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DIFFUSED SOLUTE-SOLVENT INTERFACE WITH POISSON–BOLTZMANN ELECTROSTATICS: FREE-ENERGY VARIATION AND SHARP-INTERFACE LIMIT

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Abstract

A phase-field free-energy functional for the solvation of charged molecules (e.g., proteins) in aqueous solvent (i.e., water or salted water) is constructed. The functional consists of the solute volumetric and solute-solvent interfacial energies, the solute-solvent van der Waals interaction energy, and the continuum electrostatic free energy described by the Poisson–Boltzmann theory. All these are expressed in terms of phase fields that, for low free-energy conformations, are close to one value in the solute phase and another in the solvent phase. A key property of the model is that the phase-field interpolation of dielectric coefficient has the vanishing derivative at both solute and solvent phases. The first variation of such an effective free-energy functional is derived. Matched asymptotic analysis is carried out for the resulting relaxation dynamics of the diffused solute-solvent interface. It is shown that the sharp-interface limit is exactly the variational implicit-solvent model that has successfully captured capillary evaporation in hydrophobic confinement and corresponding multiple equilibrium states of underlying biomolecular systems as found in experiment and molecular dynamics simulations. Our phase-field approach and analysis can be used to possibly couple the description of interfacial fluctuations for efficient numerical computations of biomolecular interactions.

Keywords and phrases

variational implicit-solvent model; diffused solute-solvent interface; Poisson–Boltzmann theory; matched asymptotic analysis; sharp-interface limit

1. Introduction

The solvation of charged molecules such as DNAs and proteins in aqueous solvent (i.e., water or salted water) is a fundamental biological process. Implicit-solvent models provide efficient predictions of the solvation free energies and equilibrium conformations of underlying molecular systems [35]. In such a model, the solvent molecules and ions are treated implicitly and their effects are coarse-grained. In a large class of implicit-solvent

models, the solute-solvent interface that separates the solvent region from solutes is used to calculate the surface energy and electrostatic energy. The later is often done by solving Poisson's or the Poisson–Boltzmann equation with the dielectric coefficient close to 1 and 80 in the solute and solvent regions, respectively [7,16,27,38]. In a variational implicit-solvent model (VISM) [19,20,44], one determines the solvation free energies and stable equilibrium conformations by minimizing a macroscopic free-energy functional of all possible solute-solvent interfaces, i.e., dielectric boundaries.

Let us denote by $\Omega \subset \mathbb{R}^3$ the region of an underlying solvation system; cf. Figure 1.1. Assume that there are total N solute atoms located at $x_1, \ldots, x_N$ inside Ω and carrying partial charges $Q_1, \ldots, Q_N$, respectively. Assume also that there are M ionic species in the solvent, and denote by c_j^∞ and $q_j = z_j e$ the bulk concentration and charge for the jth ionic species, respectively, where z_j is the valence and e elementary charge. Let Γ be a closed and smooth surface, a possible solute-solvent interface, that encloses all $x_1, \ldots, x_N$ and that divides Ω into two regions: the solute region Ω_p (p stands for protein) and the solvent region Ω_w (w stands for water). The VISM solvation free-energy functional is then defined for all such solute-solvent interface Γ by

$$F[\Gamma]=P\mathrm{Vol}(\Omega_p)+\gamma_0\mathrm{Area}(\Gamma)+\rho_w\int_{\Omega_w}U(x)\,dx+\int_\Omega\left[-\frac{\varepsilon_\Gamma}{2}|\nabla\psi|^2+\rho_f\psi-\chi_w V(\psi)\right]dx. \quad (1.1)$$

The first term here is the energy of creating a solute cavity in the solvent against the pressure difference P between the solvent liquid and solute vapor. The second term is the surface energy with γ_0 being the constant surface tension. For simplicity, we neglect the Tolman correction to the surface tension [40]. The third term is the energy of the van der Waals (vdW) type interaction between the solute atoms x_i ($1 \le i \le N$) and continuum solvent, where ρ_w is the constant bulk solvent density. The interaction potential U is often defined by

$$U(x)=\sum_{i=1}^{N}U_{\mathrm{LJ}}^{(i)}(|x-x_i|),$$

where each

$$U_{\mathrm{LJ}}^{(i)}(r)=4\varepsilon_i\left[\left(\frac{\sigma_i}{r}\right)^{12}-\left(\frac{\sigma_i}{r}\right)^{6}\right]$$

is a Lennard-Jones potential, and all the parameters ε_i of energy and σ_i of length are given.

The last term is the electrostatic free energy, where ψ is the electrostatic potential, ε_Γ is the coefficient of permittivity, ρ_f is a fixed charge density approximating the solute point charges $\sum_{i=1}^{N}Q_i\delta_{x_i}$ with δ_{x_i} being the Dirac delta function at x_i, χ_w is the characteristic function of the solvent region Ω_w, and $V(\psi)$ describes the ionic contribution to the

electrostatic interaction. Here, ions are assumed to be in an equilibrium macroscopically; and the equilibrium ionic concentrations are given by the Boltzmann distributions through the electrostatic potential ψ [7, 27]. The potential ψ is the solution to a boundary-value problem of the dielectric-boundary Poisson–Boltzmann equation

$$\nabla \cdot \varepsilon_\Gamma \nabla \psi - \chi_{\mathrm{w}} V'(\psi) = -\rho_{\mathrm{f}} \quad \text{in } \Omega, \quad (1.2)$$

$$\psi = \psi_\infty \quad \text{on } \partial\Omega, \quad (1.3)$$

where ψ_∞ is a given function on the boundary $\partial\Omega$. The coefficient ε_Γ is defined by

$$\varepsilon_\Gamma(x) = \begin{cases} \varepsilon_{\mathrm{p}}\varepsilon_0 & \text{if } x \in \Omega_{\mathrm{p}}, \\ \varepsilon_{\mathrm{w}}\varepsilon_0 & \text{if } x \in \Omega_{\mathrm{w}}, \end{cases} \quad (1.4)$$

where ε_{p} and ε_{w} are the dielectric coefficients (relative permitivities) of the solute and solvent regions, respectively, and ε_0 is the vacuum permittivity. In general, $\varepsilon_{\mathrm{p}} \approx 1$ and $\varepsilon_{\mathrm{w}} \approx 80$. In the classical Poisson–Boltzmann theory,

$$V(\psi) = \beta^{-1} \sum_{j=1}^{M} c_j^\infty \left(e^{-\beta q_j \psi} - 1\right),$$

where $\beta = 1/(k_{\mathrm{B}}T)$ is the inverse thermal energy with k_{B} the Boltzmann constant and T absolute temperature. Different forms of $V(\psi)$ can be used for the linearized or size-modified Poisson–Boltzmann equation [26, 45]. More complicated forms $V = V(\psi, \nabla\psi)$ involving both ψ and $\nabla\psi$ can be used to model effects such as the ionic concentration dependent dielectric response but can also be more complicated for implementation [2,23,29].

Cheng *et al*. [9,10,12,41,44] developed a highly accurate, compact coupling interface method for solving the dielectric-boundary Poisson–Boltzmann equation and a robust level-set method to minimize the VISM functional (1.1). The normal velocity in the level-set formulation is the (normal component of) effective boundary force defined to be the negative variational derivative $-\delta_\Gamma F[\Gamma] : \Gamma \to \mathbb{R}$ of the free-energy functional $F[\Gamma]$ with respect to the location change of interface Γ. Let n denote the unit normal to the interface Γ pointing from the solvent region Ω_{w} to solute region Ω_{p}. We have [5,9–11,28,44]

$$-\delta_\Gamma F[\Gamma] = P + 2\gamma_0 H - \rho_{\mathrm{w}} U + \frac{1}{2}\left(\frac{1}{\varepsilon_{\mathrm{p}}\varepsilon_0} - \frac{1}{\varepsilon_{\mathrm{w}}\varepsilon_0}\right)\left(\varepsilon_\Gamma \frac{\partial\psi}{\partial n}\right)^2 + \frac{1}{2}(\varepsilon_{\mathrm{w}}\varepsilon_0 - \varepsilon_{\mathrm{p}}\varepsilon_0)|\nabla_\Gamma \psi|^2 + V(\psi) \quad \text{on } \Gamma, \quad (1.5)$$

where H is the mean curvature that is positive if Ω_{p} is a sphere and $\nabla_\Gamma = (I - n \otimes n)\,\nabla$, with I the identity matrix, is the surface gradient along Γ.

While successful initially [9, 12, 22, 41, 44], the sharp-interface VISM needs to be improved in several aspects. The most critical one is to include the description of fluctuations, both around the solute-solvent interface and in the bulk solvent. Such fluctuations are particularly crucial in the transition of one equilibrium conformation to another and in sampling different states to accurately predict the free energies of underlying biomolecular systems. It is certainly possible to describe interfacial fluctuations within a sharp-interface framework. But several implementational difficulties can arise. For instance, the extension of normal velocity in the level-set method can be hard for a moving fluctuating interface. Moreover, fluctuations can nucleate and coalesce small bubbles (water regions) inside solutes, making it hard to solve the dielectric boundary Poisson–Boltzmann equation in a sharp-interface formulation. In seeking for an alternative approach, we notice that initial theoretical and computational studies of interfacial fluctuations using a diffused-interface approach seem promising [3,17,24]. We therefore propose in this work a diffused-interface approach to the solvation of charged molecules. In a slight different language, this is a phase-field approach as it is well appreciated that the solvent-solute interface in a biomolecular system resembles a liquid-vapor interface, and the solvent and solute can be regarded as two different phases [6,42]. The phase-field approach has been widely used in studying interface problems arising in many scientific areas, such as materials physics, complex fluids, biomembranes, and cell motility, cf. e.g., [1, 13, 18, 25, 31, 37] and the references therein.

Our phase-field model is governed by the free-energy functional

$$F_\xi[\phi]=P\int_\Omega \phi^2 \mathrm{d}x+\gamma_0\int_\Omega \left[\frac{\xi}{2}|\nabla\phi|^2+\frac{1}{\xi}W(\phi)\right]\,\mathrm{d}x+\rho_{\mathrm{w}}\int_\Omega(\phi-1)^2U\,\mathrm{d}x+\int_\Omega\left[-\frac{\varepsilon(\phi)}{2}|\nabla\psi_\phi|^2+\rho_{\mathrm{f}}\psi_\phi-(\phi-1)^2V(\psi_\phi)\right]\,\mathrm{d}x \quad (1.6)$$

for all phase fields $\varphi:\Omega\to\mathbb{R}$, where the electrostatic potential ψ_φ is the solution to the boundary-value problem of Poisson–Boltzmann equation with a diffused dielectric boundary

$$\nabla\cdot\varepsilon(\phi)\nabla\psi_\phi-(\phi-1)^2V'(\psi_\phi)=-\rho_{\mathrm{f}} \quad \text{in } \Omega, \quad (1.7)$$

$$\psi_\phi=\psi_\infty \quad \text{on } \partial\Omega. \quad (1.8)$$

Here $\xi>0$ is a small number. With a low free energy, a phase field φ should be close to two values, say, 0 and 1, respectively, in the solvation region Ω, except a thin transition layer that represents the dielectric boundary. The sets $\{\varphi\approx 0\}$ and $\{\varphi\approx 1\}$ represent the solvent and solute regions, respectively. With such a convention, the first term in (1.6) corresponds to that in (1.1), describing the volumetric energy. The second term in (1.6), in which,

$$W(\phi)=18\phi^2(1-\phi)^2,$$

approximates the surface energy [30, 33, 39]. The third term in (1.6) corresponds to that in (1.1), describing the energy of solute-solvent interaction. Finally, the last term in (1.6) corresponds to that in (1.1), describing the electrostatic free energy. In this term, $\varepsilon(\varphi)$ is

defined to be a smooth function of φ that interpolates the piecewise constant dielectric coefficient: $\varepsilon(0) = \varepsilon_w\varepsilon_0$ and $\varepsilon(1) = \varepsilon_p\varepsilon_0$. We shall require that $\varepsilon'(0) = \varepsilon'(1) = 0$. Note that the electrostatic potential ψ_φ depends on φ.

