Theory of stabilization for liquid films containing polymers

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Theory of stabilization for liquid films containing polymers 高分子を含んだ液膜の安定性解析

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泡を利用する製品において、泡の安定化は重要である [1]。工 業分野では泡の安定化のために界面活性剤に加えて、高分子も 使用されている [2]。これまで高分子を考慮して泡の安定性を解 析した理論は確立されていない。本研究の目的は高分子を含ん だ液膜における高分子の膜安定性に対する寄与を理論的に明ら かにすることである。

本研究では高分子の影響に注目するため、先行研究の実験で 高分子と界面活性剤の相互作用が顕著 [3, 4] であった高分子と界 面活性剤が異符号に帯電している系を扱う。先行研究では、高分 子濃度の大小で液膜の挙動が異なる [5] と報告されているため、 本研究では高分子濃度の希薄領域と濃厚領域のそれぞれに対し て理論モデルを構築した。以下では各濃度領域における先行研 究および本研究の理論について述べる。

濃厚領域では、界面活性剤と高分子が気液界面でゲル状の複合体を形成し [3]、液膜の崩壊時間はゲルネットワーク密度の上昇に応じて延びると報告さ れている [6]。私は図1のようにゲル状複合体が液膜中を満たしていると考 えて、ゲル薄膜の揺らぎの時間発展をモデル化することでゲルが膜安定性に 与える影響の解析を試みた。ゲル薄膜の安定性解析から、膜の体積弾性と分 子間力の競合によって膜の安定・不安定が決定すること、摩擦が膜の崩壊時 間を延長させることを予言した。また、摩擦の効果は高分子の体積分率上昇 に応じて増大することが分かった [7]。

希薄領域では、分離圧という膜中に働く反発力が濃度上昇に対して極小値 を示し、膜は破裂することが報告されている[4]。つまり、膜はある濃度領 域でのみ不安定になる。私は液膜中の高分子は互いに離れていると考えて、 図2のように1つの高分子の形態に注目し、形態変化が分離圧に与える影 響の解析を試みた。高分子形態と分離圧の関係から、高分子が2つの気液界 面を架橋する構造をとる時のみ、高分子のエントロピー弾性によって膜同士 が引きつけられ、分離圧が負になることを予言した[8]。

以上から、先行研究の実験結果と定性的に一致する2つの理論モデルが示された。

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図1 濃厚領域:ゲル薄膜の模式図。表 面張力、膜中の体積弾性、分子間力の3 つの力で静水圧が決まる。ゲルネット ワークと溶媒との摩擦が溶媒の流れを遅 くする。



図2 希薄領域:正に帯電し た界面活性剤と負に帯電し た高分子を含んだ液膜の模 式図。高分子は静電相互作 用により、2つの気液界面を 架橋する。

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Abstract

Foams are familiar materials that are used widely in industrial applications such as foods and cosmetics. In some of these applications, foams are stabilized by surfactants and polymers. In previous researches, foams stabilized by both surfactants and polymers were analyzed by using the concepts that have been developed for the foams stabilized only by surfactants. We focus on the role of polymers in the foam.

Considering the fact that the role of polymers depends on the polymer concentrations, we have constructed models to predict the stability of liquid films for two polymer concentration regimes. In the high concentration regime, we derive the time evolution of the surface fluctuation by treating the film as a gel. In the dilute regime, we predict the disjoining pressure by taking into account the polymer conformation. Our theories agree with the previous experiments qualitatively.

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Chapter 1

Introduction

Liquid foams are applied in the food and cosmetic industries owing to their various functions, including detergent, thermal insulation and sensory optimization.^{1,2} In the applications mentioned above, the stability of foams is of practical importance and thus has been widely investigated.^{3,4} Although the stabilization mechanism of foams stabilized by surfactants has been well revealed so far,^{3,5} the foams that are applied in industry (shampoo bubbles, the foams of beers and cappuccino foams) are outside the applicability of previous researches since foams applied in industry contain polymers. Polymers have large conformational degree of freedom. Therefore, the size of the polymers must be important in thin foam films since the polymers are longer than small molecules. We have to take into account the role of polymers to understand the stabilization mechanism of the foams stabilized by polymers and surfactants. In this thesis, we present two theories which predict the stability of foams containing surfactants and polymers by introducing the role of polymers to conventional theories.

1.1 Background

Our theories in this thesis are based on polymer physics, and the conventional theories^{3,5–7} for the stability of foams containing pure surfactants. We present the basis of the foam stability and the role of polymers which is treated in this thesis.

1.1. BACKGROUND

1.1.1 Liquid film stabilized by surfactants

Single liquid films have been frequently discussed instead of foams, Figure 1.1.³ These single films can be considered to be the building blocks of the macroscopic foams. In general, liquid films are naturally unstable; however, they can be stabilized by adding surfactants. These molecules comprise of a polar group and an apolar tail. They stabilize the liquid film by localizing at the air-water interface. We present the widely used measurement, which characterizes the stability of the liquid film, and two conventional theories, which describe the liquid film stabilized by surfactants.



Figure 1.1: Microscopic foam is a assembly of single liquid films.

Surface elasticity

Surface elasticity is originated from the surface density fluctuation of surfactants. The surfactants are messed up by thermal energy, and then generate the restoring force to keep the surface density uniform. Similarly, the fluctuation of the air/liquid interface is created through a spontaneous process caused by thermal motion. Foam films rupture when surface fluctuations increase such that the two interfaces collide. Surface elasticity suppresses the surface fluctuation.⁷

Thin-film pressure balance

The stability of the thin liquid film has been evaluated by thin-film pressure balance. This method was established by Mysels and Exerowa.^{9,10} With this method, the repulsive force between two air/liquid interfaces, called disjoining pressure, can be measured. Figure 1.2



Figure 1.2: The apparatus for measuring the repulsive force between two air/liquid interfaces.⁸ The liquid film is formed from a droplet in a hole (diameter of *ca.*1mm) that is drilled into a porous glass disk with a pore size of *ca.*10 μ m. The film holder is placed in the sealed box. The pressure inside the box is changed by using a pump.

shows the equipment for measuring the disjoining pressure ΔP in the film as a function of the film thickness. The thickness is determined interferometrically.¹¹

DLVO theory

DLVO (Derjaguin-Landau-Verwey-Overbeek) theory predicts the equilibrium distance between two charged walls filled with liquid.⁶ The distance is determined by the balance of electric repulsions and van der Waals (VDW) attractions. Originally, the target of this theory is the dispersion of colloids in solutions. The colloids disperse in the solution when the electrostatic repulsion is larger than the VDW attraction. In contrast, the colloids aggregate when the electric repulsion is smaller than the VDW attraction. By neglecting the size of surfactants localized at the air-water interface, the interface can be treated as the charged wall. The dispersion of colloids corresponds to the stability of liquid films.

Considering the air/liquid interface decorated by surfactants as a charged wall, we introduce the disjoining pressure in the liquid film decorated by negative charged surfactants only.¹² The disjoining pressure is the difference between the electrostatic repulsion and

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van der Waals attraction. We explain this two forces.



Figure 1.3: Schematic picture of the distribution of the counterions. The surfactants and the counterions are charged negative and positive, respectively.

The polar group of surfactants is ionized when the surfactants are in water. Owing to the charge neutrality, the counterions of the surfactants are oppositely charged. Figure 1.3 shows that the counterions in water, and surfactants localized at air/water interfaces have positive and negative charge, respectively. The electrostatic repulsion is determined by the translation entropy of the counterions. We calculate the electrostatic potential ϕ and the counterions density ρ_+ to obtain the electrostatic repulsion by solving the Poisson equation for the system in Figure 1.3 as follows:

$$\frac{d^2\phi}{dz^2} = -\frac{e}{\epsilon} \, [\rho_+(z)], \tag{1.1.1}$$

where e and ϵ is elementary charge and dielectric constant, respectively. The number of the counterions is constant since the counterions are liberated from the surfactants. The conservation of the counterions has the form

$$\int_{-L/2}^{L/2} \rho_+(z) dz = 2\sigma.$$
 (1.1.2)

where σ and L are the surface charge determined by the surfactant density and the distance between two walls, respectively. The boundary conditions are considered as follows:

$$\phi(0) = 0, \left. \frac{d\phi}{dz} \right|_{z=0} = 0.$$
 (1.1.3)

These conditions are because of the symmetry. We use the Boltzmann distribution for the counterion density, $\rho_{+} = n_0 e^{-e\phi/k_{\rm B}T}$ where n_0 is the counterions density at the middle plane and $k_{\rm B}T$ is the thermal energy. $k_{\rm B}$ and T are the Boltzmann constant and temprature, respectively. The Poisson equation are rewritten as follows:

$$\frac{d^2\tilde{\phi}}{dz^2} = -4\pi l_{\rm B} n_0 \mathrm{e}^{-\tilde{\phi}},\tag{1.1.4}$$

where $\tilde{\phi}$ is the rescaled electrostatic potential, $\tilde{\phi} = e\phi/k_{\rm B}T$, and $l_{\rm B}$ is the Bjerrum length as

$$l_{\rm B} = \frac{e^2}{4\pi\epsilon} \frac{1}{k_{\rm B}T} = \frac{e^2\beta}{4\pi\epsilon}.$$
(1.1.5)

We use the inverse constant $\beta = 1/k_{\rm B}T$, for simplicity. Equation (1.1.4) is called Poisson-Boltzmann equation. By solving this equation, we obtain the counterions density. We can calculate the electrostatic repulsion from the counterions density. Details are in Appendix A. Here, we show the electrostatic repulsion as follows:

/

$$\Pi_{0} = \begin{cases} \frac{2\sigma}{L} k_{\rm B}T, & \text{when } \pi l_{B}\sigma L \ll 1 \\ \\ \left(\frac{\pi}{\beta e}\right)^{2} \frac{2\epsilon}{L^{2}} + \frac{4\sigma}{L} k_{\rm B}T. & \text{when } \pi l_{B}\sigma L \gg 1 \end{cases}$$
(1.1.6)

We obtain the electrostatic repulsion for two cases in which the distance between two walls is short and long. The repulsive force is sensitive to the distance between two walls and surface charge density.

The van der Waals attraction has a form

$$\Pi_{\rm VDW} = -\frac{A_{\rm H}}{6\pi L^3} \tag{1.1.7}$$

where $A_{\rm H}$ is Hamaker constant. Hamaker constant has a relevance to the dielectric constant of media because VDW interaction is originated from quantum-statical fluctuations.¹² When the media are air and water, $A_{\rm H} \sim 10^{-20} {\rm J.6}$

All the above, the disjoining pressure has a form

$$\Pi_{\rm disjoin} = \Pi_0 - \frac{A_{\rm H}}{6\pi L^3}.$$
 (1.1.8)

The competition between the electrostatic repulsion and van der Waals attraction determines the stability of liquid films. When L is small, the electrostatic repulsion is proportional to 1/L. Since the VDW attraction is proportional to $1/L^3$, the liquid film becomes eventually unstable as the film is thinner.

1.1.2 Experiments of the liquid film containing polymers

The studies about the foam containing polymers has been reported for over fifty years¹³ and attracting the attention so far. We introduce the recently researches.

When the liquid film is formed from the polymer-dilute solution, the disjoining pressure measurement has shown that the sign of the charged polymer and the surfactant have a relevance to the film stability.¹⁴ Adding the likely charged polyelectrolytes has no significant effect on the stability. In the system of oppositely charged polyelectrolytes and surfactants, the disjoining pressure has the minimum value against the polyelectrolyte concentration, and then the liquid film ruptures. Previous researchers have explained this interesting behavior through the DLVO theory. However, the DLVO theory does not take into account the conformation of polymers.

When the liquid film is formed from the polymer-rich solution, the disjoining pressure becomes an oscillatory function against the film thickness.¹⁵ The oscillation indicates structure in the film and has been explained phenomenologically. The surface rheology¹⁶ measurement and the ellipsometry¹⁷ have shown that the polymers and the surfactants form gel-like complexes on the air/liquid interface. Furthermore, the direct observation has shown that surface gels retard the deformation of the liquid film.¹⁸ Thus, some experiments prove that the liquid film has the gel-like complex. However, the theory for the time evolution of the film stability is not established.

In this thesis, we will take into account the role of the polymer written in the following section.

1.1.3 Role of polymers

Polymers are series of hundreds or thousands monomers. In general, polymers are treated as a simply long chain because it is difficult to take into account the effect of all monomer in one polymer.¹⁹ The simple long chain model has been successful to explan for the physical property of polymers. In the following sections, we present the two elasticity originated by polymers. One is an entropic elasticity originated by one polymer. The other is an elasticity and friction originated by the network of many polymers.

Entropic elasticity of polymer chain

A polymer is treated as a molecule composed by a series of freely jointed segments. The distribution of the end-to-end distance is given by the Gaussian distribution since the distance is expressed as the sum of independent variables. Therefore, the polymer is described by the Gaussian chain in the thermostatic system.¹⁹ The freely segments rotate driven by the thermal energy.

The polymer tries to shrink when we change the end-to-end distance longer from the equilibrium distance. This is because the number of the polymer conformation decreases. In other wards, the shrink of the polymer results from the entropy reduction. This elas-

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ticity is called the entropic elasticity. The elastic force $f_{\rm p}$ has the form

$$f_{\rm p} = \frac{3k_{\rm B}T}{Nb^2}R,\tag{1.1.9}$$

where $k_{\rm B}$ is Boltzmann constant. The entropy elasticity is proportional to the temperature T.



