Streaming potential studies of colloid, polyelectrolyte and protein deposition

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Abstract
Recent developments in the electrokinetic determination of particle, protein and polyelectrolyte monolayers at solid/electrolyte interfaces, are reviewed. Illustrative theoretical results characterizing particle transport to interfaces are presented, especially analytical formulae for the limiting flux under various deposition regimes and expressions for diffusion coefficients of various particle shapes. Then, blocking effects appearing for higher surface coverage of particles are characterized in terms of the random sequential adsorption model. These theoretical predictions are used for interpretation of experimental results obtained for colloid particles and proteins under convection and diffusion transport conditions. The kinetics of particle deposition and the structure of monolayers are analyzed quantitatively in terms of the generalized random sequential adsorption (RSA) model, considering the coupling of the bulk and surface transport steps. Experimental results are also discussed, showing the dependence of the jamming coverage of monolayers on the ionic strength of particle suspensions. In the next section, theoretical and experimental results pertaining to electrokinetics of particle covered surfaces are presented. Theoretical models are discussed, enabling a quantitative evaluation of the streaming current and the streaming potential as a function of particle coverage and their surface properties (zeta potential). Experimental data related to electrokinetic characteristics of particle monolayers, mostly streaming potential measurements, are presented and interpreted in terms of the above theoretical approaches. These results, obtained for model systems of monodisperse colloid particles are used as reference data for discussion of experiments performed for polyelectrolyte and protein covered surfaces. The utility of the electrokinetic measurements for a precise, in situ determination of particle and protein monolayers at various interfaces is pointed out.

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1. Introduction

Understanding deposition (irreversible adsorption) mechanisms of colloids and bioparticles at solid/liquid interfaces is of major significance for a variety of fields ranging from geophysics, material and food sciences, pharmaceutical and cosmetic industries, medical sciences, electrophoresis, chromatography, catalysis, etc.

Especially significant seem protein adsorption processes, which are involved in blood coagulation, artificial organ failure, plaque formation, fouling of contact lenses, heat exchangers, ultrafiltration and membrane filtration units. On the other hand, controlled protein deposition on various surfaces is a prerequisite of their efficient separation and purification by chromatography, filtration, for biosensing, bioreactors, immunological assays, etc.

Besides practical importance in the fields mentioned above, irreversible absorption of particles at various interfaces is of major significance for basic colloid science, because interesting clues on the dynamics of these processes can be extracted from the kinetics of these processes, from the maximum coverage and the topology of particle layers [1–14].

Owing to its significance, particle deposition has been extensively studied both theoretically [15–23] and experimentally, using mostly direct methods such as optical microscopy [24–28] AFM [4,5,7–9], reflectometry [10,29–34], and other methods [35–39]. Because of high precision of measurements, these results, obtained mostly for monodisperse latex or silica particles, gold particles or dendrimers, can be used as convenient reference data for protein deposition studies, which are also considerably more complicated [40–50].

However, despite numerous studies devoted to the subject of protein deposition kinetics there still appear discrepancies, even conflicting reports in the literature dealing with this subject. This situation is largely caused by the limited availability of direct experimental techniques working in situ, under dynamic conditions, e.g., in systems exposed to laminar flows, applied to enhance mass transfer rates.

Often the solution depletion methods have been used to determine the amount of proteins adsorbed at solid/liquid interfaces [40]. Although convenient to apply, these methods can become inaccurate, because of possible adsorption of solute molecules on glass walls and entrapment in pores. Also, transport conditions in such systems consisting of protein solutions in contact with stirred suspension of larger particles (substrate surfaces) are rather poorly defined. Moreover, no insight into the local coverage density or the structure of the adsorbed layer can be gained because the actual surface area of the substrate is not well known.

More precise are the gravimetric methods, especially the quartz microbalance (QCM) technique [40,51,52], although in this method the force is determined rather than the mass of adsorbed protein layer. As a result the signal depends not only on the mass of the protein but also on the structure of the adsorbed layer and its hydrodynamic resistance. Therefore, the amount of adsorbed protein alone cannot be uniquely determined, and tedious calibration procedures are needed. Last but not least, the substrate surfaces are practically limited to silver coated quartz plates.

More reliable are optical methods like ellipsometry and reflectometry [45,53,54], or surface plasmon resonance (SPR) [40], which can be applied for in situ measurements. However, they also require careful calibration and are most effective for a high coverage range, preferably multilayer coverages.

Very precise and effective for the low coverage range are the isotope labeling [42,55,56] and the fluorescence methods, like the total internal fluorescence (TIRF) method [46–48]. However, they are rather tedious for application and expensive because specific tags must be attached to proteins, which may change their properties in comparison with native proteins.

One of few precise and efficient methods for determining particle and protein deposition is based on electrokinetic measurements, most frequently the streaming potential [43,44,57,58] changes induced by deposition of particles at solid/liquid interfaces. The method allows for in situ measurement of deposition kinetics, and the precision of coverage determination, comparable with 1% of a monolayer, which, is unprecedented by any other method. Usually experiments of this type involving colloid particles and proteins have been accomplished exploiting the Poiseuille flow, either in the circular [57,58] or parallel plate channel [43,44,59–64] configurations. A characteristic feature of such a flow pattern is that the adsorbed particles are effectively immersed in a simple shear ambient flow, prevailing at channel walls [59,60].

Recently, an efficient approach aimed at complex characterization of protein monolayer formation at polymeric substrates has been developed [65]. The method is based on combination of electrokinetic (streaming potential and streaming current) measurements carried out in the microslot setup with in situ reflectometric interface spectroscopy and QCM.

Although the electrokinetic techniques proved successful in determining protein adsorption kinetics [43,44,57,58,65], their widespread use was hindered because of the lack of appropriate theoretical background. Therefore, they remained relative methods, requiring calibration. Basic experimental studies with the aim of performing such calibrations have been performed using colloid particle suspensions [59–64]. These experiments have been interpreted theoretically in terms of the hydrodynamic model developed in Refs. [59,60], which considered in an exact manner the damping of convection currents of ions in the vicinity of adsorbed particles. Within the framework of this model, which is in principle the first order extension of the Smoluchowski approach for bare surfaces [66], two constants have been calculated, characterizing additive effects stemming from particles and the interface. However, this linear model is exact in the limit of the low particle coverage only. For describing higher surface coverage effects, fitting functions of exponential type have been proposed, whose validity was justified empirically, by a good agreement with experimental data [59,60,64]. Quite recently a major progress has been achieved in this field since exact numerical calculations have been performed, which allowed one to determine theoretically the dependence of the streaming potential of particle covered surfaces for the entire range of coverage met in practice, i.e., up to 0.5 [67]. Also, interesting theoretical results for nonspherical particles (linear aggregates) have been reported in the literature [68].

Therefore, the goal of this paper is to review theoretical and experimental results pertaining to electrokinetic measurements of particle deposition at solid/liquid interfaces, with the emphasis focused on the possibility of using these data to evaluate quantitatively the protein and polyelectrolyte coverage, e.g., their concentration for the ppb range.

Accordingly, the organization of the paper is the following. In the first section illustrative theoretical results characterizing particle transport to interfaces are presented, especially analytical formulæ for the limiting flux under various deposition regimes and expressions for diffusion coefficients of various particles. Then, the blocking effects appearing for higher particle coverage are shortly characterized in terms of the random sequential model (RSA). The coupling of the bulk and surface transport steps is discussed. Experimental results illustrating characteristic features of particle deposition under convection and diffusion transport conditions are discussed.

In the next section, theoretical and experimental results pertaining to electrokinetics of particle covered surfaces are presented. Theoretical models, both analytical and numerical, are discussed, enabling a quantitative evaluation of the streaming current and the streaming potential as a function of particle coverage and their surfaces properties (zeta potential). Experimental data applicable to electrokinetic characteristics of particle monolayers, mostly the streaming potential measurements, are presented and interpreted in terms of the above theoretical approaches. These results, obtained for model systems of
monodisperse colloid particles are used as reference data for discussion of the more complicated experiments performed for poly-electrolyte and protein covered surfaces.

The utility of the electrokinetic measurements for a precise, in situ determination of particle and protein monolayers at interfaces is pointed out.

2. Particle transfer and deposition

2.1. The convective-diffusion theory

As discussed previously [14] a typical kinetic run, i.e., the dependence of the surface concentration of particles $N$ on the deposition time $t$, can be schematically illustrated by the curve shown in Fig. 1. After the short transition time $t_1$, a quasi-stationary state is attained, characterized by a linear increase in $N$ with the deposition time. Then, the kinetic curve levels off and $N$ attains its maximum value $N_\infty$ (often referred to as the jamming, saturation, limiting or plateau coverage).

The characteristic time of attaining the maximum coverage is denoted rather than the time, one can obtain kinetic runs similar to that shown in Fig. 1.

The first relaxation time $t_1$ can be estimated from the simple dependence

$$t_1 = \frac{\delta_d^2}{D}$$

where $\delta_d$ is the diffusion boundary layer thickness and $D$ is the particle diffusion coefficient.

Because for the colloid particle size range, $D$ varies between $10^{-8}$ and $10^{-7} \text{cm}^2\text{s}^{-1}$ and $\delta_d$ is of the order of $10^{-4} \text{cm}$ ($1\mu \text{m}$) under typical convective transport conditions [14], $t_1$ is typically of the order of 0.1–1 s. This is a negligible value in comparison with the time of particle deposition experiments varying usually between $10^2$ and $10^5$ s [13,35–38].

On the other hand, the second relaxation time $t_2$ can be estimated from the formula

$$t_2 = \frac{N_{\infty}}{k_b n_b}$$

where $k_b$ is the mass transfer rate under the steady-state conditions and $n_b$ is the uniform concentration of particles in the bulk.

Note that according to Eq. (2) the relaxation time $t_2$ decreases proportionally to the concentration of particles.

It can be estimated from Eq. (1) that for typical parameters describing colloid suspensions $N_{\infty} = 10^9 \text{cm}^{-2}$, $k_b = 10^{-4} \text{cm}^2\text{s}^{-1}$, $n_b = 10^{10} \text{cm}^{-3}$, the second relaxation time is $10^8$ s.

In the case of diffusion-controlled transport, $t_2$ can be calculated from the formula [69]

$$t_2 = \frac{N_{\infty}^2}{D n_b^2}$$

In this case the relaxation time $t_2$ decreases proportionally to the square of the bulk concentration of particles.

It can be estimated from Eq. (3) that for typical parameters characterizing colloid suspensions, $N_{\infty} = 10^9 \text{cm}^{-2}$, $n_b = 10^{10} \text{cm}^{-3}$, $D = 10^{-8} \text{cm}^2\text{s}^{-1}$, the second relaxation time is $10^8$ s, which is much larger than the convection relaxation time. This indicates unequivocally that the diffusion transport conditions are by orders of magnitude less effective than the convection deposition regime.

As can be deduced from these estimations there are two essential parameters, which quantitatively characterize particle deposition kinetics at interfaces:

(i) the initial deposition rate (governed by the mass transfer rate constant $k$), when the blocking effects stemming from the presence of adsorbed particles are negligible,

(ii) the maximum or jamming coverage $N_{\infty}$ governed by the adsorbed layer topology.

Hence, the major goal of a successful theoretical approach would be to predict values of $k$ and $N_{\infty}$ as a function of particle size, shape, concentration in the suspension, flow rate and configuration, interface shape, ionic strength and pH, and other physicochemical parameters.

Usually, the initial deposition problem is analyzed in terms of the convective-diffusion theory, formulated by Levich [70] and then extended by others [11,12,14,71,72] to incorporate specific force fields generated by interfaces. On the other hand, the considerably more complicated problem of predicting the maximum, mono- and multilayer coverage, as well as the structure of particle monolayers, can be effectively treated in terms of various mutations of the random sequential adsorption (RSA) model [14–23].

The convective-diffusion theory is based on the continuity (mass conservation) equation, which assumes the form [14]

$$\frac{\partial n}{\partial t} = -\nabla \cdot \mathbf{j} + \nabla \cdot \left[ \mathbf{D} \nabla n + \frac{1}{kT} (\nabla \nabla \phi)n - U_n n \right]$$

where $n$ is the particle number concentration (local quantity), $\mathbf{j}$ is the particle flux vector given explicitly by the formula

$$\mathbf{j} = -\mathbf{D} \nabla n + \frac{1}{kT} (\mathbf{D} \nabla \phi)n + U_n n.$$
interface, external force potential, etc., and \( \mathbf{U}_0 = \mathbf{M} \cdot \mathbf{F}_0 + \mathbf{M} \cdot \mathbf{T}_0 \) is the particle velocity resulting from hydrodynamic forces \( \mathbf{F}_0 \) and torques \( \mathbf{T}_0 \).

It is to remember, however, that by formulating Eq. (4) all hydrodynamic and specific interactions among particles were neglected. Moreover, the diffusion tensor occurring in Eq. (4) was assumed to be independent of the particle concentration \( n \) and its gradient. As a consequence of these simplifying assumptions, Eq. (4) remains strictly valid for diluted suspensions of non-interacting particles only. However, it still may be a useful approximation for calculating the transfer and deposition rates of particles because the volume fraction of particles in these processes \( \rho_v = n v_1 \) (where \( v_1 \) is the volume of a single particle) is usually of the order of 0.01 and less.

It is useful to derive the limiting forms of Eqs. (4) and (5) because their analytical solutions are impractical in the general case due to a complex dependence of the specific interaction potential on the distance from the interface.

If all specific interactions are neglected as well as hydrodynamic boundary effects, Eq. (4) simplifies to the form called the Smoluchowski–Levich equation [14]

\[
\frac{\partial n}{\partial t} = D \nabla^2 n - \frac{D}{k_T} \nabla \cdot (F n) - \nu \nabla n
\]  

(6)

where \( \mathbf{V} \) is the unperturbed (macroscopic) fluid velocity vector.

If the external force \( \mathbf{F} \) and the flow vanish (diffusion controlled transport conditions), the Smoluchowski equation is reduced to the simple form

\[
\frac{\partial n}{\partial t} = D \nabla^2 n.
\]  

(7)

The non-stationary Eq. (7), which is linear in respect to \( n \), can be solved analytically (using for example the Laplace transformation method) for many situations of practical interest, e.g., adsorption on a spherical interface from a finite or infinite volume [73–75].

Assuming the steady-state and neglecting external forces, Eq. (6) reduces to the simple form

\[
\nabla^2 n - \rho_e \mathbf{V} \cdot \nabla n = 0
\]  

(8)

where \( \rho_e = \frac{V_0 L_{ch}}{D_n} \) is the dimensionless Peclet number, \( \nabla V = \frac{1}{V_{ch}} \mathbf{V}, L_{ch} \) is the characteristic length scale and \( V_{ch} \) is the characteristic convection velocity.

Eq. (8), often called the convective-diffusion equation, was exploited widely for the description of the transfer of particles to collectors of various geometry [3,24–26,70–72].

The boundary conditions for Eqs. (4)–(8) are specified in the form of the perfect sink model, expressed as

\[
n = 0 \quad \text{at} \quad z = \delta_m \\
n = n_b \quad \text{for} \quad z \to \infty
\]  

(9)

where \( \delta_m \) is the primary minimum distance, \( z \) is the separation in distance from the interface and \( n_b \) is the uniform bulk particle concentration.