We study our proposed phase-field solvation free-energy functional (1.6), and the corresponding relaxation dynamics. Our main results are as follows:

1. We prove the well-posedness of the boundary-value problem of Poisson–Boltzmann equation (1.7) and (1.8), and obtain some bounds for the electrostatic potential; cf. Theorem 2.1;
2. We derive, first intuitively and then rigorously, the first variation of the phase-field free-energy functional (1.6)

$$\delta_\phi F[\phi]=2P\,\phi-\gamma_0\left[\xi\Delta\phi-\frac{1}{\xi}W'(\phi)\right]+2\rho_w(\phi-1)U-\frac{1}{2}\varepsilon'(\phi)|\nabla\psi|^2-2(\phi-1)V(\psi);$$

   cf. Theorem 3.1;
3. We consider the relaxation dynamics $\partial_t\varphi = -\delta_\varphi F[\varphi]$ for $\varphi = \varphi(x, t)$ with t denoting the time variable. Using the method of matched asymptotic analysis [4, 14, 15, 34, 36], we show that, in the sharp-interface limit, the normal velocity of the solute-solvent interface is exactly the boundary force (1.5) in the original sharp-interface variational approach; cf. Theorem 5.1.

Several remarks are in order. First, our diffuse-interface model (1.6) differs from our previous one [30,43] significantly in that we use the Poisson–Boltzmann equation, rather than the Coulomb-field approximation [8, 41] which requires no solution of partial differential equations, to describe the electrostatic interaction. Second, our relaxation dynamics $\partial_t\varphi = -\delta_\varphi F[\varphi]$ is a non-conservative dynamics with respect to the phase-field function φ. In fact, the relaxation process can change the volume of solute region $\{\varphi \approx 1\}$. The amount of ions, however, are controlled through their bulk concentrations $c_j^\infty\,(j=1,\ldots,M)$ that are input parameters. Third, the surface energy term described by the gradient-square and double-well terms in our phase-field energy functional (1.6) coincides with the part in an effective Hamiltonian for the large-scale solvent density in the Lum–Chandler–Weeks theory of solvation [32].

The rest of the paper is organized as follows: In Section 2, we prove the existence and uniqueness of, and provide bounds for, the solution to the Poisson–Boltzmann equation with a diffused dielectric boundary that is given by a phase field. In Section 3, we derive the first variation of the phase-field free-energy functional. In Section 4, we use the matched asymptotic analysis to study the relaxation dynamics in a fast and the regular time scales. In Section 5, we continue our matched asymptotic analysis for a slow time scale to show that the sharp-interface limit of the relaxation dynamics is exactly the same as in the original sharp-interface variational model.

2. Poisson–Boltzmann Electrostatics with a Diffused Dielectric Boundary

We make the following assumptions:

(A1) The solvation region Ω is a bounded, connected, open set with a sufficiently smooth boundary $\partial\Omega$. All $x_1, \ldots, x_N$ are given points in Ω. All P, γ_0, ρ_w, ε_p, and ε_w are positive constants with $\varepsilon_p < \varepsilon_w$. The function $\rho_f \in L^\infty(\Omega)$. The function $\psi_\infty \in W^{1,\infty}(\Omega)$;

(A2) The function $U : \mathbb{R}^3 \setminus \{x_1, \ldots, x_N\} \to \mathbb{R}$ is continuously differentiable and bounded below. Moreover, $\lim_{x\to x_i} U(x) = +\infty$ for each i ($1 \le i \le N$) and $\lim_{x\to\infty} U(x) = 0$;

(A3) The function $\varepsilon \in C^1(\mathbb{R})$. There exist positive numbers $\varepsilon_{\min}$, $\varepsilon_{\max}$, and $\varepsilon'_{\max}$ such that $\varepsilon_{\min} \le \varepsilon(\varphi) \le \varepsilon_{\max}$ and $|\varepsilon'(\phi)| \le \varepsilon'_{\max}$ for all $\varphi \in \mathbb{R}$. Moreover, $\varepsilon(0) = \varepsilon_w\varepsilon_0$, $\varepsilon(1) = \varepsilon_p\varepsilon_0$, $\varepsilon'(0) = \varepsilon'(1) = 0$, and $\varepsilon'(\varphi) \ne 0$ if $0 < \varphi < 1$;

(A4) The function $V \in C^2(\mathbb{R})$. It is strictly convex. Moreover, $V(0) = \min_{s\in\mathbb{R}} V(s) < V(s)$ for any $s \ne 0$, $V(\pm\infty) = +\infty$, and $V'(\pm\infty) = \pm\infty$.

Here are two examples of the function $\varepsilon = \varepsilon(\varphi)$ with all the desired properties.

Example 1.

$$\varepsilon(\phi) = \begin{cases} \varepsilon_w\varepsilon_0 & \text{if } \phi \le 0, \\ \dfrac{\varepsilon_p\varepsilon_0 e^{\tan(\pi(\phi-1/2))} + \varepsilon_w\varepsilon_0 e^{-\tan(\pi(\phi-1/2))}}{e^{\tan(\pi(\phi-1/2))} + e^{-\tan(\pi(\phi-1/2))}} & \text{if } 0<\phi<1, \\ \varepsilon_p\varepsilon_0 & \text{if } \phi \ge 1. \end{cases}$$

In fact, this is a C^∞-function. Moreover, for any integer $m \ge 1$, $\varepsilon^{(m)}(\varphi) = 0$ for all $\varphi \notin (0, 1)$ and $\varepsilon^{(m)}(\varphi) \ne 0$ for all $\varphi \in (0, 1)$.

Example 2.

$$\varepsilon(\phi) = \begin{cases} \varepsilon_w\varepsilon_0 & \text{if } \phi \le 0, \\ \frac{1}{2}(\varepsilon_w\varepsilon_0 - \varepsilon_p\varepsilon_0)\cos\pi\phi + \frac{1}{2}(\varepsilon_w\varepsilon_0 + \varepsilon_p\varepsilon_0) & \text{if } 0<\phi<1, \\ \varepsilon_p\varepsilon_0 & \text{if } \phi \ge 1. \end{cases}$$

In what follows, we shall denote by C a generic constant that may depend on Ω, ρ_f, ψ_∞, and ε but is independent of $\phi \in H_0^1(\Omega)$. We shall also denote by $C(\varphi)$ a generic constant that can depend on φ in addition to Ω, ρ_f, ψ_∞, and ε. The following theorem is our main result in this section:

Theorem 2.1

For any $\phi \in H_0^1(\Omega)$ there exists a unique weak solution $\psi_\varphi \in H^1(\Omega)$ to the boundary-value problem (1.7) *and* (1.8), *i.e., $\psi_\varphi = \psi_\infty$ on $\partial\Omega$ in the sense of trace and*

$$\int_\Omega [\varepsilon(\phi)\nabla\psi_\phi \cdot \nabla\eta + (\phi-1)^2 V'(\psi_\phi)\,\eta]\,dx = \int_\Omega \rho_f\,\eta\,dx \quad \forall \eta \in H_0^1(\Omega). \quad (2.1)$$

Moreover, $\psi_\varphi \in L^\infty(\Omega)$ *and*

$$\|\psi_\phi\|_{H^1(\Omega)} \le C\,(1+\|\phi\|_{L^2(\Omega)}), \quad (2.2)$$

$$\|\chi_{\{\phi\neq 1\}}\psi_\phi\|_{L^\infty(\Omega)} \le C, \quad (2.3)$$

$$\|\psi_\phi\|_{L^\infty(\Omega)} \le C\left(1+\|\phi\|^2_{H^1(\Omega)}\right). \quad (2.4)$$

Proof—We divide our proof in three steps.

Step 1: Let $\hat{\psi_\varphi} \in H^1(\Omega)$ be the unique weak solution to the boundary-value problem $-\nabla \cdot \varepsilon(\varphi)\nabla\hat{\psi_\varphi} = \rho_f$ in Ω and $\hat{\psi_\varphi} = \psi_\infty$ on $\partial\Omega$. This means that $\hat{\psi_\varphi}$ is the unique function in $H^1(\Omega)$ such that $\hat{\psi_\varphi} = \psi_\infty$ on $\partial\Omega$ and

$$\int_\Omega \varepsilon(\phi)\nabla\hat{\psi}_\phi \cdot \nabla\eta\,dx = \int_\Omega \rho_f\,\eta\,dx \quad \forall \eta \in H_0^1(\Omega). \quad (2.5)$$

Since $0 < \varepsilon_{\min} \le \varepsilon(\varphi) \le \varepsilon_{\max}$ for all $\varphi \in \mathbb{R}$, we have by the standard elliptic theory (cf. Theorem 8.3 and Theorem 8.16 in [21]) that $\hat{\psi_\varphi} \in H^1(\Omega) \cap L^\infty(\Omega)$, and

$$\|\hat{\psi}_\phi\|_{H^1(\Omega)} + \|\hat{\psi}_\phi\|_{L^\infty(\Omega)} \le C. \quad (2.6)$$

Step 2: We define I: $H_0^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$I[u] = \int_\Omega \left[\frac{\varepsilon(\phi)}{2}|\nabla u|^2 + (\phi-1)^2 V(u+\hat{\psi}_\phi)\right] dx \quad \forall u \in H_0^1(\Omega).$$

It is easy to see that $\inf_{u\in H_0^1(\Omega)} I[u]$ is finite. By the direct method in the calculus of variations, there exists a unique minimizer $u \in H_0^1(\Omega)$ of I over $H_0^1(\Omega)$.