Figure 1.4: Schematic picture of the Gaussian chain composed by N segments. The vector of *i*-th segments and the end-to-end vector are represented by \mathbf{r}_i and \mathbf{R} , respectively. The length of segments and end-to-end distance is $|\mathbf{r}_i| = b$ and $|\mathbf{R}| = R$, respectively.

Formation of polymer networks

Previous research has reported that polymers bond each other chemically or physically, and then form the network. If the network is composed by soluble polymers, the network contains liquid. This structure is called a gel or a sol. Gels are harder than sols. We introduce two interesting property of the gel though gels and sols exhibit many complex phenomena. They are the elasticity and the friction.

The elasticity of the gel is composed by the shear modulus and the osmotic modulus. The shear modulus results from the bond of the network. The network tries to shrink when the gel is deformed since the subchains of the network have the entropic elasticity. The osmotic modulus results from the mixing entropy between the polymer and the solvent. When the gel is deformed, the volume fraction of the solvent in the gel change from that of the equilibrium state. This deviation of the volume fraction drive the elastic force to restore the equilibrium volume fraction.

The solvent flow is retarded by the polymer network in the gel. The retardation by the friction between the obstacle and the solvent is well known such as Poiseuille flow.²⁰ The gel has many microscopic obstacle because of the network. Therefore, the solvent flow in the gel can be treated as the solvent flow in porous materials. The retarded flow in the porous materials is describer by Darcy's law.²¹ This law indicate that the flow rate is determined by the friction between the obstacle and the solvent, and insensitive the distance from the interface of the material.

1.2 Outline of this thesis

The scope of our study is making theoretical model to predict the stability of liquid films containing surfactants and polymers. We suggest two theories for the stability of liquid films containing surfactants and polymers as the following procedure. The scope of three theories is the different each other for polymer concentration.

In chapter 2, we mention about the stability and durability of the liquid film in high polymer concentration regime. We take into account a gel for the analysis and discuss the liquid film instability induced by the surface fluctuations of the film.

In chapter 3, we mention about the stability of the liquid film in low polymer concentration regime. We focus on the polymer conformation in the liquid film and discuss the disjoining pressure by using four models classified with respect to the polymer concentration.

In chapter 4, we discuss all of the prediction in the above chapters.

Chapter 2

High polymer concentration regime

In a large polymer concentration, polymers overlap each other. Because the fluctuation of the segment density is small, the fraction of the polymer can be treated by a simple mean field theory. We treat the liquid films containing plenty of polymers as the system in which the distribution of the polymers is homogeneous such as a gel macroscopically. By modeling the foam film stabilized by the polymers as the gel film, we construct a theoretical model to predict the stability and durability of the foam. We analyze the time evolution of the surface fluctuations of the gel film because the film ruptures when the magnitude of the fluctuations grows with time. The van der Waals interactions, the surface tension, and the elasticity and friction of the gel are taken into account. Our theory predicts that the gel elasticity enhances the stability of the foam film and that the friction between the solvent and the polymer network results in the retardation of the thinning of the film. In conclusion, the gel composed with the concentrated polymer solution plays an important role in the stability and durability of foams.

2.1 Conventional research

The stability of the liquid film decorated by surfactants has been well investigated by taking into account the surface elasticity. The surfactants suppress the fluctuation since they generate the restoring force to keep the surface density uniform. Consequently, they yield a large surface elasticity. The mechanism of stabilization due to the surface elasticity is known as the Gibbs-Marangoni effect.^{3,5,7} To address the dynamics of the fluctuations, one must take into account the fact that the solvent flows are driven by the surface fluctuations. The liquid flow in liquid films decorated by surfactants has been simplified as a Poiseuille flow²⁰ or as a uniform liquid flow parallel to the surfaces of the film.²² A film with effectively rigid surfaces induced by the surfactants exhibits relatively slow flow, limited by the shear viscosity. The above model is successful when the liquid film is decorated by low molecular weight surfactants and when the concentration of surfactant is low.^{20, 22}

In the above conventional theories, the viscosity of the solvent represents the effect of polymers on the film stability. Such description is based on the assumption that nothing to disturb the solvent flow is in the liquid film. However, adding polymers to foam films decorated by the surfactants can change the behavior of the foam film dramatically. Direct observation has shown that surfactants and polymers stabilize the film through a gel-like structure.^{18,23} Experiments using ellipsometry have shown that adding surfactants and polymers leads to the formation of complexes on the surface.^{17,24} For the stability of films containing gel-like structures, conventional theories based on the surface elasticity and the viscosity seem insufficient. For example, even though the complexes exist on the inside of the liquid films, the bulk contribution has not been taken into account.

2.2 Scope of this theory

The bulk structures due to the complexes yield a bulk elasticity and may suppress the fluctuation of liquid films to maintain the film thickness. They also act as a porous material and change the Poiseuille flow into the retarded flow which is insensitive to the distance from the air/liquid interface via the friction between the solvent and the complex.²¹ Such a retarded solvent flow may retard the kinetics of the fluctuation in the foam film.

In this thesis, the stability and the durability of liquid films with gel-like structures are examined. We treat a liquid film containing plenty of polymers as a gel film and consider the bulk elasticity and the friction of the gel. By analyzing the time evolution of surface fluctuations, we predict that the bulk elasticity stabilizes the foam film and that the friction increases the durability of the foam film.

2.3 Model

We consider a single foam film in Figure 2.1.^{12, 22} Assuming that the thickness of the film is sufficiently smaller than the lateral dimension, we consider infinite film area. The foam film is decorated by low molecular weight surfactants and soluble polymers. We assume that these molecules are assembled into a gel-like structure^{17, 18, 23, 24} that fills the entire region of the foam film. The foam film ruptures when the surface fluctuations increase until the two surfaces collide. The fluctuations are generated by a spontaneous process caused by thermal motion. In early stages, the magnitude of the fluctuations is small compared to the film thickness. According to the symmetry with respect to the middle plane of the film, we treat a half of the system. We use the Onsager principle, which states



Figure 2.1: Schematic picture of the gel film. We use the Monge representation, z = h(x, y), which is defined by the distance between the middle plane and the surface.¹²

that the dynamics are determined by minimizing the Rayleighian, R, to derive the time evolution equation of the film fluctuation.¹⁹ R is composed of the time derivative of free energy F and the energy dissipation function Φ , and has the form

$$R = \frac{\partial F}{\partial t} + \Phi. \tag{2.3.1}$$

2.3.1 The free energy of the gel film

The free energy of the gel film has an approximate form

$$F[h(x,y)] = \iint \left[k(h-h_0)^2 - \frac{A_{\rm H}}{12\pi h^2} + \gamma \sqrt{1 + h_x^2 + h_y^2} \right] dxdy$$

$$\simeq \iint \left[k(h-h_0)^2 - \frac{A_{\rm H}}{12\pi h^2} + \frac{\gamma}{2} (2 + h_x^2 + h_y^2) \right] dxdy$$
(2.3.2)

$$h_x = \frac{\partial h(x,y)}{\partial x}, \quad h_y = \frac{\partial h(x,y)}{\partial y}.$$
 (2.3.3)

In Table 2.1, the parameters used in our theory are summarized. The first term represents the elastic energy of the gel, where the osmotic modulus is $\tilde{k} = kh_0$ for cases in which the deformation is uniform in the z-coordinate. The equilibrium thickness, $h(x, y) = h_0$, is defined as the thickness when the structure of the complex is formed. In Equation (2.3.2), we assume that the osmotic modulus per unit area, \tilde{k} , is symmetric with respect to $h > h_0$ and $h < h_0$. This treatment is effective when the gel is connected in the entire film. We also use this assumption to estimate the film stability when the gel comprises of two separate surface gels at both surfaces. Note that the osmotic modulus, k, is zero when $h > h_0$ in a further precise treatment. We will discuss it in details in section 2.6. The second term represents the free energy due to the van der Waals interactions between the air phases via the liquid film with the Hamaker constant, $A_{\rm H}$. The third term represents the surface free energy with the surface tension, γ .¹²

Table 2.1: Parameters

h_0	Equilibrium thickness
q	Wavenumber
γ	Surface tension
$ ilde{k}$	Osmotic modulus
$A_{\rm H}$	Hamaker constant
ξ	Friction coefficient
ϕ	Volume fraction

2.3.2 The time derivative of the free energy

The time derivative of the free energy has the form

$$\frac{\partial F}{\partial t} \simeq \iint dx dy \Big[\dot{h} \Big\{ 2k(h-h_0) + \frac{A_{\rm H}}{6\pi h^3} \Big\} + \gamma \Big\{ \dot{h}_x h_x + \dot{h}_y h_y \Big\} \Big], \tag{2.3.4}$$

where $\dot{h} = \partial h / \partial t$. We focus on the x-component of last term and integrate partially,

$$\int \dot{h}_x h_x dx = \int \frac{\partial}{\partial x} (\dot{h}h_x) dx - \int \dot{h}h_{xx} dx$$

$$= \left[\dot{h}h_x \right]_{-\infty}^{\infty} - \int \dot{h}h_{xx} dx$$

$$= -\int \dot{h}h_{xx} dx$$
(2.3.5)
(2.3.5)

$$h_{xx} = \frac{\partial^2 h(x,y)}{\partial x^2} \tag{2.3.6}$$

We here for simplicity assume that the surface fluctuations are zero at the edge:

$$\dot{h}(\infty) = \dot{h}(-\infty) = 0.$$
 (2.3.7)

The same treatment is applied for the y-component. The time derivative has a form

$$\frac{\partial F}{\partial t} \simeq \iint dx dy \Big[\dot{h} \Big\{ 2k(h-h_0) + \frac{A_{\rm H}}{6\pi h^3} - \gamma(h_{xx} + h_{yy}) \Big\} \Big]$$
(2.3.8)

2.3.3 The energy dissipation function in the gel film

The energy dissipation function, Φ , due to the friction between the complex and solvent has the form

$$\Phi(\mathbf{v}_{\rm p}, \mathbf{v}_{\rm s}) = \frac{1}{2} \iiint \xi(\mathbf{v}_{\rm p} - \mathbf{v}_{\rm s})^2 d\mathbf{r}, \qquad (2.3.9)$$

where $\mathbf{v}_{p} = (v_{px}, v_{py}, v_{pz})$ and $\mathbf{v}_{s} = (v_{sx}, v_{sy}, v_{sz})$ are the velocity fields of the gel network and the solvent, respectively, and $d\mathbf{r} = (dx, dy, dz)$ is the volume integral over the entire film. We assume that the velocities of the gel network is much slower than that of the solvent, $v_{sx} \gg v_{px}$, $v_{sy} \gg v_{py}$. It is further assumed that the velocity of the gel and solvent perpendicular to the surface equal, $v_{sz} = v_{pz}$, because the complexes are in the solvent and the typical thickness of the film, h_0 , is much smaller than the lateral dimension of the film. With these treatments, the energy dissipation function is rewritten in an approximate form

$$\Phi(\mathbf{v}_{\mathrm{p}}, \mathbf{v}_{\mathrm{s}}) \simeq \frac{1}{2} \iiint \xi(v_{\mathrm{s}x}^{2} + v_{\mathrm{s}y}^{2}) d\mathbf{r}$$

$$= \frac{h}{2} \iint \xi \mathbf{v}_{\mathrm{s}||}^{2} dx dy$$
(2.3.10)

where $\mathbf{v}_{s||} = (v_{sx}, v_{sy}, 0)$ is the velocity of solvent in the direction parallel to the surface.

2.3.4 Mass conservation

We have to minimize the Rayleighian with respect to \dot{h} and $\mathbf{v}_{\mathbf{s}||}$ with the condition of mass conservation to link the lateral solvent flow with the perpendicular film fluctuation. The condition of mass conservation has the form

$$\nabla \cdot \left[\phi \mathbf{v}_{\mathrm{p}} + (1 - \phi) \mathbf{v}_{\mathrm{s}}\right] = 0. \tag{2.3.11}$$

2.3. MODEL

Being classified into x, y-components and z-component, this equation is rewritten as follow:

$$\nabla_{||} \cdot [\phi \mathbf{v}_{\mathbf{p}||} + (1 - \phi) \mathbf{v}_{\mathbf{s}||}] + \frac{\partial}{\partial z} [\phi v_{\mathbf{p}z} + (1 - \phi) v_{\mathbf{s}z}] = 0$$

$$\rightarrow \quad \frac{\partial}{\partial z} [\phi v_{\mathbf{p}z} + (1 - \phi) v_{\mathbf{s}z}] = -(1 - \phi) \nabla_{||} \cdot \mathbf{v}_{\mathbf{s}||}$$

$$(2.3.12)$$

We approximately treat the volume fraction of the gel, ϕ , as a constant since the fluctuation is small. Now, we apply the *lubrication approximation* to the equation (2.3.11). This approximation is generally accepted in a system in which the thickness is much smaller than the lateral dimension.^{12,25} Integrating the equation (2.3.11) with respect to z from 0 to h provides the form

$$[\phi v_{pz} + (1-\phi)v_{sz}]_0^h \simeq \nabla_{||} \cdot \int_0^h -(1-\phi)\mathbf{v}_{s||} dz, \qquad (2.3.13)$$

where the differentiation symbol of the right side goes out of integration because the lateral differential of the velocity of the solvent is independent of vertical direction in the film.^{12,25} According to the symmetry of the film, the velocity is zero at the mid-plane, $v_{pz} = v_{sz} = 0$. Since the surface of the gel film, z = h, has the complex or the solvent, the left side of this equation becomes \dot{h} . Thus, the incompressibility is described as

$$\dot{h} = -h(1-\phi)\nabla_{||} \cdot \mathbf{v}_{\mathbf{s}||}.$$
(2.3.14)

2.3.5 The Rayleighian of the gel film

According to the Equations (2.3.1), (2.3.8) and (2.3.10), the Rayleighian thus has the form

$$R[\dot{h}, \mathbf{v}_{\rm s||}] = \iint dx dy \left[\dot{h} \left\{ 2k(h-h_0) + \frac{A_{\rm H}}{6\pi h^3} - \gamma(h_{xx} + h_{yy}) \right\} + \frac{h}{2} \xi \mathbf{v}_{\rm s||}^2 - p \left\{ \dot{h} + h(1-\phi) \nabla_{||} \cdot \mathbf{v}_{\rm s||} \right\} \right]$$
(2.3.15)

where p denotes pressure and acts as the Lagrange multiplier to ensure the condition of mass conservation, equation (2.3.14).

