Surface and zeta potentials of charged permeable nanocoatings

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An electrokinetic (zeta) potential of charged permeable porous films on solid supports generally exceeds their surface potential, which often builds up to a quite high value itself. Recent work provided a quantitative understanding of zeta potentials of thick, compared to the extension of an inner electrostatic diffuse layer, porous films. Here, we consider porous coatings of a thickness comparable or smaller than that of the inner diffuse layer. Our theory, which is valid even when electrostatic potentials become quite high and accounts for a finite hydrodynamic permeability of the porous materials, provides a framework for interpreting the difference between values of surface and zeta potentials in various situations. Analytic approximations for the zeta potential in the experimentally relevant limits provide a simple explanation of transitions between different regimes of electro-osmotic flows, and also suggest strategies for its tuning in microfluidic applications.

Keywords: Electroosmosis; porous coatings; zeta-potential; surface potential

I. INTRODUCTION

A century ago von Smoluchowski [1] proposed an equation to describe a plug electro-osmotic flow in a bulk electrolyte that emerges when an electric field \( E \) is applied at tangent to a charged solid surface. He related the velocity in the bulk \( V_\infty \) to the electrokinetic (zeta) potential of the surface \( Z \). For canonical solid surfaces with no-slip hydrodynamic boundary condition, simple arguments lead to \( Z = \Psi_s \), where \( \Psi_s \) is the surface (electrostatic) potential. However, the problem is not that simple and has been revisited in last decades. For example, even ideal solids, which are smooth, impermeable, and chemically homogeneous, can modify the hydrodynamic boundary conditions when poorly wetted [2], and the emerging hydrophobic slippage can augment \( Z \) compared to the surface potential [3-6]. Furthermore, most solids are not ideal but rough and heterogeneous. This can further change, and quite dramatically, the boundary conditions [7] leading to a very rich electro-osmotic behavior and, in some situations (e.g. superhydrophobic surfaces), providing a huge flow enhancement compared to predicted by the Smoluchowski model [8-10].

The defects or pores of the wettable solids also modify the hydrodynamic boundary condition [11]. Besides, the local electro-neutrality is broken not only in the outer diffuse layer as it occurs for impenetrable surfaces [12-13], but also in the inner one [14]. Moreover, even when the porous coating includes a globally electro-neutral region, only mobile absorbed ions can react to an applied electric field [15]. Consequently, the electric volume force that drives the electro-osmotic flow in the electro-neutral bulk electrolyte is now generated inside the porous material too. This suggests that one can significantly impact the electro-kinetic response of the whole macroscopic system, i.e. of the bulk electrolyte, just by using various permeable nanometric coatings at the solid support, such as polyelectrolyte networks, multilayers, and brushes [16-19], or ultrathin porous membrane films [20-22].

The emerging flow is strongly coupled to the electrostatic potential profile that sets up self-consistently, so the latter becomes a very important consideration in electroosmosis involving porous surfaces. Electrostatic potentials, \( \Psi_s \) and \( \Psi_0 \) at the solid support, have been studied theoretically over several decades. In most of these studies weakly charged surfaces or thick compared to the Debye length porous films have been considered [14,23-25]. Very recently Silkina et al. [25] reported a closed-form analytic solution for \( \Psi_0 \), obtained without a small potential assumption, which is valid for porous films of any thickness. These authors also proposed a general relationship between \( \Psi_s \) and \( \Psi_0 \), but made no attempts to derive simple asymptotic approximations for surface potentials that could be handled easily.

The connection between the electro-osmotic velocity and electrostatic potentials have been reported by several groups [23,25,27,29], and these models are frequently invoked in the interpretation of the electrokinetic data [30]. However, despite its fundamental and practical significance, the zeta-potential of porous surfaces has received so far little attention, and its relation to \( \Psi_s \) has remained obscure until recently. Some authors concluded that the zeta-potential ‘loses its significance’ [24], ‘irrelevant as a concept’ [31] or ‘is undefined and thus nonapplicable’ [27], while others reported that \( Z \) typically exceeds \( \Psi_s \) [32,33], but did not attempt to relate their results to the inner flow and emerging liquid velocity at the porous surface. This was taken up only recently in the paper by Vinogradova et al. [15], who carried out calculations of the zeta potential for thick coatings of an arbitrary volume charge density. These authors predicted that \( Z \) is generally augmented com-
pared to the surface electrostatic potential, and related this enhancement to a finite hydrodynamic permeability of the porous film. However, this work cannot be trivially extended to the case of non-thick films, where inner electrostatic potential profiles are always, and often essentially, inhomogeneous. These profiles can be calculated assuming that electrostatic potentials are low [14], but such an assumption becomes unrealistic in many situations. Recently, Silkina et al. [26] derived rigorous upper and lower bounds on $Z$ of non-thick films, by lifting an assumption of low electrostatic potential. However, we are unaware of any prior work that investigated the connection of the zeta potential of non-thick films with their finite hydrodynamic permeability.

