Convergence of Phase-Field Free Energy and Boundary Force for Molecular Solvation

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June 14, 2016

Abstract

We study a phase-field variational model for the solvaiton of charged molecules with an implicit solvent. The solvation free-energy functional of all phase fields consists of the surface energy, solute excluded volume and solute-solvent van der Waals dispersion energy, and electrostatic free energy. The surface energy is defined by the van der Waals–Cahn–Hilliard functional with squared gradient and a double-well potential. The electrostatic part of free energy is defined through the electrostatic potential governed by the Poisson–Boltzmann equation in which the dielectric coefficient is defined through the underlying phase field. We prove the continuity of the electrostatics—its potential, free energy, and dielectric boundary force—with respect to the perturbation of dielectric boundary. We also prove the Γ-convergence of the phase-field free-energy functionals to their sharp-interface limit, and the equivalence of the convergence of total free energies to that of all individual parts of free energy. We finally prove the convergence of phase-field forces to their sharp-interface limit. Such forces are defined as the negative first variations of the free-energy functional; and arise from stress tensors. In particular, we obtain the force convergence for the van der Waals–Cahn–Hilliard functionals with minimal assumptions.

Key words and phrases: solvation free energy, phase field, van der Waals–Cahn–Hilliard functional, Poisson–Boltzmann equation, Γ-convergence, convergence of boundary force.

1   Introduction

We study the convergence of a phase-field variational model to its sharp-interface limit for the solvation of charged molecules. In this section, we present first the sharp-interface then the phase-field models of molecular solvation. We also describe our main results and discuss their connections to existing studies. To ease the presentation, the quantities are only formally defined in this section; their precise definitions are given in Section 2.

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1.1 A Sharp-Interface Variational Model of Solvation

We denote by $\Omega \subset \mathbb{R}^3$ the entire solvation region. It is divided into a solute (e.g., protein) region Ω_p (p for protein) that contains solute atoms located at $x_1, \ldots, x_N$, and solvent region Ω_w (w for water), separated by a solute-solvent (e.g., protein-water) interface Γ. The solute atomic positions $x_1, \ldots, x_N$ are given and fixed. A solute-solvent interface is treated as a dielectric boundary as it separates the low dielectric solutes from high dielectric solvent. In a variational implicit-solvent model, an optimal solute-solvent interface is defined as to minimize the solvation free-energy functional of all the possible interfaces $\Gamma \subset \Omega$ that enclose $x_1, \ldots, x_N$ [11, 12, 33, 37]:

$$F[\Gamma] = P_0 \mathrm{Vol}\,(\Omega_\mathrm{p}) + \gamma_0 \mathrm{Area}\,(\Gamma) + \rho_0 \int_{\Omega_\mathrm{w}} U(x)\,dx + F_\mathrm{ele}[\Gamma]. \tag{1.1}$$

The first term of $F[\Gamma]$ describes the work it takes to create the solute region Ω_p in a solvent medium at hydrostatic pressure P_0, where $\mathrm{Vol}\,(\Omega_\mathrm{p})$ is the volume of Ω_p. The second term is the solute-solvent interfacial energy, where γ_0 is an effective, macroscopic surface tension. The third term, in which ρ_0 is the constant bulk solvent density, is the solute-solvent interaction energy described by a potential U that accounts for the solute-excluded volume and solute-solvent van der Waals attraction. The interaction potential U is often given 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 with parameters ε_i of energy and σ_i of length.

The last term is the electrostatic free energy. In the classical Poisson–Boltzmann theory, it is defined to be [2, 7, 10, 18, 29, 36, 37]

$$F_\mathrm{ele}[\Gamma] = \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \psi_\Gamma|^2 + \rho \psi_\Gamma - \chi_{\Omega_\mathrm{w}} B(\psi_\Gamma) \right] dx, \tag{1.2}$$

where $\psi = \psi_\Gamma$ is the electrostatic potential. It solves the boundary-value problem of the Poisson–Boltzmann equation [2, 7, 36, 37]

$$\nabla \cdot \varepsilon_\Gamma \nabla \psi - \chi_{\Omega_\mathrm{w}} B'(\psi) = -\rho \qquad \text{in } \Omega, \tag{1.3}$$

$$\psi = \psi_\infty \qquad \text{on } \partial\Omega. \tag{1.4}$$

Here, the dielectric coefficient ε_Γ (in the unit of vacuum permittivity) is defined by $\varepsilon_\Gamma(x) = \varepsilon_\mathrm{p}$ if $x \in \Omega_\mathrm{p}$ and $\varepsilon_\Gamma(x) = \varepsilon_\mathrm{w}$ if $x \in \Omega_\mathrm{w}$, where ε_p and ε_w are the dielectric coefficients (relative permittivities) of the solute and solvent regions, respectively. In general, $\varepsilon_\mathrm{p} \approx 1$ and $\varepsilon_\mathrm{w} \approx 80$. The function $\rho : \Omega \to \mathbb{R}$ is the density of solute atomic charges. It is an approximation of the point charges $\sum_{i=1}^{N} Q_i \delta_{x_i}$, where Q_i is the partial charge carried by the ith atom at x_i and δ_{x_i} denotes the Dirac mass at x_i ($1 \le i \le N$). The function χ_A is the characteristic function of A.

The function $\psi_\infty : \partial\Omega \to \mathbb{R}$ is a given boundary value of ψ_Γ. The term $B(\psi_\Gamma)$ models the ionic effect and the function B is given by

$$B(s) = k_{\mathrm{B}}T \sum_{j=1}^{M} c_j^\infty \left(e^{-q_j s/(k_{\mathrm{B}}T)} - 1 \right),$$

where k_{B} is the Boltzmann constant and T absolute temperature, and c_j^∞ and $q_j = z_j e$ are the bulk concentration and charge for the jth ionic species, respectively, with z_j the valence and e elementary charge. Note that $B'' > 0$ on $\mathbb{R}$; so B is strictly convex. We assume there are M species of ions in the solvent. Moreover, in the bulk, the charge neutrality is reached: $\sum_{j=1}^{M} q_j c_j^\infty = 0$. This implies that $B'(0) = 0$, and hence B is also minimized at 0.

For a smooth dielectric boundary Γ, we denote by ν its unit normal pointing from the solute region Ω_{p} to the solvent region Ω_{w}. We define the normal component of the boundary force (per unit surface area) as the negative variation, $-\delta_\Gamma F[\Gamma] : \Gamma \to \mathbb{R}$, of the solvation free energy $F[\Gamma]$ (cf. (1.1)). It is given by [5, 7–9, 19, 34, 37]

$$-\delta_\Gamma F[\Gamma] = -P_0 - 2\gamma_0 H + \rho_0 U - \frac{1}{2}\left(\frac{1}{\varepsilon_{\mathrm{p}}} - \frac{1}{\varepsilon_{\mathrm{w}}}\right)\left(\varepsilon_\Gamma \frac{\partial \psi_\Gamma}{\partial \nu}\right)^2$$
$$- \frac{1}{2}(\varepsilon_{\mathrm{w}} - \varepsilon_{\mathrm{p}})\, |\nabla_\Gamma \psi_\Gamma|^2 - B(\psi_\Gamma) \qquad \text{on } \Gamma, \tag{1.5}$$

where H is the mean curvature, defined as the average of principal curvatures, positive if Ω_{p} is convex, ψ_Γ is electrostatic potential defined by (1.3) and (1.4), and $\nabla_\Gamma = (I - \nu \otimes \nu)\nabla$, with I the identity matrix, is the surface gradient along Γ.

1.2 A Phase-Field Variational Model of Solvation

To incorporate more detailed physical and chemical properties in the solute-solvent interfacial region, such as the asymmetry of dielectric environment, Li and Liu [20], and Sun *et al.* [31] constructed and implemented a related phase-field model for the solvation of charged molecules (cf. also [21, 35]). In such a model, a phase field $\phi : \Omega \to \mathbb{R}$, a continuous function that takes values close to 0 and 1 in Ω except in a thin transition layer, is used to describe the solvation system. The solute and solvent regions (or phases) are approximated by $\{\phi \approx 1\}$ and $\{\phi \approx 0\}$, respectively, and the thin transition layer is the diffuse solute-solvent interface. Let $\xi > 0$ be a small number. The phase-field solvation free-energy functional of phase fields $\phi : \Omega \to \mathbb{R}$ is [20, 21, 31, 35]:

$$F_\xi[\phi] = P_0 \int_\Omega \phi^2 \, dx + \gamma_0 \int_\Omega \left[\frac{\xi}{2}|\nabla\phi|^2 + \frac{1}{\xi}W(\phi)\right] dx + \rho_0 \int_\Omega (\phi - 1)^2 U \, dx + F_{\mathrm{ele}}[\phi], \tag{1.6}$$

where

$$F_{\mathrm{ele}}[\phi] = \int_\Omega \left[-\frac{\varepsilon(\phi)}{2}|\nabla\psi_\phi|^2 + \rho\psi_\phi - (\phi - 1)^2 B(\psi_\phi)\right] dx, \tag{1.7}$$

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and $\psi = \psi_\phi$ solves the boundary-value problem of the phase-field Poisson–Boltzmann equation

$$\nabla \cdot \varepsilon(\phi)\nabla\psi - (\phi - 1)^2 B'(\psi) = -\rho \qquad \text{in } \Omega, \tag{1.8}$$

$$\psi = \psi_\infty \qquad \text{on } \partial\Omega. \tag{1.9}$$

All the four terms in (1.6) correspond to those in the sharp-interface free-energy functional (1.1). The second integral term, in which

$$W(\phi) = 18\phi^2(1 - \phi)^2, \tag{1.10}$$

is the van der Waals–Cahn–Hilliard functional [4, 27, 32] (sometimes called the Allen–Cahn functional [1]) that is known to Γ-converge to the area of solute-solvent interface as $\xi \to 0$ [24, 30]. The pre-factor 18 is so chosen that

$$\int_0^1 \sqrt{2W(t)}\, dt = 1.$$

In the last term of electrostatic free energy, the dielectric coefficient $\varepsilon = \varepsilon(\phi)$ is constructed to be a smooth function, taking the values ε_p and ε_w in the solute region $\{\phi \approx 1\}$ and solvent region $\{\phi \approx 0\}$, respectively [20,31]. The first variation of the functional $F_\xi[\phi]$ is given by [20,31]

$$\delta_\phi F_\xi[\phi] = 2P_0\,\phi + \gamma_0 \left[-\xi\Delta\phi + \frac{1}{\xi}W'(\phi) \right] + 2\rho_0(\phi - 1)U$$

$$- \frac{1}{2}\varepsilon'(\phi)|\nabla\psi_\phi|^2 - 2(\phi - 1)B(\psi_\phi). \tag{1.11}$$

We remark that the van der Waals–Cahn–Hilliard functional in the phase-field model (1.6) is exactly the interfacial free energy defined through the macroscopic component of water density in the Lum-Chandler-Weeks solvation theory [22], where though the electrostatics is not included. It has been recognized that such interfacial free energy is crucial in the description of hydrophobic interactions [3, 6, 22].

1.3 Main Results and Connections to Existing Studies

In this work, we study the limit properties of the phase-field free-energy functionals (1.6) in terms of their sharp-interface limit. We prove the following:

(1) The convergence of the phase-field Poisson–Boltzmann electrostatics to the corresponding sharp-interface limit. More precisely, if a sequence of phase fields converge to a characteristic function of a subset of Ω, then the corresponding sequences of electrostatic potentials, electrostatic free energies, and forces converge to their respective sharp-interface counterparts; cf. Theorem 3.2 and Theorem 3.3;

(2) The free-energy convergence. There are two main results concerning such convergence. First, the Γ-convergence of phase-field free-energy functionals to the corresponding sharp-interface limit; cf. Theorem 2.1. The existence of a global minimizer of the sharp-interface free-energy functional F is then a consequence of this Γ-convergence; cf. Corollary 2.1. The proof of Γ-convergence is similar to that for the van der Waals–Cahn–Hilliard functional.

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Care needs to be taken for the solute-solvent interaction part, i.e., the third term in (1.1) and that in (1.6). In particular, we construct the recovering sequence as the same canonical phase fields for the van der Waals–Cahn–Hilliard functional [24, 30]. Second, the equivalence of the convergence of total free energies and that of the individual parts of free energy (volume, surface, solute-solvent van der Waals interaction, and electrostatics); cf. Theorem 2.2;

(3) The force convergence: if a sequence of phase fields converge to a characteristic function and the corresponding solvation free energies converge to the sharp-interface free energy, then the corresponding phase-field forces converge to their sharp-interface counterpart. In fact, each individual part of the force converges to the corresponding sharp-interface part; cf. Theorem 2.3. There are two non-trivial parts in the proof of this force convergence. One is the proof of electrostatic force convergence, which is Theorem 3.3. The other is the proof of surface force convergence, i.e., the force convergence for the van der Waals–Cahn–Hilliard functional. Due to its general interest, we state and prove a separate theorem, Theorem 2.4, for the surface force convergence. All the different kinds of forces are defined as the first variations of the corresponding parts of the free-energy functionals. These forces are shown to arise from stress tensors. Our results on force convergence are then stated in terms of the weak convergence of corresponding stress tensors.

Our work is closely related to the analysis in [21] and [20]. In [21], Li and Zhao study a similar but simpler phase-field model in which the electrostatic free energy is described by the Coulomb-field approximation [8, 33], without the need of solving a dielectric Poisson or Poisson–Boltzmann equation. They obtain the Γ-convergence of the phase-field free-energy functionals to the respective sharp-interface functional. They also prove the existence of a global minimizer of the sharp-interface free-energy functional. In [20], the authors obtain the well-posedness of the phase-field Poisson–Boltzmann equation and derive the variation (1.11). Using the matched asymptotic analysis, they also show that, in the sharp-interface limit as $\xi \to 0$, the relaxation dynamics $\phi_t = -\delta_\phi F_\xi[\phi]$ approaches that of the sharp-interface governed by $v_n = -\delta_\Gamma F[\Gamma]$, where v_n is the normal velocity of the sharp boundary. We shall use some of the results on the Poisson–Boltzmann electrostatics obtained in [20].

We remark that the force convergence for (a subsequence of) van der Waals–Cahn–Hilliard functionals is proved in [26] under the assumption that corresponding sequence of free energy is bounded and that

$$\sup_{0<\xi\ll 1} \int_\Omega \frac{1}{\xi}\left[-\xi\Delta\phi_\xi + \frac{1}{\xi}W'(\phi_\xi)\right]^2 dx < \infty, \tag{1.12}$$

where ϕ_ξ ($0 < \xi \ll 1$) is the underlying family of phase fields; cf. also [16, 17, 23, 25, 26, 28] and the references therein. These assumptions provide additional regularities that allow one to show the equi-partition of the free energy, the existence of variation of the varifold corresponding to the limit of Radon measures

$$\left[\frac{\xi}{2}|\nabla\phi_\xi|^2 + \frac{1}{\xi}W(\phi_\xi)\right] dx,$$

and the rectifiability of the varifold. Here, we only assume the convergence of phase fields to a characteristic function and the corresponding convergence of the van der Waals–Cahn–Hilliard free energies to that of the sharp-interface counterpart, i.e., the perimeter of the limit set.

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The free-energy convergence is a natural assumption as the free energies can converge to a different number even if the sequence of phase fields converge to the same limit characteristic function; see an example constructed in Subsection 2.3. Our proof of force convergence involves no varifolds. It is rather based on the observation that the free-energy convergence implies the asymptotic equi-partition of energy, and that the gradients of phase fields are controlled asymptotically by their projections onto the direction normal to the limit interface. Note that, without the additional assumption (1.12), we do not have the necessary regularities, and in turn we have to define the limit force in a weak sense through stress tensors. Consequently, the force convergence is proved as the weak convergence of stress tensors.

1.4 Organization of the Rest of Paper

In Section 2, we state our assumptions and main theorems. We also define forces and their corresponding stresses. In Section 3, we present results on the Poisson–Boltzmann electrostatics. These include a unified result on the well-posedness of the Poisson–Boltzmann equation, the continuity of the electrostatic free energy with respect to the change of dielectric regions, and the convergence of phase-field dielectric boundary force to the sharp-interface limit. In Section 4, we prove the Γ-convergence of the phase-field free-energy functionals to their sharp-interface limit. We also prove that the convergence of total free energies is equivalent to that of individual parts of free energy. Finally, in Section 5, we first prove the convergence of all the individual and total phase-field forces to their sharp-interface counterparts for the solvation free-energy functional, except the surface force. We then focus on the proof of such surface that corresponds to the van der Waals–Cahn–Hilliard functional for a general n-dimensional space with $n \geq 2$.

2 Main Theorems

2.1 Assumptions

Unless otherwise stated, we assume the following throughout the rest of paper:

(A1) The set $\Omega \subset \mathbb{R}^3$ is nonempty, open, connected, and bounded with a C^2 boundary $\partial\Omega$. The integer $N \geq 1$ and all points $x_1, \ldots, x_N$ in Ω are given. All P_0, γ_0, and ρ_0 are positive numbers. The functions $\rho \in H^1(\Omega) \cap L^\infty(\Omega)$ and $\psi_\infty \in W^{2,\infty}(\Omega)$ are given;

(A2) The function $U : \mathbb{R}^3 \to \mathbb{R} \cup \{+\infty\}$ satisfies

$$U(x_i) = +\infty \quad \text{and} \quad \lim_{x \to x_i} U(x) = +\infty \quad (i = 1, \ldots, N), \quad \text{and} \quad \lim_{x \to \infty} U(x) = 0.$$

Restricted onto $\mathbb{R}^3 \setminus \{x_1, \ldots, x_N\}$, U is a C^1-function with

$$U_{\min} := \inf\{U(x) : x \in \mathbb{R}^3\} \in (-\infty, 0].$$

Moreover, U is not integrable in the neighborhood of each x_i $(1 \leq i \leq N)$ in the following sense: for any measurable subset $\omega \subset \mathbb{R}^3$,

$$\int_\omega U \, dx = +\infty \quad \text{if there exists } i \in \{1, \ldots, N\} \text{ such that } \inf_{r>0} \frac{|\omega \cap B(x_i, r)|}{r^3} > 0,$$

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where $|Q|$ denotes the Lebesgue measure of Q in $\mathbb{R}^3$; (In what follows, measure means the Lebesgue measure, unless otherwise stated.)

(A3) The numbers ε_{p} and ε_{w} are positive and distinct. The function $\varepsilon \in C^1(\mathbb{R})$ and it satisfies that $\varepsilon(\phi) = \varepsilon_{\mathrm{w}}$ if $\phi \leq 0$, $\varepsilon(\phi) = \varepsilon_{\mathrm{p}}$ if $\phi \geq 1$, and $\varepsilon(\phi)$ is monotonic in $(0,1)$; (Two examples of such a function ε are given in [20].)

