

# Forces between CTAB-Covered Glass Surfaces Interpreted as an Interaction-Driven Surface Instability

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We examine recently reported forces between glass surfaces immersed in solutions of an adsorbing charged amphiphile (CTAB). The collapse of electrostatic double layer repulsion in such systems had been the occasion for suspecting the existence of hydrophobic attraction at surprisingly large,  $\sim 10$  nm, separations. Now, following the reasoning of a surface-instability model of "hydrophobic" interactions, we combine the Derjaguin approximation for the interaction of oppositely curved surfaces with general thermodynamic Maxwell relations and Gibbs adsorption isotherms. This combination creates a procedure to analyze chemically sensitive forces between macroscopic surfaces while explicitly including the chemical potentials of adsorbing species. At least in this system where solution conditions are specified, puzzling long-range attractive forces turn out either to be the consequence of an instability in the amount of adsorbed CTAB, driven by the changes in the intersurface separation, or to be a simple van der Waals force between surfaces whose separations are diminished by layers of adsorbed amphiphile. There appears to be no need in this case to assume the existence of more abstruse mechanisms.

## Introduction

In their recent report on forces between glass surfaces immersed in cetyltrimethylammonium bromide (CTAB) solutions, Parker *et al.*<sup>1</sup> have provided additional information on what has been called a "long-range attraction between macroscopic hydrophobic surfaces".<sup>2</sup> Their measurements, with a modified surface force apparatus, extend similar observations of forces between mica surfaces in the presence of CTAB. It was the unexpected collapse of electrostatic double layer repulsion between mica surfaces pushed together in CTA<sup>+</sup> solutions that elicited the conjecture of an additional and unexpected attractive "hydrophobic" force<sup>3</sup> of unspecified origin. A clue to an alternate interpretation was provided by Kekicheff *et al.*<sup>4</sup> who, using CTAB purified by recrystallization, found results so different from the earlier papers that it was "not possible to obtain an estimate of this [hydrophobic] force".

An alternative, less dramatic interpretation is a surface-instability model<sup>5</sup> describing this collapse in terms of CTAB adsorption and desorption. Negatively charged mica (or glass) adsorbs positively charged amphiphiles first by electrostatic (at small surface coverage), and later (at larger surface coverage) by hydrophobic, interactions. The electrostatic potential that builds up on the surface is a price paid for this adsorption. As surfaces are pushed together, the electrostatic interaction energy increases until that electrostatic price of charging/adsorption is too high for the surfaces to remain charged. The result is a sudden desorption/neutralization. The surfaces simply collapse as further force is applied. This relation of *intersurface* and *intrasurface* energetics led to a simple, successful test and to a quantitative formulation of the measured forces in terms of traditional surface chemistry.<sup>5</sup> The effects of a similar mechanism of surface interaction driven adsorption instability have also been seen in the forces between ethoxylated amine surfactant covered mica surfaces.<sup>6</sup>

The Parker *et al.*<sup>1</sup> data on forces between spherical glass surfaces provide another opportunity to test that surface-

instability model. The electrostatic double layer repulsive force and the force applied upon collapse are given as a function of the submicellar concentration, or chemical potential, of CTAB in the bathing solution. There is a chemical vs physical competition here: the "pressure" of CTA<sup>+</sup> to adsorb and charge the surface vs the physical pressure to push those surfaces together. The shifting balance in this competition emerges clearly.

In addition to testing the surface-instability model with the new data, we re-examine the results for the one CTAB concentration where their data showed a net attraction, rather than repulsion and collapse. In this case, the surfaces are neutral because the net charge of positive adsorbed CTA<sup>+</sup> and Br<sup>-</sup> ions balances the negative charge of the underlying glass surface. This remaining attraction can be identified with straightforward van der Waals attraction as long as one realizes that in this force-balance system distances are known only to within an additive constant and that the interaction distance is less than that between bare-glass surfaces by the amount of a CTA<sup>+</sup> monolayer adsorbed to each facing surface.

## Thermodynamic Analysis

The main physical content of our proposal is that as the surfaces with adsorbed CTA<sup>+</sup> are pushed together, the adsorption/desorption equilibrium responds to the changes in separation. In this respect it is closely related to the charge regulation idea introduced by Ninham and Parsegian<sup>7</sup> for the adsorption of ions, the specific novelty here being the form of the surface free energy describing the nature of the *intrasurface* interactions and taken to be based on the adsorption isotherm energy.

