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Motion of a Cylindrical Dielectric Boundary

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Abstract

The interplay between geometry and electrostatics contributes significantly to hydrophobic interactions of biomolecules in an aqueous solution. With an implicit solvent, such a system can be described macroscopically by the dielectric boundary that separates the high-dielectric solvent from low-dielectric solutes. This work concerns the motion of a model cylindrical dielectric boundary as the steepest descent of a free-energy functional that consists of both the surface and electrostatic energies. The effective dielectric boundary force is defined and an explicit formula of the force is obtained. It is found that such a force always points from the solvent region to solute region. In the case that the interior of a cylinder is of a lower dielectric, the motion of the dielectric boundary is initially driven dominantly by the surface force but is then driven inward quickly to the cylindrical axis by both the surface and electrostatic forces. In the case that the interior of a cylinder is of a higher dielectric, the competition between the geometrical and electrostatic contributions leads to the existence of equilibrium boundaries that are circular cylinders. Linear stability analysis is presented to show that such an equilibrium is only stable for a perturbation with a wavenumber larger than a critical value. Numerical simulations are reported for both of the cases, confirming the analysis on the role of each component of the driving force. Implications of the mathematical findings to the understanding of charged molecular systems are discussed.

Keywords

Charged molecules; dielectric boundaries; surface energy; electrostatic energy; effective dielectric boundary force; linear stability

1 Introduction

We consider a system of molecular solvation that occupies a region $\Omega \subset \mathbb{R}^3$. It consists of two regions Ω_- and Ω_+ that are separated by an interface Γ . One of these regions is the solvent region and the other is the solute region. The interface Γ is the dielectric boundary. We study the motion of such a boundary as the steepest descent of the free-energy functional

$$F[\Gamma] = \gamma_0 \text{Area}(\Gamma) + \int_{\Omega} \frac{1}{2} \rho \psi_{\Gamma} dV, \quad (1.1)$$

where $\psi_{\Gamma} : \Omega \rightarrow \mathbb{R}$ is the electrostatic potential determined by Poisson's equation

$$\nabla \cdot \varepsilon_{\Gamma} \nabla \psi_{\Gamma} = -\rho \quad \text{in } \Omega, \quad (1.2)$$

together with some boundary conditions. Here the first term in (1.1) is the surface energy with $\gamma_0 > 0$ the surface energy density, a given constant. The second term is the electrostatic energy in which $\rho : \Omega \rightarrow \mathbb{R}$ is the charge density, a given function. The electrostatic energy depends on the dielectric boundary Γ through the position-dependent dielectric coefficient $\varepsilon_{\Gamma} : \Omega \rightarrow \mathbb{R}$ in Poisson's equation (1.2):

$$\varepsilon_{\Gamma}(x) = \begin{cases} \varepsilon_- & \text{if } x \in \Omega_-, \\ \varepsilon_+ & \text{if } x \in \Omega_+, \end{cases} \quad (1.3)$$

where ε_- and ε_+ are the dielectric coefficients of Ω_- and Ω_+ , respectively. At normal conditions, the values of these coefficients are often taken to be close to 1 in the solute region and close to 80 in the solvent region in the unit of vacuum permittivity.

The motion of the dielectric boundary is governed by $V_n = -M \delta_{\Gamma} F[\Gamma]$. Here V_n is the normal velocity (the normal component of velocity) of the dielectric boundary Γ , $M > 0$ is a mobility constant which will be set to be 1 for simplicity, n is the unit normal at the boundary pointing from Ω_- to Ω_+ , and δ_{Γ} is the variational derivative with respect to the location change of Γ . The variation of surface area is $2H$, where H is the mean curvature (i.e., the average of principal curvatures), positive if the region inside the boundary is a sphere. Let us denote by $E[\Gamma]$ the electrostatic energy, i.e.,

$$E[\Gamma] = \int_{\Omega} \frac{1}{2} \rho \psi_{\Gamma} dV. \quad (1.4)$$

The following explicit formula of the variational derivative $\delta_{\Gamma} E[\Gamma]$ has been recently obtained [21] (cf. also [5,6,29]):

$$\delta_{\Gamma} E[\Gamma] = \frac{1}{2} \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) |\varepsilon_{\Gamma} \nabla \psi_{\Gamma} \cdot n|^2 + \frac{1}{2} (\varepsilon_+ - \varepsilon_-) (I - n \otimes n) \nabla \psi_{\Gamma}^2, \quad (1.5)$$

where I denotes the 3×3 identity matrix. Notice that the normal component $\varepsilon_{\Gamma} \nabla \psi_{\Gamma} \cdot n$ of the electric displacement and the tangential component $(I - n \otimes n) \nabla \psi_{\Gamma}$ of the electric field $-\nabla \psi_{\Gamma}$ are continuous across the dielectric boundary Γ . We define the effective dielectric boundary force to be the negative variation $-\delta_{\Gamma} E[\Gamma]$ [5,6,21,29].

The study presented here is based on a simplified model along the line of implicit-solvent approach to charged molecular systems [25]. In fact, both the surface and electrostatic energies in (1.1), together with a solute-solvent van der Waals interaction energy, constitute the mean-field free-energy functional that is central in the recently developed variational implicit-solvent models of the biomolecular interactions in an aqueous solution; cf. [13, 14] and [7–9, 27, 29]. Implemented numerically by a robust level-set method [23, 24, 26], the variational implicit-solvent approach has successfully predicted stable equilibrium solute-solvent interfaces (i.e., dielectric boundaries) and the corresponding solvation free energies for small and large molecules in solution. Such an approach has also captured capillary

evaporation in hydrophobic confinement and corresponding multiple equilibrium states [2,7–9,27,29].

Electrostatic interactions are fundamental in charged molecular systems [12, 17]. It is remarkable that continuum dielectric models can predict well basic properties of such interactions in which complex molecular structures are often determined by atomic details; cf. e.g., [19, 20, 31] and the references therein. Indeed, if Ω_- is the solute region and Ω_+ is the solvent region, then $\epsilon_- < \epsilon_+$ in general. Consequently, one observes from (1.5) and our definition that the normal n points from Ω_- to Ω_+ that the dielectric boundary force always directs from the solute region to solvent region. This gives a quantitative interpretation of the phenomenon that charged solutes immersed in solvent generate an electric field that drives the surrounding solvent molecules to the solutes [12]. A significant consequence of the observation is that a neutral cavity close to a charged solute (e.g., a protein) will move away from the solute due to the dielectric boundary force. This important charge effect to the hydrophobic interaction in biomolecules has been captured recently by the level-set variational implicit-solvent modeling of BphC, a two-domain protein [29].

Despite of the initial success of the variational implicit-solvent modeling of molecular solvation, challenges remain in the understanding on the charge effect, particularly in terms of the competition between surface energy and electrostatic energy. For instance, little is known on the stability of equilibrium dielectric boundaries governed by our underlying motion law. Such stabilities are crucial to biomolecular conformational changes such as protein folding [2, 22, 30]. In addition, it is interesting to understand the time scale of singularity formation in the combined motion when compared with the motion by mean curvature alone.

We consider in this work a model system of a cylindrical dielectric boundary Γ defined as the graph of a function $r = u(z)$ in the cylindrical coordinates (r, θ, z) . We assign Ω_- and Ω_+ to be the regions defined by $r < u(z)$ and $r > u(z)$, respectively. Let us denote by $r = u(z, t)$ the function that represents the evolving cylindrical boundary $\Gamma(t)$ at time t . The motion law $V_n = -\delta_\Gamma F[\Gamma]$, with (1.5) and (1.2), then becomes

$$\begin{cases} u_t = \gamma_0 \left(\frac{u_{zz}}{1+u_z^2} - \frac{1}{u} \right) - \frac{1}{2} \left(\frac{1}{\epsilon_-} - \frac{1}{\epsilon_+} \right) \frac{[\epsilon_{\Gamma(t)} (\psi_r - u_z \psi_z)]^2}{\sqrt{1+u_z^2}} - \frac{1}{2} (\epsilon_+ - \epsilon_-) \frac{(u_z \psi_r + \psi_z)^2}{\sqrt{1+u_z^2}}, \\ \nabla \cdot \epsilon_{\Gamma(t)} \nabla \psi = -\rho, \end{cases} \quad (1.6)$$

together with some boundary and initial conditions, where a subscript t , r or z denotes the corresponding partial derivative, and $\nabla \cdot$ and ∇ are the divergence and gradient, respectively, in Cartesian coordinates. It is clear that the mean-curvature term in (1.6) tends to reduce the surface area of the dielectric boundary. The role of electrostatic force is different in two different cases. If $\epsilon_- < \epsilon_+$, then the electrostatic force always directs inward to the axis of cylinder. Therefore, after an initial period of reducing the surface energy, the boundary then moves inward faster than that by the mean-curvature flow alone. If $\epsilon_- > \epsilon_+$, then the competition of the two components of the force determines some equilibrium boundaries. The stability and long-time behavior of such equilibrium boundaries will depend on the relative magnitude of the surface tension γ_0 and that of dielectric coefficients ϵ_- and ϵ_+ .

Here is a summary of our main results.

