm e}$, this yields $0 < \tau_{\rm f}^{-1} < 1$. For a typical case $n_{\rm f}/n_{\rm e} \simeq 1.4$, $\alpha_f \simeq 0.4$. This analysis thus predicts a fission rate constant $\tau_{\rm f}^{-1}$ that increases with increasing concentration, or a lifetime $\tau_{\rm f}$ that decreases with concentration as $\tau_{\rm f} \propto (\rho - c_{\rm c})^{-\alpha_f}$. This trend is opposite to that predicted by Eq. (105) for the stepwise reaction model, which predicts micelle dissociation lifetime $\tau_{\rm d}$ that instead increases with increasing concentration.

By substituting Eq. (126) for $\tau_{\rm d}^{-1}$ into Eq. (122) for τ_2^{-1}, while assuming $\kappa_{\rm e} \gg 1$ and $\kappa_{\rm e} \propto X$, we obtain

$$\frac{1}{\tau_2} \propto \frac{X^{n_{\rm f}/n_{\rm e}}}{1 + (\sigma_{\rm m}^2/q)X}. \tag{128}$$

Equations (126) and (128) are analogous to Eqs. (105) and (107), which give corresponding predictions for systems controlled by association and dissociation. While Eqs. (105) and (107) were previously known, Eqs. (126) and (128) to the best of our knowledge are new.

VIII. REDUCED MODELS

We now consider the construction of a complete but approximate dynamical model for a homogeneous surfactant solution as a set of ODEs for a small number of variables. Construction of such requires a set of related choices of a set of primary dynamical variables and approximate relations for their time derivatives. The analysis presented here allows the construction of models in which the primary variables are micelle number concentration $c_{\mathrm{m}}(t)$, average micelle aggregation number $q(t)$, and, optionally, the variance $\sigma_{\mathrm{m}}^2(t)$.

Given expressions for $dc_{\mathrm{m}}(t)/dt$ and $dq(t)/dt$, the corresponding derivative $dc_1(t)/dt$ can always be inferred for a homogeneous system from the constraint of constant total surfactant concentration $\rho = c_1(t) + c_{\mathrm{m}}(t)q(t)$, which implies that

$$\frac{dc_1}{dt} = -c_{\mathrm{m}}\frac{dq}{dt} - q\frac{dc_{\mathrm{m}}}{dt}. \tag{129}$$

Unimer concentration can thus be treated as an auxiliary variable rather than a primary variable when considering homogeneous systems.

Suitable expressions for the rate of change of $q(t)$ and (if desired) $\sigma_{\mathrm{m}}^2(t)$ have been given in Sec. IV. To construct a model in which $\sigma_{\mathrm{m}}^2(t)$ is retained as a primary variable, we may use Eq. (65) for $dq(t)/dt$ and Eq. (67) for $d\sigma_{\mathrm{m}}^2(t)/dt$. To construct a simpler but slightly less accurate model in which $\sigma_{\mathrm{m}}^2(t)$ is not retained, we may instead use (66) for $dq(t)/dt$. In either case, we expect the resulting equations to correctly describe evolution of these variables during either the two-stage relaxation of a weakly perturbed micellar system or during the rapid dissociation of unstable micelles that is expected in systems with $c_1 < c_{\mathrm{d}}$.

Construction of a generally applicable approximation for the net rate dc_{m}/dt of micelle creation requires more thought. The main conceptual challenge that we face is the need to treat situations in which c_1 is greater than or less than c_{d} somewhat differently, because of the different physical mechanisms at play in these cases. For simplicity, we focus hereafter on systems in which the slow process is adequately described by the stepwise reaction model.

In systems with $c_1(t) > c_{\mathrm{d}}$ and $q(t) > n_{\mathrm{t}}(c_1(t))$, changes in $c_{\mathrm{m}}(t)$ occur by rare micelle association and dissociation events. In this case, it is appropriate to use the GKRS theory to approximate dc_{m}/dt. This yields a model of the form

$$\frac{dc_{\mathrm{m}}}{dt} = k_a(c_1) - k_d(c_1)c_{\mathrm{m}}, \tag{130}$$

where $k_a(c_1) \propto e^{-\beta\Delta W_{\mathrm{a}}(c_1)}$ and $k_d(c_1) \propto e^{-\beta\Delta W_{\mathrm{d}}(c_1)}$ are the association and dissociation rate constants given in Eqs. (94) and (95), respectively. In this case, micelles are created and destroyed by rare events while the average aggregation number of existing micelles remains very close to $q^*(c_1)$.

