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# Analysis on Sharp and Smooth Interface

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ANALYSIS ON SHARP AND SMOOTH INTERFACE

by

ELIZABETH HAWKINS

(Under the Direction of Zhan Chen)

ABSTRACT

In biology, minimizing a free energy functional gives an equilibrium shape that is the most stable in nature. The formulation of these functionals can vary in many ways, in particular they can have either a smooth or sharp interface. Minimizing a functional can be done through variational calculus or can be proved to exist using various analysis techniques. The functionals investigated here have a smooth and sharp interface and are analyzed using analysis and variational calculus respectively. From the latter we find that there exists a minimizing surface for the functional; from this numerical and variational approaches to the problem can be justified. Comparatively, from the former we find the condition for extremum and its second variation. The second variation is commonly used to analyze stability of a surface that is a solution to the functional so having a surface is necessary.

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# LIST OF SYMBOLS

| | |
|---|---|
| $L^p(U)$ | $p$-integrable functions on a region $U$ |
| $W^{1,p}(U)$ | $p$-integrable functions with $p$-integrable derivatives on a region $U$ |
| $W_0^{1,p}(U)$ | for $p > 1$, functions in $W^{1,p}(U)$ that vanish on $\partial\Omega$ |
| $C^\infty(U)$ | smooth functions on a region $U$ |
| $C_c^\infty(U)$ | continuous and compactly supported functions on a region $U$ |
| $\|f\|_{L^p(U)}$ | $L^p$ norm of a function, $f$, on a region $U$ |
| $f \cdot g$ | Inner product of vector valued functions $f$ and $g$ |
| $f \otimes g$ | Cross product of vector valued functions $f$ and $g$ |
| $S$ | Shape operator of a point on a surface |
| $K$ | Gaussian curvature of a point on a surface |
| $H$ | mean curvature of a point on a surface |
| $\delta I$ | First variation of a functional $I$ |
| $\delta^2 I$ | Second variation of a functional $I$ |
| $cl(U)$ | The Closure of a region U |

# CHAPTER 1

# INTRODUCTION

When a solute is placed in a solvent there are many interactions occurring and hence many different models. These models can be categorized into two different categories, implicit solvation models and explicit solvation models. The explicit model represents the solvent in atomic detail, so it requires extensive sampling. The implicit model replaces the solvent with a dielectric continuum so it is comparatively less accurate but does not require extensive sampling. Furthermore implicit solvation models result in less degrees of freedom compared to the explicit which makes them the preferred model.

Interactions within the implicit model is described by solvation energies. These energies are defined to be the free energies of transferring the solute from a vacuum to the solvent environment. Now these interactions include the electrostatic interactions. Electrostatic interactions occur whenever a charged molecule exists in an aqueous environment, an environment containing water. Note that this means the solvent is aqueous by assumption for the model. This assumption is allowed since most biological processes occur in water.

Now assuming that the solute is charged, electrostatic interactions occur in the solute-solvent model. These interactions are important for analyzing the structure of the molecule and modelling the macro-molecule. Furthermore, the model can be arbitrarily separated into a polar and non-polar part; the polar part being the collection of electrostatic energy related terms and non-polar the converse. This means that if an uncharged solute is placed in a solvent, it would be modelled only by a non-polar part; otherwise considering only the non-polar part does not give a complete picture.

Now within the implicit solvation model there must be a beginning and end of the solute. This separation of the solute atoms and the solvent is called the interface of the model. The most recent definitions of the interface are influenced by the fundamental laws of physics. They utilize PDE to generate a surface for the macro-molecule. This is done by embedding the atomic information instead of using a given surface. Additionally, in biology, minimizing the free energy reduces the possibility of a reaction occurring thus resulting in an equilibrium shape. Consequently it is natural for the interface to be determined by this minimization. Thus a series of differential geometric based interface models was introduced which minimizes a surface free energy functional.

Within these definitions there are two types of interface, sharp and smooth. Sharp interfaces can be naturally imagined to be the physical surface of a molecule while smooth interfaces allows an overlap of the solute and solvent regions. For sharp interfaces, the solvation model is based on differential geometry. From this model, variational analysis derives a PDE which generates the surface of the macro-molecule. Comparatively, smooth interfaces are more the true boundary because it allows an overlap of the solute and solvent regions.

In this work, I will prove the existence of a global minimizer for a general functional based on an existing solvation free energy functional with both polar and non-polar parts as well as an extended new non-polar energy functional within the framework of smooth interface. Then for the sharp interface model proposed in [7] I will re-derive the perturbations of the first fundamental form, area, and volume. This will be used to give the first and second variation of an energy functional on a sharp interface. The proof and variation are the basis for a numerical approach to the energy functional. The variation in particular is useful for analyzing the stability of equilibrium.

# CHAPTER 2

# EXISTENCE OF A MINIMIZER ON A SMOOTH INTERFACE

## 2.1 Full Existing Solvation Free Energy Functional

Let $\Omega \subset \mathbb{R}^3$ be a bounded and connected Lipschitz domain composed of three disjoint subdomains with Lipschitz boundaries:

- $\Omega_m$: solute (molecular) region;
- $\Omega_s$: solvent region;
- $\Omega_b$: solute-solvent mixing region.

We define a characteristic function for the solvent $u : \mathbb{R}^3 \to \mathbb{R}$ :

$$u(x) = \begin{cases} 1 & \text{for } x \in \Omega_1 \\ 0 \le u \le 1 & \text{for } x \in \Omega_b \\ 0 & \text{for } x \in \Omega_0 \end{cases}$$

such that $\Omega_1$ is the subset of $\Omega_m$ where $u = 1$ everywhere and $\Omega_0$ is the subset of $\Omega_s$ where $u = 0$ everywhere. We will consider the functional proposed by Z. Chen, N.A Baker, and G.W Wei [6]

$$\begin{aligned} I[u,\psi] = \int_\Omega \gamma|\nabla u| + pu + &\rho_0(1-u)U^{att} + u\rho_m\psi - \frac{1}{2}\epsilon(u)\nabla\psi^2 \\ &- (1-u)k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right) dr \end{aligned}$$

with the amendment of $|\nabla u|^q$ for $1 < q \le 2$. The amended functional is then

$$\begin{aligned} I[u,\psi] = \int_\Omega \gamma|\nabla u|^q + pu + &\rho_0(1-u)U^{att} + u\rho_m\psi - \frac{1}{2}\epsilon(u)\nabla\psi^2 \\ &- (1-u)k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right) dr \end{aligned}$$

where $\int_\Omega \gamma|\nabla u|^q dr$ is used to describe the surface energy of the macromolecule. It measures the disruption of intermolecular and/or intramolecular bonds that occur when a surface is created. Of interest, $p$ is the hydrodynamic pressure. It is the mechanical work of creating the vacuum of a biomolecular size in the solvent. $\rho_0$ is the solvent bulk density and $U^{att}$ is the attractive portion of the van der Waals potential at point $r$. It represents the attractive dispersion effects near the solvent- solute interface.

We have that $\psi$ is the electrostatic potential whose domain is the whole computational domain $\Omega$. The term associated with $u$ is the electrostatic free energy of the solute and that with $(1-u)$ is the electrostatic free energy of the solvent. We define $\gamma$ to be surface tension, $\epsilon_s$ and $\epsilon_m$ the dialectic constants of the solvent and solute, $T$ temperature, $k_B$ the Boltzmann constant, $c_i$ and $q_i$ the bulk concentration and charge of the *i*th ionic species respectively, $N_c$ the number of ionic species, and $\rho_m = \sum_j Q_j \delta(r - x_j)$ as the density of the molecular charges with $Q_j$ being the partial charge on an atom located at $x_j$. Note that $\epsilon_m < \epsilon_s$ and $U^{att} < 0$. Also we denote $\epsilon(u) = u\epsilon_m + (1-u)\epsilon_s$ and $\psi$ the electrostatic potential. Clearly $\epsilon_s \geq \epsilon(u) \geq \epsilon_m$ and $\epsilon(u) \geq 0$ a.e.. in $\Omega$ since $u \geq 0$ in $\Omega$. Now the polar and non-polar part of $I[u, \psi]$ are

$$I_p[u,\psi] = \int_\Omega u\rho_m\psi - \frac{1}{2}\epsilon(u)|\nabla\psi|^2 - (1-u)k_BT\sum_{i=1}^{N_c} c_i\left(e^{-\psi q_i/k_BT} - 1\right) dr$$

and

$$I^q_{np}[u] = \int_\Omega \gamma|\nabla u|^q + pu + \rho_0(1-u)U^{att}dr,$$

respectively, so that $I[u,\psi] = I_p[u,\psi] + I^q_{np}[u]$.

Taking the 1st variation with respect to $\psi$ gives the following boundary value problem of the generalized Poisson Boltzmann equation

$$\begin{cases} \nabla(\epsilon(u)\nabla\psi) - (1-u)\sum_{i=1}^{N_c} c_iq_i(e^{-\psi q_i/k_BT}) & = -\rho_m u \text{ in } \Omega \\ & = \psi_\infty \text{ on } \partial\Omega \end{cases} \tag{2.1}$$

From this we can determine for each $u \in W^{1,q}(\Omega)$ a $\psi \in A^q$. So minimizing $I_p[u,\psi]$ is equivalent to minimizing

$$I_p[u] = \int_\Omega u\rho_m\psi - \frac{1}{2}|\nabla\psi|^2\epsilon(u) - (1-u)k_BT\sum_{i=1}^{N_c} c_i\left(e^{-\psi q_i/k_BT} - 1\right)$$

such that $\psi = \psi_\infty$ on $\partial\Omega$. The admissible functions for each $1 < q \leq 2$ for $u$ and $\psi$ are

$$X^q = \{u \in W^{1,q}(\Omega) : 0 \leq u \leq 1 \text{ a.e. on } \Omega,\, u = i \text{ on } \partial\Omega_i\}$$

$$A^q = \{v \in H^1(\Omega) : v = \psi_\infty \text{ on } \partial\Omega\},$$

respectively, and $\psi_\infty \in C^\infty(cl(\Omega))$.

