

Interaction of Ionic Solution with Permeable Membranes: a Variational Approach

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Abstract. The movement of ionic solutions is an essential part of biology and technology. Fluidics, from nano-to microfluidics, is a burgeoning area of technology which is all about the movement of ionic solutions, on various scales. Many cells, tissues, and organs of animals and plants depend on osmosis, as the movement of fluids is called in biology. Indeed, the movement of fluids through channel proteins (that have a hole down their middle) is fluidics on an atomic scale. Ionic fluids are complex fluids, with energy stored in many ways. Ionic fluid flow is driven by gradients of concentration, chemical and electrical potential, and hydrostatic pressure. In this paper, a series of sharp interface models are derived for ionic solution with permeable membranes. By using the energy variation method, the unknown flux and interface conditions are derived consistently. We start from the derivation the generic model for the general case that the density of solution varies with ionic solvent concentrations and membrane is deformable. Then the constant density and fix membrane cases are derived as special cases of the generic model.

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1 Introduction

Osmosis moves ionic solutions throughout biology and technology. It is hard to find a more widespread phenomenon. All biology occurs in ionic solutions [1, 2] that move on many scales, including atomic scales smaller than nanometers, and a great deal of chemistry involves ionic movement as well. The modern technology of fluidics — macro, micro and nano — usually moves water and ions and thus involves osmosis at every scale. Indeed, the modern names “x-fluidics” (where x=nano, micro, and someday pico) may be viewed as a renaming of a classical [3], if not ancient word [4] into more modern language.

Ionic solutions involve energy stored in many forms, pressure, concentration, electric and electrochemical potential, steric interactions, and chemical energy (We define ‘chemical’ forces between atoms as those that significantly change the spatial distribution of electrons in the atoms. In this definition, dielectric interactions are not a chemical force. More precisely, force produced by the induced charge, that is proportional to the local electric field, is not a chemical force. Dispersion forces arise from the quantum fluctuations in induced (‘dielectric’) forces and so are not considered chemical in this definition). At the same time, ionic solutions always include flows of many types, usually in a coherent consistent way. Here, ‘Consistent’ means that all variables satisfy all equations and all boundary conditions with one set of parameters. Ions interact and move as components of complex fluids [5–12]. The solution itself flows more or less as water itself would move (without the ions). Water molecules and ions move (partly) by bulk flow, that is to say, they move (partly) by convection described classically by Navier Stokes equations. Water molecules and ions also move (partly) by diffusion. Ions move (partly) because of the electric field. Water also moves in an electric field because of dielectrophoresis [13,14] when the electric field is nonuniform i.e., $|\nabla E| > 0$, where E is the electric field. Each of these flows varies with location and is described by field equations — typically partial differential equations in space and time — along with boundary conditions, that idealize the physics of the particular setup in which the flows occur. So ionic solutions are complex fluids [5, 15, 16].

The theory of complex fluids has developed consistent theories for many complex systems [10,17–19] that are mixtures (or even ionic solutions) with components that store energy. Variational methods deal successfully with magnetohydrodynamics systems [20], liquid crystals, polymeric fluids [11,12], colloids and suspensions [17,21] and electrorheological fluids [22]. The variational approach is widely used to analyze complex fluids because it derives field equations and boundary (or interface boundary) conditions, rather than assumes them. Once energy and dissipation functionals are defined by a physical model, the interaction terms in the field equations for each flow (bulk flow, diffusional

flow, and electrical migration) are determined by algebra and analysis with minimal adjustable parameters. All variables satisfy all equations with one set of parameters when the analysis is done correctly. Results fit experiments, over a range of conditions with one set of parameters, if the original functional equations — from which the field equations are derived — are a correct enough model of the physics of the system, and the description of the constraints and boundary conditions is adequate.

The Energetic Variational Approach (EnVarA) of Liu, et al., has been applied to ionic solutions of interest in references [16, 23–27]. EnVarA combines the Least Action Principle of Hamiltonian dynamics with the Maximum Dissipation Principle of Onsager (who used the dissipation function of Rayleigh) [5, 16] into a set of field equations, typically in Eulerian coordinates. Variations are taken with respect to two different variables, position and flow rate. The resulting field equations are written in one set of coordinates — usually Eulerian — with push-forward and pull-back methods. The obtained system is always thermodynamically consistent.

However, due to flow map constraints, EnVarA normally assumes the system is closed, which means that vanishing boundary conditions are used. When an interface is present within the system, not just on the boundaries, phase field method is used to smooth the solutions (or flow map) across the boundary condition. When the internal interface is permeable for fluid, phase field methods provide challenges. For many problems in biology and other applications, internal boundaries are main drivers of the process of interest, for example cell volume control and electroporation [28–31] and hemo/electrodialysis [32–34].

Most field theories do not include boundary conditions in their original form and the result of that is boundary conditions are an afterthought, which may not be consistent with the field equations. What we want to do is to include the interface or boundary as a part of the theory. Sometimes the equations behave differently near the boundary, and the boundary layer theory is a classical example. Boundary (or interface boundary) constraints of the physical problem can be converted into mathematical boundary conditions using the energy variational method [35–40]. The maximum dissipation principle (attributed to Onsager [41, 42] developed from the work of Rayleigh [43, 44] is often used to describe sharp interfaces [5, 16]. Here we combine the energy variational approach (to field equations) with the sharp interface approach to physical constraints and use the combination to analyze a classical osmotic cell [3, 45, 46], two baths separated by a semipermeable membrane — with flows driven by electrical, diffusion, and pressure fields, neglecting for the moment the steric and chemical forces of non-ideal solutions, or heat driven flows. Liu and colleagues have had some success creating what we call ‘thermal dynamics’ that deals consistently with heat driven flows in the spirit of EnVarA and the theory of complex fluids [47–49].

Our analysis of osmotic flow is in the spirit of a variational approach, combining elements of EnVarA and a sharp interface analysis that itself uses variational ideas. We also deal explicitly with the variation of the density of a solution with concentration [50] responsible for the difference between molal and molar concentration units, taught to

everyone who makes up solutions (from solid solutes) in a laboratory [51]. This density dependence may be important in some experimental setups and conditions.

The paper is organized as follows. The mathematical model for a permeable membrane is developed in Section 2. The development depends on several unknown variables. In Section 3, those variables are developed for the case where solution density is a function of ion concentration. Those unknown variables are evaluated for the case of constant density in Section 4. A historical section and discussion conclude the paper.

2 General framework

We consider the dynamics of a fluid with ions passing through a seim-permeable membrane in the traditional setup of physical chemists and biologists [46, 52–57] following [58, 59]. We use the sharp interface model [35, 37, 38, 40, 60] to derive detailed specific conditions on the membrane. Let Ω^\pm denote two compartments separated by a membrane Γ where $\Omega = \Omega^+ \cup \Omega^-$ (see Fig. 1). \mathbf{D}^\pm is the electric displacement vector field of classical electrodynamics and c_i^\pm is the distribution of the of i_{th} ($i = 1, \dots, N, \dots, Np$) species of particles in domain Ω^\pm , respectively. More precisely, from 1_{st} to N_{th} , it is ionic particle and from $N + 1_{th}$ to Np_{th} , it is electroneutral particle. ρ^\pm and \mathbf{u}^\pm are the density and velocity of solutions in left and right compartments, respectively.

Kinematic Assumptions. Based on the Maxwell's equations and conservation law for the mass of each ionic species, we have the following equations

$$\left\{ \begin{array}{ll} \nabla \cdot \mathbf{D}^\pm = \sum_{i=1}^N z_i e c_i^\pm, & \text{in } \Omega^\pm, \\ \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (c_i^\pm \mathbf{u}^\pm) = -\nabla \cdot \mathbf{j}_i^\pm, \quad i = 1, \dots, Np, & \text{in } \Omega^\pm, \\ \rho^\pm \left(\frac{\partial \mathbf{u}^\pm}{\partial t} + (\mathbf{u}^\pm \cdot \nabla) \mathbf{u}^\pm \right) = \nabla \cdot (\boldsymbol{\sigma}_\eta^\pm + \boldsymbol{\sigma}_e^\pm), & \text{in } \Omega^\pm, \\ \frac{\partial \rho^\pm}{\partial t} + \nabla \cdot (\rho^\pm \mathbf{u}^\pm) = 0, & \text{in } \Omega^\pm, \end{array} \right. \quad (2.1)$$

where z_i is the valence of the i_{th} species, e is the elementary charge, \mathbf{j}_i^\pm is the flux of the i_{th} species $\boldsymbol{\sigma}_\eta^\pm$ is the viscous stress, and $\boldsymbol{\sigma}_e^\pm$ is the electric stress in domain Ω^\pm , respectively. $\boldsymbol{\sigma}_\eta^\pm$ and $\boldsymbol{\sigma}_e^\pm$ are symmetric tensors.

If we neglect the magnetic forces, there exist an electric field \mathbf{E}^\pm and electric potential ϕ^\pm such that $\mathbf{D}^\pm = \epsilon_0 \epsilon_r^\pm \mathbf{E}^\pm = -\epsilon_0 \epsilon_r^\pm \nabla \phi^\pm$, where $\epsilon_0 \epsilon_r^\pm$ is the dielectric constant in domain Ω^\pm , respectively. We assume the dielectric constant ϵ_r^\pm (units: dimensionless) and the permittivity $\epsilon_0 \epsilon_r^\pm$ (units: farads/meter) are each a single real number and do not deal with the nonideal properties of ionic solutions, despite our understanding of their significance, and the importance of nonideality in general [1, 61, 62]. We have to start somewhere and we have our hands full with the mathematics needed to deal consistently with these idealized cases. When we do reach to include nonideality, we anticipate difficulties. Even the proper formulation of the field equations (with flow) in the nonideal case remains an open question.

For the interface condition of the surface Γ , also based on conservation law [63], we assume that on Γ

$$\begin{cases} \frac{dX}{dt} = v, \\ D^\pm \cdot n = Q(x), \\ \rho^\pm u^\pm \cdot n - \rho^\pm v \cdot n = Q_\rho, \\ u^\pm \cdot \tau = v \cdot \tau, \\ [\sigma_\eta + \sigma_e] \cdot n - [Q_\rho u] = F_{mb} \\ j_i^\pm \cdot n + c_i^\pm (u^\pm - v) \cdot n = J_i(x), \quad i = 1, \dots, Np, \end{cases} \quad (2.2)$$

where $X(\cdot, t)$ is the trajectories of points on the membrane, $v = v_\tau + v_n n$ is the velocity of membrane with normal vector n and tangential vector τ , $[f] = f^+ - f^-$ is the difference of f across the interface Γ . We also assume that $u^\pm = v = 0$ on $\partial\Gamma$, i.e., we assume the edge (or boundary) of membrane is fixed. Here $Q(x)$, $Q_\rho(x)$, and $J_i(x)$ are surface charge density, solution flux and ion flux on the interface, respectively. F_{mb} is the membrane force induced by mechanical and dielectric properties of membrane.

In the next, we will derive the explicit forms of j_i^\pm , σ_e^\pm , $Q(x)$, Q_ρ , $J_i(x)$ and F_{mb} based on the second law of thermodynamics generalized to deal with flows driven by different forces.