We first of all examine the adsorption instability in phenomenological (thermodynamic) terms. We take into account the Derjaguin approximation<sup>8</sup> used in the interpretation of virtually all measurements of interactions between the oppositely curved surfaces of mica or glass. Forces between two interacting spheres are plotted as a ratio  $F/R$  which is taken to be proportional to the energy of interaction  $E(D)$  per unit area of equivalent planar surfaces

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$$\left(\frac{F}{R}\right) = \pi E(D) = -\pi \int_{\infty}^D P(D) dD \quad (1)$$

Here,  $P(D)$  is the pressure between equivalent parallel planar surfaces of the same composition so that  $E(D)$  is the surface energy density between planar surfaces relative to infinite separation. (For the crossed-cylinder geometry of mica in the conventional surface force apparatus there is a factor  $2\pi$  rather than  $\pi$  in the above relation.)

It is at this juncture that we can see a connection between the chemical and physical kinds of work that are done on the interacting surfaces. The way the experiments are done is to change CTA<sup>+</sup> concentration or its chemical potential  $\mu$  and to change continuously at slow but finite driving rates the distance  $D$  between surfaces while measuring the resulting force. (A completely equivalent view can be taken where the independent variable is the force or pressure between surfaces and separation distance is the resulting dependent variable. We have formulated the energy with  $D$  as the independent variable since the experiments are done by continuously varying  $D$ .) Force curves are measured with different driving speeds to determine the importance of hydrodynamic forces. For the force curves reported in ref 1, hydrodynamic effects can be neglected (P. Claesson, personal communication).

Thermodynamically the change in free energy of interaction per unit area between equivalent planar surfaces is expressed in terms of two variables,  $\mu$  and  $D$ ,

$$dE(\mu, D) = -N(\mu, D) d\mu - P(\mu, D) dD \quad (2)$$

The first, chemical, term ( $-N(\mu, D)d\mu$ ) is the Gibbs adsorption isotherm; it says that the sensitivity to chemical potential of free energy per unit area is proportional to the surface excess number  $N(\mu, D)$  of CTA's per unit area. The second, physical, term ( $-P(\mu, D)dD$ ) comes from the pressure vs separation work. (The sign recognizes that a decrease in separation against positive  $P$  will increase surface energy.)

Because at separations greater than the collapse distance,  $D_{\text{coll}} \leq D \leq \infty$ ,  $E = E(\mu, D)$  is a continuous function of  $\mu$  and  $D$ , there is a Maxwell relation between  $N(\mu, D)$  and  $P(\mu, D)$

$$-\left.\frac{\partial P(\mu, D)}{\partial \mu}\right|_{D, \dots} = -\left.\frac{\partial N(\mu, D)}{\partial D}\right|_{\mu, \dots} \quad (3)$$

Through this relation we connect the measured change in energy,  $\partial E(\mu, D)/\partial \mu = \partial(F/\pi R)/\partial D$ , with the number of associated surface-excess CTAB molecules  $N(\mu, D)$  per unit area relative to the number  $N_{\infty}(\mu) = N(\mu, D \rightarrow \infty)$  at infinite separation. A similar use of Maxwell relations for adsorption affecting colloidal interactions is given in refs 19 and 20.

Because  $P(D)$  is the derivative  $-\partial(F/\pi R)/\partial D$ , where  $F/\pi R$  goes through a maximum at or very near a collapse point,  $P$  must approach zero at  $D_{\text{coll}}$ . If the only significant interaction between surfaces is electrostatic repulsion due to CTAB adsorption, then at the collapse point ( $D_{\text{coll}}$ ) the charge on the surfaces must be zero.

Consider now the set of reversible force curves at separations between the collapse distance  $D_{\text{coll}}$  and  $D \rightarrow \infty$ . Since the work  $E(D_{\text{coll}})$  needed to go between these two positions,  $(F/\pi R)_{\text{coll}}$ , is an integral over the whole reversibly accessible pressure vs separation range,

$$\left(\frac{F}{\pi R}\right)_{\text{coll}} = -\int_{\infty}^{D_{\text{coll}}} P(D) dD \quad (4)$$

the change in  $(F/\pi R)_{\text{coll}}$  with a change in CTAB concentration or chemical potential  $\mu$  translates into a derivative of pressure

$P(D)$  with respect to  $\mu$ .

$$\frac{\partial(F/\pi R)_{\text{coll}}}{\partial \mu} = -\int_{\infty}^{D_{\text{coll}}} \frac{\partial P(\mu, D)}{\partial \mu} dD = \int_{\infty}^{D_{\text{coll}}} \left(\frac{\partial N(\mu, D)}{\partial D}\right) dD = \Delta N_{\text{coll}} \quad (5)$$

This relation provides an instructive connection between  $\Delta N_{\text{coll}}$ , the change in the surface-excess number of CTABs at infinite vs collapse separations, and the sensitivity to CTA activity of the collapse energy  $E(D_{\text{coll}}) = (F/\pi R)_{\text{coll}}$ . It has the form

$$\frac{\partial(F/\pi R)_{\text{coll}}}{\partial \mu} = \pi(N(D_{\text{coll}}) - N(D_{\infty})) = \pi \Delta N_{\text{coll}} \quad (6)$$