We have that $I_p[u]$ may have a maximum, not a minimum. So we will denote for any given $u \in X^q$,

$$E_u[\psi] = -I_p[u] = \int_\Omega -u\rho_m\psi + \frac{1}{2}|\nabla\psi|^2\epsilon(u) + (1-u)k_BT\sum_{i=1}^{N_c} c_i\left(e^{-\psi q_i/k_BT} - 1\right).$$

**Theorem 2.1.** *For any $u \in X^q$, there exists a unique $\psi_u \in A^q$ such that*

$$E_u[\psi_u] = \min_{\psi\in A^q} E_u[\psi] < \infty.$$

*Moreover, $\psi_u$ is the unique solution to the Poisson-Boltzmann boundary value problem with*

$$\|\psi_u\|_{H^1(\Omega)} + \|\psi_u\|_\infty \leq C. \tag{2.2}$$

*Proof:* We have $u \in W^{1,q}(\Omega)$ so $\epsilon(u) \in W^{1,q}(\Omega)$ and it is bounded since and $\epsilon_m \leq \epsilon(u) \leq \epsilon_s$. By elliptic theory, the boundary value problem

$$\begin{cases} \nabla\cdot(\epsilon(u)\nabla\psi) + \rho_m u & = 0 \text{ in } \Omega \\ & = \psi_\infty \text{ on } \partial\Omega \end{cases}$$

has a unique weak solution $\hat{\psi}_u$ satisfying

$$\|\hat{\psi}_u\|_{H^1(\Omega)} + \|\hat{\psi}_u\|_\infty \leq C = C(\psi_\infty).$$

So we have that

$$\int_\Omega \epsilon(u)\nabla\hat{\psi}_u \cdot \nabla\eta = \int_\Omega u\rho_m\eta, \quad \forall \eta \in H_0^1(\Omega) \tag{2.3}$$

Now denote $B(v) = k_BT\sum_{i=1}^{N_c} c_i(e^{-vq_i/k_BT}-1)$. Then $B'(v) = -\sum_{i=1}^{N_c} c_iq_ie^{-vq_i/k_BT}$. Since the system is neutral, we have $B'(0) = -\sum_{i=1}^{N_c} c_iq_i = 0$. Consider then $B'(+\infty)$; given the system is neutral we have an equal negative charge for each positive charge. So then $B'(+\infty) = +\infty$. Similarly, $B'(-\infty) = -\infty$. We have that,

$$B''(v) = \frac{1}{k_BT}\sum_{i=1}^{N_c} c_i(q_i)^2e^{-vq_i/k_BT} > 0.$$

So $B$ is strictly convex with $\min_{v\in\mathbb{R}} B(v) = B(0)$.

Define $\widetilde{E_u}[\psi] : H_0^1(\Omega) \to \mathbb{R}\cup\{\infty\}$ by

$$\widetilde{E_u}[\psi] = \int_\Omega \frac{1}{2}\epsilon(u)|\nabla\psi|^2 + B(\psi+\hat{\psi}_u). \tag{2.4}$$

We have for $\hat{\psi}_u, \psi \in A^q$ that $\psi - \hat{\psi}_u \in H_0^1(\Omega)$. Then,

$$\begin{aligned}\widetilde{E_u}[\psi-\hat{\psi}_u] &= \int_\Omega \frac{1}{2}\epsilon(u)|\nabla(\psi-\hat{\psi}_u)|^2 + B(\psi)\\ &= \int_\Omega \frac{1}{2}\epsilon(u)(|\nabla\psi|^2 + |\nabla\hat{\psi}_u|^2) - \epsilon(u)\nabla\psi\cdot\nabla\hat{\psi}_u + B(\psi).\end{aligned}$$

Also by (2.3) we know

$$\int_\Omega \epsilon(u)\nabla\hat{\psi}_u\cdot\nabla(\psi-\hat{\psi}_u) = \int_\Omega \epsilon(u)\nabla\hat{\psi}_u\cdot\nabla\psi - \epsilon(u)|\nabla\hat{\psi}_u|^2 = \int_\Omega u\rho_m\psi - u\rho_m\hat{\psi}_u.$$

So,

$$\int_\Omega \epsilon(u)\nabla\hat{\psi}_u\cdot\nabla\psi = \int_\Omega \epsilon(u)|\nabla\hat{\psi}_u|^2 + u\rho_m\psi - u\rho_m\hat{\psi}_u.$$

Then combining these we get,

$$\begin{aligned}\widetilde{E_u}[\psi-\hat{\psi}_u] &= \int_\Omega \frac{1}{2}\epsilon(u)|\nabla\psi|^2 - \frac{1}{2}\epsilon(u)|\nabla\hat{\psi}_u|^2 - u\rho_m\psi + u\rho_m\hat{\psi}_u + B(\psi)\\ &= E_u[\psi] - \int_\Omega \frac{1}{2}\epsilon(u)|\nabla\hat{\psi}_u|^2 - u\rho_m\hat{\psi}_u.\end{aligned}$$

Hence,

$$E_u[\psi] = \widetilde{E_u}[\psi - \hat{\psi}_u] + \int_\Omega \frac{1}{2}\epsilon(u)|\nabla\hat{\psi}_u|^2 - u\rho_m\hat{\psi}_u.$$

Now consider the Lagrangian of (2.4), $L[p,z] = \frac{1}{2}\epsilon(u)|p|^2 + B(z+\hat{\psi}_u)$ so $L[p,z] \geq \frac{1}{2}\epsilon_m|p|^2 + C_0$ since $\min B(v) = B(0)$. Hence, $L[p,z]$ is coercive. Now, $p = (p_1, p_2, p_3)$ so $L[p,z] = \frac{1}{2}\epsilon(u)(p_1^2 + p_2^2 + p_3^2) + B(z+\hat{\psi}_u)$ and

$$\sum_{i,j} L_{p_ip_j}[p,z]\xi_i\xi_j = \epsilon(u)(\xi_1^2 + \xi_2^2 + \xi_3^2) \geq 0.$$

So the map $p \mapsto L[p,z]$ is convex for all $z$. Thus by calculus of variations and the strict convexity of $\widetilde{E_u}$, there exists a unique global minimizer $\bar{\psi}_u$ of $\widetilde{E_u}$ so that,

$$\widetilde{E_u}[\bar{\psi}_u] = \min_{\psi\in H_0^1(\Omega)} \widetilde{E_u}[\psi] < \infty$$

Consider $\psi_u = \hat{\psi}_u + \bar{\psi}_u \in A^q$. We have that,

$$\begin{aligned}E_u[\psi_u] &= \widetilde{E_u}[\bar{\psi}_u] + \int_\Omega \frac{1}{2}\epsilon(u)|\nabla\hat{\psi}_u|^2 - u\rho_m\hat{\psi}_u dr\\ &= \min_{\psi\in H_0^1(\Omega)} \widetilde{E_u}[\psi] + \int_\Omega \frac{1}{2}\epsilon(u)|\nabla\hat{\psi}_u|^2 - u\rho_m\hat{\psi}_u dr\end{aligned}$$

and since $\hat{\psi}_u \in H^1(\Omega)$ is a fixed unique solution to (2.1) for a given $u$,

$$E_u[\psi_u] = \min_{\psi\in A^q} E_u[\psi] < \infty.$$

□

Since $B(v)$ is strictly convex, there exists a $\lambda > 0$ such that

$$B'(\lambda + \hat{\psi}_u) > 1 \text{ and } B'(-\lambda + \hat{\psi}_u) < -1.$$

Let $m$ be the Lebesgue measure, and suppose $m\{\bar{\psi}_u > \lambda\} > 0$ or $m\{-\lambda > \bar{\psi}_u\} > 0$. We define

$$\widetilde{\psi} = \begin{cases} \lambda & \text{on } \{\bar{\psi}_u > \lambda\} \\ \bar{\psi}_u & \text{on } \{-\lambda \leq \bar{\psi}_u \leq \lambda\} \\ -\lambda & \text{on } \{\bar{\psi}_u < -\lambda\} \end{cases}$$

We have then that $\widetilde{E_u}[\widetilde{\psi}] \leq \widetilde{E_u}[\bar{\psi}_u]$ which contradicts the uniqueness of $\bar{\psi}_u$. So,

$$|\bar{\psi}_u| \leq \lambda \text{ a.e..}$$

So $\bar{\psi}_u$ is essentially bounded and

$$\|\bar{\psi}_u\|_\infty < \infty. \tag{2.5}$$

For the next theorem, we will need the following lemma from S. Dai, B. Li, and J. Lu [2].

**Lemma 2.1.1.** *Let $1 < p < \infty$ and $\psi_k \in L^p(\Omega)$ be such that*

$$\sup_k \|\psi_k\|_{L^p(\Omega)} < \infty. \tag{2.6}$$

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

*Proof:* [3, Lemma 3.1]

**Theorem 2.2.** *Let $u_k, u \in X^q$ such that*

$$\sup_k \|u_k\|_{W^{1,q}(\Omega)} < \infty \textit{ and } u_k \to u \textit{ in } L^q(\Omega).$$

*Let $\psi_k, \psi \in A^q$ correspond to*

$$E_{u_k}[\psi_k] = \min_{w \in A^q} E_{u_k}[w] \textit{ and } E_u[\psi] = \min_{w \in A^q} E_u[w].$$

*Then $\psi_k \to \psi$ in $H^1(\Omega)$ and $E_{u_k}[\psi_k] \to E_u[\psi]$.*

*Proof:* By Theorem 2.1, $\psi_k$ and $\psi$ are solutions to the Poisson Boltzmann equation (2.1) for all $k$, so we have

$$\int_\Omega \epsilon(u_k)\nabla\psi_k \cdot \nabla\eta + (1-u_k)B'(\psi_k)\eta dr = \int_\Omega u_k\rho_m\eta dr \quad \forall\eta \in H_0^1(\Omega) \text{ and } \forall k \tag{2.7}$$

$$\int_\Omega \epsilon(u)\nabla\psi \cdot \nabla\eta + (1-u)B'(\psi)\eta dr = \int_\Omega u\rho_m\eta dr \quad \forall\eta \in H_0^1(\Omega) \tag{2.8}$$

Clearly we have that $\{\psi_k\}$ is bounded in $H^1(\Omega)$ so there exists a subsequence $\{\psi_{k_j}\}$ that converges weakly in $H^1(\Omega)$. Then by the Rellich-Kondrachov, strongly in $L^p(\Omega)$ for any $p \in [1, 6)$, and a.e. in $\Omega$ to some $\psi^* \in H^1(\Omega)$. Note that $\psi^*$ may not be $\psi$. Furthermore, the corresponding subsequence $\{u_{k_j}\}$ converges a.e.. in $\Omega$. By (2.2)

$$(\|\psi_k\|_{H^1(\Omega)} + \|\psi_k\|_{L^\infty(\Omega)}) \leq M < \infty \ \forall k \tag{2.9}$$

$$(\|\psi\|_{H^1(\Omega)} + \|\psi\|_{L^\infty(\Omega)}) < \infty.$$

$A^q$ is convex and strongly closed in $H^1(\Omega)$, so $A^q$ is sequentially weakly closed. Hence $\psi^* \in A^q$.

