

A Deliberation on Nanobubbles at Surfaces and in Bulk

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Surface and bulk nanobubbles are two types of nanoscopic gaseous domain that have recently been discovered in interfacial physics. Both are expected to be unstable to dissolution because of the high internal pressure driving diffusion and the surface tension which squeezes the gas out, but there is a rapidly growing body of experimental evidence that demonstrates both bubble types to be stable. However, the two types of bubbles also differ in many respects: surface nanobubble stability is most probably assisted by the nearby wall, which can

repel the water (in the case of hydrophobicity), accept physisorbed gas molecules, and reduce the surface area through which outfluxing can occur; bulk nanobubbles, on the other hand, must stabilise themselves. This is perhaps through ionic shielding, perhaps through diffusive shielding, or perhaps through both. Herein, the features of both bubble types are described individually, their common and disparate features are discussed, and emerging applications are examined.

1. Introduction

The scientific world has welcomed three new types of immersed gaseous domain in recent years, each leading to new fundamental ideas as well as bringing expectation for applications. In brief, these are surface nanobubbles (nanoscopic spherical cap bubbles found at the solid/liquid interface),^[1–13] micropancakes (quasi-two-dimensional gaseous domains at the solid/liquid interface),^[14–18] and bulk nanobubbles (nanoscopic spherical bubbles in dense suspension in bulk liquids)^[19,20] (see Figure 1).

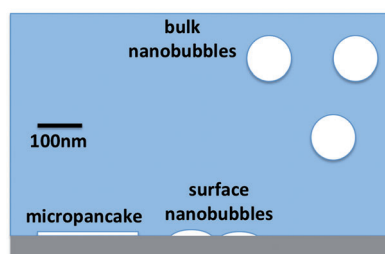


Figure 1. The three types of nanoscopic gaseous domain recently observed in the literature. Micropancakes are found at the solid/liquid interface, with typical widths of several hundred nanometres to micrometres, but only 1–2 nm in height. Surface nanobubbles are also found at the solid/liquid interface and have typical radii of curvature of 100–1000 nm, with heights and widths of 5–20 and 50–100 nm, respectively. Bulk nanobubbles are found in bulk solutions, with typical radii of curvature of 50–100 nm.

The reason for the intrigue with all three types of gaseous domain is their observed longevity.^[20–24] Of the three, the surface nanobubble field is the strongest. The micropancake field is growing, but the actual structural form of these gaseous domains is currently unknown. Bulk nanobubbles are an upcoming field, with the most obvious question other than their stability being whether they are related to surface nanobubbles in namesake alone, or whether the link is stronger.

Our aim here is to give a brief overview of both types of nanobubble, focussing on their possible stabilising mechanisms and potential applications. We shall begin with surface nanobubbles, which have been discussed in detail in recent reviews.^[11,12,25] We shall then proceed by describing bulk nanobubbles before drawing comparison between the two and looking ahead to the future. To avoid confusion between surface and bulk nanobubbles, we shall use “surface” when discussing points specific to surface nanobubbles and “bulk” when describing specific points of bulk nanobubbles. If we drop the prefix, this means we are making a statement about nanobubbles in general.

We omit micropancakes in the following discussion. The link between them and surface nanobubbles is not yet fully established and too many unknowns exist to give a coherent story. Needless to say, mere knowledge of their existence is sufficient to follow the proceeding text.

2. Surface Nanobubbles

Surface nanobubbles are nanoscopic gaseous domains found at the solid/liquid interface. They are spherical cap-shaped bubbles, typically a few tens of nanometres in height, h , and

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a few hundred nanometres in width, a . This means that their typical radii of curvature, R , are $(a^2 + h^2)/2h \approx 100 \text{ nm} - 1 \mu\text{m}$, and their internal (Laplace) pressures, assuming the surface tension of pure water, are $p = p_0 + 2\gamma/R \approx 2 - 10 \text{ atm}$, where p_0 and γ are the ambient pressure and surface tension, respectively.^[6,26] Thus, they should dissolve on a timescale of $\tau \approx 1 - 10 \mu\text{s}$. However, surface nanobubbles are found to exist for at least 10–11 orders of magnitude longer than this classical prediction,^[21] so can be considered stable.

The existence of surface nanobubbles was first hypothesised by Parker, Claesson, and Attard^[1] in 1994, as a possible explanation for the long-range hydrophobic attraction. However, it was a further 7 years before surface nanobubbles were found experimentally, initially by Ishida et al.^[27] and Lou et al.,^[2] both using atomic force microscopy (AFM).

