Hydrophobic attraction forces in asymmetric aqueous films between hydrophobized mica/bare mica surfaces

Jan Christer Eriksson [a,*], Ulf Henriksson [b], Atte Kumpulainen [a]

[a] *Division of Surface Chemistry, Department of Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*
[b] *Division of Physical Chemistry, Department of Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

Dedicated to Professor Ivan B. Ivanov (LCPE, University of Sofia) on the occasion of his 70th birthday.

Abstract

The water-structure-based, quasi-thermodynamic theory published several years ago of hydrophobic interaction forces in symmetric aqueous films [J.C. Eriksson, S. Ljunggren, P.M. Claesson, J. Chem. Soc., Faraday Trans. 2 (85) (1989) 163] has been generalized to encompass asymmetric films between, e.g. a hydrophobized mica surface and a bare mica surface. The interaction pressures derived on this basis are in good agreement with the experimental data recorded by Claesson et al. [P.M. Claesson, P.C. Herder, C.E. Blom, B.W. Ninham, J. Colloid Interface Sci. 118 (1987) 68]. Hence, additional support is gathered for the original claim that the hydrophobic attraction is related with hydrogen-bond-dependent cluster formation processes in water contacted with a hydrophobic solid surface.

1. Introduction

In addition to the ordinary DLVO interaction forces usually operating across thin films (van der Waals attraction and electrostatic repulsion), the long-range hydrophobic attraction is since long well documented. It arises for thin aqueous films sandwiched between molecularly smooth and homogeneous hydrophobic film faces. A few years ago, the vast literature on this topic was thoroughly reviewed by Christenson and Claesson [1]. In order to rationalize the hydrophobic attraction, a variety of mechanisms have been suggested and some of them have been scrutinized in considerable detail. For a critical discussion of this issue we refer to a book chapter recently written by Eriksson and Yoon [2].

So far, general agreement as to the cause of the hydrophobic attraction has not been reached. The perhaps most straightforward theoretical approach, yet to be falsified, might be the one forwarded by Eriksson et al. in 1989 that is based on the notion of an enhanced structure formation for water in the close vicinity of a hydrophobic solid surface [3]. Conceptually, this approach goes back to the original propositions of Blake and Kitchener [4], and of Israelachvili and Pashley [5]. In a similar vein, Derjaguin and Churaev [6] referred to the hydrophobic attraction in terms of the "structural component of the disjoining pressure".

Surface interaction data for asymmetric films between a hydrophobic and a bare hydrophilic solid surface have been presented by Claesson et al. [7] and Tsao and Evans [8] (hydrophobized mica/bare mica), and by Yoon et al. [9] (silanized silica/bare glass). By and large the data reported by the two last-mentioned groups are compatible with those of Claesson et al. Tsao and Evans claimed that electrostatic correlation forces alone may account for the attraction observed beyond the DLVO scheme, whereas Claesson et al. additionally, invoked surface-induced water structure generation as a possible origin of the hydrophobic attraction.

In their original paper, Eriksson et al. [3] treated the case of a thin water film between two *identical* hydrophobic surfaces submerged in bulk water, using a square-gradient, order parameter approach. They showed that by means of such an approach, satisfactory agreement could be obtained for short as well as large

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* Corresponding author.
E-mail address: janchrister.eriksson@surfchem.kth.se (J.C. Eriksson).

surface separations. The purpose of the present paper is to extend the previous treatment to encompass *asymmetric* film systems, e.g. a thin aqueous film between a hydrophobized mica surface and a bare mica surface, or between a hydrophobic solid surface and a solid surface covered by ethylene-oxide, or hydroxyl groups.

2. General model features

The model set up in reference [3] for the symmetric hydrophobic attraction case was based on the following notions:

1. By increasing the order parameter, s_0, which characterizes the organization of the contact monolayers of water molecules (relative to the bulk water state), the corresponding interfacial free energy excesses become reduced, thus lowering the overall film tension, γ^f.
2. As a consequence of the co-operative coupling among water molecules, surface-attached, structurally organized clusters of water molecules form at each of the two film faces. Their concentration diminishes with the distance, x, away from the hydrophobic surface toward the mid-plane, implying that the order parameter function $s(x)$ likewise diminishes with x in the same range. When the two hydrophobic solid surfaces are brought closer and the respective order parameter profiles start to overlap, the (weak) structural response occurring in the thin water film is further amplified.
3. The resulting total film tension γ^f arising within the water film depends on the detailed course of the order parameter function $s(x)$, because free energy penalties are connected with local s-values larger than the bulk value as well as with steep gradients $|ds/dx|$.

