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Van der Waals interactions with soft interfaces

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Abstract

Many naturally occurring microbiological and synthetic polymer systems have soft interfaces due, e.g., to the presence of polymer brushes at the surfaces. The initial interactions (before contact) in such systems are typically physical rather than chemical in origin, e.g. electrostatic or van der Waals forces. We calculate the form of the summed van der Waals interaction energies U_{HS} and U_{SS} between two bulk systems separated by a distance D , when one (U_{HS}) or both (U_{SS}) of their surfaces are soft. We find that the summed interactions diverge weakly as $D \rightarrow 0$, $U_{HS} \sim -1/D$ and $U_{SS} \sim -\ell n(1/D)$, and comment upon the applicability of these results.

1. Introduction

Physical interactions such as van der Waals forces, electrostatic interactions, and hydrogen bonding dominate the first interactions between biological systems such as, for example, (i) casein micelles (complex-structured fat globules) in milk [1–3], (ii) Gram-negative bacteria such as, e.g., *Pseudomonas aeruginosa* [4], and (iii) (bacterial) membrane vesicles [4]. Casein micelles do not aggregate due to the stabilizing existence of κ -casein polymers, which form a brush-like structure on the surface of the micelle. Aggregation can be brought about by the hydrolysis of the brush using enzymes, such as takes place in cheese-making (see, e.g., [3]). *P. aeruginosa* cells initially interact weakly with a surface in order to detect whether the surface environment is suited to the eventual formation of a biofilm [5]. The physical interactions between a pair of such bacteria or between bacteria and bacterial membrane vesicles are of scientific and practical importance. Questions concerned with which forces, if any, play dominant roles in physical attachment or aggregation processes are of relevance in understanding and possibly manipulating the initial attachment of bacteria to surfaces, with applications in the food and health industries.

Van der Waals forces between surfaces have been studied, both experimentally and theoretically, for nearly a century (see, e.g., [6]). In the last 25 years, measurements have

been made of hard surfaces with well defined geometries [7]. Recently other geometries and systems [8] were considered. There is a long history of theoretical studies of soft interfaces such as polymer brushes [9–11]; more recently, experimental studies, e.g. [12–16] and references therein, have been carried out. The purpose of this paper is to communicate the form of the Van der Waals interaction between two soft surfaces or between a soft surface and a hard surface.

By a hard surface, we mean one that exhibits small fluctuations and an abrupt, effectively discontinuous, change in number density on a length-scale small compared to the characteristic length-scale of the measurements. By a soft surface, we mean one that exhibits a change in number density from outside the system to inside it on length-scales large compared to those characterizing the measurements. In the latter case, if thermal energies are sufficiently large that the soft surface undergoes random fluctuations on timescales short compared to the movement of the two systems, then the surface can be modelled as having translational invariance in a plane parallel to the surface and a continuous change in mass density perpendicular to it. In this note, we do not consider the roles of nanoscale length fluctuations, on the grounds that, under our assumptions, they take place on a much faster timescale than the movements of the macroscopic objects possessing the soft surfaces. The surface we have in mind is, e.g., that of a heterogeneous polymer brush. The outer (bilayer) membrane of *P. aeruginosa* PAO1, for example, possesses an outer layer of lipopolysaccharides (LPSs) characterized by a hydrocarbon chain layer (~ 2 nm thick), a KDO-core region (~ 1 – 2 nm), and an O-side-chain region possessing (charged or uncharged) sugar polymers which vary in length from 0 nm (O side-chain absent) to ~ 40 nm [16–19]. Experiments on such systems have been interpreted using DLVO or XDLVO theory [20–22], or the Alexander–de Gennes model [9–11] of a polymer brush. We stress that our calculations are most likely to be relevant for length scales intermediate between short-range (< 1 nm) interactions and the mesoscale ($> 10^3$ nm, characteristic of, e.g., bacteria).

Systems with a soft interface frequently involve a relaxed polymer brush which can exhibit a decrease in mass density from a value characteristic of the dense brush at the attachment surface, to zero as the distance from the attachment surface increases (figure 1). The region of decreasing density might be a substantial fraction of the brush thickness if the polymers exhibit a wide range of lengths, as they appear to do in the case of, e.g., *P. aeruginosa* PAO1 [5]. Here we calculate the form of the summed van der Waals interaction between (a) a hard surface and a soft one and (b) two soft surfaces.

