On the thermodynamic stability of bubbles, immiscible droplets, and cavities

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Nanobubbles filled with air or a variety of pure gases are observed to persist in bulk water for weeks and months. Nanoemulsions consisting of oil droplets in water are also remarkably stable against coagulation, with lifetimes up to weeks even if not coated with surfactants. The inverse system of nanodroplets of water in oil is also accessible for study and application. Voids on the nanoscale are formed in simulations of water under strong tension and are stable during the time of the simulation. The stability of these nano-entities is ultimately determined by the molecular-level structure of their interfaces. However, a thermodynamic theory might also be capable of providing some insight. We therefore consider spherical gas nanobubbles, immiscible liquid nanodroplets, and nanocavities formed in water under negative pressure on the same footing, and give a unified thermodynamic analysis of these systems. In all cases, mechanical equilibrium (local free energy maximum or minimum) is expressed by the Laplace equation, and thermodynamic stability (local free energy minimum) follows from the radius dependence of surface tension. All of them would be unstable if their surface tensions were constant. Data from the literature allow construction of numerical examples for cavities and gas nanobubbles. Spectroscopic data are cited in support of an interfacial water structure in gas nanobubbles and water droplets in oil that differ from their flat surface counterparts. The observed longevity of nanobubbles in particular has been thought to violate fundamental principles of diffusion and solubility. A close look at the Laplace equation and its derivation shows why this widespread belief is incorrect.

Introduction

The controlled suspension of small particles in liquids has been the primary focus of colloid science for more than a century, and with technological advances the nanoscale has received increasing emphasis. Nanobubbles in water, filled with air or oxygen for example, have a variety of actual and potential biomedical, water purification, food production, and commercial applications.1–3 Water cavitation under negative pressure is an inherent feature of green plant physiology and function,4 and the nanoscale void spaces formed in simulations of strongly stretched water can provide interesting information about hydrogen-bonded structure in these conditions.5,6 The properties of nanoemulsions consisting of nanoscale oil droplets in water with their applications in food and pharmaceutical products have been extensively reviewed.7 Nanobubbles, emulsions, and cavities are usually studied as separate fields of scientific research, but it is desirable from a fundamental point of view to recognize how they might be related, particularly in regard to their stability. We therefore give in this paper a unified thermodynamic analysis of the three systems. The limitations of a thermodynamic theory are well understood to preclude direct molecular-scale insight into the interfacial structure underlying stability. Nonetheless, our results may be helpful in focusing attention on what these systems may have in common and how they differ.

Suspensions of gas-filled nanobubbles in water and other solvents can be prepared by a variety of techniques and are observed to be stable over long periods of time.1,3,8–12 Although their numbers eventually dwindle, they persist for days, weeks or months, even up to a year. A fundamental experimental study of nitrogen nanobubbles in water prepared under atmospheric conditions was reported by Ohgaki et al.8 The average radius of the bubbles was 50 nm, and their lifetimes were up to two weeks. The measured internal pressure of the nitrogen bubbles was about 60 atm. The Raman peaks of gas-phase nitrogen and nitrogen molecules homogeneously dissolved in water can be distinguished. The Raman spectrum of nitrogen in the bubble/water system was found to be dominated by the gas-phase peak, indicating that “almost no nitrogen molecules are dissolved homogeneously in the aqueous solution, and that the vast majority are present in the form of nitrogen nanobubbles”. The pressure of the nitrogen gas inside these small bubbles is much larger than atmospheric. In this situation the bubbles should disappear in a fraction of a second, as the nitrogen gas diffuses outward according to the expertly solved moving-boundary
problem formulated by Epstein and Plesset in their influential 1950 paper.\textsuperscript{1,12} The observed longevity of the nitrogen bubbles, measured in weeks, stands in stark contrast.

The stability of nanobubbles has indeed long been considered as an apparent violation of classical theory. In their interesting article, “A History of Nanobubbles”, Alheshibri et al. present a Laplace Pressure Bubble Catastrophe as creating thermodynamic instability of nanobubbles.\textsuperscript{1} The basis for their thinking is the independent discovery by Young and Laplace that surface tension causes the pressure inside a spherical bubble to be greater than outside.\textsuperscript{14,15} Henry’s law for the solubility of the gas in the exterior aqueous phase in response to the higher pressure inside the bubble is then reasoned to create a Laplace Pressure Catastrophe that uncontrollably destabilizes a bubble, causing it to grow by inward diffusion until it is removed from the solution through buoyancy, or to lose all of its gas molecules by outward diffusion and thereby shrink from existence. The Laplace Pressure Catastrophe is not observed, however, leading the authors of the History to wonder if an emphasis on solubility and diffusion “has somehow clouded our understanding of nanobubbles”. We will agree that it has.

We begin this paper with a statement of the Laplace equation and Rowlinson and Widom’s insightful derivation of it.\textsuperscript{14} A clear understanding of both leads to recognition that neither Epstein–Plesset diffusion nor the Laplace Pressure Bubble Catastrophe have a physical basis, so it is not surprising that neither of them is observed to occur. Neither provides a basis for an expectation that a nanobubble will be quickly extinguished.