We have by definition of $u_{k_j}$ that

$$\epsilon(u_{k_j}) \leq \epsilon_s. \tag{2.10}$$

Then by the Dominated Convergence Theorem and $u_{k_j} \to u^*$ a.e. in $\Omega$

$$\epsilon(u_{k_j}) \to \epsilon(u) \text{ a.e. in } \Omega.$$

Similarly by (2.2)

$$|B'(\psi_{k_j})| \leq C$$

then by the Dominated Convergence Theorem and $\psi_{k_j} \to \psi^*$ a.e. in $\Omega$

$$B'(\psi_{k_j}) \to B'(\psi^*) \text{ in } L^2(\Omega). \tag{2.11}$$

by the triangle inequality,

$$\lim_{j\to\infty} \int_\Omega (\epsilon(u_{k_j})\nabla\psi_{k_j} - \epsilon(u)\nabla\psi^*) \cdot \nabla\eta + (1 - u_{k_j})B'(\psi_{k_j})\eta - (1 - u)B'(\psi^*)\eta$$
$$\leq \lim_{j\to\infty} \int_\Omega (\epsilon(u_{k_j}) - \epsilon(u))\nabla\psi_{k_j} \cdot \nabla\eta + \epsilon(u)(\nabla\psi_{k_j} - \nabla\psi^*) \cdot \nabla\eta + (u - u_{k_j})B'(\psi_{k_j})\eta$$
$$+ (1 - u)(B'(\psi_{k_j}) - B'(\psi^*))\eta.$$

Recall that $\epsilon(u_{k_j})$ is uniformly bounded and $\epsilon(u_{k_j}) \to \epsilon(u)$ in $L^1(\Omega)$ then

$$\epsilon(u_{k_j}) \to \epsilon(u) \text{ in } L^2(\Omega). \tag{2.12}$$

then by Holders inequality we get

$$\lim_{j\to\infty} \int_\Omega (\epsilon(u_{k_j}) - \epsilon(u)) \nabla\psi_{k_j} \cdot \nabla\eta = 0$$

By (2.11),

$$\lim_{j\to\infty} \int_\Omega (1-u)(B'(\psi_{k_j}) - B'(\psi^*))\eta = 0$$

Now using (2.2), we have that we have that $\nabla\psi_{k_j} \rightharpoonup \nabla\psi^*$ in $L^2(\Omega)$ . Furthermore by, $\psi_{k_j} \rightharpoonup \psi^*$ in $H^1(\Omega)$ and (2.2) we have that

$$\psi_{k_j} - \quad {}^* \rightharpoonup 0 \text{ in } L^2(\Omega) \tag{2.13}$$

so that

$$\lim_{j\to\infty} \int_\Omega \epsilon(u)(\nabla\psi_{k_j} - \nabla\psi^*) \cdot \nabla\eta = 0$$

Finally by (2.11)

$$\lim_{j\to\infty} \int_\Omega (1-u)(B'(\psi_{k_j}) - B'(\psi^*))\eta = 0.$$

Combining these we get

$$\lim_{j\to\infty} \int_\Omega (\epsilon(u_{k_j})\nabla\psi_{k_j} - \epsilon(u)\nabla\psi^*) \cdot \nabla\eta + (1-u_{k_j})B'(\psi_{k_j})\eta - (1-u)B'(\psi^*)\eta = 0$$

so

$$\int_\Omega \epsilon(u)\nabla\psi^* \cdot \nabla\eta + (1-u)B'(\psi^*)\eta = \int_\Omega u\rho_m \eta dr \;\; \forall \eta \in C_c^1(\Omega), \tag{2.14}$$

where $C_c^1(\Omega)$ is the set of compactly supported $C^1$ mappings. $C_c^1(\Omega)$ is dense in $H_0^1(\Omega)$ so (2.14) is true for any $\eta \in H_0^1(\Omega)$. However, we previously established the uniqueness of the solution $\psi$ for $u$. Thus, $\psi = \psi^*$ in $A^q$.

Now consider, $\lim_{j\to\infty} \int_\Omega \epsilon(u_{k_j})|\nabla\psi_{k_j} - \nabla\psi|^2$. We have by (2.2) that

$$|B(\psi_{k_j})| \leq D < \infty.$$

Combining this with (2.2) and bound of $u_{k_j}$, we apply the Dominated Convergence Theorem so that

$$\lim_{j\to\infty}\int_\Omega (1-u_{k_j})B(\psi_{k_j})(\psi_{k_j}-\psi_\infty)dr = \int_\Omega (1-u)B(\psi)(\psi-\psi_\infty)dr.$$

Now by replacing $\eta$ with $\psi_{k_j}-\psi_\infty \in H_0^1(\Omega)$ in (2.7)

$$\begin{aligned}
&\lim_{j\to\infty}\int_\Omega \epsilon(u_{k_j})\nabla\psi_{k_j}\cdot\nabla(\psi_{k_j}-\psi_\infty)+(1-u_{k_j})B'(\psi_{k_j})(\psi_{k_j}-\psi_\infty)dr \\
&\qquad= \lim_{j\to\infty}\int_\Omega \epsilon(u_{k_j})|\nabla\psi_{k_j}|^2-\epsilon(u_{k_j})\nabla\psi_{k_j}\cdot\psi_\infty+(1-u_{k_j})B'(\psi_{k_j})(\psi_{k_j}-\psi_\infty)dr \\
&\qquad= \lim_{j\to\infty}\int_\Omega u_{k_j}\rho_m(\psi_{k_j}-\psi_\infty)dr
\end{aligned}$$

so we can write

$$\lim_{j\to\infty}\int_\Omega \epsilon(u_{k_j})|\nabla\psi_{k_j}|^2 \tag{2.15}$$

$$=\lim_{j\to\infty}\int_\Omega \epsilon(u_{k_j})\nabla\psi_{k_j}\cdot\psi_\infty-(1-u_{k_j})B'(\psi_{k_j})(\psi_{k_j}-\psi_\infty)+u_{k_j}\rho_m(\psi_{k_j}-\psi_\infty)dr \tag{2.16}$$

Now consider

$$\lim_{j\to\infty}\int_\Omega (\epsilon(u_{k_j})\nabla\psi_{k_j}-\epsilon(u)\nabla\psi)\cdot\nabla\psi_\infty$$

By the triangle inequality

$$\begin{aligned}
&\lim_{j\to\infty}\int_\Omega (\epsilon(u_{k_j})\nabla\psi_{k_j}-\epsilon(u)\nabla\psi)\cdot\nabla\psi_\infty \\
&\qquad\le \lim_{j\to\infty}[\int_\Omega (\epsilon(u_{k_j})-\epsilon(u))\nabla\psi_{k_j}\cdot\nabla\psi_\infty+\int_\Omega \epsilon(u)(\nabla\psi_{k_j}-\nabla\psi)\cdot\nabla\psi_\infty]
\end{aligned}$$

By (2.12) and $\nabla\psi_{k_j}\to\nabla\psi$ in $L^2(\Omega)$, we apply Holders inequality so that

$$\lim_{j\to\infty}\int_\Omega (\epsilon(u_{k_j})-\epsilon(u))\nabla\psi_{k_j}\cdot\nabla\psi_\infty = 0.$$

By, (2.13)

$$\lim_{j\to\infty}\int_\Omega \epsilon(u)(\nabla\psi_{k_j}-\nabla\psi)\cdot\nabla\psi_\infty = 0$$

Now combining these,

$$\lim_{j\to\infty}\int_\Omega (\epsilon(u_{k_j})\nabla\psi_{k_j} - \epsilon(u)\nabla\psi)\cdot\nabla\psi_\infty = 0$$

So

$$\lim_{j\to\infty}\int_\Omega \epsilon(u_{k_j})\nabla\psi_{k_j}\cdot\nabla\psi_\infty = \int_\Omega \epsilon(u)\nabla\psi\cdot\nabla\psi_\infty$$

Then by this and (2.14), equation (2.15) becomes

$$\begin{aligned}
&\lim_{j\to\infty}\int_\Omega \epsilon(u_{k_j})|\nabla\psi_{k_j}|^2 dr\\
&\quad = \lim_{j\to\infty}\int_\Omega u_{k_j}\rho_m(\psi_{k_j}-\psi_\infty) + \epsilon(u_{k_j})\nabla\psi_{k_j}\cdot\psi_\infty - (1-u_{k_j})B'(\psi_{j_k})(\psi_{k_j}-\psi_\infty)dr\\
&\quad = \int_\Omega u\rho_m(\psi-\psi_\infty) + \epsilon(u)\nabla\psi\cdot\psi_\infty - (1-u)B'(\psi)(\psi-\psi_\infty)dr \qquad (2.17)
\end{aligned}$$

Similarly, replacing $\eta$ with $\psi-\psi_\infty\in H_0^1(\Omega)$ in (2.8)

$$\begin{aligned}
&\int_\Omega \epsilon(u)\nabla\psi\cdot\nabla(\psi-\psi_\infty) + (1-u)B'(\psi)(\psi-\psi_\infty)dr\\
&\quad = \int_\Omega \epsilon(u)\nabla\psi\cdot\nabla\psi - \epsilon(u)\nabla\psi\cdot\psi_\infty + (1-u)B'(\psi)(\psi-\psi_\infty)dr\\
&\quad = \int_\Omega u\rho_m(\psi-\psi_\infty)dr
\end{aligned}$$

So we can write,

$$\int_\Omega (1-u)B'(\psi)(\psi-\psi_\infty)dr = \int_\Omega u\rho_m(\psi-\psi_\infty) + \epsilon(u)\nabla\psi\cdot\psi_\infty - \epsilon(u)\nabla\psi\cdot\nabla\psi dr \quad (2.18)$$

Then replacing (2.18) into (2.17),

$$\begin{aligned}
\lim_{j\to\infty}\int_\Omega \epsilon(u_{k_j})|\nabla\psi_{k_j}|^2 dr &= \int_\Omega u\rho_m(\psi-\psi_\infty) + \epsilon(u)\nabla\psi\cdot\psi_\infty - u\rho_m(\psi-\psi_\infty)\\
&\qquad - \epsilon(u)\nabla\psi\cdot\psi_\infty + \epsilon(u)|\nabla\psi|^2 dr\\
&= \int_\Omega \epsilon(u)|\nabla\psi|^2 dr \qquad (2.19)
\end{aligned}$$

We know that for $\{u_k\}$ and corresponding $\{\psi_k\}$, we have a subsequence $\{u_{k_j}\}$ and corresponding subsequence $\{\psi_{k_j}\}$ such that $u_{k_j} \to u$ a.e. in $\Omega$ and $\psi_{k_j} \to \psi$ in $L^2(\Omega)$ and a.e. in $\Omega$. Then replacing $\psi^*$ with $\psi$ in (2.11), we have

$$\lim_{j\to\infty} \int_\Omega -u_{k_j}\rho_m\psi_{k_j} + (1-u_{k_j})B(\psi_{k_j}) = \int_\Omega -u\rho_m\psi + (1-u)B(\psi).$$

Then combining this and (2.19) we have $E_{u_{k_j}}[\psi_{k_j}] \to E_u[\psi]$ and so $E_{u_k}[\psi_k] \to E_u[\psi]$. $\square$

**Theorem 2.3.** *For each* $1 < q \leq 2$*, there exists a* $u \in X^q$ *such that*

$$I^q_{np}[u] = \min_{w\in X^q} I^q_{np}[w] < \infty$$

*Proof:* Since $u \in W^{1,q}(\Omega)$

$$I^q_{np}[u] = \int_\Omega \gamma|\nabla u|^q + pu + \rho_0(1-u)U^{att} \geq \int_\Omega \gamma|\nabla u|^q - \rho_0|U^{att}|.$$

Since $m(\Omega) < \infty$ we have that $\int_\Omega \rho_0|U^{att}| < \infty$; hence there exists a $\beta > 0$ so that,

$$I^q_{np}[u] \geq \gamma\|\nabla u\|^q_{L^q(\Omega)} - \beta. \tag{2.20}$$

So $I^q_{np}[u]$ is coercive for any $q \in (1,2]$ and there exists an $\inf_{z\in X^q} I^q_{np}[z]$. We may choose a sequence of $u_k \in X^q$ such that $I^q_{np}[u_k] \to \inf_{z\in X^q} I^q_{np}[z]$.