(A4) The function $B \in C^2(\mathbb{R})$ is strictly convex with $B(0) = \min_{s \in \mathbb{R}} B(s) = 0$. Moreover, $B(\pm\infty) = \infty$ and $B'(\pm\infty) = \pm\infty$.

2.2   Theorems on Free-Energy Convergence

We denote
$$\mathcal{A} = \left\{ u \in H^1(\Omega) : u = \psi_\infty \text{ on } \partial\Omega \right\}. \tag{2.1}$$

For any $\phi \in L^4(\Omega)$, we define $E_\phi : \mathcal{A} \to \mathbb{R} \cup \{\infty, -\infty\}$ by

$$E_\phi[u] = \int_\Omega \left[\frac{\varepsilon(\phi)}{2} |\nabla u|^2 - \rho u + (\phi - 1)^2 B(u) \right] dx. \tag{2.2}$$

Since $B(u) \geq 0$, $E_\phi[u] > -\infty$ for any $u \in \mathcal{A}$. By Theorem 3.1, the functional $E_\phi : \mathcal{A} \to \mathbb{R} \cup \{+\infty\}$ has a unique minimizer $\psi_\phi \in \mathcal{A}$ that is also the unique weak solution of the corresponding boundary-value problem of the Poisson–Boltzmann equation: (1.3) and (1.4) if ϕ is the characteristic function of the solute region with boundary Γ; and (1.8) and (1.9) if $\phi \in H^1(\Omega)$ is a general phase field. Moreover, in both cases,

$$F_{\mathrm{ele}}[\phi] = -E_\phi[\psi_\phi] = -\min_{u \in \mathcal{A}} E_\phi[u].$$

This is exactly the electrostatic free energy $F_{\mathrm{ele}}[\Gamma]$ defined in (1.2) in the sharp-interface setting or $F_{\mathrm{ele}}[\phi]$ in (1.7) in the phase-field setting.

Let us fix $\xi_0 \in (0,1)$. We consider the phase-field functionals $F_\xi : L^1(\Omega) \to \mathbb{R} \cup \{\pm\infty\}$ for all $\xi \in (0, \xi_0]$ [20,31]:

$$F_\xi[\phi] = \begin{cases} P_0 \int_\Omega \phi^2\, dx + \gamma_0 \int_\Omega \left[\frac{\xi}{2}|\nabla\phi|^2 + \frac{1}{\xi} W(\phi) \right] dx + \rho_0 \int_\Omega (\phi-1)^2 U\, dx + F_{\mathrm{ele}}[\phi] \\ \qquad \text{if } \phi \in H^1(\Omega), \\ +\infty \qquad \text{otherwise.} \end{cases} \tag{2.3}$$

Note that F_ξ never takes the value $-\infty$, as U is bounded below and $F_{\mathrm{ele}}[\phi]$ is finite for any $\phi \in H^1(\Omega)$.

Let D be a nonempty, bounded, and open subset of $\mathbb{R}^n$ for some $n \geq 2$. We recall that a function $u \in L^1(D)$ has bounded variations in D, if

$$|\nabla u|_{BV(\Omega)} := \sup \left\{ \int_D u \operatorname{div} g\, dx : g \in C_c^1(D, \mathbb{R}^n), |g| \leq 1 \text{ in } D \right\} < \infty,$$

where $C_c^1(D, \mathbb{R}^n)$ denotes the space of all C^1-mappings from D to $\mathbb{R}^n$ that are compactly supported inside D; cf. [13,15,38]. If $u \in W^{1,1}(D)$ then $|\nabla u|_{BV(\Omega)} = \|\nabla u\|_{L^1(D)}$. The space

$BV(D)$ of all $L^1(D)$-functions that have bounded variations in D is a Banach space with the norm

$$\|u\|_{BV(D)} := \|u\|_{L^1(D)} + |\nabla u|_{BV(D)} \qquad \forall u \in BV(D).$$

For any Lebesgue-measurable subset $A \subseteq \mathbb{R}^n$, the perimeter of A in D is defined by [13, 15, 38]

$$P_D(A) := |\nabla \chi_A|_{BV(D)}.$$

We define the sharp-interface free-energy functional $F_0 : L^1(\Omega) \to \mathbb{R} \cup \{\infty, -\infty\}$ by

$$F_0[\phi] = \begin{cases} P_0|A| + \gamma_0 P_\Omega(A) + \rho_0 \int_{\Omega \setminus A} U \, dx + F_{\text{ele}}[\phi] & \text{if } \phi = \chi_A \in BV(\Omega), \\ +\infty & \text{otherwise.} \end{cases} \tag{2.4}$$

If $\phi = \chi_A \in BV(\Omega)$, where $A \subset \Omega$ is an open subset with a smooth boundary Γ and the closure $\overline{A} \subset \Omega$, then $F_0[\phi] = F[\Gamma]$ as defined in (1.1). Note that the functional F_0 never takes the value $-\infty$.

We use the notation $\xi_k \searrow 0$ to indicate that $\{\xi_k\}$ is a sequence of real numbers such that $\xi_1 > \xi_2 > \cdots$ and $\xi_k \to 0$ as $k \to \infty$. We always assume that $\xi_1 \in (0, \xi_0]$. The following theorem on free-energy convergence is proved in Section 4:

Theorem 2.1 (Γ-convergence of free-energy functionals). *For any sequence $\xi_k \searrow 0$, the sequence of functionals $F_{\xi_k} : L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$ $(k = 1, 2, \dots)$ Γ-converges to the functional $F_0 : L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$ with respect to the $L^1(\Omega)$-convergence. This means precisely that the following two properties hold true:*
  (1) *The liminf condition. If $\phi_k \to \phi$ in $L^1(\Omega)$ then*

$$\liminf_{k \to \infty} F_{\xi_k}[\phi_k] \geq F_0[\phi]; \tag{2.5}$$

  (2) *The recovering sequence. For any $\phi \in L^1(\phi)$, there exist $\phi_k \in L^1(\Omega)$ $(k = 1, 2, \dots)$ such that $\phi_k \to \phi$ in $L^1(\Omega)$ and*

$$\limsup_{k \to \infty} F_{\xi_k}[\phi_k] \leq F_0[\phi]. \tag{2.6}$$

We remark that this result does not follow immediately from the stability of Γ-convergence under continuous perturbations. In fact, the solute-solvent interaction term (i.e., the third term) and the electrostatics term (i.e., the fourth term) in the phase-field functional (2.3) are not simple continuous perturbations of the van der Waals–Cahn–Hilliard functionals. The convergence of those terms require more than the $L^1(\Omega)$-convergence of underlying phase-field functions.

The following corollary of the above theorem provides the existence of minimizers of the corresponding sharp-interface free-energy functional:

Corollary 2.1. *There exists a measurable subset $G \subseteq \Omega$ with finite perimeter $P_\Omega(G)$ in Ω such that $F_0[\chi_G] = \min_{\phi \in L^1(\Omega)} F_0[\phi]$, which is finite.*

The next result, also proved in Section 4, is of interest by itself. It states that each component of the free energy converges to its sharp-interface analog, if the total free energy converges.

Theorem 2.2. *Let $\xi_k \searrow 0$, $\phi_k \in H^1(\Omega)$ $(k = 1, 2, \dots)$, and $G \subseteq \Omega$ be measurable with $P_\Omega(G) < \infty$. Assume that $\phi_k \to \chi_G$ a.e. in Ω and $F_{\xi_k}[\phi_k] \to F_0[\chi_G]$ with $F_0[\chi_G]$ finite. Then*

$$\lim_{k \to \infty} \int_\Omega \phi_k^2 dx = |G|, \tag{2.7}$$

$$\lim_{k \to \infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx = P_\Omega(G), \tag{2.8}$$

$$\lim_{k \to \infty} \int_\Omega (\phi_k - 1)^2 U \, dx = \int_{\Omega \setminus G} U \, dx, \tag{2.9}$$

$$\lim_{k \to \infty} F_{\text{ele}}[\phi_k] = F_{\text{ele}}[\chi_G]. \tag{2.10}$$

All the limits are finite.

2.3 Definition of Force and Theorems on Force Convergence

2.3.1 Force in the Phase-Field Model

Let $\xi \in (0, \xi_0]$. We define the individual forces as vector-valued functions on Ω as follows:

$$f_{\text{vol}}(\phi) = 2P_0 \phi \nabla \phi \qquad \qquad \text{if } \phi \in H^1(\Omega),$$

$$f_{\xi,\text{sur}}(\phi) = \gamma_0 \left[-\xi \Delta \phi + \frac{1}{\xi} W'(\phi) \right] \nabla \phi \qquad \qquad \text{if } \phi \in H^2(\Omega),$$

$$f_{\text{vdW}}(\phi) = 2\rho_0 (\phi - 1) U \nabla \phi \qquad \qquad \text{if } \phi \in H^1(\Omega),$$

$$f_{\text{ele}}(\phi) = \left[-\frac{\varepsilon'(\phi)}{2} |\nabla \psi_\phi|^2 - 2(\phi - 1)B(\psi_\phi) \right] \nabla \phi \qquad \qquad \text{if } \phi \in H^1(\Omega),$$

where $\psi_\phi \in \mathcal{A}$ is electrostatic potential corresponding to ϕ, i.e., the solution to the boundary-value problem of Poisson–Boltzmann equation (1.8) and (1.9); cf. Theorem 3.1. If $\phi \in H^2(\Omega)$, we define the total force

$$f_\xi(\phi) = f_{\text{vol}}(\phi) + f_{\xi,\text{sur}}(\phi) + f_{\text{vdW}}(\phi) + f_{\text{ele}}(\phi). \tag{2.11}$$

Note that these forces are given as $-\nabla \phi$ multiplied by the negative first variations of the volume, surface, van der Waals solute-solvent interaction, electrostatics, and the total free energy, respectively; cf. (1.11). Note also that a phase field ϕ of lower free energy is close to the characteristic function of solute region. The direction $-\nabla \phi$ then points from the solute to solvent region, same as the direction ν in the sharp-interface force (1.5).

The forces can be also defined by the method of domain variations. Given $V \in C_c^1(\Omega, \mathbb{R}^n)$, we define $x = x(t, X)$ with $t \in (-t_0, t_0)$ for some $t_0 > 0$ small and $X \in \Omega$ by $\dot{x} = V(x)$ and $x(0, X) = X$. This defines a family of transformations $T_t : \Omega \to \Omega$ with $T_t(X) = x(t, X)$. For a smooth phase field ϕ, these transformations define the perturbations $\phi \circ T_t$ of ϕ. For the phase-field functional F_ξ, one then defines naturally the force to be $-(d/dt)|_{t=0} F_\xi[\phi \circ T_t]$, the negative

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variation of the phase-field free-energy functional F_ξ at ϕ with respect to these perturbations. Note that

$$T_t(X) = X + tV(X) + o(t) \quad \text{as } t \to 0.$$

Hence,

$$(\phi \circ T_t)(X) = \phi(X) + t\nabla\phi(X) \cdot V(X) + o(t) \qquad \text{as } t \to 0.$$

Therefore,

$$-\frac{d}{dt}\bigg|_{t=0} F_\xi[\phi \circ T_t] = -\frac{d}{dt}\bigg|_{t=0} F_\xi[\phi + t\nabla\phi \cdot V + o(t)] = -\delta_\phi F_\xi[\phi]\nabla\phi \cdot V.$$

By (2.11), this differs from $-f_\xi(\phi) \cdot V$ only by a sign. This sign difference results from our choice of force direction as discussed above.

We now define the corresponding individual stress tensors (with respect to the underlying coordinate system) by

$$T_{\text{vol}}(\phi) = P_0\phi^2 I \qquad\qquad\qquad \text{if } \phi \in L^4(\Omega), \qquad (2.12)$$

$$T_{\xi,\text{sur}}(\phi) = \gamma_0 \left\{ \left[\frac{\xi}{2}|\nabla\phi|^2 + \frac{1}{\xi}W(\phi)\right] I - \xi\nabla\phi \otimes \nabla\phi \right\} \qquad \text{if } \phi \in H^1(\Omega), \qquad (2.13)$$

$$T_{\text{vdW}}(\phi) = \rho_0(\phi - 1)^2 U I \qquad\qquad \text{if } \phi \in L^4(\Omega), \qquad (2.14)$$

$$T_{\text{ele}}(\phi) = \varepsilon(\phi)\nabla\psi_\phi \otimes \nabla\psi_\phi - \left[\frac{\varepsilon(\phi)}{2}|\nabla\psi_\phi|^2 + (\phi - 1)^2 B(\psi_\phi)\right] I \quad \text{if } \phi \in L^4(\Omega). \qquad (2.15)$$

Note that we assume $\phi \in L^4(\Omega)$, as our double-well potential $W = W(\phi)$ defined in (1.10) is a polynomial of degree 4. Moreover, that $\phi \in L^4(\Omega)$ is necessary for the term $(\phi - 1)^2$ in the functional $F_\xi[\phi]$ defined in (1.6) and $F_{\text{ele}}[\phi]$ defined in (1.7) to be in $L^2(\Omega)$. Note also that we have the Sobolev embedding $H^1(\Omega) \hookrightarrow L^4(\Omega)$.

We recall that the divergence of a tensor field $T = (T_{ij})$, denoted $\nabla \cdot T$ or $\text{div}\, T$, is the vector field with components $\partial_j T_{ij}$ ($i = 1, 2, 3$), if exist. For a differentiable vector field $V : \Omega \to \mathbb{R}^3$ that has components V_i ($i = 1, 2, 3$), the gradient ∇V is the matrix-valued function with the (i, j)-entry $\partial_j V_i$. For any 3×3 matrices A and B, we define $A : B = \sum_{i,j=1}^3 A_{ij}B_{ij}$. We also define $|A|$ by $|A|^2 = \sum_{i,j=1}^3 |A_{ij}|^2$. It is straightforward to generalize these definition and notation to $\mathbb{R}^n$ for any $n \geq 2$.

The following lemma indicates that the phase-field forces defined above arise from the corresponding stress tensors. Moreover, lower regularities of phase field ϕ are needed to define the stress tensors:

Lemma 2.1. *We have for almost all points in Ω that*

$$f_{\text{vol}}(\phi) = \nabla \cdot T_{\text{vol}}(\phi) \qquad\qquad\qquad \textit{if } \phi \in H^1(\Omega), \qquad\qquad (2.16)$$
$$f_{\xi,\text{sur}}(\phi) = \nabla \cdot T_{\xi,\text{sur}}(\phi) \qquad\qquad\qquad \textit{if } \phi \in H^2(\Omega), \qquad\qquad (2.17)$$
$$f_{\text{vdW}}(\phi) = \nabla \cdot T_{\text{vdW}}(\phi) - \rho_0(\phi - 1)^2\nabla U \qquad \textit{if } \phi \in H^1(\Omega), \qquad\qquad (2.18)$$
$$f_{\text{ele}}(\phi) = \nabla \cdot T_{\text{ele}}(\phi) + \rho\nabla\psi_\phi \qquad\qquad\quad \textit{if } \phi \in W^{1,\infty}(\Omega). \qquad\qquad (2.19)$$

Moreover, we have for any $V \in C_c^1(\Omega, \mathbb{R}^3)$ that

$$\int_\Omega f_{\mathrm{vol}}(\phi) \cdot V \, dx = -\int_\Omega T_{\mathrm{vol}}(\phi) : \nabla V \, dx \qquad \textit{if } \phi \in H^1(\Omega), \tag{2.20}$$

$$\int_\Omega f_{\xi,\mathrm{sur}}(\phi) \cdot V \, dx = -\int_\Omega T_{\xi,\mathrm{sur}}(\phi) : \nabla V \, dx \qquad \textit{if } \phi \in H^2(\Omega), \tag{2.21}$$

$$\int_\Omega f_{\mathrm{vdW}}(\phi) \cdot V \, dx = -\int_\Omega \left[T_{\mathrm{vdW}}(\phi) : \nabla V + \rho_0(\phi-1)^2 \nabla U \cdot V \right] dx$$
$$\textit{if } \{x_1, \dots, x_N\} \cap \mathrm{supp}\,(V) = \emptyset \quad \textit{and} \quad \phi \in H^1(\Omega), \tag{2.22}$$

$$\int_\Omega f_{\mathrm{ele}}(\phi) \cdot V \, dx = -\int_\Omega \left[T_{\mathrm{ele}}(\phi) : \nabla V - \rho \nabla \psi_\phi \cdot V \right] dx \qquad \textit{if } \phi \in W^{1,\infty}(\Omega). \tag{2.23}$$

Proof. The identities (2.16) and (2.18) follow from direct calculations. All the identities (2.20)–(2.23) follow from (2.16)–(2.19) and integration by parts. Therefore, it remains only prove (2.17) and (2.19).

Let $\phi \in H^2(\Omega)$ and $i \in \{1,2,3\}$. We have by the definition of $T_{\xi,\mathrm{sur}}(\phi)$ and using the summation convention that

$$\partial_j T_{\xi,\mathrm{sur},ij}(\phi) = \gamma_0 \partial_j \left\{ \left[\frac{\xi}{2} \partial_k \phi \partial_k \phi + \frac{1}{\xi} W(\phi) \right] \delta_{ij} - \xi \partial_i \phi \partial_j \phi \right\}$$

$$= \gamma_0 \left\{ \xi \partial_{ik} \phi \partial_k \phi + \frac{1}{\xi} W'(\phi) \partial_i \phi - \xi \partial_{ij} \phi \partial_j \phi - \xi \partial_i \phi \Delta \phi \right\}$$

$$= \gamma_0 \left[-\xi \Delta \phi + \frac{1}{\xi} W'(\phi) \right] \partial_i \phi,$$

where $\delta_{ij} = 1$ if $i = j$ and 0 otherwise. This is the ith component of the force vector $f_{\xi,\mathrm{sur}}$; (2.17) is thus proved.