Interesting analytical solutions describing particle deposition rate can be derived upon solving analytically the above limiting equations. For example, in the case of diffusion-controlled transfer of particles to a spherically shaped interface (collector) of radius \( R \) (representing either a liquid drop, a gas bubble or a solid particle (see Table 1)) the flux of particles is described by the following equation, first derived by Smoluchowski [76]

\[
-J_d = \left[ \frac{D_{12}}{a + R} + \frac{D_{12}}{k_T n_b} \right]^{1/2} n_b
\]  

(10)

where \( J_d \) is the particle adsorption flux, \( D_{12} = D + D_c \) is the diffusion coefficient of the particle relative to the collector (which may undergo diffusion in the general case) \( D_c \) is the collector diffusion coefficient and \( a \) is the particle radius. Obviously, for stationary collectors, \( D_c = 0 \).

As can be deduced from Eq. (10), for longer times, when \( (a + R)^2 / D_{12} t < 1 \), the flux attains a steady-state value equal to

\[
-J_d = \frac{D_{12}}{a + R} n_b = k_c n_b
\]  

(11)

where \( k_c = \frac{D_{12}}{a + R} \) is the mass-transfer rate constant.

It can be estimated by assuming \( a = R = 100 \) nm that the relaxation time \( t_e \) equals \( 4 \times 10^{-2} \) s. For \( a = 1000 \) nm the relaxation time becomes 1 s.

From Eq. (11) one can deduce that for \( R \to \infty \) (adsorption on a planar interface), the flux remains unsteady for all times and is given by the well-known expression

\[
-J_d = k_c n_b = \left( \frac{D}{k_T} \right)^{1/2} n_b.
\]  

(12)

As can be noticed, the flux vanishes with time proportionally to \( t^{-1/2} \), which means that particle adsorption on planar interfaces, driven by diffusion alone, becomes a very inefficient mode of transport for long times.

By integrating Eq. (12), one obtains the expression for surface concentration of adsorbed particles

\[
N = 2 \left( \frac{D}{k_T} \right)^{1/2} n_b.
\]  

(13)

This equation can be exploited to determine the particle diffusion coefficient by experimentally measuring the surface concentration \( N \) of irreversibly adsorbed particles as a function of time.

Analogous solutions for a two flat interface system (plates) shown schematically in Table 1 are the following

\[
k_c = 2D \sum_{i=1}^{(2l-1)^2} e^{\frac{(2l-1)^2 \pi^2 x^2}{4a^2}}
\]  

(14)

\[
N = h \left[ 1 - \frac{8}{\pi^2} \sum_{i=1}^{(2l-1)^2} e^{\frac{(2l-1)^2 \pi^2 x^2}{4a^2}} \right] n_b
\]  

Because the diffusion transport in the case of planar interfaces becomes very ineffective for long times, one often applies fluid convection in experiments, either in the form of stirring or in a more controlled manner, e.g., by creating flows of a desired configuration and intensity. In this way, particles are brought to the region close to interfaces, which makes their concentration uniform, except for a thin layer called the diffusion boundary layer \( \delta_d \) [14].

In the case of convection-driven transport, \( t_e \) is often negligible in comparison with typical experimental times, thus one can use for describing particle transfer rates the stationary convective-diffusion equation, Eq. (8). This equation can be further simplified for many situations of practical interest to one-dimensional forms, with the perpendicular fluid component independent of the position over the collector, as is the case for the rotating disk [69] or impinging-jet collectors [14]. Interfaces exposed to such kind of flows are called uniformly accessible surfaces. In this case, one can express the mass transfer coefficient in the general form [14]

\[
k_c = -J_d / n_b = \frac{D}{L_{ch} \Gamma^{4/3}} \left( \frac{C_{pe} \rho_e}{3} \right)^{1/3}
\]  

(15)

where \( \Gamma^{4/3} = 0.893 \) is the Euler gamma function value for \( 4/3 \) and \( C_{pe} \) is the dimensionless constant depending on the flow configuration.
Table 1
Bulk transfer rate constants (reduced flux) $k_c$ and surface concentration expressions for uniformly accessible surfaces.

| Surface and flow configuration | Transfer rate constant $k_c = |j|/n_b \text{ cm}^{-1}$ | Surface concentration of particles $N$ [cm$^{-2}$] |
|-------------------------------|--------------------------------|----------------------------------|
| Solid sphere in a quiescent suspension | $(D + D_c)/\eta$ + $(D + D_c)^{3/2}$ | $(D + D_c) n_b t + 2(D + D_c)^{1/2} n_b$ |
| Planar interface in a quiescent suspension | $(D/\eta)^{1/2}$ | $2(D/\eta)^{1/2} n_b$ |
| Two plate system in a quiescent suspension | $2D/\eta \sum_{l=1}^{\infty} e^{-2(l-1)^2/\eta}$ | $h \left[ 1 - \frac{8}{n^2} \sum_{l=1}^{\infty} \frac{e^{-2(2l-1)^2/\eta}}{(2l-1)^2} \right] n_b$ |
| Sphere in uniform suspension flow$^{**}$ (near stagnation point) | $0.889 A_f^{1/3} \eta^{1/3} \nu^{2/3}$ valid for $\theta < \frac{\pi}{2}$ | $k_c n_b t$ |
| The rotating disk | $0.620 A_f^{1/3} \nu^{1/3} \eta^{2/3}$ | $k_c n_b t$ |
| Radial impinging-jet$^{****}$ | $0.776 A_f^{1/3} \nu^{1/3} \eta^{2/3}$ | $k_c n_b t$ |
| | $0.530 A_f^{1/3} \nu^{1/3} \eta^{2/3}$ | $k_c n_b t$ |

Remarks; definitions.
The above expressions were derived by neglecting all specific and hydrodynamic (short-range) interactions, as well as surface blocking effect.

$D$ — diffusion coefficient of particles.
$D_c$ — diffusion coefficient of the collector.
$n_b$ — number concentration of the suspension in the bulk [cm$^{-3}$].

$*$ The flow parameter $A_f$ is given by the expression.

$$A_f(Re) = \frac{3}{2} \left( 1 + \frac{D}{1 + 0.249 Re^{0.95}} \right) \text{ for } Re = \frac{2V_{\infty}}{\nu} < 300$$

$**$ $A_f$ flow parameter (dimensionless).

$\alpha_1 = 4.03 + 0.628 Re - 1.89 \times 10^{-7} Re^2$ for $h/R = 1, Re < 20$

$\alpha_2 = 1.78 + 0.186 Re + 3.4 \times 10^{-7} Re^2$ for $h/R = 1.6, Re < 20$

$\alpha_3 = 1.438 + 0.337 Re + 1.25 \times 10^{-7} Re^2$ for $h/R = 2, Re < 20$

$\alpha_4$ for other Re number and $(h/R)$ are given in Ref. [14].

$V_{\infty} = Q/n\eta^2$

$Re = 2V_{\infty} R/\nu$

$Q$ — volumetric flow rate in the capillary tube.
Analytical expressions for $k_c$ are collected in Table 1 for some surfaces of practical interest. They have been calculated using Eq. (15), the definition of the Peclet number, and by substituting $L_{ch} = a$ [14].

As can be noticed, in all cases $k_c$ increases proportionally to $D_m^{2/3}$ rather than to $D_m$ as intuitively expected. Because $D_m$ is inversely proportional to particle size, this means that the convective flux decreases as $a^{-2/3}$ with particle radius. It is also interesting to observe that $k_c$ is rather insensitive to the fluid velocity $V_m$, increasing in all cases proportionally to $V_m^{3/2}$, except for the case of the rotating disk where $k_c$ remains proportional to $V_m = 0.886 \langle \Omega t \rangle^{1/2}$, where $\Omega$ is the disk angular velocity.

In the case of non-uniformly accessible surfaces, expressions for $k_c$ can be derived for symmetric flows, using the two-dimensional form of Eq. (8) [14]. For small colloidal particles, when the interception effect can be neglected, one can express $k_c(x)$, which is now a local quantity, in the general form

$$k_c(x) = \frac{D}{L_{ch} \Gamma \left(\frac{4}{3}\right)} g_c(x),$$

where $g_c(x)$ is the dimensionless function of the tangential coordinate $x$.

The integration of the local mass transfer rate over the entire collector surface gives the averaged expression for rate constant in the form:

$$\langle k_c \rangle = \frac{1}{2} \sum \int k_c(x) dS(x) = \frac{D}{L_{ch} \Gamma \left(\frac{4}{3}\right)} \langle g_c \rangle = \frac{D}{L_{ch} \Gamma \left(\frac{4}{3}\right)} \langle Sh \rangle,$$

where $\langle Sh \rangle = \langle k_c \rangle \frac{a}{\eta}$ is the averaged mass transfer Sherwood number. As can be deduced from Eq. (17), the averaged flux, which is independent of the tangential coordinate, increases proportionally to $Pe^{1/3}$ for all collectors, except for the fluid sphere.

For the sake of convenience the local and average flux expressions for various collectors are given in Table 2.

It is interesting to observe that in the case of parallel-plate and cylindrical channels, widely used for protein deposition studies by the streaming potential method, the expressions for the local mass transfer rates are [60]:

$$k_c = 0.776 \left(\frac{V_m^{3/2}}{R^{3/2} \chi^{1/3}} \right)^{4/3},$$

(parallel–plate channel) (18)

$$k_c = 0.854 \left(\frac{V_m^{3/2}}{R^{3/2} \chi^{1/3}} \right)^{4/3},$$

(cylindrical channel) (19)

where $b$ is the half width of the parallel-plate channel, $\chi = x/L$ is the dimensionless distance from the inlet to the channel, $L$ is its length, $R$ is the cylindrical channel radius,

$$\langle V \rangle = \frac{2}{3} V_m = \frac{P b^2}{3 \eta L},$$

is the averaged fluid velocity in the channel, $P$ is hydrostatic pressure drop along the channel and $\eta$ is the dynamic viscosity of the fluid.

In the case of the cylindrical channel one has

$$\langle V \rangle = \frac{1}{2} V_m = \frac{P R^2}{8 \eta L}.$$ (21)

Note that the local flux for both the parallel-plate and the cylindrical channel diverges for $\chi = 0$ (entrance to channels) proportionally to $\chi^{-1/3}$. This non-physical behavior is caused by the postulate that the initial particle concentration distribution in the channel was uniform up to the interface. In reality, at the entrance area, the suspension is devoid of particles in the thin layer adjacent to the interface. By considering this, the singularity occurring in Eq. (18) is eliminated [77].

The flux averaged over the entire channel area is

$$k_c = \langle k_c \rangle = 1.1646 \left(\frac{V_m^{3/2}}{D_m^{2/3} \chi^{1/3}} \right)^{1/3}. \frac{P b^2}{3 \eta L}.$$ (22)

In the case of the cylindrical channel one has

$$k_c = \langle k_c \rangle = 1.281 \left(\frac{V_m^{3/2}}{D_m^{2/3} \chi^{1/3}} \right)^{1/3} \frac{P R^2}{8 \eta L}.$$ (23)

It is interesting to note that the local flux in this channel attains a value equal to the average flux at the distance $\chi = \frac{1}{2} b = 0.296$ from the entrance.

It is to mention, however, that the above analytical expressions for the mass transfer rates are strictly valid for the nanoparticle size range. For larger particles, of the size of micrometers, the kinetics of their transfer to interfaces can be predicted more accurately by solving the governing mass-balance equation, Eq. (4), which incorporates the effects of interception, specific, external and hydrodynamic forces in an exact manner. Numerical solutions of this equation for collectors of practical interest are discussed in detail elsewhere [14,72].

Implementation of the above equations also requires the knowledge of the diffusion coefficient of particles, which can be calculated from the Stokes–Einstein relationship

$$D = \frac{kT}{6 \pi a \langle R_H \rangle^{-1}}$$

where the quantity $\langle R_H \rangle$ is defined as the orientation averaged hydrodynamic radius of a particle of arbitrary shape.

Obviously for solid spheres $\langle R_H \rangle$ is equal to the sphere radius $a$. For a solid sphere doublet $\langle R_H \rangle = 1.39 a$ [78], for a triplet (linear aggregate) $\langle R_H \rangle = 1.73 a$ [79,80] and for a linear aggregate composed of $n_i$ equal sized spheres one has [81]

$$\langle R_H \rangle = \frac{n_i}{\ln 2n_i} - 0.25 a = \frac{1}{\ln 2} \left(\frac{L}{2}\right).$$ (25)

where $\lambda = \frac{a}{\langle R_H \rangle}$ is the length of the aggregate (see Table 3).

For particles having the shape of prolate spheroids, one can derive the analytical expression [14,82]

$$\langle R_H \rangle = \left(\frac{1 - \frac{b}{a}}{\frac{b}{a}}\right)^{1/2} a \frac{1}{\cosh(\frac{b}{a})}.$$ (26)

where $a$ is the spheroid longer axis and $b$ is the shorter axis (see Table 3).

In the limit of very large axis ratio parameter $\lambda = \frac{a}{b}$ Eq. (26) becomes

$$\langle R_H \rangle = \frac{n_i}{\ln 2} a = \frac{1}{\ln 2} \left(\frac{L}{2}\right).$$ (27)

On the other hand, for oblate spheroids, their hydrodynamic radius is given by the expression [14,82]

$$\langle R_H \rangle = \left(\frac{1 - \frac{b}{a}}{\frac{b}{a}}\right)^{1/2} a \frac{1}{\cos(\frac{b}{a})}.$$ (28)

where $a$ is the spheroid longer axis and $b$ is the shorter axis.

In the limit of large axis ratio parameter $\lambda = \frac{b}{a}$ Eq. (28) becomes

$$\langle R_H \rangle = \frac{2}{\pi} a.$$ (29)
For the sake of convenience, expressions for $R_i$ for these and other particle shapes, including bent spheroids and sphere aggregates forming semi-circles and circles, are collected in Table 3.

It is to mention that the limitation of the expressions for $k_e$ is that they are valid for initial stages of particle deposition only, when disturbances to their transport stemming from previously adsorbed particles remain negligible. With the progress of particle adsorption, there appear deviations from linearity, in respect to the time, caused by the following main reasons:

(i) particle desorption phenomena

(ii) volume exclusion effects induced by pre-adsorbed particles.

The former effect is important for reversible systems when the energy minimum depth is not too long, which is usually the case for particle size below 10 nm. The effect of desorption can be considered in a quite simple way by analyzing the specific particle-interface energy profile, which enables one to evaluate explicitly the desorption rate constant $k_d$, either analytically or numerically. Then, the kinetic boundary conditions for bulk transport equations in a linear form with respect to bulk suspension concentration and surface coverage can be formulated. Such boundary value problems can be solved analytically for many cases of practical interest, e.g., for diffusion transport to spherical or planar interfaces in contact with suspensions of particles [6,69,73,74].

---

### Table 2

Definitions and bulk transfer rates (local and averaged) for non-uniformly accessible surfaces.

