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VARIATIONAL IMPLICIT SOLVATION WITH SOLUTE MOLECULAR MECHANICS: FROM DIFFUSE-INTERFACE TO SHARP-INTERFACE MODELS*

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Abstract. Central in a variational implicit-solvent description of biomolecular solvation is an effective free-energy functional of the solute atomic positions and the solute-solvent interface (i.e., the dielectric boundary). The free-energy functional couples together the solute molecular mechanical interaction energy, the solute-solvent interfacial energy, the solute-solvent van der Waals interaction energy, and the electrostatic energy. In recent years, the sharp-interface version of the variational implicit-solvent model has been developed and used for numerical computations of molecular solvation. In this work, we propose a diffuse-interface version of the variational implicit-solvent model with solute molecular mechanics. We also analyze both the sharp-interface and diffuse-interface models. We prove the existence of free-energy minimizers and obtain their bounds. We also prove the convergence of the diffuse-interface model to the sharp-interface model in the sense of Γ-convergence. We further discuss properties of sharp-interface free-energy minimizers, the boundary conditions and the coupling of the Poisson–Boltzmann equation in the diffuse-interface model, and the convergence of forces from diffuse-interface to sharp-interface descriptions. Our analysis relies on the previous works on the problem of minimizing surface areas and on our observations on the coupling between solute molecular mechanical interactions with the continuum solvent. Our studies justify rigorously the self consistency of the proposed diffuse-interface variational models of implicit solvation.

Key words. solvation, solute molecular mechanics, implicit solvent, surface energy, van der Waals interaction, electrostatics, motion by mean curvature, sharp interface, diffuse interface, Γ-convergence

AMS subject classifications. 35J, 49S, 92C

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1. Introduction.

The interaction between biomolecules (such as proteins, nucleic acids, and lipid membranes) and their surrounding aqueous solvent (such as water or salted water) contributes significantly to the structure, dynamics, and functions of an underlying biomolecular system. Such interactions can be described efficiently by implicit-solvent (or continuum-solvent) models [19, 37]. In such a model, the solvent molecules and ions are treated implicitly and their effects are coarse-grained; cf. Figure 1.1. The description of the solvent is thus reduced to that of the solute-solvent interface (i.e., the dielectric boundary) and the related macroscopic quantities, such as the surface tension, dielectric coefficients, and bulk solvent density. Implicit-solvent models are complementary to the more accurate but also more expensive explicit-solvent models such as molecular dynamics simulations, which often provide sampled statistical information rather than direct thermodynamic descriptions.

With an implicit solvent, the conformation of a biomolecular system in equilibrium is described by all the atomic positions of solute molecules together with the solute-solvent interface. In the recently developed variational implicit-solvent model,

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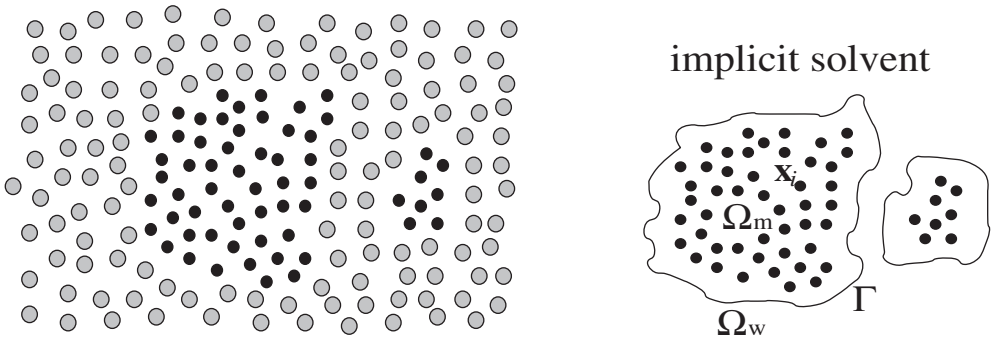

FIG. 1.1. *Schematic descriptions of a solvation system. Left: In a fully atomistic model, both the solute atoms (small dark dots) and solvent molecules (large gray dots) are degrees of freedom of the system. Right: In an implicit-solvent model, the solvent molecules are coarse-grained and the solvent is treated as a continuum. The solvent region* $\Omega_{\rm w}$ *and the solute region* $\Omega_{\rm m}$ *are separated by the solute-solvent interface (i.e., the dielectric boundary)* Γ. *The solute atoms are located at* $x_1, \ldots, x_N$ *inside* $\Omega_{\rm m}$.

such equilibrium solute atomic positions and solute-solvent interfaces are defined to minimize an effective free-energy functional; cf. [15, 16] and [9, 43] for more details. In a simple setting, the free-energy functional has the form

$$F[X,\Gamma] = E[X] + \gamma \mathrm{Area}(\Gamma) + \int_{\Omega_{\rm w}} U(X,x)\,dx. \tag{1.1}$$

Here the first term $E[X]$ is the potential energy of molecular mechanical interactions of solute atoms located at $x_1, \ldots, x_N$ inside the solute region $\Omega_{\rm m}$ (cf. Figure 1.1) and $X = (x_1, \ldots, x_N)$. The molecular mechanical interactions include the chemical bonding, bending, and torsion; the short-distance repulsion and the long-distance attraction; and the Coulombic charge-charge interaction.

The second term is an effective surface energy of the solute-solvent interface Γ that separates the solute region $\Omega_{\rm m}$ from the solvent region $\Omega_{\rm w}$, where γ is an effective surface energy density, assumed to be a constant. (The subscripts m and w stand for molecule and water, respectively.)

The last term models the solute-solvent interactions by an interaction potential $U(X,x)$ that is defined on all (X,x) with $X = (x_1, \ldots, x_N) \in \Omega_{\rm m}^N$ ($\Omega_{\rm m}^N = \Omega_{\rm m} \times \cdots \times \Omega_{\rm m}$ with N copies of $\Omega_{\rm m}$) and $x \in \Omega_{\rm w}$. There are mainly two types of solute-solvent interactions. One is the nonelectrostatic dispersive interaction that includes the repulsion due to the excluded-volume effect and the van der Waals attraction. Such interactions can be modeled by $\rho_w U_{\rm vdW}$, where $\rho_{\rm w}$ is the bulk solvent density and $U_{\rm vdW}$ is the potential defined by

$$U_{\rm vdW}(X,x) = \sum_{i=1}^{N} U_i(|x - x_i|). \tag{1.2}$$

Here, each $U_i(|x - x_i|)$ is the interaction potential between the solute particle at x_i and a solvent molecule or an ion located at $x \in \Omega_{\rm w}$. Practically, one can take the pairwise interaction U_i to be a Lennard-Jones potential

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

with ε_i and σ_i being effective parameters. The other is the electrostatic interaction for which the solute-solvent interface Γ is used as the dielectric boundary. In an implicit-solvent approach, the electrostatic interaction energy is often obtained by solving the Poisson–Boltzmann equation [12, 21, 24, 32, 40]. However, by using the Coulomb-field or Yukawa-field approximation, we can obtain, without solving the Poisson–Boltzmann equation, good approximations of the electrostatic interaction energy [5, 43]. In the Coulomb-field approximation, the electrostatic energy density is given by [43]

$$U_{\mathrm{ele}}(X,x) = \frac{1}{32\pi^2\varepsilon_{\mathrm{v}}}\left(\frac{1}{\varepsilon_{\mathrm{w}}} - \frac{1}{\varepsilon_{\mathrm{m}}}\right)\left|\sum_{i=1}^{N}\frac{Q_i(x-x_i)}{|x-x_i|^3}\right|^2,$$

where ε_{v} is the vacuum permittivity (often denoted by ε_0 in literature), ε_{m} and ε_{w} are the relative permittivities of the solute and solvent, respectively, and Q_i is the charge carried by the solute atom located at x_i. (Typical values of ε_{m} and ε_{w} are around 1 and 80, respectively.) The total solute-solvent interaction potential is then given by

$$U(X,x) = \rho_{\mathrm{w}} U_{\mathrm{vdW}}(X,x) + U_{\mathrm{ele}}(X,x), \qquad X \in \Omega_{\mathrm{m}}^N,\ x \in \Omega_{\mathrm{w}}. \tag{1.3}$$

For a fixed set of solute atoms $X = (x_1, \ldots, x_N)$, a solute-solvent interface Γ with a low free energy tends to minimize its surface area. On the other hand, the solute-solvent interaction modeled by the third term in (1.1) prevents the interface from being too close to the solute atoms located at x_i $(1 \le i \le N)$.

In [6], Cheng et al. developed a robust level-set method to minimize numerically the free-energy functional (1.1) for a fixed set of solute atoms X. The idea is to move an initially guessed solute-solvent interface that may have a large free energy in the direction of steepest descent of free energy, until a (local) minimizer is reached. The "velocity" of the moving interface is therefore given by the effective interface or boundary force that is defined to be the negative variational derivative of the free-energy functional with respect to the location change of the interface. This method has been improved, generalized, and applied to many more systems ranging from small molecules to proteins [7, 8, 9, 38, 43]. Extensive numerical results with comparison with molecular dynamics simulations have demonstrated the success of the level-set variational solvation in capturing the hydrophobic interaction, multiple equilibrium states of hydration, and fluctuations between such states.

In this work, we first propose a diffuse-interface variational implicit-solvent model, as an alternative to the original variational implicit-solvent model that uses a sharp-interface formulation, for molecular solvation. We then prove that the diffuse-interface model converges to the corresponding sharp-interface model in the sense of Γ-convergence.

Diffuse-interface approaches have been widely used in studying interface problems arising in many scientific areas, such as materials physics, complex fluids, and biomembranes; cf., e.g., [1, 4, 10, 14, 17, 22, 25, 30, 39] and the references therein. In a diffuse-interface model, an interface separating two regions is represented by a continuous function that takes values close to one constant in one of the regions and another constant in the other region, but smoothly changes its values from one of the constants to another in a thin transition region. Both the sharp-interface and the diffuse-interface approaches have their own advantages and disadvantages. Existing studies have shown that interfacial fluctuations can be described in a diffuse-interface approach [3, 26]. Such fluctuations are particularly crucial in the transition of one equilibrium conformation to another in a biomolecular system.

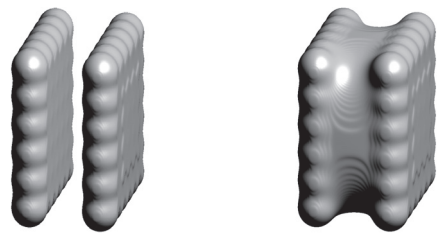

FIG. 1.2. *Numerical computations of a two-plate system based on the diffuse-interface version of the variational implicit-solvent model. Left: a tight-wrap equilibrium conformation. Right: a dewetting equilibrium conformation.*

Our diffuse-interface model is governed by the effective free-energy functional

$$F_\varepsilon[X,\phi] = E[X] + \gamma \int_\Omega \left[\frac{\varepsilon}{2}|\nabla\phi(x)|^2 + \frac{1}{\varepsilon}W(\phi(x))\right] dx + \int_\Omega [\phi(x)-1]^2\, U(X,x)\, dx. \tag{1.4}$$

Here $\varepsilon > 0$ is a small parameter. As in the sharp-interface variational solvation model, $X = (x_1, \ldots, x_N)$ and x_i is the position of the ith solute atom ($1 \le i \le N$). All the solute atoms are located inside the entire solvation region Ω. The function $\phi : \Omega \to \mathbb{R}$, often called an order parameter, describes the location of solute-solvent interface. The first term $E[X]$ is the same as in the sharp-interface model; cf. (1.1). The second term is an approximation of the surface energy of the solute-solvent interface, where the parameter γ is the constant surface energy density as before and the function $W = W(s)$ is a double-well potential with the two wells at $s = 0$ and $s = 1$ of equal depth. The last term is the solute-solvent interaction energy with the potential $U(X,x)$ being the same as in the sharp-interface model; cf. (1.3).

