Stability of surface and bulk nanobubbles

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Abstract

The existence of stable nanoscopic gaseous domains in liquids, or nanobubbles, has attracted both scepticism and intrigue, since classical theory predicts that spherical gas bubbles cannot achieve stable equilibrium. Can we prove these gaseous domains exist, and if they do, how do they survive? We critically review contemporary theoretical perspectives of the stability of surface and bulk nanobubbles, and explain how experiments either vindicate or disprove them. We then conclude with a discussion of unanswered questions and propose future directions for the field at large.

1. Introduction

A bubble is a spherical void in a continuum of liquid—a system that occurs everywhere in nature and industry where gases interact with liquids. Bubbles exhibit a bewildering range of behaviours over ten orders of magnitude in space and time, the result of a confluence of multiple effects—capillarity, viscosity, inertia, confinement, geometry and diffusive gas transport among them. While cavitation bubbles predominantly containing vapour lead short ($\sim \mu$s) and violent lives, emitting shockwaves and even light as they evolve [1], bubbles of atmospheric gas attached to the walls of a glass of cold water are long-living. A sufficiently large and untethered bubble, however, will rise through the containing liquid by buoyancy (see Fig. 1(a)) and pop as a fast liquid jet as the liquid-gas interfaces of the bubble and the liquid pool meet [2].

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The last two decades have seen substantial academic and industrial interest in bubbles of nanoscopic dimensions. Such *nanobubbles* are expected to exist in two forms: either attached onto surfaces ('surface nanobubbles') or freely suspended spherical bubbles ('bulk nanobubbles'), see Fig. 1(b). Industrial interest originates from the idea that dynamically stable and small bubbles will avoid the typical demise by buoyancy, allowing them to intervene in applications ranging from water treatment, lake remediation, fabrication of foams, cleaning of fouled surfaces, to the treatment of diseases [3]. The objects known also as 'ultrafine bubbles' are at the centre of a burgeoning industry valued by the Wall Street Journal at US$10 billion in 2020 [4].

Considering the maturity of the industry around nanobubbles, it may come as a surprise that the academic intrigue over nanobubbles is about whether they even exist, and if so, how they manage to survive. A broad corpus of experiments over the last 20 years stands at odds with the widely accepted classical prediction that spherical bubbles are unstable to diffusion under standard conditions. Growing calls to deploy nanobubbles in ambitious but risky frontiers such as human medicine make it necessary to bridge the yawning gap between industrialization and fundamental understanding as quickly as possible.

The aim of this paper is to critically survey recent theoretical developments about surface and bulk nanobubbles. This paper focuses on the historical problem of nanobubbles containing atmospheric gases, and largely neglects emergent systems of nanobubbles that are produced under extreme conditions such as boiling or electrochemistry. Our review discusses stability theories for surface nanobubbles and bulk nanobubbles, and novel recent insights from computational studies, as well as a critical perspective about the advantages and limitations of some of these contemporary viewpoints. We conclude with an outlook of future directions and open problems.

2. Why can't a spherical bubble survive?

The scientific intrigue over nanobubbles originates from the classical expectation that nanobubbles should not survive. Consider a spherical bubble that predominantly contains atmospheric gases (as opposed to a vapour bubble), and which is present in an infinite volume of liquid; we neglect buoyancy at the moment. One of the most celebrated theories in fluid dynamics is that, being a permeable interface, the transport of dissolved gas between the bubble and the surrounding liquid obeys the diffusion equation $c_t = D\nabla^2 c$, where D is the diffusion constant, t is time (the subscript denotes a derivative), ∇^2 is the Laplace operator

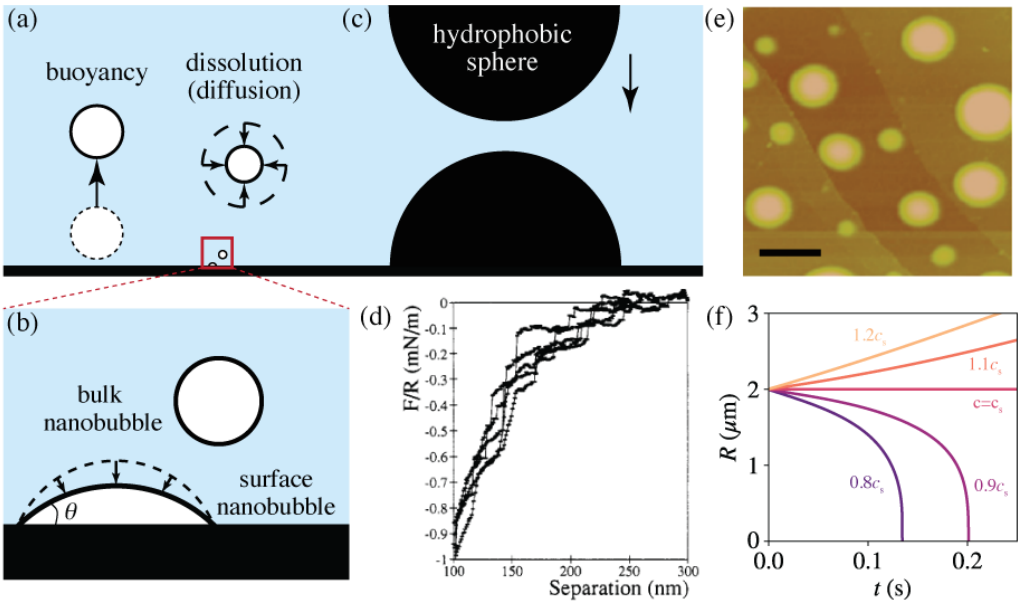

Figure 1: (a) The fates of a bubble: a macroscopic ($\gg \mu$m) bubble will rise up the liquid until it meets the top of the liquid-gas surface, or dissolves by diffusive transport. (b) Schematic representations of a surface and a bulk nanobubble. (c) The 'origin story' of surface nanobubbles. SFA experiments [5] resolve the interaction force between immersed hydrophobic spheres. (d) Parker *et al.* [5] attributed discrete steps in the interaction force between immersed hydrophobic spheres to surface nanobubbles. (e) Image of surface nanobubbles as seen in tapping mode AFM, from Teshima *et al.* [6]. (f) The 'Laplace pressure bubble catastrophe' [3]. The dynamics of bubble radii $R(t)$ as the gas concentration in the liquid is adjusted from below saturation $c < c_s$, to above saturation $c > c_s$. In the former case, a bubble will dissolve into bulk liquid, and in the latter it will grow without bound. The point $c = c_s$ is an unstable equilibrium, and in practical situations, perturbations in solubility (e.g. from temperature variations) will steer the bubble towards one or the other aforementioned outcomes.

and c is the concentration field. Using a well-known exact solution [7], Epstein and Plesset [8] suggested that the dynamic equation of a spherical bubble obeys

$$\frac{dR}{dt} = -\frac{D}{\rho_g}\left(\frac{P_0}{k_H} + \frac{2\gamma}{k_H R} - c_\infty\right)\left(\frac{1}{R} + \frac{1}{\sqrt{\pi D t}}\right), \tag{1}$$

where ρ_g is the density of gas and γ is the surface tension. The conversion between c and R is facilitated by Henry's law, which states that the dissolved gas concentration in the liquid phase adjacent to the bubble is proportional to the internal pressure P in the gas phase of the bubble.