In systems with $c_1(t) < c_{\mathrm{d}}$ or $c_1(t) > c_{\mathrm{d}}$ but $q(t) < n_{\mathrm{t}}(t)$, micelles instead become unstable to rapid shrinkage by unimer expulsion. In this situation, unimer expulsion leads to a rapid decrease in $q(t)$ and micelles are destroyed rather suddenly when $q(t)$ approaches zero. In this case, dc_{m}/dt should be described by an expression that treats micelles as having been destroyed when their aggregation number reaches or approaches $n = 1$. In a dynamical model that tracks $q(t)$ but not $\sigma_{\mathrm{m}}^2(t)$, the derivative dc_{m}/dt could modelled relatively simply by an expression of the form

$$\frac{dc_{\mathrm{m}}}{dt} = -D(q)c_{\mathrm{m}}, \tag{131}$$

in which $D(q)$ is a rate of destruction that is zero for q greater than some critical value (e.g., for $q > 10$) but that becomes rapidly larger with decreasing n. Neither the exact functional form nor the magnitude of the function $D(q)$ is particularly important, as long $D(q)$ is large enough so that $c_{\mathrm{m}}(t)$ reaches zero before $q(t)$ reaches zero. Conceptually, the simplest variant of this would be to take $c_{\mathrm{m}}(t)$ to drop suddenly to zero when $q(t)$ reaches 1, thus implicitly assuming monodisperse micelles that all simultaneously finish dissociating when $q(t) \to 1$. More realistic variants could be constructed within the context of a model that retains $\sigma_{\mathrm{m}}^2(t)$ as a primary variable, by making D a function of $\sigma_{\mathrm{m}}^2(t)$ as well as $q(t)$, but this would not change the essential features of the phenomena.

A general dynamical model must allow for both of these mechanisms for changes in $c_{\mathrm{m}}(t)$. Both mechanisms can be combined in a physically motivated manner by taking dc_{m}/dt to be a sum of the form

$$\frac{dc_{\mathrm{m}}}{dt} = -D(q)c_{\mathrm{m}} - S(c_1, q)[k_a(c_1) - k_d(c_1)c_{\mathrm{m}}], \tag{132}$$

in which $S(c_1, q)$ is "switching" function that approaches 1 for $c_1 > c_{\mathrm{d}}$ and $q > n_{\mathrm{t}}(c_1)$, but that rapidly approaches zero for either $c_1 < c_{\mathrm{d}}$ or for $c_1 > c_{\mathrm{d}}$ but $q < n_{\mathrm{t}}(c_1)$.

A general nonlinear dynamical model for a homogeneous solution can thus be constructed by using the results of Sec. IV for $dq(t)/dt$ and, optionally, $d\sigma_{\mathrm{m}}^2(t)/dt$, while using an expression of the form suggested in Eq. (132) for dc_{m}/dt. Remaining unspecified details, such as the exact functional forms of the functions $D(q)$ and $S(c_1, q)$, are not expected to strongly affect resulting predictions.

IX. CONCLUSIONS

This article presents a self-contained discussion of the theory of kinetics in homogeneous micelle-forming surfactant systems in a form suitable for describing large deviations from equilibrium. Results of this analysis are used as a starting point for the discussion of inhomogeneous systems in the accompanying article [64].

The analysis of fast stepwise processes given in Sec. IV provides general nonlinear expressions for the net rate dq/dt of micelle growth by stepwise processes and the corresponding rate of change $d\sigma_{\mathrm{m}}^2/dt$ of the variance. The resulting expression for dq/dt is given in its simplest form in Eq. (66). This yields dynamical behavior in which $q(t)$ always migrates in the direction of decreasing micelle formation free energy $W_n(c_1)$. This yields gradient-search dynamics in which $q(t)$ evolves toward a local equilibrium value $n_{\mathrm{e}}(c_1)$ in weakly perturbed micellar systems, but in which $q(t)$ decreases steadily towards zero via unimer expulsion in systems with either a subcritical value of q or a subcritical unimer concentration $c_1 < c_{\mathrm{d}}$. A somewhat more accurate model with similar qualitative behavior can be obtained by combining Eq. (65) for $dq(t)/dt$ and Eq. (67) for $d\sigma_{\mathrm{m}}^2/dt$ to describe the coupled equations for the first and second moments.