In our case, and many others [17,35,37,38,60], the total energy functional is the sum of the kinetic energy part $E_{kin}(\rho, u)$, internal energy $E_{int}(c_i, \phi)$ and surface energy $E_\Gamma(\phi, \gamma_0)$. The internal energy is composed of the electrostatic energy part $E_{es}(\phi)$, and the Gibbs free energy of particles $E_{par}(c_i)$. The total energy functional is the precise statement of our field model (that is to say our physical model without boundary ($\partial\Omega$) constraints or conditions). And the total energy functional is given by

$$\begin{aligned} E^{tot} &= E_{kin} + E_{int} + E_\Gamma \\ &= E_{kin} + E_{es} + E_{par} + E_\Gamma \\ &= \sum_{\pm} \int_{\Omega^\pm} (e_{kin}^\pm + e_{es}^\pm + e_{par}^\pm) dx + \int_\Gamma (e_\Gamma + \gamma_0) dS \\ &= \sum_{\pm} \int_{\Omega^\pm} \left\{ \frac{1}{2} \rho^\pm |u^\pm|^2 + \frac{1}{2} E^\pm \cdot D^\pm + k_B T \sum_i^{Np} c_i^\pm \ln \left(\frac{c_i^\pm}{c_0} \right) \right\} dx + \int_\Gamma \left(\frac{C_m}{2} [\phi]^2 + \gamma_0 \right) dS, \end{aligned} \quad (2.3)$$

where c_0 is a characteristic ion density, C_m is membrane capacitance, γ_0 is the membrane surface tension. In the following, square brackets always denote the jumps across the interface. The dissipation functional is defined as

$$\begin{aligned} \Delta &= \sum_{\pm} \int_{\Omega^\pm} 2\eta^\pm |D_\eta^\pm|^2 dx + \sum_{\pm} \int_{\Omega^\pm} \lambda^\pm |\nabla \cdot u^\pm|^2 dx \\ &\quad + \int_{\Omega^\pm} \sum_i R_i^\pm |j_i^\pm|^2 dx + \int_\Gamma G_1(J_i) dS + \int_\Gamma G_2(Q_\rho) dS, \end{aligned} \quad (2.4)$$

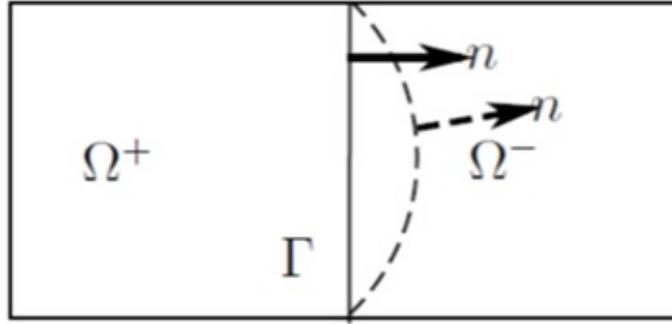


Figure 1: Schematic of a flexible membrane. Solid line is initial shape of membrane and the dashed line denotes the deformed membrane. \mathbf{n} is the normal vector of membrane Γ from the left compartment Ω^+ to the right compartment Ω^- .

where $\mathbf{D}_\eta = (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)/2$ is rate of strain, η^\pm and λ^\pm is the two Lamé constants [63], R_i^\pm are the resistance of i_{th} particles in the bulk region. The first three terms in dissipation functional are the dissipation induced by fluid friction, volume change and particles diffusion in the bulk region. The last two terms are the dissipation induced by irreversible osmosis on the membrane. The forms of $G_1(x) \geq 0$ and $G_2(x) \geq 0$, for any x , will be discussed later.

We start from the most general case that the membrane is deformable (see Fig. 1) and fluid density is a function of ion density $\rho = \hat{\rho}(c_1^\pm, \dots, c_{Np}^\pm)$. Based on the biological applications, here we consider the case that ρ weakly depends on the ion concentration.

During the derivation, the following generalized Reynolds transfer formula [64,65] is used repeatedly when the membrane is permeable

$$\begin{aligned} & \frac{d}{dt} \sum_{\pm} \int_{\Omega^\pm(t)} f^\pm dx & (2.5) \\ &= \sum_{\pm} \int_{\Omega^\pm(t)} \frac{\partial f^\pm}{\partial t} dx + \int_{\Gamma} [f] \mathbf{v} \cdot \mathbf{n} dS \\ &= \sum_{\pm} \int_{\Omega^\pm(t)} \left(\frac{Df^\pm}{Dt} + f^\pm \nabla \cdot \mathbf{u}^\pm \right) dx - \int_{\Gamma} \left[\frac{f}{\rho} \right] Q_\rho dS - \int_{\partial\Omega} f^\pm \mathbf{u}^\pm \cdot \mathbf{n} dS, \end{aligned}$$

where $\int_{\partial\Omega(t)} f^\pm dS = \int_{\partial\Omega \cap \bar{\Omega}^+} f^+ dS + \int_{\partial\Omega \cap \bar{\Omega}^-} f^- dS$, $\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla$ is the material derivative. Based on the results in [40, 66, 67] we have the following formula for surface defined function f ,

$$\frac{d}{dt} \int_{\Gamma(t)} f dS = \int_{\Gamma(t)} (\dot{f} + f \nabla_{\Gamma} \cdot \mathbf{v}) dS \tag{2.6}$$

$$\begin{aligned}
&= \int_{\Gamma(t)} \left(\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + f \nabla_{\Gamma} \cdot \mathbf{v} \right) dS \\
&= \int_{\Gamma(t)} \left(\frac{\partial f}{\partial t} + v_n \partial_n f + \mathbf{v}_{\tau} \cdot \nabla_{\Gamma} f + f \nabla_{\Gamma} \cdot \mathbf{v} \right) \\
&= \int_{\Gamma(t)} \frac{\partial f}{\partial t} + v_n \partial_n f dS + \int_{\partial\Gamma(t)} f \mathbf{v}_{\tau} \cdot \mathbf{n}_m dl - \int_{\Gamma(t)} f H \mathbf{n} \cdot \mathbf{v} dS \\
&= \int_{\Gamma(t)} \left(\frac{d^n f}{dt} \right) dS - \int_{\Gamma(t)} f H \mathbf{n} \cdot \mathbf{v} dS,
\end{aligned}$$

where $\nabla_{\Gamma} = \nabla - \mathbf{n}(\mathbf{n} \cdot \nabla)$ is the surface gradient operator, $\dot{f} = \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f$ is the material derivative on the membrane, $\frac{d^n f}{dt} = \frac{\partial f}{\partial t} + v_n \partial_n f$ is the normal time derivative, \mathbf{n}_m is the unit outward normal vector of membrane at the edge $\partial\Gamma$, i.e., $\mathbf{n}_m \cdot \mathbf{n} = 0$, $\mathbf{n}_m \cdot d\mathbf{l} = 0$ and $H = -\nabla \cdot \mathbf{n}$ is the mean curve of membrane Γ . Here we used the fact that $\mathbf{v} = \mathbf{0}$ on $\partial\Gamma$ in our model.

The following useful lemma states that the a normal time derivative of normal vector on the surface only depends on normal component of membrane velocity.

Lemma 2.1. *Let \mathbf{n} and $\mathbf{v} = v_n \mathbf{n} + \mathbf{v}_{\tau}$ be the outward normal vector and velocity of membrane Γ , respectively. Then we have the following result*

$$\frac{d^n \mathbf{n}}{dt} = -\nabla_{\Gamma} v_n.$$

The proof of Lemma 2.1 is presented in Appendix A. Now we begin to derive the full model. If we take the derivative of the energy (2.3),

$$\frac{dE^{tot}}{dt} = \frac{dE_{kin}}{dt} + \frac{dE_{es}}{dt} + \frac{dE_{par}}{dt} + \frac{dE_{\Gamma}}{dt} =: I_1 + I_2 + I_3 + I_4 \quad (2.7)$$

According to careful calculation (details are presented in Appendix B), Eq. (2.7) can be written as

$$\begin{aligned}
\frac{dE^{tot}}{dt} &= -\sum_{\pm} \int_{\Omega^{\pm}} \boldsymbol{\sigma}_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \left(\boldsymbol{\sigma}_e^{\pm} - \epsilon_0 \boldsymbol{\epsilon}_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) \right) : \nabla \mathbf{u}^{\pm} dx \\
&\quad + \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} \nabla \tilde{\mu}_i^{\pm} \cdot \mathbf{j}_i^{\pm} dx - \int_{\Gamma} \sum_{i=1}^{Np} [\tilde{\mu}_i] J_i dS \\
&\quad + \sum_{\pm} \int_{\Omega^{\pm}} \left(-\sum_{i=1}^{Np} k_B T c_i^{\pm} - p_c^{\pm} \left(1 - \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i^{\pm} \right) \right) \nabla \cdot \mathbf{u}^{\pm} dx \\
&\quad + \int_{\Gamma} (\mathbf{F}_{mb} + [Q \nabla \phi]) \cdot \mathbf{v}_{\tau} dS + \int_{\Gamma} (\mathbf{F}_{mb} \cdot \mathbf{n} + [F_n] - (e_{\Gamma} + \gamma_0) H) v_n dS \\
&\quad + \int_{\Gamma} \left[\frac{F_{\rho}}{\rho} \right] Q_{\rho} dS + \int_{\Gamma} [\phi] \frac{d^n}{dt} (C_m[\phi] - Q) dS - I_b, \quad (2.8)
\end{aligned}$$

where $\tilde{\mu}_i^\pm = \mu_i^\pm - p_c^\pm \frac{\partial_i \rho^\pm}{\rho^\pm}$, $i = 1, \dots, Np$, with

$$\mu_i^\pm = \begin{cases} z_i e \phi^\pm + k_B T \left(\ln \left(\frac{c_i^\pm}{c_0} \right) + 1 \right), & \text{for } i = 1, \dots, N, \\ k_B T \left(\ln \left(\frac{c_i^\pm}{c_0} \right) + 1 \right), & \text{for } i = N+1, \dots, Np, \end{cases} \quad (2.9)$$

$$I_b = I_{1b} + I_{2b} + \int_{\partial\Omega} \left(p_c^\pm \sum_i \frac{\partial_i \rho^\pm}{\rho^\pm} \right) \mathbf{j}_i^\pm \cdot \mathbf{n} \, dS, \quad (2.10)$$

$$\begin{aligned} F_n &= Q \nabla \phi \cdot \mathbf{n} + \left(\sum_{i=1}^{Np} k_B T c_i + 2e_{es} + e_{par} - \sum_{i=1}^{Np} c_i \mu_i \right) - \nabla_\Gamma \cdot \left(\nabla_\Gamma \left(\frac{\epsilon_0 \epsilon_r}{2} \phi^2 \right) \right) + \phi (\partial_n \mathbf{D} \cdot \mathbf{n}) \\ &= Q \partial_n \phi + \left(2e_{es} - \sum_{i=1}^N c_i z_i e \phi \right) - \nabla_\Gamma \cdot \left(\nabla_\Gamma \left(\frac{\epsilon_0 \epsilon_r}{2} \phi^2 \right) \right) + \phi (\partial_n \mathbf{D} \cdot \mathbf{n}) \\ &= Q \partial_n \phi + \left(\epsilon_0 \epsilon_r |\nabla_\Gamma \phi|^2 + \epsilon_0 \epsilon_r |\partial_n \phi|^2 - \sum_i c_i z_i e \phi \right) \\ &\quad - \left(\epsilon_0 \epsilon_r |\nabla_\Gamma \phi|^2 + \epsilon_0 \epsilon_r \phi \Delta_\Gamma \phi \right) + \phi (\partial_n \mathbf{D} \cdot \mathbf{n}) \\ &= - \left(\sum_{i=1}^N c_i z_i e \phi + \epsilon_0 \epsilon_r \phi \Delta_\Gamma \phi - \phi \partial_n \mathbf{D} \cdot \mathbf{n} \right) = - (\phi \nabla \cdot \mathbf{D} + \epsilon_0 \epsilon_r \phi \Delta_\Gamma \phi - \phi \partial_n \mathbf{D} \cdot \mathbf{n}) \\ &= - (\phi \partial_n \mathbf{D} \cdot \mathbf{n} + \phi \nabla_\Gamma \cdot \mathbf{D} + \epsilon_0 \epsilon_r \phi \Delta_\Gamma \phi - \phi \partial_n \mathbf{D} \cdot \mathbf{n}) \\ &= - (\phi \nabla_\Gamma \cdot \mathbf{D}_\Gamma - \mathbf{D} \cdot \mathbf{n} \phi H + \epsilon_0 \epsilon_r \phi \Delta_\Gamma \phi) = Q \phi H, \end{aligned} \quad (2.11)$$

$$F_\rho = -Q_\rho u_n + \mathbf{n} \cdot (\boldsymbol{\sigma}_\eta + \boldsymbol{\sigma}_e) \cdot \mathbf{n} + \left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) + Q \partial_n \phi - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i + \frac{\rho |u_n|^2}{2}. \quad (2.12)$$