1. We present a simpler and direct derivation of the variational derivative (1.5), using the fact that the boundary is a graph of function.

2. For the case $\varepsilon_- > \varepsilon_+$, we present a linear stability analysis of a circularly cylindrical equilibrium boundary. Our analysis shows that the equilibrium boundary is linearly unstable against perturbations with wavenumber smaller than a critical value.
3. For both cases, we numerically solve the system of partial differential equations (1.6). Our numerical method is a “cylindrical version” of the Coupling Interface Method (CIM) developed in [10,11,28].
4. We report our numerical simulations to show how the competition between the surface and electrostatic forces can affect the motion of dielectric boundary in terms of time scales and boundary shapes, and to confirm our linear stability analysis for the case $\varepsilon_- > \varepsilon_+$.

The rest of the paper is organized as follows: In Section 2, we describe the free-energy functional and motion law for a cylindrical dielectric boundary. In Section 3, we derive part of the boundary force that arises from the variation of the electrostatic energy. In Section 4, we present a linear stability analysis for the case $\varepsilon_- > \varepsilon_+$. In Section 5, we describe briefly our numerical methods for solving the system of evolution equations (1.6), together with boundary and initial conditions. In Section 6, we report our numerical simulation results. Finally, in Section 7, we draw our conclusions.

2 Free-Energy Functional and Motion Law

We represent the cylindrical dielectric boundary Γ by a function $r = u(z)$ ($z \in \mathbb{R}$) in the cylindrical coordinates (r, θ, z) with $r = \sqrt{x^2 + y^2}$. We assume that the function $r = u(z)$ is smooth and L -periodic for some $L > 0$. We also assume that $0 < u(z) < R_\infty$ for all $z \in \mathbb{R}$, where $R_\infty > 0$ is a given constant. Denote in the cylindrical coordinates

$$\begin{aligned}\Omega &= \{(r, \theta, z) \in \mathbb{R}^3 : 0 \leq r < R_\infty, 0 < z < L\}, \\ \Omega_- &= \{(r, \theta, z) \in \Omega : 0 \leq r < u(z), 0 < z < L\}, \\ \Omega_+ &= \{(r, \theta, z) \in \Omega : u(z) < r < R_\infty, 0 < z < L\}, \\ \Gamma &= \{(r, \theta, z) \in \Omega : r = u(z), 0 < z < L\}.\end{aligned}$$

Here Γ is the boundary that separates the cylindrical domain Ω into Ω_- and Ω_+ . See Figure 2.1.

Let $\gamma_0 > 0$ be a constant. Let $\varepsilon_\Gamma : \Omega \rightarrow \mathbb{R}$ be the piecewise constant function defined by (1.3), where ε_- and ε_+ are two given and distinct positive constants. Extend ε_Γ L -

periodically in the z direction. Let $\rho = \rho(r, z)$ with $r = \sqrt{x^2 + y^2}$ be a smooth function defined for all $r < R_\infty$ with $r = \sqrt{x^2 + y^2}$ and $z \in \mathbb{R}$. We assume that ρ is L -periodic in z . We denote by

$\mathcal{A}$ the class of functions $\phi = \phi(r, z)$, with $r = \sqrt{x^2 + y^2} \leq R_\infty$ and $z \in \mathbb{R}$, such that $\phi \in H^1(\Omega)$, $\phi(r, z)$ is L -periodical in z and $\phi(R_\infty, z) = 0$ for all $z \in (0, L)$ (in the sense of trace). Here and below we use the standard notation of Sobolev spaces [1,15].

We consider the free-energy functional $F[\Gamma]$ defined in (1.1), where the potential $\psi = \psi_\Gamma \in \mathcal{A}$ is the unique weak solution to the following boundary-value problem of Poisson's equation

$$\begin{cases} \nabla \cdot \varepsilon_{\Gamma} \nabla \psi = -\rho & \text{in } \Omega, \\ \psi = \psi(r, z) \text{ is } L\text{-periodic in } z, \\ \psi(R_{\infty}, z) = 0 & \forall z \in \mathbb{R}. \end{cases} \quad (2.1)$$

Notice that for simplicity we consider the homogeneous Dirichlet boundary condition on the part $r = R_{\infty}$ of the boundary of Ω . For a general, nonzero Dirichlet boundary data $\psi_{\infty} = \psi_{\infty}(z)$, we can extend it to a small neighborhood of the part $r = R_{\infty}$ of the boundary of Ω , and replace ψ_{Γ} by $\psi_{\Gamma} - \psi_{\infty}$. The system (2.1) is equivalent to the following elliptic interface problem [20]

$$\begin{cases} \varepsilon_{-} \Delta \psi = -\rho & \text{in } \Omega_{-}, \\ \varepsilon_{+} \Delta \psi = -\rho & \text{in } \Omega_{+}, \\ \llbracket \psi \rrbracket = 0 & \text{on } \Gamma, \\ \llbracket \varepsilon_{\Gamma} \partial_n \psi \rrbracket = 0 & \text{on } \Gamma, \\ \psi = \psi(r, z) \text{ is } L\text{-periodic in } z, \\ \psi(R_{\infty}, z) = 0 & \forall z \in \mathbb{R}, \end{cases} \quad (2.2)$$

where Δ is the Laplacian in Cartesian coordinates, $\llbracket v \rrbracket = v|_{\Omega_{+}} - v|_{\Omega_{-}}$ denotes the jump across Γ of a function v from Ω_{-} to Ω_{+} , and n is the unit normal at Γ pointing from Ω_{-} to Ω_{+} .

Note that the cylindrical boundary Γ has the surface representation

$$x = u(z) \cos \theta, \quad y = u(z) \sin \theta, \quad z = z.$$

In Cartesian coordinates, the unit normal n at a point of Γ , $(u(z), \theta, z)$ in cylindrical coordinates and $(u(z) \cos \theta, u(z) \sin \theta, z)$ in Cartesian coordinates, is given by

$$n = \frac{1}{\sqrt{1+u'(z)^2}} (\cos \theta, \sin \theta, -u'(z)). \quad (2.3)$$

For a smooth function $\varphi = \varphi(r, z)$ with $r = \sqrt{x^2 + y^2}$, the gradient $\nabla \varphi = (\varphi_x, \varphi_y, \varphi_z)$ at a point (r, θ, z) in cylindrical coordinates is $\nabla \varphi = (\varphi_r \cos \theta, \varphi_r \sin \theta, \varphi_z)$. If the point $(r, \theta, z) = (u(z), \theta, z)$ is on the boundary Γ , then the normal derivative of φ is

$$\partial_n \varphi = \nabla \varphi \cdot n = \frac{\varphi_r - u' \varphi_z}{\sqrt{1+u'^2}}. \quad (2.4)$$

In the orthogonal decomposition

$$\nabla \varphi = (\partial_n \varphi) n + (I - n \otimes n) \nabla \varphi, \quad (2.5)$$

we have by direct calculations that

$$(I - n \otimes n) \nabla \varphi = \frac{u' \varphi_r + \varphi_z}{1+u'^2} (u' \cos \theta, u' \sin \theta, 1). \quad (2.6)$$

The variational derivative of the free-energy functional (1.1) with respect to the location change of boundary Γ and to the defined unit normal n at Γ is a function on Γ , denoted $\delta_\Gamma F[\Gamma] : \Gamma \rightarrow \mathbb{R}$. It is given by

$$\delta_\Gamma F[\Gamma] = -\gamma_0 \left[\frac{u''}{(1+u'^2)^{3/2}} - \frac{1}{u(1+u'^2)^{1/2}} \right] + \frac{1}{2} \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \frac{[\varepsilon_\Gamma (\psi_r - u' \psi_z)]^2}{1+u'^2} + \frac{1}{2} (\varepsilon_+ - \varepsilon_-) \frac{(u' \psi_r + \psi_z)^2}{1+u'^2} \quad (2.7)$$

for any $(u(z), \theta, z) \in \Gamma$, where $\psi = \psi_\Gamma \in \mathcal{A}$ is the weak solution to (2.1), u and its derivatives are evaluated at z , and ψ and its partial derivatives are evaluated at $(u(z), z)$. Notice that the two squared terms correspond to the normal component of $\varepsilon_\Gamma \nabla \psi$ and the tangential component of $\nabla \psi$, respectively; cf. (1.5), (2.4), and (2.6).