In this paper, we provide analytical solutions to electro-osmotic flows in and outside uniformly charged non-thick porous coatings, with the focus on their zeta potential and its relation to the surface potential. Ionic solutions are described using the non-linear mean-field Poisson-Boltzmann theory. For simplicity, here we treat only the symmetric monovalent electrolyte, but it is rather straightforward to extend our results to multivalent ionic systems. As any approximation, the Poisson-Boltzmann formalism has its limits of validity, but it always describes very accurately the ionic distributions in ionic systems. As any approximation, the Poisson-Boltzmann theory is build up self-consistently and defined, besides $H$, by two lengths, $\lambda_D \propto c_\infty^{1/2}$ and $\ell \propto \kappa^{1/2}$. The application of a tangential electric field, $E$, leads to an electro-osmotic flow of solvent that depends on the Brinkman screening length $\Lambda$.

In Sec. II we give basic principles, brief summary of known relationships, and formulate the problem. Solutions to electro-osmotic velocities and zeta-potentials are derived in Sec. III. We illustrate the theory and validate it numerically in Sec. IV. Implications for the use of non-thick porous films to enhance EO flows at different salt concentration are discussed in Sec. V followed by concluding remarks in Sec. VI.

II. MODEL, GOVERNING EQUATIONS, AND SUMMARY OF KNOWN RELATIONSHIPS

The system geometry is shown in Fig. 1. The properties of the sketched heterogeneous supported film are, of course, related to its internal structure and can be evaluated in specific situations, but here we do not try to solve the problem at the scale of the individual pores. Instead, motivated by the theory of heterogeneous media [26,37], we replace such a real coating by an imaginary homogeneous one, which ‘macroscopically’ behaves in the same way and possess effective properties, such as a volume charge density or a hydrodynamic permeability. Thus, we consider a homogeneous permeable film of a thickness $H$, which sets a length scale for our problem, of a volume charge density $\kappa$, taken positive without loss of generality. The film is in contact with a semi-infinite 1:1 electrolyte of bulk ionic concentration $c_\infty$, permittivity $\varepsilon$, and dynamic viscosity $\eta$. Ions obey Boltzmann distribution, $c_\pm(z) = c_\infty \exp(\mp \psi(z))$, where $\psi(z) = e\Psi(z)/(k_B T)$ is the dimensionless electrostatic potential, $e$ is the elementary charge, $k_B$ is the Boltzmann constant, $T$ is a temperature, and the upper (lower) sign corresponds to the cations (anions). The inverse Debye screening length of an electrolyte solution, $\kappa \equiv \lambda_D^{-1}$, is defined as usually, $\kappa^2 = 8\pi \epsilon k_B c_\infty$, with the Bjerrum length $\ell_B = e^2/\epsilon k_B T$. The Debye length defines a new (electrostatic) length scale and is the measure of the thickness of the outer diffuse layer, where the local electro-neutrality is broken. We emphasize that it is independent on the film charge.

The system subjects to a weak tangential electric field $E$, so that in steady state $\psi(z)$ is independent of the fluid flow. For our geometry the concentration gradients at every location are perpendicular to the direction of the flow, it is therefore legitimate to neglect advection. Consequently, the dimensionless velocity of an electro-osmotic flow, $\nu(z) = \frac{4\pi \ell_B \eta}{eE} V(z)$, satisfies the generalized Stokes equation

$$v'' - \kappa^2 v' \Theta(H - z) = \psi'' + \kappa^2 \rho \Theta(H - z),$$

where $'$ denotes $d/dz$, with the index $[i,j]$ standing for “in” ($z \leq H$) and “out” ($z \geq H$), $\Theta(z)$ is the Heaviside step function, $\kappa = \Lambda^{-1}$ is the inverse Brinkman length, and $\rho = \frac{\theta}{2e c_\infty}$. For small volume charge and/or high electrolyte concentration $\rho$ is small and below we refer such coatings to as weakly charged. For large volume
charge and/or dilute electrolyte solutions $\rho$ is large and we term these films strongly charged.

At the wall we apply a classical no-slip condition, $v_0 = v_i(0) = 0$, and at the surface the condition of continuity of velocity, $v_s(H) = v_i(H)$, and shear rate, $v'_s(H) = v'_i(H)$, is imposed. Far from the surface, the solution of Eq. (1) should satisfy $v'_i \to 0$ at $z \to \infty$ to provide a plug flow. The velocity at $z \to \infty$ is constant and is equal to $-\zeta$.

The dimensionless zeta-potential, $\zeta = eZ/(k_BT)$ is given by [15, 26]

$$\zeta = \psi_s - v_s,$$  \hspace{1cm} (2)

where $\psi_i = e\Psi_i/(k_BT)$ and $v_s = \Psi(H)$. Note that $-v_s$ represents the velocity jump inside the porous film. Since the film is much thinner than any of the macroscopic dimensions, the outer liquid appears to slip at the velocity $-\zeta$, along the porous surface. We, therefore, refer $-\zeta$ as the (positive definite) slip velocity.

Silkina et al. [26] carried out calculations in the limit of zero and infinite $\mathcal{K}H$ and concluded that for films of an arbitrary thickness at $\mathcal{K}H \to 0$

$$-v_s \approx \Delta \psi + \frac{\rho(\mathcal{K}H)^2}{2}, \quad \zeta = \psi_0 + \frac{\rho(\mathcal{K}H)^2}{2},$$  \hspace{1cm} (3)

and

$$-v_s \approx 0, \quad \zeta \approx \psi_s$$  \hspace{1cm} (4)

when $\mathcal{K}H \to \infty$. Here $\psi_0 = \psi(0)$ is the wall potential, $\psi_s = \psi(H)$ is the surface potential, and $\Delta \psi = \psi_0 - \psi_s$ is the drop of the electrostatic potential in the coating.

