Exploring the stability and dynamics of nanobubbles

Tan, Beng Hau

2017

<http://hdl.handle.net/10356/72533>

<https://doi.org/10.32657/10356/72533>

EXPLORING THE STABILITY AND DYNAMICS OF NANOBUBBLES

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

EXPLORING THE STABILITY AND DYNAMICS OF
NANOBUBBLES

TAN BENG HAU

an experimental, theoretical and numerical study

January 2017

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Dedicated to my parents,
Siew Luan Choo and Tan Boon Hock.

ABSTRACT

Nanoscale domains of gas in liquids, known as nanobubbles, have received substantial attention as much for their unusual fundamental properties as for their potential applications in microfluidics or cleaning. Due to the inability of the widely-used atomic force microscopy (AFM) to observe dynamic events, many basic properties of nanobubbles remain to be understood, such the strength of the line pinning that appears to facilitate their remarkable stability. Through experiments, theory and numerical simulations, we resolve some open questions in nanobubbles, with a particular focus on their dynamics and stability mechanisms.

The first half of this thesis focuses on issues related to surface nanobubbles. To address an on-going problem with contamination, we demonstrate a method to distinguish between nanobubbles and polymeric drops of contamination by applying predominantly vertical or lateral forces on these objects. We make the first direct estimates of the line pinning on nanobubbles, through dynamic imaging with optical fluorescence microscopy. Since typical nucleation techniques are easily contaminated and lead to an uncontrollable distribution of nanobubbles, our results will be useful in developing techniques to control the distribution of nanobubbles for various applications.

The second half of this thesis pertains to the observation of nanobubbles in an electron microscope. These nanobubbles appear not to be stabilised by the line pinning or oversaturation that sustain surface nanobubbles. We show instead that imaging conditions typical in a transmission electron microscope stabilises these nanobubbles by increasing the liquid's viscosity by orders of magnitude. Our results provide mechanistic understanding to the long-standing and puzzling observation that a wide range of phenomena in fluids imaged with electron microscopy appear to be significantly damped.

ACKNOWLEDGEMENTS

My supervisor Claus-Dieter Ohl has offered me a great degree of freedom and support to pursue my research. I cherish very much the hours he has spent on me to share his advice and intuition on research matters, but also to provide much needed counsel on personal matters. I have learned most from Dieter by his example. His fondness for tinkering with side projects for no other reason than genuine curiosity inspires my own passion for science.

My co-supervisor Evert Klaseboer has a meticulous style and exacting standards which have often motivated me to think very long and hard about how to improve every aspect of my work. Evert takes a “tough love” approach in his mentoring but it has been very important for my development as a scientist. My unofficial co-co-supervisor, Rogerio Manica, is also in the same vein. Thank you both for pushing me to improve, and never giving up.

My thanks to the Agency for Science, Technology and Research (A*Star) for funding my PhD via the A*Star Graduate Scholarship. Kasthuri Devi and Shahrena Asnawi handle my administrative needs at A*Star promptly, professionally and flexibly. At NTU I thank Chua Si Yun, Lee Yean Chin, Tony Gan, and professor Chee Yeow Meng.

I am deeply grateful to have the chance to pursue two university degrees, especially as it almost didn’t happen. My grades in high school were not good enough for the public universities in Singapore. As luck would have it, the then-head of the physics department in NTU, Alfred Huan, opened the intake of the physics course to a number of mediocre students including myself. But for that stroke of luck, I would not have had the opportunity to experience the depth, freedom and variety of a university education.

The multinational ‘bubbles’ in the Cavitation Lab make research life varied and a lot of fun. In no particular order: Fenfang, Roberto, Minh, Dr Zeng, Tandiono, Julien, Jiaming, Robin, Raghu, Firdaus, Longquan, Weiwei, Santosh, Tatsuya, Yuanxiang, Luong, Milad, Hema and Anne. It was a pleasure to work with all of you in some capacity or other.

In my day-to-day work, I work most closely with the nanobubbles team. It is my great honour to be mentored by An Hongjie, who in addition to being a *bona fide* AFM expert, is one of the most easy-going and most generous spirited people you could ever meet. Almost everything else I know in the laboratory was taught in one way or another by Chan Chon U, who is one of the most talented scientists that

I know. Manish Arora was a great mentor to me and gently oriented me into the world of surface nanobubbles. I worked with Meera Mohan trying to understand the nanobubbles she first observed in TEM and am grateful for the chance to work with her on this challenging topic.

I'm fortunate to have the chance to pick the brains or work with many great mentors from A*Star, NUS, NTU and elsewhere. Thanks to Derek Chan, Leong Fong Yew, Tran Si Bui Quang, Wang Qiang, and Wang Jianfeng. I spent plenty of time discussing various ideas with Su Haibin and Chapter 2 in particular was inspired by his perceptive questions. At NUS I had a short but fruitful collaboration with Duane Loh, which has led to Chapter 8 of this thesis. I am grateful to have received his mentorship for hours at a time, on many topics ranging from tips to improve my code, to impromptu courses to refresh a pitiful grasp of solid state physics. Plus, Duane's gift of *Numerical Recipes* is one of the best I have ever received.

I am the proud son of a career civil servant nurse and a port worker. My parents lived through a world war, grew up as emaciated children in most destitute time in my country's history, and spent decades working on modest salaries to put their children through school. The creature comforts that I enjoy today owe everything to their sacrifices. My sister, Eng Yong, for her admirable ability to stay cheerful even in challenging times. Thanks to Tinah, for caring for our family. My cousins, *che ches* Ah Noi, Nancy and Julie, are some of the most grounded and pure-hearted people I have met.

Finally, my wife Kelly, for showing me how to love someone with all your heart and soul.

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ACRONYMS

AFM	atomic force microscopy
APS	ammonium persulphate
CCD	charge coupled device
ESEM	environmental scanning electron microscopy
HOPG	highly ordered pyrolytic graphite
MSD	mean squared displacement
MD	molecular dynamics

PDMS polydimethylsiloxane

RDF radial distribution function

TIRFM total internal reflection fluorescence microscopy

TEM transmission electron microscopy

INTRODUCTION

It is our common experience that when bubbles deposit on an immersed surface, or drops of water on a dry one, their contact angles are universal – independent of the droplet size. This curious observation traces its origin back to Young's equation, which states that the contact angle depends only on the balance of interfacial energies at the three phase line of the object. A bubble or a droplet should have a contact angle that is defined only by the unique combination of the liquid and the substrate.

This simple picture works well in the macroscale, but inevitably breaks down when the size of a droplet or a bubble is in the micro or nanoscale. At this scale, physical and chemical heterogeneities on the substrate start to become significant, and even properties of the liquid that were once thought to hold to a molecular scale, such as the surface tension diverge from their bulk values. As we will see, the inability of soft objects to achieve the uniquely identifiable contact angles of their macroscopic counterparts is behind much of the fundamental intrigue about surface nanobubbles, and also the more banal matter of distinguishing nanobubbles from other soft matter, such as contamination.

1.1 THE MYSTERY OF SURFACE NANOBUBBLES

Surface nanobubbles were discovered by accident in the 1990s when Parker *et al.* [1] found an unexpected long-ranged attractive force between two immersed hydrophobic spheres at separations of up to 100 nm, well in excess of the ~ 1 nm regime in which van der Waals forces are expected to act. Even more surprisingly, the force curves were *stepped* rather than continuous, as one would expect in classical physics. The interpretation of Parker *et al.* was that the steps originated from nanoscopic bubbles of a characteristic height $h \sim 10$ nm pulling the spheres together.

The first experiments to directly visualise surface-attached nanobubbles were performed by Lou *et al.* [2] and Ishida *et al.* [3] in 2000. The first topological images of nanobubbles made by gentle tapping mode atomic force microscopy (AFM) found spherically-capped domains with heights $h \sim 10$ nm and base radii $L \sim 100$ nm, in agreement with the hypothesis of Parker *et al.* The work of Lou *et al.* is particularly notable for pioneering the now widely-used technique of solvent exchange. The process of flushing the substrate alternately

2 INTRODUCTION

Figure 1.1: Early evidence of surface nanobubbles. (a) Discrete steps in the force curves between two hydrophobic spheres. Reprinted with permission from Parker *et al.* [1], copyright the American Chemical Society. (b) The first known AFM images of surface nanobubbles nucleated by solvent exchange. Reprinted with permission from Lou *et al.* [2], copyright American Vacuum Society.

with water and organic solvent generates a sufficiently large oversaturation of gas within the liquid to support the nucleation of a dense population of nanobubbles.

Despite resolving the initial mystery of the long-ranged hydrophobic force, the nanobubbles themselves have proven to be even more mysterious, possessing some anomalous properties that have still not been fully explained. Unexpectedly, the contact angles of nanobubbles, are not only universally smaller than predicted by Young's equation but appear to be independent of the substrate. But perhaps the most astonishing property of surface nanobubbles is their longevity. The well-established diffusion theory of Epstein and Plesset [4] predicts that a spherical nanobubble with radius $R = 1 \mu\text{m}$ in bulk liquid should dissolve within a diffusive timescale $\tau \sim R^2/D \sim 0.1 \text{ ms}$. Yet surface nanobubbles have been observed to persist for at least several days with no imminent sign of dissolution [5], a discrepancy which stretching orders of magnitude.

Due to the stark differences between the experiments and the expectation of classical physics, the existence of surface nanobubbles was hotly disputed for much of the history of the field and even outright denied in the pages of the journal *Nature* [6]. However, over time, various groups in the field have built up a strong body of results proving the existence of nanobubbles and their gaseous nature. A few of the landmark papers in this area include the first observations of nanobubbles with both fluorescence microscopy [7] and interference microscopy [8], nanobubbles dissolving under continuous

degassing [9, 10], infrared spectroscopy to find chemical signals of gases [10], or even quartz microbalance measurements [11] to detect minute differences in weight induced by the presence of nanobubbles on a substrate.

Much of the historical research efforts in nanobubbles have focused on measuring and understanding their basic properties. Yet there remain a number of significant experimental and theoretical challenges towards their understanding.

1.2 WHEN CONTAMINATION STRIKES

The field of nanobubbles is known to be fraught with issues with reproducibility and contamination. There is only broad agreement between research groups on certain ‘stylised facts’ such as that the contact angles are much smaller than would be expected, but the quantities measured by research groups differs considerably. This comes as a surprise considering that nucleation experiments are often performed using commonly-available liquids (usually just water and ethanol) and atomically-flat graphite.

Only in the last two years, Berkelaar *et al.* [12] unexpectedly found that the use of disposable medical syringes and cannulas can lead to the nucleation of polymer droplets instead of the gaseous nanobubbles that were expected. The droplets originate from the use of biologically inert silicone oils to lubricate needles and syringe barrels to reduce topical pain when delivering injections during medical care. In Figure 1.2 we compare liquid nanodroplets of polydimethylsiloxane with surface nanobubbles nucleated on the same substrate, which unexpectedly have the same contact angle of 22° . Like surface nanobubbles, nanodroplets also exhibit unexpectedly small contact angles and behave identically under various imaging loads. To further complicate the picture, it has been reported that oil nanodroplets can be deliberately produced using a protocol similar to the water-ethanol exchange for nanobubbles [13, 14].

The key observation by Berkelaar *et al.* that plastic syringes – used widely in the field – are a source of contamination in nucleation experiment has cast doubt on the entire body of work on nanobubbles spanning two decades. Moreover, AFM methods are apparently incapable of distinguishing between nanobubbles, nanodroplets, or even a combination or both on the same substrate.

Methods have already been developed to distinguish gaseous from liquid bodies, but each has its issues. Degassing experiments performed by Zhang *et al.* [5] found that only some of the objects in the experiments disappeared. It is not fully clear whether the objects that did survive were oil droplets (the authors of [5] would

Figure 1.2: Liquid droplets or gas bubbles? The objects in these AFM scans have the same contact angle of about 22° . (a) Nanodroplets of polydimethylsiloxane. The z-range is 21 nm. Image reproduced from [12], with courtesy of R. P. Berkelaar. (b) Surface nanobubbles produced by solvent exchange; liquids are delivered with a glass syringe. The z-range is 49.5 nm. The substrate in both figures is highly ordered pyrolytic graphite (HOPG). Scale bars are 1 μm .

likely dispute that), or whether cooperative effects from surrounding nanobubbles can sustain them. More recently, various methods in optical microscopy have been developed to distinguish between bubbles and droplets easily. Seo *et al.* [15] have shown that gaseous nanobubbles and oil droplets can be tagged unambiguously using fluorescent dyes. And if seeing is believing, the demonstrative experiments of Chan *et al.* [16] provide the most convincing evidence of all in Figure 1.3. Their experiments with optical total internal reflection fluorescence microscopy show that moving a contact line over a nanobubble causes it to pop upon exposure to the ambient atmosphere, but pin strongly on an oil droplet or a spherical solid particle. But fluorescence microscopy methods require the objects to be permanently changed by coating them with fluorescent dyes for identification, or to be destroyed upon identification, which would preclude their further use in practice.

Given the ongoing contamination issue, there is urgent interest in developing a simple ‘touchstone’ [17] to distinguish between nanodroplets and nanobubbles, but using AFM in particular. This is because the vast majority of papers in the literature characterise nanobubbles with AFM, and also because the optical microscopy methods require specialised equipment. An AFM-based method would also be able to identify nanobubbles on an object-by-object basis, without permanently destroying them.

Figure 1.3: Seeing is believing – in TIRFM experiments, (a) surface nanobubbles burst when a three-phase contact line runs over it, exposing it to the ambient atmosphere, but (b-c) the same contact line pins strongly as it passes over a liquid drop and a solid particle. Scale bars are $1\ \mu\text{m}$ in (a) and $2\ \mu\text{m}$ in (b-c). Figure used with permission from [16].

1.3 WHAT STABILISES NANOBUBBLES?

Even after a long period of study the most basic question about nanobubbles has not been answered: how do they persist for so much longer than expected? Over the years a wide variety of theories have been put forward to account for the remarkable stability of nanobubbles.

Figure 1.4: Theories of nanobubble stability. (a) Contamination barrier. (b) Dynamic equilibrium *via* a recirculating flow. (c) Contact line pinning.

Some of the theories were later disproven by experiment. The hypothesis by Ducker [18] that the nanobubbles might be covered in a gas-impermeable contamination barrier (Figure 1.4(a)) was undermined by experiments proving the permeability of the water-bubble interface [10] and the apparent indifference of the nanobubbles to the addition of a wide variety of ionic additives and surfactants [19]. Brenner and Lohse [20] suggested that the rapid outflux of gas from the nanobubble could be counteracted by a flow recirculating gas back into the bubble (Figure 1.4(b)); the bubble being perpetually stable because the two effects mutually cancel so that there is no net flux of gas. However, this explanation plainly violates the laws of thermodynamics – some external source of energy must sustain the recirculation. Despite an initial claim by Seddon *et al.* [21] that a vertical jet of water with an estimated speed of ~ 2 m/s was observed above a population of nanobubbles was measured with an AFM tip, subsequent particle tracking experiments by two independent groups [7, 22] have not found the purported recirculating flows.

In recent years, increasing attention has been devoted to the experimental curiosity that nanobubbles exhibit contact line pinning, which is to say that they grow and shrink only by changing their heights, while maintaining a fixed footprint (see Figure 1.4(c)). Weijs and Lohse [23] were the first to show that nanobubbles shrink far more slowly in a pinned mode than a spherical bubble in the bulk. A spherical bubble in the bulk, or a surface bubble that is unpinned, has a reduced radius of curvature when it shrinks and thus a larger Laplace pressure; the shrinkage accelerates in time. On the other hand, a pinned nanobubble has an increased radius of curvature and a lower Laplace pressure, and the shrinkage decelerates. Yet, in their theory, the nanobubbles ought to shrink gradually over time and dissolve within about 12 hours, whereas experiments suggest they remain virtually unchanged over days [9].

The missing ingredient in this picture appears to have been the oversaturation of gas in the liquid. Lohse and Zhang [24], as well as Chan *et al.* [25], have shown that the bubble can reach an equilibrium in oversaturated liquid, and therefore be sustained indefinitely. But perhaps the most appealing aspect about the pinning-oversaturation theory is that the equilibrium is stable, meaning that it will achieve an equilibrium contact angle no matter what the angle was at the point of nucleation. This theory has also received independent support from thermodynamic lattice density functional theory simulations which have found both oversaturation and pinning being critical for thermodynamic equilibrium. Yet there are some outstanding issues that remain to be understood about pinning.

First, we do not know how large the pinning force is. Given that nanobubbles are known to have contact angles that are far smaller

than expected by Young's equation, it has been popularly suggested that the experimentally observed contact angle is related to the Young contact angle θ_0 by

$$\cos \theta = \cos \theta_0 - \frac{\tau}{\gamma R}, \quad (1.1)$$

where γ is the surface tension, R is the radius of curvature of the bubble, and τ defined as the *line tension*, which is to be interpreted as an excess free energy active at the contact line. Although this is not exactly a direct measure of the pinning, the line tension measurement is popular in the literature as τ can be calculated conveniently by fitting a distribution of radii R and contact angles obtained by AFM to equation 1. Unfortunately, there is little consensus on how large the line tension should be, with estimates [26–29] varying over three orders of magnitude and both positive and negative values reported. Perhaps a more direct measure would be to subject nanobubbles to invasive forces strong enough to trigger their unpinning. However, nanobubbles have so far been known to be impervious to invasive contact line AFM [30] and cavitation-induced shockwaves [31]. There is therefore a need to devise a method to detach nanobubbles from their substrates, and then estimate the force required to do so.

Second, we do not understand what factors trigger the onset of pinning in nanobubbles. Given that nanodroplets are known to shrink in both the pinned and unpinned modes, it would be reasonable to expect that nanobubbles can exist in both modes, too. Yet surface nanobubbles have only ever been observed to exist in a pinned state. Can nanobubbles exist in both modes, and if so, what determines the dominant dynamical mode? Given that there is very little control over the sizes of nucleated nanobubbles, there is significant interest in creating nanobubbles of a desired size by turning the pinning on and off as required.

1.4 NANOBUBBLES IN THE ELECTRON MICROSCOPE

When water is confined between graphene sheets and imaged in a transmission electron microscope (TEM), domains of nanobubbles with a radius of about 10 nm are often observed. These observations were first reported into the literature by Shin *et al.* [32], although my colleague Meera Mohan was likely to be the first to observe this phenomenon some two years prior [33].

These small nanobubbles contradict almost everything that we know about the surface nanobubbles that have been widely studied for the last two decades. Unlike the usual surface nanobubbles, which have a footprint radius of about 100 nm and are invariably pinned to their substrates, the ones observed in TEM shrink in an unpinned mode

and dissolve into bulk liquid over ~ 10 seconds. This is a remarkably slow dissolution time, considering that the dissolution of a $R = 10$ nm nanobubble should take $\tau \sim R^2/D \sim 10$ ns.

We have already discussed a number of potential theories of nanobubble stability and pointed out that the pinning and oversaturation hypothesis of Lohse and Zhang seems to be the most promising of them all. Yet whatever is sustaining the nanobubbles in TEM cannot be either line pinning (since the bubbles shrink smoothly and continuously), or oversaturation (reaction-diffusion modelling by Schneider *et al.* [34] suggests that the beam-induced radiolysis only produces gases up to their saturation concentrations – that is, producing zero oversaturation).

One important clue towards understanding the stability mechanism in this system is the apparent observation that the fluid dynamics of water in the electron microscope environment appears to be universally damped. From measuring the mean-squared displacements (MSD) of nanoparticles embedded in a 10 nm water nanodroplet, Lu *et al.* [35] found a diffusion constant 9 orders smaller than would be expected in bulk liquid. Liquid droplets slide and depin about 8 orders more slowly than expected from a fluid dynamic scaling [36, 37]. Both liquid droplets and gaseous nanobubbles coalesce with each other on a timescale up to 9 orders longer [38] than expected [39]. Notably, all of these findings can be reconciled with their theoretical predictions if the liquid's viscosity is assumed to be orders of magnitude larger than its usual value in the bulk. If it were true that the liquid viscosity is substantially larger than bulk water, then, according to the Stokes-Einstein equation, the diffusion constant

$$D = \frac{k_B T}{6\pi\eta a}, \quad (1.2)$$

where k_B is the Boltzmann constant, T temperature, η the viscosity and a the effective radius of a water molecule, would reduce by a proportionate amount. However, the idea that the liquid could be highly viscous has faced strong resistance in the literature. If it is true that there is such a viscosity buildup, it would be essential to propose a feasible mechanism that can generate one.

1.5 GUIDE TO THIS THESIS

This thesis is organised as follows. Various mechanisms have been proposed to explain the long lifetimes of surface nanobubbles. In Chapter 2 we show from thermodynamic principles that the gas pressure in a nanobubble is simultaneously satisfied by the Young-Laplace equation and by Henry's law, providing independent confirmation of

a class of theories which suggest that surface nanobubbles are stabilised by a combination of line pinning and oversaturation of liquid.

