Petsev et al. Reply: Tan et al. [1] provide a thoughtful analysis suggesting that, while our model in Ref. [2] appears correctly derived, it may not predict significantly reduced contact angles in common experimental nanobubble systems (e.g., mica, HOPG, hydrophobized silicon, etc.) due to the choice of adsorption constant K_{eq}^A. Given the absence of direct measurements of K_{eq}^A for nanobubble-relevant substrates, discussion that aims to pin down this value is important. Tan et al. [1] indirectly estimate that K_{eq}^A ranges between 10^{-13} and 10^{-9} Pa^{-1}, 3–7 orders of magnitude smaller than the smallest value we considered. They correctly state that the influence of gas adsorption on nanobubble morphology is negligible for $K_{eq}^A \leq 10^{-8}$.

We highlight recent work by Teshima et al. [3] that investigates surface nanobubbles with molecular dynamics simulations. These authors estimate $K_{eq}^A = 0.43 \times 10^{-7}$ and $K_{eq}^A = 1.53 \times 10^{-7}$ Pa^{-1} for the two different solid-gas interactions representative of N$_2$ nanobubbles on graphene and agree that their values are "significantly smaller than the K_{eq}^A values used in Petsev's study"; however, their values are not as dramatically small as in Tan et al.'s [1] analysis. Moreover, Teshima et al. observe the angle-reducing adsorption effect in their simulations for smaller nanobubbles, and their contact angles agree with our model's prediction using the measured K_{eq}^A [see Fig. 4(b) in Ref. [3]]. Therefore, while gas adsorption may not be significant for all substrates and nanobubble sizes, the effect does not appear completely negligible.

While Tan et al.'s analysis [1] is valuable, more work is necessary to accurately determine the adsorption constant, which may vary widely due to material-specific factors. To illustrate this, we estimate K_{eq}^A using a simple statistical mechanical model, showing that K_{eq}^A is highly sensitive to molecular interaction parameters and can span orders of magnitude. First, we write the Langmuir adsorption constant as [2]

$$K_{eq}^A = \Lambda^3 \zeta / k_B T. \tag{1}$$

Here, ζ is the partition function for a single adsorbed molecule, and Λ is its thermal de Broglie wavelength. In the harmonic oscillator approximation, ζ is given by [4]

$$\zeta(T) = q_x q_y q_z \exp(-U_{00}/k_B T), \tag{2}$$

where q_x, q_y, and q_z are one-dimensional harmonic-oscillator partition functions and U_{00} is the potential energy minimum for the adsorbed molecule on the surface. The vibrational partition functions are [4]

$$q_x = q_y = q_z = \frac{\exp(-\Theta/2T)}{1 - \exp(-\Theta/T)}, \tag{3}$$

with $\Theta = h\nu/k_B$. This simple model assumes a perfectly flat substrate and single-layer adsorption. The two unknown quantities are the vibrational frequencies for
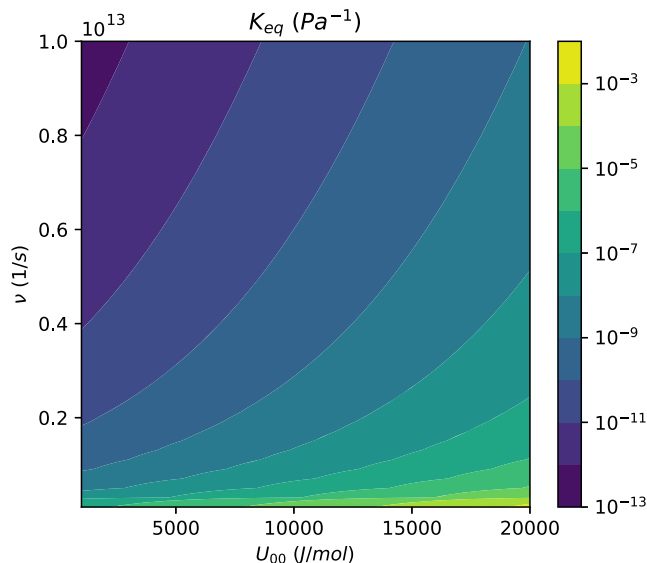

FIG. 1. Estimate for the adsorption constant as a function of the molecular vibrational frequency and interaction potential energy minimum.

the adsorbed molecule, ν, and the molecule-wall interaction energy U_{00}. Note that ν describes vibrations of the position of the molecule in the potential well and *not* intramolecular bond vibrations. Hill [4] suggests that ν is typically "a little less than 10^{12} sec^{-1}" and provides values for argon adsorbing to an unspecified substrate: $\nu = 5 \times 10^{12}$ s^{-1} and $U_{00} = 6276$ kJ/mol. At $T = 293.15$ K for N$_2$, the estimate for K_{eq}^A is indeed low at 3.89×10^{-11} Pa^{-1}. However, absent precise values for the vibrational frequencies, K_{eq}^A is very sensitive to ν for realistic choices. Figure 1 shows the estimated K_{eq}^A as a function of both ν and U_{00} for frequencies ranging from 10^{11} to 10^{13} s^{-1} and energies 2–20 kJ/mol. While sizable regions have very low ($<10^{-8}$) adsorption constants, the possible values of K_{eq}^A can range between 10^{-2} and 10^{-13}, 11 orders of magnitude. Therefore, our model may not apply to all nanobubble systems, but it remains unclear where different substrates lie in the space in Fig. 1 and if Tan et al.'s argument [1] holds for all experimentally relevant substrates or a subset. Future theoretical and experimental analysis may give further insight into this important problem.

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