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Bridging-Cluster Model for Hydrophobic Attraction

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A new model is proposed to account for the long-range hydrophobic attraction repeatedly observed for thin water films between two stable (solid) hydrophobic surfaces. The model is based on the notion of structurally organized, elongated water clusters that span the gap between the hydrophobic surfaces. Two features are noted: (i) Mixing entropy due to the mixing of the clusters and the remainder of the water in the thin film is explicitly taken into account. (ii) A term is invoked that depends inversely on the film thickness, which accounts for the free-energy change associated with reorganizing the film as the film thickness varies. Fitting to experimental surface force data resulted in parameter values of reasonable magnitudes. The model developed covers film thicknesses from about 2 nm and above. On this basis, the amazingly long range of the hydrophobic attraction can be attributed to the formation of bridging, quasi-cylindrical clusters having a radius on the order of 1 to 2 nm.

Introduction

Most investigations of hydrophobic attraction during the past few decades have been based on employing the surface force apparatus (SFA) developed by Israelachvili et al.¹ or atomic force microscopy (AFM). The state of affairs as to the origin of this attraction that early on was observed by Israelachvili and Pashley² has recently been reviewed^{3–5} and was summarized by Christenson and Claesson,³ who stated that the concept of a hydrophobic interaction force by and large stands for

(i) a fairly short-range but strongly attractive force that is much stronger than a van der Waals force;

(ii) an attraction of variable strength and range caused by the presence of small bubbles sporadically adhering to hydrophobic surfaces;⁶

(iii) a very long-range attractive force with exponential decay operating between certain hydrophobic surfaces, in particular, those hydrophobized by means of Langmuir–Blodgett deposition on mica or silica or adsorption from a solution of an ionic amphiphile.

Let us briefly recall a model surface force experiment with a thin water film between two plane-parallel, atomically smooth, laterally homogeneous, stable hydrophobic surfaces (Figure 1).

To establish the equality of the chemical potentials everywhere, a lateral tension γ^f develops in the thin film that at large thickness will be equal to twice the interfacial tension of the hydrophobic surface/water interface (i.e., about 100 mN m⁻¹). To keep the film at a certain thickness h , an extra pressure, positive (repulsive) or negative (attractive), has to be applied to counteract the disjoining pressure operating inside the film. It is well known

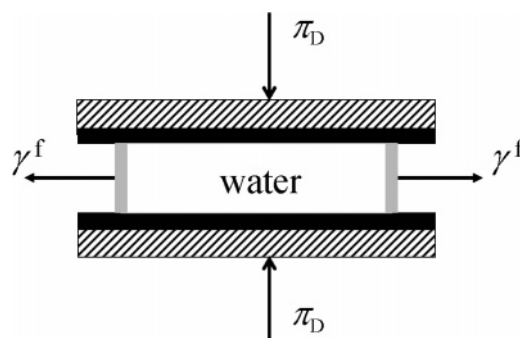


Figure 1. Sketch of a thin water film between two plane-parallel hydrophobic surfaces. A mechanical film tension γ^f is acting in the lateral directions. π_D counterbalances the disjoining pressure operating in the direction of the normal to the surface.

that the relation between the equilibrium film tension γ^f and the disjoining pressure π_D is generally given by

$$\left(\frac{\partial \gamma^f}{\partial h}\right)_{T,p,\text{all chemical potentials}} = -\pi_D \quad (1)$$

To derive the film tension change, $\Delta\gamma^f$, arising from a decrease in thickness from $h = \infty$ where $\pi_D = 0$, that is, beyond the range of the surface forces, to some smaller thickness h , we can integrate eq 1 while supposing the bulk phase state to remain the same:

$$\Delta\gamma^f \equiv \gamma^f(h) - \gamma^f(\infty) = -\int_{\infty}^h \pi_D dh \quad (2)$$

According to the Derjaguin approximation,⁷ the surface force F between two crossed cylinders (or sphere/plate) measured by means of an SFA/AFM device is given by

$$F = 2\pi R \Delta\gamma^f \quad (3)$$

It has become common practice, however, to report “normalized” surface forces in the form of F/R corresponding to $2\pi\Delta\gamma^f$ for the above standard case rather than the more fundamental film tension change $\Delta\gamma^f$ for plane-parallel film faces.

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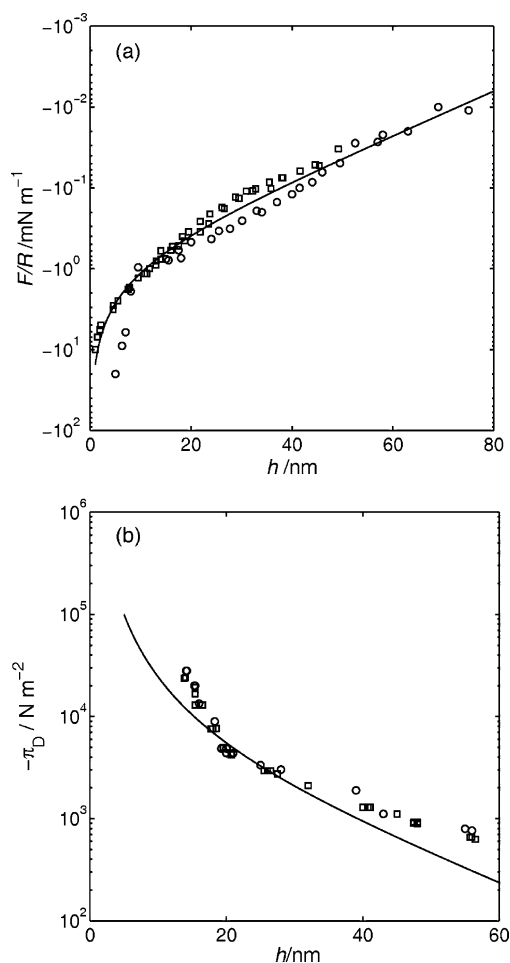


Figure 2. (a) Surface forces reported by Claesson and Christenson⁸ (○) and Lin et al.⁹ (□) using LB-deposited DODA⁺ monolayers on mica. The data points due to Claesson and Christenson for separations of less than 10 nm are special because they were obtained using a much stiffer spring than in all other cases. (b) Disjoining pressure data reported by Tsao et al.¹⁰ using mica surfaces hydrophobized by means of the adsorption of DODA⁺ in acetate form (○) and DEDA⁺ (dieicosyldimethylammonium bromide, □) from cyclohexane solution and a surface force apparatus. The solid curves correspond to eqs 5 and 6, respectively, with $b^{-1} = 15.8$ nm and $B = 0.50$ mN m⁻¹.