To obtain numerically equilibrium conformations of a charged molecular system, we fix the small parameter $\varepsilon > 0$ and solve numerically the equations of the gradient-flow of the free-energy functional (1.4),

$$\begin{cases} \dot{X} = -\nabla_X F_\varepsilon[X,\phi], \\ \partial_t \phi = -\delta_\phi F_\varepsilon[X,\phi], \end{cases}$$

for $X = X(t)$ and $\phi = \phi(x,t)$. Here and below, a dot on top denotes the derivative with respect to t, ∇_X denotes the gradient with respect to $X = (x_1, \ldots, x_N)$, and δ_ϕ denotes the variational derivative with respect to ϕ. Explicitly, the gradient-flow equations are

$$\begin{cases} \partial_t \phi = \gamma\left[\varepsilon\Delta\phi - \dfrac{1}{\varepsilon}W'(\phi)\right] - 2(\phi-1)U(X,\cdot) \qquad \text{in } \Omega, \\ \dot{X} = -\nabla_X E[X] - \displaystyle\int_\Omega [\phi(x)-1]^2\, \nabla_X U(X,x)\, dx. \end{cases} \tag{1.5}$$

The second equation is equivalent to the N vector-equations

$$\dot{x}_i = -\nabla_{x_i} E[X] - \int_\Omega [\phi(x)-1]^2\, \nabla_{x_i} U(X,x)\, dx, \qquad i = 1, \ldots, N.$$

In Figure 1.2, we show our diffuse-interface computational results of a two-plate molecular system that has been used as a prototype system in many molecular dynamics and continuum simulations [6, 7, 28, 29, 33, 43]. Each plate consists of 6×6

neutral atoms that are fixed in each of the two computations. We observe that the diffuse-interface model captures the two local minimizers of the system. We shall report more diffuse-interface computational results in our subsequent work.

The main body of this work is an analysis of the variational implicit-solvent models, both the sharp-interface and the diffuse-interface versions, for molecular solvation. Specifically, we prove the following:

(1) The sharp-interface free-energy functional $F = F[X, \Gamma]$, defined in (1.1), is minimized by a set of solute atoms X and the boundary of a measurable subset $A \subseteq \Omega$ that has a finite perimeter in Ω. Moreover, the minimum free energy can be approximated by the free energies of boundaries of sets that contain small balls centered at x_i $(1 \leq i \leq N)$; cf. Theorems 2.1 and 2.2.

(2) The existence of free-energy minimizers of the diffuse-interface free-energy functionals F_ε, defined in (1.4), and the bounds on such minimizers and on the minimum free energies; cf. Theorem 3.1.

(3) The convergence of the minimum free energies and the free-energy minimizers of the diffuse-interface free-energy functionals (1.4) to those of the corresponding sharp-interface free-energy functional (1.1); cf. Theorems 4.1, 4.2, and 4.3.

In addition, we discuss several issues. These include the regularity and other properties of sharp-interface free-energy minimizers, the boundary conditions in the diffuse-interface model, the convergence of the diffuse-interface forces to the sharp-interface forces, and the coupling of the Poisson–Boltzmann description of the electrostatic interaction in the diffuse-interface modeling. We discuss both the forces acting on the solute atoms and the dielectric boundary forces.

Our analysis relies on some of the properties of the underlying models, in particular the interplay between the solute particles X and the field ϕ, and on the existing studies on the diffuse-interface approximations of the motion by mean curvature with the constant-volume constraint [27, 34, 35, 41].

We notice that a diffuse-interface model for solvation is proposed in [11], where the surface energy is modeled by the integral of $\gamma|\nabla S|$ with γ being the surface energy density and S a field similar to our ϕ. However, there are no terms in the total free-energy functional G_{total} (cf. equation (7) in [11]) that can keep the field S to be close to two distinct values so that the system region can be partitioned into the solute and solvent regions by the field S. Unless an equilibrium boundary or field S is a priori known, the minimization of the total free-energy functional will smooth out the field S to reduce the surface energy.

In section 2, we describe the main assumptions on the interaction potentials $E[X]$ and $U(X, x)$. We also prove the existence of minimizers for the sharp-interface free-energy functional (1.1). In section 3, we prove the existence of minimizers for the diffuse-interface free-energy functional (1.4). We also prove some properties of such minimizers. In section 4, we prove the convergence of the minimum free energies and free-energy minimizers in passing the diffuse-interface to the sharp-interface description. Some lemmas are used in the proof. These lemmas are proved in the appendix. Finally, in section 5, we discuss several issues on the properties of sharp-interface free-energy minimizers, the boundary conditions, the convergence of forces, and the coupling of the Poisson–Boltzmann equation in the diffuse-interface modeling.

2. Sharp-interface free-energy minimizers. Let Ω be a nonempty, open, connected, and bounded subset of $\mathbb{R}^3$ with a Lipschitz-continuous boundary $\partial\Omega$. We use an overline to denote the closure of a set. So, $\overline{\Omega}$ is the closure of Ω in $\mathbb{R}^3$. Let

$N \geq 1$ be an integer and denote

$$O_N = \left\{ X = (x_1, \ldots, x_N) \in (\mathbb{R}^3)^N : x_i \neq x_j \text{ if } i \neq j \text{ for } 1 \leq i, j \leq N \right\}.$$

Clearly O_N is an open subset of $(\mathbb{R}^3)^N$. Let $E : \overline{\Omega}^N \to \mathbb{R} \cup \{+\infty\}$ satisfy the following assumptions:

(E1) $E[X] = +\infty$ if $X \in \overline{\Omega}^N \setminus (\Omega^N \cap O_N)$ and $E[X]$ is finite if $X \in \Omega^N \cap O_N$. Moreover, the restriction of E onto $\Omega^N \cap O_N$ is a continuous function.

(E2) $E_{\min} := \inf_{X \in \overline{\Omega}^N} E(X)$ is finite.

(E3) $E[X] \to +\infty$ as $\min_{1 \leq i < j \leq N} |x_i - x_j| \to 0$.

(E4) $E[X] \to +\infty$ as $\min_{1 \leq i \leq N} \operatorname{dist}(x_i, \partial\Omega) \to 0$.

The function $E = E[X]$ with $X = (x_1, \ldots, x_N)$ models the potential of the molecular mechanical interactions among the solute atoms located at $x_1, \ldots, x_N$. Assumption (E1) states that $E[X] = +\infty$ if two different atoms occupy the same position, i.e., $x_i = x_j$ for some i and j with $i \neq j$, or an atom is on the boundary, i.e., $x_i \in \partial\Omega$ for some i. Parts of assumption (E1) and assumption (E3) describe the repulsion of solute atoms. Parts of assumption (E1) and assumption (E4) can be viewed as a consequence of the assumption that $E[X] \to +\infty$ as $\min_{1 \leq i \leq N} |x_i - \overline{X}| \to 0$, where $\overline{X} = (1/N) \sum_{i=1}^N x_i$ is the geometrical center of the solute atoms. This models the connectivity of these atoms as a network. In practice, the open set Ω is an underlying computational region, and the solute atoms will be always kept inside Ω.

Let $U : \overline{\Omega}^N \times \overline{\Omega} \to \mathbb{R} \cup \{+\infty\}$ satisfy the following assumptions:

(U1) $U(X, x) = +\infty$ if $(X, x) = (x_1, \ldots, x_N, x) \in \overline{\Omega}^{N+1} \setminus \left((\Omega^N \times \overline{\Omega}) \cap O_{N+1} \right)$ and $U(X, x)$ is finite if $(X, x) \in (\Omega^N \times \overline{\Omega}) \cap O_{N+1}$. Moreover, the restriction of U onto $(\Omega^N \times \overline{\Omega}) \cap O_{N+1}$ is a continuous function.

(U2) $U_{\min} := \inf_{\overline{\Omega}^N \times \overline{\Omega}} U(X, x)$ is finite.

(U3) $U(X, x) \to +\infty$ as $\min_{0 \leq i < j \leq N} |x_i - x_j| \to 0$, where $x_0 = x$.

The function $U = U(X, x)$ describes the solute-solvent interactions. Parts of assumption (U1) and assumption (U3) model the repulsion in such interactions.

We recall that a function $f \in L^1(\Omega)$ is said to have bounded variations in Ω if

$$\int_\Omega |\nabla f| \, dx := \sup \left\{ \int_\Omega f \operatorname{div} g \, dx : g \in C_c^1(\Omega, \mathbb{R}^3), |g| \leq 1 \text{ in } \Omega \right\} < \infty, \tag{2.1}$$

where $C_c^1(\Omega, \mathbb{R}^3)$ denotes the space of all C^1-mappings from Ω to $\mathbb{R}^3$ that are compactly supported inside Ω; cf. [18, 23, 44]. If $f \in W^{1,1}(\Omega)$, then the value defined by (2.1) is the same as $\|\nabla f\|_{L^1(\Omega)}$. The space $BV(\Omega)$ of all $L^1(\Omega)$-functions that have bounded variations in Ω is a Banach space with the norm

$$\|f\|_{\mathrm{BV}(\Omega)} := \|f\|_{L^1(\Omega)} + \int_\Omega |\nabla f| \, dx \qquad \forall f \in BV(\Omega).$$

For any $A \subseteq \mathbb{R}^3$, we denote by χ_A the characteristic function of A: $\chi_A(x) = 1$ if $x \in A$ and $\chi_A(x) = 0$ if $x \notin A$. If A is Lebesgue measurable, then the perimeter of A in Ω is defined by [18, 23, 44]

$$P_\Omega(A) := \int_\Omega |\nabla \chi_A| \, dx.$$

We denote

$$\mathcal{M}_0 = \left\{ (X, A) : X \in \overline{\Omega}^N, A \subseteq \Omega, A \text{ is Lebesgue measurable} \right\}.$$

Let $\gamma > 0$ be given. For any $(X, A) \in \mathcal{M}_0$, we define

$$F_0[X, A] = E[X] + \gamma P_\Omega(A) + \int_{\Omega \setminus A} U(X, x)\, dx. \tag{2.2}$$

Since E and U are bounded below, $F_0(X, A) > -\infty$. If $A \subset \Omega$ is open and smooth, with a finite perimeter in Ω, then $F_0(X, A) = F(X, \Gamma)$, where $\Gamma = \partial A$ and F is defined in (1.1) with $\Omega_{\mathrm{w}} = \Omega \setminus A$. Therefore, $F_0 : \mathcal{M}_0 \to \mathbb{R} \cup \{+\infty\}$ describes the free energy of a solvation system with A being the solute region.

