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Additional Attraction between Surfactant-Coated Surfaces

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A simple model that shows an additional attraction between solvated surfactant-coated systems is developed. The model simply calculates the van der Waals attraction between the solvated surfactant layers. This attraction was previously neglected as it was expected to have a small energetic contribution. This is indeed the case; however, despite the small energetic contribution the force is large. In other words, although the expression that we get is small in energy, it is large in force. This is particularly important for surface force balance measurements, where using the developed expression, some apparent discrepancies between measured and theoretical values may now have a possible explanation, and especially those associated with surfactant-coated surfaces. We apply the new expression to a given system, and compare with the experimental results. © 2002 Elsevier Science (USA)

Key Words: **surface force apparatus (SFA); functional group; refractive index; thin layer; vdW forces; colloids; suspensions; Hamaker constant.**

INTRODUCTION

Surfaces modified by surfactants have found uses ranging from stabilizing colloidal dispersions (1) to magnetic disk storage devices (2) in computers. Experimentally, an important tool for characterization of such systems is the surface force balance (see, for example, (3, 4)). Interactions between surfaces bearing solvated surfactant layers using the surface force balance (SFB) (5–7, 17, 18) show in all the investigated systems (see, for example, (3, 4)) an attractive well. Particularly, this attractive well is always much bigger than the calculated London–van der Waals (vdW) attraction between two such opposing surfaces, as is noted in those references, and left there as a puzzle. The calculation of the theoretical vdW attraction in these references takes into account the mica–mica attraction across the solvent medium (mica being the material on which surface the surfactants are grafted in the SFB). The contribution of the surfactant layers to the vdW attraction was neglected in these studies probably because the medium was assumed to have a Hamaker constant similar to that of the solvated surfactant chains. This would result in a very small energetic contribution. Additionally the surfactant layer is quite thin, which would further decrease the energetic contribution of this layer, and would also require establishment of a proper expression for the energy contribution from thin shells (8)—a work that one would not do in order just to discover that the energetic contribution is negligible.

Indeed, as is shown in the following sections, the contribution of the surfactant layers to the total vdW *energy* is small in part because of the similar refractive indices (and hence similar Hamaker constants), and in part because of the thinness of the two layers. However, particularly because of the small thicknesses, this contribution has such a force law that makes the *force*—the derivative of the energy—high, and thus the theory may still be consistent with the SFB measurements, which measure forces rather than energies. At the same time colloidal stability is still obeyed since the energetic contribution of the surfactant layers is small.

Apart from proposing an explanation for the additional attractive force between surfactant-coated surfaces, we also calculate the value of such a contribution for one specific case. We also confirm that adding the additional attraction to the total expression for the energy still corresponds to a stable colloidal suspension in this particular case.

LONDON–VAN DER WAALS ENERGY BETWEEN TWO OPPOSING SHELLS

The first stage is to write the expression for the vdW attraction between two shells that will mimic the two surfactant layers. The general case was already established (8), and we only write here the corresponding derivative for our specific geometry, including the cylindrical case of the SFA.

Two solid spherical particle of radii R_1 and R_2, a distance d apart (d is the shortest distance between the surfaces of the particles), have a London–van der Waals attraction energy

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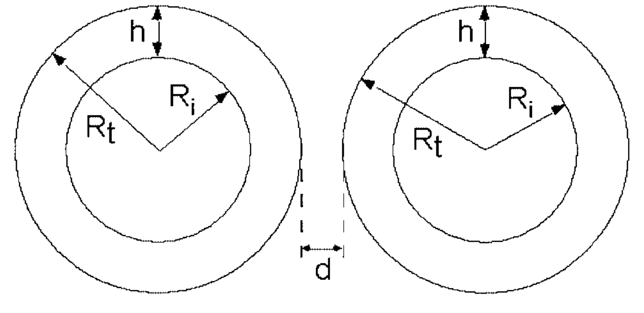

FIG. 1. A schematic representation of the model for vdW energy between two shells.

