Adhesion of hard spheres under the influence of double-layer, van der Waals, and gravitational potentials at a solid/liquid interface
(simulation/Brownian dynamics/Boltzmann factor)

B. Sengers†, P. Schaal‡, F. J. Bafaluy§, F. J. G. Cuisinier*, J. Talbot||, and J.-C. Voegel*

*Institut National de la Santé et de la Recherche Médicale, Contrat Jeune Formation 92-04, Centre de Recherches Odontologiques, Université Louis Pasteur, 1, place de l'Hôpital, 67000 Strasbourg, France; ‡Institut Charles Sadron, 6, rue Bousingsault, 67083 Strasbourg Cedex, France; §Ecole Européenne des Hautes Etudes des Industries Chimiques, Centre National de la Recherche Scientifique, Unité de Recherche Associée 405, BP 296F, 1, rue Blaise Pascal, 67008 Strasbourg Cedex, France; ||Department de Física, Universitat Autonoma de Barcelona, 08193 Bellaterra Barcelona, Spain; and ||School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

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ABSTRACT The deposition process of colloidal particles or microorganisms on flat surfaces is analyzed by means of computer simulations. Interparticle interactions (double layer and van der Waals) and weak gravitational forces are taken into account; hydrodynamic interactions, on the other hand, are neglected. In particular, the deposition probability as a function of the deposition location of a particle in the presence of one or two identical fixed particles is discussed. It is shown, in particular, that the ratio of the adhesion probabilities at a given location $r$, for particles subject to weak gravitation, in the presence and in the absence of the interparticle interaction $U(r)$ follows approximately a Boltzmann law $\exp(-U(r)/kT)$, even though the adsorption process is fully irreversible. This result validates, as far as the distribution function of particles on a surface is concerned, Adamczyk's assumption [Adamczyk, Z., Zembala, M., Siwek, B. & Warszynski, P. (1990) J. Colloid Interface Sci. 140, 123–137] that the adhesion process of Brownian particles can be modeled by a random sequential adsorption model with an adsorption probability equal to $\exp(-U(r)/kT)$.

1. Introduction

Microbial adhesion depends on a complicated interplay of various forces acting between the biological particles and the surface (1). Deposition and adhesion of, for instance, oral microorganisms is the first step of the development of dental caries, and, more generally, bacterial adhesion may induce various infectious diseases (2). Two main questions are thus of importance: why do microorganisms adhere to a given surface and how do they distribute over the surface? These problems have been addressed by Busscher et al. (3–5), who studied the interaction of bacteria and cells with solid surfaces and showed that the adhesion of microorganisms is governed by short-range interaction forces. Hence the precise nature of the surface/organism forces plays a minor role in the distribution of the particles on the surface. Rather, the latter is governed primarily by interparticle interactions such as electrostatic, van der Waals, or hydrodynamic forces. Since they have similar long-range interactions but are in other respects much simpler, suspensions of latex or polystyrene particles have been used as model systems for the study of the deposition process. The adhesion probability and the distribution of such particles on surfaces have already been analyzed under various flow conditions (6, 7). Presently, we will limit ourselves only to static conditions for the solution in contact with the adhesion surface.

Based on experimental studies, Feder (8) proposed that the irreversible adsorption of proteins may be described by the random sequential adsorption (RSA) model. Some features of the deposition of latex particles can also be described by this model (9). However, even though it takes surface exclusion effects into account, it neglects all other interactions between adsorbed and adsorbing particles, as well as diffusion of the latter toward the adsorption surface (10). Adamczyk (11) has proposed to take interparticle interactions into account by modifying the RSA rules so that, at each adhesion trial, the probability of success at a position $r$ is proportional to $\exp(-U(r)/kT)$, $U(r)$ being the potential acting between the trial particle and the particle already deposited on the surface. Such an assumption is, however, not at all obvious. Simulations taking into account the diffusion process of the adhering particles, subject to hard-sphere interactions, have shown that the adsorption law proposed by Adamczyk is not observed (12)—i.e., that the adsorption probability depends on $r$ for all positions that do not result in an overlap between particles. However, if hydrodynamic interactions are taken into account (13), the adsorption probability is actually almost independent of $r$ for all allowed positions. Indeed, the component of the diffusion tensor perpendicular to the surface decreases more rapidly with the particle/surface separation than the parallel components of the tensor. Particles thus have time to randomize their position during the adhesion process.