2.4 Stability analysis of gel films

2.4.1 Time evolution equation for the film thickness

By taking the functional derivative with respect to \dot{h} , we derive the form

$$p = 2k(h - h_0) + \frac{A_{\rm H}}{6\pi h^3} - \gamma(h_{xx} + h_{yy}).$$
(2.4.1)

This equation represents the force balance in the foam film. Similarly, by taking the functional derivative with respect to $\mathbf{v}_{\mathbf{s}||}$, the velocity of the solvent, $\mathbf{v}_{\mathbf{s}||}$, is derived in the form

$$\xi \mathbf{v}_{\rm s||} = -(1-\phi)\nabla_{||}p. \tag{2.4.2}$$

This equation is called Darcy's law, which represents the velocity of solvents in a porous material.²¹ For simplicity, we use the boundary conditions that the velocity of the solvent is zero on the edge, $\mathbf{v}_{s||}|_{x=\infty} = \mathbf{v}_{s||}|_{x=-\infty} = \mathbf{v}_{s||}|_{y=\infty} = \mathbf{v}_{s||}|_{y=-\infty} = 0$, to derive equation (2.4.2).

Using the equations (2.3.14), (2.4.1) and (2.4.2), we derive the time evolution equation of the film thickness:

$$\dot{h} = h \frac{(1-\phi)^2}{\xi} \nabla_{||}^2 \Big[2k(h-h_0) + \frac{A_{\rm H}}{6\pi h^3} - \gamma(h_{xx} + h_{yy}) \Big].$$
(2.4.3)

2.4.2 Linear approximation

We analyze the time evolution of a small fluctuation, δh defined by

$$h(\boldsymbol{\rho}, t) = h_0 + \delta h(\boldsymbol{\rho}, t), \qquad (2.4.4)$$

where $\rho = (x, y)$. With this approximation, the each term of the Equation (2.4.3) has approximate forms

$$\begin{cases} 2k(h-h_0) = 2k\delta h\\ \frac{A_{\rm H}}{6\pi h^3} \simeq \frac{A_{\rm H}}{6\pi h_0^3} \left(1 - 3\frac{\delta h}{h_0}\right)\\ h_{xx} = \delta h_{xx}\\ h_{yy} = \delta h_{yy} \end{cases}$$
(2.4.5)

Neglecting the higher order term of δh , we get the time evolution equation of the surface fluctuations in early stage as follow:

$$\delta \dot{h} = h_0 \frac{(1-\phi)^2}{\tilde{\xi}} \nabla_{||}^2 \Big[2k\delta h + \frac{A_{\rm H}}{6\pi h_0^3} \Big(1 - 3\frac{\delta h}{h_0} \Big) - \gamma(\delta h_{xx} + \delta h_{yy}) \Big]$$

$$= h_0 \frac{(1-\phi)^2}{\tilde{\xi}} \nabla_{||}^2 \Big[2k\delta h - \frac{A_{\rm H}}{2\pi h_0^4} \delta h - \gamma(\delta h_{xx} + \delta h_{yy}) \Big]$$
(2.4.6)

We represent δh in a Fourier series,

$$\delta h(\rho, t) = \sum_{\mathbf{q}} \delta h_{\mathbf{q}}(t) e^{i\mathbf{q}\cdot\boldsymbol{\rho}}$$
(2.4.7)

where **q** is defined as $\mathbf{q} = (q_x, q_y)$. By linearizing the right side of equation (2.4.3) with respect to δh , we can rewrite the time evolution equation in the form

$$\frac{\partial \delta h_{\mathbf{q}}}{\partial t} = \alpha \delta h_{\mathbf{q}} \tag{2.4.8}$$

with

$$\alpha = -h_0 \ \kappa q^2 \Big[\gamma q^2 + 2 \Big(k - \frac{A_{\rm H}}{4\pi h_0^4} \Big) \Big], \tag{2.4.9}$$

where κ is the Darcy constant defined as $\kappa = (1 - \phi)^2 / \xi$. The solution of equation (2.4.8) has the form $\delta h_{\mathbf{q}}(t) = \delta h_{\mathbf{q}}(0) \exp(\alpha t)$. Thus, the stability of the foam film is determined by the sign of α : the film is stable when $\alpha < 0$ because the fluctuation is suppressed and is unstable when $\alpha > 0$ because the fluctuation increases. Even when α is positive, the collapse of the film becomes slower as α becomes smaller.

2.5 Results

Our theory predicts the characteristic growth rate of the fluctuations as

$$\alpha^* = 4h_0 \frac{\kappa}{\gamma} \left| k - \frac{A_{\rm H}}{4\pi h_0^4} \right|^2$$
(2.5.1)

and the characteristic wave number of the fluctuations as

$$q^* = \sqrt{\frac{2}{\gamma} \left| k - \frac{A_{\rm H}}{4\pi h_0^4} \right|}.$$
 (2.5.2)

Thus, we obtain the normalized growth rate as a function of the normalized wave number as follow:

$$\frac{\alpha}{\alpha^*} = \begin{cases} -\tilde{q}^2(\tilde{q}^2 - 1) & \text{when } \frac{A_{\rm H}}{4\pi h_0^4} > k \\ -\tilde{q}^2(\tilde{q}^2 + 1) & \text{when } \frac{A_{\rm H}}{4\pi h_0^4} < k \end{cases}$$
(2.5.3)

where the normalized wave number $\tilde{q} = q/q^*$.

According to α and α^* , we can explain the stability and durability of the gel film. The growth rate $\alpha(q)$ converges to two master curves depending on the relative magnitudes of k and $A_{\rm H}/4\pi h_0^4$, as shown in Figure 2.2. The gel film is unstable when $\alpha > 0$ if k is smaller than $A_{\rm H}/4\pi h_0^4$ and q is smaller than q^* (the upper half of Orange line), see the equation (2.4.8). In contrast, the gel film is stable when $\alpha < 0$ if k is smaller than $A_{\rm H}/4\pi h_0^4$ and q is larger than q^* (the bottom half of orange line) or k is larger than $A_{\rm H}/4\pi h_0^4$ (blue line). Even when α/α^* is positive, the collapse of the gel film becomes slower as α^* becomes smaller.



Figure 2.2: The growth rate, α , is shown as a function of the wave number, q. The rescaled inverse time constant plotted against the rescaled wavenumber. Orange and blue lines show the cases in which the elastic forces are smaller and larger than van der Waals forces, respectively.

2.6 Discussion

We refer to the relationship between the dominant parameters, α^* and q^* , and their constituents, k, κ and γ . The osmotic modulus k determines the sign of α . Hence, the bulk elasticity is important for the stability. The Darcy constant κ determines the value of α . Therefore, the friction is also important for the durability. The surface tension, γ , determines the lateral length scale of the fluctuation. The fluctuation increases with time when q is smaller than q^* . The foam film, even when the elasticity is small, $k < A_{\rm H}/4\pi h_0^4$, is stable when the lateral length of the foam film is smaller than $1/q^*$. Hence, the surface tension stabilizes small foam films. Thus, the bulk elasticity and the friction of the gel dominate the stability and durability of the foam decorated by polymer/surfactant complexes.

The Darcy constant κ and the osmotic modulus k may be experimentally accessible. The Darcy constant κ is the parameter that represents the friction and the volume fraction of complexes in the gels. This constant is probably characterized by measuring the drainage of foams. The osmotic modulus, k, represents the repulsive force between the interfaces. The osmotic modulus is characterized by measuring the applied pressure under which a foam film shows instability.^{9,10,26}

The gelation of the aqueous foam film by two mechanisms other than polymer/surfactant complexes has been reported. One mechanism involves lamellar liquid crystals comprising of surfactants and salts.^{27,28} A lamellar liquid crystal is also called a surfactant crystal because the surfactants are arranged as crystal structure. They behave similar to gels macroscopically as they are hydrated by polar group. The other mechanism consists of polymers cross-linked by ions.²⁹ The polymers and ions form a framework structure in the foam film. The drainage of the foam containing polymers cross-linked by ions becomes slower as the concentration of the cross-linker increased.²⁹ The increase in the degree of cross-linking correlates with the increase in the volume fraction, ϕ , and then the decrease in the Darcy constant, κ . Our theory agrees with the previous experiments qualitatively.

The above results and discussion are derived from the assumption that the size of the surface gel is comparable to the thickness of the foam film. We argue that the ratio of these two length scales determines the stabilizing mechanism of foam films. When a foam film is thinner than h_0 , the film is stabilized by bulk elasticity, as the complexes are packed and form the gel-like structure. In contrast, when a foam film is thicker than h_0 , the film is stabilized by surface elasticity since the entire foam film is not filled with the complexes that exist on the surface. Thus, bulk elasticity stabilizes a foam film when the foam film is not stabilized by surface elasticity and then it thins. This crossover may depend on the polymer and the surfactant concentration during the solution preparation. Although we treat the osmotic modulus is symmetric for $h = h_0$ for simplicity, we can predict the lower bound of the film stability. It is because the foam film becomes more stable as the film becomes thicker. The osmotic modulus k for $h > h_0$ describes the attracting force in the unstable foam film which has surface elasticity.

2.7 Summary

We proposed a theory on the stability and durability of a liquid film decorated by surfactants and polymers. Here, we assume that surfactants and polymers form a complex similar to a gel that spans the entire film. The gel suppresses and retards the foam film fluctuation. The contributions of the gel to the foam film are classified into two types: bulk elasticity and friction. We predict that the bulk elasticity contributes to the stabilization of the foam film and that the friction in the foam film prolongs the lifetime of the film.

Chapter 3

Low polymer concentration regime

On dilute polymer regime below the overlap concentration c^* , the mean field assumption for polymer local concentrations is not valid because the polymers are separated from each other.³⁰ The effect of polymers on the stability of liquid films should thus be investigated microscopically. To highlight the roles played by the conformation of polymers, we take into account the entropic elasticity of polymers and the electrostatics in the liquid film because the neat air/water interfaces are charged by surfactants or OH⁻ ions.^{31,32} Liquid films are stable when the repulsive force is larger than the attractive force, such as van der Waals force.^{14,31} Thus, we analyze the repulsive force between two air-liquid interfaces and construct a theoretical model to characterize the stability of liquid films.

3.1 Conventional research

Kristen and Klitzing reviewed the stability measurements of foam films containing polymers and surfactants.¹⁴ The conventional experiments are classified into three groups. One is the liquid film containing the likely charged polyelectrolytes and surfactants. Another is the oppositely charged polyelectrolyte/surfactant systems. The last one is the polyelectrolyte/surfactant systems in which one or both is not charged. In previous experiments, the liquid film stability is characterized by thin-film pressure balance.^{8,14,31} With this method, the repulsive forces called disjoining pressure can be measured with the porous-plate technique, developed by Mysels and Exerowa.^{9,10} The experiments has reported that the stability of the liquid film containing the oppositely charged polyelectrolytes and surfactants is dramatically different compared to that of the film containing the pure surfactants,³³ while the system of the likely charged polyelectrolytes and surfactants has no significant effect on the stability.³⁴ It is because that the oppositely charged polyelectrolyte/surfactant forms surface complexes induced by electrostatic attractions, and the likely charged polyelectrolytes are repelled from the surfactants on the surface of foams.

They argued that DLVO forces (refer to 1.1.1) which consist of electrostatic and van der Waals interactions explain the stability of liquid films containing polyelectrolytes and surfactants.¹⁴ In the system of oppositely charged polyelectrolytes and surfactants, the disjoining pressure has the minimum value (\sim thousands of pascals) against the polyelectrolyte concentration, and then the liquid film ruptures when the thickness is \sim 10nm. The instability can be induced by the decrease of the electric repulsion since the concentration when the film ruptures is the isoelectric point (IEP). However, the DLVO theory is the same to the stability analysis for the liquid film containing surfactants only. Therefore, the electric charge of the polymer only is taken into account in the theory.

3.2 Scope of this theory

For simplicity, the stability of the liquid film containing the oppositely charged polyelectrolyte/surfactant complexes is described in this thesis. This is because hydrogen bonds and hydrophobic interactions are comparable to electric interactions in the polyelectrolyte/surfactant systems in which one or both is not charged.²³ The effect of neglected terms might be described the charge ratio between polyelectrolytes and surfactants.

