Nanobubbles: the big picture

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Abstract

Nanobubbles, whose existence on hydrophobic surfaces immersed in water has previously been inferred from measurements of long-ranged attractions between such surfaces, are directly imaged by tapping mode atomic force microscopy. It is found that the nanobubbles cover the surfaces in an irregular, interconnected or close-packed network whose morphology is dependent on pH and whose lifetimes are at least of the order of hours. Their height is of the order of 30 nm and their radius of curvature is of the order of 100–300 nm. It appears that the nanobubbles form from a solution supersaturated with air. A thermodynamic and statistical mechanical analysis of the homogeneous nucleation of liquid droplets from a supersaturated vapour shows that although a single droplet can be in equilibrium with a finite volume of gas, for a gas reservoir the equilibrium state is represented by a single macroscopic droplet, which grows by collisions and by Ostwald ripening. It is concluded that the electric double-layer repulsion between neighbouring nanobubbles on the hydrophobic surface plays a role in their stabilisation.

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1. Introduction

Colloid science, which deals with the interaction of microscopic particles in liquids, with the adhesion of particles to surfaces and to each other, and with the stability of dispersions of particles, is based upon the balance of the van der Waals attraction and the electric double-layer repulsion, with additional contributions from polymer depletion, bridging, and entropic restriction, and from solvent structuring. The van der Waals
attraction arises from correlated electrodynamic fluctuations and has an effective range of 1 nm or so, whereas the electric double-layer repulsion arises from the surface charge of the colloids and has a range of 1–100 nm, depending upon the electrolyte concentration. The radius of gyration generally determines the range of polymeric forces, and solvation forces have a range of several molecular diameters.

A new attractive force emerged in the latter quarter of the 20th century that was orders of magnitude stronger than the van der Waals attraction and that had a measurable range of 10–100 nm [1,2]. The force was found between hydrophobic (water repellent) surfaces, and, although somewhat variable, was measured in a number of laboratories, (see Ref. [3] and references therein). A wide ranging debate about its origins ensured [4–6], with the initially controversial but ultimately compelling proposal being that the attraction was due to the bridging of submicroscopic bubbles (nanobubbles) that existed on the hydrophobic surfaces [3,7]. This mechanism was based upon the observation of steps in the force at long range, signifying a bridging event [3], and the form and magnitude of the attraction was consistent with thermodynamic calculations of the force due to a bridging bubble [3,8]. The idea was supported by subsequent de-aeration experiments [9,10], which showed the range of the attraction decreased in de-aerated water. Consensus finally emerged following the observation of a rapidly decaying repulsion prior to the onset of the attraction at long range [11], which signified the presence of pre-existing bubbles on the surface, and which phenomenon was confirmed by a number of later studies [12–15].

Despite this weighty but admittedly indirect evidence, there remains a very strong objection to the existence of nanobubbles. The Laplace–Young equation states that the pressure inside a bubble is greater than the external pressure by an amount inversely proportional to the radius,

\[ p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{R_b} \]

where \( \gamma \) is the surface tension and \( R_b \) is the radius. Accordingly, a 10 nm nanobubble would have an internal pressure of 144 atm, and it should rapidly dissolve as it cannot be in equilibrium with the atmosphere. The challenge is to reconcile the Laplace–Young equation with the experimental evidence for the existence of nanobubbles, and to explore further the origins and properties of the nanobubbles.

2. Forces and images

Fig. 1 shows the attractive force measured between two hydrophobic surfaces (radius 1 mm) in water [3]. The higher resolution and density of the data compared to earlier measurements revealed steps or discontinuities in the force at large separations. These were taken to represent the attachment to the approaching surface of a bubble already on the apposite surface. The bridging bubble subsequently grows laterally and gives rise to the measured attraction. It can be seen from the figure that the force is fitted in detail by a thermodynamic calculation involving six bridging bubbles of radius 300 nm placed strategically off the central axis.