One consequence of the Epstein-Plesset equation is that all spherical gas bub-

bles are diffusively *unstable* in practical situations. We can prove this by directly solving Eq. (1) across a range of dissolved gas concentrations c_∞, with respect to its saturation concentration $c_s = (2\gamma/R + P_0)/k_H$, where k_H is the Henry constant, see Fig. 1(f). In an undersaturated liquid $c_\infty < c_s$, the bubble shrinks until it dissolves completely; this process is accelerative since the Laplace pressure $P_0 + 2\gamma/R$ driving the shrinkage diverges as R decreases. In oversaturated liquid $c > c_s$, reciprocal arguments apply, but in practice the main cause for demise is that the bubble rises out of the liquid once work done on it by buoyancy $\sim \rho R^4 g$ exceeds the thermal energy $\sim k_B T$. (Balancing these terms yields $R \approx \sqrt[4]{k_B T/\rho g} \sim 1$ μm.) This leaves the final possibility, $c_\infty = c_s$. Although a first glance of Eq. (1) suggests the bubble stabilizes here, explicit solution reveals that the point is an unstable equilibrium. Any transient gradients of temperature and solubility would therefore nudge the bubble into either unbounded growth or dissolution. We should also note that these theoretical predictions are upheld by experimental validation, down to the resolution limits of the experimental techniques used. A long distance microscope can resolve bubble sizes as small as $R \approx 5$ μm [9], while careful resistive pulse experiments by Berge [10] probe bubble radii as small as $R \approx 1.5$ μm.

3. Surface nanobubbles

The story of surface nanobubbles has its roots not in fluid dynamics, but in the development of a liquid-medium surface force apparatus (SFA) by Jacob Israelachvili, which heralded a generation of study in fundamental interactions between liquid-immersed surfaces (see Fig. 1(c) and Ref. [11]). SFA measurements predict the existence of a 'short-ranged hydrophobic interaction' with a range of about a nanometer, which is found to be attractive or repulsive depending on the choice of spheres and the intervening liquid. In 1994, Parker, Claesson and Attard [5] reported a 'long-ranged interaction' at the $\sim$ 100 nm length scale. Unlike the interaction curve at the $\sim$ 1 nm range, which varies continuously, the long-ranged interaction was unexpectedly discrete, presenting random (but not quantized) jumps (see Fig. 1(d)). Parker, Claesson and Attard attributed the jumps to gaseous 'nanobubbles'. A new field of soft matter was born.

The postulated existence of surface nanobubbles immediately invited scepticism on both experimental and theoretical grounds. Experimental objections centred around the inability to reproduce the findings by Parker, Claesson and Attard [5]; some neutron scattering experiments did not reproduce their key assumption that bubbles are entrained on water immersed hydrophobic surfaces [12, 13].

The theoretical objections centred around the categorical prediction by Epstein and Plesset that spherical bubbles should dissolve within $\sim 1\ \mu$s of nucleation.

Theoretical objections notwithstanding, experiments—particularly tapping mode atomic force microscopy [14, 15, 16, 17, 6], see Fig. 1(e)—over the last two decades have confirmed the presence of stable, flat, spherically capped surface nanobubbles on liquid-immersed surfaces (often, but not always hydrophobic) with heights $h \sim 10-100\,$nm and footprint radii $L \sim 100-1000\,$nm. The experimental objections were addressed by the eventual realization that surface nanobubbles do not always spontaneously nucleate on immersed surfaces, but specific nucleation techniques (which compel nucleation by increasing local gas oversaturation) will quite reproducibly produce nanobubbles on demand. The field has also had to overcome a widespread issue with contamination, which we discuss in detail in a companion paper.

In short, experiments reveal that surface nanobubbles possess the following properties:

1. Surface nanobubbles survive for as long as researchers have bothered to wait, which in this case is about four weeks.
2. Their contact angles are small as measured from the gas phase, regardless of the combination of liquid or substrate, and typically range from 5-20°. Curiously, the angles are unrelated to the Young contact angle measured at the macroscale.
3. They are stable in some types of liquids, notably water, but then dissolve when immersed in some organic solvents, such as ethanol [18, 19].
4. In water, surface nanobubbles are often found on hydrophobic surfaces such as silanized silicon wafer, but also on hydrophilic substrates such as highly ordered pyrolytic graphite (HOPG), or even glass.
5. Upon a change to the dissolved gas concentration c_∞ in the liquid, the bubbles grow or shrink into a new height over several hours [15].
6. When dissolved gas is removed from the liquid, surface nanobubbles shrink but remain stable [14, 15]. Surface nanobubbles survive the removal of as much as 80% of the dissolved gas in the bulk liquid [20]. This is remarkable because the Epstein-Plesset theory predicts that spherical gas bubbles dissolve immediately once the dissolved gas concentration falls below exact saturation.

In the rest of this section we outline the major theoretical milestones in arriving at a theory of stability for surface nanobubbles that is capable of explaining all of these major properties.

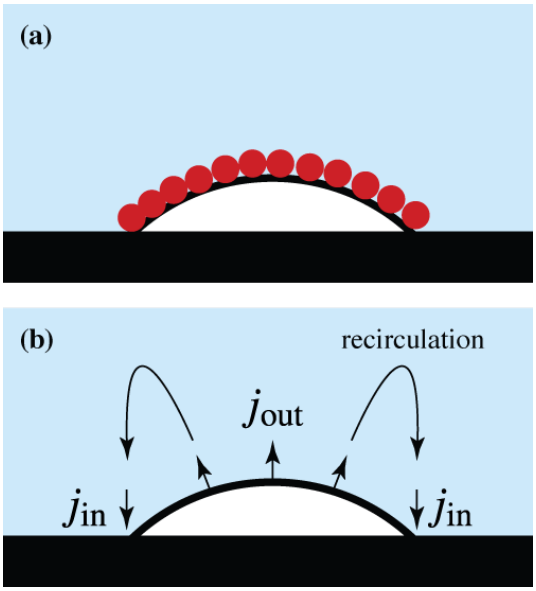

Figure 2: (a) The contaminant barrier hypothesis supposes that surface nanobubbles are coated in a layer of organic contamination that renders them entirely impermeable to gas. (b) The dynamic equilibrium model [21] assumes that gas outflux j_{out} is compensated by an influx near the substrate, j_{in}. Continuity implies the existence of a large-scale recirculation flow with typical velocity 1 m/s [22], though experiments subsequently failed to find evidence of such flows [18, 23].

