Surface conservation laws at microscopically diffuse interfaces

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Abstract

In studies of interfaces with dynamic chemical composition, bulk and interfacial quantities are often coupled via surface conservation laws of excess surface quantities. While this approach is easily justified for microscopically sharp interfaces, its applicability in the context of microscopically diffuse interfaces is less theoretically well-established. Furthermore, surface conservation laws (and interfacial models in general) are often derived phenomenologically rather than systematically. In this article, we first provide a mathematically rigorous justification for surface conservation laws at diffuse interfaces based on an asymptotic analysis of transport processes in the boundary layer and derive general formulae for the surface and normal fluxes that appear in surface conservation laws. Next, we use nonequilibrium thermodynamics to formulate surface conservation laws in terms of chemical potentials and provide a method for systematically deriving the structure of the interfacial layer. Finally, we derive surface conservation laws for a few examples from diffusive and electrochemical transport.
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Keywords: Surface conservation laws; Transport theory; Interface structure; Asymptotic analysis

1. Introduction

It is well known that the chemical composition of an interface plays an important role in its dynamics (both its motion and the evolution of its chemical composition). A few interesting and important examples include the effect of surfactants on surface tension [1–3], the charging dynamics of electrochemical double layers [4–8], electrokinetic phenomena [9–20] and soap film dynamics [21,22]. Unfortunately, theoretical modeling of the interaction between chemical composition and interfacial dynamics can be quite challenging because it involves coupling dynamics at the macroscopic scale away from the interface with a microscopic model for the interfacial region. Sometimes it may not even be clear which microscopic model is appropriate for a particular problem. Many successful approaches based on the notion of an excess surface concentration [23–25] have been developed and applied to a wide-range of problems. While this approach is well-founded for microscopically sharp interfaces, the theoretical foundations for this methodology in the context

of microscopically diffuse interfaces (especially for dynamic interfaces) do not appear to have been thoroughly explored.

For microscopically diffuse interfaces (i.e., interfaces where the chemical composition smoothly varies across the interface), the notion of a surface excess concentration and dynamics of surface excess quantities can be rigorously justified via asymptotic analysis. In this article, we present a general procedure based on asymptotic analysis for deriving surface conservation laws (including derivation of the structure of the interfacial layer) that couple dynamics in the bulk with dynamics of the interfacial region and demonstrate the application of our formulation to example problems in diffusive and electrochemical transport. Our results are only valid in the "sharp interface" limit (i.e., when the distance over which the volume density of the diffuse species varies is small relative to macroscopic length scales of the problem). Fortunately, this limit is the only one that is physically meaningful—if an interface is too diffuse, it may not be appropriate to treat it as an interface in the first place.

In previous work involving surface conservation laws, the thickness and boundaries of the interfacial layer are often defined in an ad hoc manner [6,7,25]. While this approach yields

surface conservation laws of the correct form, it leaves the definition of surface quantities, which are computed by integrating over the thickness of the interfacial layer, ambiguous. In contrast, our derivation uses asymptotic analysis to more rigorously define surface quantities that appear in surface conservation laws. Previous work also focuses primarily on surface conservation laws in the absence of transport within the interface itself [3,26–31] and deriving the surface conservation laws in the context of specific problems [4–7,10]. Our derivation unifies these earlier results by providing a general framework for deriving surface conservation laws for application to a wide range of transport problems. We only require that, near the surface, the flux for the transport process scales in the same manner as a linear combination of gradients of field variables. Fortunately, these types of fluxes are very common in transport theory [32]. We emphasize that the formulation of surface conservation laws we present is not based on phenomenological physical arguments; rather, they are a direct consequence of the asymptotic analysis. Moreover, the generality of our formulation allows us to derive surface conservation laws for nonlinear transport processes when the bulk is far from equilibrium (e.g., electrochemical transport of around metallic particles at large applied fields) and for systems with complex interfacial structure. To the authors' knowledge, surface conservation laws for these types of problems have not been previously derived.

2. Surface conservation laws

When studying chemically active interfaces, the state of the interface is commonly described at macroscopic scales by specifying the excess surface concentrations of all chemical species. Intuitively, excess surface concentrations are defined as the amount of material per unit area of surface after the material in the "bulk" has been removed from the interfacial region. However, this definition is physically and mathematically ambiguous—in the region near the interface, how is one to distinguish between material that is part of the bulk and material that is part of the interface? The ambiguity of this definition was recognized long ago by Gibbs [33–35] and is typically dealt with by arbitrarily selecting a concentration, C^*, at some point within the interface (when viewed at a microscopic length scale) to be the reference "bulk" concentration [23,24,36]. Any deviation of the concentration near the interface from C^* is treated as a contribution to the excess surface concentration. In terms of this reference concentration, the excess surface concentration is defined as the integral of $(C–C^*)$ over the thickness of the interface.

While somewhat inelegant from a theoretical perspective, this formulation of excess surface concentration has been used quite successfully for studying interfaces of equilibrium systems. For systems in thermal equilibrium, the excess surface concentrations can be related to other thermodynamic variables, such as bulk concentrations and other excess surface concentrations via adsorption isotherms [1,23,24,37,38]. However, when the dynamics of surface species is important (e.g., fast adsorption–desorption kinetics, nonnegligible surface-diffusion), isotherm models need to be replaced by sur-
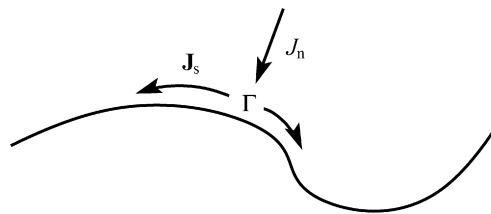

Fig. 1. Schematic diagram of fluxes at an interface. Note that the surface excess concentration Γ and the surface fluxes J_s are defined only on the interface itself.

face conservation laws for the excess surface concentrations which provide dynamic coupling between bulk concentrations and excess surface concentrations:

$$\frac{\partial \Gamma}{\partial t} = -\nabla_s \cdot \mathbf{J}_s + J_n. \tag{1}$$

Here Γ, $\mathbf{J}_s$ and J_n are the surface excess concentration, the surface flux and the normal flux, ∇_s denotes a surface derivative, and the sign on the normal flux is chosen to be positive when the flux is into the boundary layer (see Fig. 1). In this situation, the thermodynamic definition of excess surface concentrations becomes unsatisfactory because all of the variables in (1) depend implicitly on the choice of C^* whose governing equation and relationship to other macroscopic variables may be difficult to derive.