Despite the rapidly growing knowledge on surface nanobubbles, the acceptance of them as “nanoscopic gaseous bubbles” did not arrive until the spectroscopic measurements of Zhang, Khan, and Ducker in 2007, who showed that surface nanobubbles were indeed composed of gas^[21] (shown in that work as the presence of rotational fine structure from carbon dioxide-saturated water), rather than being simply bulk contamination.^[28] The work of Zhang, Khan, and Ducker^[21] really set surface nanobubbles in stone as being gas-filled bubbles.

AFM has proven to be an essential tool for investigating surface nanobubbles.^[2-4,9,18,29,30] However, the necessity for experimental techniques other than AFM is clear: in AFM, a nanoscopic spherical-cap probe is rapidly (10^4 Hz) tapped against the substrate. Every time the probe leaves the substrate the liquid pressure between the two solids diverges such that dissolved gases can accumulate at that position.^[31] Thus, it was previously thought that surface nanobubbles may have been seen with AFM because of the technique used. However, the number of experimental techniques has since been extended to include the quartz crystal microbalance (QCM),^[32,33] surface plasmon resonance (SPR)^[21] and rapid cryo-fixation,^[34] with the non-intrusive techniques of spectroscopy and QCM showing conclusively that surface nanobubbles occur naturally.

Not only do surface nanobubbles have unusually extended lifetimes, they also exhibit several other peculiar phenomena; for example, the (gas-side) contact angle, θ , made between the liquid/gas interface and the solid/gas interface is always of the order $10 - 30^\circ$, regardless of the hydrophob/philicity of the substrate used.^[2-4,6,7,10,26,30,34-41] The contact angle is usually considered to be a material constant, depending (strongly) on the solid, liquid and (weakly on the) gas type.

To confuse matters more, the contact angle is found to strongly depend on the gas type^[41]—this is peculiar inasmuch as the macroscopic contact angle has its strongest dependencies on the solid and liquid types, whilst its weakest dependence is on gas type (one can easily show this by degassing the air above a water meniscus in a glass beaker; the contact angle of the meniscus hardly changes despite the fact that the gas phase is being replaced by a low-density water vapour phase). The solution to the two observations above is that the nanobubbles are actually sat on top of a densely adsorbed

layer of gas molecules, which may provide a useful conduit for gas replenishment.

The unusual values and dependencies of surface nanobubble contact angles leads to an unusual feature: the gas inside a nanobubble must always be of Knudsen type^[25,42-44] (i.e. the gas molecules very rarely collide with each other, rather collisions occur more often with the solid substrate and the liquid/gas interface). This can be readily shown since the Knudsen number (the ratio of the mean free path, λ , to the bubble height) is [Eq. (1)]:

$$Kn = \frac{\lambda}{h} = \frac{kT}{\sqrt{2}\sigma R(p_0 + 2\gamma/R)} \frac{1}{(1 - \cos \theta)} \quad (1)$$

where kT is the thermal energy and σ is the collisional cross section of the gas molecules. In the small bubble limit of $2\gamma/R \gg p_0$, Kn is surprisingly only dependent on the contact angle, surface tension, and collisional cross section, as [Eq. (2)]:

$$Kn \approx \frac{kT}{2\sqrt{2}\sigma\gamma} \frac{1}{(1 - \cos \theta)} \quad (2)$$

It is easy to show that Knudsen behaviour, defined here as $Kn > 1$, is observed for contact angles of $\theta \leq 30^\circ$ (with a small gas-type dependency), such that all nanobubbles in the literature to date are indeed filled with Knudsen gas (see Figure 2). We shall discuss the implications of this below.

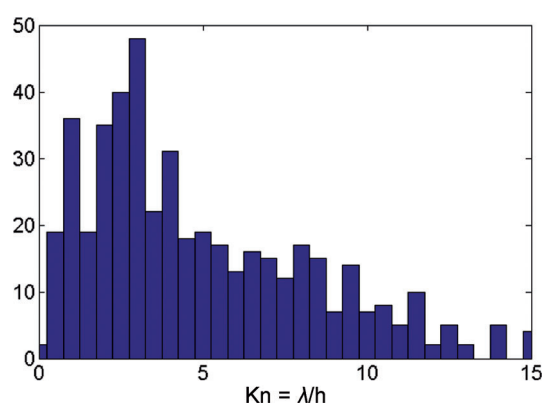


Figure 2. Typical Knudsen numbers for surface nanobubbles in the literature. The internal gas is generally of Knudsen type. The data are for different gas types and different temperatures. Extracted from ref. [41].