For dioctadecyldimethylammonium (DODA⁺)-covered mica surfaces submerged in pure water, approximate agreement is found among the surface force data recorded by Claesson and Christenson,⁸ Lin et al.,⁹ and Tsao et al.¹⁰ (cf. Figure 2). Note in particular in Figure 2a the exponential behavior at large thickness and the amplification “knee” as a salient feature for small thickness.

Attempts to Unravel the Origin of Hydrophobic Attraction.

To rationalize the experimentally observed hydrophobic attraction, a variety of mechanisms have been suggested. Some of them have even been scrutinized in considerable detail, but a final clarification has so far not been attained. A paper mostly dealing with the theoretical understanding of the hydrophobic force was presented by Spalla.¹¹ Furthermore, papers by Tsao, Evans, and Wennerström¹² and Craig, Ninham, and Pashley¹³ incorporate

illuminating discussions about the possible origin of the hydrophobic force. More recently, Israelachvili and co-workers have begun reexamining the whole issue.^{9,14} In two later papers from this group,^{4,15} they argue that the long-range hydrophobic attraction is actually an electrostatic correlation attraction¹⁶ whereas the “true” hydrophobic attraction has a much shorter range. Recently it has been found, however, that the long-range attraction observed for a series of alkyltrimethylammonium surfactants adsorbed on silica at the charge neutralization concentration can hardly be attributed to an electrostatic correlation effect.¹⁷ Moreover, it has been observed that a long-range attraction of the anticipated strength is also present for water-exposed gold surfaces hydrophobized by means of thiol surfactants, which are free of surface charges, without noting any signs of bubble attachment.¹⁸ Earlier, upon experimenting with surfaces of the same kind, Ederth linked the occurrence of small steps in the surface force curves to the bridging of adhering nanobubbles and the consequent onset of hydrophobic attraction.¹⁹

A rather straightforward theoretical approach, yet to be falsified, is the one forwarded by Eriksson et al. based on the notion of enhanced structure formation for water in the vicinity of a hydrophobic solid surface using a square-gradient order parameter approach.²⁰ By means of this approach, satisfactory agreement could be established with experimental surface force data for short as well as large surface separations. Yet, no convincing molecular explanation was furnished for the long-range character of the effect. Because our previous model is nevertheless of importance for the development of the molecular model presented in this article, it is summarized below in some detail. It was based on the following premises:

(i) The final water state in the film reflects a balance between the favorable molecular reorganization occurring in the first (contact) layer of water molecules and the induced, unfavorable, though rather modest restructuring of the remainder of the film. These free-energy changes are characterized by an order parameter $s(x)$ that we may assume mirrors the local density in an inverse manner.

(ii) By increasing the order parameter s_0 that characterizes the organization of the two contact monolayers of water molecules (relative to the bulk water state), the corresponding interfacial free energy becomes reduced, thus reducing the overall excess free energy of the film.

(iii) As a consequence of the co-operative coupling among water molecules, a surface-induced water structure is propagated toward the core of the water film in such a manner that the order parameter function $s(x)$ diminishes with the distance from the hydrophobic surface toward the midplane. When the two hydrophobic solid surfaces are brought closer together and the respective order parameter profiles start to overlap, the (weak) structural response occurring in the thin water film is further amplified.

The resulting film tension arising inside the water film depends on the detailed course of order parameter function $s(x)$. This is

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because free-energy penalties are connected with local s values larger than the bulk value as well as with steep gradients ds/dx . As to the free-energy excess per unit area of a symmetric water film of a certain thickness h , we can start out by writing

$$\omega^f = \omega_{\text{il}}^f - c_1 s_0 + \int_{-h/2}^{h/2} \left[c_2 s^2(x) + \frac{1}{2} c_3 \left(\frac{ds}{dx} \right)^2 \right] dx \quad (4)$$

where a formalism is employed that conceptually is rather close to the so-called 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 midplane, whereas ω^f is the grand Ω potential of the film per unit area and ω_{il}^f stands for its initial value prior to adjustment of the order parameter function. Three additional constants are involved: (i) c_1 , accounting for the lowering of the film tension due to organizing each of 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. Finally, we note that the form chosen for the ansatz given by eq 4 relies on a number of mathematical considerations that are presented in ref 20.

Upon minimizing ω^f with respect to order parameter function $s(x)$ (i.e., taking the functional derivative of eq 4), additionally minimizing with respect to the s_0 parameter, and finally invoking the Derjaguin approximation, one obtains the hydrophobic attraction force for the cylinder–cylinder case as the surprisingly simple two-parameter expression²⁰

$$\frac{F}{R} = 2\pi\Delta\gamma^f = -B \left[\coth\left(\frac{bh}{2}\right) - 1 \right] \quad (5)$$

with parameters $B = \pi c_1^2 / (8c_2 c_3)^{1/2}$ and $b^{-1} = (c_3 / 2c_2)^{1/2}$ and where $\Delta\gamma^f = \Delta\omega^f$ is the film tension difference between fully equilibrated, plane-parallel water films of a certain thickness h and $h = \infty$, respectively. For sufficiently large film thicknesses, the right side of eq 5 equals $-2B \exp(-bh)$; that is, in the weak overlap regime, we predict $\ln(-F/R)$ to be a linear function of h , in agreement with experiments. In this range, b^{-1} has a decay length nature. However, for thin enough water films, the surface force is given roughly by $-2B/bh$; in other words, it depends inversely on the thickness h .