We focus on the conformation of one polyelectrolyte and take into account the entropic elasticity of the polyelectrolyte to discuss the liquid film formed. The polyelectrolytes are adsorbed alone to the surfactants since they are oppositely charged for the surfactants and isolated each other in dilute solution. Therefore, the number of the adsorbed polymers is classified into three group(0, 1, 2) by using the lattice model as shown in Figure 3.1. In this chapter, we derive the conformation of the adsorbed polymer and the disjoining pressure at each lattice site.



Figure 3.1: Schematic picture of the lattice model for the liquid film with polyelectrolytes and surfactant mixture. Treating the air/liquid interface as the adsorption site for the polyelectrolyte, the lattice pairs are classified into three group against the number of the adsorbed polyelectrolytes.

3.3 Conformation of polymers adsorbed on surfactants

In this section, we derive the conformation of the polymer adsorbed to the surfactants for two systems. One is the system in which the polymer is adsorbed to one side. The other is the system in which the polymer is adsorbed to both sides. The adsorption to one side represents the limit where the distance between two interfaces is large.

The conformation of the polymer has relevance to the surfactants through the electrostatic interaction. Thus, we minimize the free energy and predict the conformation by taking into account the entropic elasticity and the electrostatic interaction. To focus on these two interactions, we consider the conformation of the strongly charged polymer.

3.3.1 Plane adsorption model



Figure 3.2: A simple lattice box for the adsorbed polymer. We treat the width and height of the lattice box as d and L, respectively. The surface charge becomes zero since the oppositely charged segment of the polymer approaches the surface. The polymer adsorbed by the electric attraction can be treated as the grafted polymer.

By treating the polymer as a lattice box and the interface having the surfactants as a charged wall as shown in Figure 3.2, we derive the simple conformation of the polymer adsorbed to one side. The polymer is adsorbed to the surfactants through the electric attraction. The segment of the polymer and the surfactant close to each other can be treated as the non-charged segment due to the electric neutrality. For simplicity, we assume that the counter ions of surfactants freed by the adsorption distribute uniformly in the system. This is because the electric interaction of the polymer is screened when the polymer is strong charged. The free energy of the adsorbed polymer has a form

$$F = \frac{kL^2}{2} + k_{\rm B}Td^2 \int_0^\infty \rho_+ (\ln \rho_+ - 1) dz$$

$$+ \frac{ed^2}{2} \int_0^\infty (\rho_+ - C)\phi \, dz - \lambda \Big[d^2 \int_0^\infty \rho_+ dz - CLd^2 \Big],$$
(3.3.1)

where the entropic elasticity has the form

$$k = \frac{3k_{\rm B}T}{(N - \sigma d^2)a^2}$$
(3.3.2)

and the charge density of the polymer has the form

$$C(z) = \begin{cases} \frac{1}{L} \left(\frac{N}{d^2} - \sigma \right) & (0 \le z \le L) \\ 0 & (z \ge L) \end{cases}$$

$$(3.3.3)$$

and the Lagrange multiplier is λ . The first term represents the entropic elasticity of the polymer¹⁹ where N is the number of the segments and σ is the surface density of the electric charge, and a is the length of the segment. This elasticity is inversely proportional to the number of remained segment which is not adsorbed, $N - \sigma d^2$, see the equation (1.1.9). The second term represents the entropy of the counterion liberated from the polymer where the counterion density is ρ_+ . The third term represents the electrostatic energy where e is an elementary charge. Using the method of Lagrange multipliers, we fix the number of the counterion in the fourth term.

To simplify the free energy, we reduce the variable of the equation. According to the functional derivative of the equation (3.3.1) with respect to ρ_+ ,³⁵ the density of the counterion has a form

$$n_0 = e^{\lambda\beta}$$

$$\rho_+ = n_0 e^{-\beta e\phi}$$
(3.3.4)

where n_0 is a constant depending on the Lagrange coefficient and the density of the counterion ρ_+ has relevance to the electrostatic potential ϕ . Here, we introduce an Poisson-Boltzman equation, $d^2\phi/dz^2 = -e(\rho_+ - C)/\epsilon$. Substituting (3.3.4) and the Poisson-Boltzmann equation, we obtain

$$F = \frac{kd^2}{2} - \frac{\epsilon d^2}{2} \int_0^\infty \left(\frac{d\phi}{dz}\right)^2 dz - d^2 \int_0^L eC(z)\phi \ dz - n_0 k_{\rm B} T d^2 \int_0^\infty e^{-\beta e\phi} dz + k_{\rm B} T d^2 \ln n_0 \ CL.$$
(3.3.5)

Using the functional derivative of the Equation (3.3.5) with respect to ϕ , we can confirm

the Poisson-Boltzmann equation of this system.

$$\frac{d^2 \tilde{\phi}(z)}{dz^2} = 4\pi l_{\rm B} \{ -n_0 \mathrm{e}^{-\tilde{\phi}} + C(z) \}, \qquad (3.3.6)$$

where a dimensionless potential $\tilde{\phi} = \beta e \phi$ is the electric potential rescaled with the thermal energy $k_{\rm B}T$, and the Bjerrum length $l_{\rm B}$ is the distance in which an electric interaction is comparable to thermal energy. Multiplying both side of the Equation (3.3.6) by $d\tilde{\phi}/dz$, the equation has a form

$$\frac{d}{dz}\left\{\frac{1}{2}\left(\frac{d\tilde{\phi}(z)}{dz}\right)^{2}\right\} = 4\pi l_{\rm B}\left\{-n_{0}\frac{d}{dz}e^{-\tilde{\phi}} + C(z)\frac{d\tilde{\phi}(z)}{dz}\right\}.$$
(3.3.7)

Integrating this equation with respect to z from 0 to h provides the form

$$\left(\frac{d\tilde{\phi}}{dz}\right)^{2} = \begin{cases} 8\pi l_{\rm B}(n_{0}{\rm e}^{-\tilde{\phi}} + C\tilde{\phi}) + C_{0}({\rm const.}) & (0 \le z \le L) \\ \\ 8\pi l_{\rm B}n_{0}{\rm e}^{-\tilde{\phi}} + C_{1}({\rm const.}) & (z \ge L) \end{cases}$$
(3.3.8)

Owing to the electric neutrality at z = 0, the boundary condition has a form

$$\tilde{\phi}(0) = 0, \left. \frac{d\tilde{\phi}(z)}{dz} \right|_{z=0} = \left. \frac{d\tilde{\phi}(z)}{dz} \right|_{z=\infty} = 0.$$
(3.3.9)

Furthermore, the counterion density becomes zero at long distance,

$$\rho_+(\infty) = n_0 e^{-\tilde{\phi}(\infty)} = 0.$$
(3.3.10)

Comparing the Equation (3.3.8) to the boundary conditions, we have the integral constants as follows:

$$C_0 = -8\pi l_{\rm B} n_0, \quad C_1 = -8\pi l_{\rm B} \rho_-(\infty) = 0.$$
 (3.3.11)

Thus,

$$\left(\frac{d\tilde{\phi}(z)}{dz}\right)^{2} = \begin{cases} 8\pi l_{\rm B}(n_{0}{\rm e}^{-\tilde{\phi}} - n_{0} + C\tilde{\phi}) & (0 \le z \le L) \\ \\ 8\pi l_{\rm B}n_{0}{\rm e}^{-\tilde{\phi}} & (z \ge L) \end{cases}$$
(3.3.12)

From the continuous condition of the electric field at z = L, the potential at z = L is

$$(n_0 e^{\tilde{\phi}_L} - n_0 + C\tilde{\phi}_L) = n_0 e^{\tilde{\phi}_L}.$$

$$\rightarrow \underline{\tilde{\phi}_L} = \frac{n_0}{\underline{C}}$$
(3.3.13)

We derive the potential in two regimes.

 $({
m I})z\geq L$

By integrating with variable separation, the potential has a form

$$-\sqrt{8\pi l_{\rm B} n_0} dz = e^{\tilde{\phi}/2} d\tilde{\phi} \tilde{\phi} = 2 \ln \left[\frac{\kappa z}{\sqrt{2}} - C_2(\text{const.})\right], \quad \kappa = \sqrt{4\pi l_{\rm B} n_0} \tag{3.3.14}$$

Due to the boundary condition at z = L, the potential becomes

$$\widetilde{\phi}(z) = 2\ln\left[\frac{\kappa(z-L)}{\sqrt{2}} + e^{\frac{n_0}{2C}}\right] \qquad (z \ge L)$$
(3.3.15)

$(\mathrm{II}) 0 \leq z \leq L$

The electric energy is smaller than the thermal energy because the electric interaction is screened by the counterions. By introducing $e^{\tilde{\phi}} \simeq 1 + \tilde{\phi} + \frac{\tilde{\phi}^2}{2}$ under $\tilde{\phi} \ll 1$ to the Equation (3.3.12), we obtain the equation as follows:

$$\begin{pmatrix} d\tilde{\phi} \\ dz \end{pmatrix} = \sqrt{8\pi l_B n_0} \sqrt{\tilde{\phi} + \frac{\tilde{\phi}^2}{2} + \frac{C}{n_0}} \tilde{\phi}$$

$$= \sqrt{4\pi l_B n_0} \sqrt{(\tilde{\phi} + a)^2 - a^2}, \qquad a = 1 - \frac{C}{n_0}.$$
(3.3.16)

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By integrating with variable separation, the potential has a form

$$-\kappa z + C_3(\text{const.}) = \cosh^{-1}\left(\frac{\tilde{\phi}}{a} + 1\right)$$
(3.3.17)

Due to the boundary condition at z = 0, $C_3 = \cosh^{-1}(1) = 0$. Therefore, the potential becomes

$$\underbrace{\tilde{\phi}(z) = \left(1 - \frac{C}{n_0}\right) \left[\cosh(\kappa z) - 1\right] \qquad (0 \le z \le L)$$
(3.3.18)

Furthermore, the potential at z = L is

$$\tilde{\phi}_L = \left(1 - \frac{C}{n_0}\right) \left[\cosh(\kappa L) - 1\right]$$
(3.3.19)

Summarizing above, the potentials is written as follows:

$$\tilde{\phi}(z) = \begin{cases} \left(1 - \frac{C}{n_0}\right) \left[\cosh(\kappa z) - 1\right] & (0 \le z \le L) \\ \\ -2\ln\left[\frac{\kappa(z-d)}{\sqrt{2}} + e^{\frac{n_0}{2C}}\right] & (z \ge L) \end{cases}$$
(3.3.20)

where $\kappa = \sqrt{4\pi l_{\rm B} n_0}$. κ^{-1} is called the Debye length.⁶ To obtain n_0 , we compare the Equation (3.3.13) and (3.3.19).

$$\frac{n_0}{C} = \left(\frac{C}{n_0} - 1\right) \left[\cosh(\kappa L) - 1\right]$$

$$\rightarrow \frac{C}{n_0} = \frac{1}{2} \left(\sqrt{\frac{\cosh(\kappa L) + 3}{\cosh(\kappa L) - 1}} + 1\right)$$
(3.3.21)

We approximate this equation for two limits. One of them is the case in which the length of the polymer is much longer than the Debye length. The other one is the case in which the length of the polymer is much shorter than the Debye length. $({
m I})\kappa L\gg 1$

$$\frac{C}{n_0} \simeq \frac{1}{2} \left(\sqrt{\frac{\mathrm{e}^{\kappa L}}{\mathrm{e}^{\kappa L}}} + 1 \right) = 1$$

$$\rightarrow \underline{n_0} \simeq C$$
(3.3.22)

Thus,

$$\tilde{\phi}(z) = \begin{cases} 0 & (0 \le z \le L) \\ \\ 2\ln\left[\frac{\kappa(z-L)}{\sqrt{2}} + e^{\frac{1}{2}}\right] & (z \ge L) \end{cases}$$
(3.3.23)

where $\kappa = \sqrt{4\pi l_{\rm B}C}$.

 $(\mathrm{II})\kappa L\ll 1$

$$\frac{C}{n_0} \simeq \frac{1}{2} \left(\sqrt{1 + \frac{8}{(\kappa L)^2} + 1} \right) \simeq \frac{\sqrt{2}}{\kappa L} + \frac{1}{2}$$

$$\rightarrow \underline{n_0} = 2\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma\right)^2$$
(3.3.24)

Thus,

$$\tilde{\phi}(z) = \begin{cases} 2\pi l_{\rm B} C z^2 & (0 \le z \le L) \\ 2\ln\left[2\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma\right)(z - L) + e^{\pi l_{\rm B} L(\frac{N}{d^2} - \sigma)}\right] & (z \ge L) \end{cases}$$
(3.3.25)

where $\kappa = 2\sqrt{2}\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma\right)$. Comparing the Equation (3.3.22) and (3.3.24), the overlap length L' has a form

$$C = 2\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma\right)^2$$

$$\rightarrow \underline{L'} = \frac{1}{2\pi l_{\rm B}(\frac{N}{d^2} - \sigma)}. \qquad \left(0 \le d \le \sqrt{\frac{N}{\sigma}}\right)$$
(3.3.26)
A phase diagram and non-dimensionalization

We describe the phase diagram for the electric potential $\tilde{\phi}$ as a function against the height of the box L and the width of the box d.