We introduce the working principles of AFM and TIRFM in Chapter 3, utilised over the next few chapters. In Chapter 4 we handle the issue of widespread contamination nucleation experiments by showing a technique in which nanobubbles and nanodroplets of oil contamination can be distinguished through careful AFM characterisation.

In Chapter 5, we report the first dynamic TIRFM observations of a nanobubble shrinking in an unpinned mode, before experiencing a transition to a pinned state. Then, in Chapter 6, we demonstrate a method to deduce the substrate pinning force acting on a surface nanobubble by observing how they respond to being pulled by a microscopic AFM tip.

The second half of this thesis pertains to nanobubbles that are observed in the TEM. These bubbles are remarkable in the sense that they have internal pressures well in excess of the typical surface nanobubbles studied in the preceding chapters. In Chapter 7 we show that these bubbles obey the same governing equations as the nanobubbles studied at larger scales, but appear to be stabilised by an orders of magnitude buildup in viscosity. Yet this viscosity enhancement theory is not well-accepted due a lack of experimental evidence.

To fill this gap, we outline in Chapter 8 a plausible mechanism for the strong viscous damping that appears to be observed in a wide variety of TEM experiments, including bubble dynamics. By subjecting a water box to electric fields, we show that the liquid's viscosity can be raised by orders of magnitude under typical imaging conditions in TEM.

WHAT IS THE PRESSURE IN A NANOBUBBLE?

The most important open question about surface nanobubbles pertains to their remarkable stability against diffusion. Nanobubbles survive for days without apparent change to their morphology, in remarkable contrast with the well-established theory of Epstein and Plesset, which predicts a sub-second shrinkage. Recent theories based on the diffusion equation suggest that nanobubbles attain an equilibrium contact angle provided their contact lines are pinned, and that the ambient liquid is supersaturated with gas. However, it is unclear whether these two factors alone can confer a nanobubble with thermodynamic stability, or whether a confluence of additional factors (such as diffusive shielding) is required. Here, we confirm from thermodynamics that the combination of supersaturation and pinning alone allows a nanobubble to achieve thermodynamic equilibrium.

2.1 INTRODUCTION

Figure 2.1: Schematic of a surface nanobubble. A surface nanobubble is typically a spherical cap with footprint radius $L \sim 100$ nm, height $h \sim 10$ nm, and an effective radius of curvature $R = (L^2 + h^2)/2h$ which is in the order of $R = 1$ μ m.

Surface nanobubbles are long-lived, spherically capped domains that are found attached onto hydrophobic substrates immersed in both water and non-aqueous liquids. Typically they measure about ~ 100 nm in footprint radius L and ~ 10 nm in height h , as we show in Figure 2.1. Although their existence is now confirmed by the weight of overwhelming experimental evidence through various modes of microscopy [8, 15, 40], their long lifetimes have always been considered to be implausible from the framework of well-established classical theories [41]. By modelling the gas transport from a spheri-

cal bubble with the diffusion equation, Epstein and Plesset [4] predict that a spherical gas bubble of $R \sim 1 \mu\text{m}$ should shrink on a subsecond timescale, a result which stands in remarkable contrast with the experimental finding that surface nanobubbles with similar radii of curvature survive for *days* with little apparent change to morphology [9].

The challenge in rationalising the vast difference between experiments and theory has motivated various groups to develop explanations ranging from the hypothesis that nanobubbles are covered in a barrier of gas-impermeable contamination [5, 18], to a recirculating flow that dynamically replenishes gas lost through diffusion [20], shown schematically in Figure 1.4.

The most recent developments in the theoretical understanding on nanobubbles has been focused on the experimental curiosity that nanobubbles exhibit contact line pinning, which is to say that they grow and shrink only by changing their heights, while maintaining a fixed footprint (see Figure 1.4(c)). Weijs and Lohse [23] were the first to show that nanobubbles shrink far more slowly in a pinned mode than a spherical bubble in the bulk. A spherical bubble in bulk liquid, or a surface bubble that is unpinned, has a reduced radius of curvature when it shrinks and thus a larger Laplace pressure; the shrinkage accelerates in time. On the other hand, a pinned nanobubble has an increased radius of curvature and a lower Laplace pressure, and the shrinkage decelerates. Yet, in their theory, the nanobubbles ought to shrink gradually over time and dissolve within about 12 hours, whereas experiments suggest they remain virtually unchanged over days [9].

The missing ingredient in this picture appears to have been the oversaturation of gas in the liquid. Two groups – Lohse and Zhang [24], as well as Chan *et al.* [25] – showed that with the assumption of contact line pinning and the coupling of the bubble's gas pressure to the liquid-phase gas concentration c_L by Henry's law, the contact angle of a surface-attached nanobubble obeys

$$\frac{d\theta}{dt} = -\frac{Dc_{\text{sat}}}{L^2\rho_G}(1 + \cos\theta)^2 f(\theta) \left(\frac{2\gamma}{LP_0} \sin\theta - \zeta \right), \quad (2.1)$$

where θ is the contact angle, ρ_G the density of gas, D is diffusion constant, L the footprint radius of the bubble, $f(\theta)$ is a geometric factor that can be obtained from an exact solution of the quasi-static diffusion equation [24, 40], and the oversaturation ζ is defined as a function of gas concentration c_L , such that

$$\zeta = \frac{c_L}{c_{\text{sat}}} - 1. \quad (2.2)$$

Since c_{sat} is the saturation concentration of gas in the liquid, a super-saturated liquid has $\zeta > 0$. By inspecting Equation 2.1 it is evident that the nanobubble can achieve zero molecular flux

$$\zeta = \frac{2\gamma}{LP_0} \sin \theta_e > 0, \quad (2.3)$$

thus guaranteeing a nanobubble's *indefinite* stability. In fact, one can go so far as to demonstrate that the equilibrium is a *stable* one [24, 25], which is to say that no matter what the nanobubble's contact angle was at the point of nucleation, it will always tend towards $\theta_e = \arcsin(LP_0\zeta/2\gamma)$, so long as its ambient liquid is oversaturated. Without pinning, the equilibrium is unstable – any slight perturbation of L or θ from the exact values that lead to $\zeta = 0$ would cause the bubble to either grow indefinitely, or shrink and dissolve into the bulk liquid.

Apart from its prediction of a stable equilibrium, the pinning and oversaturation theory is appealing because of its use of only well established laws, such as the Young-Laplace equation and Henry's law; for providing a reasonable mechanism for nanobubbles to attain a universally small contact angle relative to the one expected by Young's equation¹; and its implication that the pinning would also act as a mechanism to resist Ostwald ripening of nanobubbles [43]. Finally, the idea that both pinning and oversaturation are required for the stability of surface nanobubbles has received independent support from numerical lattice density functional theory calculations by Liu *et al.* [44] (which in fact predates the theoretical model itself [24, 25]).

However, the theoretical picture is still not complete. The fact that nanobubbles barely change in morphology when left to equilibrate over several days strongly suggests that they are locally in a state of thermodynamic equilibrium, in addition to being in dynamic (or diffusive) equilibrium. However, the construction of a diffusive equilibrium in theory does not automatically imply the attainment of thermodynamic equilibrium. Nowhere is this point more apparent than in the work of Brenner and Lohse [20], who hypothesised that nanobubbles are dynamically replenished by recirculating flow of gas. Unfortunately, their explanation does not satisfy conservation of energy, since some external driving mechanism is required to sustain the recirculating flow. Despite an early claim by Seddon *et al.* [21] that a ~ 1 m/s flow was detectable with an AFM tip, subsequent experiments by two independent groups have failed to uncover evidence of any strong recirculating flows around nanobubbles [7, 22].

One particular concern is whether the use of standard thermodynamic equations such as the Young-Laplace relation for the pres-

¹ On graphite, the contact angle measured from the gas phase would be expected to be about 90° , compared to the $20\text{--}50^\circ$ observed in experiments [42].

sure or Henry's law hold down to the nanoscale. The validity of the Young-Laplace relation has only recently been shown to hold to a molecular length scale by convincing molecular dynamics simulations [45]; moreover, over the relatively large length scale of a nanobubble, curvature corrections to the Laplace pressure would be insignificant. However, the same is not true for Henry's law. There is solid theoretical ground to suspect that Henry's law might be significantly altered at the highly-curved interface between water and a gas nanobubble. According to the Gibbs-Duhem equation $Nd\mu = VdP$ (see Appendix B for a derivation), the pressure shift across a curved interface (which scales with its radius of curvature as $1/R$) is directly coupled to the chemical potential μ [46] and therefore directly affects the thermodynamic equilibrium of the nanobubble itself. The potentially significant influence of curvature to the thermodynamic balance has led to some colleagues in the field suggesting [40] that the gas pressure in a nanobubble could be given by an equation similar to the Kelvin equation, as opposed to the Laplace equation.

Although it is important to understand the stability of surface-attached nanobubbles from a thermodynamic perspective, there have so far been few studies in this area [47, 48]. In one notable study, Colaço *et al.* [47] consider the liquid-vapour equilibrium over a curved bubble interface essentially by deriving the bubble analogue to the well-known Kelvin equation for the vapour pressure surrounding a water droplet. Yet this approach attracted strong criticism by Seddon and Zandvliet [49], especially because nanobubbles do not just contain water vapour, but have been shown to contain atmospheric gases [5, 42].

In this chapter, we derive an expression for the gas pressure in surface-attached nanobubbles at thermodynamic equilibrium, considering the effects of both water and dissolved gases.

2.2 THERMODYNAMIC EQUILIBRIUM OF SURFACE NANOBUBBLES

In Figure 2.2 we show a nanobubble with base radius L and contact angle θ that has settled on a solid substrate immersed in a layer of water. Since experiments suggest that nanobubbles barely change in morphology over several days, and because the liquid thickness (mm) is much thicker than the height of the nanobubbles (nm) in practice, we assume that the nanobubbles are in a locally closed thermodynamic equilibrium. Note that the top surface of the liquid is itself in equilibrium with the outside world, such that P_L is coupled to the atmospheric pressure P_0 .

For a curved surface, and using appropriate subscripts for liquid (L), gas (G) and interface (LG), the liquid-gas thermodynamic equilib-

Figure 2.2: Schematic of the thermodynamic system.

rium of a system of k components requires that the total differential entropy is zero, $dS_L + dS_G + dS_{LG} = 0$. By applying the first law of thermodynamics $TdS = dU + PdV - \sum_i \mu^i dN^i$ individually to each phase and applying conservation of energy U

$$dU_{LG} + dU_L + dU_G = 0, \quad (2.4)$$

conservation of volume V (the interface is assumed to take up no volume)

$$dV_G + dV_L = 0 \quad (2.5)$$

and conservation of molecule number N

$$dN_{LG}^i + dN_L^i + dN_G^i = 0 \quad (2.6)$$

we obtain

$$\begin{aligned} dS_{\text{tot}} = & \left(\frac{1}{T_G} - \frac{1}{T_{LG}} \right) dU_G + \left(\frac{1}{T_L} - \frac{1}{T_{LG}} \right) dU_L \dots \\ & + \left(\frac{P_G}{T_G} - \frac{P_L}{T_L} \right) dV_G + \sum_i \left(\frac{\mu_G^i}{T_G} - \frac{\mu_{LG}^i}{T_{LG}} \right) dN_G^i \dots \\ & + \sum_i \left(\frac{\mu_L^i}{T_L} - \frac{\mu_{LG}^i}{T_{LG}} \right) dN_L^i - \frac{\gamma}{T_{LG}} dA = 0. \end{aligned} \quad (2.7)$$

Here γ is the surface tension of the dividing interface between the liquid and gas phases, A is the surface area of the spherical cap interface, and R is the radius of curvature of the interface (i.e. the radius of curvature of the nanobubble). Setting the expressions in each pair of parentheses to be zero yields the following conditions for equilibrium:

$$T_L = T_G = T_{LG}, \quad (2.8)$$

$$\mu_L^i(P_L, T_L) = \mu_G^i(P_G, T_G) = \mu_{LG}^i(P_{LG}, T_{LG}), \quad (2.9)$$

$$P_G = P_L + \frac{2\gamma}{R}. \quad (2.10)$$

In the derivation of Equation 2.10, we fold the dA differential into the dV_G term in Equation 2.7 using the geometric relation $dA/dV = 2/R$, derived for a spherical cap geometry in Appendix B.

2.3 CHEMICAL POTENTIAL SHIFTS

The conditions for equilibrium are defined for arbitrarily many chemical species. We simplify this by considering a solution containing a solvent (i.e. water), and a solute (nitrogen). In a weak solution containing solute with concentration c , the liquid-phase chemical potentials μ_L^{water} and μ_L^{solute} are shifted [50, 51] by $-k_B T c_L$ and $k_B T \ln(c_L/c_{\text{sat}})$ respectively, where c_L is the concentration of solute in the water and c_{sat} is the saturation concentration.

The chemical potential μ can be defined with respect to a reference by integrating the Gibbs-Duhem equation $d\mu = (V/N)dP$. In the liquid phase, incompressibility means that V/N is not a function of P , and using the vapour pressure P_∞ as the reference for the water solvent and P_L for the solute gives [51, 52]

$$\mu_L^{\text{water}}(P_L, T) = \mu_L^{\text{water},0}(P_\infty, T) + v_L^{\text{water}}(P_L - P_\infty) - k_B T c_L \quad (2.11)$$

$$\mu_L^{\text{solute}}(P_L, T) = \mu_L^{\text{solute},0}(P_L, T) + k_B T \ln(c_L/c_{\text{sat}}). \quad (2.12)$$

In the gas phase, the ideal gas equation of state $V/N = k_B T/P$ applies, and integrating the Gibbs-Duhem equation with respect to the same reference points leads to a chemical potential with

$$\mu_G^{\text{water}}(P_G, T) = \mu_G^{\text{water},0}(P_\infty, T) + k_B T \ln\left(\frac{P_G^{\text{water}}}{P_\infty}\right), \quad (2.13)$$

$$\mu_G^{\text{solute}}(P_G, T) = \mu_G^{\text{solute},0}(P_L, T) + k_B T \ln\left(\frac{P_G^{\text{solute}}}{P_\infty}\right). \quad (2.14)$$

Note that according to Dalton's law, each chemical species contributes a *partial pressure* to the gas pressure, i.e. $P_G^{\text{water}} + P_G^{\text{solute}} = P_G$. We can rewrite this contribution as a mole fraction, where if c_G is defined

as the fraction of solute molecules in the gas phase, the gas phase chemical potentials then become

$$\mu_G^{\text{water}}(P_G, T) = \mu_G^{\text{water},0}(P_\infty, T) + k_B T \ln \left(\frac{P_G}{P_\infty} \frac{c_G}{1 + c_G} \right), \quad (2.15)$$

$$\mu_G^{\text{solute}}(P_G, T) = \mu_G^{\text{solute},0}(P_L, T) + k_B T \ln \left(\frac{P_G}{P_L} \frac{1}{1 + c_G} \right). \quad (2.16)$$

To satisfy thermodynamic equilibrium for water and the solute, we pair up Equation 2.11 with Equation 2.15 (for the water), and Equation 2.12 with Equation 2.16 (for the solute). This procedure gives the pair of coupled equations

$$k_B T \ln \left(\frac{P_G}{P_\infty} \frac{c_G}{1 + c_G} \right) = v_L^{\text{water}}(P_L - P_\infty) - k_B T c_L, \quad (2.17)$$

$$\frac{1}{1 + c_G} = \frac{c_L}{c_{\text{sat}}} \frac{P_G}{P_L}, \quad (2.18)$$

which are to be simultaneously satisfied. We can further combine these equations to give the equation of a nanobubble which incorporates the effect of dissolved atmospheric gas,

$$P_G = \frac{c_L P_L}{c_{\text{sat}}} + P_\infty \exp \left[(P_L - P_\infty) \frac{v_L^{\text{water}}}{k_B T} - c_L \right]. \quad (2.19)$$

The only unknown in Equation 2.19 is the liquid pressure P_L . What is it? In an experimental setting, we may assume that the ambient liquid is in turn at thermodynamic equilibrium with the outside world, and thus $P_L = P_0$, where P_0 is the atmospheric constant. It is then clear that for a typical dissolved gas concentration $c_L \sim 10$ ppm, $v_L^{\text{water}} \sim 10^{-29} \text{ m}^3/\text{molecule}$, $P_0 \sim 10^5 \text{ Pa}$, $P_\infty \sim 10^3 \text{ Pa}$ and $T = 300 \text{ K}$, the term in the exponential of Equation 2.19 is almost zero. Since $P_0 \gg P_\infty$ we can state the gas pressure in the bubble as

$$P_G \approx \frac{c_L}{c_{\text{sat}}} P_0 + P_\infty \approx \frac{c_L}{c_{\text{sat}}} P_0 \quad (2.20)$$

to a good approximation. In the limit where no solute is present, the chemical potential shifts in Equation 2.11, 2.16 owing to the weak solution vanish and it can be shown [53] that the balance of the water's chemical potentials in the gas and liquid phases lead to the Kelvin equation for a water vapour bubble $P_G = P_\infty \exp(-2\gamma v_L^{\text{water}} / R k_B T)$.

Note that our analysis so far presents two separate expressions for the gas pressure in the nanobubble. While Equation 2.10 is the familiar Young-Laplace equation given by the requirement for mechanical equilibrium between the bubble, Equation 2.20 states the gas pressure as a consequence of the presence of a dissolved gas in the liquid. By construction these quantities should be equal. Equating the two expressions for gas pressure and noting that the base radius of a

nanobubble R is related to its radius of curvature R and equilibrium contact angle θ_e by $L = R \sin \theta_e$, we have

$$\zeta = \frac{2\gamma}{LP_0} \sin \theta_e. \quad (2.21)$$

We therefore recover the exact condition for diffusive equilibrium (Equation 2.3) developed in the pinning-and-supersaturation models [24, 25]. The reason for the equivalence is that the bubble's gas pressure as a function of concentration, Equation 2.20, is a re-statement of Henry's law $P_G = k_H c_L$, since for a planar interface $P_0 = k_H c_{\text{sat}}$. Our formulation recovers Henry's law as a consequence of thermodynamic equilibrium instead of assuming its validity from the outset. It suggests that the effect of the nanobubble's curvature has a negligible effect on the chemical potential balance, and thus that planar values of Henry's law calculated in experiments are applicable.

2.4 CONCLUSIONS

In this chapter, we show from thermodynamic principles that pinning of a nanobubble and the oversaturation of the ambient liquid are required for the stability of a nanobubble. In the approximation of a single species of dissolved gas, our result reproduces exactly the expression derived by Lohse and Zhang [24] and Chan *et al.* [25].

The significance of our result is that it shows from basic thermodynamics that well-established relations such as the Young-Laplace equation and Henry's law hold in the nanoscale, and that the presence of a highly curved liquid-gas interface does not significantly affect the thermodynamic equilibrium.

However, there remain serious discrepancies between theory and experiment that need to be clarified going forward. An *et al.* [54] used a temperature difference method to nucleate nanobubbles, by introducing cold water on a heated hydrophobic graphite substrate. The morphologies of nanobubbles measured by AFM ($\theta \approx 15^\circ$, $L < 100$ nm) in that work suggest a very strong oversaturation of about $\zeta \approx 3 - 5$ is required to sustain them, well in excess of the oversaturation of $\zeta \approx 1$ that the temperature difference method was expected to generate. Note that the pinning-and-supersaturation theories make the strict requirement that the bubbles be sustained by supersaturated liquid – if ζ falls below several percent, nanobubbles will still dissolve into bulk water within μs [25]. Yet we would expect that a liquid layer with thickness $\ell = 1$ cm left to equilibrate with its surroundings should completely lose its oversaturation $\zeta \rightarrow 0$ over a diffusive timescale $\tau \sim \ell^2/D \sim 10$ hours [23], after which time the nanobubbles should perish. So the question would be why the excess

gas saturation in the *open* system of An *et al.* persists for days, when it should equilibrate back to $\zeta = 0$ over a timescale of 10 hours.

Clearly, if the newly proposed pinning and supersaturation models of nanobubble stability are to be widely accepted, the reason why the oversaturation itself persists longer than the diffusive timescale must be identified. One logical explanation put forward by Brenner and Lohse [20] is that a hydrophobic potential at the substrate inhibits the diffusive transport of gas molecules escaping from the liquid into the atmosphere. As they point out, the competing effects of diffusion and substrate attraction from some hydrophobic potential ϕ compels the gas concentration in the liquid to become a function of distance from the substrate, *i.e.* $c(z) \sim \exp(-\phi(z)/k_B T)$, rather than being a constant. This idea has support from the molecular dynamics simulations of Dammer and Lohse [55], who report that dissolved gas in liquid builds up preferentially at a hydrophobic wall (without nucleating into nanobubbles) to $\zeta \sim 100$ in the first few molecular diameters adjacent to the wall.

3

THE MICROSCOPY OF SURFACE NANOBUBBLES

In this chapter the basic principles of two contrasting, but complementary methods of imaging surface nanobubbles are introduced.

