Journal of Colloid and Interface Science **247,** 255–257 (2002)
doi:10.1006/jcis.2001.8165, available online at http://www.idealibrary.com on IDEAL®

LETTER TO THE EDITOR

Effective Spring Description of a Bubble or a Droplet Interacting with a Particle

It is shown that the interaction of a particle with a liquid drop or a gas bubble may be quantitatively described over the whole distance regime by treating the fluid interface as a Hookean spring. An algorithm suitable for analyzing atomic force microscopy data suitable for a calculator or a spread-sheet is given and applied to data for oil drops.

Key Words: **bubble; droplet; particle interaction; atomic force microscopy.**

INTRODUCTION

Colloid probe force measurements with the atomic force microscope (AFM) have shown that air bubbles (1–4) and oil droplets (5–9) behave as simple Hookean springs in the so-called constant compliance regime. A recent theoretical analysis has confirmed this experimental finding, showing that the experimentally applied loads are well within the linear regime, and that the effective spring constant is practically equal to the surface tension of the interface (10). Earlier theoretical work on deformable fluid interfaces provides numerical support for the experimental and analytic conclusion (11–13). In the opinion of the present authors, recent numerical computations (9, 14) also exhibit the Hookean nature of the interface, although it should be noted that the original authors (9, 14) concluded that the interface was *not* Hookean (15).

Since the bubble or drop behaves as a simple spring in the constant compliance regime, which is the region of largest load, it must necessarily also be Hookean in the region of weaker loads prior to contact. The reason that the measured force is not a linear function of drive distance prior to contact is that the separation between the particle surface and the fluid interface is not constant there, whereas in contact it is (10). Nevertheless, if this change in separation can be calculated, one has the possibility of describing particle–bubble and particle–droplet interactions simply and quantitatively using little more than Hooke's law. The purpose of this letter is to give an algorithm that accomplishes this goal and to show by comparison with experiment that it is accurate in both the precontact and the post-contact regimes.

Consider a particle of radius R_p interacting with a very much larger bubble or droplet of undeformed radius R_0. The interaction pressure between surfaces separated by h is taken to be an electrical double-layer repulsion,

$$p(h) = Pe^{-\kappa h}, \qquad [1]$$

where κ^{-1} is the Debye screening length of the electrolyte, and the preexponential coefficient is

$$P = 2\epsilon_0\epsilon_r(4k_B T\kappa/q)^2\gamma_1\gamma_2, \qquad [2]$$

with ϵ_0 being the permittivity of free space, ϵ_r the dielectric constant of the electrolyte, k_B Boltzmann's constant, T the absolute temperature, and q the ion charge. The nonlinear Poisson–Boltzmann theory has been used here to renormalize the surface potentials ψ (16),

$$\gamma_i = \tanh\frac{q\psi_i}{4k_B T}, \quad i = 1, 2. \qquad [3]$$

This double-layer expression is for asymmetric surfaces in a binary symmetric electrolyte. It is exact (within Poisson–Boltzmann theory) at large separations at all potentials. It may, however, become inaccurate at small separations (large forces) where nonlinear effects, steric repulsions, and van der Waals forces may additionally contribute.

When the particle is forced toward the bubble or droplet it causes a dimple to form. It has been shown that the radius of curvature in the contact region, R_w, is related to the applied load, F, by (10)

$$R_w = R_0\frac{F\kappa R_p + 4\pi\gamma R_p}{F\kappa R_0 - 4\pi\gamma R_p}, \qquad [4]$$

where γ is the surface tension of the interface. The wrap radius varies between $-R_0$ for low loads (the negative value arises because the curvature is here measured external to the droplet or bubble) and R_p for high loads, where the interface is almost concentric with the particle. The load is related to the central or closest separation of the actual surfaces by (10)

$$F = \frac{2\pi R_p R_w}{\kappa[R_w - R_p]}p(h_a), \qquad [5]$$

where h_a is the actual physical surface separations, as distinct from the nominal separation h_n, which ignores the deformation of the interface (see below). For the present purposes it is more convenient to express the separation as a function of load. In view of the Poisson–Boltzmann force law, Eq. (1), this is

$$h_a = \kappa^{-1}\ln\frac{2\pi R_p R_w P}{\kappa F[R_w - R_p]}. \qquad [6]$$

One can now generate a separation versus load curve simply by regarding the load as the independent variable. The maximum load that can be applied before rupture of the interface is $F^* = 2\pi\gamma R_p$ (10, 17).