Now let $\phi \in W^{1,\infty}(\Omega)$. By Theorem 3.1, ψ_ϕ is bounded on $\chi_{\{\phi \neq 1\}}$. Since $\phi \in W^{1,\infty}(\Omega)$, we have

$$\varepsilon(\phi) \Delta \psi_\phi = -\rho - \varepsilon'(\phi) \nabla \phi \cdot \nabla \psi_\phi + (\phi-1)^2 B'(\psi_\phi) \in L^2(\Omega).$$

Hence $\psi_\phi \in H^2(\Omega)$. By direct calculations using the fact that ψ_ϕ solves the Poisson–Boltzmann equation, we obtain

$$\partial_j T_{\mathrm{ele},ij} = \partial_j(\varepsilon(\phi) \partial_i \psi_\phi \partial_j \psi_\phi) - \delta_{ij} \partial_j \left[\frac{1}{2} \varepsilon(\phi) \partial_k \psi_\phi \partial_k \psi_\phi + (\phi-1)^2 B(\psi_\phi) \right]$$

$$= \varepsilon'(\phi) \partial_j \phi \partial_i \psi_\phi \partial_j \psi_\phi + \varepsilon(\phi) \partial_{ij} \psi_\phi \partial_j \psi_\phi + \varepsilon(\phi) \partial_i \psi_\phi \Delta \psi_\phi$$

$$\quad - \frac{1}{2} \varepsilon'(\phi) \partial_i \phi |\partial \psi_\phi|^2 - \varepsilon(\phi) \partial_{ik} \psi_\phi \partial_k \psi_\phi - 2(\phi-1) \partial_i \phi B(\psi_\phi) - (\phi-1)^2 B'(\psi_\phi) \partial_i \psi_\phi$$

$$= \left[\nabla \cdot \varepsilon(\phi) \nabla \psi_\phi - (\phi-1)^2 B'(\psi_\phi) \right] \partial_i \psi_\phi - \left[\frac{\varepsilon'(\phi)}{2} |\nabla \psi_\phi|^2 + 2(\phi-1) B(\psi_\phi) \right] \partial_i \phi$$

$$= -\rho \partial_i \psi_\phi - \left[\frac{\varepsilon'(\phi)}{2} |\nabla \psi_\phi|^2 + 2(\phi-1) B(\psi_\phi) \right] \partial_i \phi, \qquad i = 1,2,3,$$

proving (2.19). $\qquad\square$

2.3.2 Force in the Sharp-Interface Model

Let G be an open subset of Ω such that the closure $\overline{G} \subset \Omega$, the boundary ∂G is C^2, and $x_i \in G$ $(i = 1, \ldots, N)$. Denote by ν the unit vector on ∂G that points from G to $G^c = \Omega \setminus G$. Following (1.1) (with $\Gamma = \partial G$) or (2.4) (with $A = G$), and (1.5) (with $\Gamma = \partial G$), we define the individual volume, surface, van der Waals, and electrostatic forces on the boundary ∂G as vector-valued functions on ∂G as follows:

$$f_{0,\text{vol}}[\partial G] = -P_0 \nu, \tag{2.24}$$

$$f_{0,\text{sur}}[\partial G] = -2\gamma_0 H \nu, \tag{2.25}$$

$$f_{0,\text{vdW}}[\partial G] = \rho_0 U \nu, \tag{2.26}$$

$$f_{0,\text{ele}}[\partial G] = \left[-\frac{1}{2} \left(\frac{1}{\varepsilon_\text{p}} - \frac{1}{\varepsilon_\text{w}} \right) |\varepsilon(\chi_G) \nabla \psi_{\chi_G} \cdot \nu|^2 \right.$$
$$\left. - \frac{1}{2} (\varepsilon_\text{w} - \varepsilon_\text{p}) \left| (I - \nu \otimes \nu) \nabla \psi_{\chi_G} \right|^2 - B(\psi_{\chi_G}) \right] \nu. \tag{2.27}$$

We also define the total boundary force to be

$$f_0[\partial G] = f_{0,\text{vol}}[\partial G] + f_{0,\text{sur}}[\partial G] + f_{0,\text{vdW}}[\partial G] + f_{0,\text{ele}}[\partial G].$$

In (2.25), H is the mean curvature of ∂G, defined as the average of the principal curvatures, and is positive if G is convex. In (2.27), $\psi_{\chi_G} \in \mathcal{A}$ is the electrostatic potential corresponding to χ_G; cf. Theorem 3.1. It satisfies $\psi_{\chi_G}|_G \in H^2(G)$ and $\psi_{\chi_G}|_{G^c} \in H^2(G^c)$. Moreover (cf. [18, 19]),

$$-\varepsilon_\text{p} \Delta \psi_{\chi_G} = \rho \qquad \text{in } G, \tag{2.28}$$

$$-\varepsilon_\text{w} \Delta \psi_{\chi_G} + B'(\psi) = \rho \qquad \text{in } G^c, \tag{2.29}$$

$$\psi_{\chi_G}|_G = \psi_{\chi_G}|_{G^c} \qquad \text{on } \partial G, \tag{2.30}$$

$$\varepsilon_\text{p} \nabla \psi_{\chi_G}|_G \cdot \nu = \varepsilon_\text{w} \nabla \psi_{\chi_G}|_{G^c} \cdot \nu \qquad \text{on } \partial G. \tag{2.31}$$

The quantity $\varepsilon(\chi_G) \nabla \psi_{\chi_G} \cdot \nu$ in (2.27) is the common value of both sides of (2.31). By (2.30), the tangential gradient $(I - \nu \otimes \nu) \nabla \psi_{\chi_G}$ in (2.27) is the same when ψ_{χ_G} is restricted onto either side of the boundary ∂G.

We recall that the stress tensors $T_{\text{vol}}(\chi_G)$, $T_{\text{vdW}}(\chi_G)$, and $T_{\text{ele}}(\chi_G)$ are defined in (2.12), (2.14), and (2.15), respectively, with ϕ replaced by χ_G. The following lemma indicates that the forces defined above in (2.24)–(2.27) also arise from stress tensors in the sharp-interface model and that only lower regularity of the subset G is needed to define the stresses:

Lemma 2.2. *Let G be an open subset of Ω such that the closure $\overline{G} \subset \Omega$ and the boundary ∂G is C^2. Let ν denote the unit vector ν on ∂G that points from G to G^c. We have for any $V \in C_c^1(\Omega, \mathbb{R}^n)$ that*

$$\int_{\partial G} f_{0,\text{vol}}[\partial G] \cdot V \, dS = -\int_\Omega T_{\text{vol}}(\chi_G) : \nabla V \, dx, \tag{2.32}$$

$$\int_{\partial G} f_{0,\text{sur}}[\partial G] \cdot V \, dS = -\gamma_0 \int_{\partial G} (I - \nu \otimes \nu) : \nabla V \, dS, \tag{2.33}$$

$$\int_{\partial G} f_{0,\text{vdW}}[\partial G] \cdot V \, dS = - \int_{\Omega} \left[T_{\text{vdW}}(\chi_G) : \nabla V + \rho_0 (1 - \chi_G)^2 \nabla U \cdot V \right] dx$$

$$\text{if } \{x_1, \ldots, x_N\} \cap \text{supp}\,(V) = \emptyset, \tag{2.34}$$

$$\int_{\partial G} f_{0,\text{ele}}[\partial G] \cdot V \, dS = - \int_{\Omega} \left[T_{\text{ele}}(\chi_G) : \nabla V - \rho \nabla \psi_{\chi_G} \cdot V \right] dx. \tag{2.35}$$

Proof. Eq. (2.32) follows from the identity $I : \nabla V = \nabla \cdot V$ and an application of the divergence theorem. Eq. (2.33) follows from our definition of force $f_{0,\text{sur}}$ and the known result (cf. Lemma 10.8 in [15]):

$$\int_{\partial G} 2H \nu \cdot V \, dS = \int_{\partial G} (I - \nu \otimes \nu) : \nabla V \, dS.$$

Assume each $x_i \notin \text{supp}\,(V)$ $(1 \le i \le N)$. Noticing that ν points from G to $G^c = \Omega \setminus G$, we have by the definition of $T_{\text{vdW}}(\chi_G)$ (cf. (2.14)) and the divergence theorem that

$$\int_{\Omega} \left[T_{\text{vdW}}(\chi_G) : \nabla V + \rho_0 (1 - \chi_G)^2 \nabla U \cdot V \right] dx$$

$$= \rho_0 \int_{G^c} (U \nabla \cdot V + \nabla U \cdot V) \, dx$$

$$= \rho_0 \int_{G^c} \nabla (UV) \, dx$$

$$= -\rho_0 \int_{\partial G} U \nu \cdot V \, dS,$$

leading to (2.34). Finally, Eq. (2.35) is part of Theorem 3.3 that is proved in Section 3. □

2.3.3 Force Convergence

Let D be a nonempty, open, and bounded subset of $\mathbb{R}^n$ with $n \ge 2$. For any measurable subset G of D with $\overline{G} \subset D$ and $P_D(G) < \infty$, we denote by $\partial^* G$ the reduced boundary of G and by $\|\partial G\| = \mathcal{H}^{n-1} \llcorner (\partial^* G \cap D)$ the perimeter measure of G in D, where $\mathcal{H}^{n-1}$ denotes the $(n-1)$-dimensional Hausdorff measure [13, 15, 38]. We also denote by $\nu : D \to \mathbb{R}^n$ the unit outer normal of $\partial^* G$. We recall that $|\nu| = 1$ $\|\partial G\|$-a.e. and

$$\int_G \nabla \cdot g \, dx = \int_{\partial^* G} g \cdot \nu \, d\mathcal{H}^{n-1} \qquad \forall g \in C_c^1(\Omega, \mathbb{R}^n). \tag{2.36}$$

The following result states that the convergence of total force is equivalent to that of individual forces; its proof is given in Section 5:

Theorem 2.3 (Force convergence for the solvation free-energy functional). *Let G be a measurable subset of Ω such that $\overline{G} \subset \Omega$, $P_\Omega(G) < \infty$, and $F_0[\chi_G]$ is finite. Let $\xi_k \searrow 0$ and $\phi_k \in H^1(\Omega)$ $(k = 1, 2, \ldots)$ be such that $\phi_k \to \chi_G$ a.e. in Ω and $F_{\xi_k}[\phi_k] \to F_0[\chi_G]$. Then we have for any $V \in C_c^1(\Omega, \mathbb{R}^3)$ that*

$$\lim_{k \to \infty} \int_\Omega T_{\text{vol}}(\phi_k) : \nabla V \, dx = \int_\Omega T_{\text{vol}}(\chi_G) : \nabla V \, dx, \tag{2.37}$$

$$\lim_{k\to\infty} \int_\Omega T_{\xi_k,\mathrm{sur}}(\phi_k) : \nabla V \, dx = \gamma_0 \int_{\partial^* G} (I - \nu \otimes \nu) : \nabla V \, d\mathcal{H}^2, \tag{2.38}$$

$$\lim_{k\to\infty} \int_\Omega \left[(T_{\mathrm{vdW}}(\phi_k) : \nabla V + \rho_0(\phi_k - 1)^2 \nabla U \cdot V \right] dx$$

$$= \int_\Omega \left[T_{\mathrm{vdW}}(\chi_G) : \nabla V + \rho_0(\chi_G - 1)^2 \nabla U \cdot V \right] dx \quad \text{if } \{x_1, \dots, x_N\} \cap \mathrm{supp}\,(V) = \emptyset, \tag{2.39}$$

$$\lim_{k\to\infty} \int_\Omega [T_{\mathrm{ele}}(\phi_k) : \nabla V - \rho \nabla \psi_{\phi_k} \cdot V] \, dx = \int_\Omega [T_{\mathrm{ele}}(\chi_G) : \nabla V - \rho \nabla \psi_{\chi_G} \cdot V] \, dx. \tag{2.40}$$

The force convergence for the van der Waals–Cahn–Hilliard functional is the main part of the above theorem. Since this functional is rather a general model, we state separately the result of its force convergence for a general n-dimensional space. For simplicity of notation, we define the stress tensor $T_\xi(\phi)$ to be the same as $T_{\xi,\mathrm{sur}}(\phi)$ defined in (2.13), except we take $\gamma_0 = 1$, i.e., we define for a function ϕ of n-variables

$$T_\xi(\phi) = \left[\frac{\xi}{2} |\nabla \phi|^2 + \frac{1}{\xi} W(\phi) \right] I - \xi \nabla \phi \otimes \nabla \phi,$$

where I is the $n \times n$ identity matrix.

Theorem 2.4 (Force convergence for the van der Walls–Cahn–Hilliard functional). *Let Ω be a nonempty, bounded, and open subset of $\mathbb{R}^n$. Let G be a nonempty, measurable subset of Ω such that $\overline{G} \subset \Omega$ and $P_\Omega(G) < \infty$. Assume $\xi_k \searrow 0$ and $\phi_k \in H^1(\Omega)$ $(k = 1, 2, \dots)$ satisfy that $\phi_k \to \chi_G$ a.e. in Ω and that*

$$\lim_{k\to\infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx = P_\Omega(G). \tag{2.41}$$

Then we have for any $\Psi \in C_c(\Omega, \mathbb{R}^{n\times n})$ that

$$\lim_{k\to\infty} \int_\Omega T_{\xi_k}(\phi_k) : \Psi \, dx = \int_{\partial^* G} (I - \nu \otimes \nu) : \Psi \, d\mathcal{H}^{n-1}. \tag{2.42}$$

If, in addition, $\phi_k \in W^{2,2}(\Omega)$ $(k = 1, 2, \dots)$, G is open, and ∂G is of C^2, then we have for any $V \in C_c^1(\Omega, \mathbb{R}^n)$ that

$$\lim_{k\to\infty} \int_\Omega \left[-\xi_k \Delta \phi_k + \frac{1}{\xi_k} W'(\phi_k) \right] \nabla \phi_k \cdot V \, dx = -(n-1) \int_{\partial G} H \nu \cdot V \, dS. \tag{2.43}$$

We remark that the assumption of the above theorem requires the convergence of free-energy, i.e., (2.41). Such convergence is not guaranteed by the assumptions that $\phi_k \to \chi_G$ a.e. in Ω and $\phi_k \to \chi_G$ in $L^1(\Omega)$. This is expected as not every such sequence is a recovery sequence of the Γ-convergence. In particular, let G be an open subset of Ω with a smooth boundary ∂G and $\overline{G} \subset \Omega$, and let β be any real number such that

$$\beta \geq \sigma := \int_0^1 \sqrt{2W(s)} \, ds.$$

(We have $\sigma = 1$ for our choice of W.) We show that there exist $\phi_k \in H^1(\Omega)$ $(k = 1, 2, \dots)$ such that

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(1) $\phi_k \to \chi_G$ a.e. in Ω and $\phi_k \to \chi_G$ in $L^1(\Omega)$;

(2) $\displaystyle\lim_{k\to\infty} \int_\Omega \left[\frac{\xi_k}{2}|\nabla\phi_k|^2 + \frac{W(\phi_k)}{\xi_k} \right] dx = \beta P_\Omega(G).$

Let $a > 0$ and define $W_a(s) = W(s)/a$ $(s \in \mathbb{R})$. For each $k \geq 1$, we define $q_k : [0,1] \to \mathbb{R}$ by

$$q_k(t) = \int_0^t \frac{\xi_k}{\sqrt{2[W_a(\tau) + \xi_k]}}\, d\tau \qquad \forall t \in [0,1].$$

Clearly, q_k is a strictly increasing function of $t \in [0,1]$ with $q_k(0) = 0$, $\lambda_k := q_k(1) \in (0, \sqrt{\xi_k/2})$, and $q_k(t) \leq t$ for any $t \in [0,1]$. Let $g_k : [0, \lambda_k] \to [0,1]$ be the inverse of $q_k : [0,1] \to [0, \lambda_k]$. By using the formula of derivatives of inverse functions, we obtain

$$g_k'(s) = \frac{1}{\xi_k}\sqrt{2[W_a(g_k(s)) + \xi_k]} \qquad \forall s \in [0, \lambda_k].$$

We extend g_k onto the entire real line by defining $g_k(s) = 0$ for any $s < 0$ and $g_k(s) = 1$ for any $s > \lambda_k$. Denote now by $d : \Omega \to \mathbb{R}$ the signed distance function to the boundary $\partial G : d(x) = \text{dist}\,(x, \partial G)$ if $x \in G$ and $d(x) = -\text{dist}\,(x, \partial G)$ if $x \in G^c$. Let $\xi_k \searrow 0$. Define $\phi_k : \Omega \to [0,1]$ by $\phi_k(x) = g_k(d(x))$ $(x \in \Omega)$. Then $\phi_k \to \chi_G$ a.e. in Ω and $\phi_k \to \chi_G$ in $L^1(\Omega)$ [24, 30]. Moreover, since ∂G is smooth, we have for a.e. $x \in \Omega$ and k large enough that

$$|\nabla\phi_k(x)| = |g_k'(d(x))\nabla d(x)| = \frac{1}{\xi_k}\sqrt{2\,[W_a(\phi_k(x)) + \xi_k]}.$$

Note for any $s \in [0,1]$ that $\phi_k(x) = s$ if and only if $d(x) = q_k(s)$, and $q_k(s) \leq \lambda_k \to 0$ as $k \to \infty$. Since ∂G is smooth, we have (cf. Lemma 4 in [24] and Lemma 2 in [30]) that

$$\lim_{k\to\infty}\sup_{0\leq s\leq 1} \mathcal{H}^{n-1}(\{x \in \Omega : \phi_k(x) = s\})$$
$$= \lim_{k\to\infty}\sup_{0\leq s\leq 1} \mathcal{H}^{n-1}(\{x \in \Omega : d(x) = q_k(s)\})$$
$$= P_\Omega(G).$$

Consequently, applying the co-area formula and the Lebesgue Dominated Convergence Theorem, we obtain that

$$\lim_{k\to\infty} \int_\Omega \left[\frac{\xi_k}{2}|\nabla\phi_k|^2 + \frac{W(\phi_k)}{\xi_k} \right] dx$$

$$= \lim_{k\to\infty} \int_\Omega \left(\frac{\sqrt{W_a(\phi_k) + \xi_k}}{\sqrt{2}} + \frac{aW_a(\phi_k)}{\sqrt{2\,[W_a(\phi_k) + \xi_k]}} \right) |\nabla\phi_k|\, dx$$

$$= \lim_{k\to\infty} \int_0^1 \mathcal{H}^{n-1}(\{x \in \Omega : \phi_k(x) = s\}) \left(\frac{\sqrt{W_a(s) + \xi_k}}{\sqrt{2}} + \frac{aW_a(s)}{\sqrt{2\,[W_a(s) + \xi_k]}} \right) ds$$

$$= P_\Omega(G) \int_0^1 \frac{1+a}{\sqrt{2}}\sqrt{W_a(s)}\, ds$$

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$$= \frac{1+a}{2\sqrt{a}} \sigma \, P_\Omega(G).$$

If $\beta = \sigma$, we can take $a = 1$. If $\beta > \sigma$, we have two choices of $a > 0$ such that $\beta = (1+a)\sigma/(2\sqrt{a})$. Thus for any $\beta \geq \sigma$ we can find ϕ_k $(k = 1, 2, \ldots)$ that satisfy (1) and (2).

3 The Poisson–Boltzmann Electrostatics

We first present some basic results regarding the boundary-value problem of Poisson–Boltzmann equation and the corresponding electrostatic free energy for a function $\phi : \Omega \to \mathbb{R}$ that describes the dielectric environment. These results unify and improve those of Theorem 2.1 in [19] and Theorem 2.1 in [20]. We recall that the set $\mathcal{A}$ and functional E_ϕ are defined in (2.1) and (2.2), respectively.

