Current Opinion in Colloid & Interface Science 22 (2016) 51–58

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Forces between extended hydrophobic solids: Is there a long-range hydrophobic force?

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ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form 16 February 2016
Accepted 16 February 2016
Available online 27 February 2016

Keywords:
Please note that this is a submission for the special issue on "Weak Self-Assembly"

ABSTRACT

Thirty years ago there was considerable excitement over the first report of a long-ranged "hydrophobic force" between solids that were not wet by water (Israelachvili and Pashley, *Nature* 1982, *300*, 341–342). Many of the subsequent measurements have been reexamined and found not to support the existence of a long-range hydrophobic force. The principal difficulty was that hydrophobic solids frequently experience other forces, which obscured or were mistaken for a hydrophobic force. In this paper, we review the surviving evidence for a long-range hydrophobic force and find that there is only supporting evidence in a total of two papers, one old and one new, where net attractive forces were measured at separations greater than about 5–6 nm. Thus the evidence is scarce. In contrast there are new experiments showing no such force, thereby arguing against the universality of a measureable hydrophobic force beyond about 6 nm. Since solvent water is common to the experiments, such evidence makes it difficult to describe a universal mechanism for a long-ranged hydrophobic force based on water structure. There are also new measurements that are consistent with a hydrophobic force with a decay length in the range 0.3–1.0 nm. In particular, attractive forces have been measured on small radius surfaces (8–50 nm) consistent with a hydrophobic force with a decay length of 0.5–0.6 nm, and a variety of net repulsive measurements are consistent with an attractive hydrophobic force that has a decay length of 0.3–1.0 nm. We also discuss some new measurements, which are consistent with cavitation, and not a surface force that acts at a distance.

1. Introduction

In this review, we examine experimental measurements of surface forces between extended hydrophobic solids in aqueous solution. When water is limited in extent by two solid boundaries, the hydrogen-bonding network that exists in bulk is necessarily interrupted. When the boundary solids are hydrophobic, potential hydrogen bonding sites are lost and so the molar free energy in the film is greater than in the bulk. At smaller separations, confined water must be removed to bulk, resulting in a lower energy, and thus an attractive force. This appears to be a simple topic that should have been well understood by now, but it is not. On the theoretical and modeling side, water is complicated because of the extended three-dimensional hydrogen-bonding network. It is the existence of this network that stimulated the idea that perturbations from the interface should be transmitted over a "long" range — greater than the several molecular diameter range of structural force that is expected [1] and observed [2] for simple fluids. On the experimental side, it has been surprisingly difficult to prepare clean, extended, hydrophobic solids, and to provide an unambiguous attribution of forces to hydrophobicity. Previous notable reviews of this area include those by Christenson and Claesson [3•], Meyer et al. [4•], and recently by Donaldson et al. [5••] and Tabor et al. [6••]. Most measurements of attractive "hydrophobic forces" have later been found to be not *directly* attributable to surface hydrophobicity, but due to other mechanisms, most commonly, (1) bridging of one or more preformed interfacial nanobubbles [7–9•] and (2) correlations between surface dipoles [10,11•,12•]. Although these cases will be discussed briefly, the purpose of this review will be to focus on the very few measurements that other reviews have not already attributed to these effects. A summary of some new results is shown in Fig. 1. Many surface forces asymptote to zero force at large separation, so do not have a definite range. When the forces are exponential, the decay length is a measure of range, but otherwise the "range" in this paper is an approximate term used to indicate where the measured forces become lost in the noise. Among the measurements shown, the maximum range of attractive force is about 20 nm and a few have no measurable force at distances beyond 6 nm.

2. Extended hydrophobic surfaces

2.1. Surface forces

The hydrophobic *effect* is a molecular scale effect that manifests as attraction between apolar solutes in water because of inability of the

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http://dx.doi.org/10.1016/j.cocis.2016.02.006
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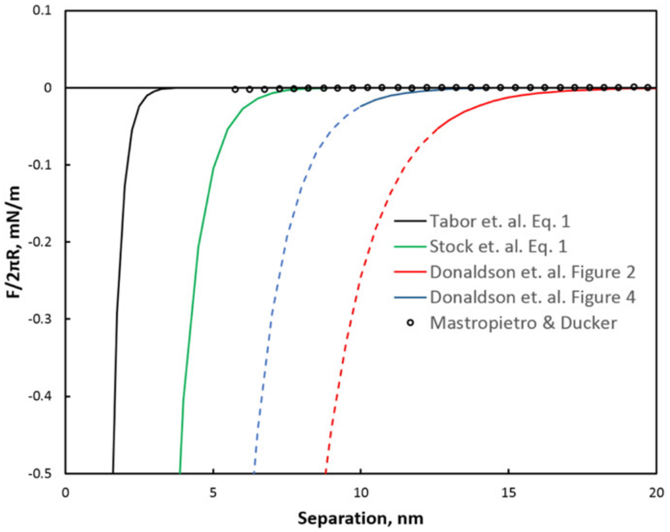

Fig. 1. Comparison of normalized hydrophobic force vs separation from recent publications. For Tabor et al. [13••], the figure shows an equation that the authors fitted to their data. For Stock et al. [14••], the data is also a fit equation from the authors, and the total force is very similar to the hydrophobic force contribution for separations less than about 6 nm. For both Donaldson et al. curves [5••], the figure shows the author's fit equation. The solid portions are for the region where data was measured and the dotted lines are interpolations. The total force was attributed to the hydrophobic force. For Mastropietro and Ducker [15••], the symbols represent measurements. In that case, most of the force was attributed to van der Waals force.