Eqs. (3) and (4) represent rigorous upper and lower bounds that constrain the attainable values of slip velocity and zeta-potential. In many regimes, however, these bounds are not close enough to obviate the need for calculations flows over porous surfaces of a finite $\mathcal{K}H$.

It follows from Eq. (1) that to calculate electro-osmotic velocity we have to find the distribution of electrostatic potentials that satisfy the nonlinear Poisson-Boltzmann equation

$$\psi_{ii}'' = \kappa^2 (\sinh \psi_i - \rho \Theta (H - z)), \hspace{1cm} (5)$$

and to obtain simple expressions for $\psi_0, \psi_s$, and $\Delta \psi$. We assume that the wall is uncharged, $\psi_i(0) = 0$, and set $\psi_i(H) = \psi_p(H)$ and $\psi_i'(H) = \psi_i'(H)$ at the surface of the coating.

The solution of Eq. (5) satisfying $\psi_i \to 0$ at $z \to \infty$ is the same as for an impenetrable wall of the same $\psi_s$ [34]

$$\psi_i(z) = 4 \arctanh [\gamma e^{-\kappa(z-H)}],$$  \hspace{1cm} (6)

where $\gamma = \tanh \frac{\psi_s}{4}$.

Ions of an outer electrolyte can permeate inside the porous film, giving rise to their homogeneous equilibrium distribution in the system, with the enrichment of anions in the film. When $\mathcal{K}H(1 + \rho^2)^{1/4} \gg 1$ the film becomes thick compared to the inner diffuse layer, with an extended ‘bulk’ electro-neutral region (where intrinsic-" coating charge is completely screened by absorbed electrolyte ions, is formed). The potential in this region is usually referred to as the Donnan potential, $\psi_D$. Note that Eq. (5) immediately suggests that $\psi_D = \arcsinh(\rho)$ since in the electro-neutral area $\psi''_i$ vanishes. A systematic treatment of the influence of the Brinkman length on the zeta-potential of thick films was contained in a paper published by Vinogradova et al. [15]. Here we will focus on the case of films of

$$\mathcal{K}H(1 + \rho^2)^{1/4} \gg 1$$  \hspace{1cm} (7)

that can be termed non-thick. For weakly charged films of $\rho \ll 1$ this implies that $\mathcal{K}H = O(1)$ or smaller. The more interesting strongly charged coatings of $\rho \gg 1$ can be considered as non-thick when $\mathcal{K}H \sqrt{\rho} \gg 1$ and are thin when $\mathcal{K}H \sqrt{\rho} \ll 1$.

Non-thick films do not contain an electro-neutral portion, where the intrinsic volume charge is fully screened by absorbed ions. Consequently, their $\psi_0$ given by [26]

$$\psi_0 = \ln \left[ \frac{2 + (\rho \kappa H)^2 + \rho H \sqrt{4 + (\kappa H)^2(1 + \rho^2)}}{2 + \rho(\kappa H)^2} \right],$$  \hspace{1cm} (8)

is smaller than the Donnan potential.

The surface potential, $\psi_s$, and the potential drop in the film, $\Delta \psi = \psi_0 - \psi_s$, are related to $\psi_0$ as [6, 26]

$$\psi_s \equiv \psi_0 - \frac{\cosh \psi_0 - 1}{\rho}, \quad \Delta \psi = \frac{\cosh \psi_0 - 1}{\rho}. \hspace{1cm} (9)$$

The inner $\psi$-profile of a non-thick film is given by [26]

$$\psi_i(z) = \psi_0 - \frac{\rho}{2} (kz)^2 [1 - \mathcal{F}],$$  \hspace{1cm} (10)

where

$$\mathcal{F} = \frac{\sinh \psi_0}{\rho} \hspace{1cm} (11)$$

represents the fraction of the screened film intrinsic charge at $z = 0$.

The surface potential is then

$$\psi_s \approx \psi_0 - \frac{\rho}{2} (kH)^2 [1 - \mathcal{F}].$$  \hspace{1cm} (12)

III. ELECTROSTATIC POTENTIALS VS. ZETA-POTENTIAL

The expression for an outer velocity can be written as [15, 26]

$$v_o(z) = v_i + \psi_i(z) - \psi_s,$$  \hspace{1cm} (13)
where \( \psi_0 \) is given by Eq. (6) and \( \psi_s \) obeys Eq. (12). Therefore, in order to obtain a detailed information concerning zeta-potential a calculation of \( v_s \) arising due to the inner flow is required.

Using then (2) we conclude that the \( \rho_K \) on s is two limits, depending on how strong the dimensionless volume charge density is.