3.1 ATOMIC FORCE MICROSCOPY

An atomic force microscope (AFM) can be best described as 'walking blind'. Once a rectangular scan area of interest is defined, a microscopic probe mounted on a cantilever scans the region line by line. A schematic of an AFM is shown in Figure 3.1 to demonstrate the essential working principle. To measure tiny variations accurately, an infrared laser beam is reflected off the cantilever and into a photodiode which is sensitive to vertical and lateral motion. The photodiode converts a mechanical signal from the probe into an electrical one which recovers the surface topography of the sample. The deflection measured at the photodiode is measured against a feedback system which adjusts the scanner's z (perpendicular) displacement to maintain a constant deflection or oscillation amplitude on the cantilever.

Figure 3.1: Working principle of an AFM – a photodiode picks up minute shifts due to deflections in a cantilever as it is subjected to surface forces. Image courtesy of C. Roduit under a Creative Commons Attribution-ShareAlike license.

There are different imaging modes possible for AFM which depend on the motion of the tip.

Figure 3.2: Basic modes of an AFM: the conventional contact mode, which is tracked by a feedback mechanism to ensure a constant cantilever deflection; and tapping mode, which is tracked according to the cantilever's oscillation amplitude. Illustration of the cantilever is courtesy of C. Roduit under a Creative Commons Attribution-ShareAlike license.

Conventionally, AFM is performed in *contact mode*. The feedback system maintains the tip at a consistent deflection, see Figure 3.2, by sending a voltage to the piezoelectric positioning element to adjust the tip deflection. In this way, the voltage issued by the feedback system becomes a measure of the topography of the sample. Since contact mode effectively drags the tip across the object it images, it has the distinct disadvantage of delivering large lateral forces onto the sample.

Because contact mode is relatively invasive, soft objects such as surface nanobubbles are mostly imaged using *tapping mode* AFM¹. Here, the cantilever is pre-selected to oscillate close² to its resonance frequency and with an amplitude that is in the order of 10 nm. The feedback system works to keep the oscillation amplitude constant, see Figure 3.2. When the tip approaches the object or substrate, the oscillation becomes significantly damped due to tip-sample interaction. Compared with contact mode, the oscillation-based feedback mechanism in tapping mode provides a rich array of information beyond the usual three-dimensional topography. At the interface of soft objects, not only does the amplitude of the oscillation change, but also its phase. This is crucial in distinguishing between soft objects and the background substrate.

In recent years, the use of *peak force tapping* mode has become an increasingly popular choice to image nanobubbles due to its ability to carefully control the imaging force delivered during AFM characterisation. As in tapping mode, the cantilever is set to oscillate, but far from its resonance (~ 1 kHz, compared to about 30-50 kHz for a

¹ Tapping mode is also known as amplitude modulation or intermittent contact mode.

² In practice, within 5% of its resonance.

typical AFM cantilever in water). The tip approaches and retracts vertically, to and from the sample, once every 0.1 ms or so [56], capturing a force curve once during every such cycle. The feedback mechanism ensures that the maximum force exerted on the tip is kept at a constant value that can be set by the user. The additional channels of information available to users of tapping mode AFM are also available in peak force tapping mode. In particular, phase signals are returned in quadrature and inphase components.

3.1.1 Characterising nanobubbles with AFM

Typically, nanobubbles are nucleated on an atomically-flat highly ordered pyrolytic graphite (HOPG) substrate using the solvent exchange process pioneered by Lou *et al.* [2]. In this section I will briefly describe a typical protocol used to produce and characterise surface nanobubbles in AFM. To ensure a closed environment for the continuous flow of liquids through a flow cell, a rubber O-ring is used to create a sealed environment, and silicone tubing connected to the inlet and outlets in the cantilever holder, shown in Figure 3.3.

Figure 3.3: Schematic of a typical AFM flow cell to create a closed environment for in-liquid AFM.

Due to well-known issues with contamination we take care to clean all surfaces that come into contact with the liquid. The HOPG substrate is cleaved with Scotch tape, to expose a fresh working surface immediately before experiments commence. We use only a 10 ml glass syringe and a metal needle to deliver liquids into a flow cell. Before the experiment, the silicone O-ring, tubings, glass syringe barrels and plungers, and metal needles are washed for 20 minutes each in acetone, isopropyl alcohol and ethanol under sonication. The cantilever is cleaned with oxygen plasma (Harrick Plasma, United States) for about 20 seconds, and this process also renders it hydrophilic for AFM characterisation. Finally, the flow cell itself is washed with copi-

ous amounts of ethanol and deionised water³. All the items washed are blown dry with a fresh stream of nitrogen.

To perform solvent exchange, the flow cell is first filled with deionised water (18.2 M Ω cm, Sartorius, Germany), thus immersing the HOPG substrate in liquid. Then, 10 ml of ethanol is used to displace the water, and finally, another 10 ml of water is introduced to displace the ethanol. Because the water-ethanol exchange is exothermic and introduces thermal fluctuations that may affect imaging, we wait for several minutes to allow the imaging conditions to settle before engaging the AFM. The AFM characterisation is performed with the BioScope Catalyst (Bruker Corporation).

Figure 3.4: 3D image of surface nanobubbles on HOPG imaged in peak force mode, at a peak force $F_p = 80$ pN. The scan size is $4 \times 4 \mu\text{m}$. The z-limit of the image is 30 nm.

In Figure 3.4 we show a three-dimensional height image in a typical AFM scan of a HOPG substrate decorated with surface nanobubbles using the solvent exchange method. The nanobubbles are imaged in water, using a relatively soft silicon nitride cantilever (ScanAsyst Fluid, Bruker Corporation) with nominal spring constant $k = 0.7$ N/m, and a resonant frequency of 100 kHz in air. In the image the flat terraces of the HOPG are clearly visible. Surface nanobubbles measuring ~ 100 nm and ~ 10 nm appear to avoid the cleave steps, consistent with previous studies [57].

Solvent exchange is not the only method to produce surface attached nanobubbles. There are a number of different possible nucle-

³ Due to the sensitive electronics on board it would not be advisable to subject the cantilever holder to harsh organic solvents or sonication.

ation protocols based on liquid exchange, all of which are based on a significant difference in solubility between the liquids exchanged. These include:

HOT-COLD WATER EXCHANGE Guan *et al.* [58] have previously shown that nanobubbles can be nucleated by successively exchanging warm water (40°C) with refrigerated cold water. An alternative method to nucleate nanobubbles without exchange is simply to refrigerate water overnight and warm it up, a process which also induces an oversaturation of gas in the liquid.

SALT WATER EXCHANGE Guo *et al.* [59] and Liu *et al.* [60] have shown that nanobubbles can be formed by exchanging water with saline solutions.

A common feature of these alternative exchange methods is that the footprint radii of nanobubbles produced is generally smaller than those nucleated with solvent exchange. This might be related to the fact that the solvent exchange creates a substantially larger supersaturation in the water than other exchange methods. The solubility difference between water and ethanol is about 3 times [61]. This means that when highly soluble ethanol is replaced with water, the excess gas content from the ethanol creates an supersaturation of 300% in the water that displaces it. On the other hand, the solubility difference between water at 4°C and 40°C generates a supersaturation of only about 150%.

3.2 TOTAL INTERNAL REFLECTION FLUORESCENCE MICROSCOPY

Although AFM provides accurate characterisation of soft objects at the nanoscale, it has the distinct disadvantage of being blind and slow – the line-by-line scanning of an AFM rules it out as a method to observe dynamical processes. Total internal reflection fluorescence microscopy, or TIRFM, was first developed to observe surface nanobubbles by Chan and Ohl [7], allowing nucleation processes to be observed in real time with optical microscopy. With a sufficiently sensitive camera, TIRFM can capture processes with a temporal resolution of 0.01 s, about four orders of magnitude faster than what an AFM can reasonably achieve.

The principle of TIRFM is that a beam of light starts to reflect internally (as oppose to diffracting through) a material when its angle of incidence exceeds a certain threshold. In this case, total internal reflection occurs at a critical angle of $\theta \approx \arcsin(n_w/n_g) \approx 61^\circ$, where $n_w = 1.33$ and $n_g = 1.52$ are the indices of refraction of water and glass. The total internal reflection generates an evanescence regime immediately above the glass. The evanescence decays exponentially with a penetration depth (defined as the height at which

the intensity of evanescence decays to $1/e$) in the region of $z_0 = \lambda(4\pi/\sqrt{(n_g \sin \theta)^2 - n_w^2}) \sim 100$ nm, where λ is the wavelength of the light.

In practice, a green ($\lambda = 532$ nm) continuous wave laser with a power < 2 mW is used as an excitation source, taking particular care to use as little power as possible to avoid photobleaching of the dye. The laser beam is steered through the side port of a microscope and into the base of a $60\times$ oil-immersion objective. The beam then reflects internally off a coverslip to produce an evanescent region in the immersed region immediately above the coverslip.

Figure 3.5: Working principle of TIRFM: fluorescent dye molecules that are within the evanescence region release a fluorescent signal.

To visualise nanobubbles within the evanescent zone, a suitable fluorescent dye is added to the water. The dye coats the nanobubbles and the substrate, and so long as it is within the 100 nm-thick evanescent zone, dye molecules absorb excitation and emit fluorescence, see Figure 3.5. Once the initial excitation has been removed with suitable filters, nanobubbles appear in the microscope image as brightly contrasted regions against a dark background⁴.

3.3 CHARACTERISING NANOBUBBLES WITH TIRFM

Since AFM is blind and slow, it is desirable to observe nucleation and dynamic events with optical microscopy. This would require us to use a substrate such as glass that allows optical access to the substrate and the nanobubbles. We now describe a typical protocol used to nucleate nanobubbles for TIRFM. A setup for a typical TIRFM experiment is shown in Figure 3.6. The nanobubbles are nucleated within the confines of a PDMS microchannel that is tightly bonded to a glass coverslip.

⁴ This seems counter-intuitive because dye molecules attached to the substrate are by definition lower and exposed to a stronger excitation. However, the dye has a much stronger affinity for a liquid-gas interface than the substrate, collecting in a greater concentration and appearing far brighter at the bubble than at the substrate.

Figure 3.6: Schematic of a TIRFM setup.

Since the microchannels are made with the same PDMS material that has caused issues with contamination that we have described in Chapter 1, we must therefore take careful precautions to ensure that no residual oils are left on the channels after they are cured and hardened. A slab of PDMS containing about 20 microchannels etched by lithography is washed with copious amounts of ethanol and isopropyl alcohol before it is cut, plasma cleaned (20 s, Harrick Plasma, United States), and then bonded onto a glass coverslip. To ensure that the resulting objects are indeed gaseous, we perform the contact line experiment described by Chan *et al.* [16]. We introduce a moving contact line by using a pressure controller to gently flush air into the channel *via* one of the inlets; the nanobubbles pop when a three-phase contact line runs over it. When channels are prepared with the aforementioned protocol we do not observe any instances in which a contact line pins or jumps over a circular object as would be characteristic for a liquid PDMS droplet.

We perform solvent exchange by flushing water and ethanol alternatively into the channel. Typically we exchange the liquids at 10 $\mu\text{L}/\text{min}$; the flow rate appears to determine the rate at which nucleation is occurring [7], with nanobubbles nucleating almost instantaneously at high flow rates of about 50 $\mu\text{L}/\text{min}$, and over several minutes at low flow rates below 5 $\mu\text{L}/\text{min}$. After exchange of water-ethanol-water, the coverslip becomes populated with surface nanobubbles, as shown in Figure 3.7.

Figure 3.7: Nanobubbles nucleated with solvent exchange imaged in TIRFM. The scale bar is 5 μm .

3.4 CONCLUSIONS

In this chapter we have introduced two common methods of imaging nanobubbles: atomic force microscopy (AFM), and total internal reflection fluorescence microscopy (TIRFM). These methods have contrasting pros and cons. While AFM can image nanobubbles to an arbitrarily small spatial resolution, its line-by-line scanning prevents dynamic processes from being observed. On the other hand, TIRFM easily images dynamic processes – the temporal resolution is limited only by the availability of fluorescence – but is unfortunately diffraction-limited.

Since both methods are complementary, they can be combined and performed simultaneously. When nanobubbles are nucleated over a thin transparent substrate, optical access by TIRFM comes from underneath the sample, while the AFM accesses the substrate from above. Simultaneous characterisation with AFM-TIRFM allows us to enjoy the best of both worlds. We demonstrate one such application in Chapter 6, by measuring pinning forces on nanobubbles as they are pulled with a precisely manoeuvred AFM tip.

DISTINGUISHING BETWEEN NANOBUBBLES AND NANODROPLETS WITH AFM

The widespread application of surface-attached nanobubbles and nanodroplets in biomedical engineering and nanotechnology is limited by numerous experimental challenges, in particular, the possibility of contamination in nucleation experiments. These challenges are complicated by recent reports that it can be difficult to distinguish between nanoscale drops and bubbles. Here we identify clear differences in the mechanical responses of nanobubbles and nanodroplets under various modes of AFM imaging which subject the objects to predominantly vertical or lateral forces.

4.1 NUCLEATING NANOBUBBLES AND NANODROPLETS ON A COMMON SUBSTRATE

To avoid the well-known contamination issues outlined in Chapter 1 there is a need in this study to use an unambiguous method to produce surface nanobubbles. Several groups have already reported on nucleation of nanobubbles nucleated via electrolysis and more details can be found in papers by Yang *et al.* [62] and Zhang *et al.* [63]. By performing electrolysis on a freshly-cleaved slab of HOPG (ZYA grade, MikroMasch) immersed in 10 mM sodium phosphate solution, we avoid the need for liquids to pass through plastic syringes, cannulas or other sources of polymeric contamination. To complete an electrolysis circuit the HOPG was used as an anode and a platinum wire immersed in the liquid used as a cathode. When a DC potential of 5 V is applied for 90 seconds, the substrate becomes populated with hydrogen bubbles, some of which can be observed with the naked eye. To produce nanodroplets, we dilute polydimethylsiloxane (PDMS) with de-ionised water to 1:10000 (vol/vol), as described by Berkelaar *et al.* [12].

A baseline distribution of sizes and contact angles was established by imaging nanobubbles and nanodroplets separately with tapping mode AFM. The nanoscopic contact angles of the objects were calculated by least-square fits of the cross-sectional profile to a spherical cap. As shown in Figure 4.1, the nanobubbles' fitted contact angles were virtually height-independent¹ ($\theta \approx 20^\circ$), whereas the nanodroplets' contact angles increased ($30^\circ < \theta < 60^\circ$) with height. The

¹ The reason for the angular independence is that the contact angle is expected to be a function of the properties of the liquid and substrate only, as was clarified by Lohse and Zhang [24].

Figure 4.1: (left) Schematic of quantities used for the nanobubbles. The nanoscopic contact angle is defined from the gas phase. (right) Distribution of contact angles of nanobubbles (red triangles) nucleated by electrolysis and nanodroplets (blue dots) from a dilute oil solution.

contact angles are measured from the gas phase for nanobubbles and from the oil phase for the nanodroplets.

4.2 PEAK FORCE IMAGING: RESPONSE OF NANOBUBBLES AND NANODROPLETS TO VERTICAL FORCES

The most direct way to compare nanobubbles and nanodroplets is to introduce them onto a common substrate. We first electrolysed water to generate bubbles, and later introduced oil drops by adding dilute oil solution, allowing both types of objects to appear on the same scan.

We selected an area containing two nanodroplets and one nanobubble with similar lateral radii, shown in Figure 4.2. To observe the effects of varying the imaging force on drops and bubbles, we used peak force tapping mode AFM. In this mode, the maximum vertical force on the cantilever is used as a feedback mechanism, allowing soft objects to be imaged with a *peak force* F_p that is typically of the order 0.1 to 1 nN, but can be controlled to an accuracy of ~ 10 pN [64–66].

We then performed successive AFM scans at $F_p = 0.5$ to 10 nN. The morphology of nanodroplets and nanobubbles changed significantly with increasing F_p . At 0.5 nN, the height profiles of nanodroplets and nanobubbles were well-fitted to spherical caps (Figure 4.2(c-d)). With increasing F_p , the nanobubble in Figure 4.2(a) became smaller in base radius and height, before disappearing completely at $F_p = 5.0$ nN. A nanodroplet also shrank in base radius and height with an increase in F_p , but at $F_p > 3$ nN appeared as a *sombrero*: a spherical cap sitting

Figure 4.2: Response of nanobubbles to changing peak forces $F_p = 0.5, 1.0, 3.0, 5.0$ nN. (a) Height images. The z-limit is 20 nm. (b) Phase images. The z-limit is 11.5°. (c-d) Height profiles for the nanodroplet at the bottom-left of (a), and the nanobubble. The angles cited are calculated from least-squares fits to a spherical cap. Note the emergence of a flat wetting layer for the oil nanodroplets at high peak force.

on a flat molecular layer. Remarkably, the molecular layer was highly resistant to vertical loading and remained in the height image at up to $F_p = 20$ nN, maintaining a thickness of 1-2 nm. Molecular layers of ~ 1 -2 nm thickness at the contact lines of spreading PDMS drops have previously been observed by ellipsometry [67], though this layering is still not well understood.

We can prove that neither the nanobubbles nor the nanodroplets were physically moved or destroyed by peak force imaging. Phase images of both types of objects (Figure 4.2(b)) show that even though the objects disappear from the height image at high forces, the nanobubbles and nanodroplets are still in place. Details of the phase image calculation from the raw inphase and quadrature signals in peak force mode are presented in Appendix A. Moreover, when F_p was reduced from 5.0 to 0.5 nN, all the objects restored their original heights, base radii, and positions.

The way we created the objects on the system – with bubbles created first, and drops introduced later – leaves open the possibility that the bubbles may have been coated with oils. To investigate this scenario, AFM scans were taken in peak force mode before and five hours after dilute oil solution was introduced into the system. Some bubbles exhibited an increase of contact angle from 18-20° to 30-54°,

Figure 4.3: Nanobubbles coated in oil also exhibit nanometric wetting layers. Profiles are recorded in peak force mode. (top) Height profiles comparing a nanobubble, imaged at $F_p = 0.3$ nN (blue dots), an oil-coated nanobubble, imaged at $F_p = 0.3$ nN (green triangles), and an oil-coated nanobubble imaged at a large force of $F_p = 5$ nN. (bottom) A zoomed-in profile reveals that the apparently ‘flat’ profile of the oil-covered nanobubble scanned at a large force has a height of approximately 1-2 nm.

see Table 1. As surface nanobubbles are stable against diffusion for several weeks without significant changes to morphology [42], the difference in contact angle must arise only from the change in interfacial energy balance at the nanobubble’s three-phase line due to oil depositing on top of the nanobubbles. When F_p was increased incrementally, nanobubbles no longer disappeared from the scan image at $F_p = 5.0$ nN but maintained a nanometric layer, similar to the oil nanodroplets, see Figure 4.3.

The presence of a nanometric layer under strong AFM scanning is a tell-tale sign of contamination, resolving a contradiction raised by three recent papers imaging nanobubbles in peak force mode. Zhao *et al.* [66] and Yang *et al.* [64] found that nanobubbles disappeared from the scan image at $F_p = 1.25$ -2 nN, restoring their original heights when F_p was reduced to 0.2 nN. Our results are in broad agreement with these two reports. On the other hand, Walczyk *et al.* [65] report that nanobubbles (~ 20 nm height, ~ 100 nm width) remained visible when F_p reached 27 nN. While the vast majority of work in the liter-

BUBBLE	$\theta_{\text{before}} (^{\circ})$	$\theta_{\text{after}} (^{\circ})$
1	18	33
2	19	43
3	18	49
4	20	54
5	19	50

Table 1: Contact angles of nanobubbles before and after incubating in dilute oil solution for 5 hours.

ature nucleated nanobubbles by solvent exchange or electrolysis [42, 68], they were able to nucleate the objects simply by delivering water with a disposable syringe. Our results suggest that the robust layers visible at high peak forces in Walczyk *et al.* [65] were not nanobubbles, but polymeric contamination originating from plastic syringes.

4.3 CONTACT MODE IMAGING: RESPONSE OF NANOBUBBLES AND NANODROPLETS TO LATERAL FORCES

Soft objects are usually imaged in non-invasive tapping or peak force mode AFM, rather than the conventional contact mode. In these modes, the tip height is adjusted rapidly (once in $100 \mu\text{s}$ in peak force mode [56]) by a feedback mechanism to ensure that the tip and sample only contact intermittently. The imaging force is hence predominantly vertical, while avoiding strong lateral forces. In contrast, feedback in contact mode controls the cantilever deflection rather than the tip height, and this imparts a strong lateral force on the objects imaged.

To observe the influence of strong lateral deformation on nanobubbles and nanodroplets, we nucleated the objects separately on HOPG substrate and performed scans in peak force mode both before (Figure 4.4(a) and (d)) and after (Figure 4.4(c) and (f)) a contact mode scan with an estimated imaging force of $F_c = 5 \text{ nN}$ (Figure 4.4(b) and (e)). Before contact mode imaging, the deflection sensitivity (in units of m/volts) S_d was calibrated. The imaging force F_c can be estimated from the equation $F_c = kS_d(a_0 - a_v)$, where k is the spring constant of the cantilever, a_0 the set point and a_v the vertical deflection signal (both in volts) reading before the AFM was engaged. Figure 4.4(a)-(c) show that nanobubbles on the substrate were neither moved nor destroyed by contact mode scanning. Some irregularly-shaped particles, likely dirt, were removed by the scanning. We were unable to unpin nanobubbles from the substrate, even when F_c was increased to $\approx 50 \text{ nN}$. On the contrary, the distribution of nanodroplets was completely altered at $F_c = 5.0 \text{ nN}$, either by merging with other nanodroplets or being removed from the scan area (Figure 4.4(f)).