solute to hydrogen bond to water. If the molecules are small, a hydrogen bonding network can be maintained, but only with a decrease in entropy of the water molecules. There is then an increase in the entropy of water when two hydrophobic molecules coalesce in water, which can be considered to be an attractive force. The hydrophobic effect is a major driving force in molecular self-assembly. Compared to single molecules, extended hydrophobic surfaces place even more constraints on water molecules, and it is generally not possible to maintain the hydrogen bonding network [16•]. Eriksson et al. [17•] described a mechanism for an attractive hydrophobic force between two solids which is akin to the hydrophobic effect: the loss of entropy in a thin film between hydrophobic surfaces leads to a greater free energy. When the film thins, this high free-energy water is removed to bulk, resulting in a lower energy and thus an attractive force. This is the opposite effect to the repulsive force that is expected between surfaces that bond strongly to water — hydrophilic surfaces [18,19]. The similar but opposite nature of the hydrophobic and hydration force has been highlighted in a recent review and described as the “Hydra” model [4•]. The open question is then: will the force decay with a characteristic length of a water molecule diameter (~0.25 nm), or is there another characteristic length, for example, related to the hydrogen bonding network? For the purpose of this review, “long-range” will mean a force with a decay length that is significantly greater than the size of a water molecule.

Before discussing long-range forces, we remark that it is clear that there are large effects of hydrophobicity at “zero” range. Hydrophobic surfaces produce a high water contact angle, and indeed this is the default definition of hydrophobicity on a macroscopic scale. Consistent with the high contact angle, there is a large adhesion between two hydrophobic materials in water, a feature that is heavily exploited in mineral or oil separation by froth flotation. The important questions are the extent to which an attractive force operates over a *finite range—more than several molecular diameters*, and exceeds the van der Waals force. The van der Waals force is almost ubiquitous, so the hydrophobic force must be of the same order, or larger, in magnitude to be of practical importance. There is also a large and exciting field of hydrophobic surfaces that considers very rough or structured surfaces, particularly applied to wetting problems. This review will be restricted to relatively flat and smooth surfaces, that is, solids that have a roughness of less than a few nanometers.

Unfortunately there is as yet no molecular scale theory for hydrophobic forces, but many investigators have modeled data with an exponentially decaying form. For example, the original pioneering work by Israelachvili and Pashley [20••,21••] used an equation of the following form for the energy per unit area, E_a, between two flat plates:

$$E_A = -C\ \exp\left(-\frac{s}{\lambda}\right) \tag{1}$$

where C is a constant, s is the separation and λ is the decay length of the hydrophobic force. Subsequently, the group of Israelachvili suggested the “Hydra” equation: [5••]

$$E_A = -2\gamma\ Hy\ \exp\left(-\frac{s}{\lambda}\right) \tag{2}$$

where γ is the interfacial tension between water and the hydrophobic surface, Hy is the fraction of hydrophobic area, ranging from 1 for fully hydrophobic, to 0 for an indifferent surface and to negative values for hydrophilic surfaces. Thus repulsive hydration forces can be characterized with the same equation. The Hydra equation replaces the fitted constant, C, of Eq. (1) with a material property, the surface tension, and a coverage, which could potentially be measured.

2.2. Dewetting in thin films between hydrophobic solids

The simplest experimental manifestation of hydrophobicity is a high water contact angle. Without any need for molecular arguments, Yushchenko et al. [22] described that, during the approach of two particles with contact angle exceeding 90°, the water film between the particles becomes thermodynamically unstable compared to the formation of a vapor cavity between the particles. The separation at which this occurs depends on various parameters, but is on the order of 100 nm. The free energy of formation of the vapor phase is:

$$\Delta G = A_{SV}(\gamma_{SV} - \gamma_{SL}) + A_{LV}\gamma_{LV} + \Delta\mu\Delta n, \tag{3}$$

where A is the area of an interface, γ is the surface tension, and S, L, and V refer to the solid, liquid, and vapor phases respectively. $\Delta\mu$ is the difference in chemical potential between the vapor and liquid, and Δn is the amount of vapor that forms in the cavity. $\Delta\mu\Delta n$ is equal to $V\Delta P$ where V is the volume of the vapor phase and ΔP is the pressure difference between the liquid and vapor (the Laplace Pressure). The high value of γ_{SL} for a hydrophobic material compared to hydrophilic materials lowers the energy of formation of the vapor phase. Once the vapor phase has formed, both the reduced pressure within the vapor capillary and the resolved component of γ_{SL} act to rapidly draw the particles together [23].

When the solids are in contact, or for very thin films, there is no activation barrier for formation of the capillary. But for thicker films (i.e. a greater separation between the particles), Yushchenko et al. [22] found that the activation energy for growth of the vapor phase normal to s scales like the square of the separation between the particles, making the formation of the vapor cavity decreasingly likely at larger s. Even for films as thin as 1 nm, they found that the activation energy is about 100 kT, making formation of the vapor film unlikely.

This idea has been confirmed by more recent theory and molecular simulation. By introducing a slowly varying density field, Lum et al. [16•] showed that the water is only metastable between hydrophobic surfaces from thick films down to films of about 5 nm, at which point the vapor phase becomes stable. Leung et al. showed that for two flat solids with contact angles of 135° and a micron-sized contact areas separated by 1.4 nm, the rate for cavity formation was $10^{11}\ \mathrm{s}^{-1}$ [24]. For a