Fortunately, for many problems, there is a natural way to define C^* in terms of bulk concentrations (which almost always have relatively straightforward governing equations). Define C^* to be the limit of the corresponding bulk concentration, $C(x)$, as x approaches the interface. Unlike thermodynamic definitions of the excess concentration which are defined in terms of a reference concentration chosen at microscopic length scales and suffer from the difficulty of relating that reference concentration to macroscopic variables, the choice of C^* just described is directly related to macroscopic variables because it is explicitly defined in terms of those variables. Note that C^* is not necessarily a constant; it may still be a function of position along the surface of the interface.

Equation (1) seems physically intuitive: the time rate of change in the surface concentration results from a combination of surface diffusion and flux from the bulk. However, it is important to remember that the equation describes the evolution of excess concentrations, not absolute concentrations. Thus, $\mathbf{J}_s$ and J_n must be carefully defined so that they contribute solely to changes in the excess concentration, not to changes in reference concentration C^*. Even excellent discussions of surface conservation laws, such as [25], often overlook this subtle point. One purposes for this article is to bring attention to this issue and provide a systematic method, based on fundamental physical principles, for defining and calculating the fluxes that appear in surface conservation laws at microscopically diffuse interfaces.

For microscopically sharp interfaces, such as the monolayer interfaces that arise in problems involving surfactants at liquid–gas interfaces [1–3] or the compact layer in electrochemical systems [24,37], $\mathbf{J}_s$ and J_n are very simply defined because the bulk truly extends all the way to the interface. As a result,
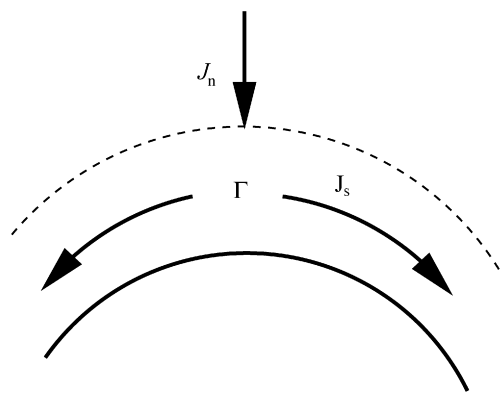
Fig. 2. Schematic diagram of a microscopically diffuse interface. The dashed line represents the outer "edge" of the boundary layer, which is not at a mathematically well-defined location. Note that in addition to the fluxes within the boundary layer, it is possible for the interface to possess fluxes that physically reside on the microscopic interface itself. For some systems, these "microscopic" surface fluxes may provide a significant contribution to the total surface flux in the boundary layer.

the excess surface concentration is the amount of material per unit surface area that resides precisely on the interface. In other words, the excess surface concentration is the absolute surface concentration. Thus, the surface can truly be thought of as a distinct phase, and a conservation law argument based on a balance of fluxes into a "control volume" on the interface is mathematically valid. As a result, J_n is the flux of bulk material normal to the surface and $\mathbf{J}_s$ is the flux within the surface itself driven by transport processes intrinsic to the interface (e.g., surface diffusion in a lipid bilayer).

That surface conservation laws hold for microscopically sharp interfaces is not surprising. What is interesting is that $\mathbf{J}_s$ and J_n can be defined in such a way that surface conservation laws also hold for microscopically diffuse interfaces (see Fig. 2). For instance, in their studies of the evolution of surface excess concentrations of electrolyte around colloid particles [4,5,10], Dukhin, Deryagin, and Shilov made use of surface conservation laws for excess ion concentration to couple ion transport in the bulk to the behavior of the electrical double layer. A key observation about microscopically diffuse interfaces is that surface transport within the boundary layer near the interface is driven by the same transport processes that occur in the bulk. In contrast, at microscopically sharp interfaces, surface transport could potentially be completely different from bulk transport because the underlying physical processes driving surface transport (which are related to the specific nature of the interface) might be fundamentally different.

Unfortunately, the derivation of surface conservation laws for microscopically sharp interfaces is not valid for diffuse interfaces because the notion of a surface "control volume" is no longer well-defined. The main problem is the lack of a distinct separation between the bulk and the interfacial region. Rather, there is a thin region near the interface over which concentrations vary rapidly. Intuitively, what we would like to do is define surface quantities by directly integrating over the boundary layer. This procedure, however, must be carried out carefully

in order to obtain physically meaningful results. The basic idea in deriving surface conservation laws, which we shall elaborate on in the next section, is that all integrations over the boundary layer should involve only excess quantities; integration of absolute quantities leads to divergent results.

It is important to note that (1) neglects contributions due to motion and deformation of the interface (e.g., terms involving convection in the normal direction and surface dilation [11,39,40]). Since our analysis sheds no new insight for these terms, we shall ignore them to simplify the discussion.

2.1. Dimensionless formulation of equations

In deriving the general form for $\mathbf{J}_s$ and J_n involved in surface conservation laws for microscopically diffuse interfaces, it is convenient to examine all equations in nondimensional form. To avoid confusion when reintroducing dimensions, let us take a moment to fix the physical scales used in the nondimensionalization process. At the macroscopic scale, the spatial coordinates, (X, Y, Z), are scaled by the characteristic size of the system, L. At the microscopic scale, the tangential, (x, y), and normal, z, spatial coordinates are scaled by L and δ, respectively, where δ is the characteristic thickness of the interfacial layer. Time, t, is scaled by the bulk diffusion time scale, $\tau = L^2/D$. Concentrations, c_i, are nondimensionalized by taking the reference concentration to be the maximum physically realizable concentration, c_{max}. Bulk, $\mathbf{F}_i$, and surface fluxes, $\mathbf{J}_i$, are scaled using $c_{max}L/\tau$ and $c_{max}L^2/\tau$, respectively. Other physical variables that appear later in this article are nondimensionalized as follows. The electric potential, ϕ, is scaled by the thermal voltage $k_B T/e$, where k_B is Boltzmann's constant and e is the absolute charge of an electron. Thermodynamic energy variables, U and F, and the entropy, S, are scaled using $k_B T$ (the thermal energy) and k_B, respectively. Table 1 gives a summary of the physical scales used to nondimensionalize equations in this article.