Figure 4.4: Response of nanobubbles and nanodroplets to an invasive contact mode scan. AFM height images of nanobubbles (a-c) and PDMS nanodroplets (d-f) before and after an invasive contact mode scan. The nanobubbles survive invasive scanning, while the nanodroplets' distribution is irreversibly altered, suggesting a drastic difference in substrate pinning. (a), (c), (d), and (f) are peak force mode height images captured at $F_p = 0.3$ nN. (b) and (e) are captured by contact mode imaging (imaging force is $F_c = 5$ nN). Scan size: $5 \mu\text{m} \times 5 \mu\text{m}$. Height scale: 50 nm for (a-c); 100 nm for (d-f).

To understand why nanodroplets are unpinned and swept away in contact mode imaging, we make a few estimates. According to Young's equation, the contact angle of a surface-attached soft object is defined only by the interfacial energies at its three phase line. In contact mode, the tip imparts a steady lateral force onto the object (see Figure 3.2), which deforms the object from one side, changing its approaching and receding angles. The object depins once the difference in angles – hysteresis – has reached a certain amount. Since this threshold is unknown, we instead exploit the fact that bubbles and drops possess an effective spring constant [69] in the same order of magnitude as the surface tension of the object [70]. The force exerted on the objects can then be estimated from the distance of deformation x to be $F \sim \gamma_{pw}x$, where γ_{pw} is the PDMS-water interface tension. In the experiments, the PDMS-water interface has a surface tension of 40 mN/m [71], and the nanodroplets have a typical base radius ~ 200 nm. Assuming that the maximum deformation of the drop is in the same order as the base radius, the threshold force to trigger the un-

pinning of the drop in contact mode AFM can be estimated to be 4 nN, in agreement with our experimental observation. On the other hand, in peak force mode, the intermittent contact between tip and object minimised contact angle hysteresis. Nanodroplets were thus able to withstand large vertical forces of ~ 10 nN without unpinning.

The force threshold required to unpin a nanobubble from its substrate remains unresolved. If nanobubbles and nanodroplets are pinned to their substrates by an identical force per unit length, and knowing that the interfacial energy of water-air is about double that of water-PDMS (72 versus 40 mJ/m²), the force threshold to unpin a bubble from the surface in contact mode should be approximately double that of a PDMS drop with same lateral size, i.e. $F_c \approx 10$ nN. However, we were unable to unpin nanobubbles at any imaging force in both imaging modes used here.

4.4 FORCE CURVES ON NANOBUBBLES AND NANODROPLETS

Figure 4.5: Cantilever deflection versus piezo z -displacement on the (a) HOPG substrate, (b) PDMS nanodroplet, (c) nanobubble and (d) nanobubble contaminated with PDMS. The approach curves are given in blue and the retraction curves are red. The tip-object slopes m on the approach curves in (c) and (d) were calculated with a least-square fit.

We also examined the tip-object interaction with AFM force spectroscopy. The tip-sample interaction is quantified by tracking the cantilever's vertical deflection as it moves down towards (approach) and away (retract) from the sample. The force curves are read right-to-left.

Figure 4.5 shows the deflection-displacement curve on the bare HOPG substrate. When the tip is far away from the substrate ('in liquid'), the deflection is zero. The deflection then increases linearly as the tip comes into contact with the HOPG substrate ('substrate'); the slope of the deflection-displacement curve gives a measure of the effective stiffness of the substrate.

We next show the force curves when the tip comes into contact first with a nanodroplet (Figure 4.5(b)) or a nanobubble (Figure 4.5(c)) before contacting the substrate. The tip-bubble interaction is characterised by a linear slope in the deflection-piezo displacement curve, which is consistent with theory [69] and experiments [19, 72]. In our limited testing, this linear dependence occurs independent of the type of salt used in the electrolysis and probe wettability. Theory suggests that the tip-bubble interaction is linear [70] provided the magnitude of deformation by the tip is within a compliance regime [69, 73]. We assume that nanobubbles fall within this regime because the maximum deformation of a spherically-capped nanobubble is its height $h \sim 50$ nm, which is small compared to its radius of curvature $R_c \sim 1$ μ m. We note the caveat that in very pure systems, the initial contact between the AFM tip and the bubble is marked with a pronounced snap-in [19], but this is suppressed in our case, perhaps due to disruption of electric double layer forces by electrolyte ions. However, the snap-in itself does not affect the linear dependence of the bubble-tip interaction. On the other hand, the tip-nanodroplet interaction is non-linear. Sharp kinks are observed in the approach curve in Figure 4.5(b), representing a jump-to-contact with the substrate when the gradient of van der Waals forces between the oil and the tip overcomes the cantilever's spring constant [74].

4.5 CONCLUSIONS

In this chapter, we have identified a number of robust indicators to distinguish between nanobubbles and nanodroplets when they are imaged in AFM, such as force curves and response to primarily vertical or lateral imaging forces.

The indicators can be summarised in the following points:

- A. Nanobubbles disappear cleanly and completely under large vertical forces in peak force mode (< 3 nN), while oil-covered nanobubbles or oil nanodroplets maintain a nanometric wetting layer when subjected to large peak forces (> 5 nN).
- B. Nanobubbles are very strongly pinned to their substrate and survive intense contact mode scanning, while nanodroplets are easily unpinned by lateral forces.

- c. Force curves on nanobubbles and oil-covered nanobubbles are linear in the region where the tip interacts with the bubble, but an AFM tip on a pure nanodroplet experiences a strong, non-linear jump to contact.

Our findings address a very urgent need in the field of nanobubbles to distinguish between gaseous objects and polymeric contamination which occurs easily during nucleation experiments. Although other methods of distinguishing between nanobubbles and contamination already exist, the results in this chapter are of particular significance because currently existing tests are destructive and require specialised optical techniques inaccessible to the majority of research groups which image nanobubbles with AFM.

5

PINNING TRANSITION IN SHRINKING SURFACE NANOBUBBLES

The unusual stability of surface-attached nanobubbles is thought to originate from the contact line pinning observed in most experiments. However, due to the inability of traditional modes of imaging nanobubbles to capture dynamic processes, it is not understood what factors cause the pinning and how large its magnitude is. Here we show with optical fluorescence microscopy that relatively large (footprint radius $L \sim 10 \mu\text{m}$) nanobubbles nucleated on a glass substrate initially shrink in an unpinned mode, before becoming stabilised when contact line pinning becomes dominant at $L \approx 1.5 \mu\text{m}$. By modelling the pinning transition with an energy balance we estimate that the pinning force is in the order of 30 mN/m .

5.1 INTRODUCTION

Figure 5.1: Shrinkage modes of surface nanobubbles. (a) In an unpinned shrinkage, the nanobubble shrinks by maintaining its contact angle while changing its footprint radius. (b) In a pinned shrinkage, the nanobubble shrinks by changing its height or contact angle, while the footprint radius L remains constant.

Surface-attached nanobubbles are gaseous domains found attached onto immersed substrates. These objects turn out to be of significant interest not only for their potential applications in the control of flows in micro and nanofluidic environments [75], but also in the fundamental understanding of the nanoscale physics of soft matter. Among the curious characteristics that nanobubbles are notable for are contact angles which are universally smaller than predicted by Young's equation [5, 68], and their stability against diffusion over timescales that are up to ten orders of magnitude longer than expected [4, 40–42].

In general, sessile soft objects deposited on a substrate, such as droplets and bubbles, can evolve in one of two basic modes [76], as they accumulate or lose material. They grow or shrink in either (a)

an *unpinned mode* in which the object grows or shrinks in its footprint radius while maintaining its contact angle; and (b) a *pinned mode* in which it evolves only in height, while maintaining a fixed footprint radius. A third mode, called ‘stick-jump’, alternates between the two basic modes, leading to the observation of discrete jumps in the footprint radius [77, 78].

Unlike liquid droplets, which are known to exhibit both of the basic dynamic modes, atomic force microscopy (AFM) experiments suggest that nanobubbles exhibit contact line pinning [9, 23]. Since the temporal resolution of AFM is in the order of several minutes, dynamical processes during nucleation cannot be resolved. In the current theoretical understanding, nanobubbles are thought to be indefinitely stable under contact line pinning, but in the unpinned mode they are thought to dissolve within a timescale faster than can be captured with AFM [24, 25]. Regardless, the influence of line pinning is still not well understood – how large is it, and under what conditions does it become significant?

In this chapter, we make an important advance in the understanding of the line pinning on nanobubbles by observing with total internal reflection fluorescence microscopy (TIRFM) an *unpinned* shrinkage of nanobubbles, and their subsequent transition to a pinned state.

5.2 EXPERIMENT

Figure 5.2: Schematic of the TIRFM setup. To nucleate nanobubbles, cold water is introduced to a coverslip heated by a heating stage. The heating was stopped once liquid was introduced into the microchannel.

Nanobubbles are nucleated by introducing cold water at 10°C onto a glass coverslip (no. 1, Menzel-Gläser, Germany) that was pre-heated for 10 minutes with a stage-heater with temperature probe (Bruker Corporation, United States). Due to weak thermal coupling, a water droplet dispensed the middle of the coverslip reaches a maximum temperature of 40°C when the heating stage was set to 150°C. Cold water was delivered to the substrate via a polydimethylsiloxane (PDMS) microchannel which was fabricated using standard techniques, plasma cleaned, and then bonded onto the glass coverslip in a low-humidity environment at room temperature for 24 hours. This procedure bonds the glass weakly enough for the channel to be removable for further characterisation, but is sufficiently strong to avoid leakage of liquids. Heating was stopped once the liquid was introduced into the microchannel.

To visualise the nanobubbles in TIRFM, 2.5 μM rhodamine 6G (Sigma-Aldrich, Germany) fluorescent dye was added to the cold water before it was introduced into the microchannel. A laser beam ($\lambda = 532\text{ nm}$) is steered through a 60 $\times$ oil-immersion microscope objective (Olympus, Japan) such that it reflects internally off the bottom of the coverslip and generates an evanescent region immediately above it. Dye molecules fluoresce under excitation of the evanescence, and when the initial excitation is removed with a suitable filter, nanobubbles appear as a bright object contrasted against the dark background, as shown in Figure 5.2(a). Images are captured at 2 frames/s using an sCMOS camera (Zyla 5.5, Andor, Northern Ireland). Note that times cited in this Letter are reported from the start of the recording, which was about 90 seconds after water was injected into the microchannel. We were not able to capture nanobubbles at the point of nucleation, or any earlier than 90 seconds, since the nanobubbles are only sparsely populated within the confines of the microchannel, and the flexing of the cooling coverslip continuously moves the TIRFM image out of its focal plane (the depth of field is within 0.5 μm).

In contrast with previous experiments, we observe nanobubbles shrinking in an unpinned mode. The nanobubble in Figure 5.3(a) initially shrinks in footprint radius L , but remarkably it stops shrinking after about 200 seconds and becomes pinned to its contact line. As it shrinks, the nanobubble leaves behind a dark circular footprint corresponding to its initial size during nucleation. When the microchannel is removed and the stable bubbles characterised in tapping mode atomic force microscopy (BioScope Catalyst, Bruker, United States) the bubbles have a contact angle of 50° as measured from the gas phase.

How do the nanobubbles nucleate? The temperature difference method of nucleating nanobubbles exploits the fact that the solubility of gas in

Figure 5.3: Unpinned shrinkage of a surface nanobubble and its transition to pinning. (a) Experimental TIRFM images of a shrinking nanobubble. The time $t = 0$ refers to the start of the recording, taken approximately 90 s after water was injected into the system. A dark circle corresponding to the original footprint of the bubble is left behind as the bubble shrinks. The nanobubble becomes pinned and fixed at its final radius after about 300 s. The scale bar is $5 \mu\text{m}$. (b) Plots of the dissolved gas concentration c_L as a function of temperature. (c) Comparison of the footprint radius of the bubble in (a) in the experiment (red dots), theoretical unpinned shrinkage curve (dashed line), and modified theory assuming a time-dependent oversaturation (red solid line). (d) Plot of the empirical time-dependent oversaturation $\zeta(t)$, Equation 5.9, used to generate the theoretical curve in (c), for $\tau = 80$.

water is higher in cold water as compared to warm water, for which an empirically-determined fitting curve [79] is shown in Figure 5.3(b). It is convenient to define the oversaturation as a function of the dissolved gas concentration c and its solubility c_{sat}

$$\zeta = \frac{c_L}{c_{\text{sat}}} - 1. \quad (5.1)$$

The use of cold water creates an oversaturation in the liquid relative to the heated substrate, and by reading values off Figure 5.3(b) we deduce that the oversaturation prevalent at the time of nucleation is approximately $\zeta_{\text{nuc}} = c(10)/c(40) - 1 \approx 0.52$. Note that this oversaturation only applies at the point of nucleation and changes in time, since the solubility of water c_{sat} is temperature dependent.

Nanobubbles with base radius L embedded in a liquid with oversaturation ζ evolve according to the diffusion equation. Since nanobubbles are experimentally known to evolve very slowly, the dynamics can be modelled in the quasi-static limit with the Laplace equation.

Lohse and Zhang [24] have shown that the rate of change of mass of the bubble obeys

$$\frac{dm}{dt} = -\pi L D \Delta c f(\theta), \quad (5.2)$$

where the geometric term

$$f(\theta) = \frac{\sin \theta}{1 + \cos \theta} + 4 \int_0^\infty \frac{1 + \cosh 2\theta\tau}{\sinh 2\pi\tau} \tanh[(\pi - \theta)\tau] d\tau \quad (5.3)$$

originates from an exact solution for a spherical cap geometry derived by Popov [80], and Δc is the difference in gas concentration between the ambient liquid and the bubble which drives the diffusion

$$\Delta c = \left(P_0 + \frac{2\gamma}{R} \right) \frac{1}{k_H} - c_L, \quad (5.4)$$

where γ is surface tension and k_H is the Henry's law constant. Note that by substituting Henry's law for a planar interface $P_0 = k_H c_{\text{sat}}$, Equation 5.4 can be written as a function of the oversaturation ζ :

$$\Delta c = c_{\text{sat}} \left(\frac{2\gamma}{L P_0} \sin \theta - \zeta \right). \quad (5.5)$$

A dynamical equation for the nanobubble can be determined by obtaining a second equation for dm/dt from the spherically-capped nanobubble's mass

$$m = \pi L^3 \rho_G \frac{\cos^3 \theta - 3 \cos \theta + 2}{3 \sin^3 \theta} \equiv \pi L^3 \rho_G g(\theta). \quad (5.6)$$

In the unpinned mode, L is time-varying, while θ is fixed. When the derivative of Equation 5.6 with respect to $L(t)$ is taken and equated with Equation 5.2, we obtain the dynamic equation in the unpinned mode

$$\frac{dL}{dt} = -\frac{D c_{\text{sat}}}{3 L \rho_G g(\theta)} \left(\frac{2\gamma}{L P_0} \sin \theta - \zeta \right). \quad (5.7)$$

When the derivative of Equation 5.6 is taken with respect to $\theta(t)$ instead, we obtain the dynamic equation of a pinned nanobubble

$$\frac{d\theta}{dt} = -\frac{D c_{\text{sat}}}{L^2 \rho_G} (1 + \cos \theta)^2 f(\theta) \left(\frac{2\gamma}{L P_0} \sin \theta - \zeta \right). \quad (5.8)$$

Despite the superficial similarity between the appearance of Equations 5.8 and 5.7, nanobubbles in the unpinned mode have a very different fate to those in the pinned mode. Although both equations predict an equilibrium at $\zeta = 2\gamma \sin \theta / L P_0$, it can be shown that the unpinned mode is in an unstable equilibrium and the pinned mode is in a stable equilibrium [24, 25]. Physically, this means that a pinned nanobubble in sufficiently oversaturated liquid will always attain an

equilibrium contact angle $\theta = \arcsin(\zeta LP_0/2\gamma)$ from any starting θ . On the other hand, a nanobubble shrinking in the unpinned mode can only be stable at some unique ζ ; outside this value it dissolves into bulk liquid. This expectation is confirmed by a full numerical solution of the unpinned shrinkage expression (Equation 5.7, dashed line) for $\zeta_{\text{start}} = 0.29$, which predicts a lifetime under 100 s.

To model the experimental data we assume that nanobubbles with contact angle $\theta = 50^\circ$ are shrinking purely in the unpinned mode, since the experimental curve is smooth rather than step-wise as would be expected for a mixed-mode shrinkage [77]. We modify the solution of Equation 5.7 by assuming a time-dependent oversaturation $\zeta(t)$ that matches what is known about the oversaturation at the start and end of the experiment. The initially heated coverslip rapidly cools back to the laboratory temperature before the first images in Figure 5.3(a) were recorded. Even though the cured PDMS is known to be gas permeable, significant volumes of gas leak only in the event that the relative pressures between the internal and external environments are in the order of 0.1 atm [81]. Since the relative pressure in our system is zero (see Figure 5.2), we may assume that gas loss through the channel is minimal and excess dissolved gas from the cold water remains in the system during the timescale of the experiment. We thus infer that oversaturation at the start of the experiment is $\zeta_{\text{start}} = c(10)/c(25) - 1 \approx 0.29$. At the end of experiment, the nanobubble reaches an equilibrium radius of $1.5 \mu\text{m}$, which implies an equilibrium oversaturation $\zeta_{\text{end}} = 2\gamma/P_0 L_{\text{final}} \sin \theta \approx 0.74$. A suitable continuous function, shown in Figure 5.3(d), which transitions between ζ_{start} and ζ_{end} is

$$\zeta(t) = -\frac{\zeta_{\text{start}} - \zeta_{\text{end}}}{2} \tanh \frac{t - \tau}{\tau} + \frac{\zeta_{\text{start}} + \zeta_{\text{end}}}{2}, \quad (5.9)$$

where the transition timescale is estimated to be $\tau = 80$ s (see Appendix C). When the nanobubble base radius L is solved in the unpinned mode using the time-dependent oversaturation $\zeta(t)$ (Equation 5.9) as an input, we obtain a theoretical curve (red line) in Figure 5.3(c) that fits the experimental data points well. Note that to achieve this fitting the diffusion constant D in both theoretical curves plotted in Figure 5.3(c) was 240 times smaller than the expected value of $2 \times 10^{-9} \text{ m}^2/\text{s}$. The reduced diffusion constant could be justified by the coating of fluorescent dye (necessary for TIRFM visualisation) on the bubbles inhibiting the diffusion of gas from the nanobubbles, as was also suggested by a previous study [25].

However, the pinning transition model presents a conceptual difficulty: it requires that the ambient liquid surrounding the nanobubble becomes *more* oversaturated in time (see Figure 5.3(d)), contrary to the expectation that in time the liquid should equilibrate to $\zeta = 0$.

We hypothesise that the existence of an attractive potential at the substrate inhibits the loss of gas to the outside world, ensuring that the localised oversaturation surrounding the nanobubbles remains elevated. This view has support from molecular dynamics simulations which find a substantial buildup of oversaturation at the liquid-wall interfaces of hydrophobic substrates [55]. Although the possibility that the rhodamine dye contributes to such a hydrophobic potential (thus influencing the oversaturation) in our experiments cannot be ruled out, we believe that the buildup in oversaturation is a universal phenomenon. In previous work, An *et al.* [54] have shown that nanobubbles nucleated by a temperature difference method on a hydrophobic graphite substrate appeared to be sustained by an oversaturation $\zeta \approx 5$, even though the nucleation method only produces an oversaturation $\zeta \approx 1$.

5.3 TRANSITION TO PINNING

At what point does a nanobubble shrinking in an unpinned mode start to become pinned? In Figures 5.4(a)-(b) we compare the initial radius of the nanobubbles L_{before} , estimated by measuring the dark footprints in the TIRFM images (see Figure 5.3(a)), with the final radius of each nanobubble in its pinned state ranging $L_{\text{after}} = 1.5$ to $2 \mu\text{m}$. The onset of pinning is triggered by competing effects. Physically, the shrinking of a nanobubble in the constant angle unpinned mode leads to a loss in surface area $S = 2\pi L^2 / \sin \theta$, which in its differential form is $dS = (4\pi\gamma L / \sin \theta) dL$. Assuming that the contact line exerts a force F over the nanobubble's circumference, the work done is $dW = 2\pi F dL$. In Figure 5.4(c) we show how the balance of these effects evolves as a nanobubble changes in radius L . A nanobubble shrinks when the pinning energy cannot overcome the change in surface energy induced by bubble shrinkage, i.e. $dW < dS$, and conversely is stable against shrinkage when $dW > dS$. At the threshold radius L_{after} in which the two effects mutually cancel, we find that the pinning force is

$$F = \frac{2\gamma L_{\text{after}}}{\sin \theta}. \quad (5.10)$$

Applying Equation 5.10 to the nanobubbles in this system suggests a pinning force in the range of $0.2\text{--}0.4 \mu\text{N}$, or 30 mN/m when normalised over the nanobubble's footprint perimeter. Since the glass is neither chemically (due to the presence of the dye) nor physically (due to its inherent roughness) homogeneous, some spread in the stable footprint radius L_{after} and the pinning force F is expected. The magnitude of the pinning force we calculate here is in line with theoretical predictions of the pinning force of nanobubbles nucleated on heterogeneous substrates by Liu and Zhang [82].