$E_{\mathrm{sph}}(R_1, R_2, d)$ which is given by (9)

$$E_{\mathrm{sph}}(R_1, R_2, d) = -\frac{A}{6}\left\{\frac{2R_1R_2}{2(R_1+R_2)d+d^2} + \frac{2R_1R_2}{4R_1R_2+2(R_1+R_2)d+d^2} + \ln\left[\frac{2(R_1+R_2)d+d^2}{4R_1R_2+2(R_1+R_2)d+d^2}\right]\right\}, \quad [1]$$

where A is the Hamaker constant appropriate to the interaction of the spherical material across the medium between the spheres.

Consider now two identical solid spheres of radius R_t. Imagine each sphere is composed of two parts: one being the spherical core of radius R_i $(=R_t - h)$ (see Fig. 1) and the other part the spherical shell of thickness h with $R_i + h$ $(=R_t)$ and R_i as the outer and inner radii, respectively.

Let $E_{\mathrm{shell}}(R_i + h, R_i, d) = E_G$ (shell, shell) be the interaction energy between two identical shells. This is a function of the outer radius $R_i + h$ of the shells, the inner radius R_i of the shells, and the closest distance d between the shells. We write the total interaction between the two solid spheres of the same radius R_t as

$$E_G\,(\text{sphere, sphere}) = E_G\,(\text{shell, shell}) + E_G\,(\text{core, core}) + 2E_G\,(\text{core, shell}), \quad [2]$$

where $E_G(x, y)$ is the interaction energy between a geometrical body x and a geometrical body y, subjected to the geometrical conditions of Fig. 1. For instance, E_G (core–shell) is a function that describes the vdW interaction energy between the spherical core (radius R_i) and the spherical shell ($R_i + h$, R_i for outer and inner radii) when separated by a closest distance $d + h$ apart. Similarly we can write

$$E_G\,(\text{core, shell}) = E_G\,(\text{core, sphere}) - E_G\,(\text{core, core}). \quad [3]$$

Substituting Eq. [3] into Eq. [2] and rearranging we get

$$E_G\,(\text{shell, shell}) = E_G\,(\text{sphere, sphere}) - 2E_G\,(\text{sphere, core}) + E_G\,(\text{core, core}). \quad [4]$$

Finally in the notations of Eq. [1] this reads as

$$E_{\mathrm{shell}}(R_i + h, R_i, d) = E_{\mathrm{sph}}(R_i + h, R_i + h, d) - 2E_{\mathrm{sph}}(R_i + h, R_i, d + h) + E_{\mathrm{sph}}(R_i, R_i, d + 2h), \quad [5]$$

and since all terms on the right-hand side of Eq. [5] are known from Eq. [1], then Eq. [5] is analytic. Equation [5] describes the vdW energy between two identical shells. The force F_{shell}, which corresponds to the energy E_{shell}, is simply $F_{\mathrm{shell}} = (\partial E_{\mathrm{shell}}/\partial d)$. Writing the term for the force is straightforward (a derivative of the analytic Eq. [5]). To simplify the resulting expression (which is rather lengthy) we write an approximate expression for F_{shell}/R for the case of $R \gg d, h$. We first obtain $F_{\mathrm{shell}}/R = 1/R(\partial E_{\mathrm{shell}}/\partial d)$ and then neglect terms of order d/R or smaller than 1. This yields

$$\frac{F_{\mathrm{shell}}}{R} = \frac{1}{R}\frac{\partial E_{\mathrm{shell}}}{\partial d} = \frac{A}{12}\left(\frac{1}{d^2} + \frac{1}{(2h+d)^2} - \frac{2}{(h+d)^2}\right) \quad R \gg d, h. \quad [6]$$

Equations [5] and [6] describe the nonretarded (19) vdW interactions of two thin layers. We note w.r.t. Eq. [6] that according to the Derjaguin approximation (10) for $R \gg d$, $F_{\mathrm{GL}}/R = 1/2\, F_C/R_C = \pi E_A$, where F_{GL} and F_C are the forces between spherical and crossed cylindrical objects respectively, and E_A is the interaction energy per unit area between two infinite parallel flat objects, all obeying the same force—distance law. The relation to F_C allows us to compare with the SFB measurements in which the surfaces are crossed cylinders. The experimental data of the SFA are given as F_C/R_C and the relation to E_A shows that it is possible to compare different experiments by normalizing the measured force by the cylinder radius. For the case of the force law in Eq. [6], we need to replace F_{GL} with F_{shell}, and then the energy per unit area E_A corresponds to parallel flat membranes, as can be derived in a different way (11). Note that for SFB measurements, $R_C \gg d, h$.