The dimensional form of any of the equations in this article can be obtained by first replacing each dimensionless variable with its associated dimensional variable divided by the appropriate characteristic scale and then multiplying the entire equation by an appropriate physical scale to restore units to the equation.[1] For instance, if the dimensionless concentration, c, appears in a dimensionless equation, it should be replaced by C/c_{max} when re-dimensionalizing the equation.

2.2. Derivation of Eq. (1) for microscopically diffuse interfaces

To derive surface conservation laws of the form (1) at microscopically diffuse interfaces, our goal is to appropriately define Γ, $\mathbf{J}_s$ and J_n in terms of macroscopic variables. Our approach will be to use asymptotic analysis [41,42] to carefully integrate concentrations and fluxes over the boundary layer.

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[1] Note that differential operators will also need their units restored.

Table 1
Summary of physical scales used to nondimensionalize equations

Physical quantity	Variable(s)	Physical scale
Spatial coordinate	X, Y, Z, x, y	L (macroscopic length scale)
Spatial coordinate	z	δ (microscopic length scale)
Time	t	$\tau = L^2/D$ (bulk diffusion time scale)
Concentration	c_i	c_{max} (maximum physically realizable concentration)[a]
Bulk flux	$\mathbf{F}_i, J_n^i$	$c_{max} L/\tau$
Surface flux	$\mathbf{J}_s^i$	$c_{max} L^2/\tau$
Electric potential	ϕ	$k_B T/e$ (thermal voltage)
Energy	U, F	$k_B T$ (thermal energy)
Entropy	S	k_B

[a] $c_{max} = 1/a^3$, where a^3 is the characteristic volume of each solute/solvent particle.

We begin by writing the conservation law that governs the time evolution of a chemical species in the bulk:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{F}, \tag{2}$$

where c is the concentration and $\mathbf{F}$ is the flux. For our derivation, we assume that there is no flux of material through the interface[2] itself so that $\partial \mathbf{F}/\partial n = 0$ and that the spatial coordinates in (2) have been nondimensionalized using a characteristic macroscopic length scale. In these units, the thickness of the boundary layer over which c varies rapidly is $O(\epsilon)$, where $\epsilon \equiv \delta/L$ is the ratio of the interfacial and macroscopic length scales.

We study the "sharp interface" limit (defined as the limit $\epsilon \to 0$) by taking (2) for the outer equations and deriving the inner equations by rescaling the spatial coordinates. In the following discussion, we shall distinguish inner and outer variables by using the hat (ˆ) and bar accents (¯), respectively. Also, we shall use (X, Y, Z) (upper case variables) and (x, y, z) (lower case variables) to represent the outer and inner spatial coordinates, respectively. Since the focus will be on the region immediately neighboring the surface, we shall take (x, y) to be Cartesian coordinates tangential to the interface and z to be the coordinate normal to the interface.

Rescaling (2) using the inner coordinates $(x, y, \epsilon z) = (X, Y, Z)$, we find that the governing equations in the boundary layer are

$$\frac{\partial \hat{c}}{\partial t} = -\nabla_s \cdot \hat{\mathbf{F}}_s - \frac{1}{\epsilon^2} \frac{\partial \hat{\mathbf{F}}_n}{\partial z}, \tag{3}$$

where the subscripts s and n indicate tangential and normal components of the flux and divergence operator, respectively. Note that in (3), we have implicitly assumed that in changing to the inner coordinates, the normal derivative of the normal flux $\hat{\mathbf{F}}_n$ picks up a factor of $1/\epsilon$ because

$$\hat{\mathbf{F}}_n(x, y, z) = \epsilon \bar{\mathbf{F}}_n(X, Y, Z). \tag{4}$$

This relationship between the inner and outer normal fluxes is a direct consequence of our requirement that, near the interface,

$\mathbf{F}$ scales in the same manner as a linear combination of gradients of macroscopic field variables:

$$\mathbf{F} = \sum_i f_i(c_1, c_2, \ldots, c_n)\nabla c_i, \tag{5}$$

where f_i are arbitrary functions of $c_1, c_2, \ldots, c_n$. For fluxes of the form (5), the factor of ϵ in (4) arises from the fact that the flux itself involves derivatives of space. We emphasize, however, that for our general analysis, we only require that fluxes satisfy (4) without regard for the origin of this relationship.

Next, we derive an evolution equation for the excess concentration in the boundary layer:

$$\gamma(x, y, z, t) = \hat{c}(x, y, z, t) - c^*(x, y, t), \tag{6}$$

where $c^*(x, y, t) \equiv \lim_{Z \to 0} \bar{c}(X, Y, Z, t)$. Notice that we have chosen the reference concentration to be the limit of the bulk concentration as the interface is approached. Taking the time derivative of this equation and using inner and outer evolution equations, (2) and (3), we find that

$$\frac{\partial \gamma}{\partial t} = \left(-\nabla_s \cdot \hat{\mathbf{F}}_s - \frac{1}{\epsilon^2} \frac{\partial \hat{\mathbf{F}}_n}{\partial z}\right) - \left(-\nabla_s \cdot \mathbf{F}_s^* - \lim_{Z \to 0} \frac{\partial \bar{\mathbf{F}}_n}{\partial Z}\right), \tag{7}$$

where $\mathbf{F}^* \equiv \lim_{Z \to 0} \bar{\mathbf{F}}$.

To obtain an evolution equation for the surface excess concentration Γ, it is tempting to integrate this equation over the boundary layer. Unfortunately, naive integration over the entire range of the inner variable can lead to divergent integrals. For example, integrating the last term on the right-hand side of (7) leads to

$$\int_0^\infty \left(\lim_{Z \to 0} \frac{\partial \bar{\mathbf{F}}_n}{\partial Z}\right) \mathrm{d}z = \left(\lim_{Z \to 0} \frac{\partial \bar{\mathbf{F}}_n}{\partial Z}\right) \int_0^\infty \mathrm{d}z = \infty. \tag{8}$$

Clearly, we have made an error in the asymptotic integration because the boundary layer has an $O(\epsilon)$ width and all of the integrands are $O(1)$, which suggests that all of the integrals should be $O(\epsilon)$ quantities.