Figure 5.4: Onset of pinning in nanobubbles. (a) Schematic of the footprint radius L_{before} before shrinkage and when the bubble is pinned, L_{after} . (b) A comparison of L_{before} and L_{after} , captured from TIRFM images after the experiment. In general the bubbles shrink to about half their original radius. (c) Schematic of the energy balance between the loss of a shrinking nanobubble's surface energy dS (in the direction of the arrow, as the bubble shrinks) and the work done by line pinning dW ; the bubble is pinned at L_{after} when the two contributions are equal. (d) Histogram of the estimated pinning force F on the nanobubbles in this system; when normalised by the footprint radius of the bubble L_{after} we find that the pinning force is in the region of 30 mN/m.

5.4 CONCLUSIONS

In summary, we report a transition of shrinking nanobubbles from an unpinned to a pinned state. Our results present some new insights into the fundamental physics of nanobubbles. First, we have provided the first direct experimental evidence that the onset of contact line pinning stabilises nanobubbles, as has been theorised by various groups [9, 23–25, 82]. Second, we have shown that line pinning plays a key role in determining the equilibrium size of a nanobubble. In previous work, Chan *et al.* [7] nucleated surface nanobubbles using solvent exchange which were all smaller than $L \approx 1.5 \mu\text{m}$, none of which were observed to shrink. In the context of our findings, the nanobubbles in that work can be understood to be nucleated in the stable region

in which line pinning dominates (green region in Figure 5.4(d)) and therefore do not shrink any further in their footprint radius, while the relatively large nanobubbles $L_{\text{before}} > 2 \mu\text{m}$ in our experiments are nucleated in a dynamically-unstable region and shrink until they reach the stable region.

RESOLVING THE PINNING FORCE ON NANOBUBBLES WITH SIMULTANEOUS MICROSCOPY

Many of the remarkable properties of surface nanobubbles, such as unusually small contact angles and long lifetimes, are related to the force that pins them onto their substrates. This pinning force is yet to be quantified experimentally. Here, surface-attached nanobubbles are pulled with an atomic force microscope (AFM) tip while their mechanical responses are simultaneously observed with total internal reflection fluorescence microscopy (TIRFM).

6.1 INTRODUCTION

Surface nanobubbles are gaseous domains attached onto wetted surfaces. They possess unusual properties such as long lifetimes and anomalously small contact angles, both of which remain to be fully understood [40, 42, 68].

It is thought that the key to both properties lies in the experimentally-observed contact line pinning of nanobubbles, which constrains them to grow or shrink only in height, while their footprint areas remain fixed. While no single explanation for the long lifetimes of nanobubbles has gained wide acceptance, a strong consensus has emerged from theoretical, experimental and computational studies [9, 23, 24, 44, 82, 83] that substrate pinning is essential for nanobubble stability. Moreover, a popular explanation for the unusually small contact angles of nanobubbles observed in experiments is that the contact line pinning manifests as a *line tension* τ , changing the bubble's nanoscopic contact angle predicted by Young's law, namely $\cos \theta_c = (\gamma_{sv} - \gamma_{sl})/\gamma$, to $\cos \theta = \cos \theta_c - \tau/\gamma R$, where R is the radius of curvature and the subscripts in γ refer to the solid, liquid and vapour phases.

Although it is now agreed that nanobubbles are strongly pinned to their surfaces, the strength of the pinning never been determined accurately. Experimental efforts to quantify contact line pinning have centred on a direct measure of the pinning force or line tension. Traditionally, most research groups favour the line tension approach, since this quantity can be easily computed by fitting a distribution of nanobubbles contact angles and radii to three-dimensional atomic force microscopy (AFM) data [42]. Unfortunately, this method leads to conflicting estimates for τ [26, 28, 29, 59, 84] which span three orders of magnitude and include both positive and negative values [42].

An alternative approach is to subject nanobubbles to strong forces, in the hopes of triggering their unpinning or destruction. Remarkably, however, no method is yet known to unpin nanobubbles, even when they are subjected to intense contact mode scanning in AFM [30] or cavitation-induced shockwaves [31]. The magnitude of the substrate pinning therefore remains an open question.

An understanding of pinning is also important in controlling the distribution of surface-attached bubbles for applications such as the reduction of drag in microfluidics [75, 85], surface cleaning [86] and even graphene transfer [87]. In typical nucleation experiments, exchanging water and organic solvent over a surface [2] creates an uncontrollable distribution of bubbles on the substrate. To tailor the use of nanobubbles for specific applications, it is also important to understand how large a force is required to move or destroy these objects if they appear in undesirable locations.

Even though it has long been desired to measure the strength the contact line pinning, widely-used methods such as AFM cannot provide the dynamic imaging required to understand how strong forces interact with nanobubbles, or to determine a threshold force at which nanobubbles can unpin from their substrate. In this chapter, we perform the first *direct* measure of pinning force on nanobubbles by observing their mechanical response to being pulled with a precisely manoeuvred AFM cantilever.

6.2 EXPERIMENT

Figure 6.1: Schematic of the simultaneous AFM-TIRFM setup.

Micro and nanobubbles are nucleated on a glass coverslip (no. 1, Menzel-Gläser, Germany) by exchanging water, ethanol and water

within the confines of a polydimethylsiloxane (PDMS) microchannel, as shown in Figure 6.1. 2.5 μM rhodamine 6G (Sigma-Aldrich, Germany) fluorescent dye was added to both exchange liquids to visualise the bubbles in TIRFM. PDMS channels were fabricated with standard techniques and plasma-cleaned for 30 seconds before bonding them onto the coverslip in a low-humidity, room temperature environment for 24 hours¹. This ensures that the channel is removable for AFM characterisation, while providing sufficient sealing to avoid leakage of liquids during nanobubble nucleation. Although contamination from PDMS is known to be a significant issue in nucleation experiments – leading to the formation of oil droplets instead of nanobubbles – we have verified that objects nucleated using the above-mentioned protocol are gaseous [16].

In TIRFM, a laser beam ($\lambda = 532 \text{ nm}$) is steered through a $60\times$ oil-immersion microscope objective (Olympus, Japan) and reflects internally on the bottom of a glass coverslip, generating an evanescent region above its top surface [7]. Under excitation by the evanescent, dye attached onto the bubbles fluoresces, and when the excitation is removed using suitable filters, nanobubbles appear as highly contrasted regions against the dark background as shown in Fig. 1(b). To ensure that the nanobubbles remain immersed during AFM characterisation, a reservoir of 1 ml of deionised water is dispensed around the channel before removing it. The nanobubbles are then imaged in tapping mode AFM (Bioscope Catalyst, Bruker, United States) using a gold-coated cantilever (NSC-19/Cr-Au, MikroMasch) with a nominal spring constant $k = 0.5 \text{ N/m}$. The AFM tips are hydrophobic when used as received, but plasma cleaning (Harrick Plasma, United States) for 20 seconds renders them hydrophilic.

Simultaneous TIRFM and AFM images (Figure 6.2(a)-(b)) of a $20 \times 20 \mu\text{m}^2$ area show the advantages of each imaging mode. Optical microscopy allows instantaneous and dynamic imaging over areas of $\sim 100 \times 100 \mu\text{m}^2$. On the other hand, the superior spatial resolution of AFM is evident, embodied by the appearance of tiny nanobubbles that are not visible in the optical image due to the diffraction limit (Figure 6.2(b)). An AFM height profile of one of the bubbles is shown in Figure 6.2 (c) and is fitted to a spherical cap by the least-squares method (red line). The fitted contact angle of 28.2° is defined from the less dense gas phase and is consistent with previous reports [40, 42, 68]. However, we note that this angle should not be considered definitive, since the contribution of dye to the interfacial energy balance at the bubble's three-phase line may alter the contact angle from a 'pure' system.

¹ A more typical protocol to bond the channel to the glass would be to leave the microchannel in a hot oven overnight, though the microchannel would not be removable in this case.

Figure 6.2: Simultaneous AFM-TIRFM microscopy of nanobubbles. (a) TIRFM image of nanobubbles nucleated by solvent exchange within a removable channel. A glowing in the middle of the image (marked with an arrow) corresponds to the position of the AFM tip. (b) AFM image of the same feature; the AFM picks up the presence of tiny bubbles that are too small to be resolved optically. Scale bars in (a-b) are $5\ \mu\text{m}$. (c) Height profile of the nanobubble marked in white in (b), fitted to a spherical cap (red line). The fitted contact angle is 28.2° .

The precise control provided by AFM allows us to measure the mechanical response of nanobubbles to pulling under tapping mode AFM. A schematic representation of the pulling is depicted in Figure 6.3(a). In tapping mode AFM, the oscillation amplitude of the tip is kept constant by a feedback mechanism which monitors the input amplitude signal with respect to a reference *setpoint*. A lower setpoint corresponds to a larger amplitude drop and a stronger tip-sample interaction.

Careful control of the lateral position of the tip as well as the tip-object contact allows for the manipulation of individual nanobubbles. First, the tip is manoeuvred to a suitable position just inside the contact line of a selected nanobubble without contacting it (here, a setpoint beyond 100% is used). Second, the tip is made to penetrate the bubble and contact strongly onto the substrate by reducing the

$t = 50$ to 60 s in Figure 6.3(c). No bubbles were successfully unpinned with a hydrophilic tip.

6.3 ESTIMATING THE PINNING FORCE ON NANOBUBBLES

The ability to observe the deformation of bubbles by the AFM tip allows the pulling force induced by the tip to be estimated. The work done by the anchored tip to pull out a neck of length h leads to a change in surface energy $\gamma\Delta S$ in the bubble, where γ is the surface tension and $\Delta S = S_{\text{pulled}} - S_{\text{unpulled}}$ is the difference in surface energy between the unpulled, spherically-capped nanobubble, and at its maximal extension. Equating these terms leads to

$$F = \frac{\gamma\Delta S}{h}. \quad (6.1)$$

We estimate ΔS from the optical TIRFM images by detecting the footprint, calculating the effective radius of curvature, and taking a surface of revolution about the bubble's axis of symmetry while enforcing the experimentally-observed contact angle of the nanobubble in the integration. More details are presented in Appendix D.

Figure 6.4: (a) Pulling force F (calculated from Equation 6.1) exerted by an AFM tip on nanobubbles, and (b) F normalised by the perimeter of the unpulled nanobubble.

The calculated values of the maximum force F exerted by the tip are shown in Figure 6.4(a). The nanobubbles that survived the pulling

were subjected to $F \sim 0.05 \mu\text{N}$ before their necks collapsed, while those that were successfully unpinned were generally subjected to $F \sim 0.1 \mu\text{N}$. Since the neck length h is defined as the maximum extension just before the nanobubble starts to slide along the substrate, the maximum force exerted by the tip on the unpinned bubbles is equivalent to the pinning force by the substrate for the bubbles denoted by green points on Figure 6.4(a). Since the absolute pinning force is a function of the nanobubble's size, we also plot the *pinning strength*, defined as the force normalised by the footprint perimeter of the unpinned nanobubble $F/2\pi L$ in Figure 6.4(b). The normalisation identifies a threshold pinning strength of about 5 mN/m, and can reach up to ~ 20 mN/m. Variations in pinning strength are presumably due to chemical and physical heterogeneities along the substrate.

This estimate of the pinning force is consistent with previous theoretical and experimental work in the literature. In particular, our measurements agree with the lattice density functional theory calculations of Liu *et al.* [82] which predict a pinning force per unit length within an order of magnitude of the surface tension. Our measurements also reinforce previous experiments that show nanobubbles comfortably surviving up to 50 nN of force from invasive AFM scanning in contact mode [88].

6.4 PULLING STABILITY OF A NANOBUBBLE

It is clear from our experiments that the maximum force that can be exerted by the tip on the bubble depends on the stability of the neck that is pulled out by the tip, since the neck pinches off and collapses beyond a certain extension. The neck is a minimum energy surface [89–91] formed by an interface which spans two co-axial rings separated by a distance x . Since the free energy of the interface is proportional to its surface area, the minimal energy configuration of the interface is equivalent to finding its minimal surface area. This surface of revolution is $S[r] = 2\pi \int r \sqrt{1 + (\dot{r})^2} dr$. The interfacial profile $r(x)$ that generates the minimal surface area can then be found from variational calculus to be $r\ddot{r} = 1 + \dot{r}^2$. The general solution of this equation is the catenary [92]

$$r(x) = a \cosh(x/a + c), \quad (6.2)$$

where a and c are constants determined by the boundary conditions. This argument can be extended to the neck pulled out of a surface-attached nanobubble, a schematic of which is shown in Figure 6.5. The neck, whose cross-section is a truncated sphere, can also be described by a catenary since the angular dependence factor 2π drops out during the derivation of Equation 6.2. The boundary conditions at the two footprint radii at each end of the neck are then $L_{\text{tip}} =$

Figure 6.5: Stability of nanobubbles against pulling. (a) The neck region describes a catenoid with footprint radius L_{base} at the bubble's base, L_{tip} at the tip, and length x (see Figure 6.3 for a top view). (b) The stability threshold of the neck as a function of $w = h/2L_{\text{tip}}$ and $\alpha = L_{\text{base}}/L_{\text{tip}}$. Points that lie above the theoretical curve (black line) are unstable. The experimental points (green squares) represent bubbles unpinned from their substrates by hydrophobic tips; these points notably fall within the stable region.

$a \cosh c$ and $L_{\text{base}} = a \cosh(h/a + c)$. The classical calculation requires the radius of curvature R (see Figure 6.3(a)), but this cannot be resolved in our experiment. Instead, we utilise the experimentally observable footprint radii L . We justify this by noting that a spherical cap with constant contact angle θ obeys $L = R \sin \theta$ and thus $L_{\text{base}}/L_{\text{tip}} = R_{\text{base}}/R_{\text{tip}}$. By also defining $X = L_{\text{tip}}/a$, $w = h/2L_{\text{tip}}$, and $\alpha = L_{\text{base}}/L_{\text{tip}}$, Salkin *et al.* [93] showed that the equation for L_{base} can be expressed as the non-linear equation

$$\sinh^2(wX) - X^2(1 - 2\alpha \cosh(wX) + \alpha^2) = 0. \quad (6.3)$$

A stable neck exists when one or more roots for Equation 6.3 can be found. By iteratively searching for roots with a parameter sweep of X and w , it can be shown that every unique neck configuration $\alpha = L_{\text{base}}/L_{\text{tip}}$ possesses a unique maximum stretching length h (see the Appendix D). After the neck is stretched beyond its threshold length h_{max} , Equation 6.3 has no roots and the neck is no longer stable. (Note that the boundary values a and c do not influence h_{max} .) This calculation is then repeated for $1 < \alpha < 5$ to obtain the stability threshold curve in Figure 6.5(b). Our experiments show reasonable agreement with the stability theory (Figure 6.5(b)) – the bubbles tolerate a certain amount of stretching before the neck becomes unstable and pinches off. We also find that the bubbles which successfully unpin and start to slide along the substrate (green square points, Figure 6.5(b)) lie within the stable region, as expected.

The preceding analysis suggests that the key to unpinning nanobubbles from their substrate lies in a relatively large neck radius L_{tip} and low α , which promotes neck stability. It is also apparent from Figure 6.3(b)-(c) that hydrophobic tips are more likely to unpin nanobubbles, since the necks that they pull out from the nanobubbles are considerably wider than the thin ones pulled out by hydrophilic tips. However, it is not immediately clear why hydrophobic tips have significant variation in the neck width, leading to some nanobubbles unpinning and others not. It is likely that the hydrophobic tips in our experiments, which are not cleaned, contain some nanorough heterogeneities leading to a spread in observed contact angles at the neck.

6.5 CONCLUSIONS

In this chapter, we have measured the pinning force on nanobubbles by stretching them with a precisely-manoeuvred AFM tip to the point that they begin to slide along their substrate, and observing their mechanical deformation with optical microscopy. We deduce that nanobubbles are pinned by a force of $\sim 0.1 \mu\text{N}$, or on a normalised scale, a pinning strength in the region of $\sim 10 \text{ mN/m}$. To our knowledge this is the first experimental measurement of the pinning force on nanobubbles.

These results have important implications for both applications and fundamental understanding of nanobubbles. Knowledge of the magnitude of pinning would greatly facilitate efforts to reduce drag in confined environments [75] by being able to manipulate nanobubbles into desired distributions. On the fundamental side, measuring line pinning is clearly crucial to the understanding of how surface nanobubbles stabilise. To provide a sense of how strongly pinned the nanobubbles are, they are known to survive highly invasive contact mode AFM scanning which delivers lateral forces in the order of 10 nN, as we have demonstrated in Chapter 4. The forces required to unpin nanobubbles reported here are at least an order of magnitude in excess of that.

NANOBUBBLES IN AN ELECTRON MICROSCOPE

We study the dynamics of ~ 10 nm nanobubbles formed in a water layer between two graphene sheets positioned 30-50 nm apart. Under a 120 kV electron beam, the nanobubbles coalesce with each other and dissolve into the bulk liquid at a characteristic timescale of 10 s. The timescale of merger between nanobubbles and the dissolution timescale of the bubbles suggest that they are shrinking within an ambient liquid that is significantly more viscous than bulk water. Without the line pinning that can indefinitely sustain a surface-attached nanobubble, we hypothesise that the electron beam itself induces an orders of magnitude increase in viscosity which stabilises the nanobubbles against a rapid shrinkage.

7.1 INTRODUCTION

The properties of liquid-gas interfaces at the nanoscale have significant implications for fundamental biological processes. The accidental discovery in the 1990s that nanobubbles mediate a long-ranged hydrophobic attraction [1, 94, 95] is of particular interest, because hydrophobic interactions in water control the assembly and collapse of biological soft matter such as micelle formation and protein folding [96, 97].

Unfortunately, the existence of stable nanobubbles in water appears to be ruled out by well-established theories. The classical theory of Epstein and Plesset [4] predicts that micron-sized bubbles are expected to dissolve in bulk water [42] within microseconds. Yet the existence of nanobubbles is an experimental fact, demonstrated in a wide variety of experimental methods [40, 42] such as AFM [68, 98], scanning transmission X-ray [99] and various modes of optical microscopy [7, 8, 16]. Nanobubbles are reported to exist both in bulk water [100, 101] and attached to surfaces [42, 68, 102].

Despite significant interest in the field of nanobubbles, many fundamental properties about them remain unknown due to the shortcomings of existing experimental techniques used to characterise nanobubbles. Surface nanobubbles are typically imaged with atomic force microscopy (AFM), which provides excellent spatial resolution but is too slow to capture dynamic processes [40]. Optical microscopy methods [7, 8] provide the dynamic imaging that was previously lacking, but have diffraction-limited spatial resolutions of about ~ 100 nm. The use of electron-based microscopy techniques such as transmission electron microscopy (TEM) and environmental scanning electron mi-

croscopy (ESEM) are particularly appealing in this context, with their capability to offer dynamic imaging at spatial resolutions far better than what AFM can offer.

Since the imaging resolution in TEM is largely limited by the transparency of the cell membrane to electron transmission, the introduction of graphene liquid cells by Yuk *et al.* [103] has finally made the observation of nanoscale fluid processes with electron microscopy viable. Graphene's atomic thickness, electron transparency, flexibility, and impermeability to small molecules make it particularly suitable as a liquid cell capable of trapping and observing liquids within the vacuum environment of a TEM.

Graphene liquid cells have now enabled some advances in the study of nanobubbles in confined water. Shin *et al.* [32] report shrinking and coalescence dynamics of ~ 10 nm nanobubbles imaged with TEM within a graphene liquid cell. These results are remarkable for a number of reasons. First, the radius $R \sim 10$ nm nanobubbles are significantly smaller than the typical surface nanobubbles which have been observed over the years [40, 42], or the bulk nanobubbles detected in dynamic light scattering experiments [102].

Second, the nanobubbles reported by Shin *et al.* should not even exist. Recently published models show that surface nanobubbles can be indefinitely stable if they are pinned at their contact lines to the substrate, and if the ambient liquid is oversaturated with gas [24, 25]. In Chapter 2 we have also shown that this combination also leads to thermodynamically stable surface nanobubbles. For the nanobubbles observed by Shin *et al.* to be stabilised by the mechanism proposed by Lohse and Zhang [24], they must have a pinned contact line – which is simply not observed in the experiment – and possess an oversaturation ζ in the order of

$$\zeta \sim \frac{2\gamma}{RP_0} \sim 100, \quad (7.1)$$

which is far in excess of the prediction that radiolysis induced by the electron beam would only generate enough gas to reach the saturation concentration (*i.e.* a zero oversaturation $\zeta \approx 0$) [104], let alone to exceed the saturation concentration by $\sim 100\times$.