The disjoining pressure expression that can be derived from eq 5 by differentiation with respect to h is the following:

$$\pi_D = -\frac{\partial\gamma^f}{\partial h} = -\frac{bB}{4\pi} \left[\coth^2 \frac{bh}{2} - 1 \right] \quad (6)$$

From Figure 2, one can see how closely the two-parameter expressions (eqs 5 and 6), upon inserting $B = 0.50 \times 10^{-3} \text{ N m}^{-1}$ and $b^{-1} = 15.8 \text{ nm}$, can actually represent the most reliable surface force data presented so far. Here it is worth noting that eq 6 has also been successfully applied to entirely fluid thin film systems by Paunov et al.²¹ and Angarska et al.²²

On the basis of eq 6, we can estimate the average excess free energy per water molecule in the water film taking into account that the pressure tensor must be anisotropic. Typically, in the medium separation range $h \approx 10 \text{ nm}$, we find the excess free energy to amount to about $10^{-4} k_B T$ per molecule, as compared

with the energy of a hydrogen bond at room temperature, $\sim 7k_B T$, showing that we are indeed studying very minute thermodynamic effects by means of a sensitive SFA or AFM setup. Moreover, hydrogen-bonded networks and chains of water molecules are known to be cooperatively stabilized; in other words, larger clusters are inherently more stable than small ones. This sets the stage for extended water clusters of various shapes to arise provided that the associated free-energy expenses are small enough to be counterbalanced by size fluctuation and mixing entropies, a thermodynamic scenario that is familiar from the field of surfactant aggregation.

Bridging-Cluster Theory

Model Features. Next, we invoke the notion that a thin water film between hydrophobic surfaces might become phase separated on the nanoscale,²³ containing randomly distributed quasi-cylindrical, rod-shaped clusters of water molecules that span the gap between the two hydrophobic faces. These clusters are supposed to be more organized structurally than the remainder of the film incorporating ordinary bulk and interfacial water. It follows that a cluster has to be subject to an (anisotropic) tension to be in full equilibrium with the surrounding water. The ultimate reason as to why a phase separation of this sort on the nanoscale may arise is, of course, that it provides a mechanism for the reduction of ω^f , the Ω potential per square meter of film. By analogy to the case of cylindrical surfactant aggregates, we may assume that the free ends of a rod-shaped cluster are comparatively costly from a free-energy standpoint. Thus, we can neglect the presence of both nonattached rod-shaped clusters in the core of the film and those attached by one end only to either of the hydrophobic surfaces, focusing just on the ones that span the gap between the two hydrophobic surfaces.

In the spirit of a mean-field approximation, we may imagine that the rod-shaped clusters as recorded by a snapshot would neither be entirely straight nor always and everywhere exhibiting the same diameter. The conjecture is rather that the clusters that result from the surface-induced phase separation on the average can be modeled as straight cylinders. Yet, a prerequisite is, of course, that upon varying the mean cluster radius there will be a sharp enough minimum of the cluster free energy for some particular radius. A similar requirement has to be inferred for small spherical clusters as well as for microemulsion droplets. In the latter case, the curvature dependence of the surfactant-loaded oil–water interfacial tension is generally recognized to be of crucial importance. By the same token, there has to be a certain free-energy cost restricting shape changes.

A reduction of the free energy supposedly arises from replacing both of the “ordinary” surface water/hydrocarbon contact interfaces by cluster water/hydrocarbon interfaces. To some extent, however, this reduction is likely to be counterbalanced by the free energy it takes to generate the transition zone between the outer rod part and the ordinary interfacial water next to the hydrophobic solid surface. Nevertheless, there arises an additional thermodynamic driving force of entropic origin due to mixing the clusters with the surrounding film water, by analogy to the case of a micelle-forming surfactant solution.

Thermodynamics of a Thin Water Film with Bridging Clusters. For a thin water film of area A and thickness h containing $N_c = n_c N_A$ (N_A is Avogadro’s number) bridging clusters in equilibrium with pure bulk water (cf. Figure 1), the relevant thermodynamic potential function is the grand potential $\Omega^f = G^f - \mu_{\text{w}n_w}$ of the film. For changes at constant T , p , and μ_{w} , we

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then have

$$d\Omega^f = \gamma^f dA - \pi_D A dh + \mu_c^{\text{ex}} dn_c \quad (7)$$

The film tension is thus defined by

$$\gamma^f \equiv \left(\frac{\partial \Omega^f}{\partial A} \right)_{h, n_c} \quad (8)$$

and the excess chemical potential of water in the clusters is defined by

$$\mu_c^{\text{ex}} \equiv \left(\frac{\partial \Omega^f}{\partial n_c} \right)_{h, A} \quad (9)$$

The concentration of bridging clusters in the film can be expressed by means of the fraction of the area of each of the film faces covered by cluster ends $\phi_c = N_c a_c / A = a_c / a$, where a_c is the cross-sectional area of a cluster and $a = A / N_c$ is the film area on the average available to each cluster. The equilibrium value of ϕ_c is governed by the condition $\mu_c^{\text{ex}} = 0$ in much the same way as ordinary complex formation in the bulk phase is determined by the familiar equilibrium condition $\Delta G = 0$. Writing $\Omega^f = N_c \epsilon^f$, where ϵ^f is the Ω^f potential per cluster, we obtain as the equilibrium condition

$$\frac{\mu_c^{\text{ex}}}{N_A} = \epsilon^f + N_c \left(\frac{\partial \epsilon^f}{\partial N_c} \right)_{h, A} = 0 \quad (10)$$

Noting that $A = N_c a_c / \phi_c = N_c a$ and that ϵ^f is a function merely of h and ϕ_c , we can rewrite the above equilibrium condition in the alternative forms

$$\epsilon^f + \phi_c \left(\frac{\partial \epsilon^f}{\partial \phi_c} \right)_h = 0 \quad (11a)$$

$$\epsilon^f - a \left(\frac{\partial \epsilon^f}{\partial a} \right)_h = 0 \quad (11b)$$