2.1. Surface Nanobubble Stability

If the surface tension of water is assumed to be 73 mN m^{-1} the small sizes of surface nanobubbles lead to large internal Laplace pressures. Thus, their expected lifetimes from classical diffusion are $\tau \approx R^2/D \approx 10 \mu\text{s}$, where D is the diffusion constant, that is, much lower than the experimentally observed lifetimes of days.^[21,44] The most important fundamental question is thus “why are surface nanobubbles stable?” Two possible explanations have been put forward. One, by Ducker,^[23] is that a trapped layer of contaminant coats each bubble, which de-

creases the surface tension and provides a barrier to diffusion. The other, by Brenner and Lohse,^[22] is that the gas does indeed escape from part of the interface, but this outflux is exactly balanced by an influx elsewhere on the interface such that surface nanobubbles exist in a dynamic equilibrium (in fact the influx is at the three-phase line and the outflux is through the spherical cap in the model of Brenner and Lohse). On the one hand, both ideas have their merits, whilst on the other hand, they both seem lacking in certain respects. Herein we will describe the pros and cons of both ideas.

2.1.1. Contamination

The concept of stabilisation by contamination is fairly straightforward. If sufficient insoluble contaminants accumulate on the liquid/gas interface of a surface nanobubble, then two effects occur: 1) the surface tension will decrease and 2) a barrier to diffusion will be formed.^[23] One can easily imagine a solid layer, or shell, forming at the liquid/gas interface if sufficient contaminants were available.

As described earlier, the fundamental objection to the longevity of nanobubbles is the expected diffusion that arises from the combination of curvature and high surface tension. If the surface tension were reduced, then the driving force would also be reduced. Adsorption of contaminants to the liquid/gas interface reduces the surface tension and thus diminishes the driving force for dissolution. If contaminants become pinned on the bubble (e.g. insoluble polymers or oils), then as the bubbles shrink in volume through dissolution of their gaseous contents, the surface density of contamination increases at the air/water interface. The increase in the surface density of contamination further decreases the surface tension, which can fall to zero or even become negative. If the surface tension were to fall to zero the pressure difference across the interface, and thus the diffusive driving force for dissolution of the gaseous contents, would also fall to zero. Then, nanobubble dissolution should only take place due to the entropic favourability of mixing, which could take an incredibly long time. The presence of the insoluble film would also act as a diffusion barrier, slowing diffusion that might occur as a result of pressure differences.

The pros of this idea are clear: it explains why nanobubbles are stable, by diminishing both the driving force for diffusion and by providing a barrier to diffusion. However, there are a few cons too. The first argument against the contamination idea is that nanobubbles are found in many different systems with many different techniques and setups. Thus, the idea of “universal” contamination must be questioned, although it is known that even purified water contains sufficient contaminants to alter the hydrodynamic boundary condition of a bubble and extraordinary measures are required to remove this.^[45] Secondly, the effect of a barrier on the diffusion will be diminished by thermal fluctuations, which will create pores in the contaminant shell, thus leading to an overall outflux of gas with time. However, nanobubbles are stable in size, with a preferred radius of curvature.^[6,26] Finally, recent work by Das et al.^[46] showed that both ionic and non-ionic contaminants do

indeed reduce the surface tension, but this is insufficient to prevent diffusive outflux.

2.1.2. Dynamic Equilibrium

Brenner and Lohse’s “dynamic equilibrium” model^[22] exactly replenishes the diffusive outflux through the spherical cap with a gaseous influx at the contact line. The balance is stable, such that oversized surface nanobubbles should shrink whilst under-sized surface nanobubbles should grow. Hence stability is automatic: nanobubbles of any size should approach the equilibrium size. In their model, Brenner and Lohse use the near-wall gas enrichment^[47] as the replenishing gas bank. More gas accumulates at more hydrophobic walls, so hydrophobic substrates should be preferred over hydrophilic substrates for surface nanobubble nucleation.

The pros of this model are that it explains both surface nanobubble stability and the preferred surface nanobubble sizes found in experiments. However, several issues must be raised. Firstly, if an outflux and an influx are both taking place, the outfluxing gas should move back towards the gas bank to prolong the nanobubble lifetime (the gas bank is not infinite). Hence, the gas flow must be in a recirculatory stream that requires energy input to drive (obviously the nanobubbles are not in perpetual motion, since they exist within liquid droplets; droplets evaporate and evaporation generates a lot of energy—the system must eventually reach equilibrium and the recirculation fail). Secondly, the basic forms of both the outflux and influx scale in the same way with radius of curvature of the surface nanobubble ($dN/dt \propto R^0$), which means that no stable point should exist. Brenner and Lohse modify the expression for the contact angle to break the scaling equality in their model, introducing a term similar to line tension. However, the length scale over which this modification should take effect in their report is several orders of magnitude larger than in reality (70 nm as compared to 100 pm^[48]). Thirdly, the concept of “gas enrichment” was taken from a numerical paper^[47] in which the gas flux towards the wall did not have to fight against the diffusive flux away from the wall due to the presence of a surface nanobubble—the effect must be at least weaker in the presence of a surface bubble. Gas enrichment may not be the key—it is also possible that the gas molecules physisorb to the substrate and surface diffuse into the bubble (this is entropically favourable because the gas molecules effectively gain a degree of freedom by doing so; such an adsorbate may in fact be a micropancake^[14–18]). As a final note, the Brenner and Lohse model cannot explain the existence of nanobubbles on hydrophilic substrates, but nanobubbles have been found on every substrate investigated to date, with macroscopic contact angles ranging from 15° (mica) to 108° (hydrophobised silicon).

