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Possible implications of hydrophobic slippage on the dynamic measurements of hydrophobic forces

Olga I Vinogradova

Laboratory of Physical Chemistry of Modified Surfaces, Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky Prospect, 117915 Moscow, Russia

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Abstract. It was earlier shown that capillary measurements may be interpreted in favour of hydrophobic slippage. Here, the possible implications of this phenomenon as regards the dynamic technique for the hydrophobic attractive force measurements are discussed. We demonstrate that under experimental conditions discernible deviations from the Reynolds theory due to slippage may occur. Misuse of the Reynolds theory may lead to overestimation of the hydrophobic attractive force. This apparent 'extra attraction' depends critically on the driving speed, and the types of force present in the system.

1. Introduction

The surface force apparatus (SFA) uses a technique of optical interferometry to determine the separation between two crossed cylinders of molecularly smooth transparent mica. There are a number of different techniques for measuring force. In the simplest technique the force is obtained from the deflection of a cantilever spring, on which one of the cylinders is mounted [1]. This deflection method is not suitable for the measurement of strongly attractive interaction because the device is prone to cantilever instability, which occurs when the distance derivative of the attractive force is greater than the spring constant k. Instead, one often resorts to the drainage (dynamic) technique [2, 3]. In this method the end of the spring away from the cylinder is driven towards the other (fixed) cylinder with a constant driving speed. The spring is deflected as a result of both the surface force F_s, and the hydrodynamic force F_h. This technique has the advantage that the measurements can be made more rapidly. Also, the mechanical system becomes more stable (due to the presence of an additional 'repulsive' force).

It is usually assumed that the hydrodynamic force is adequately described by the Reynolds theory [2, 3], i.e. it is inversely proportional to the separation between the surfaces. The application of the Reynolds theory when the surfaces are hydrophobed must be questioned. Indeed, a considerable increase in liquid flow as compared with that expected when the no-slip condition is valid was observed in flow through hydrophobed capillaries of small diameters (see, for example, [4]). These changes may be interpreted in favour of hydrophobic slippage described by a slip length b [4, 5]:

$$\boldsymbol{v}_s = b\frac{\partial \boldsymbol{v}_s}{\partial n} \tag{1.1}$$

where $\boldsymbol{v}_s$ is the slip (tangential) velocity on the wall, and the axis n is normal to the surface. Previous work [5, 6] explored theoretically hydrodynamic interaction of curved bodies allowing slip on their surfaces, and predicted decreased hydrodynamic resistance (as compared to the Reynolds drag) when the separation becomes comparable with the slip lengths of bodies. Hence, one can expect that only part of the force found by subtracting of the Reynolds drag F_R from the total force measured may be attributable to F_s. Another part may be due to hydrophobic slippage, and will appear as a new long-range attractive force. Our aim here it is to examine this apparent 'extra attraction' under experimental conditions in the SFA.

2. Analysis

A simple force balance gives

$$F_h + F_s = F_k \tag{2.1}$$

where F_k is the restoring force of the cantilever spring. We assume here that any surface forces present are unaffected by the relative motion of surfaces and are thus the equilibrium forces. This is valid when the relative velocity is sufficiently slow compared to the characteristic relaxation times of the physical processes that give rise to F_s, which appears to be satisfied for water films and typical approach velocities in the SFA.

2.1. Hydrodynamic force

The hydrodynamic resistance to the approach of two crossed cylinders of radii R can be expressed as [5, 6]

$$F_h = -\frac{6\pi R^2 \mu}{h} \frac{\mathrm{d}h}{\mathrm{d}t} f^* \tag{2.2}$$

where μ is the bulk dynamic viscosity ($\mu = 10^{-2}$ dyn s cm^{-2} for water), and f^* is the correction for slippage that for cylinders of the same slip length b takes the form [5, 7]

$$f^* = \frac{h}{3b} \left[\left(1 + \frac{h}{6b}\right) \ln\left(1 + \frac{6b}{h}\right) - 1 \right].$$

We have chosen the value of $b \sim 10^{-5}$ cm (obtained for water in methylated silica capillaries [4]). Typically, one uses $R \sim 1$ cm in the surface force experiment.

2.2. Surface forces

We consider that only attractive forces are present. This situation is the most favourable for experiment, because the uncertainty of having to subtract out a double-layer force is avoided. Indeed, some of the measurements of hydrophobic forces (see, for example, [3]) claimed to have neutral surfaces.

In the general case, the surface attractive force presents the sum of van der Waals attraction (F_{vdw}) that is always available in the system, and some additional non-DLVO attraction, or hydrophobic interaction (F_{sh}).