Then

$$\|Du_k\|_{L^q} \leq \inf_{z\in X^q} I^q_{np}[z] < \infty$$

so $\exists M > 0$ such that

$$\|Du_k\|_{L^q(\Omega)} < M \quad \forall k.$$

We have that $u = 0$ on $\partial\Omega$, so by Poincare's inequality there exists a $C > 0$ so that

$$\|u_k\|_{L^q(\Omega)} \leq C\|Du_k\|_{L^q(\Omega)} < CM.$$

Hence

$$\|u_k\|_{W^{1,q}(\Omega)} = \|u_k\|_{L^q(\Omega)} + C\|Du_k\|_{L^q(\Omega)} < CM + M.$$

Hence $\{u_k\}$ is bounded in $W^{1,q}(\Omega)$ and there exists a subsequence not relabeled such that

$$u_k \rightharpoonup u^* \text{ in } W^{1,q}(\Omega) \tag{2.21}$$

We have then by Soblev embedding that $W^{1,q}(\Omega) \hookrightarrow L^{3q/3-q}(\Omega)$. By Hellys selection theorem there exists a bounded subsequence, not relabeled, such that

$$u_k \to u^* \in L^{3q/3-q}(\Omega) \text{ pointwise a.e. in } \Omega \tag{2.22}$$

So by (2.22) we have that

$$\lim_{k\to\infty} \int_\Omega pu_k + \rho_0(1-u_k)U^{att} = \int_\Omega pu^* + \rho_0(1-u^*)U^{att}.$$

Finally by (2.21),

$$\int_\Omega |\nabla u^*|^q \leq \liminf_{k\to\infty} \int_\Omega |\nabla u_k|^q.$$

Now given that $u^* \in X^q$

$$\inf_{z\in X^q} I^q_{np}[z] \leq I^q_{np}[u^*] \leq \inf_{z\in X^q} I^q_{np}[z].$$

So $I^q_{np}[u^*] = \inf_{z\in X^q} I^q_{np}[z]$.

□

**Theorem 2.4.** *There exists a $u \in X^q$ such that*

$$I[u] = \min_{w\in X^q} I[w] < \infty$$

*Proof:*

$$\begin{aligned} I[u] &= I^q_{np} - E_u[\psi] \\ &= \int_\Omega |\nabla u|^q + pu + \rho_0(1-u)U^{att} + u\rho_m\psi - \frac{1}{2}|\nabla\psi|^2\epsilon(u) - (1-u)B(\psi) \end{aligned}$$

Given for any $u \in X$ we have $E_u[\psi_u] \leq E_u[\psi_\infty]$. Consider $-I_p[u] = E_u[\psi]$, we have that $E_u[\psi] \leq E[\psi_\infty]$

$$\begin{aligned} E_u[\psi_\infty] &= \int_\Omega -u\rho_m\psi_\infty + \frac{1}{2}|\nabla\psi_\infty|^2\epsilon(u) + (1-u)B(\psi_\infty) \\ &\leq \rho\|\psi_\infty\|_\infty + \frac{1}{2}\epsilon_m \int_\Omega |\nabla\psi_\infty|^2 + B(\|\nabla\psi_\infty\|). \end{aligned}$$

then by (2.2) and $\psi_\infty \in H^1(\Omega)$, there exists a $C > 0$ so that

$$E_u[\psi_\infty] < C < \infty$$

and by coercitivity there exists a $D > 0$ so that

$$I[u] = I^q_{np}[u] + I_p[u,\psi] = I^q_{np}[u] - E_u[\psi] > D - C > -\infty \ \forall u \in X^q$$

So there exists a minimizing sequence $\{u_k\}$ such that

$$\lim_{k\to\infty} I[u_k] = \inf_{z\in X^q} I[z] = M.$$

Now for each $u \in X^q$

$$\begin{aligned} E_u[\psi] &= \int_\Omega -u\rho_m\psi + \frac{1}{2}|\nabla\psi|^2\epsilon(u) + (1-u)B(\psi) \\ &\geq \int_\Omega -u\rho_m\psi - uB(\psi) \\ &\geq \int_\Omega -\rho_m\|\psi\|_\infty - B(\psi) \end{aligned}$$

$\in A^q$ is the corresponding electric potential for $u$. By (2.2) and given that $B(v)$ is a strictly convex function, $B(\psi) \in (-\infty, \infty)$ for any $\psi \in A^q$. Then

$$\begin{aligned} E_u[\psi] &\geq \int_\Omega -\rho_m\|\psi\|_\infty - B(\psi) > -\infty \\ -E_u[\psi] &= I_p[u,\psi] < \infty \end{aligned}$$

Now

$$\begin{aligned} I_{np}^q[u] &= \int_\Omega |\nabla u|^q + pu + \rho_0(1-u)U^{att} \\ &\leq \|u\|_{W^{1,q}(\Omega)} + \int_\Omega p \\ &< \infty \end{aligned}$$

Hence for an arbitrary $u \in X^q$,

$$I[u] = I_{np}^q[u] + I_p[u, \psi] < \infty.$$

So $\inf_{z \in X} I[z] = M < \infty$ and for $k$ sufficiently large

$$I[u_k] \leq M + 1$$

Thus by coercitivity ,

$$\|\nabla u_k\|_{L^q(\Omega)}^q < M + 1 + \beta < \infty$$

and by Poincare's inequality there exists a $C > 0$ so that,

$$\|u_k\|_{L^q(\Omega)} < C\|\nabla u_k\|_{L^q(\Omega)} < \infty.$$

So for $k$ sufficiently large

$$\|u_k\|_{W^{1,q}(\Omega)} < \infty \text{ and } u_k \rightharpoonup u^* \text{ in } W^{1,q}(\Omega). \tag{2.23}$$

And given that $X^q$ is weakly closed in $W^{1,q}(\Omega)$, we have that $u^* \in X^q$.

Now by (2.23),

$$\int_\Omega |\nabla u^*|^q \leq \liminf_{k \to \infty} \int_\Omega |\nabla u_k|^q \tag{2.24}$$

and by the Rellich-Kondrovachov Theorem, $W^{1,q}(\Omega)$ is compactly embedded into $L^p(\Omega)$ for any $p \in [1, \frac{3q}{3-q})$ so that $u_k \to u^*$ in $L^p(\Omega)$ and

$$u_k \to u^* \text{ a.e.. in } \Omega \tag{2.25}$$

Then by (2.24), (2.25), and Fatou's Lemma, we have

$$I^q_{np}[u^*] \le \liminf_{k\to\infty} I^q_{np}[u_k]. \tag{2.26}$$

By Theorem (2.2),

$$\lim_{k\to\infty} I_p[u_k] = -\lim_{k\to\infty} E_{u_k}[\psi_k] = -E_{u^*}[\psi] = I_p[u^*].$$

So combining this and (2.26), we have

$$\begin{aligned} M \le I[u^*] &= I^q_{np}[u^*] + I_p[u^*] \\ &\le \liminf_{k\to\infty} I^q_{np}[u_k] + \lim_{k\to\infty} I_p[u_k] \\ &\le \lim_{k\to\infty} I[u_k] = M. \end{aligned}$$

So, $I[u^*] = \min_{z\in X^q} I[z] < \infty$.

□

## 2.2 New Extended Non-Polar Model

We denote $\Omega_m$ the macro-molecular domain and $\Omega_s$ the solvent domain within the computational domain $\Omega$ to be Lipshitz with $\Omega = \Omega_s \cup \Omega_m$ and $m(\Omega) < \infty$. Then the region $\Omega_b = \Omega_s \cap \Omega_m$ is the region of molecules and solvent. We define a characteristic function for the solvent $u : \mathbb{R}^3 \to \mathbb{R}$ :

$$u(x) = \begin{cases} 1 & \text{for } x \in \Omega_1 \\ u \ge 0 & \text{for } x \in \Omega_b \\ 0 & \text{for } x \in \Omega_0 \end{cases}$$

such that $\Omega_1$ is the subset of $\Omega_m$ where $u = 1$ everywhere and $\Omega_0$ is the subset of $\Omega_s$ where $u = 0$ everywhere. Consider the energy functional proposed by Z. Chen and Y. Shao [8].

$$I[u] = \int_\Omega |\nabla u|^2 + 18w(u) + pu + \rho_s(1-u)U_{ss}\, d\Omega$$

where $w(u) = u^2(1-u)^2$, $\rho_s$ is a constant, and $p$ is the pressure difference. We define the admissible functions to be

$$A = \{u \in H^1(\Omega) : u \geq 0 \text{ a.e. in } \Omega \text{ and } u = 0 \text{ on } \partial\Omega_1 \text{ and } u = 1 \text{ on } \partial\Omega_0\}.$$

Now consider that

$$\begin{aligned} I[u] &= \int_\Omega |\nabla u|^2 + 18w(u) + pu + \rho_s(u-1)|U_{ss}|d\Omega \\ &> \int_\Omega |\nabla u|^2 + \rho_s(u-1)|U_{ss}|d\Omega \\ &> \int_\Omega |\nabla u|^2 d\Omega - \int_\Omega \rho_s|U_{ss}|d\Omega \\ &= \|Du\|^2_{L^2(\Omega)} - \int_\Omega \rho_s|U_{ss}|d\Omega. \end{aligned}$$

Given that $m(\Omega) < \infty$ and $\int_\Omega |U_{ss}|d\Omega < \infty$, we have that there exists $\beta > 0$ such that

$$I[u] \geq \|Du\|_{L^2(\Omega)} - \beta.$$

Thus $I[u]$ is coercive and there exists an infimum, $\inf_{z\in A} I[z]$. So then we may choose a minimizing sequence $u_k \in A$ so that $I[u_k] \to \inf_{z\in A} I[z]$ as $k \to \infty$.

We have by coercitivity that

$$\|Du_k\|_{L^2(\Omega)} \leq \inf_{z\in A} I[z] < \infty$$

so there exists an $M > 0$ such that

$$\|Du_k\|_{L^2(\Omega)} < M \quad \forall\, k.$$

Furthermore since $u = 0$ on $\partial\Omega_s$, $u_k \in H^1_0(\Omega)$. Then by Poincare's identity there exists a $C > 0$ such that

$$\|u_k\|_{L^2(\Omega)} \leq C\|Du_k\|_{L^2(\Omega)} < CM.$$

Hence,

$$\|u_k\|_{H^1(\Omega)} = \|u_k\|_{L^2(\Omega)} + \|Du_k\|_{L^2(\Omega)} < CM + M \tag{2.27}$$

so $\{u_k\}$ is bounded in $H^1(\Omega)$ and there exists a subsequence, not relabeled, so that

$$u_{k_j} \rightharpoonup u^* \text{ in } H^1(\Omega). \tag{2.28}$$

Because $A$ is convex and weak, sequentially closed, we have $u^* \in A$.