3.1. Local transport: hydrophobicity and dynamic equilibrium

The earliest attempts to rationalize the existence of surface nanobubbles focused on transport of gas in the immediate vicinity of the bubble. One potentially trivial explanation for stability is that the bubble is simply impermeable to gas, such as by a covering of contamination [24], see Fig. 2(a). However, experiments disproved this hypothesis by showing that surface nanobubbles do respond to environmental changes in dissolved gas concentration (**Property 5**) and are therefore gas permeable [14, 25].

A second major avenue was inspired by the finding in early experiments that nanobubbles nucleate on hydrophobic surfaces. Such hydrophobic surfaces attract gas in preference to water, with the consequence that the dissolved gas concentration within about 1 nm from the substrate, where short-ranged attraction is dominant, should be higher than in the bulk liquid, where the attraction diminishes [26]. Brenner and Lohse [21] argued that this reservoir of gas enrichment should contribute an influx of gas at the nanobubble's three phase line that should exactly cancel out gas outflux from the bubble, which was assumed constant over

the bubble (see Fig. 2(b)). However, what was known as the *dynamic equilibrium* model suffered from the conceptual difficulty that a convective current would be required to connect the outflux to the influx. Such an convection would not only require an external source of energy but even implies that a nanobubble should emit a strong liquid jet with a velocity of 1 m/s [22]. In any case, the dynamic equilibrium model fell out of favour after experiments from separate groups found that tracer particles seeded in the vicinity of surface nanobubbles exhibit dynamics indistinguishable from Brownian motion [18, 23].

3.2. Global transport: the traffic jam model

Instead of contending with gas transport local to a surface nanobubble, Weijs and Lohse [27] instead consider the much broader problem of gas transport *throughout* the entire liquid that hosts the surface nanobubbles. They consider a semi-infinite, one dimensional system with a surface nanobubble at one side and the top of a liquid pool on the other, see Fig. 3(a). Since the nanobubble's internal pressure is $P_0 + 2\gamma/R$ and unconditionally larger than the saturation concentration of the liquid, it serves as a source of gas oversaturation, losing its excess dissolved gas to the ambient environment over time. Consequently the Weijs-Lohse model explains for the first time the remarkably slow dynamic response of surface nanobubbles to environmental stimuli (**Property 5**): the liquid's thickness ℓ establishes its diffusion timescale $\tau \sim \ell^2/D$, extending to 10 hours when $\ell \sim 1$ cm. However, it incorrectly predicts surface nanobubbles would shrink gradually until they dissolve. Instead, experiments show that on a change of the liquid's dissolved gas concentration, surface nanobubbles reach a new equilibrium height after several hours (**Properties 1 and 5**). The model also conspicuously neglects the influence of either the liquid or the substrate (**Properties 3 and 4**).

3.3. Contact line pinning and oversaturation

In parallel to the aforementioned early ideas on local and global transport, lattice density functional theory calculations by Liu and Zhang [28, 29, 30] identified two other potential sources of stability. Experiments show that surface nanobubbles observe *contact line pinning*, maintaining a constant footprint even as they grow or shrink in height. The Liu-Zhang simulations showed that a line-pinned (imposed by either chemical or physical defects) surface nanobubble in a liquid that is oversaturated with dissolved gas achieves thermodynamic metastability.

An elegant mechanistic insight for the unexpected stability was subsequently supplied by Lohse and Zhang [31] and by Chan, Arora and Ohl [32]. Both approaches start from the realization that the unstable equilibrium experienced by a

shrinking spherical bubble is ultimately driven by its geometry. They reparameterise the dynamic equation in the Epstein-Plesset model from a spherical bubble of radius R to that of a line-pinned *spherical capped* surface nanobubble through elementary geometric identities. These theories implement contact line pinning by setting the footprint radius L constant, leading to a dynamical equation either as a function of height $h(t)$ or contact angle $\theta(t)$. With the reparameterisation, surface nanobubbles achieve stable equilibrium when [31]

$$\zeta = \frac{2\gamma}{LP_0} \sin\theta_e. \tag{2}$$

Without contact line pinning, a spherical cap bubble would be able to grow or shrink proportionally, and in that case would also experience the same unstable equilibrium experienced by freely suspended spherical bubbles.

The pinning-oversaturation model takes a key step in overcoming the conceptual difficulty in understanding why bubbles should not immediately dissolve (see Section 2). However, it also raises fresh conceptual difficulties of its own. First, it was quickly pointed out [33] that Eq. (2) requires $\zeta > 0$ for a non-zero contact angle, meaning that the pinning-oversaturation model cannot explain how surface nanobubbles can exist at ambient conditions ($\zeta = 0$, see **Property 1**), or when the liquid is degassed ($\zeta < 0$, see **Property 6**). Second, the model implies that the bulk liquid cannot be in thermodynamic equilibrium, since it is required to hold dissolved gas beyond saturation. Third, the model does not natively explain how stability is affected by the liquid and substrate (**Properties 3 and 4**).

3.4. Tying loose ends together: the TAO model

The three aforementioned models—dynamic equilibrium, traffic jam and pinning-oversaturation—pursue very different perspectives of stability and are thus not mutually exclusive. A pair of papers by Tan, An and Ohl [34, 35] argue that these ideas—when suitably modified—can be unified within a single framework.

The key issue with the pinning-oversaturation model was that the indefinite stability of a surface nanobubble is contingent on the presence of permanent gas oversaturation in the bulk liquid; this assumption is unrealistic because at thermodynamic equilibrium the bulk liquid must be exactly saturated (i.e. $\zeta = 0$). However, the framework of Brenner and Lohse [21] offers a solution to this conundrum: the solid substrate is not an inert boundary but attracts dissolved gas locally. Crucially, this local gas enrichment persists at thermodynamic equilibrium and constitutes the source of *permanent* oversaturation that was sought after

in the pinning-oversaturation model. By generalising the Lohse-Zhang condition [Eq. (2)], Tan, An and Ohl [35] yield the revised stability condition

$$\int_0^h \left(\frac{2\gamma}{LP_0} \sin\theta_e - \zeta(z) \right) dz = 0, \tag{3}$$

whose root yields the equilibrium contact angle θ_e under the influence of the potential ϕ. The TAO model maintains the stable equilibrium that is predicted by the pinning-oversaturation model. It is especially noteworthy that the geometry of the surface nanobubble enforces the equilibrium. A disproportionate portion of a spherical cap's surface area is concentrated at its footprint, and even more so as the bubble flattens (i.e. its contact angle decreases). Therefore, as a pinned surface nanobubble shrinks, an increasing proportion of its overall surface area falls within the gas enrichment zone, nudging the system towards a state that is already known to reach stable equilibrium (see section 3.3). Gas influx occurs at parts of the bubble within the interaction distance of the potential λ and outflux occurs at heights beyond it (see Fig. 3(b)). Transport is entirely local to the liquid-gas interface, dispensing with the need for the long-ranged recirculating flows that were required in the dynamic equilibrium model.

