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Analytical Models of Single Bubbles and Foams



Trinity College Dublin

Coláiste na Tríonóide, Baile Átha Cliath

The University of Dublin

Robert P. Murtagh

School of Physics

Trinity College Dublin

The University of Dublin

A thesis submitted for the degree of

Doctor of Philosophy

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Thesis 11240

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Summary

We investigate the use of analytic models of three-dimensional bubbles with deformable surfaces to study the energy of foams in equilibrium. While the idea of modelling the surfaces of bubbles as deformable minimal surfaces in three-dimensions has been explored before, this work has been limited to the mathematically exact case of a bubble with just two contacts, an unrealistic case for real three dimensional bulk foams. Here we demonstrate that by geometrically decomposing a bubble into a collection of Z circular cones with the same total volume as the original bubble, we can successfully extend this approach to estimate the energy of a bubble in a foam with any number of neighbouring bubbles over the entire range of liquid fraction. We model the interaction between bubbles as they come into contact as a constant volume deformation. The results of this approximate geometrical model are found to agree, both qualitatively and quantitatively, with the results of Surface Evolver simulations.

We show that deforming a bubble leads to an increase in the total surface area, and hence surface energy, which depends on the number of neighbours Z . Utilising the analytical nature of our model, we derive asymptotic expressions for the variation of this excess energy with deformation and liquid fraction close to the wet limit. These findings highlight the fact that the bubble-bubble interaction in three-dimensions has a logarithmic functional form which plays a dominant role very close to the wet limit. This clearly demonstrates that simply extending the Durian bubble model of harmonically interacting overlapping disks to overlapping spheres gives qualitatively incorrect results in three dimensions. Given the popularity of harmonic interaction potentials in physics, we investigate the possibility that the interaction is roughly harmonic further away from the wet limit. While we find that the variation of energy with deformation is described with a power law exponent higher than 2 for any number of contacts, we argue that for low Z , there is an intermediate range of deformations for which a harmonic potential could be used.

We build further on this minimal surface approach, extending the cone model to incorporate unequal contacts in order to model the Kelvin cell with its eight nearest neighbour bubbles and six next nearest neighbours. This requires careful incorporation of additional structural information about the solid angles of the faces and the relative distances to the different contacts, but leads us to a very accurate evaluation of the excess energy of a wet Kelvin foam over the entire range of liquid fraction. We demonstrate that structural transitions caused by the loss of contacts away from the wet limit are distinct from those at the wet limit. This illustrates that the bubble-bubble interaction is more complex than first thought and further work will be necessary in the future to fully grasp its nature.

We consider also the temporal evolution of a single bubble at a liquid surface whose shape is described by the mathematics of minimal surfaces and changes dramatically according to the size of the bubble relative to the capillary length. We demonstrate that knowing the composition of the gas is crucial to predicting how the bubble will evolve. We show that while a bubble containing nitrogen or air shrinks in time in line with what we would expect, adding a small amount of a low solubility gas, such as perfluorohexane, to the bubble leads to the opposite behaviour; the bubble is found to grow in time. For large bubbles at a liquid surface, whose shape closely resembles a hemisphere, we show that the growth of a bubble in this case obeys a power law with an exponent of a quarter. Low solubility gases are often used in experimental foam studies to inhibit coarsening and our work highlights that care must be taken when using these gases as their inclusion may significantly alter the evolution of the foam.

List of Publications

1. S. Hutzler, R. P. Murtagh, D. Whyte, S. T. Tobin and D. Weaire. *Z-cone model for the energy of an ordered foam*. *Soft Matter*, 10, 7103-7108 (2014).
2. D. Whyte, R. P. Murtagh, D. Weaire and S. Hutzler. Applications and extensions of the *Z-cone model for the energy of a foam*. *Colloids and Surfaces A*, 473, 55-59 (2015).
3. R. P. Murtagh, D. Whyte, D. Weaire and S. Hutzler. Adaptation of the *Z-cone model to the estimation of the energy of a bcc foam*. (Accepted for publication in *Philosophical Magazine Letters*)
4. R. P. Murtagh, A. J. Meagher, D. Weaire and S. Hutzler. Evolution of a bubble on a liquid surface containing one or two gas species. (In preparation)

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Dedicated to the memory of

Dr. Mary Redmond-Ussher

Chapter 1

General Introduction

1.1 Introduction

Although usually going unnoticed, foams are an indispensable part of modern society. The student of foams cannot help but be reminded of the impacts of the physics of foam on the world today. From the industrial process of mineral flotation [1], in which foam is used to separate valuable minerals such as copper and lead from their native ores by harnessing a difference in hydrophobicities (or affinity for water), to more routine shaving foam and the head of a cappuccino.

Despite there being a presumed knowledge of what is and is not a foam, given the wide range of observed physical properties and different applications, it then becomes necessary to clarify; “what exactly is a foam?”

A liquid foam is a two-phase system in which gas bubbles are dispersed in a continuous liquid phase [2, 3]. The gas phase is often present in large quantities leading to the common understanding of a foam as a collection of gas bubbles separated by continuous liquid films. Foams often exhibit similar physical properties to emulsions, which are made up of a continuous liquid phase with a liquid dispersed phase [4–7].

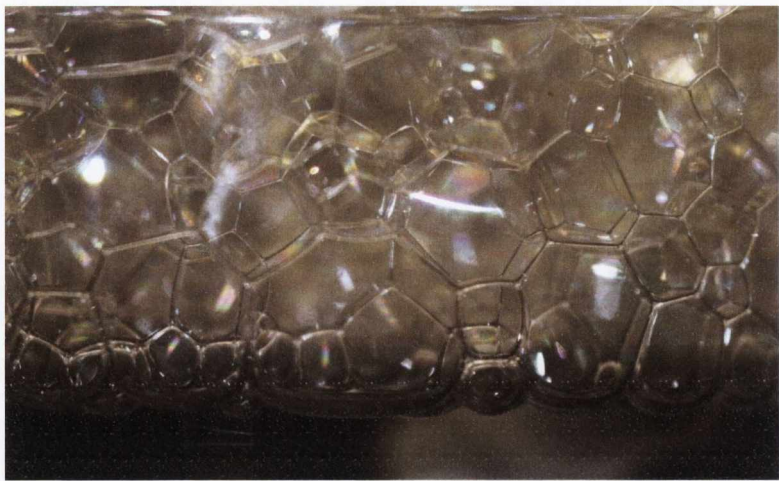
The **liquid fraction** ϕ of a foam (hereafter “foam” will be used to refer to emulsions as well as liquid foams for simplicity) is defined as the ratio of the volume of the continuous liquid phase to the total volume of the foam [2]. A foam with a very high liquid fraction ϕ is naturally referred to as a “**wet**” foam while a foam with a very low liquid fraction ϕ is referred to as a “**dry**” foam. Examples of wet and dry foams are shown in Figure 1.1.

However, most foams that we encounter have a liquid fraction somewhere between these two extremes and it is not altogether clear, theoretically, what liquid fraction demarcates a “wet” foam from a “dry” foam. As shown in Figure 1.1, a dry foam is characterised by **polyhedral** bubbles which arrange in such a way as to satisfy Plateau’s rules (see Section 1.2) while wet foam bubbles are rounded, tending to resemble a packing of spheres for high liquid fractions. In practical terms, a liquid fraction of between 15% and 18% is often taken as the boundary between wet and dry foams; a liquid fraction in this range is roughly halfway between 0% liquid fraction, which denotes the so-called **dry limit**, and 36% liquid fraction, which is called the **wet limit** or **jamming transition** above which the bubbles become separated and no longer constitute a foam [8, 9]. We will discuss the nature of the jamming transition further in Section 1.3. This distinction is not important for the arguments presented in this thesis as we will focus mostly on very wet foams.

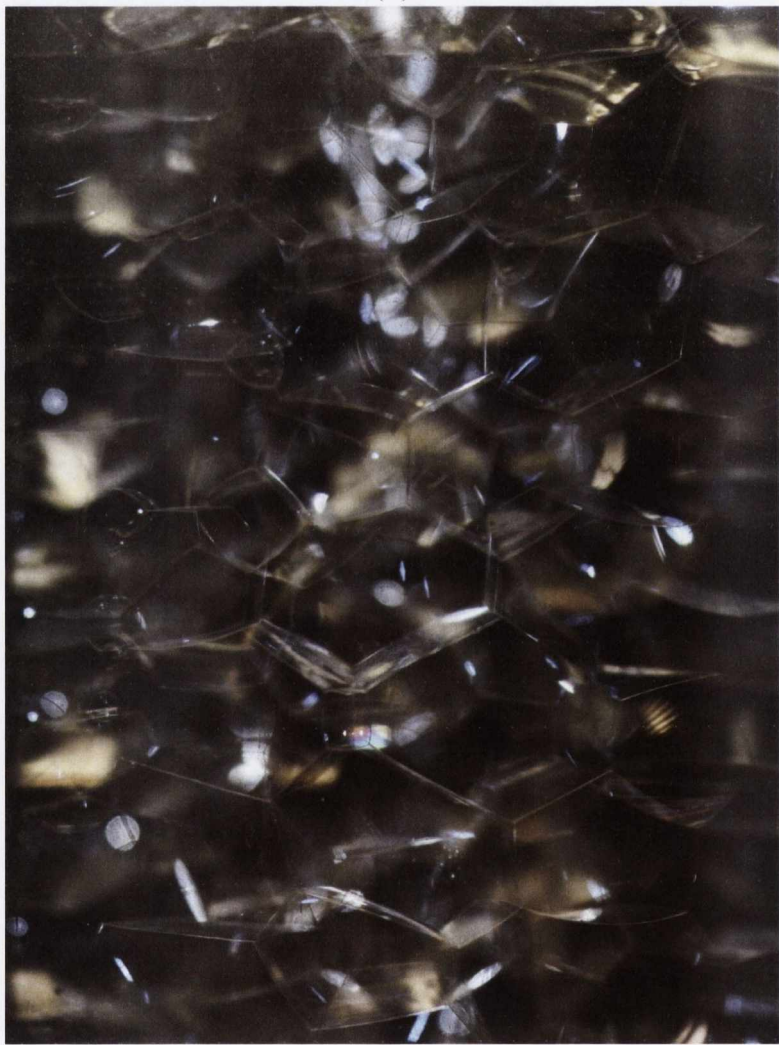
However, merely specifying a single factor of a foam, such as an average liquid fraction, is not sufficient to fully describe a foam. For example, while the average liquid fraction helps to generally identify whether a foam is wet or dry, the local liquid fraction will be higher close to the liquid pool and much lower at the top of the foam as liquid drains under gravity, as we can clearly see from Figure 1.1. Drainage of the liquid over time gives rise to a height profile for the liquid fraction which is not captured by the average liquid fraction (see Section 1.5).

The study of foams is usually split into four areas.

1. **Structure** is concerned with the geometry of soap bubbles that have been packed together, usually in the bulk of a foam.



(A)



(B)

FIGURE 1.1: Experimental images of foam with different liquid fractions ϕ . (a) Bubbles in contact with a liquid pool are visibly rounded due to their high liquid fraction. (b) In a dry foam the bubbles take on polyhedral shapes separated by thin liquid films.

2. **Drainage** relates to the motion of liquid through the channels within a foam, due to the force of gravity.
3. **Coarsening** refers to the diffusion of gas between bubbles within a foam, with the general consequence that large bubbles get larger and small bubbles get smaller.
4. **Rheology** is the study of the deformation and flow of foam in response to an applied stress.

For the most part, we will concern ourselves with foam structure, although we will discuss coarsening in Chapter 6.

1.2 Plateau's Rules for Dry Foams

The structure of foams in both the wet and dry limits is a very active area of research. In the limit of a “dry” foam (i.e as $\phi \rightarrow 0$) the bubbles become deformed (see Figure 1.1(b)). The very small amount of liquid left in the foam is distributed between the soap films which separate the polyhedra.

The first description of the equilibrium structure of a dry foam was given by Joseph Plateau in his 1873 book “Statique Expérimentale et Théorique des Liquides soumis aux seules Forces Moléculaires” [10] and it contains a set of empirical laws (known as Plateau's Rules) which are obeyed by the thin (liquid) films separating the bubbles in a dry foam. Namely,

1. Thin films can only meet three at a time forming a **Plateau border**. The angle between the films must be $\frac{2\pi}{3}$ radians.
2. No more than four Plateau borders may meet at a vertex. The angle between the Plateau borders at this vertex is the regular tetrahedral angle of $\arccos(-1/3)$ radians ($\approx 109.47^\circ$). This condition also limits the number of films meeting at a vertex to six.

3. Each thin film must have a constant mean curvature related to the Laplace pressure difference ΔP across the thin film, according to the Young-Laplace law [2, 3],

$$\Delta P = \frac{2\sigma}{R_c} \quad (1.1)$$

where σ is the surface tension and R_c is the mean radius of curvature of the film, which is constant. The Laplace pressure for a bubble (two films), rather than a single film, is simply $4\sigma/R_0$ where R_0 is the bubble radius.

Despite being known for over a hundred years, the theoretical proof of Plateau's laws was only provided in 1976 by Jean Taylor [11].

With increasing liquid fraction of the foam (above $\sim 2\%$ [2]), the Plateau borders and vertices swell, forming a liquid network in the foam for which Plateau's law no longer strictly apply.

1.3 The Wet Limit

The bubbles in a foam with a very high liquid fraction are no longer polyhedral, being better described as “more or less” spherical and the structure of such a foam can be thought of as a dense packing of spheres. The wet limit is defined as the point at which the bubbles are spheres and have only point contacts with each of their neighbouring bubbles. In Section 1.1, we referred to this as the wet limit or the jamming transition.

The liquid fraction at which this occurs is called the “**critical liquid fraction**” ϕ_c and is approximately 0.36 in three dimensions for a random-close-packing (RCP) of spheres [8]. At RCP, the interaction between neighbouring bubbles is strong enough to give stability and rigidity to the collection of bubbles forming a foam, while for higher liquid fractions the bubbles separate from each other to form a bubbly liquid.

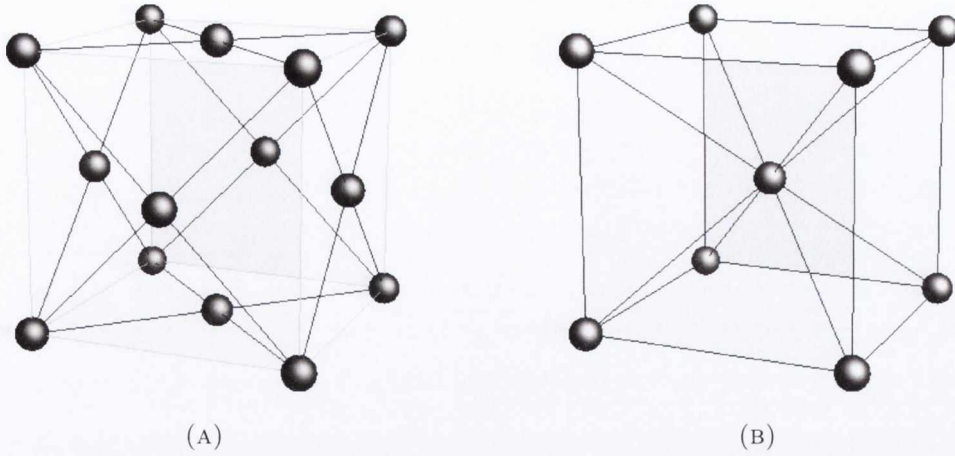


FIGURE 1.2: (a) The face-centred cubic (fcc) and (b) body-centred cubic (bcc) lattices. The critical liquid fraction associated with these structures are $\phi_c = 0.26$ and $\phi_c \approx 0.32$, respectively. Both of these structures are of relevance in monodisperse foam studies [12] and will be discussed later in this thesis with regard to the cone model (see Chapters 2, 4 and 5).

It should be noted that the value ϕ_c is different if the bubble positions are not random but are ordered, for example as a crystal lattice. For the fcc crystal lattice, shown in Figure 1.2(a), $\phi_c = 0.26$ while for the bcc crystal shown in Figure 1.2(b) $\phi_c = 1 - \frac{\sqrt{3}\pi}{8} \approx 0.32$. The fascinating subject of ordered foam structures will be discussed in greater detail in Chapter 2 in the context of the Z -cone model.

1.4 Monodisperse Foam Structures

When discussing ordering in foams, an important parameter to consider is the bubble size. For much of this work, the most convenient measure of bubble size is the **equivalent sphere radius** which we denote by R_0 . It is defined by

$$R_0 = \sqrt[3]{\frac{3V}{4\pi}}. \quad (1.2)$$

While disordered structures may be formed by foams with a wide size distribution or **polydispersity** [2], many of the most interesting **ordered** structures arise in monodisperse foams, in which all of the bubbles have the same radius R_0 [12]. Two

such monodisperse structures, the Kelvin and Weaire-Phelan structures [13, 14], are shown in Figure 1.3.

From an experimental standpoint, monodisperse foams can be made relatively easily using a flow-focussing device [15, 16] and may also be made to crystallise into well-defined ordered structures over time [17].

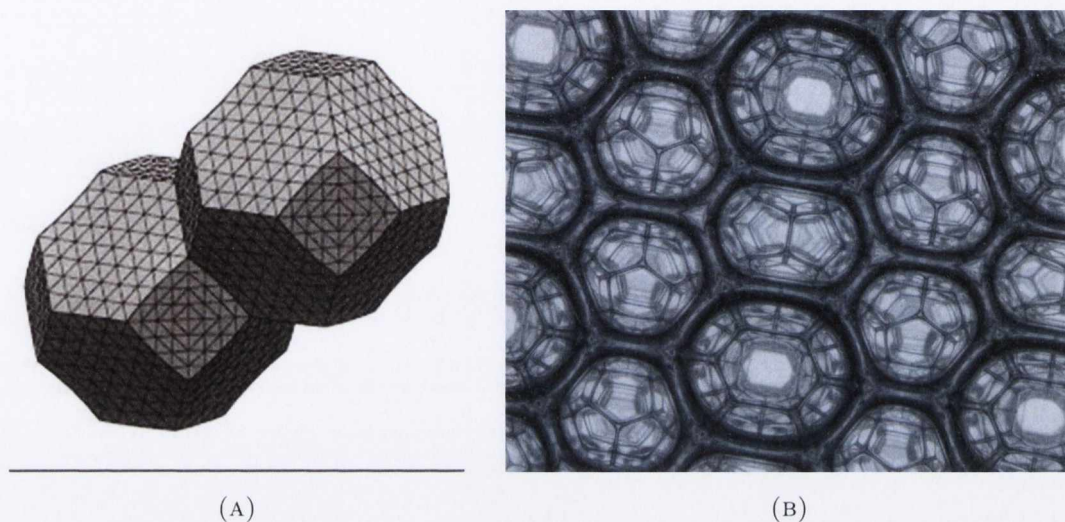


FIGURE 1.3: (a) The double bubble unit cell of Kelvin's tetrakaidecahedron with curved faces, generated using the Surface Evolver [18]. (b) Experimental image of the Weaire-Phelan structure courtesy of A. Meagher [14].

Theoretically, monodisperse foam is an often-used system in the study of packing. In fact, both experimental and theoretical approaches involving monodisperse foams have been instrumental in attempts to answer a famous question in the study of packings: which unit cell, infinitely repeated, partitions space into cells of equal volume such that a minimal amount of surface area separates the cells?

Kelvin, in his treatise “On the Division of Space with Minimal Partition Area” of 1887 [19], demonstrated using a combination of soap films on wire frames (a common representation of a bubble in a monodisperse dry foam) and simple mathematical arguments that a non-orthic truncated octahedron (or “Kelvin tetrakaidecahedron”), shown in Figure 1.3 (a), had a lower surface area to volume ratio than any of the Archimedean solids and many other common crystal structures. Surprisingly, Kelvin never evaluated the energy of his proposed structure and, indeed, this was not done until 100 years later [20]. The Kelvin tetrakaidecahedron has

been observed experimentally in real monodisperse foams on a number of occasions since 2000 [12, 21, 22]. In 1994, a unit cell structure with an even lower surface area to volume ratio by approximately 0.3% was discovered using a numerical approach by Denis Weaire and Robert Phelan [23]. The Weaire-Phelan structure was first observed experimentally in monodisperse foam by Meagher *et al.* in 2012 [14].

1.5 Osmotic Pressure

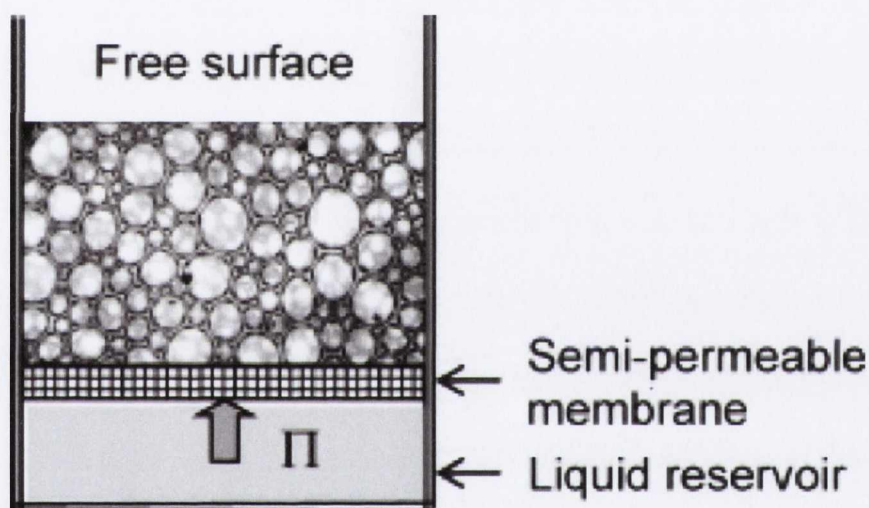


FIGURE 1.4: A schematic diagram illustrating the concept of osmotic pressure. The application of an osmotic pressure Π forces liquid out of the foam, causing the bubbles to come into closer contact, deforming their shape. This image is taken from Höhler *et al.* [12].

Thus far, our discussion has been concerned with equilibrium foam structures in the wet and dry limits. However, it is interesting to consider what happens as we transition from one limit to the other. Say, from the wet to the dry limit, corresponding to the extraction of liquid from the foam. As liquid leaves the foam, the bubbles become deformed, increasing their surface area, and hence surface energy. For a foam in equilibrium, there must be a force present to counter this increase in surface energy. This force manifests itself in the form of the **osmotic pressure**.

The osmotic pressure of a foam Π can be thought of as the force per unit area on a semi-permeable membrane placed at the interface of the foam and a liquid pool which does not allow the gas to pass through it (see Figure 1.4). As liquid passes through the membrane, the ratio of liquid to gas (i.e. the average liquid fraction ϕ) decreases and the bubbles in the foam are forced into closer contact, deforming them.

The osmotic pressure Π is formally defined by

$$\Pi = -\sigma \left(\frac{\partial S}{\partial V} \right)_{V_g = \text{const.}}, \quad (1.3)$$

where S is the total surface area of the bubbles, given by the sum of the individual bubble surface areas A_i , within a confined volume V and σ is the surface tension [24]. Note that this expression assumes that the gaseous phase is incompressible due to the need to keep the total gas volume V_g constant when taking this derivative. The limiting values of the osmotic pressure in the wet and dry limits are

$$\Pi \rightarrow 0 \quad \text{for} \quad \phi \rightarrow \phi_c, \quad (1.4)$$

and

$$\Pi \rightarrow \infty \quad \text{for} \quad \phi \rightarrow 0, \quad (1.5)$$

respectively.

The osmotic pressure is a **global** property of a foam in the sense that it depends on the total area S of the foam sample and the average liquid fraction ϕ . In an idealised crystalline foam in which each of the bubbles has the same volume (and hence equivalent sphere radius R_0), and their local packing arrangements are identical, the **local** osmotic pressure will be identical to the overall osmotic pressure for the whole foam.

From dimensional analysis, it is possible to show that the osmotic pressure scales as the surface tension σ divided by the bubble radius R_0 [5, 12]. Thus, it is common to consider instead the **reduced osmotic pressure** $\tilde{\Pi} = \frac{\Pi}{\left(\frac{\sigma}{R_0}\right)}$ [12]. As we noted in Section 1.1, in real foams the liquid fraction varies as a function of the height above the bottom of the foam $\tilde{x}$ (see Section 3.3), also known as the **reduced height**.

We can relate the change in reduced osmotic pressure $\tilde{\Pi}$ to the local liquid fraction $\phi(\tilde{x})$ at a height $\tilde{x}$ above the bottom of the foam, where it is in contact with a liquid pool [12],

$$d\tilde{\Pi} = (1 - \phi(\tilde{x}))d\tilde{x}. \quad (1.6)$$

Expressing the differentials in equation (1.6) as partial derivatives, we obtain a differential equation for the local liquid fraction profile,

$$\frac{\partial\phi(\tilde{x})}{\partial\tilde{x}} = \frac{1 - \phi(\tilde{x})}{\frac{\partial\tilde{\Pi}}{\partial\phi}} \quad (1.7)$$

where $\phi(0) = \phi_c$, the critical liquid fraction. We will consider this equation in our discussion of the Z -cone model in Chapter 3.

1.6 Surface Energy and Minimisation

The surface energy E of a bubble in a foam is directly proportional to its surface area A such that

$$E = \sigma A \quad (1.8)$$

with the constant of proportionality σ being the surface tension.

The Kelvin and Weaire-Phelan structures are sophisticated examples of a general principle which determines the structure of a foam: in equilibrium, a foam will

relax to the state of lowest surface energy to volume ratio for the given confinement conditions. The simplest and most elegant example of this principle is for a free soap bubble in air, which assumes a spherical shape [2].

In our work we are primarily concerned with the lowest surface energy configuration of a bubble confined within the bulk of an ordered monodisperse foam. In equilibrium, such a bubble has Z **discrete regions of contact** or **faces** with neighbouring bubbles. In idealised descriptions of dry foams these correspond to infinitesimally thin films covering the entire bubble surface [25] while at random close pack, the contact areas go to zero and the structure consists of spherical bubbles with point contacts.

As discussed in Section 1.5, traversing from the wet to the dry limit is achieved through the application of an osmotic pressure [2, 12, 26] leading the bubble to undergo a **constant volume deformation**.

This type of deformation is accompanied by an increase in surface energy, consistent with equation (1.8). A convenient quantity to compute is the **dimensionless (relative) excess surface energy** ε of a bubble,

$$\varepsilon \equiv \frac{E - E_0}{E_0} \quad (1.9)$$

where $E_0 = 4\pi\sigma R_0^2$ is the surface energy of an undeformed spherical bubble of the same volume with radius R_0 and E is the bubble surface energy defined in equation (1.8).

Similarly, the degree of deformation may be conveniently quantified via the **dimensionless deformation** ξ , defined as

$$\xi = \frac{R_0 - h}{R_0} \quad (1.10)$$

where h is the distance between the bubble centre and a bubble face. The dimensionless deformation ξ is related to the liquid fraction ϕ via the expression $\phi = 1 - \frac{1-\phi_c}{(\xi-1)^3}$, where ϕ_c is the critical liquid fraction [27].

We must stress here that the deformation ξ , as we have defined it in equation (1.10), is valid for both monodisperse and polydisperse systems. With the deformation being measured to the middle of the contact, it is the pressure difference between the bubbles which is the key factor here. While the Weaire-Phelan structure (see Figure 1.3(b) in Section 1.4) is a famous example of a monodisperse foam where the individual bubbles have different pressures [14, 23], it is more common for differing internal pressures to arise in polydisperse foam. In the case of equal pressures, the pressure difference across the contact is zero and the deformation is the same for each bubble. This is not true when the bubbles are of different volumes; the Laplace pressure (see Section 1.2), $P = 4\sigma/R_0$, scales with the inverse of the bubble radius R_0 and so the smaller of the two bubbles will have a higher Laplace pressure. The presence of a finite Laplace pressure across the contact leads to a curved contact. Thus, R_0 and h are different for the larger and smaller bubbles meaning that the deformation ξ calculated using equation (1.10) will be different. We will discuss this in Chapter 7.

Nonetheless for any given foam structure, the dependence of the dimensionless excess surface energy ε on the dimensionless deformation ξ may be numerically calculated using the Surface Evolver [18] (see Appendix F for details on the Surface Evolver). However, the numerical approach fails to provide us with the in depth physical description necessary to better understand foams. For example, while the bubble-bubble interaction in two dimensions is well-described by a harmonic force, this is not a good description in three dimensions, as we will see, meaning that we cannot reduce this interaction to the sort of simple spring model which pervades many fields of physics.

For this reason, recent research has focused on various simple models which attempt to reproduce the key features of the exact numerical results and will be the focus of the next chapters.

1.7 Review of Previous Theoretical Studies of the Bubble-Bubble Interaction

In this section, we will discuss some important models of the bubble-bubble interaction which directly motivate the Z -cone model that we will introduce in Chapter 2. The key feature of all of these models is that they are designed to describe a wet foam consisting of nearly spherical (or circular in 2D) bubbles. Thus, they are qualitatively distinct from models of polyhedral dry foams for which adherence to Plateau's laws (see Section 1.2) is a fundamental requirement [25].

In keeping with the tendency of physicists to study two-dimensional systems for simplicity, before exploring the more complicated three-dimensional systems, we will start our overview by looking at some key insights garnered in two dimensions.

1.7.1 Soft Disk Model and Lacasse in 2D

The so-called “soft” disk model (also known as the bubble model) refers to a simple **dynamic** model for interacting bubbles which was introduced first by Durian [28], and further developed by Langlois *et al.*, for the purposes of studying the flow behaviour of foams in two dimensions [29].

In this model, the bubbles in a wet foams are represented by a collection of disks. Below the critical liquid fraction ϕ_c , the disks interact by overlapping, illustrated in Figure 1.5 for bubbles of radii R_i, R_j , giving rise to the understanding of these disks as “soft”. Each of the overlapping disks experiences two forces due to the overlap; a simple elastic repulsion and a viscous dissipation force. It is interesting to note that this bears some similarity to dissipative particle dynamics (DPD) [30, 31], a molecular dynamics simulation technique for dynamic and rheological properties of complex fluids. Similarly to the Durian model, the particles in DPD are subjected to a conservative force between particle centres and a dissipative force. However, a key difference is that DPD includes a random force in the simulation which serves to effectively thermalise the system.

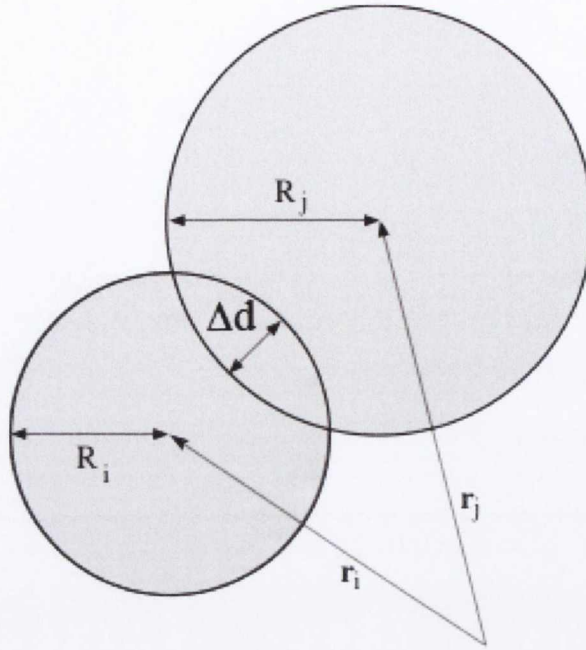


FIGURE 1.5: The force of interaction between neighbouring bubbles i and j in the soft disk model is taken to be repulsive harmonic with a spring constant proportional to the overlap Δd . This figure is reproduced from Langlois *et al.* [29].

The viscous dissipation term is an important component of this soft disk model because it contains all of the information about the liquid phase of the foam, which is not explicitly modelled. The viscous dissipation term is usually represented as a linear viscous drag,

$$F_{\text{vis}} = -c_{\text{vis}}\Delta\mathbf{v}, \quad (1.11)$$

which is directly proportional to the vector difference in bubble velocities $\Delta\mathbf{v} = (\mathbf{v}_i - \mathbf{v}_j)$. In this case, c_{vis} is a dissipation constant whose value can be varied to simulate either strongly or weakly dissipating liquid phases [32]. This is intimately linked to the **viscosity** of the liquid that plays a crucial role in the study of foam rheology [33, 34]. However, in the context of this thesis, we will not concern ourselves with this interesting topic.

However, we are primarily interested in the repulsion force which acts pairwise between bubbles. It is this force which is responsible for the forming of contacts

between bubbles as it acts along a line connecting the centres of adjacent bubbles. In the soft disk model, the repulsion force F_{SD} is considered to be an elastic spring repulsion which whose magnitude is given by

$$F_{\text{SD}} = \tilde{k} \frac{2R_{\text{av}}}{R_i + R_j} \Delta d. \quad (1.12)$$

Here, $\tilde{k}$ is a spring constant, R_{av} is the average radius of all the disks in the foam and Δd is the geometric overlap of the disks. Clearly, the term $\frac{2R_{\text{av}}}{R_i + R_j}$ becomes unity for monodisperse foams and only plays a role for polydisperse foams. This term represents the fact that deformation is dependent on polydispersity, as we noted in Section 1.6. The higher Laplace pressure of smaller bubbles means that they are harder to deform, corresponding to a stiffer spring force compared to larger bubbles.

Since we are interested in the variation of excess energy ε with the deformation ξ defined for foams rather than overlapping disks, it is useful to recast equation (1.12), which is a force, as a corresponding elastic potential. The natural analogue in this sense is

$$\varepsilon(\xi) = \tilde{k}\xi^2. \quad (1.13)$$

This model is widely implemented in numerical studies of large-scale sheared foam systems for both linear (single channel) and Couette (rotating ring) geometries [35–37]. An example of a linear geometry is shown in Figure 1.6. An important reason for this popularity is the simplicity of the force expressions and the corresponding relative efficiency with which these forces can be programmed and balanced for large numbers of bubbles.

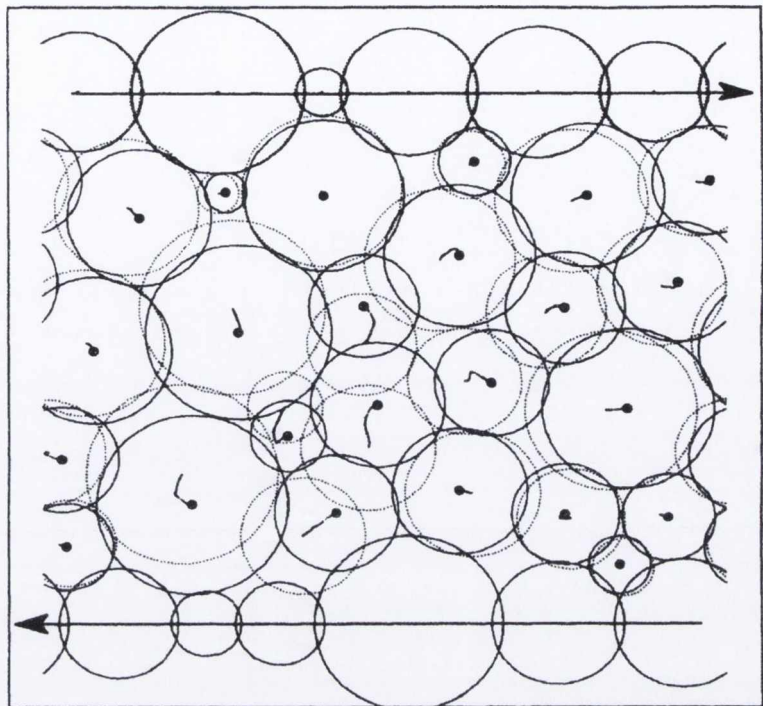


FIGURE 1.6: Durian’s overlapping “soft disk” model in a linear geometry. The row of bubbles at the top and bottom are fixed, acting as a rough boundary wall. Flow is induced in the system by moving the boundaries, known as **shearing**, as indicated by the arrows. The black points mark the centres of the disks while the black lines track the movement of the bubble centres over time. This image is reproduced from Durian [28].

While there have been numerous successes of the soft disk model in describing and predicting the bulk properties of flowing foams, it is based on the assumption of a harmonic interaction between bubbles in two-dimensions. How valid is this assumption given that this heuristic formulation of bubbles in terms of overlapping disks is far from an accurate picture of real two-dimensional foams?

The assumption of harmonicity was tested by Lacasse *et al.* [27] who performed Surface Evolver simulations (see Appendix F) of a single circular bubble confined and deformed by a number of contacts. This differs fundamentally from the soft disk model in the fact that the surface of the bubble is allowed to deform in order to find the lowest energy ε_{2D} , defined as

$$\varepsilon_{2D}(\xi) = \frac{\Lambda(\xi)}{2\pi R_0} - 1. \tag{1.14}$$

In two dimensions the excess energy is in terms not of the area but the perimeter length Λ . They also performed similar simulations in three-dimensions which we will describe in Section 1.7.3.

The results of these simulations are shown in Figure 1.7 for two, three and four contacts. The inset shows the power law scaling of these curves which indicate a power law exponent in all cases of two, at least for small deformations. This demonstrates that a harmonic potential of the form of equation (1.13) is a good description of the bubble-bubble interaction, validating its use in the soft disk model.

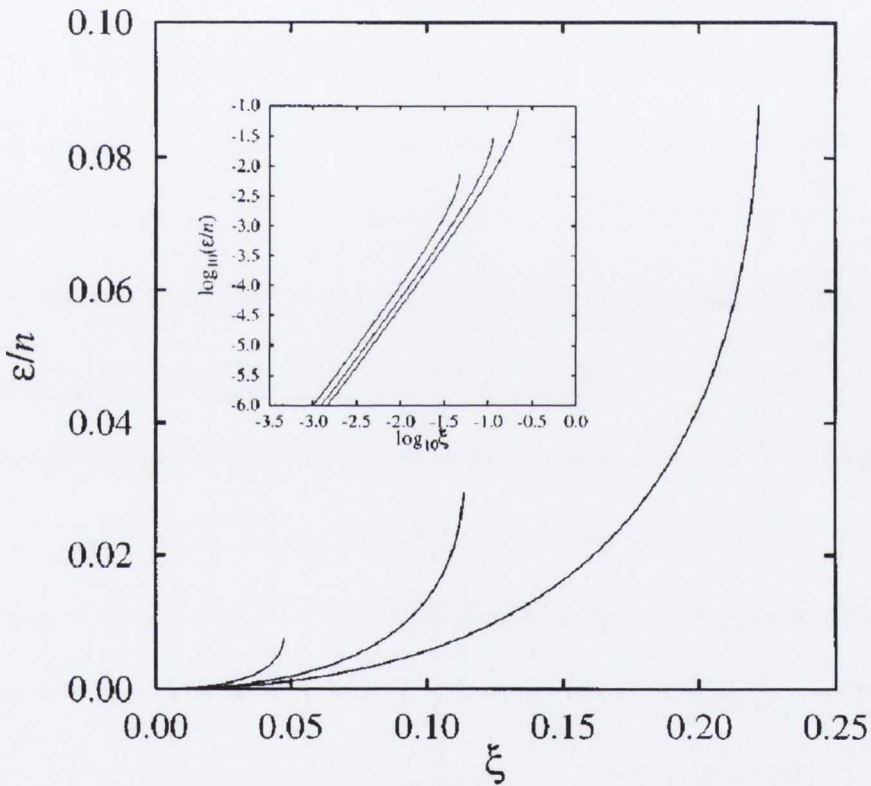


FIGURE 1.7: Variation of the excess energy ε per contact (here specified by n) as a function of deformation ξ . The curves (from right to left) are for contacts numbers $n = 2$, $n = 3$ and $n = 4$. A harmonic interaction is a good description in this case of small deformations ξ , as evidenced by the inset which shows a power law scaling with an exponent close to 2 initially. The definition of ξ in 2D is analogous to that for 3D defined in Section 1.6. This figure is reproduced from Lacasse *et al.* [27]

1.7.2 Morse and Witten

Our discussion of contacting bubbles up to this point has been confined to two dimensions where a harmonic interaction between bubbles is a good approximation for small deformations. In three dimensions, the situation is more complex and this will be reflected in the nature of the models used to describe three-dimensional bubbles under confinement. In particular, these models will introduce the concept of “softness” not through overlaps but by considering deformable surfaces via Euler-Lagrange minimisation methods [38](see Appendix A for details).

Morse and Witten [39] were the first to address the problem of the asymptotic form of the dimensionless excess surface energy ε (see Section 1.6) of a single droplet pressed against a flat surface by a dimensionless gravitational force F in a mathematical way. In equilibrium, a droplet behaves identically to a bubble (see Section 1.1) and so the findings of Morse and Witten are relevant for bubbles and we will use the term bubble to avoid confusion in this section.

A bubble pressed against a flat surface by gravity experiences an equal and opposite dimensionless force F , directed towards its geometric centre, which is distributed as a pressure over a small, circular contact of radius δ . In this case, force balance requires that $F = \pi\delta^2\Pi_i$ where Π_i is the internal pressure of the bubble. In the case of simple crystal structures and monodisperse foam, the contact area between two contacting bubbles is flat, thus we expect a similar asymptotic form for ε to that found in this case.