Theorem 3.1. *Let $\phi \in L^4(\Omega)$. There exists a unique $\psi_\phi \in \mathcal{A}$ such that*

$$E_\phi[\psi_\phi] = \min_{u \in \mathcal{A}} E_\phi[u], \tag{3.1}$$

which is finite. Moreover, $\psi_\phi \in \mathcal{A}$ is the unique weak solution to the boundary-value problem of Poisson–Boltzmann equation (1.8) and (1.9), i.e., $\psi_\phi \in \mathcal{A}$ and

$$\int_\Omega \left[\varepsilon(\phi)\nabla\psi_\phi \cdot \nabla\eta + (\phi - 1)^2 B'(\psi_\phi)\,\eta \right] dx = \int_\Omega \rho\eta \, dx \qquad \forall \eta \in H^1_0(\Omega). \tag{3.2}$$

Finally, $\psi_\phi \in L^\infty(\Omega)$ and there exists a constant $C > 0$ independent of $\phi \in L^4(\Omega)$ such that

$$\|\chi_{\{\phi \neq 1\}}\psi_\phi\|_{L^\infty(\Omega)} \leq C,$$
$$\|\psi_\phi\|_{H^1(\Omega)} \leq C \left(1 + \|\phi\|_{L^2(\Omega)} \right),$$
$$\|\psi_\phi\|_{L^\infty(\Omega)} \leq C \left(1 + \|\phi\|^2_{L^4(\Omega)} \right).$$

Proof. This is similar to that of Theorem 2.1 in [20]. First, note that $B \in C^2(\mathbb{R})$ is convex and nonnegative. By direct methods in the calculus of variations, there exists a unique $\psi_\phi \in \mathcal{A}$ that satisfies (3.1). The minimum value is finite as it is bounded above by $E_\phi[\psi_\infty] < \infty$. Next, by a comparison argument using the growth property and convexity of B (cf. the proof of Theorem 2.1 in [20]), we have $|\psi_\phi| \leq C$ a.e. on $\{\phi \neq 1\}$ for some constant $C > 0$ independent of ϕ. This is the first desired estimate. This estimate, together with the Lebesgue Dominated Convergence Theorem, allows us to obtain (3.2) for $\eta \in H^1_0(\Omega) \cap L^\infty(\Omega)$. By approximation, (3.2) is true for all $\eta \in H^1_0(\Omega)$. Finally, the fact that $\psi_\phi \in L^\infty(\Omega)$ and the other two desired estimates follow from the regularity theory for elliptic problems; cf. Theorem 8.3 and Theorem 8.16 in [14], and the proof of Theorem 2.1 in [20]. In particular, the estimate (10) in [20] provides the bound $C(1 + \|\phi\|^2_{L^4(\Omega)})$ for $\|\psi_\phi\|_{L^\infty(\Omega)}$. $\qquad\square$

The following theorem indicates that the electrostatic potential and electrostatic free energy are continuous with respect to the change of dielectric boundary:

Theorem 3.2. *Let $\phi_k \in L^4(\Omega)$ $(k = 1, 2, \dots)$ and $\phi \in L^4(\Omega)$ be such that*

$$\sup_{k \geq 1} \|\phi_k\|_{L^4(\Omega)} < \infty \quad \text{and} \quad \phi_k \to \phi \quad \text{in } L^1(\Omega). \tag{3.3}$$

Let $\psi_{\phi_k} \in \mathcal{A}$ $(k = 1, 2, \dots)$ and $\psi_\phi \in \mathcal{A}$ be the corresponding electrostatic potentials, i.e.,

$$E_{\phi_k}[\psi_{\phi_k}] = \min_{u \in \mathcal{A}} E_{\phi_k}[u] \quad (k = 1, 2, \dots) \quad \text{and} \quad E_\phi[\psi_\phi] = \min_{u \in \mathcal{A}} E_\phi[u],$$

respectively. Then, $\psi_{\phi_k} \to \psi_\phi$ in $H^1(\Omega)$ and $E_{\phi_k}[\psi_{\phi_k}] \to E_\phi[\psi_\phi]$.

To prove this and other theorems, we need the following lemma which holds true for any measurable subset $\Omega \subset \mathbb{R}^n$ of finite measure $|\Omega|$:

Lemma 3.1. *Let $1 < p < \infty$ and $\phi_k \in L^p(\Omega)$ $(k = 1, 2, \dots)$ be such that*

$$\sup_{k \geq 1} \|\phi_k\|_{L^p(\Omega)} < \infty. \tag{3.4}$$

Let $\phi \in L^1(\Omega)$. Assume either $\phi_k \to \phi$ a.e. in Ω or $\phi_k \to \phi$ in $L^1(\Omega)$. Then $\phi \in L^p(\Omega)$ and $\phi_k \to \phi$ in $L^q(\Omega)$ for any $q \in [1, p)$.

Proof. Assume $\phi_k \to \phi$ a.e. in Ω. Fatou's lemma then leads to

$$\int_\Omega |\phi|^p dx \leq \liminf_{k \to \infty} \int_\Omega |\phi_k|^p dx < \infty.$$

Hence $\phi \in L^p(\Omega)$. Let $\varepsilon > 0$. Egoroff's Theorem implies that there exists a measurable subset $A \subseteq \Omega$ such that $|A| < \varepsilon$ and $\phi_k \to \phi$ uniformly on $A^c = \Omega \setminus A$. Therefore, it follows from Hölder's inequality and (3.4) that for any $q \in [1, p)$

$$
\begin{aligned}
\limsup_{k \to \infty} \int_\Omega |\phi_k - \phi|^q dx &= \limsup_{k \to \infty} \left[\int_A |\phi_k - \phi|^q dx + \int_{A^c} |\phi_k - \phi|^q dx \right] \\
&\leq \limsup_{k \to \infty} |A|^{(p-q)/p} \|\phi_k\|^q_{L^p(\Omega)} + \limsup_{k \to \infty} \int_{A^c} |\phi_k - \phi|^q dx \\
&\leq \varepsilon^{(p-q)/p} \left(\sup_{k \geq 1} \|\phi_k\|^q_{L^p(\Omega)} \right).
\end{aligned}
$$

Hence $\phi_k \to \phi$ in $L^q(\Omega)$.

Assume now $\phi_k \to \phi$ in $L^1(\Omega)$. Then there exists a subsequence of $\{\phi_k\}$ that converges to ϕ a.e. in Ω. Applying Fatou's lemma to this subsequence, we also get $\phi \in L^p(\Omega)$. Let $1 < q < p$. Every subsequence of $\{\phi_k\}$ has a further subsequence that converges to ϕ a.e. in Ω, and hence, as proved above, converges to ϕ in $L^q(\Omega)$. Thus $\phi_k \to \phi$ in $L^q(\Omega)$. $\square$

We are now ready to prove Theorem 3.2. We use the symbol $\rightharpoonup$ to denote the weak convergence:

Proof of Theorem 3.2. For notational convenience, let us write $\psi_k = \psi_{\phi_k}$ and $\psi = \psi_\phi$. We first prove that $\psi_k \to \psi$ in $H^1(\Omega)$. It suffices to prove that any subsequence of $\{\psi_k\}$ has a further subsequence that converges to ψ in $H^1(\Omega)$.

Note by Theorem 3.1 and (3.3) that

$$\int_\Omega \left[\varepsilon(\phi_k)\nabla\psi_k \cdot \nabla\eta + (\phi_k - 1)^2 B'(\psi_k)\eta\right] dx = \int_\Omega \rho\eta \, dx \qquad \forall \eta \in H_0^1(\Omega) \quad \forall k \geq 1, \tag{3.5}$$

$$\int_\Omega \left[\varepsilon(\phi)\nabla\psi \cdot \nabla\eta + (\phi - 1)^2 B'(\psi)\eta\right] dx = \int_\Omega \rho\eta \, dx \qquad \forall \eta \in H_0^1(\Omega), \tag{3.6}$$

$$\sup_{k\geq 1} \left(\|\psi_k\|_{H^1(\Omega)} + \|\psi_k\|_{L^\infty(\Omega)}\right) < \infty \quad \text{and} \quad \psi_\phi \in L^\infty(\Omega). \tag{3.7}$$

By (3.3) and (3.7), any subsequence of $\{\psi_k\}$ has a further subsequence $\{\psi_{k_j}\}$ that converges to some $\hat\psi \in H^1(\Omega)$ weakly in $H^1(\Omega)$, strongly in $L^2(\Omega)$, and a.e. in Ω; and the corresponding sequence $\{\phi_{k_j}\}$ converges to ϕ a.e. in Ω. We prove that $\hat\psi = \psi$ in $H^1(\Omega)$ and $\psi_{k_j} \to \psi$ strongly in $H^1(\Omega)$.

Since $\mathcal{A}$ is convex and strongly closed in $H^1(\Omega)$, it is sequentially weakly closed. Hence $\hat\psi \in \mathcal{A}$. Since $\psi_{k_j} \to \hat\psi$ a.e. in Ω, by (3.7), $\hat\psi \in L^\infty(\Omega)$. By Lemma 3.1, $\phi_{k_j} \to \phi$ in $L^q(\Omega)$ for any $q \in [1, 4)$. Hence, $\varepsilon(\phi_{k_j}) \to \varepsilon(\phi)$ in $L^2(\Omega)$. Similarly,

$$(\phi_{k_j} - 1)^2 \to (\phi - 1)^2 \quad \text{in } L^{3/2}(\Omega). \tag{3.8}$$

By the compact embedding $H^1(\Omega) \hookrightarrow L^3(\Omega)$ and the weak convergence $\psi_{k_j} \rightharpoonup \hat\psi$ in $H^1(\Omega)$, we have that $\psi_{k_j} \to \hat\psi$ in $L^3(\Omega)$, and hence that

$$B'(\psi_{k_j}) \to B'(\hat\psi) \quad \text{in } L^3(\Omega). \tag{3.9}$$

Therefore, replacing ϕ_k and ψ_k in (3.5) by ϕ_{k_j} and ψ_{k_j}, respectively, and then sending $j \to \infty$, we obtain for any $\eta \in C_c^1(\Omega)$ that

$$\int_\Omega \left[\varepsilon(\phi)\nabla\hat\psi \cdot \nabla\eta + (\phi - 1)^2 B'(\hat\psi)\eta\right] dx = \int_\Omega \rho\eta \, dx.$$

Since $C_c^1(\Omega)$ is dense in $H_0^1(\Omega)$, this identity holds true also for any $\eta \in H_0^1(\Omega)$. This and (3.6), together with the uniqueness of weak solution established in Theorem 3.1, imply that $\hat\psi = \psi$ in $H^1(\Omega)$.

We now prove $\psi_{k_j} \to \psi$ in $H^1(\Omega)$. By our assumptions on ε, the fact that $\psi_{k_j} - \psi \in H_0^1(\Omega)$ $(j = 1, 2, \dots)$, and Poincaré's inequality, it suffices to prove

$$\lim_{j\to\infty} \int_\Omega \varepsilon(\phi_{k_j})|\nabla\psi_{k_j} - \nabla\psi|^2 dx = 0. \tag{3.10}$$

By (3.3) and Lemma 3.1, we have $\phi_{k_j} \to \phi$ in $L^{7/2}(\Omega)$ and hence $(\phi_{k_j} - 1)^2 \to (\phi - 1)^2$ in $L^{7/4}(\Omega)$. Similarly, by the convergence $\psi_{k_j} \to \psi$ in $L^2(\Omega)$, the embedding $H^1(\Omega) \hookrightarrow L^{14/3}(\Omega)$,

(3.7), and Lemma 3.1, we have $\psi_{k_j} \to \psi$ and hence $B(\psi_{k_j}) \to B(\psi)$ in $L^{14/3}(\Omega)$. Consequently, by Hölder's inequality,

$$\lim_{j\to\infty} \int_\Omega (\phi_{k_j} - 1)^2 B(\psi_{k_j})(\psi_{k_j} - \psi_\infty)\,dx = \int_\Omega (\phi - 1)^2 B(\psi)(\psi - \psi_\infty)\,dx.$$

Setting $\eta = \psi_{k_j} - \psi_\infty \in H_0^1(\Omega)$ in (3.5) and (3.6), we then obtain

$$\lim_{j\to\infty} \int_\Omega \varepsilon(\phi_{k_j})|\nabla\psi_{k_j}|^2 dx$$

$$= \lim_{j\to\infty} \int_\Omega \left[\varepsilon(\phi_{k_j})\nabla\psi_{k_j}\cdot\nabla\psi_\infty + \varepsilon(\phi_{k_j})\nabla\psi_{k_j}\cdot\nabla(\psi_{k_j} - \psi_\infty)\right] dx$$

$$= \lim_{j\to\infty} \int_\Omega \left[\varepsilon(\phi_{k_j})\nabla\psi_{k_j}\cdot\nabla\psi_\infty + \rho(\psi_{k_j} - \psi_\infty) - (\phi_{k_j} - 1)^2 B'(\psi_{k_j})(\psi_{k_j} - \psi_\infty)\right] dx$$

$$= \int_\Omega \left[\varepsilon(\phi)\nabla\psi\cdot\nabla\psi_\infty + \rho(\psi - \psi_\infty) - (\phi - 1)^2 B'(\psi)(\psi - \psi_\infty)\right] dx$$

$$= \int_\Omega \left[\varepsilon(\phi)\nabla\psi\cdot\nabla\psi_\infty + \varepsilon(\phi)\nabla\psi\cdot\nabla(\psi - \psi_\infty)\right] dx$$

$$= \int_\Omega \varepsilon(\phi)|\nabla\psi|^2 dx. \tag{3.11}$$

Since $\phi_{k_j} \to \phi$ a.e. in Ω, the Lebesgue Dominated Convergence Theorem implies that

$$\lim_{j\to\infty} \int_\Omega \varepsilon(\phi_{k_j})|\nabla\psi|^2 dx = \int_\Omega \varepsilon(\phi)|\nabla\psi|^2 dx. \tag{3.12}$$

It now follows from (3.11), (3.12), and the fact that $\varepsilon(\phi_{k_j}) \to \varepsilon(\phi)$ in $L^2(\Omega)$ and $\psi_{k_j} \rightharpoonup \psi$ in $H^1(\Omega)$ that

$$\lim_{j\to\infty} \int_\Omega \varepsilon(\phi_{k_j})|\nabla\psi_{k_j} - \nabla\psi|^2 dx$$

$$= \lim_{j\to\infty} \int_\Omega \left[\varepsilon(\phi_{k_j})|\nabla\psi_{k_j}|^2 - 2\varepsilon(\phi_{k_j})\nabla\psi_{k_j}\cdot\nabla\psi + \varepsilon(\phi_{k_j})|\nabla\psi|^2\right] dx$$

$$= \int_\Omega \left[\varepsilon(\phi)|\nabla\psi|^2 - 2\varepsilon(\phi)\nabla\psi\cdot\nabla\psi + \varepsilon(\phi)|\nabla\psi|^2\right] dx$$

$$= 0,$$

leading to (3.10).

We finally prove the energy convergence $E_{\phi_k}[\psi_k] \to E_\phi[\psi]$. Since $\phi_k \to \phi$ in $L^1(\Omega)$ and $\psi_k \to \psi$ in $H^1(\Omega)$, any subsequence of $\{\phi_k\}$ and the corresponding subsequence of $\{\psi_k\}$ have further subsequneces $\{\phi_{k_j}\}$ and $\{\psi_{k_j}\}$, respectively, such that $\phi_{k_j} \to \phi$ a.e. in Ω, and $\psi_{k_j} \to \psi$ in $H^1(\Omega)$ and a.e. in Ω. By (3.8), and (3.9) with ψ replacing $\hat\psi$, we have

$$\lim_{k\to\infty} \int_\Omega \left[-\rho\psi_{k_j} + (\phi_{k_j} - 1)^2 B(\psi_{k_j})\right] dx = \int_\Omega \left[-\rho\psi + (\phi - 1)^2 B(\psi)\right] dx. \tag{3.13}$$

This and (3.11) implies that $E_{\phi_{k_j}}[\psi_{k_j}] \to E_\phi[\psi]$. Hence $E_{\phi_k}[\psi_k] \to E_\phi[\psi]$. $\qquad\square$

We now state and prove the last result in this section: the convergence to the sharp-interface limit of phase-field electrostatic boundary forces, in terms of the weak convergence of the corresponding stress fields; cf. Lemma 2.1. We recall that $f_{0,\text{ele}}[\partial G]$ is defined in (2.27).