By our assumption (A4) on the function V and by (2.6), there exists $\lambda > 0$, independent of φ, such that $V'(\lambda + \hat{\psi_\varphi}) > 1$ and $V'(-\lambda + \hat{\psi_\varphi}) < -1$ a.e. on Ω. We prove that

$$|u| \le \lambda \quad \text{a. e. on } \{\phi \neq 1\}. \quad (2.7)$$

Define $u_\lambda : \Omega \to \mathbb{R}$ by

$$u_\lambda(x)=\begin{cases} -\lambda & \text{if } u(x)<-\lambda, \\ u(x) & \text{if } -\lambda \le u(x) \le \lambda, \\ \lambda & \text{if } u(x)>\lambda. \end{cases}$$

Since $I[u_\lambda] \ge I[u]$ and $|\nabla u_\lambda| \le |\nabla u|$ a.e. Ω, we have

$$\begin{aligned} \int_\Omega (\phi-1)^2 V(u+\hat{\psi}_0)\,\mathrm{d}x &= I[u]-\int_\Omega \tfrac{\varepsilon(\phi)}{2}|\nabla u|^2 dx \\ &\le I[u_\lambda]-\int_\Omega \tfrac{\varepsilon(\phi)}{2}|\nabla u_\lambda|^2 dx \\ &= \int_\Omega (\phi-1)^2 V(u_\lambda+\hat{\psi}_\phi)\,\mathrm{d}x. \end{aligned}$$

Consequently, it follows from the convexity of V and our choice of λ that

$$\begin{aligned} 0 &\ge \int_\Omega (\phi-1)^2 V(u+\hat{\psi}_\phi)\,\mathrm{d}x - \int_\Omega (\phi-1)^2 V(u_\lambda+\hat{\psi}_\phi)\,\mathrm{d}x \\ &= \int_\Omega \chi_{\{u>\lambda\}}(\phi-1)^2 \left[V(u+\hat{\psi}_\phi)-V(\lambda+\hat{\psi}_\phi)\right]\mathrm{d}x + \int_\Omega \chi_{\{u<-\lambda\}}(\phi-1)^2 \left[V(u+\hat{\psi}_\phi)-V(-\lambda+\hat{\psi}_\phi)\right]\mathrm{d}x \\ &\ge \int_\Omega \chi_{\{u>\lambda\}}(\phi-1)^2 V'(\lambda+\hat{\psi}_\phi)(u-\lambda)\mathrm{d}x + \int_\Omega \chi_{\{u<-\lambda\}}(\phi-1)^2 V'(-\lambda+\hat{\psi}_\phi)(u+\lambda)\mathrm{d}x \\ &\ge \int_\Omega \chi_{\{u>\lambda\}}(\phi-1)^2 (u-\lambda)\mathrm{d}x + \int_\Omega \chi_{\{u<-\lambda\}}(\phi-1)^2 (-u-\lambda)\mathrm{d}x \\ &= \int_\Omega \chi_{\{|u|>\lambda\}}(\phi-1)^2 ||u|-\lambda|\mathrm{d}x \\ &\ge 0. \end{aligned}$$

This leads to (2.7).

The minimizer u of I: $H_0^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$ is the weak solution to the Euler–Lagrange equation

$$\nabla \cdot \varepsilon(\phi)\nabla u - (\phi-1)^2 V'(u+\hat{\psi}_\phi)=0 \quad \text{in } \Omega,$$

i.e.,

$$\int_\Omega \left[\varepsilon(\phi)\nabla u \cdot \nabla \eta + (\phi-1)^2 V'(u+\hat{\psi}_\phi)\eta\right]\mathrm{d}x=0 \quad \forall \eta \in H_0^1(\Omega). \quad (2.8)$$

This is true by (2.7) and the Lebesgue Dominated Convergence Theorem if $\eta \in H_0^1(\Omega) \cap L^\infty(\Omega)$. For a general $\eta \in H_0^1(\Omega)$, this is also true, since $(\varphi-1)^2 V'(u+\psi_{\hat{\varphi}}) \in L^4(\Omega)$ by (2.7) and since $H_0^1(\Omega) \cap L^\infty(\Omega)$ is dense in $H_0^1(\Omega)$. The convexity of V implies that the weak solution $u \in H_0^1(\Omega)$ defined by (2.8) is unique.

If we choose $\eta = u$ in the equation of (2.8), we obtain by (2.6), (2.7), and Poincaré's inequality that

$$\|u\|^2_{H^1(\Omega)} \le C\int_{\{\phi\neq 1\}} \left|(\phi-1)^2 V'(u+\hat{\psi}_\phi)\, u\right| \,\mathrm{d}x \le C\int_\Omega (1+\phi^2)\,\mathrm{d}x,$$

leading to

$$\|u\|_{H^1(\Omega)} \le C\,(1+\|\phi\|_{L^2(\Omega)}). \quad (2.9)$$

It now follows from the regularity theory (cf. Theorem 8.16 in [21]), (2.6), (2.7), and the imbedding $H^1(\Omega) \hookrightarrow L^4(\Omega)$ that

$$\|u\|_{L^\infty(\Omega)} \le C\|(\phi-1)^2 V'(u+\hat{\psi}_\phi)\|_{L^2(\Omega)} \le C\left(1+\|\phi\|^2_{L^4(\Omega)}\right) \le C\left(1+\|\phi\|^2_{H^1(\Omega)}\right). \quad (2.10)$$

Step 3: Let $\psi_\varphi = u + \hat{\psi_\varphi}$. Then $\psi_\varphi = \psi_\infty$ on $\partial\Omega$. Moreover, (2.5) and (2.8) imply (2.1). The uniqueness of ψ_φ follows from the convexity of V and a usual argument. The estimates (2.2)–(2.4) follow from (2.6), (2.9), (2.7), and (2.10).

3. First Variation of Free-Energy Functional

We calculate the first variation of the free-energy functional F_ξ defined by (1.6). The first variation of each of the first three parts in the functional F_ξ can be obtained by routine calculations. So, we focus on the electrostatic part

$$F_{\mathrm{ele},\xi}[\phi] := \int_\Omega \left[-\frac{\varepsilon(\phi)}{2}|\nabla\psi_\phi|^2 + \rho_{\mathrm{f}}\psi_\phi - (\phi-1)^2 V(\psi_\phi)\right]\mathrm{d}x, \quad (3.1)$$

where ψ_φ is the unique solution to the boundary-value problem (1.7) and (1.8). Heuristically, if we denote by δ_φ the "derivative" with respect to φ and $\delta\varphi$ the variation of φ, and "differentiate" both sides of the above equation, then we obtain by the chain rule and product rule for differentiation that

$$\begin{aligned}\delta_\phi F_{\mathrm{ele},\xi}[\phi]\delta\phi &= \int_\Omega \left[-\tfrac{\varepsilon'(\phi)}{2}\delta\phi|\nabla\psi_\phi|^2 - \varepsilon(\phi)\nabla\psi_\phi\cdot\nabla\delta_\phi\psi_\phi + \rho_{\mathrm{f}}\delta_\phi\psi_\phi - 2(\phi-1)\delta\phi V(\psi_\phi) - (\phi-1)^2 V'(\psi_\phi)\delta_\phi\psi_\phi\right]\mathrm{d}x\\ &= \int_\Omega \left[-\tfrac{\varepsilon'(\phi)}{2}|\nabla\psi_\phi|^2 - 2(\phi-1)V(\psi_\phi)\right]\delta\phi\,\mathrm{d}x + \int_\Omega \rho_{\mathrm{f}}\delta_\phi\psi_\phi\,\mathrm{d}x - \int_\Omega[\varepsilon(\phi)\nabla\psi_\phi\cdot\nabla\delta_\phi\psi_\phi + (\phi-1)^2 V'(\psi_\phi)\delta_\phi\psi_\phi]\,\mathrm{d}x\\ &= \int_\Omega \left[-\tfrac{\varepsilon'(\phi)}{2}|\nabla\psi_\phi|^2 - 2(\phi-1)V(\psi_\phi)\right]\delta\phi\,\mathrm{d}x,\end{aligned}$$

where in the last step we used the weak form (2.1) of the Poisson–Boltzmann equation with $\eta = \delta_\varphi\psi_\varphi$. We then identify $\delta_\varphi F_{\mathrm{ele},\xi}[\varphi]$ as

$$\delta_\phi F_{\mathrm{ele},\xi}[\phi]=-\frac{\varepsilon'(\phi)}{2}|\nabla\psi_\phi|^2-2(\phi-1)V(\psi_\phi).$$

We remark that $-\delta_\varphi F_{\mathrm{ele},\xi}[\varphi]$ is an approximation of the electrostatic part of the boundary force $-\delta_\Gamma F[\Gamma]$ in (1.5) if $\varphi\approx 0$ in the solvent region and $\varphi\approx 1$ in the solute region. In fact, the *V*-terms are similar, since the perturbation $\delta\varphi$ is localized at the interface. With our notation, the unit normal $n\approx-\nabla\varphi/|\nabla\varphi|$. Moreover, $\varepsilon(\varphi)\approx\varepsilon_\Gamma$. Therefore,

$$\begin{aligned}\tfrac{\varepsilon'(\phi)}{2}|\nabla\psi_\phi|^2&=\tfrac{\varepsilon'(\phi)}{2}|\nabla\psi_\phi\cdot n|^2+\tfrac{\varepsilon'(\phi)}{2}|\nabla_\Gamma\psi_\phi|^2\\&=-\tfrac{1}{2}\tfrac{d}{d\phi}\left[\tfrac{1}{\varepsilon(\phi)}\right]|\varepsilon(\phi)\nabla\psi_\phi\cdot n|^2+\tfrac{\varepsilon'(\phi)}{2}|\nabla_\Gamma\psi_\phi|^2\\&\approx-\tfrac{1}{2}\left(\tfrac{1}{\varepsilon_{\mathrm{p}}\varepsilon_0}-\tfrac{1}{\varepsilon_{\mathrm{w}}\varepsilon_0}\right)|\varepsilon_\Gamma\nabla\psi_\phi\cdot n|^2+\tfrac{1}{2}(\varepsilon_{\mathrm{p}}\varepsilon_0-\varepsilon_{\mathrm{w}}\varepsilon_0)|\nabla_\Gamma\psi_0|^2.\end{aligned}$$

The final result is exactly the corresponding part in (1.5).

We now give a rigorous justification of our derivation. We recall that if $G:H_0^1(\Omega)\to\mathbb{R}$ is a functional and if $\varphi,\eta\in H_0^1(\Omega)$, then the first variation of *G* at φ in the "direction" η is defined to be

$$\delta_\phi G[\phi][\eta]=\lim_{t\to 0}\frac{G[\phi+t\eta]-G[\phi]}{t}=\frac{d}{dt}\Big|_{t=0}G[\phi+t\eta],$$

if the limit exists.