At this point, the dynamic response of surface nanobubbles of $\sim \mu$s remains orders of magnitude lower than the true experimental timescale (hours). To resolve this remaining shortcoming [35], TAO couple these effects—which are local to the surface nanobubble, see Fig. 3(b)—to the broader problem of global transport of dissolved gas through the liquid to the outside world (Fig. 3(a)) as first tackled by Weijs and Lohse [27]. Due to a disparity of length (nm vs. m) and time (μs vs. min) scales of the global and local problems, TAO argue that the nanobubble's contact angle can be assumed to respond instantaneously to environmental changes in gas concentration in the global problem. Thus, as they envisage it, surface nanobubbles gradually adjust to a stable equilibrium angle that is jointly determined by both the macroscopic environment (through c_∞) and the microscopic affinity ϕ between the gas and the substrate (Fig. 3(c)).

The downside of the TAO model, however, is that the effective gas-substrate potential ϕ must be known. Their calculations assume an *ad hoc* dependence with a typical attractive strength $\sim k_B T$, and an interaction distance ~ 1 nm. With these assumptions, most of the key experimental properties are explainable: surface nanobubbles reach a stable equilibrium (**Property 1**) at small contact angles (**Property 2**); respond to changes in dynamic stimuli slowly; (**Property 5**), and survive even when the liquid is strongly degassed (**Property 6**).

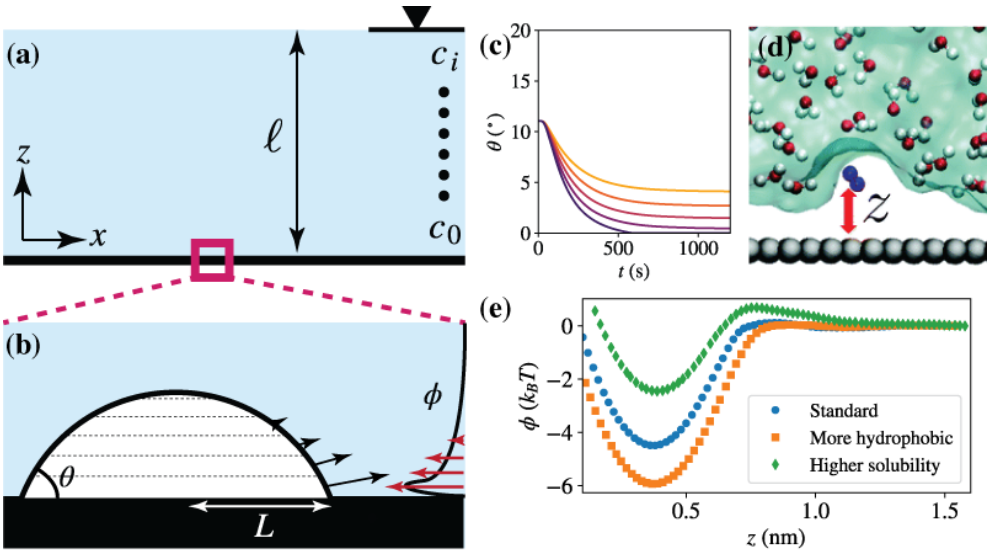

Figure 3: The interplay of liquid, gas and solid interactions affects the stability of surface nanobubbles. (a-b) The TAO model [34, 35] connects global transport effects (Ref. [27] and Fig. 2(b)) with a local gas enrichment facilitated by an effective attraction. (c) Gas enrichment implies that surface nanobubbles can survive degassing of the liquid. The curves from top to bottom (which use an ad hoc potential [35]) show a system in which 0%, 25%, 50%, 75% and 100% of the dissolved gas in the bulk liquid is removed; the nanobubble here survives 75% degassing. (d-e) The potential of mean force $\phi(z)$ between a nitrogen molecule and a water-immersed graphene substrate. The interaction for standard values is highly attractive ($-4.5k_BT$, blue circles). On a more hydrophobic surface (weaker liquid-gas interaction), the effective gas-solid attraction is stronger (orange squares). In contrast, the attraction is significantly weakened in a liquid of $5\times$ the gas solubility of water (by defining stronger liquid gas interaction; green diamonds).

3.5. The potential of mean force

Despite its successes, the TAO model is not by itself a complete framework for the stability of surface nanobubbles. It does not—directly at least—address at least two remaining key properties: how stability is affected by the identities of the liquid and the substrate (**Properties 3 and 4**). Rather, it reframes the question "what stabilizes a surface nanobubble?" into "what is the effective potential between the gas and the substrate?"

The *potential of mean force* (PMF) between the nitrogen and the liquid-immersed substrate convolves a multitude of disparate intrinsic mutual interactions between the gas molecule and the liquid-immersed substrate mediated by the molecular structure of the liquid (Fig. 3(d)). Although it can neither be experimentally nor theoretically derived, the PMF can be calculated by rare event sampling molecu-

lar dynamics, as shown by Tortora *et al.* [36]. Their calculations, see Fig. 3(e), indicate that the PMF is attractive ($\sim k_B T$) over 1 nm, consistent with the assumptions of Tan, An and Ohl [34]. When the calculated $\phi(z)$ is used in the TAO model, one recovers equilibrium contact angles in the range of 5-20°, in strikingly good agreement with experiments [37, 17], though we urge caution in making direct comparisons between experiments and MD simulations (see Section 3.6).

By varying the balance of interactions between gas, solid and liquid, the PMF calculations of Tortora *et al.* [36] provide a singularly unique perspective about how macroscopically accessible quantities like wettability and gas solubility influence the stability of surface nanobubbles. To simulate a more hydrophobic surface, they use a weaker liquid-solid interaction, which leads to a deepened attraction (orange squares, Fig. 3(e)); note that the enhanced interaction arises without modifying the interaction with the dissolved gas. In contrast, a liquid with approximately 5× the gas solubility of water, implemented by increasing the liquid-gas interaction, diminishes the attraction considerably (green diamonds, Fig. 3(e)). The reason why we describe these findings as "unique" is that they show how the liquid plays a decisive role in determining stability, even though *all* the models discussed so far conspicuously regard the liquid as a purely inert medium. These calculations therefore offer straightforward explanations for observation that surface nanobubbles can exist on both hydrophilic and hydrophobic surfaces (**Property 4**), and for their instability in organic solvents, such as ethanol (**Property 3**). These insights, along with the properties explained by the TAO model, lead to the simultaneous explanation of all six of the major experimental properties of surface nanobubbles.

3.6. Novel perspectives: adsorption effects

In parallel, several novel perspectives have also emerged in recent years. One emerging class of models suggest that strong adsorption of gas molecules to the substrate. It should be noted that adsorption effects do not necessarily contradict the ideas presented in previous sections, but their presence can lead to interesting or counterintuitive effects.

Petsev, Leal and Shell [38] argue that some portion of the gas molecules inside the nanobubble are chemisorbed to the surface, and with fewer 'free' gas molecules in the gas phase, a surface nanobubble would have a lower internal pressure and adopt a flatter shape (**Property 2**). However, the authors make the assumption that materials used in surface nanobubble experiments such as HOPG have comparable adsorption constants to metal organic frameworks and other materials specially functionalized for gas capture. Given that the adsorption constant

is exponentially dependent on adsorption enthalpy [39], these calculations may significantly overestimate the effect of adsorption on the bubble shape. Maheshwari *et al.* [40] have also suggested that gas molecules from one surface nanobubble are strongly attracted (or physisorbed) to the planar substrate, translating along it along a 'gas tunnel', before reaching a neighbouring nanobubble. If the interaction parameters do correspond to a physically occurring system, these 'gas tunnels' may allow surface nanobubbles a novel path to Ostwald ripen or coalesce, effects that are theoretically forbidden by contact line pinning [41].