Obviously the force and the energy have different distance dependences, and in order to see this different dependence we plot the two for a particular case. The case involves a previous publication (4) in which the surfactant used is oleic-trimethyl-ammonium-iodide ($CH_3(CH_2)_7CH{=}CH(CH_2)_8N^+(CH_3)_3I^-$), from now on "OTAI," which is adsorbed by its ionic head on a mica surface and solvated by the solvent medium—hexadecane (HD). The measured attraction between the surfaces in the SFB, which utilizes ~1 cm radius crossed cylinders, is in this case ~3 times bigger than the calculated one (4) based only on the vdW attraction due to the semi-infinite mica surfaces (on which the thin OTAI layer is grafted).

In order to add the energetic contributions in Eq. [5] or [6] to the previously calculated attraction between the semi-infinite surfaces (in order to compare with the experimental results), we need to know the value of the Hamaker constant associated with the attraction of one solvated surfactant layer with the other across the hexadecane medium. For the Hamaker constant, one only requires information on the refractive index of the substance (and the dielectric constant, which in our case is a negligible term). This information is not available experimentally, for a two reasons: (1) Any bulk data on OTAI are very different from its actual grafted to mica and solvated in HD form since it would include the grafted end group. This end group includes the iodide which is no longer in the system (4) (since it is replaced by the negative charge on the mica) and would give rise to an apparent higher refractive index (12). (2) It is well known that different functional groups (in a chemical compound) contribute differently to the refractive index (see, for example, Chap. 10 in Ref. (12)). Usually some average is made over these functional groups in order to obtain the average refractive index (12) of the compound. However, clearly in our case, different groups on the surfactant layer are not randomly distributed along the thickness of the layer, but rather there is some order with respect to the distance normal to the surface along the thickness of the layer. This order is expected in any set of grafted chains, and it is higher the shorter is the chain and the longer is the persistence length of the chain, and surely with the relatively short surfactant hydrophobic tail it is a dominant effect. This forces us to view the refractive index of different layers away from the mica surface individually with respect to the corresponding concentrations of the different functional groups in that layer. There are two aspects to this phenomenon: (1) How are the different functional groups distributed along the thickness of the surfactant layer? (2) What is the refractive index value that we should use for a given distribution of functional groups, or how can we calculate the refractive index based on a known distribution of functional groups? In what follows, we suggest some answer to the second question (how to calculate a contribution of a functional group to the refractive index). Then, rather than answering the first question, we check what should be the distribution so that the experimental results may finally be fitted, and discuss the deviations in case of other possible distributions.

There are three components in the hydrophobic tail of the OTAI: CH_2 groups, a $CH{=}CH$ group, and a CH_3 group. The CH_2 groups are dominant in the HD, and therefore the contribution of this group to the OTAI–OTAI interaction across HA cancels (6, 11). We are left with CH_3 group, and the $CH{=}CH$. In case the CH_3 group is concentrated at some layer away from the surface, it would contribute to a refractive index different from that of the HD. The $CH{=}CH$ group, which is nonexistent in the HD, would also contribute to an attractive three-layer Hamaker constant, and the magnitude of this contribution again depends on the concentration of this layer and its location normal to the surface. Since the HD solvent has also CH_3 groups, then the contribution of the CH_3 groups depends also on the alignment of the HD molecules, which makes it a more difficult problem, and we focus here on the $CH{=}CH$ group.