Comparing with Eq. (2.4), by taking quadratic forms of $G_1 = \sum_i \frac{g_i}{\rho^2} [\tilde{\mu}_i]^\pm$ and $G_2 = \frac{Q_\rho^2}{K(x)}$, we have

$$\left\{ \begin{array}{lll} \mathbf{j}_i^\pm = -\frac{D_i^\pm c_i^\pm}{k_B T} \nabla \tilde{\mu}_i^\pm, & i = 1, \dots, Np, & \text{in } \Omega^\pm, \\ \boldsymbol{\sigma}_\eta^\pm = 2\eta^\pm \mathbf{D}_\eta^\pm + \lambda^\pm (\nabla \cdot \mathbf{u}^\pm) \mathbf{I} - p^\pm \mathbf{I}, & & \text{in } \Omega^\pm, \\ \boldsymbol{\sigma}_e^\pm = \epsilon_0 \epsilon_r^\pm \nabla \phi^\pm \otimes \nabla \phi^\pm - \frac{\epsilon_0 \epsilon_r^\pm}{2} |\nabla \phi^\pm|^2 \mathbf{I}, & & \text{in } \Omega^\pm, \\ J_i = \frac{g_i}{(z_i e)^2} [\tilde{\mu}_i], & i = 1, \dots, N, & \text{in } \Omega^\pm, \\ J_i = L p_i [\tilde{\mu}_i], & i = N+1, \dots, Np, & \text{in } \Omega^\pm, \\ p^\pm = \sum_{i=1}^{Np} k_B T c_i^\pm + p_c^\pm \left(1 - \sum_{i=1}^{Np} \frac{\partial_i \rho^\pm}{\rho^\pm} c_i^\pm \right), & & \text{in } \Omega^\pm, \\ Q = C_m [\phi], & & \text{on } \Gamma, \\ Q_\rho = -\bar{\rho}^2 K(\mathbf{x}) \left\{ \left[\frac{F_\rho}{\rho} \right] \right\}, & & \text{on } \Gamma, \\ \mathbf{F}_{mb} \cdot \mathbf{n} = (e_\Gamma + \gamma_0) H - [F_n], & & \text{on } \Gamma, \\ \boldsymbol{\tau} \cdot \mathbf{F}_{mb} = -Q [\nabla_\Gamma \phi] \cdot \boldsymbol{\tau}, & & \text{on } \Gamma, \end{array} \right. \quad (2.13)$$

where $K(x)$, g_i and Lp_i are the water permeability, conductance of i_{th} ion, hydraulic conductivity of neutral particle on the membrane, respectively. Here we assume the resistance of i_{th} particle R_i^\pm is equal to $\frac{K_B T}{D_i^\pm c_i^\pm}$.

Remark 2.1. Here we took G_1 and G_2 as the simple quadratic functions, i.e., $G_1 = \sum_i (g_i / e^2) [\tilde{\mu}_i]^2$ and $G_2 = Q_\rho^2 / K(x)$. In fact, any flux $J(x)$ satisfying $G(x) = xJ(x) \geq 0$ could be used in order to maximize the dissipation.

Then, we have

$$[F_n] = Q[\phi]H = 2e_\Gamma H \quad \text{and} \quad -Q[\nabla_\Gamma \phi] = -\nabla_\Gamma e_\Gamma, \tag{2.14}$$

which yields

$$[(\sigma_\eta + \sigma_e)] \cdot \mathbf{n} - [Q_\rho \mathbf{u}] = \mathbf{F}_{mb} = (\gamma_0 - e_\Gamma)H\mathbf{n} - \nabla_\Gamma e_\Gamma, \tag{2.15}$$

and

$$\begin{aligned} \left[\frac{F_\rho}{\rho} \right] &= \left[\frac{1}{\rho} \left(\mathbf{n} \cdot (\sigma_\eta + \sigma_e) \cdot \mathbf{n} + \left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) + Q \partial_n \phi - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] + \left[\frac{|u_n|^2}{2} - \frac{Q_\rho u_n}{\rho} \right] \\ &= \left[\frac{1}{\rho} \left(\mathbf{n} \cdot (\sigma_\eta) \cdot \mathbf{n} + O - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] + \left[\frac{Q_\rho^2 + 2Q_\rho v_n}{2\rho^2} - \frac{Q_\rho}{\rho} \left(\frac{Q_\rho}{\rho} + v_n \right) \right] \\ &= \left[\frac{1}{\rho} \left(\mathbf{n} \cdot (\sigma_\eta) \cdot \mathbf{n} + O - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] - \left[\frac{Q_\rho^2}{2\rho^2} \right], \end{aligned} \tag{2.16}$$

where we denote $O = \sum_{i=1}^{Np} k_B T c_i$ as the osmotic pressure. Here we used the fact that v_n is continuous across the membrane.

Model for fluid with variable density. To summarize, we have the following model for fluid with variable density passing through a deformable membrane

$$\left\{ \begin{array}{ll} -\nabla \cdot (\varepsilon_0 \varepsilon_r^\pm \nabla \phi^\pm) = \sum_{i=1}^N z_i e c_i^\pm, & \text{in } \Omega^\pm, \\ \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (\mathbf{u}^\pm c_i^\pm) \\ = \nabla \cdot \left(D_i^\pm \left(\nabla c_i^\pm + \frac{z_i e}{k_B T} c_i^\pm \nabla \phi^\pm - \frac{1}{k_B T} c_i^\pm \nabla \left(p_c^\pm \frac{\partial_i \rho^\pm}{\rho^\pm} \right) \right) \right), \quad i=1, \dots, N, & \text{in } \Omega^\pm, \\ \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (\mathbf{u}^\pm c_i^\pm) \\ = \nabla \cdot \left(D_i^\pm \left(\nabla c_i^\pm - \frac{1}{k_B T} c_i^\pm \nabla \left(p_c^\pm \frac{\partial_i \rho^\pm}{\rho^\pm} \right) \right) \right), \quad i=N+1, \dots, Np, & \text{in } \Omega^\pm, \\ \rho^\pm \frac{D\mathbf{u}^\pm}{Dt} = \nabla \cdot (\sigma_\eta^\pm) + \nabla \cdot (\sigma_e^\pm), & \text{in } \Omega^\pm, \\ \frac{D\rho^\pm}{Dt} + \rho^\pm \nabla \cdot \mathbf{u}^\pm = 0, & \text{in } \Omega^\pm, \\ \rho = \hat{\rho}(c_1^\pm, \dots, c_N^\pm), & \text{in } \Omega^\pm, \end{array} \right. \tag{2.17}$$

where viscous shear stress is

$$\sigma_{\eta}^{\pm} = 2\eta^{\pm} \mathbf{D}_{\eta}^{\pm} + \lambda^{\pm} (\nabla \cdot \mathbf{u}^{\pm}) \mathbf{I} - \left(\sum_i k_B T c_i^{\pm} + p_c^{\pm} \left(1 - \sum_i \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i^{\pm} \right) \right) \mathbf{I} \quad (2.18)$$

and Maxwell stress

$$\sigma_e^{\pm} = \epsilon_0 \epsilon_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{1}{2} |\nabla \phi^{\pm}|^2 \mathbf{I} \right) \quad (2.19)$$

with interface conditions on Γ

$$\left\{ \begin{array}{l} \frac{d\mathbf{X}}{dt} = \mathbf{v}, \\ -\epsilon_0 \epsilon_r^{\pm} \nabla \phi^{\pm} \cdot \mathbf{n} = C_m [\phi], \\ j_i^{\pm} \cdot \mathbf{n} + c_i^{\pm} (\mathbf{u}^{\pm} - \mathbf{v}) \cdot \mathbf{n} = \frac{g_i}{(z_i e)^2} \left(\left[k_B T (\ln(c_i/c_0) + 1) + z_i e \phi - p_c \frac{\partial_i \rho}{\rho} \right] \right), \quad i=1, \dots, N, \\ j_i^{\pm} \cdot \mathbf{n} + c_i^{\pm} (\mathbf{u}^{\pm} - \mathbf{v}) \cdot \mathbf{n} = L p_i \left(\left[k_B T (\ln(c_i/c_0) + 1) - p_c \frac{\partial_i \rho}{\rho} \right] \right), \quad i=N+1, \dots, Np, \\ Q_{\rho} = -\bar{\rho}^2 K(x) \left\{ \left[\frac{1}{\rho} \left(\mathbf{n} \cdot \sigma_{\eta} \cdot \mathbf{n} + O - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] - \left[\frac{1}{2\rho^2} \right] Q_{\rho}^2 \right\}, \\ \rho^{\pm} (\mathbf{u}^{\pm} - \mathbf{v}) \cdot \mathbf{n} = Q_{\rho}, \\ [\sigma_{\eta} + \sigma_e] \cdot \mathbf{n} - [Q_{\rho} \mathbf{u}] = (\gamma_0 - e_{\Gamma}) H \mathbf{n} - \nabla_{\Gamma} e_{\Gamma}, \\ \mathbf{u}^{\pm} \cdot \boldsymbol{\tau} = \mathbf{v} \cdot \boldsymbol{\tau}, \end{array} \right. \quad (2.20)$$

and some appropriate boundary conditions on $\partial\Omega$.

Here the first equation is the motion of the interface; the second one means the surface charge density is proportional to potential jump with capacitance C_m ; the third and fourth equations show the transmembrane flux of substances are proportional to the jump of chemical potential; The fifth and sixth equations are the conditions for the transmembrane fluid flux which is determined by the jumps of viscous stress and osmotic stress; the seventh one is the force balance on the membrane; the last one is the continuity of fluid along the tangential directions. On the membrane force balance condition, it shows that the surface electric energy plays a role as the surface tension by defining $\gamma = \gamma_0 - e_{\Gamma}$ [60].

Remark 2.2. Here it is easy to check that the model (2.17) with interface conditions (2.20) is Galilean invariant. For the transmembrane solution flux, note that (2.20) is a quadratic equation of Q_{ρ} , which normally involves two solutions. If we denote $\delta = [1/2\rho^2] \ll 1$, one solution involves Q_{ρ}^2 as a small perturbation

$$Q_{\rho} = -\bar{\rho}^2 K(x) \left\{ \left[\frac{1}{\rho} \left(\mathbf{n} \cdot \sigma_{\eta} \cdot \mathbf{n} + O - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] \right\} + \delta \bar{\rho}^2 K(x) \left\{ \bar{\rho}^2 K(x) \left[\frac{1}{\rho} \left(\mathbf{n} \cdot \sigma_{\eta} \cdot \mathbf{n} + O - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] \right\}^2 + O(\delta^2),$$

which means Q_{ρ} is mainly driven by the hydro and osmotic pressure difference.

The other candidate solution makes Q_ρ a large quantity

$$Q_\rho = \frac{1}{\delta} \frac{1}{\bar{\rho}^2 K(x)} - \bar{\rho}^2 K(x) \left\{ \left[\frac{1}{\rho} \left(\mathbf{n} \cdot \boldsymbol{\sigma}_\eta \cdot \mathbf{n} + O - \sum_{i=1}^{N_p} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] \right\} + O(\delta),$$

which means Q_ρ is mainly driven by the density difference and does not depend on the hydrostatic and osmotic pressure. The large Q_ρ solution is not reasonable for a permeable membrane flux in that solution because the solution flux increases as density difference decreases ($\delta \rightarrow 0$). So the first solution will be chosen for our permeable membrane solution flux.

Remark 2.3. Here we considered a simple membrane mechanical energy, only including the surface tension. The derivation has been generalized to more complicated membrane energy case, for example the Helfrich bending energy [39, 68] and the neo-Hookean hyperelastic energy [69], allowing models of fascinating biological phenomena like vesicle fusion [70, 71] to include the effects of ionic composition, membrane potential, and hydrostatic pressure that are known to have significant effects in experiment and life. The detailed derivation could be found in Appendix C.