Theorem 3.3 (Convergence of dielectric boundary force). *Let $\phi_k \in L^4(\Omega)$ $(k = 1, 2, \dots)$ and $\phi \in L^1(\Omega)$ be such that*

$$\sup_{k \geq 1} \|\phi_k\|_{L^4(\Omega)} < \infty \quad \text{and} \quad \phi_k \to \phi \quad \text{a.e. in } \Omega. \tag{3.14}$$

We have for any $V \in C_c^1(\Omega, \mathbb{R}^3)$ that

$$\lim_{k \to \infty} \int_\Omega \left[T_{\text{ele}}(\phi_k) : \nabla V - \rho \nabla \psi_{\phi_k} \cdot V \right] dx = \int_\Omega \left[T_{\text{ele}}(\phi) : \nabla V - \rho \nabla \psi_\phi \cdot V \right] dx. \tag{3.15}$$

If, in addition, $\phi = \chi_G$ for some open subset G of Ω with a C^2 boundary ∂G and the closure $\overline{G} \subset \Omega$, then this limit is

$$\int_\Omega \left[T_{\text{ele}}(\chi_G) : \nabla V - \rho \nabla \psi_{\chi_G} \cdot V \right] dx = - \int_\Omega f_{0,\text{ele}}[\partial G] \cdot V \, dS. \tag{3.16}$$

Proof. We first note that, by Lemma 3.1, $\phi \in L^4(\Omega)$ and $\phi_k \to \phi$ in $L^q(\Omega)$ for any $q \in [1, 4)$. Let us denote $\psi_k = \psi_{\phi_k}$ $(k \geq 1)$ and $\psi = \psi_\phi$. Since ε is a bounded function and $\psi_k \to \psi$ in $H^1(\Omega)$ by Theorem 3.2, we have

$$\lim_{k \to \infty} \int_\Omega \varepsilon(\phi_k) \left[(\nabla \psi_k - \nabla \psi) \otimes (\nabla \psi_k - \nabla \psi) \right.$$
$$\left. + \nabla \psi \otimes (\nabla \psi_k - \nabla \psi) + (\nabla \psi_k - \nabla \psi) \otimes \nabla \psi \right] : \nabla V \, dx = 0.$$

Since $\phi_k \to \phi$ a.e. in Ω, the Lebesgue Dominated Convergence Theorem implies that

$$\lim_{k \to \infty} \int_\Omega \varepsilon(\phi_k) \nabla \psi \otimes \nabla \psi : \nabla V \, dx = \int_\Omega \varepsilon(\phi) \nabla \psi \otimes \nabla \psi : \nabla V \, dx.$$

Therefore,

$$\lim_{k \to \infty} \int_\Omega \varepsilon(\phi_k) \nabla \psi_k \otimes \nabla \psi_k : \nabla V \, dx$$
$$= \lim_{k \to \infty} \int_\Omega \varepsilon(\phi_k) \left[(\nabla \psi_k - \nabla \psi) \otimes (\nabla \psi_k - \nabla \psi) + \nabla \psi \otimes (\nabla \psi_k - \nabla \psi) \right.$$
$$\left. + (\nabla \psi_k - \nabla \psi) \otimes \nabla \psi + \nabla \psi \otimes \nabla \psi \right] : \nabla V \, dx$$
$$= \int_\Omega \varepsilon(\phi) \nabla \psi \otimes \nabla \psi : V \, dx. \tag{3.17}$$

Similarly,

$$\lim_{k \to \infty} \int_\Omega \varepsilon(\phi_k) |\nabla \psi_k|^2 \nabla \cdot V \, dx = \int_\Omega \varepsilon(\phi) |\nabla \psi|^2 \nabla \cdot V \, dx. \tag{3.18}$$

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As in the proof of Theorem 3.2, we have again by the convergence $\psi_k \to \psi$ in $H^1(\Omega)$ that

$$\lim_{k\to\infty} \int_\Omega \left[(\phi_k - 1)^2 B(\psi_k) \nabla \cdot V + \rho \nabla \psi_k \cdot V \right] dx = \int_\Omega \left[(\phi - 1)^2 B(\psi) \nabla \cdot V + \rho \nabla \psi \cdot V \right] dx.$$
(3.19)

It now follows from the definition of T_{ele} (cf. (2.15)) and (3.17)–(3.19) that

$$\lim_{k\to\infty} \int_\Omega \left[T_{\text{ele}}(\phi_k) : \nabla V - \rho \nabla \psi_{\phi_k} \cdot V \right] dx$$

$$= \lim_{k\to\infty} \int_\Omega \left\{ \varepsilon(\phi_k) \nabla \psi_k \otimes \nabla \psi_k : \nabla V - \left[\frac{1}{2} \varepsilon(\phi_k) |\nabla \psi_k|^2 + (\phi_k - 1)^2 B(\psi_k) \right] \nabla \cdot V \right.$$

$$\left. - \rho \nabla \psi_k \cdot V \right\} dx$$

$$= \int_\Omega \left\{ \varepsilon(\phi) \nabla \psi \otimes \nabla \psi : \nabla V - \left[\frac{1}{2} \varepsilon(\phi) |\nabla \psi|^2 + (\phi - 1)^2 B(\psi) \right] \nabla \cdot V - \rho \nabla \psi \cdot V \right\} dx$$

$$= \int_\Omega \left[T_{\text{ele}}(\phi) : \nabla V - \rho \nabla \psi \cdot V \right] dx.$$

This is exactly (3.15), since $\psi = \psi_\phi$.

We now prove (3.16). Denote again $\psi = \psi_\phi = \psi_{\chi_G} \in \mathcal{A}$. Denote also by V_i and ν_i ($i = 1, 2, 3$) the components of V and ν, respectively. Notice that the unit normal ν points from G to $G^c = \Omega \setminus G$. Using the conventional summation notation, we have by integration by parts that

$$\int_\Omega \left[T_{\text{ele}}(\chi_G) : \nabla V - \rho \nabla \psi_{\chi_G} \cdot V \right] dx$$

$$= \int_\Omega \left\{ \varepsilon(\chi_G) \nabla \psi \otimes \nabla \psi : \nabla V - \left[\frac{\varepsilon(\chi_G)}{2} |\nabla \psi|^2 + \chi_{G^c} B(\psi) \right] \nabla \cdot V - \rho \nabla \psi \cdot V \right\} dx$$

$$= \int_G \left(\varepsilon_{\text{p}} \partial_i \psi \partial_j \psi \partial_j V_i - \frac{\varepsilon_{\text{p}}}{2} \partial_i \psi \partial_i \psi \partial_j V_j - \rho \nabla \psi \cdot V \right) dx$$

$$+ \int_{G^c} \left[\varepsilon_{\text{w}} \partial_i \psi \partial_j \psi \partial_j V_i - \frac{\varepsilon_{\text{w}}}{2} \partial_i \psi \partial_i \psi \partial_j V_j - B(\psi) \partial_j V_j - \rho \nabla \psi \cdot V \right] dx$$

$$= \int_G \left(-\varepsilon_{\text{p}} \partial_{ij} \psi \partial_j \psi V_i - \varepsilon_{\text{p}} \partial_i \psi \partial_{jj} \psi V_i + \varepsilon_{\text{p}} \partial_{ij} \psi \partial_i \psi V_j - \rho \nabla \psi \cdot V \right) dx$$

$$+ \int_{\partial G} \left(\varepsilon_{\text{p}} \partial_i \psi |_G \partial_j \psi |_G V_i \nu_j - \frac{\varepsilon_{\text{p}}}{2} \partial_i \psi |_G \partial_i \psi |_G V_j \nu_j \right) dS$$

$$+ \int_{G^c} \left[-\varepsilon_{\text{w}} \partial_{ij} \psi \partial_j \psi V_i - \varepsilon_{\text{w}} \partial_i \psi \partial_{jj} \psi V_i + \varepsilon_{\text{w}} \partial_{ij} \psi \partial_i \psi V_j + B'(\psi) \partial_j \psi V_j - \rho \nabla \psi \cdot V \right] dx$$

$$+ \int_{\partial G} \left[-\varepsilon_{\text{w}} \partial_i \psi |_{G^c} \partial_j \psi |_{G^c} V_i \nu_j + \frac{\varepsilon_{\text{w}}}{2} \partial_i \psi |_{G^c} \partial_i \psi |_{G^c} V_j \nu_j + B(\psi) V_j \nu_j \right] dS$$

$$= \int_G (-\varepsilon_{\text{p}} \Delta \psi - \rho) \nabla \psi \cdot V \, dx + \int_{G^c} \left[-\varepsilon_{\text{w}} \Delta \psi + B'(\psi) - \rho \right] \nabla \psi \cdot V \, dx$$

$$+ \int_{\partial G} \left\{ \varepsilon_p (\nabla \psi \cdot \nu) \nabla \psi |_G \cdot V - \varepsilon_{\text{w}} (\nabla \psi \cdot \nu) \nabla \psi |_{G^c} \cdot V \right.$$

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$$+ \left[\frac{\varepsilon_{\mathrm{w}}}{2} |\nabla\psi|_{G^c}|^2 - \frac{\varepsilon_{\mathrm{p}}}{2} |\nabla\psi|_G|^2 + B(\psi) \right] V \cdot \nu \Big\} dS$$

$$= \int_{\partial G} \Big\{ \varepsilon(\chi_G)(\nabla\psi \cdot \nu)(\nabla\psi|_G - \nabla\psi|_{G^c}) \cdot V$$

$$+ \left[\frac{\varepsilon_{\mathrm{w}}}{2} |\nabla\psi|_{G^c}|^2 - \frac{\varepsilon_{\mathrm{p}}}{2} |\nabla\psi|_G|^2 + B(\psi) \right] V \cdot \nu \Big\} dS, \tag{3.20}$$

where in the last step we used (2.28)–(2.31).

The gradient $\nabla\psi$ restricted onto ∂G from either G or G^c has the decomposition

$$\nabla\psi = (\nabla\psi \cdot \nu)\nu + (I - \nu \otimes \nu)\nabla\psi \qquad \text{on } \partial G.$$

Since ψ is continuous across ∂G (cf. (2.30)), the tangential derivatives of ψ, and hence $(I - \nu \otimes \nu)\nabla\psi$, are continuous across the interface ∂G:

$$(I - \nu \otimes \nu)\nabla\psi|_G = (I - \nu \otimes \nu)\nabla\psi|_{G^c} \qquad \text{on } \partial G.$$

Thus

$$\nabla\psi|_G - \nabla\psi|_{G^c} = ((\nabla\psi|_G - \nabla\psi|_{G^c}) \cdot \nu)\nu \qquad \text{on } \partial G.$$

Moreover, restricted onto ∂G from either G or G^c,

$$|\nabla\psi|^2 = |(\nabla\psi \cdot \nu)\nu + (I - \nu \otimes \nu)\nabla\psi|^2 = |\nabla\psi \cdot \nu|^2 + |(I - \nu \otimes \nu)\nabla\psi|^2.$$

Therefore,

$$\varepsilon(\chi_G)(\nabla\psi \cdot \nu)(\nabla\psi|_G - \nabla\psi|_{G^c}) \cdot V + \left[\frac{\varepsilon_{\mathrm{w}}}{2} |\nabla\psi|_{G^c}|^2 - \frac{\varepsilon_{\mathrm{p}}}{2} |\nabla\psi|_G|^2 + B(\psi) \right] V \cdot \nu$$

$$= \left[\varepsilon_{\mathrm{p}} |\nabla\psi|_G \cdot \nu|^2 - \varepsilon_{\mathrm{w}} |\nabla\psi|_{G^c} \cdot \nu|^2 + \frac{\varepsilon_{\mathrm{w}}}{2} |\nabla\psi|_{G^c}|^2 - \frac{\varepsilon_{\mathrm{p}}}{2} |\nabla\psi|_G|^2 + B(\psi) \right] V \cdot \nu$$

$$= \left[\frac{\varepsilon_{\mathrm{p}}}{2} |\nabla\psi|_G \cdot \nu|^2 - \frac{\varepsilon_{\mathrm{w}}}{2} |\nabla\psi|_{G^c} \cdot \nu|^2 + \frac{1}{2}(\varepsilon_{\mathrm{w}} - \varepsilon_{\mathrm{p}})|(I - \nu \otimes \nu)\nabla\psi|^2 + B(\psi) \right] V \cdot \nu$$

$$= \left[\frac{1}{2}\left(\frac{1}{\varepsilon_{\mathrm{p}}} - \frac{1}{\varepsilon_{\mathrm{w}}} \right) |\varepsilon(\chi_G)\nabla\psi \cdot \nu|^2 + \frac{1}{2}(\varepsilon_{\mathrm{w}} - \varepsilon_{\mathrm{p}})|(I - \nu \otimes \nu)\nabla\psi|^2 + B(\psi) \right] V \cdot \nu$$

$$= -f_{0,\mathrm{ele}}[\partial G] \cdot V.$$

With our notation $\psi = \psi_{\chi_G}$, this and (3.20) imply (3.16). $\qquad \square$

4   Free-Energy Convergence

In this section, we first prove some lemmas. We then prove Theorem 2.1 on the Γ-convergence of free-energy functionals and its Corollary 2.1. Finally, we prove Theorem 2.2 on the equivalence of the convergence of total free energy and that of each individual part of the free energy.

The first lemma is on the existence of a phase-field minimizer for the functional F_ξ (cf. (2.3)) for each $\xi \in (0, \xi_0]$. This result will be used in proving Corollary 2.1.

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Lemma 4.1. *Let $\xi \in (0, \xi_0]$. There exists $\phi_\xi \in H^1(\Omega)$ such that*

$$F_\xi[\phi_\xi] = \min_{\phi \in H^1(\Omega)} F_\xi[\phi] = \min_{\phi \in L^1(\Omega)} F_\xi[\phi],$$

which is finite.

Proof. Let $\phi \in H^1(\Omega)$. We have by our assumptions on the functions U and ε, the fact that

$$W(s) - s^4 = 18s^2(s-1)^2 - s^4 \to +\infty \quad \text{as } s \to \infty,$$

the inequality

$$\min_{u \in \mathcal{A}} E_\phi[u] \leq E_\phi[\psi_\infty] = \int_\Omega \left[\frac{\varepsilon(\phi)}{2} |\nabla \psi_\infty|^2 - \rho \psi_\infty + (\phi - 1)^2 B(\psi_\infty) \right] dx,$$

and Hölder's inequality that

$$F_\xi[\phi] \geq \int_\Omega \left[P_0 \phi^2 + \frac{\gamma_0 \xi}{2} |\nabla \phi|^2 \right] dx + \frac{\gamma_0}{\xi} \|\phi\|_{L^4(\Omega)}^4 + \frac{\gamma_0}{\xi} \int_\Omega \left[W(\phi) - \phi^4 \right] dx$$

$$+ \rho_0 \int_{\{x \in \Omega : U(x) \leq 0\}} (\phi - 1)^2 U \, dx - E_\phi[\psi_\infty]$$

$$\geq C_1 \left(\|\phi\|_{H^1(\Omega)}^2 + \|\phi\|_{L^4(\Omega)}^4 \right) - 2 \left(\rho_0 |U_{\min}| + \|B(\psi_\infty)\|_{L^\infty(\Omega)} \right) \int_\Omega \phi^2 \, dx - C_2$$

$$\geq C_3 \left(\|\phi\|_{H^1(\Omega)}^2 + \|\phi\|_{L^4(\Omega)}^4 \right) - C_4, \tag{4.1}$$

where all C_i $(i = 1, \ldots, 4)$ are positive constants independent of $\phi \in H^1(\Omega)$.

Let $\alpha = \inf_{\phi \in H^1(\Omega)} F_\xi[\phi]$. By (4.1), $\alpha > -\infty$. Setting $\phi(x) = 1$ for all $x \in \Omega$, we have $\alpha \leq E_\xi[\phi] < \infty$. So, α is finite. Let $\phi_k \in H^1(\Omega)$ $(k = 1, 2, \ldots)$ be such that $F_\xi[\phi_k] \to \alpha$. By (4.1), $\{\phi_k\}$ is bounded in $H^1(\Omega)$. Hence, it has a subsequence, not relabeled, such that $\psi_k \to \phi_\xi$ weakly in $H^1(\Omega)$, strongly in $L^2(\Omega)$, and a.e. in Ω for some $\phi_\xi \in H^1(\Omega)$.

Since $\phi_k \to \phi_\xi$ in $L^2(\Omega)$ and U is bounded below,

$$\lim_{k \to \infty} \left[P_0 \int_\Omega \phi_k^2 \, dx + \rho_0 \int_{\{x \in \Omega : U(x) \leq 0\}} (\phi_k - 1)^2 U \, dx \right]$$

$$= P_0 \int_\Omega \phi_\xi^2 \, dx + \rho_0 \int_{\{x \in \Omega : U(x) \leq 0\}} (\phi_\xi - 1)^2 U \, dx. \tag{4.2}$$

Since $\phi_k \to \phi_\xi$ weakly in $H^1(\Omega)$,

$$\liminf_{k \to \infty} \gamma_0 \int_\Omega \frac{\xi}{2} |\nabla \phi_k|^2 dx \geq \gamma_0 \int_\Omega \frac{\xi}{2} |\nabla \phi_\xi|^2 dx. \tag{4.3}$$

Since $\phi_k \to \phi_\xi$ a.e. in Ω, Fatou's Lemma implies that

$$\liminf_{k \to \infty} \left[\gamma_0 \int_\Omega \frac{1}{\xi} W(\phi_k) \, dx + \rho_0 \int_{\{x \in \Omega : U(x) > 0\}} (\phi_k - 1)^2 U \, dx \right]$$

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$$\geq \gamma_0 \int_\Omega \frac{1}{\xi} W(\phi_\xi) \, dx + \rho_0 \int_{\{x\in\Omega:U(x)>0\}} (\phi_\xi - 1)^2 U \, dx. \tag{4.4}$$

By the Sobolev embedding $H^1(\Omega) \hookrightarrow L^4(\Omega)$, $\sup_{k\geq 1} \|\phi_k\|_{L^4(\Omega)} < \infty$. Hence it follows from Theorem 3.2 that

$$\lim_{k\to\infty} \min_{u\in\mathcal{A}} E_{\phi_k}[u] = \min_{u\in\mathcal{A}} E_{\phi_\xi}[u]. \tag{4.5}$$

Combining (4.2)–(4.5), we obtain

$$\alpha = \liminf_{k\to\infty} F_\xi[\phi_k] \geq F_\xi[\phi_\xi] \geq \alpha.$$

Hence $F_\xi[\phi_\xi] = \min_{\phi\in H^1(\Omega)} F_\xi[\phi]$. But $F_\xi[\phi] = +\infty$ if $\phi \in L^1(\Omega) \setminus H^1(\Omega)$. Hence $F_\xi[\phi_\xi] = \min_{\phi\in L^1(\Omega)} F_\xi[\phi]$. □

Next, we establish some lower bound for the functional $F_\xi = F_\xi[\phi]$ for all ϕ and ξ.