In the limit of $\frac{\delta}{R_0} \ll 1$, the deformation outside the contact region is well approximated by the solution for a point force of magnitude F which permits the use of a solution using Green’s functions. In this way, Morse and Witten found the dimensionless excess surface energy ε to be related to the dimensionless force F by the singular form,

$$\varepsilon_{MW}(\xi) = F(\xi)^2 \ln(F(\xi)). \quad (1.15)$$

This equation represents the first strong evidence for the important role played by logarithmic terms in the interaction potential between bubbles in three dimensions. Note that in equation (1.15), we have stated that F is a function of ξ directly. The analytic form of this dependence will be discussed when we come to explain the Z -cone model in Section 2.2.

So far we have only discussed the case of a bubble pressed against a flat wall by its own weight, which is an idealised system rarely encountered in practical experiments. We can extend our considerations to the case of a bubble simultaneously compressed against any number of confining walls.

1.7.3 Bubbles in a Confined Geometry

Lacasse *et al.* [27] further developed the idea of modelling bubbles not as “soft” spheres, but as truly deformable surfaces, continuing the work begun by Morse and Witten [39]. They chose to study the dimensionless excess surface energy ε of a monodisperse foam, whose bubbles are arranged in a series of crystal structures, having different contact numbers Z .

For the case $Z = 2$ only, Lacasse *et al.* adduced a complete analytic solution to the problem of determining the surface shape and all related quantities, including ε , which confirmed the presence of a logarithmic term in the bubble-bubble interaction similar to that predicted by Morse and Witten [39]. An illustration of the resulting bubble profile in this case is shown in Figure 1.8 for a range of deformations.

For $Z > 2$, these authors set aside the mathematical approach and settled instead on the simulation of confined bubbles with the Surface Evolver [18] (see Appendix F). The numerical procedure for computing the dimensionless excess surface energy of a confined bubble is as follows. A cube of volume V_0 is placed within a Z -faced polyhedron. By then tessellating the surface of the cube with triangles (periodically refining the tessellations) and allowing the vertices of the triangles to move, the Surface Evolver minimises the surface area for the **fixed volume** V_0

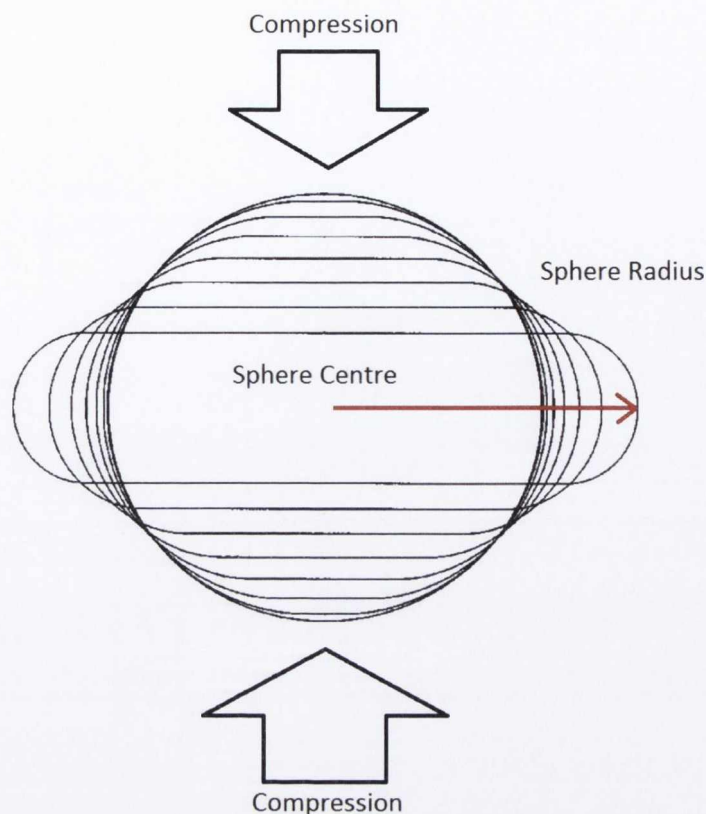


FIGURE 1.8: Numerically constructed cross-section of a bubble compressed between two parallel contacts for a number of different degrees of deformation. The bubble shape changes as a function of deformation due to the constraints of constant mean curvature and constant volume (see equation (1.1)). This figure has been adapted from Lacasse *et al.* [27].

using the conjugate gradient algorithm [40]. In the case of no bounding surfaces, the sphere gives the lowest surface area for such a volume. The deformation is carried out by moving the contacts closer together in a number of steps with the lowest surface area state being calculated at each successive step. The surface area for each deformation step is recorded and the dimensionless excess surface energy ε computed appropriately using equation (1.9). Taking small steps in deformation, the Surface Evolver can in this way provide us with data for the bubble-bubble interaction (see Appendix F) which may then be used to fit prospective interactions, as shown in Figure 1.9, or to test the results of models such as the Z -cone model, introduced in Chapter 2.

Lacasse *et al.* [27] found that the response of ε to dimensionless deformation ξ was stronger than a harmonic repulsive potential of the form assumed by models

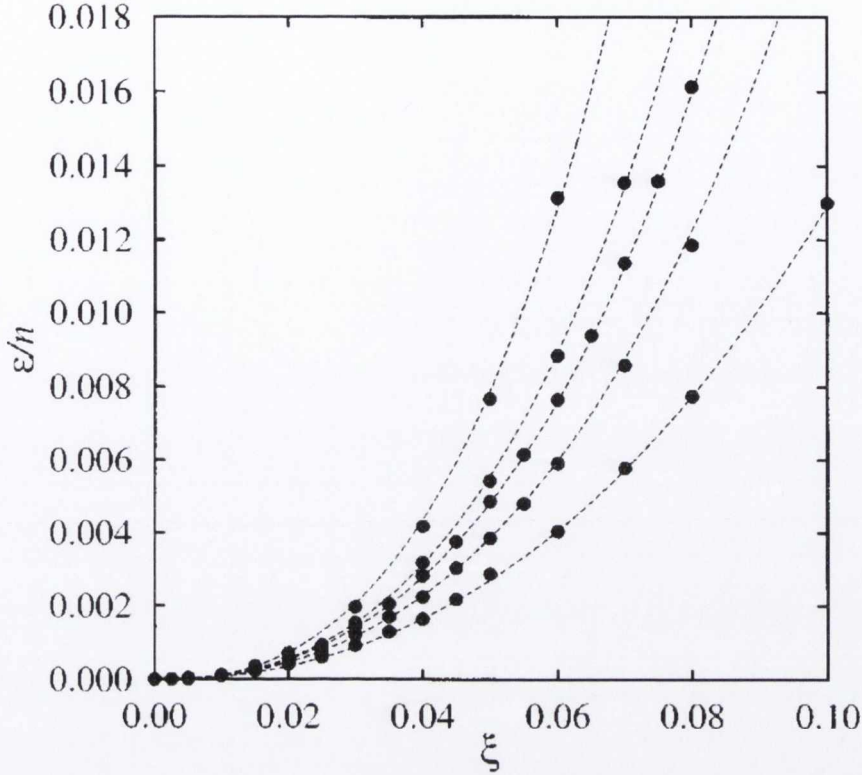


FIGURE 1.9: Variation of excess energy ε with deformation ξ in three dimensions. The curves, from right to left, represent $Z = 2, 4, 6, 8$ and 12 . They are reasonably well fit for intermediate deformations ξ by a function of the form of equation (1.16). This figure is reproduced from Lacasse *et al.* [27].

of overlapping spheres [28]. Indeed, it is clear that while a harmonic response may be approximately applicable over some range of ξ , it can never be correct since the analytic form of ε diverges logarithmically from a harmonic-like response close to the wet limit (i.e. low ξ) as Morse and Witten had previously indicated.

However, Lacasse *et al.* found that a power law of the form

$$\varepsilon_L = Z C_Z \left[\frac{1}{(1 - \xi)^3} - 1 \right]^{\alpha_Z}, \quad (1.16)$$

can be fit reasonably well to the numerical data over the range $\xi \sim 0.02 - 0.1$, with the values of the fit parameters C_Z and α_Z depending on Z . The results of these fits to their simulation data is shown in Figure 1.9.

Of particular importance is that the value of α_Z is greater than 2 for any number of contacts and appears to saturate above $Z = 12$ [27]. This illustrates that the

bubble-bubble potential in three dimensions depends critically on the confinement conditions; that is, the number of contacts of the individual bubbles. It should also be noted that C_Z varies, more strongly than α_Z [27].

However, this power law does not capture the logarithmic form of the dimensionless excess surface energy $\varepsilon(\xi)$ as $\xi \rightarrow 0$ which is present in their Surface Evolver results, and overestimates it above $\xi \approx 0.1$. As such, this power law is at best a qualitative description of the bubble-bubble interaction for intermediate deformations. Incorporating this logarithmic term into a model with multiple contacts Z will be the focus of Chapter 2.

1.8 Structure of the Thesis

This thesis is primarily concerned with mathematical models of the surface energy of bubbles and foams for a variety of structures. In Chapter 2, we will introduce the Z -cone model for the energy of a monodisperse bubble with Z identical nearest neighbours. Following the introduction of this model we will illustrate the usefulness of this model for understanding some key properties of foam in equilibrium in Chapter 3. In Chapter 4, we will model the famous Kelvin cell with the cone model by introducing next-nearest neighbours. In Chapter 5, we will make use of the extended cone model of the Kelvin cell to study the nature of contact loss in foams. Finally, in Chapter 6, a simple model for the evolution behaviour of a single bubble at a liquid surface will be described which takes into account the detailed shape of the bubble via minimal surfaces.

Chapter 2

The Z-Cone Model

As discussed in the preceding chapter, the total energy of a soap film is proportional to its surface area (see equation (1.8)), if we make the assumption that the gas and liquid are treated as incompressible. In the familiar case of a single, isolated bubble made from just one such film, the geometric shape with the lowest surface area is a sphere, while a bubble in the bulk of a foam confined by neighbouring bubbles has, in general, a more complicated geometry which does not correspond to any of the familiar Platonic or Archimedean solids.

The reason for this is the ease with which the surface of a bubble is deformed, due to the lack of static friction and rigidity which is present in solids, and it alters its shape when in contact with other bubbles or the walls of a container. This is true regardless of whether the neighbouring bubbles are randomly arranged, as in a Bernal packing [8], or whether they are ordered in a regular, crystalline fashion.

In this chapter, we shall introduce a mathematical model, namely the Z -cone model, to describe the interaction of a bubble in an ordered monodisperse foam with its neighbours. In particular, the variation of excess surface energy ε with increasing deformation will be of interest for a range of different neighbour numbers Z from two to twelve. We find excellent agreement between the variation of ε obtained from the Z -cone model and the results of simulations performed with the Surface Evolver [2] (see Appendix F for further details on the Surface Evolver).

Finally, we will comment on our results in respect of the interaction between bubbles and present analytic expressions for the variation of the excess surface energy with both deformation and liquid fraction in the wet limit. The work presented in this chapter was originally published in *Soft Matter* in 2014 [41].



FIGURE 2.1: A sphere is the global minimum of the surface area for an enclosed volume in the absence of external constraints.

2.1 Introduction

For more than two decades, Brakke's Surface Evolver [18] (see Appendix F) has provided a practical method for computing the equilibrium structures [23] of dry foam. It achieves this by approximately representing bubbles as finely tessellated surfaces made up of vertices, edges and faces, and repeatedly allowing these to move in order to relax the surface to an area minimum for a given fixed volume.

This approach can also be used to simulate wet foams in the manner outlined in Section 1.7.3, although the process of area minimisation is more difficult than in the case of dry foams. This is because the finite liquid fraction in wet foams

give the bubbles more freedom to move, significantly increasing the occurrence of topological transitions, or neighbour changes [2]. For this reason, simulations of wet foams with the Surface Evolver have tended to focus on ordered foams, as in the simulations of Lacasse *et al.* [27] and Hohler *et al.* [12], which are more effective in completely surrounding the bubbles and suppressing neighbour changes [42].

While the ability to find a lowest energy structure under certain conditions is useful in many applications [23], it is not sufficient to properly explain the physics of these systems, without reference to an underlying physical framework. In effect, the computational approach fails to provide an answer to the more interesting question: why is this structure optimal? While analytical work is often more complicated and time-consuming than the computational approach, it provides more flexibility to test the effects of different physical assumptions, thereby aiding us in understanding why the optimal structure is so.

To address this question in the present case, a natural approach is to seek a simpler physical representation or mathematical model of a bubble confined by neighbouring bubbles. Central to such a model is a description of how bubbles interact with one another. For instance, how valid is the assumption of pairwise additive potentials, as in the Durian model for example [2, 28]? What is the form of interaction (i.e. the change in surface area) between two bubbles which barely touch each other?

As we will see in the following section, attaining an accurate form for the interaction (i.e the change in surface area) between bubbles which barely touch each other is not a simple task. It will be shown to depend crucially on both the dimensionality of the system and the number of contacts.

2.2 *Z*-Cone Model

The *Z*-Cone Model is an analytical model describing the approximate equilibrium **shape**, and hence the surface area, of a bubble in the bulk of a foam, which is in contact with Z neighbouring bubbles.

It is a model, of the type of Morse and Witten and Lacasse, which treats the bubble surfaces as deformable, minimal surfaces for a fixed bubble volume V . Indeed, for one and two contacts, our *Z*-cone model reduces to the models of Morse and Witten and Lacasse, respectively (see Section 1.7). Thus, one can think of our model as the natural extension of the minimal surface approach to any number of contacts Z in three dimensions, for example the face-centred cubic structure ($Z = 12$) shown in Figure 2.2.

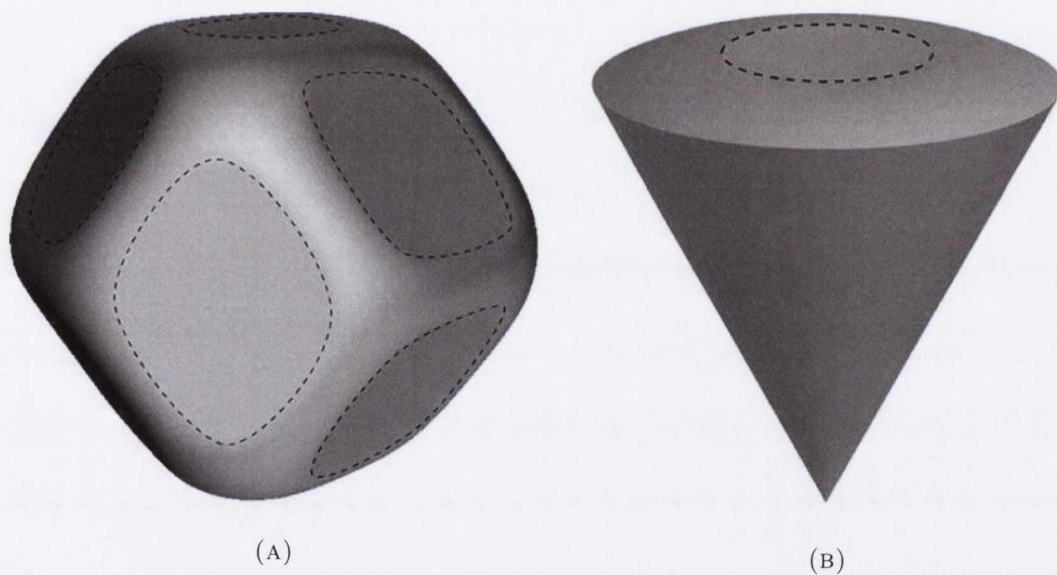


FIGURE 2.2: The shape of a bubble in a crystalline foam with Z equivalent neighbours, shown in (a) for $Z = 12$, may be approximated by an assembly of Z cones of the type shown in (b). Its flattened surface corresponds to a bubble-bubble contact.

Our ultimate goal is to provide an analytical expression for the excess energy ε in terms of important foam parameters, such as the liquid fraction ϕ .

2.2.1 Theory

Our essential geometrical approximation is inspired by the early work of Ziman on describing the Fermi-surface of copper [43]. The bubble volume V can be divided into Z equivalent sections, each of which is to be represented approximately by a circular cone (of volume $V_c = \frac{V}{Z}$), as shown in Figure 2.3. The advantage of this approximation is that it allows us to represent the bubble surface (referred to as the cap) mathematically as a surface of revolution.

The bubble surface consists of a flat disk of area $\pi\delta^2$ (the contact area of neighbouring bubbles) and an outer part which has a constant total curvature, terminating at right angles to the cone surface. The flat disk and the outer part join smoothly; there is no curvature discontinuity at the boundary.

As the liquid fraction ϕ is reduced, the contact area grows, and the separation of bubble centres s is reduced according to:

$$s = 2(h + h_c) = 2R_0(1 - \xi) \quad (2.1)$$

where h and h_c are defined as the heights of the cap and cone, respectively (see Figure 2.3). R_0 is radius of a spherical sector of volume V_c and ξ is a dimensionless deformation parameter (see Section 1.6). In the undeformed case, the radius R_0 is identical to the equivalent sphere radius defined in Section 1.4.

Our aim is to compute the dimensionless excess energy ε , defined as

$$\varepsilon(\xi) = \frac{A(\xi)}{A_0} - 1, \quad (2.2)$$

where $A(\xi)$ is the surface area of one of the cone caps, and $A_0 = 2\pi R_0^2(1 - \cos\theta)$ is the curved surface area of the undeformed cap, i.e. for $\xi = 0$.

For given ξ and solid angle Ω , we can calculate the surface area A of one of these cones and its total volume V_c analytically, as outlined below and detailed in

Appendix A. Note that because each of the cones are identical the 4π steradian solid angle of the bubble is divided equally between each contact such that

$$\theta = \arccos \left(1 - \frac{2}{Z} \right). \quad (2.3)$$

The total surface area, per contact Z , of our bubble can be written as

$$A = A_\delta + 2\pi \int_0^h r(z) \sqrt{1 + \left(\frac{dr(z)}{dz} \right)^2} dz, \quad (2.4)$$

where A_δ is the surface area of the contact and $r(z)$ is the distance from a point on curved surface to the central axis of the cone (see Figure 2.3). The second term in equation (2.4) is the general expression for the surface area (of revolution) of any curve given by $r(z)$.

The volume under this curve is given by

$$V = \pi \int_0^h r(z)^2 dz + \frac{\pi r(0)^3 \cot \theta}{3}. \quad (2.5)$$

Utilising the Euler-Lagrange formalism [38] in a similar way to Lacasse *et al.* [27], we can determine the minimum surface area A under the constraint of constant volume (for details of the method see Appendix A).

To do this, we require boundary conditions on the curvature of the surface at two points; where the curved surface meets the flat contact and where it meets the cone.

$$\left. \frac{dr(z)}{dz} \right|_{z=h} = \infty \quad (2.6)$$

$$\left. \frac{dr(z)}{dz} \right|_{z=0} = \cot \theta. \quad (2.7)$$

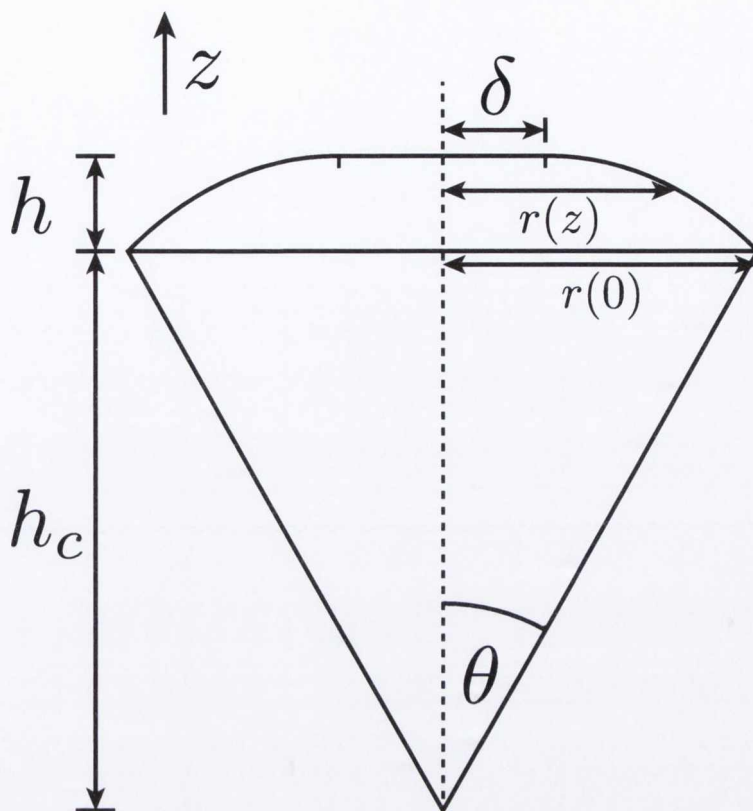


FIGURE 2.3: Two-dimensional cross-section of a cone with relevant notation. During bubble deformation, total bubble volume V and total solid angle must be conserved, according to $V = ZV_c$ and $4\pi = Z\Omega$, where $V_c = \frac{2}{3}\pi R_0^3(1 - \cos\theta)$ is the volume of a cone with opening angle $\theta = \arccos(1 - \frac{2}{Z})$, R_0 is the radius of the spherical sector (corresponding to an undeformed cone) and Ω is the solid angle of the cone.

The first of these ensures that the bubble surface meets the flat contact smoothly which models a zero contact angle where the cone is terminated by a flat disk, corresponding to a contact with a neighbouring bubble. The second ensures that the bubble surface meets the cone at a right angle.

Since the model of a bubble we present is purely geometric in nature and does not depend upon the length scale chosen (i.e. it is the same for micron and millimetre sized bubbles), it is convenient to work in dimensionless variables. In particular, we define the dimensionless length ρ_δ as

$$\rho_\delta = \frac{\delta}{r(0)}. \quad (2.8)$$

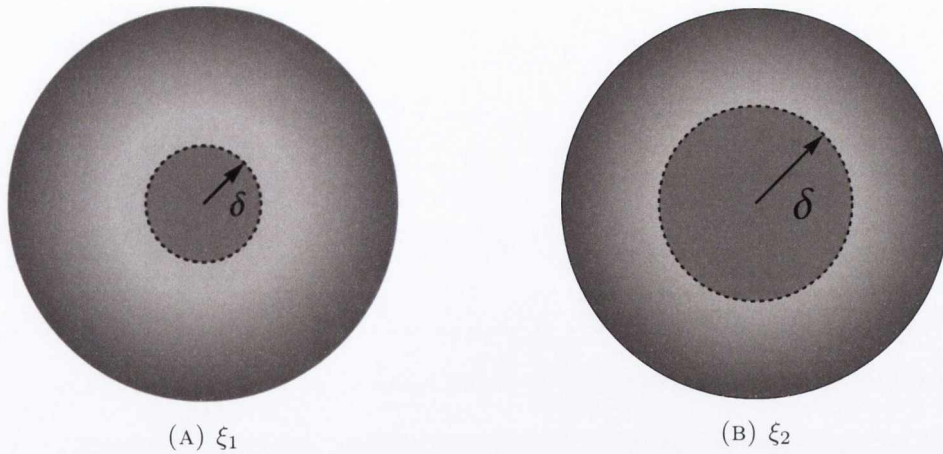


FIGURE 2.4: Top down view of a bubble-bubble contact. In the Z -cone model, the contact is always a circle; the radius δ of the contact grows as the deformation ξ increases, $\xi_1 < \xi_2$.

In these units, ρ_δ provides a dimensionless measure of the radius of the contact δ which varies from $\rho_\delta = 0$, in the wet limit to $\rho_\delta = 1$ in the dry limit, when the flat contacts cover the entire bubble surface.

A somewhat lengthy derivation, given in Appendix A, results in the following exact expression for the energy ε

$$\varepsilon(\rho_\delta, Z) = \frac{\rho_\delta^2 + \frac{Z}{\sqrt{Z-1}}(1 - \rho_\delta^2)K(\rho_\delta, Z)}{Z^{-\frac{1}{3}} \left(\frac{Z-2}{\sqrt{Z-1}} + 6J(\rho_\delta, Z) \right)^{\frac{2}{3}}} - 1. \quad (2.9)$$

The deformation is $\xi(\rho_\delta, Z)$ is expressed as

$$\xi(\rho_\delta, Z) = 1 - \left[\frac{\frac{4}{Z}}{\frac{Z-2}{2\sqrt{Z-1}} + 3J(\rho_\delta, Z)} \right]^{1/3} \left(\frac{Z-2}{2\sqrt{Z-1}} + I(\rho_\delta, Z) \right). \quad (2.10)$$

The functions $I(\rho_\delta, Z)$, $J(\rho_\delta, Z)$ and $K(\rho_\delta, Z)$ are definite elliptic integrals given, respectively, by

$$I(\rho_\delta, Z) = \int_{\rho_\delta}^1 (x^2 - \rho_\delta^2) f(x, \rho_\delta, Z) dx, \quad (2.11)$$

$$J(\rho_\delta, Z) = \int_{\rho_\delta}^1 x^2(x^2 - \rho_\delta^2) f(x, \rho_\delta, Z) dx, \quad (2.12)$$

and

$$K(\rho_\delta, Z) = \int_{\rho_\delta}^1 x^2 f(x, \rho_\delta, Z) dx, \quad (2.13)$$

with

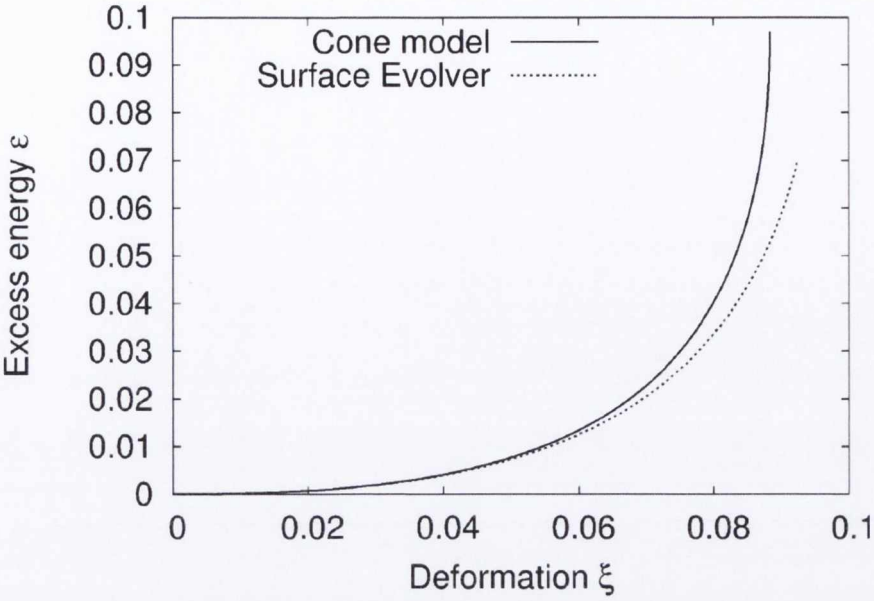
$$f(x, \rho_\delta, Z) = \left[\frac{Z^2}{4(Z-1)} x^2 (1 - \rho_\delta^2)^2 - (x^2 - \rho_\delta^2)^2 \right]^{-\frac{1}{2}}. \quad (2.14)$$

Now we have all that we need to compare with numerical results which will be the purpose of the rest of this chapter.

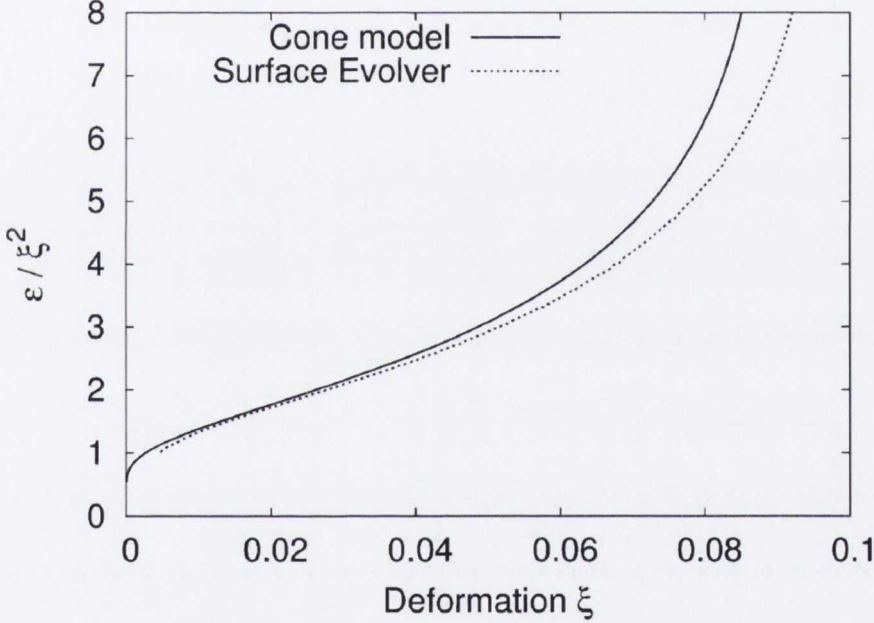
2.2.2 Dependence of Energy on Deformation and Liquid Fraction

In this section, we focus on the comparison of the cone model with Surface Evolver simulations of the face-centred cubic (fcc) structure which is observed experimentally in wet foams [12]. Our model is directly applicable in this case since each bubble has $Z = 12$ equivalent neighbours. In the dry limit, a bubble approaches a rhombic dodecahedron. We will also show the results of Surface Evolver simulations for a pentagonal dodecahedron, for which the cone model gives even better agreement.

For the face-centred cubic structure (fcc) with $Z = 12$ the analytic solution is shown in Figure 2.5(a), together with Surface Evolver calculations (see Appendix F for details), which confirm its accuracy. This shows that for $Z = 12$ the dependence on ξ is not quadratic, as stated by Lacasse *et al.* (from Surface Evolver calculations). However, for smaller values of Z and over a limited range of ξ , a quadratic



(A)



(B)

FIGURE 2.5: (a) Variation of the excess energy ε , and (b) variation in $\frac{\varepsilon}{\xi^2}$, with deformation ξ . The solid line corresponds to the Z-cone model for $Z = 12$ while the dotted line corresponds to Surface Evolver calculations for the fcc structure shown in Figure 2.2(a). Due to numerical noise near the wet limit, we were not able to produce reliable Surface Evolver data for $\xi \lesssim 0.005$. In the case of (b), a quadratic interaction potential would result in a horizontal line. Thus, the dependence of ε on ξ may be approximated by a quadratic only over a very limited range of ξ .

approximation could be made with a prefactor which is roughly proportional to Z .

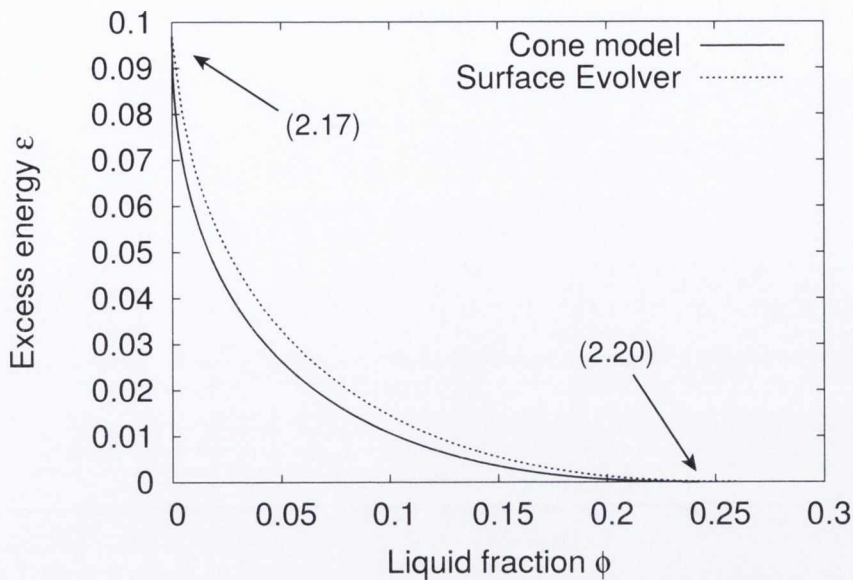


FIGURE 2.6: Variation of excess energy with liquid fraction: cone model prediction ($Z = 12$) and Surface Evolver calculation for fcc. The equations describing the wet and dry limit are marked by arrows.

That is, the contribution of each cone, which may be considered as an interaction potential with one neighbour, is approximately proportional to Z . We will return to this topic more fully in Chapter 3.

By dividing the excess energy, $\varepsilon(\xi)$ by a quadratic term we can examine more closely the true form of the interaction, particularly close to the wet limit. In Figure 2.5(b), we see deviations from a quadratic form at both small and large ξ , corresponding to the limits of a wet and dry foam. We will therefore examine the asymptotic limits, turning our attention for the moment to the variation of excess energy ε with liquid fraction ϕ , as shown in Figure 2.6.

The liquid fraction ϕ lies between 0, the dry limit, and a value ϕ_c at which the deformation vanishes (the wet limit). Liquid fraction may be expressed in terms of ξ by

$$\xi = 1 - \left(\frac{1 - \phi_c}{1 - \phi} \right)^{\frac{1}{3}}. \quad (2.15)$$

Note that derivations of this equation and the key results from the cone model, outlined in the rest of this chapter, are included in Appendix B.

For the cone model, we can show that

$$\phi_c = \frac{3 - \frac{4}{Z}}{Z - 1}. \quad (2.16)$$

In the dry limit, $\phi \rightarrow 0$, our cone model data is well described by

$$\varepsilon(\phi) = e_0 - e_1 \phi^{\frac{1}{2}} \quad (2.17)$$

which is the same form found for the Surface Evolver results, where it corresponds to the decoration of film intersections with Plateau borders of finite cross-section [2]. The values for the constants e_0 and e_1 are close to the true coefficients for the given crystal structure, they vary as

$$e_0 = \left[\frac{Z(Z-1)}{(Z-2)^2} \right]^{\frac{1}{3}} - 1 \quad (2.18)$$

and

$$e_1 \propto \frac{1}{Z} \quad (2.19)$$

respectively.

In the wet limit, $\phi \rightarrow \phi_c$, the energy varies with the liquid fraction as

$$\varepsilon(\phi) \simeq -\frac{Z}{18(1-\phi_c)^2} \frac{(\phi_c - \phi)^2}{\ln(\phi_c - \phi)}, \quad (2.20)$$

see the discussion in Section 2.2.3.

Figure 2.8(a) shows that in the case of a regular pentagonal dodecahedron, the cone model gives an even better prediction for $\varepsilon(\xi)$ than for the fcc arrangement.

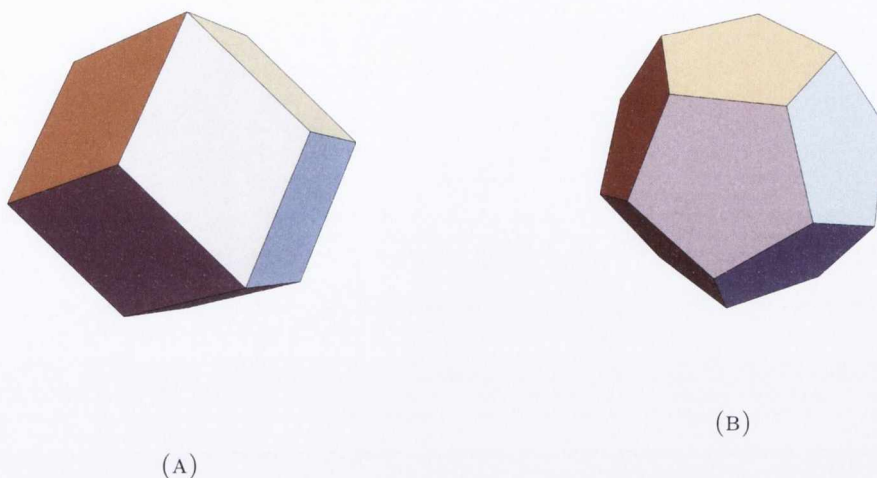


FIGURE 2.7: Voronoi cells for the (a) fcc and (b) pentagonal dodecahedral crystal structures. The pentagonal faces of the pentagonal dodecahedron are more similar in shape to the circular contacts of the *Z*-cone model than the diamond-shaped faces of the fcc.

The reason for this is the symmetry of the faces, which can be seen in Figure 2.7, particularly for larger deformations. The basic assumption about the bubble surfaces in the cone model is that they are rotationally symmetric; this means that the contact areas themselves are always circular. Thus, we can expect a better agreement between the cone model and the regular pentagonal dodecahedron compared to the diamond-shaped faces of the fcc structure, despite both these structures having the same number of contacts.

To further demonstrate the applicability of the cone model, in Figure 2.8(b) we show the case of $Z = 6$; a bubble confined in a cube.

2.2.3 Asymptotic Form of the Energy-Deformation Relation

Now turning to the variation of energy with deformation, we note that the wet limit is very subtle. As we saw in Sections 1.7.2 and 1.7.3, Morse and Witten [39] and Lacasse *et al.* [27] have derived an asymptotic form for small deformation for the dependence of excess energy ε on force F , proportional to $F^2 \ln(F^{-1})$.

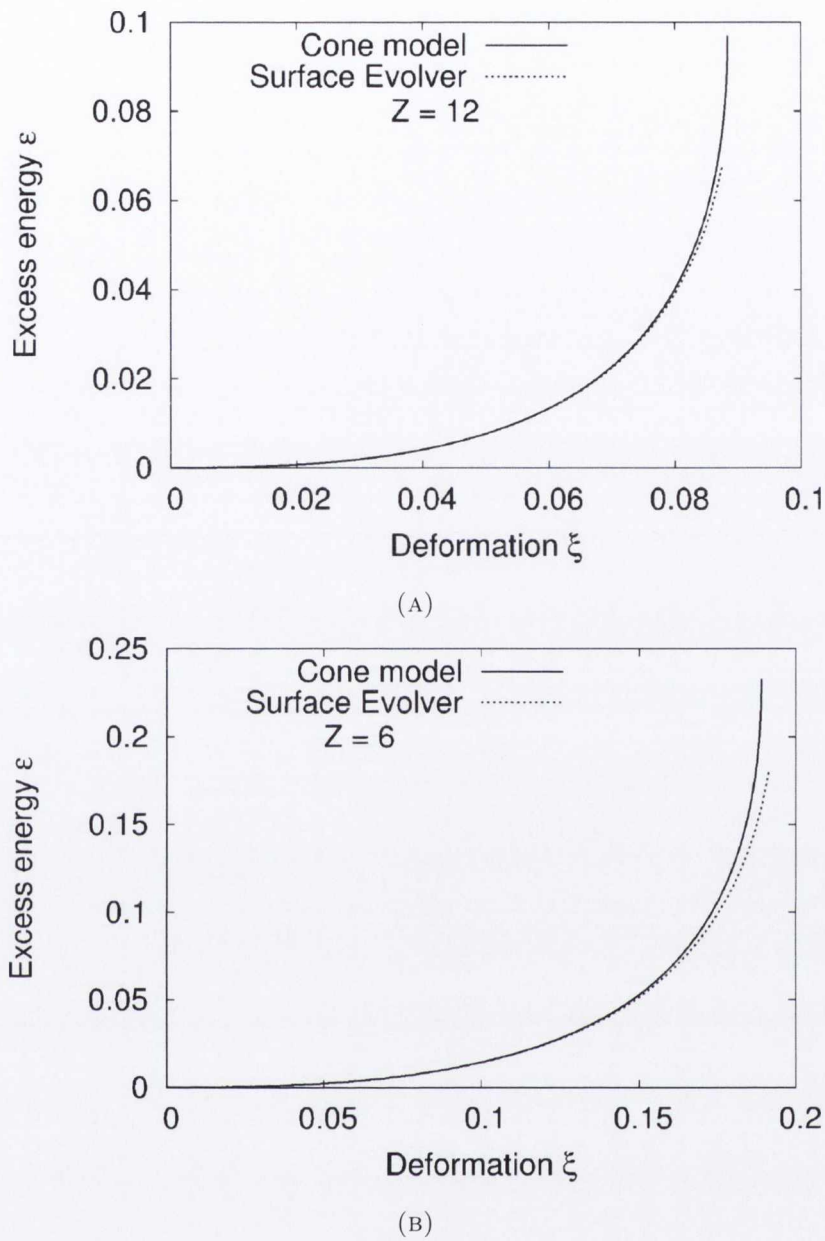


FIGURE 2.8: Comparison of cone model predictions for $\varepsilon(\xi)$ with Surface Evolver simulations for Platonic solids. (a) $Z = 12$: a pentagonal dodecahedron, and (b) $Z = 6$: a cube. We see good agreement, due to the underlying symmetry of these shapes.

This was derived for the special cases of a droplet pressed against a flat surface [39] and a drop compressed by two parallel plates (corresponding to $Z = 2$ in our Z-Cone model) [27]. For present purposes it is more convenient to consider the energy-deformation relation, which takes the corresponding asymptotic form

$$\varepsilon = mF^2 \ln(F^{-1}) \Rightarrow \varepsilon = \frac{\xi^2}{4m \ln \xi}, \quad (2.21)$$

where m is a constant. It was derived by assuming ε of the form $\varepsilon(\xi) \propto \frac{\xi^2}{\ln \xi}$.