In this article, we further investigate the influence of double-layer and van der Waals forces between the particles and between the particles and the surface during the adhesion process on the configurations of the system. Since simulations of these models require large amounts of computer time, weak gravitational forces are also introduced. At present, the inclusion of hydrodynamic interactions would impose too great a computational burden and they are therefore not taken into account. The aim of this study is, in particular, to determine whether Adamczyk's assumption is valid. A positive answer to this question would represent considerable progress in the field, since RSA-like algorithms that require much less computer time could be used.

In Section 2, we describe the simulation procedure as well as the potentials used. In Section 3, we describe the results corresponding to the adhesion of a particle in the vicinity of one and two particles fixed on the surface. We will, in particular, show that the ratio $p_{ad}(r)/p_{st}(r)$ of the adhesion probability $p_{ad}(r)$ at position $r$ by taking gravitational forces and interparticle forces into account and the adhesion probability $p_{st}(r)$ by considering only gravitational and hard-sphere forces between particles is reasonably well approxi-

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Abbreviation: RSA, random sequential adsorption.†To whom reprint requests should be addressed.
mated by a Boltzmann law: \( p_{\text{eq}}(r)/p_{\text{eq}}(r) = \exp(-U(r)/kT) \). As mentioned above, the inclusion of the hydrodynamic forces in the diffusion/adsorption process leads to uniform probability over the entire adsorption area (outside the exclusion surface). This means that \( p_r(r) \) would then become a constant. Therefore \( p_{\text{eq}}(r) \) becomes directly proportional to the exponential factor and even equal to it if \( p_r(r) \) is conveniently normalized to unity. Hence, taking hydrodynamic effects into account should further strengthen the conclusion that Adamczyk’s assumption is valid and the use of a RSA-like algorithm for description of the deposition of particles on a collector in the presence of soft interaction potentials.

2. Potential Model and Simulation Procedure

Interaction Potentials. Sphere–sphere interaction potentials. In addition to the (short range) hard-sphere potential, the moving and fixed spheres interact by electrostatic (double layer) and van der Waals potentials. The sum of all these potentials is hereafter denoted by \( U(r) \). We assume that all the particles have the same constant surface potential, \( \psi_0 \), fixed to \(-25 \text{ mV} \) (1). For this value, one can use the following expression of the double-layer potential (14)

\[
U_{\text{dl}}^{\text{M}}/kT = 2\pi\varepsilon_0\varepsilon_\text{T} R^2 \ln[1 + \exp(-\kappa R)]/kT, \tag{1}
\]

where \( \varepsilon_\text{T} \) represents the relative dielectric constant of water at \( T = 300 \text{ K} \)—i.e., \( \varepsilon_\text{T} = 77.82 \). \( \varepsilon_0 \) is the dielectric constant of vacuum, \( k \) is the Boltzmann constant, \( \kappa \) is the reciprocal of the Debye length \( (\kappa^{-1} = 0.030386 \mu\text{m} \text{ for a 1-M electrolyte at } 10^{-4} \text{ M and } 300 \text{ K}) \), and \( \delta = r - 2R \), \( r \) being the center-to-center distance of the spheres of radius \( R \) (fixed at \( 2 \mu\text{m} \) throughout this study). This potential is repulsive and finite for all values of \( \delta \approx 0 \).

The van der Waals potentials used in this study are nonretarded potentials. Indeed, our results should not depend significantly on the precise form of the potential; otherwise, our conclusion would be of no great significance. Thus, it is reasonable to use expressions for the potential that are not too difficult to handle analytically (15)

\[
U_{\text{sw}}^{\text{M}}/kT = -(A/3kT)((u^2 + 4u)^{-1} + (u^2 + 4u + 4)^{-1} + (1/2)\ln[(u^2 + 4u)/(u^2 + 4u + 4)]), \tag{2}
\]

where \( A \) is the Hamaker constant \( [A/kT = 2.5 \text{ for the combination polystyrene–water–polystyrene (16)}] \) and \( u \) is the ratio \( \delta/R \). This potential is attractive for all separations and becomes (mathematically) infinite at \( \delta = 0 \).