An addition to the model of Brenner and Lohse was recently proposed by Seddon, Zandvliet, and Lohse.^[42] The authors demonstrated that Knudsen-gas-filled nanobubbles should generate bulk liquid motion (Knudsen gas molecules have a preferred flight direction: macroscopically, the continuity of the shear-stress boundary condition across the liquid/gas inter-

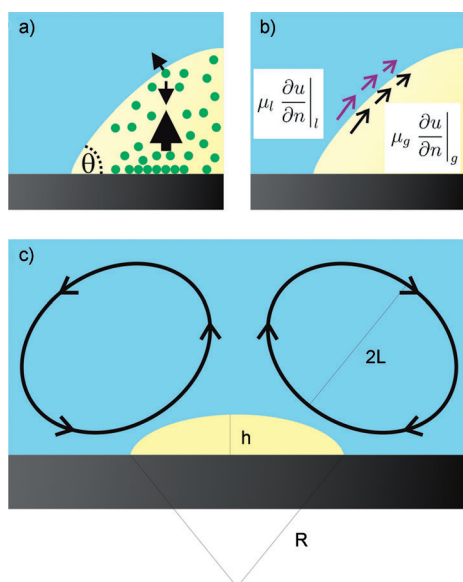


Figure 3. a) The gas inside a surface nanobubble has a preferred direction due to the Knudsen behaviour (the bulk motion arises due to 100% of the molecules moving upwards from the substrate but fewer returning back downwards, because some have dissolved at the liquid/gas interface). b) The continuity of the shear-stress boundary condition means that a bulk gas flow drives a bulk liquid flow. c) This bulk liquid flow must be a circulatory flow due to conservation of mass, which can stream the diffusive outfluxing gas back to the surface nanobubble. Reprinted with permission from American Physical Society (ref. [42]).

face drives the liquid flow (see Figure 3); microscopically, the gas molecules transfer momentum to the liquid molecules at the liquid/gas interface as the gas molecules change direction from vertical (within the surface nanobubble) to radial (within the bulk liquid)). This bulk liquid motion then streams the diffusive outfluxing gas back to the three-phase line for re-entry into the bubble, either through gas enrichment^[47] or adsorption and surface diffusion. This model explains how the diffusive outfluxing gas remains local to the nanobubble, as well as how it is transported back to the three-phase line for re-entry, but it still does not explain where the energy is coming from to drive the flow, nor does it shed light on the re-entry mechanism. But Seddon, Zandvliet, and Lohse^[42] did succeed in measuring nanoscopic force fields in the close vicinity of surface nanobubbles. Of course, measurement of a force does not demonstrate that there is a flux of gas or liquid—an electrostatic double-layer force is expected. However, the magnitudes of the force fields measured by Seddon, Zandvliet, and Lohse^[42] were consistent with that expected for liquid flow (not gaseous diffusion), plus they did not change with the purposeful addition of ionic contaminants. Note that surfactant contaminants, if present, should enhance the flow because the boundary condition then becomes one of “no slip” (the surfactant molecules should be sufficiently mobile at the liquid/gas interface for this to occur). “Hard” contaminants would completely inhibit the flow.

The principal difficulty with this model is that the maintenance of a steady state (with matching flows into and out of

the bubble) requires a source of energy or a reservoir. The small scale of this problem (10–1000 nm) makes reservoirs difficult to maintain against diffusion. Without such a source, the first law of thermodynamics would have been violated.

Net flows of gas molecules only occur down a chemical potential gradient. The flow out of the bubble is driven by a smaller chemical potential outside the bubble than inside the bubble. The flow into the bubble is driven by a smaller chemical potential inside the bubble than outside. The model hypothesises that there are regions outside the bubble where the chemical potential is both greater and lesser than inside the bubble, that is, an out-of-equilibrium situation. Flow between these regions would quickly eliminate such a potential energy gradient. Therefore there must be some means of raising the chemical potential either outside the bubble or inside the bubble, and raising the chemical potential requires an input of energy. The model hypothesises that there is a source of input, but does not specify the exact origin of this input. Possibilities could be the evaporation of the droplet, the AFM apparatus, or some temperature gradient across the setup.