Let us now consider a moving dielectric boundary $\Gamma(t)$ at time $t \in [0, T]$ for some $T > 0$. We assume that the boundary $\Gamma(t)$ can be represented by a smooth function $r = u(z, t)$ ($z \in \mathbb{R}$ and $t \geq 0$) that is L -periodical in z . The velocity of any point $(u(z, t) \cos \theta, u(z, t) \sin \theta, z)$ of Γ is $V = (u_t \cos \theta, u_t \sin \theta, 0)$. By (2.3), the normal velocity is then

$$V_n = V \cdot n = \frac{u_t}{\sqrt{1+u_z^2}}. \quad (2.8)$$

We consider the steepest descent dynamics $V_n = -\delta_\Gamma F[\Gamma]$. Hence it follows from (2.7), (2.8), and (2.1) that our governing system of equations, together with the boundary and initial conditions, for the boundary motion is

$$\begin{cases} u_t = \gamma_0 \left(\frac{u_{zz}}{1+u_z^2} - \frac{1}{u} \right) - \frac{1}{2} \left(\frac{1}{\varepsilon_-} + \frac{1}{\varepsilon_+} \right) \frac{[\varepsilon_{\Gamma(t)} (\psi_r - u_z \psi_z)]^2}{\sqrt{1+u_z^2}} \\ \quad - \frac{1}{2} (\varepsilon_+ - \varepsilon_-) \frac{(u_z \psi_r + \psi_z)^2}{\sqrt{1+u_z^2}} \quad \forall (z, t) \in (-\infty, \infty) \times (0, T], \\ u(z, t) \text{ is } L\text{-periodic in } z \text{ for each } t \in [0, T], \\ u(z, 0) \text{ is given for all } z \in (-\infty, \infty), \\ \nabla \cdot \varepsilon_{\Gamma(t)} \nabla \psi = -\rho \quad \text{in } \Omega, \\ \psi(r, z, t) \text{ is } L\text{-periodic in } z \text{ for each } (r, t) \in [0, R_\infty) \times [0, T], \\ \psi(R_\infty, z, t) = 0 \quad \forall (z, t) \in (-\infty, \infty) \times [0, T]. \end{cases} \quad (2.9)$$

In the first equation, the function u and its partial derivatives are evaluated at (z, t) and the function $\psi = \psi(r, z, t)$ and its partial derivatives are evaluated at $(u(z), z, t)$.

3 Derivation of Dielectric Boundary Force

We now fix a cylindrical dielectric boundary Γ and assume it is the graph of a smooth and L -periodical function $r = u(z)$ in the cylindrical coordinates. We assume all Ω , Ω_- , Ω_+ , ρ , and $\mathcal{A}$ are the same as defined in the previous section. To perturb the boundary Γ , we consider a family of smooth diffeomorphisms $T_t : \Omega \rightarrow \Omega$ that are parameterized by t with $0 \leq t \ll 1$ with T_0 the identity mapping. Each T_t maps the boundary Γ to $\Gamma(t) = T_t(\Gamma)$. We assume that there is a smooth function $r = u(z, t)$ ($z \in \mathbb{R}$ and $0 \leq t \ll 1$), L -periodic in z , such that the boundary $\Gamma(t)$ is the graph of this function at t with $0 < z < L$ and $u(z, 0) = u(z)$ for all z . We assume each $\Gamma(t)$ is completely inside Ω and divides Ω into two parts $\Omega_-(t) = T_t(\Omega_-)$ and $\Omega_+(t) = T_t(\Omega_+)$, with $\Omega_-(0) = \Omega_-$ and $\Omega_+(0) = \Omega_+$, respectively. For each t , let $\psi = \psi(r, z, t)$ be the unique weak solution of the boundary-value problem (2.1) with Γ replaced by $\Gamma(t)$ and $\psi(r, z)$ replaced by $\psi(r, z, t)$. We denote $\psi(r, z) = \psi(r, z, 0)$ for all (r, z) . So, $\psi = \psi(r, z)$ is

the unique weak solution to (2.1). Notice that we use the same notations $r = u(z, t)$ and $\psi = \psi(r, z, t)$ as in the last section. But we understand here these functions correspond to the mappings $T_t(0 < t \ll 1)$.

It follows from the definition (1.4), the fact that ψ is the weak solution to (2.1), and integration by parts that the electrostatic energy corresponding to the dielectric boundary $\Gamma(t)$ is

$$E[\Gamma(t)] = \int_{\Omega} \frac{1}{2} \rho \psi dV = \int_{\Omega} \left[-\frac{\varepsilon_{\Gamma(t)}}{2} |\nabla \psi|^2 + \rho \psi \right] dV. \quad (3.1)$$

We denote by n the unit normal at $\Gamma(t)$ pointing from $\Omega_-(t)$ to $\Omega_+(t)$. We define $\delta_{\Gamma} E[\Gamma] : \Gamma \rightarrow \mathbb{R}$ to be the unique function that satisfies

$$\frac{d}{dt} \Big|_{t=0} E[\Gamma(t)] = \int_{\Gamma} \delta_{\Gamma} E[\Gamma] V_n dS, \quad (3.2)$$

where V_n is the normal velocity of the boundary $\Gamma(t)$, viewed as moving boundaries, at $t = 0$. This normal velocity is given by (2.8). It is determined by the mappings T_t for small $t > 0$. We derive now

$$\delta_{\Gamma} E[\Gamma] = \frac{1}{2} \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \frac{[\varepsilon_{\Gamma} (\psi_r - u' \psi_z)]^2}{1 + u'^2} + \frac{1}{2} (\varepsilon_+ - \varepsilon_-) \frac{(u' \psi_r + \psi_z)^2}{1 + u'^2}. \quad (3.3)$$

Note that this is independent of the family of mappings T_t ($0 < t \ll 1$). Here, the function u and its derivatives are evaluated at z and the function ψ and its partial derivatives are evaluated at $(u(z)-, z)$ or $(u(z)+, z)$. Those two squared terms are common values from both sides of the boundary Γ :

$$\varepsilon_{\Gamma} (\psi_r - u' \psi_z) = \varepsilon_- (\psi_r^- - u' \psi_z^-) = \varepsilon_+ (\psi_r^+ - u' \psi_z^+), \quad (3.4)$$

$$u' \psi_r + \psi_z = u' \psi_r^- + \psi_z^- = u' \psi_r^+ + \psi_z^+, \quad (3.5)$$

where the superscripts $-$ and $+$ denote in general the restrictions from Ω_- (or $\Omega_-(t)$) and Ω_+ (or $\Omega_+(t)$), respectively.

Note that in the cylindrical coordinates the gradient of ψ is given by $\psi_r^2 + \psi_z^2$. Therefore, using the cylindrical coordinates for the integral involving the gradient of ψ , we have by (3.1) that

$$E[\Gamma(t)] = 2\pi \int_0^L \left[\int_0^{u(z,t)} -\frac{\varepsilon_-}{2} (\psi_r^2 + \psi_z^2) r dr \right] dz + 2\pi \int_0^L \left[\int_{u(z,t)}^{R_{\infty}} -\frac{\varepsilon_+}{2} (\psi_r^2 + \psi_z^2) r dr \right] dz + \int_{\Omega} \rho \psi dV.$$

We shall denote by $[[\cdot]]$ the jump across $\Gamma(t)$ from $\Omega_+(t)$ to $\Omega_-(t)$. Note that $-\varepsilon_s \Delta \psi = \rho$ in $\Omega_s(t)$ for $s = -$ and $+$ and that ψ and $\varepsilon_{\Gamma(t)} n \psi$ are continuous across $\Gamma(t)$. Consequently, using the Cartesian or cylindrical coordinates as appropriate and integration by parts, we obtain

$$\begin{aligned}
\frac{d}{dt}E[\Gamma(t)] &= -2\pi\varepsilon_- \int_0^L \left[\int_0^{u(z,t)} (\psi_r \psi_{rt} + \psi_z \psi_{zt}) r dr \right] dz \\
&\quad - \pi\varepsilon_- \int_0^L uu_t \left[(\psi_r^-)^2 + (\psi_z^-)^2 \right] dz \\
&\quad - 2\pi\varepsilon_+ \int_0^L \left[\int_{u(z,t)}^{R_\infty} (\psi_r \psi_{rt} + \psi_z \psi_{zt}) r dr \right] dz \\
&\quad + \pi\varepsilon_+ \int_0^L uu_t \left[(\psi_r^+)^2 + (\psi_z^+)^2 \right] dz + \int_\Omega \rho \psi_t dV \\
&= -\varepsilon_- \int_{\Omega_-(t)} \nabla \psi \cdot \nabla \psi_t dV - \varepsilon_+ \int_{\Omega_+(t)} \nabla \psi \cdot \nabla \psi_t dV \\
&\quad + \pi \int_0^L \llbracket \varepsilon_{\Gamma(t)} |\nabla \psi|^2 \rrbracket uu_t dz + \int_\Omega \rho \psi_t dV \\
&= \varepsilon_- \int_{\Omega_-(t)} \Delta \psi \psi_t dV - \varepsilon_- \int_{\partial \Omega_-(t)} \partial_{\hat{n}} \psi^- \psi_t^- dS \\
&\quad + \varepsilon_+ \int_{\Omega_+(t)} \Delta \psi \psi_t dV - \varepsilon_+ \int_{\partial \Omega_+(t)} \partial_{\hat{n}} \psi^+ \psi_t^+ dS \\
&\quad + \pi \int_0^L \llbracket \varepsilon_{\Gamma(t)} |\nabla \psi|^2 \rrbracket uu_t dz + \int_{\Omega_-(t)} \rho \psi_t dV + \int_{\Omega_+(t)} \rho \psi_t dV \\
&= \int_{\Gamma(t)} \varepsilon_{\Gamma(t)} \partial_n \psi \llbracket \psi_t \rrbracket dS + \pi \int_0^L \llbracket \varepsilon_{\Gamma(t)} |\nabla \psi|^2 \rrbracket uu_t dz,
\end{aligned} \tag{3.6}$$

where $\hat{n}$ denotes the exterior unit normal along $\Omega_-(t)$ or $\Omega_+(t)$, and where some of the surface integrals on $z = 0$ and $z = L$ cancel out, since ψ is L -periodical in z .