The value of \( \psi_0 \) can be generally calculated from Eq. (6), which then allows to find \( \psi_s \) and \( \Delta \psi \) from Eq. (13). Using standard manipulations we derive

\[
v_i = \left( \frac{\kappa}{K} \right)^2 \left( 1 - \frac{2\Delta \psi}{(\kappa H)^2} \right) e^{-\kappa z} - 1 + \frac{\sinh \kappa z}{\cosh \kappa H} \left[ \left( \frac{\kappa}{K} \right)^2 - \frac{2\Delta \psi}{(\kappa H)^2} \right] e^{-\kappa H} - \frac{2\Delta \psi}{\kappa H},
\]

so that at the surface

\[
v_s = \left( \frac{\kappa}{K}^2 - 2\Delta \psi \right) \left( 1 + \frac{\rho \kappa H}{(\kappa H)^2} e^{-\kappa H} - 1 - \frac{2\Delta \psi}{\kappa H} \right),
\]

Eq. (15) can be used for any values of \( \rho \) and \( \kappa H \), and in the limits of \( \kappa H \rightarrow 0 \) and \( \infty \) reduces to Eqs. (3) and (4).

When \( \kappa H \) is small, Eq. (15) can be expanded about \( \kappa H = 0 \), and to second order we obtain

\[
- v_s \approx \Delta \psi \left( 1 - \frac{(\kappa H)^2}{4} \right) + \frac{\rho \kappa H}{2} \left( 1 - \frac{5(\kappa H)^2}{12} \right)
\]

The first term in Eq. (16) is associated with the reduction of the potential, \( \Delta \psi \), in the porous film, but also depends on \( \kappa H \). The second term is associated with a body force \( \rho \kappa \) that drives the inner flow. Both terms reduce with \( \kappa H \) leading to deviations from the upper value of \( -v_s \) defined by Eq. (9). Using then (2) we conclude that the \( \zeta \)-potential can be approximated by

\[
\zeta \approx \psi_0 - \Delta \psi - \frac{\rho \kappa H}{2} \left( 1 - \frac{5(\kappa H)^2}{12} \right)
\]

Expanding \( v_i \) in Eq. (15) at large \( \kappa H \) we find

\[
- v_s \approx \frac{2\Delta \psi}{\kappa H} + \rho \left( \frac{\kappa}{K} \right)^2
\]

Eq. (18) indicates that \( v_s \) is a superposition of a flow that is linear in \( \Delta \psi \) and of a plug flow, \( \rho \left( \frac{\kappa}{K} \right)^2 \). Then it follows from Eq. (2) that

\[
\zeta \approx \psi_0 + \frac{2\Delta \psi}{\kappa H} + \rho \left( \frac{\kappa}{K} \right)^2
\]

We have calculated the inner velocity profile by solving Eq. (1) with \( \psi_i \) satisfying Eq. (10) and prescribed boundary conditions, and obtained that \( v_i \) is given by

\[
v_i = \left( \frac{\kappa}{K} \right)^2 \left( 1 - \frac{2\Delta \psi}{(\kappa H)^2} \right) e^{-\kappa z} - 1 + \frac{\sinh \kappa z}{\cosh \kappa H} \left[ \left( \frac{\kappa}{K} \right)^2 - \frac{2\Delta \psi}{(\kappa H)^2} \right] e^{-\kappa H} - \frac{2\Delta \psi}{\kappa H},
\]

A. Weakly charged coatings (\( \rho \ll 1 \))

At small \( \rho \) one can expand \( \psi_0 \) given by Eq. (6) into a series about \( \rho = 0 \), and we conclude that a sensible approximation for \( \psi_0 \) should be
\[
\psi_0 \approx \rho \kappa H \frac{\sqrt{4 + (\kappa H)^2} - \kappa H}{2}.
\] (22)

Note that \(\psi_0\) is linear in \(\rho\), but is a non-linear function of \(\kappa H\) since to derive Eq. (22) we do not make an additional assumption that \(\kappa H \ll 1\). Consequently, this and the following equations of this subsection should be valid even when \(\kappa H = O(1)\).

Expanding Eq. (9) at small \(\psi_0\) and substituting Eq. (22) we obtain

\[
\Delta \psi \approx \frac{\psi_0^2}{2 \rho} \approx \frac{\rho (\kappa H)^2 (\sqrt{4 + (\kappa H)^2} - \kappa H)^2}{8},
\] (23)

which together with (22) leads to

\[
\psi_s \approx \frac{\rho \kappa H}{4} \left( \sqrt{4 + (\kappa H)^2}^2 (2 + (\kappa H)^2) - \kappa H (4 + (\kappa H)^2) \right).
\] (24)

Note that imposing the condition of small \(\kappa H\) one can easily recover the known result of the linearized Poisson-Boltzmann theory (see Appendix A)

\[
\psi_0 \approx \rho \kappa H \left( 1 - \frac{\kappa H}{2} \right), \quad \psi_s \approx \rho \kappa H (1 - \kappa H),
\] (25)

which suggests that the \(\psi\)-profile is almost constant throughout a weakly charged thin film.

Expanding Eq. (11) at small \(\psi_0\) and using Eq. (22) we get

\[
\mathcal{F} \approx \frac{\psi_0}{\rho} = \frac{\kappa H (\sqrt{4 + (\kappa H)^2} - \kappa H)}{2} + O(\rho^2)
\] (26)

We remark that in this low \(\rho\) regime to leading order \(\mathcal{F}\) does not depend on \(\rho_0\), and is finite even if \(\rho \to 0\), where \(\psi_0 \approx 0\). At first sight this is somewhat surprising, but we recall that our dimensionless charge density is introduced by dividing the real one by the salt concentration, so that a nearly vanishing \(\rho\) simply implies that the (non-thick) film is enriched by counter-ions that partly screen its intrinsic charge.