To gain further insight, we proceed to a unified treatment of the mechanical equilibrium and thermodynamic stability of bubbles, immiscible droplets, and cavities. These spherical objects are immersed in pure water. They exist in an ideal limiting condition as closed, that is, as containing a constant number of molecules (for the cavity, the constant number is zero). We give some examples of what we have in mind. Take a droplet of oil in water. In this case, our understanding is not clouded, because “oil and water do not mix”, and the stability of an oil droplet in pure water (or a water droplet in oil) can be considered.\textsuperscript{7,16,17}

Cavities in a liquid provide another related example. Water can be literally torn apart when placed under sufficiently great tension (negative pressure), and quasi-spherical cavities have been observed in simulations of water under tension.\textsuperscript{5,6} We take seriously the description of the cavity as a void space by assuming its interior to be empty (in their analysis Min and Berkowitz neglect the number of water molecules in the cavity as well as the pressure inside as “very small”, while Menzl et al. make the still stronger statement that their cavities are “essentially voids [that] rarely contain vapor molecules”).

Gas-filled bubbles provide the third example. As mentioned, the “vast majority” of nitrogen molecules in the nitrogen nanobubble system studied by Ohgaki et al. were contained in the bubbles and “almost none” in the aqueous phase. We therefore wish to study a gas-filled nanobubble situated in pure water containing no gas molecules, in other words, when the gas has no significant solubility in water.

Our analysis proceeds under the assumptions of macroscopic thermodynamics, that is, in the thermodynamic limit, and for an ideally sharp spherical interface. We give a direct proof that all the systems under study are unstable in this context if the surface tension is assumed independent of sphere radius. But all of these systems have been observed to be stable (more precisely, metastable) for varying but significantly long periods of time. We find that some thermodynamic models for a radius-dependent surface tension support stability. To our knowledge, this study is the first to demonstrate that stability of these nanospherical systems is consistent with the macroscopic thermodynamic limit.

There is another aspect to the systems under discussion. The surfaces of gas nanobubbles are widely thought to be electrostatically charged, as suggested by measurements of “zeta potentials”.\textsuperscript{9–11} We will express skepticism, but we do ask with others\textsuperscript{8,11,18} whether a surface charge can in principle contribute toward stabilization of the bubble size. Among our results is a calculation based on the Born energy indicating that it can, but that the effect may be much too small by orders of magnitude to account for nanobubble stability.

The Laplace equation

Certainly any discussion of bubbles or droplets must assign a principal role to the Laplace equation for the pressure difference $\Delta P$ (inside minus outside) across the surface of a spherical phase of radius $R$,

$$\Delta P = \frac{2\gamma(R)}{R} \quad (1)$$

where $\gamma(R)$ is the surface tension, taken here for generality and subsequent use as inherently dependent on bubble size. The surface tension is understood to be positive (work is required to create a surface),\textsuperscript{15} so $\Delta P$ is also positive. The pressure of the material inside the bubble is greater than the pressure of the aqueous phase outside. If the “bubble” is an empty cavity, the pressure inside is zero, and the pressure of the water outside is negative. To avoid confusion with some aspects of the current theoretical literature, we specify that by “radius” we will always mean the positive distance between the center of the sphere and the surface.

The derivation of this equation can be so brief, but the physical insight it provides so important, that we wish to reproduce it here, and we can do no better than an essentially direct reading of the presentation of Rowlinson and Widom.\textsuperscript{14} Their derivation for a bubble is also applicable to an immiscible droplet or a spherical cavity. We have then a spherical bubble of radius $R$ within the body of a liquid. The tension in the surface will make the bubble collapse unless the pressure inside exceeds that outside by, say, $\Delta P$. The work of an infinitesimal change in $R$ vanishes at equilibrium, so $\Delta P dV$ equals $\gamma dA$, where $dV$ and $dA$ are the increases in volume and surface area of the bubble. Since $V = (4/3)\pi R^3$, and $A = 4\pi R^2$, we have $dV/dA = R/2$, and so $\Delta P = 2\gamma/R$, the Laplace equation.
From the derivation we see that the Laplace equation is a condition for mechanical equilibrium. It states that the net radially directed force on the bubble, as the resultant of pressure and resistance of the surface to stretching, must then vanish. The infinitesimal change in \( R \) is not brought about by a flow of gas molecules across the bubble surface. Further, the Laplace equation says nothing about the thermodynamic stability of the mechanical equilibrium. It does not distinguish between a maximum or minimum of free energy, only that the free energy (work) is at an extremum, where the forces involved (pressure and restoring surface tension) are exactly in balance.

We see also that at the Laplace equilibrium state there is a discontinuity of pressure across the bubble surface. If \( P_b \) is the pressure within the bubble, and \( P_w \) the lower pressure of the aqueous phase, the pressure discontinuously drops by the amount \( \Delta P = P_b - P_w \) as we proceed from just inside the bubble to just outside. The reason for the pressure drop is the convexity of the spherical surface (\( dV/dA = R/2 > 0 \)), which causes the tension in the surface to push on the inside of the bubble while pulling on the outside.