From eq 8 and noting again that $\phi_c = N_c a_c / A = a_c / a$, we get the following expressions for the film tension:

$$\gamma^f = - \frac{\phi_c^2}{a_c} \left(\frac{\partial \epsilon^f}{\partial \phi_c} \right)_h \quad (12a)$$

$$\gamma^f = \left(\frac{\partial \epsilon^f}{\partial a} \right)_h \quad (12b)$$

Consequently, the equilibrium condition (eq 10) can be equally well written as follows (eqs 11b, 12b):

$$\epsilon^f - a \gamma^f = 0 \quad (13)$$

This latter form corresponds to the equilibrium conditions for mixed soluble monolayers derived by Butler in 1932.²⁴ Note that eq 11b implies that insofar as equilibrium is established, $\epsilon^f / a = \omega^f$ has a minimum.

To calculate the surface force from eq 3, we need an expression for the film tension change $\Delta \gamma^f = \gamma^f(h) - \gamma^f(\infty) = \gamma^f(h) - 2\gamma^{\text{hc/w}}$, where $\gamma^{\text{hc/w}}$ stands for the interfacial tension of a single non-interacting hydrocarbon/water interface. For this purpose, let us first introduce $\Delta \epsilon^f$ by means of the relation

$$\epsilon^f = 2\gamma^{\text{hc/w}} a + \Delta \epsilon^f \quad (14)$$

Hence, $\Delta \epsilon^f$ denotes the excess free energy per cluster for a thin water film with interacting film faces as compared to a thick film without any interactions. By differentiating eq 14 with respect to a and using eq 12b, we obtain

$$\Delta \gamma^f \equiv \gamma^f - 2\gamma^{\text{hc/w}} = \left(\frac{\partial \Delta \epsilon^f}{\partial a} \right)_h = - \frac{\phi_c^2}{a_c} \left(\frac{\partial \Delta \epsilon^f}{\partial \phi_c} \right)_h \quad (15)$$

By means of these expressions, we can calculate $\Delta \gamma^f$ once $\Delta \epsilon^f$ is known as a function of cluster concentration. In addition, by combining eqs 13 and 14 it is seen that the equilibrium condition now becomes

$$\Delta \epsilon^f = a \Delta \gamma^f = \frac{\Delta \gamma^f a_c}{\phi_c} \quad (16)$$

Taking eq 15 into account, this relation apparently implies that at equilibrium $\Delta \omega^f = \Delta \epsilon^f / a$ must have a minimum.

Cluster Free Energy. We next introduce the following ansatz for the excess free energy per cluster $\Delta \epsilon^f$ in a thin water film of thickness h between two planar hydrophobic surfaces:

$$\frac{\Delta \epsilon^f}{k_B T} = \frac{2a_c \Delta \gamma_{\text{eff}}}{k_B T} + bh - \frac{c}{h} + \left(\ln \frac{\phi_c}{\phi_w} + \frac{\phi_c}{\phi_w} - 1 \right) \quad (17)$$

Here, $\phi_w = 1 - \phi_c$ and $\Delta \gamma_{\text{eff}}$ is the associated effective change in free energy per unit area upon forming the cylinder-surface contact for a long-enough rod-shaped bridging cluster. The bh term is introduced to cope with the fact that even for an elongated cluster there will be a free-energy cost equal to $b k_B T$ per unit length to make it longer. The negative c/h term accounts for the fact that the contact free energy decreases for a cluster as the film thickness decreases, in line with our previous (laterally homogeneous) theory,²⁰ vide infra. The last term, finally, is an entropic term taken from scaled-particle theory that is known to reproduce simulations of the equation of state for 2D hard discs rather accurately.²⁵ For convenience, the standard state used here is $\phi_c = \phi_w = 0.5$ although a better choice might have been $\phi_c = 0.9069$, corresponding to 2D hexagonal close-packing. It will appear from the following, however, that for the way in which the calculations have been carried out a difference of this sort is absorbed in the first term on the right side of eq 17. To calculate the equilibrium concentration of clusters, eqs 15 and 16 are put to use and combined with eq 17, resulting in

$$\frac{2a_c \Delta \gamma_{\text{eff}}}{k_B T} + bh - \frac{c}{h} + \ln \frac{\phi_c}{\phi_w} + \frac{\phi_c}{\phi_w} - 1 + \frac{1}{\phi_w^2} = 0 \quad (18)$$

When parameter values a_c , $\Delta \gamma_{\text{eff}}$, b , and c are known, eq 18 gives the particular area fraction ϕ_c of bridging clusters where for a given thickness the ω^f potential of the water film has a minimum (cf. Figure 4). The equilibrium surface force for the cylinder-cylinder case can now be calculated from eqs 3 and 15

$$\frac{1}{2\pi R} F = \Delta \gamma^f = - \frac{\phi_c^2}{a_c} \left(\frac{\partial \Delta \epsilon^f}{\partial \phi_c} \right)_h = - \frac{k_B T \phi_c}{a_c \phi_w^2} \quad (19)$$

where the rhs represents the surface pressure (with sign reversed) caused by the presence of the rod-shaped clusters. This expression