This relation says that if a number  $(N(\mu, D_{\text{coll}}) - N_{\infty}(\mu))$  of CTAB's must be pushed off (or on) a unit area of surface in order for them to collapse, then the change,  $d(F/\pi R)_{\text{coll}}$ , in the physical work to bring surfaces to the collapse point is equal to the change  $(N(\mu, D_{\text{coll}}) - N_{\infty}(\mu))d\mu$  in the Gibbs adsorption excess energies of the surfaces at infinite separation and collapse. In this way, the measured  $\partial(F/\pi R)_{\text{coll}}/\partial \mu$  is a gauge of the surface excess of CTA's. If  $N(\mu, D_{\text{coll}})$  is that number of CTA's required to neutralize surfaces, and it is essentially the same number for all cases of collapse, then it is the dependence of  $N_{\infty}(\mu)$  on  $\mu$  that is the important part of  $\partial(F/\pi R)_{\text{coll}}/\partial \mu$ .

Formally, the above analysis bears a distant resemblance to the thermodynamic treatment of  $\text{Co}^{3+}$ -condensed DNA,<sup>9</sup> the most important difference being in the geometry of the experimental setup for measurement of the intersurface forces which necessitates the Derjaguin approximation.

### A Microscopic Model

We next turn to a simple microscopic model that we proposed recently.<sup>5</sup> Isolated CTAB-covered surfaces can be either in a charged or in a completely discharged state described by the surface free energy density of the form

$$f(\varphi) = -\frac{1}{2}a\varphi^2 + \frac{1}{4}b\varphi^4 + \dots \quad (7)$$

where  $\varphi$ , the value of the electrostatic potential at the adsorbing surface, is used as an order parameter, while  $a$  and  $b$  are surface-specific phenomenological constants. Since in these measurements the locus of the charge-bearing surface is not known but to within an additive constant,  $\varphi$  itself is a phenomenological quantity. To avoid further intricate and fruitless speculation, we use  $\varphi$  values as operationally defined in the experimental papers.<sup>1,3,4</sup>

Adding to this surface free energy  $f(\varphi)$  the ordinary (Poisson-Boltzmann) electrostatic double layer interactions between two apposed charged surfaces, we derived the changes in intersurface free energy (i.e., measured forces) as well as changes in the state of the surfaces by minimizing the total free energy with respect to  $\varphi$ . For very large intersurface separations, we obtained the following minimized form for the electrostatic potential

$$\varphi_{\infty}^2 = b^{-1} \left( a - \left. \frac{\partial \sigma_{\infty}(\varphi)}{\partial \varphi} \right|_{\varphi=0} \right) \quad (8)$$

where  $\sigma_{\infty}(\varphi)$  is the functional form of the dependence of the surface charge density  $\sigma$  on electrostatic potential  $\varphi$  at infinite separation (the Grahame equation). As indicated, the derivative

TABLE 1: Measured and Computed Force Parameters<sup>a</sup>

| $(F/R)_{\text{coll}}$<br>[mN/m] | $\varphi_{\infty}$<br>[mV] | $(e_0/\sigma_{\infty})$<br>[Å <sup>2</sup> ] | $\lambda_D$<br>[nm] | $\varphi_{\infty}^2/(F/R)_{\text{coll}}$<br>[V <sup>2</sup> m/N] | $(\Delta N_{\text{coll}})^{-1}$<br>[Å <sup>2</sup> ] |
|---------------------------------|----------------------------|--|---------------------|--|--|
| Reference 3                     |                            |  |                     |  |  |
| 0.10                            | 20                         | 8300   | 7.7                 | 4.0  | ●  |
| 1.3                             | 80                         | 300  | 1.5                 | 4.9  | ●  |
| 2.8                             | 105                        | 1230   | 10.5                | 3.9  | 463  |
| 5.4                             | 140                        | 500  | 8.5                 | 3.6  | 463  |
| 9.2                             | 200                        | 42   | 2.3                 | 4.3  | 463  |
| Reference 4                     |                            |  |                     |  |  |
| 0.584                           | -55                        | 16600  | 52                  | 5.2  | ●  |
| 0.119                           | 28                         | 50000  | 70                  | 6.6  | ●  |
| 0.611                           | 65                         | 14300  | 51                  | 6.9  | 833  |
| 1.750                           | 100                        | 5260   | 40.5                | 6.3  | 833  |
| 2.879                           | 120                        | 2700   | 32                  | 5.0  | 833  |
| 4.32                            | 130                        | 2130   | 30                  | 3.9  | 833  |
| 5.437                           | 140                        | 1300   | 22                  | 3.6  | 833  |
| Reference 1                     |                            |  |                     |  |  |
| 0.07                            | -22                        | 1000   | 97.4                | 6.9  | ●  |
| 0.1                             | 18                         | 333  | 25.8                | 3.2  | ●  |
| 0.3                             | 50                         | 10000  | 17.1                | 8.3  | 2130   |
| 1.5                             | 110                        | 1470   | 13.8                | 8.0  | 866  |
| 2.3                             | 145                        | 630  | 11.9                | 9.1  | 540  |