Since $r = u(z, t)$ is smooth in (z, t) , the solution $\psi = \psi(r, z, t)$ is also smooth in t and in $(r, z) \in \Omega_s(t)$ with $s = -$ or $+$. By the continuity of ψ across $\Gamma(t)$, we have

$$\psi(u(z, t) - z, t) = \psi(u(z, t) + z, t)$$

for all z and t under consideration. Taking the derivatives with respect to t and to z , respectively, we get $\llbracket \psi_t \rrbracket = -u_t \llbracket \psi_r \rrbracket$ and $\llbracket \psi_z \rrbracket = -u_z \llbracket \psi_r \rrbracket$. Thus

$$\begin{aligned}
(1 + u_z^2) \llbracket \psi_t \rrbracket &= \llbracket \psi_t \rrbracket + u_z^2 \llbracket \psi_t \rrbracket = -u_t \llbracket \psi_r \rrbracket - u_t u_z^2 \llbracket \psi_r \rrbracket \\
&= -u_t \llbracket \psi_r \rrbracket + u_t u_z \llbracket \psi_z \rrbracket = -u_t \llbracket \psi_r - u_z \psi_z \rrbracket.
\end{aligned}$$

This, together with (2.4) and (2.8), implies that on $\Gamma(t)$

$$\begin{aligned}
\varepsilon_{\Gamma(t)} \partial_n \psi \llbracket \psi_t \rrbracket &= -\varepsilon_{\Gamma(t)} \partial_n \psi \frac{\llbracket \psi_r - u_z \psi_z \rrbracket}{\sqrt{1 + u_z^2}} \frac{u_t}{\sqrt{1 + u_z^2}} \\
&= -\varepsilon_{\Gamma(t)} \partial_n \psi (\partial_n \psi^+ - \partial_n \psi^-) V_n \\
&= -\left(\frac{1}{\varepsilon_+} - \frac{1}{\varepsilon_-} \right) \llbracket \varepsilon_{\Gamma(t)} \partial_n \psi \rrbracket^2 V_n \\
&= \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \frac{\llbracket \varepsilon_{\Gamma(t)} (\psi_r - u_z \psi_z) \rrbracket^2}{1 + u_z^2} V_n.
\end{aligned} \tag{3.7}$$

Notice that, for a smooth function $\xi: \Gamma \rightarrow \mathbb{R}$,

$$\int_\Gamma \xi(r, z) dS = 2\pi \int_0^L \xi(u(z), z) u(z) \sqrt{1 + u'(z)^2} dz.$$

It then follows from the formula of normal velocity (2.8), the orthogonal decomposition (2.5), the continuity across $\Gamma(t)$ of $\varepsilon_{\Gamma(t)} \partial_n \psi$ and $(I - n \otimes n) \nabla \psi$, the formula of the normal derivative (2.4), and the formula of tangential component of $\nabla \psi$ (2.6) that

$$\begin{aligned}
& \pi \int_0^L \llbracket \varepsilon_{\Gamma(t)} |\nabla \psi|^2 \rrbracket u u_t dz = \frac{1}{2} \int_{\Gamma(t)} \llbracket \varepsilon_{\Gamma(t)} |\nabla \psi|^2 \rrbracket V_n dS \\
& = \frac{1}{2} \int_{\Gamma(t)} (\varepsilon_+ |\nabla \psi^+|^2 - \varepsilon_- |\nabla \psi^-|^2) V_n dS \\
& = \frac{1}{2} \int_{\Gamma(t)} [\varepsilon_+ |\partial_n \psi^+|^2 - \varepsilon_- |\partial_n \psi^-|^2 + (\varepsilon_+ - \varepsilon_-) (I - n \otimes n) \nabla \psi|^2] V_n dS \\
& = \frac{1}{2} \int_{\Gamma(t)} \left\{ \left(\frac{1}{\varepsilon_+} - \frac{1}{\varepsilon_-} \right) \frac{[\varepsilon_{\Gamma(t)} (\psi_r - u_z \psi_z)]^2}{1 + u_z^2} + (\varepsilon_+ - \varepsilon_-) \frac{(u_z \psi_r + \psi_z)^2}{1 + u_z^2} \right\} V_n dS
\end{aligned}$$

Combining this with (3.6) and (3.7), and setting $t = 0$, we obtain (3.2) with $\delta_\Gamma E[\Gamma]$ given by (3.3) as desired.

4 Linear Stability for the Case $\varepsilon_- > \varepsilon_+$

We assume in this section that $\varepsilon_- > \varepsilon_+$. We also assume for simplicity that the charged density $\rho = \rho(r)$ only depends on r but not on z . We present a linear stability analysis that consists of the following steps [4]: (1) Find steady-state solutions; (2) Linearize the original nonlinear system around such a steady-state solution; (3) Solve the linearized system with initial solutions being sinusoidal perturbations of wavenumber k , and derive the dispersion relation $\omega = \omega(k)$ that is the rate of growth or decay of a perturbed front.

4.1 Steady-state solutions

Let us assume that $u_0 \in (0, R_\infty)$. Consider a circularly cylindrical boundary Γ represented by the constant function $r = u_0$ for all $z \in \mathbb{R}$ and assume it is a solution to the full system (2.9). The corresponding potential ψ_0 depends only on r . Note that the Laplacian of $\psi_0 = \psi_0(r)$ in the cylindrical coordinates is simply $(r\psi_0'(r))' / r$. By (2.9), we then obtain the equations for u_0 and $\psi_0 = \psi_0(r)$

$$\begin{cases} \frac{\gamma_0}{u_0} = \frac{1}{2} \left(\frac{1}{\varepsilon_+} - \frac{1}{\varepsilon_-} \right) |\varepsilon_\Gamma \psi_0'(u_0)|^2, \\ \frac{\varepsilon_-}{r} (r\psi_0'(r))' = -\rho(r) & \text{if } 0 < r < u_0, \\ \frac{\varepsilon_+}{r} (r\psi_0'(r))' = -\rho(r) & \text{if } u_0 < r < R_\infty, \\ \psi_0(u_0^-) = \psi_0(u_0^+), \\ \varepsilon_- \psi_0(u_0^-) = \varepsilon_+ \psi_0(u_0^+), \\ \psi_0(R_\infty) = 0. \end{cases} \quad (4.1)$$

Denote

$$\eta = 2\gamma_0 \left(\frac{1}{\varepsilon_+} - \frac{1}{\varepsilon_-} \right)^{-1} > 0.$$

After a series of calculations using the fact that ψ_0 is continuous at $r = 0$, we obtain

$$\eta u_0 = \left(\int_0^{u_0} s \rho(s) ds \right)^2, \quad (4.2)$$

$$\psi_0(r) = \begin{cases} -\frac{1}{\varepsilon_-} \int_0^r \left[\frac{1}{s} \int_0^s \tau \rho(\tau) d\tau \right] ds + C_2 & \text{if } 0 < r < u_0, \\ -\frac{1}{\varepsilon_+} \int_{u_0}^r \left[\frac{1}{s} \int_{u_0}^s \tau \rho(\tau) d\tau \right] ds + C_3 \log r + C_4 & \text{if } u_0 < r < R_\infty, \end{cases} \quad (4.3)$$

where the constants C_2 , C_3 , and C_4 are determined by

$$\begin{cases} C_2 - C_3 \log u_0 - C_4 = \frac{1}{\varepsilon_-} \int_0^{u_0} \left[\frac{1}{s} \int_0^s \tau \rho(\tau) d\tau \right] ds, \\ C_3 = -\frac{1}{\varepsilon_+} \int_0^{u_0} s \rho(s) ds, \\ C_3 \log R_\infty + C_4 = \frac{1}{\varepsilon_+} \int_{u_0}^{R_\infty} \left[\frac{1}{s} \int_{u_0}^s \tau \rho(\tau) d\tau \right] ds. \end{cases}$$

It is easy to see that the equation (4.2) has at least one solution $u_0 \in (0, R_\infty)$ provided that

$$\eta R_\infty < \left(\int_0^{R_\infty} s \rho(s) ds \right)^2.$$

Once u_0 is fixed, the solution $\psi_0 = \psi_0(r)$ is uniquely determined.