In this chapter we attempt to provide mechanistic understanding about the origin, shape and dynamics of these unusual gaseous bodies, with a view to uncovering the mechanism which sustains the nanobubbles over a remarkably long lifetime.

7.2 EXPERIMENT

ESEM images (Quanta 200 FEG, FEI) of features outside the graphene liquid cell were collected at an accelerating voltage of 20 kV. TEM

Figure 7.1: Fabrication scheme of graphene liquid cells.

(Tecnai, FEI) with an electron accelerating voltage of 120 kV and an electron dose rate of $30\text{--}50\text{ e}/(\text{\AA}^2\text{ s})$. Videos were captured at a rate of 10–20 frames/s using a CCD camera (Orius SC200, Gatan). The graphene liquid cell used in the experiments is shown schematically in Figure 7.1. Graphene is prepared from single-layer graphene films on copper foil by etching the copper away with 4% (by weight) ammonium persulphate (APS) solution. One half of the cell comprises of a sheet of graphene supported by a gold TEM grid with $80\text{ }\mu\text{m}$ square holes, overlaid with a carbon mesh (Quantifoil, Electron Microscopy Sciences) with square holes measuring $7 \times 7\text{ }\mu\text{m}^2$. A TEM image of the overlaid grids is shown in Figure 7.2. The cell is then sealed with a second graphene layer which sandwiches a $1\text{ }\mu\text{L}$ water droplet between the two membranes. Although TEM imaging occurs in a vacuum environment, the adhering graphene sheets form a seal which traps a layer of water that is estimated to be about 30–50 nm thick.

The ESEM images that we capture are able to record simultaneously in transmission and conventional mode. In the conventional mode shown in Figure 7.2(c–d), an external view of the graphene liquid cell shows the collapse of a bulge in the cell membrane. Here, the non-uniform shape and thickness of the liquid layer is apparent. The electron transparency of the graphene allows us to observe clusters of tiny nanobubbles in the liquid layer, as well.

We also observed the dynamics of individual nanobubbles in TEM, *i.e.* through a small region in the electron-transparent region within a grid in the carbon mesh. Nanobubbles of radius $\sim 10\text{ nm}$ appeared in the TEM images from the first frame of recording after the electron beam was turned on, and subsequently dissolved within a timescale of ~ 10 seconds. There is some variation in the lifetime of individual nanobubbles, which is expected due to various factors such as the non-uniform thickness of the liquid layer, heterogeneity in the electron beam, or diffusive shielding from neighbouring bubbles.

7.3 THE ORIGIN OF THE BUBBLING

Nanobubbles were already present in the image when the electron beam was switched on. The radiolysis of water is known to produce

Figure 7.2: TEM and ESEM images of the graphene liquid cell. (a) TEM image of the gold TEM grid ($80 \times 80 \mu\text{m}^2$ square holes) overlaid on a carbon mesh ($7 \times 7 \mu\text{m}^2$ square holes) and the two graphene sheets. The scale bar is $50 \mu\text{m}$. (b) A magnified view of the region in the yellow box in (a) showing detailed structure of the graphene over the grid. (c-d) ESEM images, recorded simultaneously in transmission and conventional mode, showing the collapse of a bulge in the graphene cell membrane. In transmission mode, bubbles trapped between the graphene layers are visible, circled in orange. The scale bar is 500 nm .

a wide variety of by-products, including hydrogen and oxygen. Exact calculations by Schneider *et al.* [34] suggest that the concentration of hydrogen produced by the radiolytic breakdown of water is about an order of magnitude larger than oxygen, and therefore would be the major product of the radiolysis.

However, we believe that the bubbles are *not* produced by the radiolysis of water for the following reasons. First, the presence of bubbling critically depends on the etchant used. While nanobubbles are observed when APS is used to etch the graphene, switching to iron (III) chloride does not lead to the production of any obvious bubbling. Since water is present in excess in both solutions, it is unlikely that the specific reaction causing the bubbling is the radiolytic breakdown of water. Second, the nucleation is not persistent, meaning that once all the nanobubbles in a given region were imaged, no further activity was observed. This observation is consistent with the interpretation that the chemical species causing the bubbling is present only in a limiting amount and becomes depleted by the imaging. We would expect that hydrogen nanobubbles formed by the radiolysis of water would nucleate spontaneously and continuously, since water

is always present in excess. If the radiolytic breakdown of etchant is responsible for the bubbling, then the nanobubbles should primarily contain oxygen – Gall *et al.* [105] have shown that APS breaks down to form hydrogen peroxide and oxygen gas as the major products.

7.4 INFERRING THE WATER VISCOSITY FROM MERGING NANOBUBBLES

Figure 7.3: Merging nanobubbles in TEM. (a) TEM images of merging nanobubbles. For a nanobubble of size $R_0 \sim 10$ nm, the typical timescale of shrinkage is $\tau \sim 10$ s. The scale bar is 10 nm. (b) Schematic of the merger between nanobubbles of radius R_0 .

To account for the remarkable stability of the nanobubbles, we first deduce a key property of the confined water. Experimentally, we find that nanobubbles merge within a timescale of $\tau_m \sim 0.1$ s; a typical example is shown in Figure 7.3. Nanometric gas bubbles in a liquid with the same viscosity as bulk water ought to merge within a timescale that is significantly shorter than what we observe in the experiment.

To show this we derive a scaling law for the merging timescale between nanobubbles. Due to the small size of the nanobubbles, we may assume that inertial effects are negligible, and thus consider a dynamic balance between the viscosity and the capillary force generated by a highly curved ($\sim$ nm) capillary neck that forms between the two bubbles, shown schematically in Figure 7.3. In the limit that the radius of curvature of the capillary neck r is much smaller than the radius of the merging bubble R_0 , it can be shown [106] that the Laplace pressure of the curved interface is $p_c \sim 2\gamma R_0/r^2$, where γ is

surface tension. The neck retracts within a viscous medium, whose stress may be estimated to be

$$p_v \sim \mu \frac{\partial u}{\partial r} \sim \frac{\mu}{r} \frac{dr}{dt}, \quad (7.2)$$

where μ is the dynamic viscosity of the liquid. Balancing the viscous and capillary contributions leads to the differential equation $r(dr/dt) = 2\gamma R_0/\mu$, which can be solved to give $r/R_0 = k\sqrt{t/\tau_m}$, where k is a constant of order 1 and

$$\tau_m = \frac{\mu R_0}{\gamma} \quad (7.3)$$

is the merging timescale. This scaling relation is known to hold very well in exhaustive experiments by Paulsen *et al.* [39] in which the coalescence of mm-sized gas bubbles was observed in liquids over six orders of magnitude. Equation 7.3 can now be used to infer an *effective viscosity* for the water. Substituting $R_0 \sim 10$ nm, $\gamma = 72 \times 10^{-3}$ N/m, and $\tau_m \sim 0.1$ s, the effective viscosity of the confined water is $\mu \approx 7 \times 10^5$ Pa s, a remarkable 8 orders of magnitude larger than the bulk value.

The suggestion that the water is significantly more viscous than in bulk water is disputed and not widely accepted. To put this controversy into context it is worthwhile for us to give a brief review of the literature. Surface probe microscopy experiments in which water is nano-confined to several nanometers have given conflicting results, with some studies suggesting a 6 orders' buildup in viscosity [107], and others suggesting only a modest increase to within an order of magnitude [108, 109].

Notably, however, these studies are performed outside the environment of electron microscopy, which subjects samples to bombardment by high energy electrons. Unlike the conflicting results observed in surface probe experiments, the experiments performed in the TEM environment *universally* show evidence of highly damped fluid dynamics. These experiments cover a wide variety of multi-phase phenomena, ranging from droplet merger [38], stick-slip dynamics of droplets sliding across a substrate [36], nanocrystal nucleation [110]. In a recent study, Lu *et al.* [35] attempted to infer the viscosity of the water by observing the mean squared displacements (MSD) of particles fluctuating within a 30 nm water nanodroplet. They too, found an effective viscosity nine orders of magnitude larger than bulk water. A popular criticism of the work by Lu *et al.* is that strong adhesion between the particles and the liquid cell disrupts the regular Brownian fluctuation of the particles and leads to a significant increase in the measured viscosity [111]. Yet this specific hypothesis cannot be the mechanism for the universal slowdown of such a wide variety of

fluid phenomena in the TEM, especially the fluid dynamics of pure liquid droplets and bubbles that we show in Figure 7.3.

There is therefore a need to identify a universal mechanism responsible for the large increases in apparent viscosity in the water. In Chapter 8 we will show using molecular dynamics simulations that the application of electric fields typical in TEM (~ 10 V/nm) can lead to orders-of-magnitude increases in the viscosity of water.

How does an increased liquid viscosity affect the dissolution of nanobubbles? A Brownian particle of radius a propagating within the liquid possesses a diffusion constant given by the Einstein relation $D = \lambda k_B T$, where λ is the mobility. Conventionally, the Brownian mobility is dominated by viscous drag, leading to the Stokes-Einstein relation $D = k_B T / 6\pi\mu a$. Assuming that Stokes-Einstein is valid both in bulk and confined water, proportionality implies that the diffusion constant in confined water is $D_{\text{conf}} = \mu_{\text{bulk}} D_{\text{bulk}} / \mu_{\text{conf}} \sim 10^{-18} \text{ m}^2 \text{ s}^{-1}$, nine orders smaller than the bulk value $D_{\text{bulk}} = 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

7.5 DIFFUSIVE DYNAMICS OF NANOBUBBLES

The transport of gas molecules from the nanobubble during shrinkage is governed by the diffusion equation [4]

$$\frac{\partial c}{\partial t} = D \nabla^2 c. \quad (7.4)$$

Figure 7.4: Possible shapes of the nanobubbles observed in the TEM experiments: a surface nanobubble attached to one of the liquid cell membranes, a catenoidal bubble attached to both membranes, and a freely-suspended bubble in bulk liquid.

However, the governing equation for a shrinking nanobubble is geometry dependent. Since TEM provides only a projection view of the nanobubbles, it cannot reliably distinguish between three possible configurations for the nanobubble, as we show in Figure 7.4: (a) a spherical nanobubble in bulk solution, (b) a surface nanobubble attached to only one of the two membranes of the liquid cell, and (c) a catenoid nanobubble which is simultaneously attached to both membranes.

We next proceed to derive governing equations for the case of a spherical nanobubble and a spherical cap nanobubble shrinking in an unpinned mode. For a spherical nanobubble in bulk solution, the solution of the diffusion equation can be shown to be [4, 112]

$$\frac{\partial c}{\partial r} = (c_b - c_\infty) \left(\frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right), \quad (7.5)$$

where c_b is the gas concentration in the liquid immediately adjacent to the bubble, and c_∞ is the concentration in the far-field. Dimensionally it can be shown the mass flux of gas out of the bubble obeys

$$\frac{dm}{dt} = -4\pi R^2 J = 4\pi R^2 \rho_g \frac{dR}{dt}, \quad (7.6)$$

where ρ_g is the density of the gas and the flux J obeys Fick's first law of diffusion,

$$J = -D \frac{\partial c}{\partial r}. \quad (7.7)$$

The combination of Equation 7.5-7.7 leads to the governing equation for a shrinking spherical nanobubble in the bulk,

$$\frac{dR}{dt} = -\frac{D}{\rho} (c_b - c_\infty) \left(\frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right) \quad (7.8)$$

$$= -\frac{D c_{\text{sat}}}{\rho} \left(\frac{2\gamma}{R P_0} - \zeta \right) \left(\frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right), \quad (7.9)$$

where we have defined the oversaturation ζ to depend on the saturation gas concentration c_{sat} as

$$\zeta \equiv \frac{c_\infty}{c_{\text{sat}}} - 1. \quad (7.10)$$

For a spherical cap nanobubble, an exact solution exists only in the quasi-static limit of the diffusion problem, *i.e.* the Laplace equation is solved instead. This problem was first solved by Popov [80] to resolve the formation of coffee stains in a spherically-capped droplet, and has subsequently been validated to excellent agreement in experiments [113]. In particular, the mass flux of gas (which was Equation 7.6 for a spherical gas bubble) now becomes

$$\frac{dm}{dt} = -\pi L D c_{\text{sat}} f(\theta) \left(\frac{2\gamma}{L P_0} \sin \theta - \zeta \right), \quad (7.11)$$

where

$$f(\theta) = \frac{\sin \theta}{1 + \cos \theta} + 4 \int_0^\infty \frac{1 + \cosh 2\theta\tau}{\sinh 2\pi\tau} \tanh[(\pi - \theta)\tau] d\tau \quad (7.12)$$

is a geometric term depending on the contact angle θ which emerges from the exact solution by Popov. The mass of the bubble is given by

$$m = \pi L^3 \rho_g \frac{\cos^3 \theta - 3 \cos \theta + 2}{3 \sin^3 \theta} \equiv \pi L^3 \rho_g g(\theta). \quad (7.13)$$

There are two major dynamical modes for the shrinkage of a spherical cap bubble [77]. In a *pinned* shrinkage, the bubble only shrinks by changing its height and not its footprint, thus the observed footprint radius L would be invariant in time. In an *unpinned* shrinkage the bubble shrinks proportionally by maintaining its contact angle. There also exists a third mode in which the bubble alternates between the pinned and unpinned modes, but this would lead to a shrinkage curve with discrete steps, which we do not observe in our experiments. We therefore proceed by considering the case of an unpinned, constant contact angle shrinkage. Taking the derivative of Equation 7.13 with respect to the footprint radius (and leaving θ constant) and equating with Equation 7.11 gives the governing equation for the footprint radius of a surface nanobubble shrinking in an unpinned mode,

$$\frac{dL}{dt} = -\frac{Dc_{\text{sat}}}{3L\rho_g} \left(\frac{2\gamma}{LP_0} - \zeta \right) \frac{f(\theta)}{g(\theta)}. \quad (7.14)$$

Figure 7.5: Shrinking nanobubbles in TEM, with experimental points in red dots, fitting for a bulk nanobubble in dashed line, and fitting for an unpinned surface nanobubble in solid line. The nanobubble in (a) fits the governing equation for a surface nanobubble with $Df(\theta)/g(\theta) = 2.0 \times 10^{-17} \text{ m}^2/\text{s}$, while the one in (b) is well-fitted to the governing equation for the bulk nanobubble with $D \approx 1.1 \times 10^{-18} \text{ m}^2/\text{s}$.

By using the diffusion constant D in our curve fits to the experimental data in Figure 7.5, we are able to infer an effective diffusion constant in this system. Since the fitting equations are for a spherical or a spherical cap bubble, we selected only bubbles with circular footprints, and which are isolated by at least five bubble diameters from a neighbouring bubble in order to avoid cooperative effects [114] that may sustain the nanobubbles for longer than expected. For the fitting to the dynamical equation for a bulk nanobubble (Equation 7.9), D

FIGURE	D (m ² /s)	$D \frac{f(\theta)}{g(\theta)}$ (m ² /s)	$D(72^\circ)$ (m ² /s)
5.5(a)	1.7×10^{-18}	2.0×10^{-17}	4.5×10^{-18}
5.5(b)	1.1×10^{-18}	5.0×10^{-18}	1.7×10^{-18}

Table 2: Fitting parameters for the curve fits to the dynamical equations for the surface nanobubble (Equation 7.14) and bulk nanobubble (Equation 7.9). The fitting parameters that are used in Figure 7.5 are highlighted in bold.

is the lone fitting parameter. For the fitting to a surface nanobubble, both D and the contact angle θ are unknown. However, the form of Equation 7.14 suggests that D and θ can be collapsed into the single fitting parameter $Df(\theta)/g(\theta)$ instead. Since the numerical calculations of Schneider *et al.* [34] predict that the radiolysis products of TEM reach their saturation values within a second of switching on the TEM beam, we assume $\zeta = 0$. We also use the same material parameters for a nitrogen bubble used by Lohse and Zhang [24], $c_{\text{sat}} = 0.017$ kg/m³ and $\rho_g = 1.165$ kg/m³.

Curve fits to the circular nanobubbles in our system suggest that both spherical nanobubbles in bulk and surface attached nanobubbles are present. In Figure 7.5 we plot the experimental shrinkage curves of two nanobubbles, one which is well-described by an unpinned shrinkage of a spherical cap nanobubble (Equation 7.14), and the other well-fitted to the dynamical equation for a spherical bulk nanobubble (Equation 7.9). For reference we have plotted both types of fitting curves on the same axes in order to contrast the theoretical prediction of each type of shrinkage. In general, for a shrinkage over the same radius R and same dissolution time t , a bulk nanobubble has a more gradual dissolution, while the shrinkage of an unpinned surface nanobubble accelerates in time.

Our curve fits suggest that the effective diffusion constant mediating the shrinkage of the bulk nanobubbles is in the order of $D \sim 10^{-18}$ m²/s, see Table 2. Although we do not have a value for the contact angle of the surface nanobubbles, the experiments of Shin *et al.* [32] use a virtually identical protocol to produce the graphene liquid cells, and in a folded TEM grid found that nanobubbles with a contact angle of about $\theta \approx 72^\circ$. When this contact angle is substituted into the fitted parameter $D \cdot f(\theta)/g(\theta)$ for the surface nanobubble in Figure 7.5(a), we obtain an estimated diffusion constant of $D \approx 4.5 \times 10^{-18}$ m²/s.

Our estimates of the diffusion constant of the nanobubbles in our system match with the corresponding estimate that was based on observing the timescale of bubble coalescence, Equation 7.3 to within

an order of magnitude. The fact that the diffusion constants tally to within an order of magnitude despite being estimated from two different physical phenomena suggests that the pure liquid is highly viscous.

Let us return to the last possible type of bubble, the catenoid nanobubble. We did not observe any circular nanobubbles shrinking in any other mode than the bulk and unpinned shrinkage modes that we show in Figure 7.5. However, we can say that for a typical nanobubble size of about 10 nm and a typical liquid thickness of about 30-50 nm, we would not expect catenoid nanobubbles to be abundant in our system. This is because an exact solution for the minimum surface energy suggests that a catenoid bubble with the wetting radius R_0 on each end can only have a maximum height of about $1.33R_0$ before the catenoid becomes unstable [92] and pinches off into two surface nanobubbles attached to the top and bottom membranes. Given the bulging in the graphene liquid cell we observe in Figure 7.2 we cannot rule out the possibility that catenoid nanobubbles could nucleate in a region that is extremely thin, and later pinch off into surface-attached nanobubbles as the distance between the graphene sheets becomes larger than $1.33R_0$.

7.6 NANOBUBBLES THAT DO NOT DISAPPEAR

There is one last mystery about the nanobubbles in our system. Remarkably, if the electron beam is turned off while the shrinkage is in progress and later switched back on, the bubble remains present in the image. In Figure 7.6 we show an example of a nanobubble that loses only about 50% of its initial area A_0 after a waiting time of 22 minutes. Once the beam is switched back on, the bubble in Figure 7.6 finally completes its shrinkage over 60 s.

This result is rather remarkable given that the typical shrinkage timescale of the nanobubble is in the range of 10-100 seconds. Compared to the typical diffusion constant $D \sim 10^{-18} \text{ m}^2/\text{s}$ used to fit the equations for the nanobubbles in Figure 7.5, the diffusion constant would need to be about two orders lower than this, i.e. $D \sim 10^{-20} \text{ m}^2/\text{s}$ in order for the nanobubbles to only shrink slightly in the absence of the beam. In the framework of the diffusion theory in this chapter, we do not have a satisfactory answer for this remarkable phenomenon.

7.7 CONCLUSIONS

Part of the conceptual difficulty in understanding why nanobubbles are so long-lived is that their high Laplace pressures imply that they should shrink rapidly. Surface nanobubbles are now understood to be

Figure 7.6: Nanobubbles resist shrinkage in the absence of TEM beam. (a-b) Images of two nanobubbles taken immediately before the beam was switched off for 22 minutes, and immediately after the beam is switched back on again. The bubbles have shrunk slightly after the waiting time. (c) A plot of the radius of the smaller bubble at the top-right corner of (a-b). This bubble dissolves into the liquid after about 60 s when the beam is switched back on.

stabilised by a combination of contact line pinning and oversaturation of the ambient liquid. Yet, nanobubbles observed under an electron microscope are very different from the surface nanobubbles studied with AFM, including the fact that they persist even without the benefit of contact line pinning or liquid oversaturation.

In this chapter we show that the apparent stability of the nanobubbles originates from the diffusion constant in water being significantly smaller than would be expected for bulk water. We use two very different methods to estimate the diffusion constant within the liquid – (a) by observing how rapidly nanobubbles merge, and (b) by fitting experimental images of shrinking nanobubbles to the diffusion equation, with the diffusion constant as a fitting parameter. Both estimates agree that the diffusion constant in the liquid is up to a remarkable 9 orders smaller than the bulk value for water. Although we concede

that such a strong buildup of viscosity in the water remains disputed, our conclusions are very much in line with a wide variety of TEM studies, all of which have found highly viscous fluid dynamics of droplets as they interact with surfaces [36], nanoparticles [35, 111], and so forth.