Now by the Rellich-Kondrachov, $H^1(\Omega)$ is continuously embedded into $L^6(\Omega)$. By this and Helly's selection theorem, there exists a bounded subsequence, not relabeled, such that

$$u_k \to u^* \text{ in } L^2(\Omega) \text{ and pointwise a.e. in } \Omega. \tag{2.29}$$

Furthermore, we have $u_k$ is bounded in $L^p(\Omega)$ for $1 < p \leq 6$, so

$$\int_\Omega w(u_k) = \int_\Omega u_k^2(1-u_k)^2 \leq \int_\Omega u_k^2 + u_k^4 = \|u_k\|^2_{L^2(\Omega)} + \|u_k\|^4_{L^4(\Omega)} < \infty.$$

Then there exists a subsequence not relabeled so that

$$w(u_k) \to w(u^*) \text{ a.e. in } \Omega. \tag{2.30}$$

Returning to $I[u_{k_j}]$, by (2.28),

$$\int_\Omega |\nabla u^*|^2 d\Omega \leq \liminf_{k\to\infty} \int_\Omega |\nabla u_k|^2 d\Omega.$$

By (2.29), the boundedness of $|U_{ss}|$, and Fatou's lemma we have,

$$\int_\Omega pu^* + \rho_s(u^*-1)|U_{ss}| d\Omega \leq \liminf_{i\to\infty} \int_\Omega pu_{k_j} + \rho_s(u_{k_j}-1)|U_{ss}| d\Omega.$$

By (2.30) and Fatou's lemma,

$$\int_\Omega w(u^*) d\Omega \leq \liminf_{i\to\infty} \int_\Omega w(u_{k_j}) d\Omega.$$

Now combining these we have

$$I[u^*] \leq \liminf_{i\to\infty} I[u_{k_j}]$$

and $u^* \in A$. So,

$$I[u^*] = \inf_{z\in A} I[z] = \min_{z\in A} I[z].$$

□

# CHAPTER 3

# SHARP INTERFACE

We define the region of computation $\Omega = \Omega_m \cup \Omega_s$ for solute region $\Omega_m$ and solvent region $\Omega_s$. We then consider the functional of solvation as defined by Z. Chen [7],

$$G = \gamma(Area) + p(Vol) + \int_{\Omega_s} \rho_s U^{vdW} - \frac{1}{2}\epsilon_s |\nabla\psi|^2 - k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right) + \int_{\Omega_m} \rho_m \psi - \frac{1}{2}\epsilon_m |\nabla\psi|^2 dr.$$

Here $Area$ and $Vol$ represent the surface area and volume of the macromolecule and

$$\int_{\Omega_s} \rho_s U^{vdW}\, dr, \int_{\Omega_m} \rho_m \psi\, dr$$
$$\int_{\Omega_m} \epsilon_m |\nabla\psi|^2\, dr, \int_{\Omega_s} \epsilon_s |\nabla\psi|^2\, dr$$
$$\int_{\Omega_s} k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right)\, dr$$

are other volume functionals of the form $\int_{\Omega_i} F(r)dr$. The $\gamma(Area)$ term is the surface energy; it measures the disruption of intermolecular and/or intramolecular bonds that occur when a surface is created. The $p(Vol)$ term is the mechanical work of creating the vacuum of a biomolecular size in the solvent. The other terms represent the same as previously mentioned. We use the same notation for constants as the previous functional with the addition of solvent density $\rho_s$ and $U^{vdW}(r)$ the attractive portion of the van der Waals potential at point $r$.

By calculus of variations, given a functional $I[u] = \int_U F(Du, u, x)dx$ on a region $U$. We define $I[u+v] = \int_U F(D(u+v), u+v, x)$ for an increment given by the arbitrary function $v(x) \in C_c^\infty(\mathbb{R})$. Then $\Delta I = I[u+v] - I[u]$ and we expand $I[u+v]$ using Taylor's theorem about $v = 0$,

$$I[u+v] = I[u] + I_u[u]v + I_{Du}[u]Dv + \frac{1}{2}I_{uu}[u](v)^2 + \frac{1}{2}I_{DuDu}[u](Dv)^2 + \frac{1}{2}I_{uDu}[u]v(Dv) + \frac{1}{2}I_{Duu}[u]v(Dv) + O(v^3)$$

We denote $\eta_1$ and $\eta_2$ the first and second order terms from the Taylor's expansion, then

$$\Delta I = \eta_1[v] + \eta_2[v] + O(v^3).$$

For an arbitrary constant $\tau \in \mathbb{R}$, the variation of $I$ is defined to be

$$\delta I = \eta_1[v] = \frac{\partial}{\partial \tau} I[u + \tau v]|_{\tau=0}$$

and the second variation to be

$$\delta^2 I = \eta_2[v] = \frac{1}{2}\frac{\partial^2}{\partial \tau^2} I[u + \tau v]|_{\tau=0}.$$

### 3.1 Perturbation of $|g|$

We know from calculus that for a real manifold $\Xi$ and a region $\Omega$

$$Area = \int_{\Xi} d\sigma \text{ and } Volume = \int_{\Omega} dV$$

Because both area and volume depend on $|g|$ where $g$ is the first fundamental form. Their variations include the perturbations of $|g|$. This can be found generally thus simplifying later calculations of the variation of volume and area.

We define the interface $\Gamma$ to be a closed surface in real euclidean space and $U$ an open set contained in $\Gamma$. We then define $f : U \to \mathbb{R}^3$ to be a surface patch on $\Gamma$ and $f^{\rho} = f + \rho N(u_1, u_2)$ to be a surface patch on the perturbed surface with $\rho = \epsilon\phi$ for an arbitrary function $\phi(u_1, u_2) \in C_c^{\infty}(\Omega)$ and $\epsilon \in \mathbb{R}$. We have then from J. Pruss and g. Simonett [3] that the perturbation on $g$ by $\rho$ is given in the equation,

$$g(f^{\rho}) = g - 2\rho l + \rho^2 l g^{-1} l + \nabla_{\Xi}\rho \otimes \nabla_{\Xi}\rho$$

where $l$ denotes the second fundamental form and $\nabla_{\Xi}$ is the surface gradient. For compactness, we denote $g(\rho) = g - 2\rho l + \rho^2 l g^{-1} l$. Then denoting $S = g^{-1} l$ as the shape operator,

$$g(\rho) = g[I - 2\rho g^{-1} l + \rho^2 [g^{-1} l]^2] = g[I - 2\rho S + \rho^2 S^2] = g[\rho S - I]^2.$$

So we have the perturbation of $g$ is given by,

$$g(f^\rho) = g(\rho)[I + g^{-1}(\rho)\, \nabla_\Xi \rho \otimes \nabla_\Xi \rho],$$

and the determinant $|g(f^\rho)|$ of the perturbed $g$ gives the perturbation of $|g|$

$$|g(f^\rho)| = |g(\rho)||I + g^{-1}(\rho)\, \nabla_\Xi \rho \otimes \nabla_\Xi \rho|.$$

### 3.1.1 Derivatives of the perturbation of $|g|$

We can then quickly take the derivatives of the perturbations of $|g|$ to simplify later calculations. The first order derivative is

$$\begin{aligned}\frac{\partial}{\partial \epsilon}|g(f^\rho)||_{\epsilon=0} &= \frac{\partial}{\partial \epsilon}\left(|g(\rho)||I + g^{-1}(\rho)\nabla_\Xi \rho \otimes \nabla_\Xi \rho|\right)|_{\epsilon=0} \\ &= \frac{\partial}{\partial \epsilon}|g(\rho)||_{\epsilon=0}|I + g^{-1}(\rho)\nabla_\Xi \rho \otimes \nabla_\Xi \rho||_{\epsilon=0} + \frac{\partial}{\partial \epsilon}|I + g^{-1}(\rho)\nabla_\Xi \rho \otimes \nabla_\Xi \rho||_{\epsilon=0}|g(\rho)||_{\epsilon=0}.\end{aligned}$$

Clearly, $|g(\rho)||_{\epsilon=0} = |g|$ and $|I + g^{-1}(\rho)\nabla_\Xi \rho \otimes \nabla_\Xi \rho||_{\epsilon=0} = |I| = 1$. Then $\frac{\partial}{\partial \epsilon}|g(f^\rho)|$ simplifies to

$$\frac{\partial}{\partial \epsilon}|g(f^\rho)| = \frac{\partial}{\partial \epsilon}|g(\rho)||_{\epsilon=0} + \frac{\partial}{\partial \epsilon}|I + g^{-1}(\rho)\nabla_\Xi \rho \otimes \nabla_\Xi \rho||g|.$$

Furthermore, we know that for any two vectors $a, b \in \mathbb{R}^n$ we have $|I + a \otimes b| = (1 + a \cdot b)$, so

$$\begin{aligned}\frac{\partial}{\partial \epsilon}|I + g^{-1}(\rho)\nabla_\Xi \rho \otimes \nabla_\Xi \rho||_{\epsilon=0} =& \frac{\partial}{\partial \epsilon}|I + \epsilon^2 g^{-1}(\rho)\, \nabla_\Xi \phi \otimes \nabla_\Xi \phi||_{\epsilon=0} \\ =& \frac{\partial}{\partial \epsilon}(1 + \epsilon^2(|g|^{-1}(\rho)\nabla_\Xi \phi \cdot \nabla_\Xi \phi))|_{\epsilon=0} \\ =& 2\epsilon(|g|^{-1}(\rho)\nabla_\Xi \phi \cdot \nabla_\Xi \phi)|_{\epsilon=0} + \epsilon^2 \frac{\partial}{\partial \epsilon}(|g|^{-1}(\rho)\nabla_\Xi \phi \cdot \nabla_\Xi \phi)|_{\epsilon=0} \\ =& 0.\end{aligned}$$

Hence,

$$\begin{aligned}\frac{\partial}{\partial\epsilon}|g(f^{\rho})||_{\epsilon=0} =&\frac{\partial}{\partial\epsilon}|g(\rho)||_{\epsilon=0} = \frac{\partial}{\partial\epsilon}\left(|g||\rho S - I|^2\right)|_{\epsilon=0} = |g|\frac{\partial}{\partial\epsilon}|\rho S - I|^2|_{\epsilon=0}\\ =&2g|\rho S - I||_{\epsilon=0}\frac{\partial}{\partial\epsilon}|\rho S - I||_{\epsilon=0}\\ =&2g\frac{\partial}{\partial\epsilon}|\rho S - I||_{\epsilon=0}.\end{aligned}$$

Now using Jacobi's formula and notating $adj(A)$ for the adjunct of $A$,

$$\begin{aligned}\frac{\partial}{\partial\epsilon}|\rho S - I||_{\epsilon=0} =&tr(adj(\rho S - I)|_{\epsilon=0}\phi S)\\ =&tr(adj(-I)\phi S)\\ =&-\phi tr(S).\end{aligned}$$