First, we rescale the width d by $d^* = \sqrt{\frac{N}{\sigma}}$ since the charge density of the polymer is written as $N - \sigma d^2 \ge 0$.

$$\frac{d}{d^*} = s. \quad (0 \le s \le 1) \tag{3.3.27}$$

Next, we rescale the height L by $L^* = \frac{1}{2\pi l_B \sigma}$ called the Gouy-Chapman length because the height of the box has relevance to the electric interaction.

$$\frac{L}{L^*} = t, \quad (0 \le t \le t_{\max}), \tag{3.3.28}$$

where $t_{\text{max}} = 2\pi l_{\text{B}}\sigma Na(1-s^2)$. According to these rescaled parameters, the rescaled overlap height has a form

$$\underline{t' = \frac{L'}{L^*} = \frac{1}{s^{-2} - 1}}.$$
(3.3.29)

Thus, we exhibit the phase diagram by describing the Equation (??) and (3.3.29) in Figure 3.3.



Figure 3.3: The phase diagram of the rescaled electric potential. The rescaled height is plotted against the rescaled width. Red and blue areas show cases in which the height is shorter and longer than the screening length κ^{-1} , respectively. Red area ($\kappa L \ll 1$) represents that the electric charge of the polymer is screened by the surface charge. Blue area ($\kappa L \gg 1$) represents that the charge of the polymer is remained.

The hight of the lattice box

The free energy of the adsorbed polymer is a function of two variables, L and d. We obtain the equilibrium conformation by using the derivative of the free energy. Before calculating the derivative, we simplify the free energy by substituting the Equation (3.3.12) to the free energy (3.3.5). The simplified free energy is rewritten as follow:

$$F = \frac{kL^2}{2} - n_0 k_{\rm B} T L d^2 - \epsilon d^2 \int_0^\infty (\nabla \phi)^2 dz + k_{\rm B} T \left(N - \sigma d^2 \right) \ln n_0 \tag{3.3.30}$$

The derivative of the free energy with respect to L has a form

$$\frac{dF}{dL} = \frac{\partial F}{\partial L} + \frac{\delta F}{\delta \phi} \frac{\partial \phi}{\partial L}$$
(3.3.31)

We substitute $\frac{\delta F}{\delta \phi} = 0$ to this equation because of the obtained electric potential from the functional derivative. So, the derivatives with respect to L for two regime are written as follows:

 $(\mathbf{I})\kappa L \gg 1; n_0 \simeq C$

$$\frac{\partial F}{\partial L} = kL - Ck_{\rm B}Td^2 + \frac{\epsilon d^2}{L} \int_0^\infty (\nabla\phi)^2 dz$$
(3.3.32)

We calculate the electrostatic energy.

$$\frac{\partial \tilde{\phi}(z)}{\partial z} = \begin{cases} 0 & (0 \le z \le L) \\ \\ \frac{-2}{(z-L) + \frac{1}{\kappa}\sqrt{2e}} & (z \ge L) \end{cases}$$
(3.3.33)

Therefore,

$$\int_0^\infty (\nabla\tilde{\phi})^2 dz = \int_L^\infty (\nabla\tilde{\phi})^2 dz = \frac{4}{L} \int_0^\infty \frac{du}{(u + \frac{1}{\kappa L}\sqrt{2e})^2} = \frac{4\kappa}{\sqrt{2e}}.$$
(3.3.34)

Thus,

$$\frac{\partial F}{\partial L} = \frac{3k_{\rm B}T}{(N - \sigma d^2)a^2}L - \frac{k_{\rm B}T}{L}\left(N - \sigma d^2\right) + \frac{4d^2}{\sqrt{2e}\beta e}\sqrt{\frac{\epsilon}{\beta}}\frac{1}{L^{3/2}}\sqrt{\frac{N}{d^2} - \sigma} = PL - \frac{Q}{L} + \frac{R}{L^{3/2}} = 0,$$
(3.3.35)

where

$$P = \frac{3k_{\rm B}T}{(N - \sigma d^2)a^2}, \qquad Q = k_{\rm B}T\left(N - \sigma d^2\right), \qquad R = \frac{4d^2}{\sqrt{2e}}\frac{1}{\beta e}\sqrt{\frac{\epsilon}{\beta}}\sqrt{\frac{N}{d^2} - \sigma}.$$
 (3.3.36)

(i) When L is large, we approximate the height, $L\simeq \sqrt{\frac{Q}{P}}$ by neglecting the third term. Then, the solution becomes

$$L_1 \equiv \sqrt{\frac{1}{3} a(N - \sigma d^2)}.$$
 (3.3.37)

(ii) When L is small, we approximate the height, $L \simeq \left(\frac{R}{Q}\right)^2$ by neglecting the first term. Then, the solution becomes

$$L_2 \equiv \frac{2}{e} \frac{1}{\pi l_B \sigma} \frac{1}{N/\sigma d^2 - 1},$$
(3.3.38)

where e is Napier's constant. According to these equations, the minimum and maximum values correspond to $L_{\rm max}$ and L' except for prefactars. However, the polymer has no equilibrium state when $\kappa L \gg 1$. This is because L_2 is smaller than κ^{-1} , and the maximum value L_1 is larger than the gyration size of the polymer in solutions $R_{\rm g} \sim a\sqrt{N}$.¹⁹ (II) $\kappa L \ll 1$; $n_0 = 2\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma\right)^2$

$$\frac{\partial F}{\partial L} = kL - k_{\rm B}T2\pi l_{\rm B}d^2 \left(\frac{N}{d^2} - \sigma\right)^2 + \frac{\epsilon d^2}{L} \int_0^\infty (\nabla\phi)^2 dz \qquad (3.3.39)$$

We have the electrostatic energy.

$$\frac{\partial \tilde{\phi}(z)}{\partial z} = \begin{cases} -4\pi l_{\rm B} C z & (0 \le z \le L) \\ \\ \frac{-2}{(z-L)+X}, & (z \ge L) \end{cases}$$
(3.3.40)

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where

$$X = \frac{\mathrm{e}^{\pi l_{\mathrm{B}} L(\frac{N}{d^2} - \sigma)}}{2\pi l_{\mathrm{B}}(\frac{N}{d^2} - \sigma)}.$$
(3.3.41)

Therefore,

$$\int_0^\infty (\nabla \tilde{\phi})^2 dz = (4\pi l_{\rm B})^2 \left(\frac{N}{d^2} - \sigma\right)^2 \frac{L}{3} + 8\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma\right) e^{-\pi l_{\rm B} L(\frac{N}{d^2} - \sigma)}.$$
(3.3.42)

Thus,

$$\frac{\partial F}{\partial L} = \frac{3k_{\rm B}T}{(N - \sigma d^2)a^2}L - \frac{e^2d^2}{6\epsilon} \left(\frac{N}{d^2} - \sigma\right)^2 + \frac{2k_{\rm B}Td^2}{L} \left(\frac{N}{d^2} - \sigma\right)e^{-\pi l_{\rm B}L(\frac{N}{d^2} - \sigma)}$$

$$= PL - V + \frac{W}{Le^{YL}} = 0,$$
(3.3.43)

where

$$V = \frac{e^2 d^2}{6\epsilon} \left(\frac{N}{d^2} - \sigma\right)^2, \qquad W = \frac{2k_{\rm B}T d^2}{L} \left(\frac{N}{d^2} - \sigma\right), \qquad Y = -\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma\right). \tag{3.3.44}$$

(i) When L is large, we approximate the height, $L\simeq \frac{V}{P}$ by neglecting the third term. Then, the solution becomes

$$L_3 \equiv \frac{a^2}{9d^2} 2\pi l_{\rm B} (N - \sigma d^2)^3.$$
(3.3.45)

(ii) When L is small, we approximate the height, $L \simeq \frac{W}{V}$ by neglecting the first term. In this case, the solution becomes

$$L_4 \equiv \frac{6\epsilon}{e^2} \frac{2k_{\rm B}T}{\left(\frac{N}{d^2} - \sigma\right)} = \frac{3}{\pi l_{\rm B}} \frac{1}{\left(\frac{N}{d^2} - \sigma\right)}.$$
(3.3.46)

From the above derivative, the equilibrium length L_4 is larger than the screen length $\kappa^{-1} = \left[2\sqrt{2\pi}l_{\rm B}\left(\frac{N}{d^2} - \sigma\right)\right]^{-1}$. Therefore, the free energy has no equilibrium state in this

regime. In other wards, $\partial F/\partial L$ is positive when $L < \kappa^{-1}$.

The appropriate height is zero because the free energy monotonically increase with respect to L.

The width of the lattice box

Substituting L = 0 to the free energy (3.3.30), we obtain the appropriate free energy with respect to L.

$$F = \gamma d^{2} = k_{\rm B} T \left(N - \sigma d^{2} \right) \left[\ln 2\pi l_{\rm B} + 2 \ln \left(\frac{N}{d^{2}} - \sigma \right) - 2 \right]$$
(3.3.47)

The derivative of the free energy with respect to d has the form

$$\frac{\partial F}{\partial d} = -2k_{\rm B}T\sigma d \left[\ln 2\pi l_{\rm B} + 2\ln\left(\frac{N}{d^2} - \sigma\right) - 2\right] - 4k_{\rm B}T\frac{N}{d}$$
(3.3.48)

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$$\frac{\partial F}{\partial d} = -\frac{2Nk_{\rm B}T}{d} \left[\frac{\sigma d^2}{N} \left(\ln \left[2\pi l_{\rm B} \left(\frac{N}{d^2} - \sigma \right)^2 \right] - 2 \right) + 2 \right] < 0, \qquad \left(0 \le d \le \sqrt{\frac{N}{\sigma}} \right) \quad (3.3.49)$$

The polymer spreads to the limit. Therefore, the polymer is adsorbed plainly to the surface.

3.3.2 Bridge model

The polymer is adsorbed to one surface when two walls are far. In contrast, the polymer may be adsorbed to both surfaces and bridge a gap when two walls are close as shown in Figure 3.4. We consider the conformation of the bridging polymer. For simplicity, we assume that number of the counterions from the polymer is constant in a lattice box.



Figure 3.4: Schematic picture of the adsorbed polymer as the bridge between two surfaces.

The free energy of the bridging polymer

We assume that the polymer is adsorbed isotropically to the surfaces as shown in Figure 3.5. The free energy density per unit area γ has a form

$$\gamma = \frac{k}{2} \left(\frac{h}{d}\right)^2 + \frac{e}{2} \int_{-h/2}^{h/2} \left(\rho_+ - \rho_- - C\right) \phi dz$$

+ $k_{\rm B} T \int_{-h/2}^{h/2} \rho_+ (\ln \rho_+ - 1) + \rho_- (\ln \rho_- - 1) dz$ (3.3.50)
- $\mu \left[\int_{-h/2}^{h/2} + \rho_- dz - 2\sigma \right] - \lambda \left[\int_{-h/2}^{h/2} \rho_+ dz - \frac{N}{d^2} \right]$
 $k = \frac{3k_{\rm B} T}{(N - 2\sigma d^2)a^2}$ (3.3.51)



Figure 3.5: The model of the bridging polymer. The width of the polymer is d. The distance between two walls is h.

$$C = \frac{1}{h} \left(\frac{N}{d^2} - 2\sigma \right) \tag{3.3.52}$$

According to the functional derivative, we derive the Poisson-Boltzmann equation. Substituting $\phi(z) = \int_{-h/2}^{h/2} \frac{e}{4\pi\varepsilon} \frac{\rho_+ - \rho_- - C}{|z - z'|} dz'$ to the Equation (3.3.50), we obtain the plus counterion density as follows:

$$\frac{\delta\gamma}{\delta\rho_{+}} = \int_{-h/2}^{h/2} \left[e\phi + k_{\rm B}T \ln \rho_{+} - \lambda \right] dz = 0$$

$$\Rightarrow \rho_{+} = e^{\lambda\beta} e^{-\beta e\phi} = n_{+} e^{-\tilde{\phi}}$$
(3.3.53)

The same treatment is applied for the ρ_{-} . The minus counterion density has a form

$$\rho_{-} = n_{-} \mathrm{e}^{\tilde{\phi}}.\tag{3.3.54}$$

Using the Equations (3.3.53) and (3.3.54), γ is rewritten as a function of the electric potential ϕ :

$$\gamma[\tilde{\phi}(z)] = \frac{k}{2} \left(\frac{h}{d}\right)^2 - \frac{\epsilon}{2} \int_{-h/2}^{h/2} (\nabla \phi)^2 dz - eC \int_{-h/2}^{h/2} \phi \, dz - k_{\rm B}T \int_{-h/2}^{h/2} n_+ e^{-\tilde{\phi}} - n_- e^{\tilde{\phi}} dz + \frac{Nk_{\rm B}T}{d^2} \ln n_+ + 2\sigma k_{\rm B}T \ln n_-$$
(3.3.55)

where the rescaled $\tilde{\phi} = \beta e \phi$. By using the functional derivative of $\tilde{\phi}$ for γ , we obtain the following Poisson-Boltzmann equation:

$$\nabla^2 \tilde{\phi} = 4\pi l_{\rm B} (C + n_- {\rm e}^{\tilde{\phi}} - n_+ {\rm e}^{-\tilde{\phi}}).$$
(3.3.56)