For the example of the nitrogen nanobubble, the pressure discontinuity has an important implication. If the pressure is discontinuous at the bubble surface, the concentration of the nitrogen molecules cannot be continuous there. It must also be discontinuous, contrary to the assumption of local equilibrium of nitrogen molecules at the surface that is a boundary condition essential to the Epstein–Plesset diffusion model.\(^1\)\(^,\)\(^13\) The pressure discontinuity also means that the pressure \( P_b \) in the interior of the bubble, and therefore the pressure acting on the surface from inside, cannot be taken as a pressure exerted on the water immediately surrounding the bubble from outside, as assumed in the formulation of the Laplace Pressure Bubble Catastrophe.\(^1\)

The concentration of nitrogen molecules in the water just outside the bubble is not equal to the Henry’s law saturation concentration at \( P_b \). It is equal to a much lower concentration corresponding to atmospheric conditions, just as everywhere else in the bulk aqueous phase. Therefore, since there is no gradient for diffusion outside the bubble, there is no diffusion. And since the solubility of nitrogen in the water just outside the bubble is not governed by the pressure inside the bubble, there is no Laplace pressure catastrophe.

A sharper understanding of the Laplace equation and the physics underlying it has thus removed the mystery from nanobubble longevity. The gas in the nanobubble exists in a state analogous to that of solute in an ordinary osmotic pressure arrangement at equilibrium, where escape of the solute molecules is prevented by a semi-permeable membrane. In an equilibrated bubble system, the spherical surface itself plays the role of the membrane, its tension having adjusted upward just sufficiently to check escape of the gas.

We note that the issue of thermodynamic catastrophe apparently does not exist in the field of nanoemulsions, presumably because oil and water have such a high degree of immiscibility. But confusion in a lower key about the role of Laplace pressure is there also.\(^7\) Nonvanishing solubility of the oil molecules in water is said to implicate oil molecule diffusion along a gradient of oil molecules from just outside small oil droplets with high Laplace pressure to just outside larger oil droplets with lower Laplace pressure, resulting in further growth of the latter at the expense of the former. But for the same reasons as given in this section, the Laplace pressure difference between small and large droplets does not cause a solute diffusion gradient in the surrounding liquid. Coagulation of emulsions does not involve Laplace pressure.

**Thermodynamic stability analysis**

We return to the first point in the previous section about the physics underlying the Laplace equation, that it says nothing about the stability of the mechanically equilibrated state represented by it. The Laplace equation generalizes the simple mechanical equilibrium condition \( \Delta P = 0 \) for a planar interface between two phases.\(^15\),\(^19\) For a planar surface the equality of pressures on both sides means that the force exerted by one phase on the second must be equal to the force exerted by the second phase on the first, if the system is to be at equilibrium. Otherwise, the phase at higher pressure will expand at the expense of the one with lower pressure. Mechanical equilibrium at a planar interface between two phases does not imply by itself that the two-phase system is thermodynamically stable. For stability of the equilibrium state, a second condition must apply; the isothermal compressibilities of both phases must be positive.\(^19\)

Analogously, for a single phase to be mechanically equilibrated, its pressure must be uniform throughout, but this equilibrium state is stable only if the compressibility is positive.\(^19\) A positive compressibility of a substance means that its volume decreases if the pressure on it increases. Since no known materials in nature behave otherwise (if one did, it would be unstable, and would long ago have disappeared), there is a universally intuitive understanding of equilibration and stability of planar interfaces that may not extend to curved ones. The following analysis of closed bubbles is aimed at partial correction of this situation.

We have a large body of a liquid, for example water, with volume \( V_w \) containing a constant number \( N_w \) of liquid molecules. Immersed in this liquid is a spherical phase \( b \) that we call a bubble (even if it contains an immiscible liquid). The volume of the bubble, \( V_b \), is \( (4/3)\pi R^3 \), where \( R \) is the radius of the sphere. We define “radius” in the usual way, as the positive distance between the center of the sphere and the surface, so that the volume of the bubble also has its usual meaning as a positive quantity. The bubble contains a constant number of molecules \( N_b \) (equal to zero if the bubble is an empty void). Examples were given in the Introduction of physical systems that this model might be expected to describe reasonably accurately. An example to which the model does not apply would be a liquid water droplet surrounded by its vapor in thermodynamic equilibrium (equal chemical potentials), since in that case \( N_b \) and \( N_w \) are not constant.

The two phases, \( w \) and \( b \), are separated by an interface, which we represent as an ideal two-dimensional surface containing no molecules. We realize that “such a division of the system into two physical subsystems... is not evident unless the interface is perfectly sharp, which is never the case,”\(^120\) and that an extensive theoretical literature, beginning with Gibbs himself,\(^14\) seeks “to avoid this problem.” Nonetheless we
persistent for present purposes with exactly such an idealized interface, while avoiding any attempt to describe its actual physical structure either on a Gibbsian local thermodynamic level, or atomistically (but see Discussion).

Our ideal surface is endowed with a tension that is understood to resist expansion, so to minimize its area $A$, the surface takes on a spherical shape with $A = 4\pi R^2$. The total number of molecules $N = N_w + N_b$ is constant since both $N_b$ and $N_w$ are constant. The total volume of the system is $V = V_w + V_b$, and $V$ is held constant while the component volumes can vary. The respective pressures are $P_w$ and $P_b$ (for the example of an empty cavity $P_b = 0$, and $P_w$ is negative to achieve mechanical equilibrium). The entire system is isothermal with common temperature $T$ held constant.