<sup>a</sup> Normalized collapse force,  $(F/R)_{\text{coll}}$ , from published graphs; reported surface electrostatic potential  $\varphi_{\infty}$  fitted to force-distance curves at large separation, with  $\sigma_{\infty}$  corresponding to surface charge density computed via the Grahame equation (eq 10); Debye length  $\lambda_D$  computed from reported salt concentrations. The ratio  $\varphi_{\infty}^2/(F/R)_{\text{coll}}$  is computed to test the predicted relation between surface potential and the capacity of the interaction surfaces to absorb physical work (see Figure 1).  $\Delta N_{\text{coll}} = (N(\mu, D_{\text{coll}}) - N_{\infty}(\mu))$  computed here is obtained from a fit of  $(F/R)$  data to  $\log(c)$  (see main text). The marks ● in column 6 denote those data points that fell markedly outside the fit. A more complete computation of  $\Delta N_{\text{coll}}$  for Parker *et al.* data is given in Figure 3.

in the above equation has the form of a capacitance that should be taken at  $\varphi = 0$ . In the framework of this model we were able to show<sup>5</sup> that there is an adsorption instability in the system at a critical value of the intersurface spacing, given by the following relation

$$\left(\frac{F}{R}\right)_{\text{coll}} = \pi E(D_{\text{coll}}) = \frac{1}{4}\pi \left( a - \left| \frac{\partial \sigma_{\infty}(\varphi)}{\partial \varphi} \right|_{\varphi=0} \right) \varphi_{\infty}^2 \quad (9)$$

Here,  $(F/R)_{\text{coll}}$  is the measured force  $F(\mu, D_{\text{coll}})$  per curvature radius  $R$  of interacting surfaces (crossed cylinders for mica or sphere-against-flat for glass) at the instability point.  $E(\mu, D_{\text{coll}})$  is the corresponding surface free energy between planar surfaces of identical structure, and  $\varphi_{\infty} = \varphi_{\infty}(\mu)$  is the electrostatic surface potential inferred from the force curve at large separations. The above relation suggests that at the collapse point for different values of the CTAB concentration, the ratio  $\varphi_{\infty}^2/(F/R)_{\text{coll}}$  is a constant dependent only on the nature of the interacting surfaces, a prediction verified for earlier data and further tested below.

The surface charge density that goes with the surface potential at infinite separation is deduced by means of the Grahame equation (in mks units)

$$\sigma_{\infty} = \frac{e_0}{2\pi\lambda_B\lambda_D} \text{sh} \left( \frac{e_0\varphi_{\infty}}{2kT} \right) \quad (10)$$

used in Table 1.  $\lambda_B$  is the Bjerrum length ( $\approx 7.1$  Å for univalent charges in water) and  $\lambda_D$  is the Debye length of a uni-univalent salt. Since the degree of CTAB dissociation is not known *a priori*, there is no simple relation between the surface excess of CTA and the net surface charge. All one knows is that  $\sigma_{\infty}$ , the density of charge on the surface, must be less than or equal to the  $e_0$  times  $(N(\mu, D_{\text{coll}}) - N_{\infty}(\mu))$ , the number of CTA's in excess of those that neutralize the surface.

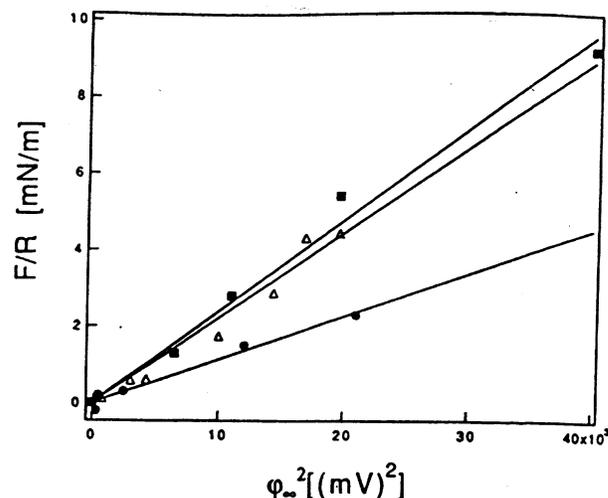


Figure 1. Testing the linear relation between the force at the collapse point  $(F/R)_{\text{coll}}$  and the square of the fitted electrostatic potential at large separations,  $\varphi_{\infty}^2$  ( $D \rightarrow \infty$ ). Data were extracted from three different measurements, two of them with mica supporting surfaces and one with a glass supporting surface: ■, data from Israelachvili and Pashley;<sup>3</sup> Δ, data from Kekicheff *et al.*;<sup>4</sup> ●, data from Parker *et al.*<sup>1</sup> The difference in slopes might indicate differences in charge and adsorptive powers of mica<sup>3,4</sup> compared to those of glass.<sup>1</sup>