A reduced dynamical model for the evolution of a homogeneous system can be constructed by combining expressions obtained here for the time derivatives of $c_1(t)$, $c_{\mathrm{m}}(t)$, $q(t)$, and (optionally) $\sigma_{\mathrm{m}}^2(t)$ as functions of the same set of primary variables. The main conceptual challenge that is encountered when attempting to construct a globally valid model is the need to use different physical models and mathematical expressions to predict $dc_{\mathrm{m}}(t)/dt$ in situations in which there is or is not a barrier to rapid stepwise dissociation. In systems with $c_1 > c_{\mathrm{d}}$ and a barrier to dissociation, dynamics in a stepwise reaction model can be described by combining the theory of Sec. IV for fast relaxation of $q(t)$ and $\sigma^2_{\mathrm{m}}(t)$ with the GKRS theory of the slow process. In systems of unstable micelles, dynamics can be described by the nonlinear theory of the fast process combined with an assumption that micelles are destroyed when $q(t)$ approaches zero. We have proposed a somewhat *ad hoc* way of combining expressions designed to describe these different situations so as to interpolate correctly between them, but have not entirely resolved this difficulty.

The analysis of slow processes in Secs. VI and VII allows for the possibility that, in different systems, the slow process may occur primarily either by stepwise association and dissociation or by micelle fission and fusion. Predictions are given here for the concentration dependence of the micelle fission lifetime and the slow relaxation time in nonionic systems in which the slow process proceeds by fission and fusion; these can be compared to previously known predictions for systems in which the slow process proceeds by association and dissociation. The two mechanisms yield qualitatively different trends, giving a micelle dissociation lifetime that increases with increasing concentration for the association-dissociation mechanism and a fission lifetime that decreases with increasing concentration for the fission-fusion mechanism. In both cases, the relevant micelle lifetime τ is found to exhibit an approximately power-law dependence $\tau^{-1} \propto (\rho - c_{\mathrm{c}})^{\alpha}$, with an exponent α that depends on the ratio of an aggregation number associated with a dynamical transition state to the value of the most probable equilibrium micelle aggregation number n_{e}. For the association-dissociation mechanism, $\alpha = n_{\mathrm{t}}/n_{\mathrm{e}} - 1$, where n_{t} is the aggregation number of the transition state for stepwise association or dissociation, for which $n_{\mathrm{t}} < n_{\mathrm{e}}$. For the fission-fusion mechanism, $\alpha = n_{\mathrm{f}}/n_{\mathrm{e}} - 1$, where n_{f} is the average aggregation number of rare micelles that undergo spontaneous fission, for which $n_{\mathrm{f}} > n_{\mathrm{e}}$.

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APPENDIX A: TIME DEPENDENCE OF THE VARIANCE

In this Appendix, we analyze the rate of change $d\sigma^2_{\mathrm{m}}(t)/dt$ of the variance of the micelle aggregation number. To begin, we introduce the notation

$$c^{(k)}_{\mathrm{m}} \equiv \sum_{n=b}^{\infty} c_n n^k \tag{A1}$$

for integer k, such that $c^{(0)}_{\mathrm{m}} = c_{\mathrm{m}}$, $c^{(1)}_{\mathrm{m}} = \rho_{\mathrm{m}}$, and

$$c^{(2)}_{\mathrm{m}} = \left(q^2 + \sigma^2_{\mathrm{m}}\right)c_{\mathrm{m}}. \tag{A2}$$

The desired derivative of $\sigma^2_{\mathrm{m}} = (c^{(2)}_{\mathrm{m}}/c_{\mathrm{m}}) - q^2$ is thus

$$\begin{aligned}\frac{d\sigma^2_{\mathrm{m}}(t)}{dt} &= \frac{d}{dt}\left(\frac{c^{(2)}_{\mathrm{m}}}{c_{\mathrm{m}}} - q^2\right)\\ &= \frac{1}{c_{\mathrm{m}}}\frac{dc^{(2)}_{\mathrm{m}}}{dt} - \frac{q^2 + \sigma^2_{\mathrm{m}}}{c_{\mathrm{m}}}\frac{dc_{\mathrm{m}}}{dt} - 2q\frac{dq}{dt}.\end{aligned} \tag{A3}$$