Remark 2.4. If we assume that $\lambda^\pm = -\frac{2}{3}\eta^\pm$ and those coefficients, like ϵ_r^\pm, η^\pm , are constant in domain Ω^\pm , respectively, the Navier-Stokes equation in (2.17) could be rewritten as

$$\rho^\pm \frac{D\mathbf{u}^\pm}{Dt} + \nabla p^\pm = \eta^\pm \Delta \mathbf{u}^\pm + \frac{\eta^\pm}{3} \nabla (\nabla \cdot \mathbf{u}^\pm) - \sum_{i=1}^N z_i e c_i^\pm \nabla \phi^\pm, \quad (2.21)$$

where we used Poisson equation and the fact

$$\begin{aligned} \nabla \cdot \boldsymbol{\sigma}_\eta^\pm &= \eta^\pm \Delta \mathbf{u}^\pm + \frac{\eta^\pm}{3} \nabla (\nabla \cdot \mathbf{u}^\pm) - \nabla p^\pm, \\ \nabla \cdot \boldsymbol{\sigma}_e^\pm &= \epsilon_0 \epsilon_r^\pm \Delta \phi^\pm \nabla \phi^\pm = - \sum_i z_i e c_i^\pm \nabla \phi^\pm. \end{aligned} \quad (2.22)$$

3 Special cases

In this section, we consider several special cases of the system in last section.

3.1 Variable density & inflexible membrane

We first assume that the membrane is inflexible $v = \mathbf{0}$ and the total energy and dissipation functional are same as in Eqs. (2.1) and (2.2). The flux interface conditions are reduced to $\rho^\pm \mathbf{u}^\pm = Q_\rho \mathbf{n}$ and $\mathbf{j}_i^\pm \cdot \mathbf{n} + c_i^\pm \mathbf{u}^\pm \cdot \mathbf{n} = J_i(x)$, on Γ . By using the similar calculation with the reduced interface conditions, Eq. (2.8) is reduced to

$$\frac{dE^{tot}}{dt} = - \sum_{\pm} \int_{\Omega^\pm} \boldsymbol{\sigma}_\eta^\pm : \nabla \mathbf{u}^\pm \, dx \quad (3.1)$$

$$\begin{aligned}
 & - \sum_{\pm} \int_{\Omega^{\pm}} \left(\sigma_e - \varepsilon_0 \varepsilon_r^{\pm} (\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{1}{2} |\nabla \phi^{\pm}|^2 \mathbf{I}) \right) : \nabla \mathbf{u} dx \\
 & + \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} (\nabla \tilde{\mu}_i^{\pm}) \cdot \mathbf{j}_i^{\pm} dx - \int_{\Gamma} \sum_{i=1}^{Np} [\tilde{\mu}_i] J_i dS \\
 & + \sum_{\pm} \int_{\Omega^{\pm}} \left(- \sum_{i=1}^{Np} k_B T c_i^{\pm} - p_c^{\pm} \left(1 - \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i \right) \right) \nabla \cdot \mathbf{u}^{\pm} dx \\
 & + \int_{\Gamma} [\phi] \frac{\partial}{\partial t} (C_m[\phi] - Q) dS + \int_{\Gamma} \left[\frac{F_{\rho}}{\rho} \right] Q_{\rho} dS + I_b.
 \end{aligned}$$

Comparing with the dissipation functional (2.4), we obtain the same results as in Eq. (2.13) without the last two equations for force balance on the membrane.

Model for an inflexible permeable membrane. To summarize, when the density of solution is a function of ion concentration, we obtained the following model for fluid passing through an inflexible permeable membrane

$$\left\{ \begin{array}{ll}
 -\nabla \cdot (\varepsilon_0 \varepsilon_r^{\pm} \nabla \phi^{\pm}) = \sum_{i=1}^N z_i e c_i^{\pm}, & \text{in } \Omega^{\pm} \\
 \frac{\partial c_i^{\pm}}{\partial t} + \nabla \cdot (\mathbf{u}^{\pm} c_i^{\pm}) \\
 = \nabla \cdot \left(D_i^{\pm} \left(\nabla c_i^{\pm} + \frac{z_i e}{k_B T} c_i^{\pm} \nabla \phi^{\pm} - \frac{1}{k_B T} c_i^{\pm} \nabla \left(p_c^{\pm} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \right) \right), & i = 1, \dots, N, \quad \text{in } \Omega^{\pm} \\
 \frac{\partial c_i^{\pm}}{\partial t} + \nabla \cdot (\mathbf{u}^{\pm} c_i^{\pm}) \\
 = \nabla \cdot \left(D_i^{\pm} \left(\nabla c_i^{\pm} - \frac{1}{k_B T} c_i^{\pm} \nabla \left(p_c^{\pm} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \right) \right), & i = N+1, \dots, Np, \quad \text{in } \Omega^{\pm} \\
 \rho^{\pm} \frac{D \mathbf{u}^{\pm}}{D t} = \nabla \cdot (\boldsymbol{\sigma}_{\eta}^{\pm}) + \nabla \cdot (\varepsilon_0 \varepsilon_r^{\pm} \nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{\varepsilon_0 \varepsilon_r^{\pm}}{2} |\nabla \phi^{\pm}|^2), & \text{in } \Omega^{\pm}, \\
 \frac{D \rho^{\pm}}{D t} + \rho^{\pm} \nabla \cdot \mathbf{u}^{\pm} = 0, & \text{in } \Omega^{\pm}, \\
 \rho = \hat{\rho}(c_1^{\pm}, \dots, c_N^{\pm}), & \text{in } \Omega^{\pm}
 \end{array} \right. \quad (3.2)$$

where viscous shear stress is

$$\boldsymbol{\sigma}_{\eta}^{\pm} = 2\eta^{\pm} \mathbf{D}_{\eta}^{\pm} + \lambda^{\pm} (\nabla \cdot \mathbf{u}^{\pm}) \mathbf{I} - \left(\sum_i k_B T c_i^{\pm} + p_c^{\pm} \left(1 - \sum_i \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i^{\pm} \right) \right) \mathbf{I}$$

with interface conditions on Γ

$$\left\{ \begin{array}{ll}
 -\varepsilon_0 \varepsilon_r^{\pm} \nabla \phi^{\pm} \cdot \mathbf{n} = C_m[\phi], \\
 \mathbf{j}_i^{\pm} \cdot \mathbf{n} + c_i^{\pm} \mathbf{u}^{\pm} \cdot \mathbf{n} = \frac{g_i}{(z_i e)^2} \left(\left[k_B T (\ln(c_i/c_0) + 1) + z_i e \phi - p_c \frac{\partial_i \rho}{\rho} \right] \right), & i = 1, \dots, N, \\
 \mathbf{j}_i^{\pm} \cdot \mathbf{n} + c_i^{\pm} \mathbf{u}^{\pm} \cdot \mathbf{n} = L p_i \left(\left[k_B T (\ln(c_i/c_0) + 1) - p_c \frac{\partial_i \rho}{\rho} \right] \right), & i = N+1, \dots, Np, \\
 Q_{\rho} = -\bar{\rho}^2 K(\mathbf{x}) \left\{ \left[\frac{1}{\rho} \left(O + \mathbf{n} \cdot \boldsymbol{\sigma}_{\eta} \cdot \mathbf{n} - \sum_i \frac{\partial_i \rho}{\rho} p_c c_i \right) \right] - \left[\frac{1}{2\rho^2} \right] Q_{\rho}^2 \right\}, \\
 \rho^{\pm} \mathbf{u}^{\pm} = Q_{\rho} \mathbf{n},
 \end{array} \right. \quad (3.3)$$

and some appropriate boundary conditions on $\partial\Omega$.

Remark 3.1. Comparing with the results for flexible membrane in Eqs. (2.17)-(2.20), we find the only difference is that there is no force balance equation for the inflexible membrane. The inflexible membrane has an unknown external force that maintains the position of membrane. Only the Dirichlet interface condition is used to describe the solvent velocity passing through the inflexible membrane. In the case that the membrane is non-permeable for fluid, an equation of osmotic velocity is not needed. In this case, the membrane moves with the fluid, i.e., $Q_\rho = 0$ (i.e., $\mathbf{u}^\pm = \mathbf{v}$); only the force balance equation $[\sigma_\eta + \sigma_e] \cdot \mathbf{n} = (\gamma_0 - e_\Gamma)H\mathbf{n} - \nabla_\Gamma e_\Gamma$ on the membrane is needed when the membrane is non-permeable for fluid.

Remark 3.2. In above interface conditions, at equilibrium state, i.e., $\mathbf{u}^\pm = \mathbf{0}$ and $Q_\rho = 0$. By using the fact that

$$\sigma_\eta^\pm = 2\eta^\pm \mathbf{D}_\eta^\pm + \lambda^\pm (\nabla \cdot \mathbf{u}^\pm) \mathbf{I} - p^\pm \mathbf{I}, \quad p^\pm = \left(\sum_{i=1}^{Np} k_B T c_i^\pm + p_c^\pm \left(1 - \sum_{i=1}^{Np} \frac{\partial_i \rho^\pm}{\rho^\pm} c_i^\pm \right) \right),$$

the mass flux interface boundary condition in Eq. (2.20) could be rewritten as

$$\begin{aligned} Q_\rho &= -\bar{\rho}^2 K(x) \left\{ \left[\frac{1}{\rho} \left(\mathbf{n} \cdot \sigma_\eta \cdot \mathbf{n} + O - \sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} c_i \right) \right] - \left[\frac{1}{2\rho^2} \right] Q_\rho^2 \right\} \\ &= -\bar{\rho}^2 K(x) \left\{ \left[\frac{1}{\rho} \left(\mathbf{n} \cdot 2\mathbf{D}_\eta \cdot \mathbf{n} + \lambda \nabla \cdot \mathbf{u} \right) - \frac{p-O}{\rho - \sum_{i=1}^{Np} \partial_i \rho c_i} \right] - \left[\frac{1}{2\rho^2} \right] Q_\rho^2 \right\}. \end{aligned}$$

In the equilibrium state, we have

$$\left[(p-O) / \left(\rho - \sum_{i=1}^{Np} \partial_i \rho c_i \right) \right] = 0. \tag{3.4}$$

In this case, the osmotic pressure is not simply balanced by the hydropressure directly. It also depends on the density. However, if we assume the density of solution linearly depends on the total ion concentration, i.e., $\rho(x) = \hat{\rho}(c_i) = \rho_0 + \alpha \sum_i c_i$, then above equation yields

$$\left[\frac{p-O}{\rho_0} \right] = \frac{[p-O]}{\rho_0} = 0, \tag{3.5}$$

which means $[p] = [O]$.

3.2 Constant density & flexible membrane

For the normal biological problem, where the bulk ion concentration is in the range of $1 \sim 300 \text{ mM}$, the density of solution has a small variation. Concentrations are very much

larger in and near ion channels, charged lipid membranes, binding proteins, enzyme active sites, and nucleic acids. In those situations, solutions are also quite nonideal and so a different treatment is needed.