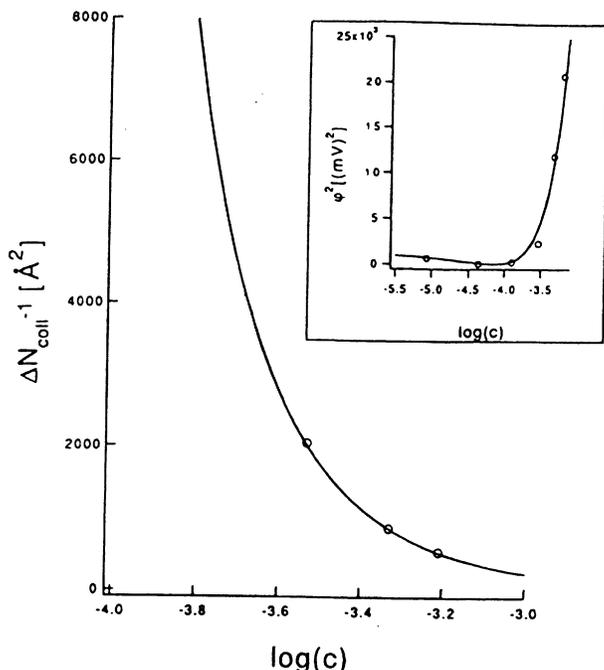
## Results and Discussion

(a)  $\varphi_{\infty}^2 \sim (F/R)_{\text{coll}}$ . Before considering the general connections between  $(F/R)_{\text{coll}}$  and  $\mu_{\text{CTA}}$  we check whether the Parker *et al.*<sup>1</sup> data obey the relation  $\varphi_{\infty}^2/(F/R)_{\text{coll}} \sim \text{constant}$ , see eq 9, verified for earlier data.<sup>5</sup> Table 1 and Figure 1 show that the constancy of the ratio  $\varphi_{\infty}^2/(F/R)_{\text{coll}}$  is well preserved in all the force curves, at least for data at higher potentials where  $(F/R)_{\text{coll}}$  is most accurately measured. To this extent, the new data by Parker *et al.*<sup>1</sup> on glass surfaces are completely consistent with the available experiments on mica surfaces<sup>3,4</sup> immersed in CTAB solutions.

Table 1 also presents values of several other parameters deduced from experiments with mica<sup>3,4</sup> and glass<sup>1</sup> surfaces. The common characteristic of all the data is the relatively small amount of surface charge  $\sigma_{\infty}$ , derived from the Grahame equation and  $\varphi_{\infty}$ , in all the experiments. An area per charge creating the observed potentials  $\varphi_{\infty}$  seems to be  $\sim 500$  Å<sup>2</sup> and greater. This is an order of magnitude greater than the expected area for a tightly packed monolayer of single-chain lipids. The general trends in the data are discernible from all the experiments.<sup>1,3,4</sup>

(b)  $\partial(F/R)_{\text{coll}}/\partial\mu = \pi\Delta N_{\text{coll}}$ . In order to get an estimate for  $\Delta N_{\text{coll}}$  in the experiment by Parker *et al.*<sup>1</sup> we eschew any assumption of the functional relationship between  $(F/R)_{\text{coll}}$  and  $\log(c)$  and try to fit the data without invoking any assumptions as to the form of the dependence of the collapse point on the CTAB concentration. We do, however, invoke the major tenet of our model that at the collapse point we have  $(F/R)_{\text{coll}} \sim \varphi_{\infty}^2(c)$ . The plot of  $\varphi_{\infty}^2(c)$  vs  $\log(c)$  should thus give us, through eq 6, the dependence  $\Delta N_{\text{coll}}(c)$ . This apparent indirect route through  $\varphi_{\infty}$  is taken in order to remain close to experimental information, where  $\varphi_{\infty}$  is provided and not  $(F/R)_{\text{coll}}$ .<sup>1</sup> Taking now the surface potentials at infinite separation,  $\varphi_{\infty}$ , as reported by Parker *et al.*<sup>1</sup> over the whole range of CTAB concentrations, we can parameterize their concentration dependence as

$$\varphi_{\infty} = A + Bc^{\alpha} \quad (11)$$



**Figure 2.** Dependence of the  $(\Delta N_{\text{coll}})^{-1}$  on the concentration of CTAB through eq 6. To stay close to the reported data,  $\varphi_{\infty}(c)$  was fitted to  $\log(c)$ , then  $(F/R)_{\text{coll}}$  was introduced assuming its proportionality to  $\varphi_{\infty}^2$ .  $\Delta N_{\text{coll}}$  goes to zero as the concentration of charge cancellation, a "point of zero charge" at infinite separation, is approached (at  $\approx 6 \times 10^{-5}$  M). The fitted dependence of  $\varphi_{\infty}(c)$  on the concentration of CTAB is  $\varphi_{\infty}(c) \approx -33.4 + 4.8 \times 10^4 \times c^{0.76}$ .

