

Influence of Dissolved Gas on the Interaction between Hydrophobic Surfaces in Water

Håkan Wennerström

Division of Physical Chemistry 1, The Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, SE-22100 Lund, Sweden

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We analyze how the interaction between two hydrophobic surfaces in water depends on the amount of dissolved gas. At equilibrium there is, for a truly hydrophobic surface with contact angle $\theta > 90^\circ$, a long range attractive force. The attraction is due to the formation of a gaseous film between the surfaces. For a completely degassed sample the gas consists of water vapor and the range of the force is of order 500 nm at ambient conditions. In the other extreme where the water is saturated with gas with respect to the atmosphere the range of the equilibrium force is determined by the hydrostatic pressure and it diverges as the distance between the surface setup and the air–water interface goes to zero. It is generally considered that the formation of a gaseous film is a kinetically very slow process so that one in practice stays on the metastable liquid branch until an instability appears at short separations. For the particular case of formation and stability of oil in water emulsions in the absence of stabilizer a degassing will affect at least two crucial steps in the process. In the formation of droplets, new interfaces are formed and separated from short distances. The presence of dissolved gas, in both oil and water, facilitates the formation of gas bubbles between the surfaces. Furthermore, the lifetime of gas bubbles adsorbed on the interface is substantially prolonged in the presence of dissolved gas and they can act as nucleation centers for the formation of a gaseous lens between two oil droplets at re-encounters.

The nature of the interaction between hydrophobic surfaces in water continues to present an enigma in colloid science.^{1–3} In a recent paper by Pashley⁴ on the stability of surfactant-free oil in water emulsions the role of dissolved gas^{5,6} is put into focus. In this Letter we present a simple analysis that shows how dissolved gas has a substantial effect on the equilibrium interaction between two hydrophobic surfaces with a contact angle $\theta > 90^\circ$. We also discuss mechanisms by which the extent of dissolved gas could influence the stability in a binary oil plus water system.

Consider the case of two identical parallel hydrophobic surfaces with area A and at a separation d immersed in a water bath at temperature T . The system is kept at an external pressure p_{ext} at the top of the container. At the position of the surfaces a distance h below the liquid vapor interface there is an additional hydrostatic pressure $p_{\text{hyd}} = \rho_{\text{H}_2\text{O}}gh$. We allow for the possibility that there is some dissolved gas, g , in the water, which in practice is nitrogen and oxygen from the air. The amount of dissolved gas is expressed through the partial pressure p_g and the saturation pressure is p_g^{eq} . The vapor pressure of the water also contributes to the total pressure in the external gas phase.

The dissolved gas acts as a molecular impurity in the water and, being hydrophobic, it will accumulate to some extent close to the hydrophobic surfaces. However, at ambient pressures typical nitrogen and oxygen saturation concentrations are of order millimolar and their surface activity is limited. At the air–water interface the liquid density goes to its bulk value on a short length scale.⁷ Also at a hydrophobic surface one expects a density depression,^{8,9} and this effect is slightly enhanced by the presence of the dissolved gas but the decay to the bulk conditions should occur on approximately the same length scale as for the air–water interface. A more significant role of the dissolved gas is that it can act as a source or sink for a local gaseous phase between the surface. It is accepted that one source

of the observed attractive interaction between hydrophobic surfaces is the occurrence of gas bubbles^{3,10,11} bridging the surfaces. We thus consider the transition from liquid to gas in the space between the surfaces. This is just one manifestation of the more general phenomenon of capillary-induced phase separation¹² (CIPS).

In a thermodynamic approach the CIPS phenomenon is seen as the competition between a surface term

$$G_{\text{surf}} = 2A(\gamma_{\text{sg}} - \gamma_{\text{sw}}) \quad (1)$$

that favors the formation of a new phase if the contact angle exceeds 90° . The surface term is balanced by a bulk term describing the free energy cost

$$G_{\text{bulk}} = kT(n_g \ln(p_g/p_g^{\text{eq}}) + n_{\text{H}_2\text{O}} \ln(p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^{\text{eq}})) \quad (2)$$

of transforming a volume Ad from the bulk to the incipient phase. Here we have assumed ideal gas behavior, which also implies the validity of Dalton's law. Furthermore γ_{ij} denotes the surface free energy between media i and j (s = solid, w = water, g = gas). The pressure is not constant within the system and the transition from liquid to gas involves a change in volume, ΔV . This gives another free energy term from the pressure–volume work

$$G_{\text{exp}} = \{(p_{\text{ext}} + p_{\text{hyd}} - (p_g + p_{\text{H}_2\text{O}}))\Delta V \quad (3)$$

For the case that the local pressure in the gas phase matches the external pressure this contribution is zero, as it should for a truly constant pressure system.