In the bulk, we can take the zero order approximation, i.e., $\rho^\pm = \rho^0$, where ρ^0 is a constant. Then the fourth equation in (2.1) is reduced to the incompressibility condition $\nabla \cdot \mathbf{u} = 0$. The kinetic energy functional is reduced to be $E_{kin} = \sum_{\pm} \int_{\Omega^\pm} \frac{1}{2} \rho^0 |\mathbf{u}^\pm|^2 dx$. The second term in dissipation functional vanishes. The interface conditions are reduced to on Γ

$$\begin{cases} \frac{d\mathbf{X}}{dt} = \mathbf{v}, \\ \mathbf{D}^\pm \cdot \mathbf{n} = Q(x), \\ \mathbf{u}^\pm \cdot \mathbf{n} - \mathbf{v} \cdot \mathbf{n} = U, \\ \mathbf{j}_i^\pm \cdot \mathbf{n} + c_i^\pm (\mathbf{u}^\pm - \mathbf{v}) \cdot \mathbf{n} = J_i(x), \quad i = 1, \dots, Np, \\ [\sigma_\eta + \sigma_e] \cdot \mathbf{n} = \mathbf{F}_{mb}, \\ \mathbf{u}^\pm \cdot \boldsymbol{\tau} = \mathbf{v} \cdot \boldsymbol{\tau} \end{cases} \quad (3.6)$$

Here the main difference between Eqs. (2.2) and (3.6) is that the velocity on the membrane is continuous since the density is continuous. Here we replaced $\frac{Q_\rho}{\rho^0}$ by new variable U . By using a similar calculation with interface conditions (3.6) and incompressibility, Eq. (2.8) is reduced to

$$\begin{aligned} \frac{dE^{tot}}{dt} = & - \sum_i \int_{\Omega^\pm} \sigma_\eta^\pm : \nabla \mathbf{u}^\pm dx - \sum_{\pm} \int_{\Omega^\pm} \left(\sigma_e^\pm - \epsilon_0 \epsilon_r^\pm \left(\nabla \phi^\pm \otimes \nabla \phi^\pm - \frac{|\nabla \phi^\pm|^2}{2} \mathbf{I} \right) \right) : \nabla \mathbf{u}^\pm dx \\ & + \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} \nabla \mu_i^\pm \cdot \mathbf{j}_i^\pm dx - \int_\Gamma \sum_i [\mu_i] J_i dS + \int_\Gamma (\mathbf{F}_{mb} + [Q \nabla \phi]) \cdot \mathbf{v}_\tau dS \\ & + \int_\Gamma (\mathbf{F}_{mb} \cdot \mathbf{n} + [F_n] - (e_\Gamma + \gamma_0) H) V_n dS \\ & + \int_\Gamma [F_\rho] U dS + \int_\Gamma [\phi] \frac{d^n}{dt} (C_m[\phi] - Q) dS + I_b, \end{aligned} \quad (3.7)$$

where $I_b = I_{1b} + I_{2b}$, chemical potential $\tilde{\mu}_i$ reduces to μ_i ; $F_n = Q\phi H$ is the same as in Eq. (2.11); and

$$F_\rho = \mathbf{n} \cdot (\sigma_\eta + \sigma_e) \cdot \mathbf{n} + \left(e_{es} + \sum_{i=1}^{Np} k_B T c_i + Q \partial_n \phi \right). \quad (3.8)$$

Model for a deformable membrane. To summarize, the model for fluid passing through a deformable membrane is

$$\left\{ \begin{array}{ll} -\nabla \cdot (\varepsilon_0 \varepsilon_r^\pm \nabla \phi^\pm) = \sum_{i=1}^N z_i e c_i^\pm, & \text{in } \Omega^\pm, \\ \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (\mathbf{u}^\pm c_i^\pm) = \nabla \cdot \left(D_i^\pm \left(\nabla c_i^\pm + \frac{z_i e}{k_B T} c_i^\pm \nabla \phi^\pm \right) \right), & i=1, \dots, N, \quad \text{in } \Omega^\pm, \\ \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (\mathbf{u}^\pm c_i^\pm) = \nabla \cdot (D_i^\pm (\nabla c_i^\pm)), & i=N+1, \dots, Np, \quad \text{in } \Omega^\pm, \\ \rho^0 \frac{D\mathbf{u}^\pm}{Dt} + \nabla p^\pm = \nabla \cdot (2\eta^\pm \mathbf{D}_\eta^\pm) + \nabla \cdot (\varepsilon_0 \varepsilon_r^\pm \nabla \phi^\pm \otimes \nabla \phi^\pm - \frac{\varepsilon_0 \varepsilon_r^\pm}{2} |\nabla \phi^\pm|^2 \mathbf{I}), & \text{in } \Omega^\pm, \\ \nabla \cdot \mathbf{u}^\pm = 0, & \text{in } \Omega^\pm, \end{array} \right. \quad (3.9)$$

where the viscous stress for incompressible fluid is

$$\boldsymbol{\sigma}_\eta^\pm = 2\eta^\pm \mathbf{D}_\eta^\pm - p^\pm \mathbf{I},$$

and pressure p is introduced as a Lagrange multiplier of incompressibility. By taking $\bar{\rho} = \rho^0$, the interface boundary conditions on Γ are

$$\left\{ \begin{array}{ll} \frac{dX}{dt} = \mathbf{v}, \\ -\varepsilon_0 \varepsilon_r^\pm \nabla \phi^\pm \cdot \mathbf{n} = C_m[\phi], \\ \mathbf{j}_i^\pm \cdot \mathbf{n} + c_i^\pm (\mathbf{u}^\pm - \mathbf{v}) \cdot \mathbf{n} = \frac{g_i}{(z_i e)^2} ([k_B T (\ln(c_i/c_0) + 1) + z_i e \phi]), & i=1, \dots, N \\ \mathbf{j}_i^\pm \cdot \mathbf{n} + c_i^\pm (\mathbf{u}^\pm - \mathbf{v}) \cdot \mathbf{n} = L p_i ([k_B T (\ln(c_i/c_0) + 1)]), & i=N+1, \dots, Np \\ \mathbf{u}^\pm - \mathbf{v} = U \mathbf{n}, \\ U = -K(x) [O + \mathbf{n} \cdot \boldsymbol{\sigma}_\eta \cdot \mathbf{n}], \\ [\boldsymbol{\sigma}_\eta + \boldsymbol{\sigma}_e] \cdot \mathbf{n} = (\gamma_0 - e_\Gamma) H \mathbf{n} - \nabla_\Gamma e_\Gamma, \end{array} \right. \quad (3.10)$$

and some appropriate boundary conditions on $\partial\Omega$ describing the experimental setup in a reasonably realistic, but idealized way. Note that the system (3.9) with interface condition (3.10) are same as the previous results 106.

Remark 3.3. Other formulations could be used for the membrane of course. Even the traditional Goldman–Hodgkin–Katz flux [60] $J_i = P_i f(z_i e [\phi] / k_B T) c_i^- (e^{[\mu_i] / k_B T} - 1)$ with $f(x) = \frac{x}{e^x - 1} = 0$, for any x , could be used to replace the Hodgkin-Huxley flux $J_i = \frac{g_i}{(z_i e)^2} [\mu_i]$.

What is really needed of course is a physical model of the water, mass, and electrical flux through the ensemble of channels, starting with atomic detail. That is not yet available, particularly because the macroscopic representation (of the ensemble of channels) needed here (i.e., in Eq. (32)) should include time dependent gating phenomena that are not properties of a single permanently open channel. The Goldman-Hodgkin-Katz and Poisson Nernst Planck formulations are representations of the behavior of single permanently open channels. Those representations need to be supplemented by an explicit theory of time (and agonist or voltage) dependent opening and closing of both single channels and ensembles of single channels before they can sensibly be used in a model like Eq. (32). Note two types of gating are involved, the stochastic open and closed gating of single channels, and the deterministic time dependent conductance called gating in the Hodgkin Huxley formulation of ensemble properties.

Remark 3.4. If the neutrality particles are taken into account, system (3.9)-(3.10) are degenerated to be

$$\begin{cases} \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (\mathbf{u}^\pm c_i^\pm) = \nabla \cdot (D_i^\pm \nabla c_i^\pm), & i = N+1, \dots, Np, & \text{in } \Omega^\pm \\ \rho^0 \frac{D\mathbf{u}^\pm}{Dt} + \nabla p^\pm = \nabla \cdot (2\eta^\pm \mathbf{D}_\eta^\pm), & & \text{in } \Omega^\pm \\ \nabla \cdot \mathbf{u}^\pm = 0, & & \text{in } \Omega^\pm \end{cases} \quad (3.11)$$

with interface boundary conditions on Γ are

$$\begin{cases} \frac{d\mathbf{X}}{dt} = \mathbf{v}, \\ \mathbf{j}_i^\pm \cdot \mathbf{n} + c_i^\pm (\mathbf{u}^\pm - \mathbf{v}) \cdot \mathbf{n} = Lp_i ([k_B T (\ln(c_i/c_0) + 1)]), & i = N+1, \dots, Np, \\ \mathbf{u}^\pm - \mathbf{v} = U\mathbf{n}, \\ U = -K(x) [O + \mathbf{n} \cdot \boldsymbol{\sigma}_\eta \cdot \mathbf{n}], \\ [\boldsymbol{\sigma}_\eta] \cdot \mathbf{n} = \gamma_0 H\mathbf{n}. \end{cases} \quad (3.12)$$

3.3 Constant density & inflexible membrane

In this section, besides the constant density, we further assume that the membrane is inflexible, i.e. $\mathbf{v} = \mathbf{0}$. Similarly, the difference between flexible and inflexible membranes is that we do not need the force balance equation on the interface. Then we could obtain the following model for fluid passing through an inflexible membrane

$$\begin{cases} -\nabla \cdot (\varepsilon_0 \varepsilon_r^\pm \nabla \phi^\pm) = \sum_{i=1}^N z_i e c_i^\pm, & \text{in } \Omega^\pm, \\ \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (\mathbf{u}^\pm c_i^\pm) = \nabla \cdot \left(D_i^\pm \left(\nabla c_i^\pm + \frac{z_i e}{k_B T} c_i^\pm \nabla \phi^\pm \right) \right), & i = 1, \dots, N, & \text{in } \Omega^\pm, \\ \frac{\partial c_i^\pm}{\partial t} + \nabla \cdot (\mathbf{u}^\pm c_i^\pm) = \nabla \cdot (D_i^\pm \nabla c_i^\pm), & i = N+1, \dots, Np, & \text{in } \Omega^\pm, \\ \rho^0 \frac{D\mathbf{u}^\pm}{Dt} + \nabla p^\pm = \nabla \cdot (2\eta^\pm \mathbf{D}_\eta^\pm) + \nabla \cdot (\varepsilon_0 \varepsilon_r^\pm \nabla \phi^\pm \otimes \nabla \phi^\pm - \frac{\varepsilon_0 \varepsilon_r^\pm}{2} |\nabla \phi^\pm|^2 \mathbf{I}), & \text{in } \Omega^\pm, \\ \nabla \cdot \mathbf{u}^\pm = 0, & \text{in } \Omega^\pm, \end{cases} \quad (3.13)$$

where the viscous stress for incompressible fluid is

$$\boldsymbol{\sigma}_\eta^\pm = 2\eta^\pm \mathbf{D}_\eta^\pm - p^\pm \mathbf{I}$$

with interface boundary conditions on Γ

$$\begin{cases} -\varepsilon_0 \varepsilon_r^\pm \nabla \phi^\pm \cdot \mathbf{n} = C_m [\phi], \\ \mathbf{j}_i^\pm \cdot \mathbf{n} + c_i^\pm \mathbf{u}^\pm \cdot \mathbf{n} = \frac{S_i}{(z_i e)^2} ([k_B T (\ln(c_i/c_0) + 1) + z_i e \phi]), & i = 1, \dots, N, \\ \mathbf{j}_i^\pm \cdot \mathbf{n} + c_i^\pm \mathbf{u}^\pm \cdot \mathbf{n} = Lp_i ([k_B T (\ln(c_i/c_0) + 1)]), & i = N+1, \dots, Np, \\ \mathbf{u}^\pm = U\mathbf{n}, \\ U = -K(x) [O + \mathbf{n} \cdot \boldsymbol{\sigma}_\eta \cdot \mathbf{n}], \end{cases} \quad (3.14)$$

and some appropriate boundary conditions on $\partial\Omega$.

4 Historical comments

Osmosis occurs in so many contexts that no one, certainly not us, can grasp its totality. The temptation then is to discuss only what we have grasped and say nothing about what is beyond our reach. Because we do know something about some important applications — and think something is better than nothing — we write this section. We hope workers in different fields will learn of each other's work, so they can benefit from each other's knowledge, experience, and enthusiasm about osmosis.

It is important also to understand that at least in biology many of the most important issues in osmosis remain open. We believe, without proof, that some of these issues will be easier to resolve when ionic solutions are treated as complex fluids with mathematics that is consistent, with all variables satisfying all field equations and interface boundary conditions with one set of unchanging parameters. We understand, however, that no one can know the consequences of a consistent analysis until it is actually performed in the experimental, technological and biological systems of interest. Details matter!