We have left the pressure difference $P_w - P_b$ as an arbitrary constant pressure difference, independent of $R$. Now we ask whether or not, as we scan through values of $R$, we will find any radii that characterize spherical bubbles mechanically equilibrated with this fixed $\Delta P$.

To answer this question, $dF/dr$ is set to zero. The roots $R$ of the equation $dF/dr = 0$ are the values of $R$ corresponding to a mechanical force $-dF/dr$ that everywhere vanishes (this is the meaning of mechanical equilibrium). From eqn (4), we can write the mechanical equilibrium condition $dF/dr = 0$ in the form of the Laplace equation,

$$R = \frac{2\gamma(R)}{\Delta P} \quad (6)$$

This yields the Laplace equation, eqn (6), is the condition for vanishing net force. From this condition, we recognize that the net zero force is the resultant of two competing tendencies. The positive surface tension $\gamma$ tends to minimize the surface area, and the bubble shrinks. If it is directed outwards, the bubble expands. If it vanishes, the bubble is in a state of mechanical equilibrium.

For the Laplace equation to be stable the right-hand side must be positive, for only then is the free energy at a minimum. If the free energy at a value of $R$ corresponding to mechanical equilibrium is at a maximum, the equilibrium is thermodynamically unstable, and thermal fluctuations immediately destroy it. Noting the minus sign, we write the stability condition as,

$$\gamma(R) - R(d\gamma/dr) < 0 \quad (8)$$

where it is understood that the left-hand side is evaluated at a value of $R$ corresponding to a state of mechanical equilibrium (i.e., a root $R$ of the Laplace eqn (6)).

### Surface tension: special cases

#### Constant surface tension

We consider a variety of special cases for the radius dependence of the surface tension $\gamma(R)$, beginning with $\gamma = const$. For this case, there is only one mechanically equilibrated radius $R = 2\gamma/\Delta P$, that is, just one solution of eqn (6). The stability condition, eqn (8), then reduces to $\gamma < 0$. Stability would therefore require a negative surface tension. But the possible reality is that $\gamma$ is positive. Therefore, the free energy is at a maximum, and the bubble is unstable if the surface tension is constant.

In a thermodynamic theory the underlying physics can remain opaque. It may be useful at this point to translate some of the calculations into words. We recall first why the surface tension is a positive quantity. If a surface separating two phases had a negative surface tension, the area of the surface would spontaneously increase without limit until the entire system consisted only of surface, and the two phases would cease to exist separately. Next, we consider the net force exerted by the surroundings of a bubble, including the surface, on the interior of the bubble. If this net force is directed inwards, the bubble shrinks. If it is directed outwards, the bubble expands. If it vanishes, the bubble is in a state of mechanical equilibrium.

The Laplace equation, eqn (6), is the condition for vanishing net force. From this condition, we recognize that the net zero force is the resultant of two competing tendencies. The positive surface tension $\gamma$ tends to minimize the surface area, and the bubble tends to contract. But the positive surface tension also creates a positive Laplace pressure difference $\Delta P$; the pressure inside the bubble is greater than the pressure outside. The pressure-volume work therefore tends to expand the sphere. At a radius $R$ corresponding to mechanical equilibrium, these two tendencies are in exact balance. But under the assumption of a constant surface tension, the pressure-volume work dominates when the radius is displaced slightly outwards, and then the sphere spontaneously expands further. When the radius is
displaced slightly inwards, the tendency toward minimal surface area dominates, and the sphere contracts further. This, in words, is the unstable response in the face of a constant surface tension to a small fluctuation away from mechanical equilibrium.

The failure of the stability condition \( \gamma < 0 \) tells us that when the positive surface tension coefficient \( \gamma \) is assumed independent of radius, the unstable state of the bubble and its surrounding liquid is entirely determined by the surface tension itself. It is reasonable to ask whether a radius dependence of the surface tension might stabilize the system. Stabilization might occur if an increase of surface area (increased radius) brings into play stronger surface forces tending to contract the bubble, in other words, if the surface tension \( \gamma \) increases when \( R \) increases. We therefore proceed to consider of models for a radius dependence of surface tension, while not departing from a “perfectly sharp” surface. We begin with a simple linear dependence on \( R \). Then we consider the Tolman approximation for \( \gamma(R) \), purely as a formal expression of a dependence on \( R \), and not as a theory attempting to explain the dependence on the basis of a departure from a perfectly sharp surface. The Tolman equation is often linearized, and we proceed to consider the linear form. Finally, we consider the radius dependence conferred on spherical surface tension if the sphere is charged. From a purely theoretical perspective, this case is interesting, because it explicitly exhibits a perfectly sharp interface that nonetheless possesses a physically realistic radius dependence of its surface tension. Discussion of the results and their placement in the context of the literature is deferred to the Discussion section.