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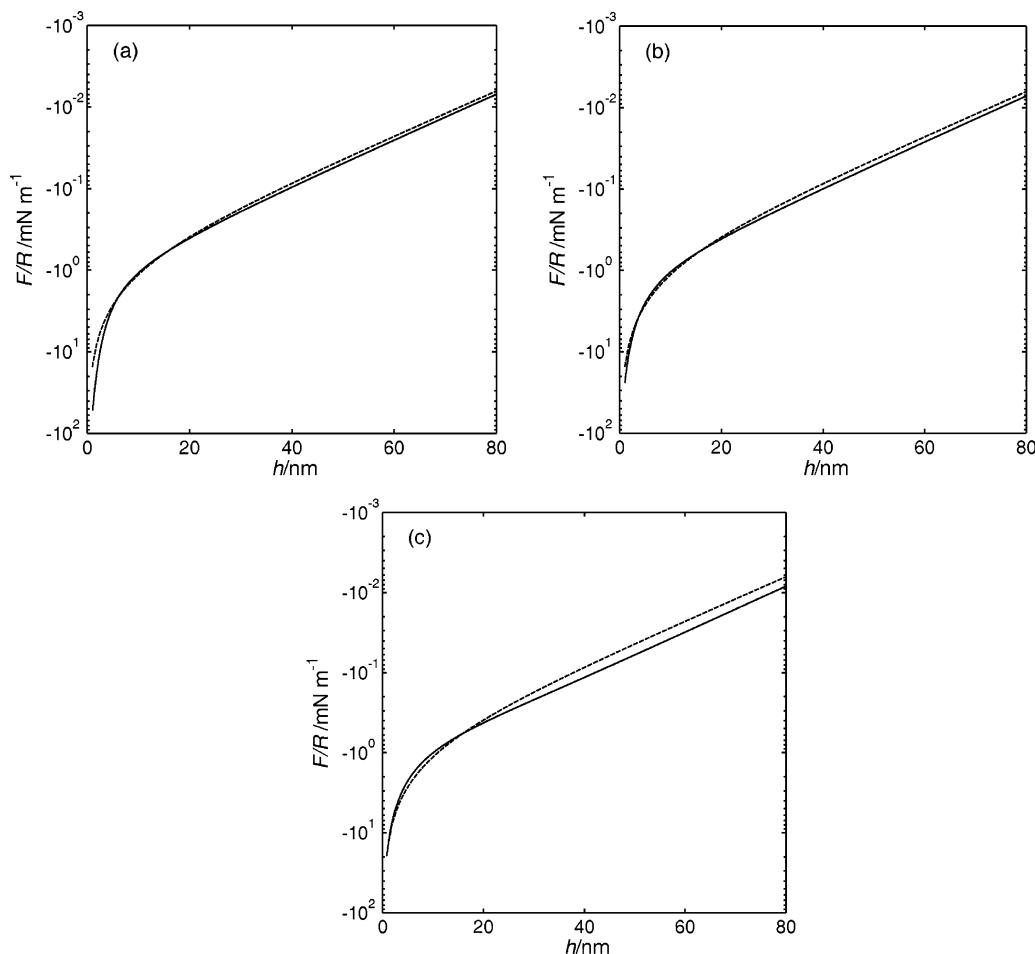


Figure 3. Surface force vs thickness (solid curves) obtained for (a) $a_c = 1 \text{ nm}^2$, $\Delta\gamma_{\text{eff}} = 6.695 \text{ mJ m}^{-2}$, and $c = 7.955 \text{ nm}$; (b) $a_c = 5 \text{ nm}^2$, $\Delta\gamma_{\text{eff}} = 0.6765 \text{ mJ m}^{-2}$, and $c = 10.72 \text{ nm}$; and (c) $a_c = 25 \text{ nm}^2$, $\Delta\gamma_{\text{eff}} = 2.798 \text{ μJ m}^{-2}$, and $c = 23.49 \text{ nm}$. The dashed lines represent eq 5 for $b^{-1} = 15.8 \text{ nm}$ and $B = 0.50 \text{ mN m}^{-1}$ in all three cases.

is not new, but it is well known to almost exactly account for the surface pressure exerted by hard discs.²⁶

Determination of the Parameter Values. From this point on, we adopt the standpoint that eq 5 primarily constitutes just a convenient mathematical representation of experimental surface force data for the case of a pure water film sandwiched between two hydrophobic surfaces. In other words, $B = 0.50 \text{ mN m}^{-1}$ and $b^{-1} = 15.8 \text{ nm}$, which give the solid curve in Figure 2a and should be considered merely as experimentally determined constants. The parameters in our model were determined as follows:

- The parameter b has the same meaning in eqs 5 and 17 as the inverse of the decay length for large separations and is fixed to $b^{-1} = 15.8 \text{ nm}$.

- Next, some particular values for a_c were chosen. For each a_c value, the behavior at large film thickness is examined. When $h \rightarrow \infty$, $\phi_w \rightarrow 1$ and eqs 18 and 19 result in the following expressions

$$\frac{2a_c\Delta\gamma_{\text{eff}}}{k_B T} + bh + \ln \phi_c = 0 \quad (20)$$

$$-\frac{F}{R} = \left(\frac{2\pi k_B T}{a_c}\right) \phi_c = \left(\frac{2\pi k_B T}{a_c}\right) e^{-2a_c\Delta\gamma_{\text{eff}}/k_B T} e^{-bh} \quad (21)$$

which can be compared with the experimental behavior at large thickness from eq 5

$$-\frac{F}{R} = 2B \exp(-bh) \quad (22)$$

Identifying the last two expressions gives

$$B = \left(\frac{\pi k_B T}{a_c}\right) e^{-2a_c\Delta\gamma_{\text{eff}}/k_B T} \quad (23)$$

from which $\Delta\gamma_{\text{eff}}$ can be determined for each chosen a_c value. It appears from eq 23 that the B constant is closely related to the work required to attach the cluster ends to the hydrophobic surfaces. For $B = 0.50 \text{ mN m}^{-1}$, we find $\Delta\gamma_{\text{eff}}$ to range from 0.003 to 0.68 mJ m^{-2} for a_c values between 25 and 5 nm^2 (i.e., in the range of microemulsion interfacial tension). One has to bear in mind, however, that to a certain extent these figures are affected by the choice of the standard state as discussed above.

- To determine the c parameter, we have, for simplicity, at first set h equal to b^{-1} . Equilibrium cluster fraction ϕ_c at this thickness was calculated from eq 19 by first making use of eq 5 to obtain F/R at the same thickness. Then the equilibrium condition of eq 18 was applied to derive a value for the c parameter.