The classical biological literature is older, and in danger of being lost to modern generations, particularly those who know more of Navier Stokes and fluidics than of the kidney or epithelia. So we provide key references to interesting biological applications. It is important to understand that these areas are central to a wide range of biological research. They are not isolated special cases. Much of classical physiology, described in detail in textbooks [52,53,55,56] concerns organs that depend on osmosis. Mori [60,72] has started a consistent analysis of osmosis and our work should be viewed as an extension of his. The reviews of Boulpaep [73], Hill [74], and Pohl [75] provide good entries to the field. Hill is particularly useful for showing the substantial controversies and their history. The analysis of osmosis in the lens, mostly from the laboratory of Richard Mathias, is notable for its success, combining field theory, molecular biology, structural biology, and measurements of hydrostatic pressure, electrical impedance, and fluxes to provide a coherent view of how the lens uses osmosis to stay alive [76–78]. That approach, expanded perhaps to explicitly use the theory of complex fluids, will help to resolve the many controversies we believe.

A great deal of work has been done on fusion of vesicles to membranes, because of its wide biological role (e.g., in the $\sim 10^{14}$ chemical synapses in our brains, with thousands of vesicles in each synapse) and medical importance in the entry of viruses into cells [70,79,80]. Most of that work only considers the elastic properties of membranes. We suggest that energy sources like diffusion, electrical potential, and convection should be included in the analysis of vesicle fusion — and membrane flow in general — to see if they are used by biology for its purposes. Experiments suggest they are.

Modern work in molecular biology and water flow is focused on the aquaporins that are thought to provide channels for water flow [81,82], or sensors controlling water flow [83,84]. Some work seeks to study osmosis in individual channels, but comparison with similar work studying current flow through channels suggests that much remains to be done. In our view, the full range of forces — electrical, diffusional, convective,

steric, and chemical — are likely to be involved in flow through water channels and so must be included in models and simulations, at least to begin with, until we discover the variables that evolution uses to control water flow on the atomic scale in the channels of aquaporins.

Sadly, osmosis and fluid flow in plants is not an area we know enough about to cite intelligently. Osmosis/fluidics reaches its most impressive heights in trees (nearly 100 meters in redwoods). Water flow in the xylem of trees — from roots to the crown — certainly needs analysis with the theory of complex fluids, if that has not already been done. There are also innumerable examples of osmosis/fluidics we do not know enough about to even name. All the more reason for readers interested in complex fluids to learn their names and study how they work. In each case, it seems clear to us that treating osmosis as the movement of a complex fluid is likely to be useful, even necessary, in biology, and everywhere else.

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A Proof of Lemma 2.1

Proof. By using the Batchelor’s method [69, 85], we have

$$\begin{aligned} \frac{d}{dt}(n)dS + \frac{d}{dt}(dS)n &= \frac{d}{dt}(ndS) = (\nabla \cdot v)ndS - (\nabla v) \cdot ndS \\ &= (\nabla \cdot vn - (\partial_n v \cdot n)n)dS - \nabla_\Gamma v \cdot ndS = (\nabla_\Gamma \cdot v)ndS - \nabla_\Gamma v \cdot nds \end{aligned}$$

and $\frac{d}{dt}dS = \nabla_\Gamma \cdot v dS$. Then we have $\frac{dn}{dt} = -\nabla_\Gamma v \cdot n$. Finally, by the definition of $\frac{d^n}{dt}$, we have

$$\begin{aligned} \frac{d^n n}{dt} &= \frac{dn}{dt} - (v_\Gamma \cdot \nabla_\Gamma)n = -\nabla_\Gamma v \cdot n - (v_\Gamma \cdot \nabla_\Gamma)n \\ &= -\nabla_\Gamma(v_n n + v_\Gamma) \cdot n - \nabla_\Gamma n \cdot v_\Gamma = -\nabla_\Gamma v_n - \nabla_\Gamma(n \cdot v_\Gamma) = -\nabla_\Gamma v_n. \end{aligned}$$

Here we used the symmetry of curvature tensor $\nabla_\Gamma n$ and $|n|^2 = 1$. □

B Time derivative of total energy calculation details

In this section, we present the details for the time derivative calculation in Section 2. For the first term I_1 , by using the last two equations in Eq. (2.1), third interface condition in (2.2) and Eq. (2.5), we have

$$I_1 := \frac{d}{dt} \sum_{\pm} \int_{\Omega^\pm} \frac{1}{2} \rho^\pm |u^\pm|^2 dx \tag{B.1}$$

$$\begin{aligned}
 &= \sum_{\pm} \int_{\Omega^{\pm}} \frac{|\mathbf{u}^{\pm}|^2}{2} \frac{D\rho^{\pm}}{Dt} dx + \sum_{\pm} \int_{\Omega^{\pm}} \rho^{\pm} \frac{D\mathbf{u}^{\pm}}{Dt} \cdot \mathbf{u}^{\pm} dx - \int_{\Gamma} \left[\frac{|\mathbf{u}|^2}{2} \right] Q_{\rho} \\
 &\quad + \sum_{\pm} \int_{\Omega^{\pm}} \frac{1}{2} \rho^{\pm} |\mathbf{u}^{\pm}|^2 \nabla \cdot \mathbf{u}^{\pm} dx - \int_{\partial\Omega} e_{kin}^{\pm} \mathbf{u}^{\pm} \cdot \mathbf{n} dS \\
 &= - \sum_{\pm} \int_{\Omega^{\pm}} \boldsymbol{\sigma}_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \boldsymbol{\sigma}_e^{\pm} : \nabla \mathbf{u}^{\pm} dx + \int_{\Gamma} [\mathbf{n} \cdot (\boldsymbol{\sigma}_{\eta} + \boldsymbol{\sigma}_e) \cdot \mathbf{u}] dS \\
 &\quad - \int_{\Gamma} \left[\frac{|\mathbf{u}|^2}{2} \right] Q_{\rho} dS + I_{1b} \\
 &= - \sum_{\pm} \int_{\Omega^{\pm}} \boldsymbol{\sigma}_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \boldsymbol{\sigma}_e^{\pm} : \nabla \mathbf{u}^{\pm} dx + \int_{\Gamma} [(\mathbf{n} \cdot (\boldsymbol{\sigma}_{\eta} + \boldsymbol{\sigma}_e) - Q_{\rho} \mathbf{u}) \cdot \mathbf{u}] dS \\
 &\quad + \int_{\Gamma} \left[\frac{u_n^2}{2} \right] Q_{\rho} dS + \sum_{\pm} \int_{\Omega^{\pm}} p_c^{\pm} \left(\sum_i^{N_p} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} (\nabla \cdot \mathbf{j}_i^{\pm} + c_i^{\pm} \nabla \cdot \mathbf{u}^{\pm}) - \nabla \cdot \mathbf{u}^{\pm} \right) dx + I_{1b}.
 \end{aligned}$$

where we used the notation $\partial_i \rho^{\pm} = \frac{\partial \hat{\rho}}{\partial c_i} (c_i^{\pm})$, the decomposition $\mathbf{u} = u_n \mathbf{n} + \mathbf{u}_{\tau}$, \mathbf{u}_{τ} is continuous on the membrane and

$$I_{1b} = \int_{\partial\Omega} \left((\boldsymbol{\sigma}_{\eta}^{\pm} + \boldsymbol{\sigma}_e^{\pm}) \cdot \mathbf{n} \right) \cdot \mathbf{u}^{\pm} dS - \int_{\partial\Omega} e_{kin}^{\pm} \mathbf{u}^{\pm} \cdot \mathbf{n} dS.$$

The colon $:$ represents the double dot of two tensors $\mathbf{A} : \mathbf{B} \equiv \sum_{ij} A_{ij} B_{ij}$.

A Lagrange multiplier p_c is introduced to assure mass conservation, when solution density is a function of ion density.

The second and third terms in Eq. (2.7) are , with the help of first two equations in (2.1) and last two equations in (2.2), given by

$$\begin{aligned}
 I_2 + I_3 &:= \frac{d}{dt} \sum_{\pm} \int_{\Omega^{\pm}} e_{es}^{\pm} dx + \frac{d}{dt} \sum_{\pm} \int_{\Omega^{\pm}} e_{par}^{\pm} dx \tag{B.2} \\
 &= \sum_{\pm} \int_{\Omega^{\pm}} \frac{\partial}{\partial t} \left(\frac{1}{2} \mathbf{E}^{\pm} \cdot \mathbf{D}^{\pm} \right) dx + \sum_{\pm} \int_{\Omega^{\pm}} \frac{\partial}{\partial t} \left(\sum_{i=1}^{N_p} k_B T c_i^{\pm} \ln \frac{c_i^{\pm}}{c_0} \right) dx + \int_{\Gamma} [e_{es} + e_{par}] \mathbf{v} \cdot \mathbf{n} dS \\
 &= \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{N_p} \left(z_i e \phi^{\pm} + k_B T \left(\ln \left(\frac{c_i^{\pm}}{c_0} \right) + 1 \right) \right) \frac{\partial c_i^{\pm}}{\partial t} dx \\
 &\quad + \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=N+1}^{N_p} \left(k_B T \left(\ln \left(\frac{c_i^{\pm}}{c_0} \right) + 1 \right) \right) \frac{\partial c_i^{\pm}}{\partial t} dx \\
 &\quad - \int_{\partial\Omega} \left(\phi^{\pm} \frac{\partial \mathbf{D}^{\pm}}{\partial t} \cdot \mathbf{n} \right) dS - \int_{\Gamma} \left[\phi \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{n} \right] dS + \int_{\Gamma} [e_{es} + e_{par}] \mathbf{v} \cdot \mathbf{n} dS \\
 &= \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{N_p} \mu_i^{\pm} \left(-\nabla \cdot \mathbf{j}_i^{\pm} - \nabla \cdot (c_i^{\pm} \mathbf{u}^{\pm}) \right) dx
 \end{aligned}$$

$$\begin{aligned}
 & - \int_{\partial\Omega} \left(\phi^\pm \frac{\partial \mathbf{D}^\pm}{\partial t} \cdot \mathbf{n} \right) dS - \int_{\Gamma} \left[\phi \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{n} \right] dS + \int_{\Gamma} [e_{es} + e_{par}] \mathbf{v} \cdot \mathbf{n} dS \\
 = & \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} \nabla \mu_i^\pm \cdot \mathbf{j}_i^\pm dx + \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} c_i^\pm (\nabla \mu_i^\pm) \cdot \mathbf{u}^\pm dx \\
 & - \int_{\Gamma} \left[\sum_{i=1}^{Np} \mu_i (\mathbf{j}_i \cdot \mathbf{n} + c_i \mathbf{u} \cdot \mathbf{n}) \right] dS - \int_{\Gamma} \left[\phi \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{n} \right] dS + \int_{\Gamma} [e_{es} + e_{par}] \mathbf{v} \cdot \mathbf{n} dS + I_{21b} \\
 = & \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} \nabla \mu_i^\pm \cdot \mathbf{j}_i^\pm dx + \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} c_i^\pm (\nabla \mu_i^\pm) \cdot \mathbf{u}^\pm dx \\
 & - \int_{\Gamma} \sum_i [\mu_i] J_i dS - \int_{\Gamma} \left[\phi \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{n} \right] dS + \int_{\Gamma} \left[\left(e_{es} + e_{par} - \sum_{i=1}^{Np} \mu_i c_i \right) \right] \mathbf{v} \cdot \mathbf{n} dS + I_{21b},
 \end{aligned}$$

where

$$\mu_i^\pm = \begin{cases} z_i e \phi^\pm + k_B T \left(\ln \left(\frac{c_i^\pm}{c_0} \right) + 1 \right), & \text{for } i=1, \dots, N, \\ k_B T \left(\ln \left(\frac{c_i^\pm}{c_0} \right) + 1 \right), & \text{for } i=N+1, \dots, Np \end{cases} \quad (\text{B.3})$$

and

$$I_{21b} = - \int_{\partial\Omega} \left(\phi^\pm \frac{\partial \mathbf{D}^\pm}{\partial t} \cdot \mathbf{n} \right) dS - \int_{\partial\Omega} \sum_{i=1}^{Np} \mu_i (\mathbf{j}_i^\pm + c_i^\pm \mathbf{u}^\pm) \cdot \mathbf{n} dS.$$