This result has not been previously stated: its validity may be checked by differentiating equation (2.21), writing $\frac{d\varepsilon}{d\xi} = F$, and keeping the lowest order terms. The curves calculated for $\varepsilon(\xi)$ using analytic functions, such as that of Figure 2.5, show a variation close to $\xi = 0$ that is consistent with the above form.

Expansion of the elliptic integrals (see Figure 2.9) involved in the limit $\xi \rightarrow 0$ reveals a logarithmic singularity of the form

$$\varepsilon = -\frac{Z\xi^2}{2\ln \xi}, \quad (2.22)$$

which is true for any value of Z .

Expressing ξ in terms of ϕ and Taylor expanding to lowest order (via ρ_δ) leads to the energy variation $\varepsilon(\phi)$ as stated above in equation (2.20). The evaluation of the elliptic integrals $I(\rho_\delta, Z)$, $J(\rho_\delta, Z)$ and $K(\rho_\delta, Z)$ and their Taylor expansions in ρ_δ are shown in Figure 2.9.

An asymptotic expression that covers a larger range of deformation may be obtained by expressing energy ε in terms of ρ_δ , resulting in

$$\varepsilon(\rho_\delta, Z) = m_1 \rho_\delta^4 (m_2 - \ln \rho_\delta), \quad (2.23)$$

with $m_1(Z) = \frac{4}{Z} \left(1 - \frac{1}{Z}\right)^2$ and $m_2(Z) = \frac{1}{4} \left(\frac{1}{1-\frac{1}{Z}} - 3\right) - \ln \left(1 - \frac{1}{Z}\right)$. Combining equation (2.23) with equation (2.10) for the deformation parameter ξ leads to the parametric plot shown in Figure 2.10 which describes the analytical result very well for values up to about $\xi \simeq 0.005$.

The anomalous asymptotic form for the interaction of bubbles, as they come into contact at the critical liquid fraction ϕ_c (equation (2.20)) appears to be general,

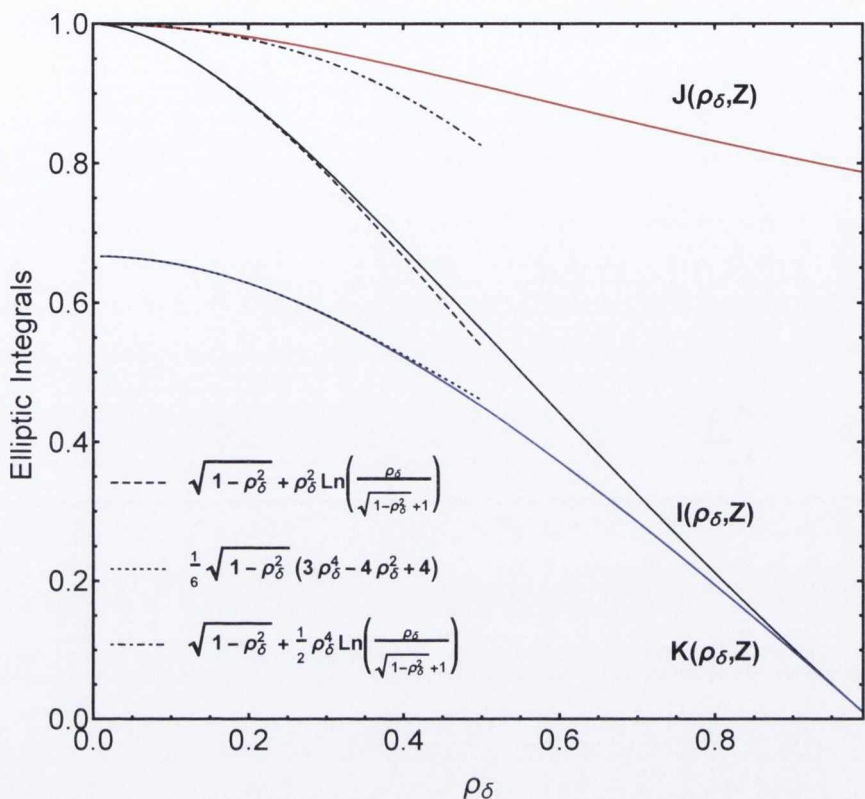


FIGURE 2.9: Variation of the elliptic integrals with ρ_δ along with their Taylor expansions in the wet limit, i.e. for $\rho_\delta \ll 1$.

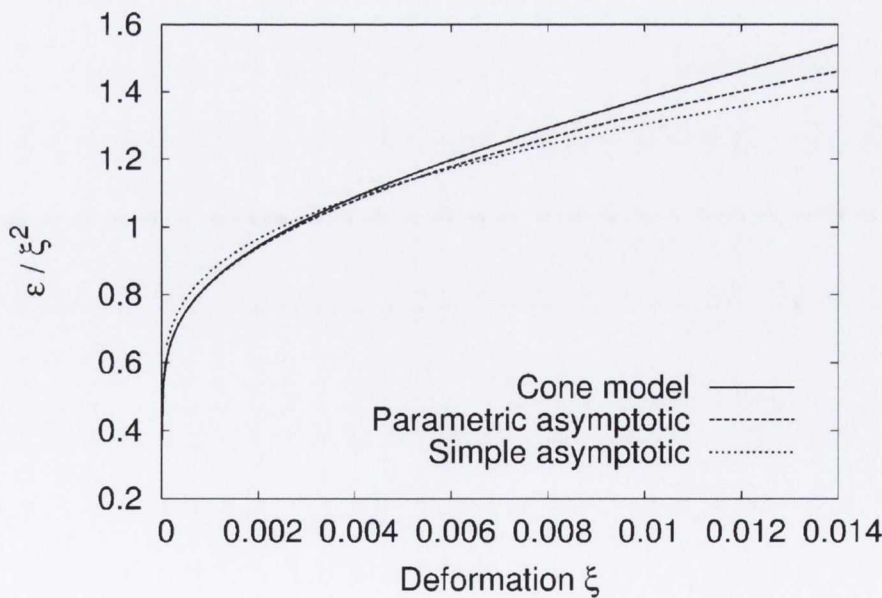


FIGURE 2.10: Asymptotic behaviour of energy ϵ/ξ^2 in the limit of small deformation, $\xi \ll 1$, for $Z = 12$. The analytic result for the cone model (solid line) is well presented by a parametric plot of the expansion of equation (2.23).

applying to any number of contacts Z near ϕ_c . However, the form of this interaction differs for contacts gained away from ϕ_c ; this is discussed in Chapter 5 where we discuss the loss of the square faces in the Kelvin structure which occurs at a liquid fraction significantly lower than the critical liquid fraction ϕ_c . Only for larger values of ξ , and over a limited range, as a decreasing function of Z , may the excess energy be reasonably well approximated by a quadratic, as will be discussed in detail in Chapter 3.

The anomalous asymptotic (logarithmic) form adds a further complication to the analysis of the approach to the wet limit in disordered foams, analogous to that of the “jamming” problem in granular materials [8, 9]. If foam is to be taken as a representative system for this problem, the validity of quadratic potentials in granular packings must be questioned.

2.3 Conclusions and Outlook

In the limit of very small bubble-bubble contacts, Morse and Witten [39] and Lacasse *et al.* [27] have suggested that the interaction between bubbles is logarithmic, rather than harmonic (see Sections 1.7.2 and 1.7.3). By treating the bubble surfaces as deformable and geometrically approximating the volume, we have introduced the Z -cone model which ties together a number of previous results [27, 39] with a single coherent picture. Importantly, our model moves away from the Durian bubble model of overlapping spheres (see Figure 1.6 in Section 1.7.1), which is predominantly used in simulations of foam rheology.

We have presented a semi-analytical relation between the energy (i.e. surface area) and the liquid fraction ϕ and correct asymptotic forms for the energy in the limits of dry and wet foam, with prefactors dependent on Z . In particular, the variation of energy with uniform, uniaxial deformation in the wet limit is consistent with the anomalous behaviour first reported by Morse and Witten [39] and Lacasse *et al.* [27], with a prefactor $\frac{Z}{2}$.

In the form presented so far, the *Z*-cone model is strictly only applicable to a limited number of cases, in which neighbours are equivalent, but it is possible to pursue its generalisation to other ordered structures. This will be explored for the Kelvin foam in Chapter 4. A further generalisation to bidisperse systems will be the subject of Chapter 7.

The asymptotic variation of energy and forces in the wet limit is of some topical importance, because a wet foam is regarded as an ideal experimental system with which to investigate jamming properties, since it has well-characterised constituents without static friction [44]. However, theories of jamming often invoke the kind of quadratic forces that we have now shown, with the *Z*-cone model, to be qualitatively inappropriate for foams, in the wet limit. Is the presence of a logarithmic force and energy specific to bubbles, for which the surfaces are not rigid but deformable and there is no static friction? While a definitive answer to this question is beyond the scope of this work, a sharp transition between harmonic and logarithmic forces for a finite rigidity of the particles seems unlikely. Thus, the results presented here for bubbles call into question the validity of quadratic potentials in granular packings.

Chapter 3

Applications of the Z -Cone Model

In Chapter 2, we introduced the Z -cone model of a bubble in the bulk of a foam to understand the properties of foams in equilibrium. From this, we were able to derive an approximate expression for the excess surface energy ε of a bubble in terms of deformation and liquid fraction which demonstrated that there is a logarithmic term which dominates the bubble-bubble interaction close to the wet limit ϕ_c . This interaction was also shown to be inexpressible as a pair potential since it depends explicitly on the number of neighbours of each of bubbles Z which may, in principle, be different for each of the bubbles forming the contact. By Taylor expanding the excess energy very close to the wet limit, we were able to determine this critical form.

The aim of this chapter is to further our analysis of the implications of the Z -cone model. While the presence of a logarithmic term at the wet limit rules out the presence of a strictly harmonic interaction, the range of deformations where this logarithmic correction is dominant is small. Away from this limit, the interaction is approximately harmonic, as discussed by Lacasse *et al.* [27]. In Section 3.1 we will show this for the Z -cone model.

We will also show how the Z -cone model can be used to determine the liquid fraction profile and osmotic pressure of a foam.

3.1 Computation of the Effective Spring Constant for the Bubble-Bubble Interaction

In this section, we will compute an effective Hookean spring constant, as a function of contact number Z , for bubble-bubble interactions using the Z -cone model. As we saw in Section 1.7.3, Lacasse *et al.* [27] proposed a power law form for the excess energy ε as a function of the deformation ξ , given by equation (1.16), with fitting parameters C_Z and α_Z .

The slightly odd form of the term in square brackets is due to the fact that this expression is equivalent to $\varepsilon = C'(\phi_c - \phi)^{\alpha_Z}$ and has been converted to deformation using the relation $\xi = 1 - \left(\frac{1-\phi_c}{1-\phi}\right)^{1/3}$. Equation (1.16) was found to agree well with Surface Evolver simulations of a bubble confined by a number of contacts Z in the range $\xi \sim 0.02 - 0.1$. In particular, α_Z was found to rise from $\alpha_Z = 2.1$ for two contacts to $\alpha_Z = 2.5$ for the fcc structure.

There are two key features of equation (1.16) which bear further investigation. Firstly, the prefactor C_Z depends on the number of contacts Z . This is consistent with our findings from Chapter 2 in which we showed that the prefactor in the logarithmic asymptotic form for the excess energy ε depends explicitly on the number of contacts Z . Secondly, the power α_Z is close to the harmonic value of $\alpha_Z = 2$.

While a power law of the form of equation (1.16) is useful, it is not easy to visualise the term in brackets as the displacement term in a Hookean spring model. As we discussed in Section 1.6 when we defined the deformation ξ for the simple structures with Z equivalent neighbours that we are considering here, the deformation can be simply related to the distance between bubble centres s which forms the basis of any spring model. For this reason, we choose to describe the bubble-bubble interaction for higher values of the deformation as

$$\varepsilon \propto \xi^\alpha. \tag{3.1}$$

Figure 3.1 shows, on a log-log plot, the variation of ε with ξ as obtained from the Z-cone model for $Z = 6$ and 12 . In this figure, a line of slope 2 would represent a truly harmonic interaction. We find that $\alpha \approx 2.2$ is satisfactory for a wide range of ξ . This is broadly in line with our expectations, based upon the results obtained by Lacasse *et al.*, and represents an interaction which lies between the harmonic case: Hooke's law, i.e. $\alpha = 2$, and the so-called Hertzian case with $\alpha = \frac{5}{2}$.

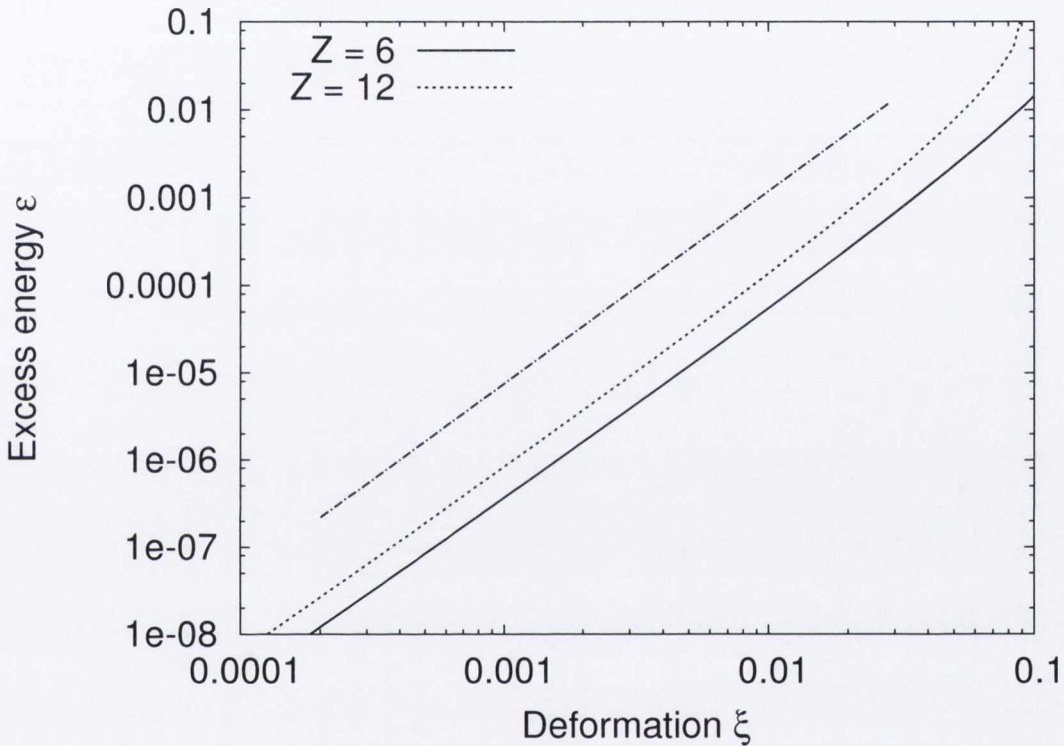


FIGURE 3.1: Dependence of excess energy on deformation for $Z = 6$ and $Z = 12$, shown on a log-log plot. A line of slope 2.2 is shown as a guide to the eye, showing that $\varepsilon \propto \xi^{2.2}$ is a good approximation over a wide range of ξ .

As $\alpha \neq 2$, we cannot refer to a true spring constant k . However, we may define an effective spring constant k_{eff} ;

$$k_{\text{eff}} = \left. \frac{\varepsilon}{\xi^2} \right|_{\xi=\xi_{\text{inf}}} \quad (3.2)$$

where ξ_{inf} is the inflection point on the plot of $\frac{\varepsilon}{\xi^2}$ as indicated in Figure 3.2. We choose this definition for k_{eff} , rather than the more conventional $k_{\text{eff}} = \left. \frac{\partial^2 \varepsilon}{\partial \xi^2} \right|_{\xi=0}$, as

the second derivative is difficult to evaluate near $\xi = 0$ due to the logarithmic form of $\varepsilon(\xi)$. The inflection point ξ_{inf} represents the value of ξ at which $\frac{\varepsilon}{\xi^2}$ has the least slope: this might reasonably be considered the point at which the approximation of harmonicity is best, since in the harmonic case $\varepsilon/\xi^2 = k$ for all ξ . It is clear from Figure 3.2 that this assumption of harmonicity is better for low Z .

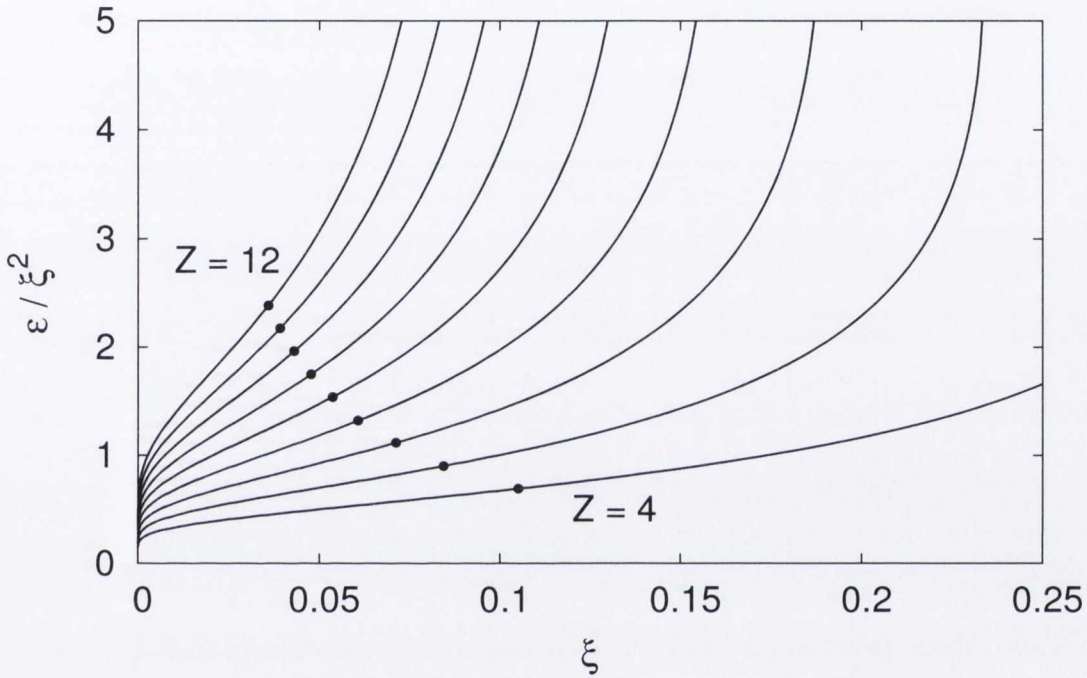


FIGURE 3.2: We use the point at which ε/ξ^2 has least slope as a function of ξ to obtain an effective Hooke's law constant k_{eff} for each value of Z . k_{eff} is found to increase with Z .

In Figure 3.3 we plot the variation of k_{eff} with the number of contacts Z . We see a relationship which is very close to linear, with the line of best fit:

$$k_{\text{eff}} = 0.21(Z - 0.75). \quad (3.3)$$

While clearly an approximation, a local force law of the form $F = k_{\text{eff}} \xi$ is worth considering in any extensions of Durian's two-dimensional model to three dimensions.

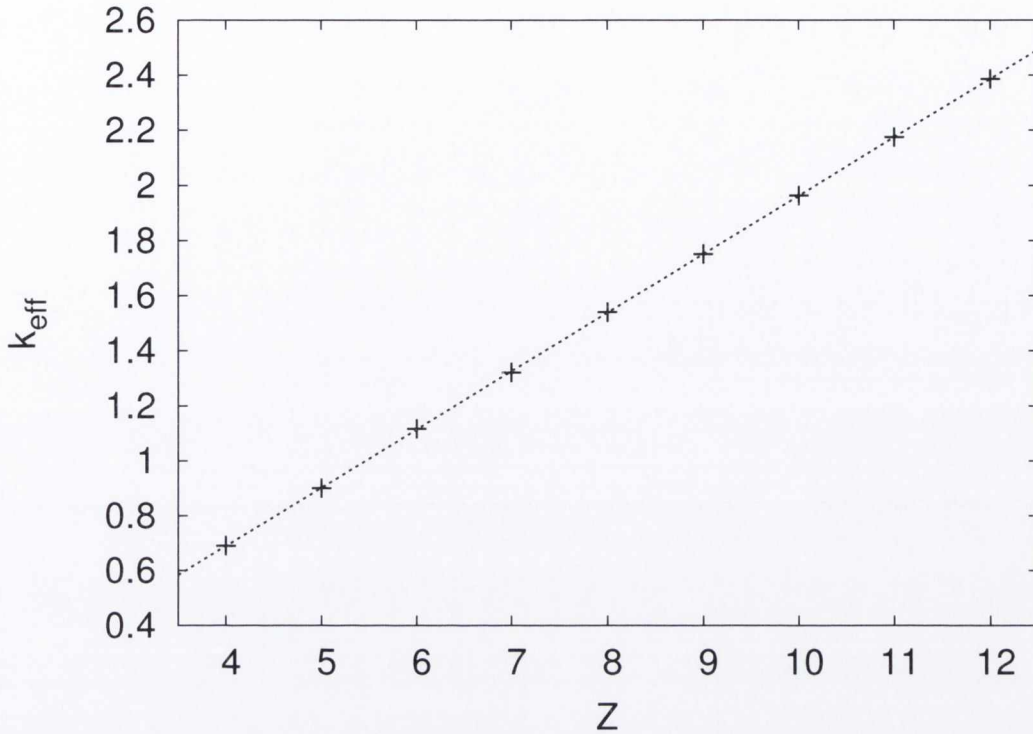


FIGURE 3.3: The variation of the effective spring constant k_{eff} with the number of contacts Z is well described by the linear relationship (3.3).

3.2 Osmotic Pressure in the Z-Cone Model

As we have seen, the Z-cone model provides us with analytic predictions for the excess energy ε as functions of both deformation ξ and liquid fraction ϕ . Using these analytic expressions, we will compute the osmotic pressure Π and from this a liquid fraction profile for a foam at equilibrium under gravity. The osmotic pressure, as it is defined in equation (1.3) is for any volume of foam V . In the Z-cone model, however, we are considering an ordered foam with identical bubbles. In this case, we can relate the reduced osmotic pressure to the excess energy ε of a single bubble in the foam [12] by

$$\tilde{\Pi}(\phi) = -3(1 - \phi)^2 \frac{\partial \varepsilon}{\partial \phi}, \quad (3.4)$$

where the derivative can be expressed as $\frac{\partial \varepsilon}{\partial \phi} = \frac{\partial \varepsilon}{\partial \xi} \frac{\partial \xi}{\partial \phi}$ (see equation (3.6)).

Figure 3.4 shows $\tilde{\Pi}(\phi)$, as computed numerically for the Z-cone model using equation (2.9).

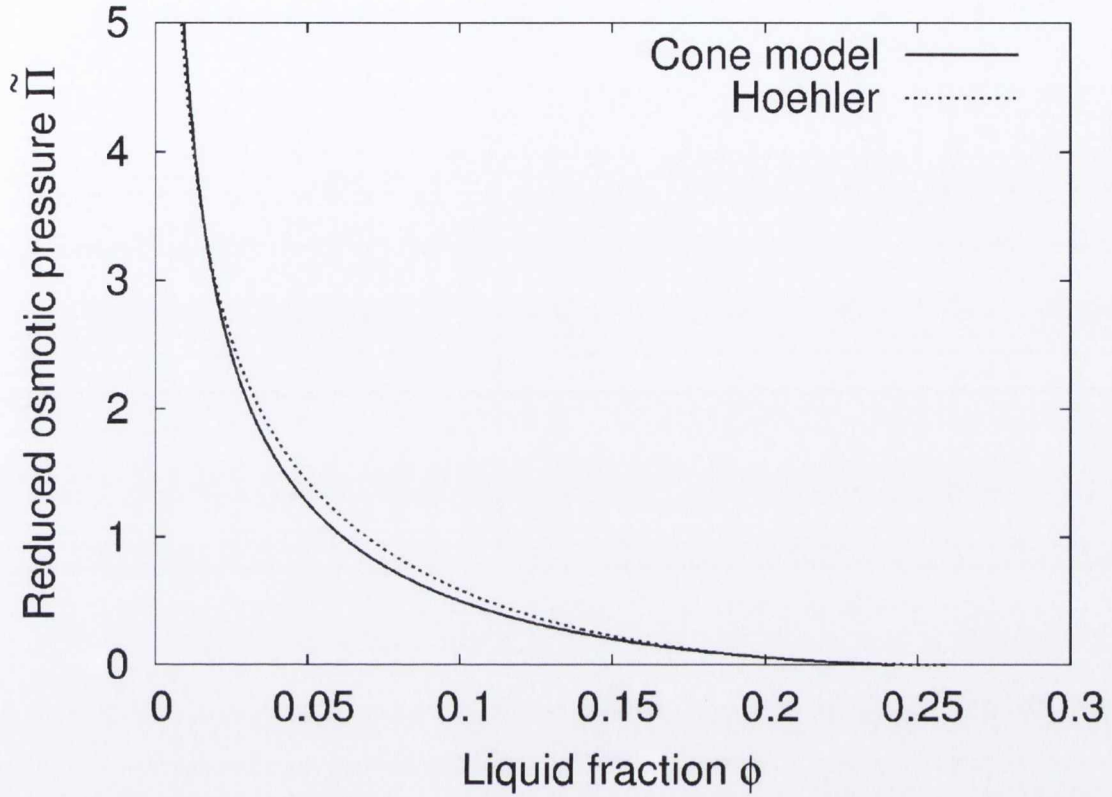


FIGURE 3.4: The variation of the reduced osmotic pressure $\tilde{\Pi}$ as a function of liquid fraction ϕ , together with an empirical relationship proposed by Höhler *et al.* to describe experimental data [12] for ordered foams. The data presented is for $Z = 12$.

The dashed line in Figure 3.4 is an empirical relationship given by

$$\frac{\Pi(\phi)}{\left(\frac{\gamma}{R}\right)} = 7.3(\phi - \phi_c)^2 \phi^{-\frac{1}{2}}, \quad (3.5)$$

which was obtained as a fit to experimental data for osmotic pressure measurements carried out by Höhler *et al.* [12]. The Z-cone model gives a good approximation to this experimental relationship over the full range of liquid fraction ϕ .

Although there is no explicit algebraic form for $\tilde{\Pi}(\phi)$ from the Z-cone model, over the entire range of liquid fraction ϕ , it is possible to provide an asymptotic

form in the wet limit. Taking equation (2.22) for the corresponding asymptotic form of $\varepsilon(\xi)$ along with the identity equation (2.15), and using the transformation $\frac{\partial \varepsilon}{\partial \phi} = \frac{\partial \varepsilon}{\partial \xi} \frac{\partial \xi}{\partial \phi}$, results in

$$\frac{\Pi(\phi)}{\left(\frac{\gamma}{R}\right)} = -\frac{Z}{3} \frac{(1-\phi)^2}{(1-\phi_c)^2} \frac{(\phi_c - \phi)}{\ln(\phi_c - \phi)} \quad (3.6)$$

in the wet limit. This is also in good agreement with Surface Evolver data with the appropriate choice of ϕ_c .

3.3 Liquid Fraction Profile

The liquid fraction profile for the Z-cone model was derived by considering the reduced osmotic pressure $\tilde{\Pi}(\phi)$ of the foam, which we defined in Section 1.5. We saw that there is a simple relationship, equation (1.6), between the local liquid fraction $\phi(\tilde{x})$ at a reduced height $\tilde{x}$ above the bottom of the foam and the reduced osmotic pressure $\tilde{\Pi}$.

The reduced height which we have introduced is defined as $\tilde{x} = \frac{xR_0}{l_0^2}$ with l_0 the capillary length. The capillary length l_0 is a characteristic length scale used in foams and is defined as the ratio of buoyancy forces to inertial forces [3] and has been used by previous authors to define a single bubble layer in a wet foam as $\frac{l_0^2}{R_0}$ [3]. Thus, the reduced height $\tilde{x}$ measures the height in the foam in terms of the number of bubble layers, and so is useful in particular for experiments.

Expanding equation (1.6) into partial derivatives, we obtain a differential equation for $\phi(\tilde{x})$ which depends on $\partial\tilde{\Pi}/\partial\phi$:

$$\frac{\partial \phi}{\partial \tilde{x}} = \frac{1 - \phi(\tilde{x})}{\frac{\partial \tilde{\Pi}}{\partial \phi}}, \text{ with } \phi(0) = \phi_c. \quad (3.7)$$

We can use equation (2.16) to obtain an expression for $\varepsilon(\phi)$ which we use with equation (3.4) to solve this differential equation numerically, yielding a liquid fraction profile for any Z . We choose $Z = 12$, as for fcc-ordered foams, and so equation (2.16) gives a critical liquid fraction $\phi_c = 0.242$. We plot the obtained liquid fraction profile in Figure 3.5, and compare it to an empirical fit to experimentally measured profiles for ordered foams [45]. Note that the experimental data has a critical liquid fraction of 0.26.

While there is good agreement between the Z -cone model with $Z = 12$ and the experimental data in the wet limit, there is a discrepancy at lower ϕ with the wetness decaying more slowly that is predicted by the Z -cone model. One possible source of this is the fact that $Z = 12$ does not hold throughout an ordered foam. When $\phi < 0.07$, bubbles tend to arrange in a Kelvin (bcc) structure more readily than fcc [12]. We will discuss the bcc structure in detail in Chapters 4 and 5.

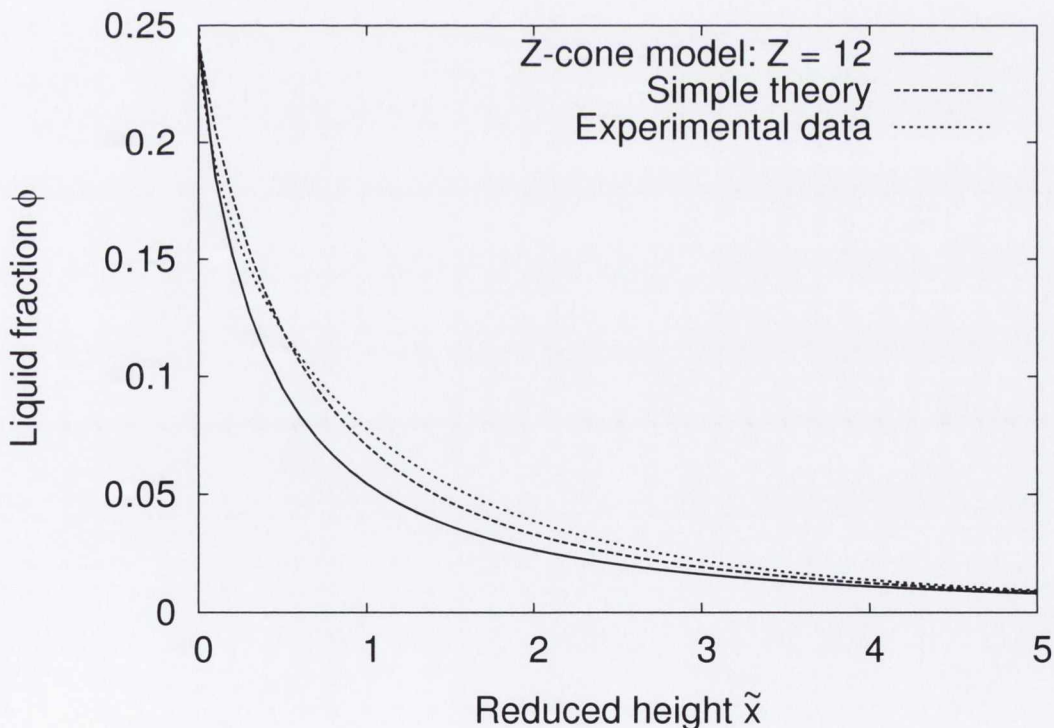


FIGURE 3.5: The liquid fraction as a function of reduced height, obtained using the Z -cone model with $Z = 12$, compared to a simple theoretical expression from [2], and to an empirical expression for ordered monodisperse foams from Maestro *et al.* [45]. The Z -cone model gives an adequate approximation of the experimental data in the wet limit.

In the same figure we have also plotted an expression for $\phi(\tilde{x})$ following from Weaire *et al.* [2]:

$$\phi(\tilde{x}) = \tilde{c} \left(\tilde{x} + \sqrt{\frac{\tilde{c}}{\phi_c}} \right)^{-2}. \quad (3.8)$$

The derivation of this expression considers the vertical variation in cross-section of a Plateau border, based on the hydrostatic pressure variation in the liquid; together with a structural constant $\tilde{c} \approx 0.333$ related to the number of Plateau borders per volume in a Kelvin foam [2]. The resulting equation (equation (3.8)), presented in this form for the first time, is a surprisingly good description of the experimental data, and has an appealingly simple form.

3.4 Conclusions and Outlook

In Chapter 2, we used the Z-cone model to identify a logarithmic form for the excess energy ε , close to the wet limit. This showed that the interaction between bubbles in this limit is clearly not harmonic, which is a commonly used model of the interaction in computer simulations, in particular the Durian model (see Section 1.7.1). However, approximate harmonicity could be inferred for the interaction slightly further away from ϕ_c . We examined the validity of such an assumption, showing that while it may represent a reasonable approximation for low Z , it is far from acceptable for Z higher than about 7. This significantly reduces the validity of such an assumption for simulations of three-dimensional foams, where the average number of contacts per bubble is typically between 12 and 14 [3]. We proposed that a more appropriate form for high numbers of contacts would be to consider a power law with an exponent of 2.2.

We have further analysed the Z-cone model from Chapter 2, using it to compute the reduced osmotic pressure $\Pi(\phi)$ as a function of liquid fraction. We have shown that the results from the Z-cone model agree well with experimental findings [12]. Expanding on the theme of asymptotic forms for the wet limit from Chapter 2,

we have derived an analytical expression for the reduced osmotic pressure $\tilde{\Pi}$ close to ϕ_c which agrees well with the results of Surface Evolver for the case of $Z = 12$. This provides further confidence in the power of our model to describe foams in equilibrium, despite the approximations used in its conception.

Furthermore, we have used the osmotic pressure to compute a liquid fraction profile for a foam which provides an adequate approximation to experimental data for the fcc structure in the wet limit. Some deviation is observed for intermediate liquid fractions which can most likely be attributed to the fact that as the liquid fraction decreases in experiment, the fcc structure ceases to be the lowest energy crystal structure with the bcc structure being strongly preferred below about $\phi = 0.07$ [12]. Due to the Z-cone model underestimating the excess energy of the fcc structure compared to the Surface Evolver (see Figure 2.6), this crossover is observed closer to $\phi = 0.1$ (see Chapters 4 and 5).

Chapter 4

Application of the Cone Model to a Kelvin Foam

In the physics of foams, the structure envisaged by Kelvin [46] has played a central role as a prototype, even though it is now known not to be the structure of lowest energy for a monodisperse dry foam [47]. The Kelvin structure is based on the bcc lattice, shown in Figure 4.1, which has eight nearest neighbours and six next nearest neighbours. Various authors have already applied Surface Evolver simulations to the dry Kelvin structure [12]. In particular, Höhler *et al.* have used it when discussing foam structure in the case of finite liquid fraction [12].

In this chapter, we will show that the Z -cone model, introduced in Chapter 2 to model bubbles in contact with Z equivalent neighbours, can be extended to a more general cone model which incorporates unequal contacts. Although various approximations are involved in the new formulation, the model retains the character of the original Z -cone model as there are no adjustable parameters. This represents the first step in extending this geometric idea to more general ordered foam structures and, as we shall see, the generalised method that we describe here can easily be adapted for other ordered structures.

As was the case for the Z -cone model, our primary goal is to present an approximation of the excess energy ε of the Kelvin cell. The results of this model will

then be compared in Section 4.3 to accurate simulations using the Surface Evolver over the full range of liquid fraction ϕ .

The cone model developed in this chapter will also enable us to revisit the question of mechanical stability of the structure and the loss of the square faces in Chapter 5, which we feel has not been adequately addressed in the literature.

4.1 Key Components of the Model

In this section, we will broadly describe how the Z -cone model, which we introduced in Chapter 2, can be extended to describe a wet Kelvin cell.

In Chapter 2, we developed the Z -cone model as an analytically tractable model that allows for the estimation of the energy of a foam consisting of identical bubbles with Z nearest neighbours. In this case, each bubble is segmented into Z equivalent pieces which are then approximated as circular cones (see Figure 2.2). Upon deformation, corresponding to the application of an osmotic pressure, the initially spherical caps of the cones become increasingly flattened. Their surface area is minimised subject to a specified constant cone volume V_c . The result is an analytic parametric expression for the excess energy ε of a bubble in terms of liquid fraction ϕ which contains no free parameters and depends only on the number of contacts.

To generalise the cone model to handle the Kelvin cell we must separate our bubble into two different types of cones corresponding to the eight hexagonal faces and six square faces that are characteristic of the Kelvin cell, see Figure 4.1(b). An illustration of this concept is shown in Figure 4.2. The presence of two different types of contacts adds a geometric complexity to the cone model meaning that several simplifying statements which we made use of in the original Z -cone model no longer hold.

As we mentioned above, the conservation of the total bubble volume V_0 is central to the Z -cone model and, for the case of identical contacts, is equivalent to keeping

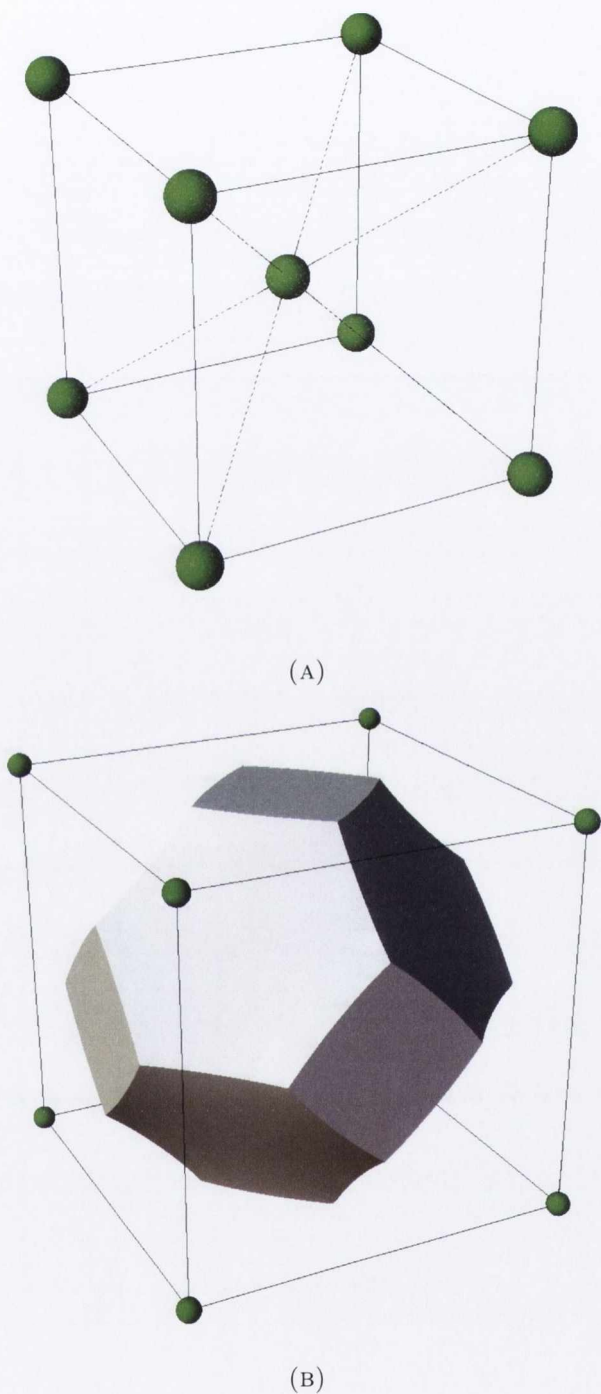


FIGURE 4.1: (a) The bcc lattice. (b) A bubble in a dry bcc foam takes the form of a Kelvin cell. The hexagonal faces are slightly warped, and the square faces are planar with convex edges.