THE CONTRIBUTION OF THE DOUBLE BOND TO THE HAMAKER CONSTANT

We first determine the highest possible refractive index of a phase composed only of $CH{=}CH$ groups n_{db} (db stands for double bond, which is the phenomenon that makes this group different), and then we dilute it to a value that is expected in the concentration of the grafted to the surface OTAI in HD.

In order to calculate n_{db} we compare a simple alkane chain with that of an identical length alkene chain. Since the only difference between those chains is the double bond (db), we may learn from this difference about n_{db}. For example, the refractive index of nonane (C_9) is 1.4050, and that of nonene (13) is 1.4190. By subtracting we get 0.014. Doing the same subtraction for tetradecene and tetradecane we get $1.438 - 1.429 = 0.009$. Apparently these two results are very different; however, in order to relate these two results we should bear in mind that the longer is the chain, the smaller would be the difference in the refractive index. For example, an infinite chain with only one double bond will have the same refractive index as the same infinite chain without this one double bond just because the concentration of the double bond is negligible in the infinite chain. Thus, in order to compare properly we need to divide the value that we get for the refractive index difference due to one double bond, by the concentration of it w.r.t the total amount of carbons in the chain (14). For example in nonene there are 9 carbons; hence the concentration of the double bond is $\frac{1}{9}$ (14), and we need to divide by $\frac{1}{9}$, or simply multiply by 9, to get $0.014/(\frac{1}{9}) = 0.014 * 9 = 0.126$. The same for tetradecene where there are 14 carbons: $0.009/(\frac{1}{13}) = 0.009 * 13 = 0.126$. Making the same calculation for 6, 8, 9, 10, and 14 carbon chains always results in the same value of 0.126 with very small deviations (especially for the smaller molecules where the double bond and the end methyl group start to interfere). Since we divide by the concentration, we in fact obtain the value that corresponds to a dens phase of double bonds.

Putting the above in general terms we may write that the refractive index $n(j, 1\,\mathrm{db})$ of an alkene with j carbons and one double bond is higher than the refractive index $n(j, 0)$ of an alkane with the same number (j) of carbons but with 0 double bonds. However, in order to know how much bigger will be the refractive index of a phase composed only of double bonds than that of only single bonds, we should divide the difference by the concentration of the double bond in the chain (divide by $1/j$ or multiple by j). A phase composed only of db's has a refractive index n_{db} of

$$n_{\mathrm{db}} = n(j, 0) + \Delta n_{\mathrm{db}}, \qquad [7]$$

where $\Delta n_{\mathrm{db}} \cong j[n(j, 1\mathrm{db}) - n(j, 0)]$.

Equation [7] (and Δn_{db}) describes the approximate difference in the refractive index of an imaginary phase composed only of db's. Our alkane medium in the experiment is hexadecane with $n_{\mathrm{hd}}(=n_3) = 1.423$; we therefore can write $n_{\mathrm{db}} \cong 1.423 + 0.126 = 1.549$.

We cannot have a dense phase of db's since the fraction of OTAI occupied adsorbing sites on the mica surface imposes an average lateral (two-dimensional) density of approximately $\frac{1}{4}$ (Ref. (4)). Thus even if all the db's are exactly at the same height from the surface (same vertical displacement), the maximal volume fraction that the db's can get is also approximately $\frac{1}{4}$. Thus, the maximal value that the refractive index n_1 of that layer or thin shell within which the db's are localized is

$$n_{1(\mathrm{max})} = (n_{\mathrm{db}} + 3n_{\mathrm{hd}})/4 = 1.4545.$$

Any vertical diffusion of the double bond would further minimize n_1. This can be written by the simple number average over the length

$$n_1 = \left[n_{1(\mathrm{max})} l_{\mathrm{db}} + n_{\mathrm{hd}}(h - l_{\mathrm{db}})\right]/h, \qquad [8]$$

where l_{db} is the length of one double bond and h is the thickness of the diffused db layer. Note that the thickness h is not necessarily that of the surfactant L (i.e., $h \le L$).