<table>
<thead>
<tr>
<th>Collector and flow configuration</th>
<th>Local rate constant $k_i(x)$</th>
<th>Averaged rate constant $k_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere in uniform flow</td>
<td>$A_i^{1/3}V_i^{1/3}D^{2/3}$</td>
<td>$0.776f_1(x) = \frac{\sin \theta}{\left(1 - \frac{1}{2}\sin 2\theta\right)^{1/3}}$</td>
</tr>
<tr>
<td>Radial impinging-jet RIJ</td>
<td></td>
<td>$0.389A_i^{1/3}V_i^{1/3}D^{2/3}$</td>
</tr>
<tr>
<td>Parallel-plate channel</td>
<td></td>
<td>$1.165A_i^{1/3}V_i^{1/3}D^{2/3}$</td>
</tr>
<tr>
<td>Plate in uniform flow</td>
<td></td>
<td>$0.678V_i^{1/2}D^{2/3}$</td>
</tr>
<tr>
<td>Cylinder in uniform flow</td>
<td></td>
<td>$0.582A_i^{1/3}V_i^{1/3}D^{2/3}$</td>
</tr>
<tr>
<td>Cylindrical channel</td>
<td></td>
<td>$1.281A_i^{1/3}V_i^{1/3}D^{2/3}$</td>
</tr>
</tbody>
</table>

For $f_i(x)$ the equation is:

$$f_i(x) = \frac{\sin x}{\left(1 - \frac{1}{2}\sin 2x\right)^{1/3}}$$
In contrast, a proper description of the volume exclusion effect (often called less accurately the surface blocking effect) is more complicated. The direct cause of the volume exclusion effect is the dynamic interactions among adsorbed and moving particles. These interactions depend not only on the particle coverage but also on their distribution over interfaces, which is in turn dependent on mechanisms of particle transfer like diffusion, flow, migration, etc. As a result of this non-linear coupling, a rigorous analysis of surface exclusion phenomena becomes impractical in the general case. However, approximate results of quite general

**Table 3**  
Averaged hydrodynamic radius \( <R_H> \) values for various particle shapes.

<table>
<thead>
<tr>
<th>Particle shape</th>
<th>( &lt;R_H&gt; ) expression</th>
<th>Remarks, Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid sphere</td>
<td>( &lt;R_H&gt; = a )</td>
<td>Analytical (Stokes law)</td>
</tr>
<tr>
<td>Fluid sphere</td>
<td>( &lt;R_H&gt; = \frac{1 + 2\eta}{\eta} a )</td>
<td>Analytical expression</td>
</tr>
<tr>
<td>Solid sphere doublet</td>
<td>( &lt;R_H&gt; = 1.39a )</td>
<td>Analytical, Ref. [78]</td>
</tr>
<tr>
<td>Solid sphere triplet</td>
<td>( &lt;R_H&gt; = 1.73a )</td>
<td>Numerical solution of the Stokes equation [81]</td>
</tr>
<tr>
<td>Solid sphere aggregate ( \lambda = n_s )</td>
<td>( &lt;R_H&gt; = 3.61a )</td>
<td>Numerical solution of the Stokes equation [81]</td>
</tr>
<tr>
<td>Solid sphere linear aggregate</td>
<td>( &lt;R_H&gt; = \frac{1}{\ln 2 - 0.25} \lambda a )</td>
<td>Asymptotic expression for ( 100 \leq n_s \leq 300 ) ( \lambda = n_s ) [81]</td>
</tr>
<tr>
<td>Prolate spheroid</td>
<td>( &lt;R_H&gt; = \left(1 - \frac{b^2}{a^2}\right) a )</td>
<td>( a&gt;b, \lambda = a/b &gt; 1 ) analytical solution</td>
</tr>
<tr>
<td>Oblate spheroids</td>
<td>( &lt;R_H&gt; = \left(1 - \frac{b^2}{a^2}\right)^{\frac{1}{2}} )</td>
<td>( a&gt;b, \lambda = a/b &gt; 1 ) analytical solution</td>
</tr>
<tr>
<td>Prolate spheroid (slender)</td>
<td>( &lt;R_H&gt; = \frac{1}{\ln 2 - 0.115} \lambda )</td>
<td>( \lambda = L/2b ) approximate solution [14], valid for ( \lambda \gg 1 )</td>
</tr>
<tr>
<td>Slender cylinder</td>
<td>( &lt;R_H&gt; = \frac{1}{\ln 2 - 0.115} \lambda )</td>
<td>( \lambda = L/2b ) approximate solution, valid for ( \lambda \gg 1 ) [14]</td>
</tr>
</tbody>
</table>
validity can be derived using various RSA approaches discussed in the next section.

2.2. Surface blocking effects

A limitation of the convective-diffusion theory discussed above is lack of the possibility of deriving information on surface blocking effects, maximum (jamming) coverages, and the structure of particle monolayers. This can be done within the framework of other approaches, exploiting statistical, rather than deterministic concepts. The most efficient in this respect seems to be the above mentioned RSA approach, whose main advantages are simplicity, flexibility and efficiency in generating large particle populations. This enables one to derive blocking functions, jamming limits for particles of various shape, pair correlation functions, and so forth. This kind of information can be then exploited as boundary conditions for the bulk transport equations, which makes it possible to solve the coupled bulk and surface transport problem in a proper way [14,69].

The general rules of the Monte Carlo type simulation scheme based on the RSA approach are [15–19,21].

(i) an adsorbing (virtual) particle is created, whose position and orientation is selected at random within prescribed limits defining the adsorption domain,

(ii) if the virtual particle fulfills prescribed adsorption criteria, it is adsorbed with unit probability and its position remains unchanged during the entire simulation process (localized and irreversible adsorption postulate),

(iii) if the adsorption criteria are violated, a new attempt is made that is fully uncorrelated with previous attempts.

It is interesting to note that the RSA model is applicable for particles of various shape and various dimensionality like a quasi one

---

Table 3 (continued)

<table>
<thead>
<tr>
<th>Particle shape</th>
<th>(\langle R_H \rangle) expression</th>
<th>Remarks, Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bent spheroid</td>
<td>[\frac{1}{\frac{1}{2} \ln 2 \lambda - 0.31} \left( \frac{L}{2b} \right)]</td>
<td>Approximate solution, (\lambda = L/2b) valid for (\lambda \gg 1) [128]</td>
</tr>
<tr>
<td>Half circle approximated by (n_s) spheres</td>
<td>[\frac{1}{\frac{1}{3} \ln 2 \lambda - 0.084} \lambda a]</td>
<td>Numerical solution valid for (100 \leq \lambda \leq 400) [81]</td>
</tr>
<tr>
<td>Bent spheroid</td>
<td>[\frac{1}{\frac{1}{4} \ln 2 \lambda - 0.002} \lambda L]</td>
<td>(L = 2nd, \lambda = L/2b \gg 1) approximate solution [128]</td>
</tr>
<tr>
<td>Circle (ring) made of (n_s) spheres</td>
<td>[\frac{1}{\frac{1}{2} \ln 2 \lambda + 0.67} \lambda a]</td>
<td>(\lambda = n_s) numerical solution valid for (100 &lt; \lambda &lt; 450) [81]</td>
</tr>
<tr>
<td>Disk</td>
<td>[\frac{2}{\pi} a]</td>
<td>Analytical, valid for (d/a \ll 1, d - disk thickness) [14]</td>
</tr>
</tbody>
</table>
dimensional (1D) adsorption on a line segment, a two-dimensional (2D) adsorption on planar surfaces of finite (surface features) or infinite extension and three-dimensional (3D), adsorption (referred to as random addition) in the space.

It is advantageous for analyzing these results to introduce the dimensionless coverage, which for the 2D case (adsorption at a surface), can be defined as

$$\Theta = \frac{S_N}{\Delta S}$$

(30)

where $S_N$ is the characteristic cross-section of the particle and $\Delta S$ is the surface area of the adsorbing domain, for example a surface feature and $N$ is the number of particles adsorbed at $\Delta S$.

For spherical particles one can define $S_N$ unequivocally as $na^2$ so

$$\Theta = \frac{na^2 N}{\Delta S}$$

(31)

On the other hand, in simulations based on the RSA scheme, particle adsorption probability for a given coverage, defined as the available surface function $ASF$ [14,16–21,18] or less properly as the blocking function [27,72,74], can be calculated as

$$ASF(\Theta) = B(\Theta) = \frac{N_{\text{succ}}}{N_{\text{att}}}$$

(32)

for $N_{\text{att}} \to \infty$, where $N_{\text{succ}}$ is the number of successful adsorption events and $N_{\text{att}}$ is the number of virtual adsorption attempts.

Usually, in these simulations, the hard particle interaction potential [14] is used for describing particle–particle interactions. On the other hand, the particle collector interactions are described by the perfect sink interaction potential, originally introduced by Smoluchowski [75]. These idealized potentials are especially suitable for colloid particles, when the double layer thickness remains smaller than particle dimensions. For nanoparticles, the exponentially decaying Yukawa repulsive potential is used [11,14], and the particle collector interactions are described by the attractive Yukawa potential.

In the case of surfaces bearing isolated adsorption centers of the size comparable with the adsorbing particles, a modified RSA simulation scheme is used whose first step consists in the deposition of sites according to the classical RSA of desired surface density $N_c/\Delta S$ and the coverage $\Theta = \frac{na^2 N_c}{\Delta S}$ (where $N_c$ is the number of centers and $a$ is the site radius). The simulations of random site adsorption can be carried out either for point-like sites distributed randomly over a homogeneous surface with the zero minimum distance [83], or for sites having finite dimensions, e.g., hard disks of the diameter $2a$, incorporated into the substrate [84], or hard spheres attached to the surface [85].

Because of its major significance, adsorption on continuous surfaces (bearing uniformly distributed centers of the size much smaller than particle dimensions) has widely been studied in terms of the RSA model described above. Most results concern hard spherical particle adsorption on planar interfaces of infinite [15–23] or finite extension [86,87].

There also exist results for polydisperse spherical particles [88] and for anisotropic hard particles of a convex shape like squares [89], rectangles (cylinders), spherocylinders (disk rectangles) and ellipses (spheroids) [17]. Results are available for particles interacting via a short range repulsive potential resulting from the electric double layers [11,12,14,22].

In these simulations one can derive not only the number of adsorbed particles in the jamming state but also under transient states, which can be physically linked to quasi-time variable. In this way the kinetics of particle deposition can be determined. For very long simulation times, the final state is achieved when no more particles can be adsorbed and the jamming coverage $\Theta_{\text{ jam}}$ is attained. This is the most important parameter, derived from RSA simulations by extrapolation, because it characterizes the interface capacity to accommodate particles. For hard spherical particles it has been determined that $\Theta_{\text{ jam}} = 0.547$ [15,18], which is markedly smaller than the maximum hexagonal packing of spheres in 2D, equal $\pi / 2 \sqrt{3} = 0.9069$ or the regular packing, equal $\pi / 4 = 0.7854$ [14]. For randomly oriented squares $\Theta_{\text{ jam}} = 0.53$ and for ellipses characterized by axis ratio 2:1, $\Theta_{\text{ jam}} = 0.583$ [17]. Values of $\Theta_{\text{ jam}}$ for particles of other shapes can be found in Ref. [14]. It is to mention that these values correspond to the side-on adsorption of particles. For elongated particles, their adsorption on quasi continuous surfaces can also occur at arbitrary orientations, which can be described in terms of the unoriented adsorption regime, analyzed in detail in Refs. [19,90,91].

It was shown in Ref. [14] that the above results can also be used for interpretation of experimental results for particles interacting via the short range Yukawa potential upon defining the effective interaction range $h^{*}$. Using this concept one can calculate the jamming coverage for interacting particles (referred to as the maximum coverage) from the simple relationship valid for both spherical and anisotropic particles

$$\Theta_{\text{max}} = \Theta_{\text{ jam}} \frac{1}{(1 + h^{*})^2}.$$  

(33)

As discussed [11,12,22], the effective interaction range $h^{*}$ remains proportional to the thickness of the electric double layer $Le = (\frac{d}{\kappa})^2$ (where $\epsilon$ is the dielectric permittivity of the solvent, $\kappa$ is the elementary charge and $l$ is the ionic strength of the electrolyte), with the proportionality constant of about two, for particle size range of 100–500 nm [14].

Further details on the dependence of the effective interaction range on the ionic strength and particle size for various particle shapes can be found in Ref. [14].

In addition to the jamming coverage, from RSA simulations one can also determine the available surface function (blocking function) which has major significance for predicting particle adsorption kinetics. It was demonstrated [16] that for not too high coverage, one can approximate the blocking function by the second order series expansion

$$B(\Theta) = 1 - C_1 \Theta + C_2 \Theta^2 + O(\Theta^3).$$  

(34)

For spheres $C_1 = 4$ and $C_2 = 6\sqrt{3} / \pi = 3.31$. For other particle shapes, the $C_1$ and $C_2$ constants are given in Ref. [14].

Results calculated from Eq. (34) reflect well the exact data derived from simulations for particle coverage $\Theta < 0.4$.

On the other hand, for $\Theta$ approaching the jamming coverage, the blocking function for spheres can be well approximated by the expression [16]

$$B(\Theta) = 2.31 \left(1 - \frac{\Theta}{\Theta_{\text{ jam}}} \right)^3.$$  

(35)

For non-spherical particles, the blocking function, for a coverage close to the jamming limit, assumes an analogous form [17]

$$B(\Theta) = C_\Theta \left(1 - \frac{\Theta}{\Theta_{\text{ jam}}} \right)^4$$  

(36)

where the dimensionless constant $C_\Theta$ varies between 2.8 and 3.2 for spheroids [14].

In the case of spheres, one can also formulate an approximate analytical expression which fits well the blocking function for the entire range of coverage [16]

$$B(\Theta) = \left[1 + 0.812 \frac{\Theta}{\Theta_{\text{ max}}} + 0.4258 \left(\frac{\Theta}{\Theta_{\text{ max}}} \right)^2 + 0.0716 \left(\frac{\Theta}{\Theta_{\text{ max}}} \right)^3 \right] \left(1 - \frac{\Theta}{\Theta_{\text{ max}}} \right)^3.$$  

(37)

where $\Theta_{\text{ max}} = 0.547$.

It is to mention that the above results have been obtained within the framework of the classical RSA model, postulating a two-dimensional adsorption of particles. In more refined approaches, referred to as the generalized RSA model, a more realistic, three-dimensional motion of particles in the adsorption layer is considered
It was demonstrated that under the conditions of a quasi-stationary transport (convective diffusion) the flux to particle covered surfaces can be expressed as [14,23]

$$j(\theta) = j_0 \frac{KB(\theta)}{1 + (K-1)B(\theta)}$$  \( (38) \)

where \( j_0 = -k_f n_0 \) is the initial flux for bare surfaces analyzed above, \( K = k_s/k_c \) is the coupling constant, \( k_s \) is the adsorption constant describing the rate of particle transfer through the adsorption layer [14] and \( B(\theta) \) is the generalized blocking function describing the effect of three dimensional particle deposition process.

Because of mathematical difficulties, the generalized blocking function \( B(\theta) \) has been evaluated in an exact way for the low coverage range only [23]. Since the deviation from the 2D function described by Eq. \( (34) \) was rather minor, it was suggested that for higher coverage range, close to jamming one can as well approximate \( B(\theta) \) by Eq. \( (37) \).

On the other hand, the deposition rate constant \( k_s \) can be evaluated as [14]

$$k_s = \frac{D}{2a_k} \left( 1 + \frac{1}{2 \ln \frac{\delta_m}{a}} \right)$$  \( (39) \)

where \( \delta_m \) is the minimum distance between the particle and the interface.

Using Eq. \( (39) \), the expression for the coupling constant \( K \) becomes

$$K = \frac{D}{2a_k} \left( 1 + \frac{1}{2 \ln \frac{\delta_m}{a}} \right) = \frac{1}{2a_k \ln \frac{\delta_m}{a}}$$  \( (40) \)

where values of the bulk transfer rate constant \( k_c \) are given in Tables 1–2.

It was shown in Ref. [14] that for a particle size below 100 nm, \( K \gg 1 \) under typical forced convection transport conditions.

Using these data one can calculate particle deposition kinetics for the entire range of coverage by numerically integrating Eq. \( (38) \).