The problem with the intuitive approach is that it makes the mistake of equating the asymptotic limit $\epsilon \to 0$ with the spatial limit $z \to \infty$. Realizing this subtle distinction (which is safe to neglect for many asymptotic analyses), we can reformulate the integration over the boundary layer as the limit of a sequence of integrals over finite intervals, which tends to the entire half-space $[0, \infty)$ as $\epsilon \to 0$. In choosing the domain of integration, we want to be sure to capture the entire boundary layer so that the notion of the total surface excess concentration is physically meaningful. In addition, we want the region of integration at the macroscopic length scale to go to zero as $\epsilon \to 0$ so that we are truly integrating over only the boundary layer. We can simultaneously achieve both of these goals by taking the region of integration at the macroscopic length scale (i.e., where Z is the variable in the normal direction) to be $[0, \alpha]$ where $\alpha = O(\epsilon^p)$ with $0 < p < 1$. Since the width of the boundary layer is $O(\epsilon)$, this choice of α ensures that the integration region completely covers the boundary layer but tends to 0 in the asymptotic limit.

Even with this choice of integration region, we must still exercise care to make sure that all integrands are of excess

[2] This assumption may be relaxed in situations where there are processes intrinsic to the interface (e.g., chemical reactions).

quantities so that integrations over the inner coordinate are convergent. The key idea is that only excess concentrations are asymptotically integrable, absolute concentrations are not. This restriction suggests that we rewrite (7) as

$$\frac{\partial \gamma}{\partial t} = -\nabla_s \cdot \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) - \frac{1}{\epsilon^2} \frac{\partial \hat{\mathbf{F}}_n}{\partial z} + \lim_{Z \to 0} \frac{\partial \bar{\mathbf{F}}_n}{\partial Z}. \tag{9}$$

Integrating this equation over the boundary layer (at the macroscopic length scale), we obtain

$$\int_0^\alpha \frac{\partial \gamma}{\partial t} \, dZ = -\int_0^\alpha \nabla_s \cdot \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) dZ - \frac{1}{\epsilon^2} \int_0^\alpha \frac{\partial \hat{\mathbf{F}}_n}{\partial z} \, dZ$$
$$+ \int_0^\alpha \left(\lim_{Z \to 0} \frac{\partial \bar{\mathbf{F}}_n}{\partial Z} \right) dZ. \tag{10}$$

Changing from the outer to the inner coordinate for all of the integrals except the last term yields

$$\epsilon \int_0^{\alpha/\epsilon} \frac{\partial \gamma}{\partial t} \, dz = -\epsilon \int_0^{\alpha/\epsilon} \nabla_s \cdot \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) dz - \frac{1}{\epsilon} \int_0^{\alpha/\epsilon} \frac{\partial \hat{\mathbf{F}}_n}{\partial z} \, dz$$
$$+ \int_0^\alpha \left(\lim_{Z \to 0} \frac{\partial \bar{\mathbf{F}}_n}{\partial Z} \right) dZ$$
$$= -\epsilon \int_0^{\alpha/\epsilon} \nabla_s \cdot \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) dz - \frac{1}{\epsilon} \hat{\mathbf{F}}_n(x, y, \alpha/\epsilon)$$
$$+ \alpha \left(\lim_{Z \to 0} \frac{\partial \bar{\mathbf{F}}_n}{\partial Z} \right). \tag{11}$$

Note that to move from the first to the second line in the above equations, we have explicitly integrated the normal derivative and applied the no flux boundary condition, $\frac{\partial \hat{\mathbf{F}}}{\partial n}(z = 0) = 0$. Expanding the last term in (11) using a Taylor series, we find that

$$\epsilon \int_0^{\alpha/\epsilon} \frac{\partial \gamma}{\partial t} \, dz = -\epsilon \int_0^{\alpha/\epsilon} \nabla_s \cdot \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) dz - \frac{1}{\epsilon} \hat{\mathbf{F}}_n(x, y, \alpha/\epsilon)$$
$$+ \bar{\mathbf{F}}_n(X, Y, \alpha) - \bar{\mathbf{F}}_n(X, Y, 0) + O(\alpha^2). \tag{12}$$

Finally, recalling that $\hat{\mathbf{F}}_n(x, y, \alpha/\epsilon) = \epsilon \bar{\mathbf{F}}_n(X, Y, \alpha)$, the above equation can be simplified to

$$\epsilon \int_0^{\alpha/\epsilon} \frac{\partial \gamma}{\partial t} \, dz = -\epsilon \int_0^{\alpha/\epsilon} \nabla_s \cdot \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) dz$$
$$- \bar{\mathbf{F}}_n(X, Y, 0) + O(\alpha^2). \tag{13}$$

By choosing $1/2 < p$ in the definition of α, we find that the $O(\alpha^2)$ term becomes negligible compared to the remaining terms in the $\epsilon \to 0$ limit so that the leading order asymptotic equation describing surface concentration evolution satisfies

$$\epsilon \int_0^\infty \frac{\partial \gamma}{\partial t} \, dz = -\epsilon \int_0^\infty \nabla_s \cdot \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) dz - \bar{\mathbf{F}}_n(X, Y, 0). \tag{14}$$

From this equation, it is clear how we should define the surface excess concentration, surface flux and normal flux to arrive at the surface conservation law (1):

$$\Gamma \equiv \epsilon \int_0^\infty \gamma \, dz, \tag{15}$$

$$\mathbf{J}_s \equiv \epsilon \int_0^\infty \left(\hat{\mathbf{F}}_s - \mathbf{F}_s^* \right) dz, \tag{16}$$

$$J_n \equiv \bar{\mathbf{F}}(X, Y, 0) \cdot \hat{n} = -\mathbf{F}_n^*. \tag{17}$$

The sign difference between J_n and $\bar{\mathbf{F}}_n$ is merely a byproduct of the choice of orientation for the local coordinate system in our analysis. As mentioned earlier, the sign convention for the normal flux is that J_n be positive when the direction of the flux is into the boundary layer.

It is worth mentioning that the presence of the ϵ in the time dependent term and the surface flux term in (14) indicates that the relative importance of these terms relative to bulk transport (i.e., the normal flux term) may depend on the choice of timescales and the magnitude of surface transport. This observation is elaborated upon in the examples discussed in Sections 3 and 4.