We denote by $B(y, r)$ the open ball in $\mathbb{R}^3$ centered at $y \in \mathbb{R}^3$ with radius $r > 0$. For convenience in the analysis of the solute effect, we introduce the following.

Definition 2.1. *Let $X = (x_1, \dots, x_N) \in \Omega^N \cap O_N$ and $\sigma > 0$. We call $B(X, \sigma) := \cup_{i=1}^N B(x_i, \sigma)$ a σ-core of X in Ω associated with the potential $U(X, \cdot)$, or simply an X-core, if the following are satisfied:* (1) $B(X, \sigma) \subseteq \Omega$; (2) $\overline{B(x_i, \sigma)} \cap \overline{B(x_j, \sigma)} = \emptyset$ *if* $i \neq j$; *and* (3) $U(X, x) \geq 0$ *for all* $x \in B(X, \sigma)$.

It follows from assumption (U3) that $B(X, \sigma)$ is an X-core if $X \in \Omega^N \cap O_N$ and $\sigma > 0$ is sufficiently small.

Our first theorem asserts the existence of a global minimizer of the sharp-interface free-energy functional $F_0 : \mathcal{M}_0 \to \mathbb{R} \cup \{+\infty\}$. This is a standard result and can be proved by the direct methods in the calculus of variations. To show how the solute atoms located at $x, \dots, x_N$ can be analyzed, here we give a complete proof of the theorem.

Theorem 2.1. *There exists $(X, A) \in \mathcal{M}_0$ such that*

$$F_0[X, A] = \inf_{(Y,B) \in \mathcal{M}_0} F_0[Y, B].$$

Moreover, this minimum value is finite.

Proof. Let $\alpha = \inf_{(Y,B)\in\mathcal{M}_0} F_0[Y, B]$. Since E and U are bounded below, $\alpha > -\infty$. Fix $X_0 \in \Omega^N \cap O_N$. Let $A_0 = B(X_0, \sigma)$ be an X_0-core. Then $(X_0, A_0) \in \mathcal{M}_0$. Note that $U(X_0, \cdot)$ is bounded on $\overline{\Omega} \setminus A_0$. Hence $F_0[X_0, A_0] < \infty$, and α is finite. There now exist $(X_k, A_k) \in \mathcal{M}_0$ $(k = 1, 2, \dots)$ such that $\lim_{k\to\infty} F_0[X_k, A_k] = \alpha$ and that $F_0[X_k, A_k]$ is finite for each $k \geq 1$. The lower boundedness of E and U implies that $\{P_\Omega(A_k)\}_{k=1}^\infty$ is bounded. This further implies that the sequence

$$\int_{\Omega \setminus A_k} U(X_k, x)\, dx \quad (k = 1, 2, \dots)$$

is bounded and finally that $\{E[X_k]\}_{k=1}^\infty$ is bounded.

Since $\{X_k\}_{k=1}^\infty$ is bounded, it has a subsequence, not relabeled, such that $X_k \to X$ as $k \to \infty$ for some $X \in \overline{\Omega}^N$. It follows from the boundedness of $\{E[X_k]\}_{k=1}^\infty$ and our assumptions on E that $X \in \Omega^N \cap O_N$. Moreover, the continuity of E at X implies that

$$\lim_{k\to\infty} E[X_k] = E[X]. \tag{2.3}$$

By the boundedness of $\{P_\Omega(A_k)\}_{k=1}^\infty$ and the compact embedding $BV(\Omega) \hookrightarrow L^1(\Omega)$, there exists a subsequence of $\{\chi_{A_k}\}$, not relabeled, such that $\chi_{A_k} \to \chi_A$ in $L^1(\Omega)$ for some Lebesgue measurable set $A \subseteq \Omega$. Moreover,

$$P_\Omega(A) \le \liminf_{k\to\infty} P_\Omega(A_k). \tag{2.4}$$

Clearly $(X, A) \in \mathcal{M}_0$. Passing to a further subsequence of $\{\chi_{A_k}\}_{k=1}^\infty$ if necessary, we may assume that $\chi_{A_k} \to \chi_A$ a.e. in Ω. Applying Fatou's lemma and using the fact that $\chi_{A_k} \to \chi_A$ in $L^1(\Omega)$, we obtain

$$\begin{aligned}
&\liminf_{k\to\infty} \int_{\Omega\setminus A_k} U(X_k, x)\, dx \\
&\quad = \liminf_{k\to\infty} \left\{ \int_\Omega \chi_{\Omega\setminus A_k}(x) \left[U(X_k, x) - U_{\min}\right] dx + \int_\Omega \chi_{\Omega\setminus A_k}(x) U_{\min}\, dx \right\} \\
&\quad = \liminf_{k\to\infty} \int_\Omega \chi_{\Omega\setminus A_k}(x) \left[U(X_k, x) - U_{\min}\right] dx + \lim_{k\to\infty} \int_\Omega \chi_{\Omega\setminus A_k}(x) U_{\min}\, dx \\
&\quad \ge \int_\Omega \chi_{\Omega\setminus A}(x) \left[U(X, x) - U_{\min}\right] dx + \int_\Omega \chi_{\Omega\setminus A}(x) U_{\min}\, dx \\
&\quad = \int_{\Omega\setminus A} U(X, x)\, dx. \qquad (2.5)
\end{aligned}$$

Now (2.3), (2.4), and (2.5) imply

$$F_0[X, A] \le \liminf_{k\to\infty} F_0[X_k, A_k].$$

Hence $F_0[X, A] = \alpha$. ∎

We now prove that the minimum value of the free-energy functional $F_0 : \mathcal{M}_0 \to \mathbb{R} \cup \{+\infty\}$ can be approximated by free energies of certain "regular" subsets. To this end, we denote by $\mathcal{A}_0$ the class of subsets $E \cap \Omega$ such that

(1) E is an open subset of $\mathbb{R}^3$ with a nonempty, compact, C^∞ boundary ∂E;
(2) $\partial E \cap \Omega$ is C^2;
(3) $\mathcal{H}_2(\partial E \cap \partial\Omega) = 0$.

Here and below $\mathcal{H}_2(S)$ denotes the two-dimensional Hausdorff measure of a set $S \subseteq \mathbb{R}^3$. We denote

$$\mathcal{R}_0 = \{(X, A) \in \mathcal{M}_0 : X \in \Omega^N \cap O_N, A \in \mathcal{A}_0, \text{ and } A \text{ contains an } X\text{-core}\}. \tag{2.6}$$

THEOREM 2.2. *We have*

$$\inf_{(X,A)\in\mathcal{M}_0} F_0[X, A] = \inf_{(X,A)\in\mathcal{R}_0} F_0[X, A]. \tag{2.7}$$

To prove this theorem, we need two lemmas. We denote by $\sigma_k \downarrow 0$ if $\sigma_1 > \cdots > \sigma_k > \cdots$ and $\lim_{k\to\infty} \sigma_k = 0$.

LEMMA 2.1. *Let $(X, A) \in \mathcal{M}_0$. Let $\sigma_k > 0$ $(k = 1, 2, \dots)$ be such that $\sigma_k \downarrow 0$ and that $B(X, \sigma_k)$ $(k = 1, 2, \dots)$ are all X-cores. We have*

$$\limsup_{k\to\infty} F_0[X, A \cup B(X, \sigma_k)] \le F_0[X, A]. \tag{2.8}$$

Proof. If $F_0[X,A]=\infty$, then (2.8) is true. Assume $F_0[X,A]<\infty$. Since both E and U are bounded below, this implies that $P_\Omega(A)<\infty$. Moreover,

$$\begin{aligned}\limsup_{k\to\infty} P_\Omega(A\cup B(X,\sigma_k)) &\le \limsup_{k\to\infty}\,[P_\Omega(A)+P_\Omega(B(X,\sigma_k))]\\ &= P_\Omega(A)+\lim_{k\to\infty} P_\Omega(B(X,\sigma_k)) = P_\Omega(A).\end{aligned} \tag{2.9}$$

It is easy to verify that for each $k\ge 1$

$$\Omega\setminus A = [\Omega\setminus(A\cup B(X,\sigma_k))]\cup[B(X,\sigma_k)\setminus A] \quad \text{and} \quad [\Omega\setminus(A\cup B(X,\sigma_k))]\cap[B(X,\sigma_k)\setminus A]=\emptyset.$$

Since $U(X,x)\ge 0$ for all $x\in B(X,\sigma_k)$ for each $k\ge 1$, we then have

$$\begin{aligned}\int_{\Omega\setminus(A\cup B(X,\sigma_k))} U(X,x)\,dx &\le \int_{\Omega\setminus(A\cup B(X,\sigma_k))} U(X,x)\,dx + \int_{B(X,\sigma_k)\setminus A} U(X,x)\,dx\\ &= \int_{\Omega\setminus A} U(X,x)\,dx, \qquad k=1,2,\dots.\end{aligned}$$

This, (2.9), and (2.2) (the definition of F_0) imply (2.8). ∎

LEMMA 2.2. *Let $(X,A)\in\mathcal{M}_0$ be such that $X\in\Omega^N\cap O_N$, $P_\Omega(A)<\infty$, and A contains an X-core. Then for each integer $k\ge 1$ there exists $A_k\subseteq\mathcal{A}_0$ such that A_k contains an X-core and*

$$\lim_{k\to\infty} F_0[X,A_k]=F_0[X,A]. \tag{2.10}$$

This lemma is very similar to Lemma 1 in [34] and Lemma 1 in [41]. The volume constraint there, which gives rise to rather technical difficulties, is replaced here by the integral term in the free-energy functional F_0.

Proof of Lemma 2.2. Assume A contains an X-core $B(X,\sigma)$. Since $P_\Omega(A)<\infty$, there exists $u\in \mathrm{BV}(\mathbb{R}^3)\cap L^\infty(\mathbb{R}^3)$ such that $u=\chi_A$ in Ω and

$$\int_{\partial\Omega} |\nabla u|\,dx = 0; \tag{2.11}$$

cf. (3) in [34]. Notice that $u=1$ on $B(X,\sigma)$. By using mollifiers, we can construct $u_k\in C^\infty(\mathbb{R}^3)$ $(k=1,2,\dots)$ such that $u_k=1$ in $B(X,\sigma/2)$ $(k=1,2,\dots)$, $u_k\to u$ in $L^1(\Omega)$, and using (2.11)

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

cf. sections 2.8 and 2.16 in [23]. For a given $t\in\mathbb{R}$, we define $E_k=\{x\in\mathbb{R}^3 : u_k(x)>t\}$ $(k=1,2,\dots)$. Clearly, each E_k is an open subset of $\mathbb{R}^3$. Following the proof of Lemma 1 in [34] and Lemma 1 in [41], there exist $t\in(0,1)$ and a subsequence of $\{E_k\}_{k=1}^\infty$, not relabeled, that satisfy the following properties: (1) for each $k\ge 1$, $E_k\supseteq B(X,\sigma/2)$; (2) for each k, the boundary ∂E_k is nonempty, compact, and C^∞; and $\partial E_k\cap\Omega$ is C^2; (3) for each $k\ge 1$, $\mathcal{H}_2(\partial E_k\cap\partial\Omega)=0$; (4) $\chi_{E_k\cap\Omega}\to\chi_A$ in $L^1(\Omega)$ as $k\to\infty$; and (5) $P_\Omega(E_k\cap A)\to P_\Omega(A)$ as $k\to\infty$.