2. Theory. Van der Waals interactions involving polymer brushes

We assume that we can represent the two surfaces under consideration as parallel planes separated by a distance D , and that the remainder of the objects occupy their respective half-spaces (figure 1). We assume that the motions of the two mesoscopic objects are very much slower than those of the polymer brush, so that the latter can be approximated by an average number density that is independent of the position parallel to the surfaces. In our calculation we use the classical approach (Hamaker summation method) [7, 23]. We assume additivity of atomic-scale $-C/r^6$ interactions between infinitesimal volumes of space that are characterized by the average number density $\rho(\vec{r})$ present in these volumes. For simplicity, we assume that the interaction strength C is independent of the atomic moiety.

Consider two mesoscale objects, 1 and 2, and let the vectors \vec{r}_1 and \vec{r}_2 locate two infinitesimal volumes, $dv(\vec{r}_1)$ and $dv(\vec{r}_2)$, on objects 1 and 2 respectively. Then, under our assumptions, the van der Waals interaction between these two objects can be obtained by integrating the $-C/r^6$ interaction between each pair of infinitesimal volumes that comprise

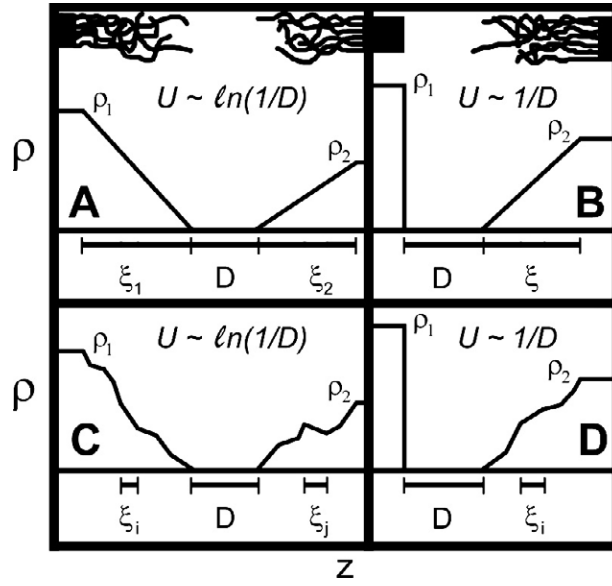


Figure 1. Number-density distributions describing the time-averaged polymer distributions as a function of position perpendicular to the two parallel surfaces. (A), (B) Soft surfaces with constant slopes: two soft surfaces (A); one soft and one hard surface (B). (C), (D) Soft surfaces with varying slopes: two soft surfaces (C); one soft and one hard surface (D).

the two objects:

$$U_{12} = -C \int_1 dv(\vec{r}_1) \int_2 dv(\vec{r}_2) \frac{\rho_1(\vec{r}_1) \rho_2(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|^6}. \quad (1)$$

Here, C is the coefficient of the intermolecular pair potential, $\rho_1(\vec{r}_1)$ and $\rho_2(\vec{r}_2)$ are the number densities of the two objects, and the integrations are over their volumes. The simplest case is the interaction between two homogeneous semi-infinite objects of constant densities (figure 1(B) with $\xi = 0$), oriented with their faces parallel. We define the two objects as uniformly filling the two half-spaces $-\infty < z \leq -D/2$ (object 1) and $D/2 \leq z < \infty$ (object 2), with constant number densities equal to ρ_1 and ρ_2 inside the objects and zero outside, and a single interaction coefficient C . To calculate the interaction energy per area (A) between the two facing surfaces, we use cylindrical polar coordinates (t, φ, z), so that equation (1) becomes

$$\frac{U(D)}{A} = - \int_0^{2\pi} d\varphi \int_0^\infty t dt \int_{D/2}^\infty dz_1 \int_{-\infty}^{-D/2} dz_2 \frac{C \rho_1 \rho_2 s}{[t^2 + (z_1 - z_2)^2]^3} = - \frac{\pi}{12} \frac{C \rho_1 \rho_2}{D^2} = \frac{-A_H}{12\pi D^2}, \quad (2)$$

where the Hamaker constant $A_H = \pi^2 C \rho_1 \rho_2$ has dimensions of energy (Joules) [24]. Equation (2) shows that the $1/r^6$ atomic-scale interaction gives rise to a $1/D^2$ mesoscale interaction. Hunter [25] and Tadmor [8] list various mesoscale van der Waals interactions between objects of different shapes that possess hard surfaces. With hard surfaces, such interactions are all power laws: $U \sim D^{-\alpha}$, where D is some distance characterizing the separation between the two objects. When the mass density goes smoothly to zero on a sufficiently large scale, however, a different result is obtained.