One of the most radical theoretical ideas about surface nanobubbles is the claim that surface nanobubbles are not gaseous at all, but are quasi-liquid condensates with a density comparable to liquid nitrogen, even at room temperature and pressure [42]. If they exist, ultradense condensates would be of monumental importance to society, since the transportation and handling of dilute gases is the single biggest technological bottleneck to the widespread adoption of clean hydrogen technologies. It should be pointed out that claims of ultradense bubbles in MD simulations have a history stretching up to 15 years [43, 44, 45], but has come into renewed focus recently due to experiments that claim *quantitative* agreement with the MD simulations [42, 46]. However, the mechanistic details of the quasi-liquid condensate hypothesis need to be carefully resolved. One can understand that gas might be present at higher densities within the 1 nm interaction distance of the PMF (see Fig. 3(e)), but this leaves open the question of what is holding gas molecules to the tune of $200\times$ the density of an ideal gas beyond the interaction distance, where the gas-substrate PMF is zero.

These examples reflect the hazards of drawing literal inspiration from molecular dynamics simulations. It is frequently overlooked that MD studies currently do not simulate realistically gas-solvated liquids. Nitrogen dissolves in liquid at a mole fraction of 10^{-5} [47], implying that a bubble containing just 10-100 gas molecules would require system sizes of $10^6 - 10^7$ molecules, out of the reach of most computational research groups today. Consequently, *all* MD studies that we are aware of suffer from the common flaw of using unrealistically high mole fractions of $10^{-3} - 10^{-2}$, that is, hundreds to thousands of times beyond their true saturation concentration. In our view, the ultrahigh densities reported across more than a decade's worth of MD simulations [43, 45, 48, 42] may well be an artifact of the extreme oversaturations unique to MD. Moreover, MD studies typically deploy periodic boundary conditions that prevent the excess oversaturation from exiting the computational domain. Thus, gas molecules in an MD system exist in an frustrated metastable state in which gas molecules are left with no other recourse but to accumulate at high density within the nanobubble.

3.7. Novel perspectives: is contact line pinning necessary for stability?

A recent fluorescence microscopy study by Bull *et al.* [49] suggests that surface nanobubbles can survive without contact line pinning, invalidating the theoretical foundations established by the pinning-oversaturation model (see Section 3.3). By repeatedly cycling ethanol and water over a substrate, they observe that surface nanobubbles nucleate on the same locations on glass, but on a copolymer brush, the nucleation sites are not reproducible. Unlike the glass, the authors suggest that the polymer brush continuously reconfigures as it absorbs solvent, smoothing out physical defects that they presume contribute to contact line pinning. However, reconfiguration of the mobile tails of the copolymer brush also means that the chemical heterogeneity landscape of the surface will also dynamically change; thus the irreproducible nucleation on copolymer brushes has a potentially trivial explanation unrelated to line pinning. Further, the authors appear to have the fundamental misconception that only physical defects contribute to contact line pinning, leading them to neglect at least two other sources of contact line pinning in their experiments. Contact lines can be immobilized on atomically flat surfaces if the surface contains chemical heterogeneities [50, 51], or if the substrate is sufficiently soft, in which case pinning is triggered [52, 53] through an out-of-plane elastocapillary force [54]. Follow up claims that surface nanobubbles are stable without contact line pinning should therefore control for at least three sources of contact line pinning: physical heterogeneity, chemical heterogeneity and softness.

4. Bulk nanobubbles

Much like surface nanobubbles, the story of bulk nanobubbles started as a theoretical construct, tracing back to approximately the middle of the last century. Theoretical considerations predict that pure water needs to be stretched by a tensile stress in the order of a thousand atmospheres before the onset of cavitation. However, experiments *universally* find that bubbles spontaneously form in water at vastly smaller tensile stresses, even when special effort is taken to ensure the purity of the water. The most persistently presented explanation for the dramatic reduction of tensile stress of water is that the liquid contains compressible pockets of *cavitation nuclei* [55], which would respond more readily to stress variations than the pristine liquid. Such nuclei can be entrained in crevices in vessels bearing liquid, present on flat immersed surfaces (i.e. surface nanobubbles), or suspended in the bulk liquid (bulk nanobubbles).

The difficulty, however, is in experimental validation of this theoretical construct. There are a wide variety of techniques to characterise surface nanobubbles that are fixed onto surfaces, and perhaps more importantly, experimental techniques that corroborate that the objects are gaseous. In the case of bulk nanobubbles there is no shortage of methods that claim to be able to produce them; unfortunately there is no experimental technique that is able to authoritatively prove that the objects produced are actually gaseous.

Bulk nanobubbles are predominantly characterized by dynamic light scattering (DLS). In short, a coherent light source such as a laser is directed into the liquid, creating a speckle as light scatters off suspended objects. One or more photodetectors that are aligned oblique to the illumination axis measure the temporal persistence of the resulting speckle, recovering a histogram of particle sizes. Although it is widely used, DLS cannot distinguish among bubbles, droplets or particles, a fatal limitation in a field that has a long history of irreproducible results and contaminated results. DLS results can drastically change if liquids are redistilled [56] or, even more alarmingly, DLS spectra attributed to nanobubbles can disappear when care is taken to clean experimental vessels [57].

Having prefaced with the caveat that DLS experiments are not definitive, we briefly outline the properties that DLS attribute to bulk nanobubbles:

1. Bulk nanobubbles have an implied radius ~ 100 nm.
2. The implied radii of bulk nanobubbles has a maximum of several hundred nanometers, generally well below the 1 μm limit beyond which buoyancy dominates and the bubble will rise out of the liquid.
3. The implied radii of bulk nanobubbles is responsive to ionic chemical additives; although there is considerable scatter in experiments between individual groups, there is consensus that the bubble radius increases with a decrease in a liquid's Debye length.

In the last few years, the experimental literature has fissured into two camps. One camp unequivocally proclaims to have adduced undisputable evidence for the existence of bulk nanobubbles in pure water [58, 59]. The other is adamant that the experiments clearly rule out that bulk nanobubbles can exist in pure water, and that such objects can likely only exist when armoured with particles or some other coating [60, 61, 62]. The ongoing debate has occasionally taken an ugly turn, with one group describing sceptics of bulk nanobubbles as basing their conclusions on "either questionable experimentation or sheer speculation" [58].