2.3. Formulation in terms of chemical potentials

In general, it is best to express driving forces for fluxes in terms of gradients of chemical potentials [38,43]:

$$\mathbf{F}_i = -c_i \left(\sum_j L_{ij} \nabla \mu_j \right) + u c_i, \tag{18}$$

where the L_{ij} are mobility coefficients[3] that relate the drift velocity of species i to the gradient of the chemical potential of species j and u is the background velocity that contributes to advective transport. Note that in order to satisfy (4), we require that the normal component of the background velocity, u_n, at the interface must vanish.

Substituting this expression into (16) and (17) and rearranging a bit, we obtain

$$\mathbf{J}_s^i = -\Gamma_i \left(\sum_j L_{ij} \nabla_s \mu_j^* \right) + \Gamma_i u_s^* + \epsilon \int_0^\infty \hat{c}_i \left(\hat{u}_s - u_s^* \right) dz$$
$$- \epsilon \int_0^\infty \hat{c}_i \nabla_s \left(\sum_j L_{ij} \left(\hat{\mu}_j - \mu_j^* \right) \right) dz, \tag{19}$$

$$J_n^i = -c_i^* \left(\sum_j L_{ij} \frac{\partial \mu_j^*}{\partial n} \right), \tag{20}$$

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[3] In dimensional form, mobility coefficients are related to diffusion coefficients via the Einstein relation: $D_{ij} = kT L_{ij}$. With our choice of energy scale, the dimensionless Einstein relation is $D_{ij} = L_{ij}$.

where we have imposed $\hat{u}_n = 0$, u_s is the tangential component of the background velocity, and the superscript i indicates on the $\mathbf{J}_s$ and J_n indicates that these fluxes are for the ith species.

The expression for $\mathbf{J}_s^i$ can be simplified because the last integral term is equal to zero. As (3) shows, a rescaling of the conservation law associated with (18) to the inner coordinate yields the leading order equation:

$$\frac{\partial}{\partial z}\left[c_i\left(\sum_j L_{ij}\frac{\partial \hat{\mu}_j}{\partial z}\right)\right] = 0. \tag{21}$$

Integrating this equation and using asymptotic matching for the boundary conditions as $z \to \infty$, we find that at leading order,

$$\sum_j L_{ij}\hat{\mu}_j = \sum_j L_{ij}\mu_j^* \tag{22}$$

in the inner layer. That is, special linear combinations of the chemical potentials involving the mobility coefficients are constant in the normal direction and slowly varying in the tangential direction. Equation (21) has the following physical interpretation: in the sharp interface limit, the interfacial layer is always in quasi-equilibrium at the bulk diffusion time scale, $\tau = L^2/D$. It is important to note that at faster time scales, which may be appropriate for systems with external forcing, this result may break down because the time derivative term could balance the normal flux term when (3) is rescaled to the faster time scale.

Using this observation, $\mathbf{J}_s^i$ becomes

$$\mathbf{J}_s^i = -\Gamma_i\left(\sum_j L_{ij}\nabla_s\mu_j^*\right) + \Gamma_i u_s^* + \epsilon\int_0^\infty \hat{c}_i\left(\hat{u}_s - u_s^*\right)\mathrm{d}z. \tag{23}$$

The surface conservation law for transport follows directly from these results:

$$\frac{\partial \Gamma_i}{\partial t} = \nabla_s \cdot \left[\Gamma_i\left(\sum_j L_{ij}\nabla_s\mu_j^*\right) + \Gamma_i u_s^* + \epsilon\int_0^\infty \hat{c}_i\left(\hat{u}_s - u_s^*\right)\mathrm{d}z\right]$$
$$- c_i^*\left(\sum_j L_{ij}\frac{\partial \mu_j^*}{\partial n}\right). \tag{24}$$

It is worth mentioning that the surface transport term (the term involving the surface divergence) does not always contribute to the leading order surface conservation law. Whether the surface transport term must be retained at leading order depends on the magnitudes of Γ_i (which depends implicitly on bulk field variables) and the tangential component of bulk chemical potential gradients. Interestingly, when the surface transport term is significant, the surface conservation law depends explicitly on the small parameter ϵ (through Γ_i).

Theoretical derivation of interfacial structure

While surface conservation laws may be derived by substituting *arbitrary* models for the structure of the boundary layer into (15)–(17), the quasi-equilibrium nature of the interfacial layer allows us to theoretically derive the boundary layer structure from the chemical potential using (22). Starting with a free energy for the system that incorporates the physical effects we

wish to include, chemical potentials may be easily computed as the functional derivatives of the free energy with respect to the concentrations of the individual species[4]:

$$\mu_i = \delta F/\delta c_i, \tag{25}$$

where F is the total free energy of the system. Thus, formulating the transport equations in terms of chemical potentials yields a systematic method for deriving boundary layer structure and surface conservation laws directly from fundamental physical principles without resorting to ad hoc models for the interfacial layer. We shall demonstrate this general approach for several example problems in the next two sections.

3. Applications to neutral solutions

In this section, we present surface conservation laws for neutral solutions. Because we have formulated surface conservation laws in terms of chemical potentials, derivation of the integrated fluxes for these systems is a straightforward application of the formulae in Section 2.3. For simplicity, we shall assume that fluid flow is absent.

3.1. Dilute solutions

For dilute solutions of a single neutral species, we can write the free energy, F, for the system as

$$F = U - TS = \int c\Phi + c(\log c - 1)\,\mathrm{d}x, \tag{26}$$

where U, T and S are the internal energy, the absolute temperature (scaled to 1 in dimensionless units) and entropy of the system, respectively, c is the concentration of solute, and Φ is the energy of interaction between solute particles and the surface (per unit concentration of solute particles). Note that the free energy density per unit concentration of solute in (26) is determined up to an arbitrary additive constant, which we take to be -1 ($-kT$ in dimensional form) to simplify the expression for the chemical potential (derived below). The interaction energy, $\Phi(z)$, between solute particles and the surface extends over a distance ϵ (typically a few molecular diameters) and can account for hydrophobic interactions, polarization effects, etc. $\Phi(z)$ essentially gives the affinity of the solute particles for the surface. Note that in the dilute solution approximation, solute particles do not directly interact with each other or with solvent particles.