More recent measurements with the atomic force microscope (AFM) have revealed a repulsion prior to the attractive jump into contact (Fig. 2) [11]. The repulsion is
Fig. 1. The steps in the attractive force at long range measured between macroscopic (radius 2 mm), hydrophobic surfaces in water that led to the original idea that nanobubbles existed on such surfaces and that their bridging was responsible for the hydrophobic attraction. The line is a thermodynamic calculation of the force fitted with six bridging bubbles. Reproduced with permission from Ref. [3]. Copyright 1994 Am. Chem. Soc.

Fig. 2. The rapidly decaying repulsion prior to the onset of the long-range attraction that confirmed the pre-existence of the nanobubbles on the hydrophobic surfaces. Reproduced with permission from Ref. [11]. Copyright 1998 Am. Phys. Soc.
Fig. 3. Phase (A, 10° valley to peak), and height (B, 30 nm valley to peak), scanning probe tapping mode images of hydrophobic surfaces in water at pH 5.6 showing the features that are interpreted as nanobubbles. Reproduced with permission from Ref. [16]. Copyright 2001 Am. Phys. Soc.

so rapidly decaying and the separation is so large that it is unlikely to originate from the hydrophobic surfaces themselves, but rather it signifies an interaction between one surface and something sticking out from the other surface. The fact that this object subsequently disappears upon the jump into solid–solid contact provides strong evidence that the object is a nanobubble that was already on the surface prior to the approach of the second surface. The soft compliance region evident approaching hard contact appears to be due to the finite rate of lateral spreading of the bridging nanobubble [8,11].

Those workers who accepted the evidence summarised above for the existence of nanobubbles had imagined them as isolated hemispherical objects sparsely distributed on the hydrophobic surfaces. Therefore, it came as a surprise that the scanning probe tapping mode images of hydrophobic surfaces obtained by Tyrrell and Attard [16] revealed them as irregularly shaped and forming a close-packed, almost interconnected network that virtually covers the surface with a film of gas (Fig. 3).

The evidence that the features indeed represent nanobubbles comes from the phase images, which show that the features are composed of a softer material than the substrate. Further, after contact mode imaging which showed a featureless substrate with less than 0.5 nm root mean square roughness indicating that the features had been scraped aside and destroyed, the nanobubbles re-emerged virtually unchanged within about 20 min [16,17]. Additional evidence was obtained by flushing the cell with ethanol, for which the surface is lyophilic (contact angle 29°), compared to water, for which the surfaces are lyophobic (contact angle 101°). Whereas in water immediately preceding and immediately succeeding the ethanol, the surfaces showed an attractive jump into contact, a strong adhesion, and tapping mode images of nanobubbles; in ethanol there was no attraction, no adhesion, and the tapping mode images were featureless [17].
The fact that the nanobubbles are not circular in cross-section indicates that the forces that pin the contact line or that resist its motion are large compared to the surface tension that seeks to minimise the area of the liquid-vapour interface (see the conclusion below). The variability in the size and shape of the nanobubbles indicates that the nanobubbles are not strictly in thermodynamic equilibrium with each other and with their surrounds. Whereas previous workers had assumed that the separation at which the surfaces jumped into contact equalled the height of the nanobubbles above the surface, and that this equalled their radius of curvature, the images in Fig. 3 show that their height (∼30 nm) is somewhat greater than the position of the jump (∼20 nm, not shown), and that this is substantially less than the radius of curvature at their apex (∼100–300 nm).

3. Nanobubble stability

The nanobubble network imaged in Fig. 3 is reminiscent of the morphology of water droplets condensing on a surface from a supersaturated vapour. In view of the Laplace–Young equation, the convexity of the nanobubbles in Fig. 3 evidently precludes them from being in equilibrium with the atmosphere. An alternative hypothesis is that they are in equilibrium with a supersaturated solution. The possible origin of the supersaturation will be discussed in the concluding section. Here the problem is posed in the language of statistical mechanics as homogeneous nucleation theory, with the particular manifestation being the condensation of liquid droplets from a supersaturated vapour.