The derivative $dc^{(2)}_{\mathrm{m}}/dt$ is given by

$$\begin{aligned}\frac{dc^{(2)}_{\mathrm{m}}}{dt} &= \sum_{n=b}^{\infty}\frac{dc_n}{dt}n^2 = \sum_{n=b}^{\infty}(I_{n-1} - I_n)n^2\\ &= I_{b-1}b^2 + \sum_{n=b}^{\infty}[(n+1)^2 - n^2]I_n\\ &= I_{b-1}b^2 + \sum_{n=b}^{\infty}(2n+1)I_n,\end{aligned} \tag{A4}$$

where the second line is obtained from the first by applying a summation by parts. Upon substituting Eq. (A4) for $dc^{(2)}_{\mathrm{m}}/dt$, Eq. (43) for dc_{m}/dt, and Eq. (45) for dq/dt into Eq. (A3), we obtain

$$\frac{d\sigma^2_{\mathrm{m}}(t)}{dt} = 2A + B + C, \tag{A5}$$

where

$$A = \frac{1}{c_{\mathrm{m}}}\sum_{n=b}^{\infty}(n-q)I_n, \tag{A6}$$

$$B = \frac{1}{c_{\mathrm{m}}}\sum_{n=b}^{\infty}I_n, \tag{A7}$$

$$C = \frac{1}{c_{\mathrm{m}}}\left[(q-b)^2 - \sigma^2_{\mathrm{m}}\right]I_{b-1}. \tag{A8}$$

Note that B is equivalent to the r.h.s. of Eq. (52) for dq/dt during a fast process and can thus be approximated by using the results of our analysis of this quantity.

By using Eq. (40) for I_n, we may express A as a sum

$$A = A_U + A_D, \tag{A9}$$

$$A_U = \frac{1}{c_{\mathrm{m}}}\sum_{n=b}^{\infty}c_n(n-q)U_n, \tag{A10}$$

$$A_D = \frac{-1}{c_{\mathrm{m}}}\sum_{n=b}^{\infty}(n-q)k_n(c_{n+1} - c_n)\ , \tag{A11}$$

in which

$$U_n \equiv k_n(e^{-\beta\Delta W_n} - 1). \tag{A12}$$

Here A_U is a contribution to A arising from the drift velocity U_n, while A_D is a contribution arising from a diffusive flux.

Using summation by parts to evaluate A_D yields

$$A_D = \frac{1}{c_{\mathrm{m}}}\sum_{n=b}^{\infty}k_{n-1}c_n + A_S = \langle k_{n-1}\rangle_{\mathrm{m}} + A_S, \tag{A13}$$

where A_S is a boundary term given by

$$A_S \equiv \frac{c_b}{c_{\mathrm{m}}}k_{b-1}(b-1-q). \tag{A14}$$

We then obtain

$$A_D \simeq k(q) - k' + A_S \tag{A15}$$

by approximating k_n as a linear function of n within the average $\langle k_{n-1}\rangle_n$.

To evaluate A_U, we first express it as an average

$$A_U = \langle (n-q)U\rangle_{\mathrm{m}}. \tag{A16}$$

Approximating U_n by a Taylor expansion to linear order about $n = q$ then yields

$$A_U \simeq U'(q)\sigma_{\mathrm{m}}^2. \tag{A17}$$

Evaluating the derivative $U'(q)$ and neglecting subdominant terms then yields

$$A_U \simeq [-k\beta W'' e^{-\beta W'} + k'(e^{-\beta W'} - 1)]\sigma_{\mathrm{m}}^2, \tag{A18}$$

where all functions of n on the r.h.s. are evaluated at $n = q$, and where we have neglected higher order terms of order $k'(\beta W'')$ and $k(\beta W'')^2$.

The final result for $d\sigma_{\mathrm{m}}^2(t)/dt$ given in Eq. (67) is obtained by substituting Eq. (A15) A_D and Eq. (A18) for A_U into Eq. (A11), using Eq. (66) to approximate $B \simeq dq/dt$, ignoring the boundary terms C and A_S that are proportional to I_{b-1} or c_b, and keeping only the dominant contributions in the resulting sum, ignoring terms that are higher order in k'/k and $\beta W''$.

APPENDIX B: LINEAR DYNAMICS OF FAST PROCESSES

This Appendix presents some details of the derivation of linearized models for the fast process. We consider small deviations from a final equilibrium state with a unimer concentration $\bar{c}_1$. In this context, symbols with overbars denote values obtained in this equilibrium state, such as $\bar{n}_{\mathrm{e}} \equiv n_{\mathrm{e}}(\bar{c}_1)$. Symbols preceded by a "δ" denote deviations from equilibrium values, so that $\delta c_1 \equiv c_1 - \bar{c}_1$, $\delta q \equiv q - q^*(\bar{c}_1)$, and $\delta n_{\mathrm{e}} \equiv n_{\mathrm{e}}(c_1) - n_{\mathrm{e}}(\bar{c}_1)$.