Assume again that we have two homogeneous, solid objects, 1 and 2, of constant number densities ρ_1 and ρ_2 filling the half space with $-\infty < x, y < \infty$. Attached to them are brushes

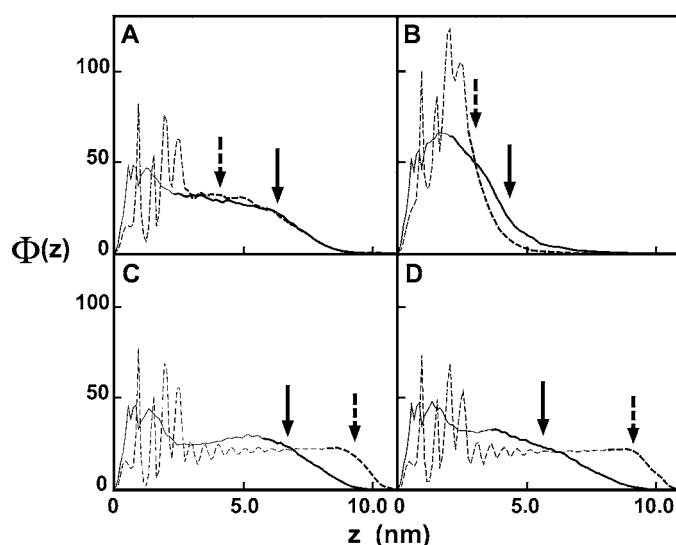


Figure 2. Simulation of a model of a polymer brush formed by a monolayer of LPS molecules from the outer layer of the outer membrane of a Gram-negative bacterium that illustrates the formation of a density gradient at a soft interface. The hydrocarbon chain distribution has been omitted. Number-density, $\Phi(z)$, as a function of distance z away from the hydrophobic core of the outer membrane. Monovalent ions from NaCl are represented by a Debye screening length $\kappa^{-1} = 0.3 \text{ nm}^{-1}$. Solid (dashed) lines and arrows are with (without) CaCl_2 . Arrows and thicker lines indicate the soft-interface regions relevant to this paper. (A), (B) Uncharged O side-chains with hydrogen bonding excluded (A) and included (B). (C), (D) Charged O side-chains with hydrogen bonding excluded (C) and included (D).

possessing boundary layers of thicknesses ξ_1 and ξ_2 . These boundary layers can be nanometers in extent; in figure 2 we show the results of computer simulations of such brushes (below). The edges of the brushes are separated by a distance D . The densities of the brushes decrease linearly, from ρ_1 or ρ_2 at the surfaces of attachment to the homogeneous objects to zero at the edges of the brushes; it is this kind of behaviour that characterizes what we refer to as ‘soft’. We begin by assuming that the dependence of number-density upon distance is linear (figure 1).

The densities as functions of z are shown in figure 1(A), where we have arbitrarily chosen $\rho_1 \geq \rho_2$ and $\xi_1 \geq \xi_2$. Assuming a single interaction coefficient C and performing the integration of equation (1), we obtain the remarkably compact expression

$$\frac{U(\rho_1, \rho_2, \xi_1, \xi_2, D)}{A} = \frac{-A_H}{12\pi\xi_1\xi_2} \ln \left[1 + \frac{\xi_1\xi_2}{D(D + \xi_1 + \xi_2)} \right] \quad (3)$$

$$= \frac{A_H}{12\pi\xi_1\xi_2} \ln \left[1 - \frac{\xi_1\xi_2}{(D + \xi_1)(D + \xi_2)} \right]. \quad (4)$$