The sum of both potentials, \( U_{\text{ss}} = U_{\text{dl}}^{\text{M}} + U_{\text{sw}}^{\text{M}} \) (Fig. 1) exhibits a high repulsive barrier \( (U_{\text{dl}}^{\text{M}}/kT = 700) \), which renders contact between particles practically impossible. If this barrier height were of the order of a few \( kT \) or lower, the particles would coagulate in the solution and adhesion experiments would not be feasible. Thus, the precise value of the maximum of the potential is not of great importance as long as it prevents the coagulation process in the suspension. Fig. 1 Inset shows that \( U_{\text{dl}}^{\text{M}}/kT \) has a secondary minimum of depth \( \sim 0.63 \mu\text{m} \) located at \( r/2R = 1.07 \), corresponding to \( \delta = 0.28 \mu\text{m} \)—i.e., 9 times the value of the Debye length given above. This secondary minimum should not be too deep (absolute value smaller than \( kT \)) in order to prevent any flocculation mechanism. All the values chosen in this study are typical experimental conditions.

Sphere-plane potentials. We assume that the plane has a surface potential \( \psi_0 = 0 \). The expression for the sphere-plane double-layer potential, \( U_{\text{sp}}^{\text{M}} \), then simplifies and is given by (14, 17)

\[
U_{\text{sp}}^{\text{M}}/kT = \frac{\pi\varepsilon_0\varepsilon_\text{T} R^2}{2}\ln[1 + \exp(-\kappa R)]/kT, \tag{3}
\]

where \( \delta = z - R \) represents the separation distance between the sphere and the plane, and \( z \) is the altitude of the sphere center. The other symbols were defined previously. We note that this potential is not 0 but is attractive at all distances, as already emphasized by Visser (17). The nonretarded van der Waals potential, \( U_{\text{sp}}^{\text{M}} \), is given by (18)

\[
U_{\text{sp}}^{\text{M}}/kT = -(A/3kT)((u^2 + 4u)^{-1} + (u^2 + 4u + 4)^{-1} + (1/2)\ln[(u^2 + 4u)/(u^2 + 4u + 4)]], \tag{4}
\]

and is also attractive at all distances. Due to the fact that \( A \) does not vary substantially from one system to another, the same value of \( A \) for the sphere–sphere and sphere–surface interactions is taken. The sum of these two contributions, \( U_{\text{sp}}^{\text{M}} \), is always attractive and its interaction range is of the order of \( R \).

Simulation Procedure. One particle is permanently fixed on the adsorbing plane, with its center at the position \( (0, 0, R) \). Throughout the one fixed particle case, the moving particle starts from a point at height \( h \) and lateral distance \( d = d_{\text{start}} \) \( (d \text{ is the distance from the center of the diffusing particle to the vertical Oz axis}) \). The chosen starting height, \( h = 4R \), is sufficiently large so that the particle is practically not influenced initially by either of the potentials.

The movement of a particle in the bulk is governed by the following form of Langevin’s equation (19)

\[
r(t + \Delta t) = r(t) + (DF/kT) \Delta t + \Delta r_B, \tag{5}
\]

where \( D \) represents the diffusion coefficient assumed to be constant even at small sphere–sphere or sphere–plane separation

\[
D = kT/6\pi\eta R, \tag{6}
\]

\( \eta \) being the viscosity of the fluid \( [0.8513 \times 10^{-3} \text{ kg m}^{-1} \text{s}^{-1} \text{ for water at } 300 \text{ K} (20)] \). Thus, the position \( r(t + \Delta t) \) of the particle at time \( t + \Delta t \) is derived from its position \( r(t) \) at time \( t \) by taking into account the deterministic displacement \( (DF/kT)\Delta t \) and the Brownian (random) displacement \( \Delta r_B \).
corresponding to the time step $\Delta t$. If a collision would occur between the moving and fixed particles, the step is not performed and a new displacement is generated. If the particle touches the plane, it is adsorbed and the coordinates of its center are recorded. This particle is then discarded and a new trajectory is initiated from the fixed position $(d_{\text{start}}, h)$. It is assumed that during the time interval $\Delta t$, the forces and particle velocity are constant. The components of $\Delta \mathbf{r}$ are normal deviates with moments of first order equal to zero and of second order given by $2D\Delta t$ and are derived from uniformly distributed random numbers as explained in ref. 21.