To describe small perturbations, it is sufficient to consider a model for $W(n, c_1)$ as a quadratic function

$$W(n, c_1) \simeq W_e(c_1) + \tfrac{1}{2}W''[n - n_{\mathrm{e}}(c_1)]^2, \tag{B1}$$

in which $W_e(c_1) = W(n_{\mathrm{e}}(c_1), c_1)$ is the local minimum value of $W(n, c_1)$, and in which W'' is a constant coefficient. This model yields a Gaussian equilibrium distribution for which $q^*(c_1) = n_{\mathrm{e}}(c_1)$ and $(\sigma_{\mathrm{m}}^*)^2 = k_BT/W''$.

The deviations δq and δq^* are both related to δc_1, and thus to each other. Conservation of total monomer concentration $\rho = c_1 + c_{\mathrm{m}}q$ in a system with constant c_{m} implies that

$$\delta c_1 = -c_{\mathrm{m}}\delta q. \tag{B2}$$

Linearization of the partial equilibrium condition, using Eq. (25) for $dq^*(c_1)/dc_1$, yields

$$\delta q^* \simeq \frac{(\sigma_{\mathrm{m}}^*)^2}{\bar{c}_1}\delta c_1 \tag{B3}$$

to first order in deviations. Substituting Eq. (B2) for δc_1 into Eq. (B3), we find that

$$\delta q^* = -\frac{c_{\mathrm{m}}\sigma_{\mathrm{m}}^2}{\bar{c}_1}\delta q = -\kappa_{\mathrm{p}}\delta q, \tag{B4}$$

where $\kappa_{\mathrm{p}} \equiv c_{\mathrm{m}}(\sigma_{\mathrm{m}}^*)^2/\bar{c}_1$.

Linearization of the simplified form for dq/dt given in Eq. (66) yields the linear ODE

$$\frac{d(\delta q)}{dt} \simeq -\frac{1}{\tau_\sigma}(\delta q - \delta q^*(c_1)), \tag{B5}$$

where τ_σ is defined by Eq. (68). Using Eq. (B4) for δq^* then yields Eq. (69).

Linearization of the coupled equations defined by Eqs. (65) and Eq. (67), in which we again use Eq. (B4) for δq^*, yields Eqs. (71) and (72).

APPENDIX C: CONTINUUM DIFFUSION MODEL

In this Appendix, we consider predictions for the fast process of a continuum model in which n is treated from the outset as a continuum variable, and in which the cluster number concentration $c(n, t)$ is governed by Eqs. (47) and Eq. (48). Let $c_{\mathrm{m}}^{(p)}$ denote an integral

$$c_{\mathrm{m}}^{(p)} \equiv \int_b^\infty dn\, c(n, t)n^p \tag{C1}$$

for integer p. Let $c_{\mathrm{m}} = c_{\mathrm{m}}^{(0)}$ and $\rho_{\mathrm{m}} = c_{\mathrm{m}}^{(1)}$. Let $\langle B\rangle_{\mathrm{m}}$ denote the number average of a micelle property $B(n)$, as defined by an integral

$$\langle B\rangle \equiv \frac{1}{c_{\mathrm{m}}}\int_b^\infty dn\, B(n)c(n). \tag{C2}$$

Let $q = \langle n\rangle_{\mathrm{m}} = \rho_{\mathrm{m}}/c_{\mathrm{m}}$ and $\sigma_{\mathrm{m}}^2 = \langle n^2\rangle_{\mathrm{m}} - q^2$. Throughout this Appendix, we use a continuous notation for functions of n, in which $W(n, c_1) = W_n(c_1)$ and $k(n) = k_n^-$. Symbols with primes denote derivatives or partial derivatives with respect to n, such as $W' = \partial W(n, c_1)/\partial n$.

Using Eq. (47) for $\partial c(n, t)/\partial t$ and Eq. (47) for $I(n, t)$, we find that

$$\frac{dc_{\mathrm{m}}^{(p)}}{dt} \equiv -\int_b^\infty dn\, n^p\frac{\partial I(n, t)}{\partial n}. \tag{C3}$$

Using integration by parts to evaluate the above integral yields

$$\frac{dc_{\mathrm{m}}}{dt} \equiv I(b, t) \tag{C4}$$

for $p = 0$ and

$$\frac{dc_{\mathrm{m}}^{(p)}}{dt} \equiv \int_b^\infty dn\, pn^{p-1}I(n, t) + b^pI(b, t) \tag{C5}$$

for all $p \geqslant 1$.