Equations (3) and (4) constitute our main formal results for the summed van der Waals interactions between soft planar interfaces. There are two interesting limits of equations (3) and (4). The first is when the two objects are far apart compared to the brush thickness, so that $D \gg (\xi_1 + \xi_2)$. Then equations (3) and (4) become

$$\frac{U(\rho, \xi, D)}{A} \approx \frac{-A_H}{12\pi D^2} \left[1 - \frac{(\xi_1 + \xi_2)}{D} \right], \quad (5)$$

which agrees with equation (2) when $(\xi_1 + \xi_2)/D \rightarrow 0$, and identifies the first-order correction

in the brush thickness. The second limit is when the two surfaces are very close together, so that $1/D \gg (1/\xi_1 + 1/\xi_2)$; in this case, we obtain the interesting result that the interaction diverges weakly like a logarithm:

$$\frac{U(\rho, \xi, D)}{A} \sim \frac{-A_H}{12\pi \xi_1 \xi_2} \ln \left[\frac{1}{D(1/\xi_1 + 1/\xi_2)} \right]. \tag{6}$$

The case in which the left-hand object is hard ($\xi_1 \rightarrow 0$) and the right-hand one possesses a soft surface ($\xi_2 > 0$), as shown in figure 1(B), is easily treated and the result is

$$\frac{U(\rho_1, \rho_2, \xi, D)}{A} = \frac{-A_H}{12\pi D(D + \xi_2)}. \tag{7}$$

This interaction diverges like $1/D$ as the two objects approach each other ($D \ll \xi_2$). The case of two hard surfaces ($\xi_2 \rightarrow 0$) again yields equation (2).

One can extend these results to flat surfaces of otherwise semi-infinite objects that are coated with more complex soft layers than those described above. We assume that the mass density along the z -axis, averaged over the xy -plane, can be described by piecewise linear combinations of densities as shown in figures 1(C) and (D). A calculation similar to the previous one shows that, for small values of D , the attractive interaction between two such complex soft interfaces (figure 1(C)) diverges logarithmically as $\ln(1/D)$. If one surface is soft while the other is hard (figure 1(D)), then the attractive interaction diverges like $1/D$.

Finally, we present the results for the case in which the cross-section of the brush follows a parabolic function. Scaling (e.g. [11]) and self-consistent field methods [26–30] predict a parabolic number density dependence upon distance from the plane z , and computer simulations [31, 32] gave the same results. Here we present the results for the van der Waals interaction between two semi-infinite objects, as above, but now with parabolic polymer brushes on their surfaces, and between two such objects, one with a hard surface and the other possessing a parabolic polymer brush. The case of two polymer brushes is given in (8a) and (8b), while the case of the single polymer brush and the hard surface is obtained by putting $\xi_1 = 0$.

$$\begin{aligned} \rho_1(z_1) &= \rho_1 & -\infty < z_1 \leq -D/2 - \xi_1 \\ \rho_1(z_1) &= s_1(z_1 + D/2) - K_1(z_1 + D/2)^2/2, & -D/2 - \xi_1 < z_1 \leq -D/2 \\ \rho_1(z_1) &= 0 & -D/2 < z_1 < \infty \end{aligned} \tag{8a}$$

$$\begin{aligned} \rho_2(z_2) &= 0 & -\infty < z_2 < D/2 \\ \rho_2(z_2) &= s_2(z_2 - D/2) - K_2(z_2 - D/2)^2/2, & D/2 \leq z_2 < D/2 + \xi_2 \\ \rho_2(z_2) &= \rho_2 & D/2 + \xi_2 \leq z_2 < \infty. \end{aligned} \tag{8b}$$

As before, the edge of the left-hand brush is at $z_1 = -D/2$, while that of the right-hand brush is at $z_2 = D/2$. The van der Waals interaction energy of two brushes is of the form

$$U_{SS} = U_{11} + U_{12} + U_{21} + U_{22} + U_{HS} + U_{HH} \tag{9}$$

where the first four terms describe the interactions between the two brushes alone and the fifth describes the two interactions between the brush on one and the bulk body of the other, while the last describes the interaction between the two bulk objects with a hard surface (equation (2)) but separated by a distance $D + \xi_1 + \xi_2$. When $D \rightarrow \infty$ for finite ξ_1 and ξ_2 , then $U_{SS} \sim 1/D^2$. When $D \ll \xi_1$ and $D \ll \xi_2$ as $D \rightarrow 0$, we find that the only divergent term in U_{SS} comes from that proportional to $s_1 s_2$, $U_{SS} \sim -\pi C s_1 s_2 \ln(1/D)$, as we found above for the case of a linear dependence of the number-density upon z (equation (6)).