For two parallel planar surfaces the gap between them will be completely filled with either liquid or gas at equilibrium. In the latter case a meniscus will appear at the rim of the macroscopic surfaces. This meniscus is pinned by the rim and

a local equilibrium will be established between the gas phase of fixed volume and the liquid. Under such circumstances the partial pressure in the gas is simply the equilibrium pressure at the given temperature. For a completely degassed sample we then have $p_g = 0$ and $p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^{\text{eq}}$, whereas for a liquid saturated with air $p_g + p_{\text{H}_2\text{O}} = p_{\text{ext}}$. For both these cases the free energy contribution from eq 2 is equal to zero, whereas the pressure volume term of eq 3 provides an energy penalty for forming the gas phase. The distance d_{crit} at which a gaseous phase should appear is obtained by balancing the contributions from eqs 1 and 3 and

$$d_{\text{crit}} = 2\Delta\gamma/(p_{\text{ext}} + p_{\text{hyd}} - p_g - p_{\text{H}_2\text{O}}) \quad (4)$$

where $\Delta\gamma = \gamma_{\text{sw}} - \gamma_{\text{sg}}$. For a completely degassed sample $p_g = 0$ and with typical values of $\Delta\gamma = 25 \text{ mJ/m}^2$, $T = 298 \text{ K}$ giving an equilibrium water vapor pressure of 250 Pa and with $p_{\text{ext}} = 1 \times 10^5 \text{ Pa}$ the calculated value for the critical distance is $d_{\text{crit}} \approx 500 \text{ nm}$,¹³ as long as the hydrostatic pressure is only moderately strong. In the other extreme when the system is saturated with gas, the only resistance for the formation of gas between the surface arises from the hydrostatic pressure and¹⁰

$$d_{\text{crit}} = 2\Delta\gamma/p_{\text{hyd}} \quad (5)$$

For surfaces located 1 cm below the interface $p_{\text{hyd}} \approx 100 \text{ Pa}$ and $d_{\text{crit}} \approx 0.5 \text{ mm}$. For both the degassed and the saturated system the equilibrium transition to a gaseous film occurs at very large separations.

The corresponding equilibrium force, F , is easily obtained by noting that once the gaseous film has appeared, a change of distance between the surfaces only amounts to decreasing the volume of the gas phase and

$$F/\text{area} = -(p_{\text{ext}} + p_{\text{hyd}} - p_g - p_{\text{H}_2\text{O}}) \quad (6)$$

for $d < d_{\text{crit}}$ and zero otherwise.

In practice, it is the forces between particles with curved surfaces that are more relevant. A virtue of considering equilibrium conditions is that one can apply the Derjaguin approximation also for the CIPS case¹² although the system is not laterally homogeneous. However, a requirement is that the radius of the particles should be larger than d_{crit} , which is not always fulfilled. If no one can estimate that a gaseous lens will form at a separation of closest approach between particles of the same order as the particle radius, then a strong attractive force appears.

For the case of a capillary-induced phase separation, the application of the Derjaguin approximation yields a force that increases linearly with decreasing separation. This results also emerge explicitly from eqs 1–3. Long-range forces with the characteristic linear dependence of the force between curved surfaces have been observed.^{14–16} However, when the attraction between hydrophobic surfaces is measured, one does not observe a long range force with the characteristics predicted above for cases where the theory should apply.³ The accepted explanation is, there is such a large barrier for nucleating the gaseous phase¹⁷ that the system in reality remains on the metastable liquid branch up to relatively short separations $\leq 10 \text{ nm}$. Even though the barrier for gas formation is high, it is clear that it is relatively lower in the presence of dissolved gas than in its absence and the short-range instability should be met at a somewhat larger separation in this case.