Consider a supersaturated system of $N$ molecules in a volume $V$ in equilibrium with a heat reservoir of temperature $T$. The constrained partition function for the case that there are $M$ identical droplets of volume $v = 4\pi R_b^3/3$ containing $n$ molecules is [20]

$$Z(M, n, R_b|N, V, T) = A^{-3N} \int_V \frac{dr^N}{N!} e^{-\beta U}$$

$$= \frac{1}{M!} \left[ A^{-3n} \int_{V - Mc} dr_1 \int_v \frac{dr^{n-1}}{n!} e^{-\beta U_1} \right]^M$$

$$\times \left[ A^{-3(N - Mn)} \int_{V - Mc} (N - Mn)! \frac{dr^{N - Mn}}{(N - Mn)!} e^{-\beta U_v} \right] e^{-\beta U_b}$$

$$= \frac{1}{M!} \left( \frac{V}{v} \right)^M Z(n, v, T)^M Z(N - Mn, V - Mc, T) e^{-\beta \gamma AM}, \quad (1)$$

where $A = 4\pi R_b^2$ is the area of a droplet. Boltzmann’s constant times the logarithm of this is the constrained total entropy, and in general multiplying the latter by $-T$ gives
the constrained thermodynamic potential [18]. For the present cloud of droplets, one obtains

\[
F(M, n, R_b | N, V, T) = M \left[ v f(n/v, T) + \gamma A + k_B T \ln \frac{Mv}{V} - k_B T \right] + (V - Mv) f((N - Mn)/(V - Mv), T). \tag{2}
\]

Here the Helmholtz free energy densities of the bulk liquid and vapour phases appear. If one now assumes that the vapour phase is so much greater than the liquid phase that it forms a reservoir unaffected by the droplets that is characterised solely by its chemical potential and its pressure, then one obtains

\[
F(M, n, R_b | S, T) = M \left[ v f(n/v, T) + \gamma A + k_B T \ln \frac{Mv}{V} - k_B T \right] - M \mu N + Mpv + \text{const}. \tag{3}
\]

If one further assumes that the translational term is negligible, that the gas is ideal, and that the liquid is incompressible with density \( \rho_l \), then after some algebra one obtains the classical expression for the free energy of droplet formation [19],

\[
F(M, n, R_b | S, T) = M \left[ 4 \pi R_b^2 \gamma - \frac{4}{3} \pi R_b^3 \rho_l \ln S \right], \tag{4}
\]

where the supersaturation ratio is \( S = p/p_{\text{coex}} \). Although not essential to the theory, the surface tension of a planar interface was used throughout, since it is known that curvature corrections are negligible for droplets beyond several molecular diameters in radius [21]. The equation of state of Nicolas et al. [22] was used to calculate the Helmholtz free energy densities.

Fig. 4 shows the free energy of a single liquid droplet constrained by its radius, Eq. (2) (but in equilibrium at each \( R_b \) with respect to the number of atoms). The energy barrier to nucleation is evident in the inset; the so-called critical radius is \( R^* \approx 1.5 \sigma \). Because this is a finite-sized system, the vapour is depleted as the droplet grows and the supersaturation ratio is not constant. It can be seen that the classical theory is quite accurate at small radii, but that it overestimates the height of the barrier (the supersaturation ratio used in the classical theory is the final one; the initial supersaturation ratio was negative). The classical theory predicts that the drop will grow without bound, whereas the present theory predicts that it will reach a stable radius at \( R_0 \approx 10 \sigma \) where it is in equilibrium with the vapour. For smaller radii than this equilibrium radius, the chemical potential of the vapour phase is higher than that of the liquid phase, whereas for larger radii the vapour is depleted to the extent that its chemical potential is less than the liquid. It can be seen in Fig. 4 that the present theory predicts quite accurately the radius obtained in the molecular dynamics simulation of the droplet by El Bardouni et al. [23].

Several conclusion can be drawn from Fig. 4. The approximation for the constrained free energy of a droplet, Eq. (2), is quite accurate. Further, it is necessary to take into account the depletion of the gas phase by the growing droplet, at least for the finite system used in the computer simulation. Also, a droplet can reach equilibrium with a supersaturated atmosphere of finite size.
Fig. 4. Constrained free energy of a single liquid drop growing from a supersaturated vapour of Lennard-Jones atoms ($N = 3375$, $V = (31.74\sigma)^3$, $T = 0.65\epsilon/k_B$). The solid line is the full theory for a finite gas phase [20], and the dashed line is the classical idealised theory for a gas reservoir using the final supersaturation ratio $S_f = 5.03$. The arrow signifies the molecular dynamics equilibrium radius [23].