An additional problem with the dynamic equilibrium hypothesis is that it predicts a preferred bubble size, whereas nanobubbles are often observed with very heterogeneous size ranges.^[44]

3. Bulk Nanobubbles

The existence of surface nanobubbles is now firmly established following many different investigations from a number of groups. Far less common are reports of the existence of bulk nanobubbles. One could posit that this is because they are less stable in the bulk or that appropriate techniques for their investigation have not yet been developed. In principle, a nanobubble in the bulk should be less stable than one of the same volume at an interface. The bulk nanobubble has a larger gas/liquid interface to allow diffusion of gas out of the bubble. Also, the curvature of the surface bubble is greater, thus leading to a greater pressure differential across the interface for a bulk bubble of the same volume. Nonetheless, several groups have presented evidence for their existence.

The most startling evidence for bulk nanobubbles is the recent work by Ohgaki et al., who report small nitrogen, methane and argon bulk nanobubbles of radius ≈ 50 nm that are stable for up to 2 weeks.^[20] The bulk nanobubbles, which were produced by mechanical means that led to extreme supersaturation, were imaged from freeze-fracture replicas by scanning electron microscopy (SEM) and were produced in such large quantities that the bulk density of the solution was substantially reduced.

In other work, researchers at the Chinese University of Hong Kong used dynamic light scattering to investigate the existence of bulk nanobubbles.^[49] The slow mode of relaxation was interpreted as arising from bulk nanobubbles and was used to show that, in the presence of organic molecules, bulk nanobubbles are stable. Furthermore, repeated filtering can remove them and subsequent (gentle) sparging with gas can restore them (which suggests that the nucleation centres must

at least remain). Other work has shown that bulk nanobubbles can be used to induce an attractive depletion attraction between surfaces^[50] and that the addition of salt can lead to the aggregation and coalescence of bulk nanobubbles.^[51] However, as yet most reports of bulk nanobubbles have not been independently validated and, as such, have not received wide attention. As these reports are recent we can expect that the issue might be resolved in the next few years. Currently, there are claims that the slow mode of relaxation is due to contaminants associated with the organic species present in solution,^[52] whereas others report results consistent with nanobubbles.^[53]

The literature does contain a report from the 1960s that strongly infers a role for bulk nanobubbles. Nuclear scientists Sette and Wanderlingh^[19] showed in a careful study that the threshold ultrasound power required for the production of bubbles in bulk solution is altered by the influence of cosmic neutrons. Moreover, the influence of neutrons is long lasting. If neutrons in depositing their energy produce bulk nanobubbles that take several hours to decay, then by shielding their apparatus the production of bulk nanobubbles was prevented, thereby raising the cavitation threshold energy required to observe macroscopic bubbles, as seen in Figure 4. They went on

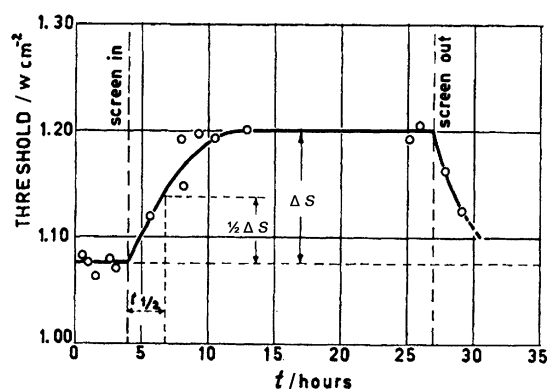


Figure 4. Ultrasound is used to cause cavitation in a bath of water. Here, the ultrasound threshold energy is plotted. Addition of a lead screen around the container ($t \approx 5$ h) led to a $\approx 10\%$ increase in the ultrasound energy required to induce cavitation. Removing the lead screen ($t \approx 27$ h) led to the required ultrasound energy decreasing back. The conclusion is that neutrons, which are prevented from entering the water when the lead screen is in place, act as nuclei for cavitation. Image is reprinted with permission from American Physical Society (ref. [19]).

to show that a neutron source within the lead screen can reduce the cavitation threshold to baseline levels. The implication of this report is that bulk nanobubbles at low concentrations may be constantly created by cosmic radiation and, as such, are ubiquitous, perhaps influencing many phenomena.

Significantly, the existence of bulk nanobubbles may influence our understanding of the stability and formation of surface nanobubbles. One mechanism for the formation of surface nanobubbles is that they form by collision of bulk bubbles with an interface. Some explanations for nanobubble stability

only apply to surface nanobubbles,^[22,42] whereas other explanations can also be applied to bulk nanobubbles^[23] (see Section 2.1). Thus, the existence and manipulation of bulk nanobubbles can be seen as a significant test for different theories of surface nanobubbles and may (or may not) be crucial in resolving the true nature of surface nanobubbles. Whilst acknowledging that the existence of stable, long-lived nanobubbles is not currently widely accepted, for the purpose of this discussion we will assume that they do exist and explore the implications of their existence.