We solve this equation. The electric field is zero at middle plane owing to the symmetry. Furthermore, the electric field is zero on the surfaces due to the electric neutrality by the adsorption of the polymer. The boundary conditions is written as follows:

$$\frac{d\phi}{dz}\Big|_{z=h/2} = \frac{d\phi}{dz}\Big|_{z=-h/2} = \frac{d\phi}{dz}\Big|_{z=0} = 0$$
(3.3.57)

$$\phi(0) = 0 \tag{3.3.58}$$

$$\phi\left(\frac{h}{2}\right) = \phi\left(-\frac{h}{2}\right) \tag{3.3.59}$$

By multiplying both side of the Equation (3.3.56) by $\nabla \tilde{\phi}$ and integrating, we obtain the following equation:

$$\left(\frac{d\tilde{\phi}}{dz}\right)^2 = 8\pi l_{\rm B}(C\tilde{\phi} + n_-{\rm e}^{\tilde{\phi}} + n_+{\rm e}^{-\tilde{\phi}}) + C_0(\text{const.})$$
(3.3.60)

Due to the boundary condition at z = 0, the integral constant has a form

$$C_0 = -8\pi l_{\rm B}(n_+ + n_-). \tag{3.3.61}$$

Therefore,

$$\left(\frac{d\tilde{\phi}}{dz}\right)^2 = 8\pi l_{\rm B} (C\tilde{\phi} + n_-(\mathrm{e}^{\tilde{\phi}} - 1) + n_+(\mathrm{e}^{-\tilde{\phi}} - 1)).$$
(3.3.62)

Owing to the two boundary conditions at z = h/2 and z = -h/2,

$$0 = C\tilde{\phi}_{h/2} + n_{-}(\exp(\tilde{\phi}_{h/2}) - 1) + n_{+}(\exp(-\tilde{\phi}_{h/2}) - 1), \qquad (3.3.63)$$

$$0 = C\tilde{\phi}_{-h/2} + n_{-}(\exp(\tilde{\phi}_{-h/2}) - 1) + n_{+}(\exp(-\tilde{\phi}_{-h/2}) - 1).$$
(3.3.64)

Let us consider that the counterion is filled up in the polymer because the polymer is strongly charged. We use the approximation: $\tilde{\phi} \ll 1$. Due to this approximation, the boundary condition at z = h/2 has an approximate form

$$0 \simeq C\tilde{\phi}_{h/2} + n_{-}\tilde{\phi}_{h/2} + n_{+}\tilde{\phi}_{h/2}$$

= $(C + n_{-} - n_{+})\tilde{\phi}_{h/2}.$ (3.3.65)

To complete the above equation, we have to consider the cases in which either $C+n_--n_+ = 0$ or $\tilde{\phi}_{h/2} = 0$. At first, we treat the case in which $C + n_- - n_+ \neq 0$ and $\tilde{\phi}_{h/2} = 0$. The Equation (3.3.62) has an approximate form

$$\left(\frac{d\tilde{\phi}}{dz}\right)^2 \simeq 8\pi l_{\rm B}(C+n_--n_+)\tilde{\phi}.$$
(3.3.66)

Solving this equation, we obtain the following equation:

$$\sqrt{\tilde{\phi}} = \pm \sqrt{2\pi l_{\rm B}(C + n_- - n_+)}z + C_1.$$
(3.3.67)

Due to the boundary condition at z = 0, this equation has a form

$$\tilde{\phi} = 2\pi l_{\rm B} (C + n_- - n_+) z^2, \qquad (3.3.68)$$

where $C_1 = 0$. Comparing the derivative of the solution to the electric field at z = h/2, we find the following relation:

$$\frac{\partial \tilde{\phi}}{\partial z}\Big|_{z=h/2} = 2\pi l_{\rm B} (C+n_--n_+)h \neq 0.$$
(3.3.69)

The case in which $C + n_- - n_+ \neq 0$ and $\tilde{\phi}_{h/2} = 0$ is improper. Next, we consider the case in which $C + n_- - n_+ = 0$. The Equation (3.3.66) changes to a form

$$\left(\frac{d\tilde{\phi}}{dz}\right)^2 \simeq 0. \tag{3.3.70}$$

Therefore,

$$\tilde{\phi} = 0. \tag{3.3.71}$$

where the electric field is zero at z = 0. Thus, the electric potential is constant in the system, and then the ions distribute uniformly.

$$\rho_{-} = \frac{2\sigma}{h}, \quad \rho_{+} = \frac{N}{hd^2}$$
(3.3.72)

The free energy density (3.3.50) changes to a form

$$\gamma = \frac{k}{2} \left(\frac{h}{d}\right)^2 + k_{\rm B} T \int_{-h/2}^{h/2} \frac{N}{hd^2} (\ln \frac{Nv_0}{hd^2} - 1) + \frac{2\sigma}{h} (\ln \frac{2\sigma v_0}{h} - 1) dz$$

$$= \frac{k}{2} \left(\frac{h}{d}\right)^2 + \frac{Nk_{\rm B} T}{d^2} (\ln \frac{Nv_0}{hd^2} - 1) + 2\sigma k_{\rm B} T (\ln \frac{2\sigma v_0}{h} - 1),$$
(3.3.73)

where the volume of the monomer is $v_0 = a^3$.

The area of the bridging polymer

According to the Equation (3.3.73), the free energy F has a form

$$F = \gamma d^{2}$$

$$= \frac{3k_{\rm B}T}{2} \left(\frac{h}{a}\right)^{2} \frac{1}{N - 2\sigma d^{2}} + Nk_{\rm B}T \left(\ln\frac{Nv_{0}}{hd^{2}} - 1\right) + 2\sigma d^{2}k_{\rm B}T \left(\ln\frac{2\sigma v_{0}}{h} - 1\right)$$
(3.3.74)

To obtain the area of the bridging polymer, we perform the width d derivative of the free energy.

$$\frac{\partial F}{\partial d} = \frac{2Nk_{\rm B}T}{d} \left[3\left(\frac{h}{a}\right)^2 \frac{\sigma d^2}{N(N-2\sigma d^2)^2} - 1 + \frac{2\sigma d^2}{N} \left(\ln\frac{2\sigma v_0}{h} - 1\right) \right]$$
(3.3.75)

The derivative $\frac{\partial F}{\partial d} = 0$ has a form

$$3\left(\frac{h}{Na}\right)^{2}\frac{\frac{\sigma d^{2}}{N}}{\left(1-\frac{2\sigma d^{2}}{N}\right)^{2}}-1+\frac{2\sigma d^{2}}{N}\left\{\ln\left(\frac{aN}{h}\frac{2\sigma a^{2}}{N}\right)-1\right\}=0.$$
(3.3.76)

where $d \neq 0$. The system of the bridging polymer is allowed in the distance below the full length of the polymer, h < Na. We can approximate the above equation by using $\frac{h}{Na} \ll 1$.

$$3\left(\frac{h}{Na}\right)^{2} \frac{1}{\left(1 - \frac{2\sigma d^{2}}{N}\right)^{2}} + 2\left\{\ln\left(\frac{aN}{h}\frac{2\sigma a^{2}}{N}\right) - 1\right\} \simeq 0$$
(3.3.77)

Thus, the width of the bridging polymer has a form

$$d_{\text{bridge}} = \sqrt{\frac{N}{2\sigma}} \sqrt{1 - \sqrt{\frac{3}{2} \left(\frac{h}{Na}\right)^2 \left\{1 - \ln\left(\frac{aN}{h}\frac{2\sigma a^2}{N}\right)\right\}^{-1}}} \sim \sqrt{\frac{N - h/a}{2\sigma}}.$$
 (3.3.78)

Above the all, the polymer bridges two surfaces as an extended conformation and the all remained segments are adsorbed to the surface.

3.4 Disjoining pressure

To estimate the contribution of the polymer for the stability of the liquid film, we calculate the disjoining pressure.

3.4.1 Both side adsorption

Due to the plain adsorption, we treat the adsorbed polymer and the interface as a neutral wall, Figure (3.6). The counterions originated from the interfaces and the polymers distribute uniformly.



Figure 3.6: Schematic picture of two interfaces with the polymers. Owing to the adsorption of the polymer, the electric charge of the interfaces is zero.

We treat the density of plus charged counterion and minus charged counterion as ρ_+ and ρ_- , respectively. The number per unit area of the counterions has a form

$$\int_{0}^{h} \rho_{+} dz = \int_{0}^{h} \rho_{-} dz = 2\sigma.$$
(3.4.1)

where the surface charge density is σ . According to the uniformly distribution, the densi-

ties has a form

$$\rho_{+} = \rho_{-} = \frac{2\sigma}{h}.$$
(3.4.2)

The free energy density contains the entropy of the counterions since the electrostatic energy is zero due to the electric neutrality. Then, the free energy density γ has a form

$$\gamma(z) = k_{\rm B}T \int_0^h \rho_+ (\ln \rho_+ - 1) + \rho_- (\ln \rho_- - 1)dz$$

= $4\sigma k_{\rm B}T \left[\ln \left(\frac{2\sigma}{h} - 1 \right) \right]$ (3.4.3)

Thus, the disjoining pressure has a form

$$\Pi_{2} = -\frac{\partial \gamma}{\partial h}$$

$$= -4\sigma k_{\rm B}T \frac{\partial}{\partial h} \left[\ln \left(\frac{2\sigma}{h} - 1 \right) \right]$$

$$= \frac{4\sigma}{h} k_{\rm B}T.$$
(3.4.4)

3.4.2 Plane adsorption



Figure 3.7: Schematic picture of two interfaces with the polymers. Owing to the adsorption of the polymer, the electric charge of the interfaces is zero at one side.

Owing to the plain adsorption, we treat the adsorbed polymer and the interface as a

neutral wall, Figure (3.7). The Poisson-Boltzmann equation for this system has the form

$$\nabla^2 \tilde{\phi} = -4\pi l_{\rm B}(\rho_+ - \rho_-) \qquad (0 < z < L) \tag{3.4.5}$$

where ρ_+ and ρ_- are the positive charged counterion and the negative charged counterion, respectively. The boundary conditions for the charge neutrality are considered as follows:

$$\tilde{\phi}(h) = \tilde{\phi}_h = 0, \left. \frac{d\tilde{\phi}}{dz} \right|_{z=h} = 0.$$
(3.4.6)

Using this condition, we define the constant n_0 representing the density of the counterions at z = h as follows:

$$\rho_{+} = n_0 e^{-\tilde{\phi}}, \quad \rho_{-} = n_0 e^{\tilde{\phi}}.$$
(3.4.7)

We consider the case in which the the number of the counterions is constant. This conditions have the form

$$\int_{0}^{h} \rho_{+} dz = 2\sigma, \quad \int_{0}^{h} \rho_{-} dz = \sigma.$$
 (3.4.8)

where σ is the surface charge density. The Poisson-Boltzmann equation (3.4.5) is rewritten as follow:

$$\frac{d^2\tilde{\phi}}{dz^2} = 8\pi l_{\rm B} n_0 \sinh(\tilde{\phi}). \tag{3.4.9}$$

Multiplying both side of this equation by $d\tilde{\phi}/dz$, we obtain the following equation:

$$\left(\frac{d\tilde{\phi}}{dz}\right)^2 = 16\pi l_{\rm B} n_0 \cosh(\tilde{\phi}) + C_0. \tag{3.4.10}$$

Owing to the boundary condition at z = h, this equation change to the form

$$\left(\frac{d\tilde{\phi}}{dz}\right)^2 = 16\pi l_{\rm B} n_0 \Big[\cosh(\tilde{\phi}) - \cosh(\tilde{\phi}_h)\Big]. \tag{3.4.11}$$

We approximate this equation by using $\tilde{\phi} \ll 1$ because the counterions screen the elec-

trostatic interaction of the charged surface. Integrating the approximated equation, we obtain the following equation:

$$\sqrt{8\pi l_{\rm B} n_0} z + C_1 = \int \frac{d\tilde{\phi}}{\sqrt{\tilde{\phi}^2 - \tilde{\phi}_h^2}} = -\cosh^{-1}\left(\frac{\tilde{\phi}}{\tilde{\phi}_h}\right). \tag{3.4.12}$$

Substituting z = h to this equation, we obtain $C_1 = -\sqrt{8\pi l_{\rm B} n_0} h$. Then, the electrostatic potential becomes

$$\tilde{\phi}(z) = \tilde{\phi}_h \cosh[\kappa(h-z)], \qquad (3.4.13)$$

where $\kappa = \sqrt{8\pi l_{\rm B} n_0}$. At z = 0, the potential becomes

$$\tilde{\phi}_0 = \tilde{\phi}_h \cosh[\kappa h]. \tag{3.4.14}$$

Owing to the boundary condition at z = 0, $\left. \frac{d\tilde{\phi}}{dz} \right|_{z=0} = -4\pi l_{\rm B}\sigma$, we find the following relation from the Equation (3.4.11):

$$\frac{\pi l_B \sigma^2}{n_0} = \cosh(\tilde{\phi}_0) - \cosh(\tilde{\phi}_h) \simeq \frac{\tilde{\phi}_0^2}{2} - \frac{\tilde{\phi}_h^2}{2}.$$
(3.4.15)

This approximation is because of the potential screening, $\tilde{\phi} \ll 1$. Substituting the Equation (3.4.14) to this equation, we obtain the following equation:

$$\frac{2\pi l_B \sigma^2}{n_0} \simeq \tilde{\phi}_0^2 \tanh^2(\kappa h). \tag{3.4.16}$$

Focusing on $tanh(\kappa h)$, we obtain n_0 as a function of $\tilde{\phi}_0$ for the cases in which the distance between two walls is long and short.