Computing the functional derivative of (26), we obtain an expression for the chemical potential

$$\mu = \log c + \Phi. \tag{27}$$

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[4] This expression for the chemical potential implicitly assumes that the system is locally in thermal equilibrium. Given this assumption, it is easy relate (25) to the definition from equilibrium thermodynamics by recognizing that the functional derivative of the total free energy with respect to concentration is merely the partial derivative of the free energy density with respect to concentration, which yields the local chemical potential of the system at each point in space.

As we showed in Section 2.3, in the interfacial layer, $\hat{\mu}$ is equal to μ^* in the normal direction, which leads to a Boltzmann distribution for the concentration:

$$\hat{c}(z) = \exp\big(\mu^* - \Phi(z)\big). \tag{28}$$

We can rewrite this expression in terms of the bulk concentration just outside of the interfacial layer by observing that $c^* = e^{\mu^*}$ from asymptotic matching and the fact that the solute surface interaction decays far away from the surface. Thus, we find that

$$\hat{c}(z) = c^* e^{-\Phi(z)}. \tag{29}$$

Note that this is exactly the boundary layer profile obtained by Anderson et al. using the *assumption* that the interfacial layer is in equilibrium [44].

The surface excess concentration of solute, Γ, is the integral of the excess concentration over the boundary layer:

$$\Gamma = \epsilon \int_0^\infty \big(\hat{c}(z) - c^*\big)\,\mathrm{d}z = \epsilon \int_0^\infty c^*\big(e^{-\Phi(z)} - 1\big)\,\mathrm{d}z. \tag{30}$$

After the integral in this expression has been explicitly evaluated, the surface conservation law for dilute solutions of neutral solutes is derived by substituting the surface excess concentration (30) and the chemical potential (27) into (24), which leads to the following transport equation for the surface excess concentration:

$$\frac{\partial \Gamma}{\partial t} = L\left[\nabla_s \cdot \big(\Gamma \, \nabla_s \log c^*\big) - \frac{\partial c^*}{\partial n}\right], \tag{31}$$

where L is the nondimensional mobility coefficient for solute particles. It is interesting to observe that the driving force for surface transport and the source term for transport between the bulk and interfacial regions depend only on the concentration in the bulk. This result is generally true for transport problems where fluid flow is negligible.

3.2. Concentrated solutions

For concentrated solutions of a single neutral species, the size of the individual solute particles cannot be neglected and steric effects must be accounted for. Bulk solutions are considered concentrated when the dimensionless parameter $\nu = a^3 c_{\max}$, which represents the bulk volume fraction of solute, is not small. In this case, we can use concentrated solution theory to qualitatively describe bulk transport. However, even when $\nu \ll 1$, concentrated solution theory may be necessary if the surface interaction energy, Φ, is strong enough to condense particles near the surface. As for dilute solutions, we begin by writing the free energy for the system using ideal solution theory [45]:

$$F = U - TS$$
$$= \int c\Phi + \big[c \log c + (1-c) \log(1-c)\big]\,\mathrm{d}x, \tag{32}$$

where the last term in F accounts for the entropy of the solvent particles, assuming they have the same size as the solute particles. This classical model for steric effects, dating back at least

to Bikerman [46], can be derived by taking the continuum limit of a discrete model with solute and solvent molecules restricted to a regular lattice. As such, it can be good approximation for solid solutions, such as lithium intercalation oxides [47], although it substantially underestimates steric effects in liquids. It would be straightforward to apply our general derivation of surface conservation laws to more accurate approximations of the entropy of hard-sphere liquids [48], so we proceed with this simple first approximation.

Taking the functional derivative of (32), we find that the chemical potential for concentrated solutions is given by

$$\mu = \log\left(\frac{c}{1-c}\right) + \Phi. \tag{33}$$

Note that unlike dilute solutions, there is a maximum concentration for the solute that arises from the sharp increase in the chemical potential at high solute concentrations (low solvent concentrations) caused by the solvent's entropic contribution to the free energy.

As before, we can derive the concentration profile of solute atoms by using the fact that, within the interfacial layer, the chemical potential is constant in the direction normal to the surface:

$$\hat{c}(z) = \exp\big(\mu^* - \Phi(z)\big)\big[1 + \exp\big(\mu^* - \Phi(z)\big)\big]^{-1}. \tag{34}$$

For concentrated solutions, the simple Boltzmann distribution for the quasi-equilibrium concentration profile in the normal direction is replaced by a Fermi–Dirac-like distribution with a maximum concentration of 1 ($c_{\max} = 1/a^3$ in dimensional form). Note that expression of $\hat{c}(z)$ in terms of the bulk concentration, c^*, outside of the interfacial layer does not lead to a significant simplification of (34). The surface excess concentration is found by integrating (34) over the interfacial layer.

To derive the surface conservation law for concentrated neutral solutions, we substitute (33) and the expression for the surface excess concentration into the general formula for the surface conservation law in terms of chemical potentials (24).

4. Application to electrolytes

In electrochemical systems, the solute particles are electrically charged, so transport processes are affected by electric fields (both self-generated and externally applied). When modeling electrochemical systems, it is common to model transport in the bulk separately from the response of the double layer at surfaces. Surface conservation laws justify and generalize the usual phenomenological approaches for coupling bulk and double layer dynamics. In this section, we discuss surface conservation laws for dilute and concentrated electrolyte solutions. As we shall see, the key difference between these two cases is the microscopic model that must be used to describe the electrical double layer.