Theorem 3.1

Let $\phi\in H_0^1(\Omega)$. Let $\psi_\varphi\in \mathrm{H}^1(\Omega)$ be the weak solution of the corresponding boundary-value problem (1.7) and (1.8). Let $\eta\in L^\infty(\Omega)\cap H_0^1(\Omega)$. *Then*

$$\delta_\phi F_{\mathrm{ele},\xi}[\phi][\eta]=\int_\Omega\left[-\frac{1}{2}\varepsilon'(\phi)|\nabla\psi_\phi|^2-2(\phi-1)V(\psi_\phi)\right]\eta\,dx. \quad (3.2)$$

To prove the theorem, we need the following lemma:

Lemma 3.2

Let $\phi\in H_0^1(\Omega)$ *and* $\eta\in L^\infty(\Omega)\cap H_0^1(\Omega)$. *Let* $t\in\mathbb{R}$ *with* $|t|\le 1$. *Let* ψ_φ *and* $\psi_{\varphi+t\eta}$ *be the weak solutions to the boundary-value problems of Poisson–Boltzmann* equation (1.7) *and* (1.8) *corresponding to* φ *and* $\varphi+t\eta$, *respectively. Then there exists a constant* $C=C(\varphi,\eta)>0$ *that may depend on both* φ *and* η *such that*

$$\|\psi_{\phi+t\eta}-\psi_\phi\|_{H^1(\Omega)} \le C(\phi,\eta)|t| \quad \text{if } |t| \le 1.$$

Proof—By the weak form for ψ_φ and that for $\psi_{\varphi+t\eta}$, cf. (2.1), we have for any $\zeta \in H_0^1(\Omega)$ that

$$\int_\Omega [\varepsilon(\phi)\nabla\psi_\phi\cdot\nabla\zeta+(\phi-1)^2V'(\psi_\phi)\zeta]\,dx=\int_\Omega \rho_{\mathrm{f}}\,\zeta\,\mathrm{d}x,$$
$$\int_\Omega [\varepsilon(\phi+t\eta)\nabla\psi_{\phi+t\eta}\cdot\nabla\zeta+(\phi+t\eta-1)^2V'(\psi_{\phi+t\eta})\,\zeta]\,dx=\int_\Omega \rho_{\mathrm{f}}\,\zeta\,dx.$$

It follows from these two equations with $\zeta = \psi_{\varphi+t\eta} - \psi_\varphi$, the property of ε, and the convexity of V that

$$\begin{aligned}
&\varepsilon_{\min}\|\nabla(\psi_{\phi+t\eta}-\psi_\phi)\|^2_{L^2(\Omega)}\\
&\le \int_\Omega \varepsilon(\phi)\nabla(\psi_{\phi+t\eta}-\psi_\phi)\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&=\int_\Omega \varepsilon(\phi)\nabla\psi_{\phi+t\eta}\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx-\int_\Omega \varepsilon(\phi)\nabla\psi_\phi\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&=-\int_\Omega[(\varepsilon(\phi+t\eta)-\varepsilon(\phi))]\nabla\psi_{\phi+t\eta}\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&+\int_\Omega \varepsilon(\phi+t\eta)\nabla\psi_{\phi+t\eta}\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx-\int_\Omega \varepsilon(\phi)\nabla\psi_\phi\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&=-\int_\Omega[(\varepsilon(\phi+t\eta)-\varepsilon(\phi)]\nabla\psi_{\phi+t\eta}\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&-\int_\Omega[(\phi+t\eta-1)^2-(\phi-1)^2]\,V'(\psi_{\phi+t\eta})\,(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&-\int_\Omega(\phi-1)^2[V'(\psi_{\phi+t\eta})-V'(\psi_\phi)]\,(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&\le -\int_\Omega[(\varepsilon(\phi+t\eta)-\varepsilon(\phi))]\nabla\psi_{\phi+t\eta}\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&-\int_\Omega[(\phi+t\eta-1)^2-(\phi-1)^2]\,V'(\psi_{\phi+t\eta})\,(\psi_{\phi+t\eta}-\psi_\phi)\,dx\\
&\le \varepsilon'_{\max}|t|\|\eta\|_{L^\infty(\Omega)}\|\nabla\psi_{\phi+t\eta}\|_{L^2(\Omega)}\|\nabla(\psi_{\phi+t\eta}-\psi_\phi)\|_{L^2(\Omega)}\\
&+(2|t|\|\eta(\phi-1)\|_{L^2(\Omega)}+t^2\|\eta^2\|_{L^2(\Omega)})\|V'(\psi_{\phi+t\eta})\|_{L^\infty(\Omega)}\|\psi_{\phi+t\eta}-\psi_\phi\|_{L^2(\Omega)}.
\end{aligned}$$

Since $|t| \le 1$, we have by (2.2) and (2.4) that both $\|\psi_{\varphi+t\eta}\|_{H^1(\Omega)}$ and $\|V'(\psi_\varphi + t\eta)\|_{L^\infty(\Omega)}$ are bounded by some constants that can depend on φ and η. An application of Poincaré's inequality then implies the desired inequality.

Proof of Theorem 3.1—For any t with $|t| \ll 1$, we denote by $\psi_{\varphi+t\eta}$ the weak solution to the boundary-value problem (1.7) and (1.8) with $\varphi + t\eta$ replacing φ. Setting $\psi_{\phi+t\eta}-\psi_\phi \in H_0^1(\Omega)$ as the test function in the corresponding weak formulation for $\psi_{\varphi+t\eta}$, we obtain

$$\begin{aligned}
&\int_\Omega \rho_{\mathrm{f}}\,(\psi_{\phi+t\eta}-\psi_\phi)\,\mathrm{d}x=\int_\Omega \varepsilon(\phi+t\eta)\nabla\psi_{\phi+t\eta}\cdot\nabla(\psi_{\phi+t\eta}-\psi_\phi)\,\mathrm{d}x+\int_\Omega(\phi+t\eta-1)^2V'(\psi_{\phi+t\eta})(\psi_{\phi+t\eta}-\psi_\phi)\,\mathrm{d}x\\
&=\tfrac{1}{2}\int_\Omega \varepsilon(\phi+t\eta)\,(|\nabla\psi_{\phi+t\eta}|^2+|\nabla\psi_{\phi+t\eta}-\nabla\psi_\phi|^2-|\nabla\psi_\phi|^2)\,\mathrm{d}x+\int_\Omega(\phi+t\eta-1)^2V'(\psi_{\phi+t\eta})(\psi_{\phi+t\eta}-\psi_\phi)\,\mathrm{d}x.
\end{aligned}$$

Consequently, by the definition of the functional $F_{\mathrm{ele},\xi}$ (cf. (3.1)), we have

$$\begin{aligned}
&F_{\mathrm{ele},\xi}[\phi+t\eta]-F_{\mathrm{ele},\xi}[\phi]\\
&=\int_\Omega\left[-\tfrac{\varepsilon(\phi+t\eta)}{2}|\nabla\psi_{\phi+t\eta}|^2+\tfrac{\varepsilon(\phi)}{2}|\nabla\psi_\phi|^2+\rho_{\mathrm{f}}\,(\psi_{\phi+t\eta}-\psi_\phi)\right.\\
&\left.-(\phi+t\eta-1)^2V(\psi_{\phi+t\eta})+(\phi-1)^2V(\psi_\phi)\right]\,dx\\
&=\int_\Omega\tfrac{1}{2}\varepsilon(\phi+t\eta)|\nabla\psi_{\phi+t\eta}-\nabla\psi_\phi|^2dx\\
&-\int_\Omega\tfrac{1}{2}[\varepsilon(\phi+t\eta)-\varepsilon(\phi)]|\nabla\psi_\phi|^2dx\\
&-\int_\Omega[(\phi+t\eta-1)^2-(\phi-1)^2]\,V(\psi_\phi)\,dx\\
&-\int_\Omega(\phi+t\eta-1)^2\,[V(\psi_{\phi+t\eta})-V(\psi_\phi)-V'(\psi_{\phi+t\eta})(\psi_{\phi+t\eta}-\psi_\phi)]\,dx\\
&=:\Lambda_1(t)-\Lambda_2(t)-\Lambda_3(t)-\Lambda_4(t),
\end{aligned}\tag{3.3}$$

where $\Lambda_i(t)$ (i = 1, …, 4) denote the corresponding integrals.

By Lemma 3.2, we have

$$\left|\frac{\Lambda_1(t)}{t}\right|\le\frac{\varepsilon_{\max}}{2|t|}\|\psi_{\phi+t\eta}-\psi_\phi\|^2_{H^1(\Omega)}\le C(\phi,\eta)t\to 0\quad\text{as } t\to 0.\tag{3.4}$$

Since $\eta\in L^\infty(\Omega)$, we have for a.e. $x\in\Omega$ that

$$\frac{1}{t}[\varepsilon(\phi+t\eta)-\varepsilon(\phi)]=\varepsilon'(\phi+\theta t\eta)\eta\to\varepsilon'(\phi)\eta\quad\text{as } t\to 0,$$

where $\theta=\theta(x)\in[0,1]$. The Lebesgue Dominated Convergence Theorem then implies that

$$\lim_{t\to0}\frac{\Lambda_2(t)}{t}=\int_\Omega\frac{1}{2}\varepsilon'(\phi)|\nabla\psi_\phi|^2\eta\,dx.\tag{3.5}$$

Similarly, since $\psi_\varphi\in L^\infty(\Omega)$ by Theorem 2.1,

$$\lim_{t\to0}\frac{\Lambda_3(t)}{t}=\int_\Omega 2(\phi-1)V(\psi_\phi)\eta\,dx.\tag{3.6}$$

Let $a\in\mathbb{R}$ and define $g(b)=V(b)-V(a)-V'(b)(b-a)$ for all $b\in\mathbb{R}$. Note that $g(a)=0$ and $g'(b)=-V''(b)(b-a)$. By Taylor's expansion,

$$g(b)=g(a)+g'(a+\mu(b-a))(b-a)=-\mu V''(a+\mu(b-a))(b-a)^2,$$

where $\mu=\mu(b)\in[0,1]$. With $a=\psi_\varphi$ and $b=\psi_{\varphi+t\eta}$, we obtain by (2.4), the Cauchy–Schwarz inequality, the imbedding $H^1(\Omega)\hookrightarrow L^4(\Omega)$, and Lemma 3.2 that

$$\begin{aligned}\left|\frac{\Lambda_4(t)}{t}\right| &\le \frac{C(\phi,\eta)}{t}\int_\Omega(\phi+t\eta-1)^2|\psi_{\phi+t\eta}-\psi_\phi|^2dx\\ &\le \frac{C(\phi,\eta)}{t}\|(\phi+t\eta-1)^2\|_{L^2(\Omega)}\|\psi_{\phi+t\eta}-\psi_\phi\|^2_{L^4(\Omega)}\\ &\le \frac{C(\phi,\eta)}{t}\|(\phi+t\eta-1)^2\|_{L^2(\Omega)}\|\psi_{\phi+t\eta}-\psi_\phi\|^2_{H^1(\Omega)}\\ &\to 0 \quad \text{as } t\to 0.\end{aligned} \tag{3.7}$$

Now (3.2) follows from (3.3)–(3.7).

The next theorem provides the formula of first variation of the solvation free-energy functional F_ξ defined in (1.6). It follows from Theorem 3.1 and routine calculations. We thus omit the proof.