The two media we consider are hexadecane (refractive index n_3) and the db-rich phase (refractive index n_1). The nonretarded Hamaker constant for two identical phases 1 interacting across a medium 3 is given by the excellent approximation (6)

$$\begin{aligned} A &= \frac{3kT}{4}\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)^2 + \frac{3h\nu_{\mathrm{e}}}{16\sqrt{2}}\frac{\left(n_1^2 - n_3^2\right)^2}{\left(n_1^2 + n_3^2\right)^{3/2}} \\ &\cong \frac{3h\nu_{\mathrm{e}}}{16\sqrt{2}}\frac{\left(n_1^2 - n_3^2\right)^2}{\left(n_1^2 + n_3^2\right)^{3/2}} \quad \text{for hydrocarbon chains,} \qquad [9] \end{aligned}$$

where k is the Boltzmann constant, T is the temperature, ε_1 and ε_3 are the static dielectric constants of the two media, h is the Planck constant, and ν_{e} is the so-called plasma frequency of the free electron gas, and is the main electric absorption frequency in the UV, typically around $3 \times 10^{15}\ \mathrm{s}^{-1}$ (6).

Similarly we can estimate the corresponding values of $\varepsilon_{\mathrm{db}}$, $\varepsilon_{1(\mathrm{max})}$, and ε_1. We note though that for hydrocarbon systems the contribution of the first (ε-dependent) term of Eq. [9] is negligible (see values in Ref. (6)) compared with the second one, and we neglect it.

In order to predict what should be the additional attraction due to the surfactant layer in general and the db contribution in particular, we need to know what is the thickness of this layer and where the db is located (at what height from the surface). This should involve energy minimization, which takes into account the stiffness of the chains, the entropic gain in increasing the thickness, and the enthalpic gain in decreasing the thickness. This is beyond the scope of this paper, and here we merely describe how the db attractive contribution changes with the thickness of the db layer, and whether it can possibly explain the apparent discrepancy between theory and measurements in force measurements of surfactant-coated surfaces. The Hamaker constant A is therefore a function of the thickness of the db layer. Substituting Eq. [8] in Eq. [9] gives this h dependence:

$$A \cong \frac{3h\nu_{\mathrm{e}}}{16\sqrt{2}}\frac{\left[\frac{1}{h^2}\left(n_{1(\mathrm{max})} l_{\mathrm{db}} + n_3(h - l_{\mathrm{db}})\right)^2 - n_3^2\right]^2}{\left[\frac{1}{h^2}\left(n_{1(\mathrm{max})} l_{\mathrm{db}} + n_3(h - l_{\mathrm{db}})\right)^2 + n_3^2\right]^{3/2}}. \qquad [10]$$

THE TOTAL ENERGY

All parameters in Eq. [10] are known constants except for h, which is also the only unknown parameter in Eqs. [5] and [6]. Thus, substituting Eq. [10] into Eq. [5] or [6] adds no degrees of freedom to the expressions for the shells. By substituting Eq. [10] into Eq. [5] or [6], we may finally fit the experimental data of Ref. (4). Yet, in order to give a full description of the energy between the surfaces, we incorporate the osmotic repulsion due to the steric effects of the OTAI layer as was derived in Ref. (4), and write for the osmotic repulsive energy

$$E_{\mathrm{S}} = \frac{kT}{a^3}\left(\ln\frac{1}{1-\Phi} - \Phi\right)\left(\frac{\pi\delta^2}{12}(6R + L - \delta)\right), \qquad [11]$$

where a is the monomer dimension, Φ is the concentration of the surfactants between the surfaces, and δ is the maximal depth with which the two OTAI layers overlap ($\delta = 2L - D$).