**Linear dependence on size**

We investigate whether stability can be induced for some radius inside a range of possible radii where the dependence of surface tension on radius is linear,

\[
\gamma(R) = \alpha + \beta R
\]

with \( \alpha \) and \( \beta \) constant coefficients. A physically realistic theory using this ansatz for \( \gamma(R) \) must be consistent with positive values for three quantities: the spherical bubble radius \( R \), the mechanically equilibrated pressure difference \( \Delta P \), and the surface tension \( \gamma(R) \) itself. With \( \gamma(R) = \alpha + \beta R \), the requirement for stability, eqn (8), reduces to \( \alpha < 0 \) regardless of the value of \( R \), so in the expression for \( \gamma(R) \) we take the coefficient \( \alpha \) to be negative. Then it is necessary for a positive value of \( \gamma(R) \) that the coefficient \( \beta \) be positive.

The requirement for mechanical equilibrium is the Laplace eqn (6). Substituting \( \gamma(R) = \alpha + \beta R \) into this equation, we easily extract the only root \( R \) of this equation,

\[
R = \frac{2\alpha}{\Delta P - 2\beta}
\]

For \( R \) to be positive, \( \Delta P \) must be less than \( 2\beta \), since \( \alpha < 0 \) and \( \beta > 0 \). If we choose a fixed \( \Delta P > 0 \), then this \( \Delta P \) is restricted to the interval \( 0 < \Delta P < 2\beta \). Calculating \( \gamma(R) = \alpha + \beta R \) with eqn (10) for \( R \), we get

\[
\gamma(R) = \frac{2\Delta P}{\Delta P - 2\beta}
\]

which is positive, since \( \alpha < 0 \) and \( 0 < \Delta P < 2\beta \).

We conclude that a mechanically equilibrated and thermodynamically stable spherical bubble of radius \( R \) given by eqn (10) is consistent with a size-dependent surface tension \( \gamma(R) = \alpha + \beta R \), \( \alpha < 0 \), \( \beta > 0 \), and a positive pressure difference \( \Delta P < 2\beta \). It is understood that the expression for \( \gamma(R) \) need not hold outside some range of \( R \) that includes the stable radius.

**The Tolman dependence**

The Tolman expression is,

\[
\gamma(R) = \frac{\gamma_0}{1 + 2\delta/R}
\]

where \( \gamma_0 \) and \( \delta \) are constants, the latter with units of length. Again, we assume that this form holds within some range of \( R \) values and ask if there are any stable radii in this range. With this expression for \( \gamma(R) \) we find a single positive root of the Laplace eqn (6), \( R = 2(\gamma_0/\Delta P - \delta) \) if the length \( \delta \) is chosen to be less than \( \gamma_0/\Delta P \). A bubble with this radius is mechanically equilibrated, but is it stable? We compute from eqn (12),

\[
\gamma = -\frac{\gamma_0 \Delta P}{(1 + 2\delta/R)^2}
\]

which is positive for any radius and any value of \( \delta \). Therefore the stability condition, eqn (8), is never satisfied, and a bubble in Laplace equilibrium but with a Tolman surface tension is always unstable.

**Linear dependence on inverse radius**

Next we examine a linear version of eqn (12),

\[
\gamma(R) = \gamma_0 \left(1 - \frac{2\delta}{R}\right)
\]

The stability requirement, eqn (8), reduces to,

\[
R < 4\delta
\]

which in particular requires \( \delta > 0 \).

The requirement for mechanical equilibrium, whether stable or not, is the Laplace eqn (6),

\[
R = \frac{2\gamma_0}{\Delta P} \left(1 - \frac{2\delta}{R}\right)
\]

which expands into a quadratic equation for the variable \( R \),

\[
R^2 - R \gamma_0 R + 2\delta \gamma_0 = 0
\]

In writing this equation, we have presented a mechanically equilibrated radius \( R_0 \) for a hypothetical spherical phase with constant surface tension \( \gamma_0 \), i.e., \( R_0 \) is defined by a Laplace formula,

\[
R_0 = \gamma_0 \Delta P
\]

We can write explicit formulas for the two solutions of eqn (17), but a direct analysis of the polynomial \( f(R) = R^2 - R \gamma_0 R + 2\delta \gamma_0 \) is more instructive. We see directly that
$f(R) > 0$ for all values of $R \leq 0$, and from the first two derivatives of $f(R)$, we conclude that there is a single extremum, a minimum, at $R = (1/2)R_0$, where $f = R_0 \left( 2\delta - \frac{1}{4}R_0 \right)$. So for $\delta > (1/8)R_0$, $f(R)$ is positive for all $R$, and the two roots must be a pair of complex conjugates, that is, there are no equilibrated spheres of any radius given this surface tension. But if $\delta < (1/8)R_0$, then $f(R)$ is negative at its minimum, and there are two positive real roots $R_+ > (1/2)R_0$ and $R_- < (1/2)R_0$.

The radius $R_+$ corresponds to an equilibrated but unstable sphere, since $R_+ > (1/2)R_0 > (1/2)(8\delta) = 4\delta$, a violation of the stability condition eqn (8). But then this solution $R_+$ of the Laplace equilibrium condition represents a maximum of free energy, and so the other root $R_-$ is at a free energy minimum, since there are only two solutions of the Laplace equation (it cannot be a maximum, since then there would be two maxima, which would have to be separated by a minimum, hence three solutions of the Laplace equation, but there are only two). Since $R_+$ is then a stable radius, it must be less than $4\delta$, the stability condition. But it must also be greater than $2\delta$ to meet the requirement of a positive surface tension. Therefore there is a stable radius $R_-$ somewhere in the interval $2\delta < R_- < 4\delta$.