Theorem 3.3

Let $\phi \in H_0^1(\Omega)$ *and* $\eta \in L^\infty(\Omega)\cap H_0^1(\Omega)$ *be such that*

$$\int_\Omega(\phi-1)^2U\,dx<\infty \quad \text{and} \quad \int_\Omega\eta^2U\,dx<\infty.$$

Let $\psi_\varphi \in H^1(\Omega)$ *be the unique weak solution to the boundary-value problem* (1.7) *and* (1.8) *corresponding to* φ. *Then*

$$\delta_\phi F_\xi[\phi][\eta]=\int_\Omega\left\{\gamma_0\xi\nabla\phi\cdot\nabla\eta+\left[2P\phi+\frac{\gamma_0}{\xi}W'(\phi)+2\rho_w(\phi-1)U-\frac{\varepsilon'(\phi)}{2}|\nabla\psi_\phi|^2-2(\phi-1)V(\psi_\phi)\right]\eta\right\}dx.$$

If in addition $\varphi \in H^2(\Omega)$ then the integral of $\nabla\varphi\cdot\nabla\eta$ becomes that of $-\Delta\varphi\eta$. Therefore, we shall denote

$$\delta_\phi F_\xi[\phi]=2P\phi-\gamma_0\left[\xi\Delta\phi-\frac{1}{\xi}W'(\phi)\right]+2\rho_{\mathrm{w}}(\phi-1)U-\frac{\varepsilon'(\phi)}{2}|\nabla\psi_\phi|^2-2(\phi-1)V(\psi_\phi), \tag{3.8}$$

and call it the first variation of F_ξ at φ.

4. Relaxation Dynamics: Fast and Regular Time Scales

We now consider the relaxation dynamics $\partial_t\varphi = -\delta_\varphi F_\xi[\varphi]$. By Theorem 3.3, this dynamics is described by the following initial-boundary-value problem for the phase field $\varphi = \varphi(x, t)$ and the corresponding electrostatic potential $\psi = \psi(x, t)$:

$$\partial_t\phi=-2P\,\phi+\gamma_0\left[\xi\Delta\phi-\frac{1}{\xi}W'(\phi)\right]-2\rho_{\mathrm{w}}(\phi-1)U+\frac{1}{2}\varepsilon'(\phi)|\nabla\psi|^2+2(\phi-1)V(\psi), \tag{4.1}$$

$$\nabla\cdot\varepsilon(\phi)\nabla\psi-(\phi-1)^2V'(\psi)=-\rho_{\mathrm{f}}, \tag{4.2}$$

$$\phi=0 \quad \text{on } \partial\Omega, \quad (4.3)$$

$$\psi=\psi_\infty \quad \text{on } \partial\Omega, \quad (4.4)$$

together with some initial condition for φ. If the solution $\varphi = \varphi(x, t)$ and $\psi = \psi(x, t)$ are smooth, then we have by (1.6), (3.8), the chain rule, and integration by parts that

$$\begin{aligned}\frac{d}{dt}F_\xi[\phi(\cdot,t)] &= \int_\Omega \partial_t\phi\,\delta_\phi F_\xi[\phi]\,dx - \int_\Omega [\varepsilon(\phi)\nabla\psi\cdot\nabla\partial_t\psi - \rho_f\partial_t\psi + (\phi-1)^2V'(\psi)\partial_t\psi]\,dx \\ &= -\int_\Omega (\partial_t\phi)^2 dx \le 0,\end{aligned}$$

where the vanish of the second integral follows from the weak formulation for (4.2) with the test function $\partial_t\psi$. Therefore, the energy decays, explaining the terminology “relaxation dynamics”.

Assume $0 < \xi \ll 1$. We expect that, after a short time period, the solution φ will take the value close to 0 or 1 in most of the region Ω, due to the fast reaction described by the term $-(1/\xi)W'(\varphi)$. Moreover, in the regions $\{\varphi \approx 0\}$ and $\{\varphi \approx 1\}$, the leading-order term of the electrostatic potential should solve the boundary-value problem (4.2) and (4.4), as the electrostatic relaxation is instantaneous: there is no $\partial_t\psi$ term. In the subsequent long time period, the relaxation dynamics is mainly the motion of the interface that separates the two regions $\{\varphi \approx 0\}$ and $\{\varphi \approx 1\}$. It is reasonable to assume that the early fast time scale is determined by the basic reaction-diffusion equation

$$\partial_t\phi = \xi\Delta\phi - \frac{1}{\xi}W'(\phi),$$

as again the electrostatic relaxation is instantaneous. Perturbing the unstable constant equilibrium solution $\varphi_0(x) = 1/2$ by $\delta \exp(ik \cdot x + \omega t)$ with $|\delta| \ll 1$, we find the most unstable mode $k_c = 0$ and the corresponding fastest growth rate $\omega(k_c) = O(1/\xi)$. Therefore, the fast time scale is t/ξ. The next time scales are the regular time scale t, a slow time scale ξt, and so on.

Let us first consider the fast time scale $T = t/\xi$. We assume that

$$\phi(x,t) = \phi_0(x,T) + \xi\phi_1(x,T) + \xi^2\phi_2(x,T) + \cdots, \quad (4.5)$$

$$\psi(x,t) = \psi_0(x,T) + \xi\psi_1(x,T) + \xi^2\psi_2(x,T) + \cdots, \quad (4.6)$$

where $\varphi_i = \varphi_i(x, T)$ and $\psi_i = \psi_i(x, T)$ ($i = 0, 1, \ldots$) are smooth and bounded functions satisfying the boundary conditions

$$\phi_i=0 \quad (i \geq 0), \quad \psi_0=\psi_\infty, \quad \text{and} \quad \psi_i=0 \quad (i \geq 1) \quad \text{on } \partial\Omega. \quad (4.7)$$

Substitute φ and ψ in (4.1) by these expansions and match terms with the same orders of ξ. At the leading order $O(\xi^{-1})$, we obtain $\partial_T \varphi_0 = -\gamma_0 W'(\varphi_0)$. This equation has two stable fixed points 0 and 1. So,

$$\text{for any } x \in \Omega,\ \phi_0(x,T) \to 0 \text{ or } 1 \text{ exponentially as } T \to \infty. \quad (4.8)$$

Similarly, placing our expansions into (4.2), we obtain the leading-order $O(1)$-equation

$$\nabla \cdot \varepsilon(\phi_0)\nabla\psi_0-(\phi_0-1)^2V'(\psi_0)=-\rho_{\mathrm{f}}. \quad (4.9)$$

This is exactly (4.2), as expected. More equations corresponding to other higher powers of ξ can be obtained but they provide less useful information. We therefore need to examine the next time scale, the regular time scale.

We assume that, at the regular time scale, the solution φ and ψ have the expansions

$$\phi(x,t)=\phi_0(x,t)+\xi\phi_1(x,t)+\xi^2\phi_2(x,t)+\cdots,$$
$$\psi(x,t)=\psi_0(x,t)+\xi\psi_1(x,t)+\xi^2\psi_2(x,t)+\cdots,$$

where $\varphi_i = \varphi_i(x, t)$ and $\psi_i = \psi_i(x, t)$ ($i = 0, 1, \ldots$) are smooth and bounded functions that satisfy the boundary conditions (4.7). Note that these are functions of (x, t), different from those of (x, T) in (4.5) and (4.6). Substituting φ and ψ in (4.1) by these expansions and matching the terms with the same orders of ξ, we obtain the first two equations

$$\begin{aligned} O(\xi^{-1}): &\quad W'(\phi_0)=0, \\ O(1): &\quad \partial_t\phi_0=-2P\phi_0-\gamma_0W''(\phi_0)\phi_1-2\rho_{\mathrm{w}}(\phi_0-1)U \end{aligned} \quad (4.10)$$

$$+\frac{1}{2}\varepsilon'(\phi_0)|\nabla\psi_0|^2+2(\phi_0-1)V(\psi_0). \quad (4.11)$$

Note that Eq. (4.2) does not involve any time derivatives. Thus, substituting φ and ψ in (4.2) by their expansions, we obtain the same equation (4.9) in the leading order.

Eq. (4.10) implies that $\varphi_0 = 0$, 1, or 1/2. By (4.8), we must have $\varphi_0 = 0$ or 1. Since $\varphi_0 = 0$ on $\partial\Omega$, we have $\varphi_0 = 0$ near $\partial\Omega$. By the assumption (A2) on the function U in Section 2 and (4.11), φ_0 cannot be identically 0 in Ω. Thus, both $\{\varphi_0 = 0\}$ and $\{\varphi_0 = 1\}$ are nonempty. But φ_0 is a continuous function. This means that our above expansions for φ and ψ are valid only in the outer region, i.e., the union of $\Omega_\xi^+(t):=\{x \in \Omega:\phi(x,t) \approx 1\}$ and $\Omega_\xi^-(t):=\{x \in \Omega:\phi(x,t) \approx 0\}$. The region $\Omega_\xi^+(t)$ contains all the points x_i ($1 \leq i \leq N$). The boundary of the region $\Omega_\xi^-(t)$ contains the boundary of Ω.

We assume the inner region, a thin transition layer of width $O(\xi)$ that is complement to the outer region, centers around the closed and smooth interface $\Gamma_\xi(t) = \{x \in \Omega : \varphi(x, t) = 1/2\}$ enclosing $\Omega_\xi^+(t)$. This interface is the perturbation of a closed and smooth interface $\Gamma(t)$ that is also inside the inner region and that does not depend on ξ. We assume that all the principal curvatures of these interfaces are $O(1)$ with respect to $\xi \to 0$. For a given point x in the inner region, we denote by $s(x, t)$ the signed distance from x to $\Gamma_\xi(t)$, positive interior and negative exterior of the interface. This is a smooth function depending on ξ such that $|\nabla s(x, t)| = 1$. Let $P_t x \in \Gamma_\xi(t)$ be the projection of x onto $\Gamma_\xi(t)$, defined by $|s(x, t)| = \|x - P_t x\|$. (We use the Euclidean norm and distance.) The projection P_t depends on ξ. For $\xi > 0$ small enough, one can expect that the projection $P_t x \in \Gamma_\xi(t)$ is unique. We shall assume so. Consequently, the vector $x - P_t(x)$ is normal to $\Gamma_\xi(t)$ at $P_t x$.

