

# Quantitative Measure of Hydrophobicity: Experiment and Theory

Laura A. Deschenes, Patrick Zilaro, Laura J. Muller, John T. Fourkas,\* and Udayan Mohanty

Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02167

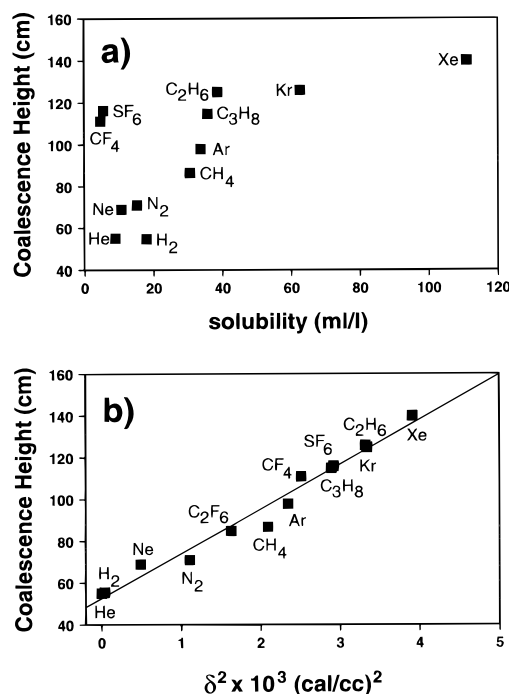
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The strength of the forces between bubbles of various hydrophobic gases is determined by monitoring the coalescence rate of bubbles. A theory is formulated to elucidate the role of hydrophobicity in the rupture of the film between two hydrophobic surfaces and to develop thereby a first-principles parameter for the strength of hydrophobic forces. The theory is shown to be in quantitative agreement with the experimental data. On the basis of these results, it is demonstrated that the vacuum is the most hydrophobic “solute” possible.

Hydrophobic interactions are ubiquitous in nature<sup>1–3</sup> and are linked intimately to processes such as the folding of proteins<sup>4</sup> and the binding of enzymes to substrates.<sup>5</sup> Accordingly, hydrophobic interactions have received considerable theoretical and experimental attention, although often with results that appear to be conflicting. While it is well accepted that the “hydrophobic effect” causes short-range attractions between hydrophobic molecules in water, it remains possible that other, long-range forces also exist between hydrophobic solutes. It has proven remarkably difficult to develop a uniform consensus on the details or even the existence of such forces, due in part to the experimental challenges of studying the interactions of relatively insoluble molecules and the lack of a unique, quantitative, nonempirical measure of the strength of hydrophobic forces.<sup>6</sup>

The water liquid/vapor interface is believed to be hydrophobic,<sup>7</sup> and it has therefore been suggested that hydrophobic forces are involved in the rupture of films between a bubble and a hydrophobic surface<sup>8</sup> and in the coalescence of bubbles.<sup>9</sup> The difficulties associated with studying insoluble molecules are circumvented with bubbles, which can be generated continuously, reproducibly, and in large numbers. Here we demonstrate that the coalescence of bubbles is a sensitive probe of hydrophobic forces. By considering the forces that lead to the rupture of the film separating two bubbles, we develop a quantitative measure of hydrophobicity that is in excellent agreement with our experimental data.

Our experimental apparatus, which is similar to that of ref 9, consists of a 140-cm tall glass column with an inner diameter of 18 mm, fitted at the bottom with a medium-porosity (30- $\mu$ m pore size) glass frit. The column is flushed with water several times before being loaded with a fixed volume of ultrapure water (Millipore Milli-Q Plus) that has been degassed<sup>10</sup> by sonication under vacuum and then allowed to return to room temperature. Careful cleaning of the column between samples with a concentrated chromic acid/sulfuric acid mixture was not found to affect experimental results, so measures to prevent the presence of small quantities of organic impurities were not deemed necessary. After the sample is loaded in the column, gas is bubbled through the frit at a flow rate of 6.4 mL/s to create uniform, small bubbles that coalesce as they rise. The qualitative nature of the results is independent of the gas flow rate used. The size of the bubbles released from the frit was observed to be the same for all gases studied. Thus, the average height above the frit at which bubbles of a predetermined size are formed serves as a sensitive indicator of the coalescence rate.



**Figure 1.** Coalescence height (at 21 °C and atmospheric pressure) as a function of (a) gas solubility and (b) square of the solubility parameter. The marker height is approximately 2 standard deviations. The solid line in (b) is a linear least-squares fit. Solubilities are from ref 11 and solubility parameters from ref 18.

For the data reported here, the “coalescence height” ( $h_c$ ) is defined as the average formation height of bubbles 1.2-cm in diameter. The coalescence height is determined by monitoring the column for 5–10 min with a video camera. Each video clip contains footage of 10–15 bubbles of the desired size. The appropriate video frames are digitized so that the coalescence height can be measured by computer, generally with a standard deviation of about 2 cm.