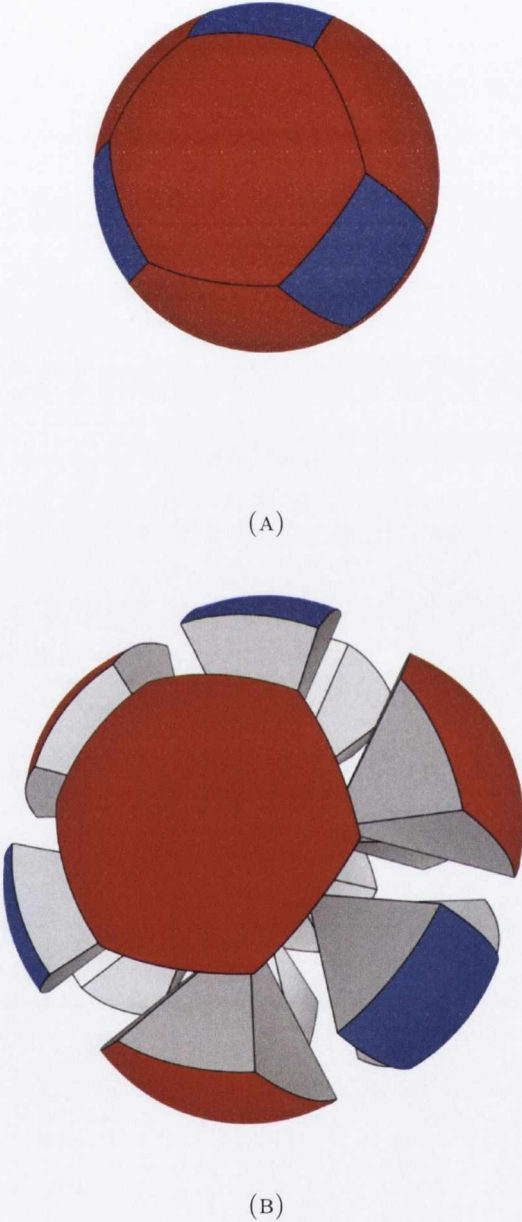


FIGURE 4.2: (a) A bubble in a Kelvin foam has eight neighbours in the $\langle 111 \rangle$ directions and six neighbours in the $\langle 100 \rangle$ directions. As the liquid fraction ϕ is reduced the eight neighbours give rise to the hexagonal faces of the Kelvin cell (see Figure 4.1) while the six neighbours form the square faces. (b) We associate each neighbour a cone, as shown here for a spherical bubble. In the cone model, each of these cones is approximated by an appropriate circular cone.

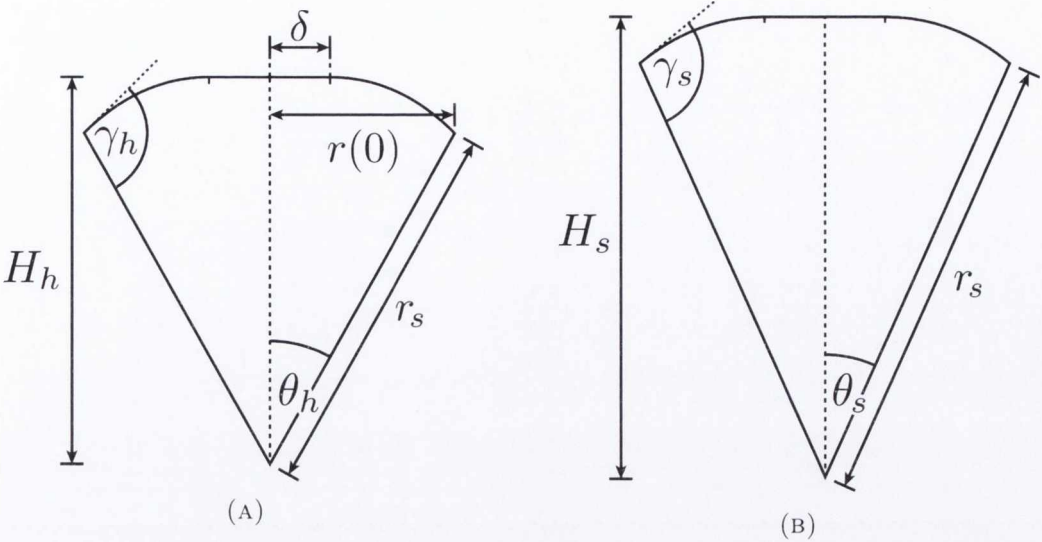


FIGURE 4.3: In the Kelvin cone model, we deal with two types of (circular) cones. Cross-sections of the (a) hexagonal contacts and (b) the square contacts are shown here with some appropriate mathematical notation. They share a common slant height denoted by r_s . The total heights H_h and H_s are different, representing the different distances to the nearest and next nearest neighbours in a bcc lattice. The ratio $\rho_{\delta_h} = \frac{\delta}{r(0)}$, along with a similar definition of ρ_{δ_s} for the square cone, feature in the derivation of the cone model expressions which is presented in Appendix D.

each of the cone volumes V_c constant. When we consider two different types of contacts we are not able to make this assumption.

While the total volume of the bubble, V_0 , is constant, the volume of each of the cones is no longer required to be constant. Indeed, the proportions of the total volume in the hexagonal and square cones are allowed to vary, as a function of liquid fraction ϕ for example, provided that the total volume of the collection of cones is equal to V_0 . The constraint on the individual cone volumes is now given by

$$8V_h + 6V_s = V_0, \tag{4.1}$$

where V_h and V_s denote the volumes of the cones associated with hexagonal and square bubble contact areas, respectively.

4.1.1 Determining the Cone Angles θ_h and θ_s

The hexagonal- and square-based cones depicted in Figure 4.2(b) are not conducive to the minimal surface approach that we use to determine the excess energy ε . To facilitate this, we must do as we did in the Z -cone model and approximate each of these angular cones as circular cones, with different opening angles for each of the sets of cones, as shown in Figure 4.3.

In the Z -cone model, the cone angles are determined by splitting the total solid angle $\Omega = 4\pi$ of the bubble equally between the Z contacts and calculating the opening angle of a circular cone encompassing this solid angle. Naturally, this simple approach is not directly applicable and must be modified for the two types of contacts in the Kelvin cell having separate opening angles θ_h and θ_s (see Figure 4.3). We choose instead to retain the values of the solid angles subtended by each type of face in the “dry” Kelvin structure. This guarantees that the sum of the solid angles subtended by the eight hexagonal and six square faces is equal to the 4π steradian solid angle of our bubble.

The solid angle taken up by any n -sided polygonal face is given, in terms of the side-length u of the polygon (in our case $u = 1$) and the distance h_n from the origin to the centre of the face, by

$$\Omega_n = 2\pi - 2n \arcsin \left(\frac{2h_n \sin \left(\frac{\pi}{n} \right)}{\sqrt{4h_n^2 + u^2 \cot^2 \left(\frac{\pi}{n} \right)}} \right). \quad (4.2)$$

The heights h_n are half the distances to the nearest and next nearest neighbours in the dry Kelvin structure; $h_n = \sqrt{\frac{3}{2}}u$ for the hexagonal faces and $h_n = \sqrt{2}u$ for the square faces.

The cone opening angles θ_h and θ_s are then calculated for these solid angles from

$$\theta_n = \arccos \left(1 - \frac{\Omega_n}{2\pi} \right). \quad (4.3)$$

4.1.2 Matching at Cone-Cone Boundaries

In light of these generalisations, in particular the possibility for the volume of the cones to vary with liquid fraction ϕ , it is natural to ask how these cones can be combined to accurately replicate a Kelvin cell?

For two cones to meet each other, they are required to have a common slant height r_s (see Figure 4.3). In addition, their curved caps should meet smoothly, i.e. the curved caps making up the bubble surface should have no sharp corners. In the original Z -cone model, the presence of identical cones automatically ensures the first of these conditions while the second was satisfied by requiring each of the curved caps to meet their respective cones at right angles (see equation (2.7) and Figure 2.3).

While the requirement of a common slant height r_s for both the square and the hexagonal cones in the case of the Kelvin cell can be used to constrain the possible values of the other parameters, for example the cone volumes, the second condition is more tricky. To ensure that the cones meet smoothly, we need the angles made between the curved caps and the cones, denoted by γ_h and γ_s (see Figure 4.3), to sum to 180 degrees. Note that there is a subtlety here related to the geometry of the Kelvin cell. From Figure 4.2 it is clear that while the square cones meet with hexagonal cones on all four of their sides, the hexagonal cones meet with square cones on only half of their sides. Thus, γ_h will be slightly different for hexagon-hexagon and hexagon-square boundaries and the γ_h which we use in the model is, consequently, intermediate between the precise values in the Kelvin cell. Incorporating this, we find that the cones in the Kelvin cell meet smoothly provided that

$$2\gamma_h + \gamma_s = \frac{3\pi}{2}. \quad (4.4)$$

Similarly to the generalised volume condition above, the angles γ_h and γ_s are no longer fixed, as in the basic Z -cone model.

4.1.3 Additional Constraints

Thus far in this section, we have shown how a bubble in a wet Kelvin foam can be described using a combination of two types of cones. We have also illustrated that the physical considerations of constant bubble volume and a smooth bubble surface at the point where two cones meet, are sufficient to relate the cone volumes V_h and V_s , and the angles γ_h and γ_s .

However, these two conditions alone are not enough to uniquely determine the values of these parameters for any given liquid fraction ϕ . We must use some additional information in order to do this and complete our cone mode description of the Kelvin cell.

The first additional constraint we introduce on the model is due to the geometry of the bcc structure (see Figure 4.1). As we noted in Section 4.1.1 when discussing solid angles in the dry Kelvin, the distances from the centre of the bubble to the square and hexagonal faces are known. Indeed the ratio of these distances is $\frac{h_h}{h_s} = \frac{\sqrt{3}}{2} \approx 0.866$. In our cone model approximation of circular cones, the equivalent ratio of the height of the two cones (see Figure 4.3) is required to be

$$\nu = \frac{H_h}{H_s} = \frac{\cos \theta_h}{\cos \theta_s} = 0.864434. \quad (4.5)$$

It is important to stress that the height ratio between the faces given by equation (4.5), remains constant as the liquid fraction is varied for the Kelvin cell. Since ν is less than one, this implies that a bubble in a Kelvin foam, which is spherical at $\phi_c \sim 0.32$, will initially gain only the eight hexagonal contacts corresponding to nearest neighbour bubbles (in the bcc lattice, see 4.1) as the liquid fraction is brought below ϕ_c . The square faces only form later, at a lower liquid fraction ϕ^* , which depends on the shape of the surface as a function of liquid fraction. This loss of the square faces will be discussed further in Chapter 5.

The final additional constraint on our model is that the internal pressure p_i in each of the neighbouring cones should be equal. In physical terms, this is simply

the statement that pressure does not depend on the position in the bubble. The internal pressure of a bubble is responsible for the curvature of its surface and, by considering the work done to increase the volume of each cone by a small amount ΔV_i , we arrive at the following expression for the internal pressure of a cone,

$$p_i = \frac{\Delta E_i}{\Delta V_i^*} - 2\pi r_{s_i} \cos \gamma_i \cos \theta_i \frac{\Delta r_{s_i}}{\Delta V_i^*}, \quad (4.6)$$

where Δr_{s_i} is the slant height change of a cone, ΔE_i is the surface energy change and ΔV_i^* is the change in the volume associated with the curved surface of the bubble. For a derivation of this expression, as well as full mathematical details for the general cone model presented here, see Appendix D.

The above constraints are sufficient to uniquely determine all of the variables in our extended cone model and to write the excess surface energy ε for the Kelvin model as

$$\varepsilon = \frac{8A_h + 6A_s}{4\pi} - 1, \quad (4.7)$$

where A_h and A_s are the areas of the square and hexagonal cones. The precise mathematical expressions for these quantities are somewhat unsavoury and not important for the discussion below. As such, they are left to Appendix D.

Now that we have outlined the key elements necessary to extend the cone model to the Kelvin structure we are, in principle, ready to evaluate the excess energy ε , as given in equation (4.7), for any liquid fraction ϕ . However, it is necessary first to make a remark about the excess energy of the dry Kelvin foam, as we will make use of this in Section 4.3 as a reference when looking at the relative difference between the results of the cone model and Surface Evolver.

4.2 Excess Energy of the Dry Kelvin Cell

When considering the energy of the Kelvin structure, it is worth recalling what Kelvin himself was able to do at the outset [46]. He was concerned only with the dry foam limit of $\phi = 0$, for which he produced a remarkably accurate description of the bubble shape which came to bear his name, shown in Figure 4.1(b). He recognised the importance of crystal symmetry which implies that the quadrilateral faces are flat, while the hexagonal ones are not, and applied Plateau’s rules for the angles of intersection of faces, together with the requirement that the total curvature of the hexagonal faces is everywhere zero. His numerical calculation by hand of the approximate form of the hexagonal faces was a veritable tour de force.

But Kelvin did not proceed to estimate the surface area of his new structure, even though this bore directly on the motivation for the work. It appears that this was first evaluated one hundred years later, when Princen and Levinson [20] computed the surface area numerically by using a discretisation into flat segments.

The result was expressed in terms of the relative surface area $\frac{A}{A_0}$, where A_0 is the surface area of a sphere with the same volume of the polyhedron. Note that the relative surface area is nothing more than $\varepsilon + 1$, according to our definition of excess energy ε from Section 1.6. The computed value of $\frac{A}{A_0}$ for the Kelvin cell is 1.0970, a decrease from the value of 1.0990 for the planar-faced truncated octahedron, which to Princen and Levinson appeared “surprisingly small” [20].

However, it is possible to offer an alternative estimate of the dry Kelvin excess energy by adjusting the angles of the truncated octahedron to conform with Plateau’s rules (see Section 1.2) and which may have applications to other such structures. In this way, we obtain a value of $\frac{A}{A_0} = 1.0968$. As this is not central to our discussion in this chapter, we leave a discussion of the details of this estimate to Appendix E. We were also able to obtain a value of $\varepsilon_{K_0} = 0.0970$ from Surface Evolver calculations which agree with the value of Princen and Levinson.

We will shift our focus in the following section to using a comparison of the extended cone model outlined above with Surface Evolver simulations.

4.3 Excess Energy for Finite Liquid Fraction

Figure 4.4 shows the variation of the dimensionless excess energy $\varepsilon(\phi)$ with liquid fraction, obtained from both the Surface Evolver and the extended cone model above.

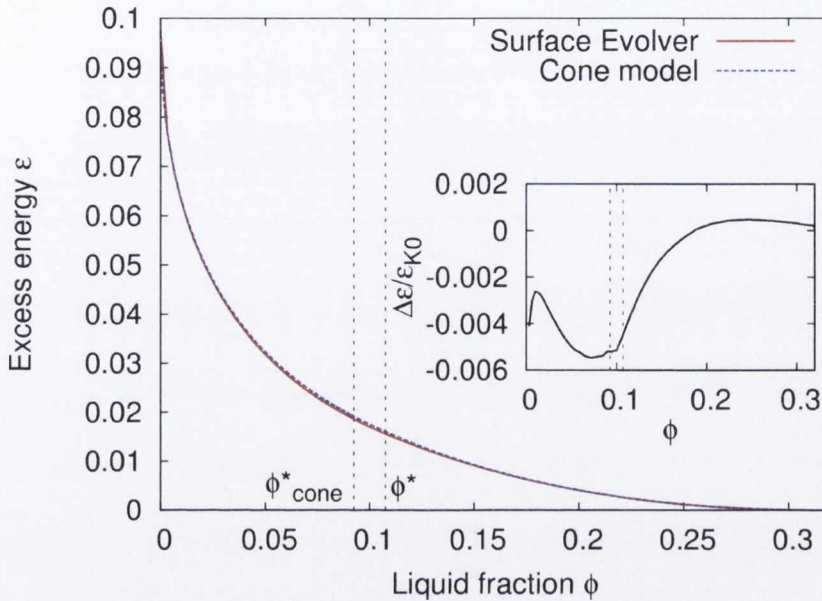


FIGURE 4.4: Variation of dimensionless excess energy ε with liquid fraction ϕ for the Kelvin structure, obtained from Surface Evolver calculations (solid line), and its approximation using the generalised cone model (dashed) outlined in Section 4.1. The values in the dry limit ($\phi = 0$) are $\varepsilon_0 = 0.0970$ from the Surface Evolver and $\varepsilon_{0C} = 0.0980$ from the cone model. Increasing ϕ leads to the loss of the six square faces. This takes place at $\phi^* = 0.108$ for Surface Evolver simulations, and at $\phi_{\text{cone}}^* = 0.092$ in the cone model. These events are marked by the dashed vertical lines. The inset show the normalised difference $(\varepsilon(\phi) - \varepsilon_{\text{cone}}(\phi)) / \varepsilon_0$.

We observe that the cone model gives a very good estimation of the excess energy ε over the entire range of ϕ , with a difference not exceeding one percent of $\varepsilon_0 = \varepsilon(0)$, as shown in the inset. Indeed, the agreement is perhaps surprisingly good given the approximations we made in extending the cone model to this case. This gives us confidence that the cone model can be further extended to more general crystal structures in the future.

The cone model is first and foremost a model of wet foams and so the good agreement shown, in particular, close to the dry limit is extremely encouraging. This is

in contrast to the simple Z -cone model where the comparison with Surface Evolver is noticeably worse as the dry limit is approached, i.e. for large deformations (see Chapter 2). The reason that the cone model so closely agrees with Surface Evolver for the Kelvin structure is primarily related to the shape and relative size of the faces in the the Kelvin cell.

In Section 2.2.2, we noted that for $Z = 12$ the cone model agreed better with the pentagonal dodecahedral structure than the fcc structure due to the high symmetry of pentagonal faces (i.e. the pentagons better resembled the circular contacts assumed by the cone model than the diamond-shaped faces of the fcc cell). The degree of symmetry increases with the number of sides and so the presence of eight large hexagonal faces should significantly improve the accuracy of our approximate model. As the six square faces only account for about one quarter of the total surface area of the dry Kelvin cell, the effect of the less symmetric square faces is not as important.

The value of ϕ at which the six $\langle 100 \rangle$ contacts vanish is given by $\phi^* = 0.108$ for the exact case and $\phi_{\text{cone}}^* = 0.092$ for the cone model, indicated by the dashed lines in Figure 4.4. It is worth noting that Weaire *et al.* [48] arrived at a remarkably accurate early estimate of $\phi^* \approx 0.11$ by a crude argument based on ratios of Plateau border widths. A clear difference exists however for the value of ϕ^* from these two methods. The contact loss in the cone model precedes that in the Surface Evolver computations (i.e. at a lower liquid fraction). This discrepancy between the values of ϕ^* obtained is a direct result of the approximations of the cone model. Although our cone model agrees well with Kelvin cell due the symmetric shape of the hexagonal faces, the approximation of circular faces which we must make is not sufficiently precise here and this gives rise to the observed discrepancy. The small difference in ν , the equivalent ratio of the height of two cones, for the cone model from the value of $\frac{\sqrt{3}}{2}$ and the approximation of circular cones are also important contributing factors. This interpretation is supported by the fact that the critical liquid fraction ϕ_c for the wet limit predicted from the cone model is $\phi_{c, \text{cone}} = 0.319$ which is a very good approximation to the value of $\phi_c = 0.320$ for the Kelvin foam [2].

4.4 Conclusions and Outlook

We have shown how the Z -cone model can be extended to the Kelvin foam, where not all contacts are equivalent. The key feature of this extended model is introduction of two different sets of cones, with different opening angles θ_h and θ_s , to account for the square and hexagonal contacts in Kelvin cell. This fundamental change required us to drop a number of simplifying assumptions from the original Z -cone model; in particular, the individual volume of the cones is no longer held constant for all liquid fractions ϕ but is allowed to vary provided the total volume of the assortment of cones remains constant.

However, by utilising the geometric properties of the Kelvin structure we were able to obtain a variation of excess energy ε with liquid fraction ϕ which compared extremely well with the results of Surface Evolver calculation over the entire range of liquid fraction with the difference not exceeding 1% of the excess energy of the dry Kelvin structure (which served as a reference).

From our extended cone model we were able to obtain a value of $\phi_{\text{cone}}^* = 0.092$ for the point at which the second nearest neighbours, corresponding to the square faces of the Kelvin cell, are lost. This differs noticeably from the value of $\phi^* \approx 0.108$ obtained from Surface Evolver calculations. The source of this discrepancy was found to be the result of the approximations of the cone model. Thus while further refinements to the model may help to bridge the gap, it is unlikely that the cone model can close it entirely. Nonetheless, this discrepancy does not invalidate the usefulness of the cone model in studying the variation of the energy ε close to the loss of the square contacts, which would shed light on the interaction of bubbles away from the critical liquid fraction ϕ_c . This will be the subject of Chapter 5.

The model which we have presented here is general and a natural follow-up would be to apply this to other well-defined geometries with more than two types of contacts. A further extension of this model to curved contacts, which occurs for polydisperse bubbles or for monodisperse bubbles with different pressures (i.e.

Weaire-Phelan is the best-known example), is briefly discussed in Chapter 7. Combining these would, in effect, pave the way for a cone model which would describe a completely random foam.

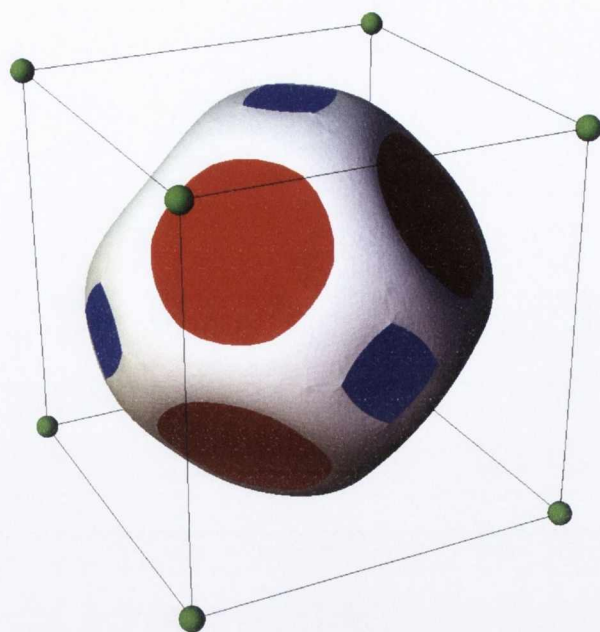
Chapter 5

Contact Losses in the Kelvin Foam

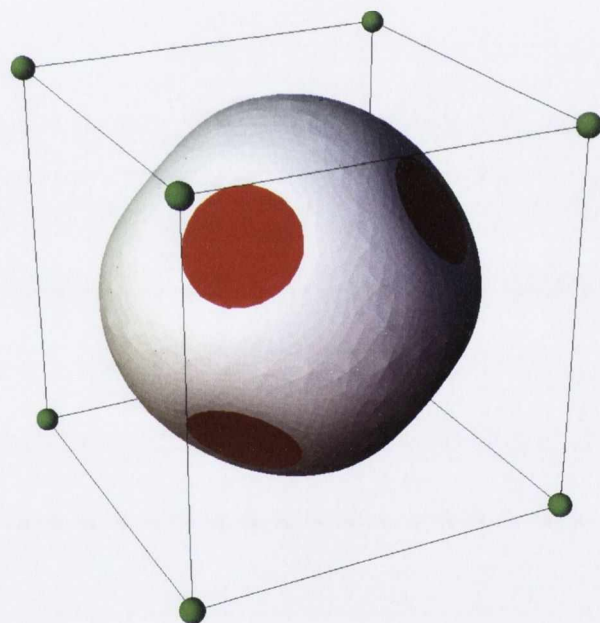
We saw in Chapter 4 that the Kelvin structure, consisting of a body-centred cubic (bcc) arrangement of bubbles (see Figure 4.1), provides a prototypical structure to extend the cone model for unequal contacts. The significance of the Kelvin foam as a prototype and our interest in it extends further, however. It also represents a well-defined structure that can be used for the study of a general feature of foams, namely the gain or loss of a face at some critical liquid fraction ϕ^* .

The Kelvin structure is stable with respect to small deformations for liquid volume fractions ϕ up to about $\phi \approx 0.11$ [13]. For $\phi > 0.11$ the Kelvin foam becomes unstable, and the close-packed fcc and hcp structures become energetically favourable [12]; the lattices for these structures are given in Section 1.4.

In experiments it is found that the fcc structure gives way to the bcc structure gradually as the liquid fraction is decreased with regions of both fcc and bcc present in the foam [12]. However, this structural transition from fcc to bcc would be sharp with the cone model, occurring precisely at a single value of the liquid fraction. The reason for this sharp transition is that the cone model treats a foam as a collection of **identical** bubbles with a precisely specified crystal geometry which is difficult to replicate in experiments.



(A)



(B)

FIGURE 5.1: Two examples of equilibrium bubble shapes in a wet bcc foam, with centres of neighbouring bubbles marked. These were generated in Surface Evolver. (a) For liquid fraction $\phi < \phi^*$, there are two sets of contacts, corresponding to the hexagonal $\langle 111 \rangle$ faces and square $\langle 100 \rangle$ faces. (b) When ϕ exceeds ϕ^* the square contacts are lost.

The loss of the six square $\langle 100 \rangle$ contacts in the Kelvin structure represents a

structural transition tied to the variation of liquid fraction. An illustration of the loss of the square faces is shown in Figure 5.1. As ϕ is increased from 0 to its maximum value of $\phi_c = 1 - \frac{\sqrt{3}\pi}{8}$, at which the bubbles are spheres (see Section 1.3), the areas of the square contacts are observed to shrink with increasing ϕ prior to disappearing at a liquid fraction $\phi^* < \phi_c$.

In examining the contact losses in the Kelvin structure, we will focus particularly on the details of the variation of excess energy ε with liquid fraction ϕ close to the liquid fraction at which contact is lost with the six neighbours in the $\langle 100 \rangle$ crystal directions. By using this generalised cone model, in addition to Surface Evolver computations (see Appendix F for further details of the Surface Evolver calculations), we will arrive at an empirical expression for the variation of energy close to this point. While it also features a logarithmic term, the functional form is distinctly different to that found for the Z-cone model (see equation (2.20)).

5.1 Shrinking of the Square Faces

In Section 4.3, we discussed the variation of the excess energy ε with liquid fraction for the Kelvin cell and noted that the square $\langle 100 \rangle$ contacts were lost at a liquid fraction ϕ^* . The precise value of $\phi^* = 0.108$ is slightly higher for the Surface Evolver (which represents the exact Kelvin cell with curved faces) than the value of ϕ_{cone}^* for the cone model due to the approximation inherent in the cone model (see Section 4.3 for further details).

This shrinking of the contact areas to zero is particularly sudden (i.e. occurs over a very short range of liquid fraction) close to ϕ^* which raises the question of whether the Kelvin structure becomes unstable due to the loss of the square contacts at ϕ^* or whether the instability occurs prior to the loss of these contacts. Indeed, the association of this contact loss with instability is not new, dating back to some incidental remarks of Weaire *et al.* [48] who were inspired by the instability of bcc metals.

The high level of precision (on the order of $\Delta\phi \sim 10^{-6}$) required to clearly resolve the position of the structural transition makes such subtle questions difficult to pursue with Surface Evolver simulations. Thus, we turn to the cone model to shed some light on the nature of this transition. In particular, we shall comment on the precise position of the instability associated with the loss of the $\langle 100 \rangle$ contacts.

Figure 5.2 shows the variation in area of both the square and hexagonal faces as a function of liquid fraction ϕ . We observe that the shape of the curves for the cone model and the Surface Evolver are similar for both the square and hexagonal cases. We also see that the square faces in the Evolver have a consistently higher area than predicted by the cone model. It is this that leads to the higher value of ϕ^* seen for in the Surface Evolver.

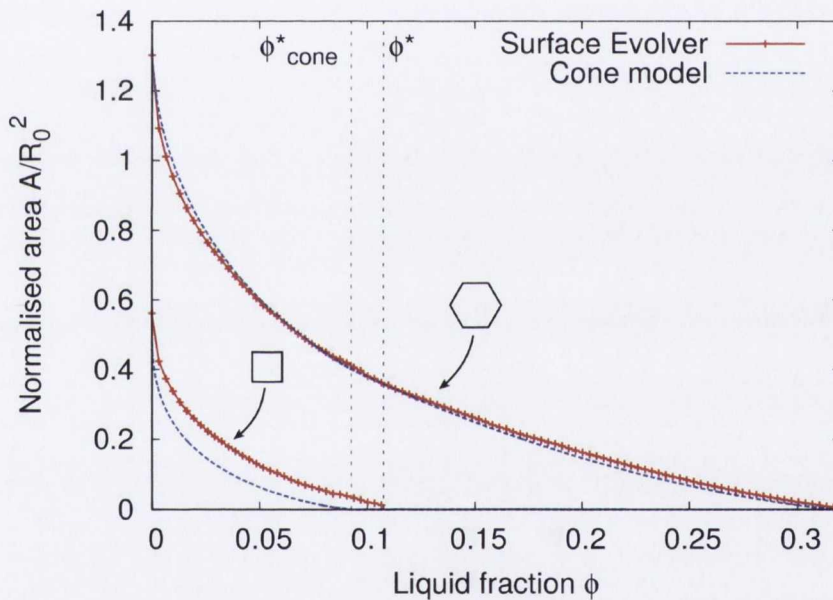


FIGURE 5.2: Variation of the areas of the hexagonal and square faces with liquid fraction ϕ , obtained from the Surface Evolver and the cone model. The areas are normalised by R_0^2 , where the volume of the bubble is $\frac{4\pi}{3}R_0^3$.

We should note that when ϕ is very slightly less than ϕ^* , we encounter problems accurately modelling the surface using Surface Evolver, due to difficulties in allowing the area of faces to go to zero. As a result, when we come to examine the nature of the contact loss around ϕ^* in the following section, we will use only data from the cone model.

5.2 Nature of the Contact Loss and Instability

The purpose of this section is to answer a question which has proved difficult to examine in the literature and to which the cone model is ideally suited: What is the effect of the loss of a face on the variation of energy?

To provide an answer to this question, we must now give closer attention to the two critical points, ϕ_{cone}^* and $\phi_{c, \text{cone}}$, at which contacts are lost with the square and hexagonal contacts in the Kelvin structure, respectively. In doing so, the results are clearer when viewed in terms of derivatives of the excess energy.

Numerical noise means that it is not practical to compute these derivatives accurately from the Surface Evolver. As we shall see, the key features of contact loss occur over a very small range of liquid fraction which practically negates the possibility of fitting the Surface Evolver data accurately.

With this in mind, we show in Figure 5.3 the variation of the derivative $\frac{d\varepsilon}{d\phi}$ as a function of liquid fraction as obtained from the cone model. While this variation is continuous, a clear discontinuity of the slope of $\frac{d\varepsilon}{d\phi}$ at the point of contact loss is revealed.

The variation of the derivative $\frac{d\varepsilon}{d\phi}$ at $\phi = \phi_{c, \text{cone}}$, as obtained from the original cone model (see Chapter 2) by differentiating equation (2.20) and keeping first order terms, is given by

$$\frac{d\varepsilon}{d\phi} = a \frac{\phi_c - \phi}{\ln(\phi_c - \phi)}, \quad (5.1)$$

where a is a constant. This describes our data well in Figure 5.4(a), as we expect from our analysis of the Z -cone model (see Chapter 2).

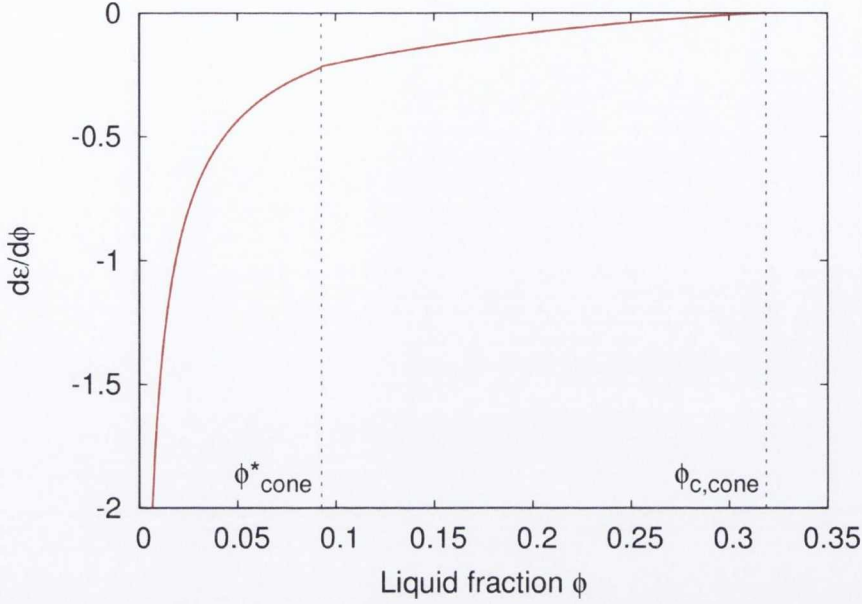


FIGURE 5.3: The derivative of the excess energy with respect to liquid fraction, $\frac{d\varepsilon}{d\phi}$ over the full range of liquid fraction obtained from the cone model. The vertical dashed lines mark the critical values of liquid fraction for which contacts are formed/lost in this structure. There is a clear discontinuity of slope at $\phi = \phi_{\text{cone}}^* = 0.092$, i.e the point at which the square faces corresponding to next-nearest neighbour contacts are formed/lost.

For $\frac{d\varepsilon}{d\phi}$ at $\phi = \phi^*$, we did not find an analytical expression from our new cone model. This is due to the additional geometrical complications which are inherent in this model, as we discussed in Chapter 4. However, the following empirical expression is a reasonably good description of the data which we show in Figure 5.4(b),

$$\frac{d\varepsilon}{d\phi} = b_1 + \frac{b_2}{(\ln(\phi_c - \phi))^2} \quad (5.2)$$

There is a clear discontinuity of the slope of $\frac{d\varepsilon}{d\phi}$ at $\phi = \phi_{\text{cone}}^*$ which is clearly visible in Figure 5.4(b).

Of note is the presence of logarithmic terms in both expressions, a feature known from studies of the bubble-bubble interactions [27, 39] (see Section 1.7). The discrepancy between the forms of equations (5.1) and (5.2) suggests that results

from bubble-bubble interactions do not directly apply to all contact losses away from the wet limit.

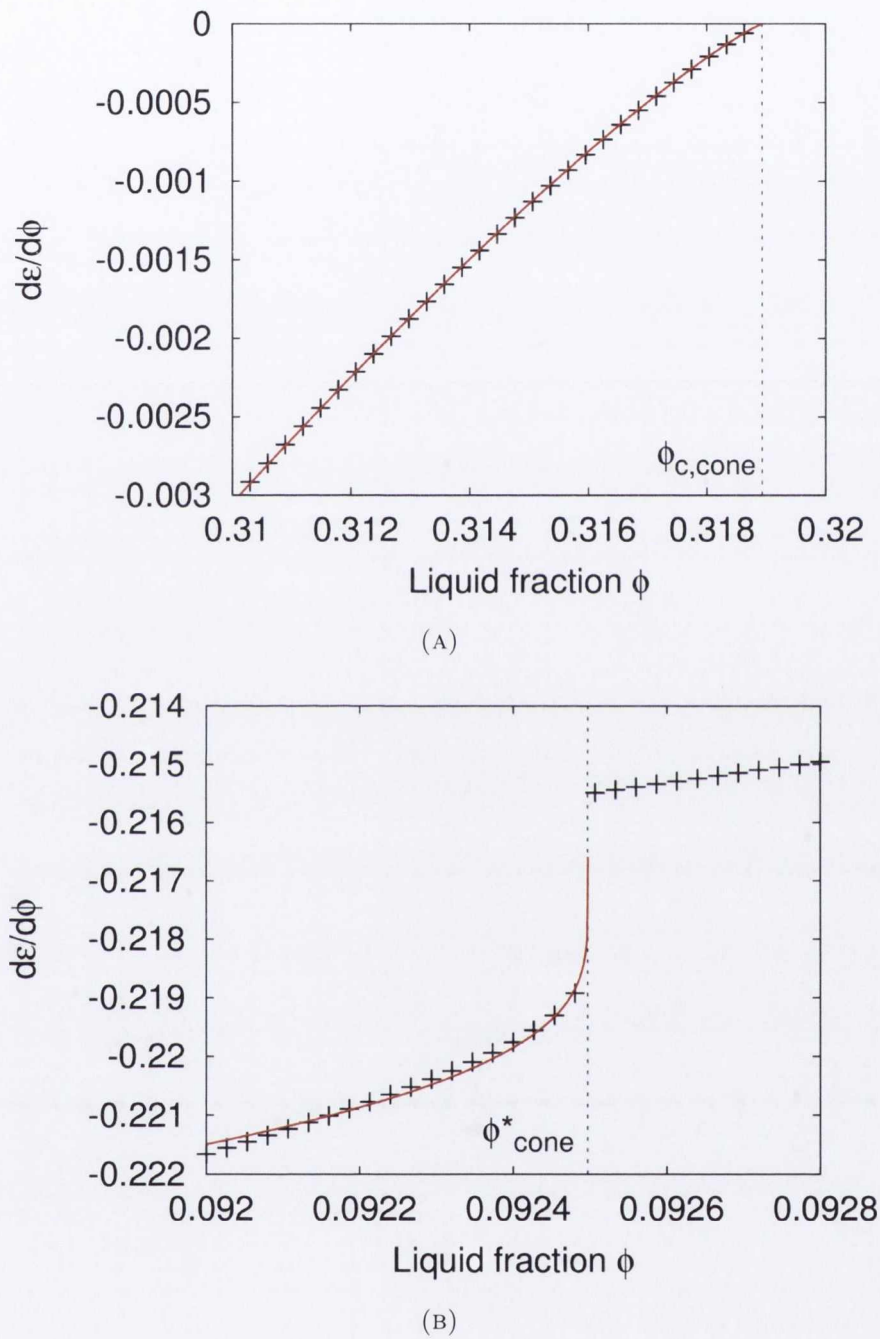


FIGURE 5.4: A closer view of the derivative of the excess energy with respect to liquid fraction near the contact loss points. (a) Near $\phi = \phi_{c,cone}$, the variation of the derivative $\frac{d\varepsilon}{d\phi}$, indicated by the points for the cone model, is well approximated by the form of equation (5.1) which is shown by a continuous line. (b) Near $\phi = \phi^*_{cone}$, the variation is quite different, and is reasonably well approximated by the proposed empirical form of equation (5.2) which is similarly shown with a continuous line.

It has been argued that the limit of mechanical stability of the Kelvin structure was due to the loss of the square faces [49]. A bcc crystal of interacting points is well known to require second-nearest-neighbour interactions to stabilise when simple pairwise potentials are applied. This appeared indeed supported by Phelan *et al.* [23] who found a negative elastic constant at values of $\phi > 0.11$, i.e. close to the value of $\phi = 0.11 \pm 0.005$ that these authors identified for the face loss. New preliminary Surface Evolver calculations suggest that the elastic constant changes sign for ϕ near ϕ^* but this work is in its nascent stages and will be investigated further in future work.

At present, the calculation of such elastic constants with the cone model is limited to the reduced uniaxial modulus $\mu(\phi)$ for simple cases of $Z = 2$ and $Z = 6$ due to their particularly simple symmetries. While the results of these early calculations are in agreement with the results of previous work by both Buzza and Cates [50] and Lacasse *et al.* [27], showing a characteristically logarithmic onset of $\mu(\phi)$ at the point of contact formation, it is not yet clear how to extend this approach to the Kelvin cell. Nonetheless, the sharp contrast in behaviour seen in Figure 5.4 for the excess energies of the different faces, suggests that further analysis of the loss of the square $\langle 100 \rangle$ could show an instability at a liquid fraction slightly lower than ϕ_{cone}^* .

5.3 Conclusions and Outlook

We have made use of the extended the cone model of Chapter 4 to investigate the variation of the excess energy ε with liquid fraction ϕ close to the loss of both the square and hexagonal contacts of the Kelvin cell.

We see two distinct contact losses; the loss of the hexagonal $\langle 111 \rangle$ faces at the wet limit, ϕ_c , and of the square $\langle 100 \rangle$ faces away from the wet limit at ϕ^* , resulting in two distinctly different variations of energy with liquid fraction. Both feature logarithmic terms in the respective derivative of energy with respect to liquid

fraction; only the face loss at ϕ_c can at this stage be analytically understood in terms of the cone model.

Using the cone model, we have also computed the variation of areas of the hexagonal and square faces close to ϕ_c and ϕ^* respectively; numerical noise hinders these calculations using the Surface Evolver.

Chapter 6

Evolution of a bubble on a liquid surface containing one or two gas species

In this chapter, we will be looking at the **shape** of a bubble at a liquid surface using the mathematics of minimal surfaces of revolution, an approach which was also at the heart of the cone model which has been introduced previously. Once again, we shall focus on the theoretical and computational aspects of the problem before utilising these to understand the results of experimental studies. In particular, we aim to model the temporal evolution of a single bubble at a liquid surface, taking account of its detailed shape, for two-component gas mixtures.

Bubbles containing more than one type of gas are increasingly being used in modern experimental foam physics. It has been shown both computationally [51] and experimentally that the addition of a low solubility gas significantly extends the lifetime of the foam [52] by resisting Ostwald ripening or “coarsening” [3]. The addition of perfluorohexane gas (PFH) to bubbles of air or nitrogen is now a standard procedure in foam drainage and rheology experiments [53] that run over several hours.

Despite the growing experimental interest in mixed gas systems for the purpose of inhibiting coarsening (over several days, as in the experiments of Meagher *et al.* [17]), there are a number of observations of **growing** mixed gas bubbles [54], particularly at foam/air interfaces, which have yet to be fully explained [55]. The origin of this behaviour is connected to the addition of relatively insoluble gases, such as PFH, to air in the bubbles [56], as we will show in this chapter.