We shall show that, to the leading order with respect to $\xi \to 0$, the interface $\Gamma(t)$, or equivalently the interface $\Gamma_\xi(t)$, does not move at this time scale. To this end, let us introduce a local coordinate system for the inner region [14, 15]. Consider an open neighborhood $D(t)$ in $\mathbb{R}^3$ that covers an $O(\xi)$-neighborhood of a part of $\Gamma_\xi(t)$. Let $Q(t) \subset \mathbb{R}^2$ be a smooth domain and $\Phi(\cdot, t) : Q(t) \to D(t) \cap \Gamma_\xi(t)$ a smooth parameterization of the patch of interface $D(t) \cap \Gamma_\xi(t)$ such that the coordinate lines $y_i = 0$ ($i = 1, 2$) are exactly the lines of principal curvature and the coordinates y_1 and y_2 of $y = (y_1, y_2) \in Q(t)$ are the corresponding arc lengths of these lines on $\Gamma_\xi(t)$. Then any point $x \in D(t)$ of the inner region can be expressed uniquely as

$$x = \Phi(y, t) + \xi z(t) n(y, t), \quad (4.12)$$

where $\Phi(y, t)$ is exactly the projection of x onto $\Gamma_\xi(t)$, $z(t) = s(x, t)/\xi$, and $n(y, t) = \nabla_x s(x, t)$ is the unit normal to the interface $\Gamma_\xi(t)$ at the projection $\Phi(y, t)$, pointing from the exterior to interior of the interface $\Gamma_\xi(t)$. We shall denote by $J = J(y, t)$ the Jacobian matrix of the mapping $\Phi(\cdot, t) : Q(t) \to D(t) \cap \Gamma_\xi(t)$. This is a 3×2 matrix at each point $y = (y_1, y_2)$ with the jth column being the vector $\partial_{y_j} \Phi(y, t)$ ($j = 1, 2$). These columns are orthonormal vectors and are tangent to the surface $\Gamma_\xi(t)$. Note that all $D(t)$, $\Phi(y, t)$, $J(y, t)$, $z(t)$, and $n(y, t)$ can depend on ξ. Both $\Phi(y, t)$ and $J(y, t)$ are $O(1)$ with respect to $\xi \to 0$. Note also that the z component of the (z, y) coordinate is a global variable, independent of the parameterization $\Phi(\cdot, t)$ of the patch of interface $D(t) \cap \Gamma_\xi(t)$.

The relation (4.12) determines locally $y = y(x, t)$ and $z = z(x, t)$ as smooth functions of x and t. In particular, $z(x, t) = s(x, t)/\xi$. Let $v = v(y, t)$ and $H = H(y, t)$ be the normal velocity and mean curvature of the point $\Phi(y, t) \in \Gamma_\xi(t)$ defined by $v(y, t) = \partial_t \Phi(y, t) \cdot n(y, t)$ and $H(y, t) = \nabla_y \cdot n(y, t)/2$, respectively. We have for any x related to (z, y) by (4.12) that

$$\nabla_x z(x, t) = \xi^{-1} n(y, t), \quad (4.13)$$

$$\Delta_x z(x, t) = 2\xi^{-1} H(y, t) + O(1), \quad (4.14)$$

$$\partial_t z(x,t) = -\xi^{-1} v(y,t), \quad (4.15)$$

$$\nabla_x y(x,t) = J(y,t) + O(\xi). \quad (4.16)$$

Eq. (4.13) follows from $n(y, t) = \nabla_x s(x, t)$ and $\xi z(x, t) = s(x, t)$. Eq. (4.14) follows from the fact that $\partial_{y_j} n$ is the jth column of J multiplied by the jth principal curvature; cf. (2.3) in [15]. Fixing x and replacing $z(t)$ by $s(x, t)$ in (4.12), differentiating both sides of this equation with respect to t, and then dotting with the unit vector $n = n(y, t)$, we then obtain (4.15). Finally, Eq. (4.16) follows from a formula for $\nabla_x y$ in Lemma 2.1 of [15]. With these, we further obtain by a series of calculations that, for any smooth functions $f = f(x, t)$ and $\tilde{f} = \tilde{f}(z, y, t)$ that satisfy $f(x, t) = \tilde{f}(z, y, t)$ with x and (z, y) related by (4.12),

$$\nabla_x f = (J\nabla_y + \xi^{-1} n \partial_z)\tilde{f} + O(\xi), \quad (4.17)$$

$$\Delta_x f = (\xi^{-1} 2H\partial_z + \xi^{-2}\partial_{zz}^2)\,\tilde{f} + O(1), \quad (4.18)$$

$$\partial_t f = (\partial_t - \xi^{-1} v\,\partial_z)\,\tilde{f}. \quad (4.19)$$

We now assume that the solutions $\varphi = \varphi(x, t)$ and $\psi = \psi(x, t)$ have the following expansions in the intersection of $D(t)$ and the inner region [4, 34, 36]:

$$\phi(x,t) = \tilde{\phi}_0(z,y,t) + \xi\tilde{\phi}_1(z,y,t) + \xi^2\tilde{\phi}_2(z,y,t) + \cdots,$$
$$\psi(x,t) = \tilde{\psi}_0(z,y,t) + \xi\tilde{\psi}_1(z,y,t) + \xi^2\tilde{\psi}_2(z,y,t) + \cdots,$$

where x and (z, y) are related by (4.12), and all $\tilde{\varphi}_i = \tilde{\varphi}_i(z, y, t)$ and $\tilde{\psi}_i = \tilde{\psi}_i(z, y, t)$ $(i = 0, 1, \ldots)$ are smooth and bounded functions. Substitute φ and ψ in (4.1) with these inner expansions, apply (4.17)–(4.19), and group terms of the same orders in terms of powers of ξ.

Equating the terms of the order $O(\xi^{-2})$, we get $\varepsilon'(\tilde{\varphi}_0)(\partial_z \tilde{\psi}_0)^2 = 0$. Since $\varphi_0 = 0$ or 1 in the outer region, we can assume that the set of points in the inner region at which $\tilde{\varphi} = 0$ or 1 has the Lebesgue measure zero. Thus, by our assumption (A3) in Section 2, $\varepsilon'(\tilde{\varphi}_0) \neq 0$ almost everywhere in the inner region. Consequently, $\partial_z \tilde{\psi}_0 = 0$ in the inner region. With this, we obtain at the next order $O(\xi^{-1})$ that

$$-v\,\partial_z\tilde{\phi}_0 = \gamma_0\left[\partial_{zz}^2\tilde{\phi}_0 - W'(\tilde{\phi}_0)\right]. \quad (4.20)$$

By matching the inner and outer solutions, we have $\tilde{\varphi}_0(z, y, t) \to 0$ if $z \to -\infty$ and $\tilde{\varphi}_0(z, y, t) \to 1$ if $z \to +\infty$. Moreover, since $\tilde{\varphi}_0$ is smooth and bounded, we have also that $\partial_z \tilde{\varphi}_0 \to 0$ as $z \to -\infty$ or ∞. Therefore, multiplying both sides of (4.20) by $\partial_z \tilde{\varphi}_0$ and integrating over z from $-\infty$ and ∞, we obtain

$$-v\int_{-\infty}^{\infty}\left(\partial_z\tilde{\phi}_0\right)^2 dz=\gamma_0\left[\frac{1}{2}(\partial_z\tilde{\phi}_0)^2-W(\tilde{\phi}_0)\right]\Big|_{z=-\infty}^{z=\infty}=0.$$

Hence $v = v(y, t) = 0$. Therefore, at the leading order of ξ, the interface does not move at the regular time scale. However, in the next long time period measured by a slow time scale, the interface still moves. Note that all these results depend only on the global variable z but not on the local variable y, i.e., not on the parametrization $\Phi(\cdot, t) : Q(t) \to D(t) \cap \Gamma_\xi(t)$.

5. Relaxation Dynamics: Slow Time Scale and Sharp-Interface Limit

We now consider the slow time scale $\tau = \xi t$ and obtain the leading order of the normal velocity for this interface motion. Based on the previous analysis, we assume at each τ the system region Ω is divided by a closed and smooth interface $\Gamma(\tau)$ into two regions $\Omega^-(\tau)$ and $\Omega^+(\tau)$, outside and inside of $\Gamma(\tau)$, respectively. We assume the principal curvatures at any point of $\Gamma(\tau)$ are of order $O(1)$ with respect to $\xi \to 0$. We have $\varphi \approx 0$ in $\Omega^-(\tau)$ and $\varphi \approx 1$ in $\Omega^+(\tau)$. Moreover, all $x_i \in \Omega^+(\tau)$ $(1 \le i \le N)$. Hence $\Omega^+(\tau)$ approximates the solute region Ω_p and $\Omega^-(\tau)$ approximates the solvent region Ω_w.

We assume that in the outer region—the region outside an $O(\xi)$ neighborhood of $\Gamma(\tau)$—the solutions φ and ψ have the expansions

$$\phi(x,t)=\phi_0(x,\tau)+\xi\phi_1(x,\tau)+\xi^2\phi_2(x,\tau)+\cdots,$$
$$\psi(x,t)=\psi_0(x,\tau)+\xi\psi_1(x,\tau)+\xi^2\psi_2(x,\tau)+\cdots,$$

where $\varphi_i = \varphi_i(x, \tau)$ and $\psi_i = \psi_i(x, \tau)$ with $\tau = \xi t$ are smooth and bounded functions that satisfy the boundary conditions (4.7). Plugging these into (4.1) and comparing the terms of the same orders of ξ, we obtain

$$O(\xi^{-1}):\quad 0=W'(\phi_0), \quad (5.1)$$

Similarly, we have by (4.2) that

$$O(1):\quad \nabla\cdot\varepsilon(\phi_0)\nabla\psi_0-(\phi_0-1)^2V'(\psi_0)=-\rho_f. \quad (5.2)$$

By (5.1) and the boundary condition for φ_0, we get $\varphi_0 = 0$ in the $\Omega^-(\tau)$ part of the outer region and $\varphi_0 = 1$ in the $\Omega^+(\tau)$ part of the outer region. In particular, as $\xi \to 0$, φ_0 converges to 1 and 0, inside and outside $\Gamma(\tau)$, respectively.

We now consider the solutions φ and ψ in the inner region, an $O(\xi)$-neighborhood of $\Gamma(\tau)$. As before, we introduce a local coordinate system for the inner region. Let $s(x, \tau)$, $P_\tau(x)$, $D(\tau)$, $Q(\tau)$, $\Phi = \Phi(y, \tau)$, $J = J(y, \tau)$, $z = z(\tau)$, $n = n(y, \tau)$, $H = H(y, \tau)$, and $v = v(y, \tau)$ be all the same as those in Section 4 with τ replacing t and $\Gamma(\tau)$ replacing $\Gamma_\xi(t)$, respectively. We relate a point $x \in D(\tau)$ in the inner region to the local coordinates (z, y) by

$$x=\Phi(y,\tau)+\xi z(\tau)n(y,\tau). \quad (5.3)$$

We still have (4.13), (4.14), and (4.16) with t replaced by τ. Eq. (4.15) is changed now to $\partial_\tau z(x,\tau) = -v(x,\tau)$. If $f(x,\tau)$ and $\tilde{f}(z,y,\tau)$ are two smooth functions and $f(x,\tau) = \tilde{f}(z,y,\tau)$ with x and (z,y) related by (5.3), then (4.17) and (4.18) still hold true; but (4.19) is changed to $\partial_\tau f = (\xi\partial_\tau - v\partial_z)\tilde{f}$.