**Dependence on electrostatic charge**

It is known that surface charge contributes to the surface tension of a sphere in a radius-dependent manner. A derivation of the relevant expression not having been provided, we give a short one here (with no claim to originality). The electrostatic free energy of a sphere with surface charge can be estimated with the Born energy,

$$F_{el} = \frac{n^2 e^2}{8\pi \varepsilon_0 R} \quad (19)$$

where $n$ is the number of elementary charges $e$ distributed uniformly on the sphere, $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon$ is the dielectric constant of the surrounding fluid. Assuming that $n$ is constant, we can differentiate with respect to radius $R$, and then use surface area $A = 4\pi R^2$ to get $dA = dA/8\pi R$. We find,

$$dF_{el} = -\frac{n^2 e^2}{64\pi \varepsilon_0 R^3} dA \quad (20)$$

The coefficient of $dA$ is an electrostatic contribution $\gamma_{el}$ to the surface tension. It is negative, implying that the electrostatic repulsions among surface charges lower the surface tension, thus favoring expansion of the bubble, as the charges tend to be as far apart as possible.

We can write $\gamma(R) = \gamma_0 + \gamma_{el}(R)$ in a form similar to eqn (14), but with the electrostatic third-order curvature term instead of the linear one. That is,

$$\gamma(R) = \gamma_0 \left( 1 - \frac{2\delta_{el}^3}{R^3} \right) \quad (21)$$

where

$$\delta_{el}^3 = \frac{n^2 e^2}{128\pi^2 \varepsilon_0 \varepsilon_0 \gamma_0} \quad (22)$$

An analysis similar to the one for linear dependence on curvature goes through, concluding that there is a stable radius $R$, and providing upper and lower bounds for it in terms of the electrostatic quantities appearing in $\delta_{el}$, $2^{1/3}\delta_{el} < R < 2\delta_{el}$.

**Discussion**

The observed stability of gas nanobubbles has long been considered puzzling, since the diffusion calculation of Epstein and Plesset suggests that small bubbles should disappear in a fraction of a second. In the first part of this paper, we have shown why the assumption of local gas equilibrium across the boundary of the bubble, crucial to the diffusion model, violates the fundamental physical principles underlying the Laplace equation for mechanical equilibrium of a liquid or gas phase surrounded by another fluid phase. For the same reason, Henry's law with a pressure equal to the pressure of the gas inside the bubble cannot be applied to calculate the gas concentration just outside the bubble, thereby invalidating the analysis of a “Laplace Pressure Bubble Catastrophe”, a catastrophe that has never been observed because it does not exist.

In the second part of the paper, we replaced one puzzle with another. If the surface tension is taken as constant, that is, independent of bubble, droplet, or cavity radius, then a mechanically equilibrated spherical phase (Laplace’s equation) is nonetheless thermodynamically unstable. It is located at a free energy maximum, not a minimum. Then the quandary of observed bubble longevity would persist, not for reasons based on a misunderstanding of the meaning of the Laplace equation, but instead because a constant surface tension cannot balance a mechanically equilibrated bubble radius in a stable manner. An obvious approach toward resolution of a puzzle set up by an assumption of constant surface tension is to abandon the assumption and see what happens if the surface tension of a bubble depends significantly on bubble radius.

In our theoretical considerations, we used the conventional definition of surface tension as the coefficient $\gamma$ in the expression $\gamma dA$ for the infinitesimal increment of work required to increase surface area $A$ by the infinitesimal amount $dA$. There are other ways to define surface tension. Using the different symbol $\Gamma$ for it to avoid confusion, we may say that incremental surface work is given by $d(\Gamma A) = \Gamma dA + Ad\Gamma$, where $d\Gamma$ in the additional term $Ad\Gamma$ represents the effect of a postulated variation of surface tension as one proceeds continuously in a normal direction through an interface endowed with three-dimensional structure. This formulation leads to a modified Laplace equation for a spherical interface. We do not use $\Gamma$ in our analysis, as its physical meaningfulness is unclear.

The expression $\gamma dA$ for the incremental work of creating surface, which is “obviously proportional to $dA$”, is a clear analogy for surfaces to bulk work $-PdV$, $-\gamma$ playing the role of surface pressure. Its use does imply a commitment to a perfectly sharp, ideally two-dimensional, surface. And just as $P$ may, and in general does, depend on volume $V$, so $\gamma$ may depend on surface area $A$, and therefore on radius $R$ for a spherical surface with $A = 4\pi R^2$. 

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We proceeded to examine four possibilities for a radius-dependent surface tension, and we will discuss each of them here in turn. We first looked at a possible effect of bubble size by assuming a linear dependence of $\gamma(R)$ on $R$, $\gamma(R) = \alpha + \beta R$. Physical realism dictates that such a dependence could apply, if at all, inside a restricted range of $R$ values short of infinity. We found that droplet, cavity, or bubble stability is consistent with such radius dependence if the intercept $\alpha$ is negative, while the slope $\beta$ is positive. A negative value of $\alpha$ violates no physical principles. A sphere of small radius $R < |\beta/|\alpha|$ would expand spontaneously but only until the crossover to positive values of surface tension. The value of the stable radius is given by eqn (10), but we are unable to give a direct numerical illustration because knowledge of the values of surface tension and stable radius from literature data does not lead to values of $\alpha$ and $\beta$ (the determinant of coefficients in eqn (9) and (10) vanishes). However, we will find a way to circumvent this problem (see below).

