

Comment on “Universal Gas Adsorption Mechanism for Flat Nanobubble Morphologies”

In a recent Letter, Petsev, Leal, and Shell (PLS) [1] intriguingly attribute the low contact angles of surface nanobubbles to adsorption of gas molecules to liquid-immersed surfaces. Although the flattening effect might plausibly occur on highly adsorbing commercial gas capture materials, we show in this Comment that the proposed effect is negligible in systems encountered experimentally and, thus, cannot be the “universal” reason for small contact angles.

The Letter uses an adsorption constant range $10^{-6} < K_{eq}^A < 10^{-4} \text{ Pa}^{-1}$ that originates from literature values of metal organic frameworks (MOFs) and carbon molecular sieves (CMSes)—functional materials renowned for their gas capture capabilities [2]. Its conclusion that adsorptive flattening is universal to all experiments assumes that the lower bound $K_{eq}^A \sim 10^{-6} \text{ Pa}^{-1}$ is easily exceeded by conventional or experimentally encountered materials like HOPG [3].

The adsorption strength of a material is typically quantified by adsorption enthalpy ΔH rather than K_{eq}^A (the latter is model dependent [4]). PLS’s indicative range relies on CO_2 adsorption to two landmark sites in Mg-MOF-74, with $K_{eq}^A = 2.49 \times 10^{-4}$ and $1.28 \times 10^{-6} \text{ Pa}^{-1}$, or $\Delta H = 42$ and 24 kJ/mol [5]. In contrast, computational [6,7] and experimental [8,9] investigations of N_2 -HOPG find $\Delta H = 2\text{--}10 \text{ kJ/mol}$. In the single-site Langmuir adsorption model used in the Letter [4],

$$K_{eq}^A = V_b e^{\Delta H/k_B T} / k_B T, \quad (1)$$

where V_b is the binding site volume. Since K_{eq}^A increases monotonically with ΔH , the K_{eq}^A of N_2 -HOPG must be smaller than the model’s lower bound.

To determine the extent of the model’s overestimate, we estimate the ratio between K_{eq}^A for N_2 -HOPG and CO_2 -Mg-MOF-74 by Eq. (1), assuming equal V_b (N_2/CO_2 have similar 0.33/0.35 nm diameters). Depending on ΔH pairs between N_2 -HOPG (2–10 kJ/mol) and CO_2 -Mg-MOF-74 (24 or 42 kJ/mol), we find $10^{-13} < K_{eq}^A < 10^{-9} \text{ Pa}^{-1}$, i.e., 3–7 orders below the lower bound. Alternatively, PLS estimate their lower bound by extrapolating the $K_{eq}^A \sim 10^{-6} \text{ Pa}^{-1}$ of CMSs to HOPG, arguing that the two are chemically similar. However, two chemically *identical* materials yield different K_{eq}^A if one possesses a higher specific surface area A and, thus, more adsorption sites $n \propto A^{3/2}$ per unit mass. While CMSs are nanoporous ($A \sim 1000 \text{ m}^2/\text{g}$ [10]), natural graphite has $A = 0.6\text{--}8.9 \text{ m}^2/\text{g}$ [11,12]; for atomically- flat HOPG, A is even smaller. Since $1/K_{eq}^A$ defines the pressure at which

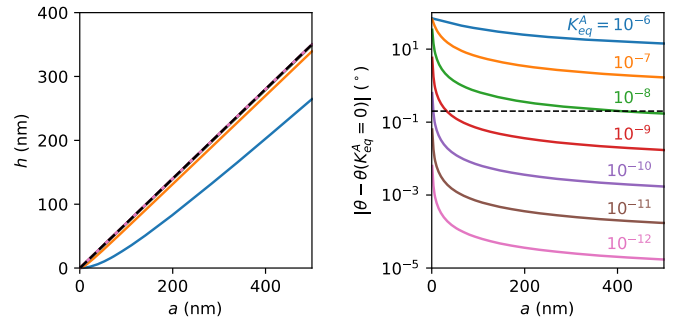


FIG. 1. Left: predicted nanobubble heights h for $10^{-12} < K_{eq}^A < 10^{-6} \text{ Pa}^{-1}$ (legend on right); the zero adsorption case is in the black dashed line. Following Fig. 2 and Eq. (5) of the Letter [1], we assume $\theta_e = 70^\circ$ and $\gamma = 73 \text{ mN/m}$. Right: contact angle reduction relative to zero adsorption case; indicative error of an atomic force microscope $\Delta\theta \sim 0.2^\circ$ is marked in the dashed line.

half of adsorption sites are occupied [4], neglecting porosity implies a 3–6 order overestimate of the N_2 -HOPG K_{eq}^A .

The model has little margin to accommodate an overestimate of the lower bound K_{eq}^A . Reevaluating Eq. (5) of the Letter [1] for $10^{-12} < K_{eq}^A < 10^{-6} \text{ Pa}^{-1}$, we find that adsorptive flattening is only marginally discernible from the zero adsorption case (Fig. 1 left, black dashed line) if $K_{eq}^A \sim 10^{-7}$ (Fig. 1, orange curve), an order below the 10^{-6} Pa^{-1} “weak adsorption” limit (Fig. 1, blue curve). The effect is negligible—i.e., not discernible by atomic force microscopy—should the true K_{eq}^A be 2 orders or more below the weak limit (Fig. 1, right).

Finally, we note that there are several other viable mechanisms [3,13]—ambient gas supersaturation in the liquid, line tension, and sensitivity of AFM imaging forces to bubble size—that can lead to unexpectedly small contact angles, without assuming unreasonably strong gas-substrate interactions. Our observations are relevant to recent reports attributing other unusual properties of surface nanobubbles to adsorption, particularly those relying on the authors’ choice of adsorption constants [14].

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