The total interaction energy between two particles of radius R, which have attached surfactants of thickness L on their surfaces, and considering a thin shell of a different Hamaker constant inside these layers, has the form

$$E_{\mathrm{tot}} = E_{\mathrm{sph}}(R, R, D) + E_{\mathrm{csh}} + E_{\mathrm{s}}. \qquad [12]$$

The first term on the r.h.s. of Eq. [12] is the vdW energy between two solid spherical particles according to Eq. [1], the second term is the contribution of the shells (Eq. [5]), and the last term is the osmotic repulsion (Eq. [11]). Each of the two db shells attracts also the solid particle on which the opposing surfactants are grafted. This should add two more (identical) terms (of the type of Eq. [3]) to Eq. [12]. However, their contribution was found to be small compared with the shell–shell interaction energy and therefore we neglected it in Eq. [12]. Using Eqs. [1], [5], [11], and [12] we calculate the different contributions to the energies for a colloidal particle of $R = 5$ nm as in the case of the ferrofluid dispersion (4), which is known to be stable (4, 15), and for $R = 1$ cm as in the SFA experiment (see Fig. 2).

In the inset to Fig. 2a we see the fit of the total interaction (Eq. [12]) to the experimental data from Ref. (4). The fit uses the value of $h = 1.62$ Å (corresponding to a Hamaker constant of $A = 1.76\ 10^{-22}$ J) when the two db-rich phases are $d = 1.7$ Å away from each other (6, 16). The theoretical curve can finally reach the depth of the measured attraction. Note that h and d are interdependent—the smaller is h, the higher is d, and thus there are more pairings of these two numbers that will give a similar result; however the values of the h and d are close to the edge of the feasible limit (6, 16). Therefore it is likely that the db