Lemma 4.2. *There exists a constant C such that for any $\phi \in H^1(\Omega)$ and any $\xi \in (0, \xi_0]$*

$$F_\xi[\phi] \geq \frac{\gamma_0}{2}\left[\xi\|\nabla\phi\|_{L^2(\Omega)}^2 + \frac{1}{\xi}\|W(\phi)\|_{L^1(\Omega)}\right] + 9\gamma_0\|\phi\|_{L^4(\Omega)}^4 + \rho_0 \int_\Omega (\phi - 1)^2 |U| \, dx + C. \tag{4.6}$$

Proof. Fix $\phi \in H^1(\Omega)$ and $\xi \in (0, \xi_0]$. Recall from (2.2) that

$$E_\phi[\psi_\infty] = \int_\Omega \left[\frac{\varepsilon(\phi)}{2}|\nabla\psi_\infty|^2 - \rho\psi_\infty + (\phi - 1)^2 B(\psi_\infty)\right] dx.$$

We have then by the definition of F_ξ (cf. (2.3)) that

$$0 \leq \frac{\gamma_0}{2}\left[\xi\|\nabla\phi\|_{L^2(\Omega)}^2 + \frac{1}{\xi}\|W(\phi)\|_{L^1(\Omega)}\right] + 9\gamma_0\|\phi\|_{L^4(\Omega)}^4 + \rho_0 \int_\Omega (\phi - 1)^2 |U| \, dx$$

$$= F_\xi[\phi] - P_0\|\phi\|_{L^2(\Omega)}^2 - \frac{\gamma_0}{2\xi}\|W(\phi)\|_{L^1(\Omega)} + 9\gamma_0\|\phi\|_{L^4(\Omega)}^4$$

$$+ \rho_0 \int_\Omega (\phi - 1)^2(|U| - U) \, dx + \min_{u\in\mathcal{A}} E_\phi[u]$$

$$\leq F_\xi[\phi] - \frac{\gamma_0}{2\xi_0}\|W(\phi)\|_{L^1(\Omega)} + 9\gamma_0\|\phi\|_{L^4(\Omega)}^4 + 2\rho_0 \int_{\{x\in\Omega:U(x)\leq 0\}} (\phi - 1)^2 |U| \, dx + E_\phi[\psi_\infty]$$

$$\leq F_\xi[\phi] - \frac{\gamma_0}{2\xi_0}\|W(\phi)\|_{L^1(\Omega)} + 9\gamma_0\|\phi\|_{L^4(\Omega)}^4 + 2\rho_0|U_{\min}| \int_\Omega (\phi - 1)^2 \, dx$$

$$+ \frac{1}{2}\max(\varepsilon_{\mathrm{p}}, \varepsilon_{\mathrm{w}})\|\nabla\psi_\infty\|_{L^2(\Omega)}^2 + \|\rho\|_{L^2(\Omega)}\|\psi_\infty\|_{L^2(\Omega)} + \|B(\psi_\infty)\|_{L^\infty(\Omega)} \int_\Omega (\phi - 1)^2 dx$$

$$= F_\xi[\phi] - \int_\Omega g(\phi) \, dx + \frac{1}{2}\max(\varepsilon_{\mathrm{p}}, \varepsilon_{\mathrm{w}})\|\nabla\psi_\infty\|_{L^2(\Omega)}^2 + \|\rho\|_{L^2(\Omega)}\|\psi_\infty\|_{L^2(\Omega)}, \tag{4.7}$$

where $g : \mathbb{R} \to \mathbb{R}$ is given by

$$g(s) = \frac{\gamma_0}{2\xi_0}W(s) - 9\gamma_0 s^4 - \left[2\rho_0|U_{\min}| + \|B(\psi_\infty)\|_{L^\infty(\Omega)}\right](s - 1)^2.$$

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Note that $\lim_{s\to\infty} g(s) = +\infty$, since $0 < \xi_0 < 1$ and $W(s) = 18s^2(s-1)^2$. Therefore, g is bounded below. Setting

$$C = |\Omega| \min_{s\in\mathbb{R}} g(s) - \frac{1}{2}\max(\varepsilon_{\mathrm{p}}, \varepsilon_{\mathrm{w}})\|\nabla\psi_\infty\|_{L^2(\Omega)}^2 - \|\rho\|_{L^2(\Omega)}\|\psi_\infty\|_{L^2(\Omega)},$$

we then obtain the desired estimate (4.6) from (4.7). $\qquad\qquad\qquad\qquad\qquad\qquad\quad\square$

The following lemma, stated for $\mathbb{R}^n$ with a general $n \geq 2$, is refinement of a standard result; it is used in the proof of Theorem 2.1 and Theorem 2.4:

Lemma 4.3. *Let Ω be a nonempty, bounded, and open subset of $\mathbb{R}^n$ with $n \geq 2$. Let G be a measurable subset of Ω with $P_\Omega(G) < \infty$. Assume that $\xi_k \searrow 0$ and $\phi_k \in H^1(\Omega)$ $(k = 1, 2, \dots)$ satisfy $\phi_k \to \chi_G$ a.e. in Ω and*

$$\sup_{k\geq 1} \int_\Omega \left[\frac{\xi_k}{2}|\nabla\phi_k|^2 + \frac{1}{\xi_k}W(\phi_k) \right] dx < \infty. \tag{4.8}$$

Define

$$\eta_k(x) = \int_0^{\phi_k(x)} \sqrt{2W(t)}\, dt \qquad \forall x \in \Omega,\ k = 1, 2, \dots$$

Then

$$\sup_{k\geq 1} \left[\|\eta_k\|_{L^{4/3}(\Omega)} + \|\eta_k\|_{W^{1,1}(\Omega)} \right] < \infty, \tag{4.9}$$

$$\eta_k \to \chi_G \text{ a.e. in } \Omega \text{ and in } L^q(\Omega) \text{ for any } q \in [1, 4/3), \tag{4.10}$$

$$P_\Omega(G) \leq \liminf_{k\to\infty} \int_\Omega |\nabla\eta_k|\, dx \leq \liminf_{k\to\infty} \int_\Omega \left[\frac{\xi_k}{2}|\nabla\phi_k|^2 + \frac{1}{\xi_k}W(\phi_k) \right] dx. \tag{4.11}$$

If, in addition, $\overline{G} \subset \Omega$, then

$$\lim_{k\to\infty} \int_\Omega \nabla\eta_k \cdot g\, dx = -\int_{\partial^* G} g \cdot \nu\, d\mathcal{H}^{n-1} \qquad \forall g \in C_c(\Omega, \mathbb{R}^n). \tag{4.12}$$

Proof. Since W is a quartic potential, we have $\sqrt{2W(t)} \leq C(1 + t^2)$ for all $t \in \mathbb{R}$. Here and below, C denotes a generic, positive constant. Therefore,

$$|\eta_k| \leq C(|\phi_k| + |\phi_k|^3) \qquad \text{a.e. in } \Omega,\ k = 1, 2, \dots$$

By (4.8), $\sup_{k\geq 1} \|\phi_k\|_{L^4(\Omega)} < \infty$. This implies that

$$\sup_{k\geq 1} \|\eta_k\|_{L^{4/3}(\Omega)} < \infty. \tag{4.13}$$

Note for each $k \geq 1$ that $\nabla\eta_k = \sqrt{2W(\phi_k)}\nabla\phi_k$ a.e. in Ω. Hence,

$$\int_\Omega |\nabla\eta_k|\, dx = \int_\Omega \left| \sqrt{2W(\phi_k)}\nabla\phi_k \right| dx \leq \int_\Omega \left[\frac{\xi_k}{2}|\nabla\phi_k|^2 + \frac{1}{\xi_k}W(\phi_k) \right] dx.$$

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This, together with (4.8) and (4.13), then implies that

$$\sup_{k \geq 1} \|\eta_k\|_{W^{1,1}(\Omega)} < \infty. \tag{4.14}$$

Now (4.9) follows from (4.13) and (4.14).

Since $\phi_k \to \chi_G$ a.e. in Ω and the integral of $\sqrt{2W(s)}$ over $[0,1]$ is 1, we have $\eta_k \to \chi_G$ a.e. in Ω. Lemma 3.1 and (4.13) imply that $\eta_k \to \chi_G$ in $L^q(\Omega)$ for any $q \in [1, 4/3)$. Hence (4.10) is proved.

By the fact that $W^{1,1}(\Omega) \hookrightarrow BV(\Omega)$ and (4.9), we have $\sup_{k \geq 1} \|\eta_k\|_{BV(\Omega)} < \infty$. Consequently, by (4.10) [13, 15, 38],

$$
\begin{aligned}
P_\Omega(G) &\leq \liminf_{k \to \infty} \int_\Omega |\nabla \eta_k| \, dx \\
&= \liminf_{k \to \infty} \int_\Omega \sqrt{2W(\phi_k)} |\nabla \phi_k| \, dx \\
&\leq \liminf_{k \to \infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx.
\end{aligned}
$$

This is (4.11).

Finally, if $g \in C_c^1(\Omega, \mathbb{R}^n)$, then it follows from (4.10) and (2.36) that

$$
\lim_{k \to \infty} \int_\Omega \nabla \eta_k \cdot g \, dx = -\lim_{k \to \infty} \int_\Omega \eta_k \nabla \cdot g \, dx = -\int_G \nabla \cdot g \, dx = -\int_{\partial^* G} g \cdot \nu \, d\mathcal{H}^{n-1}.
$$

Since $\sup_{k \geq 1} \|\eta_k\|_{W^{1,1}(\Omega)} < \infty$ by (4.9) and the perimeter measure $\|\partial G\| = \mathcal{H}^{n-1} \, \llcorner \, (\partial^* G \cap \Omega)$ is a Radon measure on Ω, the equation in (4.12) for any function $g \in C_c(\Omega, \mathbb{R}^n)$ follows from the fact that such a function can be approximated uniformly on any compact subsets of Ω by functions in $C_c^1(\Omega, \mathbb{R}^n)$. $\qquad \square$

We denote $B(\sigma) = \cup_{i=1}^N B(x_i, \sigma)$ for any $\sigma > 0$. The following is the last lemma we need to prove our Γ-convergence result:

Lemma 4.4. *Let G be a measurable subset of Ω such that $P_\Omega(G) < \infty$, $G \supseteq B(\sigma)$ for some $\sigma > 0$, and $|G| < |\Omega|$. Then there exist bounded open sets $D_k \subseteq \mathbb{R}^3$ ($k = 1, 2, \dots$) that satisfy the following properties:*
  (1) *For each $k \geq 1$, $D_k \cap \Omega \supseteq B(\sigma/2)$;*
  (2) *For each $k \geq 1$, ∂D_k is a nonempty compact hypersurface of class C^∞ and $\partial D_k \cap \Omega$ is of class C^2;*
  (3) *For each $k \geq 1$, $\mathcal{H}^2(\partial D_k \cap \partial \Omega) = 0$;*
  (4) *$|(D_k \cap \Omega) \Delta G| \to 0$ as $k \to \infty$;*
  (5) *$P_\Omega(D_k) = P_\Omega(D_k \cap \Omega) \to P_\Omega(G)$ as $k \to \infty$.*

This lemma is similar to Lemma 1 in [24] and Lemma 1 in [30]. Here we assume $G \supseteq B(\sigma)$. Moreover, part (1) above replaces the volume constraint $|D_k \cap \Omega| = |G|$ in [24, 30]. An outline of the proof of this lemma is given in the proof of Lemma 2.2 in [21]. For completeness, here we provide the main steps of proof, pointing out how the property (1) is satisfied.

Proof of Lemma 4.4. Since $P_\Omega(G) < \infty$, there exists $u \in \mathrm{BV}(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$ such that $u = \chi_G$ in Ω and

$$\int_{\partial\Omega} |\nabla u| \, d\mathcal{H}^2 = 0; \tag{4.15}$$

cf. Sections 2.8 and 2.16 in [15]. Since Ω is bounded, by using mollifiers, we can further modify u so that it is compactly supported. Notice that $u = 1$ on $B(\sigma)$. By using mollifiers again, we can construct $u_k \in C^\infty(\mathbb{R}^3)$ $(k = 1, 2, \dots)$ such that $\mathrm{supp}(u_k) \subseteq B(0, L)$ $(k = 1, 2, \dots)$ for some $L > 0$ sufficiently large, $u_k = 1$ in $B(\sigma/2)$ $(k = 1, 2, \dots)$, $u_k \to u$ in $L^1(\Omega)$, and using (4.15)

$$\lim_{k\to\infty} \int_\Omega |\nabla u_k| \, dx = |\nabla u|_{BV(\Omega)} = P_\Omega(A);$$

cf. Sections 2.8 and 2.16 in [15].

For any $t \in \mathbb{R}$, we define $D_k(t) = \{x \in \mathbb{R}^3 : u_k(x) > t\}$ $(k = 1, 2, \dots)$. Following Sections 1.24 and 1.26 in [15], and the proof of Lemma 1 in [24] and Lemma 1 in [30] (using the co-area formula and Sard's Theorem), there exists $t_0 \in (0, 1)$ and a subsequence of $\{D_k(t_0)\}$, not relabeled, that satisfy (2)–(5) in the lemma with $D_k = D_k(t_0)$ $(k = 1, 2, \dots)$. Clearly, for each $k \geq 1$, D_k is an open set with $D_k \subseteq B(0, L)$. Moreover,

$$D_k \supseteq \{x \in \mathbb{R}^3 : u_k(x) = 1\} \supseteq B(\sigma/2), \qquad k = 1, 2, \dots$$

This, and the fact that $B(\sigma) \subseteq G \subseteq \Omega$, implies part (1). $\qquad\square$

We are now ready to prove Theorem 2.1.

Proof of Theorem 2.1. Fix $\xi_k \searrow 0$.

(1) The liminf condition. Assume that $\phi_k \to \phi$ in $L^1(\Omega)$. If $\liminf_{k\to\infty} F_{\xi_k}[\phi_k] = +\infty$, then (2.5) is true. Otherwise, we may assume, without loss of generality, that

$$\lim_{k\to\infty} F_{\xi_k}[\phi_k] = \liminf_{k\to\infty} F_{\xi_k}[\phi_k] < \infty$$

and that there exists a constant $C > 0$ such that $F_{\xi_k}[\phi_k] \leq C$ for all $k \geq 1$. By the definition of functional F_ξ (cf. (2.3)), this implies that $\phi_k \in H^1(\Omega)$ for each $k \geq 1$. Hence, since $\{F_{\xi_k}[\phi_k]\}$ is bounded, it follows from Lemma 4.2 that

$$\sup_{k\geq 1} \int_\Omega \left[\frac{\xi_k}{2} |\nabla\phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx < \infty.$$

Since $W(s) = 18s^2(s-1)^2$ has exactly two minimum points 0 and 1, by a usual argument [24], there exists a subsequence of $\{\phi_k\}$, not relabeled, that converges strongly in $L^1(\Omega)$ and a.e. in Ω to χ_G for some measurable subset $G \subseteq \Omega$ of finite perimeter in Ω. Since $\phi_k \to \phi$ in $L^1(\Omega)$, we have $\phi = \chi_G$ a.e. in Ω. Since $\{F_{\xi_k}[\phi_k]\}$ is bounded, $\{\|\phi_k\|_{L^4(\Omega)}\}$ is bounded by Lemma 4.2. Hence, it follows from Lemma 3.1 that $\phi_k \to \chi_G$ in $L^q(\Omega)$ for any $q \in [1, 4)$.

Since $\phi_k \to \chi_G$ in $L^2(\Omega)$,

$$|G| = \int_\Omega \chi_G^2 \, dx = \lim_{k\to\infty} \int_\Omega \phi_k^2 \, dx. \tag{4.16}$$

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Lemma 4.3 implies that

$$P_\Omega(G) \le \liminf_{k\to\infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla\phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx. \tag{4.17}$$

By Fatou's Lemma, the convergence $\phi_k \to \chi_G$ a.e. in Ω, the convergence $\phi_k \to \chi_G$ in $L^2(\Omega)$, and the fact that U is bounded below, we obtain

$$\int_{\Omega\setminus G} U \, dx = \int_{\{x\in\Omega\setminus G : U(x)>0\}} (\chi_G - 1)^2 U \, dx + \int_{\{x\in\Omega\setminus G : U(x)\le 0\}} (\chi_G - 1)^2 U \, dx$$

$$\le \liminf_{k\to\infty} \int_{\{x\in\Omega\setminus G : U(x)>0\}} (\phi_k - 1)^2 U \, dx + \lim_{k\to\infty} \int_{\{x\in\Omega\setminus G : U(x)\le 0\}} (\phi_k - 1)^2 U \, dx$$

$$= \liminf_{k\to\infty} \int_{\Omega\setminus G} (\phi_k - 1)^2 U \, dx. \tag{4.18}$$

Since $\{\|\phi_k\|_{L^4(\Omega)}\}$ is bounded by Lemma 4.2 and $\phi_k \to \chi_G$ in $L^1(\Omega)$, Theorem 3.2 implies that

$$\lim_{k\to\infty} \min_{u\in\mathcal{A}} E_{\phi_k}[u] = \min_{u\in\mathcal{A}} E_{\chi_G}[u]. \tag{4.19}$$

The liminf inequality (2.5) now follows from (4.16)–(4.19).

(2) The recovering sequence. Let $\phi \in L^1(\Omega)$. If $F_0[\phi] = +\infty$, then we can take $\phi_k = \phi$ for all $k \ge 1$ to obtain (2.6). Assume $F_0[\phi] < \infty$. We then have $\phi = \chi_G \in BV(\Omega)$ for some measurable subset $G \subseteq \Omega$ of finite perimeter in Ω. We divide the rest of proof into two steps.

Step 1. We first consider the case that $G = D \cap \Omega$ for some bounded open set $D \subset \mathbb{R}^3$ such that the boundary ∂D is a nonempty compact hypersurface of class C^∞, $\partial D \cap \Omega$ is C^2, and $\mathcal{H}^2(\partial D \cap \partial \Omega) = 0$. It follows from a standard argument [21, 24, 30], for $\xi_k \searrow 0$, there exist $\phi_k \in H^1(\Omega)$ ($k = 1, 2, \dots$) satisfying

$$0 \le \phi_k \le \chi_G \quad \text{in } \Omega, \tag{4.20}$$

$$\phi_k = 1 \quad \text{in } G_k := \left\{ x \in G : \text{dist}(x, \partial G) \ge \sqrt{\xi_k} \right\}, \tag{4.21}$$

$$\phi_k = 0 \quad \text{in } \Omega \setminus G, \tag{4.22}$$

$$\phi_k \to \chi_G \quad \text{strongly in } L^1(\Omega) \text{ and a.e. in } \Omega, \tag{4.23}$$

$$\limsup_{k\to\infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla\phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx \le P_\Omega(G). \tag{4.24}$$

By (4.20), (4.23), and Lemma 3.1, we have $\phi_k \to \chi_G$ in $L^q(\Omega)$ for any $q > 1$. Hence

$$\lim_{k\to\infty} \int_\Omega \phi_k^2 \, dx = \int_\Omega \chi_G^2 \, dx = |G|. \tag{4.25}$$

Since $F_0[\chi_G] < \infty$, by (2.4) with G replacing A, the integral of U over $\Omega \setminus G$ is finite. Since $G = D \cap \Omega$ is open and $\partial D \cap \Omega$ is C^2, it follows from our assumptions on U, all points $x_i \in \Omega$ ($1 \le i \le N$) must be interior points of G. Consequently, there exists $r_0 > 0$ and $N_0 \ge 1$ such that $B(r_0) := \cup_{i=1}^N B(x_i, r_0) \subseteq G_k \subseteq G$ for all $k \ge N_0$. Hence, by (4.21), $\phi_k = 1$ on $B(r_0)$ for

all $k \geq N_0$. Note that U is bounded on $\Omega \setminus B(r_0)$. Therefore, by (4.21) and the convergence $\phi_k \to \chi_G$ in $L^2(\Omega)$,

$$
\begin{aligned}
\lim_{k\to\infty} \int_\Omega (\phi_k - 1)^2 U \; dx &= \lim_{k\to\infty} \int_{\Omega\setminus B(r_0)} (\phi_k - 1)^2 U \; dx \\
&= \int_{\Omega\setminus B(r_0)} (\chi_G - 1)^2 U \; dx \\
&= \int_{\Omega\setminus G} U \; dx.
\end{aligned}
\tag{4.26}
$$

By Theorem 3.2,

$$
\lim_{k\to\infty} \min_{u\in\mathcal{A}} E_{\phi_k}[u] = \min_{u\in\mathcal{A}} E_{\chi_G}[u].
\tag{4.27}
$$

Combining (4.24)–(4.27), we obtain (2.6).

Step 2. We now assume that $G \subseteq \Omega$ is an arbitrary measurable subset of finite perimeter in Ω. Since $F_0[\chi_G]$ is finite, the integral of U over $\Omega \setminus G$ is finite. This implies that $|G| > 0$. If $|G| = |\Omega|$ then $P_\Omega(G) = 0$. We can thus choose $\phi_k = \chi_G$ to get the limsup inequality (2.6). We assume now $0 < |G| < |\Omega|$.