Let $A_k=E_k\cap\Omega$ $(k=1,2,\dots)$. Clearly, for each $k\ge 1$, $A_k\in\mathcal{A}_0$ and A_k contains the X-core $B(X,\sigma/2)$. Since $U(X,\cdot)$ is bounded on $\overline{\Omega}\setminus B(X,\sigma/2)$, we have by the

fact that $\chi_{A_k} \to \chi_A$ in $L^1(\Omega)$ that

$$\lim_{k\to\infty} \int_{\Omega\setminus A_k} U(X,x)\,dx = \int_{\Omega\setminus A} U(X,x)\,dx.$$

This and the fact that $P_\Omega(A_k) \to P_\Omega(A)$ as $k \to \infty$ imply (2.10). ∎

We are now ready to prove Theorem 2.2.

Proof of Theorem 2.2. Clearly,

$$\inf_{(X,A)\in\mathcal{M}_0} F_0[X,A] \le \inf_{(X,A)\in\mathcal{R}_0} F_0[X,A].$$

By Theorem 2.1, the infimum of F_0 over $\mathcal{M}_0$, which is finite, is attained by some $(X_0, A_0) \in \mathcal{M}_0$. Clearly, $X_0 \in \Omega^N \cap O_N$ and $P_\Omega(A_0) < \infty$. Let $B(X_0, \sigma_k)$ $(k = 1, 2, \dots)$ be X_0-cores with $\sigma_k \downarrow 0$. It follows from Lemma 2.1 that

$$\begin{aligned} F_0[X_0, A_0] &\le \liminf_{k\to\infty} F_0[X_0, A_0 \cup B(X_0,\sigma_k)] \\ &\le \limsup_{k\to\infty} F_0[X_0, A_0 \cup B(X_0,\sigma_k)] \le F_0[X_0, A_0], \end{aligned}$$

leading to

$$\lim_{k\to\infty} F_0[X_0, A_0 \cup B(X_0,\sigma_k)] = F_0[X_0, A_0]. \tag{2.12}$$

For each $k \ge 1$, the set $A_0 \cup B(X_0, \sigma_k)$ has a finite perimeter in Ω. Therefore, by Lemma 2.2, there exists $A_k \in \mathcal{A}_0$ containing an X_0-core, such that

$$|F_0[X_0, A_k] - F_0[X_0, A_0 \cup B(X_0,\sigma_k)]| \le \frac{1}{k}.$$

This and (2.12) imply (2.7), since $(X_0, A_k) \in \mathcal{R}_0$ $(k = 1, 2, \dots)$. ∎

3. Diffuse-interface free-energy minimizers. We define $W : \mathbb{R} \to \mathbb{R}$ by

$$W(t) = 18t^2(1-t)^2 \qquad \forall t \in \mathbb{R}.$$

Note that

$$\int_0^1 \sqrt{W(t)}\,dt = \frac{1}{\sqrt{2}}. \tag{3.1}$$

Let $\varepsilon_0 \in (0,1)$. Let $\mathcal{M} = \overline{\Omega}^N \times H^1(\Omega)$. By the lower boundedness of the functions E and U, $F_\varepsilon[X,\phi] > -\infty$ for any $(X,\phi) \in \mathcal{M}$ and any $\varepsilon \in (0, \varepsilon_0]$, where $F_\varepsilon[X,\phi]$ is defined in (1.4). We consider the family of functionals $F_\varepsilon : \mathcal{M} \to \mathbb{R} \cup \{+\infty\}$ $(0 < \varepsilon \le \varepsilon_0)$.

THEOREM 3.1. *For each $\varepsilon \in (0, \varepsilon_0]$, there exists $(X_\varepsilon, \phi_\varepsilon) \in \mathcal{M}$ with $X_\varepsilon \in \Omega^N \cap O_N$ such that*

$$F_\varepsilon[X_\varepsilon, \phi_\varepsilon] = \inf_{(X,\phi)\in\mathcal{M}} F_\varepsilon[X,\phi], \tag{3.2}$$

and this infimum value is finite. Moreover, there exist constants C_1 and C_2 such that

$$C_1 \le \min_{(X,\phi)\in\mathcal{M}} F_\varepsilon[X,\phi] \le C_2 \qquad \forall \varepsilon \in (0, \varepsilon_0]. \tag{3.3}$$

If $(X_\varepsilon, \phi_\varepsilon) \in \mathcal{M}$ *satisfies* (3.2) *for each* $\varepsilon \in (0, \varepsilon_0]$, *then*

$$\phi_\varepsilon(x) \le 1 \qquad a.e.\, x \in \Omega \ \forall \varepsilon \in (0, \varepsilon_0]. \tag{3.4}$$

Moreover, there exists a constant C_3 *such that*

$$\begin{aligned} &\varepsilon \|\nabla \phi_\varepsilon\|^2_{L^2(\Omega)} + \frac{1}{\varepsilon}\|W(\phi_\varepsilon)\|_{L^1(\Omega)} + \|\phi_\varepsilon\|^4_{L^4(\Omega)} \\ &\quad + \left| \int_\Omega [\phi_\varepsilon(x) - 1]^2\, U(X_\varepsilon, x)\, dx \right| \le C_3 \qquad \forall \varepsilon \in (0, \varepsilon_0]. \end{aligned} \tag{3.5}$$

The following lemma provides a lower bound of the functionals F_ε $(0 < \varepsilon \le \varepsilon_0)$; it will be used in the proof of Theorem 3.1 and other results.

LEMMA 3.1. *There exists* $C_4 \in \mathbb{R}$ *such that*

$$F_\varepsilon[X, \phi] \ge C_4 + \frac{\gamma}{2}\left[\varepsilon \|\nabla \phi\|^2_{L^2(\Omega)} + \frac{1}{\varepsilon}\|W(\phi)\|_{L^1(\Omega)} + \|\phi\|^4_{L^4(\Omega)}\right] \qquad \forall (X, \phi) \in \mathcal{M}\, \forall \varepsilon \in (0, \varepsilon_0].$$

Proof. Let $(X, \phi) \in \mathcal{M}$. We have

$$\begin{aligned} F_\varepsilon[X, \phi] &\ge E_{\min} + \frac{\gamma\varepsilon}{2}\|\nabla \phi\|^2_{L^2(\Omega)} + \frac{\gamma}{2\varepsilon}\int_\Omega W(\phi)\, dx + \frac{\gamma}{2\varepsilon_0}\int_\Omega W(\phi)\, dx \\ &\quad + U_{\min}\int_\Omega (\phi - 1)^2\, dx \\ &= E_{\min} + \frac{\gamma\varepsilon}{2}\|\nabla \phi\|^2_{L^2(\Omega)} + \frac{\gamma}{2\varepsilon}\|W(\phi)\|_{L^1(\Omega)} + \frac{\gamma}{2}\|\phi\|^4_{L^4(\Omega)} + \int_\Omega g(\phi)\, dx, \end{aligned}$$

where

$$g(\phi) = \frac{\gamma}{2\varepsilon_0}\left[W(\phi) - \varepsilon_0 \phi^4\right] + U_{\min}(\phi - 1)^2.$$

Notice that $g : \mathbb{R} \to \mathbb{R}$ is continuous and $g(s) \to +\infty$ as $|s| \to +\infty$. The desired bound is now obtained by setting $C_4 = E_{\min} + |\Omega| \inf_{s \in \mathbb{R}} g(s)$. ∎

Proof of Theorem 3.1. Fix $\varepsilon \in (0, \varepsilon_0]$. Let $\beta = \inf_{(X,\phi)\in\mathcal{M}} F_\varepsilon[X, \phi]$. Fix $X \in \Omega^N \cap O_N$ and define $\phi(x) = 1$ for all $x \in \Omega$. Then $(X, \phi) \in \mathcal{M}$ and $F_\varepsilon[X, \phi] = E[X]$, which is finite. Hence $\beta < +\infty$. By Lemma 3.1, $\beta > -\infty$. Therefore β is finite. It now follows that there exist $(X_k, \phi_k) \in \mathcal{M}$ $(k = 1, 2, \dots)$ such that $F_\varepsilon[X_k, \phi_k] \to \beta$ as $k \to \infty$ and that $F_\varepsilon[X_k, \phi_k]$ is finite for each $k \ge 1$. By Lemma 3.1 and the lower boundedness of E and U, all the sequences $\|\phi_k\|_{H^1(\Omega)}$, $E[X_k]$,

$$\int_\Omega \left[\frac{\varepsilon}{2}|\nabla \phi_k|^2 + \frac{1}{\varepsilon}W(\phi_k)\right] dx, \quad \text{and} \quad \int_\Omega [\phi_k(x) - 1]^2\, U(X_k, x)\, dx$$

$(k = 1, 2, \dots)$ are bounded.

Since $\{X_k\}_{k=1}^\infty$ is bounded in $(\mathbb{R}^3)^N$, it has a subsequence, not relabeled, that converges to some $X_\varepsilon \in \overline{\Omega}^N$. By the boundedness of $\{E[X_k]\}_{k=1}^\infty$ and our assumptions on E, $X_\varepsilon \in \Omega^N \cap O_N$. Since $\{\phi_k\}_{k=1}^\infty$ is bounded in $H^1(\Omega)$, there exist $\phi_\varepsilon \in H^1(\Omega)$ and a subsequence of $\{\phi_k\}_{k=1}^\infty$, not relabeled, such that $\phi_k \rightharpoonup \phi_\varepsilon$ (weak convergence) in $H^1(\Omega)$, $\phi_k \to \phi_\varepsilon$ in $L^2(\Omega)$, and $\phi_k \to \phi_\varepsilon$ a.e. in Ω. The weak convergence $\phi_k \rightharpoonup \phi_\varepsilon$ in $H^1(\Omega)$ implies that

$$\liminf_{k\to\infty} \int_\Omega |\nabla \phi_k|^2 dx \ge \int_\Omega |\nabla \phi_\varepsilon|^2 dx.$$

By the continuities of E and U in their respective regions and Fatou's lemma, we have

$$\begin{aligned}
\beta &= \liminf_{k\to\infty} F_\varepsilon[X_k,\phi_k] \\
&\geq \lim_{k\to\infty} E[X_k] + \frac{\gamma\varepsilon}{2}\liminf_{k\to\infty}\int_\Omega |\nabla\phi_k|^2 dx + \frac{\gamma}{\varepsilon}\liminf_{k\to\infty}\int_\Omega W(\phi_k)\,dx \\
&\quad + \liminf_{k\to\infty}\int_\Omega [\phi_k(x)-1]^2\,[U(X_k,x)-U_{\min}]\,dx + U_{\min}\lim_{k\to\infty}\int_\Omega [\phi_k(x)-1]^2\,dx \\
&\geq E[X_\varepsilon] + \gamma\int_\Omega\left[\frac{\varepsilon}{2}|\nabla\phi_\varepsilon|^2 + \frac{1}{\varepsilon}W(\phi_\varepsilon)\right]dx \\
&\quad + \int_\Omega [\phi_\varepsilon(x)-1]^2\,[U(X_\varepsilon,x)-U_{\min}]\,dx + U_{\min}\int_\Omega [\phi_\varepsilon(x)-1]^2\,dx \\
&= F_\varepsilon[X_\varepsilon,\phi_\varepsilon] \\
&\geq \beta.
\end{aligned}$$

This proves (3.2).