It is clear that \(\psi_0, \psi_s,\) and \(\Delta \psi\) are small, so is \(v_s\) given by Eq. (16). Consequently, \(\zeta\) is also generally small and we do not discuss it here in detail. However, it would be worthwhile to mention that an upper bound on \(\zeta\) in this case is

\[
\zeta \approx \rho \kappa H \frac{\sqrt{4 + (\kappa H)^2}}{2},
\] (27)

which together with (24) gives \(\zeta / \psi_s \approx 2 + \kappa H \left(1 - \frac{(\kappa H)^2}{8}\right)\).

Thus, the electro-osmotic flow in the bulk can potentially be enhanced in more than two times compared to the Smoluchowski case.

### B. Strongly charged coatings \((\rho \gg 1)\)

We recall that for strongly charged coatings Eq. (6) reduces to [26]

\[
\psi_0 \approx 2 \arcsinh \left( \frac{\rho \kappa H}{2} \right) - \ln \left( 1 + \frac{\rho (\kappa H)^2}{2} \right).
\] (28)

Straightforward calculations show that Eqs. (20) and (21) can be transformed to

\[
\Delta \psi \approx \frac{\rho (\kappa H)^2}{2 + \rho (\kappa H)^2},
\] (29)

indicating that \(\Delta \psi \approx \mathcal{F}\) when \(\rho\) is large.

Two limits can now be distinguished depending on the value of \(\rho (\kappa H)^2\).

1. The limit of \(\rho (\kappa H)^2 \ll 1\)

We recall that since \(\rho\) is large, the film becomes thin when \(\kappa H \sqrt{\rho} \ll 1\). Therefore, such a situation is possible only for films that are truly thin or quasi-thin. We further remark that in this limit the first term in Eq. (28) dominates, so that it can be further simplified to give

\[
\psi_0 \approx 2 \arcsinh \left( \frac{\rho \kappa H}{2} \right) - \frac{\rho (\kappa H)^2}{2}
\] (31)

In turn, Eq. (29) reduces to

\[
\Delta \psi \approx \frac{\rho (\kappa H)^2}{2},
\] (32)

leading to

\[
\psi_s \approx 2 \arcsinh \left( \frac{\rho \kappa H}{2} \right) - \rho (\kappa H)^2
\] (33)

When \(\rho \kappa H\) is small, Eqs. (31) and (33) reduce to Eqs. (25), which implies that they can also be employed when \(\rho\) is small, provided \(\kappa H\) is not large.

From Eq. (17) we then find that for small \(\kappa H\) the zeta-potential can be approximated as

\[
\zeta \approx 2 \arcsinh \left( \frac{\rho \kappa H}{2} \right) - \frac{\rho (\kappa H)^2 (\kappa H)^2}{3},
\] (34)

which leads to

\[
\zeta \approx 2 \arcsinh \left( \frac{\rho \kappa H}{2} \right)
\] (35)
when $\mathcal{K}H \to 0$. However, using (33) we obtain $\zeta - \psi_s \leq \rho(\mathcal{K}H)^2$, which is small in this limit. Therefore, our asymptotic arguments suggest that even in the case of extremely large hydrodynamic permeability of the porous layer, the difference between $\zeta$ and $\psi_s$ cannot be significant. Thus a knowledge of $\psi_s$ should be sufficient to provide a realistic evaluation of $\zeta$ (and vice versa). Nevertheless, for completeness we mention that at large $\mathcal{K}H$ from (19) one can obtain

$$\zeta \approx 2 \text{arsinh} \left( \frac{\rho \mathcal{K}H}{2} \right) + \rho \left( \frac{\kappa}{\mathcal{K}} \right)^2 \left( 1 + \mathcal{K}H - (\mathcal{K}H)^2 \right),$$

(36)

which tends to $\psi_s$ given by Eq.(33) when $\mathcal{K}H \to \infty$.

2. The limit of $\rho(\mathcal{K}H)^2 \gg 1$

This limit is close to, but weaker of, the condition for a thick film $\mathcal{K}H \sqrt{\rho} \gg 1$. So, we can term these films quasi-thick.

For large $\rho(\mathcal{K}H)^2$, Eqs.(28) and (29) can be further simplified to

$$\psi_0 \approx \ln(2\rho) - \frac{2}{\rho(\mathcal{K}H)^2}, \quad \Delta \psi \approx 1 - \frac{2}{\rho(\mathcal{K}H)^2}$$

(37)

which gives the same $\psi_s$ as for thick films [15, 38]

$$\psi_s \approx \ln(2\rho) - 1$$

(38)

Substituting (37) into (17) in the limit $\mathcal{K}H \ll 1$ we obtain

$$\zeta \approx \ln(2\rho) + \frac{\rho(\mathcal{K}H)^2}{2} \left( 1 - \frac{5(\mathcal{K}H)^2}{12} \right),$$

(39)

which suggests that for quasi-thick films $\zeta$ can become very large and significantly increases $\psi_s$.