Choose $\sigma_k \searrow 0$ such that the closure of $B(\sigma_k) := \cup_{i=1}^N B(x_i, \sigma_k)$ is included in Ω, $U \geq 0$ on $B(\sigma_k)$, and $0 < |G \cup B(\sigma_k)| < |\Omega|$ for each $k \geq 1$. Denote $\widehat{G}_k = G \cup B(\sigma_k)$ for $k \geq 1$. Then $G \subseteq \widehat{G}_{k+1} \subseteq \widehat{G}_k$ for all $k \geq 1$ and $\chi_{\widehat{G}_k} \to \chi_G$ in $L^1(\Omega)$. We claim that

$$
\limsup_{k\to\infty} F_0[\chi_{\widehat{G}_k}] \leq F_0[\chi_G].
\tag{4.28}
$$

Clearly,

$$
|\widehat{G}_k| = |G| + |B(\sigma_k) \setminus G| \to |G| \quad \text{as } k \to \infty.
\tag{4.29}
$$

Moreover [15],

$$
\begin{aligned}
\limsup_{k\to\infty} P_\Omega(\widehat{G}_k) &= \limsup_{k\to\infty} P_\Omega(G \cup B_k) \\
&\leq \limsup_{k\to\infty} [P_\Omega(G) + P_\Omega(B_k)] \\
&= P_\Omega(G) + \lim_{k\to\infty} P_\Omega(B_k) \\
&= P_\Omega(G).
\end{aligned}
\tag{4.30}
$$

Since $\Omega \setminus \widehat{G}_k \subseteq \Omega \setminus \widehat{G}_{k+1}$, we have by the Lebesgue Monotone Convergence Theorem that

$$
\begin{aligned}
\lim_{k\to\infty} \int_{\Omega\setminus\widehat{G}_k} \chi_{\{x\in\Omega:U(x)>0\}} U \; dx &= \lim_{k\to\infty} \int_\Omega \chi_{\Omega\setminus\widehat{G}_k} \chi_{\{x\in\Omega:U(x)>0\}} U \; dx \\
&= \int_\Omega \chi_{\Omega\setminus G} \chi_{\{x\in\Omega:U(x)>0\}} U \; dx \\
&= \int_{\Omega\setminus G} \chi_{\{x\in\Omega:U(x)>0\}} U \; dx.
\end{aligned}
$$

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Since U is bounded below and $|\Omega \setminus \widehat{G}_k| \to |\Omega \setminus G|$,

$$\lim_{k\to\infty} \int_{\Omega\setminus\widehat{G}_k} \chi_{\{x\in\Omega:U(x)\leq 0\}} U\, dx = \int_{\Omega\setminus G} \chi_{\{x\in\Omega:U(x)\leq 0\}} U\, dx.$$

Combining the above two equations, we get

$$\lim_{k\to\infty} \int_{\Omega\setminus\widehat{G}_k} U\, dx = \int_{\Omega\setminus G} U\, dx. \tag{4.31}$$

By Theorem 3.2,

$$\lim_{k\to\infty} \min_{u\in\mathcal{A}} E_{\chi_{\widehat{G}_k}}[u] = \min_{u\in\mathcal{A}} E_{\chi_G}[u]. \tag{4.32}$$

Now, (4.28) follows from (4.29)–(4.32).

Fix an arbitrary $k \geq 1$. It follows from Lemma 4.4 that there exist open sets $D_{k,j} \subseteq \mathbb{R}^3$ ($j = 1, 2, \dots$) such that, for each $j \geq 1$ and $G_{k,j} := D_{k,j} \cap \Omega$, $G_{k,j} \supseteq B(\sigma_k/2)$, $\partial D_{k,j}$ is C^∞ and $\partial D_{k,j} \cap \Omega$ is C^2, and $\mathcal{H}^2(\partial D_{k,j} \cap \partial\Omega) = 0$, and that $|G_{k,j}\Delta\widehat{G}_k| \to 0$, which is equivalent to $\chi_{G_{k,j}} \to \chi_{\widehat{G}_k}$ in $L^1(\Omega)$, and $P_\Omega(G_{k,j}) \to P_\Omega(\widehat{G}_k)$ as $j \to \infty$. Clearly, $|G_{k,j}| \to |\widehat{G}_k|$ as $j \to \infty$. Since each $G_{k,j} \supseteq B(\sigma_k/2)$ and $\chi_{G_{k,j}} \to \chi_{\widehat{G}_k}$ in $L^1(\Omega)$,

$$\lim_{j\to\infty} \int_{\Omega\setminus G_{k,j}} U\, dx = \int_{\Omega\setminus\widehat{G}_k} U\, dx.$$

By Theorem 3.2, $\min_{u\in\mathcal{A}} E_{\chi_{G_{k,j}}}[u] \to \min_{u\in\mathcal{A}} E_{\chi_{\widehat{G}_k}}[u]$ as $j \to \infty$. Therefore,

$$\lim_{j\to\infty} F_0[\chi_{G_{k,j}}] = F_0[\chi_{\widehat{G}_k}], \quad k = 1, 2, \dots$$

By induction, we can choose $j_1 < j_2 < \cdots$ with $j_k \to \infty$ such that, with the notation $H_k = G_{k,j_k}$ for all $k \geq 1$,

$$\|\chi_{H_k} - \chi_{\widehat{G}_k}\|_{L^1(\Omega)} < \frac{1}{k} \quad \text{and} \quad |F_0[\chi_{H_k}] - F_0[\chi_{\widehat{G}_k}]| < \frac{1}{k}, \quad k = 1, 2, \dots$$

These, together with the fact that $\chi_{\widehat{G}_k} \to \chi_G$ in $L^1(\Omega)$ and (4.28), imply that

$$\lim_{k\to\infty} \|\chi_{H_k} - \chi_G\|_{L^1(\Omega)} = 0 \quad \text{and} \quad \limsup_{k\to\infty} F_0[\chi_{H_k}] \leq F_0[\chi_G]. \tag{4.33}$$

By Step 1, we can find for each $k \geq 1$ a recovering sequence $\{\phi_{k,l}\}_{l=1}^\infty$ for χ_{H_k} such that all $\phi_{k,l} \in H^1(\Omega)$ ($l = 1, 2, \dots$),

$$\lim_{l\to\infty} \|\phi_{k,l} - \chi_{H_k}\|_{L^1(\Omega)} = 0 \quad \text{and} \quad \limsup_{l\to\infty} F_{\xi_l}[\phi_{k,l}] \leq F_0[\chi_{H_k}], \quad k = 1, 2, \dots \tag{4.34}$$

By (4.33) and (4.34), and induction, we can choose $l_1 < l_2 < \cdots$ with $l_k \to \infty$ such that $\phi_{k,l_k} \to \chi_G$ in $L^1(\Omega)$ and

$$\limsup_{k\to\infty} F_{\xi_{l_k}}[\phi_{k,l_k}] \leq F_0[\chi_G].$$

The proof is complete. $\qquad\square$

Proof of Corollary 2.1. Let $\xi_k \searrow 0$. For each $k \geq 1$, let $\phi_k \in H^1(\Omega)$ be such that $F_{\xi_k}[\phi_k] = \min_{\phi \in L^1(\Omega)} F_{\xi_k}[\phi]$; cf. Lemma 4.1. By Lemma 4.2 and comparing $F_{\xi_k}[\phi_k]$ to the free energy of the constant function $\phi = 1$, the sequence $\{F_{\xi_k}[\phi_k]\}$ is bounded. Hence the corresponding sequence of the van der Waals–Cahn–Hilliard functionals of ϕ_k is also bounded. This and a usual argument [24, 30] imply that there exists a subsequence of $\{\phi_k\}$, not relabeled, such that $\phi_k \to \chi_G$ in $L^1(\Omega)$ for some measurable subset G of Ω. Theorem 2.1 then implies χ_G minimizes F_0. $\qquad\square$

We need the following elementary result in the proof of Theorem 2.2:

Lemma 4.5. *Let a_k and b_k ($k = 1, 2, \dots$), and a and b be all nonnegative numbers such that*

$$\lim_{k \to \infty} (a_k + b_k) = a + b, \quad \liminf_{k \to \infty} a_k \geq a, \quad and \quad \liminf_{k \to \infty} b_k \geq b.$$

Then

$$\lim_{k \to \infty} a_k = a \quad and \quad \lim_{k \to \infty} b_k = b.$$

Proof. Since $a_k \geq 0$ and $b_k \geq 0$ ($k = 1, 2, \dots$) and $\{a_k + b_k\}$ converges, both $\{a_k\}$ and $\{b_k\}$ are bounded. Let $\{a_{k_j}\}$ be any subsequence of $\{a_k\}$. Let $\{a_{k_{j_i}}\}$ be a further subsequence such that

$$\lim_{i \to \infty} a_{k_{j_i}} = \liminf_{j \to \infty} a_{k_j}. \tag{4.35}$$

We have then

$$a + b = \liminf_{j \to \infty}(a_{k_j} + b_{k_j}) \geq \liminf_{j \to \infty} a_{k_j} + \liminf_{j \to \infty} b_{k_j} \geq \liminf_{k \to \infty} a_k + \liminf_{k \to \infty} b_k \geq a + b,$$

leading to

$$0 \geq \left(\liminf_{j \to \infty} a_{k_j} - a \right) + \left(\liminf_{j \to \infty} b_{k_j} - b \right) \geq 0.$$

Each term in the sum is nonnegative, and hence is 0. Thus $\liminf_{j \to \infty} a_{k_j} = a$. This and (4.35) imply that $a_{k_{j_i}} \to a$ as $i \to \infty$, and hence $a_k \to a$ as $k \to \infty$. Similarly, $b_k \to b$ as $k \to \infty$. $\quad\square$

We are now ready to prove Theorem 2.2.

Proof of Theorem 2.2. Since $\{F_{\xi_k}[\phi_k]\}$ converges, it is bounded. Lemma 4.2 then implies that $\sup_{k \geq 1} \|\phi_k\|_{L^4(\Omega)} < \infty$. Since $\phi_k \to \chi_G$ a.e. in Ω, Lemma 3.1 implies that $\phi_k \to \chi_G$ in $L^q(\Omega)$ for any $q \in [1, 4)$. Hence, (2.7) follows. Moreover, Theorem 3.2 implies (2.10).

By our assumptions on U and the Lebesgue Dominated Convergence Theorem,

$$\lim_{k \to \infty} \int_{\{x \in \Omega : U(x) \leq 0\}} (\phi_k - 1)^2 U \, dx = \int_{\{x \in \Omega : U(x) \leq 0\}} \chi_{\Omega \setminus G} U \, dx. \tag{4.36}$$

Since $F_{\xi_k}[\phi_k] \to F_0[\chi_G]$ with $F_0[\chi_G]$ being finite, it follows from (2.7), (2.10), and (4.36) that

$$\lim_{k \to \infty} \left\{ \gamma_0 \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx + \rho_0 \int_{\{x \in \Omega : U(x) > 0\}} (\phi_k - 1)^2 U \, dx \right\}$$

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$$
\begin{aligned}
&= \lim_{k\to\infty} \left\{ F_{\xi_k}[\phi_k] - P_0 \int_\Omega \phi_k^2 \, dx - \rho_0 \int_{\{x\in\Omega:U(x)\le 0\}} (\phi_k - 1)^2 U \, dx + \min_{u\in\mathcal{A}} E_{\phi_k}[u] \right\} \\
&= F_0[\chi_G] - P_0|G| - \rho_0 \int_{\{x\in\Omega:U(x)\le 0\}} \chi_{\Omega\setminus G} U \, dx + \min_{u\in\mathcal{A}} E_{\chi_G}[u] \\
&= \gamma_0 P_\Omega(G) + \rho_0 \int_{\{x\in\Omega:U(x)>0\}} \chi_{\Omega\setminus G} U \, dx.
\end{aligned}
\tag{4.37}
$$

By Lemma 4.3, we have

$$
\liminf_{k\to\infty} \int_\Omega \left[\frac{\xi_k}{2}|\nabla\phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx \ge P_\Omega(G).
\tag{4.38}
$$

Fatou's Lemma implies that

$$
\liminf_{k\to\infty} \int_{\{x\in\Omega:U(x)>0\}} (\phi_k - 1)^2 U \, dx \ge \int_{\{x\in\Omega:U(x)>0\}} \chi_{\Omega\setminus G} U \, dx.
\tag{4.39}
$$

By (4.37)–(4.39) and Lemma 4.5, the inequalities (4.38) and (4.39) become equalities. Therefore (2.8) is true; and further, (2.9) is true.

Finally, since all $F_0[\chi_G]$, $|G|$, $P_\Omega(G)$, and $F_{\text{ele}}[G]$ are finite, the right-hand side of (2.9) is also finite. $\qquad\square$

5   Force Convergence

We first prove Theorem 2.3. We then focus on the proof of Theorem 2.4, which is for a general space dimension $n \ge 2$.

Proof of Theorem 2.3. Since $F_{\xi_k}[\phi_k] \to F_0[\chi_G]$, Lemma 4.2 implies that $\{\|\phi_k\|_{L^4(\Omega)}\}$ is bounded. Since, $\phi_k \to \chi_G$ a.e. in Ω, Lemma 3.1 then implies that $\phi_k \to \chi_G$ in $L^q(\Omega)$ for any $q \in [1,4)$. This implies (2.37); it also implies (2.39) as both U and ∇U are continuous on $\text{supp}(V)$. The second equation (2.38) is part of Theorem 2.4. Finally, the equation (2.40) is part of Theorem 3.3. $\quad\square$

To prove Theorem 2.4, we need the following lemma which states that the convergence of phase-field surface energies to their sharp-interface limit implies the asymptotic equi-partition of energies. Indeed, we prove that

$$
\frac{\xi_k}{2}|\nabla\phi_k|^2 - \frac{1}{\xi_k} W(\phi_k) \to 0 \quad \text{strongly in } L^1(\Omega) \text{ as } k \to \infty.
$$

This is stronger than the weak convergence of the discrepancy measures

$$
\left[\frac{\xi_k}{2}|\nabla\phi_k|^2 - \frac{1}{\xi_k} W(\phi_k) \right] dx \quad (k = 1, 2, \dots)
$$

that are defined in [17, 26]:

Lemma 5.1 (Asymptotic equi-partition of energy). *Let $\xi_k \searrow 0$, $\phi_k \in H^1(\Omega)$ ($k = 1, 2, \dots$), and $G \subseteq \Omega$ be measurable with $P_\Omega(G) < \infty$. Assume that $\phi_k \to \chi_G$ a.e. in Ω. Assume also that*

$$\lim_{k \to \infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx = P_\Omega(G). \tag{5.1}$$

Then, we have

$$\lim_{k \to \infty} \int_\Omega \left| \sqrt{\frac{\xi_k}{2}} |\nabla \phi_k| - \sqrt{\frac{W(\phi_k)}{\xi_k}} \right|^2 dx = 0, \tag{5.2}$$

and

$$\lim_{k \to \infty} \int_\Omega \left| \frac{\xi_k}{2} |\nabla \phi_k|^2 - \frac{1}{\xi_k} W(\phi_k) \right| dx = 0. \tag{5.3}$$

Proof. Define $\eta_k = \eta_k(x)$ as in Lemma 4.3. We have by Lemma 4.3 and (5.1) that

$$0 \le \limsup_{k \to \infty} \int_\Omega \left| \sqrt{\frac{\xi_k}{2}} |\nabla \phi_k| - \sqrt{\frac{W(\phi_k)}{\xi_k}} \right|^2 dx$$

$$= \limsup_{k \to \infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) - \sqrt{2W(\phi_k)} |\nabla \phi_k| \right] dx$$

$$= \lim_{k \to \infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] - \liminf_{k \to \infty} \int_\Omega \sqrt{2W(\phi_k)} |\nabla \phi_k| \, dx$$

$$= P_\Omega(G) - \liminf_{k \to \infty} \int_\Omega |\nabla \eta_k| \, dx$$

$$\le 0.$$

This proves (5.2). By (5.1) and (5.2), we have

$$\int_\Omega \left| \frac{\xi_k}{2} |\nabla \phi_k|^2 - \frac{1}{\xi_k} W(\phi_k) \right| dx$$

$$= \int_\Omega \left| \sqrt{\frac{\xi_k}{2}} |\nabla \phi_k| - \sqrt{\frac{W(\phi_k)}{\xi_k}} \right| \left| \sqrt{\frac{\xi_k}{2}} |\nabla \phi_k| + \sqrt{\frac{W(\phi_k)}{\xi_k}} \right| dx$$

$$\le \left(\int_\Omega \left| \sqrt{\frac{\xi_k}{2}} |\nabla \phi_k| - \sqrt{\frac{W(\phi_k)}{\xi_k}} \right|^2 dx \right)^{1/2} \left(2 \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] dx \right)^{1/2}$$

$$\to 0 \qquad \text{as } k \to \infty,$$

implying (5.3). $\qquad \square$

We are now ready to prove Theorem 2.4.

Proof of Theorem 2.4. Suppose (2.42) is true for any $\Psi \in C_c(\Omega, \mathbb{R}^n \times \mathbb{R}^n)$. Let $V \in C_c^1(\Omega, \mathbb{R}^n)$. Under the additional assumptions on ϕ_k $(k \geq 1)$ and G, we have by (2.21) in Lemma 2.1, (2.42) with $\Psi = \nabla V$, and (2.33) in Lemma 2.2 that

$$
\lim_{k \to \infty} \int_\Omega \left[-\xi_k \Delta \phi_k + \frac{1}{\xi_k} W'(\phi_k) \right] \nabla \phi_k \cdot V \, dx
$$
$$
= - \lim_{k \to \infty} \int_\Omega T_{\xi_k}(\phi_k) : \nabla V \, dx
$$
$$
= - \int_{\partial G} (I - \nu \otimes \nu) : \nabla V \, d\mathcal{H}^{n-1}
$$
$$
= -(n-1) \int_{\partial G} H\nu \cdot V \, dS,
$$

proving (2.43).

We now prove (2.42). We claim that it suffices to prove that

$$
\lim_{k \to \infty} \int_\Omega \xi_k \nabla \phi_k \otimes \nabla \phi_k : \Psi \, dx = \int_{\partial^* G} \nu \otimes \nu : \Psi \, d\mathcal{H}^{n-1} \qquad \forall \Psi \in C_c(\Omega; \mathbb{R}^{n \times n}). \qquad (5.4)
$$

In fact, suppose (5.4) is proved. Notice for any $a \in \mathbb{R}^n$, $|a|^2 = a \otimes a : I$. Let $\Psi \in C_c(\Omega, \mathbb{R}^{n \times n})$. Then $(I : \Psi)I \in C_c(\Omega, \mathbb{R}^{n \times n})$. Hence, it follows from Lemma 5.1 and (5.4), with $(I : \Psi)I$ replacing Ψ, that

$$
\lim_{k \to \infty} \int_\Omega \left[\frac{\xi_k}{2} |\nabla \phi_k|^2 + \frac{1}{\xi_k} W(\phi_k) \right] I : \Psi \, dx
$$
$$
= \lim_{k \to \infty} \int_\Omega \xi_k |\nabla \phi_k|^2 I : \Psi \, dx
$$
$$
= \lim_{k \to \infty} \int_\Omega \xi_k \nabla \phi_k \otimes \nabla \phi_k : (I : \Psi)I \, dx
$$
$$
= \int_{\partial^* G} \nu \otimes \nu : (I : \Psi)I \, d\mathcal{H}^{n-1}
$$
$$
= \int_{\partial^* G} I : \Psi \, d\mathcal{H}^{n-1}.
$$

This, togehter with (5.4), implies (2.42).