Due to the first equation in (2.1) and second equation in (2.2), the second term in Eq. (B.2) is rewritten

$$\begin{aligned}
 & \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} c_i^\pm \nabla \mu_i^\pm \cdot \mathbf{u}^\pm dx \quad (\text{B.4}) \\
 = & \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^N z_i e c_i^\pm \nabla \phi^\pm \cdot \mathbf{u}^\pm dx + \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} k_B T \nabla c_i^\pm \cdot \mathbf{u}^\pm dx \\
 = & \sum_{\pm} \int_{\Omega^\pm} (\nabla \cdot \mathbf{D}^\pm) (\nabla \phi^\pm \cdot \mathbf{u}^\pm) dx - \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} k_B T c_i^\pm \nabla \cdot \mathbf{u}^\pm dx \\
 & + \int_{\partial\Omega} \sum_{i=1}^{Np} k_B T c_i^\pm \mathbf{u}^\pm \cdot \mathbf{n} dS + \int_{\Gamma} \left[\sum_{i=1}^{Np} k_B T c_i \mathbf{u} \cdot \mathbf{n} \right] dS \\
 = & - \sum_{\pm} \int_{\Omega^\pm} \mathbf{D}^\pm \cdot (\nabla \mathbf{u}^\pm) \cdot \nabla \phi^\pm dx - \sum_{\pm} \int_{\Omega^\pm} \mathbf{D}^\pm \cdot (\nabla \nabla \phi^\pm) \cdot \mathbf{u}^\pm dx + \int_{\Gamma} [Q \nabla \phi \cdot \mathbf{u}] dS \\
 & + \int_{\partial\Omega} (\mathbf{D}^\pm \cdot \mathbf{n}) (\nabla \phi^\pm \cdot \mathbf{u}^\pm) dS \\
 & - \sum_{\pm} \int_{\Omega^\pm} \sum_{i=1}^{Np} k_B T c_i^\pm \nabla \cdot \mathbf{u}^\pm dx + \int_{\partial\Omega} \sum_{i=1}^{Np} k_B T c_i^\pm \mathbf{u}^\pm \cdot \mathbf{n} dS + \int_{\Gamma} \left[\sum_{i=1}^{Np} k_B T c_i \mathbf{u} \cdot \mathbf{n} \right] dS
 \end{aligned}$$

$$\begin{aligned}
&= \sum_{\pm} \int_{\Omega^{\pm}} \epsilon_0 \epsilon_r^{\pm} (\nabla \phi^{\pm} \otimes \nabla \phi^{\pm}) : \nabla \mathbf{u}^{\pm} dx + \sum_{\pm} \int_{\Omega^{\pm}} \frac{\epsilon_0 \epsilon_r^{\pm}}{2} (\nabla |\nabla \phi^{\pm}|^2) \cdot \mathbf{u}^{\pm} dx \\
&\quad + \int_{\Gamma} [Q \nabla \phi \cdot \mathbf{u}] dS + \int_{\partial \Omega} (\mathbf{D}^{\pm} \cdot \mathbf{n}) (\nabla \phi^{\pm} \cdot \mathbf{u}^{\pm}) dS \\
&\quad - \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} k_B T c_i^{\pm} \nabla \cdot \mathbf{u}^{\pm} dx + \int_{\partial \Omega} \sum_{i=1}^{Np} k_B T c_i^{\pm} \mathbf{u}^{\pm} \cdot \mathbf{n} dS + \int_{\Gamma} \left[\sum_{i=1}^{Np} k_B T c_i \mathbf{u} \cdot \mathbf{n} \right] dS \\
&= \sum_{\pm} \int_{\Omega^{\pm}} \epsilon_0 \epsilon_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} k_B T c_i^{\pm} \nabla \cdot \mathbf{u}^{\pm} dx \\
&\quad + \int_{\Gamma} [e_{es} \mathbf{u} \cdot \mathbf{n}] dS + \int_{\Gamma} [Q \nabla \phi \cdot \mathbf{u}] dS + \int_{\Gamma} \left[\sum_{i=1}^{Np} k_B T c_i \mathbf{u} \cdot \mathbf{n} \right] dS + I_{22b},
\end{aligned}$$

where

$$I_{22b} := \int_{\partial \Omega} e_{es}^{\pm} \mathbf{u}^{\pm} \cdot \mathbf{n} dS + \int_{\partial \Omega} (\mathbf{D}^{\pm} \cdot \mathbf{n}) (\nabla \phi^{\pm} \cdot \mathbf{u}^{\pm}) dS + \int_{\partial \Omega} \sum_{i=1}^{Np} k_B T c_i^{\pm} \mathbf{u} \cdot \mathbf{n} dS.$$

By using the Lemma on the interface $\Gamma(t)$, we have

$$\frac{d^n Q}{dt} = \frac{d^n \mathbf{D}}{dt} \cdot \mathbf{n} + \frac{d^n \mathbf{n}}{dt} \cdot \mathbf{D} = \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{n} + v_n \partial_n \mathbf{D} \cdot \mathbf{n} - \nabla_{\Gamma} v_n \cdot \mathbf{D},$$

which yields

$$\frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{n} = \frac{d^n Q}{dt} + \nabla_{\Gamma} v_n \cdot \mathbf{D} - v_n \partial_n \mathbf{D} \cdot \mathbf{n} = \frac{d^n Q}{dt} - \epsilon_0 \epsilon_r \nabla_{\Gamma} v_n \cdot \nabla_{\Gamma} \phi - v_n \partial_n \mathbf{D} \cdot \mathbf{n}.$$

Then the fourth term in (B.2) could be rewritten as

$$\begin{aligned}
\int_{\Gamma} \left[\phi \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{n} \right] dS &= \int_{\Gamma} [\phi] \frac{d^n Q}{dt} dS - \int_{\Gamma} [\epsilon_0 \epsilon_r \phi \nabla_{\Gamma} v_n \cdot \nabla_{\Gamma} \phi + \phi v_n \partial_n \mathbf{D} \cdot \mathbf{n}] dS \\
&= \int_{\Gamma} [\phi] \frac{d^n Q}{dt} dS + \int_{\Gamma} [\epsilon_0 \epsilon_r \nabla_{\Gamma} \cdot (\phi \nabla_{\Gamma} \phi)] v_n dS - \int_{\Gamma} [\phi \partial_n \mathbf{D} \cdot \mathbf{n}] v_n dS. \quad (\text{B.5})
\end{aligned}$$

Combining (B.2), (B.4) and (B.5) yields

$$\begin{aligned}
I_2 + I_3 &:= \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} \nabla \mu_i^{\pm} \cdot \mathbf{j}_i^{\pm} dx + \sum_{\pm} \int_{\Omega^{\pm}} \epsilon_0 \epsilon_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) : \nabla \mathbf{u}^{\pm} dx \\
&\quad - \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} k_B T c_i^{\pm} \nabla \cdot \mathbf{u}^{\pm} dx + \int_{\Gamma} \left[\left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) \mathbf{u} \cdot \mathbf{n} \right] dS + \int_{\Gamma} [Q \nabla \phi \cdot \mathbf{u}] dS \\
&\quad - \int_{\Gamma} \sum_{i=1}^{Np} [\mu_i] J_i dS - \int_{\Gamma} [\phi] \frac{d^n Q}{dt} dS
\end{aligned}$$

$$\begin{aligned}
 & - \int_{\Gamma} \left[\nabla_{\Gamma} \cdot \left(\nabla_{\Gamma} \left(\frac{\epsilon_0 \epsilon_r}{2} \phi^2 \right) \right) \right] \mathbf{v} \cdot \mathbf{n} dS + \int_{\Gamma} [\phi \partial_n \mathbf{D} \cdot \mathbf{n}] \mathbf{v} \cdot \mathbf{n} dS \\
 & + \int_{\Gamma} \left[e_{es} + e_{par} - \sum_{i=1}^{Np} c_i \mu_i \right] \mathbf{v} \cdot \mathbf{n} dS + I_{2b}
 \end{aligned} \tag{B.6}$$

where $I_{2b} = I_{21b} + I_{22b}$. For the last term in Eq. (2.7), by using the surface Reynolds formula (2.6), we obtain

$$I_4 := \int_{\Gamma} C_m[\phi] \frac{d^n}{dt}([\phi]) dS - \int_{\Gamma} ((e_{\Gamma} + \gamma_0) H \mathbf{n}) \cdot \mathbf{v} dS. \tag{B.7}$$

Combining Eqs. (B.1), (B.6) and (B.7), we have

$$\begin{aligned}
 \frac{dE^{tot}}{dt} = & - \sum_i \int_{\Omega^{\pm}} \sigma_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \left(\sigma_e^{\pm} - \epsilon_0 \epsilon_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) \right) : \nabla \mathbf{u}^{\pm} dx \\
 & + \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} \nabla \mu_i^{\pm} \cdot \mathbf{j}_i^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} k_B T c_i^{\pm} \nabla \cdot \mathbf{u}^{\pm} dx \\
 & + \sum_{\pm} \int_{\Omega^{\pm}} p_c^{\pm} \left(\sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} (\nabla \cdot \mathbf{j}_i^{\pm} + c_i^{\pm} \nabla \cdot \mathbf{u}^{\pm}) - \nabla \cdot \mathbf{u}^{\pm} \right) dx \\
 & + \int_{\Gamma} [(\mathbf{n} \cdot (\sigma_{\eta} + \sigma_e) - Q_{\rho} \mathbf{u}) \cdot \mathbf{u}] dS + \int_{\Gamma} \left[\left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) \mathbf{u} \cdot \mathbf{n} \right] dS \\
 & + \int_{\Gamma} [Q \nabla \phi \cdot \mathbf{u}] dS - \int_{\Gamma} \sum_{i=1}^{Np} [\mu_i] J_i dS - \int_{\Gamma} [\phi] \frac{d^n Q}{dt} dS \\
 & - \int_{\Gamma} \left[\nabla_{\Gamma} \cdot \left(\nabla_{\Gamma} \left(\frac{\epsilon_0 \epsilon_r}{2} \phi^2 \right) \right) \right] \mathbf{v} \cdot \mathbf{n} dS + \int_{\Gamma} [\phi \partial_n \mathbf{D} \cdot \mathbf{n}] \mathbf{v} \cdot \mathbf{n} dS \\
 & + \int_{\Gamma} \left[\left(e_{es} + e_{par} - \sum_{i=1}^{Np} \mu_i c_i \right) \right] \mathbf{v} \cdot \mathbf{n} dS + \int_{\Gamma} \left[\frac{|u_n|^2}{2} \right] Q_{\rho} dS \\
 & + \int_{\Gamma} C_m[\phi] \frac{d^n}{dt}([\phi]) dS - \int_{\Gamma} (e_{\Gamma} + \gamma_0) H \mathbf{v} \cdot \mathbf{n} dS + I_{1b} + I_{2b}
 \end{aligned} \tag{B.8}$$