3.1. Bulk Nanobubble Stability

Bulk nanobubbles differ from surface nanobubbles in two important ways. Firstly, the curvature of surface nanobubbles is low for their size due to the very high contact angles that they make with the substrate (see Section 2), whereas the size of bulk nanobubbles is directly reflected in the curvature. That is, for a given volume, a bulk nanobubble will have a much smaller radius of curvature.^[12] As such, bulk nanobubbles will have higher internal (Laplace) pressures than surface nanobubbles of the same volume. As for surface nanobubbles, the high internal pressures favour nanobubble dissolution. Secondly, bulk nanobubbles are mobile, whereas surface nanobubbles are largely immobile. Thus, bulk nanobubbles have the opportunity to collide with the walls of the container, or with each other, and thereby coalesce or rise and break at the air/water interface, all of which results in instability. Thus, the mobility of bulk nanobubbles also requires stability against coalescence with other bubbles or interfaces. How then might bulk nanobubbles be stable?

A simple explanation is that the presence of adsorbed material at the air/water interface can reduce^[49] or oppose^[23] the surface tension and thereby reduce or remove the driving force to dissolution. This material may also protect against collisions with the walls, other nanobubbles, and the free interface. This mechanism could act to stabilise small concentrations of bulk nanobubbles; however, the concentration of such species is unlikely to be sufficient to explain the stability of the large numbers of bulk nanobubbles reported by Ohgaki et al.,^[20] as the huge surface area of the bulk nanobubbles would rapidly deplete the concentration of surface-active species. Nevertheless, experiments that claim to demonstrate the existence of nanobubbles must also show that the “bubbles” are actually gaseous, and not just contaminants.

Bulk nanobubbles could be kinetically stable due to the combined action of a number of factors, all of which are necessary to confer kinetic stability:

1. Firstly, since nanobubbles are small, the buoyancy force on bulk nanobubbles is also small. Consequently, bulk nanobubbles will rise very slowly to the free surface. A bubble of radius 100 nm will have a rise velocity due to buoyancy of $\approx 20\text{--}30\text{ nm s}^{-1}$, depending on the boundary condition.^[54] One can thus expect that convective flows will dominate.

- Secondly, repulsive hydrodynamic and electrostatic double-layer forces will act to stabilise nanobubbles. That is, coalescence between nanobubbles and interactions between both nanobubbles and the container walls and nanobubbles and the free surface will be opposed by both electrostatic and hydrodynamic repulsive forces. Electrostatic double-layer repulsion arises as the air/water interface is negatively charged,^[55] whilst hydrodynamic repulsion arises from the Brownian velocity of the bulk nanobubbles. Electrolytes are found to inhibit bubble coalescence. That is, the coalescence process is slowed down but not prevented. This has recently been shown to be a purely dynamic effect and therefore may only be relevant to nanobubbles in that it may prevent coalescence during a rapid collision. It should not stabilise nanobubbles against coalescence when the collision time is large.
- A degree of metastability can be achieved when bubbles form from a supersaturated solution. This may occur if large numbers of bulk nanobubbles are produced. In this case, the dissolution of the smallest bulk nanobubbles will lead to the solution becoming supersaturated with respect to atmospheric pressure, to the extent that larger bulk nanobubbles are in equilibrium until diffusion of gas from solution decreases the pressure below the equilibrium pressure for the larger bubbles.

Supporting the above is recent work (in the current Special Issue) using molecular dynamics simulations which shows that individual nanobubbles populating large clusters are stabilised by the presence of the surrounding bulk nanobubbles, since this prevents diffusive outflux of the gaseous molecules.^[56] When the concentration of bulk nanobubbles is reduced (by increasing their separation distance) they are no longer stable (see Figure 5). Thus, it may be that bulk nanobubble solutions can only exist with such large number densities. Weijs et al. demonstrate that bulk nanobubbles are stable if the ratio of their interspace, L , to their radii is sufficiently small.^[56] In the

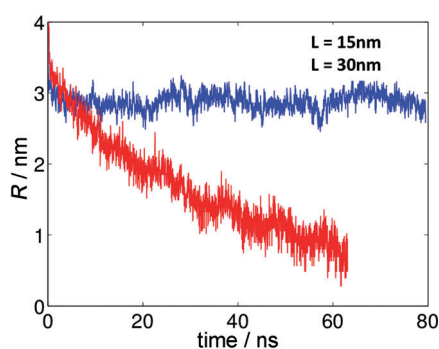


Figure 5. Molecular dynamics simulations of periodic arrays of quasi-two-dimensional Lennard–Jones bulk nanobubbles. In both cases the starting condition was a pre-formed nanobubble in bulk liquid, with periodic boundary conditions. The control parameter was the box size: for bulk nanobubbles with radii of ≈ 3 nm, a $5R$ interspacing leads to stabilisation of the array. However, doubling the box size to $10R$ and, thus, doubling the nanobubble interspacing, leads to destabilisation of the array. The blue line is for the $L = 15$ nm simulation, the red line is for the $L = 30$ nm simulation. Image is reprinted with permission from Wiley-VCH (ref. [56]).

work of Ohgaki et al.,^[20] $L/R \approx 7$, which is right on the edge of the stable region found by Weijs et al. (this is yet another difference with surface nanobubbles, where supersaturation is not required^[18]).