In the non-retarded approximation the van der Waals (dispersion) force is given by the expression

$$F_{vdw} = -\frac{RA}{6h^2} \tag{2.3}$$

where A is the Hamaker constant ($A = 2 \times 10^{-13}$ erg cm^{-2} for mica across water [1]). All the types of attractive force can be modelled with power-law [3] or exponential [8] decay.

The power-law decay is chosen to be of the form

$$F_{sh} = -\frac{RC}{h^2} \tag{2.4}$$

where C is some constant. For an upper bound of C we have chosen a value of 10^{-12} erg. In this case, with force resolution 10^{-2} dyn, the hydrophobic force is measurable to $\sim$100 nm, and $\sim$1.5 orders of magnitude larger than the van der Waals force. Thus, values of C in the range 0–10^{-12} erg represent the physically realistic regime.

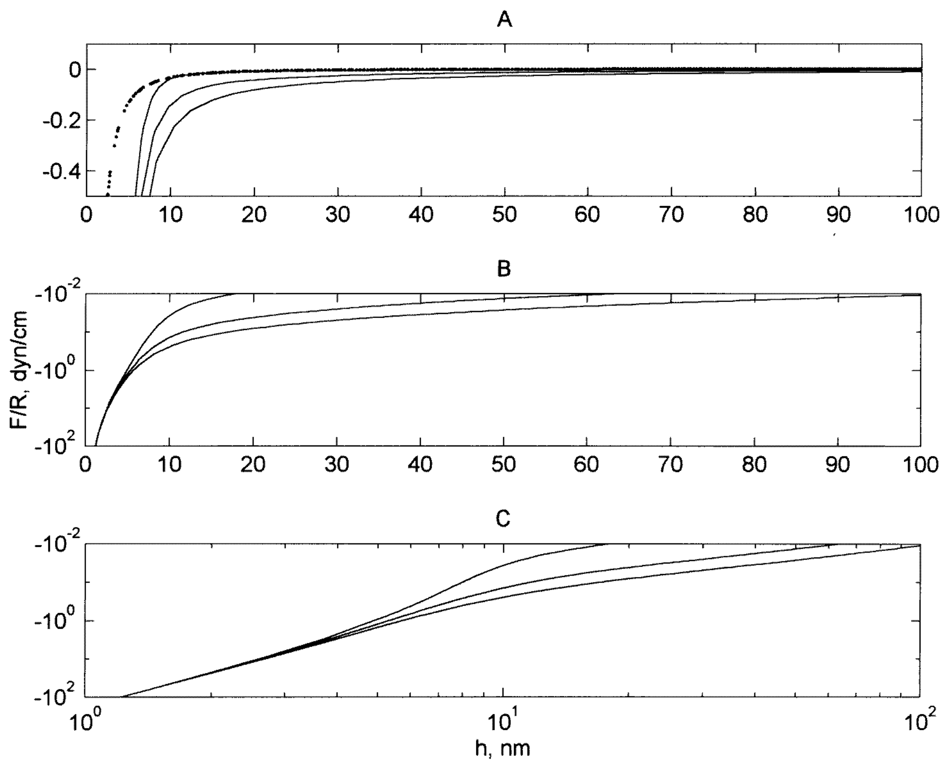

Figure 1. (A) The apparent 'extra attraction' (normalized by the radius of curvature of the surfaces) as a function of the separation expected if just a van der Waals attraction (dotted curve) acted between the surfaces. The solid curves from left to right are the computed results for $v = -1, -5, -10$ nm s^{-1}; (B) the same results replotted on a semilogarithmic scale; (C) the same values plotted on a log–log scale.

Exponential force is modelled with the expression

$$F_{sh} = -RB\exp\left(-\frac{h}{\lambda}\right) \tag{2.5}$$

where B is the prefactor, and λ is the decay length. In the general case, hydrophobic force is a double-exponential function [8]. We are interested here only in the long-range part of this exponent, so we have examined the case of $B = 1$ dyn cm^{-1} with the decay lengths 5, 10, and 15 nm.