To model AFM data one must convert the actual surface separation h_a to the nominal separation h_n. The latter is the separation that the bodies would have if they were undeformed, and it may be obtained experimentally, relative to an arbitrary zero, from the specified AFM drive distance and the measured cantilever deflection (see below). The difference between the actual and the nominal separation is the deformation of the interface. Since the bubble or droplet behaves as a simple spring of spring constant k_b, the latter is $\Delta z = -F/k_b$, and one has

$$h_n = h_a - F/k_b. \qquad [7]$$

Note that for large loads the nominal separation becomes negative, whereas the actual separation is always positive. Using the above equations one can generate

0021-9797/02 $35.00

for the drop or bubble a force versus nominal separation curve, or, more precisely, a nominal separation versus force curve. The interfacial spring constant k_b may be obtained by fitting the experimental data, or by using the analytic result that expresses it in terms of the interior contact angle and the logarithm of the ratio of length scales (10),

$$k_b^{-1} = \frac{-1}{4\pi\gamma}\left\{\ln\left[\frac{R_p}{2\kappa R_0^2}\frac{(1+\cos\theta)^2}{\sin^2\theta}\right] + \frac{4 - 5\cos\theta + 2\cos^2\theta - \cos^3\theta}{2 - \cos\theta - \cos^3\theta}\right\}. \quad [8]$$

In practice the predicted interfacial spring constant is approximately equal to the surface tension.

In the AFM experiments the drive distance ΔD and the cantilever deflection, $\Delta x = F/k_c$ (k_c is the cantilever spring constant), are known. Hence the nominal separation is

$$h_n = F/k_c - \Delta D + C. \quad [9]$$

This is relative to an arbitrary zero since the initial separation is not known. One must choose a value of the constant C that gives the proper zero of separation.

The determination of the absolute separation scale has hitherto plagued AFM measurements of soft surfaces. Gillies *et al.* (18) have recently solved the problem by shifting the experimental data for *soft* surfaces to coincide with the known force law for *rigid* surfaces in the large-separation, weak force regime. This procedure is exact, since for weak enough forces all surfaces are effectively rigid and undeformed, $h_a = h_n$. It does, however, require that the surface potentials be known. In the case of the electric double layer treated here, the force law is

$$F = 2\pi R_p \kappa^{-1} P e^{-\kappa h_n}, \quad [10]$$

assuming $R_0 \gg R_p$. Hence the nominal separation of the experiments is shifted to coincide with this rigid body force at large separations.

Figure 1 tests the present theory against the measured force for an oil drop. The data are a representative selection of that given in Figs. 3 and 4 of Ref. (8).

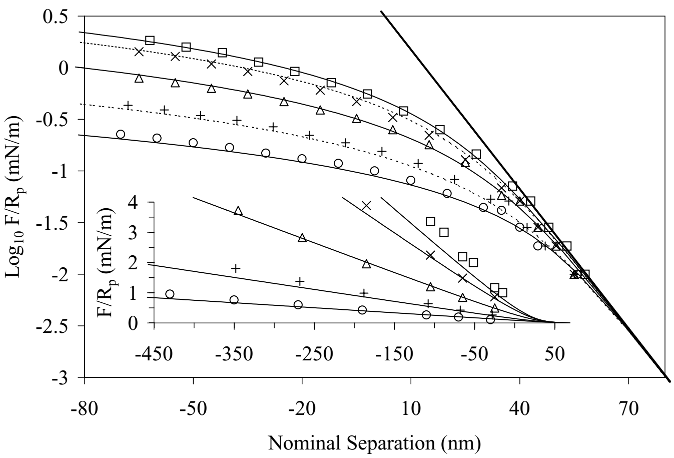

FIG. 1. AFM data (8) for an *n*-decane oil droplet ($R_b = 0.25$ mm) and silica colloid probe ($R_p = 3\ \mu$m), interacting in 1 mM $NaNO_3$ ($\kappa^{-1} = 9.65$ nm). From bottom to top the concentration of the added SDS surfactant is 3×10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} M. The zero of separation has been determined by ensuring coincidence at large separations with the renormalized linear Poisson–Boltzmann law (bold line, Eq. [1]) (18), which uses the measured zeta potentials $\psi_{SiO_2} = -70$ mV (19) and $\psi_{decane} = -100$ mV (20). The curves are the results of the present spring calculations using a fitted interfacial spring constant (see the succeeding figure).

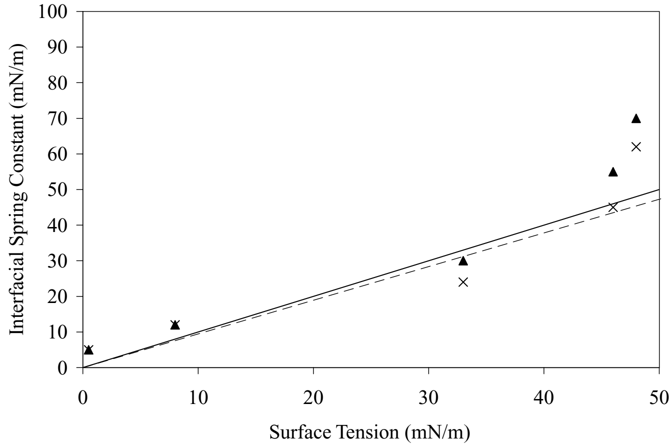

FIG. 2. The spring constant of a fluid interface as a function of the measured surface tension (8) for the respective surfactant concentrations of the preceding figure (the concentration decreases from left to right). The triangles are the fitted results used in the preceding figure, and the crosses are values obtained in Ref. (8) by fitting the slope of the constant compliance regime. The full line is $k_b = \gamma$, and the dashed line is Eq. [8] (10) with a contact angle of 90°.