This section will critically discuss the major proposed stability mechanisms for the existence or stability bulk nanobubbles and explain the degree to which

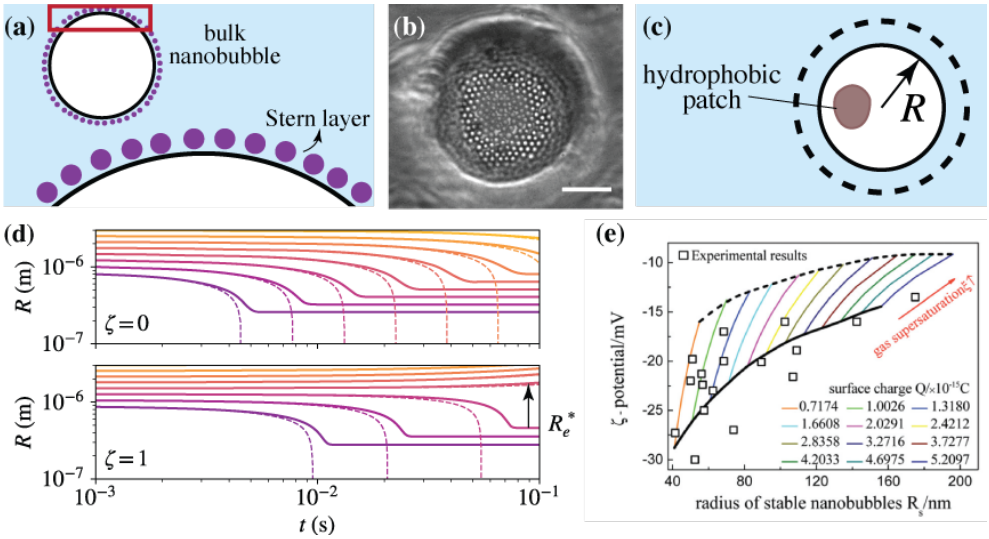

Figure 4: Contemporary perspectives of the stability of bulk nanobubbles. (a) Akulichev's model [63] proposes that, given experimental reports that bubbles are negatively charged, a diffuse electric double layer (here only the Stern layer is shown) assembles at the liquid-gas interface, whose electrostatic stress balances with the bubble's Laplace pressure. (b) A microbubble stabilized by an armour of particles. As the bubble shrinks, the particles jam together more strongly, therefore reinforcing mechanical stability. Scale bar, 30 μm. (c) Yasui's model [64] proposes that a bulk nanobubble is stabilized by a hydrophobic, gas permeable patch that experiences gas influx, balancing exactly with outflux from pristine regions of the bubble. (d-e) The models of Tan-An-Ohl [65] and Zhang-Guo-Zhang [66] extend the Akulichev model consider the gas oversaturation in the liquid; they find that oversaturation establishes a maximum size that a nanobubble can achieve. Moreover, the TAO model predicts that spherical bubbles will follow Epstein-Plesset dynamics before abruptly stabilizing at a few hundred nanometer radius.

recent experiments support or disprove them. In short, our position is that as a matter of physical principle, bulk nanobubbles can exist, but neither camp in the ongoing debate among experimentalists has authoritatively proven or disproven the existence of bulk nanobubbles.

4.1. Akulichev's model: stabilization by surface charges

It has been known since the late 19th century [67, 68] that a bubble in neutral pH liquid carries an electrical charge. When released between electrodes of opposing polarity, the bubble migrates towards the cathode. As far as we are aware, the first to link this property to the possible stability of a spherical bubble was V. Akulichev [63]. All models of bulk nanobubble stabilization by surface charges essentially rely on this single insight, with perhaps the most consistent proponent

of the idea in recent years being the group of Bunkin [69], who refer to these objects as "bubbstons".

In short, the charge stabilization model assumes that the surface charge density σ on the bubble creates an electrostatic pressure $P_e = \sigma^2/2\varepsilon_r\varepsilon_0$, where ε_0 is the permittivity of free space and ε is the relative permittivity of water. Akulichev made the key insight that P_e acts *opposite* to the Laplace pressure $P = P_0 + 2\gamma/R$. The tensile nature of surface tension means that at every point on the curved surface of the bubble, components of force tangential to the surface cancel out everywhere, leaving a component directed towards the bubble's centre. However, P_e acts in the opposite direction: surface charges mutually repel, and by similar symmetry arguments produces a force that acts radially outward—that is, opposite to the Laplace pressure. It is therefore expected that the two contributions cancel when $P(R_e) = P_e(R_e)$, leading to an equilibrium when the bubble's radius is $R = R_e$. This equilibrium can be shown to be a stable one [65, 66], avoiding the conceptual issue that afflicted surface nanobubbles for years.

This formulation invites the question of how to provide a quantitative measure of the charge density. A charged interface should lead to the assembly of dissolved ions in an electric double layer around it, and through the Poisson-Boltzmann equation one obtains, for a bubble of radius R,

$$\sigma(R) = \frac{2\varepsilon_0\varepsilon_r\kappa k_B T}{e} \sinh\left(\frac{e\psi}{2k_B T}\right) f(R). \tag{4}$$

Here, the zeta potential ψ is the electric potential at the distance from the bubble that delineates mobile bulk liquid from immobile liquid at the double layer, and $f(R)$ is a correction term that accounts for the curvature of the double layer, derived by Ohshima, Healy and White [70]. Zeta potential measurements generally find that the potential is negative and is of the order of tens of mV, consistent with a stable radius in the region of 100 nm [66].

One limitation of the classical Akulichev formulation is that it fails to consider the gas oversaturation of the ambient liquid. In the Epstein-Plesset model, gas oversaturation manifests explicitly in Eq. (1) as a perturbation to the mechanical stress balance. Most protocols that purport to produce bulk nanobubbles tend to produce clouds or suspensions of bubbles, typically by intense mechanical aeration of the liquid [3]. Since all bubbles have an internal pressure $P_0 + 2\gamma/R$ exceeding atmospheric pressure P_0, the liquid immediately surrounding them must be gas oversaturated, per Henry's law. Indeed, measurements with commercial dissolved oxygen meters suggest that water processed by commercial 'nanobub-

ble generators' have 400% the dissolved gas concentration of saturated distilled water [71].

The models of Tan, An and Ohl [65] and Zhang, Guo and Zhang [66] account for the contribution of oversaturation to the mechanical stress balance at the bubble's interface, as shown in Figs. 4(d) and (e). When oversaturation is neglected, the mechanical balance of Laplace and electrostatic pressures is *unbounded*, meaning that there is always a unique equilibrium radius R from balancing P_e and P_L. Both papers report that oversaturation establishes an unconditional maximum equilibrium radius for a bubble in the charge stabilization model. This maximum (of a few hundred nanometers) is observed experimentally in DLS experiments, and the considerable variation of this maximum in the experiments may originate from a lack of quantitative control of gas oversaturation in experiments.