One of the objections against the hypothesis of a significant viscous buildup in the TEM environment is that a suitable mechanism of such a buildup has not yet been identified. We complete this story in the next and final chapter of this thesis by proposing one possible mechanism.

VISCOSITY ENHANCEMENT OF WATER UNDER ELECTRIC FIELDS

The availability of liquid cells for in situ transmission electron microscopy (TEM) has enabled the observation of novel nanoscale phenomena in liquids, despite a modest temporal resolution. Although experiments suggest that the ambient liquid might be highly viscous, the possibility that the liquid is significantly more viscous than bulk water is still controversial and in any case the mechanism for viscous buildup is unknown. Using molecular dynamics simulations we show that the application of typical electric field strengths used in TEM can induce an increase in the water viscosity by orders of magnitude before its freezing point. Beyond the freezing point, we observe a continuous phase transition at low field and a discontinuous one at high field strengths.

8.1 INTRODUCTION

The advent of liquid cells for *in situ* transmission electron microscopy (TEM) [115] has facilitated rapid advances in the understanding of physical phenomena at the nanoscale [103]. With its ability to provide dynamic imaging at nanometer resolution, in-liquid TEM studies have uncovered novel nucleation pathways for nanoparticles and crystals [111, 116], unusual stick-slip dynamics of nanodroplets [37], nucleation of nanobubbles [32], and the formation of square ice [117].

One of the key open questions about TEM imaging is why these phenomena can even be visualised in TEM. Since the time and length scales of fluid dynamical phenomena tend to scale together, it is odd that processes occurring on a nanometer length scale can be observed over timescales of 10-100 s in TEM. Remarkably slow dynamics is *universally* observed in TEM. Table 3 lists a broad range of nanoscale phenomena that are significantly slower than the theoretical predictions. The dynamics observed appear to be consistent with a viscosity that is 6-9 orders larger than that of bulk water [36].

The suspicion that the water imaged in the TEM environment might be highly viscous has stimulated interest in measuring its viscosity. Lu *et al.* [35] measured the diffusion constant of gold nanoparticles in a 10 nm nanodroplet to be 9 orders smaller than would apply in bulk water. A straightforward application of the Stokes-Einstein equation suggests that the water is a commensurate 9 orders more viscous than bulk water. This hypothesis is not widely accepted, however. Instead, the prevailing argument, first suggested by Zheng *et al.* [110] is

Type	Theoretical	Experimental
Bubble shrinkage	$\tau \sim R^2/D \sim 10 \text{ ns}$	$\tau \sim 10 \text{ s}$ [32]
Bubble merger	$\tau \sim \eta R/\gamma \sim 0.1 \text{ ns}$	$\tau \sim 0.1 \text{ s}$ [32]
Droplet depinning	$\tau \sim \eta R/\gamma \sim 0.1 \text{ ns}$	$\tau \sim 0.1 \text{ s}$ [36]
Nanoparticle dynamics	$D \sim 10^{-9} \text{ m}^2/\text{s}$	$D \sim 10^{-18} \text{ m}^2/\text{s}$ [35]

Table 3: Comparison of nanoscale phenomena observed in TEM experiments, as compared to theoretical predictions. The orders of magnitude for bubbles/droplets are radius $R \sim 10 \text{ nm}$, diffusion constant $D \sim 10^{-9} \text{ m}^2/\text{s}$, and surface tension $\gamma \sim 10^{-1} \text{ N/m}$.

that a strong adhesion between the nanoparticles and the liquid cell membrane disrupts the Brownian motion of the particles. However, particle-substrate adhesion alone cannot account for viscous dynamics of pure liquids in the TEM as bubbles and droplets shrink [32] and coalesce with each other, or slide [37] and depin [36] from solid substrates.

Even if substantially larger water viscosities can be indisputably demonstrated, the mechanistic origin of the *universal* slowdown of nanoscale fluid dynamics has not been identified. Apart from the aforementioned adhesion hypothesis, the most promising of a limited number of potential explanations is that the hindered diffusion of molecules under nano confinement may lead to a significant rise in viscosity. Several groups using various modes of force microscopy [107, 118] have reported that water can achieve orders-of-magnitude increases in viscosity under nanometric confinement by hydrophilic substrates. However, these results are disputed – other experimental studies report only a modest increase of viscosity to within an order of magnitude [108, 109, 119].

Molecular dynamics simulations suggest that nanoconfinement cannot explain the substantial increase of viscosity observed in the in-liquid TEM experiments. Some groups predict that a pair of graphene sheets separated by several Ångströms can produce a squeezing pressure up to $\sim \text{GPa}$, enough to increase the shear viscosity by 2-3 orders of magnitude [120], or even induce freezing of a monolayer of water molecules [117, 121]. Yet these effects only come into play within a *sub-nanometer* regime, and thus cannot account for highly viscous behaviour observed in TEM liquid cells, which are confined to 10-100 nm [37, 103].

Along with a lack of convincing experimental evidence of viscosity buildup outside the electron microscopy environment, the universal dampening of fluid dynamics in TEM seems to indicate that the viscosity buildup may originate from the imaging conditions. In this chapter we test this hypothesis by molecular simulations.

8.2 PRINCIPLES OF MOLECULAR DYNAMICS

One of the most direct methods of simulating nanoscale processes is with molecular dynamics, in which a system of atoms mutually interacting under the influence of a potential V is subjected to Newton's second law,

$$m \frac{d^2 \mathbf{r}}{dt^2} = F(\mathbf{r}(t)) = -\nabla V(\mathbf{r}(t)). \quad (8.1)$$

The positions x_i and velocities v_i of the atoms are known and advanced in time according to an algorithm such as the velocity Verlet method. In this approach, the velocity is advanced in a two-step process

$$\mathbf{v}\left(t + \frac{\Delta t}{2}\right) = \mathbf{v}(t) + \frac{1}{2} \mathbf{a}(t) \Delta t, \quad (8.2)$$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t) \Delta t + \frac{1}{2} \mathbf{a}(t) \Delta t^2, \quad (8.3)$$

where the acceleration $\mathbf{a}$ is a function of the inter-atomic potential V and is advanced by

$$\mathbf{a}(t + \Delta t) = -\frac{1}{m} \nabla V(\mathbf{r}(t + \Delta t)). \quad (8.4)$$

Once $\mathbf{v}(t + \Delta t/2)$, $\mathbf{r}(t + \Delta t)$ and $\mathbf{a}(t + \Delta t)$ are known, the velocity update for a single timestep is completed with

$$\mathbf{v}(t + \Delta t) = \mathbf{v}\left(t + \frac{\Delta t}{2}\right) + \frac{1}{2} \mathbf{a}(t + \Delta t) \Delta t. \quad (8.5)$$

This procedure seems rather roundabout, especially since the velocities can be explicitly calculated from the position data $\mathbf{r}(t)$ with the update equation

$$\mathbf{v}(t) = \frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)}{2\Delta t}. \quad (8.6)$$

However, the truncation error of Equation 8.6 is $O(\Delta t^2)$, leading to unacceptably large errors in computing variables that are explicit functions of velocity, such as kinetic energy $K \sim m\mathbf{v}(t)^2$. Apart from being accurate to a higher order, the velocity Verlet algorithm has the property of being symplectic [122], meaning that it conserves the area in the position-momentum (x, p) phase space and avoids instabilities associated with non-symplectic integrators such as the Euler method.

The key to an accurate simulation critically depends on the interaction potential V between the atoms in the system. Interactions between atoms are dominated at short ranges by the Lennard-Jones potential

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (8.7)$$

and at longer ranges by the Coulombic potential

$$V_{LE} = \frac{q_i}{4\pi\epsilon_0 r}. \quad (8.8)$$

Since it is computationally prohibitive to calculate pairwise potentials between all N molecules in a water box, in practice, cut-offs are defined so that the potentials are not calculated beyond a certain distance.

Figure 8.1: Water models in MD. (a) The TIP class of rigid water models. Reproduced from Wikipedia under a Creative Commons license. (b) The TIP4P model (and a 2005 parameterisation) is able to reproduce the phase diagram of water with reasonable fidelity. Reproduced from [123] with permission, copyright of the Royal Society of Chemistry.

To model water, one must assign molecular weights to individual atoms at x_i , Lennard-Jones parameters ϵ and σ , as well as charges q_i corresponding to each atom. The exact values of these parameters are not *a priori* known, so various models propose various purely empirical parameters. The parameters are chosen in a way that matches experimental measurements of various properties of water as closely as possible.

In the TIP models (Figure 8.1), the bonds between the oxygen and hydrogen are rigidly fixed to maintain a certain bond length and bond angle. The numbers in the TIP models correspond to the number of interaction points. The basic TIP3P utilises a simple 3-site model in which the charges are located on the atoms. For increased accuracy some groups have proposed modifications to the basic model, such as placing charges on dummy atoms (labelled 'M' in Figure 8.1(a)) or lone pairs ('L'), to improve electrostatic distribution around the molecules. However, the tradeoff with a more elaborate model is increased computation time.

Despite the empirical approach of MD, these water models are generally effective in reproducing the properties of water, to the point that they are able to reproduce the entire phase diagram of water with reasonable fidelity [123], as we show here for the TIP4P potential in Figure 8.1(b). Even though MD cannot reproduce experimental measurements exactly, the ability of the simulations to closely approximate them in a wide variety of physical properties gives us confidence that molecular dynamics can provide some key insights into physical mechanisms that occur in water and other nanoscale systems.

8.3 MOLECULAR DYNAMICS SIMULATIONS

Sustained exposure to high energy electrons in a TEM can electrify the liquid cell membranes in TEMs with a surface potential in the order of 100 mV, as was found by Kelvin probe measurements by Mirsaidov *et al.* [37]. Counter ions in the liquid, which originate from buffer solutions used in TEM experiments¹ are drawn towards the membranes, forming a diffuse electric double layer. Another potential source of ions for the double layer may come from the beam-induced dissociation of water to form hydroxide and hydronium ions. Calculations with the Poisson-Boltzmann equation [124] suggest that the electric field within the double layer with a surface charge of ~ 100 mV and a bulk concentration of 1 mM can reach up to $E = 0.1$ V/nm.

We study the effects of an electric field on a box of 512 water molecules measuring $24.8 \times 24.8 \times 24.8 \text{ \AA}^3$ (corresponding to an approximate density of 1000 kg/m^3), by integrating the velocity Verlet equations with the LAMMPS solver [125]. Force interactions between water molecules were modelled using the TIP4P/2005 potential [126]. To simulate bulk conditions, periodic boundary conditions were applied on the three principal axes. The temperature of the system was constrained to 300 K using the Nosé-Hoover thermostat. After equilibration for 1 ns at zero field in the canonical NVT ensemble, the simulation was executed in the NPT ensemble (300 K and 1 atmosphere) for 5 ns and a time step of 1 fs at various electric fields. The shear viscosity was computed with the Green-Kubo formula

$$\eta = \lim_{t \rightarrow \infty} \frac{V}{k_B T} \int_0^t dt \sum_{\alpha, \beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle. \quad (8.9)$$

Here V is the system volume, and the summation is taken over the five independent components of the stress tensor $(P_{xx} - P_{yy})/2$, $(P_{yy} - P_{zz})/2$, P_{xy} , P_{yz} and P_{xz} [127]. The autocorrelation integral was computed by capturing the aforementioned stress tensor components every 1 fs, and performing the averaging over 5 ps. For the TIP4P/2005

¹ In the case of the bubbles in graphene liquid cells in Chapter 7, the ammonium persulphate used to etch graphene may be the source of ions.

potential we obtain a shear viscosity (at $E = 0$) of $\eta_{\text{bulk}} = 0.84 \text{ mPa s}$, in close agreement with the results of González and Abascal [128].

Applying a uniaxial electric field to the water molecules in this system introduces an external force to each atom, $\mathbf{F}_e \sim qE_0\hat{\mathbf{z}}$. Note that the applied electric field E_0 is *not* the electric field E that would be measured in experiment, due to a screening effect by water molecules as they are polarised by the applied field, thus $\mathbf{E} = \mathbf{E}_0 + \mathbf{P}$. The screened electric field E can be estimated by dividing the dielectric constant of water, $E \approx E_0/\epsilon_r$, where $\epsilon_r \approx 60$ for the TIP4P potential.

We vary the electric fields E over five orders of magnitude for $10^{-5} < E < 10^0$. The viscosity is initially unchanged with E until a threshold of $E \approx 10^{-3} \text{ V/nm}$, after which it begins to scale as $\eta \sim E^2$, as we show in Figure 8.2. This scaling can be accounted for by noting that the pressure estimator in MD utilises a summation of force interactions F between pairs of neighbouring atoms (i, j) [129]

$$p = \frac{1}{3V} \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \sum_{i,j}^{i \neq j} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_i \right). \quad (8.10)$$

In the large field limit, the contribution of E dominates the pressure term, and as it is a constant, can be taken out of the integral in Equation 8.9, leading to the scaling $\eta \sim E^2$. Beyond $E \approx 0.07 \text{ V/nm}$, the water begins to freeze (red points in Figure 8.2) within the simulation timescale of 1 ns.

Physically, viscosity is a measure of a liquid's resistance to shear deformation, which for water is mediated by inter-molecular hydrogen bonding. To examine the strength and extent of the hydrogen bonding we first define a hydrogen bond by the geometric criteria [130] that the donor oxygen and acceptor hydrogen have a distance of less than $2.42 \text{ \AA}$, and that the angle between the O–H bond and O...O vectors is less than 30° . We then calculated the average number of hydrogen bonds on each water molecule $\langle n_{\text{HB}} \rangle$ and the mean bond energy $\langle U_{\text{HB}} \rangle$ at the final timestep of the simulation, see Figure 8.2(b)–(c). As with the viscosity, both quantities are invariant to an increasing electric field until a threshold of about $E = 0.1 \text{ V/nm}$, at which point $\langle n_{\text{HB}} \rangle$ shifts from about 3.4 to nearly 4 hydrogen bonds per molecule, and $\langle U_{\text{HB}} \rangle$ shifts from -25 to -45 kJ/mol.

What explains the transition to the $\eta \sim E^2$ scaling at about 1 mV/nm? We expect the behaviour of water molecules with dipole moment p to be qualitatively different when their electric field interaction energy exceeds the thermal energy, that is, $pE_0 \gg k_B T$, where k_B is the Boltzmann constant and T is temperature. Since heating is not significant in TEM experiments [104] we take $T = 300 \text{ K}$, and take the

Figure 8.2: Viscosity enhancement of water under an electric field. From top to bottom, (a) viscosity η as a fraction of the bulk water viscosity $\eta_{\text{bulk}} = 0.84 \text{ mPa s}$, (b) average hydrogen bond energy $\langle U_{\text{HB}} \rangle$ and (c) average number of hydrogen bonds $\langle n_{\text{HB}} \rangle$ per water molecule as a function of applied electric field E . Note the transition to the $\eta \sim E^2$ scaling starting from 10^{-3} V/nm , and the freezing of the the water box after $E > 0.1 \text{ V/nm}$.

dipole moment for a single water molecule to be $p \sim 1 e \cdot \text{\AA}$. Then water molecules may be coerced to align with a persistent external fields when $E_0 > 0.25 \text{ V/nm}$. This is equivalently $E = E_0/\epsilon_r \sim 4 \times 10^{-3} \text{ V/nm}$, in accordance with the transition observed in Figure 8.2.

While the $\eta \sim E^2$ viscosity increase we report here is substantial, the increase only persists for four orders before the water freezes Figure 8.3, rather than the 6-9 orders that have been claimed. Moreover, our estimate that $E \sim 0.1 \text{ V/nm}$ is within the region where freezing is observed to occur, despite the fact that liquid than ice is observed in the TEM experiments [36, 111, 131].

We hypothesise that some other mechanism not accounted for in the MD simulations may suppress the onset of freezing, and therefore allow the water to remain liquid as its viscosity increases under strong electric fields. In our view, the aggregate effect of the dissociation would merely be to extend the threshold electric field strength E required to freeze the water, by introducing physical heterogeneities that inhibit the freezing of water as a whole. This would be analo-

Figure 8.3: (a) Liquid water. (b) Water freezes to hexagonal ice at $E = 0.07 \text{ V/nm}$.

gous to the inhibition of freezing by adding impurities to water – for instance, the introduction of concentrated brine can reduce the freezing point of water by about 20°C [132]. Due to the generality of the Green-Kubo formula (Equation 8.9), the onset E for freezing does not affect the viscosity estimate, allowing the $\eta \sim E^2$ scaling to hold through the freezing transition.

8.4 STRUCTURAL MOTIFS IN WATER

Figure 8.4: A rotationally invariant measure to extract structural motifs in water. (a) Definition of the planar angle between water molecules. (b) Searching a radial neighbourhood around the central oxygen atom (red circles) of one particular water molecule.

To observe the system structure on a molecule-by-molecule level we devise a rotationally-invariant measure to extract the structural motifs that the water molecules adopt under changing electric fields, shown schematically in Figure 8.4. For each water molecule, we search the immediate neighbourhood up to $r = 3.5 \text{ \AA}$ away from its central

oxygen atom. The coordinates of the three atoms in water form a plane with a characteristic normal vector. We construct a histogram of planar angles ϕ formed between each pair of plane normals. This calculation is then repeated over all the water molecules in the box to form a matrix that is binned by the oxygen atom number in the column axis and ϕ in the row axis. Finally, the matrix is filtered with a singular value decomposition to extract the dominant motifs, and hierarchical clustering (with complete linkage) is applied to rearrange and sort the rows into visually discrete clusters based on their mutual similarity² of the motifs.

Figure 8.5: Characteristic motifs of water and ice. Each row represents the distribution of planar angles ϕ in the neighbourhood of a single water molecule in the box. The distributions plotted at the bottom of the figure denote the local neighbourhoods around the oxygen atoms indicated in red and pink arrows. (a) Liquid at $E = 0$ V/nm, (b) liquid at $E = 0.00167$ V/nm, (c) hexagonal ice formed at $E = 0.07$ V/nm.

This procedure recovers characteristic motifs for water and the various types of ice. In the low field limit the planar angle distribution is almost flat except for a rise at the extremes, $\phi = 0, \pi$ which occurs due to the polarisation of molecules in the electric field. The hexagonal ice motif is characterised by two lobes at about $\pi/3$ and $\pi/6$. In the $E < 0.07$ V/nm region before the threshold E for freezing we observe the nearly uniform distribution of ϕ that is expected of liquid (Figure 8.5(a)), suggesting that there is no geometric ordering associated with the viscosity increase observed in Figure 8.2.

² The similarity is quantified by taking the Cartesian distance between each pair of rows. The distance between two clusters is defined in complete linkage as the furthest possible distance between an element from each cluster.

8.5 PHASE TRANSITION IN ELECTROFROZEN WATER

Phase transitions bring about observable changes to the long range structure of water. In Figure 8.6(a-b) we plot the radial distribution function (RDF) $g_{OO}(r)$ between oxygen atoms in the box as a function of radial displacement r from each individual molecule. By plotting the RDFs every 5000 timesteps (or 5 ps) and stacking them into a kymograph we are able to visualise the transition of liquid water into the final icy state. Comparing the RDFs before and after the phase transition, we find a gradual buildup of peaks at 4 and 7 Å.

We can confirm this gradual buildup from our previous calculation of structural motifs in the water. The matrix of motifs in Figure 8.5 give us an idea of how much of the water box is icy and how much remains liquid. By repeating this process over every saved frame in our MD trajectory (once every 5000 fs) we are able to resolve the dynamics of the phase transitions in even greater detail than the RDF kymographs shown in Figure 8.6(a-b). First, we defined the icy state as being the average motif (i.e. the mean of the pseudocolour plot, averaged over all the oxygen atoms) at the final frame of the MD trajectory. For each time step, we compute the cross-correlation between the motif of each individual water molecule and of the previously defined icy state. The motif is then defined as icy if the cross-correlation exceeds 0.9. In this way, we are able to plot the water box's iciness as a function of time, shown in Figure 8.6. For the freezing transition to hexagonal ice, we thus find an almost linear increase in the overall iciness of the box, until it plateaus at an ice fraction of about $k_{\text{ice}} \approx 0.9$.

8.6 CONCLUSIONS

In the first half of this chapter we report that strong electric fields typical in a TEM environment can induce orders of magnitude increases in the viscosity of bulk water. This finding provides theoretical support for experimental studies in TEM which report highly viscous fluid dynamics (such as in Chapter 7 of this thesis), but which have been disputed over the years due to a lack of experimental evidence in non-electronic modes of microscopy. Our results give some resolution to the puzzling ability of TEM to image nanometer scale processes at anomalously long timescales by clarifying that the unique imaging conditions of TEM slow down fluid dynamic processes to such an extent that they can be imaged at fairly modest frame rates.