To determine the role of hydrophobic forces in bubble coalescence,  $h_c$  was measured in pure water for 13 sparingly soluble gases. The coalescence height for these gases is plotted versus the solubility<sup>11</sup> in Figure 1a. Although molar solubility (or, equivalently, Ostwald solubility) is commonly used as an indicator of relative hydrophobicity, Figure 1a demonstrates clearly that solubility does not provide a quantitative scale of the strength of the forces driving bubble coalescence.<sup>6</sup> To elucidate the role of hydrophobic forces in bubble coalescence, we present a theoretical model of the coalescence process.

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We assume that the bubbles coalesce in pairs that encounter one another diffusively, at which point there is some probability that a pair will coalesce before they can diffuse apart again. The effective rate constant for this process can then be written as

$$k_{\text{eff}} = \frac{k_a k_d}{k_a + k_d} \quad (1)$$

where  $k_d$  is the rate of diffusive encounters/separations and  $k_a$  is the rate of reaction of encounter pairs.<sup>12</sup> We must therefore establish the role that hydrophobic forces play in the determination of  $k_a$ .

The film between two bubbles or a between a bubble and a hydrophobic surface is known to rupture at distances on the 1000-Å scale.<sup>8</sup> Since the hydrophobic effect operates on a distance scale that is 2 orders of magnitude smaller, bubble coalescence must be driven by other interactions with a longer distance scale. While there is experimental<sup>13</sup> evidence for such interactions, there exists as yet no consensus as to the mechanism of these long-range forces. Yaminsky and Ninham have shown that to stretch the liquid in the gap between hydrophobic surfaces requires less energy than to stretch the liquid in the bulk.<sup>15</sup> There is a consequent enhancement of thermal expansion in the direction parallel to the surfaces,<sup>15</sup> which leads to a long-range cavitation force per unit area. The operational distance scale of this mechanism is in the range of 100 Å, however, which is still too short to account for the rupture of the film between bubbles at a distance scale of 1000 Å.

Yaminsky and Ninham have also pointed out that the enhanced thermal fluctuations of water at a hydrophobic interface can lead to rupture of films on the relevant distance scale.<sup>15</sup> As two bubbles approach one another, the surface tension of the bubbles leads to a transverse stress in the film between them. Because of this stress, a large enough fluctuation in the surface of one bubble will form a "crack" that is able to propagate, thereby creating a channel between the bubbles that leads to the rupture of the film.

We proceed by assuming that the process that leads to the rupture involves one or more order parameters  $n$ . The free energy  $G$  that describes the process (which includes terms for the solvent, the solute, and the interactions between them) can be parameterized in terms of  $n$ . We denote the thermodynamic variable responsible for the driving force in the nucleation crack model by  $x$ , the fluctuations of the variable by  $\delta x$ , and the mean-square fluctuations of the variable by  $\langle(\delta x)^2\rangle$ . Fluctuations smaller than some critical size  $\delta x_{\text{min}}$  cannot nucleate a crack. Since the transverse stress decreases with increasing film thickness  $R$ ,  $\delta x_{\text{min}}$  increases with increasing  $R$ , and for thick enough films the probability of having a critical fluctuation is infinitesimal.

From fluctuation theory,<sup>16</sup> the probability that the driving force has a certain value is expressible in terms of the fluctuations  $\delta x$ :

$$P(\delta x) = \frac{1}{[2\pi\langle(\delta x)^2\rangle]^{1/2}} e^{-(\delta x)^2/2\langle(\delta x)^2\rangle} \quad (2)$$

The average transition probability per unit time for a critical fluctuation as a function of  $R$  is given by

$$\bar{W}(R) \propto \int_{\delta x_{\text{min}}(R)}^{\infty} P(\delta x) d(\delta x) = \frac{1}{2} \operatorname{erfc} \left[ \frac{\delta x_{\text{min}}(R)}{[2\langle(\delta x)^2\rangle]^{1/2}} \right] \quad (3)$$

For large enough values of the argument of the complementary error function, we can approximate

$$\bar{W}(R) \propto \frac{1}{\sqrt{2\pi}} \frac{\langle(\delta x)^2\rangle^{1/2}}{\delta x_{\text{min}}(R)} \quad (4)$$

We must now establish the connection between  $\langle(\delta x)^2\rangle$  and the identity of the gas.