Substitution of Eqs. (37) and (38) into (19) for $\mathcal{K}H \gg 1$ leads to

$$\zeta \approx \ln(2\rho) - 1 + \rho \left( \frac{\kappa}{\mathcal{K}} \right)^2 + \frac{2}{\mathcal{K}H}$$

(40)

IV. NUMERICAL RESULTS AND DISCUSSION

It is of considerable interest to compare exact numerical data with our analytical theory and to determine the regimes of validity of asymptotic results. Here we first present results of numerical solutions of Eq. (5) with prescribed boundary conditions, using the collocation method [39]. We then solve numerically the system of Eqs. (1) and (6). The exact numerical solutions will be presented together with calculations from the asymptotic approximations derived in Sec III

In Fig. 2 we plot $\psi_0$ and $\psi_s$, computed using $\mathcal{K}H = 0.8$ and 0.1, as a function of $\rho$. It is well seen that for a thinner film $\psi_0 = \psi_s$ up to $\rho \mathcal{K}H \approx 3$. On increasing $\rho$ further $\Delta \psi$ increases slowly. For a thicker film of $\mathcal{K}H = 0.8$ the potential drop in the film is always finite and $\Delta \psi$ grows much faster as $\rho$ is increased. The theoretical curves calculated from Eqs. (22) and (24) are also included in Fig. 2. The fits are quite good for $\rho \leq 2$, but at larger $\rho$ there is some discrepancy, especially for $\mathcal{K}H = 0.8$, and the theoretical potentials predicted by low $\rho$ approximations become higher than computed. Note, however, that for $\mathcal{K}H = 0.1$ the discrepancy between a linear fit and numerical calculations is negligibly small when $\rho \leq 2$.

In Fig. 3, the data sets for $\psi_0$ and $\psi_s$ obtained at smaller values of $\rho$ reproduced from Fig. 2 and plotted as a function of $\rho \mathcal{K}H$. The upper set of curves and symbols shows $\mathcal{K}H = 0.1$, the lower one corresponds to $\mathcal{K}H = 0.8$.

To examine its significance more closely, the initial portions of the $\psi$-profiles from Fig. 2 are reproduced in Fig. 3 but now plotted as a function of $\rho \mathcal{K}H$. An overall conclusion from this plot is that the approximations derived in Sec III A are very accurate when $\rho \mathcal{K}H \leq 1$. We now return to Fig. 2 and focus on the large $\rho$ portions of the
curves. As reported by Silkina et al. [26, Eq. (8) fits very accurately the numerical data for \( \psi_0 \) at any \( \rho \), so does more elegant [28], except for \( \rho \leq 1 \), where some very small discrepancy is observed. Calculations with our parameters fully confirm this conclusion, so that we do not show these data. Instead, we include \( \psi_0 \) calculated from Eqs. (31) and (37) that correspond to small and large \( \rho (kH)^2 \). It is well seen that for \( \rho \geq 10 \) the agreement with numerical data is excellent in both cases. Also included is \( \psi_o \) from [25] and [28], and we see that these asymptotic approximations coincide with the numerical data.

Fig. 4 shows the electrostatic potential drop, \( \Delta \psi \), inside the film computed for \( kH = 0.2 \) and 0.8 as a function of \( \rho \). The degree of screened intrinsic charge at the wall, \( \mathcal{F} \), calculated numerically for the same values of \( kH \) is also plotted. It is seen that \( \Delta \psi \) first increases linearly with \( \rho \) and, when \( \rho \) is getting sufficiently large, slowly approaches to unity for a film of \( kH = 0.8 \). However, in a chosen interval of \( \rho \) the potential drop of a thinner film of \( kH = 0.2 \) still continues to grow, although weakly and nonlinearly. It can be seen that the linear portions of the curves are well fitted by Eq. (23), and the nonlinear ones are reasonably well described by Eq. (29). Also included in Fig. 4 are the curves for \( \mathcal{F} \) computed using the same values of \( kH \). For strongly charged coatings \( \mathcal{F} \approx \Delta \psi \), confirming predictions of Eq. (30). When \( \rho = 0 \), \( \mathcal{F} \) is finite and its value is given by (26). This equation also predict a parabolic growth of \( \mathcal{F} \) at small \( \rho \), which is well seen in Fig. 4.

We now turn to the electro-osmotic velocity. The velocity profiles computed using three \( KH \) in the range from 0.1 (small) to 5 (relatively large) are shown in Fig. 5. They have been obtained using \( kH = 0.3 \) and \( \rho = 50 \). Note that with these parameters \( kH \sqrt{\rho} \approx 2.1 \), \( \rho (kH) = 15 \), and \( \rho (kH)^2 = 4.5 \), so in our terms we deal with a non-thick highly charged film of moderate value of \( \rho (kH)^2 \). Also included is the computed \( \psi \)-profiles for this film. As described in Sec. II, the electrostatic potential of a non-thick film is generally nonuniform throughout the system. Its maximum value (at the wall) reaches about 4.5, indicating that nonlinear electrostatic effects become significant. The theoretical curves calculated from Eq. (13) for \( \psi_o \) using \( v \), defined by Eq. (15), and from Eq. (14) for \( v_\infty \) coincide with the numerical data. It can be seen that on reducing \( \mathcal{K}H \) the value of \( -v \) increases. All outer velocity profiles are of the same shape that is set by \( \psi_0 \), indicating that the dramatic increase in \( -v \) upon decreasing \( \mathcal{K}H \) is induced by changes in \( v_o \) only. At very large \( z/H \) the curves for \( v_o \) saturate to \( v_\infty = -\zeta \) (not shown).