Figure 3 shows the different surface force functions generated for $a_c = 1, 5$, and 25 nm^2 , respectively. It appears that all three curves can rather faithfully account for the surface force function of eq 5, which implies that the choice of the a_c value by no means

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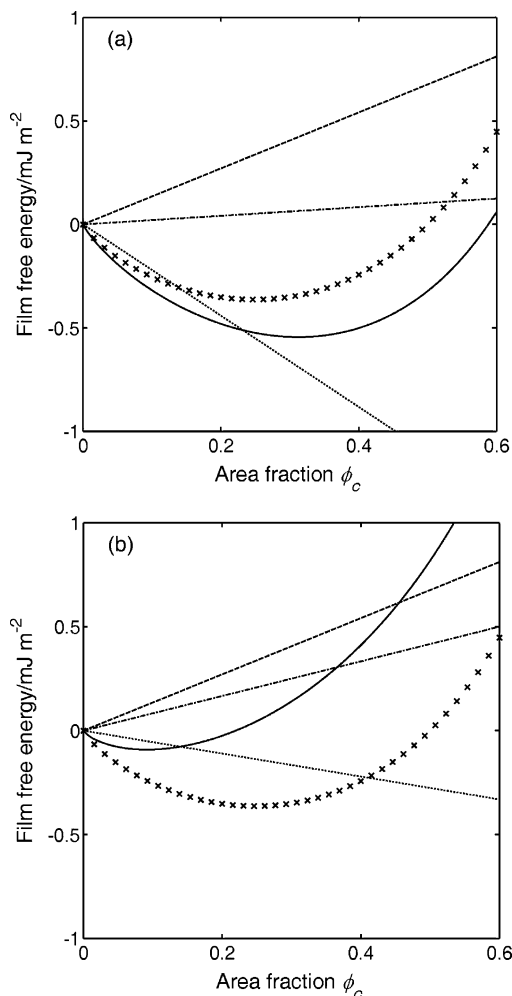


Figure 4. Different contributions to the film free energy $\Delta\omega^f$ displayed as functions of the area fraction of clusters. The parameter values inserted are $a_c = 5 \text{ nm}^2$, $\Delta\gamma_{\text{eff}} = 0.6765 \text{ mJ m}^{-2}$, and $c = 10.72 \text{ nm}$. The dashed curve shows the contribution from the $\Delta\gamma_{\text{eff}}$ -containing term, the dash-dotted line shows the contribution from the b -dependent term, and the dotted line shows the contribution from the c -dependent term whereas the curve marked by crosses represents the entropy of mixing contribution. Finally, the solid curve is the total excess film free energy. (a) $h = 4 \text{ nm}$ and (b) $h = 16 \text{ nm}$.

is crucial. Furthermore, when the above scheme is followed this choice will only to a rather modest extent affect the value derived for the c parameter. Yet one might well pick the curve obtained for $a_c = 5.0 \text{ nm}^2$ as the one to prefer. However, varying the a_c parameter alone while keeping all thermodynamic parameters fixed will yield vastly different surface force curves.

Results. Figure 4 shows how the excess free energy $\Delta\omega^f$ of the water film varies as a function of the cluster fraction ϕ_c while keeping the thickness h constant and the a_c parameter fixed to 5.0 nm^2 . Note that for both cases the entropic term is instrumental in giving rise to a minimum in the film tension and that $\Delta\gamma_{\text{eff}}$ in effect is found to be positive, equal to 0.6765 mJ m^{-2} for $B = 0.50 \text{ mN m}^{-1}$.

With the parameter values accordingly determined, $\phi_c(h)$ was calculated from eq 18 at the chosen cluster cross section $a_c = 5 \text{ nm}^2$. The corresponding surface force function was readily obtained by means of eq 19. The results of these calculations are presented in Figure 5. In Figure 5a, this particular surface force function is shown together with experimental data points, and the various contributions to the equilibrium surface force are plotted in Figure 5b, from which it appears that the entropic term

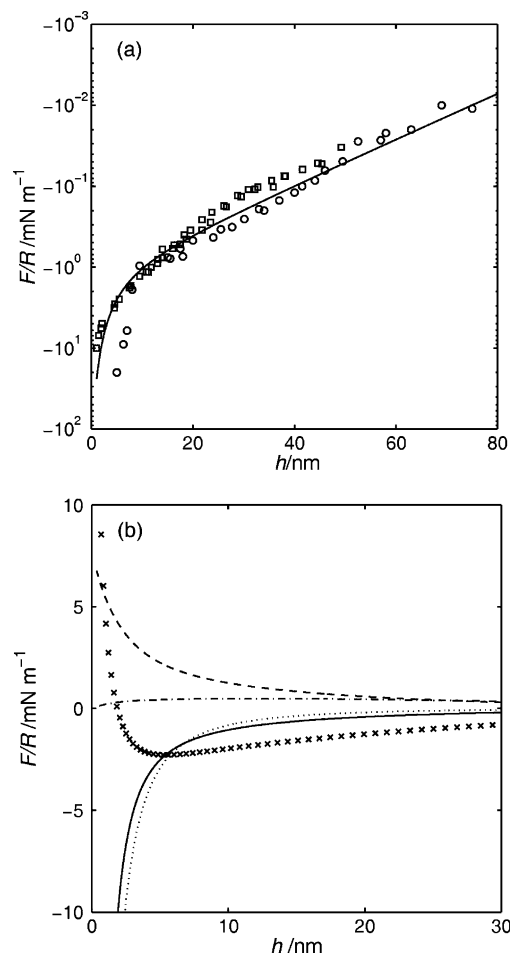


Figure 5. Surface forces calculated for $a_c = 5 \text{ nm}^2$, $\Delta\gamma_{\text{eff}} = 0.6765 \text{ mJ m}^{-2}$, and $c = 10.72 \text{ nm}$ shown with the same experimental data points that are included in Figure 2a (left) and the various components of the surface force on a linear scale (right). The solid curve represents the total surface force, the dashed curve represents the $\Delta\gamma_{\text{eff}}$ -dependent component, the dashed-dotted curve represents the b -dependent component, the dotted curve represents the c -dependent component, and the curve marked with crosses represents the component due to the entropy of mixing.

is predominant as the driving force for thickness above about 10 nm whereas the c/h term takes over the leading role for smaller thickness.