In the case of diffusion controlled transport the situation is more complicated since particle deposition kinetics can only be evaluated via numerical solutions of governing transport equations with the boundary condition at the interface having the form [69]

$$j(\theta, t) = k_s n(\delta) B(\theta)$$  \( (41) \)

where \( n(\delta) \) is the local particle concentration at the edge of the adsorption layer \( \delta \) (subsurface concentration).

2.3. Experimental results

The validity of the above theoretical predictions has been confirmed by a variety of experimental results concerning particle deposition in model systems. The most reliable results were obtained for monodisperse colloid particles using direct experimental methods, such as optical microscope observations [1,2,6,23–25,28] or AFM techniques for latex [4,5,10] colloid gold [8,34] and dendrimer suspensions [9,33]. One can also apply the electron microscopy to determine the particle coverage [39].

Most of these experimental studies are devoted to kinetic aspects of particle deposition, which allow one to determine the two most relevant parameters, namely the initial flux \( (j(0)) \) and the maximum coverage \( \delta_{\text{max}} \) as a function of particle size and ionic strength of suspensions.

Typical examples of deposition kinetics determined by Brouwer et al. [34] for colloid gold particles (averaged diameter 13.4 nm) at a silicon substrate covered by a 25 nm thick silica layer, are shown in Fig. 2. In this study, the impinging jet cell was used, combined with a reflectometric method of particle coverage determination using the thin island film theory. As can be seen, for short deposition time, all kinetic curves follow the same straight line dependence, irrespectively of the ionic strength of particle suspension, which indicates that the blocking effects were negligible. On the other hand, for longer deposition time, particle coverage attained its maximum value, which decreased with the decrease in the ionic strength. Hence, the maximum coverage for \( l = 13.6 \) mM was equal to 0.22 and for \( l = 3.6 \) mM it was equal to 0.15. This effect can be interpreted in terms of increased blocking effects stemming from the lateral repulsion among deposited particles.

It is interesting to mention that the experimental kinetic runs shown in Fig. 2 were quantitatively interpreted in terms of the RSA model using the integrated form of Eq. \( (38) \) for \( K = 45 \) (these theoretical results are depicted by solid lines in Fig. 2).

Analogous kinetic runs were reported for other convection controlled systems, for example by Kleimann et al. [10], who studied deposition of positively charged amine latex particles (averaged size of 22.5 nm) at oxidized silicon, covered by a 100 nm of thickness silica layer in the impinging jet cell, using the reflectometric method. Particle coverage was determined using the AFM measurements. However, no attempt was undertaken to analyze the kinetic runs theoretically.

Similar kinetics of particle deposition were reported by Kozlova and Santore [38] who studied deposition of silica particles (averaged diameter 460 nm, fluoroscently labeled by fluorescein) on a glass substrates covered by a thin (10 nm) silica layer and modified by positively charged polyelectrolyte, poly(dimethylylaminoethylmethacrylate) (pDMAEMA).

Analogous deposition kinetics under convective transport have been observed for proteins as well. For example Lin and Hlady [46] have determined, using the TIRF method, adsorption kinetics of HSA (human serum albumin) at silica gradient surfaces, using a parallel plate channel flow cell.

On the other hand, Wertz and Santore [48] measured deposition of BSA and fibrinogen using the TIRF method in the parallel-plate channel cell made of microscope glass slides modified by silane adsorption, at wall shear rate of 5 s\(^{-1}\) and various bulk concentrations of the protein (25–100 ppm). Their experimental results (points) for fibrinogen are shown in Fig. 3 as the dependence of the surface concentration of the protein expressed in mg/m\(^2\) on the dimensionless time of deposition \( \tau = k_{\text{cd}}/N_0 \) (where \( N_0 \) is the characteristic coverage equal to 10 mg/m\(^2\)). The solid and the dashed lines denote the theoretical results calculated by numerical integration of Eq. \( (38) \) for \( K = 2 \times 10^3 \) and \( K = 10^5 \), respectively. As can be seen in Fig. 3, the theoretical results describe properly the experimental data for the entire range of deposition time and the bulk protein concentration. It is interesting to observe, however, that the maximum coverage of fibrinogen increased slightly with its bulk concentration. This suggests that either some of protein molecules were forming a second layer due to surface aggregation or they were adsorbing end on at the surface.

It is to mention, however, that protein deposition experiments are often carried out under diffusion controlled transport. Therefore, numerous studies of colloid particle deposition under diffusion-controlled transport have been carried out using the AFM [4,5,10] or optical microscope observation methods [6] with the aim of collecting reliable reference data for interpreting protein deposition kinetics. Typical examples of kinetic runs obtained in this case of positively charged amide latex particles (average diameter 800 nm) adsorbing on bare mica are shown in Fig. 4 [92].

As can be seen, these kinetic results, expressed in terms of the square root of adsorption time \( \sqrt{t} \) resemble very closely, the dependencies predicted for convective transport, shown in Fig. 2. For the deposition time shorter than ca. 10 h (when \( \theta < 0.2 \)), particle deposition kinetics remained a linear function of \( \sqrt{t} \), independently of the ionic strength of the suspension. This result agrees with the limiting analytical solution derived from Eq. \( (13) \), which was derived...
by neglecting all blocking effects and specific interactions among particles. However, for longer times, especially at lower ionic strength of $2 \times 10^{-5}$ M, experimental results deviate from these analytical predictions, attaining maximum values, increasing with the ionic strength. This is a direct manifestation of blocking effects due to repulsion among particles. As can be seen in Fig. 4, the experimental data were quantitatively accounted for by theoretical results obtained by numerical solution of the governing diffusion equation, Eq. (7), with the boundary condition described by Eq. (41). It is interesting to observe that the theoretical results derived from the widely used Langmuir model, where the blocking function is described by $1 - \Theta / \Theta_{\text{max}}$ (dashed lines in Fig. 4) do not reflect properly the experimental kinetic runs.

For further analysis of streaming potential data for particle covered surfaces it is important to know not only the coverage of particles but also their distribution over the substrate surface. This can be qualitatively seen in Fig. 5 (part a) showing the amidine latex monolayers formed at mica for $l = 2 \times 10^{-2}$ M, $\Theta = 0.27$ and $l = 10^{-3}$ M, $\Theta = 0.44$. A short-range, liquid-like ordering of particles is clearly visible in this picture. It is interesting to mention that this micrograph was taken using optical microscopy under wet conditions, which preserved particle monolayers intact.

The structure of particle monolayers can be quantitatively characterized in terms of the pair correlation function $g(r/a)$ (often referred to as the radial distribution function) [15,16,18,21]. This function expresses the ensemble averaged probability of finding a particle pair at the center to center distance $r$ (normalized usually to particle radius $a$).

As can be seen, a characteristic feature of the $g(r/a)$ function shown in Fig. 5a, is that there is a well pronounced maximum at the distance $r/a = 3$, i.e., when the gap between particle surfaces equals one particle radius. The position of the peak is a direct indication of the range of the lateral interactions among adsorbing particles. Here, due to a large screening distance (equal to ca. 200 nm in this case), the range is comparable with the particle dimensions.

With the increase in the ionic strength, the repulsion between particles becomes smaller at short distances, because of more intense...
screening. They can, therefore, form a more compact monolayer. Accordingly, the peak in the pair correlation function appears at the distance \( r/a \) close to 2 (see Fig. 5b), which is expected for hard (noninteracting) particles.

The results shown in Fig. 5 indicate unequivocally that the maximum coverage of particles and structure of their monolayers can be regulated to a significant extent by the change in the ionic strength of particle suspensions.

The maximum particle coverage \( \Theta_{\text{max}} \), which can be determined from extrapolation of the kinetic runs, is of a primary experimental significance. Therefore, many studies have been carried out in the literature with the aim of determining this parameter as a function of the double-layer parameter \( a/Le = (a^2 e^2 kT/2e^2 I)^{1/2} \), which represents the ratio of the particle radius to the double layer thickness \( Le \).

Most of these studies were carried out using monodisperse latex particles [4–6,10], colloid gold particles [8,34] or dendrimers [9], under the diffusion transport condition or forced convection transport in the impinging-jet cells. The coverage of particles was determined by optical microscopy, AFM, electron microscopy, or reflectometry. These results obtained for various particle sizes, ionic strength and particle transport conditions are collected in Fig. 6 as the dependence of the reduced maximum coverage \( \Theta_{\text{max}}/\Theta_{\infty} \) (where \( \Theta_{\infty} = 0.547 \) is the jamming coverage for hard spheres) on the \( a/Le \) parameter. As can be observed, the experimental data collected under various conditions can well be reflected for \( a/Le > 1 \) by theoretical results derived from the RSA model, which predict a significant reduction in \( \Theta/\Theta_{\text{max}} \) for lower values of \( a/Le \), i.e., either for low ionic strength or smaller particles, because of increasing range of the repulsive double-layer interactions. The results derived from the RSA model can be approximated by the following analytical formula derived in Ref. [14]

\[
\frac{\Theta_{\text{max}}}{\Theta_{\infty}} = \frac{1}{(1 + H^*)^2}
\]

where

\[
H^* = \frac{1}{2(\phi_0)} \left[ \ln \left( \frac{\phi_0}{2\phi_{\text{ch}}} \right) - \ln \left( 1 + \frac{1}{2(\phi_0)} \ln \left( \frac{\phi_0}{2\phi_{\text{ch}}} \right) \right) \right]
\]

and \( \phi_0 \) is the repulsive interaction energy between particle pair at close separations (height of the energy barrier), and \( \phi_{\text{ch}} \) is the characteristic energy close to 1 kT [14].

On the other hand, negative deviations of experimental data from this theoretical model, which appeared for \( a/Le > 10 \), can be explained by the time of deposition experiments being too short. This conclusion is supported by the fact that theoretical results obtained for finite simulation times, corresponding to typical experimental times (empty squares in Fig. 6), correlate better with some experimental points than the theoretical results obtained for infinite times (empty triangles).

The results presented in this section enable a quantitative description of particle deposition kinetics under various transport conditions, especially evaluation of the maximum coverage, which is a prerequisite for a proper interpretation of electrokinetic measurements for particle covered surfaces discussed next.

Fig. 5. Part “a”, micrographs showing positively charged latex particles (averaged diameter 800 nm) deposited on bare mica, ionic strength \( 2 \times 10^{-5} \) M, \( pH = 5.5 \), \( T = 298 \) K, \( \Theta_s = 0.27 \), and ionic strength \( 10^{-3} \) M, \( pH = 5.5 \), \( T = 298 \) K, \( \Theta_s = 0.44 \) [91]. Part “b” the pair correlation function \( g(r) \) for the same parameters. The points denote experimental results derived from optical microscopy and the solid line denotes the theoretical results derived from the Monte-Carlo RSA simulations.
3. Electrokinetics of particle covered surfaces

As can be deduced from the previous discussion, kinetic measurements of particle deposition at solid/liquid interfaces performed via direct observation methods, although precise, are tedious and time consuming, especially for nanoparticle size range (proteins). One of the alternatives of overcoming this difficulty is the use of electrokinetic techniques, especially the streaming potential measurements, making it possible to determine under in situ conditions the kinetics of particle deposition of arbitrary size range. The utility of this method has recently been enhanced due to the availability of reference experimental data, based on direct determination of the particle coverage. These results can be quantitatively interpreted in terms of the new theoretical results derived by exact numerical solution of the electrokinetic problem of particle covered surfaces. Reviewing these results is the goal of this section.

3.1. The theoretical model

The streaming current is the result of the convective flux of ions from the thin double-layer region adjacent to solid/electrolyte interfaces. It is induced by a macroscopic flow of the fluid, usually driven by the hydrostatic pressure gradient, e.g., for channel and capillary flows, or motion of interfaces (circular disks arrangement, rotating disk).

Accordingly, the streaming current \( I_s \) defined as the amount of charge flowing per unit of time through the plane \( S \), perpendicular to the interface (see Fig. 7), can be expressed via the constitutive equation

\[
I_s = \frac{\rho_e}{\varepsilon} \int_{S} \mathbf{V} \cdot d\mathbf{S}
\]  

where \( \rho_e \) is the electric charge density, \( \mathbf{V} \) is the macroscopic fluid velocity field and \( d\mathbf{S} \) is the surface element.

Eq. (44) is valid for arbitrary interface shape provided that its local radius of curvature remains much larger than the double layer thickness \( \varepsilon \) and the particle dimension.

In formulating various theoretical approaches discussed in this section it is further assumed that the flow field is laminar in the region adjacent to the interface and that the electric charge density is governed by the Poisson–Boltzmann equation, unperturbed by the flow, i.e.,

\[
\rho_e = -e \nabla^2 \psi = e \sum_{i} z_i n_{ib} e^{-\frac{z_i e \psi}{kT}}
\]  

where \( \psi \) is the electric potential, \( z_i \) is the \( i \)-th ion valency, \( n_{ib} \) is the concentration of this ion in the bulk (it is to be noted that the SI unit system has been adopted in this work).

By considering Eq. (45) the expression for the streaming current becomes

\[
I_s = -e \int_{S} \nabla^2 \psi \mathbf{V} \cdot d\mathbf{S}
\]  

The explicit evaluation of Eq. (46) requires the knowledge of the scalar electrostatic potential field \( \psi \) and the hydrodynamic vector field \( \mathbf{V} \), which cannot be found analytically in the general case of particle covered surfaces.

However, analytical solutions can be found for shearing flows in the case of bare interfaces and in the low particle coverage regime, using the cluster expansion technique (see Appendix A). These solutions are of a quite broad utility because the simple shear appears close to most solid/
liquid interfaces exposed to laminar ambient flows, e.g., for channel flows, for the rotating disk, impinging-jets, for the uniform flow past a sphere or cylinder, etc. (see Table 2). In all these cases the macroscopic fluid flow in the x-direction parallel to interfaces can be expressed as

\[ \mathbf{V} = \mathbf{G}_o \mathbf{z} \mathbf{x} \]  

(47)

where \( \mathbf{G}_o = \left( \frac{\mathbf{b}}{\mathbf{c}} \right) \) is the shear rate at the interface, \( \mathbf{z} \) is the coordinate locally perpendicular to the interface and \( \mathbf{z} \mathbf{x} \) is the unit vector in the direction parallel to the interface and the flow.

Substituting Eq. (47) into Eq. (46) and integrating two times by parts (assuming also that the electric potential vanishes far from the interface) one obtains the general formula for the streaming current of homogeneous surfaces (in the absence of particles)

\[ -I_i = e \mathbf{G}_o \mathbf{z} = \zeta \mathbf{L} \]  

(48)

where \( I_i \) is the width of the interface (see Fig. 7), \( \mathbf{z} \) is the electric potential in the slip plane (where the liquid starts to move), usually referred to as the zeta potential [93–95].

Note that Eq. (48) does not involve the length of the interface.

It is interesting to observe that according to Eq. (48), the streaming current depends linearly on the zeta potential of the interface, although the governing Poisson–Boltzmann equation, Eq. (45), is nonlinear. Thus, Eq. (48) is valid for an arbitrary charge of the interface, electrolyte concentration and composition, including mixtures of electrolytes of arbitrary valency.

Eq. (48) can be evaluated explicitly for some geometries of major practical significance, where the shear rate at the interface is known from analytical solutions of the Navier–Stokes equation.