6.1 Introduction to Surface Bubbles

The shape of a single bubble at a liquid surface consists of two parts which meet in a circular ring of contact with a radius of x_c (see Figure 6.1). In what follows, we will regard the radius x_c as a measure of the bubble size since it is easily measured in experiments. Above the ring of contact, the bubble surface is a spherical cap in contact with the atmosphere while below this ring, the bubble is in contact with the liquid and forms a sessile droplet [57]. The examples shown in Figure 6.1 were computed numerically using a method developed by Princen [57] (for details see Appendix G), for the case of an infinitesimally thin liquid film. In reality, this liquid film has a finite thickness which is a function of both position and time. We chose a numerical approach here due to the difficulty of obtaining analytical solutions for this shape on a liquid surface. For the similar shape of a hemispherical bubble sitting atop a flat substrate with liquid Plateau borders, however, Teixeira *et al.* [58] adduced an approximate analytical solution for the shape of the Plateau borders in the limit of small Plateau border sizes.

In contrast to our discussion of the cone model, the actual bubble size x_c is crucial to our discussions in this chapter. The primary reason for this is that a bubble at the surface of a liquid is subject to the opposing forces of surface tension, which tries to draw liquid out of the bulk (effectively pushing the bubble down), and inertial forces (gravity) which cause the bubble to effectively rise out of the liquid; the interplay between these two forces determines the position of the ring of contact [2] and so the overall shape of the bubble.

The balancing of these two forces defines a length scale, known as the capillary length l_0 (see Chapter 1), which demarcates the bubble size regimes for which gravity or surface tension is the dominant force. Accordingly, the capillary length l_0 is represented by the formula

$$l_0 = \sqrt{\frac{\sigma}{\Delta\rho g}} \quad (6.1)$$

where σ represents surface tension, $\Delta\rho$ the difference in density between the liquid and gas phases and g is the acceleration due to gravity. Bubbles which are much smaller than the capillary length become gradually submerged below the liquid surface, as shown in Figure 6.1, while bubbles much larger than the capillary length are almost hemispherical. The capillary length for the commercially available detergent *Fairy Liquid*, which we use in the experiments detailed in Section 6.5 below, is $l_0 \approx 1.693\text{mm}$ [2, 59], which is fairly typical for the surfactants used in foam experiments.

Thus far we have discussed how the shape of a bubble at a liquid surface depends upon the size of the bubble. However, we have yet to comment on the mechanism by which a surface bubble evolves in time, i.e. by diffusion, or the role played by the gas composition. We pick up both of these threads in the next section which will be an introduction to diffusion in bubbles.

6.2 Diffusion in Gas Mixtures

In Chapter 1 (see Section 1.1), we noted that **coarsening** is the name given to the process of gas diffusion between neighbouring bubbles in a foam [2]; a general consequence of which is that relatively large bubbles get larger and relatively small bubbles get smaller over time. The treatment of this subject in the foams community often focusses on average bubble quantities for bulk foams. For example, it is found that the average bubble radius grows with time with a power law exponent dependent on the liquid fraction ϕ of the foam [60]. For dry foams, the

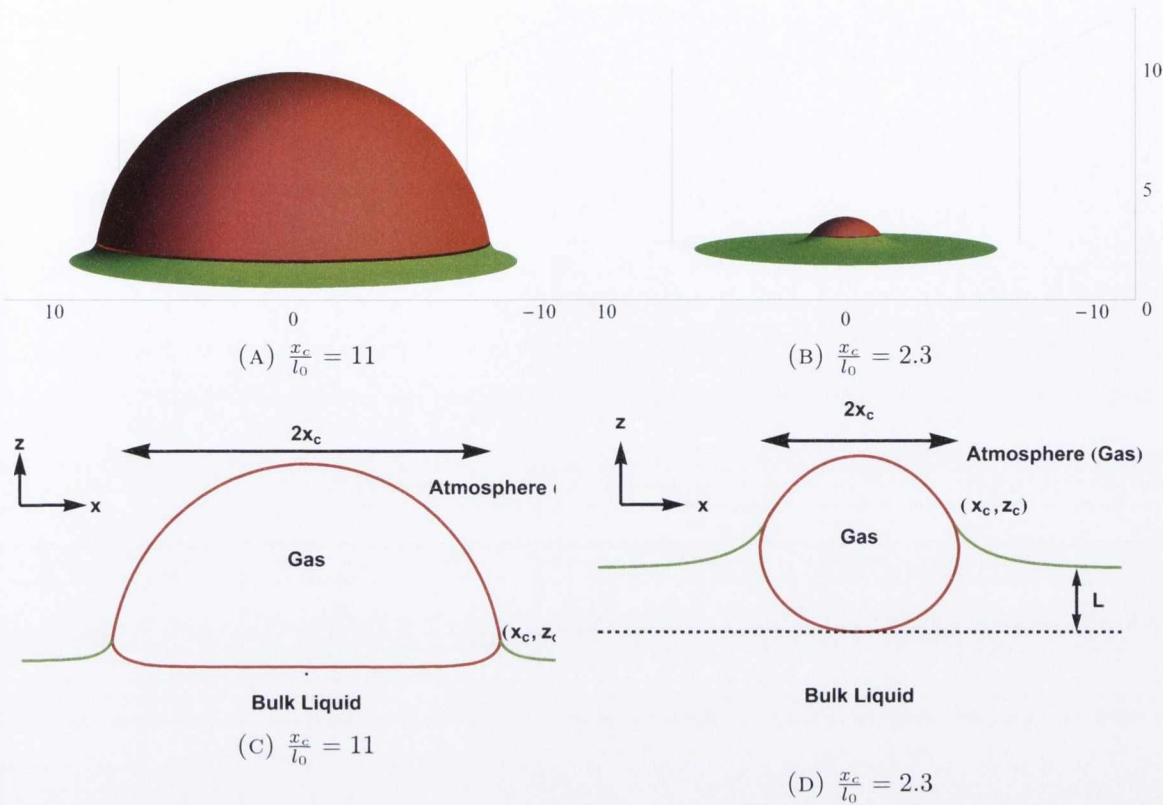


FIGURE 6.1: Exemplary calculations of the shape of a bubble on a liquid surface. (a) Bubbles much larger than the capillary length l_0 are roughly hemispherical while (b) bubbles whose size x_c is close to or below the capillary length take on more complicated shapes as they are partially submerged beneath the liquid surface. The extent of the spherical cap is shown in red while the liquid surface is shown in green. 2D cross-sections of the bubbles shown in (a) and (b) are shown in (c) and (d). (x_c, z_c) marks the ring of contact (see above) separating the spherical cap in contact with the atmosphere from the rest of the bubble. This is also the point where the liquid tail (marked in green) meets the spherical cap of width $2x_c$. L indicates the height of the liquid surface above the bottom of the bubble far from the edge of the bubble (i.e when the surface becomes flat).

average bubble radius is found to grow as $t^{1/2}$ while for wet foams, the exponent law changes to $1/3$ [61]. The introduction of insoluble gases is known to inhibit coarsening and so we focus on the diffusion characteristics of a single bubble to better understand the effect of using mixtures of gases.

Under the influence of a concentration or pressure gradient, a soap film acts as a permeable membrane, with a permeability coefficient k , allowing gas to diffuse across it. The gas pressure p_g in a bubble is higher than the atmospheric pressure P_0 (see Section 1.2) by an amount $\Delta p = p_g - P_0 = \frac{4\sigma}{R_c}$ where R_c is the radius of

curvature of the thin liquid film. This creates a pressure gradient across the surface of the bubble. Considering the soap film as a pair of surfactant layers separated by bulk liquid, it has been both proposed theoretically and observed experimentally that the permeability coefficient of the film is inversely proportional to its thickness for thick films [59, 62]. One such theoretical expression, forwarded by Princen and Mason, illustrates this point:

$$k = \frac{DH}{h_f + \frac{D}{k_{ml}}}, \quad (6.2)$$

where h_f is the film thickness, D is the diffusion coefficient of the gas, k_{ml} is the monolayer permeability and H is gas solubility. For very thin films, the permeability is controlled by the permeability of the surfactant monolayers. The permeability coefficient depends linearly on the solubility of the gas and the diffusion coefficient of the film. Also of note is that the dependence of k on the diffusion coefficient drop out if $D/k_{ml} \gg h_f$.

Diffusion through the film into the atmosphere is not the only possible diffusion mechanism for a bubble floating at a liquid surface. Gas can be exchanged with the liquid at a rate which depends upon the gas saturation level in the liquid [63]. For example, an oversaturation of gas in the liquid manifests itself as an effective overpressure in the liquid, creating a gas pressure difference between the bubble and the surrounding liquid which tends to drive gas from the liquid into the bubble. This is also known as outgassing [2, 3]. It is also possible for some gas to diffuse into the bubble from the atmosphere due to local differences in the gas concentration.

Given all of the potential processes associated with even the simplest case of a single bubble floating at a liquid surface, we are forced to make a number of simplifications to arrive at a tractable model for bubble evolution. We shall treat the permeability coefficient as a constant for each of the gases in our bubble (thus also fixing the solubilities). To do this, uniform and constant thickness in the thin film of the bubble is assumed, as is the case with experiments in which the bubble

is left to drain for twenty-four hours before measuring its permeability [3, 59]. In consideration of the bubble shape, the film is taken to be infinitesimally thin so that the radius of the ring of contact x_c can be well-defined. It then must also be assumed that the liquid is sufficiently saturated with the gases under constant temperature, to ensure that there is no net exchange of gases between the bubble and the liquid.

In making these assumptions, we can begin to build a theoretical understanding of the importance the diffusion of different gases has on the evolution of a bubble on a liquid surface. In particular, how the bubble in question develops depending on certain factors (size, capillary length, etc.) in two distinct cases:

1. **Case One:** We consider a bubble which contains a single, soluble gas that is identical to the gas in the surrounding atmosphere, albeit at a different pressure. We treat the corresponding permeability coefficient as constant in time and denote it as k_B .
2. **Case Two:** We consider a bubble which contains a mixture of two gases; one of which has the same properties as in Case One above. The second gas present is a low solubility or non-diffusive gas, which is not present in the surrounding atmosphere and has a permeability coefficient denoted by the symbol k_A . We will consider two instances in this case: one in which $k_A = 0$ which corresponds to a perfectly non-diffusing or insoluble gas and also the more realistic case of a low solubility gas where $k_A \ll k_B$.

This process of gas diffusion can be effectively modelled via Fick's First Law [59] which for a single gas, as in Case One, gives the change in the bubble volume ΔV in time Δt as

$$-\Delta V = \frac{k_B A_c \Delta p}{P_0} \Delta t, \quad (6.3)$$

where A_c is the surface area of permeation, Δp the pressure difference across the surface of the bubble and k_B is the permeability coefficient of the gas. As the total pressure difference Δp is always positive, the bubble volume **shrinks** over time

with a power law of $t^{\frac{1}{2}}$ [64, 65], as was observed previously by others, in particular Princen and Mason [59]. We will return to the discussion of this in later sections.

In the case of mixtures of gases, the situation is more complicated. Dalton's Law of partial pressure states that the total pressure in a mixture of (ideal) gases is equal to the sum of the **partial pressures** of each of the individual gases in the mixture [51]. For a mixture of ideal gases, as in Case Two (here denoted A and B), of differing permeabilities k_A and k_B we must consider not the total pressure difference in Fick's Law, but the partial pressure differences for each component of the mixture. The partial pressure of a gas in a mixture is the pressure that the gas would have if it occupied the volume of the entire mixture [51]. Mathematically, it is defined as

$$p_i = \frac{V_i}{V_{tot}} p_{tot} = x_i p_{tot} \quad (6.4)$$

where V_i is the volume of one of the component gases, V_{tot} is the total volume of the mixture (i.e. the bubble volume). The volume fraction x_i can also be thought of as the mole fraction of each gas component for gases which are similar in molecular size. With this definition for the partial pressure, the appropriate version of Fick's Law of Diffusion for a mixture of gases [59] is given by the formula

$$\begin{aligned} -\Delta V &= \sum_i^2 \frac{k_i A_c}{P_0} \Delta p_i \Delta t \\ &= A_c \Delta t \left\{ k_A \frac{(p_A - \bar{p}_A)}{P_0} + k_B \frac{(p_B - \bar{p}_B)}{P_0} \right\} \end{aligned} \quad (6.5)$$

where the barred quantities denote properties of the atmosphere (see Figure 6.1).

Comparing this expression to equation (6.3), we see that the introduction of partial pressures allows for a richer bubble evolution process than is the case for a single gas. In addition to the shrinking evident in single gas bubbles, a mixed gas bubble

may **grow** in time depending on the permeabilities k_A , k_B of the two gases and the partial pressure differences of the two gases.

The criterion which demarcates the boundary between growing and shrinking behaviour for these bubbles is obtained by considering $\Delta V = 0$ in equation (6.5). Furthermore, for the simplest case of a single bubble open to the atmosphere, we have derived a simple analytic expression (see Appendix H) for this boundary between growing and shrinking behaviour given by

$$\frac{k_A}{k_B} = 1 + \frac{1}{x_A^*} \left(\frac{P_0}{P_0 + \frac{4\sigma}{R_c}} - 1 \right). \quad (6.6)$$

Equation (6.6) expresses the fact that for any mixture of gases with a fixed ratio of permeabilities $\frac{k_A}{k_B}$ and for any bubble size R_c , there is a critical concentration x_A^* of gas A for which the bubble **neither grows nor shrinks**. This is illustrated for different bubble sizes in Figure 6.2. If the permeability of gases A and B is similar (such as nitrogen and oxygen in air) and the concentration of A is low, then the bubble is likely to shrink. However, for mixtures of PFH and air, a common mixture for inhibiting coarsening, where the permeabilities differ by orders of magnitude [66], the bubble will grow in time.

It is important to mention here that equation (6.6) (and hence Figure 6.2) is derived for a surrounding atmosphere which is “**very large**” and initially contains only gas B (see Appendix H for the full derivation). By very large, we mean that the volume of gas A which diffuses from the bubble into the atmosphere does not noticeably change the concentration of this gas A in the atmosphere. In an experiment, this will only ever be an approximation and so Figure 6.2 serves primarily as a very good qualitative description for the behaviour of a bubble of a given size (see equation (H.4) for the general form of equation (6.6) applicable to experimental systems).

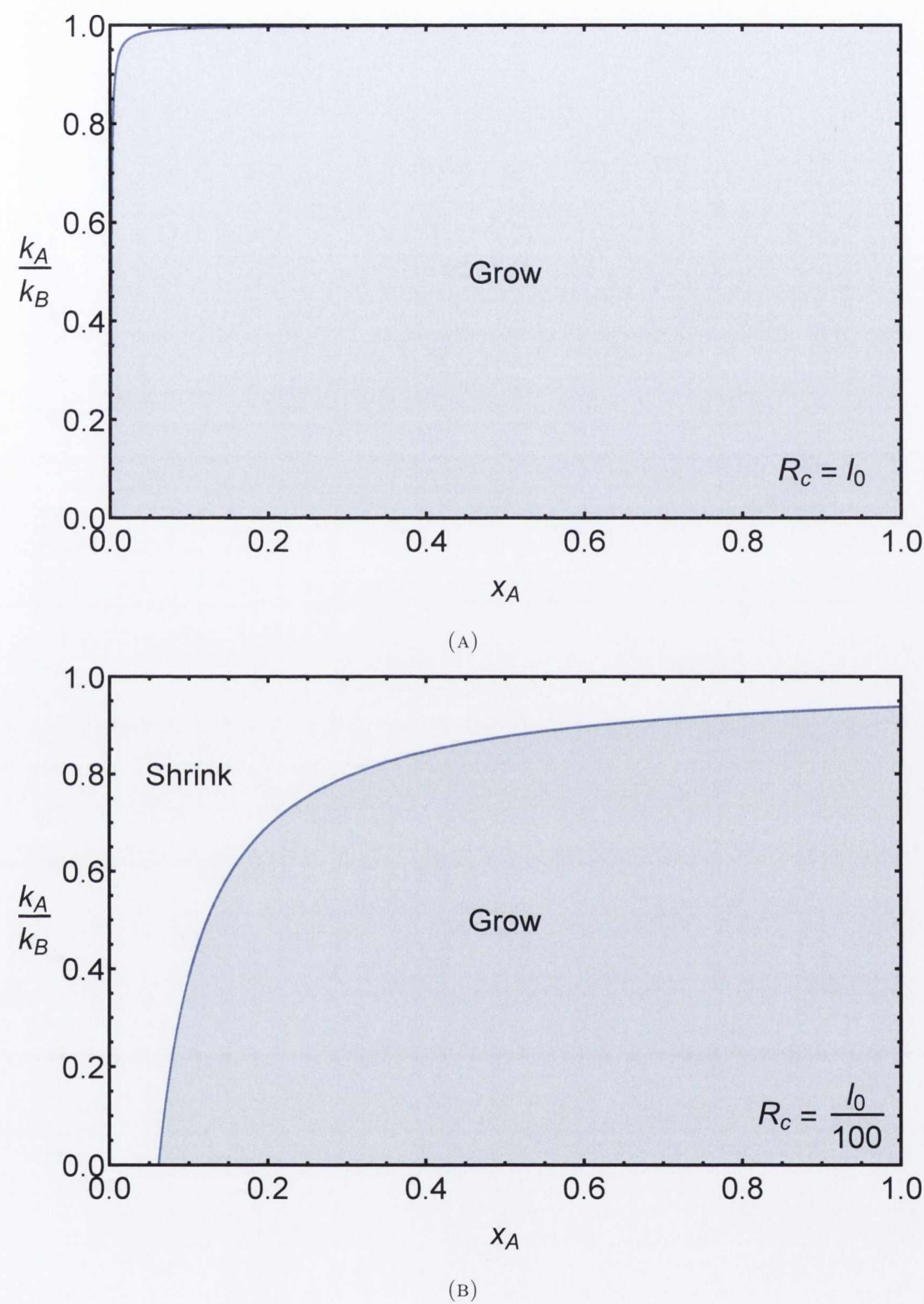


FIGURE 6.2: Phase plots of the ratio of permeabilities $\frac{k_A}{k_B}$ versus relative concentration of gas x_A for mixed gas surface bubbles at different length scales showing regions where the bubbles are expected to grow and shrink, from equation (6.6). The radius of curvature of the bubble films R_c is similar to x_c (see Appendix G) and included here as an indication of the bubble size.

Finally, we should note that we can equally well consider the critical concentration x_B^* of the second gas B in the mixture since volume conservation requires that

$$x_A + x_B = 1. \quad (6.7)$$

6.3 Simulations of the Evolution of a Single Bubble

Examining both cases described above, we will describe simulations of growing and shrinking bubbles at a liquid surface, taking into account the precise shape of the bubble. As seen in Figure 6.1, x_c is a suitable proxy for the bubble size since it is most readily measured in an experiment by photographing from above. The results of our simulation are expressed in the dimensionless quantities $\frac{x_c}{l_0}$ and $\frac{t}{\left(\frac{l_0}{k_B}\right)}$ for bubble size as a function of time. For the computation of this volume-dependent shape, an algorithm is used that was originally proposed by Princen [64]. This algorithm enables the calculation of the precise shape of the bubble as a function of time, achieved by numerical integration of a set of three coupled, ordinary differential equations describing the boundary of the bubble (see Appendix G for further details of the algorithm).

6.3.1 Case One: Simulation Results for the Shrinking Bubble

In Case One, we examine a bubble of size x_c that is initially much larger than the capillary length and contains a single, soluble gas of permeability k_B , for example nitrogen (N_2).

The volume change at each time step is calculated as a function of time from the discrete form of Fick's First Law, equation (6.3), which we introduced in Section

6.2. The contact area of permeation A_c and the pressure difference Δp are updated at each timestep.

In this case, the pressure difference is simply

$$\Delta p = \frac{4\sigma}{R_c}. \quad (6.8)$$

Figure 6.3 shows the shrinkage of the bubble size x_c as a function of time. The guiding line, shown in dashed red, indicates a power law scaling behaviour of the bubble size x_c of

$$x_c^2(t) - x_c^2(0) \propto -(t - t_0) \quad (6.9)$$

for bubbles much larger than the capillary length, as has been previously observed experimentally [65]. The near hemispherical shape of large bubbles (Figure 6.1) is at the heart of such scaling as will be demonstrated in Section 6.4.1.

It is notable that, as it comes close to the capillary length, the scaling of $x_c(t)$ breaks down due to the decrease in bubble size x_c which is accompanied by a significant deviation of the shape from a hemisphere.

Given that a bubble with a single soluble gas shrinks, it is natural to wonder where this case fits into the overall picture of growing and shrinking bubbles represented by the phase plots of Figure 6.2.

In simplest terms, the case of a single soluble gas bubble is equivalent to a mixture for which $\frac{k_A}{k_B} = 1$. Thought of in this way, it is clear that the concentration x_A is equal to zero and we can identify the single gas bubble as occupying a point at the top left corner in the phase plots of Figure 6.2. Despite the fact that the region denoting shrinking behaviour is significantly reduced for larger and larger bubbles, the top left corner will always be contained in this region and so we see that such bubbles will always shrink, irrespective of the bubble size.

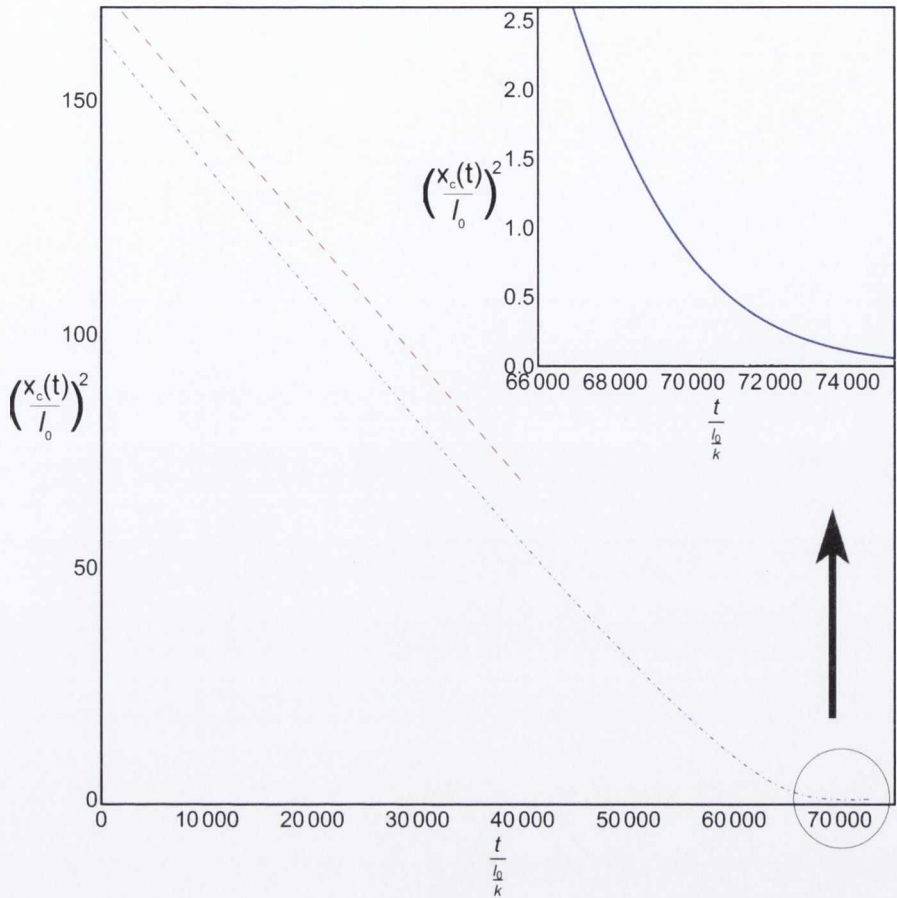


FIGURE 6.3: Computation of the time dependence of bubble size x_c for a single gas bubble, with a permeability coefficient k_B , on a liquid surface. The dot-dashed line shows the simulation data for $x_c(t)$. The red dashed line is a guide to the eye indicating the slope of the scaling $x_c^2(t) - x_c^2(0) \propto -(t - t_0)$, consistent with previous studies [65]. The inset shows the strong deviations from this scaling law for $x_c \lesssim 7l_0$.

6.3.2 Case Two: Simulation Results for the Growing Bubble

We move now to examining Case Two in which the single gas of permeability k_B (soluble) is mixed with a second gas with a different permeability k_A (insoluble).

The volume change at each time step is calculated in this case from Fick’s Law for mixtures, equation (6.5), and again, as for Case One, the contact area of permeation A_c and the partial pressure differences $\Delta p_A = p_A - \bar{p}_A$ and $\Delta p_B = p_B - \bar{p}_B$ are updated at each time step.

It is clear from Figure 6.2 that the evolution characteristics of this mixture will be more varied than the universal shrinking we observed for Case One above. The evolution of the bubble in this case will depend upon three important factors; the ratio of permeabilities $\frac{k_A}{k_B}$, the concentration x_A and the shape of the bubble, which is intrinsically linked to the bubble size x_c . In light of this, we considered a number of different scenarios; each one tailored to emphasise the effect of one of these factors.

6.3.2.1 The Effect of Shape

As we intimated in the introduction to this chapter, a key goal of this work is to identify the role of the shape of the bubble in the evolution of mixed gas bubbles. To achieve this, we simulated a bubble containing a mixture of gases with $k_A = 0$, $x_A = 0.89$ and an initial size $x_c(0)$ of one half the capillary length.

In this case, our simulation begins in the bottom right hand corner of the phase plot for this bubble size. In this scenario the partial pressure difference dominates over the Laplace pressure difference and so we expect the bubble to grow in time.

Figure 6.4 shows the evolution of radius $x_c(t)$ as a function of time in this case and we see that indeed the bubble grows in time. The evolution of x_c appears to reach a different power law scaling state to that of the shrinking gas, when it is much larger than the capillary length. Indeed, the guiding line in this case is a power law of $t^{\frac{1}{4}}$ (see Section 6.4). As with the shrinking bubble, the scaling state does not hold for small bubbles, $x_c \leq 10l_0$.

It is clear that the existence of a power law scaling in the case of a single bubble at a liquid surface is independent of the gas it contains. The determining factor is the size of the bubble relative to the capillary length l_0 .

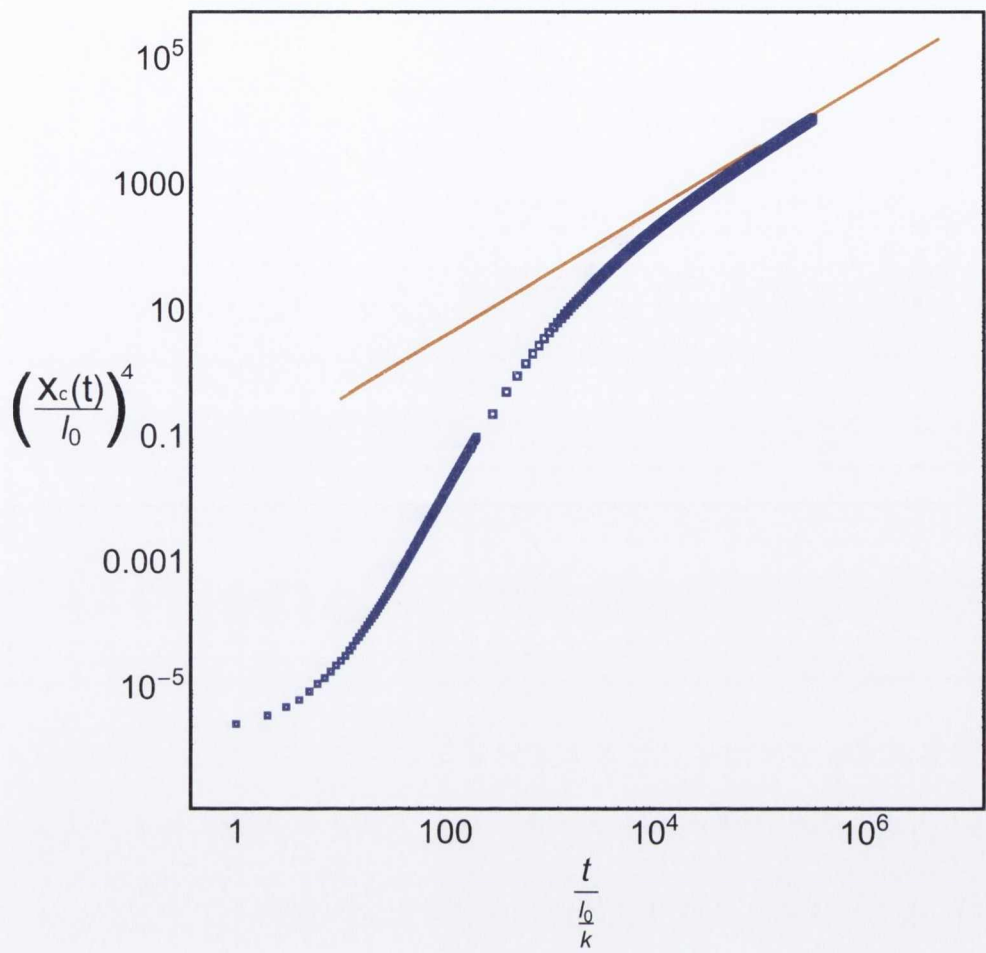


FIGURE 6.4: The time dependence of radius $x_c(t)$ for a growing bubble (as specified in the text) on a liquid surface. The (blue) squares represent $x_c(t)$ while the solid (orange) line represents has slope 1 and thus represents a power law scaling of $t^{\frac{1}{4}}$. The origins of this power law scaling are investigated below.

A bubble much larger than the capillary length assumes a roughly hemispherical shape which remains self-similar as the size increases and it is this self-similarity which causes the bubble to evolve in time with a power law scaling relationship.

Bubbles comparable in size to the capillary length have a much more complicated shape which continuously changes as the bubble is gradually submerged beneath the liquid surface. Thus, the power law evolution is not evident at small bubble sizes.

6.3.2.2 The Effect of Permeability: $k_A \ll k_B$

We showed in the previous section that the hemispherical shape of surface bubbles much larger than the capillary length l_0 gives rise to a clear power law scaling behaviour with time. However, the choice of our initial conditions, in particular the choice of $k_A = 0$, represent a special case.

In real experimental systems (see Section 6.5), it is not always possible to ignore the relatively small, yet non-zero, permeability coefficient k_A of the low solubility gas component. Previous studies [66, 67] have shown that the permeability coefficients of many of the common anti-coarsening hydrocarbon mixtures (e.g. perfluorocarbons) are only 1 – 3 orders of magnitude smaller than that of air (containing mostly nitrogen). In particular, Sarkar et al. [66] reported a value for the permeability coefficient of PFH of $k_{\text{PFH}} \approx \frac{k_{N_2}}{20}$.

To investigate the effect of permeability on bubble evolution, we considered again a bubble with the same initial size and concentration as in Section 6.3.2.1. In this case, however, we replaced the permeability condition $k_A = 0$ for the insoluble gas component with a more realistic value of $k_A = \frac{k_B}{20}$.

In this simulation the volume change of our bubble, calculated using equation (6.5), is again dominated by the partial pressures differences of the component gases. Unlike for the case of $k_A = 0$, both of the terms in equation (6.5) are non-zero. Thus, the time evolution of our bubble is then a competition of the two diffusion processes; one which draws gas B in, causing the bubble to grow, and a second, slower process which drives our low solubility gas, of permeability $k_A \ll k_B$, out of the bubble. The results of the simulations are shown in Figure 6.5, which

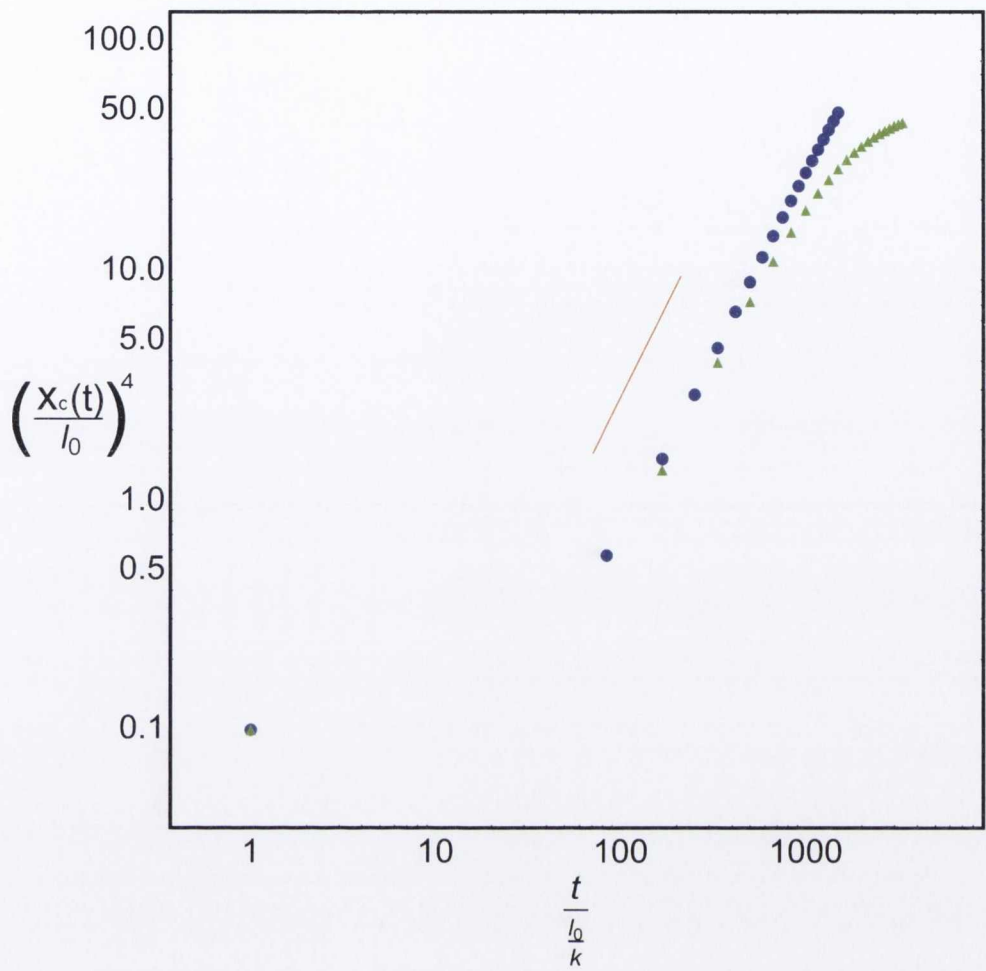


FIGURE 6.5: Simulated evolution of a bubble of radius x_c containing a mixture of gases with $k_A \ll k_B$. The circles represents the case of $k_A = 0$, as in Figure 6.4, while the triangles are for a $k_A = \frac{k_B}{20}$. Treating $k_A \neq 0$ has the effect of slowing the bubble growth compared to the case $k_A = 0$. The orange line is a guide to the eye and corresponds to a power law (over a limited range) with a higher exponent of 0.32, compared to the exponent of 0.25 for the case $k_A = 0$.

compares the growth of a bubble with a finite value of $k_A = \frac{k_B}{20}$ to that with $k_A = 0$. It is clear that this has a qualitative effect on the evolution of the bubble.

Firstly, although the bubble still grows in time, this happens at a slower rate than for the case $k_A = 0$. Secondly, the bubble does not grow to be as large as in the insoluble case and indeed appears to asymptotically approach a limiting size. As the volume of the bubble increases, the partial pressure difference of the gases in the bubble approaches equilibrium more gradually and the effect of the finite solubility of gas A is observed. If the partial pressure differences become small

enough, the effect of the insoluble gas A leaving the bubble becomes more evident. As a result, the bubble does not reach the size regime in which a power law can be clearly identified.

Having shown that including a finite permeability for the insoluble gas component in a mixture slows the growth of a bubble at a liquid surface, we wish to investigate whether, under suitable conditions, we can expect such a bubble to stop growing and for the bubble to begin shrinking.

To investigate this possibility, we again altered our simulation of a bubble at a liquid surface containing a mixture of gases. In this case, we again considered $k_A = \frac{k_B}{20}$ but significantly reduced our initial concentration $x_A = 0.15$ and reduced the initial bubble size to $x_c(0) \sim \frac{l_0}{5}$. The choice of these initial conditions ensures that our simulation begins close to the boundary between growing and shrinking behaviour (see Figure 6.2) ensuring that a switch from growing to shrinking behaviour would occur in a reasonable time. The results of this simulation are shown in Figure 6.6.

Figure 6.6(a) shows the evolution of the bubble size $x_c(t)$ as a function of time in this case. We see that the bubble initially grows in time under the influence of partial pressure differences, similarly to Figures 6.4 and 6.5. However, the finite permeability of the gases leads to a slowing of this growth and indeed, for longer times, the bubble begins to shrink in time. At the maximum of this curve, the partial pressure differences are no longer dominant over the Laplace pressure differences and the bubble passes from a growing regime to a shrinking regime (see Figure 6.2).

Figure 6.6(b) shows the corresponding evolution of the concentration $x_A(t)$ with time. We observe that the concentration of gas A decreases as the evolution of the bubble proceeds; steeply decreasing initially before levelling out. This behaviour is directly linked to the transition from a growing bubble regime to a shrinking regime, as can be seen from Figure 6.6(c). We observe that the maximum value of the bubble size x_c occurs around $x_A = 0.02$, at a time $t/(l_0/k) = 10$ approximately halfway through the simulation. Below this concentration, the slope of the curve is

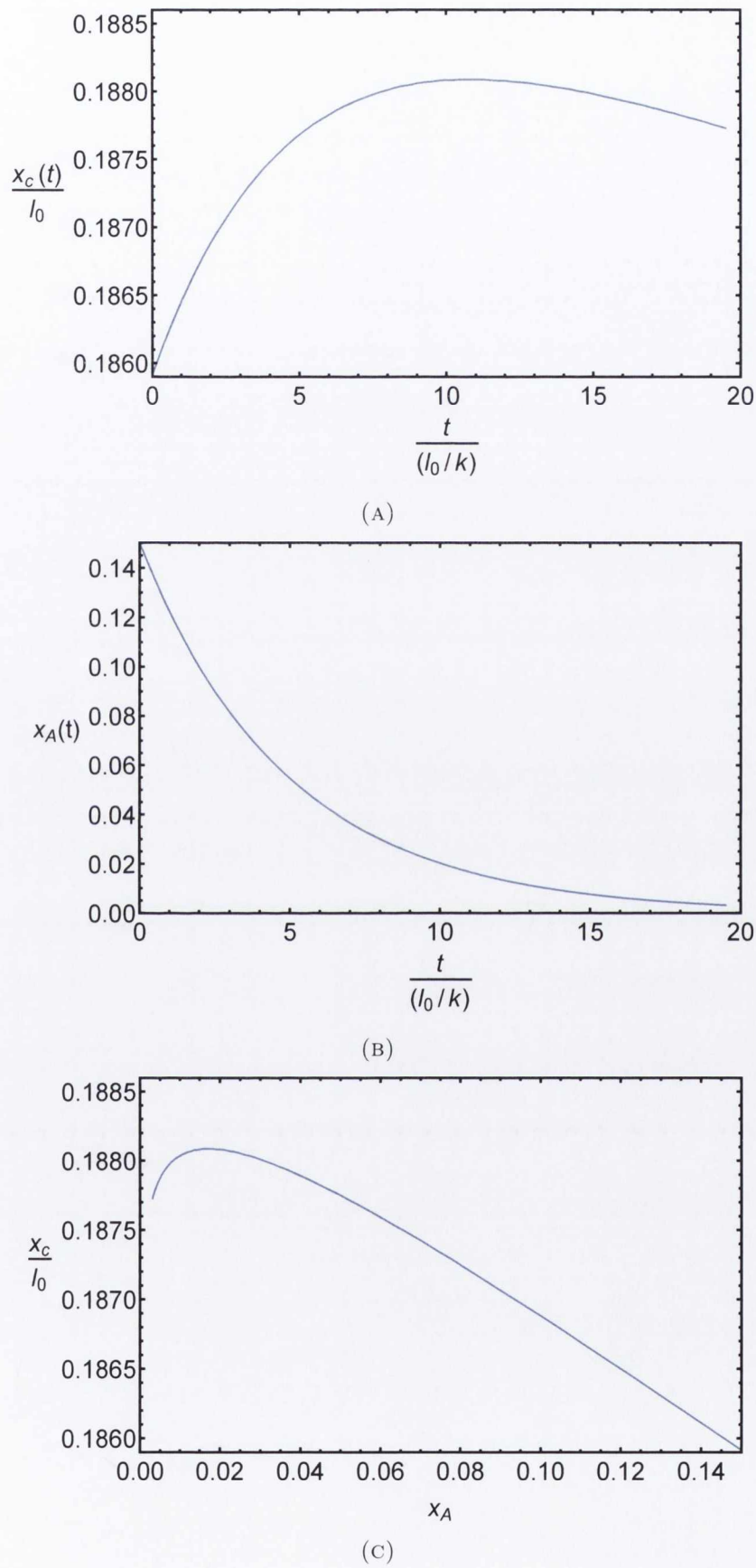


FIGURE 6.6: (a) Time dependence of a bubble smaller than the capillary length l_0 containing a mixture of gases with initial concentration $x_A = 0.15$ and $\frac{k_A}{k_B} = \frac{1}{20}$. (b) The corresponding time dependence of the concentration x_A . (c) Plot of the bubble size versus the concentration x_A . The bubble grows for a time under the influence of partial pressures before the Laplace pressure becomes the dominant driver of the diffusion. At this point, the bubble begins to shrink. This corresponds to crossing from one region to another in Figure 6.2.

steeper (i.e. once the bubble shrinks) indicating that the changes in x_A with time become progressively smaller. However, even as the bubble shrinks the change in concentration remains negative which indicates that once the bubble crosses from a growing regime to a shrinking regime, it remains in this regime thereafter.