The case of one brush interacting with a hard surface is obtained by setting $\xi_1 = 0$, and the calculation gives

$$U_{\text{HS}} = -\frac{\pi C \rho_1}{6} \left[\frac{\rho_2}{2(D + \xi_2)^2} + s_2 \left(-\frac{\xi_2}{2(D + \xi_2)^2} - \frac{1}{2(D + \xi_2)} + \frac{1}{2D} \right) - \frac{K_2}{2} \left(-\frac{\xi_2^2}{2(D + \xi_2)^2} - \frac{\xi_2}{(D + \xi_2)} + \ln(D + \xi_2) - \ln(D) \right) \right]. \quad (10)$$

When $D \rightarrow \infty$ for finite ξ_2 , then $U_{\text{HS}} \sim 1/D^2$. When $D \ll \xi_2$ as $D \rightarrow 0$, we find that the only divergent terms in U_{HS} are

$$U_{\text{HS}} \sim -\frac{\pi C \rho_1}{12} \left[\frac{s_2}{D} + K_2 \ln(D) \right]. \quad (11)$$

The term in equation (11) that is proportional to K_2 is not so much a repulsion as a reduction of the term in equation (11) that is proportional to s_2/D (the only term to appear in the linear-slope model above), and reflects the decreasing slope of the brush number density. Note that, because boundary conditions will differ, depending upon the system, we have not applied them to relate s_j , ξ_j , K_j and ρ_j ($j = 1, 2$).

It is clear that the change from a $1/D^2$ interaction, when the two surfaces are treated as ‘hard’, to a $\ln(1/D)$ interaction, when they are ‘soft’, is determined by whether the brush density changes effectively discontinuously or whether it exhibits a finite slope at the edge of the brush. In a real situation, there will be a competition between the various diverging terms (e.g. those in equation (11)), and the dependence can be a combination of these terms—which can change as the separation of the brushes changes.

These interactions, and those described elsewhere, can be combined with continuum electrostatic interactions to give an appropriate DLVO theory of the surface. However, as has been pointed out elsewhere, e.g. [20, 33], DLVO theory is not really suited to model such polymeric surfaces on scales similar to, or less than, those of the brush. The reason is at least twofold: (a) in replacing the end of the brush by a continuum of average thickness ξ , we lose the possibility of including many-body effects of ions and polyions on brush structure, and (b) if two brushes try to overlap, then they will repel each other, which can change their thickness and density. If the brush thickness is not calculated self-consistently, then the brush repulsion or attraction is accounted for only in an *ad hoc* way. Nonetheless, our finding that van der Waals interactions between two soft surfaces, as modelled here, diverges only weakly as $\ln(1/D)$ when they approach each other, serves to emphasize (a) the importance of considering distance dependences other than $1/D^2$, and (b) the importance of other interactions, particularly electrostatic interactions, in biological systems (e.g. [34]).

3. Computer simulation

Finally, we show that a minimal model of a charged or uncharged polymer brush at a bacterial surface, under a range of different conditions, does exhibit a number-density distribution as a function of distance from a membrane to which it is tethered, of the form that we have described here. The intent of this calculation is to illustrate that such soft profiles arise in naturally occurring systems. We have performed Monte Carlo computer simulations, e.g. [35], to calculate the dependence of the number-density of a tethered semi-flexible polymer brush upon the distance perpendicular to the plane of a membrane tethering surface. This model is intended to represent the amphiphilic lipopolysaccharide (LPS) molecules in the outer layer of the outer membrane of a Gram-negative bacterium at $T = 300$ K. In these molecules, hydrocarbon chains are connected to a glucosamine segment which is connected to the KDO core. The

form of the (charged) glucosamine–KDO-core segments of each LPS approximately represents those of *P. aeruginosa* PAO1 [4]. The polysaccharides (the O side-chains) attached to the other end of the KDO-core segment, and forming the polymer brush, can be uncharged (A-band LPS) or charged (B-band LPS). A charged O side-chain is composed of repeat groups of sugar trimers carrying charges (+, −, −). In the model, each sugar group is represented by a sphere, and the spheres are connected by bonds [34]. Both hydrogen-bonding and electrostatic interactions were included, but not van der Waals forces. The hydrocarbon chain region of an LPS molecule was represented by a large sphere that served only to anchor the KDO-core–O-side-chain segment of the molecule in the membrane plane. The aqueous medium, in which the sugar groups were embedded, and containing monovalent ions, was represented by a linearized Poisson–Boltzmann continuum, e.g. [7], with a Debye screening length κ^{-1} . The outer layer of the membrane was composed of 100 LPS molecules, and periodic boundary conditions were used along the x - and y -axes, which define the membrane plane. LPS molecules could oscillate perpendicular to the membrane plane (the z -axis) and the bond-stretching algorithm was used [36]. We considered cases in which each O side-chain contained 15 sugar groups (five trimers in the case of B-band LPS). Figure 2 shows the number-densities (number per 1 Å thick slab, parallel to the membrane plane) of sugar groups, for both charged and uncharged O side-chains, with hydrogen bonding included or ignored, in the presence or absence of CaCl_2 with $\kappa = 0.3 \text{ nm}^{-1}$. Ca^{2+} and Cl^- ions arising from CaCl_2 are represented by charged spheres.