For example, in the case of a rectangular channel of the cross-section \( 2b \times 2c \) (where \( 2b \) is the channel height and \( 2c = l \) is the channel width) the expressions for the average shear rates at the base and side walls are [14]

\[ G_1 = \mathbf{G}_o \left[ 1 - \frac{b}{c} f \left( \frac{b}{c} \right) \right] \]  

(49)

\[ G_2 = \mathbf{G}_o f \left( \frac{b}{c} \right) \]

where \( \mathbf{G}_o = \frac{\mathbf{P} b}{\mathbf{L}} \) and \( \mathbf{P} \) is the hydrostatic pressure gradient along the channel of the length,

\[ f \left( \frac{b}{c} \right) = \frac{16}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \tan \left( \frac{2n+1}{2b} \right) \]  

(50)

It is interesting to observe that the function \( f(b/c) \) varies little with the channel shape assuming the value of 0.5 for a channel with square cross-section \( (b = c) \) and 0.54 in the limiting case of parallel-plate channel, where \( b/c \ll 1 \). Hence,

\[ G_1 = G_2 = \frac{1}{2} \mathbf{G}_o \]  

(51)

for channel with square cross-section and

\[ G_1 \approx \mathbf{G}_o \left[ 1 - 0.54 \frac{b}{c} \right] \]

\[ G_2 \approx 0.54 \mathbf{G}_o \]  

(52)

for a parallel-plate channel.

Using Eqs. (48) and (49) one can formulate the following expression for the streaming current for a rectangular channel

\[ -I_i = 4e \mathbf{G}_o c \left[ \zeta \left( 1 - \frac{b}{c} f \left( \frac{b}{c} \right) \right) + \frac{b}{c} \zeta f \left( \frac{b}{c} \right) \right] \]  

(53)

where \( \zeta_1 \) is the zeta potential of the two base walls and \( \zeta_2 \) is the zeta potential of the two side walls.

It is interesting to observe that in the case when all channel walls are of the same material (characterized by equal zeta potentials, \( \zeta_1 = \zeta_2 \)), Eq. (53) simplifies to the limiting form independent of the channel shape (cross-section)

\[ -I_i = 4e \mathbf{G}_o c \zeta_1 = 4e \frac{P b c}{\mathbf{L}} \zeta_1 = -I_{0i}. \]  

(54)

On the other hand, for the parallel-plate channel, where \( b/c \ll 1 \) (which is usually the case in experimental studies) the expression for \( I_i \) becomes

\[ -I_i = 2e \mathbf{G}_o c \left[ 1 - 0.54 \frac{b}{c} \left( 1 - \frac{\zeta_2}{\zeta_1} \right) \right] \zeta_1. \]  

(55)

From Eq. (55) one can estimate the correction associated with the fact that the side walls of a parallel-plate channel are usually made of a different material than the base walls [substrate surface studies]. For \( b/c = 1/20 \) (which is a typical value for many experimental works [59,60,64]) assuming \( \frac{\zeta_2}{\zeta_1} = 0.5 \), the correction is 0.014. In the extreme case of \( \frac{\zeta_2}{\zeta_1} = 0 \), the correction equals 0.027. These values are significantly smaller than other experimental errors, connected mostly with the electrode asymmetry potential and surface conductivity.

For a cylindrical plate channel (capillary) with the radius \( R_c \), the perimeter of the capillary is \( l = 2\pi R_c \) and we have \( \mathbf{G}_o = \frac{P R_c}{2\pi L} [14] \). Accordingly, Eq. (48) becomes

\[ -I_i = e \frac{P R_c^2}{2\pi L} \zeta_1 = -I_{0i} \]  

(56)

where \( \frac{P}{L} \) is the hydrostatic pressure gradient along the capillary of the length \( L \).

The above equations for \( I_i \) are valid for \( \frac{b}{c} \ll 1 \), in the case of the parallel plate channel and \( \xi \ll 1 \), in the case of the capillary.

Because of the appearance of the streaming current, electric charge is transported away from the double layer region adjacent to the interface, which results in the appearance of an electric potential difference, referred to as the streaming potential \( E_s \). This generates a backward electric current \( I_s = -I_i \) due to the electric conductance of the cell. As discussed in Refs. [93,94] the streaming potential is connected with the streaming current by the Ohmic dependence

\[ E_s = -I_i R_c = I_i R_e \]  

(57)

where \( R_e \) is the overall electric resistance of the cell governed mainly by the specific conductivity of the electrolyte in the cell.

However, for dilute electrolytes and thin channels, the contribution stemming from surface conductance starts to play a significant role [94,95], thus special procedures are to be undertaken to correct for this effect. Thus, in the general case \( R_e \) can be expressed as

\[ R_e = \frac{L}{\Delta \Sigma K_e} = \frac{L}{\Delta \Sigma (K_e + K_s)} \]  

(58)

where \( \Delta \Sigma_s \) is the channel cross-section area, \( K_e \) is the specific conductivity due to electrolyte and \( K_s \) is the surface conductivity, depending in the general case on the channel shape.

Considering Eq. (57) one can derive from Eq. (53) the following formula for the streaming potential in the case of the rectangular channel

\[ E_s = E_{0s} \left[ 1 - \frac{b}{c} f \left( \frac{b}{c} \right) \left( 1 - \frac{\zeta_2}{\zeta_1} \right) \right] \]  

(59)
where  

$$E_0 = 2\varepsilon Pb^2 R_e \zeta_i = \varepsilon P a L \zeta_i$$  \hspace{1cm} (60)$$

is the value of the streaming potential for the parallel-plate channel (for $b/a \ll 1$).

For the cylindrical channel one obtains an identical expression

$$E_0 = \frac{P\pi R_e^2}{\eta L} \zeta_i = \varepsilon P a L \zeta_i.$$  \hspace{1cm} (61)

As can be noticed, when introducing the specific conductivity, the expressions for the streaming potential are the same for arbitrary channel cross-sections if the walls are made of the same material. This is so, however, only if the surface conductivity contribution can be neglected.

It is interesting to observe that Eq. (61) was first derived by Smoluchowski [66].

As can be noticed, the zeta potential of surfaces, which is a quantity of primary experimental interest for characterizing their electrical state, can be calculated by measuring experimentally the slope of the dependence of $E_s$ on $\Theta$ once the electric conductivity of the channel is known.

3.2. Theoretical results for particle covered surfaces

It is to mention, however, that all the above formulae are valid for a homogeneous charge distribution over interfaces and for uniform (position independent) flows. When particles are present at interfaces (see Fig. 7), both these conditions are violated. Particles disturb the electric charge distribution near interfaces and the macroscopic flow $\mathbf{V}$ in their vicinity.

In principle, Eq. (44) could be used to evaluate the streaming current in this case if the charge distribution $\rho_i$, and the liquid velocity $\mathbf{V}$ were known as a function of particle position, coverage and their distribution over interfaces. This would require a solution of the nonlinear Poisson–Boltzmann and Navier–Stokes equations for such many body problems, which poses insurmountable difficulties at present time. Therefore, theoretical results have been derived for some limiting cases only, for example, for the low coverage [59,60] and the thin double layer regimes [67]. It was postulated moreover that the ion distribution in the vicinity of the particles is not perturbed by the local flow, governed by the linear Stokes equations [59,60,67].

With this assumption, exact analytical expressions for the streaming current of particle covered surfaces were derived in Refs. [59,60] in the limit of low coverage

$$I_i(\Theta) = I_{a0} \left[1 - C_i (\frac{a}{Le})^{\frac{2}{3}} + C_p (\frac{a}{Le})^{\frac{5}{3}} \frac{\zeta_i}{\zeta_p} \Theta \right]$$  \hspace{1cm} (62)$$

where $C_i$, $C_p$ are dimensionless functions of the double-layer parameter, $a/Le$, characterizing separately the effects stemming from the macroscopic flow disturbances and the electric charge density disturbances, $\zeta_i$ the zeta potential of the bare interface and $\zeta_p$ is the zeta potential of particles.

It is interesting to mention that Eq. (62) is valid for arbitrary shear flow and the interface shape provided that the range of variation of the shear rate is much larger than the particle dimension.

The dependence of $C_i$, $C_p$ on $a/Le$ was calculated numerically by solving the Poisson–Boltzmann equation and the Navier–Stokes equation for the particle-interface configuration, using the bispherical coordinate system [96,97]. The dependence of these functions on the $a/Le$ parameter calculated in this way is shown graphically in Fig. 8.

For the range of $2 < a/Le < 8$, the $C_i$, $C_p$ functions remain practically constant. For thicker double layers, $C_i$ decreases and attains the value of 8 for $a/Le = 1$, whereas the $C_p$ constant slightly increases, attaining 6.7 for $a/Le = 1$ [96,97].

On the other hand for the limiting case of thin double-layers, where $a/Le \gg 1$, these functions assume the limiting values of $C_i^0 = 10.2$, $C_p^0 = 6.51$ [59,60,67].

Until now, there are no exact results available in the literature for non-spherical elongated particles, which are of considerable interest for interpretation of streaming potential measurements of polyelectrolyte covered surfaces. The only exception are the results obtained in Ref. [68] for strings of rigid spherical particles forming linear aggregates obtained using the multipole expansion method. From these numerical results describing the hydrodynamic force per a single sphere, it can be predicted that for a two particle aggregate, $C_i^0 = 7.99$ for the side on (parallel) orientation and 13.1 for the perpendicular orientation. For an aggregate composed of 10 spheres one has, $C_i^0 = 6.84$ for the side on orientation and 30.8 for the
perpendicular orientation. As can be noticed, the difference between parallel and perpendicular orientations is very significant, which suggests that the streaming current or streaming potential measurements can be used as a sensitive tool for detecting polyelectrolyte or protein orientations at interfaces. In Table 4 values of the $C^0$ constant for various aggregates are collected for the side-on orientation averaged in the adsorption plane, for perpendicular orientation and for averaged end on with $S_i = n_i a^2$ in Eq. (30).

For interpretation of experimental results it is advantageous to rewrite Eq. (62) in a reduced form. For a charged interface

$$T_i = E_i = 1 - C_i \theta + \frac{C_p}{S_i} \Theta$$

(63)

where $T_i = \frac{F}{l_{ch}}$, $E_i = E / \Theta$ and the reduced quantities are $-l_{ch} = \frac{2 \pi G_0 C_p}{S_i}$ and $E_{ch} = \frac{1}{\Theta}$. In the case of neutral interfaces,

$$T_i = E_i = C_p \theta$$

(64)

where $T_i = \frac{F}{l_{ch}}$, $E_i = E / E_{ch}$ and the reduced quantities are $-l_{ch} = \frac{2 \pi G_0 C_p}{S_i}$ and $E_{ch} = \frac{1}{\Theta}$.

We emphasize that the reduced streaming current $T_i$ (or, equivalently, the streaming potential $E_i$) does not depend on parameters describing either the electric resistance or geometry of the cell. Hence $T_i$ or $E_i$ can be used as a universal quantity characterizing the effect of adsorbed particles alone. In particular, it can be applied to determine the particle coverage. It should be noted that the slope of the dependencies of $T_i$ or $E_i$ on the particle coverage, accessible experimentally, is much higher that unity. For example, in the case of neutral particles it is equal to 10.2 (in the limit of thin double-layers) and equal to 16.7 in the case of particles charged oppositely to the interface. Therefore, electrokinetic methods for evaluation of particle coverage that are based on measurements of the streaming current or streaming potential can achieve high sensitivity, even for low coverages of the order of 1%.

In principle, such electrokinetic methods can be used to determine particle coverage also in the high-coverage regime. However, Eq. (63) is valid only in the limit of low coverage (approximately for $\theta < 0.05$), which restricts its wider use in practice. Therefore, correction functions have been proposed in Refs. [59,60], accounting for the fact that for higher coverage the flow and electric charge density perturbations resulting from separate particles are no more additive. Accordingly, Eq. (63) was generalized to the form

$$T_i = E_i = 1 - A_i(\theta) \Theta + A_p(\theta) \frac{C_p}{S_i} \Theta$$

(65)

where

$$A_i(\theta) = \frac{1 - e^{-C_i \theta}}{\Theta}$$

$$A_p(\theta) = \frac{1 - e^{-C_p \theta}}{\Theta}$$

(66)

These results have been successfully used for interpretation of experimental data obtained for monodisperse polymeric particle suspensions [59,60,64,96,97], silica particles [61–63] and polyelectrolytes [98,99].

Recently, exact theoretical results have been derived in the limit of thin double layers [67], which can be used to determine the range of validity of these semi-empirical correction functions. These results were obtained by evaluating numerically the flow in the vicinity of adsorbed particles using the multipole expansion method [100–102], for the coverage range up to 0.5. Moreover, in the case of lower coverage range, analytical results have been derived by applying the cluster expansion method. As shown in the

<table>
<thead>
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<th>Table 4</th>
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<tr>
<td>Values of the $C^0$ constant (upper row) and the $C_p$ constant (lower row) for linear aggregates adsorbed at a solid interface (calculated using the results given in Ref. [68]).</td>
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<tr>
<td>Configuration</td>
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<tr>
<td>Flow</td>
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<tr>
<td>Side on (averaged over $\alpha$)</td>
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<tr>
<td>6.51</td>
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<tr>
<td>Perpendicular to interface</td>
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<tr>
<td>6.51</td>
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<tr>
<td>End on (averaged over $\alpha$ and $\beta$)</td>
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<td>6.51</td>
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Appendix A, the functions $A_i(\theta)$, $A_p(\theta)$ appearing in Eq. (65) can be expressed, in the form of the power series expansion

$$
A_i(\theta) = 10.2 - 59.43\theta + 2920\theta^2 + 0(\theta^3)
$$

$$
A_p(\theta) = 6.51 - 36.82\theta + 1810\theta^2 + 0(\theta^3)
$$

(67)

Eq. (67) was derived by assuming an equilibrium distribution of particles in the adsorption layer. In the case of the RSA configuration, the expansion has the form (cf. the Appendix A)

$$
A_i(\theta) = 10.2 - 59.43\theta + 2960\theta^2 + 0(\theta^3)
$$

$$
A_p(\theta) = 6.51 - 36.82\theta + 1840\theta^2 + 0(\theta^3)
$$

(68)

Accordingly the power series expansion for the reduced streaming current/potential assumes in the case of an equilibrium configuration of particles the following form

$$
\bar{I}_i = \bar{E}_i = \theta + (59.43 - 36.82\zeta)\theta^2 + (292 - 181\zeta)\theta^3 + 0(\theta^4)
$$

(69)

In the case of the RSA configuration, the power expansion becomes

$$
\bar{I}_i = \bar{E}_i = 1 - \frac{10.2 - 6.5\zeta\theta + (59.43 - 36.82\zeta)\theta^2}{(292 - 181\zeta)\theta^3 + 0(\theta^4)}
$$

(70)

where $\zeta = \frac{\zeta_i}{\zeta_p}$.

It is to mention however, that the expansions, Eqs. (67)–(70) are valid for low coverage only, approximately for $\theta < 0.07$.

Therefore, in Ref. [67] exact numerical calculations were performed for particle configurations at planar surfaces characterized by desired coverage (reaching 0.5 as mentioned above) with periodic boundary conditions. The multipole algorithm [100–102] has been used. Results averaged over 300–400 configurations enabled one to formulate the following analytical functions, which approximated the exact numerical results with precision better than 1%.

$$
A_i(\theta) = \frac{10.2 - 5.75\theta}{1 + 5.46\theta}
$$

$$
A_p(\theta) = \frac{6.51 - 2.38\theta}{1 + 5.46\theta}
$$

(71)

In Fig. 9 theoretical predictions derived from Eq. (71) are compared with the semi-empirical fitting functions given by Eq. (66) and the power expansion, given by Eq. (69). As can be seen, the semi-empirical function $A_i(\theta)$ agrees very well with the exact data derived from Eq. (71) for the entire range of coverage studied, whereas the function $A_p(\theta)$ systematically over predicts the exact results.