In experiment, it is common practice to enclose the entire system within a finite box to limit extraneous experimental effects (e.g. evaporation) [65]. The volume of this reservoir will decrease over time as the bubble grows, providing a mechanism for equalisation of the partial pressure differences over very long times. However, this occurs over a significantly longer time than considered in this work and so we neglect this effect in our analysis.

6.4 Simple Scaling Models for the Evolution of Ideal, Hemispherical Gas Bubbles Due to Pressure-induced Gas Diffusion

Bubbles for which the bubble size x_c greatly exceeds the capillary length are well approximated by a hemispherical shape of radius $R_c = x_c$. In this case, it is straightforward to compute the evolution of bubble size with time analytically, based on an integration of Fick's Law (see equations (6.3) and (6.5)), together with the appropriate expression for the pressure differences. In the following, we will show how this reproduces the scaling laws found in our simulations for large bubbles and shown in Figures 6.3 and 6.4 for shrinking and growing bubbles, respectively.

6.4.1 Case One: Permeability k_B

For a hemispherical bubble of radius $x_c = R_c$ on a flat surface (or equally a free spherical bubble), we have the Laplace law $\Delta p = \frac{4\sigma}{R_c}$, $A_c = 2\pi R_c^2$ and $V = \frac{2}{3}\pi R_c^3$ where σ is the surface tension of the liquid films. Inserting these into Fick's

equation (6.3) with $R_c(t_0) = R_0$ and integrating we readily obtain

$$R_c(t)^2 = R_0^2 - \frac{8\sigma k_B}{P_0}(t - t_0). \quad (6.10)$$

This is indeed the scaling behaviour that we found in our simulations of large shrinking bubbles in section 6.3.1, Figure 6.3.

6.4.2 Case Two: Permeabilities $k_B \neq 0$ and $k_A = 0$

Next, we consider the case of a hemispherical bubble on a flat surface containing two gases with k_B and $k_A \ll k_B$, respectively.

For a hemispherical bubble we have, again, $A_c = 2\pi R_c^2$ and $V = \frac{2}{3}\pi R_c^3$. Taking the dominant pressure difference to be due to partial pressure, inserting into (6.5) and integrating leads to

$$R_c(t)^4 = R_0^4 + \frac{6k_B V_A}{\pi}(t - t_0), \quad (6.11)$$

where V_A is the volume of gas B in the bubble.

This is indeed the scaling law for large bubbles as found in our simulations (see Figure 6.4). A more detailed derivation for both of these power laws is given in Appendix H.

6.5 Experimental Procedure and Results

In addition to the theoretical and simulation studies described above, experimental studies were carried out by A. Meagher to illustrate the growth law of a single, stabilised bubble at a liquid surface containing a mixture of nitrogen gas (N_2) and the compound perfluorohexane (PFH)[66].

A petri-dish was filled with this solution until an inverted meniscus was formed. This meniscus enables the accumulation of floating bubbles at the center of the dish, rather than along its boundary, allowing for accurate imaging. The petri dish was lit from below using a planar backlight and imaged from above using a CCD camera.

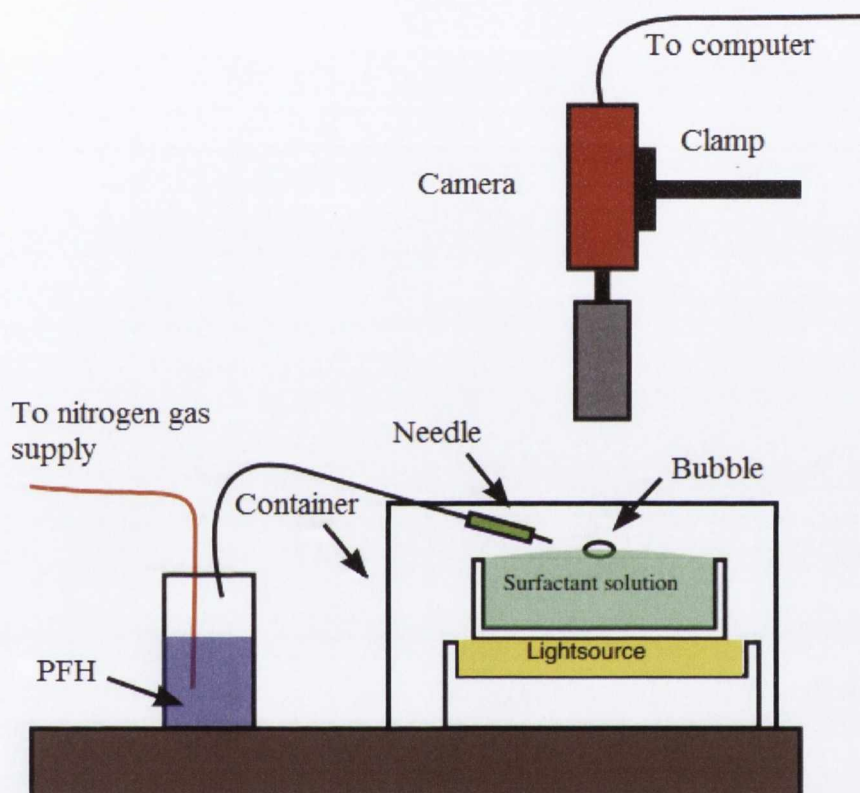


FIGURE 6.7: Experimental setup for analysing the evolution of a single bubble composed of a mixed gas.

Oxygen-free nitrogen gas was blown through a solution of 98% pure PFH, producing a two-component gas phase in the bubble. Single bubbles were then formed by injecting the resulting gas slowly into the solution of the Petri-dish using a 0.4 mm diameter needle. To increase the lifetime of the bubbles, a clear container was placed over the Petri-dish. This limited evaporation from the surface of the bubble, allowing for the production of bubbles which are stable for several hours. The bubble was then imaged every minute for the lifetime of the bubble.

Using *ImageJ* [68], the experimental images were binarised and the resulting bubble diameter (measured as twice x_c) determined using the watershed transformation [68, 69]. Due to internal reflection within the bubble bulk, a 10 % reduction was taken into account for the measured values of the bubble size x_c [69]. Typical expansion data for a single bubble is shown in Figure 6.8.

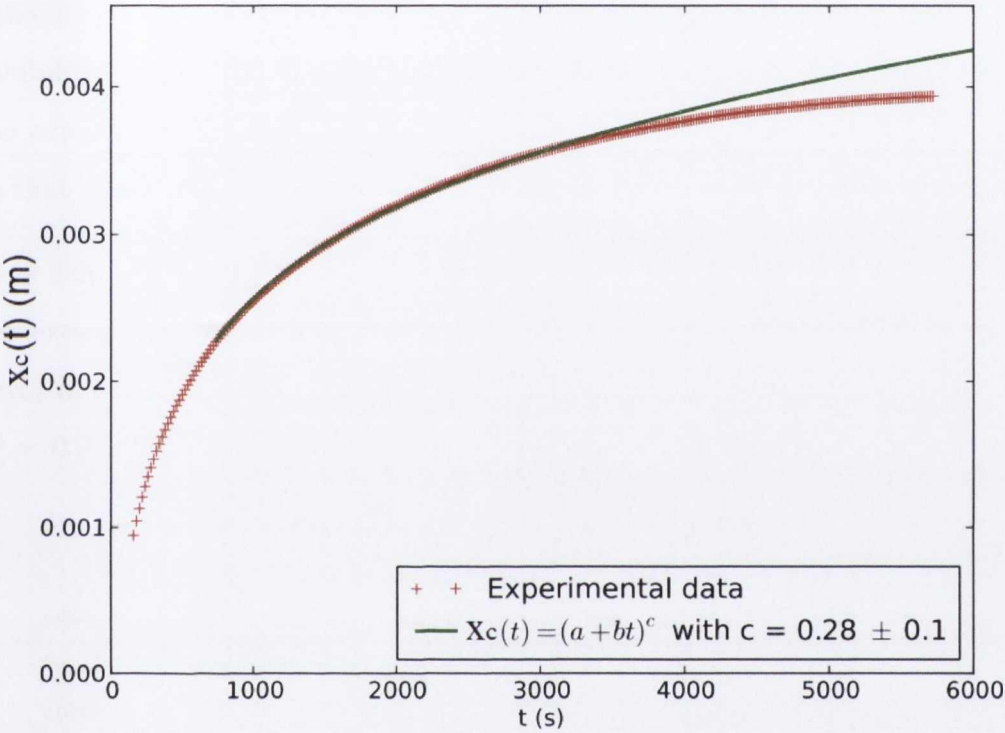


FIGURE 6.8: Evolution of the bubble size x_c with time t . The data was fitted between 580s where $x_c \approx l_0$ and 3500s using the function $x_c(t) = (a + bt)^c$, with a calculated exponent of $c = 0.28 \pm 0.01$. Deviations from this power-law fit are seen at longer times.

The smooth growth of the bubble was tracked for over an hour. During this time, it was found the bubble size x_c increased by a factor of 4. Fitted to the experimental data was an equation of the form $x_c(t) = (a + bt)^c$ in order to determine the validity of the theoretical prediction as seen in equation (6.11).

Figure 6.8 shows the result of one such experiment. It was found that the growth of the bubble size x_c was well approximated by a power law with an exponent of $c = 0.28 \pm 0.01$ in the limited range 580s to 3500s, slightly exceeding the ideal case of $c = 0.25$. In the mean of seven experiments, where the lifetime of the bubble

was less than one hour, an average exponent of $c = 0.3 \pm 0.04$ was found. Note that this is similar to the simulations of Case Two (see Figure 6.5) where a higher effective exponent of $c = 0.32 \pm 0.01$ was fitted for bubbles in the same size range as the above experimental data, consistent with the fact that our experimental bubbles do not grow large enough to reach the scaling regime where $c = 0.25$.

A clear divergence from scaling behaviour is seen at large timescales. The divergent behaviour at longer times, shown in Figure 6.8, is primarily due to the finite solubility (or equivalently permeability) of the PFH gas, leading to a reduction in the expansion rate of the bubble as this gas diffuses into the environment similar to that observed for our simulations of Case Two (i.e. $k_A \ll k_B$) in Figure 6.5.

This can be further demonstrated by the strong qualitative agreement between the experimental data and simulations of a finitely soluble PFH gas (i.e. Case Two) in Figure 6.9 for an initial concentration of $x_A = 0.89$, $k_B = 0.28 * 10^{-5}$ and $\frac{k_A}{k_B} = 0.04$.

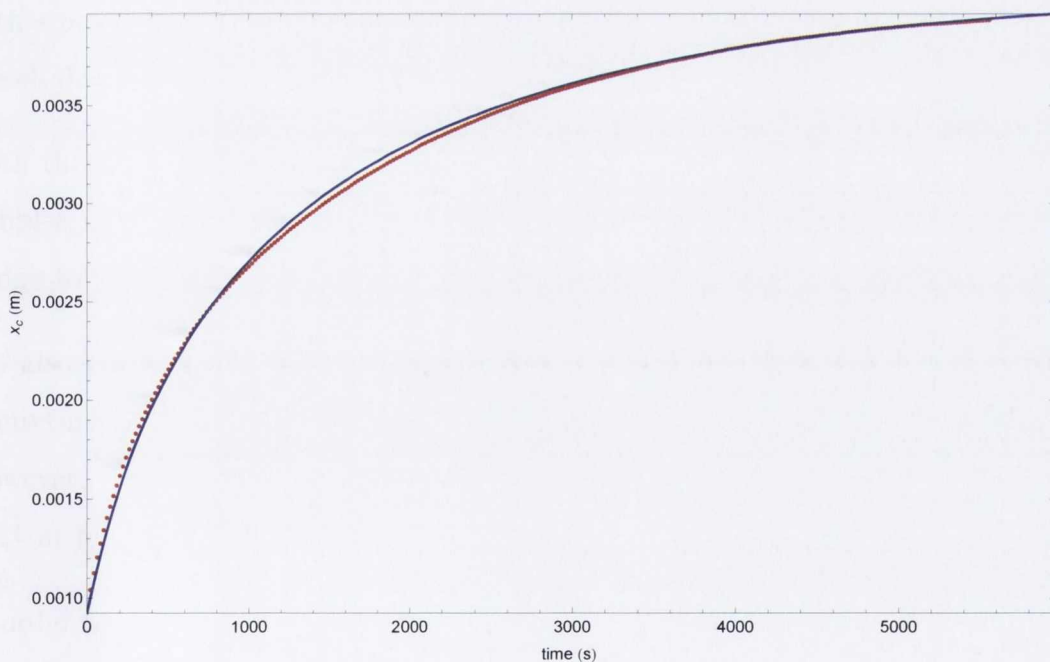


FIGURE 6.9: Comparison of the experimental data from Figure 6.8 with a similar bubble simulated as in Case Two.

6.6 Conclusions

By considering Fickian gas diffusion across the thin liquid film atop a single stabilised gas bubble floating at a liquid surface, we have been able to show, with computer simulations, theory and experiments that the gas composition of the bubble has a profound effect on the time evolution of such a bubble.

In the case that the bubble contains the same gas as the surrounding atmosphere, the bubble is seen to shrink in time, as expected. In contrast, if a fraction of completely insoluble gas ($k_B = 0$) is added to the first gas, the bubble is seen to grow in time.

However, the rate at which the bubble grows or shrinks was shown to be independent of the gas composition. Instead, the rate has been shown to depend critically on the dimensions of the bubble relative to the capillary length l_0 .

For large shrinking bubbles, it was shown that the radius x_c shrinks consistent with a power law as $-(t - t_0)^{\frac{1}{2}}$. In the case of large growing bubbles, their growth is well described by a power law scaling as $t^{\frac{1}{4}}$.

Both these power laws can be obtained from models that consider hemispherical bubbles; deviations are to be expected for bubbles smaller than the capillary length l_0 due to the partial submersion of the bubble in the underlying liquid.

We also conducted some preliminary experiments in which a bubble containing a mixture of nitrogen and perfluorohexane gas was observed to grow in time. However, the experimental data was seen to deviate from the predicted power law of $t^{\frac{1}{4}}$ at longer times.

In order to understand these experimental observations, we developed more realistic simulations which considered k_B to be very small but non-zero. In this case, the evolution of the bubble was seen to shift qualitatively from a scaling law towards the experimental evolution behaviour at long times. Thus, we can conclude that deviations from the predicted scaling law are due primarily to the finite solubility of the secondary gas component in experimental situations.

Chapter 7

Conclusion and Outlook

In this thesis we have seen that analytic models of bubbles based on the mathematically rich area of minimal surfaces provide us with a convenient and powerful way to study the energy of foams in equilibrium and the bubble-bubble interaction. We have also demonstrated how such models can be combined with a dynamic framework, in particular gas diffusion, to successfully model experimental systems.

We began by considering how a single bubble in the bulk of a foam with Z neighbours could be thought of as a collection of Z equal cones, each of the cones corresponds to a single contact with a neighbouring bubble. By considering the bubble surfaces to be deformable we showed how this simple geometric idea could be used to explore the bubble-bubble interaction in three dimensions as a function of liquid fraction. The analytic expressions for the additional surface energy of the bubbles which we derive highlight the role played by logarithmic terms in the bubble-bubble interaction in the wet limit. In particular, it shows that simply extending the Durian bubble model of harmonically interacting overlapping disks to overlapping spheres is not theoretically justified in the wet limit.

We then went on to extend the cone model to incorporate unequal contacts by considering the Kelvin cell with its eight nearest neighbour bubbles and six next nearest neighbours. This we did by carefully incorporating additional structural information, in this case details about the solid angles of the faces and the relative

distances to the different contacts, leading us to very accurately evaluate the excess energy, in agreement with Surface Evolver simulations, of a wet Kelvin foam over the entire range of liquid fraction. We demonstrated that structural transitions caused by the loss of contacts away from the wet limit are distinct from those at the wet limit. This illustrates that the bubble-bubble interaction is more complex than first thought and further work will be necessary in the future to fully grasp its nature.

Having shown that bubbles in the bulk of a foam could be described with analytical models involving minimal surfaces, we shifted our focus to another situation where minimal surfaces play a significant role. We considered the evolution of a single bubble at a liquid surface and demonstrated that knowing the composition of the gas is crucial to predicting how the bubble will evolve. In particular, we demonstrated that while a bubble containing nitrogen (or air) shrinks in time in line with what we would expect, adding a small amount of a low solubility gas to the bubble leads to the opposite behaviour. The bubble is found to grow in time. For large bubbles at a liquid surface, whose shape closely resembles a hemisphere, we were able to show that the growth of a bubble in this case obeys a power law with an exponent of a quarter. Low solubility gases are often used in experimental foam studies to inhibit coarsening and this work has highlighted that care must be taken when using these gases as their inclusion may significantly alter the evolution of the foam.

In the future, we hope to extend this work, focusing in particular on further developing the cone model towards describing a completely random foam. While this goal is still some way away, we have made some progress in this direction by adapting the cone model for curved bubble-bubble contacts, as detailed below.

7.1 Cone Model with Curved Contacts

We have seen thus far that the cone model is an effective way of studying the surface energy properties of foams made up of identical bubbles. One thing we have

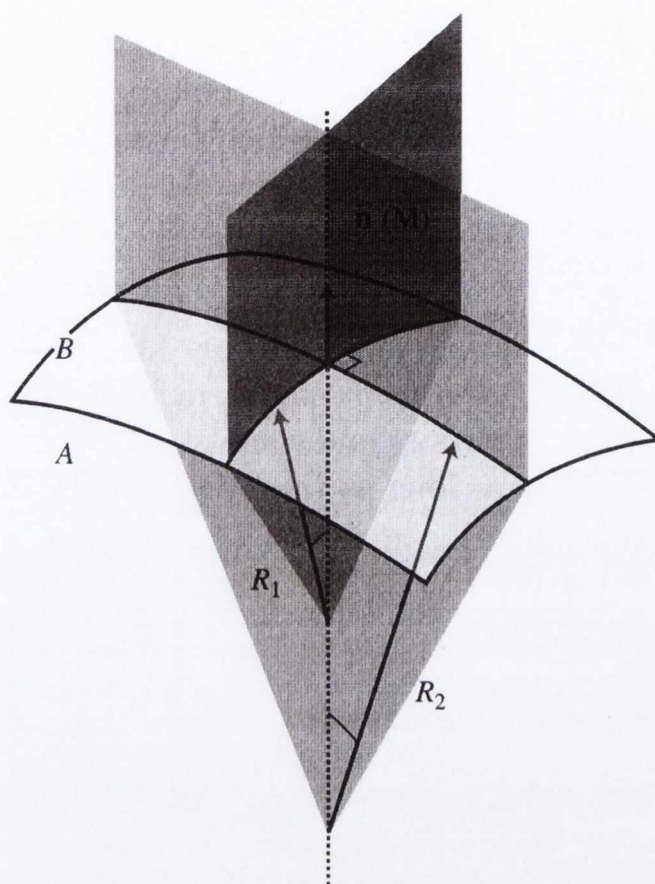


FIGURE 7.1: Schematic diagram of an interface between two bubbles A and B which is curved when there is an internal pressure difference between the bubbles. In general, the curvature is measured by the two principal radii of curvature R_1 and R_2 (which are perpendicular to each other) which are related to the pressure difference via the Young-Laplace law (see Section 1.2). For rotationally symmetric films, the radii of curvature are the same and denoted by R_c . This image has been reproduced from [3].

kept constant in our previous analyses, however, is the curvature of the bubble-bubble contacts; we have only considered ordered foam in which the pressure in all of the bubbles is the same. In this case, the approximation of rotational symmetry inherent in our model, implies a planar, circular interface between neighbouring bubbles.

Here we extend the cone model to deal with the case of bubbles with differing internal pressures. In general, this leads to a curvature of the interface which is described by two principal radii of curvature, as shown in Figure 7.1 [3]. Using

rotational symmetry, however, the picture is simpler as the interface is a spherical cap with a single radius of curvature R_c . While the Weaire-Phelan structure (see 1.3(b)) is a famous example of a monodisperse foam where the individual bubbles have different pressures [23], it is more common for differing internal pressures to arise in polydisperse foam. As we hinted in Section 1.6, a difference in bubble size will have an effect on the bubble-bubble interaction because the deformation ξ will be different for the larger and the smaller bubbles for the same contact size.

At this point, we note that the mathematical derivation of the excess energy ε and ξ (for both the larger and smaller bubbles) for curved contacts is similar in style to that outlined in Appendix A for the Z -cone model. However, the presence of curved contacts introduces some additional complications which are relevant to the details of our Euler-Lagrange formalism and lead to somewhat lengthy analytic expressions for ε and ξ . Thus, they are left to Appendix C.

In both the original Z -cone model and its extension to the Kelvin cell, we represented the presence of equal-sized neighbouring bubbles as flat contacts (see Figure 2.3) compressing a bubble from each of Z directions. For simplicity, we shall begin by looking at the case of a small bubble confined by larger bubbles. A convenient way to think about curved contacts is to simply replace the flat plates with spherical boundaries. A representation of this, for the case of $Z = 2$, is shown in Figure 7.2.

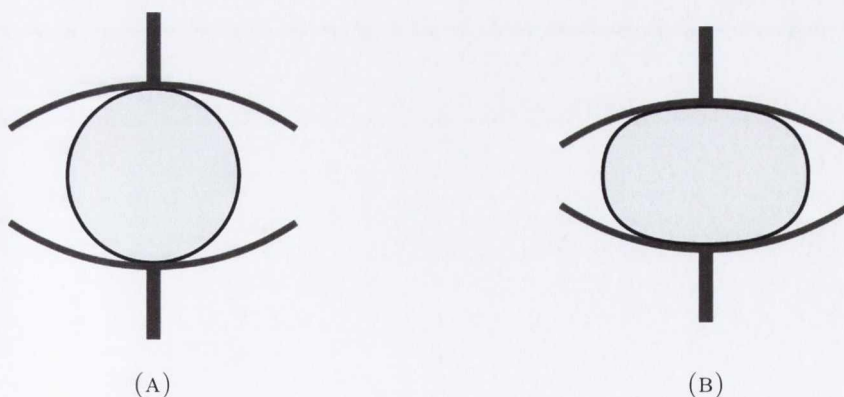


FIGURE 7.2: We investigate the case of $Z = 2$ contacts by using spherical, rather than flat, boundaries to confine the bubble, appropriate when the pressure of neighbouring bubbles is different from that of the central one.

The radius of curvature R_c of the spherical cap interface can be obtained from the Laplace pressure difference ΔP between the bubbles. In Section 1.2, we noted that the Laplace pressure difference across a single soap interface is $\Delta P = \frac{2\sigma}{R_c}$. Since a film is made up of two interfaces separated by a thin film of liquid, the radius of curvature is given by

$$R_c = \frac{4\sigma}{\Delta P}. \quad (7.1)$$

Bubbles which are smaller than their neighbours have a greater internal pressure and so the interface will curve outwards. Figure 7.3 depicts a Surface Evolver simulation performed by David Whyte of a bubble with $Z = 6$ and with higher pressure than its neighbours, so $R_c > 0$; the interfaces curve outwards. In this simulation, the curved boundaries representing the contact between bubbles are implemented not as flat surfaces but by spherical boundaries (see Figure 7.2). The surface area of the bubble is minimised at each step as these boundaries are moved inwards, deforming the bubble.

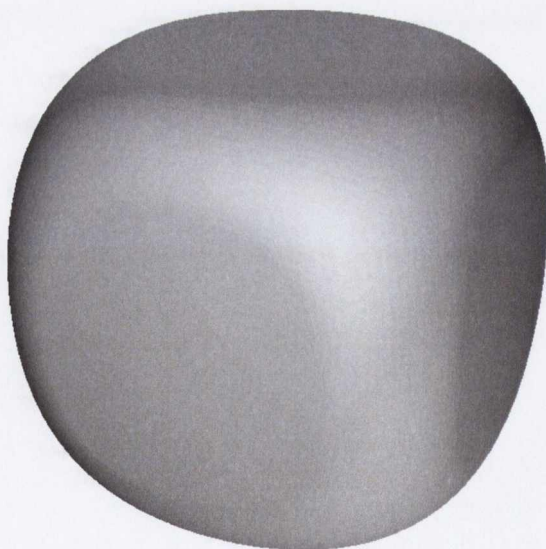


FIGURE 7.3: Surface Evolver simulation of a bubble with $Z = 6$ near the dry limit. The bubble is compressed between six plates arranged in a cube. Here, the plates are spherical caps with $R_c = 3R$, so the bubble bulges outwards.

Let us begin with the smaller of two contacting bubbles and denote its radius by R . The radius of its larger counterpart can then be written as

$$R_n = aR \quad (7.2)$$

with $a > 1$. The parameter a that we have introduced is the radial polydispersity. With the introduction of the polydispersity a , we are able to express the radius of curvature R_c of the interface between two contacting bubbles in the appealingly simple form

$$R_c = \frac{aR}{R_n - R} = \left(\frac{a}{a - 1} \right) R. \quad (7.3)$$

This follows directly from equation (7.1) by considering the pressure difference ΔP as the difference in Laplace pressures for spherical bubbles of the same volumes (see Appendix C for further details).

7.1.1 Some Preliminary Results

In Figure 7.4, we compare the results of the cone model for curved contacts with Surface Evolver simulations for $Z = 2$. In this case, the polydispersity is $a = 1.5$ which translates to a radius of curvature R_c for the interface of $3R$.

We see that the model accurately predicts the variation of excess energy over a wide range of deformations for both the small ($R_c > 0$) and large bubbles ($R_c < 0$). The shallower increase in excess energy for the larger bubble is due to our choice of deformation ξ which is measured to the centre of the curved contacts (see Section 1.6). As we expect, the model is exact for the case of a flat interface ($R_c = \infty$) as this reduces to the original Z -cone model for $Z = 2$, which is exact. While the case of $Z = 2$ is interesting, the power of the Z -cone model lies in making predictions of the excess energy for higher values of Z .

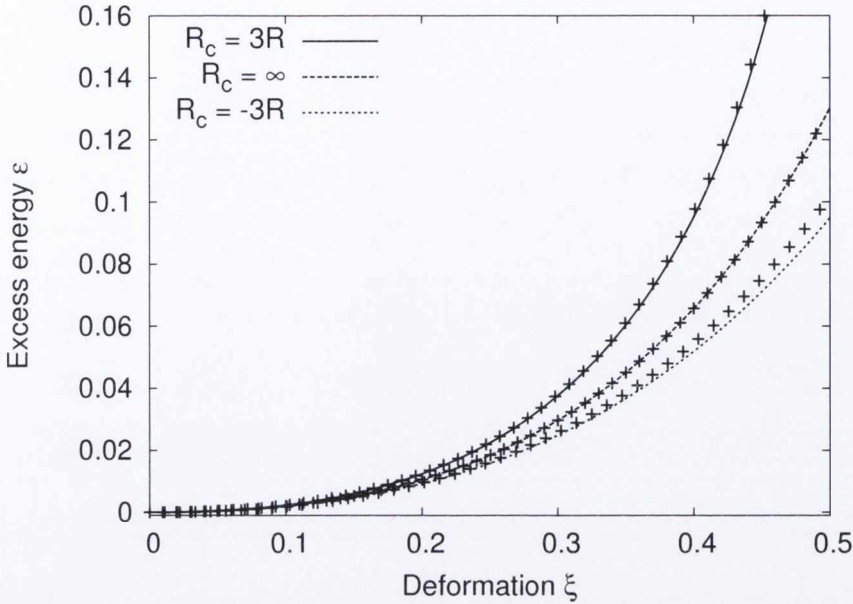


FIGURE 7.4: For a bubble with two contacts, we compare the analytic expressions for the excess energy to the results of Surface Evolver simulations. For the case of a flat interface (radius of curvature $R_c = \infty$) there is exact agreement between theory and simulation, to within numerical error. The analytic approximations for curved interfaces are good over a wide range of deformations ξ . The relative error increases with deformation, with a maximum of 8% for $R_c = -3R$ and $R_c = 3R$.

In Figure 7.5(a), we show a similar comparison of results for the case of $Z = 6$ (see Figure 7.3). As in the case of $Z = 2$, we observe very good agreement between analytical cone model results and simulation over a large range of deformations ξ . The results are not as good for the large bubbles due to the complicated shape of the surface (see Appendix C).

In Figure 7.5(b), we have divided the excess energy ε by the quadratic term ξ^2 . As in the case of flat contacts (see Chapter 2), we see deviations from a quadratic form at both small and large ξ , corresponding to the limits of wet and dry foam. In particular, we see a similar logarithmic decrease in the excess energy as we approach the wet limit as we observed for flat contacts. This shows that the fundamental form of the bubble-bubble interaction which we have elucidated earlier in this thesis for equal size bubbles is qualitatively unchanged by introducing polydispersity.

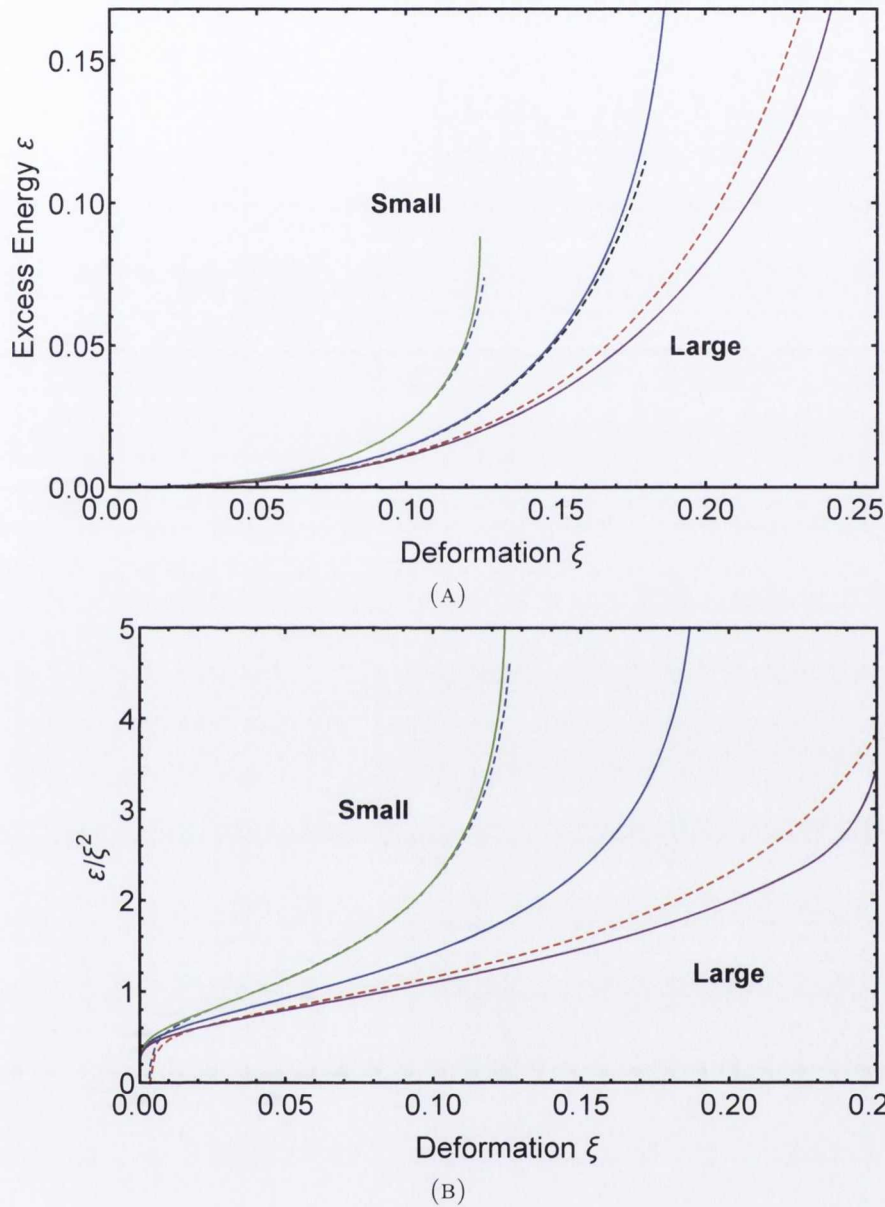


FIGURE 7.5: Comparison of (a) the variation of the excess energy ε , and (b) the variation of $\frac{\varepsilon}{\xi^2}$, with deformation ξ for $Z = 6$ computed from the cone model (solid) and Surface Evolver (dashed) for a polydispersity $a = 1.5$. The upper curves show the excess energy of the small bubble while the lower curves show the results for the large bubble. We have shown the monodisperse case, for reference, which falls between the curves for the big and small bubbles.

The polydispersity a of the system controls the degree to which the excess energy for the large and small bubble deviates from the monodisperse case. This is shown in Figure 7.6 for the case of $Z = 6$. As the polydispersity increases, the excess energies for the large and small bubbles are observed to deviate more and more from the monodisperse case.

The success of this extension to the cone model could instigate further applications of the cone model to the case of periodic bi-disperse structures, for example in the sodium chloride lattice.

7.2 Cone Model for Bubble Clusters

In extending the cone model to more and more general cases, we have yet to mention bubble clusters or adherence to Plateau's laws, in particular the 120° meeting angle for three soap films. The reason for this is simply that we have always been considering the case of a bubble in the bulk of a liquid foam. In the future, we hope to extend this model to clusters of bubbles [70–72] for which we will certainly need to take into account this meeting condition [73].

While the geometry of many bubble clusters, such as those considered by Cox and Graner [70], remains very much part of future work, we present a preliminary extension of the Z -cone model to describe the far simpler two-bubble clusters, otherwise known as bubble chains, considered by Bohn [73] which consist of two soap bubbles which are strained between two parallel surfaces. While Bohn showed that there are several configurations possible for these two bubble clusters which transition into each other as a function of the separation of the plates, we restrict ourselves to considering the chain arrangement in which the two bubbles adhere to separate plates along a contact line (equivalent to $r(0)$ for $Z = 2$, see Figure 2.3) and form a contact which is parallel to the plates. In contrast to our previous extensions of the Z -cone model, adapting the existing Z -cone model for such a bubble chain is relatively simple, requiring only two small changes to the derivation of Z -cone model given in Appendix A.

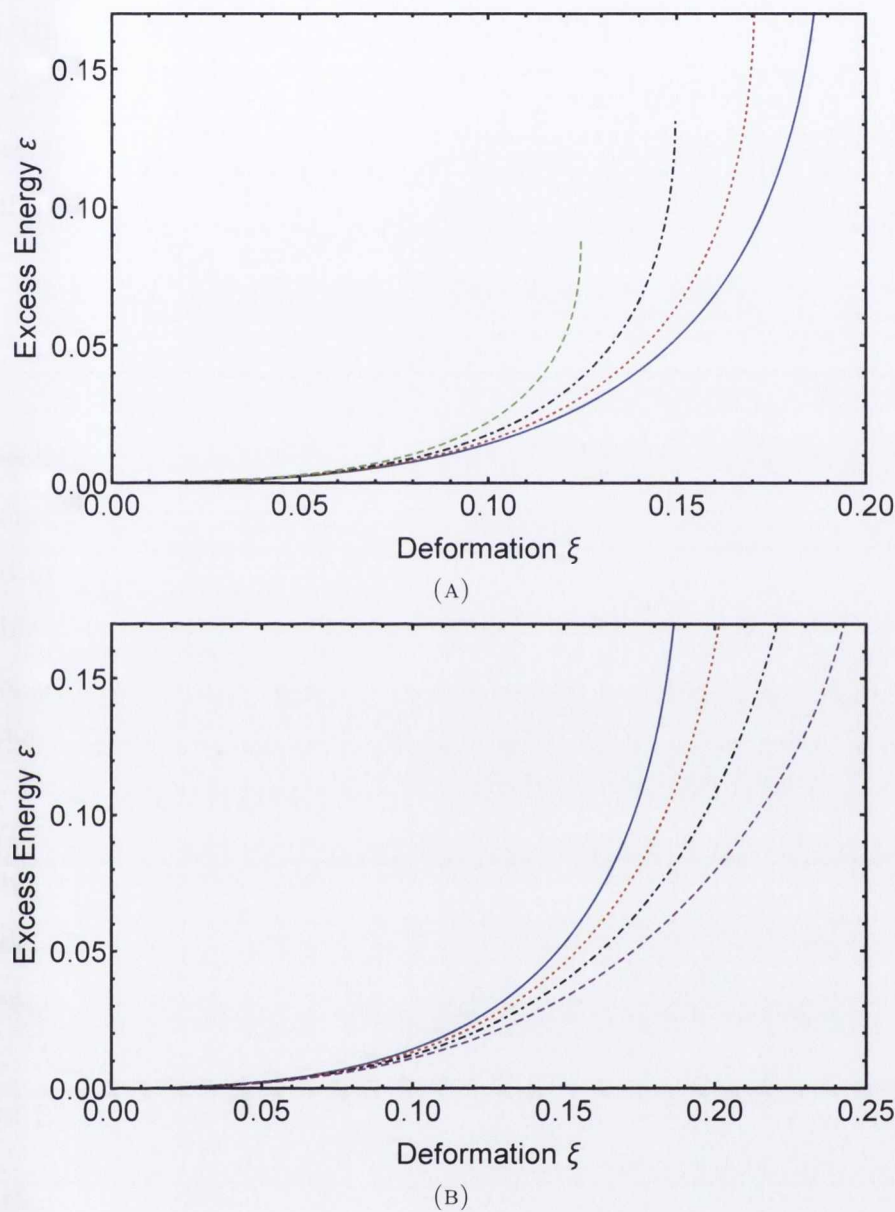


FIGURE 7.6: Variation of the excess energy of (a) the small bubble and (b) the large bubble for $Z = 6$ from the cone model for a range of values of the polydispersity a . The solid (blue) line represents the monodisperse case of $a = 1$ and serves as a reference. The dotted lines are for $a = 1.1$, the dot-dashed lines are for $a = 1.25$ and the dashed lines are for $a = 1.5$ (see Figure 7.5). As the polydispersity increases, the excess energies for the large and small bubbles move progressively further from the monodisperse case.

Firstly, we must replace the infinity in the first of the boundary conditions, equation (A.7), with the cotangent of an appropriate angle to impose the 120° angle condition at the edge of the contact. Secondly, we must remember that for these clusters, the free surface of the bubble is not a single surfactant interface separating gas in the bubble from liquid outside but a true film consisting of two such interfaces. This is simply done by doubling the contribution of the free surface to the total area of the bubble, equation (A.22).

7.2.1 Preliminary Results: Two-Bubble Chains

In this section, we present a number of preliminary results for the same two-bubble chain considered by Bohn [73], where the each bubble is initially a hemisphere with radius $R_0 = 1$. Each of these results compares our adapted Z -cone model for bubble clusters with the equivalent system for the original Z -cone model. In doing so, we clearly illustrate the effect of imposing the 120° angle condition in our model.

In Figure 7.7, we show the variation of the radii δ and $r(0)$ with distance between the bubble centres s (i.e. the separation of the parallel plates in experiment) for the two models. The reason to use s instead of deformation ξ is that the imposition of the angle condition allows for negative deformations, which is not a natural concept. Also, it is easy to compare our results directly with the experimental results of Bohn [73].

We see that for true bubble clusters, the contact between the bubbles is non-zero for distances greater than $s = 2$ (when the bubbles are hemispheres with a point contact). This agrees with the experimental results of Bohn [73] who observed that once a contact was formed between the bubbles by bring them into contact, and that this contact persisted as the plates were then separated beyond the reference position of $s = 2$. As this behaviour is not observed for the original Z -cone model, we conclude that this effect is a direct result of the angle condition.

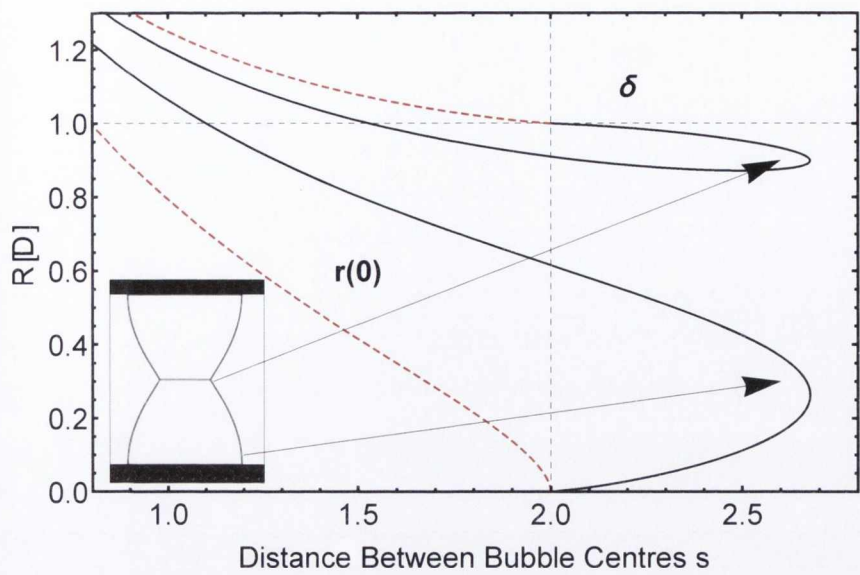


FIGURE 7.7: Comparison of the radius of the contact (upper) and of the film (lower), separating two hemispherical bubbles in a two-bubble cluster from the Z-cone model. The solid lines represent a two-bubble cluster with a 120° angle condition, as shown in the inset. The dashed lines are the corresponding quantities for the original Z-cone model (see Chapter 2).