For electrolytes, transport is driven by gradients in the electrochemical potential, so the nondimensionalized conservation laws for ionic species are given by

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (c_i \nabla \mu_i + c_i v), \tag{35}$$

where c_i are the concentration of ion i, μ_i is the electrochemical potential for species i, v is the fluid velocity, and we have assumed that all of the ions have the same diffusivity [38]. Note that the flux in this equation is just a special case of (18) where L_{ij} is an identity matrix.[5] While fluid flow plays an important role in many systems of current interest (e.g., electrokinetic microfluidic pumps and mixers [13,14,19,20]), we shall neglect it to keep the following discussion simple. In this situation, the surface conservation law (24) becomes

$$\frac{\partial \Gamma_i}{\partial t} = \nabla_s \cdot \left(\Gamma_i \nabla_s \mu_i^* \right) - c^* \frac{\partial \mu_i^*}{\partial n}. \tag{36}$$

Before considering ion transport in various special cases, we mention that for electrochemical systems, the small parameter ϵ is the ratio of the Debye screening length, λ_D, to the characteristic system size. In this article, the Debye length will be defined by

$$\lambda_D = \sqrt{\frac{\epsilon_s kT}{2e^2 C_0}}, \tag{37}$$

where ϵ_s is the dielectric constant for the electrolyte and C_0 is the average concentration of neutral salt. Alternative choices for the Debye length typically differ from this definition by an $O(1)$ multiplicative constant.

4.1. Dilute electrolytes

The free energy for general dilute electrolyte solutions is similar to the free energy for dilute neutral solutions:

$$\begin{aligned} F &= U - TS \\ &= \int \left(\sum_i c_i (\log c_i - 1) + \sum_i z_i c_i \phi - \epsilon^2 |\nabla \phi|^2 \right) dx. \end{aligned} \tag{38}$$

In this expression, the first term in the integrand is the entropic contribution from the solute particles, the second term accounts for the interaction energy between the charged particles and the electric potential, and the last term is the energy of the electric field. Note that ϵ is defined to be consistent with the definition in (37).

Taking the functional derivative of the free energy with respect to c_i, we find that the electrochemical potential of the ith ionic species takes the simple form

$$\mu_i = \log c_i + z_i \phi. \tag{39}$$

Using (39) for the electrochemical potential, (35) reduces to the commonly used Nernst–Planck equations [37,49]:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (\nabla c_i + z_i c_i \nabla \phi). \tag{40}$$

Within the double layer, the electrochemical potential is constant in the normal direction, so the concentration profile possesses a Boltzmann distribution:

$$\hat{c}_i(z) = c_i^* e^{-z_i \hat{\psi}(z)}, \tag{41}$$

where $\hat{\psi}(z) \equiv \hat{\phi}(z) - \phi^*$.

For the case of a symmetric, binary electrolyte, (41) leads to the commonly used Gouy–Chapman–Stern (GCS) model for the double layer [23,37,38,50]. It is well known that the GCS model can be theoretically justified by noting that the double layer is always in quasi-equilibrium in the sharp interface limit [51]. However, the quasi-equilibrium structure of the double layer is not at all surprising in light of our discussion in Section 2.3—it follows directly from the fact that the electrical double layer is a sharp interfacial layer.

For symmetric, binary electrolytes, we can derive explicit expressions for the excess surface concentrations. In this case, the excess concentration of each of the two ionic species is given by

$$\gamma_\pm = \hat{c}_\pm - c_\pm^* = c^* \left(e^{\mp z_\mp \hat{\psi}} - 1 \right), \tag{42}$$

where $c^* = (c_+^* + c_-^*)/2$ is the average concentration in the bulk and $z_\mp$ is the charge number for the positive ion. Following [52], this quantity is straightforward to integrate by changing the variable of integration in (15) to $\hat{\psi}$ and using the fact that

$$\frac{\partial \hat{\psi}}{\partial z} = -2\sqrt{c^*} \sinh\left(\frac{z_\mp \hat{\psi}}{2} \right) \tag{43}$$

for the GCS model. Carrying out the integration, we find that the excess surface concentration of species i is given by

$$\Gamma_\pm = \frac{2\epsilon \sqrt{c^*}}{z_\mp} \left(e^{\mp z_\mp \zeta/2} - 1 \right), \tag{44}$$

where $\zeta = \hat{\phi}(0) - \phi^*$ is the zeta-potential [23,37,38] across the diffuse part of the double layer. Using this expression for $\Gamma_\pm$ in (36), the surface conservation law for symmetric, binary electrolytes is fully specified in terms of bulk field variables and boundary conditions, and the structure of the boundary layer has been completely integrated out.

Because the charge density and neutral salt concentration are both important components of the response of an electrochemical system, it is interesting to derive surface conservation laws for these quantities [8,52]. Toward this end, we define ϵq and ϵw to be the surface charge density and surface excess neutral salt concentration, respectively[6]:

$$\begin{aligned} \epsilon q &= \frac{\epsilon}{2} \int_0^\infty (\gamma_+ - \gamma_-) \, dz \\ &= \frac{1}{2} (\Gamma_+ - \Gamma_-) = -\frac{2\epsilon \sqrt{c^*}}{z_+} \sinh\left(\frac{z_+ \zeta}{2} \right), \end{aligned} \tag{45}$$

$$\begin{aligned} \epsilon w &= \frac{\epsilon}{2} \int_0^\infty (\gamma_+ + \gamma_-) \, dz \\ &= \frac{1}{2} (\Gamma_+ + \Gamma_-) = \frac{4\epsilon \sqrt{c^*}}{z_+} \sinh^2\left(\frac{z_+ \zeta}{4} \right). \end{aligned} \tag{46}$$

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[5] In dimensional form, L_{ij} would be a scalar multiple of the identity matrix.

[6] The factor of $1/2$ in the definition of q is present for mathematical convenience. The total surface charge density is $2\epsilon q$.

Using (45) and (46), we can combine the surface conservation laws for individual ions (36) and write out the electrochemical potential in terms of c^* and ϕ^* to obtain

$$\epsilon \frac{\partial q}{\partial t} = \epsilon \nabla_s \cdot \left(q \nabla_s \log c^* + z_+ w \nabla_s \phi^* \right) - z_+ c^* \frac{\partial \phi^*}{\partial n}, \qquad (47)$$

$$\epsilon \frac{\partial w}{\partial t} = \epsilon \nabla_s \cdot \left(w \nabla_s \log c^* + z_+ q \nabla_s \phi^* \right) - \frac{\partial c^*}{\partial n}. \qquad (48)$$

Since we have explicit expressions for q and w, (47) and (48) are completely specified in terms of bulk field variables yielding surface conservation laws that can serve as effective boundary conditions for the bulk equations written in terms of these field variables [8,51,52].