In the second half of this chapter we devise a novel method to analyse phase transitions of liquid water that is electrofrozen to ice on a molecule-by-molecule level. By extracting the distribution of planar angles around individual water molecules, we were in effect able to

measure the 'iciness' of the neighbourhood of each water molecule. Our rotationally invariant measure also provides us with a measure of how individual water molecules contribute to the freezing transition.

Figure 8.6: The continuous phase transition when water freezes at $E = 0.07$ V/nm. (a) RDFs of the water box at various times t stacked into a kymograph. (b) The RDF of the box before and after the phase transition to hexagonal ice. (c) The iciness of the water box, calculated by taking the cross-correlation of the the planar angle distribution of each water molecule with the hexagonal ice motif.

CONCLUSIONS AND OUTLOOK

This dissertation studies the dynamics and stability mechanism of gas nanobubbles with experiments, theory and numerical calculations.

9.1 CONCLUSIONS

There is strong consensus that line pinning is essential for the stability of surface nanobubbles. The oversaturation and pinning theory of Lohse and Zhang predicts that nanobubbles can achieve an equilibrium contact angle, based on well-established equations such as Young-Laplace equation and Henry's law. Yet, in principle, the large curvature of a nanobubble can disrupt the thermodynamic equilibrium of a nanobubble with its surroundings. In Chapter 2 we show that this effect is small, thus confirming that the fundamental assumptions behind the theory of Lohse and Zhang are sound.

In Chapter 4 we show that despite previous reports that suggest that surface nanobubbles cannot be easily distinguished from contamination, careful AFM characterisation provides several robust indicators of polymeric contamination. One highlight is that surface nanobubbles disappear cleanly under strong vertical imaging forces, but oil nanodroplets maintain a thin nanometer wetting layer under strong lateral forces. We also show that the nanodroplets are easily swept away by lateral forces, but nanobubbles are very robust to them.

In the subsequent chapters we quantified the magnitude and onset conditions for the line pinning on nanobubbles from optical microscopy. In Chapter 5 we provide the first experimental images of nanobubbles shrinking in both an unpinned mode, and its transition to a pinned state. In particular, the threshold radius at which a shrinking nanobubble becomes pinned suggests a pinning force per unit length of about 30 mN/m. This order of magnitude matches a more direct measurement in Chapter 6, in which the deformation of a nanobubble is observed with TIREM as it is pulled with an AFM tip to the point that it detaches from its substrate.

The latter half of the thesis pertains to the observation of nanobubbles with *in situ* TEM. Remarkably, neither type of bubble appears to be stabilised by the pinning or oversaturation that sustains the more conventional nanobubbles that we have seen from Chapters 4 to 6.

Curve fits to the diffusion equation suggest that both bulk and surface nanobubbles are present in the system, and additionally suggest that they are stabilised by virtue of the liquid being orders of magnitude more viscous than bulk water. We provide a physical mechanism for this viscosity enhancement in Chapter 8, by showing in molecular dynamics simulations that the viscosity of water scales with the square of an applied electric field.

Going forward, there are a number of important issues in the field of surface and bulk nanobubbles that are worth investigating.

9.2 STABILITY OF NANOBUBBLES

The theoretical investigation in Chapter 2 provides support for the stability theory developed by Lohse and Zhang [24] from thermodynamic first principles. However, a comparison with experiment proves problematic. Experiments show the nanobubbles are sustained by oversaturations that are far larger than expected [54]. Indeed, the remaining theoretical question is why substantial oversaturations can survive for days when the diffusive timescale of a typical system is only in the order of $\tau \sim \ell^2/D \sim 10$ hours.

One possible explanation is that a hydrophobic attraction at the substrate [20, 133] acts against the diffusion and sustains the localised oversaturation near the substrate at a sufficiently high value. This idea deserves further investigation, and to do so, one could extend the results of Lohse and Zhang [24] to model what happens to ζ and the equilibrium contact angle of a nanobubble when the hydrophobic potential at the substrate is taken into consideration.

9.3 MEASURING PINNING FORCES

The investigations in Chapter 5 and Chapter 6 using optical microscopy provide some useful starting points in the investigation of how the substrate plays a role in facilitating the stability of surface nanobubbles.

Even though AFM is blind and slow, it still has an important role to play in future studies about substrate pinning. While TIRFM is an elegant imaging technique that caters for dynamic visualisation, the fluorescent dyes themselves may have some unknown influence on the pinning strength. And perhaps the key limitation of TIRFM is that it can only be used for transparent, thin and optically-compatible substrates, ruling out a wide variety of potential substrates. Ultimately, it is still desirable to develop a method to measure pinning forces using purely mechanical means, such as with laterally-sensitive modes of AFM.

Further studies in this area could include a systematic experimental measurement of pinning forces as the substrate is modified with chemical or physical heterogeneities. Numerical calculations [82] suggest that physical and chemical heterogeneities should increase substrate pinning. While it is not straightforward to pattern a substrate with physical heterogeneities (*via* etching, for example), it is relatively easy to change the wettability of substrates via chemical treatment such as silanisation.

9.4 DO BULK NANOBUBBLES EXIST?

Arguably the biggest controversy in the field of nanobubbles concerns the existence of bulk nanobubbles. Certainly, it is known that these gaseous bodies can be stabilised by coating them with particles; this is the basis of ultrasound contrast agents. It is the claim that pure gaseous bodies exist in the nanoscale that is controversial. Theoretically, bulk nanobubbles should not be stable, since their Laplace pressures $P \sim 1/R$ diverge catastrophically as they shrink in radius.

An alarming development in the field is that a substantial body of research in the literature has taken the existence of bulk nanobubbles for a fact [134–136], without having first verified its gaseous nature. Bulk nanobubbles are usually studied with dynamic light scattering. When light from a laser interacts with small particles in liquid, it scatters in various directions and fluctuates in time. The intensity autocorrelation function is able to discriminate between larger and smaller particles, and thus recover a size distribution of particles suspended in the liquid, provided that they are smaller than ~ 100 – 200 nm.

Unfortunately, dynamic light scattering cannot reliably distinguish between solid dirt particles and gaseous bodies. This limitation makes it all the more crucial to carefully design control experiments that can overcome this unfortunate limitation. In one of the few works to devise control experiments, Häbich *et al.* [137] found that the nanoscale bodies in their experiments fail a number of simple tests for a gaseous nature. One important finding was that the distribution of particle sizes hardly changed upon degassing. Perhaps most significantly, when the authors purified the liquids by double distillation, they found a sharply reduced scattering intensity, strongly hinting that the ~ 100 nm objects that take for granted to be gaseous nanobubbles could be dirt or contamination originating from the liquids themselves. This example shows the clear importance of designing control experiments in situations where gaseous bubbles cannot be distinguished from contamination.

Going forward, there are two exciting tracks of research that can be considered. Experimentally, the existence of gaseous bulk nanobub-

bles may be definitively resolved if a control experiment can be designed that tests the particles unambiguously for their gaseous nature. Since light scattering measurements are dynamic, a change in pressure in the liquid chamber would lead to an immediate and visible shift in the size distribution of compressible objects observed in experiments, thus providing indisputable evidence for the existence of bulk nanobubbles.

Theoretically, it would be important to explore any mechanisms that can facilitate the stability of bulk nanobubbles. Currently, there is little doubt that a single isolated bulk nanobubble will dissolve rapidly into bulk liquid. However, diffusive shielding in a cloud of bulk nanobubbles [114] may help sustain them. How densely populated must such a cloud be to sustain bulk nanobubbles for several hours (as was recently claimed by [136])?

Part I
APPENDICES

CALCULATION OF PHASE IMAGES IN PEAK FORCE MODE

In the proprietary peak force mode in AFM systems made by Bruker, the phase image is not returned directly as a raw signal, but in in-phase and quadrature components. The signal driving the peak force modulation is $V = V_0 \sin \omega t$, where V_0 is the raw vibrational amplitude in volts. A lock-in amplifier convolves these signals into an in-phase component $X = V_0 \sin \omega t \sin(\omega t + \phi) = \frac{V_0}{2} [\cos \phi - \cos(2\omega t + \phi)]$, and a quadrature component in which the signal is shifted by $\pi/2$ radians, namely $Y = \frac{V_0}{2} [\sin \phi - \sin(2\omega t + \phi)]$. To eliminate the time dependence, the feedback system applies a low pass filter, giving the raw outputs

$$V_i = \frac{V_0}{2} \cos \phi, \quad (\text{inphase}) \quad (\text{A.1})$$

$$V_q = \frac{V_0}{2} \sin \phi. \quad (\text{quadrature}) \quad (\text{A.2})$$

The phase image can then be calculated from a point-by-point calculation of $\phi = \arctan(V_q/V_i)$, in units of radians.

B

THE THERMODYNAMICS OF SURFACE
NANOBUBBLES

B.1 THE GIBBS-DUHEM EQUATION

The Gibbs free energy G can be expressed in two equivalent ways:

$$G = \mu N \quad (\text{B.1})$$

and

$$G = U - TS + PV, \quad (\text{B.2})$$

where U is the potential energy, T is temperature, S is entropy, P is pressure and V is volume. Taking the differential form and equating these expressions gives

$$\mu dN + Nd\mu = dU - TdS - SdT + PdV + VdP. \quad (\text{B.3})$$

The combined first and second law of thermodynamics is

$$dU = TdS - PdV + \mu dN \quad (\text{B.4})$$

Combining Equations B.3 and B.4 and taking constant temperature condition gives the Gibbs-Duhem equation

$$Nd\mu = VdP. \quad (\text{B.5})$$

Clearly, the exact form of the chemical potential depends on the equation of state VdP . In an incompressible liquid, we obtain a equation of the form

$$\mu_L^i = \mu_L^{i,0} + (V/N)(P_L - P_{\text{ref}}), \quad (\text{B.6})$$

while in the gas phase, the ideal gas relation $V/N \equiv k_B T/P$, leading to a chemical potential with the general form

$$\mu_G^i = \mu_G^{i,0} + k_B T \ln \left(\frac{P_G}{P_{\text{ref}}} \right). \quad (\text{B.7})$$

B.2 THE YOUNG-LAPLACE EQUATION

In Equation 2.7 we infer the Young-Laplace equation for the mechanical equilibrium of a nanobubble from the differential change in entropy,

$$dS_{\text{tot}} = \dots + \left(\frac{P_G}{T_G} - \frac{P_L}{T_L} \right) dV_G - \frac{\gamma}{T_{LG}} dA. \quad (\text{B.8})$$

In the case that the nanobubble is a sphere of radius r , the surface area $A = 4\pi r^2$ and the volume is $V = 4\pi r^3/3$, and thus

$$dA = \frac{2}{r}dV_G. \quad (\text{B.9})$$

In this way the dV_G term becomes zero when $P_G = P_L + 2\gamma/r$. We now generalise the Young-Laplace equation for a spherical cap nanobubble. The volume and surface area of a spherical cap nanobubble can be expressed as a function of its footprint radius L and contact angle θ

$$V_G = \pi L^3 \frac{\sin \theta (2 + \cos \theta)}{3(1 + \cos \theta)^2} \quad (\text{B.10})$$

$$A = \frac{2\pi L^2}{1 + \cos \theta}. \quad (\text{B.11})$$

Then we have

$$\frac{dA}{dV_G} = \frac{dA}{d\theta} \frac{d\theta}{dV_G} \quad (\text{B.12})$$

$$= \frac{2\pi L^2 \sin \theta}{(1 + \cos \theta)^2} \frac{(1 + \cos \theta)^2}{\pi L^3}. \quad (\text{B.13})$$

Note that with the spherical cap relation $L = R \sin \theta$ we can simplify this to

$$dA = \frac{2}{R}dV_G. \quad (\text{B.14})$$

In other words, the radius in the Young-Laplace equation, Equation 2.10, is simply the radius of curvature of the bubble.

C

ESTIMATE OF THE TRANSITION TIMESCALE TIMESCALE

Figure C.1: Estimation of the transition timescale by matching the time required for the bubble's footprint radius (captured in experiment) to reach 90% of its final value, to the time required for the oversaturation to reach 90% of its final value.

The time-dependent oversaturation $\zeta(t)$ used in the model, Equation 5.9, uses the transition timescale τ as an input parameter. We would therefore like to match the onset of the oversaturation's approach to its final value ζ_{end} with the nanobubble's approach to its final radius when it is pinned.

To do this we obtain a suitable reference value from experimental values of the nanobubble's radius, see Figure C.1. When $t = 200$ s,

the footprint radius L in the experiment is $1.69 \mu\text{m}$, or about 0.9 of the distance, $\Delta L = 3.3 - 1.5 = 1.8 \mu\text{m}$, between the maximum and minimum radii of the nanobubble. The reason for choosing the factor $k = 0.9$, rather than (for instance) $k = 0.99$, is to ensure that the reference distance $(1 - k)\Delta L$ is larger than the error in the footprint radius L calculated from the image processing (refer to Figure C.1).

We now construct a value of τ for Eq. 9, which ensures that at $t = 200$ the oversaturation is 90% of its value at pinned equilibrium, $0.9\zeta_{\text{end}}$. Since $\lim_{x \rightarrow \infty} \tanh((t - \tau)/\tau) = 1$ we seek a solution for which $\tanh((200 - \tau)/\tau) = 0.9$ for $t = 200$. This is equivalent to finding the root of the equation

$$y(\tau) = \tanh \frac{200 - \tau}{\tau} - 0.9, \quad (\text{C.1})$$

from which we find a transition timescale $\tau \approx 80 \text{ s}$.

D

ON THE STABILITY OF A CATENOID

D.1 ESTIMATION OF THE BUBBLE'S SURFACE ENERGY

Figure D.1: Estimation of the bubble's surface energy. From experimental measurements of the footprint (marked in red), we recover the radius of curvature and perform a surface of revolution integration about the bubble's axis of symmetry x .

The optical images recovered from TIREM give the footprint of the object. To recover the surface area S of the object and thus its surface energy $E = \gamma S$, we divide the thresholded image into slices (see Figure D.1) and recover the radius of curvature R of a slice with footprint radius ℓ using $\ell = R \sin \theta$, where we have assumed $\theta \approx 30^\circ$ from experimental AFM measurements. With this estimated radius of curvature we perform a surface of revolution integral about the x axis $S = 2\theta \int R \sqrt{1 + (R')^2} dx$, where the prime denotes a derivative in the x direction, and the conventional 2π is replaced with 2θ to ensure that only the truncated portion (outlined in red, Figure D.1) is calculated.

D.2 DERIVATION OF THE STABILITY EQUATION

In this section, we derive the stability condition for a catenoid formed by a soft interface between two coaxial rings of unequal radii, displayed as Equation 6.3 in the main text. The stability condition was

originally provided for soap films by Salkin *et al.* [93], although a detailed derivation was not provided.

As explained in the main text, the general solution of the minimum energy surface is the catenary $r(x) = a \cosh(x/a + c)$, where a and c are constants to be determined by the boundary conditions. In the case of the bubble pulling (Figure 6.5), the boundary condition at the bubble's tip is

$$r(0) = a \cosh c = L_{\text{tip}}, \quad (\text{D.1})$$

while the base satisfies

$$r(h) = a \cosh\left(\frac{h}{a} + c\right) = L_{\text{base}}. \quad (\text{D.2})$$

Using the identity $\cosh(A + B) = \cosh A \cosh B + \sinh A \sinh B$ yields from Equation D.2

$$\cosh(h/a) \cosh c + \sinh(h/a) \sinh c = L_{\text{base}}/a. \quad (\text{D.3})$$

Using the identity $\sinh^2 x = \cosh^2 x - 1$, we have

$$\cosh(h/a) \cosh c \pm \sinh(h/a) \sqrt{\cosh^2 c - 1} = L_{\text{base}}/a. \quad (\text{D.4})$$

We now make a few substitutions. First, from the boundary condition (Equation 6.2), we let $\cosh c = X = L_{\text{tip}}/a$, $w = h/2L_{\text{tip}}$ (see note¹), and $\alpha = L_{\text{base}}/L_{\text{tip}}$ (see note²). Hence,

$$L_{\text{base}}/a = \alpha X, \quad (\text{D.5})$$

$$h/a = wX. \quad (\text{D.6})$$

Then Equation D.4 now reads

$$X \cosh(wX) \pm \sinh(wX) \sqrt{X^2 - 1} = \alpha X. \quad (\text{D.7})$$

Rearranging and taking the square on both sides gives

$$X^2(\cosh^2(wX) - 2\alpha \cosh(wX) + \alpha^2) = \sinh^2(wX)(X^2 - 1). \quad (\text{D.8})$$

Finally, using the identity $\cosh^2 x - \sinh^2 x = 1$ gives us the non-linear equation

$$f(X, w, \alpha) = \sinh^2(wX) - X^2(1 - 2\alpha \cosh(wX) + \alpha^2) = 0. \quad (\text{D.9})$$

Equation D.9 describes the stability condition of a minimal energy surface formed between two coaxial rings of unequal radius. The physical meaning is that a stable catenary with the physical parameters (X, w, α) will have roots in Equation D.9.

¹ In the notation of the original problem, $w = h/R_{\text{tip}}$, but R_{tip} is not directly accessible by experiment. However, since $\theta \approx \pi/6$ and $R_{\text{tip}} = L/\sin \theta$ then we have $w \approx h/2L_{\text{tip}}$.

² In the notation of the original problem, $\alpha = R_{\text{base}}/R_{\text{tip}}$. Since the footprint radius L is related to the radius of curvature by $R = L \sin \theta$ and no significant hysteresis is expected to occur in the y -axis of Figure D.1, we then have $R_{\text{base}}/R_{\text{tip}} = L_{\text{base}}/L_{\text{tip}}$.

D.3 STABILITY THRESHOLD FOR A CATENOID

Figure D.2: Stability threshold for a catenoid. (a) Numerical solutions of the stability condition (Equation D.9) for varying values of $w = h/L_{\text{tip}}$ and fixed $\alpha = 1$. For small values of w two roots of Equation D.9 exist. At the maximum extension $w_{\max} = h_{\max}/L_{\text{tip}}$, there is just one root and beyond $w_{\max}$ there are no roots, indicating that the catenoid is no longer stable. (b) A plot of the first and second roots of Equation D.9 for $\alpha = 1$.

We now detail how to compute the theoretical curve (black line, Figure 6.3) for the stability threshold of a catenoid between coaxial rings of different radii. We start from Equation D.9. Note that a (which is embedded in X) is not known in general, but performing a parameter sweep of (X, w, α) eliminates the need to evaluate a . We proceed by solving the non-linear Equation D.9 as a function of (w, X) for various values of $1 < \alpha < 5$.

Plots of Equation D.9 for varying values of $1 < w = h/L_{\text{tip}} < 1.4$ and constant $\alpha = 1$ are shown in Figure D.2(a). It is clear that for a small extension h , there are two roots to Equation D.9 (we ignore the trivial root at $X = 0$), but converges to a single root at $w_{\max} \approx 1.33$. Therefore, as shown in Figure D.2(b), for an interface between coaxial rings of equal radii ($\alpha = 1$), the maximum distance that the rings can be separated is given by $w_{\max} \approx 1.33$. This is a well-known result which can be derived in a more specific manner [92]. The theoretical curve in Figure 6.3 of the main text is then obtained by repeating the above-mentioned calculation iteratively for $1 < \alpha < 5$.

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PUBLICATIONS

- ¹T. S. B. Quang, F. Y. Leong, H. An, B. H. Tan, and C.-D. Ohl, "Growth and wetting of water droplet condensed between micron-sized particles and substrate," *Sci. Rep.* **6**, 30989 (2016).
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DECLARATION

For the work in this thesis I, Beng Hau Tan (BHT) have worked with Hongjie An (HA), Meera Kanakamma Mohan (MK), Zahava Barkay (ZB), Trung Dung Luong (TDL), Haibin Su (HS), N. Duane Loh (NDL), and Claus-Dieter Ohl (CDO). Some parts of this thesis are reproduced or adapted from pre-prints, manuscript drafts, or publications listed in the *Publications* page. Unless otherwise stated below, all work presented in this thesis is my own.

Chapter 2 – BHT developed the theory. The project was supervised by HS and CDO. The project was initiated by discussions with Haibin Su and written notes by Derek Y.C. Chan.

Chapter 3 – BHT and HA performed AFM characterisation and analysed data. The project was supervised by CDO. The manuscript for this work was written by HA and BHT.

Chapter 4 – BHT performed simultaneous AFM-TIRFM imaging. HA performed AFM microscopy. BHT and HA analysed data. The project was supervised by CDO. The manuscript for this work was written by BHT.

Chapter 5 – BHT performed simultaneous AFM-TIRFM imaging. HA performed AFM microscopy. BHT and HA analysed data. The project was supervised by CDO. The manuscript for this work was written by BHT and HA.

Chapter 6 – MKM performed TEM imaging. ZB performed SEM imaging. BHT and MKM analysed data. The project was supervised by UM and CDO. The manuscript for this work was written by BHT.

Chapter 7 – BHT performed molecular dynamics simulations. BHT, NDL and TDL developed analysis software. BHT, NDL, TDL, HA and CDO analysed data. The project was supervised by NDL and CDO. The manuscript for this work was written by BHT and NDL.

Singapore, January 2017