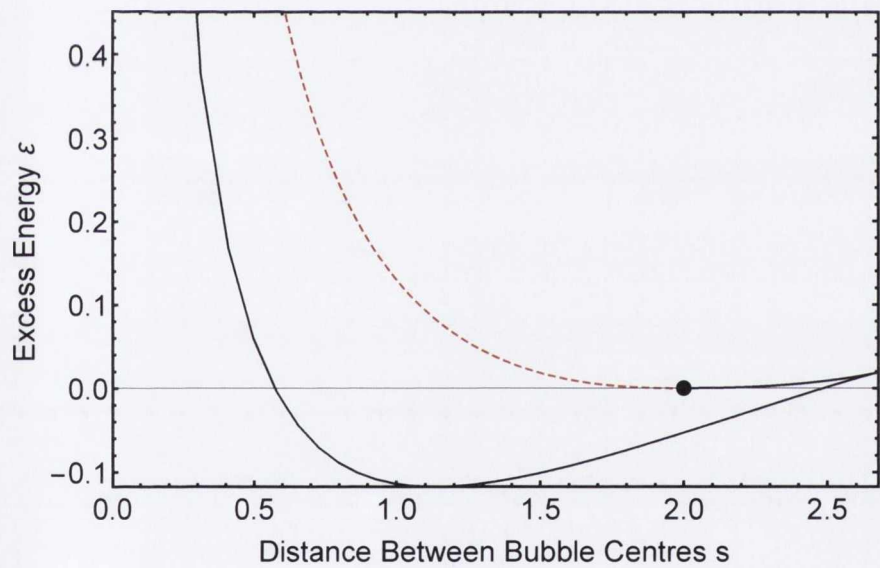


FIGURE 7.8: Comparison of the variation of excess energy ε with distance between bubble centres s for the two models. We see that the Z-cone model (solid) is well-behaved as the bubble as brought into contact, while the adapted model for bubble clusters (solid) shows a variety of additional features. In particular, we observe that the excess energy is double-valued for $s > 2$. Naturally, this is unphysical and the experimental system is observed to occupy the lowest energy configuration for each s .

Figure 7.8 shows a comparison between the excess energies ε for the two models. As

we expect, the excess energy for the original Z -cone model increases monotonically as the bubbles are brought into contact.

However, the variation of the excess energy is more complicated for the bubble cluster. We observe that there are two values of ε for each values of $s \geq 2$. The upper branch of the dashed curve corresponds to an unstable configuration which is not realised experimentally as bubbles will always jump to the lowest energy configuration available.

While the work presented here is still in its infancy, the successful replication of experimental results could spur further development of the model to more complicated bubble clusters [70] in the future.

Appendix A

Derivation of the Z-Cone Model

In this appendix, we provide a derivation of the excess energy ε and deformation ξ for the monodisperse Z-Cone model. We recall from Chapter 2 that the Z-cone model divides a spherical bubble up into Z equivalent sections, as shown in Figure A.1, which are approximated as spherical cones (see Figure 2.3). Each of these cones is associated with a neighbouring bubble and the cap of each cone represents the surface area of the bubble which is minimised under the constraint of volume conservation.

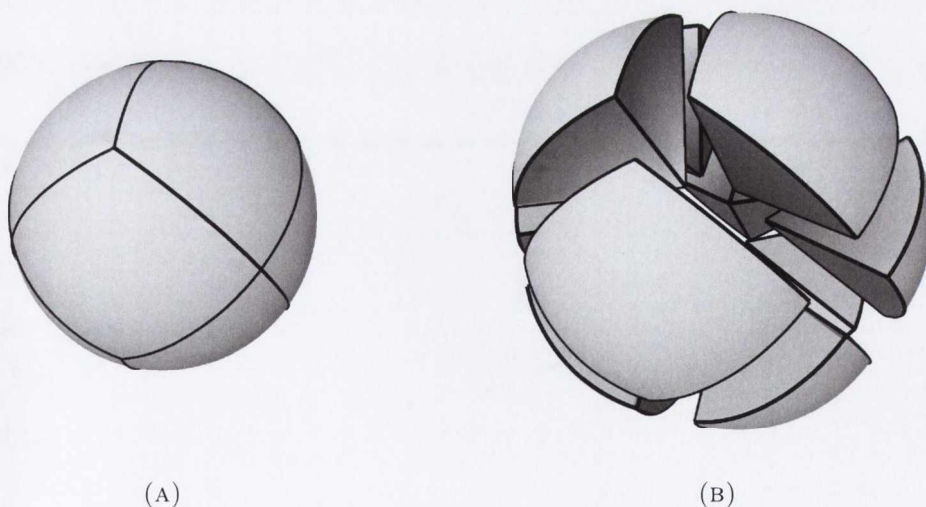


FIGURE A.1: A bubble can be divided up into Z equivalent sections; one for each neighbour. Here we show this for a bubble in an fcc-ordered foam, with $Z = 12$. In the Z-cone model, each of the sections (b) is approximated by a spherical cone whose cap is flattened by contact with a neighbouring bubble.

The total surface area A , per contact Z , of our bubble can be written as

$$A = A_\delta + 2\pi \int_0^h r(z) \sqrt{1 + \left(\frac{dr(z)}{dz}\right)^2} dz, \quad (\text{A.1})$$

where A_δ is the surface area of the contact. In the case of flat contacts $A_\delta = \pi\delta^2$. The second term in this equation is the general expression for the surface area (of revolution) of any curve given by $r(z)$ [38]. The volume V under this curve is given by

$$V = \pi \int_0^h r(z)^2 dz + \frac{\pi r(0)^3 \cot \theta}{3}. \quad (\text{A.2})$$

Minimising this surface area under the constraint of constant volume is the subject of the calculus of variations and requires the Euler-Lagrange formalism [38]. In general, the Euler-Lagrange equation is given by

$$\frac{dL\left(r(z), \frac{dr(z)}{dz}, z\right)}{dr(z)} - \frac{d}{dz} \frac{dL\left(r(z), \frac{dr(z)}{dz}, z\right)}{d\left(\frac{dr(z)}{dz}\right)} = 0. \quad (\text{A.3})$$

Fortunately, the Lagrangian function L that we consider does not depend explicitly on the coordinate z

$$L\left(r(z), \frac{dr(z)}{dz}\right) = 2r(z) \sqrt{1 + \left(\frac{dr(z)}{dz}\right)^2} - \lambda r(z)^2. \quad (\text{A.4})$$

In this special case, we can make a significant simplification of our minimisation problem by using an integrated form of the Euler-Lagrange equation (equation (A.5)) whose derivation we give here

$$\begin{aligned}
\int \frac{dL}{dr(z)} dr(z) - \int \frac{d}{dz} \frac{dL}{d\left(\frac{dr(z)}{dz}\right)} dr(z) &= \int 0 dr(z), \\
C + L - \int \frac{d}{dz} \left(\frac{dL}{d\left(\frac{dr(z)}{dz}\right)} \right) dr(z) &= 0, \\
L - \int \frac{d}{dr(z)} \left(\frac{dr(z)}{dz} \left(\frac{dL}{d\left(\frac{dr(z)}{dz}\right)} \right) \right) dr(z) &= -C, \\
L - \int d \left(\frac{dr(z)}{dz} \left(\frac{dL}{d\left(\frac{dr(z)}{dz}\right)} \right) \right) &= -C, \\
\therefore \frac{dr(z)}{dz} \frac{dL}{d\left(\frac{dr(z)}{dz}\right)} - L &= C, \tag{A.5}
\end{aligned}$$

where C is an unknown integration constant. Equation (A.5) is known as Beltrami's Identity and is at the heart of the calculus of variations [38]. For example, it is used instead of the standard Euler-Lagrange equation (equation (A.3)) in solving the brachistochrone ("shortest-time") problem [74]; this classic problem, first proposed by Johann Bernouilli in 1696, involves finding "the curve joining two points such that a bead starting from rest at the higher point will slide without friction along the curve and reach the lower point in the shortest possible time". [74].

Inserting our Lagrangian function and its derivative into Beltrami's Identity we obtain

$$-\frac{2r(z)}{\sqrt{1 + \left(\frac{dr(z)}{dz}\right)^2}} + \lambda r(z)^2 = C. \tag{A.6}$$

The unknown constants λ and C are determined by imposing the following boundary conditions on the equation:

$$\left. \frac{dr(z)}{dz} \right|_{z=h} = \infty \quad (\text{A.7})$$

$$\left. \frac{dr(z)}{dz} \right|_{z=0} = \cot \theta. \quad (\text{A.8})$$

The first of these ensures that the bubble surface meets the flat contact smoothly while the second ensures that the bubble surface meets the cone at a right angle.

By splitting the 4π steradian solid angle of our bubble equally between each contact we obtain the solid angle Ω of a cone, with opening angle θ (see Figure 2.3),

$$\begin{aligned} \Omega &= \int_0^{2\pi} \int_0^\theta \sin \theta' d\theta' d\chi' \\ &= 2\pi(1 - \cos \theta) \\ &= \frac{4\pi}{Z}. \end{aligned} \quad (\text{A.9})$$

From this we can see that θ is directly related to the number of neighbours Z via

$$\theta = \arccos \left(1 - \frac{2}{Z} \right). \quad (\text{A.10})$$

Using these conditions in equation (A.6) we have, after some algebra, that

$$\Rightarrow \frac{r(z)}{\sqrt{1 + \left(\frac{dr(z)}{dz} \right)^2}} = \frac{r(0)(r(z)^2 - \delta^2)}{(r(0)^2 - \delta^2) \sqrt{1 + \frac{(Z-2)^2}{4(Z-1)}}}. \quad (\text{A.11})$$

Rescaling this equation in terms of the dimensionless quantities $\rho(z) = \frac{r(z)}{r(0)}$ and $\rho_\delta = \frac{\delta}{r(0)}$ yields

$$\Rightarrow \sqrt{1 + \left(\frac{dr(z)}{dz} \right)^2} = \frac{\rho(z) \frac{Z}{2\sqrt{Z-1}} (1 - \rho_\delta^2)}{\rho(z)^2 - \rho_\delta^2}. \quad (\text{A.12})$$

This is a *dimensionless* first-order differential equation which can be solved by integrating it between the limits of ρ_δ and $\rho(z)$. Rearranging this equation for dz and noting that $dr(z) = r(0) d\rho(z)$, we find that

$$\int_{-h}^z dz = z + h = r(0)I(\rho(z), \rho_\delta, Z) \quad (\text{A.13})$$

and so

$$z = -h + r(0)I(\rho(z), \rho_\delta, Z). \quad (\text{A.14})$$

where $I(\rho(z), \rho_\delta, Z)$ is a definite elliptic integral defined below.

By considering $\rho(z = 0) = 1$ in equation (A.14), we obtain the important identity

$$r(0) = \frac{h}{I_\delta(\rho_\delta, Z)}, \quad (\text{A.15})$$

allowing us to express the bubble profile as

$$z(\rho(z), \rho_\delta, Z) = h \left[\frac{I(\rho(z), \rho_\delta, Z)}{I_\delta(\rho_\delta, Z)} - 1 \right]. \quad (\text{A.16})$$

The elliptic integrals $I(\rho(z), \rho_\delta, Z)$ and $I_\delta(\rho_\delta, Z)$, which need to be evaluated numerically, are given by

$$I(\rho(z), \rho_\delta, Z) = \int_{\rho_\delta}^{\rho(z)} (x^2 - \rho_\delta^2) f(x, \rho_\delta, Z) dx \quad (\text{A.17})$$

and

$$I_\delta(\rho_\delta, Z) = \int_{\rho_\delta}^1 (x^2 - \rho_\delta^2) f(x, \rho_\delta, Z) dx, \quad (\text{A.18})$$

with

$$f(x, \rho_\delta, Z) = \left[\frac{Z^2}{4(Z-1)} x^2 (1 - \rho_\delta^2)^2 - (x^2 - \rho_\delta^2)^2 \right]^{-\frac{1}{2}}. \quad (\text{A.19})$$

The volume V of our single cone is equal to $\frac{1}{Z}$ of the volume of a spherical bubble so that $V = \frac{4\pi R_0^3}{3Z}$. Inserting this expression into equation (A.2) and solving for $r(0)$ yields

$$r(0) = \frac{h}{I_\delta(\rho_\delta, Z)} = R_0 \left[\frac{\left(\frac{4}{Z}\right)}{3J_\delta(\rho_\delta, Z) + \frac{Z-2}{2\sqrt{Z-1}}} \right]^{\frac{1}{3}} \quad (\text{A.20})$$

where $J_\delta(\rho_\delta, Z)$ is another elliptic integral given by

$$J_\delta(\rho_\delta, Z) = \int_{\rho_\delta}^1 x^2 (x^2 - \rho_\delta^2) f(x, \rho_\delta, Z) dx. \quad (\text{A.21})$$

Equation (A.20) reduces to $R_0 \sin \theta$, the familiar case of a simple cone, in the limit as $\rho_\delta \rightarrow 0$. The constraint of volume conservation intuitively requires $r(0)$ (and hence h_c) to increase with increasing deformation to counteract the decrease in the height h .

Making use of equations (A.12), (A.13) and (A.20), we can re-express the surface area per contact A as

$$A(\rho_\delta, Z) = \pi R_0^2 \left(\frac{\left(\frac{4}{Z}\right)}{3J_\delta(\rho_\delta, Z) + \frac{Z-2}{2\sqrt{Z-1}}} \right)^{\frac{2}{3}} \left[\rho_\delta^2 + \frac{Z}{\sqrt{Z-1}} (1 - \rho_\delta^2) K_\delta(\rho_\delta, Z) \right] \quad (\text{A.22})$$

where $K_\delta(\rho_\delta, Z)$ is further elliptic integral given by

$$K_\delta(\rho_\delta, Z) = \int_{\rho_\delta}^1 x^2 f(x, \rho_\delta, Z) dx. \quad (\text{A.23})$$

The dimensionless excess surface energy is defined as

$$\varepsilon(\rho_\delta, Z) = \frac{A(\rho_\delta, Z)}{A_0(Z)} - 1 \quad (\text{A.24})$$

where $A_0(Z)$ is the surface area of the top of a spherical sector corresponding to our undeformed cone. From simple geometry, this is

$$A_0(Z) = 2\pi R_0^2(1 - \cos \theta) = \frac{4\pi R_0^2}{Z}. \quad (\text{A.25})$$

Combining Z of these spherical sectors recovers the total surface area of a spherical bubble of $4\pi R_0^2$, as expected.

Therefore, the dimensionless excess energy is

$$\varepsilon(\rho_\delta, Z) = \frac{\rho_\delta^2 + \frac{Z}{\sqrt{Z-1}}(1 - \rho_\delta^2)K_\delta(\rho_\delta, Z)}{Z^{-\frac{1}{3}}\left(6J_\delta(\rho_\delta, Z) + \frac{Z-2}{\sqrt{Z-1}}\right)^{\frac{2}{3}}} - 1. \quad (\text{A.26})$$

The dimensionless deformation is defined, to the middle of the flat contact, as

$$\xi = 1 - \frac{h + h_c}{R_0} \quad (\text{A.27})$$

where the height of a cone h_c is given by

$$h_c = r(0)\frac{Z-2}{2\sqrt{Z-1}}. \quad (\text{A.28})$$

Using equation (A.20), this dimensionless deformation is

$$\xi(\rho_\delta, Z) = 1 - \left(\frac{\left(\frac{4}{Z}\right)}{3J_\delta(\rho_\delta, Z) + \frac{Z-2}{2\sqrt{Z-1}}}\right)^{\frac{1}{3}} \left[\frac{Z-2}{2\sqrt{Z-1}} + I_\delta(\rho_\delta, Z)\right]. \quad (\text{A.29})$$

Appendix B

Asymptotic Wet Limit Expansions

In this appendix, we provide derivations for a number of results for the Z -cone model which we stated in Chapter 2. In particular, we will show how the deformation $\xi(\phi)$ is related directly to the liquid fraction ϕ . Using this, we will also show how to derive an expression for the critical liquid fraction ϕ_c in terms of the number of contacts Z for the Z -cone model. We also illustrate how to obtain asymptotic form for the excess energy ε as functions of both ξ and ϕ in the wet limit.

B.1 Deformation ξ and Liquid Fraction ϕ

B.1.1 Derivation of $\varepsilon(\xi)$

The purpose of this section is to show how an analytical form for deformation $\xi(\phi)$ is obtained.

We begin by considering not the liquid fraction ϕ but the associated gas fraction ϕ_g which is defined in terms of the liquid fraction as

$$\phi_g = 1 - \phi. \quad (\text{B.1})$$

Physically, the gas fraction ϕ_g for a foam is simply given by the ratio of the total bubble volume V_0 to the total volume of the Voronoi cell V_{vor} of the crystal arrangement under consideration. Namely,

$$\phi_g = \frac{V_0}{V_{\text{vor}}}. \quad (\text{B.2})$$

The critical gas fraction is similarly defined as

$$\phi_{g,c} = \frac{V_0}{V_{\text{vor},c}}, \quad (\text{B.3})$$

where $V_{\text{vor},c}$ is the volume of the Voronoi cell in the wet limit. Taking the ratio of the previous two equations we find that

$$\frac{\phi_{g,c}}{\phi_g} = \frac{V_{\text{vor}}}{V_{\text{vor},c}}. \quad (\text{B.4})$$

While the specific formula for volume depends on the shape of the Voronoi cell, we note that the overall shape of the cell remains the same. As an example, for cones the volume of the critical volume is $V_{\text{vor},c} = \frac{\pi}{3} R_0^3 \tan^2 \theta$ while for more deformed cases $V_{\text{vor}} = \frac{\pi}{3} H^3 \tan^2 \theta$. Thus, we see that equation (B.4) simplifies to

$$\frac{\phi_{g,c}}{\phi_g} = \left(\frac{H}{R_0} \right)^3 \quad (\text{B.5})$$

Since deformation in the Z-cone model is defined as $\xi = 1 - \frac{H}{R_0}$ we can immediately see that

$$\frac{\phi_{g,c}}{\phi_g} = (1 - \xi)^3 \quad (\text{B.6})$$

If we now switch from gas to liquid fraction using equation (B.1), we can relate liquid fraction ϕ directly to the deformation ξ as

$$\boxed{\xi(\phi) = 1 - \left(\frac{1 - \phi_c}{1 - \phi} \right)^{\frac{1}{3}}}. \quad (\text{B.7})$$

B.1.2 Critical Liquid Fraction ϕ_c for the Z-cone Model

We recall from Appendix A that the cone angle θ is related to Z via $\theta = \arccos(1 - (2/Z))$. Rewriting this we obtain.

$$\cos^2 \theta = \left(1 - \frac{2}{Z} \right)^2. \quad (\text{B.8})$$

By simple trigonometry transform from a cosine to a tangent in the following way

$$\tan^2 \theta = \frac{1}{\cos^2 \theta} - 1 = \frac{4(Z - 1)}{(Z - 2)^2} \quad (\text{B.9})$$

In the Z -cone model, the volume of a single cone is $V_0 = \frac{4\pi}{3Z} R_0^3$. Combining this with equation (B.3) we obtain the result

$$\boxed{\phi_c = \frac{3 - \frac{4}{Z}}{Z - 1}}. \quad (\text{B.10})$$

B.2 Logarithmic Terms in the Wet Limit

Here we give a brief derivation of the wet limit asymptotic form for the excess energy ε in the Z -cone model. For simplicity, we will use the case of $Z = 2$ but the method employed is equally valid for any value of Z .

We recall from Appendix A (also see Chapter 2) that the excess energy ε for the Z -cone model is given by

$$\varepsilon(\rho_\delta, Z) = \frac{\rho_\delta^2 + \frac{Z}{\sqrt{Z-1}} (1 - \rho_\delta^2) K_\delta(\rho_\delta, Z)}{Z^{-\frac{1}{3}} \left(6J_\delta(\rho_\delta, Z) + \frac{Z-2}{\sqrt{Z-1}} \right)^{\frac{2}{3}}} - 1 \quad (\text{B.11})$$

To find the asymptotic form of this in the wet limit, we will need to Taylor expand this expression for $\rho_\delta \rightarrow 0$. However, before we can do this, it is necessary to expand the elliptic integrals $J_\delta(\rho_\delta, Z)$ and $K_\delta(\rho_\delta, Z)$ (given by equations (A.21) and (A.23)). To fourth-order these are given by

$$J_{\rho_\delta \rightarrow 0} = \frac{1}{6} \sqrt{1 - \rho_\delta^2} (3\rho_\delta^2 - 4\rho_\delta^2 + 4) \quad (\text{B.12})$$

and

$$K_{\rho_\delta \rightarrow 0} = \sqrt{1 - \rho_\delta^2} + \frac{1}{2} \rho_\delta^4 \ln \left(\frac{\rho_\delta}{\sqrt{1 - \rho_\delta^2} + 1} \right). \quad (\text{B.13})$$

Inserting these into equation (B.11) and simplifying, keeping highest order terms, we obtain an expression for the excess energy for $Z = 2$ of

$$\varepsilon(\rho_\delta)_{\rho_\delta \rightarrow 0} = \frac{\rho_\delta^4}{-1 - 4 \ln \left(\frac{\rho_\delta}{2} \right)} + O(\rho_\delta^5). \quad (\text{B.14})$$

By similarly expanding the deformation, given by equation (A.29), and simplifying, we obtain after a somewhat lengthy computation the following expression for $\varepsilon(\xi)$ in the limit of $\rho_\delta \rightarrow 0$

$$\varepsilon(\xi)_{\rho_\delta \rightarrow 0} = -\frac{\xi^2}{\ln \xi - \ln 4} + O(\xi^4) \approx -\frac{\xi^2}{\ln \xi}. \quad (\text{B.15})$$

For higher values of Z , this equation (B.15) becomes

$$\boxed{\varepsilon(\xi) = -\frac{Z\xi^2}{2 \ln \xi}} \quad (\text{B.16})$$

From equation (B.16) for $\varepsilon(\xi)$ we obtain an expression for $\varepsilon(\phi)$ in the wet limit. This we do by Taylor expanding equation (B.7) around ϕ_c to first order so that

$$\xi(\phi) \approx \frac{\phi_c - \phi}{3(1 - \phi_c)} \tag{B.17}$$

and substituting this expression into equation (B.16) obtaining

$$\varepsilon(\phi) \simeq -\frac{Z}{18(1 - \phi_c)^2} \frac{(\phi_c - \phi)^2}{\ln\left(\frac{\phi_c - \phi}{3(1 - \phi_c)}\right)}. \tag{B.18}$$

In the limit as $\phi \rightarrow \phi_c$ we may further approximate this as

$$\varepsilon(\phi) \simeq -\frac{Z}{18(1 - \phi_c)^2} \frac{(\phi_c - \phi)^2}{\ln(\phi_c - \phi)}.$$

(B.19)

Appendix C

Cone Model for curved contacts

We demonstrated in Chapter 7 that the cone model could be extended to deal with curved bubble-bubble contacts. Curvature of the contacts between neighbouring bubbles occurs when the bubbles have different internal pressures. As we pointed out in Section 7.1, this most commonly occurs for bubbles in a polydisperse foam.

The derivation of the excess energy ε and deformation ξ in this case is similar to that given in Appendix A for the Z-Cone Model with flat contacts. As such, the aim of this appendix is to provide sufficient analytical expressions to reproduce the figures provided in Chapter 7 for the Z-Cone Model with curved contacts for both the relatively small and relatively large bubbles.

C.1 Curved Contact Model

Beginning with the smaller of the contacting bubbles (of radius R), we saw in Section 7.1 that the radius of neighbouring bubbles R_n can be written as $R_n = aR$ with $a > 1$. Since a smaller radius implies a higher Laplace pressure, the contact between the bubbles is curved “out” from the smaller of the bubbles, as shown in Figure 7.2. The Laplace pressure difference between bubbles of radius of R and R_n is given by

$$\Delta P = \frac{4\sigma}{R} - \frac{4\sigma}{R_n} = 4\sigma \frac{(a-1)}{aR} \quad (\text{C.1})$$

where σ is the surface tension.

The radius of curvature R_c of the contact between the bubbles is expressed in terms of the Laplace pressure difference ΔP as

$$R_c = \frac{4\sigma}{\Delta P}. \quad (\text{C.2})$$

Substituting the explicit form for ΔP , equation (C.1), into this expression and simplifying gives

$$R_c = \left(\frac{a}{a-1} \right) R. \quad (\text{C.3})$$

The introduction of curved interfaces introduces two new angles $\theta_{\min}$ and α into our model. The angle $\theta_{\min}$ is similar to the cone angle θ and corresponds to the angle made between the z-axis of the cone and a line from the edge of the (curved) contact to the apex of the cone. The second angle α is introduced to account for the (spherical) geometry of the contact (see Figure C.1). As discussed above, the contact between the bubbles takes the shape of a spherical cap, which can be viewed simply as the top of a sphere which has been cut off by a plane. The angle α is the angle this plane, perpendicular to the symmetry axis of the cone, makes with the spherical cap.

For each Z and a , there are unique values of $\theta_{\min}$ and α obtained by numerically solving

$$\widehat{I}_\delta(\rho_\delta, \theta_{\min}, Z) = \frac{\rho_\delta}{\tan \theta_{\min}} - \frac{Z-2}{2\sqrt{Z-1}} \quad (\text{C.4})$$

and

$$\sin \alpha = \rho_\delta \left(\frac{a-1}{a} \right) \left[\frac{\left(\frac{4}{Z} \right) - \left(\frac{a}{a-1} \right)^3 (2 - 3 \cos \alpha + \cos^3 \alpha)}{3\widehat{J}_\delta(\rho_\delta, \theta_{\min}, Z) + \frac{(Z-2)}{2\sqrt{Z-1}}} \right]^{\frac{1}{3}}, \quad (\text{C.5})$$

where the ρ_δ is defined, similarly to the Z -cone model as the ratio of the width of the contact (see $r_{\min}$ in Figure C.1 below) divided by the maximum width of the cone (i.e $r(0)$).

The dimensionless excess energy for the small bubble $\varepsilon(\rho_\delta, \theta_{\min}, \alpha, Z, a)$ is written as

$$\begin{aligned} \varepsilon(\rho_\delta, \theta_{\min}, \alpha, Z, a) = & \frac{Z}{4} \left(\frac{\left(\frac{4}{Z}\right) - \left(\frac{a}{a-1}\right)^3 (2 - 3 \cos \alpha + \cos^3 \alpha)}{3\hat{J}_\delta(\rho_\delta, \theta_{\min}, Z) + \frac{(Z-2)}{2\sqrt{Z-1}}} \right)^{\frac{2}{3}} \\ & \left[\rho_\delta^2 + \left(\frac{a}{a-1}\right)^2 (1 - \cos \alpha)^2 \left(\frac{\left(\frac{4}{Z}\right) - \left(\frac{a}{a-1}\right)^3 (2 - 3 \cos \alpha + \cos^3 \alpha)}{3\hat{J}_\delta(\rho_\delta, \theta_{\min}, Z) + \frac{(Z-2)}{2\sqrt{Z-1}}} \right)^{-\frac{2}{3}} \right. \\ & \left. + \frac{Z}{\sqrt{Z-1}} (1 - \rho_\delta^2) \hat{K}_\delta(\rho_\delta, \theta_{\min}, Z) \right] - 1. \quad (\text{C.6}) \end{aligned}$$

The dimensionless deformation for the small bubble $\xi(\rho_\delta, \theta_{\min}, \alpha, Z, a)$, measured to the middle of the curved contact, is expressed as

$$\begin{aligned} \xi(\rho_\delta, \theta_{\min}, \alpha, Z, a) = & 1 - \left(\frac{a}{a-1}\right) (1 - \cos \alpha) \\ & - \left(\frac{\left(\frac{4}{Z}\right) - \left(\frac{a}{a-1}\right)^3 (2 - 3 \cos \alpha + \cos^3 \alpha)}{3\hat{J}_\delta(\rho_\delta, \theta_{\min}, Z) + \frac{(Z-2)}{2\sqrt{Z-1}}} \right)^{\frac{1}{3}} \left[\frac{Z-2}{2\sqrt{Z-1}} + \hat{I}_\delta(\rho_\delta, \theta_{\min}, Z) \right]. \quad (\text{C.7}) \end{aligned}$$

The definite elliptic integrals $\hat{I}_\delta(\rho_\delta, \theta_{\min}, Z)$, $\hat{J}_\delta(\rho_\delta, \theta_{\min}, Z)$ and $\hat{K}_\delta(\rho_\delta, \theta_{\min}, Z)$ are given by:

$$\hat{I}_\delta(\rho_\delta, \theta_{\min}, Z) = \int_{\rho_\delta}^1 \left[(x^2 - \rho_\delta^2) - \rho_\delta \sin \theta_{\min} \frac{Z}{2\sqrt{Z-1}} (x^2 - 1) \right] \hat{f}(x, \rho_\delta, \theta_{\min}, Z) dx, \quad (\text{C.8})$$

$$\hat{J}_\delta(\rho_\delta, \theta_{\min}, Z) = \int_{\rho_\delta}^1 x^2 \left[(x^2 - \rho_\delta^2) - \rho_\delta \sin \theta_{\min} \frac{Z}{2\sqrt{Z-1}} (x^2 - 1) \right] \hat{f}(x, \rho_\delta, \theta_{\min}, Z) dx, \quad (\text{C.9})$$

$$\hat{K}_\delta(\rho_\delta, \theta_{\min}, Z) = \int_{\rho_\delta}^1 x^2 \hat{f}(x, \rho_\delta, \theta_{\min}, Z) dx, \quad (\text{C.10})$$

with

$$\hat{f}(x, \rho_\delta, \theta_{\min}, Z) = \left[\frac{Z^2}{4(Z-1)} x^2 (1 - \rho_\delta^2)^2 - \left[(x^2 - \rho_\delta^2) - \rho_\delta \sin \theta_{\min} \frac{Z}{2\sqrt{Z-1}} (x^2 - 1) \right]^2 \right]^{-\frac{1}{2}}. \quad (\text{C.11})$$

For the large bubble, the determinations of the excess energy and deformation are more complicated than for the associated small bubble. The reason for this is that the curving “in” of the contacts leads to a “dimpling” of the surface of the large bubble, as shown schematically in Figure C.1.

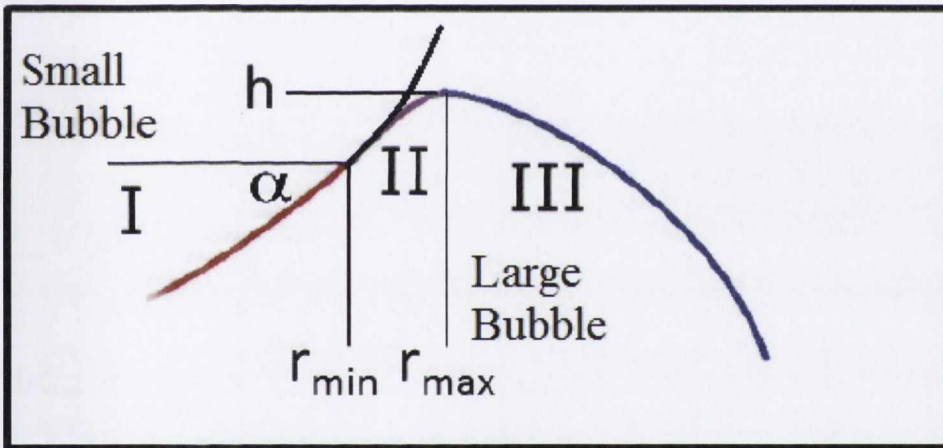


FIGURE C.1: Sketch of the contact between a large and small bubble. The red line indicates the common curved contact between the bubbles, indicated by Region I, which extends to a distance $r_{\min}$ from the centre of the contact. Regions II (purple) and III (blue) represent the free surface of the large bubble which is “dimpled”, with $r_{\max}$ indicating the maximum (vertical) height of the bubble h . The angle α is the interior angle made at $r_{\min}$ between the curved contact (red line) and plane perpendicular to the axis of symmetry of the cone.

The black line shows the surface of the small bubble.

Physically, the presence of region II is a consequence of requiring the surfaces of the two bubbles to meet smoothly at the edge of the contact, denoted here by $r_{\min}$. In simple terms, we cannot have a sharp point at the edge of the contact and so a dimple of some width is necessary. The free surface of the bubble is composed of

both II and III. We see immediately that region II presents a challenge to the cone model description of such a bubble since this approach relies upon the mathematics of minimal surfaces of revolution. In particular, we require the value of $r(z)$ (see Appendix A) to be **single-valued** for a given height h , which is not the case for the dimpled surface.

To overcome this limitation, we consider the area and volume of each of the three regions **separately** using the cone model and then combining them to obtain the final excess energy, requiring only the total volume of the bubble to be constant. Introducing two dimensionless radii $\rho_{\min}$ and $\rho_{\max}$ (similar to ρ_δ) for the large bubble, we are able to determine an expression for the dimensionless excess energy for the large bubble $\varepsilon(\rho_{\min}, \rho_{\max}, \theta_{\min}, \alpha, Z, a)$ in the form

$$\begin{aligned} \varepsilon(\rho_{\min}, \rho_{\max}, \theta_{\min}, \alpha, Z, a) = & \frac{Z}{4} \left(\frac{\left(\frac{4}{Z}\right) + (a-1)^{-3} (2 - 3 \cos \alpha + \cos^3 \alpha)}{3 \left[\tilde{J}_\delta(\rho_{\max}, Z) + \check{J}_\delta(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) \right] + \frac{Z-2}{2\sqrt{Z-1}}} \right)^{\frac{2}{3}} \\ & \left[\rho_{\min}^2 + (a-1)^{-2} \left(\frac{\left(\frac{4}{Z}\right) + (a-1)^{-3} (2 - 3 \cos \alpha + \cos^3 \alpha)}{3 \left[\tilde{J}_\delta(\rho_{\max}, Z) + \check{J}_\delta(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) \right] + \frac{Z-2}{2\sqrt{Z-1}}} \right)^{-\frac{2}{3}} (1 - \cos \alpha)^2 \right. \\ & \left. + 2(\rho_{\max}^2 - \rho_{\min}^2) \check{K}_\delta(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) + \frac{Z}{\sqrt{Z-1}} (1 - \rho_{\max}^2) \tilde{K}_\delta(\rho_{\max}, Z) \right] - 1. \end{aligned} \quad (\text{C.12})$$

The dimensionless deformation for the large bubble $\xi(\rho_{\min}, \rho_{\max}, \theta_{\min}, \alpha, Z, a)$, again measured to the middle of the curved contact, is expressed as

$$\begin{aligned} \xi(\rho_{\min}, \rho_{\max}, \theta_{\min}, \alpha, Z, a) &= 1 + \frac{1 - \cos \alpha}{a - 1} \\ &- \left(\frac{\left(\frac{4}{Z}\right) + (a - 1)^{-3} (2 - 3 \cos \alpha + \cos^3 \alpha)}{3 \left[\tilde{J}_{\delta}(\rho_{\max}, Z) + \check{J}_{\delta}(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) \right] + \frac{Z-2}{2\sqrt{Z-1}}} \right)^{\frac{1}{3}} \\ &\left[\frac{Z-2}{2\sqrt{Z-1}} + \check{I}_{\delta}(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) + \tilde{I}_{\delta}(\rho_{\max}, Z) \right]. \end{aligned} \quad (\text{C.13})$$

The definite elliptic integrals defined for the large bubble are given by

$$\check{I}_{\delta}(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) = \int_{\rho_{\min}}^{\rho_{\max}} \sin \theta_{\min} \rho_{\min} (x^2 - \rho_{\max}^2) \check{f}(x, \rho_{\min}, \rho_{\max}, \theta_{\min}, Z) dx, \quad (\text{C.14})$$

$$\check{J}_{\delta}(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) = \int_{\rho_{\min}}^{\rho_{\max}} \sin \theta_{\min} \rho_{\min} x^2 (x^2 - \rho_{\max}^2) \check{f}(x, \rho_{\min}, \rho_{\max}, \theta_{\min}, Z) dx, \quad (\text{C.15})$$

$$\check{K}_{\delta}(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) = \int_{\rho_{\min}}^{\rho_{\max}} x^2 \check{f}(x, \rho_{\min}, \rho_{\max}, \theta_{\min}, Z) dx, \quad (\text{C.16})$$

$$\tilde{I}_{\delta}(\rho_{\max}, Z) = \int_{\rho_{\max}}^1 (x^2 - \rho_{\max}^2) \tilde{f}(x, \rho_{\max}, Z) dx, \quad (\text{C.17})$$

$$\tilde{J}_{\delta}(\rho_{\max}, Z) = \int_{\rho_{\max}}^1 x^2 (x^2 - \rho_{\max}^2) \tilde{f}(x, \rho_{\max}, Z) dx, \quad (\text{C.18})$$

$$\tilde{K}_{\delta}(\rho_{\max}, Z) = \int_{\rho_{\max}}^1 x^2 \tilde{f}(x, \rho_{\max}, Z) dx, \quad (\text{C.19})$$

with

$$\check{f}(x, \rho_{\min}, \rho_{\max}, \theta_{\min}, Z) = \left[x^2(\rho_{\min}^2 - \rho_{\max}^2)^2 - \sin^2 \theta_{\min} \rho_{\min}^2 (x^2 - \rho_{\max}^2)^2 \right]^{-\frac{1}{2}}, \quad (\text{C.20})$$

and

$$\tilde{f}(x, \rho_{\max}, Z) = \left[\frac{Z^2}{4(Z-1)} x^2 (1 - \rho_{\max}^2)^2 - (x^2 - \rho_{\max}^2)^2 \right]^{-\frac{1}{2}}. \quad (\text{C.21})$$

These equations reduce to the expressions for the monodisperse Z -Cone Model of Appendix A in the case of $a = 1$, as expected.

However, simply writing these expressions is not enough and we need to determine the dimensionless ratios $\rho_{\min}$ and $\rho_{\max}$ in order to actually calculate the excess energy and deformation for the large bubble. Effectively, we need to determine how large this “dimpling” of the surface is. Due to the complex nature of the geometry shown in Figure C.1, this can only be done in a limited extent at this time by numerically solving

$$\rho_{\min} = (a-1)^{-1} \sin \alpha \left(\frac{\left(\frac{4}{Z}\right) + (a-1)^{-3} (2 - 3 \cos \alpha + \cos^3 \alpha)}{3 \left[\tilde{J}_{\delta}(\rho_{\max}, Z) + \check{J}_{\delta}(\rho_{\min}, \rho_{\max}, \theta_{\min}, Z) \right] + \frac{Z-2}{2\sqrt{Z-1}}} \right)^{-\frac{1}{3}} \quad (\text{C.22})$$

for the paired values of $\rho_{\min}$ and $\rho_{\max}$ which give the smallest excess energy provided $\rho_{\min} < \rho_{\delta}$ and $\rho_{\min} < \rho_{\max}$.

It is clear from this that our system of equations is not complete, requiring one further equation to determine both $\rho_{\min}$ and $\rho_{\max}$, independently. While by definition, $\rho_{\min} = \rho_{\max}$ in the extreme limits of $\xi = 0$ and $\xi = 1$, we have yet to ascertain the precise relationship between them between these limits; although we expect region II to be comparatively small for all deformations. This is supported by the good agreement, seen in Section 7.1, between the results of Surface Evolver and

the model presented here, for which we assumed that $\rho_{\min} = \rho_{\max}$. Determining the size of region II analytically will be the subject of future work.

Appendix D

Derivation of the Kelvin Cone Model

We recall from Chapter 4 that we can generalise the Z -cone model to describe the Kelvin cell by separating our bubble into two different types of cones, corresponding to the eight hexagonal and six square faces of the Kelvin cell. In this appendix, we provide a derivation of the excess energy ε and liquid fraction ϕ for this model. We will also show how the internal pressure of a cone p_i is derived.

D.1 Excess Energy for the Kelvin Cell

The introduction of two sets of cones does not fundamentally alter the Euler-Lagrange minimisation procedure demonstrated in detail, for the Z -cone model, in Appendix A. The most notable difference is that, in this case, we cannot express the cone angles θ_h and θ_s in terms of the number of neighbours Z as we did in the Z -cone model.

The total surface area A of each cone is still written as

$$A = A_\delta + 2\pi \int_0^h r(z) \sqrt{1 + \left(\frac{dr(z)}{dz}\right)^2} dz, \quad (\text{D.1})$$

where A_δ is the surface area of the contact. Similarly, the volume V under this curve is given by

$$V = \pi \int_0^h r(z)^2 dz + \frac{\pi r(0)^3 \cot \theta}{3}. \quad (\text{D.2})$$

Indeed, the method for computing the excess energy ε can be followed exactly from that detailed in Appendix A, with the following two caveats.