$(I)\kappa h \gg 1$

Owing to $\tilde{\phi} \ll 1$, the conservation of the counterions (3.4.8) change to a form

$$n_0 \int_0^h 1 - \tilde{\phi} \, dz = 2\sigma, \qquad n_0 \int_0^h 1 + \tilde{\phi} \, dz = \sigma.$$
 (3.4.17)

3.4. DISJOINING PRESSURE

The Equation (3.4.16) change to a form

$$n_0 = \frac{2\pi l_B \sigma^2}{\tilde{\phi}_0^2},$$
 (3.4.18)

by the use of $tanh(\kappa h) \simeq 1$. Substituting this equation to the conditions of conservation (3.4.8), we rewrite the conservation to the form

$$h - \int_0^h \tilde{\phi} \, dz = \frac{\tilde{\phi}_0^2}{\pi l_{\rm B} \sigma}, \qquad h + \int_0^h \tilde{\phi} \, dz = \frac{\tilde{\phi}_0^2}{2\pi l_{\rm B} \sigma}.$$
 (3.4.19)

The second term of the left side has the form

$$\int_{0}^{h} \tilde{\phi} \, dz = \frac{\tilde{\phi}_{h}}{\kappa} \sinh(\kappa h) = \frac{\tilde{\phi}_{0}}{\kappa} \tanh(\kappa h) \simeq \frac{\tilde{\phi}_{0}}{\kappa}.$$
(3.4.20)

Therefore, we obtain the electric potential at z = 0 and the density of counterions at z = h as follow:

$$\tilde{\phi}_0 = \sqrt{\frac{4\pi l_B \sigma h}{3}}, \qquad n_0 = \frac{3\sigma}{2h}.$$
(3.4.21)

We consider the electric potential as $|\tilde{\phi}| = \tilde{\phi}$ since the surface is positive charged at z = 0. (II) $\kappa h \ll 1$

The Equation (3.4.16) change to the form

$$n_0 = \frac{1}{|\tilde{\phi}_0|} \frac{\sigma}{2h},\tag{3.4.22}$$

by the use of $tanh(\kappa h) \simeq \kappa h$. The integral of the electric potential has the form

$$\int_0^h \tilde{\phi} \, dz = \frac{\tilde{\phi}_0}{\kappa} \tanh(\kappa h) \simeq \tilde{\phi}_0 h. \tag{3.4.23}$$

The conditions of conservation change the form

$$h - \tilde{\phi}_0 h = 4h\tilde{\phi}_0, \qquad h + \tilde{\phi}_0 h = 2h\tilde{\phi}_0.$$
 (3.4.24)

We obtain the electrostatic potential at z = 0 and the density of counterions at z = h as follow:

$$\tilde{\phi}_0 = \frac{1}{3}, \qquad n_0 = \frac{3\sigma}{2h}.$$
(3.4.25)

Disjoining pressure

To get the disjoining pressure, we describe the free energy density per unit area and perform the *L*-derivative of the free energy density. The free energy density γ has a form

$$\gamma = k_{\rm B}T \int_0^h \rho_+ (\ln \rho_+ - 1) + \rho_- (\ln \rho_- - 1) \, dz + \frac{e}{2} \int_0^h \{\rho_+ - \rho_-\} \phi \, dz - \lambda \Big[\int_0^h (\rho_+ + \rho_-) \, dz - 3\sigma \Big],$$
(3.4.26)

where λ is the Lagrange multiplier. By using the Poisson-Boltzmann equation, we rearrange the free energy density to the form

$$\gamma = -k_{\rm B}T \int_0^h \rho_+ + \rho_- \, dz - \frac{\epsilon}{2} \int_0^h (\nabla \phi)^2 \, dz + 3\sigma \ln n_0 k_{\rm B}T.$$
(3.4.27)

where $n_0 = e^{\lambda\beta}$. The derivative of the free energy density with respect to L has the form

$$\frac{\partial \gamma}{\partial L} = \frac{\epsilon}{2h} \int_0^h (\nabla \phi)^2 \, dz - \frac{k_{\rm B}T}{h} \int_0^h 2n_0 \cosh(\tilde{\phi}) \, dz. \tag{3.4.28}$$

Here, we rearrange the Equation (3.4.11) to the form

$$-\frac{\epsilon}{2}(\nabla\phi)^2 + k_{\rm B}T \ 2n_0\cosh(\tilde{\phi}) = k_{\rm B}T \ 2n_0\cosh(\tilde{\phi}_h). \tag{3.4.29}$$

Substituting this equation to the derivative of the free energy density with respect to L, we obtain the disjoining pressure as follow:

$$\Pi_{\text{plain}} = k_{\text{B}}T \ 2n_0 \cosh(\tilde{\phi}_h) = \frac{3\sigma}{h} k_{\text{B}}T, \qquad (3.4.30)$$

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where $\tilde{\phi}_h = 0$ from the boundary condition (3.4.6).

3.4.3 Bridge

Substituting $d_{\rm bridge} \sim \sqrt{\frac{N-h/a}{2\sigma}}$ to the free energy (3.3.74), we rewrite the free energy to a form

$$F = \frac{3k_{\rm B}Th}{2a} + Nk_{\rm B}T \left[\ln\left(\frac{2\sigma v_0}{h}\frac{1}{1-\frac{h}{Na}}\right) - 1 \right] + \left(N - \frac{h}{a}\right)k_{\rm B}T \left(\ln\frac{2\sigma v_0}{h} - 1\right)$$
(3.4.31)

According to the *h*-derivative of the free energy, we obtain the force exerting two surfaces,

$$\frac{\partial F}{\partial h} = \frac{3k_{\rm B}T}{2a} + Nk_{\rm B}T\left(-\frac{1}{h} + \frac{1}{Na-h}\right) - \frac{k_{\rm B}T}{a}\left(\ln\frac{2\sigma h}{h} - 1\right) - \left(N - \frac{h}{a}\right)\frac{k_{\rm B}T}{h}.$$
 (3.4.32)

Therefore, the disjoining pressure $\Pi_{\rm bridge}$ has a form

$$\Pi_{\text{bridge}} = -\frac{\partial F}{\partial h} \left(\frac{1}{d_{\text{bridge}}} \right)^2 = 2\sigma k_{\text{B}} T \left[-\frac{3}{2Na(1-\frac{h}{Na})} + \left\{ \frac{1}{h(1-\frac{h}{Na})} - \frac{1}{Na(1-\frac{h}{Na})^2} \right\} + \left\{ \frac{1}{h} + \frac{1}{Na(1-\frac{h}{Na})} \left(\ln \frac{2\sigma v_0}{h} - 1 \right) \right\} \right].$$
(3.4.33)

The first term represents the entropic elasticity of the polymer which attracts two surfaces. The second terms represent the reduction of the placement area, and the liberation of the counterions on the polymer. The third terms represent he reduction of the placement area, and the liberation of the counterions on the surface.

3.5 Results

We summarize the disjoining pressures above.

$$\Pi_{0} = \begin{cases} \left(\frac{\pi}{\beta e}\right)^{2} \frac{2\epsilon}{L^{2}} + \frac{4\sigma}{L} k_{\rm B}T, & \text{when} \quad \pi l_{B}\sigma L \gg 1 \\ \\ \frac{2\sigma}{L} k_{\rm B}T, & \text{when} \quad \pi l_{B}\sigma L \ll 1 \end{cases} \\ \Pi_{2} = \frac{4\sigma}{L} k_{\rm B}T, & \\ \Pi_{\rm plain} = \frac{3\sigma}{L} k_{\rm B}T, & \\ \Pi_{\rm bridge} = 2\sigma k_{\rm B}T \left[-\frac{3}{2Na(1-\frac{h}{Na})} + \left\{\frac{1}{h(1-\frac{h}{Na})} - \frac{1}{Na(1-\frac{h}{Na})^{2}}\right\} + \left\{\frac{1}{h} + \frac{1}{Na(1-\frac{h}{Na})}\left(\ln\frac{2\sigma v_{0}}{h} - 1\right)\right\}\right]. \end{cases}$$
(3.5.1)

The effective disjoining pressure has the van der Waals attraction, $-\frac{A_{\rm H}}{6\pi h^3}$. Therefore, the disjoining pressure measured in experiments has a form

$$\Pi = \Pi_{\rm disjoin} - \frac{A_{\rm H}}{6\pi h^3}.$$
(3.5.3)

We plot Π against the film thickness h by using the parameters in Table (3.1).



Figure 3.8: Disjoining pressure plotted against the thickness of the lattice box decorated by the surfactants only. The overlap thickness $(\pi l_{\rm B}\sigma)^{-1} = 40$ [nm]. The disjoining pressure has the maximum value at h = 4.4 [nm].



Figure 3.9: Disjoining pressure plotted against the thickness of the lattice box containing two polymers. The disjoining pressure has the maximum value at h = 3.1[nm].



Figure 3.10: Disjoining pressure plotted against the thickness of the lattice box containing one polymers. The polymer is adsorbed to one surface. The disjoining pressure has the maximum value at h = 3.6[nm].



Figure 3.11: Disjoining pressure plotted against the thickness of the lattice box containing one polymers. The polymer bridges a gap between two surfaces. The disjoining pressure has the maximum value at h = 3.1[nm].

Table 3.1: Parameters

N	Number of segments	100
a	Segment length	1[nm]
σ	Surface charged density	$0.01 [nm^{-}2]$
$A_{\rm H}$	Hamaker constant	$10^{-20}[J]$

We exhibit the maximum values as follow:



Figure 3.12: The maximum values of the disjoining pressure.

3.6 Discussion

3.6.1 The overestimation of the osmotic pressure

The disjoining pressure profiles have the maximum values at a few nanometers thickness. The comparison of the maximum values shows that the value of the bridging model is larger than that of the plain adsorption. These behaviors can not explain the minimum value of the disjoining pressure against the polymer concentration. We consider this nonconformance is caused by the confinement of counterions in the lattice box. If counterions are confined in the box, the osmotic pressure becomes large. In the previous experiment, the excess counterions probably go out of the lattice box since the liquid film touches the porous materials. The excess osmotic pressure induced by the confinement may cause the non-conformance when the film thickness is thin.

Here, let us look back the film thickness in which the disjoining pressure becomes the minimum value. The liquid film ruptures at ~ 10 nm. Paying attention to the pressure at ~ 10 nm, we find out the negative disjoining pressure in only Figure 3.11. Thus, we can obtain the maximum value of the disjoining pressure agreeing with the experiment by solving the confinement of counterions. We should consider the counterions elimination except for the ions attracted by the electrostatic interaction.

3.6.2 Computational simulation of polymer conformation

We assumed the one polymer is adsorbed to the both side in bridge model. When the distance between two surfaces is longer than the full length of the polymer, the one polymer can not bridge the gap. Consequently therefore, the probability of the polymer bridging is sensitive to the ratio of the polymer length and the gap. In this thesis, we confirm the occurrence of the polymer bridging in some cases. The study about the dependency of the probability on the gap between two surfaces is a future task.

Using the self consistent field calculation on the basis of Edwards equation³⁰ through the code "SUSHI" included in the OCTA system,³⁶ we examine the volume fraction of the segments to predict the conformation of polymers. We put strongly charged polymers into solution between two charged walls in canonical ensemble. The conformation of the polymer is determined by the entropic elasticity and the electrostatic interaction. In Table 3.2, the conditions are summarized.

Table 3.2: Condition

Simlation	SCF
Ensemble	Canonical
Surface charge density	$0.01 [C/m^2]$
Volume fraction of monomer	0.05%

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Model

We calculate two systems. In the first one, the polymers can move freely as shown in Figure 3.13a. In the last one, we focus on the polymers for which the center part is in the middle plane by using mask method as shown in Figure 3.13b. We compare the free energy between two systems to evaluate the probability of the polymer bridging.



(a) The polymers can move freely. Owing to the electrostatic interaction, the polymer is adsorbed to the charged wall since the polymers and the walls are oppositely charged.



(b) Because of focusing the polymer which the center part is in the middle plane, all segments of the polymers can not be adsorbed to one wall. The polymers bridge the gap when the polymer is longer than the gap.

Figure 3.13: Schematic pictures of the simulation model for the strongly charged polymers in solution between two charged walls.

We calculate the cases in which the distance of the gap is the length of 50 segments whose length is 0.6nm, the Bjerrum length in water, and change the degree of the polymerization from 10 to 60.

Result

We plot the volume fraction distribution of the polymer segments and the ions between two walls in Figure 3.14 and 3.15. In the case in which the polymer can move freely, the most segments are adsorbed to the walls. In the case in which the center part of the polymer is in the middle plane, the end parts are adsorbed to the walls because the volume fraction of the polymer at walls is not zero. The free energy difference becomes smaller as the degree becomes larger in Figure 3.16. The free energy difference is smaller than $0.03 k_{\rm B}T$. Thus, the polymer which bridges the gap exists with a high probability though further consideration is necessary.



Figure 3.14: The volume fraction plotted against the distance between two walls for the system in which the polymers can move freely. The length of polymer is 60 monomer length. The most segments are adsorbed to the walls.



Figure 3.15: The volume fraction plotted against the distance between two walls for the system in which the polymers can move freely. The length of polymer is 60 monomer length. Each end of the polymer is adsorbed to the each wall.