The lower bound in (3.3) follows from Lemma 3.1. Thus we need only to prove the upper bound in (3.3). Fix $X^* = (x_1^*,\ldots,x_N^*) \in \Omega^N \cap O_N$. Let $B(X^*,2\sigma) = \cup_{i=1}^N B(x_i^*,2\sigma)$ be an X^*-core with $\sigma\in(0,\varepsilon_0)$. Let $\varepsilon\in(0,\sigma]$. Define $h_\varepsilon:[0,2\sigma]\to\mathbb{R}$ by

$$h_\varepsilon(r) = \begin{cases} 1 & \text{if } 0\leq r<2\sigma-\varepsilon, \\ \dfrac{2\sigma-r}{\varepsilon} & \text{if } 2\sigma-\varepsilon\leq r\leq 2\sigma. \end{cases}$$

Define $\phi_\varepsilon^*:\Omega\to\mathbb{R}$ by

$$\phi_\varepsilon^*(x) = \begin{cases} 0 & \text{if } x\in\Omega\setminus B(X^*,2\sigma), \\ h_\varepsilon(|x-x_i^*|) & \text{if } x\in B(x_i^*,2\sigma), \quad i=1,\ldots,N. \end{cases}$$

Clearly $\phi_\varepsilon^*\in H^1(\Omega)$. Moreover, using the spherical coordinates we have that

$$\begin{aligned}
\int_\Omega\left[\frac{\varepsilon}{2}\left|\nabla\phi_\varepsilon^*\right|^2 + \frac{1}{\varepsilon}W\left(\phi_\varepsilon^*\right)\right]dx &= 4\pi N\int_0^{2\sigma}\left[\frac{\varepsilon}{2}\left|h_\varepsilon'(r)\right|^2 + \frac{1}{\varepsilon}W\left(h_\varepsilon(r)\right)\right]r^2\,dr \\
&= \frac{2\pi N}{\varepsilon}\int_{2\sigma-\varepsilon}^{2\sigma}\left[1+2W\left(h_\varepsilon(r)\right)\right]r^2\,dr \\
&\leq 8\pi\sigma^2 N\left[1+2\max_{0\leq s\leq 1}W(s)\right]. \qquad (3.6)
\end{aligned}$$

Since $\phi_\varepsilon^*=1$ on $B(X^*,\sigma)$ and $U(X^*,\cdot)$ is bounded on $K:=\overline{\Omega}\setminus B(X^*,\sigma)$, we have

$$\int_\Omega [\phi_\varepsilon^*(x)-1]^2\,U(X^*,x)\,dx = \int_K [\phi_\varepsilon^*(x)-1]^2\,U(X^*,x)\,dx \leq |K|\sup_{x\in K}|U(X^*,x)|. \qquad (3.7)$$

For each $\varepsilon\in(\sigma,\varepsilon_0]$, we define $\phi_\varepsilon^*=\phi_\sigma^*\in H^1(\Omega)$. It follows from (3.6) that

$$\begin{aligned}
\int_\Omega\left[\frac{\varepsilon}{2}\left|\nabla\phi_\varepsilon^*\right|^2 + \frac{1}{\varepsilon}W\left(\phi_\varepsilon^*\right)\right]dx &\leq \frac{\varepsilon_0}{\sigma}\int_\Omega\left[\frac{\sigma}{2}\left|\nabla\phi_\sigma^*\right|^2 + \frac{1}{\sigma}W\left(\phi_\sigma^*\right)\right]dx \\
&\leq 8\pi\sigma\varepsilon_0 N\left[1+2\max_{0\leq s\leq 1}W(s)\right]. \qquad (3.8)
\end{aligned}$$

Setting

$$C_2 = E[X^*] + 8\pi\gamma\sigma\varepsilon_0 N\left[1 + 2\max_{0\le s\le 1} W(s)\right] + |K|\sup_{x\in K}|U(X^*, x)|,$$

which is independent of $\varepsilon \in (0, \varepsilon_0]$, we obtain the upper bound in (3.3) by (1.4) (the definition of F_ε), (3.6), (3.8), and (3.7) (which includes the case that $\varepsilon = \sigma$).

Assume now $\varepsilon \in (0, \varepsilon_0]$ and $(X_\varepsilon, \phi_\varepsilon) \in \mathcal{M}$ satisfies (3.2). Denote by $|S|$ the Lebesgue measure of a Lebesgue measurable subset S of $\mathbb{R}^3$. Assume $|\{x \in \Omega : \phi_\varepsilon(x) > 1\}| > 0$. Define

$$\hat{\phi}_\varepsilon(x) = \begin{cases} \phi_\varepsilon(x) & \text{if } \phi_\varepsilon(x) \le 1, \\ 2 - \phi_\varepsilon(x) & \text{if } \phi_\varepsilon(x) > 1. \end{cases}$$

Clearly, $\hat{\phi}_\varepsilon \in H^1(\Omega)$. Moreover, $|\nabla\hat{\phi}_\varepsilon| = |\nabla\phi_\varepsilon|$ and $(\hat{\phi}_\varepsilon - 1)^2 = (\phi_\varepsilon - 1)^2$ a.e. $x \in \Omega$. If $\phi_\varepsilon(x) > 1$, then $|\hat{\phi}_\varepsilon(x)| < |\phi_\varepsilon(x)|$ and $|\hat{\phi}_\varepsilon(x) - 1| = |\phi_\varepsilon(x) - 1| > 0$. Hence $W(\hat{\phi}_\varepsilon) < W(\phi_\varepsilon)$ on $\{x \in \Omega : \phi_\varepsilon(x) > 1\}$. Consequently, $F_\varepsilon(X_\varepsilon, \hat{\phi}_\varepsilon) < F_\varepsilon(X_\varepsilon, \phi_\varepsilon)$. This contradicts (3.2). Therefore, (3.4) holds true.

Finally, the inequality (3.5) follows from (3.3), Lemma 3.1, and the lower boundedness of E and U. ∎

4. Convergence of minimum free energies and free-energy minimizers. We first prove the convergence of the global minimum free energies and the global free-energy minimizers.

THEOREM 4.1. *Let $\varepsilon_k \in (0, \varepsilon_0]$ $(k = 1, 2, \dots)$ be such that $\varepsilon_k \downarrow 0$. For each $k \ge 1$, let $(X_{\varepsilon_k}, \phi_{\varepsilon_k}) \in \mathcal{M}$ be such that*

$$F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}] = \min_{(X,\phi)\in\mathcal{M}} F_{\varepsilon_k}[X, \phi]. \tag{4.1}$$

Then there exists a subsequence of $\{(X_{\varepsilon_k}, \phi_{\varepsilon_k})\}_{k=1}^\infty$, not relabeled, such that $X_{\varepsilon_k} \to X_0$ in $(\mathbb{R}^3)^N$ for some $X_0 \in \Omega^N \cap O_N$ and $\phi_{\varepsilon_k} \to \chi_{A_0}$ in $L^{4-\lambda}(\Omega)$ for any $\lambda \in (0, 1)$ and for some measurable subset $A_0 \subseteq \Omega$ that has a finite perimeter in Ω. Moreover,

$$\lim_{k\to\infty} F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}] = F_0[X_0, A_0] \tag{4.2}$$

and

$$F_0[X_0, A_0] = \min_{(X,A)\in\mathcal{M}_0} F_0[X, A]. \tag{4.3}$$

To prove this theorem, we need two lemmas. These lemmas provide the liminf and limsup conditions that are essential for the Γ-convergence of the diffuse interfaces to the sharp interfaces. The proofs of these lemmas are given in the appendix.

LEMMA 4.1. *Let $\varepsilon_k \in (0, \varepsilon_0]$ $(k = 1, 2, \dots)$ be such that $\varepsilon_k \downarrow 0$. Let $(X_{\varepsilon_k}, \phi_{\varepsilon_k}) \in \mathcal{M}$ $(k = 1, 2, \dots)$ satisfy*

$$\sup_{k\ge 1} F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}] < \infty. \tag{4.4}$$

Then there exist a subsequence of $\{(X_{\varepsilon_k}, \phi_{\varepsilon_k})\}_{k=1}^\infty$, not relabeled, a point $X_0 \in \Omega^N \cap O_N$, and a measurable set $A_0 \subseteq \Omega$ with a finite perimeter in Ω such that, as $k \to \infty$, $X_{\varepsilon_k} \to X_0$ in $(\mathbb{R}^3)^N$ and $\phi_{\varepsilon_k} \to \chi_{A_0}$ in $L^{4-\lambda}(\Omega)$ for any $\lambda \in (0, 1)$. Moreover,

$$F_0[X_0, A_0] \le \liminf_{k\to\infty} F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}]. \tag{4.5}$$

We recall that $\mathcal{R}_0$ is defined in (2.6).

LEMMA 4.2. *Let $(X, A) \in \mathcal{R}_0$. Let $\varepsilon_k \in (0, \varepsilon_0]$ $(k = 1, 2, \dots)$ with $\varepsilon_k \downarrow 0$. Then there exist $\phi_{\varepsilon_k} \in H^1(\Omega)$ $(k = 1, 2, \dots)$ such that $\phi_{\varepsilon_k} \to \chi_A$ in $L^p(\Omega)$ for any $p \in [1, \infty)$ as $k \to \infty$ and*

$$\limsup_{k\to\infty} F_{\varepsilon_k}[X, \phi_{\varepsilon_k}] \le F_0[X, A]. \tag{4.6}$$

We are now ready to prove Theorem 4.1.

Proof of Theorem 4.1. By Theorem 3.1, the sequence $\{F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}]\}_{k=1}^{\infty}$ is bounded. By Lemma 4.1, there exists a subsequence of $\{(X_{\varepsilon_k}, \phi_{\varepsilon_k})\}_{k=1}^{\infty}$, not relabeled, a point $X_0 \in \Omega^N \cap O_N$, and a measurable set $A_0 \subseteq \Omega$ with a finite perimeter in Ω such that, as $k \to \infty$, $X_{\varepsilon_k} \to X_0$ in $(\mathbb{R}^3)^N$ and $\phi_{\varepsilon_k} \to \chi_{A_0}$ in $L^{4-\lambda}(\Omega)$ for any $\lambda \in (0, 1)$. Moreover,

$$F_0[X_0, A_0] \le \liminf_{k\to\infty} F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}]. \tag{4.7}$$

Let $(X, A) \in \mathcal{R}_0$. It follows from Lemma 4.2 that for the sequence $\varepsilon_k \downarrow 0$, there exist $\psi_{\varepsilon_k} \in H^1(\Omega)$ (hence $(X, \psi_{\varepsilon_k}) \in \mathcal{M}$) $(k = 1, 2, \dots)$ such that

$$\limsup_{k\to\infty} F_{\varepsilon_k}[X, \psi_{\varepsilon_k}] \le F_0[X, A]. \tag{4.8}$$

It now follows from (4.7), (4.1), and (4.8) that

$$F_0[X_0, A_0] \le \liminf_{k\to\infty} F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}] \le \limsup_{k\to\infty} F_{\varepsilon_k}[X, \psi_{\varepsilon_k}] \le F_0[X, A].$$

Since $(X, A) \in \mathcal{R}_0$ is arbitrary, this, (4.1), and Theorem 2.2 imply that

$$F_0[X_0, A_0] = \liminf_{k\to\infty} F_{\varepsilon_k}[X_{\varepsilon_k}, \phi_{\varepsilon_k}] = \inf_{(X,A)\in\mathcal{R}_0} F_0[X, A] = \inf_{(X,A)\in\mathcal{M}_0} F_0[X, A]. \tag{4.9}$$

Hence (4.3) is true. Finally, passing to a further subsequence of $\{(X_{\varepsilon_k}, \phi_{\varepsilon_k})\}_{k=1}^{\infty}$ if necessary, we can replace in (4.9) the liminf by the lim to obtain (4.2).