4. Relationship between Bulk and Surface Nanobubbles

Now that we have outlined the two different types of nanobubble, the obvious question is whether the two are related other than in namesake alone. Clearly the stabilising mechanisms cannot be exactly the same: surface nanobubbles benefit from their broken symmetry provided by the wall.^[42] However, a more generic relationship would be if bulk nanobubbles contained Knudsen gas, so we begin here with the same simple mean-free-path calculation that we used for surface nanobubbles, but this time for bulk nanobubbles. In this case, there is no nanobubble “height”, so the requirement for Knudsen behaviour is dependent on the radius of curvature, that is [Eq. (3)]:

$$Kn = \frac{\lambda}{R} = \frac{kT}{\sqrt{2}\sigma R(p_0 + 2\gamma/R)} \quad (3)$$

In the small bubble limit of $p_0 R \ll 2\gamma$ [Eq. (4)]:

$$Kn \approx \frac{kT}{2\sqrt{2}\sigma\gamma} \quad (4)$$

which is independent of R . For a typical gas (N_2) in pure water at ambient temperature, $Kn = 0.04$ and the gas is not of Knudsen type. In fact, rewriting the collisional cross section as πd^2 , where d is the molecular diameter, only mythical gases with kinetic diameters smaller than 0.8 \AA would possess Knudsen gas (the smallest molecular diameter of gases is helium, with $d \approx 1.0 \text{ \AA}$). From this analysis, it is clear that bulk nanobubbles are never “Knudsen” bubbles, whereas surface nanobubbles always are.

This does not end the current discussion, however, since we must now address whether or not bulk and surface nanobubbles can be converted from one type to the other. If a good coverage of surface nanobubbles was required on a substrate, it would be useful if simply flowing a bulk nanobubble suspension over the surface gave this result. Similarly, it would be equally useful to be able to create bulk nanobubble suspensions from rapid surface nanobubble nucleation and subsequent wall detachment. (Note that the latter of these is less likely to occur if the hydrodynamic shielding argument of Weijs et al.^[56] is confirmed—we envisage that insufficient nanobubbles would be detached on a small enough timescale to create a sufficiently closely packed bulk nanobubble suspension for stabilisation, unless the liquid channel was itself nanoscopic.)

Neither transition has yet been demonstrated, but the transition from bulk to surface nanobubbles could be initially tested using a simple flow-through experiment. Similarly, capacitance measurements of the liquid in a nanochannel during the elec-

trolytic generation of surface nanobubbles would give a first test of the transition from surface to bulk nanobubbles. In both cases the topographical transition would only be inferred, either from the detection of excess surface nanobubbles a posteriori in the former example, or from increased capacitance in the latter. However, full evidence of both transitions could be better demonstrated with the forceful wall attachment and detachment of nanobubbles using, for example, laser tweezers.^[57,58] The technique becomes rapidly complex: nanobubbles are smaller than the diffraction limit of the tweezers, so clever surface design is required to overcome this.^[59,60] Detaching a surface nanobubble and measuring its lifetime as a function of bulk nanobubble number density would clearly give invaluable information on the stability of the transition; so too would driving a bulk nanobubble onto a wall.

The issue of transition seems more readily achievable using molecular dynamics simulations. Attachment and detachment can be investigated through the application of body forces to an existing nanobubble. Again, attachment and detachment should be investigated as a function of nanobubble/gas molecule number density.

5. Possible Applications of Nanobubbles

If one was interested in possible applications of nanobubbles, the cause of their stability would not be too important, only the mere fact that they were indeed stable. Thus, we now proceed to highlight a few areas where nanobubbles may or have already found practical use.