4.2 Perturbations and linearized systems

We assume the solution (u, ψ) to the full system (2.9) is given by

$$u = u(z, t, \tau) = u_0 + \tau u_1(z, t) + \cdots, \quad (4.4)$$

$$\psi = \psi(r, z, t, \tau) = \psi_0(r) + \tau \psi_1(r, z, t) + \cdots, \quad (4.5)$$

where τ is a parameter small in magnitude, both $u_1 = u_1(z, t)$ and $\psi_1 = \psi_1(r, z, t)$ are L -periodic in z , and dots represent terms of order τ^2 or higher as $\tau \rightarrow 0$. The function $r = u(z, t, \tau)$ defines the moving boundary $\Gamma(t)$. We assume that the initial position of dielectric boundary is given by

$$u(z, 0, \tau) = u_0 + \tau u_1(z, 0).$$

To the leading order, the dielectric boundary that defines ψ is the steady-state boundary $r = u_0$. Insert ψ defined in (4.5) into the two Poisson's equations in (2.9). The $O(1)$ -terms are exactly those Poisson's equations in (4.1). The $O(\tau)$ terms are

$$\begin{aligned} \Delta \psi_1 &= 0 & \text{if } 0 < r < u_0, \\ \Delta \psi_1 &= 0 & \text{if } u_0 < r < R_\infty. \end{aligned}$$

At the dielectric boundary $\Gamma(t)$ defined by $r = u(z, t, \tau)$ of the form (4.4), we have

$$\begin{aligned} \psi(r, z, t, \tau) &= \psi(u_0 + \tau u_1(z, t) + O(\tau^2), z, t, \tau) \\ &= \psi_0(u_0 + \tau u_1(z, t) + O(\tau^2)) + \tau \psi_1(u_0 + \tau u_1(z, t) + O(\tau^2), z, t) + O(\tau^2) \\ &= \psi_0(u_0^s) + \tau [u_1(z, t) \psi_0'(u_0^s) + \psi_1(u_0^s, z, t)] + O(\tau^2), \end{aligned}$$

where $s = +$ or $-$. The continuity of ψ at $r = u(z, t, \tau)$ (cf. (2.9)) implies, to the leading order, the continuity of ψ_0 at $r = u_0$, i.e., $\psi_0(u_0^-) = \psi_0(u_0^+)$, and to the order $O(\tau)$, the first interface condition for $\psi_1 = \psi_1(r, z, t)$

$$u_1(z, t)\psi'_0(u_0^-) + \psi_1(u_0^-, z, t) = u_1(z, t)\psi'_0(u_0^+) + \psi_1(u_0^+, z, t) \quad \text{for all } (z, t).$$

By (2.4), we have at the dielectric boundary $r = u(z, t, \tau)$ from either side $s = -$ or $+$ that

$$\begin{aligned} \partial_n \psi(r^s, z, t, \tau) &= \frac{\partial_r \psi(u(z, t, \tau)^s, z, t, \tau) - \partial_z u(z, t, \tau) \partial_z \psi(u(z, t, \tau)^s, z, t, \tau)}{\sqrt{1 + (\partial_z u(z, t, \tau))^2}} \\ &= \psi'_0(u_0^s + \tau u_1(z, t)) + \tau \partial_r \psi_1(u_0^s, z, t) + O(\tau^2) \\ &= \psi'_0(u_0^s) + \tau [u_1(z, t)\psi''_0(u_0^s) + \partial_r \psi_1(u_0^s, z, t)] + O(\tau^2). \end{aligned} \quad (4.6)$$

Therefore, to the leading order of the continuity of $\varepsilon_{\Gamma(t)} \psi$ at $r = u(z, t, \tau)$, we obtain the continuity of $\varepsilon_{\Gamma} \psi_0$ at $r = u_0$. To the order $O(\tau)$, we obtain the second interface condition for ψ_1

$$\varepsilon_- [u_1(z, t)\psi''_0(u_0^-) + \partial_r \psi_1(u_0^-, z, t)] = \varepsilon_+ [u_1(z, t)\psi''_0(u_0^+) + \partial_r \psi_1(u_0^+, z, t)] \quad \text{for all } (z, t).$$

By (4.3) one easily verifies that

$$\varepsilon_- \psi''_0(u_0^-) = \varepsilon_+ \psi''_0(u_0^+) = \frac{1}{u_0^2} \int_0^{u_0} r \rho(r) dr - \rho(u_0). \quad (4.7)$$

Therefore the second interface condition for ψ_1 reduces to

$$\varepsilon_- \partial_r \psi_1(u_0^-, z, t) = \varepsilon_+ \partial_r \psi_1(u_0^+, z, t) \quad \text{for all } (z, t). \quad (4.8)$$

The boundary conditions that $\psi = 0$ and that $\psi_0 = 0$ at $r = R_\infty$ lead to

$$\psi_1(R_\infty, z, t) = 0 \quad \text{for all } (z, t).$$

We now consider the equation of motion for u , cf. (2.9). By (4.4) and (4.5), we have ${}_z u = O(\tau)$ and ${}_z \psi = O(\tau)$. Hence

$$(\partial_r \psi \partial_z u + \partial_z \psi)^2 = O(\tau^2). \quad (4.9)$$

At the dielectric boundary $r = u(z, t, \tau)$ we have (cf. (4.6))

$$\begin{aligned} [\varepsilon_+ (\partial_r \psi(u(z, t, \tau)^+, z, t, \tau) - \partial_z u(z, t, \tau) \partial_z \psi(u(z, t, \tau)^+, z, t, \tau))]^2 &= \varepsilon_+^2 [\psi'_0(u_0^+ + \tau u_1(z, t)) + \tau \partial_r \psi_1(u_0^+, z, t)]^2 + O(\tau^2) \\ &= \varepsilon_+^2 [\psi'_0(u_0^+) + \tau u_1(z, t)\psi''_0(u_0^+) + \tau \partial_r \psi_1(u_0^+, z, t)]^2 + O(\tau^2) \\ &= [\varepsilon_+ \psi'_0(u_0^+)]^2 + 2\tau \varepsilon_+^2 \psi'_0(u_0^+) [u_1(z, t)\psi''_0(u_0^+) + \partial_r \psi_1(u_0^+, z, t)] + O(\tau^2). \end{aligned} \quad (4.10)$$

By the continuity of ψ_0 at $r = u_0$ (cf. (4.1)), (4.7), and (4.8), the sign $+$ can be changed to the sign $-$. Inserting u defined in (4.4) into the equation of motion, the first equation in (2.9), we obtain by (4.9) and (4.10), to the leading order, the first equation in (4.1) for the steady-state solution $r = u_0$, and to the order $O(\tau)$ the following equation for $u_1 = u_1(z, t)$:

$$\partial_t u_1 = \gamma_0 \left(\partial_z^2 u_1 + \frac{u_1}{u_0^2} \right) - \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \varepsilon_+^2 \psi_0'(u_0^+) [\psi_0''(u_0^+) u_1(z, t) + \partial_r \psi_1(u_0^+, z, t)].$$

We summarize the linearized system of equations for $u_1 = u_1(z, t)$ and $\psi_1 = \psi_1(r, z, t)$ as follows:

$$\begin{cases} \partial_t u_1 = \gamma_0 \partial_z^2 u_1 + \left[\frac{\gamma_0}{u_0^2} - \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \varepsilon_+^2 \psi_0'(u_0^+) \psi_0''(u_0^+) \right] u_1 \\ - \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \varepsilon_+^2 \psi_0'(u_0^+) \partial_r \psi_1(u_0^+, z, t) \quad \forall z \in \mathbb{R} \quad \forall t > 0, \\ u_1(z, t) \text{ is } L\text{-periodic in } z \in \mathbb{R} \text{ for all } t \geq 0, \\ u_1(z, 0) \text{ is given for all } z \in \mathbb{R}, \\ \Delta \psi_1 = 0 \quad \text{if } 0 < r < u_0, \\ \Delta \psi_1 = 0 \quad \text{if } u_0 < r < R_\infty, \\ \psi_1(u_0^+, z, t) - \psi_1(u_0^-, z, t) = -u_1(z, t) [\psi_0'(u_0^+) - \psi_0'(u_0^-)] \quad \forall z \in \mathbb{R} \quad \forall t > 0, \\ \varepsilon_- \partial_r \psi_1(u_0^-, z, t) = \varepsilon_+ \partial_r \psi_1(u_0^+, z, t) \quad \forall z \in \mathbb{R} \quad \forall t > 0, \\ \psi_1(r, z, t) \text{ is } L\text{-periodic in } z \in \mathbb{R} \text{ for all } r \in [0, R_\infty) \text{ and } t > 0, \\ \psi_1(R_\infty, z, t) = 0 \quad \forall z \in \mathbb{R} \quad \forall t > 0. \end{cases} \quad (4.11)$$

Notice that potential ψ_1 is related to the function u_1 through the first interface condition.