Beyond its obvious utility for computer simulations, where it can be used to predict the size and stability of the droplet, it is arguable that the present theory is also applicable to the real world. The correct thermodynamic limit for a cloud is $N \to \infty$, $V \to \infty$, $M \to \infty$, with $N/V$ and $M/V$ both constant. In other words, the number of vapour atoms per droplet is not infinite. Related to this point is the fact that the growing droplet depletes the vapour in its vicinity, and due to the slow diffusion of the vapour it effectively comes to equilibrium with the local supersaturation. The classical theory can never predict such a local equilibrium despite the fact that clouds (and froths and foams and emulsions) tend to have fairly well-defined radii at any given stage in their evolution.

To explore this issue further, the constrained thermodynamic potential for two droplets in a finite-sized supersaturated system is shown in Fig. 5. It can be seen that the equilibrium state consists of a single large droplet. However, there is a local extremum for two smaller droplets of equal size. This extremum is unstable (it is a saddle point), but because it is rather flat it is likely in practice to be long-lived. The mechanism for the instability is known as Ostwald ripening, where the larger droplet cannibalises the smaller one. One concludes from Fig. 5 that as a cloud evolves the number of droplets decrease but their size increases.

4. Discussion and conclusion

The thermodynamic calculations have implications for the nature and stability of nanobubbles. The curved interfaces revealed by the images indicate that the aqueous phase is supersaturated with gas. However, whilst it is possible for such bubbles to be
in equilibrium with the local supersaturation, one expects them to grow over time at a rate controlled by the diffusion of dissolved gas through the solution. The images in Fig. 3 have the appearance of the late stages in evolution of the bubbles. The fact that they are essentially close packed, and their irregular cross-section and interconnections, indicate that they are limited in their lateral growth by their neighbours. The mechanism for this is undoubtedly the electric double-layer repulsion between their surfaces. The change in morphology of the nanobubbles imaged in Fig. 6 shows that at low charge (pH 3) the bubbles are larger, more irregular, and more interconnected than at high charge (pH 9.4). Such repulsive interactions with neighbours decouples the radius of curvature from the height and the lateral extent of the nanobubbles.
The origin of the supersaturation of the water is unclear. In both the atomic force microscope and the surface forces apparatus the chamber is sealed from the atmosphere after filling with saturated water. Also in both cases, heating of the fluid by either the light-lever laser or the interferometric incandescent globe will lead to supersaturation, although the magnitude of this effect is unknown. Another source of supersaturation is the entrainment of air during the passage of the surfaces through the air–water interface, or during the pumping of the solution through the chamber. More experiments involving controlled gassing and degassing and the temporal evolution of the forces and images are called for.

There are a number of practical implications of nanobubbles. Their presence on hydrophobic surfaces and their bridging accounts for the instability of lyophobic dispersions, the measured long-range attraction and the strong and irreversible adhesion of such colloid particles. Nanobubbles offer the novel possibility of controlling such interactions by varying the amount and type of gas supersaturation of the solution. The fact that the nanobubbles appear to cover hydrophobic surfaces with essentially a gas film also changes the way such surfaces are viewed. In particular, from the point of view of changing the nature of the surface by chemical reaction or by physical adsorption, it appears that more attention should be paid to the liquid–vapour interface than has previously been the case. Finally, an interesting and unexpected consequence of this emerging picture of hydrophobic surfaces concerns the flow of water next to such surfaces and the motion of hydrophobic particles in water. Evidently, nanobubble films greatly reduce the drag compared to the stick boundary conditions traditionally assumed in hydrodynamics. This may account for the finite slip lengths that have been measured in hydrophobed capillaries [24], and can be exploited in applications involving the motion of macroscopic objects in water.

References