More extensive comparison of the results, stemming from the exact and the semi-empirical approaches for various particle to interface zeta potential ratio $\zeta_p/\zeta_i$ is shown in Fig. 10. As can be seen, the theoretical results derived from both approaches agree well for $\zeta_p/\zeta_i < 0$, (where the absolute value of particle zeta potential is much smaller than the interface zeta potential). However, the deviation increases for higher values of particle zeta potential, where $\zeta_p/\zeta_i < 0$.

It is interesting to observe that for higher coverage range, i.e., for $\Theta > 0.3$, the exact values of the reduced streaming potential $E_i$ become practically constant. This is in accordance with the so called Smoluchowski principle, discussed extensively in Refs. [103,104]. Using this principle it can be predicted that the streaming potential of homogeneous disperse systems becomes independent of the concentration of particles and their shape in the limit of thin double-layers.

As can be seen in Fig. 10, however, the Smoluchowski principle, is apparently not obeyed for the low coverage range in the case of $\zeta_p/\zeta_i = 1$, corresponding to rough interface produced by deposition of particles of the same zeta potential. Thus, for $\theta < 0.2$, it is predicted that the reduced streaming potential of such composite surfaces decreases monotonically with the coverage (roughness degree) attaining the limiting value of 0.73, irrespectively of the size of the roughness. This means that zeta potential of rough surfaces measured by the streaming potential method is expected to be 27% smaller than the zeta potential for smooth surfaces. In this context, an experimental confirmation of the decrease of the streaming potential with the increase in the surface roughness would be of a major significance, although difficult to realize.

It seems, therefore, that despite a significant progress in theoretical calculations of the streaming potential for particle covered surfaces, there is need for theoretical calculations in the domain of the rough surfaces, thick double-layers, non-spherical particles and multilayer coverage of spherical particles. Also, further theoretical studies are needed in order to unequivocally determine the physical reason for the deviation from the Smoluchowski principle for the low coverage range.
3.3. Experimental results for particle covered surfaces

Most of the results discussed in this section were obtained using the parallel plate channel arrangement devised originally by van Wagenen and Andrade [105] and then used extensively to determine electrokinetic characteristics of bare surfaces (mica and silica slides) [106-108] and protein covered surfaces [43,44]. Similar cells have been exploited widely for measuring streaming potential of particle covered surfaces, most often mica modified by adsorption of simple ions or cationic surfactants [59,60,64,96] or modified glass [61,62]. The essential part of such a cell, described in detail in Refs. [59,60,106,107], is the parallel plate channel produced by clamping together two Teflon blocks and two mica sheets separated by a gasket whose thickness determines the channel height 2b (being usually of the order of 100–400 μm). Since the width of such cells 2c is of the order of 0.3–1 cm, the b/c parameter is typically much smaller than 0.1, therefore the correction due to side walls made of Teflon is of the order of a few percent, as estimated above.

The cell is completed with two compartments containing streaming potential electrodes (Ag/AgCl) connected with an electrometer of high resistance. The other electrode pair (platinum) is used for measuring the electric conductance of the cell. The electrolyte or suspension flow through the channel is driven either by gas (nitrogen) pressure [105-108], pumping [61,62] or by regulating the levels of the two electrolyte reservoirs [59,60,64]. The pressure drop along the channel is measured by pressure transducers or, in the case of hydrostatic pressure driven flow, by a cathetometer.

The advantages of such a cell are large working area increasing measurement precision, possibility of adsorption of desired solutes or particles, a capability for direct in situ microscope observation of surfaces without drying and simple theoretical interpretation of the results. However, a disadvantage of the parallel-plate channel cells is its tedious and time consuming assembling prior to experiment, sealing problems and the necessity of determining in every experiment the correction due to surface conductance of the cell.

These disadvantages were partially eliminated in the micro-slit streaming potential cell described in Refs. [94,109–111]. In this cell the distance between substrate plates forming the parallel plate channel can be regulated between wide limits (1–50 μm), which allows one to determine precisely the surface conductance of the cell. Another advantage of such an arrangement is that substrate plates (10 per 20 mm) are suitable for experimental examination by other techniques such as XPS, AFM, ellipsometry and wetting angle.

In measurements of protein deposition kinetics, circular channel cells were also used [57,58], whose construction is much simpler than the above parallel plate channel cells. However, the range of capillary materials available for such studies is rather limited, there also appear significant problems with cleaning and examination of surfaces by microscopy or other surface oriented techniques.

Problems with sealing and tedious cell assembling can be definitively eliminated using the cell developed in Ref. [112], based on the rotating disk principle. In this case, the liquid flow along the surface is driven by the centrifugal force appearing due to the rotation of a circular disk with an attached substrate surface. This arrangement is especially suitable for measuring kinetics of streaming potential changes although the measurement is less precise because of small values of the streaming potential (usually below 1 mV) and a strong dependence of the signal on the positioning of electrodes relative to the disk center.

3.3.1. Characteristics of bare surfaces

Because of its high precision, the streaming potential method has been widely used to characterize various substrate surfaces, mostly mica.

For example, Scales et al. [106] determined the dependence of zeta potential of muscovite mica as a function of pH, showing that it varied between −30 mV and −80 mV for pH = 4 and pH > 6, respectively (at constant ionic strength of 0.001 M KCl). The dependence of mica zeta potential on concentration of various monovalent salts (LiCl, NaCl, KCl, CsCl) was also determined for fixed pH = 5.8. For low salt concentration the limiting value of the zeta potential of mica was −120 mV, which increased with salt addition up to −80 mV for 0.01 M LiCl and NaCl solutions and −40 mV for 0.01 M KCl. The difference in zeta potential observed for various salts was attributed to the specific adsorption of cations (countercations). The highest zeta potential of mica equal to −20 mV was determined for 0.001 M HCl. It is interesting to observe that no zeta potential reversal of mica as a function of pH was observed, which suggests that this substrate shows no isoelectric point.

A similar behavior was observed in the case of fused silica whose zeta potential was also determined using the parallel plate streaming potential cell [104]. For pH = 3 the zeta potential of mica was −20 mV for 0.001 M KCl, and −5 mV for 0.1 M KCl. The latter value is subject to a considerable error because of very low signal due to the high conductivity of the electrolyte solution. For pH > 7 the zeta potential decreased to −100 mV for 0.001 M KCl and −40 mV for 0.1 M KCl.

In Ref. [106] the case of divalent cations such as calcium Ca2+ was also studied. It was shown that the zeta potential of mica increased to about −10 mV for 0.01 M CaCl2 solution (pH = 5.8).

A similar behavior was observed in Ref. [64] in the case of MgCl2 solutions, where the zeta potential of mica was increased from −70 mV for 10−5 M salt solution to −15 mV for 3×10−3 M salt solution.

On the other hand, in the case of LaCl3 an inversion of the zeta potential of mica to positive values was observed for the salt concentration above 3×10−4 M, with the maximum value attaining 35 mV for 0.01 M solution of salt [106].

These results suggest that the zeta potential of mica can be adjusted within broad limits by variation of pH and composition of the supporting electrolyte. This can be exploited in model studies aimed at verification of theoretical approaches describing zeta potential of particle covered surfaces.

3.3.2. Particle covered surfaces

Few basic studies for particle covered surfaces have been carried out because of considerable experimental problems associated with particle monolayer deposition of controlled coverage and structure, which can resist vigorous shearing flows in the channel. Most of the
results reported in the literature have been obtained for mica substrate and monodisperse polymeric particles (polystyrene latex or melamine latex) using the parallel plate channel cell. The main goal of these studies was to determine the validity of the correction functions $A_i(\Theta)$, $A_p(\Theta)$, to reflect the streaming potential variation of surfaces covered with particles. In order to do so, two series of experiments have been carried out [64]:

(i) for amphoteric latex particles, whose zeta potential was reduced to zero by pH variation,

(ii) for neutral surfaces whose zeta potential became zero upon adsorption of a cationic surfactant.

In Fig. 11 results derived from the first series of experiments are presented in the form of the dependence of the reduced streaming potential of mica $E_r = E_i(\Theta)/E_{s0}$ (where the scaling variable was the streaming potential measured for bare substrate $E_{s0}$ under the same physicochemical conditions) on particle coverage $\Theta$. It is interesting to mention that the particle coverage in these experiments was determined directly by optical microscope observations. Experimental values of the particle coverage determined in this way were in a good agreement with theoretical predictions of the convective-diffusion theory discussed above.

The points in Fig. 11 denote experimental results obtained for polymeric latex particles of the size 1130 nm (triangles) and 1530 nm (inverse triangles) whose zeta potential was reduced to zero by pH change to 7 [64]. The solid line represents the exact theoretical results obtained from Eq. (65) with the correction functions given by Eq. (71) and the dashed-dotted line shows the results calculated using the exponential fitting function, Eq. (66). As can be seen, the theoretical results derived from both models, which agree with each other very well, reflect properly the experimental data for the entire range of particle coverage (up to 0.45). Hence, the results shown in Fig. 11, obtained for neutral particles have a major significance, showing clearly that the hydrodynamic effects alone, associated with flow damping in the vicinity of deposited particles, induce a considerable change in the effective zeta potential. In other words, zeta potential of particle covered (heterogeneous) surfaces is determined not only by the value of the particle zeta potential as commonly assumed, but also by the flow damping effects controlled by the coverage of particles and their distribution on surfaces. This is a direct manifestation of the fact that electrokinetic phenomena are of a non-equilibrium nature, depending on hydrodynamic rather than thermodynamic conditions.

It is also interesting to observe that the slope of the dependence of the reduced streaming potential on the particle coverage is very large (initially equal to 10.2 as predicted by the theory) that suggests that the presence of adsorbed particles (even uncharged) can be precisely detected by the streaming potential measurements, especially for the low coverage range $\Theta<0.1$, where other experimental methods fail.

However, additional systematic studies performed for smaller particle sizes, and other values of ionic strength, where the $a/\ell$ parameter assumes larger values comparable with unity, are needed in order to determine precisely the range of applicability of the above theoretical approach.

In Fig. 12 the results derived from the second series of experiments are presented. In this case, the charge of mica substrate was reduced to zero by reversible adsorption of the cationic surfactant DTACl (used at the concentration of $1.2 \times 10^{-4}$ M, pH = 5.5 [64]). Under these conditions, the zeta potential of a polystyrene latex (average diameter 870 nm) was 45 mV. As previously, particle coverage was determined under wet, in situ conditions using optical microscope observations. The solid line in Fig. 12 shows the exact theoretical results obtained from Eq. (65) with the correction functions given by Eq. (71) and the dashed-dotted line shows the results calculated using the exponential fitting function. As can be seen, the theoretical results derived from the exact model deviate from the approximate model, being of about 15% smaller for particle coverage 0.2. Since the experimental data lie between both theoretical curves, it is difficult to unequivocally state which model is more appropriate. It seems, therefore, desirable to perform systematic experiments for a much broader range of surface coverage, particle size and zeta potential.

Experimental data are also available for intermediate cases of charged particles adsorbed at charged interfaces, characterized by various $\zeta_p/\zeta_i$ parameter values. Such results obtained for polystyrene latex particles 470 nm in diameter at mica modified by adsorption of Mg$^{++}$ ions are shown in Fig. 13 [64,97]. As mentioned, the addition of MgCl$_2$ increased monotonically the zeta potential of mica, which attained the value of $-25$ mV (for $10^{-3}$ M MgCl$_2$, pH = 5.5). The zeta potential of latex, remained for the same conditions at the level of 67 mV, which produced a high value (in absolute terms) of the parameter $\zeta_p/\zeta_i = -2.7$. It is worthwhile mentioning that in this case of highly charged particles adsorbing at weakly charged interfaces (full squares and curve 3 in Fig. 13) the sensitivity of the streaming potential measurements remained especially high, for a broad range of coverage $0<\Theta<0.3$ because of the large slope of the $E_r vs. \Theta$ dependence. This suggests that in order to create convenient conditions for detecting particles via the streaming potential measurement, the zeta potential of substrates is to be kept low (in absolute terms) compared to the zeta potential of particles. As can be seen, for $\zeta_p/\zeta_i = -2.7$, the experimental results are in a better agreement with the theoretical results derived using the exact functions $A_i(\Theta)$ and $A_p(\Theta)$ (described by Eq. (71)) than with the results derived using the approximate exponential function, given by Eq. (66).

On the other hand, in the case of no MgCl$_2$ addition, the zeta potential of latex was equal to 54 mV, whereas the zeta potential of mica $-120$ mV which gives $\zeta_p/\zeta_i = -0.44$. As can be seen in Fig. 13, the experimental results obtained in this case are well reflected by both theoretical models (curve 1), which agree well with each other.

It is also interesting to observe that this holds true also for the experimental data obtained by Michelmore and Hayes [63] who determined streaming current for negatively charged silica particles (trade name Monosphere) having the diameter of 1000 nm for $10^{-3}$–$10^{-4}$ M KCl solutions. As the substrate, mica sheets were used, modified by adsorption of di(aminopropyl) trimethoxysilane, which resulted in the inversion of the zeta potential of mica. This attained 63–87 mV (for $10^{-3}$–$10^{-4}$ M KCl). As can be seen in Fig. 13 the results

![Fig. 11. The dependence of the reduced streaming potential of mica $E_r$ on particle coverage $\Theta$. The points denote experimental results obtained for polystyrene latex particles whose zeta potential was reduced to zero by pH change, pH=7, $I=10^{-4}$ M, NaCl, $T=293$ K [64]. The solid line represents the exact theoretical results [67], the dashed-dotted line shows the results calculated using the exponential fitting function, Eq. (66).](image-url)
of Michelmore and Hayes [63] are in good agreement with the data obtained for latex particles, and the theoretical predictions based on Eq. (71).

However, in the case of smaller Monospher silica particles 250 and 500 nm in diameter the results obtained in Ref. [63], deviated from these theoretical predictions, because the dependence of the reduced streaming current on the particle coverage was less steep than the theory predicts. This was probably caused by the presence of aggregates in the suspension, especially for the particle of 250 nm diameter which were very hard to fully disperse. This is a likely explanation considering the theoretical predictions for the $\bar{C}_i$ constant for aggregates, given in Table 4. One can see, that for an aggregation degree larger than 10, the $\bar{C}_i$ constant decreased considerably, attaining values below 6, in comparison with the value of 10.2 corresponding to single particle deposition.

Additionally, the true size of particles was not measured in these experiments, which could produce a higher uncertainty of the results.

Another type of electrokinetic measurements for particle covered surfaces has been performed by Vincent et al. [113] who determined the electrophoretic mobility of negatively charged latex particles (average diameter 3200 nm) covered to a controlled extent under diffusion transport conditions by positively charged latex particles of the average diameter 195 nm. The positive latex coverage was determined indirectly by the solution depletion method. In Fig. 14 results obtained in these experiments (for ionic strength range $10^{-4}$–$10^{-2}$ M NaCl, $\zeta/p = -0.86$) are plotted as the dependence of the reduced electrophoretic mobility (normalized by its value for large latex particles) on the particle coverage reaching 0.4. The surface coverage was recalculated for the absolute coverage $\Theta = \pi a^2/N$, whereas in the original work it was normalized using the maximum hexagonal packing of spheres equal to 0.91. Because the theoretical results described by Eq. (65) apply to arbitrary simple shear flow, which prevails near larger particles undergoing an electrophoretic motion, they can be used for interpretation of the experimental results of Vincent et al. [113]. As can be seen in Fig. 14, these theoretical results are in a reasonable accordance with the experimental data for the entire range of coverage, with the exponential model performing slightly better than the exact theoretical model.

