Nonlinear dynamics in micellar surfactant solutions. II. Diffusion

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We discuss diffusion in micellar surfactant solutions in a form appropriate for analyzing experiments that involve large deviations from equilibrium. A general nonlinear dynamical model for inhomogeneous systems is developed that describes the effects of diffusion and micelle kinetics as a set of coupled partial differential equations for unimer concentration, micelle number concentration, average micelle aggregation number, and, optionally, the variance of the micelle aggregation number. More specialized models are developed to describe slow dynamics in situations in which the system stays in a state of partial local equilibrium or full local equilibrium. As an illustrative example of a nonlinear transport phenomenon, we discuss a simple model of diffusion from an initially homogeneous micellar solution to a rapidly created absorbing interface with fast unimer adsorption.

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I. INTRODUCTION

This is the second of two papers that present a discussion of dynamics in micelle-forming surfactant in a form that allows analysis of large deviations from equilibrium. The first article [1], hereafter referred to as "article I," discusses reaction kinetics and dynamical phenomena in spatially homogeneous solutions. The present article instead discusses the additional effects of diffusion in inhomogeneous systems. The first several sections after this introduction present a very general nonlinear model of dynamics in inhomogeneous systems, and reduced models to describe situations in which the system has reached partial or full equilibrium. The penultimate section presents a qualitative discussion of a simplified model of interfacial adsorption that exhibits several nonlinear phenomena characteristic of experiments involving transport from a micellar solution to a rapidly generated interface.

Several authors have previously constructed linearized models of surfactant transport in weakly inhomogeneous micellar solutions, using a variety of simplifying assumptions [2–11]. Such models allow analysis of linear tensiometry experiments that measure changes in interfacial tension caused by small amplitude step or oscillatory changes in interfacial area. In early work, Lucassen [2] introduced and solved a simple model that describes the solution as a binary mixture of unimers and monodisperse micelles, while treating micelle dissociation and association as pseudo-elementary reactions. Subsequently, Noskov [4–7] and Dushkin *et al.* [8,9] independently constructed closely related linear models that are based on the stepwise reaction model, and that reduce to the kinetic theory of Aniansson and Wall when applied to homogeneous systems.

The nonlinear analysis of diffusion presented here was motivated primarily by the authors' interest in processes that involve surfactant diffusion to an initially bare or rapidly expanded interface. During early stages of such a process, rapid adsorption of unimers tends to strongly suppress the unimer concentration near the interface. If the subsurface unimer concentration remains suppressed below the CMC long enough for micelles to dissolve, this can lead to formation of a micelle-free region near the interface. Several authors have discussed the resulting appearance and growth of micelle-free regions during interfacial adsorption within the context of a relatively simple "two-zone" model [12–17]. The two-zone model assumes the existence of a micelle-free region near the interface that is separated by a moving boundary from a region in which micelles are still present. All of the variants of this model discussed in previous work have assumed for simplicity that micelle creation and destruction is rapid enough to maintain full local reaction equilibrium between unimer and micelle species. In Sec. V we discuss the formation and evolution of micelle-free zones during interfacial adsorption within the context of a more general nonlinear transport theory that allows for effects of limitations on the rate of micelle destruction.

The contents of the remainder of this article are as follows: Sec. II presents a general analysis of diffusion in polydisperse micellar solutions governed by stepwise reaction kinetics. This analysis yields an approximate reduced model that can be formulated as a set of partial differential equations for the unimer concentration c_1, micelle number concentration c_m, average aggregation number q, and (optionally) the variance σ_m^2 of the micelle aggregation number. Section III presents a nonlinear model for slow dynamics systems that have reached a state of partial local equilibrium, in which q has reached local equilibrium with c_1, but in which c_m and c_1 have not yet reached local reaction equilibrium. This analysis is shown to recover the corresponding linear transport model

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of Dushkin *et al.* [8,9] when applied to weakly perturbed systems. Section IV presents a further simplified model to describe inhomogeneous systems that have reached full local equilibrium, in which both c_m and q have reached equilibrium with the local unimer concentration c_1. Section V presents a qualitative discussion of the dynamics of systems that contain a micelle-free region and a micellar region separated by a moving boundary, using a simple model of diffusion to an absorbing boundary as an example. Section VI summarizes our conclusions.

Throughout this article, equations in article I are referenced by equation number preceded by "I.," so that, e.g., Eq. (I.32) denotes Eq. (32) of article I.

II. DIFFUSION

We consider diffusion in inhomogeneous micellar solutions. For simplicity, we assume the validity of a stepwise reaction model. Let $c_n(\mathbf{r},t)$ denote the concentration of n-mers at position $\mathbf{r}$ and time t. The evolution of $c_n(\mathbf{r},t)$ by diffusion and reaction in a stationary fluid is governed for each $n \geqslant 1$ by a reaction-diffusion equation

$$\frac{\partial c_n}{\partial t} = D_n \nabla^2 c_n + G_n, \tag{1}$$

in which D_n is the diffusivity of n-mers and G_n is the local rate of generation of n-mers by stepwise reactions. Explicit expressions for G_n are given in Eq. (I.33) for $n > 1$ and in Eq. (I.34) for $n = 1$.

To simplify our notation, we only explicitly consider diffusion in a stationary fluid. Corresponding equations for situations involving advection of surfactant by an known solvent velocity field $\mathbf{v}(\mathbf{r},t)$ can, however, be obtained by simply replacing partial derivatives with respect to time by corresponding material derivatives, by making the substitution

$$\frac{\partial}{\partial t} \to \frac{\partial}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla} \tag{2}$$

throughout the analysis.

A. Micelle statistical properties

Consider the time derivatives of the micelle number concentration $c_m(\mathbf{r},t)$ defined in Eq. (I.16) and the micellar surfactant concentration $\rho_m(\mathbf{r},t)$ defined in Eq. (I.17). Exact expressions for partial derivatives of these quantities with respect to time may be computed by combining the definitions of these quantities as summations over species concentrations, as given in Eqs. (I.16) and (I.17), with the transport equation for each species, Eq. (1). Using Eq. (I.33) for G_n, for $n \geqslant b$, we obtain

$$\frac{\partial c_m}{\partial t} = \nabla^2 \sum_{n=b}^{\infty} D_n c_n + \sum_{n=b}^{\infty} (I_{n-1} - I_n), \tag{3}$$

$$\frac{\partial \rho_m}{\partial t} = \nabla^2 \sum_{n=b}^{\infty} D_n n c_n + \sum_{n=b}^{\infty} n(I_{n-1} - I_n). \tag{4}$$

The diffusive terms in Eqs. (3) and (4) may be written more compactly by defining a power-law averaged micelle diffusivity $D_m^{(k)}$ for arbitrary non-negative integer k as a ratio

$$D_m^{(k)} \equiv \frac{\sum_{n=b}^{\infty} D_n n^k c_n}{\sum_{n=b}^{\infty} n^k c_n}. \tag{5}$$

The quantity $D_m^{(0)} = \langle D_n \rangle_m$ is the number averaged micelle diffusivity, while $D_m^{(1)}$ is a "mass" averaged diffusivity. By using these definitions and repeating the summations by parts used in article I to simplify the remaining sums in Eqs. (3) and (4), we obtain

$$\frac{\partial c_m}{\partial t} = \nabla^2 \left(D_m^{(0)} c_m\right) + \left(\frac{dc_m}{dt}\right)_{rxn}, \tag{6}$$

$$\frac{\partial \rho_m}{\partial t} = \nabla^2 \left(D_m^{(1)} \rho_m\right) + \left(\frac{d\rho_m}{dt}\right)_{rxn}, \tag{7}$$

in which we have introduced the symbols

$$\left(\frac{dc_m}{dt}\right)_{rxn} \equiv I_{b-1}, \tag{8}$$

$$\left(\frac{d\rho_m}{dt}\right)_{rxn} \equiv \sum_{n=b}^{\infty} I_n + I_{b-1} b \tag{9}$$

to denote the contributions to $\partial c_m/\partial t$ and $\partial \rho_m/\partial t$ that arise directly from stepwise reactions, rather than diffusion. These reactive contributions are identical to the expressions given in Eqs. (I.43) and (I.44) for dc_m/dt and $d\rho_m/dt$ in homogeneous systems.

The quantities c_m and ρ_m are the zeroth and first moments of the micelle number concentration c_n. A general expression for the time derivative of the kth moment is given in the Appendix for arbitrary integer k. The expression for the second moment ($k = 2$) is used to compute the time derivative of the variance σ_m^2. The resulting general expressions for derivatives of the zeroth, first, and second moments, given here in Eqs. (6), (7), and (A3), have all been given previously by Danov *et al.* [10,11]. Because Danov *et al.* considered a model in which D_n was assumed to be independent of n within the micellar range, however, they did not distinguish among $D_m^{(0)}$, $D_m^{(1)}$, and $D_m^{(2)}$.