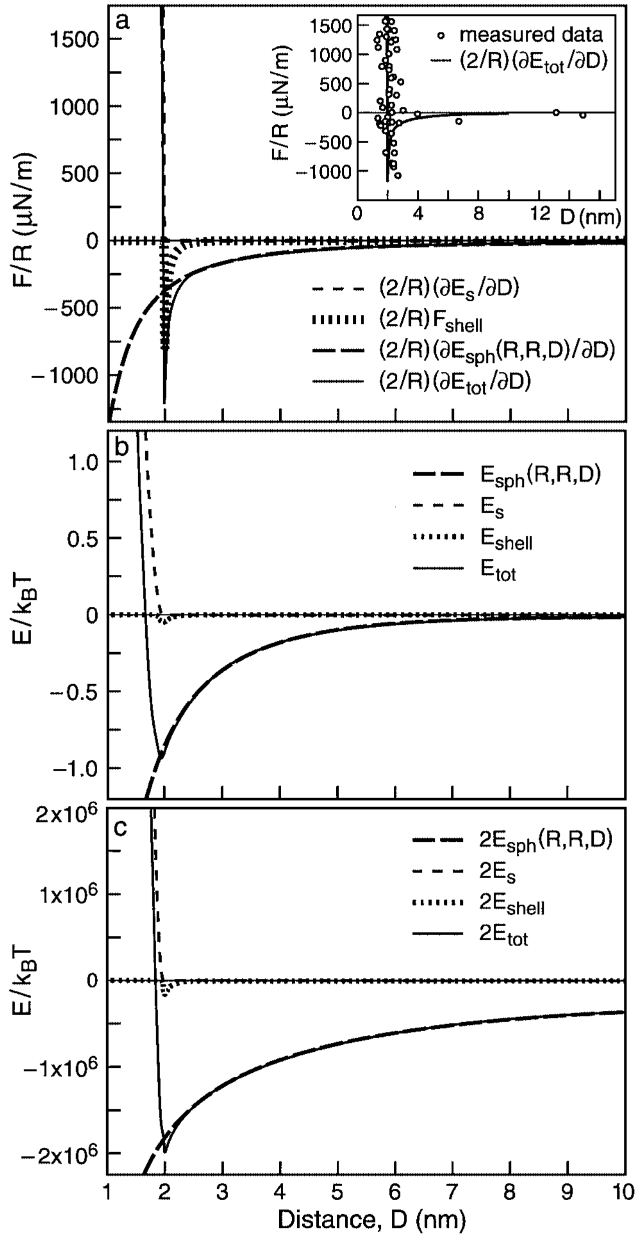

FIG. 2. Calculated values using Eqs. [1], [5], [11], and [12] for the interaction between two OTAI-covered surfaces across hexadecane. (a) The deduced forces normalized by the radius between crossed cylinders of $R_C = 1$ cm, coated with OTAI, versus the closest separation between the cylinder surfaces. The inset shows the total force (deduced from Eq. [12]) compared with data from Ref. (4). (b) Energies between OTAI-coated spherical particles of $R = 5$ nm versus the closest separation between the surfaces of the particles. This size corresponds to the commercial Fe_3O_4 particles whose suspension is stabilized with such a surfactant (15). (c) Deduced energies between crossed cylinders of $R_C = 1$ cm (as in (a), but for energies rather than forces). We see that whereas the shell contribution (the attractive contribution associated with the surfactant layer) to the force in (a) is very large, the corresponding contribution to the energy is very small. The Hamaker constant for calculating the vdW interaction between the solid particles is $A = 9 \times 10^{-21}$ J for (a) and (c) (corresponding to mica surfaces as in the SFA), and $A = 7 \times 10^{-20}$ J for (b) (corresponding to Fe_3O_4 interacting across HD (4)). For the shell–shell interaction we used $A = 1.76\ 10^{-22}$ J as discussed in the text.

contribution is in fact smaller, and is only one part of the additional attraction. Other components of the additional attraction due to the surfactant layers should include the contribution of the methyl groups, and also a possible flattening of the surfaces which would increase the area of contact, and therefore would enhance the contribution of these two groups. Nonetheless, the fit shows that the surfactant layer can explain the experimental attraction which is three times deeper than that previously calculated without the surfactant attraction, and as we show later on, this deep attraction in the force has a negligible energetic contribution, which is a phenomenological requirement.

In Fig. 2a we see the calculated interactive F/R between two crossed cylinders according to the previously developed equations, and the fitted h and d. The three contributions to the total force between the surfaces are considered: the vdW attraction between the solid particles, the vdW attractions between the db shells, and the steric repulsion. It is shown in Fig. 2a that the shell contribution to the attractive force is the most significant one, and about twice the vdW attraction between the solid particles.

In contrast to the large attractive *force* attributed to the shell–shell interaction and shown in Fig. 2a, the corresponding attractive *energy* between the small ferrofluid particles is small, as shown in Fig. 2b. This attraction hardly influences the total attraction, which is only slightly deeper than the vdW attraction between the solid particles (E_{sph} curve). This assures that the above theory would still correspond to a stable colloidal suspension, which is a phenomenological requirement (15). To realize this apparent discrepancy between the energy and $F_C/R_C(=2(\partial E_{\mathrm{GL}}/\partial D)/R)$, we show in Fig. 2c the energies that correspond to the forces in Fig. 2a, i.e., that correspond to crossed cylinders with a radius of 1 cm. The relative contribution of the shell–shell interaction energy to the total energy is a bit larger than that of the 5-nm spherical particles simply because the Hamaker constant of the solid ferroparticles (commercial colloidal dispersion (15)) across hexadecane is larger than that of mica across hexadecane (SFB experiment), and not because of the different sizes of the particles. However, the contribution of the shells to the total energy is still very small. This shows that it is only the force—that is the derivative of the shell–shell interaction energy—that is significantly high (although the energy contribution of the shell–shell interaction is relatively small).

CONCLUSIONS

In conclusion, we show in this paper how a very small energetic "spike," which is a result of a surfactant layer that covers a surface, may cause a negligible energetic contribution, but a substantial force contribution. The force is so high only because of the spike shape of the energy, which results in a very high derivative with the distance. This phenomenon is a possible explanation for the very high attractive forces measured with SFB of surfactant-coated mica surfaces, whereas the corresponding colloidal findings suggested an attractive force that is smaller and an attractive energy and smaller than kT).

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14. The fact that there is a need to divide by the concentration of the double bond is obvious; however, the way the concentration is defined is not obvious. We tried a few definitions of concentrations that gave slightly different results. The definition of the concentration with respect to the number of carbons (which gave the best results) is therefore phenomenological.
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