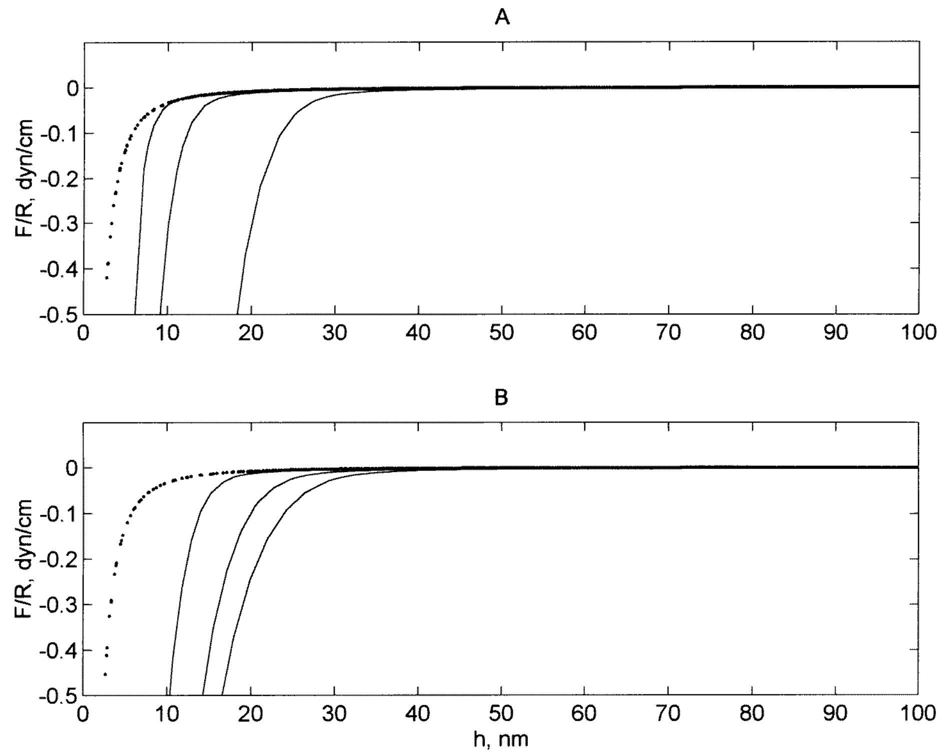

Figure 2. The apparent 'extra attraction' (normalized by the radius of curvature of the surfaces) as a function of the separation expected if hydrophobic attraction acted between the surfaces ($v = -1$ nm s^{-1}). The dotted line shows the van der Waals attraction. The solid curves from left to right are (A) the results computed by using (2.4) for $C = 0, 10^{-13}, 10^{-12}$ erg; (B) the results calculated using (2.5) for $\lambda = 5, 10, 15$ nm.

2.3. The restoring force of the cantilever spring

This is proportional to the instantaneous deflection of the spring from its equilibrium position multiplied by the spring constant k. For a standing start one can write

$$F_k = k(h - h_0 - vt) \tag{2.6}$$

where h_0 is the initial separation between the cylinders, and v is the driving speed. We have used the spring constant of 10^5 dyn cm^{-1}. This appears to be typical for spring stiffness used in water systems. It is reasonable to choose such a distance h_0 that exceeds both the radius of action of the surface forces, as well as the range of possible deviations from the Reynolds theory due to slippage. So, we have used $h_0 = 2 \times 10^{-5}$ cm. We have chosen driving speeds of -1, -5, and -10 nm s^{-1}. The lower value of v is just the speed used in reference [3] (where the authors have endeavored to keep the hydrodynamic force as small as possible in order to minimize the effects of any deviations from the Reynolds theory).

In general it is impossible to obtain a solution of differential equation (2.1) taking into account (2.2), (2.3), (2.4), (2.5) and (2.6) in closed form. This equation is then solved numerically. To calculate the drainage curve $h(t)$ we used a fourth-order Runge–Kutta method. Then, from computed $h(t)$ it was possible to calculate force–distance curves for time-dependent forces F_k and F_h. The Reynolds drag F_R was then found by dividing F_h

by the correction for slippage f^*. The apparent 'extra attraction' is consequently given by $F_h - F_R$.

3. Results and discussion

The effect of varying driving speed on deviations from the Reynolds theory on the supposition that only non-retarded van der Waals surface force is present is illustrated in figure 1. For comparison, the van der Waals force is shown as a dotted line. We see that there is an experimentally significant 'extra attraction', coming in at about ∼15–100 nm depending on driving speed. This appears to approximate an exponential with two decay lengths, and looks somewhat like a power law with an exponent of roughly −2. In other words, it exhibits the same functional dependence as that for the hydrophobic attractive force. The magnitude however is not large enough to account for the observed difference between the DLVO theory and experiment that is usually interpreted in favour of hydrophobic attraction [8].

The situation can change dramatically if some additional attractive forces are present. This leads to substantial increase in the deviations from the Reynolds theory (see figure 2) even at low driving speed. We believe that the poor agreement of the drainage results with conventional results [3] might be due to these deviations.

To distinguish the deviations from the DLVO theory from those from the Reynolds theory it is necessary to perform the drainage rate measurements always at several driving speeds. If so, the hydrophobic attraction is exactly defined. On the other hand this allows one to evaluate the value of the slip length. However, fifteen years on from the first reports on hydrophobic attractive force, we are still lacking systematic data on this dependence.

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