As to the deterministic force $\mathbf{F}$ appearing in Eq. 5, two cases are examined: (i) $\mathbf{F}$ is the sum of the sphere–sphere and sphere–plane double-layer and van der Waals forces (derived from the corresponding potentials given above) and the gravitational force $F_g$; (ii) $\mathbf{F}$ is the sum of the sphere–plane double-layer and van der Waals forces and of the gravitational force. The latter is given by

$$F_g = -(4/3)\pi R^2 \rho g \mathbf{z}, \quad [7]$$

where $\rho (\approx 0.055$ g/ml) represents the difference of specific mass between the material of the particles and the bulk fluid, $g = 9.81$ ms$^{-2}$, and $\mathbf{z}$ is the unit vector of the vertical Oz axis. The additivity of the sphere–sphere and sphere–plane potentials assumes that the deposited particle does not modify the properties of the surface and vice versa. This may not be very accurate, but, in the absence of a better model, it appears to be a reasonable starting point.

To produce precise simulations, the mean distance $\langle \Delta r \rangle$ traveled by a particle in each step must be small relative to the characteristic distance over which the potential can be considered as only slowly varying. The reduction in step length as the diffusing particle moves toward the fixed one is also required in order to avoid unrealistic passages through the potential barrier that would lead to coagulation. The time interval $\Delta t$ was determined as a function of the surface-to-surface distance of the spheres ($\delta = r - 2R$) as follows:

$$\text{if } \delta \geq R/5, \Delta t = \pi (R/100)^2/16D$$

$$\text{if } \delta < R/5, \Delta t = \pi [(R + 458)/1000]^2/16D. \quad [8]$$

In this way the potential varies by some tenths of $kT$ in each step as long as $r/2R > 1.07$. For smaller separation distances, the variation of $U_{\text{sum}}/kT$ becomes somewhat larger, but the corresponding locations of the diffusing particles are difficult to attain since by then the potential is already strongly repulsive. Indeed, as shown below, most particles adsorb at distances $r/2R > 1.07$. Under these conditions at least 96% of the moves have a length $< R/50$.

**Fig. 2.** Density of impact points as a function of the distance $r$ between the center of the fixed sphere and the center of the diffusing one, once the latter has touched the adsorbing surface. Case $i$, sphere–sphere, sphere–plane, and gravitational forces [$d_{\text{start}} = R (a); d_{\text{start}} = 3R (arrow) (c)$]; case $ii$, sphere–plane and gravitational forces [$d_{\text{start}} = R (b); d_{\text{start}} = 3R (arrow) (d)$].
For two fixed spheres, with center-to-center distance equal to $D_{12}$, the algorithm is essentially the same. The main difference, however, is that the particles start randomly from a rectangular area of dimensions $(D_{12} + 10R) \times 10R$ situated at height $6R$ above the adsorbing plane.

3. Results and Discussion

One Fixed Particle on the Surface. By means of the algorithm described in Section 2, we obtain the coordinates of the adsorption points of a sample of particles corresponding to various starting positions in the plane $z = 4R$ and for the cases $i$ and $ii$ listed above. From these coordinates, the number density is derived by dividing the number of particles located in an annulus of inner radius $r$ and outer radius $r + \delta r$ by the area of this annulus. The width $\delta r$ is fixed at 0.01 $\mu$m in all cases treated here. Fig. 1 shows that this value is indeed small compared to the width of the sphere–sphere potential well.