Figure 2(B) shows a collapse of the uncharged O side-chains brought about by the attractive hydrogen bond interactions. This is seen to a lesser extent for charged O side-chains in the presence of CaCl_2 (figure 2(D)) which serves both to screen the electrostatic interactions and provide dynamic calcium bridging between negative charges on the O side-chains, an effect which dominates hydrogen bonding. The results show that, in all cases, the number-density, as a function of distance away from the membrane surface, exhibits the type of behaviour that we have considered here. The thickness of that section of the brush ranges from ~ 15 to ~ 100 Å, almost the entire thickness of the brush.

We also estimated the characteristic time of fluctuations near the top of the brush. Measurement times larger than this characteristic fluctuation time will average over the rapidly varying motions of the monomers to give a smooth average density distribution as in figure 2. Because the dynamics of monomer motion is dominated by thermal energies at the temperatures (~ 300 K) with which we are concerned, and because, in the Monte Carlo routine, we restricted the range of movement per Monte Carlo step, Δr , to the range $0 \leq \Delta r \leq \sqrt{3} \times 10^{-1} \text{ nm}$, we could plausibly associate a fixed elapsed time, Δt , with each Monte Carlo step. By performing simulations on single free monomers and combining them with the Stokes–Einstein equation, we estimated that $\Delta t \approx 3.76 \times 10^{-12} \text{ s}$. Using this value, we then performed simulations on the polymer brush and estimated the time for a sugar monomer, at a given position along the O side-chain, to move an average distance equal to the approximate radius, $\sim 1.6 \text{ nm}$, of a single LPS molecule projected onto the membrane plane. We estimated the average time for sugar monomers to exhibit movement parallel to the membrane plane with $\langle r_{\parallel}^2 \rangle = 2.56 \text{ nm}^2$. We found that, in the upper layers of the O side-chains, these average times ranged from ~ 7.3 to $\sim 11.0 \times 10^{-8} \text{ s}$ in the absence of CaCl_2 , and from ~ 3.4 to $\sim 6.3 \times 10^{-8} \text{ s}$ when it was present. The slight difference is possibly due to the salt screening the Coulomb interaction. This number of between 3 and $11 \times 10^{-8} \text{ s}$ gives an approximate time for small-scale fluctuations near the top of the brush.

It should be noted that retardation effects change the form of the van der Waals interactions in equation (1) from $1/r^6$ to $1/r^7$ for length-scales longer than about 5–10 nm [7]. Hence the results presented here are for measurement times that are comparable to, or longer than, about 10^{-7} s , and for distances that are approximately 5–10 nm, or smaller.

4. Conclusions

We reiterate that the length scale for which our calculation might be most relevant is intermediate between that of short-range (<1 nm) interactions and the mesoscale ($>10^3$ nm) that is characteristic of, e.g., bacteria. We remark that, although the thickness of a brush might change as it approaches a hard surface or another brush, the average number density distribution can nonetheless retain the general characteristics assumed here; this is supported by scaling theory and by computer simulations. Most experimental data have been interpreted in terms of an interaction assumed to vary like $1/D^2$ but we have shown this to be untrue for the systems considered here. The observations made in this paper, that two soft surfaces interact at short distances like $\ell n(1/D)$, or that a soft surface interacts with an adjacent hard surface like $1/D$, should be taken into account in the analysis of experimental data. Finally, the weak van der Waals interaction that arises in such systems points to the importance of longer range Coulomb interactions in biological systems. Indeed, one might argue that the existence of a brush decreases the importance of the van der Waals interaction relative to electrostatic interactions, which favours some processes while inhibiting others.

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