Fig. 6 intends to indicate the range of \( \zeta \) that is encountered at different \( \mathcal{K}H \). For this numerical example we use films of \( kH = 0.2 \) and 0.8, the same as in Fig. 4 and explore the case of \( \rho = 20 \). With these parameters \( \rho (kH)^2 = 0.8 \) and 12.8. These values differ significantly and correspond to different limits (or quasi-thin and quasi-thick films) described in Sec. III, but the surface potentials, which are also shown in Fig. 6, are quite close (and not small). In the chosen range of values of \( \mathcal{K}H \), which are neither too small nor quite large, zeta po-
tentials of both films reduce strictly monotonically. We see that the value of $\zeta$ is much larger for the quasi-thick film of $xH = 0.8$, where $\zeta$ can exceed $\psi_s$ in several times. For a quasi-thin film of $xH = 0.2$ the zeta potential is higher than $\psi_s$ but not much. The parts of the $\zeta$-curves corresponding to $\mathcal{KH} \leq 1$ are well described by Eqs.(35) and (39), pointing out that this asymptotic approximations have validity well beyond the range of the original assumptions (see Sec. III). When $\mathcal{KH} \geq 2$, the decay of $\zeta$ is well consistent with predictions of Eqs.(34) and (36), indicating that the latter are also valid well outside the range of their formal applicability. As is usual, $\zeta \rightarrow \psi_s$ as $\mathcal{KH} \rightarrow \infty$.

\[ \psi (H) \approx \psi_s \left( 1 + \frac{H}{\ell} \right)^{-1/4}, \]

which is inversely proportional to the square root of the volume charge density, but does not depend on the bulk salt concentration.

The definition of dimensionless $\rho$ can then be reformulated as

\[ \rho = \left( \frac{\lambda_D}{\ell} \right)^2 \]

This suggests that it is the ratio of two electrostatic length scales of the problem that determines whether coatings are weakly or strongly charged. It is clear that an interesting “cross-over” behavior must occur for some intermediate values $c_\infty$ that corresponds to $\lambda_D \propto \ell$. We return to this important point below.

Condition (7) of a non-thick film then becomes

\[ H/L^0 \left( 1 + \left( \frac{\lambda_D}{\ell} \right)^{1/4} \right) \neq 1, \]

i.e. $H/L_{\lambda_D} \neq 1$ for weakly charged films, and $H/\ell \neq 1$ for highly charged films. It is instructive to mention that an electrostatic thickness of highly charged films is equal to $H/\ell$ and does not depends on salt. Therefore, such films are thin when $H/\ell \ll 1$, but weakly charged films are thin when $H/L_{\lambda_D} \ll 1$.

The combinations of dimensionless parameters that control $\psi_s$, $\psi_0$, and $\zeta$ can then be related to $\ell$ as

\[ \rho \psi H = \frac{\lambda_D H}{\ell^2}, \quad \rho (xH)^2 = \left( \frac{H}{\ell} \right)^2, \quad \rho (x/K)^2 = \left( \frac{\Lambda}{\ell} \right)^2 \]

Eqs.(45) illustrate that there exist several length scales, lying always in the nanometric range, which determine different regimes of the electro-osmotic flow. Another important conclusion from Eqs.(45) is that $\rho (xH)^2$ and $\rho (x/K)^2$ do not depend on the salt concentration in the bulk. Accordingly, the dependence on salt is hidden only in $pxH$, which is the function of $\lambda_D$.

Since $\rho (xH)^2$ is independent on the salt concentration, it is natural to investigate films of its relatively small and large fixed values, which is equivalent to $(H/\ell)^2 \ll 1$ and $(H/\ell)^2 \gg 1$ as follows from (45). We now fix $H = 15 \text{ nm}$, so upon increasing the salt concentration

\[ \lambda_D \text{[nm]} = \frac{0.305 \text{[nm]}}{\sqrt{c_\infty} \text{[mol/L]}}, \]

and the dependence of $\psi_s$ and $\zeta$ on $\lambda_D$ in the equations below reflects their dependence on $c_\infty$. The later is often probed in electrokinetic experiments, where a decrease of both potentials with salt is observed. We stress, however, that the measurements have been often conducted by using only a very narrow range of relatively large $c_\infty$ since existing linear theories could not provide a reasonable interpretation of data at low concentrations, where potentials are high.
from $10^{-6}$ to $10^{-2}$ mol/L, we change $H/\lambda_D$ from ca. 0.05 to 5. Let us consider two films, of $\ell = 5$ and 30 nm, which corresponds to $\varrho = 360$ and 10 kC/m$^2$. Note that the larger volume charge density is only slightly smaller than the maximal one reported in experiments [12, 43]. With the chosen values of $\varrho$, $(H/\ell)^2$ reduces from 3600 down to 0.36 for the film of $\ell = 5$ nm, and from 100 down to 0.01 for that of $\ell = 30$ nm. Therefore, with the chosen parameters both films fall to a category of non-thick, and in very dilute solutions both films are highly charged. However, as follows from Eq. (44), the film of $\ell = 5$ is quasi-thick, but that of $\ell = 30$ is quasi-thin.