The analysis of these experimental data obtained for model systems of colloid particle covered surfaces, indicates quite unequivocally that the streaming potential method can be used as a precise tool for determining particle coverage even for the range of a few percents, which is not feasible by other methods.

However, a more definite assessment of the applicability of the theoretical models requires additional experiments, involving monodisperse particles of the size below 100 nm and well defined substrate surfaces, other than mica. Similarly, measurements for nonspherical particles would be of a great value. In part, this kind of information can be derived from the streaming potential measurements performed for polyelectrolytes and proteins, discussed next.

### 3.2.3. Polyelectrolyte and protein covered surfaces

The applicability of the above theoretical approach for the interpretation of streaming potential measurements performed for polyelectrolyte covered surfaces has been confirmed in Refs. [98,99]. Two types of commonly used cationic polyelectrolytes have been studied.
(i) the poly(ethylene imine) PEI of the average molecular weight of 75 kDa [99] and (ii) poly(allylamine) PAA having the average molecular weight of 70 kDa [98]. Dynamic light scattering and AFM measurements enabled one to state that PEI molecules resemble fuzzy spheres characterized by the hydrodynamic diameter of 10.6 nm. The average number of uncompensated charges per molecule and its zeta potential dependence on pH and ionic strength was derived from microelectrophoretic measurements. These physicochemical data were exploited for a quantitative analysis of streaming potential measurements for PEI covered mica. Results of such measurements are shown in Fig. 15 as the dependence of the reduced streaming potential of mica, $E_s$, on the coverage of PEI, $C_{PEI}$. It is to mention that the coverage was expressed in absolute terms as the geometrical fraction of the surface occupied by PEI molecules whose cross-section area (foot print) was 88.2 nm [99]. The coverage was calculated using the convective theory discussed in the first section. The pH range of these experiments was 6.1–6.4, ionic strength $I = 10^{-2}$ M, NaCl, $T = 293$ K, $\zeta_i = -60$ mV, $\zeta_p = 40$ mV [99]. As can be seen in Fig. 15, the experimental data are well reflected for the entire range of $C_{PEI}$ (up to 0.4) by the theoretical model described by Eqs. (65) and (66) postulating a 3D particle-like adsorption of PEI. A characteristic feature demonstrated in these experiments is that the streaming potential of PEI covered mica is less dependent on the ionic strength, in accordance with theoretical predictions. Note also a high sensitivity of the measured streaming potential to PEI coverage, since a 100% change in the signal is observed for PEI coverage as low as 0.1. This indicates that bulk concentrations of PEI at the level of a fraction of a ppm can easily be detected by the streaming potential method. As suggested in Ref. [98] this discrepancy can be attributed to an elongated shape of the molecule. Quantitatively, this can be accounted for by exploiting the theoretical results derived in Ref. [68] (see Table 4) for rodlike particles composed of beads, which approximated quite well the real shape of PAH molecules. It can be estimated using these theoretical results that the value of $C_i$ should approach 5.6 in the limit of larger aspect ratio when a random, side-on (flat) adsorption was assumed [68]. Moreover, as shown in Table 4, this value is practically independent of the aspect ratio within the range of 20 to 100. Considering that the $C_i$ constant for elongated molecules, equals 3.4 one can use Eqs. (65) and (66) to calculate theoretical streaming potential data. Accurate values of $C_i$ are given in Table 4. As can be seen in Fig. 16 the agreement of these theoretical predictions with experimental data is satisfactory for the entire range of PAH coverage (up to 0.45).

Interestingly enough, by assuming an unoriented adsorption of PAH with a random angle of its axis relative to the plane of adsorption, the value of $C_i$ becomes 40.6 and $C_p = 24.5$ (for aspect ratio 40 pertaining to very elongated PAH molecule). As can be seen in Fig. 16, theoretical results calculated by assuming this hypothesis (depicted by dashed line) deviate completely from the experimental data, which proves quite unequivocally that PAH adsorbed mostly side on at mica surface.

Hence, the results shown in Figs. 15 and 16 indicate that from the streaming potential measurements, important clues both on the shape and conformations of polyelectrolyte molecules adsorbed at solid/liquid interfaces under in situ conditions can be derived. In particular one can easily distinguish between side on and unoriented (random) adsorption.

It has been further shown in Refs. [114–116] that the streaming potential method can be exploited as a convenient tool for characterizing the formation of polyelectrolyte multilayers on solid substrates, produced in the layer by layer deposition processes. Examples of such results are shown in Figs. 17 and 18.

In Fig. 17 experimental results obtained by the streaming potential method are shown in the case of the PEI/poly(acrylic acid) (PAA) bilayer. The first layer of this system consisted of a saturated (precursor) layer of PEI produced under diffusion transport conditions for deposition time of 20 min, from a 2 ppm solution ($pH = 5.5$, $I = 10^{-3}$ M NaCl). The zeta potential of such a layer was $\zeta_i = 40$ mV [116]. Then, a second layer of PAA of molecular weights 14 kD and 70 kD was deposited under the
same transport conditions, from 2 ppm solutions (the bulk zeta potential value of PAA, determined by microelectrophoresis was $\zeta_p = -19$ mV). The coverage of PAA was estimated using the solution of the diffusion equation.

As can be seen in Fig. 17, the dependence of $E_\varphi$, the bilayer on the PAA coverage $\Theta_{\text{PAA}}$ can be well described in the case of lower molecular weight (14kD) by the Gouy–Chapman model (described by Eq. (72), with the bilayer charge calculated in an analogous way as for PEI covered mica). This suggests that in this case, because the PAA molecule size (hydrodynamic radius of ca. 3 nm) was smaller than the PEI size (having the hydrodynamic radius of 5.3 nm), the adsorbing PAA chains were mostly adsorbing side-on, in a two-dimensional form, with little tendency to loops and tails formation.

On the other hand, in the case of higher molecular weight PAA sample (70 kD), the experimental results were better reflected by the three-dimensional model, described by Eqs. (65) and (66) with $C_i = 8.5$ and $C_p = 6$, corresponding to PAA adsorption parameters. The positive deviation of experimental data from this model, observed for lower coverage range $\Theta_{\text{PAA}}< 0.2$, can probably be attributed to penetration of PAA molecules into the PEI monolayer. For higher coverage, when all voids in the PEI monolayer were saturated the experimental results followed the 3D adsorption trend. This was so, because the hydrodynamic radius of PAA 70 kD molecules was 19.7 nm, which significantly exceeded the hydrodynamic radius of PEI molecules. Therefore, formation of tails and loops was quite likely for higher coverage of PAA.

The results shown in Fig. 17 suggest that the streaming potential measurements can be exploited as a sensitive tool for detecting conformations of adsorbed polyelectrolytes, in particular to discriminate between side-on (flat) or three-dimensional adsorption mechanism.

This technique can also be efficiently used for characterization of polyelectrolyte multilayers, which are often used for producing nanocapsule shells according to the layer-by-layer mechanism, described in refs. [117–121]. Examples of such studies are shown in Fig. 18. The reduced streaming potential (reduced zeta potential of the multilayer) of mica covered by a PAA/PSS (poly(sodium 4-styrenesulfonate) of the molecular weight of 70 kD [114]) is plotted there as a function of the number of layers. The points denote experimental results obtained in the parallel-plate channel for $pH = 7.4$, TRIS buffer, $T = 293$ K, $\zeta_i = -115$ mV (mica) and two values of ionic strength $I = 10^{-3}$ M (part a) and $I = 0.15$ (part b). As can be seen, in both cases periodic oscillations in the apparent zeta potential of the multilayer were observed indicating the formation of consecutive polyelectrolyte layer. The amplitude of these oscillations was considerably higher for the higher ionic strength (0.15 M), which indicates quite unequivocally that the layers formed under these conditions were much thicker, characterized by a three-dimensional structure composed of loops and tails of polymers. Hence, these results, although difficult for a quantitative interpretation within the framework of the theoretical approach discussed above, demonstrated the utility of the streaming potential method to characterize conformation of polyelectrolyte multilayers.

The electrokinetic methods have also been widely exploited for a qualitative determination of kinetics and mechanism of protein adsorption on flat substrates using the parallel plate configuration [43,44] and the capillary arrangement [57,58]. The pioneers in this field were Norde and Rouwendal [43] who determined changes in the streaming potential of a glass substrate (microscope slides forming the parallel plate channel) induced by adsorption of lysozyme. Kinetic runs have been obtained under the forced convection transport conditions for a broad range of lysozyme bulk concentration varied from 0.1 ppm to 10 ppm. It has been shown that the dependence of the streaming potential on adsorption time (lysozyme coverage) was linear for initial stages of adsorption, what was a major finding of this work. Although this is in accordance with the above theoretical predictions, a quantitative analysis of the data obtained in that work is not possible because the coverage of lysozyme at the substrate surface was not determined.

Analogous linear dependencies of the streaming potential of protein covered surfaces on adsorption time have been reported in Ref. [44] for bovine serum albumin (BSA), and immunoglobulin globulins IgG and in Ref. [57] for fibrinogen.

Adsorption kinetics of lysozyme using the streaming potential method was studied in detail by Ethève and Dejardin [58]. As the substrate surfaces, a bundle consisting of 1–3 silica capillaries exhibiting a rather scattered zeta potential $\zeta_i$, varying between $-23$ and $-45$ mV was used. The electrolyte flow was forced by gas pressure. The coverage of adsorbed lysozyme, labeled using iodine isotope, was determined in situ using a radioactive detector. This allowed one to express the relative streaming potential changes of capillaries in terms of the amount of adsorbed protein in $\mu$g cm$^{-2}$. A linear
dependence of the reduced streaming potential on the amount of protein adsorbed was determined in this way, although no attempt to analyze these data quantitatively was undertaken. It is to mention, however, that the maximum coverage of adsorbed protein was generally much smaller than determined in other studies reported in the literature, which suggests incomplete monolayer formation.

The experimental data of Etheve and Dejardin [58] have been interpreted quantitatively in Ref. [97] by assuming that lysozyme geometrical cross-section area was equal to 12 nm$^2$ and the zeta potential of lysozyme $\zeta_p$ varied between 20 and 29 mV. It was found that the theoretical results derived from Eqs. (15) and (16) reflect quite well the experimental data for the range of the protein coverage of up to 0.2.

Osaki et al. [65] performed interesting studies of fibronectin adsorption (a massive glycoprotein with molecular weight of ca. 440kD) on films of poly(octadecene-alt-maleic acid) (POMA) and poly(propene-alt-maleic acid) (PPMA) formed on a glass substrate. The combination of streaming potential measurements carried out in the microslit electrokinetic setup with in situ reflectometric interface spectroscopy and QCM was used in this work. These measurements allowed one to determine the dependence of adsorption mechanism and the extent of conformational changes of the protein on these two substrates, which differed significantly in hydrophobicity. It has been established that for the more hydrophobic POMA surface, fibronectin was adsorbing irreversibly under random orientation with little tendency to changes in conformation. On the other hand, adsorption on more hydrophilic PPMA films was more reversible and the protein underwent long-lasting conformational changes induced by electrostatic interactions. However, a quantitative analysis of the streaming potential changes of the substrate surfaces vs. the protein coverage has not been undertaken. These results indicate that the electrokinetic measurements can serve as an efficient tool not only for determining the amount of protein adsorption but also the protein/interface interactions and the structure of the adsorption layers.

Similar regularities as discussed above for the channel flows have also been reported in cases of protein adsorption on colloid particles, e.g., human serum albumin (HAS) on synthetic hydroxyapatite powder [122], monoclonal IgGs and their fragments on polymeric particles [lattices] [123], anti-HSA on copolymeric microspheres [124] and others [125]. Protein adsorption was studied by microelectrophoresis, which allowed one to determine zeta potential of protein covered particles. A steep, linear decrease in the relative zeta potential of particles was observed as a function of protein concentration or coverage as predicted by theory. A further quantitative analysis of these data is prevented, however, by the lack of sufficient physico-chemical data, characterizing the protein and substrate properties.

As the above examples suggest, the theoretical approach exposed in this work can be effectively used for analyzing electrokinetic measurements of protein covered surfaces. However, a precise verification of its range of applicability requires further experiments in which protein coverage is determined via direct experimental methods, e.g., the AFM method, for substrates of controlled and well defined surface properties.

4. Concluding remarks

The convective-diffusion theory makes it possible to predict initial deposition rates of particles of various shapes, as a function of their diffusion coefficient, interface geometry and flow configuration.

On the other hand, particle deposition kinetics for a higher coverage range, when the surface blocking effects play a dominant role, can be derived from the RSA model enabling one to find the jamming coverage and the structure of particle monolayers.

These theoretical results, confirmed by extensive experimental measurements for colloid particles, can be used for a proper interpretation of the streaming potential measurements performed for particle covered surfaces.

The essential finding derived from the streaming potential theory is the expression for the normalized streaming current/potential of particle covered surfaces having the form

$$\bar{I} = \bar{E} = 1 - A_1(\Theta) \Theta + A_2(\Theta) \frac{\zeta_p}{S_i} \Theta.$$  

This equation is valid for arbitrary shear flows, particle size and shape in the limit of thin double-layers.

For the low coverage regime $\Theta < 0.05$ and spherical particles, the above expression of the streaming current/potential becomes

$$\bar{I} = \bar{E} = 1 - 10.2 \Theta + 6.51 \frac{\zeta_p}{S_i} \Theta.$$  

It has been shown that this expression can be also used as a good approximation for relatively thick double-layers, provided that $a/L_e > 1$.

It has also been demonstrated theoretically that for elongated particles the expression for $\bar{I}$, $\bar{E}$ in the low coverage regime,
assuming side-on orientation becomes

\[ \bar{I}_1 = \overline{E}_1 = 1 - 5.6\theta. \]

On the other hand, for the unoriented regime (particle orientations averaged between side on and perpendicular) the constant appearing in this equation was considerably higher, increasing with the axis ratio of particles (number of beads), attaining the value of 40.6 for axis ratio of 40 (see Table 4).

These theoretical results indicate unequivocally that the measured streaming potential values depend not only on the zeta potential of particles irreversibly attached to it, immersed in an ambient laminar flow near the interface in the presence of particles.

The second term on the rhs of Eq. (A1) can be treated as the excess streaming current due to the presence of particles.

Eq. (A1) can also be formulated in an alternative form, suitable for further manipulations

\[ I_1 = I_s + N_p J_1 = I_s + \Theta I_1 \]  

(A2)

where

\[ I_s = -\varepsilon \int_S \nabla^2 \psi_0 V_0 \, dS. \]  

(A3)

\[ \Theta = \frac{S}{S_0} N_p \text{ is the average coverage of particles over the interface (} S_0 \text{ is the characteristic cross-section area of particles)} \text{ and} \ I_1 \text{, is the reduced volume integral given by the expression:} \]

\[ \overline{I}_1 = \frac{I}{S N_p} \int_I = \frac{I}{S N_p} \int_S (\rho_c U - \rho_{c_p} U_0) \, dv \]  

(A4)

where \( U = V \cdot \mathbf{i}_x \), \( dv \) is the volume element and \( I_1 \) can be treated as an average contribution to the streaming current due to one of the \( N_p \) particles adsorbed on the interface.