Figure 3.16: The free energy normalized by thermal energy $k_{\rm B}T$ plotted against the degree of polymerization. Red line shows the free energy of the system in which the polymer can move freely. Blue line shows the free energy of the system in which the center part of the polymer seems to be in the middle plane.

3.7 Summary

In this chapter, the stability of the liquid film composed by the dilute solution containing the oppositely charged polyelectrolytes and surfactants was studied. Conventional research has described the the stability of the liquid film thorough the DLVO theory⁶ considering the competition of the electrostatic repulsion and van der Waals attraction. We focused on the conformation of the polymer not only the electric charge of the polymer. Minimizing the free energy and Solving the Poisson-Boltzmann equation, we predict the disjoining pressure of the liquid film. The theory explained the instability of the film in *ca*. 10nm thickness in previous experiments qualitatively. To predict the stability more precisely, we have to eliminate the overestimation of the osmotic pressure caused by the confinement of the counterions in the lattice box.

Chapter 4

Conclusion

This thesis presented the theory of the stabilization of the liquid films containing the polymers as follows.

In chapter 2, we presented the stabilization mechanism of the liquid films composed by the polymer-rich solution. The film can be treated as a gel film because of the previous experiments. We derived the time evolution equation of the surface fluctuations in the film. The equations showed that the gel suppresses and retards the liquid film fluctuation through the bulk elasticity and friction.

In chapter 3, we presented the destabilization mechanism of the liquid films composed by the polymer-dilute solution. The conformation of the polymer must be taken into account since the polymers are isolated with each other. We constructed the bridging polymer model for the unstable liquid film and suggested that the entropic elasticity of the bridging polymer destabilize the liquid film.

The above chapters reveal that we should pay attention to a polymer concentration when adding the polymer to stabilize liquid films. If the liquid film has a little of polymer, the polymer may destabilize the film by bridging polymers. In contrast, if the liquid film has too much polymers, the macroscopic foam may become harder and longer life than expected though the film becomes stable by gels. This is an elastic structure rather than liquid foams such as styrene foams. We should promote a better understanding of a gelation to form the stable liquid foam.

Appendix A

Disjoining pressure between two charged walls



Figure A.1: Schematic picture of the distribution of the counterions. The surfactants and the counterions are charged minus and plus, respectively.

We introduce a simple case of the liquid film decorated by surfactants only¹² by treating the air/liquid interface decorated by surfactants as a charged wall. We solve the PoissonBoltzmann equation to obtain the counterions ρ_+ and the electric potential ϕ . They can be treated as uniform parallel to the walls in Figure A.1. The Poisson-Boltzmann equation has a form

$$\nabla^2 \phi = -\frac{e}{\epsilon} \left[\rho_+(z) \right],$$

$$\int_{-L/2}^{L/2} \rho_+(z) dz = 2\sigma.$$
(A.1)

The boundary conditions are considered as follows:

$$\tilde{\phi}(0) = 0, \left. \frac{d\tilde{\phi}(z)}{dz} \right|_{z=0} = 0$$

This is because the symmetry. By using $\rho_+ = n_0 e^{-\beta e\phi}$ where n_0 is the counterions density

 Table A.1: Parameters

σ	Charge density
e	Elementary charge
ρ_+	Counter ion density
ϕ	Potential

at the middle plane, the equation are rewritten as follow:

$$\nabla^2 \tilde{\phi} = -4\pi l_{\rm B} n_0 {\rm e}^{-\tilde{\phi}}, \qquad (-L/2 < z < L/2)$$
 (A.2)

where

$$l_{\rm B} = \frac{e^2}{4\pi\epsilon} \frac{1}{k_{\rm B}T} = \frac{e^2\beta}{4\pi\epsilon},$$

$$\tilde{\phi}(z) = \beta e\phi(z).$$
(A.3)

By multiplying both side of the Equation (A.2) by $\nabla \tilde{\phi}$, we obtain the following equation:

$$\frac{d}{dz} \left\{ \frac{1}{2} \left(\frac{d\tilde{\phi}(z)}{dz} \right)^2 \right\} = 4\pi l_{\rm B} n_0 \frac{d}{dz} \mathrm{e}^{-\tilde{\phi}} \tag{A.4}$$

Integrated with respect to z, the equation has a form

$$\left(\frac{d\tilde{\phi}(z)}{dz}\right)^2 = 8\pi l_{\rm B} n_0 \mathrm{e}^{-\tilde{\phi}} + C_0. \quad (C_0 = \mathrm{const.}) \tag{A.5}$$

Due to the boundary condition at z = 0, the integral constant has a form

$$0 = 8\pi l_{\rm B} n_0 + C_0$$
$$\Rightarrow \underline{C_0} = -8\pi l_{\rm B} n_0.$$

Therefore,

$$\frac{d\tilde{\phi}(z)}{dz} = \pm \sqrt{8\pi l_{\rm B} n_0} \sqrt{e^{-\tilde{\phi}} - 1}$$

$$\Rightarrow \frac{d\tilde{\phi}}{\sqrt{e^{-\tilde{\phi}} - 1}} = \pm \sqrt{8\pi l_{\rm B} n_0} dz.$$
(A.6)

Integrated both sides of this equation, the electric potential has a form

$$\tilde{\phi}(z) = \ln\{\cos^2(\sqrt{2\pi l_{\rm B} n_0} z)\}\tag{A.7}$$

The electric potential is an even function of z and has the maximum value at z = 0. Owing to $\rho_+ = n_0 e^{-\beta e\phi}$, the counterion density is written as follow:

$$\rho_+(z) = \frac{n_0}{\cos^2(\kappa z)}, \quad \kappa = \sqrt{2\pi l_B n_0} \tag{A.8}$$

Due to the conservation of the counterions, n_0 has a form

$$2\sigma = \int_{-L/2}^{L/2} \rho_{+}(z) dz = \int_{-L/2}^{L/2} \frac{n_{0}}{\cos^{2}(\kappa z)} dz$$

$$= \frac{n_{0}}{\kappa} 2 \tan(\kappa L/2)$$

$$\Rightarrow \sigma = \sqrt{\frac{n_{0}}{2\pi l_{B}}} \tan(\kappa L/2)$$

$$\Rightarrow 2\pi l_{B}\sigma = \kappa \tan(\kappa L/2), \qquad n_{0} = \frac{\kappa \sigma}{\tan(\kappa L/2)}.$$

(A.9)

Multiplying L to both sides, we find the following relation:

$$\pi l_B \sigma L = \kappa L/2 \tan(\kappa L/2) \tag{A.10}$$

Focusing on $\tan(\kappa L/2)$, we obtain n_0 as a function of L for the cases in which the distance between two walls is far or close.

(i) $\pi l_B \sigma L \gg 1$; two walls are far.

$$\kappa L/2 \simeq \frac{\pi}{2}$$

$$\Rightarrow \sqrt{2\pi l_B n_0} L = \pi$$

$$\Rightarrow n_0 = \frac{\pi}{2l_B L^2} \sim \frac{1}{L^2}.$$
(A.11)

Therefore, n_0 is proportional to inverse of L^2 .

(ii) $\pi l_B \sigma L \ll 1$; two walls are close.

Due to $\kappa L/2 \ll 1$, $\tan(\kappa L/2) \simeq \kappa L/2$. Therefore,

$$n_0 \simeq \frac{2\sigma}{L}.\tag{A.12}$$

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Furthermore, owing to $\kappa z \ll 1$, $\cos(\kappa z) \simeq 1$. Thus,

$$\rho_+(z) \simeq n_0 \simeq \frac{2\sigma}{L}.\tag{A.13}$$

 n_0 is proportional to inverse of Lm and then the density is coanstant.

Disjoining pressure

The disjoining pressure is described as follow:

$$\Pi_{\rm d} = -\left(\frac{\partial\gamma}{\partial L}\right) \tag{A.14}$$

where γ is the free energy density per unit area. The free energy density is composed of the entropy of the counterions and the electrostatic energy. So, γ has a form

$$\gamma = k_{\rm B}T \int_{-L/2}^{L/2} \rho_{+}(\ln \rho_{+} - 1)dz + \frac{\epsilon}{2} \int_{-L/2}^{L/2} (\nabla \phi)^{2} dz$$

$$= -2\sigma k_{\rm B}T + k_{\rm B}T \int_{-L/2}^{L/2} \rho_{+} \ln \rho_{+} dz + \frac{\epsilon}{2} \int_{-L/2}^{L/2} (\nabla \phi)^{2} dz \qquad (A.15)$$

$$= 2\sigma k_{\rm B}T (\ln n_{0} - 1) - \frac{\epsilon}{2} \int_{-L/2}^{L/2} (\nabla \phi)^{2} dz,$$

rearranged by the Poisson-Boltzmann equation. We calculate the second term. Owing to the Equation (A.7), the z-derivative of the electric potential has a form

$$\frac{d\tilde{\phi}}{dz} = -2\kappa \tan(\kappa z). \tag{A.16}$$

Therefore, the electrostatic energy has a form

$$\int_{-L/2}^{L/2} \left(\frac{d\tilde{\phi}}{dz}\right)^2 dz = 4\kappa^2 \int_{-L/2}^{L/2} \tan^2(\kappa z) dz$$

$$= 4\kappa^2 \left(\frac{2\tan(\kappa L/2)}{\kappa} - L\right)$$

$$= 4\kappa^2 L \left(\frac{2\tan(\kappa L/2)}{\kappa L} - 1\right).$$
(A.17)

Next, we calculate the first term of the free energy density (A.15). According to the Equations (A.11) and (A.12), the term depends on L.

(i) $\pi l_B \sigma L \gg 1$

By using the following equations:

$$n_0 = \frac{\pi}{2l_B L^2}, \quad \kappa L \simeq \pi, \quad \kappa = \sqrt{2\pi l_B n_0} = \frac{\pi}{L}, \quad l_{\rm B} = \frac{e^2}{4\pi\epsilon} \frac{1}{k_{\rm B}T} = \frac{e^2\beta}{4\pi\epsilon},$$

we obtain the free energy density as follows:

$$\gamma = 2\sigma k_{\rm B} T (\ln n_0 - 1) - \frac{2\pi\epsilon\kappa}{(\beta e)^2} \left(\frac{2\sigma}{n_0 L} - 1\right)$$

$$= 2\sigma k_{\rm B} T (\ln \frac{\pi}{2l_B L^2} - 1) - \frac{2\pi\epsilon\kappa}{(\beta e)^2} \left(\frac{\sigma 2l_B L^2}{\pi L} - 1\right)$$

$$= 2\sigma k_{\rm B} T (\ln \frac{\pi}{2l_B L^2} - 1) - \frac{2\pi^2\epsilon}{L(\beta e)^2} \left(\frac{\sigma 2l_B L}{\pi} - 1\right)$$

$$= \frac{2\sigma}{\beta} (\ln \frac{\pi^2\epsilon}{2L^2 e^2\beta} - 1) - \frac{2\pi^2\epsilon}{L(\beta e)^2} \left(\frac{\sigma 2L e^2\beta}{\pi^2\epsilon} - 1\right)$$

$$= \left(\frac{\pi}{\beta e}\right)^2 \frac{2\epsilon}{L} - \frac{4\sigma}{\beta} \ln L + \frac{2\sigma}{\beta} \left\{ \ln\left(\left(\frac{\pi}{\beta e}\right)^2 \frac{\epsilon\beta}{2}\right) - 2 \right\}.$$
(A.18)

Thus,

$$\gamma(L) = \left(\frac{\pi}{\beta e}\right)^2 \frac{2\epsilon}{L} - \frac{4\sigma}{\beta} \ln L + \text{const.}$$
(A.19)

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According to the Equation (A.14), the disjoining pressure has a form

$$\Pi_{0} = -\left(\frac{\partial\gamma}{\partial L}\right) = -\left(-\left(\frac{\pi}{\beta e}\right)^{2}\frac{2\epsilon}{L^{2}} - \frac{4\sigma}{\beta}\frac{1}{L}\right)$$

$$= \left(\frac{\pi}{\beta e}\right)^{2}\frac{2\epsilon}{L^{2}} + \frac{4\sigma}{L}k_{\mathrm{B}}T.$$
(A.20)

This means that the sum of the Maxwell stress and the osmotic pressure of the counterions.

(ii) $\pi l_B \sigma L \ll 1$

By using the following equations:

$$n_0 \simeq \frac{2\sigma}{L}, \quad l_{\rm B} = \frac{e^2}{4\pi\epsilon} \frac{1}{k_{\rm B}T} = \frac{e^2\beta}{4\pi\epsilon}$$

we obtain the free energy density as follows:

$$\gamma = 2\sigma k_{\rm B} T (\ln n_0 - 1) - \frac{2\pi\epsilon\kappa}{(\beta e)^2} \left(\frac{2\sigma}{n_0 L} - 1\right)$$

$$= 2\sigma k_{\rm B} T (\ln \frac{2\sigma}{L} - 1) - \frac{2\pi\epsilon\kappa}{(\beta e)^2} \left(1 - 1\right)$$
(A.21)

Therefore,

$$\gamma(L) = -\frac{2\sigma}{\beta} \ln L + \text{const.}$$
(A.22)

Performing the same treatment, we obtain the disjoining pressure:

$$\Pi_{0} = -\left(-\frac{2\sigma}{\beta}\frac{1}{L}\right)$$

$$= \frac{2\sigma}{L}k_{\rm B}T.$$
(A.23)

All the above, we get the disjoining pressure for two cases in which the distance between two walls is long or short.
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