4.3 Dispersion relations

We consider $u_1(z, t) = A e^{\omega t} e^{ikz}$, where $A > 0$ is a constant and $k = 2\pi k'/L$ with k' an integer. We can replace the complex-valued periodic function e^{ikz} by its real or imaginary part if necessary. By the first interface condition for ψ_1 in (4.11), we may assume that $\psi_1(r, z, t) = u_1(z, t) \phi_k(r)$. Consequently, the equation for u_1 in (4.11) leads to the following dispersion relation:

$$\omega = -\gamma_0 k^2 + \frac{\gamma_0}{u_0^2} - \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \varepsilon_+^2 \psi_0'(u_0^+) [\psi_0''(u_0^+) + \phi_k'(u_0^+)], \quad (4.12)$$

where we can replace all $+$ by $-$. Moreover, we obtain by the equations and side conditions for ψ_1 in (4.11) that

$$\begin{cases} \phi_k''(r) + \frac{1}{r} \phi_k'(r) - k^2 \phi_k(r) = 0 & \text{if } 0 < r < u_0, \\ \phi_k''(r) + \frac{1}{r} \phi_k'(r) - k^2 \phi_k(r) = 0 & \text{if } u_0 < r < R_\infty, \\ \phi_k(u_0^+) - \phi_k(u_0^-) = -[\psi_0'(u_0^+) - \psi_0'(u_0^-)], \\ \varepsilon_- \phi_k'(u_0^-) = \varepsilon_+ \phi_k'(u_0^+), \\ \phi_k(R_\infty) = 0. \end{cases} \quad (4.13)$$

The first two equations above are examples of the modified Bessel differential equation

$$x^2 y''(x) + x y'(x) - x^2 y(x) = 0.$$

It has two linearly independent solutions called the modified Bessel functions,

$$I_0(x) = \sum_{s=0}^{\infty} \frac{1}{(s!)^2} \left(\frac{x}{2}\right)^{2s} \quad \text{and} \quad K_0(x) = \int_0^{\infty} \frac{\cos(xs)}{\sqrt{1+s^2}} ds.$$

Using the change of variables $x = rk$, the solution of the above system of equations is

$$\varphi_k(r) = \begin{cases} \mu \varepsilon_+ [\psi'_0(u_0^+) - \psi'_0(u_0^-)] [K_0(kR_\infty)I_1(ku_0) + I_0(kR_\infty)K_1(ku_0)] I_0(kr) & \text{if } 0 < r < u_0, \\ \mu \varepsilon_- [\psi'_0(u_0^+) - \psi'_0(u_0^-)] [K_0(kR_\infty)I_1(ku_0) I_0(kr) - I_0(kR_\infty)I_1(ku_0) K_0(kr)] & \text{if } u_0 < r < R_\infty, \end{cases}$$

where $I_1(x) = I'_0(x)$ and $K_1(x) = -K'_0(x)$, and

$$\frac{1}{\mu} = \varepsilon_- I_1(ku_0) [I_0(kR_\infty)K_0(ku_0) - I_0(ku_0)K_0(kR_\infty)] + \varepsilon_+ I_0(ku_0) [I_1(ku_0)K_0(kR_\infty) + I_0(kR_\infty)K_1(ku_0)].$$

The dispersion relation (4.12) can be visualized using our solution for φ_k , once numerical values of the parameters in the model are given. When modeling biomolecules, one would approximately have $\gamma_0 = 0.15$, and $\varepsilon_+ = 2$ and $\varepsilon_- = 80$ in the unit of vacuum permittivity. We also choose $L = 2\pi$, $R_\infty = 10$, and $\rho(r) = 1$ for all r . The dispersion relation for these values is plotted in Figure 4.1 (Left), where we separate the contributions to $\omega(k)$ into

$$\omega_1(k) = -\left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+}\right) \varepsilon_+^2 \psi'_0(u_0^+) [\psi''_0(u_0^+) + \varphi'_k(u_0^+)]$$

and

$$\omega_2(k) = -\gamma_0 k^2 + \frac{\gamma_0}{u_0^2}.$$

We define $k_{\max} = \arg \max_k \omega(k)$, which is approximately 0.769. We also define k_0 to be the positive root of $\omega(k)$, which is approximately 2.3. We pick up $k_s = 4 > k_0$ so that $\omega(k_s)$ is negative. We plot in Figure 4.1 (Right) the graphs of φ_k for these choices of k . It is clear that, for the chosen parameters, the growth rate $\omega(k)$ is negative if and only if the wavenumber k is larger than a critical value. Therefore, the steady-state boundary $r = u_0$ is linearly unstable subject to small wavenumber perturbations but is linearly stable otherwise.

We only calculate numerically the dispersion relation for one set of parameters. But the result should be more general. In fact, with given ε_- , ε_+ , R_∞ and k , the solution φ_k of the system of equations (4.13) is completely determined by u_0 and $\psi'_0(u_0^+) - \psi'_0(u_0^-)$, both of which depend on the charge density ρ . The value u_0 is determined by (4.2) through an integral of $r\rho(r)$. The change of the sign of ρ will not affect the value of u_0 . Once u_0 is determined, the solution φ_k is completely determined by the difference $\psi'_0(u_0^+) - \psi'_0(u_0^-)$. By (4.3), we have

$$\varepsilon_- \psi'_0(u_0^-) = \varepsilon_+ \psi'_0(u_0^+) = \frac{1}{u_0} \int_0^{u_0} r \rho(r) dr.$$

This indicates that the sign of $\psi'_0(u_0^+)$, same as that of $\psi'_0(u_0^-)$, is only affected by the same integral of $r\rho(r)$. If this sign is changed, the sign of the solution ϕ_k is also changed.

Therefore, the sign of $\psi'_0(u_0^+)\phi'_k(u_0^+)$ is not changed. Consequently, by (4.12), the dispersion relation should remain the same qualitatively.

5 Numerical Methods

We choose positive integers N_r , N_z , and N_t and define $h_r = R_\infty/(N_r + 1/2)$, $h_z = L/N_z$, and $\Delta t = T/N_t$. We cover the computational region $[0, R_\infty] \times [0, L]$ by a uniform finite-difference grid with grid sizes h_r and h_z , and grid points

$$(r_i, z_j) = ((i+1/2)h_r, jh_z), \quad i=1, \dots, N_r; j=1, \dots, N_z.$$

Notice that we define r_i starting from $r_0 = h_r/2$. This is for an accurate approximation of the term $r\psi/r$ near $r=0$ in the Laplacian in cylindrical coordinates; cf. [18]. We denote $t_m = m\Delta t$ ($m=0, 1, \dots, N_t$). For any function $v = v(z, t) : [0, L] \times [0, T] \rightarrow \mathbb{R}$, we denote by $v^m = v^m(z)$ an approximation of $v(z, t_m)$ and by v_j^m approximations of $v(z_j, t_m)$ with $m=0, 1, \dots, N_t$ and $j=0, 1, \dots, N_z$. Similarly, for any function $\phi = \phi(r, z, t) : [0, R_\infty] \times [0, L] \times [0, T] \rightarrow \mathbb{R}$, we denote by $\phi^m = \phi^m(r, z)$ an approximation of $\phi(r, z, t_m)$ and by $\phi_{i,j}^m$ approximations of $\phi(r_i, z_j, t_m)$ with $i=0, 1, \dots, N_r$, $j=0, 1, \dots, N_z$, and $m=0, 1, \dots, N_t$.

We use an algorithm of alternative iteration to solve the system of equations (2.9). The iteration is on time steps $m=0, 1, \dots, N_t-1$; and each iteration consists of two steps. Let us assume that for an integer m with $0 \leq m \leq N_t-1$ we know the values of u^m and ψ^m on all the grid points. In the first step, we use the following semi-implicit scheme to solve the first equation in (2.9):

$$\frac{u^{m+1} - u^m}{\Delta t} = \gamma_0 \left[\frac{u_{zz}^{m+1}}{1 + (u_z^m)^2} - \frac{1}{u^m} \right] - \frac{1}{2} \left(\frac{1}{\varepsilon_-} - \frac{1}{\varepsilon_+} \right) \frac{[\varepsilon_\Gamma^m (\psi_r^m - u_z^m \psi_z^m)]^2}{\sqrt{1 + (u_z^m)^2}} - \frac{1}{2} (\varepsilon_+ - \varepsilon_-) \frac{(u_z^m \psi_r^m + \psi_z^m)^2}{\sqrt{1 + (u_z^m)^2}}.$$

Here u^m and u^{m+1} are functions of $z \in [0, L]$, ψ^m is a function of $(u^m(z), z)$ with $z \in [0, L]$, and Γ^m is the dielectric boundary defined by $r = u^m(z)$. The derivative u_{zz}^{m+1} and the derivative u_z^m in $1 + (u_z^m)^2$ are discretized using central differencing. The discretization of the two squared terms involving the derivatives of ψ^m in the electrostatic force will be detailed later. Due to the periodic boundary condition, the matrix of the system of linear equations resulting from the spatial discretization is not a tridiagonal matrix. It, however, can be decomposed into the sum of a tridiagonal matrix and a rank-one matrix that has the only possible nonzero entries in the four corners. With such a decomposition, the system of linear equations can be solved by solving twice a tridiagonal system.

In the second step, we use a ‘‘cylindrical version’’ of the Coupling Interface Method (CIM) [10, 11, 28] to discretize Poisson’s equation in (2.9). See more details below. We solve the

resulting system of linear equations using an algebraic multigrid method and obtain $\psi_{i,j}^{m+1}$ for all $i = 0, 1, \dots, N_r$ and $j = 0, 1, \dots, N_z$.