Expressions for time derivatives of c_m and ρ_m may be combined to obtain a corresponding time derivative of $q = \rho_m/c_m$. A straightforward calculation yields

$$\frac{\partial q}{\partial t} = D_m^{(1)} \nabla^2 q + \frac{2}{c_m} \boldsymbol{\nabla} q \cdot \boldsymbol{\nabla}\left(D_m^{(1)} c_m\right) + \left(\frac{dq}{dt}\right)_{rxn} + \frac{q}{c_m} \nabla^2 \left[\left(D_m^{(1)} - D_m^{(0)}\right) c_m\right], \tag{10}$$

in which we have introduced the notation

$$\left(\frac{dq}{dt}\right)_{rxn} \equiv \frac{1}{c_m}\left[\left(\frac{d\rho_m}{dt}\right)_{rxn} - q\left(\frac{dc_m}{dt}\right)_{rxn}\right] = \frac{1}{c_m}\left[\sum_{n=b}^{\infty} I_n + I_{b-1}(b-q)\right] \tag{11}$$

for the contribution to $\partial q/\partial t$ that arises directly from stepwise reactions. The second line of Eq. (11) is identical to the expression given in Eq. (I.45) for dq/dt in a homogeneous solution. The contribution to Eq. (10) that contains a factor

of the difference $D_{\rm m}^{(1)} - D_{\rm m}^{(0)}$ is generally small and will be neglected in subsequent discussion.

An analogous calculation of the derivative $\partial\sigma_{\rm m}^2/\partial t$ is given in the Appendix, where we obtain

$$\frac{\partial\sigma_{\rm m}^2}{\partial t} \equiv D_{\rm m}^{(2)}\nabla^2\sigma_{\rm m}^2 + \frac{2}{c_{\rm m}}\boldsymbol{\nabla}\big(D_{\rm m}^{(2)}c_{\rm m}\big)\cdot\boldsymbol{\nabla}\sigma_{\rm m}^2 + \frac{\sigma_{\rm m}^2}{c_{\rm m}}\nabla^2\big[\big(D_{\rm m}^{(2)} - D_{\rm m}^{(0)}\big)c_{\rm m}\big] + \left(\frac{d\sigma_{\rm m}^2}{dt}\right)_{\rm rxn}, \quad (12)$$

in which

$$\left(\frac{d\sigma_{\rm m}^2}{dt}\right)_{\rm rxn} = \frac{1}{c_{\rm m}}\sum_{n=b}^{\infty}(2n+1-2q)I_n + \frac{1}{c_{\rm m}}\big[(q-b)^2 - \sigma_{\rm m}^2\big]I_{b-1}. \quad (13)$$

The above expression for $(d\sigma_{\rm m}^2/dt)_{\rm rxn}$ is identical to the expression given in Eq. (I.46) for $d\sigma_{\rm m}^2/dt$ in a homogeneous solution.

The diffusive term in Eq. (7) for $\partial\rho_{\rm m}/\partial t$ can be expressed as a divergence $-\boldsymbol{\nabla}\cdot\mathbf{J}_{\rm m}$, in which

$$\mathbf{J}_{\rm m} \equiv -\boldsymbol{\nabla}\left(\sum_{n=b}^{\infty}D_n n c_n\right) = -\boldsymbol{\nabla}\big(D_{\rm m}^{(1)}\rho_{\rm m}\big) \quad (14)$$

is the flux of surfactant arising from micelle diffusion. Using the fact that $\rho_{\rm m} = c_{\rm m}q$, the micellar flux $\mathbf{J}_{\rm m}$ may also be expressed as a sum

$$\mathbf{J}_{\rm m} = -D_{\rm m}^{(1)}(q\boldsymbol{\nabla}c_{\rm m} + c_{\rm m}\boldsymbol{\nabla}q) - \rho_{\rm m}\boldsymbol{\nabla}D_{\rm m}^{(1)}. \quad (15)$$

The existence of a term proportional to $\boldsymbol{\nabla}q$ in Eq. (15) makes it clear that surfactant flux can arise from a gradient in q, as well as from a gradient in number concentration $c_{\rm m}$. To see why, consider a hypothetical situation with an inhomogeneous field $q(\mathbf{r},t)$ but homogeneous number concentration $c_{\rm m}$. In this case, inhomogeneity in q causes a corresponding inhomogeneity in $\rho_{\rm m} = c_{\rm m}q$. For simplicity, consider the case in which the cluster diffusivity D_n is independent of n, for which $\boldsymbol{\nabla}D_{\rm m}^{(1)} = 0$. In such a system, $c_{\rm m}$ would remain homogeneous, but interdiffusion of large and small micelles would tend to homogenize $q(\mathbf{r},t)$. In the case of homogeneous $c_{\rm m}$, this would also homogenize $\rho_{\rm m}(\mathbf{r},t) = c_{\rm m}q(\mathbf{r},t)$, implying the existence of a diffusive mass flux. The resulting flux for a system with $\boldsymbol{\nabla}c_{\rm m} = \boldsymbol{\nabla}D_{\rm m}^{(1)} = 0$ is given by Eq. (15) as $\mathbf{J}_{\rm m} = -D_{\rm m}^{(1)}c_{\rm m}\boldsymbol{\nabla}q$. This flux arising from mixing of micelles of different aggregation number is also the origin of the diffusive term $D_{\rm m}\nabla^2 q$ in Eq. (10) for $\partial q/\partial t$.

B. Reduced model

A slightly simplified model for the evolution of c_1, $c_{\rm m}$, and $\rho_{\rm m}$ may be obtained by introducing the following physically motivated approximations:

(1) We assume the existence of a bimodal aggregate size distribution in which ρ is dominated by contributions of unimers and proper micelles, with negligible concentrations for $n \in [2, b-1]$, so that $\rho = c_1 + c_{\rm m}q$.

(2) We assume that $D_{\rm m}^{(0)} \simeq D_{\rm m}^{(1)} \simeq D_{\rm m}^{(2)}$ as a result of the existence of a rather weak dependence of D_n on n within the width of the micelle peak. We thus use the symbol $D_{\rm m}$ to refer to any of $D_{\rm m}^{(0)}$, $D_{\rm m}^{(1)}$, or $D_{\rm m}^{(2)}$, interchangeably.

(3) We approximate $D_{\rm m}(\mathbf{r},t)$ as a function of the local average aggregation number,

$$D_{\rm m}(\mathbf{r},t) = D(q(\mathbf{r},t)), \quad (16)$$

where $D(q(\mathbf{r},t))$ denotes the value of micelle diffusivity D_n at the average aggregation number $n = q(\mathbf{r},t)$.

With these assumptions, we obtain the simplified transport equations

$$\frac{\partial c_{\rm m}}{\partial t} = \nabla^2(D_{\rm m}c_{\rm m}) + \left(\frac{dc_{\rm m}}{dt}\right)_{\rm rxn}, \quad (17)$$

$$\frac{\partial\rho_{\rm m}}{\partial t} = \nabla^2(D_{\rm m}\rho_{\rm m}) + c_{\rm m}\left(\frac{dq}{dt}\right)_{\rm rxn} + q\left(\frac{dc_{\rm m}}{dt}\right)_{\rm rxn}, \quad (18)$$

$$\frac{\partial c_1}{\partial t} = D_1\nabla^2 c_1 - c_{\rm m}\left(\frac{dq}{dt}\right)_{\rm rxn} - q\left(\frac{dc_{\rm m}}{dt}\right)_{\rm rxn}. \quad (19)$$

The corresponding auxiliary equations for $\partial q/\partial t$ and $\partial\sigma_{\rm m}^2/\partial t$ are given by

$$\frac{\partial q}{\partial t} = D_{\rm m}\nabla^2 q + \frac{2}{c_{\rm m}}\boldsymbol{\nabla}(D_{\rm m}c_{\rm m})\cdot\boldsymbol{\nabla}q + \left(\frac{dq}{dt}\right)_{\rm rxn}, \quad (20)$$

$$\frac{\partial\sigma_{\rm m}^2}{\partial t} = D_{\rm m}\nabla^2\sigma_{\rm m}^2 + \frac{2}{c_{\rm m}}\boldsymbol{\nabla}(D_{\rm m}c_{\rm m})\cdot\boldsymbol{\nabla}\sigma_{\rm m}^2 + \left(\frac{d\sigma_{\rm m}^2}{dt}\right)_{\rm rxn}. \quad (21)$$

Equations (20) and (21) can be obtained from Eqs. (10) and (12), respectively, simply by neglecting the differences between $D_{\rm m}^{(2)}$, $D_{\rm m}^{(1)}$, and $D_{\rm m}^{(0)}$, and denoting all of these quantities interchangeably by $D_{\rm m}$.

It is straightforward to confirm, by adding Eqs. (18) and (19), that this model yields a total surfactant concentration $\rho = c_1 + \rho_{\rm m}$ that satisfies a diffusion equation

$$\frac{\partial\rho}{\partial t} = -\boldsymbol{\nabla}\cdot\mathbf{J} \quad (22)$$

with a total surfactant flux

$$\mathbf{J} = -D_1\boldsymbol{\nabla}c_1 - \boldsymbol{\nabla}(D_{\rm m}\rho_{\rm m}) \quad (23)$$

given by the sum of unimer and micellar flux contributions.

To obtain a complete dynamical model, we must supplement Eqs. (17)–(21) by approximate expressions developed in article I for the reactive contributions $(dc_{\rm m}/dt)_{\rm rxn}$, $(dq/dt)_{\rm rxn}$, and (optionally) $(d\sigma_{\rm m}^2/dt)_{\rm rxn}$. We are in a position to construct either of two types of model. The more complex option, which we will refer to as model A, can be expressed using $c_1(\mathbf{r},t)$, $c_{\rm m}(\mathbf{r},t)$, $q(\mathbf{r},t)$ and $\sigma_{\rm m}^2(\mathbf{r},t)$ as primary variables. The simpler option, which we will refer to as model B, uses $c_1(\mathbf{r},t)$, $c_{\rm m}(\mathbf{r},t)$, and $q(\mathbf{r},t)$ as primary variables, but does not keep track of the variance $\sigma_{\rm m}^2(\mathbf{r},t)$.