In mathematical terms, for a symmetric water film of a certain thickness h, we can hence write

$$\gamma^f = \gamma_0^f - as_0 + \int_{-h/2}^{h/2} \left[c_2 s^2(x) + \frac{1}{2} c_3 \left(\frac{ds}{dx} \right)^2 \right] dx \qquad (1)$$

where we make use of formalism that conceptually is close to the "square-gradient approximation" frequently applied in the past to treat liquid–vapor interfaces. In this expression x is the length coordinate perpendicular to the film faces with $x=0$ for the mid-plane, whereas γ_0^f stands for the film tension prior to adjustment of the order parameter function. Three additional constants are involved: (i) a, accounting for the lowering of the film tension due to organizing the contact monolayers; (ii) c_2, accounting for the free energy rise due to having more ordered local states within the core of the film than in bulk water; and (iii) c_3, accounting for the free energy rise due to order parameter gradients, that in turn are likely to be linked to the co-operative aspects of hydrogen-bond formation in small clusters of water molecules.

Minimizing γ^f with respect to the order parameter function, $s(x)$, i.e. taking the functional derivative, yields the Euler condi-

tion

$$\frac{d^2 s(x)}{dx^2} - \frac{2c_2}{c_3} s(x) = 0 \qquad (2)$$

or,

$$\frac{d^2 s(x)}{dx^2} - b^2 s(x) = 0 \qquad (3)$$

where the constant $b = \sqrt{2c_2/c_3}$ is introduced (for thick enough films b^{-1} has the nature of a decay length). Assuming the boundary conditions $s(-h/2) = s(h/2) = s_0$, the differential Eq. (3) has the well-known (catenary) solution

$$s(x) = s_0 \frac{\cos h(bx)}{\cos h(bh/2)} \qquad (4)$$

that was central in our previous treatment of the hydrophobic attraction for the symmetric water film case [3].

For the asymmetric case, however, the solution $s(x)$ of Eq. (3) has the general form:

$$s(x) = C_1 e^{bx} + C_2 e^{-bx} \qquad (5)$$

and the boundary conditions may be written

$$s(-h/2) = C_1 e^{-bh/2} + C_2 e^{bh/2} = s_0^I \qquad (6)$$

$$s(h/2) = C_1 e^{bh/2} + C_2 e^{-bh/2} = s_0^{II} \qquad (7)$$

here, superscripts I and II refer to each of the two film faces. Thus, we can readily establish that the order parameter function $s(x)$ is given by the equation

$$s(x) = (e^{bh} - e^{-bh})^{-1} (S^{II} e^{bx} + S^I e^{-bx}) \qquad (8)$$

where

$$S^{II} = s_0^{II} e^{-bh/2} - s_0^I e^{bh/2} \qquad (9)$$

$$S^I = s_0^I e^{-bh/2} - s_0^{II} e^{bh/2} \qquad (10)$$

Moreover, by minimizing γ^f with respect to the order parameter for the contact monolayers, s_0^I and s_0^{II}, we obtain the following relationships:

$$s_0^I = \frac{b[(e^{bh} + e^{-bh})a^I + 2a^{II}]}{2c_2(e^{bh} - e^{-bh})} \qquad (11)$$

$$s_0^{II} = \frac{b[(e^{bh} + e^{-bh})a^{II} + 2a^I]}{2c_2(e^{bh} - e^{-bh})} \qquad (12)$$

which relate s_0^I and s_0^{II} to the original set of constants, i.e. a^I, a^{II}, c_2 and c_3 (recall that $b \equiv \sqrt{2c_2/c_3}$). The final expression for the film tension, γ^f, that can be derived by using Eq. (1) as the starting point is:

$$\gamma^f = \gamma_0^f - a^I s_0^I - a^{II} s_0^{II} + \frac{c_2[(S^I)^2 + (S^{II})^2]}{b(e^{bh} - e^{-bh})} \qquad (13)$$

where the values of s_0^I, s_0^{II}, S^I and S^{II} determined by Eqs. (9)–(12) have to be inserted. Accordingly, the film tension change, $\gamma^f -$

γ_∞^f arising as a result of thinning of the film from $h = \infty$ to some finite thickness h, where the film faces interact, becomes:

$$\gamma^f - \gamma_\infty^f = -a^I s_0^I - a^{II} s_0^{II} + \frac{c_2[(S^I)^2 + (S^{II})^2]}{b(e^{bh} - e^{-bh})}$$
$$+ \frac{b}{4c_2}[(a^I)^2 + (a^{II})^2] \qquad (14)$$