After these two steps, we update m and continue. We terminate the iteration if $m = N_t - 1$ or if the minimum value of u_j^m ($j = 0, 1, \dots, N_z$) is too close to 0, e.g., if

$$\min_{0 \leq j \leq N_z} u_j^m < \frac{3h_r}{2}. \quad (5.1)$$

In the rest of this section, we consider the discretization of the boundary-value problem of Poisson's equation (2.1), or equivalently (2.2), and the corresponding electrostatic force terms, the two squared terms in (3.3). We assume that $r = r(z)$ is a smooth and L -periodical function, representing a cylindrical dielectric boundary 3; cf. Figure 2.1. We assume that all Ω , Ω_+ , Ω_- , and ρ are the same as before. Let $\psi = \psi(r, z)$ be the solution of the boundary-value problem of Poisson's equation (2.1), or equivalently (2.2), which can be reformulated using the cylindrical coordinates as

$$\begin{cases} \varepsilon_- \left(\psi_{rr} + \frac{\psi_r}{r} + \psi_{zz} \right) = -\rho & \text{in } \Omega_-, \\ \varepsilon_+ \left(\psi_{rr} + \frac{\psi_r}{r} + \psi_{zz} \right) = -\rho & \text{in } \Omega_+, \\ \llbracket \psi \rrbracket = 0 & \text{on } \Gamma, \\ \llbracket \varepsilon_\Gamma \partial_n \psi \rrbracket = 0 & \text{on } \Gamma, \\ \psi \text{ is } L\text{-periodic in } z, \\ \psi(R_\infty, z) = 0 \quad \forall z \in \mathbb{R}. \end{cases} \quad (5.2)$$

We denote

$$\begin{aligned} \Omega_h &= \{(r_i, z_j) : i = 1, \dots, N_r; j = 1, \dots, N_z\}, \\ \Omega_h^+ &= \{(r_i, z_j) \in \Omega_h : (r_{i\pm 1}, z_j) \in \Omega_+ \text{ and } (r_i, z_{j\pm 1}) \in \Omega_+\}, \\ \Omega_h^- &= \{(r_i, z_j) \in \Omega_h : (r_{i\pm 1}, z_j) \in \Omega_- \text{ and } (r_i, z_{j\pm 1}) \in \Omega_-\}, \\ \Omega_h^{I,+} &= (\Omega_h \cap \Omega_+) \setminus \Omega_h^+, \\ \Omega_h^{I,-} &= (\Omega_h \cap \Omega_-) \setminus \Omega_h^-. \end{aligned}$$

5.1 Discretization of Poisson's equation with dielectric boundary

All the grid points in Ω_h^+ or Ω_h^- are regular grid points. At any of such a point (r_i, z_j) , we use the central differencing

$$\left(\psi_{rr} + \frac{\psi_r}{r} + \psi_{zz} \right)_{i,j} \approx \frac{\psi_{i+1,j} - 2\psi_{i,j} + \psi_{i-1,j}}{h_r^2} + \frac{\psi_{i+1,j} - \psi_{i-1,j}}{2r_i h_r} + \frac{\psi_{i,j+1} - 2\psi_{i,j} + \psi_{i,j-1}}{h_z^2}.$$

For a grid point $(r_0, z_j) \in \Omega_h^+ \cup \Omega_h^-$, we have

$$\varepsilon_- \left[\frac{2(\psi_{1,j} - \psi_{0,j})}{h_r^2} + \frac{\psi_{0,j+1} - 2\psi_{0,j} + \psi_{0,j-1}}{h_z^2} \right] = -\rho_{0,j},$$

where the terms involving $\psi_{-1,j}$ are canceled out.

All the grid points in $\Omega_h^{I,+}$ or $\Omega_h^{I,-}$ are interface grid points. To treat such points, we use a variation of the Coupling Interface Method (CIM) [10, 11, 28]. We first obtain some jump conditions along the coordinate directions. By the continuity of ψ and $\varepsilon_{\Gamma} \nabla \psi$ across Γ , we have by (2.4) and (3.5) that

$$\begin{cases} \llbracket \psi_z + u' \psi_r \rrbracket = \llbracket \psi_z \rrbracket + u' \llbracket \psi_r \rrbracket = 0, \\ \llbracket \varepsilon_{\Gamma} \partial_n \psi \rrbracket = \frac{\llbracket \varepsilon_{\Gamma} (\psi_r - u' \psi_z) \rrbracket}{\sqrt{1+u'^2}} = \frac{\llbracket \varepsilon_{\Gamma} \rrbracket \psi_r^+ + \varepsilon_- \llbracket \psi_r \rrbracket - u' (\llbracket \varepsilon_{\Gamma} \rrbracket \psi_z^+ + \varepsilon_- \llbracket \psi_z \rrbracket)}{\sqrt{1+u'^2}} = 0. \end{cases}$$

These lead to

$$\begin{cases} \llbracket \psi_r \rrbracket = \frac{\llbracket \varepsilon_{\Gamma} \rrbracket (u' \psi_z^+ - \psi_r^+)}{\varepsilon_- (1+u'^2)}, \\ \llbracket \psi_z \rrbracket = \frac{\llbracket \varepsilon_{\Gamma} \rrbracket (u' \psi_r^+ - u'^2 \psi_z^+)}{\varepsilon_- (1+u'^2)}, \end{cases} \quad \text{and} \quad \begin{cases} \llbracket \varepsilon_{\Gamma} \psi_r \rrbracket = \frac{\llbracket \varepsilon_{\Gamma} \rrbracket (u' \psi_z^+ + u'^2 \psi_r^+)}{1+u'^2}, \\ \llbracket \varepsilon_{\Gamma} \psi_z \rrbracket = \frac{\llbracket \varepsilon_{\Gamma} \rrbracket (u' \psi_r^+ + \psi_z^+)}{1+u'^2}. \end{cases} \quad (5.3)$$

Let us now fix $(r_i, z_j) \in \Omega_h^{I,-}$. The case that the point is in $\Omega_h^{I,+}$ is similar. Along the line of the first-order CIM (CIM1), we use the approximation

$$\left(\psi_{rr}^- + \frac{\psi_r^-}{r} + \psi_{zz}^- \right)_{i,j} \approx \frac{(\psi_r^-)_{i+\frac{1}{2},j} - (\psi_r^-)_{i-\frac{1}{2},j}}{h_r} + \frac{(\psi_r^-)_{i+\frac{1}{2},j} + (\psi_r^-)_{i-\frac{1}{2},j}}{2r_i} + \frac{(\psi_z^-)_{i,j+\frac{1}{2}} - (\psi_z^-)_{i,j-\frac{1}{2}}}{h_z}.$$

The discretization of each of the first-order partial derivative can be done exactly as that in CIM1 [11]. If the interface grid point $(r_i, z_j) \in \Omega_h^{I,-}$ satisfies certain conditions as detailed in [11], then we can use the following second-order CIM (CIM2):

$$\begin{aligned} \left(\psi_{rr}^- + \frac{\psi_r^-}{r} + \psi_{zz}^- \right)_{i,j} &\approx (\psi_{rr}^-)_{i,j} + \frac{1}{r_i h_r} \left(\psi_{i,j}^- - \psi_{i-1,j}^- + \frac{h_r^2 (\psi_{rr}^-)_{i,j}}{2} \right) + (\psi_{zz}^-)_{i,j} \\ &= \frac{2}{(2i+1) h_r^2} (\psi_{i,j}^- - \psi_{i-1,j}^-) + \left(\frac{2i+2}{2i+1} \right) (\psi_{rr}^-)_{i,j} + (\psi_{zz}^-)_{i,j}. \end{aligned}$$

The further discretization of partial derivatives in this case can be done as in CIM2 [11].

5.2 Discretization of electrostatic force terms

Given all the approximated values $u_j \approx u(z_j)$ ($j = 0, \dots, N_z$) and $\psi_{i,j} \approx \psi(r_i, z_j)$ ($i = 0, \dots, N_r$; $j = 0, \dots, N_z$), we construct approximations of $\varepsilon_{\Gamma}(\psi_r - u' \psi_z)$ and $u' \psi_r + \psi_z$ at (u_j, z_j) for all j . We need to approximate ψ_r and ψ_z at (u_j, z_j) for all j .

Let us fix j . Let (q, z_j) be the unique intersection point of the boundary Γ defined by $r = u(z)$ and the grid line $z = z_j$ i.e., $q = u(z_j)$. Notice that our underlying problem is two-dimensional due to the cylindrical symmetry, and that the boundary Γ is the graph of function $r = u(z)$ that cuts any grid line $z = z_j$ exactly once. We thus need only to discuss two cases in terms of using the CIM. In each of these cases, we choose i such that $r_i - u(z_j) < r_{i+1}$; cf. Figure 5.1.

Case 1—The boundary satisfies the two conditions $u(z_{j-1}) > r_i$ and $u(z_{j+1}) > r_i$ as in Figure 5.1 (Left), or in the analogous vertically flipped case when $u(z_{j-1}) < r_{i+1}$ and $u(z_{j+1}) < r_{i+1}$. We can then use the CIM2 to solve for $(\psi_r)_{q,j}^-$ and $(\psi_z)_{q,j}^-$ in the first case or $(\psi_r)_{q,j}^+$ and $(\psi_z)_{q,j}^+$ in the second. Notice that we essentially extrapolate $z\psi^n$ onto the boundary based on its central difference approximations at two nearby points, (r_i, z_j) and (r_{i-1}, z_j) . We compute ψ_r based on the assumption that $\psi|_{\{z=z_j\}}$ is piecewise quadratic and satisfies the interface jump condition.