We can express  $\langle(\delta x)^2\rangle$  in terms of fluctuations of the entropy  $S$  via

$$\langle(\delta x)^2\rangle \simeq \left(\frac{\partial x}{\partial S}\right)_P^2 \langle(\Delta S)^2\rangle_P \quad (5)$$

The driving force is due to fluctuations in the Gibbs free energy with the order parameter(s), so

$$x = \left(\frac{\partial G}{\partial n}\right)_V = \left(\frac{\partial G}{\partial P}\right)_V \left(\frac{\partial P}{\partial n}\right)_V \equiv VB(n) \quad (6)$$

where  $B(n)$  is a function of the order parameter. Inserting this result into eq 5 yields

$$\langle(\delta x)^2\rangle \simeq C_P \left( B \frac{\partial V}{\partial S} + V \frac{\partial B}{\partial S} \right)_P^2 \quad (7)$$

We assume that the second term in parentheses is negligible and apply the Maxwell relation for  $(\partial V/\partial S)_P$  to find

$$\langle(\delta x)^2\rangle \simeq C_P \left( B \frac{\partial T}{\partial P} \right)_S^2 \simeq C_P \left( B \frac{\kappa}{\alpha} \right)^2 \quad (8)$$

where  $\kappa$  is the isothermal compressibility,  $\alpha$  is the coefficient of thermal expansion, and we have assumed that the coefficient of isentropic compressibility is negligible. Combining this result with eq 4 yields

$$\bar{W}(R) \propto \sqrt{\frac{C_P}{2\pi}} \frac{B\kappa}{\alpha \delta x_{\text{min}}(R)} \quad (9)$$

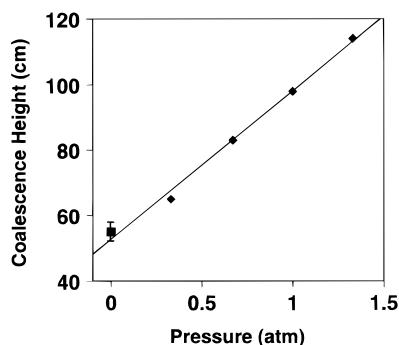
At large enough distances  $R$ , there is a vanishing probability that the film will rupture; however, the probability of rupture becomes significant below some critical value of  $R$  and is proportional to  $\kappa/\alpha$  at all distances. We therefore conclude that  $k_a$  is also proportional to  $\kappa/\alpha$ .<sup>17</sup>

The rate constants  $k_d$  and  $k_a$  are approximately independent of the bubble radius, so the measured coalescence height is proportional to

$$h_c \propto \frac{1}{k_{\text{eff}}} = \frac{1}{k_d} + K \frac{\alpha}{\kappa} \quad (10)$$

where  $K$  is a constant. The quantity  $\alpha/\kappa$  is proportional to the square of the "solubility parameter" of Hildebrand,<sup>18</sup> which we denote by  $\delta$ . The coalescence height is plotted as a function of  $\delta^2$  for each gas in Figure 1b. This plot is in excellent agreement with eq 10 establishing a direct connection among  $\delta$ , hydrophobicity (and the consequent enhancement of thermal fluctuations of the bubble surfaces), and the coalescence rate of the bubbles of a gas.<sup>19</sup>

The solubility parameter has proven particularly useful in predicting the solubility of nonpolar solutes in nonpolar liquids.<sup>18</sup> The square of the solubility parameter is proportional to the cohesive energy density of a liquid (i.e., its energy of vaporization per unit volume). The cohesive energy density of a solute that has no specific interactions with water might be expected to provide a reasonable estimate of the favorability of aqueous solvation of that solute, which in turn should be related to the hydrophobicity of the solute. Any solute that adds cohesiveness to the liquid would be expected to decrease the enhancement



**Figure 2.** Coalescence height as a function of external pressure for argon at a constant volume flow. The “zero” pressure data point is the diffusion-limited coalescence height for helium at 1 atm of external pressure. The error bar represents  $\pm 1$  standard deviation.

of thermal fluctuations at a hydrophobic interface. The implication of this result is that vacuum, by virtue of its complete lack of attractive interactions with water, is the most hydrophobic “solute” possible. Comparison of simulations of the structure of water at hydrophobic<sup>14</sup> and vacuum<sup>20</sup> interfaces supports this notion.<sup>7</sup> Thus, the coalescence height should increase linearly with the concentration of gas in the bubbles. To test this prediction,  $h_c$  was measured for argon at a range of external pressures.<sup>21</sup> The results of these experiments, which are shown in Figure 2, are in excellent agreement with the theory, further supporting the role of the solubility parameter and of hydrophobicity in the coalescence of bubbles.

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- (7) It has been noted that the comparison of the interface between liquid water and a hydrophobic surface with the interface between liquid water and water vapor should be made with caution; in particular, both the enthalpy and entropy of water molecules decrease at a hydrophobic interface and increase at the vapor interface.<sup>1</sup> However, in dissolving a hydrophobic molecule in water a cavity must still be formed, with an attendant increase in enthalpy; solvating any molecule in this cavity will lead to a decrease in enthalpy, and this enthalpy change should not be taken alone as an intrinsic feature of hydrophobicity. Furthermore, it is the orientational entropy of water that is the hallmark of hydrophobicity, and computer simulations demonstrate convincingly that this entropy is less at the vapor interface<sup>21</sup> than at a hydrophobic interface.<sup>14</sup> Water at the vapor interface is much less constrained than water at a hydrophobic interface, so the decrease in orientational entropy at the vapor interface is masked by the large increase in entropy from other degrees of freedom.
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