4.2. Stabilization by contamination

A second class of stabilization models is that the bubble is armoured by some kind of contamination, such as a particle coating. Unlike other models, there is no controversy whatsoever that this mechanism will work: particle armoured microbubbles are already widely used as ultrasound contrast agents [72, 61]. As a particle-armoured bubble shrinks, the constituent particles coating the interface jam together, exerting a mechanical stress on the interface that acts against Laplace pressure [73]. Since the jamming effect intensifies with the bubble's tendency to shrink, a particle armoured bubble will reach stable equilibrium. K. Yasui has adapted a variation of this idea specifically for bulk nanobubbles [64]. He posits that a gas-permeable hydrophobic contamination barrier may locally attract high concentrations of dissolved gas, allowing for local gas influx, while the regions that are not coated by the contamination experience the usual Epstein-Plesset outflux; the bubble is in dynamic equilibrium when these contributions balance.

However, it is an open question as to whether bulk nanobubbles are truly stabilized by a particle coating. It would be necessary to identify what sources of contamination can be found in abundance in natural systems, and once these sources are identified, to understand how or why such bubbles would universally stabilize at a radius of several hundred nanometers.

4.3. Other perspectives

Let us also discuss some alternative visions for stabilizing bulk nanobubbles. Proponents of the ultradense bubble theory (see section 3.6) have also proposed that if a bulk nanobubble's internal density were several orders of magnitude

larger— i.e. comparable to liquid nitrogen—the bubble's lifetime would increase by a few orders of magnitude to about a few seconds [44]. However, an increased density has no effect on the unstable equilibrium of the Epstein-Plesset equation [Eq. (1)], and so bulk nanobubbles cannot be long-lived, even with an ultrahigh density.

Manning has recently floated the idea that bulk nanobubbles are stabilized by virtue of the Tolman effect [74]. It is known that the surface tension of a liquid-gas interface substantially deviates from its planar value at very high curvatures $1/R$ (or very small radii of curvature R), which to leading order is

$$\gamma(R) = \gamma\left(1 - \frac{2\delta}{R}\right), \tag{5}$$

where δ is the Tolman length. Although Manning correctly argues that the point $R = 2\delta$ is one of stable equilibrium, the overall model has several notable weaknesses. First, he questionably deploys the Tolman length as a fitting parameter. For a 100 nm bulk nanobubble to be stabilized, the model demands that the Tolman length be $\delta \approx 50$ nm, which is three orders of magnitude higher than the consensus estimate (from both experiments [75] and simulations [76, 77]) of ~ 1 Å. Second, stability by the Tolman effect requires that the bubble's liquid-gas surface tension is identically *zero*. There do exist multiphase systems with ultralow (2-3 orders than the usual 10 mN/m) surface tension [78], but the demand for an interface with zero interfacial tension invites the existential question of whether a cluster of solute molecules in a solvent matrix can even be considered a bubble if not delineated by an interface of finite surface energy.

4.4. Do bulk nanobubbles exist?

We end this section by offering our answers to two controversial questions, informed by what we currently understand from these contemporary developments. First, can bulk nanobubbles exist? And second, if they do, which model is the right one?

In an effort to authoritatively prove the existence of bulk nanobubbles, the group of Barigou have performed as many as eleven different types of experiments [58] to complement the DLS measurements. Much as these strenuous efforts are commendable, we are unpersuaded that they individually or collectively constitute "conclusive proof" that bulk nanobubbles exist, because none of the eleven techniques address the fundamental inability of DLS to distinguish bubbles. To make matters worse, the most convincing experimental efforts to directly

probe compressibility of DLS light scatterers have failed to find evidence of compressible objects. The group of Craig [60] subjected water that has been processed through commercial 'nanobubble generators'—i.e. the backbone of the US$10 billion ultrafine bubble industry we alluded to in the *Introduction*—in DLS cuvettes whose liquids are subjected to compressive stresses of up to 10 atm. They find that the large stresses fail to perturb the DLS-measured histogram of particle sizes.

However, we should point out that the compressive stress experiments of Alheshibri and Craig [60] do not disprove the particle armouring or the charge stabilization models. The reason is that both models predict one-sided stability—the stabilization feedback from particle jamming or interfacial charge accelerates when the bubble shrinks, but diminishes when the bubble grows. In other words, the models predict that the size distributions of bulk nanobubbles would fail to respond noticeably to compressive stresses, but would be unstable to the application of large tensile stresses.

In our view, the study that comes the closest to proving the existence of bulk nanobubbles is a recent set of cleverly designed experiments by Jin *et al.* [79]. They optically track the shrinkage of microbubbles (whose origin and gaseous identity is much easier to ascertain than bulk nanobubbles) with darkfield microscopy. The darkfield capability becomes especially important when the objects shrink down to (or below) the optical resolution limit of brightfield imaging, and using it the authors report that the microbubbles shrink according to Epstein-Plesset dynamics before abruptly stabilizing at a few hundred nanometers. Notably, this behaviour is anticipated by the charge stabilization model of Tan, An and Ohl [65] (see Fig. 4(d)). At the equilibrium radius, the objects fluctuate with Brownian motion, indicating that they are freely suspended in the liquid and not attached onto surfaces.

4.5. Which model of bulk nanobubble stability is correct?

While experiments are yet to authoritatively prove the existence of bulk nanobubbles one way or another, there is nevertheless a large body of experimental results from DLS experiments which agree on a few broad points. The charge stabilization model is able to provide reasonable and consistent explanations for the three properties claimed by DLS experiments—i.e. its ~ 100 nm radius, the strict maximum limit for the bubble size, and the increase in implied radius as the ionic concentration is increased.

Although bubbles that are stabilized by contamination barriers indisputably exist in some contexts, it is unlikely that this is the mechanism for the stabiliza-

tion of bulk nanobubbles in all cases. Electron microscopy experiments of water claimed to be infused with nanobubbles show *featureless* voids of several hundred nanometers [80], implying that any contamination that is present has to be smaller than the $\sim 1\,\mathrm{nm}$ spatial resolution of an electron microscope. While the contamination barrier models are mechanistically quite similar to the surface charge models, the contamination barrier models do not offer a quantitative or mechanistic reason why the stable radius at should be several hundred nanometers, and nor do they explain the sensitivity of the DLS-implied bubble radius to Debye length.

Although the charge stabillization appears to be the most complete or promising mechanism for the stability of bulk nanobubbles, experimental validation is a remote possibility. Ultimately, the charge stabilization model relies on an authoritative measurement of the zeta potential of the water-gas interface. This turns out to be a formidable task. Modern zeta potentiometry of nanoscale objects is predominantly based on light scattering, and therefore suffers from the significant issues with reproducibility mentioned earlier. These measurements do, however, consistently claim that objects believed to be bulk nanobubbles have a zeta potential in the region of -10 mV. A much less frequently used technique is optical zeta potentiometry, which enjoys the clear advantage of being able to probe the zeta potential of an individual object, but also the clear disadvantage of not being able to resolve anything below the optical resolution limit (typically a few microns). The measurements of Takahashi *et al.* [81] tantalizingly show that a shrinking $\sim 10\ \mu\mathrm{m}$ microbubble (that can be verified to be of gaseous origin) will *diverge* from the planar zeta potential of -30 mV to about -60 mV before it becomes too small to be optically resolvable. It is not clear which of these perspectives is the correct one, and as a result the models are forced to make a choice. The model of Tan, An and Ohl [65] is developed around the optical zeta potentiometry experiments of Takahashi, Chiba and Li [81], while Zhang, Guo and Zhang [66] develop theirs around measurements around the much broader body of results on light scattering zeta potentiometry.