Models A and B require the use of different expressions for the evolution of variables q and $\sigma_{\rm m}^2$ that change during fast processes. In model A, $(dq/dt)_{\rm rxn}$ may be approximated by Eq. (I.65), which gives an expression that depends on $\sigma_{\rm m}^2$, q and c_1, while $(d\sigma_{\rm m}^2/dt)_{\rm rxn}$ is approximated by Eq. (I.67). In model B, $(dq/dt)_{\rm rxn}$ may be approximated by Eq. (I.66), which gives an expression that depends only on q and c_1.

The choice of an approximation for the rate $(dc_m/dt)_{rxn}$ of the slow process involves the same considerations in either model. In situations involving modest deviations from a micellar equilibrium state, for which $c_1 > c_d$ and $q > n_t$ throughout the region of interest, the net rate of micelle creation $(dc_m/dt)_{rxn}$ may be approximated by Eq. (I.93). To describe more general situations, we must use an approximation for $(dc_m/dt)_{rxn}$ of the type given in Eq. (I.132), which allows for micelle destruction either by activated processes or by shrinkage of q to nearly zero.

In Secs. III and IV, we use the general model discussed above as a starting point for the development of more specialized models of slow dynamics in regions that are assumed to have reached either partial or full local equilibrium. Both of these simplifying assumptions allow us to avoid some of the conceptual difficulties encountered when we attempt to construct a generally valid approximation for $(dc_m/dt)_{rxn}$. In the discussion of partial local equilibrium states, no expression is needed for $(dq/dt)_{rxn}$ because $q(\mathbf{r}, t)$ is determined by a partial equilibrium condition, while Eq. (I.93) may safely be used for $(dc_m/dt)_{rxn}$ because the definition of partial equilibrium requires that $c_1 > c_d$ and $q \simeq n_e(c_1) > n_t(c_1)$ throughout the region of interest. In the discussion of full local equilibrium states, no expression is needed for either $(dq/dt)_{rxn}$ or $(dc_m/dt)_{rxn}$, because in this limit dynamics is entirely controlled by diffusion rather than by reaction rate limitations.

III. PARTIAL LOCAL EQUILIBRIUM

In a system that is in partial local equilibrium, the average micelle aggregation number q at each point in space remains equal to the equilibrium value $q^*(c_1)$ corresponding to the local unimer concentration c_1, but the number concentration c_m of micelles is generally not equal to the corresponding local equilibrium value $c_m^*(c_1)$. Partial equilibrium can be reached only in regions of stable or metastable micelles where $c_1(\mathrm{r}, t) > c_d$ and where $q(\mathbf{r}, t)$ is greater than the local transition state value $n_t(c_1(\mathbf{r}, t))$. Imposing a constraint of partial local equilibrium on the reduced model yields a model in which the only independent dynamical variables are the fields $c_1(\mathbf{r}, t)$ and $c_m(\mathbf{r}, t)$, with a finite rate for the slow process, but an effectively infinite rate for the fast process.

A. Nonlinear model

The total surfactant concentration in the partial equilibrium state is given by a sum $\rho = c_1 + c_m q^*(c_1)$. The partial derivative of $\rho(\mathbf{r}, t)$ with respect to time thus obeys

$$\frac{\partial \rho}{\partial t} = \frac{\partial (c_1 + q^* c_m)}{\partial t} = (1 + \kappa_p)\frac{\partial c_1}{\partial t} + q^* \frac{\partial c_m}{\partial t}, \tag{24}$$

in which we have used the relation $c_m(\partial q^*/\partial t) = \kappa_p(\partial c_1/\partial t)$, where $\kappa_p = c_m dq^*(c_1)/dc_1$ is defined in Eq. (I.27). The overall surfactant flux $\mathbf{J}$ defined in Eq. (23) for a system in partial equilibrium may be expressed in the same notation as a sum

$$\mathbf{J} = -D_1 \nabla c_1 - \nabla(D_m c_m q^*) = -(D_1 + D_m \kappa_p)\nabla c_1 - q^* \nabla(D_m c_m) \tag{25}$$

in which we have used the relation $c_m \nabla q^* = \kappa_p \nabla c_1$. A partial differential equation for c_1 can then be obtained by combining the balance equations for ρ_m and c_m. By using Eq. (24) in the left-hand side of surfactant balance Eq. (22), using Eq. (25) for $\mathbf{J}$ in the right-hand side, and using Eq. (17) for $\partial c_m/\partial t$, we find that

$$(1 + \kappa_p)\frac{\partial c_1}{\partial t} = \nabla \cdot [(D_1 + D_m \kappa_p)\nabla c_1] + \nabla q^* \cdot \nabla(D_m c_m) - q^* \left(\frac{dc_m}{dt}\right)_{rxn}, \tag{26}$$

in which $\nabla q^* = (\kappa_p/c_m)\nabla c_1$.

A complete nonlinear model for the evolution of c_1 and c_m for systems that remain in partial local equilibrium within some region of time and space is defined by Eq. (26) for $\partial c_1/\partial t$, Eq. (17) for $\partial c_m/\partial t$, and Eq. (I.93) for the rate $(dc_m/dt)_{rxn}$ of the slow reaction.

B. Linear model

In experiments that induce only small deviations from a homogeneous equilibrium, the intermediate and late stages of relaxation can be described by a linear model of a system that remains in partial local equilibrium. Specifically, such a model is sufficient to describe linear tensiometry experiments involving changes over times much greater than the fast relaxation time τ_1. The required linear model of slow processes model was developed independently but in slightly different forms by Noskov [4–7] and Dushkin *et al.* [8,9], as discussed below.

We consider small deviations from some homogeneous equilibrium state in which $c_1 > c_d$. Let δc_1, δc_m, and δq^* represent small deviations of c_1, c_m, and q^* from their values in this reference state. The corresponding deviation $\delta\rho = \delta c_1 + \delta(q^* c_m)$ in the total surfactant concentration can be expanded to linear order as $\delta\rho = \delta c_1 + c_m \delta q^* + q^* \delta c_m$. It is convenient to express this as a sum

$$\delta\rho = \psi_1 + \psi_m, \tag{27}$$

in which we have defined contributions

$$\psi_1 \equiv \delta c_1 + c_m \delta q^*, \tag{28}$$

$$\psi_m \equiv q \delta c_m \tag{29}$$

that are proportional to $\delta c_1(\mathbf{r}, t)$ and $\delta c_m(\mathbf{r}, t)$, respectively. By expanding δq^* to linear order in δc_1 as $\delta q^* = (\sigma_m^2/c_1)\delta c_1$, and using Eq. (I.27) for $\kappa_p = c_m \sigma_m^2/c_1$, we find that

$$\psi_1 = (1 + \kappa_p)\delta c_1, \tag{30}$$

where κ_p denotes a value evaluated in the final equilibrium state.

A pair of coupled linear PDEs for ψ_1 and ψ_m may be obtained by linearizing both Eq. (26) for $\partial c_1/\partial t$ and Eq. (17) for $\partial c_m/\partial t$ and then rewriting the results in terms of ψ_1 and ψ_m. For simplicity, we will follow previous work by both Noskov and Dushkin *et al.* by treating D_m as a constant in the linearized model, and thus dropping a contribution to the

linearized equation for $dc_m/\partial t$ that is proportional to ∇D_m. This yields the coupled PDEs

$$\frac{\partial \psi_1}{\partial t} = D_p \nabla^2 \psi_1 - q\left(\frac{dc_m}{dt}\right)_{rxn}, \tag{31}$$

$$\frac{\partial \psi_m}{\partial t} = D_m \nabla^2 \psi_m + q\left(\frac{dc_m}{dt}\right)_{rxn}, \tag{32}$$

in which

$$D_p \equiv \frac{D_1 + \kappa_p D_m}{1 + \kappa_p} \tag{33}$$

is an effective diffusivity for ψ_1, i.e., for the coupled evolution of c_1 and $q^*(c_1)$.

Equation (33) yields an expression for D_p that interpolates between D_1 and D_m with increasing concentration. Recall that $\kappa_p \sim \rho_m/c_1$ in typical systems with $\sigma_m^2 \sim q$, and that typical surfactant systems have $D_1/D_m \sim 10$. With these estimates, Eq. (33), implies that $D_p \simeq D_1$ at concentrations that exceed the CMC by less than approximately one order of magnitude, for which $\kappa_p < D_1/D_m$, while $D_p \sim D_m$ at higher concentration for which $\kappa_p > D_1/D_m$. In the high concentration limit, the dependence of $q(c_1)$ upon c_1 in partial equilibrium thus causes the diffusion of unimers to be controlled by the micelle diffusivity.

We next consider the micelle reaction rate $(dc_m/dt)_{rxn}$. Linearizing Eq. (I.93) for $(dc_m/dt)_{rxn}$ yields

$$\left(\frac{dc_m}{dt}\right)_{rxn} = -\frac{1}{\tau_d}(\delta c_m - \delta c_m^*) \tag{34}$$

in which $\delta c_m^* = (c_m q/c_1)\delta c_1$ and τ_d is the equilibrium micelle dissociation lifetime defined in Eq. (I.96). Rewriting the product $q(dc_m/dt)_{rxn}$ that appears in Eqs. (31) and (32) in terms of ψ_m and ψ_1 then yields

$$q\left(\frac{dc_m}{dt}\right)_{rxn} = -\frac{1}{\tau_d}(\psi_m - \alpha\psi_1), \tag{35}$$

in which we have introduced the symbol

$$\alpha \equiv \frac{c_m q^2}{c_1(1+\kappa_p)} = \frac{\kappa_e - \kappa_p}{1+\kappa_p}. \tag{36}$$

Substitution of Eq. (35) into Eqs. (31) and (32) yields a pair of coupled linear PDEs for ψ_1 and ψ_m.