We then have the first order derivative of the perturbations of $|g|$ is

$$\frac{\partial}{\partial\epsilon}|g(f^{\rho})| = \frac{\partial}{\partial\epsilon}|g(\rho)||_{\epsilon=0} = -2g\phi tr(S) = -4g\phi H \tag{3.1}$$

where $H = \frac{1}{2}tr(S)$ is the mean curvature at a point. Now the second order derivative of the perturbation of $|g|^{1/2}$ is given by

$$\begin{aligned}\frac{\partial^2}{\partial\epsilon^2}|g(f^{\rho})||_{\epsilon=0} = \frac{\partial^2}{\partial\epsilon^2}&|g(\rho)||_{\epsilon=0}|I + g^{-1}(\rho)\nabla_{\Xi}\rho\otimes\nabla_{\Xi}\rho||_{\epsilon=0}\\ &+ |g(\rho)||_{\epsilon=0}\frac{\partial^2}{\partial\epsilon^2}|I + g^{-1}(\rho)\nabla_{\Xi}\rho\otimes\nabla_{\Xi}\rho||_{\epsilon=0}\\ &+ 2\frac{\partial}{\partial\epsilon}|g(\rho)|\frac{\partial}{\partial\epsilon}|I + g^{-1}(\rho)\nabla_{\Xi}\rho\otimes\nabla_{\Xi}\rho||_{\epsilon=0}.\end{aligned}$$

Since $\frac{\partial}{\partial\epsilon}|I + g^{-1}(\rho)\nabla_{\Xi}\rho\otimes\nabla_{\Xi}\rho||_{\epsilon=0} = 0$, we get that $\frac{\partial^2}{\partial\epsilon^2}|g(f^{\rho})||_{\epsilon=0}$ simplifies to

$$\frac{\partial^2}{\partial\epsilon^2}|g(f^{\rho})||_{\epsilon=0} = \frac{\partial^2}{\partial\epsilon^2}|g(\rho)||_{\epsilon=0} + |g|\frac{\partial^2}{\partial\epsilon^2}|I + g^{-1}(\rho)\nabla_{\Xi}\rho\otimes\nabla_{\Xi}\rho||_{\epsilon=0}$$

Consider now $\frac{\partial^2}{\partial\epsilon^2}|g(\rho)||_{\epsilon=0}$

$$
\begin{aligned}
\frac{\partial^2}{\partial\epsilon^2}|g(\rho)||_{\epsilon=0} =&\frac{\partial^2}{\partial\epsilon^2}\left(|g||\rho S - I|^2\right)|_{\epsilon=0}\\
=&|g|\frac{\partial^2}{\partial\epsilon^2}|\rho S - I|^2|_{\epsilon=0}\\
=&2g\frac{\partial}{\partial\epsilon}\left(|\rho S - I|\frac{\partial}{\partial\epsilon}|\rho S - I|\right)|_{\epsilon=0}\\
=&2g\left[\left(\frac{\partial}{\partial\epsilon}|\rho S - I||_{\epsilon=0}\right)^2 + |S|\frac{\partial^2}{\partial\epsilon^2}|\rho - S^{-1}||_{\epsilon=0}\right]\\
=&2g\left(\phi^2 tr^2\left(S\right) + 2\phi^2|S|\right).
\end{aligned}
$$

Then given that Gaussian curvature $K = |S|$ and mean curvature $H = \frac{1}{2}tr(S)$,

$$\frac{\partial^2}{\partial\epsilon^2}|g(\rho)||_{\epsilon=0} = 8g\phi^2H^2 + 4\phi^2|g|K \tag{3.2}$$

Now it remains to find $\frac{\partial^2}{\partial\epsilon^2}|I + g^{-1}(\rho)\nabla_\Xi\rho\otimes\nabla_\Xi\rho||_{\epsilon=0}$,

$$
\begin{aligned}
\frac{\partial^2}{\partial\epsilon^2}|I + g^{-1}(\rho)\nabla_\Xi\rho\otimes\nabla_\Xi\rho||_{\epsilon=0} =&\frac{\partial^2}{\partial\epsilon^2}(1 + \epsilon^2(|g|^{-1}(\rho)\nabla_\Xi\phi\cdot\nabla_\Xi\phi))|_{\epsilon=0}\\
=&2(|g|^{-1}(\rho)\nabla_\Xi\phi\cdot\nabla_\Xi\phi)|_{\epsilon=0}\\
=&2(|g|^{-1}\nabla_\Xi\phi\cdot\nabla_\Xi\phi)\\
=&2\sum_{i,j}g_{ij}^{-1}\phi_i\phi_j.
\end{aligned} \tag{3.3}
$$

Finally by (3.3) and (3.2) we have that the second order derivative of the perturbation on $|g|$ is

$$\frac{\partial^2}{\partial\epsilon^2}|g(f^\rho)| = |g|\left(8\phi^2H^2 + 4\phi^2K + 2\sum_{i,j}g_{ij}^{-1}\phi_i\phi_j\right). \tag{3.4}$$

## 3.2 Variation of Area and Volume

### 3.2.1 Variation of Area

We have that $Area$ on a real euclidean manifold, $\Xi$, is given by $Area = \int_\Xi d\sigma = \int_U |g|^{1/2}du_1du_2$. Clearly then the perturbation of $Area$ is given by

$$\int_U |g(f^\rho)|^{1/2}du_1du_2.$$

So using (3.1), the first variation of $Area$ is

$$\begin{aligned}\delta Area =&\frac{\partial}{\partial\epsilon}\int_U |g(f^\rho)|^{\frac{1}{2}}du_1du_2|_{\epsilon=0} = \int_U \frac{1}{2}|g(f^\rho)||_{\epsilon=0}^{-1/2}\frac{\partial}{\partial\epsilon}|g(f^\rho)||_{\epsilon=0}du_1du_2\\ =&\int_U \frac{1}{2}|g|^{-1/2}\frac{\partial}{\partial\epsilon}|g(f^\rho)||_{\epsilon=0}du_1du_2\\ =&\int_U \frac{1}{2}|g|^{-1/2}(-4g\phi H)du_1du_2\end{aligned}$$

$$\delta Area = -2\int_\Xi \phi H d\sigma \tag{3.5}$$

And by using (3.1) and (3.4), the second variation of $Area$ is

$$\begin{aligned}\delta^2 Area =&\frac{1}{2}\frac{\partial^2}{\partial\epsilon^2}\left(\int_U |g(f^\rho)|^{\frac{1}{2}}du_1du_2\right)|_{\epsilon=0} = \frac{\partial}{\partial\epsilon}\left(\int_U \frac{1}{4}|g(f^\rho)|^{-1/2}\frac{\partial}{\partial\epsilon}|g(f^\rho)|du_1du_2\right)|_{\epsilon=0}\\ =&\int_U\left(\frac{-1}{8}|g(f^\rho)|^{-3/2}\left(\frac{\partial}{\partial\epsilon}|g(f^\rho)|\right)^2+\frac{1}{4}|g(f^\rho)||_{\epsilon=0}^{-1/2}\frac{\partial^2}{\partial\epsilon^2}|g(f^\rho)|du_1du_2\right)|_{\epsilon=0}\\ =&\int_U \frac{-1}{8}|g|^{-3/2}\left(-4g\phi H\right)^2+\frac{1}{4}|g|^{-1/2}|g|\left(8\phi^2H^2+4\phi^2K+2\sum_{i,j}g_{ij}^{-1}\phi_i\phi_j\right)du_1du_2\\ =&\int_U |g|^{1/2}\phi^2K+\frac{1}{2}|g|^{1/2}\sum_{i,j}g_{ij}^{-1}\phi_i\phi_j du_1du_2\end{aligned}$$

Consider the operator $\nabla_\Xi\phi = \phi_i du^i$, where $u = (u_1, u_2)$ is the coordinates in the local patches. Then

$$\sum_{i,j} g_{ij}^{-1}\phi_i\phi_j = |\nabla_\Xi\phi|_g^2.$$

Because $\phi \in C_c^\infty(\mathbb{R})$, we use integration by parts so that

$$\int_\Xi |\nabla_\Xi\phi|_g^2 d\sigma = \int_\Xi (\nabla_\Xi\cdot\nabla_\Xi\phi)\phi d\sigma.$$

then

$$\int_\Xi (\nabla_\Xi\cdot\nabla_\Xi\phi)\phi d\sigma = -\int_\Xi (\Delta_g\phi)\phi d\sigma$$

for the Laplace-Beltrami operator related to $g$, $\Delta_g$. Then combining the above,

$$\int_\Xi \sum_{i,j} g_{ij}^{-1}\phi_i\phi_j d\sigma = \int_\Xi |\nabla_\Xi\phi|_g^2 d\sigma = -\int_\Xi (\Delta_g\phi)\phi d\sigma.$$

so

$$\delta^2 Area = \int_\Xi \phi^2 K - \frac{1}{2}(\Delta_g\phi)\phi d\sigma \tag{3.6}$$

### 3.2.2 Variation of Volume and other Volume Functionals

Let $x = (x_1, x_2, x_3)$ be coordinates in $\mathbb{R}^3$. Denote the reference domain by $\Omega_m$, its boundary by $\Xi$. Let $N_m$ be the outward point unit normal field of $\Xi$. Given $\phi \in C_c^\infty(\Xi)$, consider the normal variation $f^{\epsilon\phi} : \Xi \times (-a, a) \to \mathbb{R}^3 : (p, \epsilon) \mapsto p + \epsilon\phi N_m$ for a sufficiently small positive constant $a$. Set $\Xi_{\epsilon = f^{\epsilon\phi}(\Xi,\epsilon)}$ and denote by $\Omega_\epsilon$ the region enclosed by $\Xi_\epsilon$ with $d\sigma_\epsilon$ the surface element of $\Xi_\epsilon$. Let $N_\epsilon$ be the outward point unit normal field of $\Xi_\epsilon$.