(N.B.: a form chosen *only* for mathematical convenience), where  $c$  is CTAB molar concentration. We obtain  $\alpha = 0.76$ ,  $A = -33.4$  mV, and  $B = 4.8 \times 10^4$  mV. This fitted dependence of  $\varphi_{\infty}(c)$  is then used to obtain  $(F/R)_{\text{coll}}$  through the linear relation  $(F/R)_{\text{coll}} \sim \varphi_{\infty}^2(c)$  over the full range of concentrations. The coefficient in the linear relation is  $8.45$  ( $\text{mV}^2/\text{N}$ ), and the expression nicely fits the entire set of data (see Figure 2). The  $(F/R)_{\text{coll}}$  value at  $c = 4.59 \times 10^{-5}$  M CTAB vanishes since that is the concentration at which the surface potential is apparently zero due to the charge balance between positive CTA<sup>+</sup> ions and the negative charges on the supporting glass. In that case, no force needs to be applied for the surfaces to come together. It will be treated separately in the next section.

In Figure 2 (inset) we show first of all the fitted values of  $\varphi_{\infty}^2(c)$  vs the CTAB chemical potential  $\mu \sim kT \log(c)$ . The curve obviously has two branches: below and above the point of zero charge. We use the branch above the point of zero charge to obtain a continuous dependence of  $\Delta N_{\text{coll}}$  on  $\log(c)$ . The reciprocal of this difference is plotted in Figure 2 (main graph) in order to show it as the change in area per charge going from infinite separation to collapse. Obviously, as the charge-neutralizing CTAB concentration is approached (near  $c = 4.59 \times 10^{-5}$  M), the difference  $(N(\mu, D_{\text{coll}}) - (N_{\infty}(\mu)) = \Delta N_{\text{coll}} \rightarrow 0$ .

There is only one data point reported below this neutral-surface concentration. There, the surfaces are negative due to incompletely neutralized glass; the main characteristics of the charging process probably differ from those in the positively charged branch analyzed here. For these reasons, negatively charged surfaces will not be considered more than they have been in the previous section.

In the case of other experiments the analysis cannot be as straightforward as for the Parker *et al.* data, since screening is provided not only by the CTAB but as well by the background salt (KBr, NaCl, etc.) used in the experiments. If we nevertheless apply our method to the Pashley *et al.* and Kekicheff *et al.*

data, we get a surprisingly good linear relationship between  $(F/R)_{\text{coll}}$  and  $\mu$ , and the value of  $(\Delta N_{\text{coll}})^{-1}$  obtained in this way is displayed in Table 1. We suspect that this is probably due to the fact that CTA chemical potentials depend primarily on CTAB concentration and only secondarily on the activity coefficient created by added salt.

(c) **Net-Attractive Force Curve.** The particular case of charge neutralization requires asking what attracts the surfaces when  $\varphi_{\infty}(c) = 0$ . Parker *et al.*<sup>1</sup> note that although the force curves at larger values of CTAB concentration ( $\geq 10^{-5}$  M) are indeed consistent with a repulsion–instability model, the single force curve at the CTAB concentration corresponding to complete surface neutralization ( $4.59 \times 10^{-5}$  M) shows "attractive forces much higher than predicted by van der Waals interaction". To draw this conclusion requires that the actual separation between CTA-adhering surfaces be known to nanometer accuracy.

One feature of the force balance devices on which long-range attractive forces have been measured is the care that must be taken to define distances of separation to within a correct additive constant. This feature is particularly clear with the modified surface force apparatus used by Parker *et al.*<sup>1</sup> where only the up/down displacement of a spherical probe and planar substrate are observable. The "zero" of contact is in fact ambiguous also from unreported deformation of surfaces estimated to be as great as  $\sim 3.2$  nm (P. Claesson, personal communication).