Aside from differences in notation, Eqs. (31)–(36) are equivalent to the linear transport equations obtained by Dushkin *et al.* [8,9] to describe slow processes in which the system remains in partial equilibrium. They are also nearly equivalent to those obtained somewhat earlier by Noskov [4–7]. The only essential difference between the theories of slow processes presented by Noskov and by Dushkin *et al.* appears to be that Noskov incorrectly used the bare unimer diffusivity D_1 to describe the diffusion of the component proportional to δc_1 in the analog of Eq. (31), rather than the diffusivity D_p defined in Eq. (33), which was first identified by Dushkin *et al.* See, for example, Eq. (1.8) of Noskov's 1989 article [4] or Eqs. (75) and (76) of his 2002 review article [7]. This oversight appears to be a result of a failure to explicitly analyze the balance equation for total surfactant concentration $\rho(\mathbf{r}, t)$, rather than considering only $c_1(\mathbf{r}, t)$ and $c_m(\mathbf{r}, t)$, and a resulting failure to include the effect of surfactant flux that arise from gradients in average aggregation $q(\mathbf{r}, t)$.

C. Approach to full local equilibrium

Equation (35) implies that deviations from a reference equilibrium state of the form $\psi_m = \alpha\psi_1$ do not induce any net micelle creation. This occurs because $(dc_m/dt)_{rxn} = 0$ in any equilibrium state, and because a deviation of this form corresponds to an infinitesimal change from one equilibrium state to another, induced by an infinitesimal change in c_1. Equation (I.23) implies that the change δc_m^* in equilibrium micelle concentration induced by a change δc_1 in unimer concentration is given by $\delta c_m^* = (q c_m/c_1)\delta c_1$. The corresponding change in $\psi_m = q\delta c_m$ is thus $\psi_m = (q^2 c_m/c_1)\delta c_1$. Comparing this to the corresponding change in $\psi_1 = (1+\kappa_p)\delta c_1$, as given in Eq. (30), we find that $\psi_m = \alpha\psi_1$ for such a change in equilibrium state.

When applied to the relaxation of a homogeneous perturbation, this linear model reduces to the Aniansson-Wall linear theory of the slow process; this can be shown as follows. In a homogeneous system, Eqs. (31) and (32) reduce to a pair of linear ordinary differential equations that can be expressed in matrix form as

$$\frac{d}{dt}\begin{bmatrix}\psi_1 \\ \psi_m\end{bmatrix} = \frac{1}{\tau_d}\begin{bmatrix}-\alpha & 1 \\ \alpha & -1\end{bmatrix}\begin{bmatrix}\psi_1 \\ \psi_m\end{bmatrix}. \tag{37}$$

It is straightforward to show that the 2×2 matrix on the right-hand side (r.h.s.) of Eq. (37) has one vanishing eigenvalue and one negative eigenvalue given by $-\tau_d^{-1}(1+\alpha)$. Using Eq. (36) for α, one may also show that

$$\tau_2^{-1} = \tau_d^{-1}(1+\alpha), \tag{38}$$

where τ_2 is the slow relaxation time of Aniannsson and Wall, given here in Eq. (I.101). The eigenvector with an eigenvalue $-\tau_2^{-1}$, or a relaxation time τ_2, is a vector $[\psi_1, \psi_m] \propto [1, -1]$ that leaves the total concentration $\delta\rho = \psi_1 + \psi_m$ unchanged. The eigenvector with a vanishing eigenvalue, and thus a vanishing relaxation rate, is a vector $[\psi_1, \psi_m] \propto [1, \alpha]$ that corresponds to an infinitesimal change in equilibrium state. The model thus predicts a single exponential relaxation of homogeneous perturbations to a state with the same total surfactant concentration as the initial state, with a relaxation time equal to the slow time predicted by Aniansson and Wall.

Inhomogeneous systems are expected to establish a state of full local equilibrium either when allowed to relax sufficiently long after a temporary perturbation or when subjected to a sufficiently slowly varying perturbation, e.g., as in a low-frequency oscillatory perturbation. Such a state is characterized by a relationship

$$\psi_m(\mathbf{r}, t) \simeq \alpha\psi_1(\mathbf{r}, t) \tag{39}$$

for all $\mathbf{r}$, leading to a negligible net micelle creation rate, $(dc_m/dt)_{rxn} \simeq 0$. By substituting Eq. (39) for ψ_m into Eq. (32) and then adding Eqs. (31) and Eq. (32), one may show that, in this limit, ψ_1 obeys a diffusion equation

$$\frac{\partial \psi_1}{\partial t} = D_e \frac{\partial^2 \psi_1}{\partial z^2} \tag{40}$$

with an effective diffusivity

$$D_e = \frac{D_p + \alpha D_m}{1+\alpha} \tag{41}$$

for systems that remain in full local equilibrium. By using Eq. (33) for D_p and Eq. (36) for α, we obtain an alternative form

$$D_e = \frac{D_1 + \kappa_e D_m}{1+\kappa_e}. \tag{42}$$

Because the perturbation fields δc_1, δc_m, ψ_m, and ψ_1 are all proportional to one another in this linearized model, each of these fields obeys an analogous diffusion equation with diffusivity D_e. Note that $D_e \simeq D_1$ in a submicellar concentration with $\rho < c_c$, for which $\kappa_e \ll 1$, and that $D_e \simeq D_m$ in a micellar solution, for which $\kappa_e \gg 1$. Micelle diffusion dominates overall diffusive flux in micellar solutions because the local equilibrium condition strongly suppresses gradients in unimer concentration.

Consider relaxation of a system that is subjected to a small perturbation at time $t = 0$. The analysis given in this section assumes partial equilibration, and so is valid only at times $t \gg \tau_1$. At intermediate times, $\tau_1 \ll t \ll \tau_2$, effects of the micelle reaction rate $(dc_m/dt)_{rxn}$ remain negligible. To describe this time range, we may thus set $(dc_m/dt)_{rxn} \simeq 0$ in Eqs. (31) and (32) to obtain a pair of uncoupled diffusion equations for ψ_1 and ψ_m with effective diffusivities D_p and D_m, respectively. At very late times $t \gg \tau_2$, we expect the system to reach a state of full local equilibrium in which ψ_1 obeys Eq. (40), and in which $\psi_m = \alpha\psi_1$.

IV. FULL LOCAL EQUILIBRIUM

We now consider nonlinear dynamics in systems that have reached full local equilibrium. A system is in full local equilibrium when the micelle number concentration $c_n(\mathbf{r}, t)$ for all n is equal to the equilibrium value corresponding to the local unimer concentration, such that

$$c_n(\mathbf{r}, t) = c_n^*(c_1(\mathbf{r}, t)) \tag{43}$$

for all n. This condition implies that both the micelle number concentration c_m and micellar surfactant concentration ρ_m obey local equilibrium conditions

$$c_m(\mathbf{r}, t) = c_m^*(c_1(\mathbf{r}, t)), \tag{44}$$

$$\rho_m(\mathbf{r}, t) = \rho_m^*(c_1(\mathbf{r}, t)), \tag{45}$$

as does the average aggregation number $q = \rho_m/c_m$.

The assumption of full local equilibrium is expected to be valid during the final stages of relaxation of an inhomogeneous system after a transient perturbation, such as an expansion or contraction of an interface, or in an oscillatory measurement performed at sufficiently low frequency. Full local equilibrium requires relaxation of both the fast and slow processes, and is thus expected to be obtained after a sudden perturbation when the time since the perturbation becomes much greater than the slow time τ_2, or during an oscillatory measurement if the oscillation frequency is much less than τ_2^{-1}.

In any full local equilibrium state, inhomogeneities in unimer concentration $c_1(\mathbf{r}, t)$ are strongly suppressed in regions with a non-negligible micelle concentration $\rho_m(\mathbf{r}, t)$. This is a direct result of the local equilibrium condition, which requires that $\nabla c_1 = \kappa_e^{-1}\nabla\rho_m$, where $\kappa_e \sim (\rho_m/c_c)q$. Because average aggregation number $q(\mathbf{r}, t)$ is related to unimer concentration by an equilibrium condition, $q(\mathbf{r}, t) = q^*(c_1(\mathbf{r}, t))$, the average aggregation number must also be nearly homogeneous in micellar regions. Because the average micelle diffusivity D_m is approximated as a function of q, this also implies that the average micelle diffusivity D_m must be nearly homogeneous where micelles are present. For simplicity, we thus assume that $\nabla D_m \simeq 0$ throughout this section, thus effectively treating D_m as a constant in the case of full local equilibrium.