For the symmetric case ($a^I = a^{II} = a/2$) this expression can be rewritten in the more lucid form

$$\gamma^f - \gamma_\infty^f = -\left(\frac{B}{2\pi}\right)[\cot h(bh/2) - 1] \qquad (15)$$

where the constant B equals $\pi a^2/\sqrt{8c_2c_3}$, demonstrating full consistency with our previous treatment [3]. Note that according to the Derjaguin approximation the surface force measured by means of a surface force apparatus equipped with cylindrically shaped surfaces is equal to $2\pi(\gamma^f - \gamma_\infty^f)$.

For the asymmetric case that is primarily considered here, for which $a^I = a/2$; $a^{II} = 0$, Eq. (14) can be written in a form analogous to Eq. (15), that is,

$$\left(-\frac{F}{R}\right)^{asym} = -\left(\frac{B}{2}\right)[\cot h(bh) - 1] \qquad (16)$$

Comparing this expression with Eq. (15) we note that the surface force anticipated for the asymmetric film is reduced in two ways: (i) the proportionality constant is a factor of two less and (ii) the decay length, $b^{-1}/2$, is half of the decay length for the symmetrical case (b^{-1}). The latter observation appears more clearly by writing Eqs. (15) and (16) in approximate, exponential forms:

$$\left(-\frac{F}{R}\right)^{sym} \cong 2B\exp(-bh) \qquad (17)$$

$$\left(-\frac{F}{R}\right)^{asym} \cong B\exp(-2bh) \qquad (18)$$

valid for large thicknesses.

Generally, the interaction (or disjoining) pressure is obtained from Eq. (14) in accordance with the purely thermodynamic relation

$$\left(\frac{\partial \gamma^f}{\partial h}\right)_{T, p, \text{solute conc.}} = -\pi_D \qquad (19)$$

i.e., by differentiating the film tension function with respect to h. For the asymmetric film case ($a^I = a/2$; $a^{II} = 0$), using Eq. (16) we can thus derive the expression:

$$\pi_D^{asym} = -\left(\frac{Bb}{4\pi}\right)\sin h^{-2}(bh) \qquad (20)$$

The analogous expression for the symmetrical case is:

$$\pi_D^{sym} = -\left(\frac{Bb}{2\pi}\right)\sin h^{-2}\left(\frac{bh}{2}\right) \qquad (21)$$

These expressions evidently imply that the interaction pressure π_D^{asym} is generally less than π_D^{sym} by more than a factor of two

(in fact, according to the present theory by about a factor of ten for a 10 nm thick film).

3. Comparison with experimental results

The experiments for asymmetric aqueous films between hydrophobized and bare mica surfaces carried out by Claesson et al. [7], were based on determining attractive interaction pressures and corresponding jump distances by employing a surface force apparatus using a set of cantilevers with different spring constants. In order to suppress an electrostatic attraction observed in the case of pure water, KBr was added to the bulk water phase. For 0.1 and 0.01 M KBr, the interaction pressure data indicated the presence of one and the same non-DLVO attraction pressure, supposedly of hydrophobic or electrostatic (correlation) origin.

In Fig. 1 the data points recorded by Claesson et al. [7] for 0.1 and 0.01 M KBr solutions are marked. The full-drawn curve represents the π_D-function predicted on the basis of the theory presented in the previous section (Eq. (20)). The following values of the constants were inserted: $a^I = 32.5\,\text{mJ}\,\text{m}^{-2}$ (same as in [3] for the symmetrical case); $a^{II} = 0\,\text{mJ}\,\text{m}^{-2}$; $c_2 = 0.35009 \times 10^9\,\text{J/m}^3$; $c_3 = 1.74764 \times 10^7\,\text{J/m}$. These latter c_2- and c_3-values were obtained earlier in reference [3] by fitting to the surface force data of Claesson and Christensen [10] for the symmetrical case of two hydrophobized mica surfaces submerged in water. It is seen that the agreement is satisfactory, except, perhaps, for small film thicknesses where one might contemplate to complement the linear *ansatz* for the interfacial response function, $-a^{II}s_0^{II}$, with a quadratic term (cf. reference [3]). Moreover, upon comparing with the corresponding π_D-function for the symmetrical case, one notes that the attraction pressures for the asymmetrical case are significantly more than a factor of two less, as was pointed out by Claesson et. al. [7].
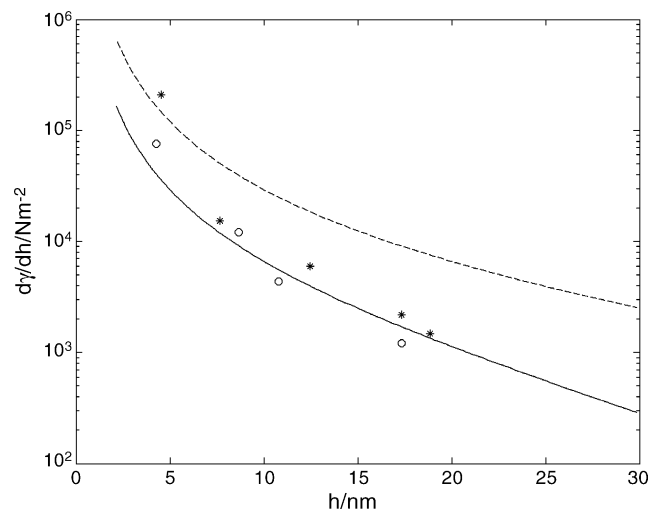