When one considers the case of two hydrophobic surfaces that are originally in contact and then separated in an aqueous

medium, the problem of nucleating the gas phase is less relevant. If there is no driving force for the liquid to enter the gap between the surfaces, the void will rather be filled with water vapor or gas previously dissolved in the medium. The equilibrium force required to separate the surfaces is clearly much smaller for a system saturated with gas than for a degassed system. As the gap widens, a bubble bridging the two surfaces develops until it finally becomes thermodynamically unstable and the gas redissolves.¹⁸

In a recent paper⁴ Pashley reports that emulsion stability is strongly affected by the presence of dissolved gas. It is clear that the equilibrium CIPS force is not operating in this case, similar to what is found in surface force experiments. On the other hand the analysis of the equilibrium conditions suggests two mechanisms that should both, and possibly in combination, affect the properties of the system. The dispersion of a bulk oil phase into droplets in water necessarily involves a stage where freshly formed hydrophobic surfaces are separated from each other. The analysis presented above demonstrates that under those conditions with the surface in proximity the gaseous phase is strongly favored. Under these conditions the presence of dissolved gas could make a substantial difference for the transient behavior. One can also note that the solubility of gases such as nitrogen and oxygen are a factor of 5–10 higher in hydrocarbons than in water so the oil can also be a significant reservoir for gas molecules. A further effect is that once gas bubbles are formed either floating in the bulk or, more likely, adsorbed to a hydrophobic surface, their lifetime is strongly affected by conditions in the bulk. For a degassed sample, the gas in the bubbles can dissolve rapidly and the bubble disappears, whereas for a system saturated in gas the dissolution process goes by an Ostwald ripening mechanism and bubbles remain in the system for much longer times and they can act as nucleation centers for the formation of a gaseous lens between two particles as they approach one another.

References and Notes

- (1) Pashley, R. M.; Israelachvili, J. N. *Colloids Surf.* **1981**, 2, 169.
- (2) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992.
- (3) Christensson, H. K.; Claesson, P. M. *Adv. Colloid Interface Sci.* **2001**, 91, 391.
- (4) Pashley, R. M. *J. Phys. Chem. B* **2003**, 107, 1714.
- (5) Craig, V. S. J.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* **1993**, 97, 10192.
- (6) Karaman, M. E.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* **1996**, 100, 15503.
- (7) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Clarendon Press: Oxford, U.K., 1982.
- (8) Forsman, J.; Jönsson, B.; Woodward, C. E.; Wennerström, H. *J. Phys. Chem. B* **1997**, 101, 4253.
- (9) Jensen, T. R.; Østergaard Jensen, M.; Reitzel, N.; Balashev, K.; Peters, G. H.; Kjaer, K.; Bjørnholm, T. *Phys. Rev-Lett.* **2003**, 90, 1952.
- (10) Parker, J. L.; Claesson, P. M.; Attard, P. *J. Phys. Chem.* **1994**, 98, 8468.
- (11) Carambassis, A.; Jonker, L. C.; Attard, P.; Rutland, M. W. *Phys. Rev. Lett.* **1998**, 80, 5357.
- (12) Evans, D. F.; Wennerström, H. *The Colloidal Domain. Where Physics, Chemistry Biology and Technology Meet*, 2nd ed.; Wiley: New York, 1999.
- (13) In ref 8 we arrived at a somewhat shorter estimate of d_{crit} due to an unwarranted condition of pressure matching between the gas in the slit and the external pressure.
- (14) Wennerström, H.; Thuresson, K.; Linse, P.; Freyssingeas, E. *Langmuir* **1998**, 14, 5664.
- (15) Petrov, P.; Olsson, U.; Wennerström, H. *Langmuir* **1997**, 13, 3331.
- (16) Freyssingeas, E.; Thuresson, K.; Nylander, T.; Joabsson, F.; Lindman, B. *Langmuir* **1998**, 14, 5877.
- (17) Yaminsky, V. V.; Yushchenko, V. S.; Amelina, E. A.; Shchukin, E. S. *J. Colloid Interface Sci.* **1983**, 96, 301.
- (18) Christensson, H. K.; Claesson, P. M. *Science* **1988**, 239, 390.