Because the cluster density change accompanying the structural reorganization increases only slightly and gradually in a hyperbolic manner when the film thickness shrinks and the same holds true for the cluster concentration (Figure 6), the average density would hardly be affected at all except for a film thickness smaller than about 2 nm where $\phi_c \approx 0.5$ (Figure 6).

Before closing this section, let us recall that the disjoining pressure π_D , which can be expressed as $\pi_D^{\text{cluster}} \phi_c$, can be obtained from the calculated surface force function (Figure 5a) and eq 1. It is noteworthy that the cluster tension $-\pi_D^{\text{cluster}}$ becomes practically independent of h and approaches $bk_B T/a_c = 5.2 \times 10^4 \text{ N m}^{-2}$ for large enough surface separations, which is most readily verified by using the relation

$$\left(\frac{\partial\omega}{\partial h}\right)_a = -\pi_D = \frac{k_B T}{a_c} \phi_c \left(b + \frac{c}{h^2}\right) \quad (24)$$

that follows from eqs 7 and 17.

c/h Term. On the basis of the above calculations, we find that it is crucial to include a term that depends inversely on the film

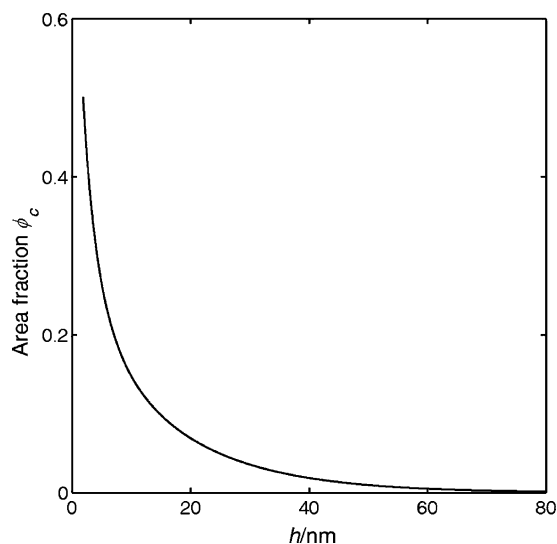


Figure 6. Area fraction of clusters plotted vs film thickness h for the main case: $a_c = 5 \text{ nm}^2$, $\Delta\gamma_{\text{eff}} = 0.6765 \text{ mJ m}^{-2}$, and $c = 10.72 \text{ nm}$.

thickness, such as the c/h term, in order to be able to reproduce the “knee” of the experimental surface force function observed in the middle range at about 10 nm in film thickness. Moreover, our previous laterally homogeneous film model²⁰ includes a contribution of this kind as a salient feature. Going back to eq 4 and ref 20, we can show that for small thickness ($h \ll b^{-1}$) this expression reduces to approximately

$$\omega^f = \omega_{\text{fil}}^f - c_1 s_0 + c_2 s_0^2 h \quad (25)$$

where, as before, ω_{fil}^f denotes the Ω potential per square meter prior to restructuring the film. This is so because $s(x)$ turns out to be nearly constant and equal to s_0 of the contact monolayers. Minimization with respect to s_0 means that for fully equilibrated, laterally homogeneous water films we will have

$$\gamma^f = \omega_{\text{fil}}^f - \frac{c_1^2}{4c_2 h} \quad (26)$$

Evidently, this expression implies that for thin water films the attractive force grows in magnitude as $1/h$ when the film gets thinner, as we have already noted in the text below eq 5.

Correspondingly, we may assume that two terms of the same kind as the s_0 -containing terms of eq 25 (viz., $-2a_c k_{\text{surf}} \Delta s_0 + a_c h k_{\text{cyl}} \Delta s_0^2$) have to be included in our primary cluster free-energy expression (that will result in eq 17) where $\Delta s_0 = s_0(h) - s_0(\infty)$ is the thickness-dependent order parameter of a bridging cluster. These terms thus account for the free-energy changes due to varying the state of order of the clusters. They vanish, of course, for comparatively thick films. Note that the thermodynamic parameters k_{surf} and k_{cyl} related to the end contact surfaces and core volume of a bridging cluster, respectively, do not need to turn out exactly the same as c_1 and c_2 in eq 25 because the corresponding theoretical frameworks are different. By minimizing this free-energy contribution with respect to the Δs_0 parameter, we obtain

$$\Delta s_0 = \frac{k_{\text{surf}}}{h k_{\text{cyl}}} \quad (27)$$

and the following expression for the intrinsic cluster free energy emerges:

$$\Delta\epsilon_{\text{cluster}} = 2\Delta\gamma_{\text{eff}} a_c + b h k_B T - \left(\frac{k_{\text{surf}}^2 a_c}{k_{\text{cyl}} h} \right) \quad (28)$$

This expression covers, as it should, the first three terms of eq 17, showing that we are in fact able to rationalize the c/h term as a consequence of the ordering of the contact layers of the water clusters that bridge the hydrophobic surfaces (which is supposed to be favorable) but is counterbalanced by the surface-induced ordering occurring in the remainder of the bridging cluster (which is unfavorable). We then have the obvious relation

$$c \equiv \frac{k_{\text{surf}}^2 a_c}{k_{\text{cyl}} k_B T} \quad (29)$$

To summarize, in the present model we assume surface-driven structure formation to occur, that is limited to the bridging clusters. For the generation of these clusters, their mixing with the rest of the water in the film and the associated increase in entropy is of vast importance. In our previous theory, essentially the same ordering mechanism was inferred for all of the (laterally homogeneous) water films. Another difference is that in the present model we in principle rely just on the first three terms on the right side of eq 4 in order to account for the thermodynamics of the ordering process.