1. Evolution of $q(t)$

Using the above relations for $d\rho_{\mathrm{m}}/dt$ and dc_{m}/dt, it is straightforward to show that

$$\begin{aligned}\frac{dq(t)}{dt} &= \frac{d}{dt}\left(\frac{\rho_{\mathrm{m}}}{c_{\mathrm{m}}}\right) = \frac{1}{c_{\mathrm{m}}}\frac{d\rho_{\mathrm{m}}}{dt} - \frac{q}{c_{\mathrm{m}}}\frac{dc_{\mathrm{m}}}{dt} \\ &= \frac{1}{c_{\mathrm{m}}}\int_b^\infty dn\, I(n, t) + \frac{1}{c_{\mathrm{m}}}(b - q)I(b, t).\end{aligned} \tag{C6}$$

Using Eq. (48) for I and applying integration by parts to the term arising from the diffusive flux then yields

$$\frac{dq}{dt} \equiv \langle V\rangle_{\mathrm{m}} + \frac{1}{c_{\mathrm{m}}}(b - q)I(b, t), \tag{C7}$$

in which

$$V = -k\beta W' + k' \tag{C8}$$

is the continuum expression for the aggregation number velocity.

To describe a fast process, we may drop the term proportional to $I(b, t)$ in Eq. (C7) to obtain $dq/dt \simeq \langle V\rangle_{\rm m}$. To obtain an explicit approximation for $\langle V\rangle_{\rm m}$, we introduce approximations of W, k, and V as Taylor expansions about their values at $n = q$. Expanding $V(n)$ to quadratic order yields

$$\frac{dq}{dt} \simeq V(q) + \frac{1}{2}V''(q)\sigma_{\rm m}^2, \tag{C9}$$

exactly as in Eq. (64). The term proportional to $V''(n)$ is evaluated by treating W as a locally quadratic function and k as locally linear, and thus neglecting terms proportional to W''' and k'', to obtain $V'' = -2k'\beta W''$. Equation (74) is then obtained by substituting expressions for $V(q)$ and $V''(q)$.

2. Evolution of $\sigma_{\rm m}^2(t)$

To compute $d\sigma_{\rm m}^2/dt$, we use Eqs. (C4) and (C5) for the derivatives of $c_{\rm m}$, $\rho_{\rm m}$ and $c_{\rm m}^{(2)}$ in Eq. (A3) for $d\sigma_{\rm m}^2/dt$. This yields

$$\frac{d\sigma_{\rm m}^2}{dt} = 2A + C, \tag{C10}$$

where

$$\begin{aligned} A &= \frac{1}{c_{\rm m}}\int_b^\infty dn\,(n-q)I(n,t), \\ C &= \frac{1}{c_{\rm m}}\big[(b-q)^2 + \sigma_{\rm m}^2\big]I(b,t). \end{aligned} \tag{C11}$$

By using Eq. (48) for I, we may express A_D as a sum

$$A = A_U + A_D, \tag{C12}$$

$$A_U = \langle (n-q)U\rangle_{\rm m}, \tag{C13}$$

$$A_D = \frac{-1}{c_{\rm m}}\int_b^\infty dn\,(n-q)k(n)\frac{\partial c_{\rm m}(n,t)}{\partial n}, \tag{C14}$$

in which

$$U(n,t) \equiv -k\beta W' \tag{C15}$$

is the continuum analog of the drift velocity $U_n(t)$ defined in Eq. (A12). Integrating by parts to evaluate A_D yields

$$A_D = \langle k\rangle_{\rm m} + A_S, \tag{C16}$$

where $A_S = c(b,t)k(b)[b - q(t)]/c_{\rm m}$.

To describe fast processes, we may drop the boundary terms C and A_S that are proportional to $I(b,t)$ and $c(b,t)$, and then introduce Taylor expansions of $U(n,t)$ and $k(n)$ about q to approximate the remaining average values. Expanding $U(n,t)$ to either first or second order yields

$$\begin{aligned} A_U &\simeq U'(q)\sigma_{\rm m}^2 \\ &\simeq -[k\beta W'' + k'W']_{n=q(t)}\sigma_{\rm m}^2. \end{aligned} \tag{C17}$$

Expanding $k(n)$ to linear order then yields $A_D \simeq \langle k\rangle_{\rm m} \simeq k(q)$. Equation (75) is then obtained by combining results for A_U and A_D.

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