A. Nonlinear model

Consider the evolution of $\rho(\mathbf{r}, t)$ for a system in full local equilibrium. We assume that ρ is dominated by contributions of unimers and proper micelles, and that Eq. (I.21) thus applies. When applied to a local equilibrium state, Eq. (I.21) implies that $\rho = c_1 + \rho_m^*(c_1)$ for all $\mathbf{r}$ and t. The partial derivative $\partial\rho/\partial t$ in such a state thus satisfies

$$\frac{\partial\rho}{\partial t} = (1+\kappa_e)\frac{\partial c_1}{\partial t}, \tag{46}$$

where $\kappa_e(c_1) \equiv d\rho_m^*(c_1)/dc_1$ is the derivative defined in Eq. (I.26). Using similar notation, the total diffusion current $\mathbf{J}$ defined in Eq. (23) may be expressed as a sum

$$\mathbf{J} = -(D_1 + D_m\kappa_e)\nabla c_1, \tag{47}$$

where we have neglected a term proportional to ∇D_m for reasons discussed above. By using Eqs. (46) and (47) for the left- and right-hand sides of conservation equation (22), respectively, we obtain the nonlinear PDE

$$(1+\kappa_e)\frac{\partial c_1}{\partial t} = \nabla\cdot[(D_1 + D_m\kappa_e)\nabla c_1], \tag{48}$$

in which $\kappa_e = \kappa_e(c_1)$ is a strongly nonlinear function of local unimer concentration c_1.

Equation (48) can also be expressed equally well as a nonlinear PDE for ρ_m, rather than c_1. To do so, we simply treat c_1 as a function ρ_m rather than the reverse, and apply reasoning closely analogous to that used to obtain Eq. (48). This yields the alternate form

$$\left(\kappa_e^{-1} + 1\right)\frac{\partial\rho_m}{\partial t} = \nabla\cdot\left[\left(D_1\kappa_e^{-1} + D_m\right)\nabla\rho_m\right], \tag{49}$$

in which $\kappa_e^{-1}(\rho_m) = dc_1/d\rho_m$. Equations (48) and (49) are completely equivalent.

B. Linear model

Situations that involve only infinitesimal perturbations from a homogeneous equilibrium state can be described using a linearized version of Eq. (48). The resulting linearized theory is sufficient to describe, e.g., linear oscillatory tensiometry experiments at frequencies much less than τ_2^{-1}. Let c_1^∞ be the unimer concentration in a homogeneous equilibrium state, and

let $\delta c_1(\mathbf{r},t) = c_1(\mathbf{r},t) - c_1^\infty$. Linearization of Eq. (48) yields a diffusion equation

$$\frac{\partial(\delta c_1)}{\partial t} = D_e \nabla^2 \delta c_1 \tag{50}$$

with an effective local equilibrium diffusivity given by Eq. (42). Note that Eq. (50) is equivalent to Eq. (40), which we obtained by considering the long time behavior of a linear model of partial local equilibrium.

Note that Eq. (42) for D_e implies the dominance of unimer diffusion in submicellar states with $\rho < c_c$ and the dominance of micellar diffusion in micellar states with $\rho > c_c$. Linearization about a submicellar state in which $\rho < c_c$ yields $\kappa_e \ll 1$, giving $D_e \simeq D_1$. Linearization about a micellar state with $\rho > c_c$ instead generally yields $\kappa_e \gg 1$, giving $D_e \simeq D_m$. Micelle diffusion dominates transport in micellar states, giving $D_e \simeq D_m$, despite the presence of a non-negligible unimer concentration $c_1 \simeq c_c$, because the local equilibrium condition strongly suppresses the unimer concentration gradient $\nabla c_1 = \kappa_e^{-1} \nabla \rho_m$, and thereby suppresses unimer diffusion.

V. TRANSPORT TO AN INTERFACE

In transport problems that involve diffusion from a micellar solution to an initially bare or nearly bare interface, rapid absorption of unimers by the interface often leads to a region of strongly depressed unimer concentration near the interface. The resulting destabilization of micelles in that region can lead to the formation of a micelle-free region that is separated from a micellar region by a moving boundary. Several authors have considered simplified models for this phenomena [12–17] that assume the existence of full local equilibrium. A more complete description must allow for the effects of limitations on the rates of processes that create and destroy micelles, and for the possibility of the formation of a partial equilibrium state in the micellar region.

A. Model: Absorbing boundary

To make the discussion concrete, it is useful to consider the following model of transport from a micellar solution to an idealized absorbing interface: Consider a micellar solution that occupies a half-space $z > 0$ and that is in contact with an interface located along the plane $z = 0$. Far from the interface, the solution is in an equilibrium state with a bulk unimer concentration c_1^∞, a micelle number concentration c_m^∞ and a total surfactant concentration $\rho^\infty = c_1^\infty + \rho_m^\infty$, with $\rho^\infty > c_c$. We assume that unimers are rapidly and irreversibly adsorbed at the interface, creating an absorbing boundary condition for unimers, such that

$$c_1(z=0,t) = 0. \tag{51}$$

We also assume that adsorption is prohibited for all clusters with $n > 1$, giving a no-flux boundary condition

$$\left.\frac{\partial c_n(z,t)}{\partial z}\right|_{z=0} = 0 \quad (n > 1) \tag{52}$$

for all species other than unimers. We consider an idealized initial condition at $t = 0$ in which the solution is in a homogeneous micellar equilibrium state of concentration $\rho_m(z, t = 0) = \rho_m^\infty$ for all $z > 0$. Diffusion is initiated by instantaneous creation or introduction of the interface at $t = 0$.

The model described above is chosen for mathematical simplicity rather than realism. The absorbing boundary condition used here does not correspond to any easily realizable experiment. It does provide a reasonable model of the early time behavior during adsorption to a rapidly generated interface along which surfactant can accumulate, at times before significant accumulation has had time to occur, in the limit of fast adsorption and negligible solubility in the second phase that occupies the region $z < 0$. More realistic models of interfacial adsorption would need to consider effects of accumulation of adsorbed surfactant on the interface, finite rates of molecular adsorption and desorption, solubility in a second phase, and possibly flow, among other possible complications. We have chosen to discuss an idealized absorbing interface simply because it illustrates the nonlinear phenomena of interest in the simplest possible form.

We show in what follows that the model described above predicts rapid dissociation of micelles near the interface and corresponding formation of a micelle-free region along the interface. This occurs because the boundary condition requiring that $c_1(z,t) = 0$ along the interface guarantees the existence of a region in which the unimer concentration $c_1(z,t)$ is depressed below the c_d, and in which there is thus no barrier to dissociation. Along the plane $z = 0$, unimer insertion is completely suppressed, and the aggregation numbers of individual micelles thus shrink at a net average rate controlled by the bare expulsion constant. More generally, we expect micelles to shrink at rates comparable to an average expulsion constant throughout the region in which $c_1 < c_d$.

B. Micelle dissociation near the interface

Let τ_e denote the time at which a micelle-free region first appears, corresponding to the time at which the micelle concentration first becomes negligible at $z = 0$, i.e., for which $c_m(z=0,t) \simeq 0$ for all $t \geqslant \tau_e$. We assume in what follows that this occurs approximately when the average aggregation number $q(z,t)$ of micelles near the interface approaches zero. We focus in this article primarily on describing the behavior at times, $t > \tau_e$, after the appearance of a micelle-free region. We begin in this subsection, however, by briefly discussing behavior at earlier times, $t < \tau_e$. Our main purpose in this discussion is to establish that it is plausible for a micelle-free region to appear long before the system can establish full local equilibrium.

A lower bound on the time τ_e required for micelles to be cleared out of a region near the interface can be obtained by considering the fate of a micelle that remains adjacent to the interface throughout this process. Because the boundary condition requires that the $c_1 = 0$ along the interface, such a micelle would experience an environment in which insertion is completely suppressed, and in which micelles thus expel unimers and shrink at a rate comparable to the bare expulsion rate. The characteristic time required for a micelle to completely dissociate in such a unimer-free environment, denoted here by τ_q, is given approximately by the ratio

$$\tau_q \equiv \frac{q^\infty}{k^-}, \tag{53}$$

where q^{∞} is the bulk value of q and k^{-} denotes an average expulsion rate constant. For concreteness, let k^{-} denote the number average expulsion rate constant of micelles in the initial equilibrium state.

For typically surfactant systems, the timescale τ_q can be shown to generally be comparable to or greater than the fast time τ_1 observed in step relaxation experiments. For the sake of concreteness, consider a system with bulk equilibrium values of $q \simeq \sigma_m^2 \simeq 10^2$ typical of common surfactants. For such a system, the time τ_q defined in Eq. (53) is comparable to the characteristic timescale $\tau_\sigma \simeq \sigma_m^2/k^{-}$ for equilibrium fluctuations in aggregation number, as defined in Eq. (I.68). By Eq. (I.70), the bulk fast time τ_1 is always less than or equal to τ_σ, with $\tau_1 \sim \tau_\sigma$ at concentration slightly above the CMC and $\tau_1 \ll \tau_\sigma$ at concentrations $\rho_m^{\infty} \gg c_c$. For systems with $\tau_q \sim \tau_\sigma$, τ_q is thus generally comparable to or greater than τ_1.

In the model considered here, an individual micelle that remained very near the interface would completely dissociate in a time of order τ_q. If we assume that the appearance of a micelle-free zone occurs when micelles near the interface finish dissociating, this suggests that we should expect $\tau_e \sim \tau_q$.

The above argument is incomplete, however, because it ignores the effects of micelle diffusion. This simplified argument focuses on the fate of a hypothetical micelle that remains stationary near the interface while steadily losing unimers. Micelles that lie near the interface at some instant are not stationary, however, but tend to diffuse away from the interface and be replaced by micelles that diffuse in from more distant regions where the average micelle aggregation number is higher. This mixing of micelles of differing aggregation number causes a diffusive "smearing" of the depression in $q(z,t)$ that spreads out the region over which $q(z,t)$ is depressed near the interface, in a manner described by Eq. (20). The expected effect of micelle diffusion is thus to decrease the rate at which $q(z=0,t)$ decreases. This thereby delays somewhat the time at which $q(z=0,t)$ approaches zero and a micelle-free region appears. We thus expect to find $\tau_e > \tau_q$ when the effects of micelle diffusion are significant, and $\tau_e \sim \tau_q$ when they are negligible. Because we have already shown that $\tau_e \geqslant \tau_1$ even in the absence of micelle diffusion for typical systems, this implies that $\tau_e \geqslant \tau_1$ more generally.