Assuming that the charge density vanishes at larger distances from the interface, which is usually the case due to electrostatic screening, the domain in the volume integral, Eq. (A4) can be expressed as

\[ 0 < z < \infty \]

\[ 0 < x < L \]

\[ 0 < y < l \]

(A5)

Eq. (A2), although generally valid for particles of any shape and for arbitrary flows, is rather impractical for a direct evaluation, since it is dependent on many parameters such as the particle coverage, and distribution over interfaces, particle shape, double layer thickness, zeta potential of the particles and the interface, etc. Moreover, its explicit evaluation requires the knowledge of the fluid velocity and the electric charge density fields. The latter cannot be calculated in an exact way for the system of many particles and the interface, because of the nonlinearity of the Poisson–Boltzmann equation.

Therefore, in order to derive from Eq. (A2) meaningful results of practical interest, a series of simplifying assumptions have to be made. The first, most important is that the charge density (electrostatic field) is not too much perturbed by the velocity field, and vice versa, so they can be evaluated independently from each other. Under this assumption, the fluid velocity field in the case of low Reynolds number flows (linear Stokes flows) can be evaluated using numerical techniques for arbitrary particle distribution and coverage. However, this is not feasible at present with respect to the electric potential field, whose distribution is governed by the nonlinear Poisson–Boltzmann (PB) equation. The latter can be calculated for spherical particles in the two limiting cases (i) low coverage regime, where \( \Theta^{3/2} \ll 1 \), and (ii) thin double layer regime, where \( a / \ell \gg 1 \). In the former case, one can solve the PB equation numerically in a bipolar coordinate system, whereas in the latter case only the potential in the shear plane (particle surface) is required.

Hence, in the case (i) assuming further the additivity of the electric fields stemming from the particle and the interface, one can express the streaming current in the simple form:

\[ I_s = I_s + \Theta (C_{c_i} + C_{c_p}) \]  

(A6)
where the two constants $C_s$, $C_p$ characterizing the contribution stemming from the interface and particles, respectively, are given by the expressions

$$C_i = \frac{1}{\varepsilon_0} \sum_{p \neq N_p} \int \rho_i U \, dV$$

$$C_p = -\frac{1}{\varepsilon_0} \sum_{p \neq N_p} \int \rho_p U \, dv$$

(A7)

where $\rho_i$, $\rho_p$ are the electric charge density fields in the case of uncharged particles ($\zeta = 0$) and uncharged interface ($\zeta = 0$), respectively.

However, the electrostatic field needed for an explicit evaluation of Eq. (A7) can only be derived numerically, as done in Ref. [96].

In the case (ii), i.e., for thin double-layers, the change of electric field occurs within thin layers adjacent to the interface and particle surface, where the fluid flow becomes linear with respect to the distance from these surfaces, because of the no-slip boundary conditions.

Accordingly, fluid flow distributions in this region can be well approximated by the equation [67]

$$U_i = z_i \cdot \nabla (V - V_0) \cdot \mathbf{i}_s$$

(at the interface)

$$U_p = (r - a) \cdot \mathbf{i}_p \cdot \mathbf{V} \cdot \mathbf{i}_s$$

(at each particle surface)

(A8)

where $U_i$ is the fluid velocity component along the $x$ direction in the vicinity of the interface, $U_p$ is the $x$-component of fluid velocity near particle surfaces $\mathbf{i}_p$ is the unit vector in the $x$ axis direction, $\mathbf{i}_p$ is the vector perpendicular to the particle surfaces, pointing into the fluid and $\mathbf{r}$ is the position vector measured relative to the particle center.

Moreover, because of the thin layer assumption, the volume integral in Eq. (A4) can be reduced to the sum of surface integrals calculated over the interface and all particle surfaces. By considering this, and using Eq. (A8), one can formulate Eq. (A4) in the form

$$I_i = I_{i0} - \frac{\varepsilon_0}{\varepsilon_s} \sum_{p = 1}^{N_p} \int_{S_p} \mathbf{i}_s \cdot \nabla (V - V_0) \cdot \mathbf{i}_p \, dS_p - \frac{\varepsilon_0}{\varepsilon_s} \sum_{p = 1}^{N_p} \int_{S_p} \mathbf{i}_s \cdot \nabla \mathbf{V} \cdot \mathbf{i}_s \, dS_p.$$

(A9)

Thus, the expression for the streaming current for particle covered surfaces becomes

$$I_i = I_{i0} + \varepsilon_0 \zeta_0 \sum_{p = 1}^{N_p} \frac{A_i(\zeta) - \varepsilon_0 \zeta_0 A_p(\zeta)}{G_0}$$

(A10)

where the constants $A_i(\zeta)$, $A_p(\zeta)$ are given by the expressions

$$A_i(\zeta) = -\frac{1}{\varepsilon_0} \sum_{p = 1}^{N_p} \int \mathbf{i}_s \cdot \nabla (V - V_0) \cdot \mathbf{i}_p \, dS_p$$

$$A_p(\zeta) = -\frac{1}{\varepsilon_0} \sum_{p = 1}^{N_p} \sum_{k = 1}^{N_k} \int \mathbf{i}_s \cdot \nabla \mathbf{V} \cdot \mathbf{i}_s \, dS_p.$$

(A11)

It is interesting to mention that Eqs. (A10) and (A11) are valid for arbitrary coverage of particles, their shape (at least if it can be approximated by a configuration of touching spheres) and particle distribution over interfaces provided that the flow field near particles is known.

In the low coverage limit of spherical particles, the flow field can be evaluated analytically in the form of series solution of spherical harmonics [96] or in the form of Bessel functions [126]. However, for higher coverage range, the flow can only be evaluated numerically [69].

In the case of $\zeta \neq 0$, Eq. (A10) can be simplified to the reduced form by considering that for a simple shear ambient flow $\mathbf{V}_0 = G_0 \zeta_0 \mathbf{i}_s$, $I_{i0} = -\varepsilon_0 G_0 \zeta_0$, thus

$$\frac{I_i}{I_{i0}} = 1 - A_i(\zeta) + A_p(\zeta) \frac{\zeta_p}{\zeta_0}$$

(A12)

On the other hand, in the case of $\zeta_0 = 0$, Eq. (A10) becomes

$$\frac{I_i}{I_{i0}} = A_p(\zeta)$$

(A13)

where $\frac{I_i}{I_{i0}} = (-\varepsilon_0 G_0 \zeta_p)$. Limiting solution of practical interest can be derived from Eqs. (A10) in the case of disk-shaped (two dimensional particles) adsorbing side-on at the interface. Since, obviously in this case, the macroscopic flow is not perturbed by particles, i.e., $\mathbf{V} = \mathbf{V}_0$, thus $A_i(\zeta) = 0$ and $A_p(\zeta) = 1$, because the surface integral over all adsorbed particles equals simply their surface area $S_p$. Therefore, in this case

$$\frac{I_i}{I_{i0}} = 1 + \frac{\zeta_p}{\zeta_0} \mathbf{\Theta}.$$

(A14)

In Ref. [67] it was demonstrated that for spherical particles the functions $A_i(\zeta)$ and $A_p(\zeta)$ can be related to the hydrodynamic force exerted by the flow on the particles and a force multipole. This can be expressed as

$$A_i(\zeta) = -\frac{1}{\varepsilon_0} \sum_{k = 1}^{N_k} \left[ F_k - H_k \right] \cdot \mathbf{i}_k$$

$$A_p(\zeta) = -\frac{1}{\varepsilon_0} \sum_{k = 1}^{N_k} \frac{2}{3} \mathbf{Q}_k \cdot \mathbf{i}_k$$

(A15)

where

$$F_k = \left[ \sum_{k = 1}^{N_k} \frac{1}{2} \mathbf{Q}_k \cdot \mathbf{i}_k \right] \cdot \mathbf{i}_k$$

$$H_k = \frac{1}{3} \mathbf{Q}_k \cdot \mathbf{i}_k$$

$$\mathbf{Q}_k = \int \left[ \mathbf{i}_k \cdot \Pi \right] \mathbf{d}S_k$$

(A16)

where $\mathbf{R}_k$ denotes the position of the $k$-th sphere over the interface, $S_k$ is the surface of $k$-th sphere and $\Pi$ is the hydrodynamic stress tensor at the particle surface $S_k$, respectively.

A2. Derivation of the streaming current expressions for the low coverage regime and thin double-layers using the cluster expansion method

Hereafter we derive the limiting expressions for $A_i(\zeta)$ and $A_p(\zeta)$ for thin double layers assuming that the electrostatic field around
each particle is the same as for an isolated particle and the electrostatic field near the interface remains unperturbed.

The solution is sought in the form of a polynomial series expansion written as
\[ A_i(\Theta) = \sum_{n=1}^{\infty} C_i \Theta^n \]
\[ A_p(\Theta) = \sum_{n=1}^{\infty} C_p \Theta^n \]

where \( C_i, C_p \) are coefficients of the expansion to be determined.

The starting point of this derivation is the general expression for the 2D cluster expansion for the system of \( N_p \) particles distributed over an interface, \( S \), which can be expressed using concepts of statistical mechanics in the form [16,127]

\[ \Theta T(\Theta) = -\sum_{n=1}^{\infty} (-1)^n \frac{\Theta^n}{n!} \int \cdots \int s_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) T(\mathbf{r}) \]

where \( g \) are the \( n \)-particle correlation functions, \( \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n \) are the relative position vectors of particles forming the cluster and \( L \) is related to components of the cluster expansion evaluated for clusters, composed of \( n \)-particles.

For a 2D equilibrium distribution of hard (noninteracting) spheres the two particle (pair) correlation function \( g_2 \) can be approximated by [16]
\[ g_2(r_{12}) = 1 + \frac{S_{12}(r_{12})}{S_p} \frac{2}{4a} \quad \text{for} \quad 2a < r_{12} < 4a \]  
\[ (A19) \]

where \( S_{12}(r_{12}) = S_{12}(r_{12}) / S_p \) and
\[ S_{12}(r_{12}) = 8a^2 \cos^{-1} \left( \frac{r_{12}}{4a} - r_{12} \left( 4a^2 - \frac{r_{12}^2}{4} \right) \right)^{1/2} \]  
\[ (A20) \]
is the overlapping area of the two exclusion circles around each particle forming the pair (having the radius of 2\( a \)) and \( r_{12} \) is the distance between the particle centers.

In the case of the RSA distribution of particles the pair correlation function becomes [16]
\[ g_2 = 1 + \frac{2}{3} S_{12}(r_{12}) \Theta. \]  
\[ (A21) \]

Obviously, for \( r_{12} < 2a \), the \( g_2 \) function vanishes since particles do not penetrate into each other.

Considering the expression for \( g_2 \), Eq. (A18) can be formulated up to the third order in particle coverage, in the following form
\[ \Theta l_i = \Theta C_i C_p \left[ L_i \Theta - \frac{1}{2} L_{ii} \Theta^2 + \frac{1}{6} \left( \frac{1}{5} L_{ii} - \frac{1}{3} L_{ii} \right) \Theta^3 \right] \]
\[ + \Theta C_i C_p \left[ L_p \Theta - \frac{1}{2} L_{pp} \Theta^2 + \frac{1}{6} \left( \frac{1}{5} L_{pp} - \frac{1}{3} L_{pp} \right) \Theta^3 \right] \]
\[ + 0(\Theta^4). \]  
\[ (A22) \]

The cluster integrals appearing in Eq. (A22) are explicitly given by
\[ l_i = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{V}_0 \right) \mathbf{a}_i dS_i = 6F_{\psi_i} \]  
\[ (A23) \]
\[ l_p = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{a}_i dS_p \right) \]
\[ (A24) \]
\[ l_{12} = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{V}_0 \right) \mathbf{a}_i dS_{12} - 2l_i \]
\[ (A25) \]
\[ l_{p12} = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{a}_i dS_{p12} - 2l_p \right) \]
\[ (A26) \]
\[ l_{123} = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{V}_0 \right) \mathbf{a}_i dS_{123} - 3l_i \]
\[ (A27) \]
\[ l_{p123} = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{a}_i dS_{p123} - 3l_p \right) \]
\[ (A28) \]
\[ l_{123} = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{V}_0 \right) \mathbf{a}_i dS_{123} - 2l_i \]
\[ (A29) \]
\[ l_{p123} = -\frac{1}{\pi a^3 \Theta} \Theta \left( \mathbf{V}_i \cdot \mathbf{a}_i dS_{p123} - 2l_p \right) \]
\[ (A30) \]

where \( \mathbf{V}_i(r) \) is the flow field near a singlet (\( r \) is the distance from the particle center), \( F_{\psi_i} \) is the dimensionless force acting on one particle (singlet) normalized by \( 6\pi a^3 \Theta \), \( \mathbf{V}_{12}(r, r_{12}, \psi_i) \) is the flow near the doublet (\( r \) is the distance from one particle center, \( \psi_i \) is the angle of the vector connecting particle centers measured relative to the ambient flow direction, the \( x \)-axis), \( \mathbf{V}_{123}(r, r_{12}, r_{13}, \psi_i, \psi_2) \) is the flow near the triplet (\( r \) is the distance from one particle center, \( r_{12}, r_{13} \) are the distance between particle centers and \( \psi_i, \psi_2 \) are the angles of the vectors connecting particle centers measured relative to the ambient flow direction, the \( x \)-axis), \( < \cdot > \) means averaging over the corresponding variables (distances and orientation angles).

As can be noticed, these integrals can be evaluated explicitly if flow fields are known for clusters composed of one, two and three particles, as a function of their orientations (against the ambient flow direction) and mutual distances among particle forming a cluster. It is also worth while noticing, that in fact, all these integrals, as shown in Ref. [67] are connected to the force or its higher multipoles associated with the specific particle clusters. These quantities, and so the integrals in Eq. (A22) were evaluated numerically in Ref. [67] using the efficient multipole method.

It was demonstrated in this way that for the hard sphere equilibrium distribution the expansion coefficient in the series, Eq. (A17) has the following numerical values
\[ C_{1i} = C_{1p} = 10.2 \]
\[ C_{2i} = C_{2p} = 6.51 \]
\[ C_{3i} = -59.4 \]
\[ C_{3p} = -36.8 \]
\[ C_{4i} = 292 \]
\[ C_{4p} = 181 \]  
\[ (A42) \]

It is interesting to mention that the coefficients \( C_{1i}^0 \) and \( C_{1p}^0 \) have been calculated previously in Ref. [59].
In the case of the RSA distribution the only modification of Eq. (A24) is
\[
\bar{\Gamma}_i = \bar{\epsilon}_i = 1 - A_i(\theta) + A_i(\theta)\bar{\zeta} = 1 - (10.2 - 6.51)\bar{\zeta} - (59.43 - 36.82)\bar{\zeta}^2 + (292 - 181)\bar{\zeta}^3 + 0(\theta^4)
\]
where \(\bar{\zeta} = \frac{\Xi}{S_i}\).

In the case of a RSA configuration, the power expansion becomes
\[
\bar{\Gamma}_i = \bar{\epsilon}_i = 1 - (10.2 - 6.51)\bar{\zeta} - (59.43 - 36.82)\bar{\zeta}^2 - (296 - 184)\bar{\zeta}^3 + 0(\theta^4).
\]

In the case of a neutral interface, where, \(\zeta_i = 0\) these expressions become
\[
I_1(\theta) = 6.510 - 36.82\theta^2 + 181\theta^5 + 0(\theta^6); \text{equilibrium configuration}
\]
\[
I_1(\theta) = 6.510 - 36.82\theta^2 + 184\theta^4 + 0(\theta^6); \text{RSA configuration}. \quad (A29)
\]

References