The perturbation of $Volume$ is given by

$$Volume(\rho) = \int_{\Omega_\epsilon} dx.$$

Here $\beta$ and $a$ denote

$$\begin{aligned} a(\rho) =& (I - \rho l)^{-1} \nabla_\Xi \rho \\ \beta(\rho) =& (1 + |a(\rho)|^2)^{-1/2} \end{aligned}$$

with $\nabla_\Xi$ being the surface gradient operator on $\Xi$, $l$ and $S$ being the second fundamental form and the shape operator on $\Xi$, respectively. By the Continuity Equaiton, c.f. the book Partial Differential Equations by Emmanuele DiBenedetto [9],

$$\begin{aligned} \frac{\partial}{\partial\epsilon} Volume(\rho) =& \frac{\partial}{\partial\epsilon} \int_{\Omega_\epsilon} dx \\ =& \int_{\Xi_\epsilon} (N_\epsilon | N_m) \phi \, d\sigma_\epsilon \\ =& \int_\Xi (\beta(\epsilon\phi)(N_m - a(\epsilon\phi)) | N_m) \phi \, d\sigma_\epsilon \\ =& \int_\Xi \phi(u) |I - \rho S| \, d\sigma, \end{aligned}$$

and

$$\begin{aligned} \frac{\partial^2}{\partial\epsilon^2} Volume(\rho) =& \frac{\partial}{\partial\epsilon} \int_\Xi \phi(u) |I - \rho S| \, d\sigma \\ =& \int_\Xi \phi \frac{\partial}{\partial\epsilon} |I - \rho S| \, d\sigma. \end{aligned}$$

Clearly then

$$\delta Volume = \frac{\partial}{\partial \epsilon}\int_{\Omega_\epsilon} dx|_{\epsilon=0} = \int_{\Xi} \phi(u)\alpha(0)\, d\sigma = \int_{\Xi} \phi d\sigma. \tag{3.7}$$

Recall

$$\frac{\partial}{\partial \epsilon}|I - \epsilon\phi S||_{\epsilon=0} = -\phi tr(S).$$

Then

$$\delta^2 Volume = \frac{1}{2}\frac{\partial^2}{\partial \epsilon^2} Volume(\rho)|_{\epsilon=0} = \frac{1}{2}\int_{\Xi} \phi \frac{\partial}{\partial \epsilon}|I - \rho S||_{\epsilon=0}\, d\sigma = -\frac{1}{2}\int_{\Xi} \phi^2 tr(S)\, d\sigma$$

$$\delta^2 Volume = -\int_{\Xi} \phi^2(u) H\, d\sigma \tag{3.8}$$

Recall that the full energy functional $g$ is given by

$$\begin{aligned} G =& \gamma(Area) + p(Vol) + \int_{\Omega_m} \rho_m \psi - \epsilon_m |\nabla\psi|^2 + \int_{\Omega_s} \rho_s U^{vdW} \\ & - \int_{\Omega_m} k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i / k_B T} - 1\right) - \int_{\Omega_s} \epsilon_s |\nabla\psi|^2. \end{aligned}$$

So to take the variation of $g$, we must find the variation of the other volume functionals. Consider a general function $F : \Omega \to \mathbb{R}$. In a tubular neighbourhood of $\Xi$, we can write $F(u_1, u_2, \epsilon)$, where $(u_1, u_2)$ are coordinates in local patches of $\Xi$ and $\epsilon$ is normal variation parameter. Then, the perturbation of a general volume integral is

$$\int_{\Omega_\epsilon} F(x)\, dx.$$

By the Continuity Equaiton, c.f. the book Partial Differential Equations by Emmanuele DiBenedetto [9] and $N_\epsilon = \beta(\epsilon\phi)(N_m - a(\epsilon\phi))$, we have that

$$\begin{aligned} \frac{\partial}{\partial \epsilon}\int_{\Omega_\epsilon} F(x)\, dx &= \int_{\Xi_\epsilon} (N_\epsilon | N_m)\phi F\, d\sigma_\epsilon \\ &= \int_{\Xi} (\beta(\epsilon\phi)(N_m - a(\epsilon\phi))|N_m)\phi F\, d\sigma_\epsilon \\ &= \int_{\Xi} \phi(u) F(u, \epsilon)|I - \rho S|\, d\sigma. \end{aligned}$$

Then

$$\delta \int_{\Omega_m} F(r)dr = \frac{d}{d\epsilon}\int_{\Omega_\epsilon} F(x)\,dx\Big|_{\epsilon=0} = \int_{\Xi} \phi F\,d\sigma.$$

We have that over the entire computational domain $\Omega$, $\delta \int_\Omega F(r)dr = 0$. Furthermore, $\Omega = \Omega_m \cup \Omega_s$ so that

$$\delta \int_{\Omega_s} F(r)dr = \delta(\int_{\Omega} F(r)dr - \int_{\Omega_m} F(r)dr) = -\int_{\Xi} \phi d\sigma \tag{3.9}$$

So the first variations of the volume functionals are:

$$\delta \int_{\Omega_s} \rho_s U^{vdW} dr = -\int_{\Xi} \phi\rho_s U^{vdW} d\sigma$$
$$\delta \int_{\Omega_m} \rho_m \psi dr = \int_{\Xi} \phi\rho_m \psi d\sigma$$
$$\delta \int_{\Omega_m} \epsilon_m |\nabla\psi|^2 dr = \int_{\Xi} \phi\epsilon_m |\nabla\psi|^2 d\sigma$$
$$\delta \int_{\Omega_s} \epsilon_s |\nabla\psi|^2 = -\int_{\Xi} \phi\epsilon_s |\nabla\psi|^2 d\sigma$$
$$\delta \int_{\Omega_s} k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right) = -\int_{\Xi} k_B T \phi \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right) d\sigma$$

Similarly, the second variation is given by

$$\begin{aligned}
\delta^2 \int_{\Omega_m} F(r)dr =& \frac{1}{2}\frac{\partial^2}{\partial\epsilon^2}\int_{\Omega_\epsilon} F(x)\,dx \\
=& \frac{1}{2}\frac{\partial}{\partial\epsilon}\int_{\Xi} \phi(u)F(u,\epsilon)|I-\rho S|\,d\sigma \\
=& \frac{1}{2}\int_{\Xi} \phi[\frac{\partial}{\partial\epsilon}F(u,\epsilon)|_{\epsilon=0}\alpha(0) + F\frac{\partial}{\partial\epsilon}|I-\rho S||_{\epsilon=0}]d\sigma \\
=& \frac{1}{2}\int_{\Xi} \phi[\phi(\nabla F\cdot N_m) + F\frac{\partial}{\partial\epsilon}|I-\rho S||_{\epsilon=0}]d\sigma
\end{aligned}$$

Recall

$$\frac{\partial}{\partial\epsilon}|I-\epsilon\phi S||_{\epsilon=0} = -\phi tr(S).$$

So finally we find the second variation of an arbitrary volume fumctional is

$$\delta^2 \int_{\Omega_m} F(r)dr = \frac{1}{2}\int_{\Xi} \phi^2[(\nabla F\cdot N_m) - F\,tr(S)]d\sigma = \frac{1}{2}\int_{\Xi} \phi^2[(\nabla F\cdot N_m) - 2F\,H]d\sigma.$$

Now over the entire compuational domain $\Omega$, we know that $\delta^2 \int_\Omega F(r)dr = 0$, so given that $\Omega = \Omega_s \cup \Omega_m$

$$\delta^2 \int_{\Omega_s} F(r)dr = \delta^2 (\int_\Omega F(r)dr - \int_{\Omega_m} F(r)dr) = -\frac{1}{2}\int_\Xi \phi^2 [(\nabla F \cdot N_m) - 2F\,H] d\sigma. \quad (3.10)$$

We can now find the second variation of all the remaining volume functionals:

$$\delta^2 \int_{\Omega_s} \rho_s U^{vdW} dr = \int_\Xi \phi^2 (-\frac{1}{2}\rho_s \nabla U^{vdW} \cdot N_m + \rho_s U^{vdW} H) d\sigma$$

$$\delta^2 \int_{\Omega_s} k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i / k_B T} - 1\right) dr = -\int_\Xi \phi^2 k_B T (-\frac{1}{2}\nabla (\sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i / k_B T} - 1\right)) \cdot N_m + H \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i / k_B T} - 1\right)) d\sigma$$

$$\delta^2 \int_{\Omega_m} \rho_m \psi dr = \int_\Xi \rho_m \phi^2 (\frac{1}{2}\nabla \psi \cdot N_m - H\psi) d\sigma$$

$$\delta^2 \int_{\Omega_m} \frac{1}{2}\epsilon_m |\nabla \psi|^2 dr = \int_\Xi \phi^2 \epsilon_m \frac{1}{2} (\frac{1}{2}\nabla |\nabla \psi|^2 \cdot N_m - H|\nabla \psi|^2) d\sigma$$

$$\delta^2 \int_{\Omega_s} \frac{1}{2}\epsilon_s |\nabla \psi|^2 dr = -\int_\Xi \phi^2 \epsilon_s \frac{1}{2} \left(-\frac{1}{2}\nabla |\nabla \psi|^2 \cdot N_m + H|\nabla \psi|^2\right) d\sigma$$

## 3.3 Variation of $G_{np}$

We will first simplify $g$ by considering just the non-polar part $G_{np}$

$$G_{np} = \gamma(Area) + p(Vol) + \int_{\Omega_s} \rho_s U^{vdW} dr.$$

For the non-polar case, we have that the first and second variations are

$$\delta G_{np} = \int_\Xi \phi(-2\gamma H + p - \rho_s U^{vdW}) d\sigma,$$

and

$$\delta^2 G_{np} = \int_\Xi \phi^2 (\gamma K - Hp - \frac{1}{2}\rho_s \nabla U^{vdW} \cdot N_m + \rho_s H U^{vdW}) - \frac{1}{2}\gamma(\Delta_g \phi)\phi d\sigma$$

Now the neccessary condition for extremum in this case is $G_{np} = 0$ which gives the equality

$$-2\gamma H + p - \rho_s U^{vdW} = 0.$$

Using this the second variation can be simplified to

$$\begin{aligned}\delta^2 G_{np} =& \int_\Xi \phi^2(\gamma K - Hp + \gamma\nabla H\cdot N_m + H(-2\gamma H + p)) - \frac{1}{2}\gamma(\Delta_g\phi)\phi d\sigma\\
=& \int_\Xi \phi^2(\gamma K + \gamma\nabla H\cdot N_m - 2\gamma H^2) - \frac{1}{2}\gamma(\Delta_g\phi)\phi d\sigma\\
=&\gamma\int_\Xi \phi^2(K + \nabla H\cdot N_m - 2H^2) - \frac{1}{2}(\Delta_g\phi)\phi d\sigma\end{aligned}$$