A micellar region in which $c_1(z,t) > c_d$ always exists further from the interface, outside the region of strongly depressed unimer concentration $c_1(z,t) < c_d$ near the interface. Perturbations in both $c_1(z,t)$ and $q(z,t)$ extend to some extent into this region, where fast processes tend to drive the system towards a state of partial local equilibrium. We expect this micellar region to reach a state of partial local equilibrium after a time of order the fast time τ_1 after introduction of an interface. Because $\tau_e > \tau_1$, we thus expect this region to reach partial local equilibrium somewhat before a micelle-free region appears. We assume in what follows that this remaining micellar region can then remain in partial local equilibrium as the micelle-free region expands.

The time required for the micellar region of such a system to reach full local equilibrium is generally expected to be of order the bulk slow τ_2. The time τ_2 exceeds both τ_σ and τ_1 by a factor proportional to $\exp(\Delta W_d/k_BT)$, in which ΔW_d denotes the barrier to dissociation in the bulk equilibrium state. In systems with weakly soluble surfactants, this Arrhenius factor can be arbitrarily large. We will assume in what follows that, in systems that exhibit widely disparate fast and slow times as the result of the existence of a barrier $\Delta W_d \gg k_BT$, τ_2 will often be much greater than τ_e as well as τ_1.

A more complete treatment of the relationship between τ_e and τ_2 would require a detailed analysis of the effects of micelle diffusion upon τ_e, which is beyond the scope of this article. An analysis of this kind has, however, been given in the Ph.D. thesis of one of the authors [18] and will also be presented in a forthcoming journal publication. That analysis confirms that it is typical to observe $\tau_2 \gg \tau_e$ in systems of sparingly soluble surfactants in which $\tau_2 \gg \tau_1$. Here, we simply treat the existence of systems for which $\tau_1 \leqslant \tau_e \ll \tau_2$ as a plausible hypothesis for systems with $\tau_1 \ll \tau_2$, and discuss some qualitative aspects of the behavior expected in this case.

When the assumption that $\tau_1 \leqslant \tau_e \ll \tau_2$ is satisfied, one should expect to observe two different stages of development at times $t > \tau_e$, after the appearance of a micelle-free zone. At intermediate times $\tau_e < t \ll \tau_2$, we expect a state with a growing micelle-free region in which partial equilibrium has been established in the micellar region but full local equilibrium has not yet been reached. At very late times, $t \gg \tau_2$, we expect the system to reach a state of full local equilibrium, of the kind whose existence was simply assumed in previous work on two-zone models. These two stages of development are discussed in Secs. V D and V C, respectively, We have chosen to discuss the final stage of full local equilibrium first, in Sec. V C, simply because this stage is conceptually simpler and more mathematically tractable.

C. Late times: Full local equilibrium

In this subsection, we consider behavior of a system with $\tau_e \ll \tau_2$ at very late times, $t \gg \tau_2$, after full local equilibrium has been established, and long after the appearance of a micelle-free region at time τ_e. Behavior in this final time regime can be discussed either at the level of the nonlinear model developed in Sec. IV or, more approximately, at the level of the two-zone model introduced in earlier several studies. We consider both approaches and the relationship between them.

1. Nonlinear PDE

Evolution of a system that remains in full local equilibrium can be described by the nonlinear model developed in Sec. IV, by starting from either Eq. (48) for $c_1(z,t)$ or, equivalently, Eq. (49) for $\rho_m(z,t)$. In the one-dimensional geometry of interest here, Eq. (48) reduces to

$$(1+\kappa_e)\frac{\partial c_1(z,t)}{\partial t} = \frac{\partial}{\partial z}\left[(D_1 + D_m\kappa_e)\frac{\partial c_1(z,t)}{\partial z}\right]. \tag{54}$$

Equation (49) reduces to a corresponding PDE for $\rho_m(z,t)$, in which terms arising from unimer contributions are multiplied by κ_e^{-1}. The presence of the strongly nonlinear function $\kappa_e(c_1)$ in both these equations leads to behavior in which different terms dominate at locations with concentrations above and below the CMC, as discussed in greater detail below.

It is straightforward to show that Eq. (54) admits a similarity solution of the form

$$c_1(z,t) = c_c F(y_1), \tag{55}$$

in which

$$y_1 = z/\sqrt{4D_1 t}, \tag{56}$$

and $F(y_1)$ is an unspecified function of a single variable. Upon substituting Eq. (55) into the PDE of Eq. (54), we find that $F(y_1)$ must solve a nonlinear ODE

$$-2(1+\kappa_e)y_1 \frac{dF(y_1)}{dy_1} = \frac{d}{dy_1}\left[(1+R\kappa_e)\frac{dF(y_1)}{dy_1}\right], \tag{57}$$

where $R \equiv D_m/D_1$, with boundary conditions requiring $F(0) = 0$ and $F(\infty) = c_1^\infty/c_c$. Behavior at times $t \gg \tau_2$ is controlled by this similarity solution, in which all length scales expand with time as $t^{1/2}$. If the solution contains a micelle-free region, the width of this region must thus increase as $t^{1/2}$.

Consider the qualitative nature of solutions of Eqs. (48) or (49) during transport to an absorbing boundary. Assume that $\rho(z,t)$ is a monotonically increasing function of z. Let $h(t)$ denote the value of z at which $\rho(h(t),t) = c_c$, which is very near the point at which $\kappa_e(c_1(z,t)) = 1$. The existence of a similarity solution of the form given in Eqs. (55) and (56) implies that $h(t)$ must increase as $h(t) \propto t^{1/2}$. Because ρ_m^* and κ_e are both very sharply increasing function of ρ in this regime, we expect to find local values of $\rho_m^* \simeq 0$ and $\kappa_e \ll 1$ throughout almost all of a region $z < h(t)$ in which $\rho(z,t) < c_c$, which is thus an essentially micelle-free region. We instead expect to find $\rho_m^* \simeq \rho - c_c$ and $\kappa_e \gg 1$ throughout the region $z > h(t)$ in which $\rho > c_c$, which is a micellar region.

Consider the nature of transport within the micelle-free region $z < h(t)$, where $\rho(z,t) < c_c$ and $\rho_m(z,t) \simeq 0$. Wherever ρ is more than a few percent less than c_c, $\kappa_e \ll 1$, and so the contributions to Eqs. (47) and (48) that are proportional to κ_e all become negligible. In this case, Eq. (47) yields a one-dimensional flux $J(z,t) \simeq -D_1 \partial c_1/\partial z$ given by the unimer contribution alone, while Eq. (48) reduces to a 1D unimer diffusion equation,

$$\frac{\partial c_1}{\partial t} \simeq D_1 \frac{\partial^2 c_1}{\partial z^2}. \tag{58}$$

In the absence of micelles, transport is thus controlled by unimers.

Next consider the micellar region $z > h(t)$ in which $\rho > c_c$ and $\kappa_e \gg 1$. Here, transport can instead be shown to be dominated by micelle diffusion. To describe this region, it is convenient to start from the one-dimensional analog of Eq. (49) for $\rho_m(z,t)$. Because $\kappa_e^{-1} \ll 1$ in this limit, Eq. (49) may be approximated by dropping terms proportional to κ_e^{-1} to obtain a micelle diffusion equation

$$\frac{\partial \rho_m}{\partial t} \simeq D_m \frac{\partial^2 \rho_m}{\partial z^2}. \tag{59}$$

In the same limit, the overall flux $J(z,t)$ is dominated by micelle diffusion, giving $J(z,t) \simeq -D_m \partial \rho_m/\partial z$. Micelle contributions dominate in this limit because the local equilibrium condition strongly suppresses variations in c_1, thus yielding very small values for the time derivative $\partial c_1/\partial t$ and the gradient ∇c_1 of c_1 that appear as unimer contributions to accumulation and flux, respectively. Micelle diffusion thus dominates transport in this region, despite the fact that c_1 is itself generally not negligible, because c_1 is nearly constant.

This discussion suggests a picture in which a micelle-free zone in the region $z < 0$ is separated by a narrow transition region from a micellar zone occupying $z > h(t)$. The transition region corresponds to a region of space in which κ_e is of order unity. Because $\kappa_e \sim 1$ only within a narrow range of values of ρ near $\rho \simeq c_c$, we expect this transition region to correspond to a correspondingly narrow region of space near the plane $z = h(t)$.

The mechanism by which surfactant is transported must thus rapidly cross over from micelle diffusion in the micellar region $z > h(t)$ to unimer diffusion in the micelle-free region $z < h(t)$, with negligible flux of micelles into the region $z < h(t)$. In order for this to occur without rapid accumulation of surfactant in the transition region, micelles that enter the transition region from the micellar region must be destroyed within the transition region, while the unimers generated by dissociation form a source for the unimer flux into the micelle-free region. The model thus implies the existence of a narrow region with a very high unimer generation rate $G_1(z,t)$ near the plane $z = h(t)$.