An even more intractable problem with proving the validity of the charge stabilization model lies with the ambiguity over what these experiments are actually measuring in the first place. Each zeta potentiometry technique estimates zeta potential by interrogating an unknown cross-section of the electric double layer. This ambiguity is not limited to experiments [82]. Whereas experiments at least agree about the sign and order of magnitude of the zeta potential, simulations nearly universally report that the water-air interface is positively charged, and *highly* acidic! Fortunately, the charge stabilization models do not necessarily require the net charge on the interface to be negative—the models work equally well

with a positive net charge—but the question of what the experiments are actually measuring remains frustratingly open.

5. Outlook

Significant strides have been made in the theoretical understanding of both surface and bulk nanobubbles in the last few years, yet there remain a number of interesting open problems worth pursuing.

5.1. Experimental validation of theory

Although the models presented in this paper comprehensively account for the main properties of both surface and bulk nanobubbles, the prospect of a comprehensive experimental validation remains distant. With surface nanobubbles, the path towards full experimental validation of the TAO model will depend on the ability to experimentally resolve the potential between a gas molecule and an immersed substrate. Force microscopy techniques such as SFA or AFM measure the interaction between a probe and the immersed surface, as opposed to the interaction between a single molecule and an immersed surface that is required by the model.

In the case of bulk nanobubbles, we envisage that the surface charge model can be authoritatively proven or disproven by extending the *in situ* pressurization techniques pioneered by Alheshibri and Craig [60] to probe the compressibility of objects subjected to *tensile* stresses, and not just compressive ones. Although the lack of response of objects claimed to be bulk nanobubbles to compressive stresses is theoretically expected, a finding that they are also resilient to tensile stresses would re-open the theoretical debate in this field. The experiments of Jin *et al.* [79] offers the most promising path to proving the existence of bulk nanobubbles, as it allows one to track the shrinkage of microbubbles (whose gaseous origin can be easily and unambiguously ascertained) and ascertain their presence even when they are too small to be distinguished by standard brightfield microscopy.

5.2. Solvent exchange

One of the most intriguing subplots of the surface nanobubble story concerns the matter of producing them. About 20 years ago, it was accidentally discovered by Lou *et al.* [83] that surface nanobubbles nucleate on a surface that is initially wetted with an organic solvent of high gas solubility, before the liquid is replaced

with water, which has a much lower solubility. The phenomenon of *solvent exchange* is remarkably simple and efficacious compared to techniques such as nanodispensing, but the mechanistic principles behind its ability to nucleate nanobubbles are poorly understood. A beautifully designed MD study by Xiao *et al.* [84] that attempts to simulate solvent exchange reveals a remarkable paradox: when a poor solvent of gas dissolves a good one, dissolved gas is advected *towards* the substrate and against its putative concentration gradient! Then, the dissolved gas assembles at large concentrations adjacent to the substrate, triggering nucleation by driving down the nucleation energy barrier [85].

5.3. Molecular dynamics simulations

The inability of MD simulations to simulate realistically gas-saturated liquids (Section 3.6), means that we urge caution when using MD simulations to draw quantitative inferences about how surface nanobubbles behave under experimental conditions. Nevertheless, due to their ability to probe length and time scales inaccessible by experiment, MD studies have and will continue to provide illuminating qualitative insights about nanobubbles and other fluid dynamical or transport processes at the nanoscale. A non-exhaustive list of recent insights include nucleation by solvent exchange [84], pinning and force balance at the contact line [51, 86], and an impressive computational validation of the salient ideas of the pinning-oversaturation model [50].

We expect that MD simulations of realistically gas-saturated liquid will become feasible in future. The most obvious path to feasibility is that further improvements to computational power that allow million-atom simulations to become commonplace, facilitating explicit simulation of 10 ppm liquids. A more technically sophisticated path would lie in the development of coarse graining or hybrid molecular-continuum techniques [87, 88] that would allow systems such as nanobubbles to be investigated with vastly reduced computational resources. Among the complications in simulating weak solutions, however, is the need to handle chemical potential shifts (particularly of the dissolved gas solute) under a coarse-graining operation.

5.4. The thermodynamics of nanobubbles

Given the longevity of nanobubbles and their ability to reach a stable dynamic equilibrium, the tempting conclusion is that nanobubbles are in a state of thermodynamic equilibrium. It has however proven somewhat difficult to establish this authoritatively in a thermodynamic framework. Unfortunately, the typical approach is to take the approximation that atmospheric gases have no contribution

to the system's free energy, and therefore regard a nanobubble as a vapour bubble. An early paper [89] taking this approach was sharply criticised by Seddon and Zandvliet [90] because surface nanobubbles predominantly contain atmospheric gases, which would behave dramatically differently from pure vapour bubbles, but the criticisms equally apply to several other papers as well.

The best attempt to account for the presence of dissolved gas within a thermodynamic theory of surface nanobubbles comes from Zargarzadeh and Elliott [85], which in turn builds on seminal papers by C. A. Ward and colleagues [91]. It is our view that intriguing questions concerning the interplay of thermodynamics and wettability of surface nanobubbles, such as the breakdown of contact angle reciprocity between nanobubbles and nanodroplets [92], will require atmospheric gases to be explicitly treated.

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Appendix A. Highlighted papers

Appendix A.1. Of outstanding interest

- Brenner and Lohse [21]: The first paper to implicate substrate hydrophobicity in the stability of surface nanobubbles.
- Tortora *et al.* [36]: Provides mechanistic explanations for stability or instability of surface nanobubbles on hydrophilic surfaces and organic solvents.
- Tan, An and Ohl [35]: Reconciles three distinct perspectives of surface nanobubbles [21, 27, 31] into a single framework.
- Lohse and Zhang [31]: The first paper to mechanistically explain how surface nanobubbles can achieve stable equilibrium.

Appendix A.2. Of special interest

- Maheshwari *et al.* [50]: Molecular dynamics simulations that numerically and qualitatively confirm the key ideas of the pinning-oversaturation model, such as stability of contact line pinned surface nanobubbles to dissolution.
- Xiao *et al.* [84]: A beautifully designed simulation study qualitatively resolving gas transport processes during solvent exchange.
- Zhang, Guo and Zhang [66]: A theory for stability of bulk nanobubbles building on the Akulichev model of charge stabilization that also takes ambient liquid oversaturation into account.
- Weijs and Lohse [27]: Explained the remarkably slow response of surface nanobubbles to environmental stimuli.
- Zargarzadeh and Elliott [85]: Describes the stability of surface nanobubbles from a thermodynamic perspective; this is one of the few papers of its kind to correctly handle the presence of dissolved gas in the liquid.
- Liu and Zhang [29]: The first to propose that surface nanobubbles can be stabilized by gas oversaturation and contact line pinning.

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