4.2. Concentrated electrolytes

The simplest theory of transport in concentrated electrolytes is based on the free energy

$$\begin{aligned} F &= U - TS \\ &= \int \left(\sum_i c_i \log c_i + \left(1 - \sum_i c_i \right) \log \left(1 - \sum_i c_i \right) \right. \\ &\quad \left. + \sum_i z_i c_i \phi - \epsilon^2 |\nabla \phi|^2 \right) dx. \end{aligned} \qquad (49)$$

As for concentrated neutral solutions, steric effects are included by adding a contribution from the solvent entropy as in (32), assuming that the molecules of all species present in the system (including the solvent) are of the same size. This model, due to Bikerman [46], has been developed by a number of authors [53–59]. As noted above, it may be accurate for solid electrolytes but significantly underestimates the entropy of liquid electrolytes and thus only provides a first approximation of steric effects [48]. It is important to mention that there are more sophisticated (and accurate) theories involving statistical density functional theory [60–63]. Unfortunately, these theories are generally more cumbersome to analyze and often require advanced numerical methods in order to gain physical insight [59].

Next, we derive electrochemical potentials for the ith ionic species by taking the functional derivative of the free energy with respect to the ith concentration:

$$\mu_i = \log \left(\frac{c_i}{1 - \sum_j c_j} \right) + z_i \phi. \qquad (50)$$

Following Kilic et al. [64], this expression for the electrochemical potential leads to a modified Nernst–Planck equation for ion transport

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left(\nabla c_i + z_i c_i \nabla \phi + \left[\frac{c_i}{1 - \sum_j c_j} \right] \sum_j \nabla c_j \right). \qquad (51)$$

Notice that, unlike dilute electrolytes, the transport of different ionic species are directly coupled via the last term in the flux.

Following our previous procedure, we can derive the concentration profile of each ionic species within the double layer by using the fact that each of the μ_i must be constant in the normal direction. This observation leads to a linear system of equations for the ionic concentrations, which is easily solved to yield

$$\hat{c}_i(z) = \frac{\exp(\mu_i^* - z_i \hat{\phi}(z))}{1 + \sum_j \exp(\mu_j^* - z_j \hat{\phi}(z))}. \qquad (52)$$

As for concentrated neutral solutions, the concentration profiles have a Fermi–Dirac-like form.

A little further progress can be made for the special case of symmetric, binary electrolytes. The excess concentrations of the ionic species in this case are given by

$$\gamma_\pm = \hat{c}_\pm - c_\pm^* = c^* \left[\frac{e^{\mp z_\mp \hat{\psi}}}{1 + 2\nu \sinh^2(z_\mp \hat{\psi}/2)} - 1 \right], \qquad (53)$$

where c^*, $\hat{\psi}$ and ν are as defined in our discussion of dilute electrolytes and concentrated neutral solutions. Unfortunately, integration of these excess concentrations for the concentrated electrolyte model does not yield a particularly simple expression for the surface excess concentration [59]:

$$\begin{aligned} \Gamma_\pm &= \mp \operatorname{sgn}(\zeta) z_\mp \epsilon \sqrt{\frac{2}{\nu} \log \left(1 + 2\nu \sinh^2(z_\mp \zeta/2) \right)} \\ &\quad + (1 - \nu)\epsilon \int_0^{z_\mp \zeta} \frac{\cosh u - 1}{1 + 2\nu \sinh^2 u} \\ &\quad \times \left[\frac{2}{\nu} \log \left(1 + 2\nu \sinh^2 u \right) \right]^{-1/2} du. \end{aligned} \qquad (54)$$

Combining this expression for the surface excess concentration and the electrochemical potential for concentrated electrolytes (50) yields the surface conservation law for concentrated, symmetric binary electrolytes.

4.3. Dominant terms in electrochemical surface conservation laws

In general, the relative importance of the terms in a set of surface conservation laws (written in any form) may depend on the choice of time scales and the magnitude of surface transport. In the context of electrochemical transport, we find that the boundary conditions applied in many theoretical studies are merely the leading order form (in different asymptotic and physical regimes) of the surface conservation laws derived in the previous section. For instance, in induced charge electroosmosis problems in dilute solutions at weak applied electric fields [19,20], ϵq and ϵw remains $O(\epsilon)$ quantities. Thus, compared to the normal flux term, the surface flux term is negligible and the time-dependent term is only important at short times, $t = O(\epsilon)$. In this situation, the double layer charging equation (47) becomes [19,20]:

$$\frac{\partial q}{\partial \tilde{t}} = \sigma \frac{\partial \phi}{\partial n}, \qquad (55)$$

where $\sigma = c^*$ is the bulk conductivity of the solution and time has been rescaled using $\tilde{t} = t/\epsilon$ so that the dynamics are on the RC time scale [8,19,20]. At $t = O(1)$ time scales, only the

normal flux remains an $O(1)$ quantity, so we are left with a "insulator" boundary condition for the electric potential:

$$\sigma \frac{\partial \phi}{\partial n} = 0. \tag{56}$$

At higher applied fields or for highly charged particles [4–7, 52], the dilute solution electrolyte model leads to surface excess concentrations as large as $O(1/\epsilon)$ for some of the ionic species in the double layer. As a result, surface currents becomes important and evolution of ionic concentrations within the double layer occurs on an $O(1)$ time scale. In this situation, no terms in (36) are negligible, so we must retain all terms in (47) and (48).

5. Summary

In this article, we have presented a general formulation and derivation of surface conservation laws at microscopically diffuse interfaces. Because surface conservation laws form the crucial connection between bulk and interfacial dynamics, it is important to know that they are theoretically well-founded. Our work fills this apparent void in the literature and provides a solid theoretical foundation based on techniques from asymptotic analysis. Our analysis has also led to explicit formulae for the surface and normal fluxes involved in surface conservation laws. In addition to formulae for arbitrary interfacial models, we have presented a formulation of surface conservation laws for the important class of interfacial models derived using the principles of nonequilibrium thermodynamics. This formulation provides a method for developing interfacial models in a systematic and physically sound manner. Finally, we have demonstrated the derivation of surface conservation laws in the specific contexts of diffusive and electrochemical transport. We emphasize, however, that surface conservation laws are very general and apply to a wide-range transport processes. The basic approach is to first specify (or derive) a model for the interfacial layer and then to compute the surface excess concentrations and surface flux using the general formulae presented in this article.

Acknowledgments

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