The nominal separation was obtained by shifting the original data horizontally to coincide at large separations with the force law for a rigid surface, following the protocol developed by Gillies *et al.* (18). The zeta potential measured for oil drops is in the range −100 to −125 mV for SDS concentrations between 0.01 and 1 mM (20). In the present calculations it has been fixed at −100 mV for all cases; at these high potentials the renormalized potential is insensitive to the precise value. The calculations took the force as the independent variable, and used Eqs. [4], [6], and [7] to obtain the nominal separation. The present calculations were carried out using an elementary spreadsheet. The interfacial spring constant k_b was treated as a fitting parameter. Figure 2 shows that the fitted value is on the order of the surface tension, and that it is in reasonable agreement with the analytic formula, Eq. [8].

It can be seen that the present theory that treats the drop as a simple spring is quantitatively accurate not only in the constant compliance region (inset) but also in the precontact regime where the force is not a linear function of the nominal separation. It may be concluded that treating an air bubble or a liquid drop as a Hookean spring yields a viable description of particle interactions that is accurate, simple, and generally applicable to systems with known surface potentials.

ACKNOWLEDGMENT

The support of the Australian Research Council is gleefully acknowledged.

REFERENCES

1. Ducker, W. A., Xu, Z., and Israelachvili, J. N., *Langmuir* **10,** 3279 (1994).
2. Butt, H.-J., *J. Colloid Interface Sci.* **166,** 109 (1994).
3. Fielden, M. L., Hayes, R. A., and Ralston, J., *Langmuir* **12,** 3721 (1996).
4. Preuss, M., and Butt, H.-J., *Langmuir* **14,** 3164 (1998).
5. Basu, S., and Sharma, M. M., *J. Colloid Interface Sci.* **181,** 443 (1996).
6. Mulvaney, P., Perera, J. M., Biggs, S., Grieser, F., and Stevens, G. W., *J. Colloid Interface Sci.* **183,** 614 (1996).
7. Snyder, B. A., Aston, D. E., and Berg, J. C., *Langmuir* **13,** 590 (1997).
8. Hartley, P. G., Grieser, F., Mulvaney, P., and Stevens, G. W., *Langmuir* **15,** 7282 (1999).
9. Aston, D. E., and Berg, J. C., *J. Colloid Interface Sci.* **235,** 162 (2001).
10. Attard, P., and Miklavcic, S. J., *Langmuir* **17,** 8217 (2001).

11. Bachmann, D. J., and Miklavcic, S. J., *Langmuir* **12,** 4197 (1996).
12. Miklavcic, S. J., *Phys. Rev. E* **54,** 6551 (1996).
13. Chan, D. Y. C., Dagastine, R. R., and White, L. R., *J. Colloid Interface Sci.* **236,** 141 (2001).
14. Bhatt, D., Newman, J., and Radke, C. J., *Langmuir* **17,** 116 (2001).
15. The discrepancy appears to arise from the definition of Hookean interface. Here and earlier (10) the usual definition is used, namely that there is a linear relation between the force and the position of the interface. The change in the position of the interface is in general not equal to the change in drive displacement nor to the change in separation. All authors agree that the force is not a strictly linear function of the displacement, and that it is not a linear function of the separation (9–14). However, Aston and Berg (9) and Bhatt *et al.* (14) have concluded from this that the interface is not Hookean, which suggests that these authors are using a definition of a Hookean interface different to that normally used.
16. Attard, P., *J. Phys. Chem.* **99,** 14,174 (1995).
17. Miklavcic, S. J., and Attard, P., *J. Phys. A: Math. Gen.* **34,** 7849 (2001).
18. Gillies, G., Prestidge, C. A., and Attard, P., *Langmuir* **17,** 7955 (2001).
19. Hartley, P. G., Larson, I., and Scales, P. J., *Langmuir* **13,** 2207 (1997).
20. Nespolo, S. A., Bevan, M. A., Chan, D. Y. C., Grieser, F., and Stevens, G. W., *Langmuir* **17,** 7210 (2001).

Phil Attard[1]
Stan J. Miklavcic[2]

Ian Wark Research Institute
University of South Australia
Mawson Lakes
South Australia 5095
Australia
E-mail: phil.attard@unisa.edu.au

Received July 11, 2001; accepted December 10, 2001

[1] To whom correspondence should be addressed.
[2] Permanent address: Department of Science and Technology, Campus Norrköping, Linköping University, Bredgatan 33–34, S-601 74, Norrköping, Sweden.