By using the fact that

$$\begin{aligned}
 & \sum_{\pm} \int_{\Omega^{\pm}} \left(p_c^{\pm} \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \nabla \cdot \mathbf{j}_i^{\pm} \right) dx \\
 = & - \sum_{\pm} \int_{\Omega^{\pm}} \nabla \cdot \left(p_c^{\pm} \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \cdot \mathbf{j}_i^{\pm} dx + \int_{\Gamma} \left[\left(p_c \sum_{i=1}^{Np} \frac{\partial_i \rho}{\rho} \right) \mathbf{j}_i \cdot \mathbf{n} \right] dS \\
 & + \int_{\partial \Omega} \left(p_c^{\pm} \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \mathbf{j}_i^{\pm} \cdot \mathbf{n} dS
 \end{aligned}$$

$$\begin{aligned}
&= -\sum_{\pm} \int_{\Omega^{\pm}} \nabla \left(p_c^{\pm} \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \cdot \mathbf{j}_i^{\pm} dx + \int_{\Gamma} \left[p_c \sum_{i=1}^{Np} \frac{\partial_i \rho}{\rho} \left(J_i - \frac{c_i}{\rho} Q_{\rho} \right) \right] dS \\
&\quad + \int_{\partial\Omega} \left(p_c^{\pm} \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \mathbf{j}_i^{\pm} \cdot \mathbf{n} dS \\
&= -\sum_{\pm} \int_{\Omega^{\pm}} \nabla \left(p_c^{\pm} \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \cdot \mathbf{j}_i^{\pm} dx + \int_{\Gamma} \left[\sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} \right] J_i dS \\
&\quad - \int_{\Gamma} \left[\sum_{i=1}^{Np} p_c \frac{\partial_i \rho}{\rho} \frac{c_i}{\rho} \right] Q_{\rho} dS + \int_{\partial\Omega} \left(p_c^{\pm} \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \mathbf{j}_i^{\pm} \cdot \mathbf{n} dS. \tag{B.9}
\end{aligned}$$

Eq. (B.8) could be rewritten as

$$\begin{aligned}
\frac{dE^{tot}}{dt} &= -\sum_i \int_{\Omega^{\pm}} \boldsymbol{\sigma}_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \left(\boldsymbol{\sigma}_e^{\pm} - \epsilon_0 \boldsymbol{\epsilon}_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) \right) : \nabla \mathbf{u}^{\pm} dx \\
&\quad + \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} \nabla \tilde{\mu}_i^{\pm} \cdot \mathbf{j}_i^{\pm} dx - \int_{\Gamma} \sum_{i=1}^{Np} [\tilde{\mu}_i] J_i dS \\
&\quad + \sum_{\pm} \int_{\Omega^{\pm}} \left(-\sum_{i=1}^{Np} k_B T c_i^{\pm} - p_c^{\pm} \left(1 - \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i \right) \right) \nabla \cdot \mathbf{u}^{\pm} dx \\
&\quad + \int_{\Gamma} \left[\left((\boldsymbol{\sigma}_{\eta} + \boldsymbol{\sigma}_e) \cdot \mathbf{n} - Q_{\rho} \mathbf{u} + \left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) \mathbf{n} + Q \nabla \phi \right) \cdot \mathbf{u} \right] dS \\
&\quad + \int_{\Gamma} \left[e_{es} + e_{par} - \sum_{i=1}^{Np} \mu_i c_i + \phi \partial_n \mathbf{D} \cdot \mathbf{n} - \nabla_{\Gamma} \cdot \left(\nabla_{\Gamma} \left(\frac{\epsilon_0 \boldsymbol{\epsilon}_r}{2} \phi^2 \right) \right) \right] \mathbf{v} \cdot \mathbf{n} dS \\
&\quad + \int_{\Gamma} \left[-p_c \sum_{i=1}^{Np} \frac{\partial_i \rho}{\rho^2} c_i + \frac{|u_n|^2}{2} \right] Q_{\rho} dS \\
&\quad + \int_{\Gamma} [\phi] \frac{d^n}{dt} (C_m[\phi] - Q) dS - \int_{\Gamma} (e_{\Gamma} + \gamma_0) H \mathbf{v} \cdot \mathbf{n} dS + I_b \\
&= -\sum_{\pm} \int_{\Omega^{\pm}} \boldsymbol{\sigma}_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \left(\boldsymbol{\sigma}_e^{\pm} - \epsilon_0 \boldsymbol{\epsilon}_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) \right) : \nabla \mathbf{u}^{\pm} dx \\
&\quad + \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} \nabla \tilde{\mu}_i^{\pm} \cdot \mathbf{j}_i^{\pm} dx - \int_{\Gamma} \sum_{i=1}^{Np} [\tilde{\mu}_i] J_i dS \\
&\quad + \sum_{\pm} \int_{\Omega^{\pm}} \left(-\sum_{i=1}^{Np} k_B T c_i^{\pm} - p_c^{\pm} \left(1 - \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i \right) \right) \nabla \cdot \mathbf{u}^{\pm} dx \\
&\quad + \int_{\Gamma} \left\{ \left[(\boldsymbol{\sigma}_{\eta} + \boldsymbol{\sigma}_e) \cdot \mathbf{n} - Q_{\rho} \mathbf{u} + \left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) \mathbf{n} + Q \nabla \phi \right] \right\} \cdot \mathbf{v}_{\tau} dS
\end{aligned}$$

$$\begin{aligned}
 & + \int_{\Gamma} \left[\left((\sigma_{\eta} + \sigma_e) \cdot \mathbf{n} - Q_{\rho} \mathbf{u} + \left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) \mathbf{n} + Q \nabla \phi \right) \cdot \mathbf{n} u_n \right] dS \\
 & + \int_{\Gamma} \left[e_{es} + e_{par} - \sum_{i=1}^{Np} \mu_i c_i + \phi \partial_n \mathbf{D} \cdot \mathbf{n} - \nabla_{\Gamma} \cdot \left(\nabla_{\Gamma} \left(\frac{\epsilon_0 \epsilon_r}{2} \phi^2 \right) \right) \right] \mathbf{v} \cdot \mathbf{n} dS \\
 & + \int_{\Gamma} \left[-p_c \sum_{i=1}^{Np} \frac{\partial_i \rho}{\rho^2} c_i + \frac{|u_n|^2}{2} \right] Q_{\rho} dS \\
 & + \int_{\Gamma} [\phi] \frac{d^n}{dt} (C_m[\phi] - Q) dS - \int_{\Gamma} (e_{\Gamma} + \gamma_0) H \mathbf{v} \cdot \mathbf{n} dS + I_b \\
 = & - \sum_{\pm} \int_{\Omega^{\pm}} \sigma_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx - \sum_{\pm} \int_{\Omega^{\pm}} \left(\sigma_e^{\pm} - \epsilon_0 \epsilon_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) \right) : \nabla \mathbf{u}^{\pm} dx \\
 & + \sum_{\pm} \int_{\Omega^{\pm}} \sum_{i=1}^{Np} \nabla \tilde{\mu}_i^{\pm} \cdot \mathbf{j}_i^{\pm} dx - \int_{\Gamma} \sum_{i=1}^{Np} [\tilde{\mu}_i] J_i dS \\
 & + \sum_{\pm} \int_{\Omega^{\pm}} \left(- \sum_i k_B T c_i^{\pm} - p_c^{\pm} \left(1 - \sum_{i=1}^{Np} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i \right) \right) \nabla \cdot \mathbf{u}^{\pm} dx \\
 & + \int_{\Gamma} (\mathbf{F}_{mb} + [Q \nabla \phi]) \cdot \mathbf{v}_{\tau} dS \\
 & + \int_{\Gamma} \left[\frac{\left((\sigma_{\eta} + \sigma_e) \cdot \mathbf{n} - Q_{\rho} \mathbf{u} + \left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) \mathbf{n} + Q \nabla \phi \right)}{\rho} \right] \cdot \mathbf{n} Q_{\rho} dS \\
 & + \int_{\Gamma} \left(\mathbf{F}_{mb} + \left[\left(e_{es} + \sum_{i=1}^{Np} k_B T c_i \right) \mathbf{n} + Q \nabla \phi \right] \right) \cdot \mathbf{n} v_n dS \\
 & + \int_{\Gamma} \left[e_{es} + e_{par} - \sum_{i=1}^{Np} \mu_i c_i + \phi \partial_n \mathbf{D} \cdot \mathbf{n} - \nabla_{\Gamma} \cdot \left(\nabla_{\Gamma} \left(\frac{\epsilon_0 \epsilon_r}{2} \phi^2 \right) \right) \right] v_n dS \\
 & + \int_{\Gamma} \left[-p_c \sum_{i=1}^{Np} \frac{\partial_i \rho}{\rho^2} c_i + \frac{|u_n|^2}{2} \right] Q_{\rho} dS \\
 & + \int_{\Gamma} [\phi] \frac{d^n}{dt} (C_m[\phi] - Q) dS - \int_{\Gamma} (e_{\Gamma} + \gamma_0) H v_n dS + I_b, \tag{B.10}
 \end{aligned}$$

where

$$\begin{aligned}
 \tilde{\mu}_i^{\pm} &= \mu_i^{\pm} - p_c^{\pm} \frac{\partial_i \rho^{\pm}}{\rho^{\pm}}, \quad i = 1, \dots, Np, \\
 I_b &= I_{1b} + I_{2b} + \int_{\partial \Omega} \left(p_c^{\pm} \sum_i \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} \right) \mathbf{j}_i^{\pm} \cdot \mathbf{n} dS.
 \end{aligned}$$

C Membrane mechanical properties

Membrane mechanical properties can be included in the analysis by modify Eq. (2.7). Assuming that E_m is the energy induced by mechanical properties of the membrane, the fourth term of Eq. (2.7) I_4 yields

$$\begin{aligned} I_4 &:= \frac{d}{dt} \int_{\Gamma(t)} \left(\gamma_0 + C_m [\phi]^2 \right) dS + \frac{dE_m}{dt} \\ &= \int_{\Gamma} C_m [\phi] \frac{d^n}{dt} ([\phi]) dS - \int_{\Gamma} ((e_{\Gamma} H \mathbf{n} - \mathbf{F}_m)) \cdot \mathbf{v} dS, \end{aligned} \quad (\text{C.1})$$

where we used the results [39], $\frac{dE_m}{dt} = \int_{\Gamma(t)} \frac{\delta E_m}{\delta \Gamma} \cdot \mathbf{v} dS$ and denotes $\mathbf{F}_m = \frac{\delta E_m}{\delta \Gamma}$. Then the rate of total energy change is

$$\begin{aligned} \frac{dE^{tot}}{dt} &= - \sum_i \int_{\Omega^{\pm}} \sigma_{\eta}^{\pm} : \nabla \mathbf{u}^{\pm} dx \\ &\quad - \sum_{\pm} \int_{\Omega^{\pm}} \left(\sigma_e^{\pm} - \epsilon_0 \epsilon_r^{\pm} \left(\nabla \phi^{\pm} \otimes \nabla \phi^{\pm} - \frac{|\nabla \phi^{\pm}|^2}{2} \mathbf{I} \right) \right) : \nabla \mathbf{u}^{\pm} dx \\ &\quad + \sum_{\pm} \int_{\Omega^{\pm}} \sum_i \nabla \tilde{\mu}_i^{\pm} \cdot \mathbf{j}_i^{\pm} dx - \int_{\Gamma} \sum_i [\tilde{\mu}_i] J_i dS \\ &\quad + \sum_{\pm} \int_{\Omega^{\pm}} \left(- \sum_i K_B T c_i^{\pm} + p_c^{\pm} \left(1 - \sum_i \frac{\partial_i \rho^{\pm}}{\rho^{\pm}} c_i \right) \right) \nabla \cdot \mathbf{u}^{\pm} dx \\ &\quad + \int_{\Gamma} (\mathbf{F}_{mb} - \mathbf{F}_m + [Q \nabla \phi]) \cdot \mathbf{v}_{\tau} dS \\ &\quad + \int_{\Gamma} (\mathbf{F}_{mb} \cdot \mathbf{n} + [F_n] - (e_{\Gamma} H - \mathbf{F}_m \cdot \mathbf{n})) v_n dS \\ &\quad + \int_{\Gamma} \left[\frac{F_{\rho}}{\rho} \right] Q_{\rho} dS + \int_{\Gamma} [\phi] \frac{d^n}{dt} (C_m [\phi] - Q) dS - I_b. \end{aligned} \quad (\text{C.2})$$

Then we obtain the force balance equation on a membrane with mechanical properties.

$$[\sigma_{\eta} + \sigma_e] \cdot \mathbf{n} - [Q_{\rho} \mathbf{u}] = -e_{\Gamma} H \mathbf{n} - \nabla_{\Gamma} e_{\Gamma} + \mathbf{F}_m. \quad (\text{C.3})$$

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