We define $\tilde{F}_0 : \overline{\Omega}^N \times L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$\tilde{F}_0[X, \phi] = \begin{cases} F_0[X, A] & \text{if } X \in \overline{\Omega}^N \text{ and } \phi = \chi_A \text{ for some measurable } A \subseteq \Omega, \\ +\infty & \text{otherwise.} \end{cases}$$

We also define $\tilde{F}_\varepsilon : \overline{\Omega}^N \times L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$ for each $\varepsilon \in (0, \varepsilon_0]$ by

$$\tilde{F}_\varepsilon[X, \phi] = \begin{cases} F_\varepsilon[X, \phi] & \text{if } X \in \overline{\Omega}^N \text{ and } \phi \in H^1(\Omega), \\ +\infty & \text{otherwise.} \end{cases}$$

Lemmas 4.1 and 4.2 now imply the following.

THEOREM 4.2. *Let $\varepsilon_k \in (0, \varepsilon_0]$ $(k = 1, 2, \dots)$ be such that $\varepsilon_k \downarrow 0$. Then the sequence of functionals $\{\tilde{F}_{\varepsilon_k}\}_{k=1}^{\infty}$ Γ-converges to $\tilde{F}_0$ with respect to the metric of $(\mathbb{R}^3)^N \times L^1(\Omega)$.*

By Theorem 4.2 and the general theory of Γ-convergence, or by those arguments used in [27], we have the following.

THEOREM 4.3. *Let (X, ϕ) be an isolated local minimizer of $\tilde{F}_0 : \overline{\Omega}^N \times L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$. Let $\varepsilon_k \in (0, \varepsilon_0]$ $(k = 1, 2, \dots)$ with $\varepsilon_k \downarrow 0$. Then there exist $(X_{\varepsilon_k}, \phi_{\varepsilon_k}) \in \overline{\Omega}^N \times L^1(\Omega)$ $(k = 1, 2, \dots)$ such that for each $k \ge 1$, $(X_{\varepsilon_k}, \phi_{\varepsilon_k})$ is a local minimizer of $\tilde{F}_{\varepsilon_k} : \overline{\Omega}^N \times L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$, and $(X_{\varepsilon_k}, \phi_{\varepsilon_k}) \to (X, \phi)$ in $\overline{\Omega}^N \times L^1(\Omega)$ as $k \to \infty$.*

5. Discussions.

5.1. Properties of sharp-interface free-energy minimizers. For simplicity, let us fix the set of solute atoms $X = (x_1, \dots, x_N) \in \Omega^N \cap O_N$ and consider the sharp-interface free-energy functional $F_0[X, A]$, defined in (2.2), as a functional of all measurable sets $A \subseteq \Omega$. We expect a global or local minimizer A of this functional to be regular and to contain an X-core. The regularity of A should be similar to that of a minimal surface; cf., e.g., [23]. The important property that A contains an X-core, which has been always true numerically [6, 7, 9, 43], can be related to the following stronger but still realistic assumption: there exists $\sigma_0 > 0$ such that for any $\sigma \in (0, \sigma_0)$

$$\int_{B(X,\sigma)\cap\Omega} U(X, x)\, dx = +\infty.$$

More detailed analysis on the diffuse-interface free-energy minimizers may help prove the property that a sharp-interface minimizer A contains an X-core.

5.2. Boundary conditions. In solving the systems of equations of the gradient flow (1.5), one would like to impose the homogeneous Dirichlet boundary condition $\phi = 0$ on $\partial\Omega$, since the solvent region is described by $\phi \approx 0$. With such a boundary condition, we need to redefine the diffuse-interface free-energy functional $\tilde{F}_\varepsilon : \overline{\Omega}^N \times L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$\tilde{F}_\varepsilon[X, \phi] = \begin{cases} F_\varepsilon[X, \phi] & \text{if } X \in \overline{\Omega}^N \text{ and } \phi \in H_0^1(\Omega), \\ +\infty & \text{otherwise.} \end{cases}$$

The Γ-limit with respect to the metric of $(\mathbb{R}^3)^N \times L^1(\Omega)$ of any sequence of functionals $\{\tilde{F}_{\varepsilon_k}\}_{k=1}^\infty$, where $\varepsilon_k \in (0, \varepsilon_0]$ $(k = 1, 2, \dots)$ are such that $\varepsilon_k \downarrow 0$, is $\tilde{F}_0 : \overline{\Omega}^N \times L^1(\Omega) \to \mathbb{R} \cup \{+\infty\}$, which is now defined by

$$\tilde{F}_0[X, \phi] = \begin{cases} F_0[X, A] + \displaystyle\int_{\partial\Omega} \left| \int_0^{\phi(x)} \sqrt{2W(t)}\, dt \right| dx & \text{if } \phi = \chi_A \in BV(\Omega) \text{ for some } A \subseteq \Omega, \\ +\infty & \text{otherwise,} \end{cases}$$

where $X \in \overline{\Omega}^N$; see [35]. (Note that in [35] the coefficient of the gradient-squared term in the energy functional is ε, not $\varepsilon/2$.) In numerical computations, the steady-state solution ϕ to the system of equations (1.5) often vanishes at the boundary $\partial\Omega$. For such ϕ, the additional integral term in the Γ-limit then vanishes.

5.3. Convergence of forces. There are two different types of forces in a solvation system that can be described by variational implicit-solvent models. One is the force acting on the solute atoms located at $x_1, \dots, x_N$. The force acting on x_i is defined to be $-\nabla_{x_i} F_0[X, A]$ for the sharp-interface model and $-\nabla_{x_i} F_\varepsilon[X, \phi]$ with $\varepsilon \in (0, \varepsilon_0]$ for the diffuse-interface model. Let us assume that the potentials E and U are continuously differentiable in their respective domains of finite values. Based on

formal calculations, we denote

$$f_0[X,A] = -\nabla_X E[X] - \int_{\Omega\setminus A} \nabla_X U(X,x)\,dx \qquad \forall (X,A)\in\mathcal{M}_0,$$
$$f_\varepsilon[X,\phi] = -\nabla_X E[X] - \int_{\Omega} [\phi(x)-1]^2\,\nabla_X U(X,x)\,dx$$
$$\forall (X,\phi)\in\mathcal{M} \text{ and } \forall \varepsilon\in(0,\varepsilon_0].$$

If the integrals exist, then these $3N$-component vectors represent the forces acting on $X=(x_1,\dots,x_N)$ in the sharp-interface and diffuse-interface descriptions, respectively. Note that the surface energy terms in F_0 and F_ε do not contribute to the forces acting on solute atoms. Intuitively, we shall have the convergence that $f_\varepsilon\to f_0$ in some sense as $\varepsilon\to 0$. But one needs to identify conditions under which such convergence holds.

Another type of force is the dielectric boundary force. In the sharp-interface model governed by the free-energy functional $F[X,\Gamma]$ that is defined in (1.1), the dielectric boundary force—more precisely the normal component of the effective dielectric boundary force—is defined as $-\delta_\Gamma F[X,\Gamma]$, the negative variational derivative of the free energy with respect to the location change of the dielectric boundary Γ. The variational derivative $\delta_\Gamma F[X,\Gamma]$ is a function defined on Γ. It is known that for any fixed $X\in\Omega^N\cap O_N$ [6, 9, 43]

$$\delta_\Gamma F[X,\Gamma](x) = \gamma H(x) - U(X,x) \qquad \forall x\in\Gamma, \tag{5.1}$$

where $H=H(x)$ is the mean curvature at $x\in\Gamma$. See also [31] for the formula of the dielectric boundary force when the full coupling of the electrostatics using the Poisson–Boltzmann equation is used.

It is now natural to ask if the corresponding diffuse-interface forces will converge to the sharp-interface ones. The variation with respect to the field ϕ of the diffuse-interface free-energy functional F_ε defined in (1.4) is

$$\delta_\phi F_\varepsilon[X,\phi] = \gamma\left[-\varepsilon\Delta\phi + \frac{1}{\varepsilon}W'(\phi)\right] + 2(\phi-1)U(X,\cdot),$$

assuming the smoothness of ϕ, where $X\in\Omega^N\cap O_N$ is fixed. This variation is a function defined on the entire region Ω. Suppose that $\varepsilon_k\in(0,\varepsilon_0]$ $(k=1,2,\dots)$ are such that $\varepsilon_k\downarrow 0$ and $\phi_{\varepsilon_k}\in H^1(\Omega)$ $(k=1,2,\dots)$ are such that $\phi_{\varepsilon_k}\to\chi_A$ in $L^2(\Omega)$ for some smooth open set $A\subset\Omega$. We then expect that the related γ-terms,

$$\gamma\left[-\varepsilon\Delta\phi_{\varepsilon_k} + \frac{1}{\varepsilon_k}W'(\phi_{\varepsilon_k})\right], \qquad k=1,2,\dots,$$

will converge in some sense to $-\gamma H_{\partial A}$ with $H_{\partial A}$ being the mean curvature of the boundary of A. This is intuitively true, but we are not aware of a proof in the literature.

For the related U-terms, we have that

$$2\,(\phi_{\varepsilon_k}-1)\,U(X,\cdot)\to -\chi_{\Omega\setminus A}U(X,\cdot) \qquad \text{in } \Omega,$$

which is different from the last term in (5.1). Such difference arises naturally from the definition of these variational derivatives: $\delta_\phi F_\varepsilon[X,\phi]$ is the variational derivative with

respect to the field ϕ, while $\delta_\Gamma F[X,\Gamma]$ is the variational derivative with respective to the boundary Γ. Notice that the later is not the variational derivative of the functional $F_0[X,A]$, which is defined in (2.2), with respect to the variation of the set A. It is therefore interesting to design a new form, if necessary and possible, to replace the U-term in the diffuse-interface free-energy functional, define a suitable derivative or force for such a functional, and prove that all the energies, forces, and interfaces will converge correctly to the corresponding sharp-interface quantities.