The simplest form for the van der Waals attraction energy between two plane parallel surfaces is an inverse-square relation which, with an ambiguity of an additive constant in separation, will have the form (see Figure 5)

$$\left(\frac{F}{R}\right) \cong \pi E_{\text{vdw}}(D) = \frac{H}{12(D - D_0)^2} \quad (12)$$

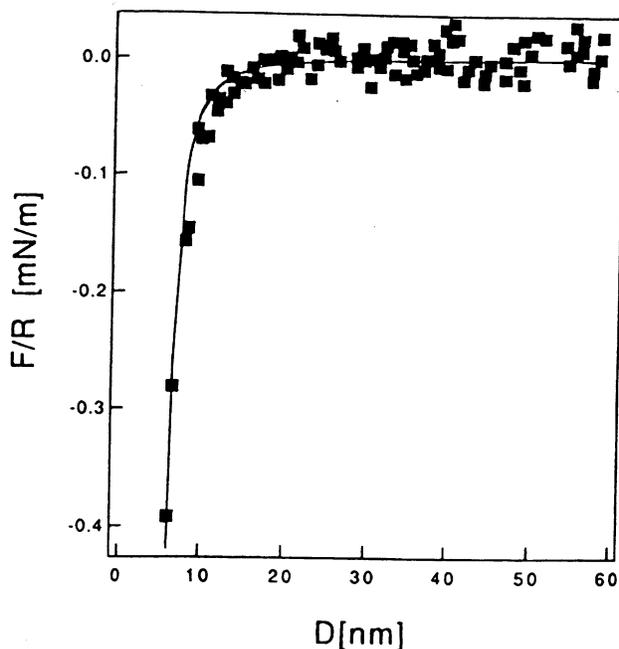
Fitting of the  $\varphi_{\infty} = 0$  data gives ordinary van der Waals attraction with a Hamaker coefficient  $H \approx 1.7 \times 10^{-20}$  J and displacement in the origin by  $D_0 \approx 4.3$  nm, see Figure 3.

This value of  $D_0$  is consistent with adsorbed monolayers of CTA of thickness  $D_0/2 \approx 21$  Å on either surface (CTA<sup>+</sup> itself has 16 carbons in the chain and could be longer than this  $D_0/2$  if in completely extended conformation). Incidentally, this is also reasonably close to the thickness of the adsorbed CTA layer  $\approx 15$  Å obtained independently in a recent measurement with optical interferometry by Kekicheff and Spalla.<sup>10</sup> The value of the Hamaker constant and the displacement in the van der Waals plane are both quite reasonable.

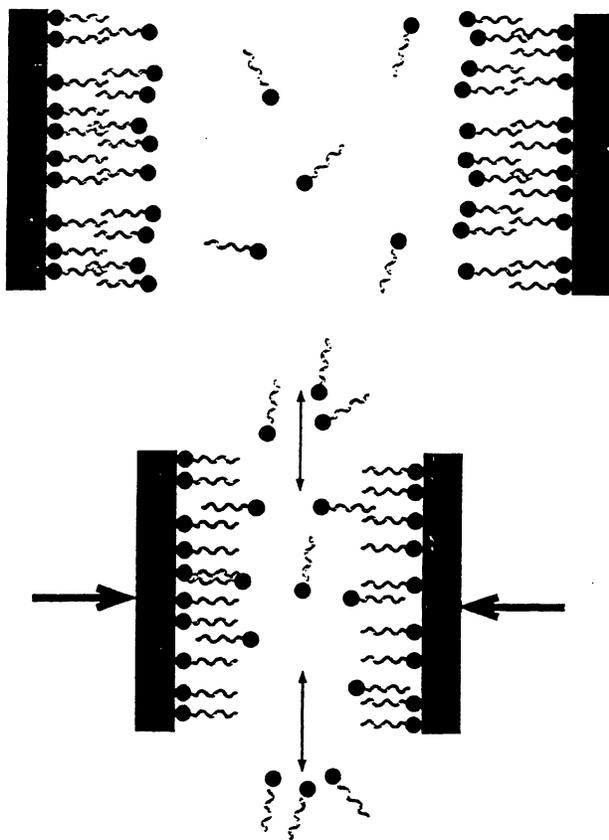
Unfortunately, any significant contribution from an adsorbed layer necessitates use of a more elaborate formula that includes van der Waals interactions between all interfaces:<sup>16</sup>

$$E(D) = \frac{1}{12\pi} \left[ \frac{H}{(D - D_0)^2} - \frac{2H'}{\left(D - \frac{D_0}{2}\right)^2} + \frac{H''}{D^2} \right] \quad (13)$$

This relation, with two additional unknowns, cannot be precisely fitted with data as scattered as those presented in ref 1. Nevertheless, pursuing such a fit, beginning with previously fitted  $H$  and  $D_0$ , we obtain  $H = 1.68 \times 10^{-20}$  J,  $H' = 0.0228 \times 10^{-20}$  J,  $H'' = 0.006 \times 10^{-20}$  J, and  $D_0 = 4.3$  nm, and indeed the first term in eq 13 gives in this case the principal contribution to the van der Waals force. (This is different from the case of lipids coating mica probably because of the greater refractive index of mica than that of glass.<sup>16</sup>)