We assume now the following local expansions in the inner region:

$$\phi(x,t)=\tilde{\phi}_0(z,y,\tau)+\xi\tilde{\phi}_1(z,y,\tau)+\xi^2\tilde{\phi}_2(z,y,\tau)+\cdots,$$
$$\psi(x,t)=\tilde{\psi}_0(z,y,\tau)+\xi\tilde{\psi}_1(z,y,\tau)+\xi^2\tilde{\psi}_2(z,y,\tau)+\cdots,$$

where $\varphi_i = \tilde{\varphi}_i(z,y,\tau)$ and $\psi_i = \tilde{\psi}_i(z,y,\tau)$ ($i = 0, 1, \ldots$) are smooth and bounded functions, and x and (z,y) are related by (5.3). We also have by (5.3) that

$$U(x)=U(\Phi(y,\tau)+\xi z(\tau)n(y,\tau))=\tilde{U}_0(y,\tau)+O(\xi).$$

where $\tilde{U}_0(y,\tau) = U(\Phi(y,\tau))$. If $x = \Phi(y,\tau) \in \Gamma(\tau)$ then $\tilde{U}_0(y,\tau) = U(x)$.

Plug these expansions into (4.1) and equate the terms with the same power of ξ to obtain

$$O(\xi^{-2}): \quad 0=\partial_z\tilde{\psi}_0, \quad (5.4)$$

$$\begin{aligned} O(\xi^{-1}): &\quad 0=\partial_{zz}^2\tilde{\phi}_0-W'(\tilde{\phi}_0).\\ O(1): &\quad -v\partial_z\tilde{\phi}_0=-2P\tilde{\phi}_0+\gamma_0\left[2H\tilde{\phi}_0+\partial_{zz}^2\tilde{\phi}_1-W''(\tilde{\phi}_0)\tilde{\phi}_1\right]-2\rho_w(\tilde{\phi}_0-1)\tilde{U}_0 \quad (5.5)\end{aligned}$$

$$+\frac{1}{2}\varepsilon'(\tilde{\phi}_0)\left[|\nabla_{\Gamma(\tau)}\tilde{\psi}_0|^2+(\partial_z\tilde{\psi}_1)^2\right]+2(\tilde{\phi}_0-1)V(\tilde{\psi}_0). \quad (5.6)$$

In obtaining (5.4), we use the fact that $\varphi_0 = 0$ or 1 in the outer region to assume that $\tilde{\varphi}_0 \in (0, 1)$ and hence $\varepsilon'(\tilde{\varphi}_0) \neq 0$ almost everywhere in the inner region. Eq. (5.4) is used to obtain (5.5) and (5.6). By (5.4), $\tilde{\psi}_0(z,y,\tau) = \tilde{\psi}_0(0,y,\tau)$ is the value of $\tilde{\psi}_0$ at the point $\Phi(y,\tau) \in \Gamma(\tau)$. Note that the surface graident term $\nabla_{\Gamma(\tau)}\tilde{\psi}_0$ in (5.6) is an $O(\xi)$-approximation of $J\nabla_y\tilde{\psi}_0$ by (4.16) and the fact that columns of J are orthogonal to n:

$$\begin{aligned}\nabla_{\Gamma(\tau)}\tilde{\psi}_0&=(I-n\otimes n)\nabla_x\tilde{\psi}_0=(I-n\otimes n)D_xy\nabla_y\tilde{\psi}_0\\&=(I-n\otimes n)J\nabla_y\tilde{\psi}_0+O(\xi)=J\nabla_y\tilde{\psi}_0+O(\xi).\end{aligned}$$

Similarly, plugging the inner expansions of φ and ψ into (4.2), we obtain by (5.4) and the fact that columns of $J = J(y,\tau)$ are orthogonal to the normal $n = n(y,\tau)$ that

$$O(\xi^{-1}): \quad \partial_z \left[\varepsilon(\tilde{\phi}_0)\partial_z \tilde{\psi}_1\right] = 0. \quad (5.7)$$

Fix $x = \Phi(y, \tau) \in \Gamma(\tau)$. Let us employ the following matching conditions [4, 34, 36]:

$$\lim_{z\to\pm\infty} \tilde{\phi}_0(z, y, \tau) = \phi_0^{\pm}(x, \tau), \quad (5.8)$$

$$\lim_{z\to\pm\infty} \tilde{\psi}_0(z, y, \tau) = \psi_0^{\pm}(x, \tau), \quad (5.9)$$

$$\tilde{\psi}_1(z, y, \tau) = (\psi_1^{\pm} + z\nabla\psi_0^{\pm} \cdot \nabla s)(x, \tau) + o(1) \quad \text{as } z \to \pm\infty, \quad (5.10)$$

where $\phi_0^{\pm}(x, \tau) = \lim_{\alpha\to 0^{\pm}} \phi_0(x + \alpha\nabla s(x, \tau))$ and $\psi_i^{\pm}(x, \tau) = \lim_{\alpha\to 0^{\pm}} \psi_i(x + \alpha\nabla s(x, \tau))$. Since $\varphi_0 = 0$ in $\Omega^-(\tau)$ and $\varphi_0 = 1$ in $\Omega^+(\tau)$, we have by (5.5) and (5.8) that

$$\tilde{\phi}_0(z, y, \tau) = \tilde{\phi}_0(z) = \frac{1}{2} + \frac{e^{3z} - e^{-3z}}{2(e^{3z} + e^{-3z})}. \quad (5.11)$$

We now derive the following matching condition that will be used later:

$$\partial_z \tilde{\psi}_1(z, y, \tau) = \nabla\psi_0^{\pm}(x, \tau) \cdot \nabla s(x, \tau) + o(1) \quad \text{as } z \to \pm\infty. \quad (5.12)$$

Let us rewrite the matching condition (5.10) as

$$\tilde{\psi}_1(z, y, \tau) = \psi_1^{\pm}(x, \tau) + z\nabla\psi_0^{\pm}(x, \tau) \cdot \nabla s(x, \tau) + g^{\pm}(z, y, \tau)$$

for some smooth functions $g^+ = g^+(z, y, \tau)$ $(z > 0)$ and $g^- = g^-(z, y, \tau)$ $(z < 0)$ such that $g^{\pm}(z, y, \tau) = o(1)$ as $z \to \pm\infty$, respectively. Thus

$$\partial_z \tilde{\psi}_1(z, y, \tau) = \nabla\psi_0^{\pm}(x, \tau) \cdot \nabla s(x, \tau) + \partial_z g^{\pm}(z, y, \tau). \quad (5.13)$$

By (5.7), we have $\partial_z \tilde{\psi_1}(z, y, \tau) = h(y, \tau)/\varepsilon(\tilde{\varphi_0}(z))$ for some smooth and bounded function $h = h(y, \tau)$ independent of z. This and (5.13) imply that $\partial_z g^{\pm}$ are bounded as $z \to \pm\infty$. Moreover, with these two equations and (5.11), we obtain

$$|\partial_{zz}^2 g^{\pm}(z, y, \tau)| = \left|\partial_{zz}^2 \tilde{\psi}_1(z, y, \tau)\right| = \left|\partial_z \left[\frac{h(y, \tau)}{\varepsilon(\tilde{\psi}_0(z))}\right]\right| \le \frac{6\varepsilon'_{\max}|h(y, \tau)|}{\varepsilon_{\max}^2} e^{-6z}.$$

Consequently, for any $A_2 > A_1 > 0$,

$$\left|[\partial_z g^+(A_2)]^2-[\partial_z g^+(A_1)]^2\right|=\left|\int_{A_1}^{A_2}\partial_z\left[(\partial_z g^+)^2\right]\,dz\right|\le 2\int_{A_1}^{A_2}|\partial_z g^+|\,|\partial_{zz} g^+|\,dz\to 0$$

as $A_1, A_2 \to \infty$. Therefore, $(\partial_z g^+)^2 \to a^+$ as $z \to \infty$ for some $a^+ \ge 0$. We must have $a^+ = 0$, since $g^+ \to 0$ as $z \to \infty$. Therefore $\partial_z g^+ \to 0$ as $z \to \infty$. Similarly $\partial_z g^- \to 0$ as $z \to -\infty$. Hence (5.12) follows from (5.13).

We now show that ψ_0 solves the Poisson–Boltzmann equation with the dielectric boundary $\Gamma(\tau)$. By (5.4), ψ_0 is independent of z. Therefore, (5.2), the matching condition (5.9), and the boundary condition $\psi_0 = \psi_\infty$ on $\partial\Omega$ allow us to determine ψ_0 in the outer region. Moreover, the matching condition (5.9) implies that $\tilde{\psi}_0=\psi_0^+=\psi_0^-$ on $\Gamma(\tau)$. Integrating both sides of Eq. (5.7) over z from $-\infty$ to ∞, we obtain by (5.12) that $\varepsilon_w\varepsilon_0\nabla\psi_0^-\cdot n=\varepsilon_p\varepsilon_0\nabla\psi_0^+\cdot n$ on $\Gamma(\tau)$. These, together with (5.2) and (4.7), imply that ψ_0 is the solution to the elliptic interface problem

$$\begin{cases} \varepsilon_w\varepsilon_0\Delta\psi_0-V'(\psi_0)=-\rho_f & \text{in } \Omega^-(\tau),\\ \varepsilon_p\varepsilon_0\Delta\psi_0=-\rho_f & \text{in } \Omega^+(\tau),\\ \psi_0^-=\psi_0^+ & \text{on } \Gamma(\tau),\\ \varepsilon_w\varepsilon_0\nabla\psi_0^-\cdot n=\varepsilon_p\varepsilon_0\nabla\psi_0^+\cdot n & \text{on } \Gamma(\tau),\\ \psi_0=\psi_\infty & \text{on } \partial\Omega. \end{cases} \tag{5.14}$$

This is equivalent to the boundary-value problem of the Poisson–Boltzmann equation (1.2) and (1.3) with ψ replaced by ψ_0 [27].