5.4. Coupling the Poisson–Boltzmann equation. A more accurate description of the electrostatic interaction in a charged molecular system is to use the Poisson–Boltzmann equation for the electrostatic potential ψ [12, 21, 24, 32, 40]

$$-\nabla\cdot\varepsilon_\Gamma\nabla\psi+\chi_{\rm w}V'(\psi)=\rho_X \qquad \text{in } \Omega,$$

together with some boundary conditions. Here Γ is the dielectric boundary that separates the solute region $\Omega_{\rm m}$ from the solvent region $\Omega_{\rm w}$ (cf. Figure 1.1), ε_Γ is the variable dielectric coefficient equal to one constant value $\varepsilon_{\rm m}$ in $\Omega_{\rm m}$ and another $\varepsilon_{\rm w}$ in $\Omega_{\rm w}$, $X=(x_1,\ldots,x_N)$, and ρ_X is the fixed charge density that consists of point charges Q_i at the solute atoms x_i $(i=1,\ldots,N)$. Such point charges can often be approximated by smooth functions. The term $-V'(\psi)$ is the density of charges of the mobile ions in the solvent, determined by the Boltzmann distribution. The function $\chi_{\rm w}$ is the characteristic function of the solvent region $\Omega_{\rm w}$. Once the electrostatic potential ψ is known, the electrostatic free energy is then determined as

$$E_{\rm ele}[\Gamma]=\int_\Omega\Big[-\frac{\varepsilon_\Gamma}{2}|\nabla\psi|^2+\rho_X\psi-\chi_{\rm w}V(\psi)\Big]\,dx.$$

To couple the Poisson–Boltzmann equation in the diffuse-interface model, we propose the free-energy functional

$$\begin{aligned}F_\varepsilon[X,\phi]&=E[X]+\gamma\int_\Omega\left[\frac{\varepsilon}{2}|\nabla\phi|^2+\frac{1}{\varepsilon}W(\phi)\right]\,dx+\rho_{\rm w}\int_\Omega\left[\phi(x)-1\right]^2U_{\rm vdW}(X,x)\,dx\\&\quad+\int_\Omega\left[-\frac{\hat\varepsilon(\phi)}{2}|\nabla\psi|^2+\rho_X\psi-(\phi-1)^2V(\psi)\right]dx,\end{aligned}\tag{5.2}$$

in which the electrostatic potential ψ is determined by the diffuse-interface version of the Poisson–Boltzmann equation

$$-\nabla\cdot\hat\varepsilon(\phi)\nabla\psi+(\phi-1)^2V'(\psi)=\rho_X \qquad \text{in } \Omega,\tag{5.3}$$

together with some boundary conditions. In (5.2), $\rho_{\rm w}$ is the constant, bulk solvent density and $U_{\rm vdW}$ is solute-solvent interaction potential defined in (1.2). In (5.2) and (5.3),

$$\hat\varepsilon(\phi)=\varepsilon_{\rm m}\phi^2+\varepsilon_{\rm w}(1-\phi)^2.$$

We shall present more details of this diffuse-interface model and report our related numerical simulations of molecular systems in our subsequent work.

It is now natural to ask if the free-energy functional F_ε, defined in (5.2), and its related quantities, such as the free-energy minimizers, minimum free-energy values, forces, and the electrostatic potentials, will converge to their sharp-interface counterparts as $\varepsilon\to 0$.

Appendix. We now prove Lemmas 4.1 and 4.2. Our proofs are based on the previous works [2, 13, 34, 35, 36, 41, 42]. For completeness, we give all the necessary details.

Proof of Lemma 4.1. We have by Lemma 3.1 and (4.4) that

$$\sup_{k\geq 1}\left[\varepsilon_k\|\nabla\phi_{\varepsilon_k}\|^2_{L^2(\Omega)}+\frac{1}{\varepsilon_k}\|W(\phi_{\varepsilon_k})\|_{L^1(\Omega)}+\|\phi_{\varepsilon_k}\|^4_{L^4(\Omega)}\right]<\infty. \tag{A.1}$$

Hence $\{\phi_{\varepsilon_k}\}_{k=1}^\infty$ is bounded in $L^2(\Omega)$. It then follows from (4.4) and the fact that

$$E_{\min}\leq E[X_{\varepsilon_k}]\leq F_{\varepsilon_k}[X_{\varepsilon_k},\phi_{\varepsilon_k}]-\int_\Omega U_{\min}\left(\phi_{\varepsilon_k}-1\right)^2dx,\qquad k=1,2,\dots,$$

that $\{E[X_{\varepsilon_k}]\}_{k=1}^\infty$ is bounded. Since $\{X_{\varepsilon_k}\}_{k=1}^\infty$ is bounded, it has a subsequence, not relabeled, that converges to some $X_0\in\overline{\Omega}^N$. By the boundedness of $\{E[X_{\varepsilon_k}]\}_{k=1}^\infty$ and our assumptions on E, we must have $X_0\in\Omega^N\cap O_N$.

Define $G:\mathbb{R}\to\mathbb{R}$ by

$$G(t)=\int_0^t\sqrt{W(s)}\,ds\qquad\forall t\in\mathbb{R}.$$

Direct calculations lead to

$$G(t)=\begin{cases}\dfrac{1}{\sqrt{2}}\left(2t^3-3t^2\right) & \text{if } t<0,\\[2mm] \dfrac{1}{\sqrt{2}}\left(3t^2-2t^3\right) & \text{if } 0\leq t\leq 1,\\[2mm] \sqrt{2}+\dfrac{1}{\sqrt{2}}\left(2t^3-3t^2\right) & \text{if } t>1.\end{cases}$$

Therefore,

$$|G(t)|\leq\sqrt{2}+\frac{3}{\sqrt{2}}\left(|t|^3+t^2\right)\qquad\forall t\in\mathbb{R}. \tag{A.2}$$

For each $k\geq 1$, we define $\psi_{\varepsilon_k}:\Omega\to\mathbb{R}$ by $\psi_{\varepsilon_k}(x)=G(\phi_{\varepsilon_k}(x))$ for all $x\in\Omega$. It follows from (A.1), (A.2), and Hölder's inequality that $\{\psi_{\varepsilon_k}\}_{k=1}^\infty$ is bounded in $L^{4/3}(\Omega)$. Moreover,

$$\begin{aligned}\int_\Omega|\nabla\psi_{\varepsilon_k}|\,dx&=\int_\Omega|\nabla G(\phi_{\varepsilon_k})|\,dx=\int_\Omega|G'(\phi_{\varepsilon_k})\nabla\phi_{\varepsilon_k}|\,dx=\int_\Omega\left|\sqrt{W(\phi_{\varepsilon_k})}\nabla\phi_{\varepsilon_k}\right|dx\\ &\leq\frac{1}{\sqrt{2}}\int_\Omega\left[\frac{\varepsilon_k}{2}|\nabla\phi_{\varepsilon_k}|^2+\frac{1}{\varepsilon_k}W(\phi_{\varepsilon_k})\right]dx,\qquad k=1,2,\dots.\end{aligned} \tag{A.3}$$

This and (A.1) imply that $\{\nabla\psi_{\varepsilon_k}\}_{k=1}^\infty$ is bounded in $L^1(\Omega)$. Therefore, $\{\psi_{\varepsilon_k}\}_{k=1}^\infty$ is bounded in $W^{1,1}(\Omega)$. By the compact embedding $W^{1,1}(\Omega)\hookrightarrow L^1(\Omega)$, there exists a subsequence of $\{\psi_{\varepsilon_k}\}_{k=1}^\infty$, not relabeled, such that $\psi_{\varepsilon_k}\to\psi_0$ in $L^1(\Omega)$ and $\psi_{\varepsilon_k}\to\psi_0$ a.e. in Ω for some $\psi_0\in L^1(\Omega)$.

Note that $G:\mathbb{R}\to\mathbb{R}$ is bijective and its inverse $G^{-1}:\mathbb{R}\to\mathbb{R}$ is continuous. Set $\phi_0=G^{-1}(\psi_0):\Omega\to\mathbb{R}$. Clearly ϕ_0 is measurable. By the definition of ψ_{ε_k}, we have $\phi_{\varepsilon_k}=G^{-1}\left(\psi_{\varepsilon_k}\right)$ $(k=1,2,\dots)$. The continuity of G^{-1} implies that $\phi_{\varepsilon_k}\to\phi_0$ a.e. in

Ω. By (A.1), $\|W(\phi_{\varepsilon_k})\|_{L^1(\Omega)} \to 0$ as $k \to \infty$. Fatou's lemma then implies that

$$\int_\Omega W(\phi_0)\,dx \le \liminf_{k\to\infty} \int_\Omega W(\phi_{\varepsilon_k})\,dx = 0.$$

Since W is continuous, $W \ge 0$, and $W = 0$ only at 0 and 1, we have $\phi_0 = \chi_{A_0}$ a.e. in Ω for some measurable set $A_0 \subseteq \Omega$.

Let $\eta > 0$. Since $\phi_{\varepsilon_k} \to \phi_0$ a.e. in Ω, Egoroff's theorem asserts that there exists a measurable subset $\Omega_\eta \subseteq \Omega$ such that $|\Omega - \Omega_\eta| < \eta$ and $\phi_{\varepsilon_k} \to \phi_0$ uniformly on Ω_η. Fix $\lambda \in (0,1)$. We have by Hölder's inequality that

$$\begin{aligned}\int_{\Omega\setminus\Omega_\eta} |\phi_{\varepsilon_k} - \phi_0|^{4-\lambda} dx &\le |\Omega - \Omega_\eta|^{\lambda/4} \left(\int_{\Omega\setminus\Omega_\eta} |\phi_{\varepsilon_k} - \phi_0|^4 dx \right)^{1-\lambda/4} \\ &\le \eta^{\lambda/4} \|\phi_{\varepsilon_k} - \phi_0\|_{L^4(\Omega)}^{4-\lambda}, \qquad k = 1, 2, \ldots.\end{aligned}$$

This, (A.1), and the uniform convergence $\phi_{\varepsilon_k} \to \phi_0$ on Ω_η imply that

$$\begin{aligned}\limsup_{k\to\infty} \int_\Omega |\phi_{\varepsilon_k} - \phi_0|^{4-\lambda}\,dx &\le \limsup_{k\to\infty} \int_{\Omega_\eta} |\phi_{\varepsilon_k} - \phi_0|^{4-\lambda}\,dx \\ &\quad + \limsup_{k\to\infty} \int_{\Omega\setminus\Omega_\eta} |\phi_{\varepsilon_k} - \phi_0|^{4-\lambda} dx \\ &\le \eta^{\lambda/4} \sup_{k\ge1} \|\phi_{\varepsilon_k} - \phi_0\|_{L^4(\Omega)}^{4-\lambda}.\end{aligned}$$

Since $\eta > 0$ is arbitrary, we obtain that $\phi_{\varepsilon_k} \to \phi_0$ in $L^{4-\lambda}(\Omega)$.