Fig. 1. Experimental attractive interaction pressures determined by Claesson et al. (reference [7]) for asymmetric aqueous films between a hydrophobized mica surface and a bare mica surface submerged in 10^{-1} (stars) and 10^{-2} M KBr (open circles). The full-drawn line represents the predicted interaction pressure π_D according to the present theory. The dashed line represents the interaction pressure between two (charge-free) hydrophobized mica surfaces in water.
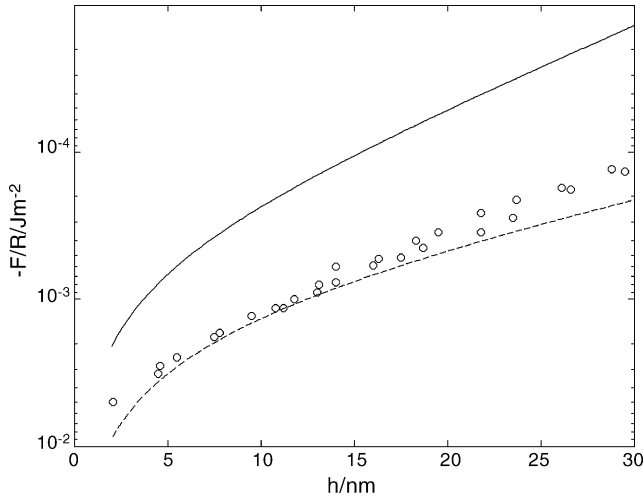
Fig. 2. The absolute value of the normalized surface force $-2\pi(\gamma^f - \gamma^f_\infty)$ plotted vs. the film thickness, h, for the asymmetric (full-drawn line) and symmetric (dashed line) film cases discussed in the text.

In Fig. 2 the corresponding surface force functions are plotted in the form $\log[-2\pi(\gamma^f - \gamma^f_\infty)/\text{mJ m}^{-2}]$. It is seen that the characteristic amplification observed for symmetric aqueous films between identical hydrophobic surfaces for small values of h is likewise present for an asymmetric aqueous film between hydrophobized mica/bare mica surfaces. Note, in addition, that the ratio of the slopes for large h approaches 2 (asym/sym) as discussed above. More recent experimental data due to Lin et al. [11] for the symmetrical case of two hydrophobized mica surfaces are also marked, showing good agreement with the earlier results of Claesson and Christenson [10] on which the parameter estimates in reference [3] were based (dashed line).