2. Two-zone model

The two-zone model provides a slightly simplified version of the picture discussed above. The version considered here, which is the same as that used in several previous studies, combines an assumption of full local equilibrium with an idealized description of the change in equilibrium behavior at the CMC. This description assumes that micelles are completely absent ($\rho_m = 0$) wherever $\rho < c_c$, and that $c_1 = c_c$ wherever $\rho > c_c$.

In the resulting model, at any time t, there exists a micelle-free region $z < h(t)$ near the interface and a micellar region $z > h(t)$ separated by a moving boundary along the plane $z = h(t)$. Throughout the micelle-free region $z < h(t)$, $\rho_m(z,t) = 0$, $c_1(z,t) < c_c$. In this region, transport occurs only by unimer diffusion, so that $J(z,t) = -D_1(\partial c_1/\partial z)$ and $c_1(z,t)$ satisfies Eq. (58). Throughout the micellar region $z > h(t)$, $c_1(z,t) = c_c$, and $\rho_m(z,t) = \rho(z,t) - c_c$. Here transport occurs only by micelle diffusion, so that $J(z,t) = -D_m(\partial \rho_m/\partial z)$ and $\rho_m(z,t)$ satisfies Eq. (59).

The two-zone model does not attempt to resolve the transition region near the plane $z = h(t)$ within which micelles dissociate, treating this as a mathematical surface. Continuity of unimer and micelle concentrations across the plane $z = h(t)$ implies that

$$c_1(h(t),t) = c_c, \quad \rho_m(h(t),t) = 0 \tag{60}$$

at any time t. Continuity of surfactant flux across this plane is imposed by matching the micellar flux in the region $z > h(t)$ with the unimer flux in the micelle-free region, giving a boundary condition

$$D_1 \left.\frac{\partial c_1}{\partial z}\right|_{z=h^-(t)} = D_m \left.\frac{\partial c_m}{\partial z}\right|_{z=h^+(t)}. \tag{61}$$

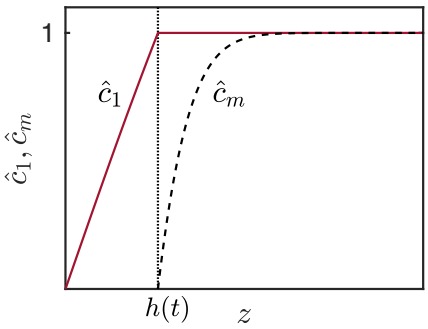

FIG. 1. Depiction of the behavior of normalized unimer concentration c_1 and micelle concentration c_m as a function of distance z from an interface during adsorption to an absorbing boundary for a system in full local equilibrium, as predicted by the two-zone model. Unimer and micelle concentrations normalized by corresponding bulk concentrations are denoted here by $\hat{c}_1 = c_1(z,t)/c_c$ (solid line) and $\hat{c}_m = c_m(z,t)/c_m^\infty$ (dashed line), as also indicated by labels. The boundary between the micelle-free and micellar regions is located at $z = h(t)$ and indicated by the dotted vertical line.

Here the notation $z = h^-(t)$ indicates a value evaluated in the micelle-free region by approaching $z = h(t)$ from below, while $z = h^+(t)$ indicates a value evaluated in the micellar region by approaching $z = h$ from above. The existence of nonzero micellar flux $-D\partial c_m/dz$ towards the interface from the micellar side of the plane $z = h(t)$ and a vanishing micellar flux on the micelle-free side implies that all micelles that diffuse to this boundary are destroyed there and converted into unimers along this plane. The two-zone model is thus defined by the unimer diffusion equation of Eq. (58) in the region $z < h(t)$, the unimer diffusion equation of Eq. (59) in the region $z > h(t)$, the boundary conditions of Eqs. (60) and (61) along the plane $z = h(t)$, an absorbing boundary condition requiring that $c_1(0,t) = 0$ at $z = 0$, and a bulk boundary condition requiring that $\rho_m(z = \infty, t) = \rho_m^\infty$.

Figure 1 depicts an example of the behavior of the normalized unimer concentration $c_1(\hat{z},t) = c_1(z,t)c_1^\infty$ and normalized micelle concentration $c_m(\hat{z},t) = c_m(z,t)/c_m^\infty$ as predicted by the two zone model. This shows a solution of the two-zone model described above for a system with $\rho_m^\infty/c_c = 3$ and $D_1/D_m = 10$. A more complete analysis of the solution of this model, which is analytically solvable, will be presented elsewhere. The solution of the full nonlinear model, which is not shown, would differ from the behavior shown here by introducing a slight smearing of the "cusps" (i.e., discontinuities in slope) of $c_1(z,t)$ and $c_m(z,t)$ along the plane $z = h(t)$.

D. Intermediate times: Partial local equilibrium

We now consider the intermediate time behavior of a system with widely disparate bulk fast and slow times, at times $\tau_e < t < \tau_2$. During this intermediate time regime, we expect to find a micelle-free region near the interface, as well as a micellar region further from the interface. These are presumably separated by a narrower transition region within which micelles dissociate, as in the case of full local equilibrium.

At times $t \ll \tau_2$, the micellar region is characterized by the existence of a state of partial local equilibrium but a negligible rate $(dc_m/dt)_{rxn}$ of the slow process. Within this region, $c_1(z,t)$ and $c_m(z,t)$ must thus approximately satisfy Eqs. (26) and (17) with $(dc_m/dt)_{rxn} = 0$, giving

$$(1+\kappa_p)\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial z}\left[(D_1 + \kappa_p D_m)\frac{\partial c_1}{\partial z}\right] + D_m \frac{\partial c_m}{\partial z}\frac{\partial q^*}{\partial z}$$
$$\frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial z^2}. \tag{62}$$

The diffusion equation for $c_1(z,t)$ in Eq. (62) allows for formation of a significant decrease in unimer concentration $c_1(z,t)$ with decreasing z within the micellar region. This is a somewhat subtle but important difference from the case of full local equilibrium, in which gradients in c_1 are almost entirely suppressed within the micellar region.

The decrease in $c_1(z,t)$ within decreasing z within the micellar region causes a corresponding decrease in the local dissociation barrier $\Delta W_d(c_1(z,t))$ with decreasing z, and a corresponding increase in the dissociation rate constant $k_d(c_1(z,t))$. We assume that the micelle dissociation rate exhibits a maximum with respect to z at some plane $z = h(t)$ along which the c_1 has decreased enough to allow relatively facile dissociation. We assume that dissociation is localized near this plane, which acts as an effective boundary between micelle-free and micellar regions. Let $c_p = c_1(z = h, t)$ denote the local unimer concentration along this plane. Because $\Delta W_d(c_1)$ is assumed to be prohibitive at $c_1 = c_1^\infty$ but vanishes in the limit $c_1 = c_d$, we assume that $c_d \leqslant c_p \leqslant c_1^\infty$. In the case of an extremely large equilibrium barrier $\Delta W_d(c_1^\infty) \gg k_B T$ and times $t \ll \tau_2$, we expect $\Delta W_d(c_1)$ to remain prohibitive except for c_1 nearly equal to c_d, giving $c_p \simeq c_d$.

The assumptions underlying the above discussion can be codified as a two-zone model analogous to that constructed for the case of full-local equilibrium. The model is based on the following assumptions:

(1) Micelles are excluded from a region $z < h(t)$ in which $c_1 < c_p$. Within this region, $c_m = 0$ and $c_1(z,t)$ satisfies a diffusion equation

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial z^2}. \tag{63}$$

(2) Micelle dissociation occurs only within a narrow region near the plane $z = h(t)$.

(3) The micellar region $z > h(t)$ is in a state of partial local equilibrium in which $q(z,t) = q^*(c_1(z,t))$. Within this region, $c_1(z,t)$ and $c_m(z,t)$ satisfy Eq. (62)

Continuity of $c_1(z,t)$ and $c_m(z,t)$ along the plane $z = h(t)$ implies that

$$c_1(h(t),t) = c_p, \quad c_m(h(t),t) = 0 \tag{64}$$

at any time t. Mass conservation also requires that the unimer diffusion current $J_1(z,t) = -D\partial c_1/\partial z$ in the micelle-free region match the total flux in the micellar region along the boundary $z = h(t)$, giving a boundary condition

$$D_1 \left.\frac{\partial c_1}{\partial z}\right|_{z=h^-(t)} = (D_1 + D_m\kappa_p)\left.\frac{\partial c_1}{\partial z}\right|_{z=h^+(t)} + q^* \left.\frac{\partial (D_m c_m)}{\partial z}\right|_{z=h^+(t)}, \tag{65}$$

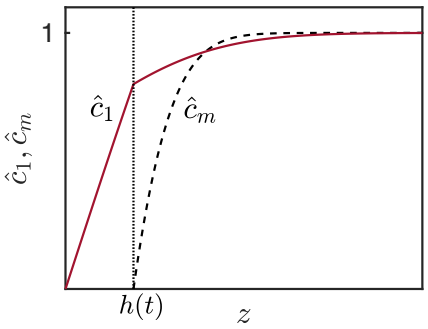

FIG. 2. Schematic depiction of c_1 and c_m for a system with a micelle-free region at times $t \ll \tau_2$, during which the micellar region is in partial local equilibrium. Unimer and micelle concentrations normalized by corresponding bulk concentrations are denoted here by $\hat{c}_1 = c_1(z,t)/c_1^\infty$ (solid line) and $\hat{c}_m = c_m(z,t)/c_m^\infty$ (dashed line), as also indicated by labels. The boundary between micelle-free and micellar regions is at $z = h(t)$ and is indicated by a vertical dotted line. Behavior shown here is representative of a system with parameters similar to those used in Fig. 1, with $(\sigma_m^*)^2 \simeq q^* \simeq 10^2$ in the bulk state and $c_p/c_c = 0.8$.

in which the r.h.s. is $-J(z,t)$ in the micellar region, as given by Eq. (25).