## 3.4 VARIATION OF $G$

We now take the first and second variation of $G$ using the formulas previously found and denote $\epsilon_c = |\epsilon_s - \epsilon_m|$. The first variation is then

$$\begin{aligned}\delta G =& \frac{\partial}{\partial\epsilon}(\gamma(Area) + p(Vol) + \int_{\Omega_m}\rho_m\psi - \frac{1}{2}\epsilon_m|\nabla\psi|^2 dr + \int_{\Omega_s}\rho_s U^{vdW}\\
&- k_B T\sum_{i=1}^{N_c} c_i\left(e^{-\psi q_i/k_B T} - 1\right) - \int_{\Omega_s}\frac{1}{2}\epsilon_s|\nabla\psi|^2 dr)|_{\epsilon=0}\\
=& \int_\Xi -2\phi H\gamma + p\phi - \phi\rho_s U^{vdW} + \phi\rho_m\psi - \frac{1}{2}\phi\epsilon_m|\nabla\psi|^2 + \frac{1}{2}\phi\epsilon_s|\nabla\psi|^2\\
&+ k_B T\phi\sum_{i=1}^{N_c} c_i\left(e^{-\psi q_i/k_B T} - 1\right) d\sigma\\
=& \int_\Xi \phi(-2\gamma H + p - \rho_s U^{vdW} + \rho_m\psi + \frac{1}{2}|\nabla\psi|^2\epsilon_c + k_B T\sum_{i=1}^{N_c} c_i\left(e^{-\psi q_i/k_B T} - 1\right))d\sigma,\end{aligned}$$

and the second variation is

$$\begin{aligned}
\delta^2 G =& \frac{\partial^2}{\partial \epsilon^2}[\gamma(Area) + p(Vol) + \int_{\Omega_m} \rho\psi - \frac{1}{2}\epsilon_m |\nabla\psi|^2 + \int_{\Omega_s} \rho_s U^{vdW} - \frac{1}{2}\epsilon_s |\nabla\psi|^2 \\
& - k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right) dr] \\
=& \int_{\Xi} \gamma(\phi^2 K - \frac{1}{2}(\Delta_g \phi)\phi) - \phi^2 Hp + \phi^2(-\frac{1}{2}\rho_s \nabla U^{vdW} \cdot N_m + \rho_s U^{vdW} H) \\
& + \rho_m \phi^2 (\frac{1}{2}\nabla\psi \cdot N_m - H\psi) - \phi^2 \epsilon_m \frac{1}{2}(\frac{1}{2}\nabla|\nabla\psi|^2 \cdot N_m - H|\nabla\psi|^2) \\
& - \phi^2 \epsilon_s \frac{1}{2}\left(-\frac{1}{2}\nabla|\nabla\psi|^2 \cdot N_m + H|\nabla\psi|^2\right) \\
& - \phi^2 k_B T(-\frac{1}{2}\nabla(\sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right)) \cdot N_m + H \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right)) d\sigma \\
=& \int_{\Xi} \phi^2 [(\gamma K + H(\rho_s U^{vdW} - p - \rho_m \psi - \frac{\epsilon_c}{2}|\nabla\psi|^2 - k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right)) \\
& + \frac{1}{2}\nabla[-\rho_s U^{vdW} + \rho_m \psi + \frac{\epsilon_c}{2}|\nabla\psi|^2 + k_b T(\sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right))] \cdot N_m] \\
& - \frac{1}{2}\gamma(\Delta_g \phi)\phi d\sigma.
\end{aligned}$$

Now the necessary condition for a minimizer is $\delta G = 0$, so we get two equalities

$$\begin{aligned}
2\gamma H =& p - \rho_s U^{vdW} + \rho_m \psi + \frac{1}{2}\epsilon_c |\nabla\psi|^2 + k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right) \\
2\gamma \nabla H =& \nabla(-\rho_s U^{vdW} + \rho_m \psi + \frac{1}{2}\epsilon_c |\nabla\psi|^2 + k_B T \sum_{i=1}^{N_c} c_i \left(e^{-\psi q_i/k_B T} - 1\right))
\end{aligned}$$

Then using these, we can simplify $\delta^2 G$ to

$$\delta^2 G = \gamma \int_{\Xi} \phi^2 (K - 2H^2 + \nabla H \cdot N_m) - \frac{1}{2}(\Delta_g \phi)\phi d\sigma$$

### 3.5 VARIATION OF $Area$ WITH CONSTANT $Volume$

Now we consider the variation of $Area$ with the constraint that $Volume = C$ for a constant $C > 0$. So the equation $p(Volume) = p \int_{\Omega_m} dV$ is the isoperimetric constraint of this problem. Then utlizing Lagrangian multipliers method,

$$\nabla A = \lambda \nabla V \text{ so } \nabla A - \lambda \nabla V = 0.$$

This is equivelant to ,

$$\delta(A - \lambda V) = 0$$

then from the previous formulas we have that

$$\int_{\Xi} (-2\gamma H - \lambda p)\phi d\sigma = 0.$$

Then for an extremum,

$$-2\gamma H = \lambda p \text{ hence } H = -\frac{\lambda p}{2\gamma} = -D \tag{3.11}$$

for a constant $D > 0$. A. D. Alexandrov proved that a compact embedded surface in $\mathbb{R}^3$ with constant mean curvature and $H \neq 0$ must be a sphere. So we have that

$$H = \frac{1}{r} \text{ and } K = \frac{1}{r^2} \tag{3.12}$$

Now we substitute $\lambda = \frac{-2\gamma H}{p}$. Then using the previous formulas for $Area$ and $Volume$, the second variation is

$$\begin{aligned} \delta^2(\gamma A - p\lambda V) = & \int_{\Xi} \gamma\phi^2 K - \gamma\frac{1}{2}(\Delta_g \phi)\phi - 2\gamma\phi^2 H^2 d\sigma \\ = & \gamma \int_{\Xi} \phi^2[K - 2H^2] - \frac{1}{2}(\Delta_g \phi)\phi d\sigma \end{aligned}$$

So using polar coordinates for a point $(u_1, u_2, z) = (r\cos\theta_1 \sin\theta_2, r\sin\theta_1\sin\theta_2, r\cos\theta_2)$, (3.12), and the usual Laplace-Beltrami operator on the sphere $\Delta_s$

$$\begin{aligned} \delta^2(\gamma A - p\lambda V) = & \gamma \int_{\Xi} \phi^2(\frac{1}{r^2} - 2\frac{1}{r^2}) - \frac{1}{2}(\Delta_s \phi)\phi \\ = & \gamma \int_{\Xi} -\phi^2\frac{1}{r^2} - \frac{1}{2}(\Delta_s \phi)\phi \end{aligned}$$

# CHAPTER 4

# CONCLUSION

This work approaches the problem of minimizing an energy functional on a smooth and sharp interface utilizing analysis and calculus of variations respectively. First we considered the functional proposed by Z. Chen, N.A Baker, and G.W Wei [6] with a smooth interface; however we amended the term $\int_\Omega \gamma|\nabla u|$ by $\int_\Omega \gamma|\nabla u|^q$. The resulting functional is coercive and we proved that it has a minimizer for $1 < q \leq 2$. This means for $q \approx 1$, the amended functional has a minimizer which supports approaching the problem numerically. In further work, I will pursue proving the original functional in [6] has a minimizer using the results from this. After this functional, we considered the an extended non-polar energy proposed by Z. Chen and Y. Shao [8]. This functional was shown to have a minimizer, and in further work we can combine this result with the associated polar part to minimize the full energy functional.

For the sharp interface we considered the functional defined by Z. Chen [7]. The variations of a functional can be used to prove the existence of a minimizer, but this seldom works because the second variation needs to be strictly positive. However, the variations are always useful for finding the necessary conditions for extrema and analyzing the stability of a minimizer. Before approaching the stability of entire energy functional, we consider a simpler case of area with constant volume. This constraint is allowable in our model because the protein's volume won't change if only the shape is changed. We were able to infer from the necessary condition for extrema that the minimizing shape is a sphere; this is a well known result for this isoperimetric problem. From here we can use spherical harmonics and the second variation to analyze the stability of the sphere. In a future work we can apply the same approach to $G_{np}$ and $G$ under the constraint of constant volume.

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# APPENDIX

**Theorem A.1.** *(Rellich-Kondrachov Theorem)*

*Let $\Omega \subset \mathbb{R}^n$ be an open, bounded Lipschitz domain, and let $1 \leq p < n$. Set $p^* := \frac{np}{n-p}$.*

*Then the Sobolev space $W^{1,p}(\Omega)$ is continuously embedded in the $L^p$ space $L^{p^*}(\Omega)$ and is compactly embedded in $L^q(\Omega)$ for every $1 \leq q < p^*$.*

**Theorem A.2.** *(Holders Inequality)*

*Let $(S, \Sigma, \mu)$ be a measure space and let $p, q \in [1, \infty]$ with $1/p + 1/q = 1$. Then, for all measurable real- or complex-valued functions $f$ and $g$ on $S$,*

$$\|fg\|_{L^1} \leq \|f\|_{L^p}\|g\|_{L^q}.$$

**Theorem A.3.** *(Fatou's Lemma)*

*If $\{f_n\}$ is a sequence of non-negative measurable functions, then*

$$\int \liminf_{n\to\infty} f_n d\mu \leq \liminf_{n\to\infty} \int f_n d\mu$$

**Theorem A.4.** *(Poincare's Identity)*

*Let $p$, so that $1 \leq p < \infty$ and $\Omega$ a subset bounded at least in one direction. Then there exists a constant $C$, depending only on $\Omega$ and $p$, so that for $(u)_\Omega = \int_\Omega u d\mu$*

$$\|u - (u)_\Omega\|_{L^p(\Omega)} \leq C\|\nabla u\|_{L^p(\Omega)}.$$

**Theorem A.5.** *(Helly's Selection Theorem)*

*Let $U$ be an open subset of $\mathbb{R}$ and let $f_n : U \to \mathbb{R}$, $n \in \mathbb{N}$, be a sequence of functions. Suppose that $(f_n)$ has uniformly bounded total variation on any $W$ that is compactly embedded in $U$. That is, for all sets $W \subset U$ with compact closure $\bar{W} \subset U$,*

$$\sup_{n\in\mathbb{N}} \left( \|f_n\|_{L^1(W)} + \left\| \frac{df_n}{dt} \right\|_{L^1(W)} \right) < \infty,$$

*where the derivative is taken in the sense of tempered distributions; and* $(f_n)$ *is uniformly bounded at a point. Then there exists a subsequence* $f_{n_k}$, $k \in \mathbb{N}$, *of* $f_n$ *and a function* $f : U \to \mathbb{R}$, *locally of bounded variation, such that*

$f_{n_k}$ *converges to* $f$ *pointwise; and* $f_{n_k}$ *converges to* $f$ *locally in* $L^1$, *i.e., for all* $W$ *compactly embedded in* $U$,

$$\lim_{k\to\infty} \int_W \|f_{n_k}(x) - f(x)\| = 0;$$

*and, for* $W$ *compactly embedded in* $U$,

$$\left\|\frac{df}{dt}\right\|_{L^1(W)} \leq \liminf_{k\to\infty} \left\|\frac{df_{n_k}}{dt}\right\|_{L^1(W)}.$$

**Theorem A.6.** *(Dominated Convergence Theorem)*

*Let* $\{f_n\}$ *be a sequence of complex-valued measurable functions on a measure space* $(S, \Sigma, \mu)$. *Suppose that the sequence converges pointwise to a function* $f$ *and is dominated by some integrable function* $g$ *in the sense that*

$$\|f_n(x)\| \leq g(x)$$

*for all numbers* $n$ *in the index set of the sequence and all points* $x \in S$. *Then* $f$ *is integrable and*

$$\lim_{n\to\infty} \int_S \|f_n - f\| d\mu = 0$$

*which also implies*

$$\lim_{n\to\infty} \int_S f_n d\mu = \int_S f d\mu$$

**Theorem A.7.** *Assume the the Lagrangian* $L$ *satisfies the coercitivity inequality and is convex in the variable* $P$. *Suppose also that the admissible set* $A$ *is nonempty.*

*Then there exists a* $u \in A$ *so that*

$$I[u] = \min_{w\in A} I[w].$$

**Theorem A.8.** *(Jacobi's formula)*

*For any differentiable map* $A$ *from* $\mathbb{R}$ *to* $n \times n$ *matrices,* $d\det(A) = tr(adj(A)dA)$.