We considered a radius dependence conforming to a suggestion of Tolman, eqn (12). We used the Tolman equation purely as a formal expression for a radius dependence, and not as a theory of surface tension. In our use, the surface is perfectly sharp. As a theory, Tolman derived his expression from the efforts of Gibbs to describe an actual physical interface as an object of tangible, if narrow, width. If the surface tension is then dependent on where it is measured within this thin layer of $R$ values, it emerges as dependent on $R$. It is for this reason that the Tolman expression, as a theory, leads to a dependence on curvature $1/R$. For this reason, also, the Tolman length $\delta$, as a theoretical object, is tiny, since it is a measure of the width of the surface. The dependence on radius that is our present subject arises from a qualitatively different perspective. There is nothing fundamentally inconsistent in defining the surface tension of a perfectly sharp interface as possessing a dependence on radius, and we did so. Of course a physical interpretation is desirable, and forthcoming below.

Today the Tolman expression, considered as a theory, might be regarded as primarily of historical interest, as the higher-order terms implicit in it beyond linear have been regarded as doubtful, including by Tolman himself.\textsuperscript{20,21} Nonetheless it continues to be used\textsuperscript{25,26} for example, by Menzl et al.\textsuperscript{6} to fit their simulated data on cavitation. We found that it leads to an unstable cavity or bubble of any radius, regardless of the value of the Tolman length $\delta$, positive or negative. The Tolman approximation, like the assumption of a constant surface tension, is inconsistent with the observed stability of cavities and gas nanobubbles, at least in the context of macroscopic thermodynamics and a perfectly sharp interface.

We proceeded to look at a linearized form of the Tolman approximation, eqn (14).\textsuperscript{5,20,27–31} We found that the stability condition, eqn (15), requires a positive Tolman length. The cavities in water under negative pressure observed in simulations by Min and Berkowitz\textsuperscript{2} were on the size scale of 1 nm. Values of simulated cavity radius were not directly reported, presumably because the observed cavities are not perfect spheres, but a numerical fit using the linearized Tolman approximation yielded an average value $R = 1.11$ nm and an average $\delta = 0.15$ nm. Our stability analysis locates a stable radius somewhere in the interval $2\delta$ to $4\delta$, that is, between 0.30 nm and 0.60 nm in this case, somewhat smaller than the values reported by Min and Berkowitz. A representative cavity radius from Fig. 2 of Menzl et al.\textsuperscript{6} is $R = 1$ nm, and their reported value of $\delta$ is 0.195 nm. Values of $R$ in the interval 2$\delta$ to 4$\delta$ are in the range 0.4 nm to 0.8 nm, somewhat less than the representative $R$ value (but Menzl et al. also find cavities with radii in this range, see their Fig. 2).

If we apply our prediction from the assumed linear curvature dependence of surface tension to nitrogen nanobubbles of 50 nm radius, we find from the interval $2\delta < R < 4\delta$ in which this stable radius is located that $\delta$ is somewhere between 13 and 25 nm. The stable bulk nitrogen nanobubbles generated in water in the experiments of Ohgaki et al.\textsuperscript{8} were typically of 50 nm radius, 6 MPa internal pressure (about 60 atm), and surface tension about twice the familiar flat open surface value 0.072 J m$^{-2}$ for water. The reader is referred to the experimental section of the original paper for methods and procedures. With an intermediate choice $\delta = 17$ nm, the following statement is correct, that the expression $\gamma(R)/\gamma_0 = 1 - (3/4R)$, taken in the neighborhood of $R = 50$ nm with $\gamma_0 = 0.45$ J m$^{-2}$, is consistent with the reported experimental data. Note that when $R$ is set equal to 50 nm in this expression, the value it gives for $\gamma(R)$ is 0.144 J m$^{-2}$, about twice the flat air/water value, as reported by the authors.

The representation of the data just given is not unique. If we linearize $1/R$ around some fixed value $R_0$ (i.e., $R^{-1} = R_0^{-1} - (R/R_0)$) from a first-order Taylor expansion, use the result in eqn (14), and then compare with $\gamma(R) = \alpha + \beta R$, we can identify $\alpha/\gamma_0 = 1 - (4\delta/R_0)$, and $\beta/\gamma_0 = 2\delta/R_0^2$. Note that $\beta > 0$, and if $R_0$ is chosen as a stable radius, then $\alpha < 0$ since $R_0 < 4\delta$. Using $\delta = 17$ nm, $R_0 = 50$ nm, we find that the linear expression $\gamma(R)/\gamma_0 = -0.36 + 0.0136 R_0$ same as above, also represents the data of Ohgaki et al. in the neighborhood of $R = 50$ nm.