Case 2—The boundary satisfies the four conditions: $u(z_{j-2}) < r_{i+1}$, $u(z_{j-1}) > r_{i+1}$, $u(z_{j+1}) < r_i$, and $u(z_{j+2}) > r_i$ as shown in Figure 5.1 (Right), or analogous conditions for the three other cases corresponding to horizontal or vertical flips of the figure. As expected, failing to satisfy one of these four conditions will allow us to use one of the other two cases. For this case, we can now use (5.3) at the interface point (q, z_j) to obtain (with $(q, j) = (q, z_j)$)

$$(\psi_z)_{q,j}^+ = \frac{\varepsilon_- \llbracket (\psi_r)_{q,j} \rrbracket (1 + u_j'^2) + \llbracket \varepsilon_\Gamma \rrbracket (\psi_r)_{q,j}^+}{\llbracket \varepsilon_\Gamma \rrbracket u_j'}. \quad (5.4)$$

Thus, we only need to compute $(\psi_r)_{q,j}^+$ and $(\psi_r)_{q,j}^-$. These can be approximated by extrapolation from both sides, due to the fact that there is only one intersection point of the interface and the line $\{z = z_j\}$. It is important in this case that we are guaranteed that $|u_j'| > 2$, because this eliminates the problem of the singularity of (5.4) when $u_j' = 0$.

6 Numerical Results

We use the following parameters in our numerical simulations: $L = 2\pi$, $R_\infty = 10$, $\gamma_0 = 0.15$, and $\rho(r, z) = 1$ for all (r, z) . We consider two cases $\varepsilon_- < \varepsilon_+$ and $\varepsilon_- > \varepsilon_+$.

6.1 The case $\varepsilon_- < \varepsilon_+$

We choose $\varepsilon_- = 2$ and $\varepsilon_+ = 80$. The initial boundary is the graph of the function

$$u(z) = 2.025 + 0.1 \sin(5z).$$

In Figure 6.1, we plot snapshots of the moving, cylindrical boundary at $t = 0, 1/2$, and $3/2$. In this case, both components of the boundary force that arise from the surface energy and electrostatic energy, respectively, push the boundary toward the cylindrical axis. Let us define the mean position of the boundary $r = u(z, t)$ by $\bar{r}(t)$ as a function of time t with

$$\bar{r}(t) = \frac{1}{L} \int_0^L u(z, t) dz.$$

It is clear that the mean position moves monotonically toward the position $r = 0$. In the meantime, the boundary is flattened by the mean-curvature part of the boundary force.

6.2 The case $\varepsilon_- > \varepsilon_+$

We now choose $\varepsilon_- = 80$ and $\varepsilon_+ = 2$. In this case, there is a steady state of the dielectric boundary that is a circular cylinder of radius $r = u_0$ determined by (4.2). Our linear stability

analysis in Section 4 shows that such a steady state is stable with respect to a sinusoidal perturbation if and only if the wavenumber k of the perturbation is larger than a critical value. Here, we test numerically such stability and instability of the boundary. Note that the parameters we use here for our numerical calculations are the same as those used for the plot of the dispersion relation in Figure 4.1.

In Figure 6.2, we show some snapshots of the moving boundary that starts as a sinusoidal perturbation of the steady state $r = u_0 \approx 1.35$:

$$u(z, 0) = u_0 + 10^{-3} \sin z.$$

The wavenumber of the perturbation is $k = 1$. It is smaller than the critical value; so $\omega(k) > 0$. We observe from Figure 6.2 that the amplitude of the wavy boundary increases as predicted by our linear stability analysis; cf. Figure 4.1.

We now set the initial boundary to be the graph of

$$u(z, 0) = u_0 + 10^{-3} \sin(5z)$$

with the wavenumber $k = 5$ larger than the critical value so that the growth factor is negative. We show in Figure 6.3 some snapshots of the moving boundary with such an initial boundary. It is clear that the amplitude of the wavy boundary decreases quickly as predicted by our linear stability analysis. Notice that after $t = 30$, the growth of an unstable mode is observed. This is due to the machine round-off error that gives rise to an effective perturbation of the steady state $r = u_0$ with a very small wavenumber. Our analysis summarized in Figure 4.1 shows that such a perturbation should lead to the growth of amplitude of the wavy perturbation. In Figure 6.4, we plot the change of each part of the energy during the time evolution of the dielectric boundary. It is clear that the total energy decays. This is expected since the motion law is the steepest descent of the corresponding free-energy functional. Notice that, while the surface energy decays, the electrostatic energy increases, at a late stage when the round-off error induces an effective perturbation with a linearly unstable wavenumber.

We finally examine the nonlinear instability of the steady state $r = u_0$. We choose the initial boundaries to be

$$u(z, 0) = u_0 + 10^{-3} \quad \text{and} \quad u(z, 0) = u_0 - 10^{-3},$$

respectively. We then solve the full system (2.9) of the boundary motion. Our numerical results are plotted in Figure 6.5. They indicate that the steady state $r = u_0$ is unstable. Notice that in this case ρ and $u(z, 0)$ are independent of z . Thus one expects that the solution u should also be independent of z for $t > 0$; cf. (2.9). Therefore, the dependence of the solution u on z at $t = 30$ shown in the left of Figure 6.5 is again the instability due to an effective perturbation from the machine round-off error.

7 Conclusions

We have studied the motion of a cylindrical dielectric boundary as the steepest descent of a free energy consisting of the surface and electrostatic energies. We derive the effective

dielectric boundary force as the negative variation of electrostatic energy with respect to the location change of the dielectric boundary. It is found that this force always points from the high dielectric region to the lower dielectric region. In the case that the interior region of the cylindrical boundary is of high dielectric, the balance between the surface energy and electrostatic energy leads to the existence of steady states that are circular cylinders. Our linear stability analysis shows that such a state is stable with respect to sinusoidal perturbations if and only if the wavenumber of perturbation is larger than a critical value. We have also developed numerical methods for solving the full system of partial differential equations governing the underlying motion of dielectric boundary. Our numerical results confirm our analysis.

Our results on the case that the interior of a cylinder is of a lower dielectric, i.e., the interior is the region of a charged molecule, agree with the general understanding on the relaxation of dielectric boundaries. See, e.g., [2, 16, 22, 30]. The case that the interior of a cylinder is of a higher dielectric is particularly interesting. Such an interior region corresponds to that of water molecules and ions often found deep inside a large protein molecule [2, 3, 22]. Our qualitative studies show that the structure of water molecules and ions inside a charged molecule is in general unstable. This seems to be a correct picture for many systems [22, 30]. However, sometimes water molecules can stay inside a protein permanently or for a very long time, possibly because there is not enough space for the trapped water molecules to escape. Our models and results then do not explain this. A simple reason is that our evolution equations only describe the relaxation of system rather than the real, highly nonequilibrium dynamics. To accurately capture more important features, such as the kinetics of the wet-dry transition, we will have to include more effects in our models.

Our simplified model has allowed us to analyze mathematically the motion of a dielectric boundary driven by the competition between the surface and electrostatic energies. With such a model we can address several issues for further mathematical studies. One of them is the singularity formation, particularly in comparison with the motion by mean curvature alone. Another is how such a model, combined with a noise term, can describe the fluctuation of the motion of dielectric boundary. In applications to the solvation of real charged molecules that are often far more complicated, we need to add the van der Waals interaction between solute particles and solvent molecules that are coarse grained. We also need to consider the ionic effect by using more accurate continuum electrostatic models, such as the Poisson–Boltzmann approximation. The study of the resulting mathematical models will then be interesting and challenging.

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Figure 2.1.

Graphical representation of a cylindrical dielectric boundary Γ separating the regions Ω_- and Ω_+ . Top: The three-dimensional geometry. Bottom: The two-dimensional projection.

Figure 4.1.

Left: The graphs of $\omega(k)$, $\omega_1(k)$, and $\omega_2(k)$, with $\omega(k) = \omega_1(k) + \omega_2(k)$. Right: The graphs of $\phi_k(r)$ for $k = k_{\max}$, k_0 , k_s , where $k_{\max} = 0.769$, $k_0 = 2.315$, and $k_s = 5$. Each $\phi_k(r)$ is discontinuous at $u_0 \approx 1.35$.

Figure 5.1.

Two cases that the boundary Γ intersects grid lines. Left: Case 1. Right: Case 2.

Figure 6.1.
Snapshots of projected, moving cylindrical boundaries at different times.

Figure 6.2.

Snapshots of projected, moving cylindrical boundary at different times. The initial boundary is a sinusoidal perturbation of the steady state $r = u_0$ with a linearly unstable mode.

Figure 6.3.

Snapshots of projected moving cylindrical boundary at different times. The horizontal and vertical axes are the z and r axes, respectively, in each plot. The initial boundary is a sinusoidal perturbation of the steady state $r = u_0$ with a linearly stable mode.

Figure 6.4.
Different parts of the total energy as functions of time.

Figure 6.5.

Motion of the dielectric boundary starting from $u(z, 0) = u_0 + \epsilon$ (Left) and $u(z, 0) = u_0 - \epsilon$ (Right) with $\epsilon = 10^{-3}$. The profile corresponding to $t = 30$ on the left shows a small wavenumber instability due to round-off errors.