We finally derive the motion law for the interface $\Gamma(\tau)$. For notational simplicity, let us skip writing the variables y and τ for a moment. Multiplying both sides of (5.6) by $\tilde{\phi}_0'$ and integrating over z from $-\infty$ to ∞, we obtain that

$$-vS=\int_{-\infty}^{\infty}R_1(z)\tilde{\phi}_0'(z)\,dz+\int_{-\infty}^{\infty}R_2(z)\tilde{\phi}_0'(z)\,dz+\int_{-\infty}^{\infty}R_3(z)\tilde{\phi}_0'(z)\,dz, \tag{5.15}$$

where by (5.11)

$$\begin{aligned} S&:=\int_{-\infty}^{\infty}\left[\tilde{\phi}_0'(z)\right]^2 dz=\int_{-\infty}^{\infty}\frac{36e^{12z}}{(e^{6z}+1)^4}dz=\int_0^{\infty}\frac{6x}{(x+1)^4}dx=1,\\ R_1(z)&:=-2P\tilde{\phi}_0-2\rho_w(\tilde{\phi}_0-1)\tilde{U}_0+2(\tilde{\phi}_0-1)V(\tilde{\psi}_0),\\ R_2(z)&:=\gamma_0\left[2H\partial_z\tilde{\phi}_0+\partial_{zz}^2\tilde{\phi}_1-W''(\tilde{\phi}_0)\tilde{\phi}_1\right],\\ R_3(z)&:=\tfrac{1}{2}\varepsilon'(\tilde{\phi}_0)\left[|\nabla_{\Gamma(\tau)}\tilde{\psi}_0|^2+(\partial_z\tilde{\psi}_1)^2\right]. \end{aligned} \tag{5.16}$$

Since $\tilde{U}_0$ and $V(\tilde{\psi}_0)$ are independent of z, we have

$$\begin{aligned}\int_{-\infty}^{\infty} R_1(z)\tilde{\phi}_0'(z)\,\mathrm{d}z &= -2P\int_{-\infty}^{\infty}\tilde{\phi}_0\tilde{\phi}_0'\,\mathrm{d}z + 2\left[V(\tilde{\psi}_0)-\rho_{\mathrm{w}}\tilde{U}_0\right]\int_{-\infty}^{\infty}\left(\tilde{\phi}_0-1\right)\tilde{\phi}_0'\,\mathrm{d}z\\ &= -P\tilde{\phi}_0^2\big|_{z=-\infty}^{z=\infty} + \left[V(\tilde{\psi}_0)-\rho_{\mathrm{w}}\tilde{U}_0\right]\left(\tilde{\phi}_0-1\right)^2\big|_{z=-\infty}^{z=\infty}\\ &= -P+\rho_{\mathrm{w}}U-V(\psi_0),\end{aligned} \tag{5.17}$$

where we have on $\Gamma(\tau)$ that $\tilde{U}_0 = U$, and that $\tilde{\psi_0} = \psi_0$ by (5.4) and (5.9).

By integration by parts and the fact that $\tilde{\phi}_0'(\pm\infty)=\tilde{\phi}_0''(\pm\infty)=0$, we have

$$\int_{-\infty}^{\infty}\partial_{zz}^2\tilde{\phi}_1\tilde{\phi}_0'\,dz=\int_{-\infty}^{\infty}\tilde{\phi}_0'''\tilde{\phi}_1\,dz.$$

Therefore, by (5.16) and (5.5), we have

$$\int_{-\infty}^{\infty}R_2(z)\tilde{\phi}_0'(z)\mathrm{d}z=2\gamma_0 H+{}_0\int_{-\infty}^{\infty}\partial_z\left[\tilde{\phi}_0''-W'(\tilde{\phi}_0)\right]\tilde{\phi}_1\,\mathrm{d}z=2\gamma_0 H. \tag{5.18}$$

Now, since $\tilde{\psi}_0=\psi_0^-=\psi_0^+$ on $\Gamma(\tau)$, we have $\nabla_{\Gamma(\tau)}\tilde{\psi}_0=\nabla_{\Gamma(\tau)}\psi_0^-=\nabla_{\Gamma(\tau)}\psi_0^+=\nabla_{\Gamma(\tau)}\psi_0$. Consequently,

$$\begin{aligned}\int_{-\infty}^{\infty}R_3(z)\tilde{\phi}_0'(z)\,\mathrm{d}z &= \tfrac{1}{2}\int_{-\infty}^{\infty}\varepsilon'(\tilde{\phi}_0)\left[|\nabla_{\Gamma(\tau)}\tilde{\psi}_0|^2+(\partial_z\tilde{\psi}_1)^2\right]\tilde{\phi}_0'\,\mathrm{d}z\\ &= \tfrac{1}{2}(\varepsilon_{\mathrm{p}}\varepsilon_0-\varepsilon_{\mathrm{w}}\varepsilon_0)|\nabla_{\Gamma(\tau)}\psi_0|^2+\tfrac{1}{2}\int_{-\infty}^{\infty}\varepsilon'(\tilde{\phi}_0)(\partial_z\tilde{\psi}_1)^2\tilde{\phi}_0'\mathrm{d}z.\end{aligned} \tag{5.19}$$

Rewrite (5.7) as $\varepsilon(\tilde{\phi}_0)\partial_{zz}^2\tilde{\psi}_1=-\varepsilon'(\tilde{\phi}_0)\tilde{\phi}_0'\partial_z\tilde{\psi}_1$. With this and (5.12), we have

$$\begin{aligned}\tfrac{1}{2}\int_{-\infty}^{\infty}\varepsilon'(\tilde{\phi}_0)(\partial_z\tilde{\psi}_1)^2\tilde{\phi}_0'\,\mathrm{d}z &= \tfrac{1}{2}\varepsilon(\tilde{\phi}_0)(\partial_z\tilde{\psi}_1)^2\big|_{z=-\infty}^{z=\infty}-\int_{-\infty}^{\infty}\varepsilon(\tilde{\phi}_0)\partial_z\tilde{\psi}_1\partial_{zz}^2\tilde{\psi}_1\mathrm{d}z\\ &= \tfrac{1}{2}\varepsilon_{\mathrm{p}}\varepsilon_0|\nabla\psi_0^+\cdot n|^2-\tfrac{1}{2}\varepsilon_{\mathrm{w}}\varepsilon_0|\nabla\psi_0^-\cdot n|^2+\int_{-\infty}^{\infty}\varepsilon'(\tilde{\phi}_0)(\partial_z\tilde{\psi}_1)^2\tilde{\phi}_0'\mathrm{d}z.\end{aligned}$$

Note that the last term on the right-hand side doubles the term on the left-hand side. This and the third equation in (5.14) then lead to

$$\begin{aligned}\tfrac{1}{2}\int_{-\infty}^{\infty}\varepsilon'(\tilde{\phi}_0)(\partial_z\tilde{\psi}_1)^2\tilde{\phi}_0'\mathrm{d}z &= \tfrac{1}{2}\varepsilon_{\mathrm{w}}\varepsilon_0|\nabla\psi_0^-\cdot n|^2-\tfrac{1}{2}\varepsilon_{\mathrm{p}}\varepsilon_0|\nabla\psi_0^+\cdot n|^2\\ &= \tfrac{1}{2}\left(\tfrac{1}{\varepsilon_{\mathrm{w}}\varepsilon_0}-\tfrac{1}{\varepsilon_{\mathrm{p}}\varepsilon_0}\right)|\varepsilon_{\Gamma(\tau)}\nabla\psi_0\cdot n|^2,\end{aligned} \tag{5.20}$$

where $\varepsilon_{\Gamma(\tau)}$ is defined in (1.4) with $\Gamma(\tau)$ replacing Γ.

Finally, it follows from (5.15)–(5.20) that

$$v = P - 2\gamma_0 H - \rho_w U + \frac{1}{2}\left(\frac{1}{\varepsilon_p \varepsilon_0} - \frac{1}{\varepsilon_w \varepsilon_0}\right)|\varepsilon_{\Gamma(\tau)} \nabla \psi_0 \cdot n|^2 + \frac{1}{2}(\varepsilon_w \varepsilon_0 - \varepsilon_p \varepsilon_0)|\nabla_{\Gamma(\gamma)} \psi_0|^2 + V(\psi_0).$$

Since our normal n points from the interior to exterior and mean curvature $H = \nabla \cdot n/2$, opposite to that in the sharp-interface model (cf. the description above Eq. (1.5)), this is exactly the normal velocity $v_n = -\delta_\Gamma F[\Gamma]$ in the sharp-interface model (cf. (1.5)).

We summarize our analysis in the following:

Theorem 5.1

Assume as above the existence of a closed and smooth interface $\Gamma(\tau)$*, the outer and inner expansions for the solutions* φ *and* ψ *to the initial-boundary-value problem* (4.1)–(4.4)*, and the corresponding matching conditions. Then the following are true:*

1. *As* $\xi \to 0$*, the leading order of the phase-field function* φ *converges to* 1 *in* $\Omega^+(\tau)$ *and* 0 *in* $\Omega^-(\tau)$, respectively;
2. *The leading-order of the electrostatic potential is the unique solution to the boundary-value problem of the Poisson–Boltzmann* equation (1.2) *and* (1.3);
3. *As* $\xi \to 0$*, the normal velocity of the interface* $\Gamma(\tau)$ *converges to the boundary force* $-\delta_\Gamma F[\Gamma]$ *in* (1.5)*, with* $\Gamma(\tau)$ *replacing* Γ*, as in the sharp-interface model.*

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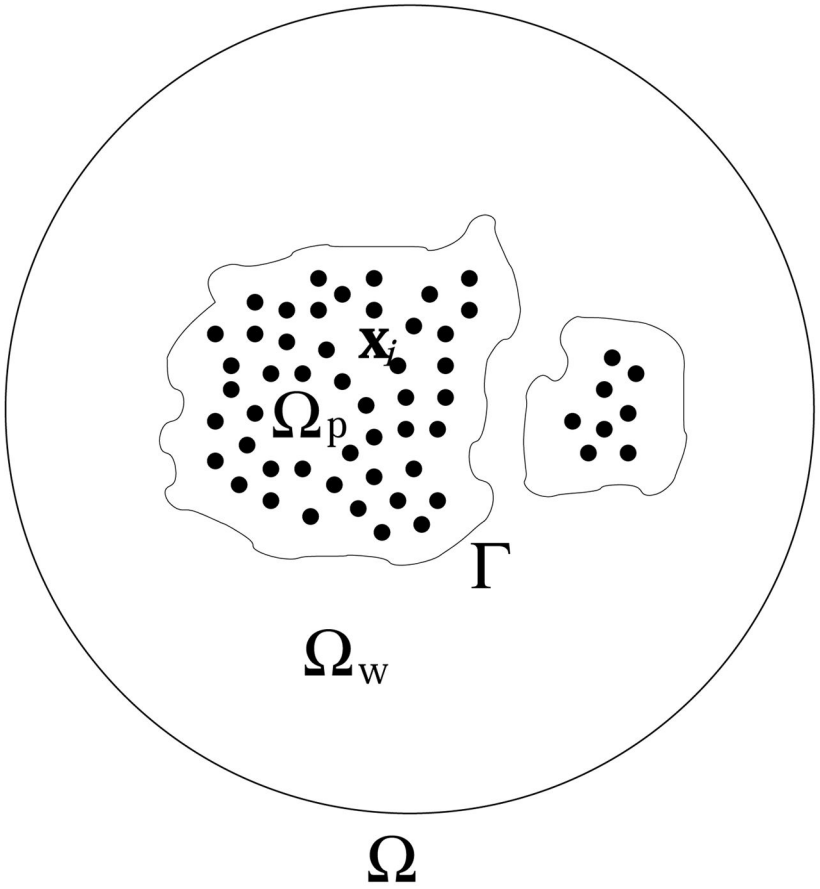

Fig. 1.1.

A schematic view of a solvation system with an implicit solvent. A solute-solvent interface Γ separates the solute region Ω_P (p stands for protein) from the solvent region Ω_W (w stands for water). Dots represent solute atoms located at x_i carrying partial charges $Q_i(i = 1, \ldots, N)$.