It remains to prove (5.4). Fix $\Psi \in C_c(\Omega, \mathbb{R}^n \times \mathbb{R}^n)$ and let $\sigma > 0$. Recall that the reduced boundary $\partial^* G$ has the decomposition [13, 15, 38]

$$
\partial^* G = \left(\bigcup_{j=1}^\infty K_j \right) \bigcup Q,
$$

where K_j $(j = 1, 2, \dots)$ are disjoint compact sets, each being a subset of a C^1-hypersurface $S_j \subset \Omega$, and $Q \subset \partial G$ with $\|\partial G\|(Q) = 0$. The vector $\nu(x)$ at some $x \in K_j$ for some j is the normal to S_j. Moreover,

$$
\sum_{j=1}^\infty \mathcal{H}^{n-1}(K_j) = \mathcal{H}^{n-1}(\partial^* G) = \|\partial G\|(\Omega) = P_\Omega(G) < \infty. \qquad (5.5)
$$

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Let J be large enough so that

$$\sum_{j=J+1}^{\infty} \mathcal{H}^{n-1}(K_j) < \sigma. \tag{5.6}$$

Since K_j $(j = 1, \ldots, J)$ are disjoint, there exist disjoint open sets $U_j \subset \overline{U}_j \subset \Omega$ such that $K_j \subset U_j$ $(j = 1, \ldots, J)$. For each j $(1 \leq j \leq J)$, we define $d_j : U_j \to \mathbb{R}$ to be the signed distance to S_j for which the sign is chosen so that $\nu(x) = \nabla d_j(x)$ if $x \in K_j$; and extend d_j to Ω by setting $d_j = 0$ on $\Omega \setminus U_j$. We also choose $\zeta_j \in C_c^1(\Omega)$ be such that $0 \leq \zeta_j \leq 1$ on Ω, $\zeta_j = 1$ in a neighborhood of K_j, $\operatorname{supp}(\zeta_j) \subset U_j$, and $\zeta_j \nabla d_j \in C_c(\Omega, \mathbb{R}^n)$. Define $\nu_J : \Omega \to \mathbb{R}^n$ by

$$\nu_J = \sum_{j=1}^{J} \zeta_j \nabla d_j.$$

Note that $\nu_j \in C_c(\Omega, \mathbb{R}^n)$, $|\nu_j| \leq 1$ on Ω, and $\nu_j = \nu$ on each K_j $(1 \leq j \leq J)$.

We rewrite $\xi_k \nabla \phi_k \otimes \nabla \phi_k$ as

$$\xi_k \nabla \phi_k \otimes \nabla \phi_k = \left(\sqrt{\xi_k} \nabla \phi_k + \sqrt{\xi_k} |\nabla \phi_k| \nu_J \right) \otimes \sqrt{\xi_k} \nabla \phi_k$$

$$+ \left(\sqrt{\frac{2W(\phi_k)}{\xi_k}} - \sqrt{\xi_k} |\nabla \phi_k| \right) \nu_J \otimes \sqrt{\xi_k} \nabla \phi_k$$

$$- \nu_J \otimes \sqrt{2W(\phi_k)} \nabla \phi_k. \tag{5.7}$$

We claim:

(1) $\displaystyle \limsup_{k \to \infty} \int_\Omega \left| \sqrt{\xi_k} \nabla \phi_k + \sqrt{\xi_k} |\nabla \phi_k| \nu_J \right|^2 dx \leq 4\sigma$;

(2) $\displaystyle \sup_{k \geq 1} \left\| \sqrt{\xi_k} \nabla \phi_k \right\|_{L^2(\Omega)} < \infty$;

(3) $\displaystyle \lim_{k \to \infty} \int_\Omega \left[\sqrt{\xi_k} |\nabla \phi_k| - \sqrt{\frac{2W(\phi_k)}{\xi_k}} \right]^2 dx = 0$;

(4) $\displaystyle \lim_{k \to \infty} \int_\Omega \nu_J \otimes \sqrt{2W(\phi_k)} \nabla \phi_k : \Psi \, dx = - \int_{\partial^* G} \nu_J \otimes \nu : \Psi \, d\mathcal{H}^{n-1}$.

If all these claims are true, then it follows from (5.7) and (5.6) that

$$\limsup_{k \to \infty} \left| \int_\Omega \xi_k \nabla \phi_k \otimes \nabla \phi_k : \Psi \, dx - \int_{\partial^* G} \nu \otimes \nu : \Psi \, d\mathcal{H}^{n-1} \right|$$

$$\leq \limsup_{k \to \infty} \int_\Omega \left| \left(\sqrt{\xi_k} \nabla \phi_k + \sqrt{\xi_k} |\nabla \phi_k| \nu_J \right) \otimes \sqrt{\xi_k} \nabla \phi_k : \Psi \right| dx$$

$$+ \limsup_{k \to \infty} \int_\Omega \left| \left(\sqrt{\frac{2W(\phi_k)}{\xi_k}} - \sqrt{\xi_k} |\nabla \phi_k| \right) \nu_J \otimes \sqrt{\xi_k} \nabla \phi_k : \Psi \right| dx$$

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$$+\left|\lim_{k\to\infty}\int_\Omega \nu_J\otimes\sqrt{2W(\phi_k)}\nabla\phi_k:\Psi\,dx+\int_{\partial^*G}\nu\otimes\nu:\Psi\,d\mathcal{H}^{n-1}\right|$$

$$\leq\limsup_{k\to\infty}\left[\int_\Omega\left|\sqrt{\xi_k}\nabla\phi_k+\sqrt{\xi_k}|\nabla\phi_k|\nu_J\right|^2 dx\right]^{1/2}\left(\sup_{k\geq 1}\left\|\sqrt{\xi_k}\nabla\phi_k\right\|_{L^2(\Omega)}\right)\|\Psi\|_{L^\infty(\Omega)}$$

$$+\limsup_{k\to\infty}\left[\int_\Omega\left(\sqrt{\xi_k}|\nabla\phi_k|-\sqrt{\frac{2W(\phi_k)}{\xi_k}}\right)^2 dx\right]^{1/2}$$

$$\cdot\left(\sup_{k\geq 1}\|\sqrt{\xi_k}\nabla\phi_k\|_{L^2(\Omega)}\right)\|\Psi\|_{L^\infty(\Omega)}$$

$$+\left|\int_{\partial^*G}(\nu_J-\nu)\otimes\nu:\Psi\,d\mathcal{H}^{n-1}\right|$$

$$\leq\sqrt{4\sigma}\left(\sup_{k\geq 1}\left\|\sqrt{\xi_k}\nabla\phi_k\right\|_{L^2(\Omega)}\right)\|\Psi\|_{L^\infty(\Omega)}+2\|\Psi\|_{L^\infty(\Omega)}\sum_{j=J+1}^\infty\mathcal{H}^{n-1}(K_j)$$

$$\leq\sqrt{4\sigma}\left(\sup_{k\geq 1}\left\|\sqrt{\xi_k}\nabla\phi_k\right\|_{L^2(\Omega)}\right)\|\Psi\|_{L^\infty(\Omega)}+2\sigma\|\Psi\|_{L^\infty(\Omega)}.$$

Since $\sigma>0$ is arbitrary, this proves (5.4).

We now prove all of our claims. Claim (2) follows from the assumption (2.41) of the energy convergence and the assumption that $P_\Omega(G)<\infty$. Claim (3) is (5.2) in Lemma 5.1. Claim (4) follows from (4.12) in Lemma 4.3, which implies that for any $j\in\{1,\dots,n\}$

$$\lim_{k\to\infty}\int_\Omega\partial_{x_j}\eta_k h\,dx=-\int_{\partial^*G}\nu_j h\,d\mathcal{H}^{n-1}\qquad\forall h\in C_c(\Omega),$$

where $\nabla\eta_k=\sqrt{2W(\phi_k)}\nabla\phi_k$.

Proof of Claim (1). Noting that $|\nu_J|\leq 1$, we have for each $k\geq 1$ that

$$\frac{1}{2}\int_\Omega\left|\sqrt{\xi_k}\nabla\phi_k+\sqrt{\xi_k}|\nabla\phi_k|\nu_J\right|^2 dx$$

$$=\frac{1}{2}\int_\Omega\left(\xi_k|\nabla\phi_k|^2+\xi_k|\nabla\phi_k|^2|\nu_J|^2+2\xi_k|\nabla\phi_k|\nabla\phi_k\cdot\nu_J\right)dx$$

$$\leq\int_\Omega\left(\xi_k|\nabla\phi_k|^2+\xi_k|\nabla\phi_k|\nabla\phi_k\cdot\nu_J\right)dx$$

$$=\int_\Omega\left[\frac{\xi_k}{2}|\nabla\phi_k|^2+\frac{W(\phi_k)}{\xi_k}\right]dx+\int_\Omega\left[\frac{\xi_k}{2}|\nabla\phi_k|^2-\frac{W(\phi_k)}{\xi_k}\right]dx$$

$$+\int_\Omega\left[\sqrt{\xi_k}|\nabla\phi_k|-\sqrt{\frac{2W(\phi_k)}{\xi_k}}\right]\sqrt{\xi_k}\nabla\phi_k\cdot\nu_J\,dx$$

$$+\int_\Omega\sqrt{2W(\phi_k)}\nabla\phi_k\cdot\nu_J\,dx$$

$$=:I_1(k)+I_2(k)+I_3(k)+I_4(k). \tag{5.8}$$

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By (5.1),
$$\lim_{k\to\infty} I_1(k) = P_\Omega(G).$$

By Lemma 5.1 on the asymptotic equi-partition of energy,
$$\lim_{k\to\infty} I_2(k) = 0.$$

By Claim (2) and Claim (3),
$$\lim_{k\to\infty} I_3(k) = 0.$$

By (4.12) in Lemma 4.3,
$$\lim_{k\to\infty} I_4 = -\int_{\partial^* G} \nu \cdot \nu_J \, d\mathcal{H}^{n-1}$$
$$= -\sum_{j=1}^{J} \mathcal{H}^{n-1}(K_j) - \sum_{j=J+1}^{\infty} \int_{K_j} \nu \cdot \nu_J \, d\mathcal{H}^{n-1}.$$

Therefore, continuing from (5.8), we have by (5.5), (5.6), and the fact that $|\nu \cdot \nu_J| \leq 1$ that

$$\limsup_{k\to\infty} \frac{1}{2} \int_\Omega \left| \sqrt{\xi_k} \nabla \phi_k + \sqrt{\xi_k} |\nabla \phi_k| \nu_J \right|^2 dx$$
$$\leq P_\Omega(G) - \sum_{j=1}^{J} \mathcal{H}^{n-1}(K_j) - \sum_{j=J+1}^{\infty} \int_{K_j} \nu \cdot \nu_J \, d\mathcal{H}^{n-1}$$
$$= \sum_{j=J+1}^{\infty} \mathcal{H}^{n-1}(K_j) - \sum_{j=J+1}^{\infty} \int_{K_j} \nu \cdot \nu_J \, d\mathcal{H}^{n-1}$$
$$\leq 2 \sum_{j=J+1}^{\infty} \mathcal{H}^{n-1}(K_j)$$
$$\leq 2\sigma,$$

proving Claim (1). The proof is complete. □

References

[1] S. M. Allen and J. W. Cahn. A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening. *Acta Metall.*, 27:1085–1095, 1979.

[2] D. Andelman. Electrostatic properties of membranes: The Poisson–Boltzmann theory. In R. Lipowsky and E. Sackmann, editors, *Handbook of Biological Physics*, volume 1, pages 603–642. Elsevier, 1995.

[3] B. J. Berne, J. D. Weeks, and R. Zhou. Dewetting and hydrophobic interaction in physical and biological systems. *Annu. Rev. Phys. Chem.*, 60:85–103, 2009.

[4] J. W. Cahn and J. E. Hilliard. Free energy of a nonuniform system. I. interfacial free energy. *J. Chem. Phys.*, 28:258–267, 1958.

[5] Q. Cai, X. Ye, and R. Luo. Dielectric pressure in continuum electrostatic solvation of biomolecules. *Phys. Chem. Chem. Phys.*, 14:15917–15925, 2012.

[6] D. Chandler. Interfaces and the driving force of hydrophobic assembly. *Nature*, 437:640–647, 2005.

[7] J. Che, J. Dzubiella, B. Li, and J. A. McCammon. Electrostatic free energy and its variations in implicit solvent models. *J. Phys. Chem. B*, 112:3058–3069, 2008.

[8] H.-B. Cheng, L.-T. Cheng, and B. Li. Yukawa-field approximation of electrostatic free energy and dielectric boundary force. *Nonlinearity*, 24:3215–3236, 2011.

[9] L.-T. Cheng, Y. Xie, J. Dzubiella, J. A. McCammon, J. Che, and B. Li. Coupling the level-set method with molecular mechanics for variational implicit solvation of nonpolar molecules. *J. Chem. Theory Comput.*, 5:257–266, 2009.

[10] M. E. Davis and J. A. McCammon. Electrostatics in biomolecular structure and dynamics. *Chem. Rev.*, 90:509–521, 1990.

[11] J. Dzubiella, J. M. J. Swanson, and J. A. McCammon. Coupling hydrophobicity, dispersion, and electrostatics in continuum solvent models. *Phys. Rev. Lett.*, 96:087802, 2006.

[12] J. Dzubiella, J. M. J. Swanson, and J. A. McCammon. Coupling nonpolar and polar solvation free energies in implicit solvent models. *J. Chem. Phys.*, 124:084905, 2006.

[13] L. C. Evans and R. F. Gariepy. *Measure Theory and Fine Properties of Functions*. CRC Press, Boca Raton, FL, 1992.

[14] D. Gilbarg and N.S. Trudinger. *Elliptic Partial Differential Equations of Second Order*. Springer, 2nd edition, 1983.

[15] E. Giusti. *Minimal Surfaces and Functions of Bounded Variation*. Birkhauser, Boston, 1984.

[16] J. E. Hutchinson and Y. Tonegawa. Convergence of phase interfaces in the van der Waals–Cahn–Hilliard theory. *Calc. Var. Partial Differential Equations*, 10:49–84, 2000.

[17] T. Ilmanen. Convergence of the Allen–Cahn equation to Brakkes motion by mean curvature. *J. Diff. Geom.*, 38:417–461, 1993.

[18] B. Li. Minimization of electrostatic free energy and the Poisson–Boltzmann equation for molecular solvation with implicit solvent. *SIAM J. Math. Anal.*, 40:2536–2566, 2009.

[19] B. Li., X.-L. Cheng, and Z.-F. Zhang. Dielectric boundary force in molecular solvation with the Poisson–Boltzmann free energy: A shape derivative approach. *SIAM J. Applied Math.*, 71:2093–2111, 2011.

[20] B. Li and Y. Liu. Diffused solute-solvent interface with Poisson–Boltzmann electrostatics: Free-energy variation and sharp-interface limit. *SIAM J. Applied Math*, 75:2072–2092, 2015.

[21] B. Li and Y. Zhao. Variational implicit solvation with solute molecular mechanics: From diffuse-interface to sharp-interface models. *SIAM J. Applied Math.*, 73(1):1–23, 2013.

[22] K. Lum, D. Chandler, and J. D. Weeks. Hydrophobicity at small and large length scales. *J. Phys. Chem. B*, 103:4570–4577, 1999.

[23] M. Mizuno and Y. Tonegawa. Convergence of the Allen–Cahn equation with Neumann boundary conditions. *SIAM J. Math. Anal.*, 47:1906–1932, 2015.

[24] L. Modica. The gradient theory of phase transitions and the minimal interface criterion. *Arch. Rational Mech. Anal.*, 98:123–142, 1987.

[25] P. Padilla and Y. Tonegawa. On the convergence of stable phase transitions. *Commun. Pure Applied Math.*, LI:551–579, 1998.

[26] M. Röger and R. Schätzle. On a modified conjecture of De Giorgi. *Math. Z.*, 254:675–714, 2006.

[27] J. S. Rowlinson. Translation of J. D. van der Waals' "The thermodynamic theory of capillarity under the hypothesis of a continuous variation of Density". *J. Stat. Phys.*, 20:197–244, 1979.

[28] N. Sato. A simple proof of convergence of the Allen–Cahn equation to Brakkes motion by mean curvature. *Indiana Univ. Math. J.*, 57:1743–1751, 2008.

[29] K. A. Sharp and B. Honig. Electrostatic interactions in macromolecules: Theory and applications. *Annu. Rev. Biophys. Chem.*, 19:301–332, 1990.

[30] P. Sternberg. The effect of a singular perturbation on nonconvex variational problems. *Arch. Rational Mech. Anal.*, 101:209–260, 1988.

[31] H. Sun, J. Wen, Y. Zhao, B. Li, and J. A. McCammon. A self-consistent phase-field approach to implicit solvation of charged molecules with Poisson–Boltzmann electrostatics. *J. Chem. Phys.*, 143:243110, 2015.

[32] J. D. van der Waals. Thermodynamische theorie der capillariteit in de onderstelling van continue dichtheidsverandering. *Verhand. Kon. Akad. v Wetensch. Amst.*, Sect. 1, 1893 (in Dutch).

[33] Z. Wang, J. Che, L.-T. Cheng, J. Dzubiella, B. Li, and J. A. McCammon. Level-set variational implicit solvation with the Coulomb-field approximation. *J. Chem. Theory Comput.*, 8:386–397, 2012.

[34] L. Xiao, Q. Cai, X. Ye, J. Wang, and R. Luo. Electrostatic forces in the Poisson–Boltzmann systems. *J. Chem. Phys.*, 139:094106, 2013.

[35] Y. Zhao, Y. Kwan, J. Che, B. Li, and J. A. McCammon. Phase-field approach to implicit solvation of biomolecules with Coulomb-field approximation. *J. Chem. Phys.*, 139:024111, 2013.

[36] H. X. Zhou. Macromolecular electrostatic energy within the nonlinear Poisson–Boltzmann equation. *J. Chem. Phys.*, 100:3152–3162, 1994.

[37] S. Zhou, L.-T. Cheng, J. Dzubiella, B. Li, and J. A. McCammon. Variational implicit solvation with Poisson–Boltzmann theory. *J. Chem. Theory Comput.*, 10(4):1454–1467, 2014.

[38] W. P. Ziemer. *Weakly Differentiable Functions: Sobolev Spaces and Functions of Bounded Variation.* Springer, New York, 2002.