For a fixed starting position, the angular distribution of adsorbed particles within an annulus is, of course, nonuniform. However, only the angle-averaged radial distribution is of interest for the present study, since all the sphere–sphere potentials are spherically symmetric.

Fig. 2 shows the adsorption density as a function of the center-to-center distance $r$ in the case where the starting points of the diffusing particles are defined by $h = 4R$, $d_{\text{start}} = R$ (Fig. 2 a and b; sample size, $10^4$ particles) and $h = 4R$, $d_{\text{start}} = 3R$ (Fig. 2 c and d; sample size, $10^4$ particles). Fig. 2 a and c clearly shows that the interparticle potential prevents the adsorption of particles at distances smaller than $\approx 2.14R$, corresponding to the positions shielded by the interparticle potential peak. The adsorption probability then rises abruptly up to its maximum value, corresponding to the secondary interparticle potential minimum. A second maximum in the adsorption probability is visible in Fig. 2 c and d, coincident with the starting position at $d_{\text{start}} = 3R$. This results from the accumulation of particles on the surface in the vicinity of the vertical projection of their starting position, the movement being only weakly hindered by the presence of the fixed particle. To isolate the effect of the sphere–sphere component of the potential model on the adsorption position, we study the evolution of the ratio of the probabilities $p_{\text{gu}}(\tau)/p_g(\tau)$, where $p_{\text{gu}}(\tau)2\pi r dr$ is the probability that a particle subject to potentials of model $i$ adsorbs at a radial distance $r$ and $r + dr$. $p_{\text{gu}}(\tau)2\pi r dr$ is a similar quantity for potential model $ii$. Fig. 3 represents the evolution of this ratio (i.e., the ratio of the data given in Fig. 2 c and d, respectively) as a function of $r$ for the case where $d_{\text{start}} = 3R$. The Boltzmann factor $\exp(-[U_{\text{d}}(r) + U_{\text{us}}(r)]/kT)$ is also shown. To a good approximation, the ratio $p_{\text{gu}}(\tau)/p_g(\tau)$ is given by the Boltzmann law, even though the deposition process is totally irreversible. A similar result is obtained for a starting position $d_{\text{start}} = R$. However, due to extensive computer time, we simulated only $10^4$ successful adsorption attempts and the signal-to-noise ratio is thus less favorable.

Two Fixed Particles on the Surface. For our conclusion concerning the ratio $p_{\text{gu}}(\tau)/p_g(\tau)$ to be general, it has also to be verified when at least two particles are fixed at the surface. To this end, we repeated the simulations with two spheres placed on the adsorption plane at a center-to-center distance $D_{12} = 4.2R$, the center-to-center line being parallel to the Ox axis. This distance was chosen so that particles can adhere in the vicinity of both spheres simultaneously and then interact with both spheres. For larger center-to-center distances, the one fixed sphere conclusions apply. Due to prohibitive computer time, it was not possible to investigate other interparticle separations. However, for smaller interparticle distances, the system should again behave like the isolated particle case due to the fact that the particles act as a unique body with a more complicated shape. The particles started from a random position in a plane of height $h = 6R$ above the adsorbing plane. After each adsorption the coordinates of the particle are recorded and the particle is withdrawn. A new particle then starts. This procedure was performed twice: by taking into account all the interactions already mentioned (case $i$), and by omitting the sphere–sphere interaction (case $ii$). For any position on the plane the corresponding sphere–sphere potential $U_{\text{us}}$ is calculated. One can then build up a histogram of the number of particles as a function of $U_{\text{us}}$ in case $i$. In case $ii$, even though $U_{\text{us}}$ is not included in the simulations, it can be calculated at the impact point by assuming additivity of the potentials of the two spheres. Hence, the positions of the particles from simulation $ii$ can also be classified with respect

![Fig. 3](image-url)  
**Fig. 3.** Ratio of simulated densities corresponding to cases $i$ and $ii$ for $d_{\text{start}} = 3R$. Continuous line represents the Boltzmann factor $\exp(-U_{\text{us}}/kT)$.
to \( U_{as} \). The ratio of these histograms that have a common abscissa scale, together with the Boltzmann factor, is given in Fig. 4.