Firstly, due to the introduction of the different opening angles θ_h and θ_s angles for the hexagonal and square cones, along with the associated angles γ_s and γ_h shown in Figure 4.3, will alter the second of the boundary conditions, equation (A.8). It is now given by

$$\left. \frac{dr(z)}{dz} \right|_{z=0} = \cot \Gamma_i, \quad (\text{D.3})$$

where the angles Γ_h and Γ_s are related to γ_h and γ_s via

$$\Gamma_i = \gamma_i + \theta_i - \frac{\pi}{2}. \quad (\text{D.4})$$

The angles Γ_h and Γ_s are the angles made by the curved surfaces of the cones and a line perpendicular to the z -axis extending from the axis to the edge of the cones. In the monodisperse Z -cone model (and in the wet limit of the Kelvin cell), they are simply given by

$$\Gamma_i = \theta_i. \quad (\text{D.5})$$

Secondly, the volume of each cone is no longer given simply by $V_c = \frac{4\pi}{3Z} R_0^3$. We recall from Section 4.1 that, in the case of the Kelvin cell, we must introduce a **global volume** constraint given by

$$8V_h + 6V_s = V_0, \quad (\text{D.6})$$

in contrast to the **local volume** constraint which applies to the regular *Z*-Cone model, which keeps the volume of each of the cones independently constant. Here V_h and V_s naturally denote the volumes of the cones associated with the hexagonal and square faces, respectively. Dividing both sides by V_0 , we have

$$8q_h + 6q_s = 1. \quad (\text{D.7})$$

where $q_h = V_h/V_0$ and $q_s = V_s/V_0$. The quantities q_h and q_s are fractions of the total volume V_0 taken up by any one of the square or hexagonal cones.

With these definitions of q_i , we can now clearly define the volume V_i of any cone as

$$V_i = \frac{4\pi R_0^3}{3} q_i. \quad (\text{D.8})$$

Incorporating these two small changes into the derivation of the original *Z*-cone model, we readily obtain the surface area A_i of any individual cone as

$$A_i(\rho_{\delta_i}, \theta_i, \Gamma_i, q_i) = \pi R_0^2 \left(\frac{4q_i}{3J(\rho_{\delta_i}, \Gamma_i) + \cot \theta_i} \right)^{\frac{2}{3}} [\rho_{\delta_i}^2 + 2(1 - \rho_{\delta_i}^2)K(\rho_{\delta_i}, \Gamma_i)]. \quad (\text{D.9})$$

As in the original *Z*-cone model, the variables ρ_{δ_h} and ρ_{δ_s} are ratios of the contact size δ of each cone to the width of the cone (see Figure 4.3).

The elliptic integrals $I(\rho_{\delta_i}, \Gamma_i)$, $J(\rho_{\delta_i}, \Gamma_i)$ and $K(\rho_{\delta_i}, \Gamma_i)$ are defined as

$$I(\rho_{\delta_i}, \Gamma_i) = \int_{\rho_{\delta_i}}^1 \sin \Gamma_i(x^2 - \rho_{\delta_i}^2) f(x, \rho_{\delta_i}, \Gamma_i) dx, \quad (\text{D.10})$$

$$J(\rho_{\delta_i}, \Gamma_i) = \int_{\rho_{\delta_i}}^1 \sin \Gamma_i x^2 (x^2 - \rho_{\delta_i}^2) f(x, \rho_{\delta_i}, \Gamma_i) dx, \quad (\text{D.11})$$

and

$$K(\rho_{\delta_i}, \Gamma_i) = \int_{\rho_{\delta_i}}^1 x^2 f(x, \rho_{\delta_i}, \Gamma_i) dx \quad (\text{D.12})$$

with

$$f(x, \rho_{\delta_i}, \Gamma_i) = [x^2(1 - \rho_{\delta_i}^2)^2 - \sin^2 \Gamma_i (x^2 - \rho_{\delta_i}^2)^2]^{-\frac{1}{2}}. \quad (\text{D.13})$$

The dimensionless excess energy ε for the Kelvin cone model is given by

$$\varepsilon(\rho_{\delta_h}, \rho_{\delta_s}, \theta_h, \theta_s, \Gamma_h, \Gamma_s, q_h, q_s) = \frac{8A_h(\rho_{\delta_h}, \theta_h, \Gamma_h, q_h) + 6A_s(\rho_{\delta_s}, \theta_s, \Gamma_s, q_s)}{4\pi} - 1 \quad (\text{D.14})$$

D.2 Liquid Fraction for the Kelvin Cell

Now we recall from Appendix B that the liquid fraction ϕ is simply equal to $\phi = 1 - \phi_g$ where ϕ_g is the total gas fraction. The total gas fraction can be easily determined because it is given by the ratio of the total bubble volume V_0 to the volume of the Voronoi cell such that

$$\begin{aligned} \phi_g &= \frac{V_0}{8V_{h_{vor}} + 6V_{s_{vor}}} \\ &= \frac{V_0}{8\left(\frac{\pi}{3}H_h^3 \tan^2 \theta_h\right) + 6\left(\frac{\pi}{3}H_s^3 \tan^2 \theta_s\right)}. \end{aligned} \quad (\text{D.15})$$

We have used the fact that the Voronoi cell which surrounds each of the cones in our geometric construction is a right-circular cone, with a volume given by $V_i = \frac{\pi}{3} H_i^3 \tan^2 \theta_i$.

Up to this point, we have largely considered the hexagonal and square cones in isolation, connected only by the total volume constraint. However, for these cones to constitute a realistic model of a foam, we require the two types of cone to have a common slant height r_s , for both the deformable cones and the Voronoi cones. Furthermore, we know that in the exact Kelvin cell, the ratio of distances $\frac{H_h}{H_s}$ from the centre of the bubble to each of the faces maintains a constant ratio of $\frac{\sqrt{3}}{2}$, at least for the isotropic deformation which we consider here. Combining these two ideas, we find that for the cone model, the ratio of distances to the faces of the Kelvin cell is slightly different from stated above. It is given by

$$\Rightarrow \frac{H_h}{\cos \theta_h} = \frac{H_s}{\cos \theta_s} = \nu = 0.864434. \quad (\text{D.16})$$

Inserting this relation, equation (D.16) into equation (D.15), along with height H_h of the hexagonal cone given by

$$H_h = R_0 \left(\frac{4q_h}{3J(\rho_{\delta_h}, \Gamma_h) + \cot \theta_h} \right)^{\frac{1}{3}} [I(\rho_{\delta_h}, \Gamma_h) + \cot \theta_h], \quad (\text{D.17})$$

and simplifying, we obtain the liquid fraction $\phi = 1 - \phi_g$ for the cone model applied to the Kelvin cell as

$$\boxed{\phi(\rho_{\delta_h}, \theta_h, \theta_s, \Gamma_h, q_h) = 1 - \frac{3J(\rho_{\delta_h}, \Gamma_h) + \cot \theta_h}{2q_h [I(\rho_{\delta_h}, \Gamma_h) + \cot \theta_h]^3 \left(4 \tan^2 \theta_h + \left(\frac{3}{v^3} \right) \tan^2 \theta_s \right)}}. \quad (\text{D.18})$$

The arguments presented here are general, and can be applied to describe a foam structure with more than two different types of cones. For more than two different types of cones, we simply need to specify the ratios of distances ν_i to each of the

different sets of faces, taking the nearest neighbours as a reference. Indicating the nearest neighbour contacts by the the index nn we have

$$\nu_i = \frac{H_{nn}}{H_i} = \frac{\cos \theta_{nn}}{\cos \theta_i}. \quad (\text{D.19})$$

Thus, the liquid fraction can be expressed for any number of cones by

$$\phi(\rho_{\delta_{nn}}, \theta_{nn}, \Gamma_{nn}, q_{nn}, \theta_i, Z_i, \nu_i) = 1 - \frac{3J(\rho_{\delta_{nn}}, \Gamma_{nn}) + \cot \theta_{nn}}{q_{nn} [I(\rho_{\delta_{nn}}, \Gamma_{nn}) + \cot \theta_{nn}]^3} \cdot \frac{1}{\sum_i \frac{Z_i}{\nu_i^3} \tan^2 \theta_i}. \quad (\text{D.20})$$

This has the form $\phi = 1 - G(\rho_{\delta_1}, \theta_1, \Gamma_1, q_1)M(\theta_i, Z_i, \nu_i)$ where G is a function of the nearest neighbour variables only while M encodes the details of the structure.

D.3 Pressure p_i

We stated in Chapter 4, that in order to provide a sufficient number of constraints to uniquely determine all of the variables involved in the extended cone model, we need to consider the internal pressure of our bubble.

The internal pressure of a bubble is higher than the atmospheric pressure, giving rise to the curvature of the surface. In the cone model, the pressure p_i in each of the cones must be equal so we will only discuss a single cone in what follows. In order to calculate the pressure p_i , we rely on a simple thermodynamic argument regarding the work done to increase the volume of the cone while keeping the size of the contact δ_i constant.

We begin by considering the volume of a cone as the sum of two parts, V'_i and V_i^* , such that

$$V_i = V'_i + V_i^*. \quad (\text{D.21})$$

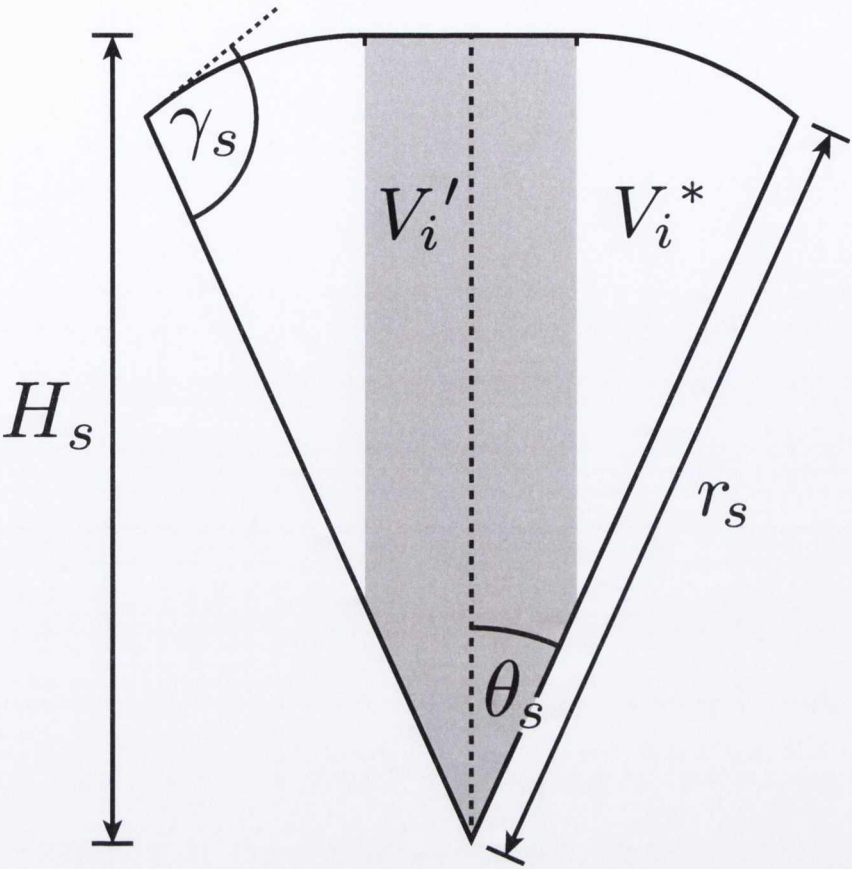


FIGURE D.1: Cross-section of a square cone for the Kelvin cone model. The shaded region V_i' is the volume which we associate with the contact while V_i^* is the volume associated with the free surface of the cone

The volume V_i' is the volume associated with the contact, indicated by the grey region in Figure D.1, while the remaining volume V_i^* is associated with the free surface of the cone.

If we now consider a small change to the volume of our cone, as though we were blowing it up, but crucially, the size of the contact δ_i remained the same (i.e. δ_i is constant). This change in volume ΔV_i is simply

$$\Delta V_i = \Delta V_i' + \Delta V_i^* = \frac{4}{3}\pi R_0^3(q_i^* - q_i) = \frac{4}{3}\pi R_0^3\Delta q_i. \tag{D.22}$$

However, we are not interested in ΔV_i itself but the individual volume changes ΔV_i^* . From the discussion above is it clear that ΔV_i^* can be obtained simply as

$$\Delta V_i^* = \Delta V_i - \Delta V_i'. \quad (\text{D.23})$$

The work W_i done in changing the volume of the cone by the small amount ΔV_i is the sum of two terms. The first term is the work done in increasing the volume (and hence surface area) of the free surface of the cone by ΔV_i^* .

$$W_{\Delta V_i^*} = p_i \Delta V_i^*. \quad (\text{D.24})$$

The second term is the work done by the surface tension σ to reduce the curvature of the free surface as the slant height of the cone increases. For a positive volume change of the cone, the work done in this case is given by

$$W_{\sigma_i} = 2\pi r_{s_i} \Delta r_{s_i} \cos \theta_i \cos \gamma_i. \quad (\text{D.25})$$

The total work done is equal to the total change in energy E_i of the cone such that

$$\Delta E_i = W_{\Delta V_i^*} + W_{\sigma_i} = p_i \Delta V_i^* + \cos \gamma_i 2\pi r_{s_i} \Delta r_{s_i} \cos \theta_i. \quad (\text{D.26})$$

Simply rearranging this equation for p_i gives us an equation for the pressure in cone as it is deformed

$$\boxed{p_i = \frac{\Delta E_i}{\Delta V_i^*} - 2\pi r_{s_i} \cos \gamma_i \cos \theta_i \frac{\Delta r_{s_i}}{\Delta V_i^*}}. \quad (\text{D.27})$$

There is a final technical note which needs to be made here. Increasing the volume of a cone in this way while keeping the contact radius δ_i constant does not imply that the associated ρ_{δ_i} is constant. Denoting quantities for the larger volume cone with tildes and using the definition $\rho_{\delta_i} = \frac{\delta_i}{r_i(0)}$ we see that

$$\widetilde{\rho_{\delta_i}} \widetilde{r_i}(0) = \rho_{\delta_i} r_i(0). \tag{D.28}$$

Inserting the appropriate form of $r_i(0)$ for the extended cone model (similar to equation (A.20) for the Z -cone model) we find that $\widetilde{\rho_{\delta_i}}$ is given, for the larger volume, by

$$\widetilde{\rho_{\delta_i}} = \left(\frac{q_i (3J(\widetilde{\rho_{\delta_i}}, \Gamma_i) + \cot \theta_i)}{\widetilde{q_i} (3J(\rho_{\delta_i}, \Gamma_1) + \cot \theta_i)} \right)^{\frac{1}{3}} \rho_{\delta_i}. \tag{D.29}$$

This equation is necessary for explicit calculation of the pressure p_i defined above.

Appendix E

Estimating the Energy of the Dry Kelvin Cell

In the course of describing the excess energy ε of the Kelvin cell with the cone model (see Chapters 4 and 5), we noticed that the energy E of the dry Kelvin foam (not the excess energy here), which is proportional to the surface area A (see equation (1.8)), can be well estimated in a very elementary way, which may have applications to other cases.

The natural first approximation to the Kelvin cell is the Voronoi cell of the bcc lattice (see Figure 4.1(a)). This corresponds to the truncated octahedron, with fourteen flat faces which are planes equidistant from first and second nearest neighbour bubbles. The angles between these planes do not conform to Plateau's equilibrium rules (see Section 1.2), that is, they are not 120° . The equilibrium structure, therefore, has slightly lower energy. Our objective is to estimate the reduction in energy ΔE when the Voronoi structure with energy E_V is relaxed,

$$\Delta E = E_V - E. \tag{E.1}$$

We first note that the Voronoi structure can be held in equilibrium by applying additional external forces at the edges of the quadrilateral faces, to compensate for the mismatch of surface tensions (see Figure E.1).

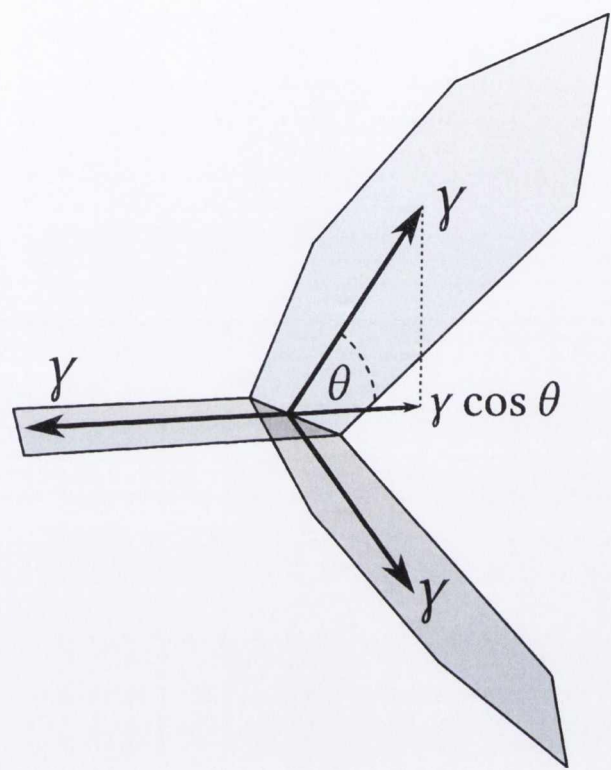


FIGURE E.1: If a surface tension γ is associated with the faces of the truncated octahedron, it is not in equilibrium. This sketch shows the forces due to surface tension acting at an edge between a quadrilateral face and two hexagons in 3D. Note that in the unrelaxed truncated octahedron 2θ equals the tetrahedral angle (i.e. $2\theta = \arccos(-1/3) \approx 109.47^\circ$) in accordance with Plateau’s Laws (see Section 1.2).

We then proceed to estimate the work done by these fictitious forces as they are continuously reduced to zero. For each increment of such a change, the work is simply force times displacement. To incorporate the latter, we approximate the curved edges of the square face as parabolic, and the force as conforming to Hooke’s Law. A short calculation then gives the relative surface area A/A_0 as

$$\frac{A}{A_0} = 1.0968. \tag{E.2}$$

Kusner and Sullivan sketch the computation of a lower bound for the energy of a Kelvin cell [75] using a similar argument to above, resulting in $A/A_0 \geq 1.0954$.

Appendix F

Simulating Bubbles in a Confined Geometry with the Surface Evolver

The Surface Evolver software [18] developed by Prof. Kenneth Brakke is widely used in computational modelling of surfaces driven by surface tension, such as soap bubbles, subject to a variety of constraints. We have made use of the Surface Evolver to evaluate the excess energy ε of a single bubble in an ordered foam to provide a comparison with the results obtained from the cone model. This was necessary because of the inherent experimental difficulties of stabilising, imaging and measuring the surface area of a bubble in the bulk of a foam, particularly close to the wet limit. We wish to acknowledge the help of David Whyte in particular and also Steven Tobin for help, with regard to performing these simulations.

In simplest terms, the Surface Evolver works by representing a continuous surface, such as a liquid film, approximately as a series of points joined together by directed straight edges forming a mesh of triangular **facets**. A normal vector is assigned to each of the facets to specify whether it faces inwards or outwards. This is important because we define a **body** such as a bubble as a list of facets which all point in the same direction.

Once a bubble is defined in this way, it is possible to constrain it to have a certain fixed volume. The success of this approach can be seen in the example of a spherical bubble which is initially specified as a crude cubic lattice of points connected by edges. Once this tessellation has been defined, its correspondence to a sphere is improved by further subdividing into smaller triangles and by allowing the vertices to move in order to minimise the total surface area. This minimisation is done here using the method of conjugate gradient descent [18]. By implementing a series of refinements of the tessellation and minimisation steps, the cube becomes more rounded and we obtain a better and better approximation of a spherical bubble. Increasing the number of tessellations significantly increases the memory required to store the configuration and slows down the minimisation procedure and the degree of refinement used must be tailored to the accuracy required.

To simulate the contact of such a spherical bubble with Z neighbouring bubbles in a crystalline arrangement, we define a series of planes in the direction of the neighbouring bubbles. These planes are treated as impenetrable barriers, with the bubble surface constrained to lie strictly within this arrangement of planes. These planes are initially defined to be situated slightly beyond the edge of the bubble and the deformation proceeds by moving the planes steadily closer to the bubble in a series of steps. Each time the bounding planes are moved in, the surface of the bubble is refined and minimised with the final value of the surface area A being stored before moving on to the next stage. This method was also used for comparison with the curved contact cone model of Chapter 7 with the flat planes being replaced by curved planes whose curvature was specified to match the radius of curvature of the contact.

While the deformation ξ is clearly defined at each time step by the position of the planes, the excess energy $\varepsilon = A/A_0 - 1$ is more subtle. This is due to the fact that it depends crucially on the value of A_0 , the surface area of the initial spherical bubble. For accurate comparison with the cone model, which is only limited by the accuracy with which the numerical integrals can be performed, the degree of tessellation in this case needs to be high (we refined and minimised at least five times in each of our simulations).

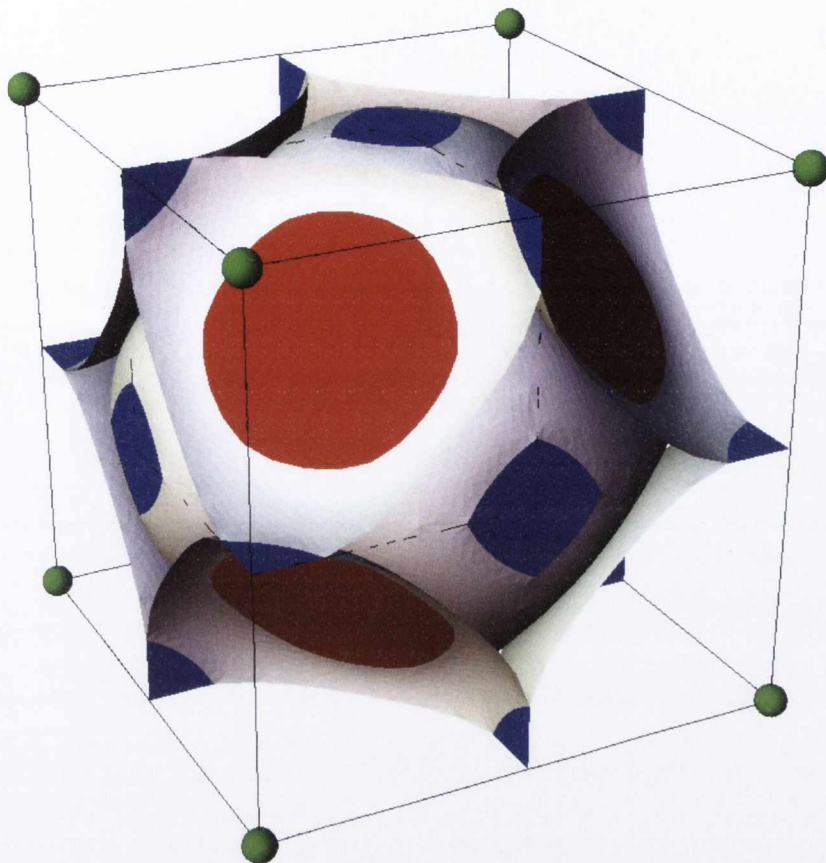


FIGURE F.1: The equilibrium structure for a Kelvin foam, including all surfaces within the conventional cell. The $\langle 111 \rangle$ contact faces are shown in red, and the $\langle 100 \rangle$ faces in blue. This is built, exploiting the reflectional symmetries, from a representative cell one eighth the size of this cell. Indeed, the full foam can be built from reflected and translated copies of such a representative cell.

The Kelvin foam consists of repeated translated copies of the conventional bcc for a foam shown in Figure F.1. The procedure for simulating this Kelvin cell with the Surface Evolver was different to that for the Z -cone model. For simplicity, we can exploit some of the symmetries of the conventional cell; namely, reflectional symmetry in the x , y and z directions. Brakke and Sullivan [76] exploit even more symmetries to yield a minimal representation of the full dry Kelvin foam. Hence we arrive at a reduced cell, which has one eighth of the volume of the conventional cell, and is composed of a cube containing one eighth of a bubble at each of two opposite corners. This increases the speed of computation considerably.

We begin with a very roughly triangulated approximation of the configuration in Figure F.1, with appropriate film edges constrained to lie within the faces of the

cube, i.e. planes of reflection. The energy minimisation process ensures that films will meet these planes at 90° , as required for smoothness. We note that in order to faithfully represent the full foam, films which lie in these planes (in this case, the blue $\langle 100 \rangle$ faces) are given half of their ‘real’ surface tension. Hence we give the red $\langle 111 \rangle$ contact faces a tension of 2 and all other faces a tension of 1. Iterated mesh refinements and gradient-descent minimisations yield the configuration shown in Figure 4.1(b).

Appendix G

Computation of the Bubble Shape

The purpose of this appendix is to briefly outline how the precise shape of a single bubble at a liquid surface (see Figure 6.1) is calculated, using an algorithm developed by Princen [57]. This procedure forms an integral part of the simulations of gas diffusion in bubbles which we discussed in Chapter 6.

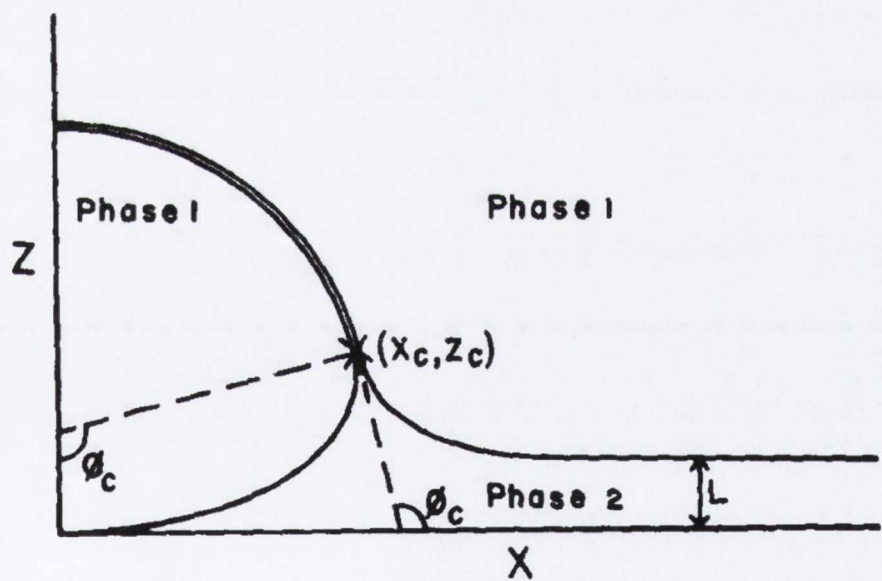


FIGURE G.1: Schematic 2-D cross-section of a gas bubble (Phase 1) at the surface of a liquid (Phase 2). The point (x_c, z_c) marks a ring of contact above which the bubble is in contact with the gaseous atmosphere. L represents the height of the liquid surface above the bottom of the bubble while ϕ_c is the angle made between the normal at (x_c, z_c) and the negative z -direction. This figure is reproduced from Princen [57].

The 2D cross-section of a surface bubble, represented schematically in Figure G.1, is described by the following three **shape equations** [57]:

$$\frac{1}{R_1} + \frac{1}{R_2} = cz + \frac{2}{b}, \text{ (interface between bubble and bulk-liquid)} \quad (\text{G.1})$$

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{R_c}, \text{ (spherical cap)} \quad (\text{G.2})$$

$$\frac{1}{R_1} + \frac{1}{R_2} = c(z - L), \text{ (distorted liquid surface).} \quad (\text{G.3})$$

As we described in Section 6.1, above the point (x_c, z_c) the bubble shape is a spherical cap with a radius of curvature R_c . The other interfaces are more complicated, however, with the radii of curvature, R_1 and R_2 , of each of the interfaces given by

$$\frac{1}{R_1} = \frac{\frac{d^2 z}{dx^2}}{[1 + (\frac{dz}{dx})^2]^{3/2}} \quad (\text{G.4})$$

and

$$\frac{1}{R_2} = \frac{\frac{dz}{dx}}{x[1 + (\frac{dz}{dx})^2]^{1/2}}. \quad (\text{G.5})$$

The radius of curvature at the bottom of the bubble is given by b and c is given by

$$c = \frac{1}{l_0^2} = \frac{\Delta \rho g}{\sigma}, \quad (\text{G.6})$$

where l_0 is the capillary length (see equation (6.1)). L is the height of the flat liquid surface above the bottom of the bubble and is related to our other simulation parameters by the relation $L = \frac{2}{c}(\frac{2}{R_c} - \frac{1}{b})$.

The algorithm for solving this system for the shape of the bubble begins by specifying the volume of the initial bubble. The radius of curvature R_c of the bulk interface is given by $R_c = \frac{x_c}{\sin \phi_c}$ [57], where x_c is the experimentally observed bubble radius (viewed from above) and ϕ_c is the angle made between the normal at (x_c, z_c) and the negative z -direction.

The spherical cap and bulk-liquid interfaces must have a common slope of $\tan \phi_c$ at the critical point (x_c, z_c) . Utilising this condition, the system of equations is then solved (in our case using the ode45 equation solver method from Matlab.) for a value of ϕ_c satisfying the boundary conditions of total bubble volume and slope matching at the intersection point. We obtain the value of the critical point (x_c, z_c) , the radius of curvature R_c as well as the area of permeation A_c of the bulk interfacial film. This completely specifies the shape of the bubble for this volume. Thus we can apply an appropriate form of Fick's Law (see Section 6.3) to allow us to obtain a new bubble volume and the process is repeated.

Appendix H

Gas Diffusion in Bubbles

In this appendix, we provide derivations for the key analytical results presented in our discussion of the diffusion characteristics of a single gas bubble in Chapter 6. As we did in Chapter 6, we will differentiate between bubbles containing a single, soluble gas of permeability k_B and bubbles containing a mixture of two gases (A and B) with different permeabilities k_A and k_B . We shall refer to these two cases as Case One and Case Two, respectively (see Section 6.2).

H.1 Boundary Between Growing and Shrinking

We recall from Chapter 6 that the diffusion of gas between bubbles proceeds according to pressure gradients, with gas flowing from regions of higher pressure to lower pressure according to Fick's First Law of Diffusion [59]. The total gas pressure p_g in a single bubble is higher than the atmospheric pressure P_0 by an amount Δp equal to the Laplace pressure

$$\Delta p = p_g - P_0 = \frac{4\sigma}{R_c}, \quad (\text{H.1})$$

where R_c is the radius of curvature of the diffusing film.

For Case One, this pressure difference causes the bubble to shrink in time (according to equation (6.3)), as seen in Figure 6.3. We noted that, due to the simplicity of equation (H.1), R_c decreases as the bubble shrinks, causing shrinking bubbles to continue shrinking until it becomes entirely submerged beneath the liquid surface.

However, we recall that in the instance of gas mixtures, as defined in Case Two, the diffusion is driven by the partial pressures (see equation (6.4)) of the gas components, leading to the more complicated diffusion equation

$$-\Delta V = A_c \Delta t \left\{ k_A \frac{(p_A - \bar{p}_A)}{P_0} + k_B \frac{(p_B - \bar{p}_B)}{P_0} \right\}. \quad (\text{H.2})$$

Here, the barred quantities denote properties of the atmosphere. We saw in Section 6.3.2 that the introduction of partial pressures allows for bubble growth (rather than shrinking) under certain circumstances, particularly when the permeabilities k_A , k_B of the two components are significantly different.

From equation (6.4) we see that $\frac{p_A}{p_B} = \frac{x_A}{x_B}$ which allows us to rewrite equation (H.2) in the form

$$-\frac{\Delta V}{A_c \Delta t} = \frac{k_B p_B}{P_0} \left\{ \frac{k_A}{k_B} \left(\frac{x_A}{x_B} - \frac{\bar{p}_A}{p_B} \right) + \left(1 - \frac{\bar{p}_B}{p_B} \right) \right\}. \quad (\text{H.3})$$

We can rewrite (H.3) to determine a surface in phase space which separates growing behaviour from shrinking behaviour. This is done by considering $\Delta V = 0$ in (H.3), equivalent to setting the curly braces equal to zero, resulting in

$$\frac{k_A}{k_B} = \frac{\frac{\bar{p}_B}{p_{tot}} - (1 - x_A^*)}{x_A^* - \frac{\bar{p}_A}{p_{tot}}}. \quad (\text{H.4})$$

x_A^* denotes the critical value of the concentration at which $\Delta V = 0$.

In the simplest case of a mixed gas bubble open to the atmosphere which contains only the soluble gas B , the partial pressures of the gases in the atmosphere are simply given by

$$\bar{p}_A = \bar{x}_A P_0 = 0 \quad (\text{H.5})$$

$$\bar{p}_B = \bar{x}_B P_0 = P_0. \quad (\text{H.6})$$

Taking the total pressure in the bubble as $p_{tot} = p_g$ (i.e. irrespective of whether or not it is a mixture) and using (H.5) and (H.6) we further simplify equation (H.4) to obtain

$$\frac{k_A}{k_B} = 1 + \frac{1}{x_A^*} \left(\frac{P_0}{P_0 + \frac{4\sigma}{R_c}} - 1 \right). \quad (\text{H.7})$$

Equation (H.7) expresses the fact that for any mixture of gases with a fixed ratio of permeabilities $\frac{k_A}{k_B}$ and for any bubble size $R_c = \frac{x_c}{\sin \phi_c}$ (see Appendix F), there is a critical concentration x_A^* of gas A for which the bubble neither grows nor shrinks. Either side of this surface, growing or shrinking behaviour is observed (see Figure 6.2).

H.2 On Power Laws and Spherical Caps

As we noted in Section 6.4, the growing or shrinking of a surface bubble much larger than the capillary length l_0 represents a special case. In this size regime, the bubble shape is well approximated by a hemispherical bubble for which the radius of curvature R_c of the diffusing film is **equal** to the experimentally measured bubble size x_c . Further changes to the volume of these approximately hemispherical bubbles does not significantly alter the bubble shape, leading simply to a similar hemispherical bubble. The insensitivity of the overall bubble shape to changes in volume gives rise to self-similar scaling laws which are asymptotically approached

for large bubbles (i.e. they are only strictly true for exactly hemispherical bubbles). In the following sections, we will show how these scaling laws are derived analytically for perfectly hemispherical bubbles.

H.2.1 Case One: Permeability k_B

We begin our discussion of self-similar scaling with the familiar case of Case One, the shrinking bubble. Consider a hemispherical bubble of radius R_c resting atop a flat surface and containing a (soluble) gas of permeability k_B which is also present in the surrounding atmosphere. Fick's Law in this case is given

$$-\frac{dV}{dt} = \frac{k_B A_c \Delta p}{P_0}. \quad (\text{H.8})$$

For a hemispherical bubble,

$$\Delta p = \frac{4\sigma}{R_c}, \quad (\text{H.9})$$

$$A_c = 2\pi R_c^2, \quad (\text{H.10})$$

$$V = \frac{2}{3}\pi R_c^3. \quad (\text{H.11})$$

Inserting these equations (H.9) and (H.10) into equation (H.8) we obtain

$$-\frac{dV}{dt} = \frac{8\pi k_B \sigma R_c}{P_0}. \quad (\text{H.12})$$

If we now remember that the volume V on the left-hand side of this expression depends explicitly on the radius R_c we can make use of the identity

$$\frac{dV(R_c)}{dt} = \frac{dV(R_c)}{dR_c} \frac{dR_c}{dt} = 2\pi R_c^2 \frac{dR_c}{dt}. \quad (\text{H.13})$$

Inserting this result into equation (H.12) and simplifying we have that

$$R_c \frac{dR_c}{dt} = -\frac{4k_B\sigma}{P_0}. \quad (\text{H.14})$$

As we are considering a diffusion process, the change in volume is accompanied by a similar change in the radius of the hemisphere. Denoting the initial radius of the hemisphere as $R_c(t_0) = R_0$, we can integrate equation (H.14) with respect to R_c to give

$$\boxed{R_c^2(t) = R_0^2 - \frac{8k_B\sigma}{P_0}(t - t_0)}. \quad (\text{H.15})$$

We note at this point that we recover an identical expression for the self-similar shrinking of a spherical bubble. Physically, this implies that in the case of a shrinking bubble, spherical and hemispherical bubbles of the same radius (of curvature) R_c will shrink such that they will always have the same radius of curvature R_c . This is in spite of the fact that they have different volumes. We will comment on this further in the next section.

H.2.2 Case Two: $k_B \neq 0$ and $k_A = 0$

In the case where we have a mixture of gases of different solubilities ($k_A < k_B$) present, we have shown in Section H.1 that a bubble grows in time provided the volume concentration of the less soluble gas is above some critical value x_A^* . For bubbles much larger than the capillary length, the partial pressure differences are orders of magnitude larger than the Laplace pressure terms. In the extreme limit, we can neglect the Laplace pressure terms altogether such that the diffusion is driven solely by the partial pressure difference of the soluble gas B . Once again, for a hemispherical bubble we have that

$$\Delta p = x_A P_0 \quad (\text{H.16})$$

$$A_c = 2\pi R_c^2 \quad (\text{H.17})$$

$$V = \frac{2}{3}\pi R_c^3. \quad (\text{H.18})$$

As we did for Case One above, we insert these expressions into Fick's Law for gas mixtures, equation (H.2), to obtain

$$-\frac{dV}{dt} = -\frac{k_A (2\pi R_c^2) (x_A P_0)}{P_0}. \quad (\text{H.19})$$

As in the previous section, we can use the fact that the bubble volume V is a function of R_c such that

$$R_c^3 dR_c = \frac{3k_A V_A}{4\pi} dt, \quad (\text{H.20})$$

where V_A is the total volume of the insoluble gas A in the mixture, rather than its volume ratio x_A .

Integrating this from R_0 to $R_c(t)$, we find that

$$\boxed{R_c(t)^4 = R_0^4 + \frac{6k_A V_A}{\pi} (t - t_0)} \quad (\text{H.21})$$

The inclusion of a volume V_A of insoluble gas leads to a self-similar growth of the radius (of curvature) of the bubble with time.

In contrast to the case in the previous section, the term on the far right-hand side of equation (H.21) changes if a spherical bubble is considered instead of hemispherical bubble, for the same total volume of gas V_A . This difference is due to the form of the pressure difference Δp for the two cases. The presence of R_c explicitly in the pressure difference for Case One allows an additional cancellation of terms

in obtaining equation (H.14) which is not the case for Case Two. In this case, considering a spherical bubble containing a mixture of gases gives

$$\boxed{R_c(t)^4 = R_0^4 + \frac{3k_A V_A}{\pi} (t - t_0)} \quad (\text{H.22})$$

From this, we see that the rate at which the radius of curvature R_c increases depends upon the ratio of insoluble gas volume V_A to the surface area of the bubble, at least for bubbles represented by some section of a sphere (i.e. the cap of a spherical cone). To illustrate this, we present the most general form of the growth law for the case of a spherical cap.

As we did for the hemisphere, we begin by expressing the volume and surface area of a spherical cap in terms of its radius of curvature R_c . They are given by

$$V_{cap} = \frac{\pi}{3} R_c^3 (2 - 3 \cos \theta + \cos^3 \theta), \quad (\text{H.23})$$

and

$$A_{cap} = 2\pi R_c^2 (1 - \cos \theta). \quad (\text{H.24})$$

where θ is the angle between a line from the edge of the spherical cap to the centre of the sphere and a line joining the centre of the sphere to the centre of the cap. These two expressions allow us to determine the value of θ which gives one Z th the volume of a sphere. Namely,

$$\frac{V_s}{Z} = \frac{4\pi}{3Z} R_c^3 = \frac{\pi}{3} R_c^3 (2 - 3 \cos \theta + \cos^3 \theta) \quad (\text{H.25})$$

such that

$$\frac{4}{Z} = 2 - 3y + y^3 = (1 - y^2)(y + 2) \quad (\text{H.26})$$

where $y = \cos \theta$.

This equation is solved for

$$y(Z) = \frac{Z}{\sqrt[3]{-Z^3 + 2Z^2 + 2\sqrt{Z^4 - Z^5}}} + \frac{\sqrt[3]{-Z^3 + 2Z^2 + 2\sqrt{Z^4 - Z^5}}}{Z}. \quad (\text{H.27})$$

As a result of y depending exclusively on Z and not on R_c , we can simply include it in our derivation of the hemispherical case, as a prefactor, to obtain the general expression,

$$R_c(t)^4 = R_0^4 + \frac{24k_A V_A}{\pi} \left[\frac{1}{(1-y)^3(y+2)^2} \right] (t - t_0) \quad (\text{H.28})$$

This can more elegantly be expressed as

$$R_c(t) = (C_1 + C_2 t)^{1/4} \quad (\text{H.29})$$

where

$$C_1 = R_0^4 - \frac{3k_A V_A Z^2 (1 - y(Z))}{2\pi} t_0, \quad (\text{H.30})$$

$$C_2 = \frac{3k_A V_A Z^2 (1 - y(Z))}{2\pi}. \quad (\text{H.31})$$

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