The model described above is incomplete because we have not stated a precise criterion for the value c_p of the unimer concentration along the boundary $z = h(t)$. The quantitative uncertainty arising from this ambiguity is less than it might at first appear, as a result of the requirement that $c_d < c_p < c_c$ and the observation that c_d is typically only a few tens of percent below c_c. A mathematically complete but slightly simplified model, which is correct in the limit of very large bulk dissociation barriers, is obtained if we assume that the dissociation barrier remains prohibitive for all c_1 greater than c_d, and thus approximate $c_p = c_d$.

The behavior of the unimer and micelle concentrations in the case of partial local equilibrium is depicted schematically in Fig. 2. The key difference between the cases of partial and local equilibrium is the existence of a substantial deviation of c_1 from c_1^∞ within the micellar region. Though this is not shown explicitly in this figure, this variation in the unimer concentration also leads to a substantial variation in average micelle aggregation number $q(z,t)$, since q this is related to c_1 by a partial equilibrium condition. The resulting fractional deviation of q from q^∞ is generally somewhat larger than the fractional deviation of c_1 from c_1^∞, and can cause a variation of $q(z,t)$ by up to approximately a factor of 2 within the micellar region for realistic molecular parameters.

This discussion shows how the two-zone model introduced in earlier work, which relied on an assumption of full local equilibrium, can be extended in slightly modified form to describe times $t \ll \tau_2$ before full local equilibrium is established. In this case, in which the barrier to dissociation remains prohibitive in the bulk solution, the sensitivity of the dissociation rate constant to changes in unimer concentration c_1 and the existence of a gradient in c_1 nonetheless guarantee that there will exist a region near the interface in which micelle dissociation becomes sufficiently rapid to create a micelle-free region.

VI. CONCLUSIONS

Sections II–IV of this paper present a self-contained discussion of the theory of kinetics and transport in micelle-forming surfactant systems in a form suitable for describing large deviations from equilibrium. Section V discusses application of the theory to a somewhat idealized adsorption problem.

The general discussion of diffusion in Secs. II–IV focuses on the development of reduced models that describe the evolution of a polydisperse system by tracking only a few statistical properties. The reduced model constructed in Sec. II is formulated as a set of partial differential equations for $c_1(z,t)$, $c_m(z,t)$, $q(z,t)$, and, optionally, $\sigma_m^2(z,t)$. This relatively general model has been used to construct two more specialized nonlinear models to describe systems that remain in either partial or full local equilibrium. The resulting model of partial local equilibrium reduces in the limit of small deviations from equilibrium to the linearized transport model of Dushkin *et al.* . We use the discussion of adsorption given in Sec. V to show by example how the nonlinear PDEs developed in Secs. II–IV can lead naturally to behavior involving propagation of a front separating micelle-free and micellar regions within an inhomogeneous system.

Section V presents a qualitative discussion of diffusion from a micellar solution to an interface that acts as an absorbing boundary for unimers. The model considered here is chosen for mathematical simplicity, rather than realism, because it illustrates several phenomena of interest in their simplest form. Micelles can dissociate rapidly near an absorbing interface because interfacial adsorption creates a region near the interface with $c_1(z,t) < c_d$, in which there is no thermodynamic barrier to dissociation. Nonlinear dependence of the rate of micelle shrinkage upon local unimer concentration thus allows rapid micelle destruction near a bare interface even in systems that exhibit an extremely long slow time τ_2 in bulk linear relaxation experiments. As a result, a micelle-free region can appear near a freshly created interface much earlier than the time required for the remaining micellar region to reach full local equilibrium, which is of order τ_2.

After a micelle-free region appears at some time τ_e, the micelle-free region is separated from the remaining micellar region by a moving boundary that moves steadily away from the interface. Micelles dissociate and are converted into unimers near this boundary. Behavior at times $t > \tau_e$ is shown to generally involve an intermediate time regime in which the micellar region remains in partial but not full equilibrium, followed by a final stage after full local equilibrium is established. We show how the two-zone model introduced in several previous studies, which assumed the existence of full local equilibrium, can be modified so as to describe the intermediate time regime. The most important distinction between behaviors predicted at intermediate and late times is the predicted existence of substantial gradients in unimer concentration and average micelle aggregation number within the micellar region at intermediate times, in contrast to the

nearly complete suppression of these gradients after full local equilibrium is established.

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APPENDIX: TIME DEPENDENCE OF MOMENTS

The derivation of the expressions for $\partial c_{\rm m}/\partial t$ and $\partial \rho_{\rm m}/\partial t$ given in Eqs. (6) and (7) can be generalized to obtain a more general expression for the temporal derivative of any moment of the micelle size distribution. In this Appendix, we first present this general analysis and then consider the second moment to obtain expressions for derivatives of $\langle n^2\rangle_{\rm m}$ and $\sigma_{\rm m}^2$.

Let $c^{(k)}$ denote the k-moment of the micelle number concentration c_n, given by a sum

$$c_{\rm m}^{(k)} \equiv \sum_{n=b}^{\infty} c_n n^k, \tag{A1}$$

defined such that

$$\langle n^k\rangle_{\rm m} = c_{\rm m}^{(k)}/c_{\rm m}. \tag{A2}$$

Note that $c_{\rm m} = c_{\rm m}^{(0)}$ and $\rho_{\rm m} = c_{\rm m}^{(1)}$ are special cases of $c_{\rm m}^{(k)}$ with $k = 0$ and $k = 1$, respectively, while q is the first moment of the normalized distribution.

The derivative $\partial c_{\rm m}^{(k)}/\partial t$ may be computed by evaluating the derivative of the sum in Eq. (A1), using Eq. (1) for $\partial c_n/\partial t$. This yields

$$\frac{\partial c_{\rm m}^{(k)}}{\partial t} = \nabla^2\big(D_{\rm m}^{(k)} c_{\rm m}\langle n^k\rangle_{\rm m}\big) + S^{(k)}, \tag{A3}$$

where

$$S^{(k)} \equiv \sum_{n=b}^{\infty} n^k (I_{n-1} - I_n) \tag{A4}$$

is a contribution arising from stepwise reactions. Note that $S^{(0)} \equiv (dc_{\rm m}/dt)_{\rm rxn}$ and $S^{(1)} \equiv (d\rho_{\rm m}/dt)_{\rm rxn}$, while $S^{(2)}$ is the r.h.s. of Eq. (I.A4). Expressions for $S^{(0)}$, $S^{(1)}$ and $S^{(2)}$ that have been simplified by applying a summation by parts are given in article I in Eqs. (I.43), (I.44), and (I.A4), respectively.

The corresponding temporal derivative of $\langle n^k\rangle_{\rm m}$ is given by the difference

$$\frac{\partial\langle n^k\rangle_{\rm m}}{\partial t} = \frac{\partial}{\partial t}\left(\frac{c_{\rm m}^{(k)}}{c_{\rm m}}\right) = \frac{1}{c_{\rm m}}\frac{\partial c_{\rm m}^{(k)}}{\partial t} - \frac{\langle n^k\rangle_{\rm m}}{c_{\rm m}}\frac{\partial c_{\rm m}}{\partial t}. \tag{A5}$$

Using Eq. (A3) for $\partial c_{\rm m}^{(k)}/\partial t$ and Eq. (6) for $\partial c_{\rm m}/\partial t$, we obtain

$$\begin{aligned}\frac{\partial\langle n^k\rangle_{\rm m}}{\partial t} \equiv{}& D_{\rm m}^{(k)}\nabla^2\langle n^k\rangle_{\rm m} + \frac{2}{c_{\rm m}}\nabla\big(D_{\rm m}^{(k)} c_{\rm m}\big)\cdot\nabla\langle n^k\rangle_{\rm m} \\ &+ \frac{\langle n^k\rangle_{\rm m}}{c_{\rm m}}\nabla^2\big[\big(D_{\rm m}^{(k)} - D_{\rm m}^{(0)}\big)c_{\rm m}\big] \\ &+ \frac{1}{c_{\rm m}}[S^{(k)} - \langle n^k\rangle_{\rm m} I_{b-1}],\end{aligned} \tag{A6}$$

in which we have used the relation $S^{(0)} = I_{b-1}$.

The corresponding derivative of $\sigma_{\rm m}^2$ is given by a difference

$$\frac{\partial\sigma_{\rm m}^2}{\partial t} = \frac{\partial(\langle n^2\rangle_{\rm m} - q^2)}{\partial t}. \tag{A7}$$

Using Eq. (A6) with $k = 2$ for $\partial\langle n^2\rangle_{\rm m}/\partial t$ and Eq. (I.45) for $\partial q/\partial t$, we obtain Eq. (12), with a reactive term

$$\left(\frac{d\sigma_{\rm m}^2}{dt}\right)_{\rm rxn} = \frac{1}{c_{\rm m}}[S^{(2)} - 2qS^{(1)} - \langle n^2\rangle_{\rm m} I_{b-1}]. \tag{A8}$$

Equation (13) for $(d\sigma_{\rm m}^2/dt)_{\rm rxn}$ is then obtained by repeating the steps used to obtain Eq. (I.46) in Appendix A of article I, by combining Eq. (I.A4) for $S^{(2)}$ and Eq. (I.44) for $S^{(1)}$.

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