This figure shows clearly that the ratio of the adsorbing density, calculated with and without sphere–sphere interaction, follows the Boltzmann factor over a wide range of the value of the potential. However, some deviation from this law occurs for regions of the adsorbing plane where the potential is the most attractive. Indeed, the region where \(-1.26 \leq U_{as}/kT \leq -0.63\) corresponds exclusively to areas on the adsorbing surface where the adsorbed particle “feels” the influence of both fixed spheres—i.e., to impact points located mainly between them, thus covering a small fraction of the adsorbing surface. For \(-0.63 < U_{as}/kT < 0\), the potential at the adhesion position is practically influenced only by one of the two fixed particles. The positive part of the abscissa axis corresponds to the steep repulsive part of the interaction potential. The statistical significance of the results in this area is weak, since the probability for a particle to overcome the electrostatic repulsion is low and, moreover, the area where \( U_{as} = 0 \) is very small. Thus, for low to intermediate coverages, the adsorption probability ratio in the presence and absence of interparticle double-layer and van der Waals forces is well approximated by a Boltzmann law.

As a general rule, it may be assumed that in the absence of gravity—i.e., if the integration of the potential takes place for the center of mass of the adsorbing particle—this law applies if the potential wells are not significantly deeper than \(-kT\). This being the case, the diffusing particle has the opportunity, on average, to explore the potential surface before adsorbing irreversibly. In the situations investigated, the maximum well depth is approximately \(-1.26kT\) (in the case of two fixed spheres). The inclusion of gravity, however, reduces the ability of the particle to experience the potential surface. In the limit of a large density difference between the particle and the solution, the motion becomes deterministic and the resulting distribution of adsorbed particles is independent of the sphere–sphere potentials. Finite density differences were introduced to speed the calculations but are in any case representative of the density differences encountered in real systems (e.g., latex beads in water). For the actual values used, the competition between gravity and the thermalization of the particle trajectory appears marginal: for a diffusing particle to escape from the well of depth \(-1.26kT\) in the absence of gravity, we estimate roughly that an additional \(3kT\) of energy is required. This represents a “worst case” situation, and often parts of the potential surface would certainly be easier to access. However, we can conclude that reducing the density difference should result in a better agreement with the Boltzmann’s law prediction, with other conditions remaining the same. Furthermore, the above reasoning applies for the diffusion of a particle in any force field, whether it be the result of one, two, or more fixed particles. Therefore, for the system studied here, Boltzmann’s law would apply for the entire deposition process.

The arguments we have presented above are qualitative in nature, and the exact conditions under which Boltzmann’s law is expected to apply can be determined only from systematic theoretical studies of simple systems—e.g., the adsorption of disks on a line for which there is the possibility of solving the transport equations analytically.

4. Conclusion

This paper presents a computer simulation study of the adhesion of colloidal particles at solid/liquid interfaces in which the Brownian motion of the diffusing particle, as well as the double-layer, van der Waals, and gravitational forces, are taken into account.

To examine the effect of these forces, we fixed one or two spherical particles on the surface and let one particle at a time diffuse until adhesion. In this way, we were able to determine the adhesion probability as a function of either the distance to the fixed particle or of the value of the potential due to the two fixed spheres. Surprisingly, we find that the ratio of the adsorption probabilities in the presence and absence of the interparticle potential, \( p_{as}(r)/p_{as}(r) \), follows a Boltzmann law, \( \exp(-U_{as}(r)/kT) \), even though the adsorption process is irreversible. In the presence of hydrodynamic interactions, this is expected that the probability ratio \( p_{as}(r)/p_{as}(r) \) would be even more accurately represented by the Boltzmann law. Indeed, the slower decrease of the perpendicular component of the diffusion tensor with respect to the particle-to-surface separation, relative to the parallel component (13), allows the particles to randomize before reaching the surface and thus to adhere at an “equilibrium” position. Thus, it is also apparent that the law is followed more closely when the effective weight of the particle in the fluid is small. This is the case in many biological situations (e.g., bacteria always have a specific mass near that of the surrounding biofluid). For dense particles, however, this conclusion should break down.

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