Interestingly, we are able to estimate k_{cyl} by computing the difference in Gibbs free energy between ice and liquid water at room temperature, invoking the entropy of fusion of ice, $22 \text{ J K}^{-1} \text{ mol}^{-1}$, and the heat capacities, 38 and $75 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. In this way, we find $\Delta\epsilon_{\text{cluster}}(\text{cylindrical part}) = 3.3 \times 10^7 \text{ J m}^{-3}$. By assuming this energy difference to correspond to a change in Δs_0 that is roughly equal to 0.5 upon passing from bulk water to solid ice,²⁷ we get $k_{\text{cyl}} = 1.3 \times 10^8 \text{ J m}^{-3}$. Furthermore, by assuming that $\Delta s_0 \approx 0.5$ likewise holds for a thin water film of a thickness of about 0.5 nm as compared with bulk water, from eq 26 we estimate k_{surf} to be $3.3 \times 10^{-2} \text{ J m}^{-2}$. On the basis of these k_{surf} and k_{cyl} values and inserting $a_c = 5 \text{ nm}^2$, in accordance with eq 29 we find $c \approx 10 \text{ nm}$, in amazingly good agreement with our calculations presented in the previous section (i.e., in support of choosing $a_c = 5 \text{ nm}^2$).

Discussion

From a purely numerical point of view, the bridging-cluster model presented here is rather unsuccessful because the two chief parameters (B and b) of our original treatment²⁰ eventually have been replaced by four parameters (a_c , $\Delta\gamma_{\text{eff}}$, b , and c). Yet, what we have gained in return is transparency and a good deal more physical insight. The derived parameter values seem reasonable, and the two most characteristic features of the experimental surface force curves (i.e., the exponential decay for large thicknesses and the amplification of the attraction seen in the middle separation range with diminishing the film thickness) emerge naturally, without any extraneous assumptions. Contrary to the case for the original model, for the bridging-cluster model it is important to invoke the notion of entropy of mixing. For both models, the concept of surface-driven water structure generation is essential. In the case of the new bridging-cluster model, however, this structure generation is limited to the clusters present, whereas the remainder of a thin film retains the local properties of a thick film.

For a model of this kind to be at all a realistic proposition, thermodynamically significant curvature effects have to be

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present. Otherwise, it would be hard to realize how structurally reorganized bridging clusters can actually belong to an account of the equilibrium states of a thin water film. Curvature effects for spherical water clusters have been a matter of theoretical investigation for a number of years.²⁸ Here cooperative interactions enter as an important aspect. In view of the fairly high hydrogen bond energies at play and the associated entropies, sufficient curvature elasticity can be anticipated. We may note that Chaplin²⁹ has proposed an icosahedral network cluster composed of 280 water molecules with a radius of 1.29 nm to be compared with the average radius of the cylindrical clusters invoked here, 1.26 nm. Furthermore, from the value of the b parameter we estimate the interfacial tension of the cylindrical cluster surface to be about 0.1 mN m^{-1} or less. Hence, bridging quasi-cylindrical clusters cannot readily be ruled out by simply claiming that they would constitute an inconceivable structural feature in a thin water film in contact with hydrophobic surfaces. We emphasize that this type of elongated clusters belong exclusively to the thin film scenario; in the bulk and in thick films, their concentration would become vanishingly small because of unfavorable end effects.

For the present, the bridging-cluster model as presented in this article might perhaps be recognized as a bold conjecture serving to promote experimental and theoretical efforts to understand the origin of the hydrophobic attraction fully. To settle this long-debated issue, the temperature dependence of the hydrophobic attraction needs further study. However, the few results presented so far for water films between hydrophobic surfaces indicate a significant reduction of the excess entropy for a thin water film as compared with that for a thick film, as is obviously in line with the notion of structure formation.⁵

Furthermore, we note that as a rule air components might be present that fill voids in the clusters (whereby a type of linear clathrate would arise) and stabilize them thermodynamically as well as mechanically, resulting inter alia in a larger decay length b^{-1} than would otherwise arise. (See ref 14.)

Finally, the minor, though occasionally fairly significant, steps seen in the surface force versus separation curves, even without any indication of adhering/bridging bubbles, can be attributed to the nucleation of bridging clusters that is bound to require more or less activation energy depending on the closer nature of the hydrophobic surfaces. Thus, it appears that most of the (well-documented) salient features of the experimentally recorded surface force versus film thickness curves may be accounted for by invoking the notion of structurally ordered, bridging clusters of water molecules.

Conclusions

We have presented an essentially surface-thermodynamic model that can account for the most reliable surface force data available on the long-ranged hydrophobic attraction recorded for thin water films between hydrophobic surfaces. A key component is the notion of elongated, bridging clusters that are organized structurally in a different manner from the rest of the water present in the film, broadly in line with current ideas about the formation of spherical water clusters in bulk water.²⁸

By considering the free-energy changes associated with attaching the clusters to the hydrophobic surfaces, elongation of the clusters, reorganization of the clusters as their length is varied, and finally, the entropy of mixing the clusters with the rest of the water present in the film, we have generated a viable model that yields an exponential surface force dependence of the thickness for thick films as well as an amplification knee for $\sim 10 \text{ nm}$ films.

The inverse of the decay length of the surface force, as it is commonly reported, multiplied by $k_B T$, turns out to be simply the work needed per meter to elongate a (long) cluster. Furthermore, to account for the amplification of the surface force for small separations, a crucial term of the (inverse) form $-c/h$, with c denoting a constant, is included in the basic free-energy expression. This term is related to the structural reorganization of the bridging clusters taking place as the film thickness is varied. The model is characterized by two more parameters: (i) the average radius of a cluster (about 1 to 2 nm) and (ii) a parameter related to the work of attaching the bridging clusters to the hydrophobic surfaces, both of which likewise can be determined by fitting to experimental surface force results. The parameter values derived in this manner all seem reasonable, as do the cluster surface fractions and cluster tensions derived for different thicknesses.

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