4. The order parameter function s(x)

From Eqs. (8)–(12) we can derive the associated order parameter function $s(x)$ for the asymmetrical film considered by inserting the values for the constants, a^I, a^{II}, c_2 and c_3 mentioned above. In Fig. 3a $s(x)$-functions are shown for two thicknesses, $h = 7.5$ nm and $h = 15$ nm, respectively. For comparison, the corresponding $s(x)$-functions characterizing the symmetrical case ($a^I = a^{II} = 32.5$ mJ m^{-2}) are also shown (Fig. 3b). Generally, the asymmetric film is less organized than the symmetrical one. In fact, it follows from the theory presented above that the order parameter value for the mid-plane of the asymmetric film is exactly half of the value for the mid-plane of the symmetric film. In particular, it is worth observing that even the contact water monolayer at the bare mica surface is affected structurally by having a hydrophobized mica surface nearby (without, however, giving rise to any significant energetic effect). Note, in addition, that the free energy gain for the contact monolayer(s) due to adjustment of the $s(x)$-function(s) always exceeds the free energy expenditures throughout the core of the film. We emphasize that the (free) energetic effects involved here are exceedingly minute, typically on the order 5×10^{-4} kT per water molecule to be compared with the hydrogen bond energy of 7 kT.
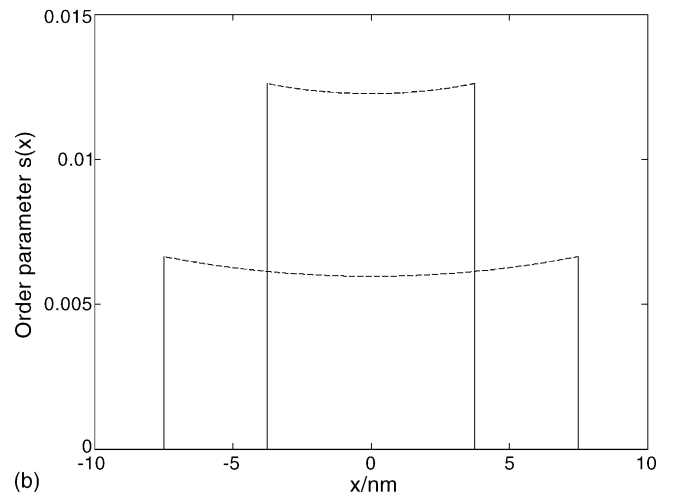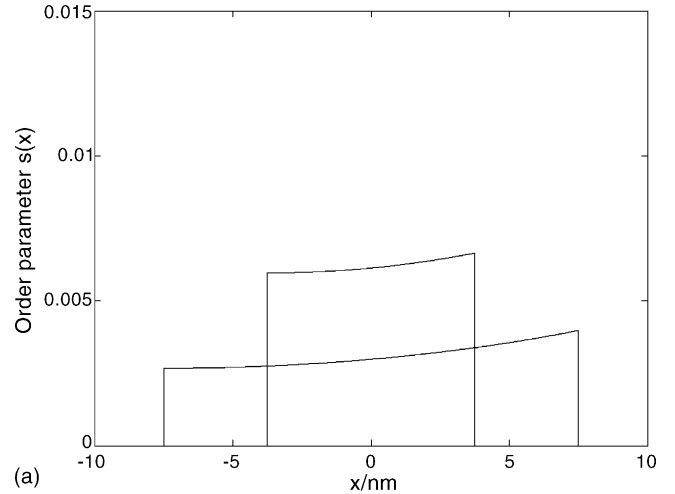

(a)

(b)

Fig. 3. The order parameter function $s(x)$ for aqueous films of thicknesses $h = 7.5$ nm and $h = 15.0$ nm, respectively, between a hydrophobized mica surface and a bare mica surface (a) and for a symmetric aqueous film between two hydrophobized mica surfaces (b).

5. Concluding remarks

The present study is founded on a straightforward extension of our previous water-structure-based theory of symmetric aqueous films between hydrophobized solid surfaces [3]. We have demonstrated that the experimental data of Claesson et al. [7] on the attractive interaction pressure for thin films of 0.01–0.1 M KBr solution, sandwiched between hydrophobized mica/bare mica surfaces, can be accounted for by reference to this broadened theoretical framework.

Conversely, this study lends, of course, additional support to the claim that the hydrophobic attraction ultimately owes its long-rangeness to the co-operative properties of the hydrogen bond, which in turn give rise to (surface-attached) clusters and chains of water molecules of variable length.

An alternative *electrostatic* mechanism, irrespective of its closer nature, is virtually ruled out as the Debye length in 0.1 M KBr is merely 0.96 nm at 25 °C. Furthermore, there were no experimental indications of any attractive bridging-air-bubble mechanism at the experimental investigations considered here.

This is hardly surprising as it would be difficult to conceive of a stable bridging bubble, devoid of excess pressure, that simultaneously satisfies the Young condition for a hydrophobized mica surface with a large contact angle against water, as well as a bare mica surface with a low contact angle against water.

Obviously, this investigation implies that a solid surface covered by *fluorocarbon* chains would be more strongly attracted to a hydrophilic surface than a solid surface covered by hydrocarbon chains. Similarly as for symmetric aqueous films between hydrophobic surfaces, a corresponding asymmetric film might be expected to give rise to a surface force of reduced magnitude at temperatures above room temperature as well as for degassed water (cf. reference [2]). Finally, it would be desirable to develop a molecularly based physical model consistent with the mathematical description presented in this paper and in reference [3].

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