



Discussion

Comment on: “On the stability of bubbles trapped at a solid–liquid interface: A thermodynamical approach”

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In a recent letter, Colaço et al. [1] presented a model for the stability of surface nanobubbles. The authors demonstrated that surface nanobubbles are stable on smooth substrates if the contact angle is greater than $\theta_c = 126.6^\circ$, and that surface roughness and encapsulation of a crevice beneath the nanobubble can increase this stability.

The reason that surface nanobubbles have attracted so much interest recently is their apparent stability [2]. They form from air dissolved within the liquid, so should diffuse back in microseconds. However they persist for at least 10 orders of magnitude longer than this expectation [3]. Trying to understand this discrepancy has led to several competing theories, including stability via a nonequilibrium mechanism of diffusive gas outflux at the apex versus attractive gas influx at the contact line [4], and stability due to diffusion-limiting contamination at the liquid–gas interface [5].

In the model of Ref. [1], they overcome the problem of diffusion by assuming the nanobubbles are made from vapor, despite the overwhelming evidence for the predominance of air [3]. They then compare the Gibb's energies between a system composed of a substrate immersed in liquid with no bubbles, and a similar system containing a single vapor bubble adhered to the substrate. The fact that they consider vapor bubbles rather than air allows them to express the chemical potential as a function of curvature, through the Kelvin equation. In their Eq. (6), Colaço et al. [1] write an expression for the stability of a nanobubble as a function of contact angle. If this expression is negative (positive) the nanobubble is stable (unstable). The authors conclude from this equation that nanobubbles are stable if the contact angle is greater than $\theta_c = 126.6^\circ$. However, their Eq. (6) is non-negative and never passes through zero, i.e. $\theta = 126.6^\circ$ is not a solution. This has led us to examine the model of Ref. [1] in more detail, and we have found some inaccuracies which, we believe, seriously affect the main conclusions that they draw.

Firstly, although not stated in Ref. [1], their two systems must be bounded by walls on all sides, since any other curvature would set up a chemical potential gradient with the curvature of the nanobubble, thus putting the system out of equilibrium. This removes any applicability of the model to describe experimental re-

sults, where most often a liquid droplet is used, and always an atmosphere–liquid interface partially exists. The initial liquid system has volume V_0 and Gibb's energy $\mu_0 N_0$. The final system's volume is the same, $V_l + V_v = V_0$, while its Gibb's energy is $\mu_l N_l + \mu_v N_v + f_A$, where f_A is a known contribution for the additional surface area, and the subscripts refer to liquid and vapor. Because the bubble is vapor rather than air, a condition for equilibrium is $\mu_l = \mu_v$. Thus, the difference in Gibb's energy between the two systems is $\Delta G = \mu_l(N_l + N_v) - \mu_0 N_0 + f_A$.

The vapor phase will have a lower density than the liquid phase in the final system. Hence, the constant volume constraint imposed above implies that particles from this liquid phase must leave the system to make room for the vapor, i.e. $N_l + N_v < N_0$. (An alternative solution to this issue would be if the pressure in the liquid phase increases above that of the nanobubble, but this would lead to annihilation of the nanobubble.) Colaço et al. [1] set the number of particles in both systems equal but it is the *difference* in energies we are interested in so *this* difference cannot be ignored.

Furthermore, we believe that the Kelvin equation is not applicable here. The Kelvin equation describes the change in chemical potential due to a change in curvature. For a liquid–vapor interface, the change in the liquid's chemical potential due to curvature is $\mu_l^{curv} - \mu_l^{flat} = \frac{V_l}{N_l} \Delta p$, the change in that of the vapor is $\mu_v^{curv} - \mu_v^{flat} = kT \log \frac{p_{curv}}{p_{flat}}$, and these two expressions must be equal to one another at equilibrium (note that it is the liquid volume that appears in the Kelvin equation and not, as used by Ref. [1], the vapor volume). In the current problem, the first system has no liquid–vapor interface so we cannot measure a *change* in its curvature. Instead, to reach the second system we must *create* an interface. Thus use of the Kelvin equation here is invalid. Instead, we would require knowledge of explicit expressions for the chemical potentials in both systems, which we do not possess.

Finally, in Ref. [1] the authors demonstrate that adding surface roughness further stabilizes surface nanobubbles. The surface roughness model is saw-tooth, and must be azimuthally symmetric in order to preserve a constant contact angle. The correct geometric factor is then $r = 1/\sin \phi$, and not the square of this as used by the authors (we note that the substrate area covered by the bubble is the same as an equivalently half-angled cone). Conceptually, adding surface area will only act to *increase* the energy of the system as $\gamma_{sv} A$.

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To conclude, we believe that the model for the stability of vaporous surface nanobubbles proposed by Colaço et al. [1] is ill-posed and incorrect. Surface nanobubbles are composed predominantly of air, not vapor, and their surprising stability remains a mystery.

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