Since $\phi_0 = \chi_{A_0}$, we have by (3.1) that

$$\psi_0(x) = G(\phi_0(x)) = \int_0^{\phi_0(x)} \sqrt{W(s)}\,ds = \begin{cases} 1/\sqrt{2} & \text{if } x \in A_0, \\ 0 & \text{if } x \in \Omega \setminus A_0. \end{cases}$$

Therefore

$$\{x \in \Omega : \psi_0(x) > t\} = \begin{cases} \Omega & \text{if } t < 0, \\ A_0 & \text{if } 0 \le t < 1/\sqrt{2}, \\ \emptyset & \text{if } t > 1/\sqrt{2}. \end{cases}$$

Noting that $P_\Omega(\Omega) = 0$, we then obtain by the Fleming–Rishel formula [20] that (A.4)

$$\int_\Omega |\nabla\psi_0|\,dx = \int_{-\infty}^{\infty} P_\Omega\{x \in \Omega : \psi_0(x) > t\}\,dt = \int_0^{1/\sqrt{2}} P_\Omega(A_0)\,dt = \frac{1}{\sqrt{2}} P_\Omega(A_0).$$

On the other hand, since $\psi_{\varepsilon_k} \to \psi_0$ in $L^1(\Omega)$, we have

$$\int_\Omega |\nabla\psi_0|\,dx \le \liminf_{k\to\infty} \int_\Omega |\nabla\psi_{\varepsilon_k}|\,dx.$$

Together with (A.3), (A.4), and (A.1), this implies that

$$P_\Omega(A_0) \le \liminf_{k\to\infty} \int_\Omega \left[\frac{\varepsilon_k}{2} |\nabla\phi_{\varepsilon_k}|^2 + \frac{1}{\varepsilon_k} W(\phi_{\varepsilon_k}) \right] dx < \infty. \tag{A.5}$$

Since $\phi_{\varepsilon_k} \to \phi_0$ a.e. in Ω, $U(X_{\varepsilon_k}, x) \to U(X_0, x)$ a.e. $x \in \Omega$, and $\phi_{\varepsilon_k} \to \phi_0$ in $L^2(\Omega)$, we obtain by Fatou's lemma that

$$\begin{aligned}
&\int_\Omega [\phi_0(x) - 1]^2 \, U(X_0, x) \, dx \\
&\quad = \int_\Omega [\phi_0(x) - 1]^2 \, [U(X_0, x) - U_{\min}] \, dx + U_{\min} \int_\Omega [\phi_0(x) - 1]^2 \, dx \\
&\quad \le \liminf_{k\to\infty} \int_\Omega [\phi_{\varepsilon_k}(x) - 1]^2 \, [U(X_{\varepsilon_k}, x) - U_{\min}] \, dx \\
&\qquad + \lim_{k\to\infty} \int_\Omega U_{\min} \, [\phi_{\varepsilon_k}(x) - 1]^2 \, dx \\
&\quad = \liminf_{k\to\infty} \int_\Omega [\phi_{\varepsilon_k}(x) - 1]^2 \, U(X_{\varepsilon_k}, x) \, dx. \qquad \text{(A.6)}
\end{aligned}$$

Now the desired inequality (4.5) follows from the definition of F_ε and F_0, the fact that $E[X_{\varepsilon_k}] \to E[X_0]$, (A.5), and (A.6). ∎

Proof of Lemma 4.2. We shall consider all $\varepsilon \in (0, \varepsilon_0]$ instead of $\{\varepsilon_k\}_{k=1}^\infty$. For each $\varepsilon \in (0, \varepsilon_0]$, we define $q_\varepsilon : [0, 1] \to \mathbb{R}$ by

$$q_\varepsilon(t) = \int_0^t \frac{\varepsilon}{\sqrt{2\varepsilon + 2W(s)}} \, ds \qquad \forall t \in [0, 1].$$

Clearly, q_ε is a strictly increasing function of $t \in [0, 1]$ with $q_\varepsilon(0) = 0$. Denote $\lambda_\varepsilon = q_\varepsilon(1) \in (0, \sqrt{\varepsilon/2})$. Let $p_\varepsilon : [0, \lambda_\varepsilon] \to [0, 1]$ be the inverse of $q_\varepsilon : [0, 1] \to [0, \lambda_\varepsilon]$. By using the formula of derivatives of inverse functions, we obtain

$$\varepsilon p_\varepsilon'(s) = \sqrt{2\varepsilon + 2W(p_\varepsilon(s))} \qquad \forall s \in [0, \lambda_\varepsilon]. \qquad \text{(A.7)}$$

We extend p_ε onto the entire real line by defining $p_\varepsilon(s) = 0$ for any $s < 0$ and $p_\varepsilon(s) = 1$ for any $s > \lambda_\varepsilon$.

Since $(X, A) \in \mathcal{R}_0$, $A \in \mathcal{A}_0$ and A contains an X-core. Thus $A = E \cap \Omega$ for some open subset E of $\mathbb{R}^3$ with a nonempty, compact, and C^∞ boundary ∂E such that $\partial E \cap \Omega$ is C^2 and $\mathcal{H}_2(\partial E \cap \partial\Omega) = 0$. We define $\phi : \Omega \to \mathbb{R}$ by

$$\phi_\varepsilon(x) = 1 - p_\varepsilon(d(x)) \qquad \forall x \in \Omega,$$

where $d : \mathbb{R}^3 \to \mathbb{R}$ is the signed distance function associated with the set E, defined by

$$d(x) = \begin{cases} -\operatorname{dist}(x, \partial E) & \text{if } x \in E, \\ \operatorname{dist}(x, \partial E) & \text{if } x \in \mathbb{R}^3 \setminus E. \end{cases}$$

Clearly, $\phi_\varepsilon \in W^{1,\infty}(\Omega)$. Moreover, $\phi_\varepsilon(x) = 1$ if $x \in A = E \cap \Omega$, $\phi_\varepsilon(x) = 0$ if $x \in \Omega \setminus A$ and $\operatorname{dist}(x, \partial E) \ge \lambda_\varepsilon$, and $0 \le \phi_\varepsilon(x) \le 1$ if $x \in \Omega \setminus A$ and $\operatorname{dist}(x, \partial E) < \lambda_\varepsilon$.

Let $p \in [1, \infty)$. We prove that $\phi_\varepsilon \to \chi_A$ in $L^p(\Omega)$. Define $p_0 : \mathbb{R} \to \mathbb{R}$ by $p_0(s) = 0$ if $s < 0$ and $p_0(s) = 1$ if $s \ge 0$. We then have $\chi_E(x) = 1 - p_0(d(x))$ for any $x \in \mathbb{R}^3 \setminus \partial E$.

Since $\partial E \cap \Omega$ is in C^2, we have $\chi_A(x) = 1 - p_0(d(x))$ a.e. $x \in \Omega$. It now follows from the co-area formula that

$$\begin{aligned}\int_\Omega |\phi_\varepsilon(x) - \chi_A(x)|^p \, dx &= \int_\Omega |p_\varepsilon(d(x)) - p_0(d(x))|^p \, |\nabla d(x)| \, dx \\ &= \int_0^{\lambda_\varepsilon} |p_\varepsilon(s) - p_0(s)|^p \, \mathcal{H}_2\left(\{x \in \Omega : d(x) = s\}\right) \, ds \\ &\le \lambda_\varepsilon 2^p \sup_{0 \le s \le \lambda_s} \mathcal{H}\left(\{x \in \Omega : d(x) = s\}\right).\end{aligned}$$

Since $\mathcal{H}_2(\partial E \cap \partial\Omega) = 0$, ∂E is smooth, and $A = E \cap \Omega$, we have (cf. Lemma 4 in [34], Lemma 2 in [41], and (1.1) in [23])

$$\lim_{\varepsilon \to 0} \sup_{0 \le s \le \lambda_s} \mathcal{H}\left(\{x \in \Omega : d(x) = s\}\right) = \mathcal{H}_2(\partial E \cap \Omega) = P_\Omega(E) = P_\Omega(A) < \infty. \tag{A.8}$$

Consequently, $\phi_\varepsilon \to \chi_A$ in $L^p(\Omega)$.

We now prove (4.6). Applying the co-area formula and using the symmetry $W(1-s) = W(s)$ for any $s \in \mathbb{R}$, we obtain

$$\begin{aligned}&\int_\Omega \left[\frac{\varepsilon}{2}|\nabla \phi_\varepsilon(x)|^2 + \frac{1}{\varepsilon} W(\phi_\varepsilon(x))\right] dx \\ &\quad = \int_\Omega \left[\frac{\varepsilon}{2}|p_\varepsilon'(d(x))|^2 + \frac{1}{\varepsilon} W(p_\varepsilon(x))\right] |\nabla d(x)| \, dx \\ &\quad = \int_0^{\lambda_\varepsilon} \left[\frac{\varepsilon}{2}|p_\varepsilon'(s)|^2 + \frac{1}{\varepsilon} W(p_\varepsilon(s))\right] \mathcal{H}_2(\{x \in \Omega : d(x) = s\}) \, ds \\ &\quad \le \left[\sup_{0 \le s \le \lambda_\varepsilon} \mathcal{H}_2(\{x \in \Omega : d(x) = s\})\right] \int_0^{\lambda_\varepsilon} \left[\frac{\varepsilon}{2}|p_\varepsilon'(s)|^2 + \frac{1}{\varepsilon} W(p_\varepsilon(s))\right] ds. \qquad \text{(A.9)}\end{aligned}$$

It follows from (A.7), the change of variables $t = p_\varepsilon(s)$, and (3.1) that

$$\begin{aligned}\int_0^{\lambda_\varepsilon} \left[\frac{\varepsilon}{2}|p_\varepsilon'(s)|^2 + \frac{1}{\varepsilon} W(p_\varepsilon(s))\right] ds &= \int_0^{\lambda_\varepsilon} \left[1 + \frac{2}{\varepsilon} W(p_\varepsilon(s))\right] ds \\ &\le \int_0^{\lambda_\varepsilon} \frac{1}{\varepsilon}\left[2\varepsilon + 2W(p_\varepsilon(s))\right] ds = \int_0^{\lambda_\varepsilon} \sqrt{2\varepsilon + 2W(p_\varepsilon(s))} p_\varepsilon'(s) \, ds \\ &= \int_0^1 \sqrt{2\varepsilon + 2W(t)} \, dt \to \int_0^1 \sqrt{2W(t)} \, dt = 1 \qquad \text{as } \varepsilon \to 0.\end{aligned}$$

Combining this, (A.8), and (A.9), we obtain

$$\limsup_{\varepsilon \to 0} \int_\Omega \left[\frac{\varepsilon}{2}|\nabla \phi_\varepsilon(x)|^2 + \frac{1}{\varepsilon} W(\phi_\varepsilon(x))\right] dx \le P_\Omega(A). \tag{A.10}$$

Notice that $U(X, \cdot)$ is continuous and bounded on $\overline{\Omega} \setminus A$, since $A \supseteq B(X, \sigma)$. Since $\phi_\varepsilon = 1$ on A for all $\varepsilon \in (0, \varepsilon_0]$ and $\phi_\varepsilon \to \chi_A$ in $L^2(\Omega)$ as $\varepsilon \to 0$, we obtain that

$$\lim_{\varepsilon \to 0} \int_\Omega \left[\phi_\varepsilon(x) - 1\right]^2 U(X, x) \, dx = \lim_{\varepsilon \to 0} \int_{\Omega \setminus A} \left[\phi_\varepsilon(x) - 1\right]^2 U(X, x) \, dx = \int_{\Omega \setminus A} U(X, x) \, dx.$$

This and (A.10) imply (4.6). ∎

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