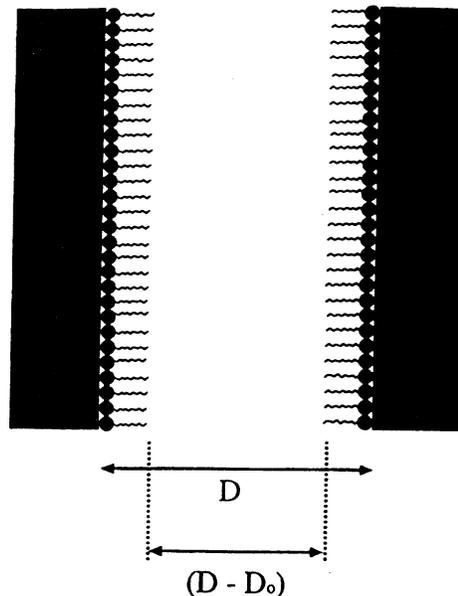


**Figure 3.** The measured normalized attractive force at complete charge neutralization (points *n* from Parker *et al.*, Figure 3) can be fit as a simple displaced van der Waals interaction (see eq 12) with Hamaker constant  $H = 1.68 \times 10^{-20}$  ( $1 \pm 0.01$ ) J and displaced plane of interaction  $D_0 = 4.3$  ( $1 \pm 0.05$ ) nm to take account of  $\approx 21$  Å monolayer on each glass surface. Because of the scatter in the data, fitting to the more accurate eq 13 does not visibly change the results.



**Figure 4.** Schematic presentation of the CTAB-glass (mica) surface system as it goes through the instability point.  $\text{CTA}^+$  ion is desorbed from the surface to the extent that the charge residing on the glass (mica) surface is neutralized.

There appears to us to be no need to invoke anomalous attractive forces for this particular set of measurements whose



**Figure 5.** Schematic presentation of the displacement of the origin of the van der Waals plane between two surfactant-covered surfaces.  $D_0/2$  is the thickness of the amphiphile monolayer and  $D$  is the separation between the bare surfaces. The leading term in the van der Waals interaction energy thus changes from  $D^{-2}$  to  $(D - D_0)^{-2}$  dependence.

connection to the van der Waals energy is

$$\left(\frac{F}{R}\right) \cong \pi E_{\text{vdw}}(D) \quad (14)$$

where  $E_{\text{vdw}}$  is the displaced van der Waals interaction free energy eq 12. The value of the fitted Hamaker constant is slightly high for a pure van der Waals force, but given the scatter in the data and ambiguity in  $D_0$ , it is not so big as to require one to assume new forces.

Recent force microscopy shows that CTAB and related single-chain lipids can settle on graphite (Manne, S.; Cleveland, J. P.; Gaub, H. E.; Stucky, G. D.; Hansma, P. K. *Langmuir* 1994, 10, 4409) and on graphite, mica, and silica (Manne, S. Personal communication, May 2, 1995) as micelles or hemimicelles—forms far different from the planar layers postulated in experimental surface force apparatus papers (refs 1, 3, 4) and used in Figure 5. The prevalence of nonlamellar lumps makes more likely the existence of a large effective “ $D_0$ ” in Figure 5 and a strong van der Waals attraction to explain the data cited in Figure 3.

Unknown to us, concurrent with our studies, Brian Pethica has developed an adsorption/desorption force model similar to that proposed here. We warmly thank him for helpful later discussions.

### Concluding Observations

There are likely to be many kinds of explanations for the many kinds of forces seen between high-energy hydrocarbon/water interfaces. At least for surfaces made hydrophobic by amphiphile adsorption, there seems to be no need to postulate anything new or dramatic. Not only could the original observations<sup>3</sup> not be quantitatively reproduced,<sup>4</sup> but also the strange forces do not even need to exist. We expect that many of the other cases of “long-range hydrophobic forces”<sup>2</sup> can be similarly explained in strictly “classical” terms. Besides the possibility of surface instabilities considered here, there can be electrostatic (fluctuation) interactions between inhomogeneous surfaces<sup>11</sup> as in the case of the long-range forces that are eradicated by small (mM) amounts of salt or by temperatures that melt the lipid

hydrocarbon chains.<sup>12</sup> The van der Waals forces due to ion fluctuation<sup>13,14</sup> are also a viable candidate for modeling interactions at very low salt concentrations.

Microscopic cavitation<sup>15</sup> has been suggested as a source of long-range forces, but attempts to detect them have not yet been successful.<sup>10</sup> Interactions that incur large, visible cavitation between macroscopic surfaces<sup>17</sup> probably represent a class of phenomena only distantly related to the "hydrophobic" force that is of such interest between nonpolar materials.

It is probably worth pointing out also that these forces of surprisingly long range have been seen only between macroscopic surfaces. Recent measurements by van der Ven *et al.*<sup>18</sup> on long-range forces between polystyrene spheres showed no evidence of the anomalously strong attractive forces; van der Waals forces sufficed to describe the attraction of particles at nanometer separations. One thus cannot take the measured long-range forces between macroscopic surfaces and use them as effective pair potentials between macromolecules or even between colloidal particles.

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