Nanoscale cleaning is incredibly important in, for example, the semiconductor processing industry. It is already widely accepted that surface nanobubbles can remove proteins that are adsorbed on substrates.^[61–64] Surface nanobubbles are thus useful cleaning agents that do not suffer from being chemically hazardous or risk damaging the surfaces.^[32,65]

Controlling slip in microfluidics is another possible application of surface nanobubbles that has received a lot of attention.^[66,67] The no-slip boundary condition governs the flow rate in microfluidic devices but, if the walls are not wetted, that is, if a nanoscopic gaseous layer exists in between the solid and liquid, the no-slip boundary condition breaks down locally at the surface of the bubble, and thus the resistance to flow is reduced in these regions. In particular, electro-osmotic flows can be amplified by wall slippage.^[68] The surface nanobubble field is rapidly gaining very good control of nucleation densities and sizes, so the ability to grow/manipulate a channel with a high coverage of nanobubbles is not far away.

Bulk nanobubbles are newer than surface nanobubbles, so it is perhaps surprising that they are already receiving attention in applications. Oxygen-filled bulk nanobubbles (either air or pure oxygen) can be used to enhance oxygen concentrations in wastewater treatment and thereby promote aerobic processes, such as in the treatment of algal blooms.^[69]

Froth flotation^[70] and depletion flocculation^[50] are two other areas where bulk nanobubbles can be used. Selective flotation and enhanced particle capture has already been demonstrated, whilst the potential to induce an attraction between hydrophil-

ic surfaces has wide industrial applications including, for example, dewatering sludges. This currently requires large concentrations of polymers and this makes it expensive. If bulk nanobubbles could be used to replace the polymer, there is not only the potential for saving money but also the process may be enhanced as bulk nanobubbles do not pose an environmental hazard and do not have to be removed or recovered from the supernatant.

A myriad of other possibilities exist. Nanobubbles could be used to nucleate larger bubbles or seed crystal growth, also perhaps to template nanoparticles (which has already been demonstrated for surface nanobubbles). As the gas within nanobubbles is under significant pressure its reactivity is increased.^[71] Thus, nanobubbles could be employed as nanoreactors, whereby reaction kinetics are enhanced without the need for expensive catalysts. For example, hydrogen and oxygen nanobubbles could be employed as reactants within a fuel cell to produce energy and water without the need for expensive and heavy catalytic systems.

The evidence that nanobubbles may be created by high-energy neutrons from cosmic radiation^[19] and that they are stable for days or weeks^[20] suggests that they may in fact be ubiquitous at low concentrations and present in vivo. The questions are thus, do they have any effect at these very low concentrations and what effect might they have if present at much higher levels? There are reports that nanobubbles have a biological impact,^[72,73] though the mechanism of action at this stage is not clear.

As nanobubbles are hydrophobic entities they will tend to associate with hydrophobic surfaces and attract hydrophobic and partially hydrophobic molecules to their surfaces. For example, most proteins will readily adsorb to the nanobubble surface via hydrophobic groups and this may result in protein denaturation. We expect that the size of the nanobubble will be important, as this will determine the interaction area between a nanobubble and a cell. Smaller nanobubbles (a few nanometres) will see the surface as a mosaic of hydrophobic and hydrophilic regions, whereas the interaction with a larger nanobubble (for example 50 nm) will blur the patchiness of the surface and an average interaction will result.

Nanobubbles may also provide a transport mechanism for gas delivery to a membrane or a cell. Gases are inherently hydrophobic, which will drive them to enter membranes and, in so doing, they will change the curvature of the membrane. This could have local effects on trans-membrane proteins or global effects on the membrane structure. Either effect will significantly alter cell function. Simulations are already beginning to grapple with this challenge.^[74] Furthermore, the nature of the nanobubble gas will be important; for example, nitrogen will be inert compared to oxygen, which may promote or interfere with biological functions.

Another possible use is ultrasound contrast agents without the need for a lipid bilayer. Various technologies are employed to deliver bubbles of appropriate sizes, including encapsulation and phase change. The availability of well-characterised, stable dispersions of bulk nanobubbles would provide for alternative ultrasound contrast agent formulations.

Finally, nanobubbles may be playing a role as nuclei for the growth of larger bubbles responsible for decompression sickness, whether these are produced by cosmic radiation or by muscle action.^[75] Thus, preventive action or treatments that minimise the number of nanobubbles may provide some protection from decompression sickness.

6. Conclusions

We have given an overview of the two fields of surface and bulk nanobubbles. Both types of nanoscopic gas bubble are intriguing and, in the preceding text, we have tried to highlight what makes them so appealing. The fundamental and applied interest both stem from the fact they are stable to bulk dissolution. Fundamentally, this is a key issue, but, for applications, the reason for the stability is irrelevant, they are stable so how can they be used?

The two types of nanobubbles seem to share the fact that they are “nano” and stable, but, beyond this, the links appear more tenuous. A lot more work is needed to determine how one type of nanobubble affects the other, or, indeed, if they can be converted from one type to the other.

Both fields are relatively new, with publications and citations increasing exponentially. We expect the fundamental issues to be answered within the next 5–10 years, but the list of possible applications is tremendous, so the subject will only get stronger.

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