The values of $\delta$ found here to stabilize the cavity and nitrogen nanobubble are quite different. We do not believe that the hydrogen-bonded water network surrounding a 1 nm void in water stabilized by 1000 atm negative pressure, on the one hand, and a 50 nm bubble containing gas at 60 atm in water at 1 atm, on the other, must be similar, and must be characterized by similar values of $\delta$. In their paper Ohgaki et al.\textsuperscript{8} presented spectroscopic evidence based on the infrared stretching frequency of the intramolecular OH bond that “the interface of nanobubbles consists of hard hydrogen bonds that are similar to the hydrogen bonds found in ice and gas hydrates”.\textsuperscript{8} An interpretation of the spectroscopic data of Ohgaki et al. might be that the interface of a 60 atm nitrogen nanobubble immersed in water, consisting as it must of some mixture of nitrogen and water molecules, features a correlated collection of imperfect clathrate-like cage structures surrounding individual nitrogen molecules, pairs of gas molecules, triples, etc.

Zdrali et al.\textsuperscript{16} have reported on an experimental study of nanoemulsions in water, consisting of droplets of hexadecane stabilized against coagulation in water by charged and uncharged surfactants, or, for some measurements, even in the absence of surfactants. The pure oil droplets in water were stable for a few weeks (private communication). The radii of these droplets are
similar to the radii of the nitrogen bubbles studied by Ohgaki et al. In the same laboratory, Smolentsev et al. conducted a spectroscopic study of radius 100 nm water droplets in oil. Their conclusion, from a method giving spectra entirely from the surface region of a few molecular layers thick, is that “the water molecules of the water droplet/hydrophobic interface appear to be much more structured than the water molecules at a planar water/air or water/hexane interface”. Again, we do not wish to bowdlerize these data with a single quotation, and the reader is encouraged to study the original source. The authors gave a tentative interpretation of their results in terms of the hydrogen-bonded structuring of water molecules around small hydrophobic protrusions into the water droplet interface.

Surface charge contributes to surface tension, and we concluded from a stability analysis of the electrostatic third-order curvature dependence, eqn (21), that a stable radius exists somewhere in the interval \(2^{1/3}\delta_{el} < R < 2\delta_{el}\), where \(\delta_{el}\) is a length given by eqn (22). An attempt at numerical analysis (not shown) suggests that the stable radius is too small by orders of magnitude to account for any bubble remotely approaching 50 nm. However, the numerical estimate is rough, and we prefer in the state of present knowledge to leave a charge effect as of possible significance.

In this Discussion section we would like to express an opinion that the evidence for the existence of significant surface charge on gas nanobubbles in pure water, whatever might be its origin, is unconvincing. It is taken for granted that measured values of negative “zeta potentials” constitute prima facie proof of a negatively charged bubble. We feel it important to emphasize that black box instruments purporting to display values of surface potentials do not measure potentials. They measure drift velocities (mobilities) in an applied external electric field. The species that we know will respond to an electric field in a system of nominally pure water containing a bubble and dissolved CO\(_2\) are the positive H\(^+\) and negative OH\(^-\) and bicarbonate ions, along with possible trace amounts of charged impurities. Asymmetries in the physical properties of these aqueous ionic species might impart asymmetries of momentum exchanges that could cause the bubble to drift even if its surface is uncharged. Such effects would disappear once the electric field is removed. This author does not know how to construct what might be a complicated hydrodynamic theory for such eventualities, but he does remain skeptical of the existence of charge on the surface of nanobubbles based only on manufacturers’ claims for zeta potentials.

The assumption that the surface of nanobubbles bears an electrostatic charge has led to peculiar theoretical considerations. For example, the observed stability with respect to size of these bubbles has been suggested as due to the creation of “electrostatic pressure”, which, acting radially inward, balances the outward Laplace pressure.9 We have explained why the Laplace pressure does not need balancing. The Laplace equation by itself is the expression of overall force balance. And of course surface charge would produce a force acting radially outward. Another idea is that adsorbed charge can compensate the surface tension arising from nonelectrostatic cohesive forces, rendering the pressure inside a nanobubble equal to the ambient pressure and the Laplace equation entirely inapplicable to nanobubbles. This conjecture is contrary to the data of Ohgaki et al. A theoretical paper reporting a stable minimum of Gibbs free energy caused by electrostatics begins with a radius-dependent integral expression \(G\) for the free energy, which is incorrect because it is not what one obtains with integration of \(dG\) containing radius-dependent Laplace and electrostatic terms. Moreover, the displayed electrostatic terms in \(G\) and the pressure difference \(\Delta P\) are mutually inconsistent. The authors then complete their cycle of errors with the claim that the equilibrium pressure inside the nanobubble equals the ambient 1 atm pressure, incorrectly invoking Henry’s law and flouting the Laplace equation.

One reason motivating many workers in this field to emphasize a surface charge on nanobubbles is that it provides a plausible explanation for the observed stability of nanobubbles toward coalescence into larger bubbles that would quickly disappear by buoyancy. Faced with a choice of conjectures, this author prefers another possibility. A collection of discrete nanobubbles does not coalesce into one large bubble, because if it did, the larger bubble might possess a radius in a range where the surface tension is constant. This large bubble would then be unstable and immediately dissociate back into smaller bubbles stabilized by radii-dependent surface tensions.

Conflicts of interest

There are no conflicts to declare.

References