The surface potential of a highly charged quasi-thick film can be obtained using Eq. (38)

$$\psi_s \approx 2 \ln \left( \frac{\lambda_D}{\ell} \right) + \ln 2 - 1$$  \hspace{1cm} (46)

and depends only on $\lambda_D/\ell$. However, when the highly-charged film is quasi-thin, $\psi_s$ obeys Eq. (33) that can be rewritten as

$$\psi_s \approx 2 \sinh \left( \frac{\lambda_D H}{2 \ell^2} \right) - \left( \frac{H}{\ell} \right)^2$$ \hspace{1cm} (47)

Thus, in this situation $\psi_s$ is defined by both $\lambda_D/\ell$ and $H/\ell$.

At high salt both films become weakly charged and quasi-thick. Therefore, to calculate $\psi_s$ one can use (A7), which gives

$$\psi_s \approx \frac{1}{2} \left( \frac{\lambda_D}{\ell} \right)^2 \varrho c_\infty^{-1}$$ \hspace{1cm} (48)

i.e. the surface potential is again controlled solely by $\lambda_D/\ell$.

![Graph of $\psi_s$ vs $c_\infty$](image)

**FIG. 8.** $\psi_s$ vs $c_\infty$ computed using $H = 15$ nm and $\ell = 5$ (upper solid curve) and 30 nm (lower solid curve). Filled and open circles are obtained from Eqs. (49) and (51). Squares show predictions of Eq. (48), and triangles mark the points of the curves, where $\lambda_D = \ell$.

In Fig. 8 we plot $\psi_s$ vs. $c_\infty$ for these two specimen examples of the films. The surface potential is quite high at $c_\infty \approx 10^{-6}$ mol/L (ca. 198 and 78 mV) and reduces with salt. At larger concentrations $\psi_s$ becomes smaller than unity and practically vanishes when $c_\infty \geq 10^{-2}$ mol/L. To specify better the branches of low and high concentrations, in Fig. 9 we have marked by black and open triangles the points, where $\lambda_D = \ell$. For an upper curve computed using $\ell = 5$ nm this is located at $c_\infty^\Delta \approx 3.7 \times 10^{-3}$ mol/L, and for a lower, of $\ell = 30$ nm, $c_\infty^\Delta \approx 10^{-4}$ mol/L. The corresponding surface potentials are $\psi_s \approx 0.5$ and 0.3. Thus, when $\lambda_D = \ell$, both films are of low surface potentials. The first film is quasi-thick, and the branch of the curve with $c_\infty \geq c_\infty^\Delta$ is well fitted by Eq. (48). Note that at $c_\infty$ the second film still remains quasi-thin and becomes quasi-thick, where $c_\infty^\Delta$ is strictly valid, only when $c_\infty \approx 10^{-3}$ mol/L. We see, however, that the fit is quite good for $c_\infty \geq c_\infty^\Delta$, although at concentrations smaller than $10^{-3}$ mol/L there is some discrepancy, and Eq. (48) slightly overestimates $\psi_s$. Also included in Fig. 8 are theoretical calculations for low salt concentrations. We see that at $c_\infty$ smaller than $c_\infty^\Delta$, Eq. (46) is very accurate for a curve of $\ell = 5$ nm, where $H/\ell = 3$. When $\ell = 30$ nm giving $H/\ell = 0.5$, Eq. (47) provides an excellent fit to numerical data. Finally, we would like to stress that it is impossible to generate a very high $\psi_s$ just by increasing $\varrho$. This is well seen in Fig. 9 where the upper curve corresponds to the film with 36 times larger $\varrho$ than that for a film corresponding to a lower curve. The ratio of the values surface potentials for these two coatings is always smaller. Its largest value is equal to 18, as follows from Eq. (48) for the high salt regime, where $\psi_s$ is small. However, when $\psi_s$ is large, its amplification with $\varrho$ is very weak (only about 2 when $c_\infty = 10^{-6}$ mol/L).

![Graph of $\zeta$ vs $c_\infty$](image)

**FIG. 9.** Zeta potential vs $c_\infty$ computed using $\Lambda = 30$ nm (upper solid curve) and 3.75 nm (lower solid curve) for a film of $H = 15$ nm and $\ell = 5$ nm. Filled and open circles are obtained from Eqs. (49) and (51). Squares show predictions of Eqs. (51) and (52). Dashed curves show upper and lower bounds on $\zeta$.

We now turn to zeta potentials, and compute the salt dependence of $\zeta$ for a film of $\ell = 5$ nm by setting $\Lambda = 30$ and 3.75 nm. These give $H/\Lambda = 0.5$ and 4, which should correspond to large and small Brinkman length regimes (see Fig. 6).

The results of numerical calculations are shown in Fig. 9. We see that the numerical curves are confined...
between lower and upper bounds on $\zeta$, and that they are of the same shape as $\psi_H$ but shifted towards larger values that depend on $\Lambda$. At $c_\infty \leq c_\infty^*$ and small $H/\Lambda$, the expression for the zeta potential can be obtained from Eq. (39)

$$\zeta \simeq 2 \ln \left( \frac{\Lambda_D}{\ell} \right) + \frac{1}{2} \left( H^2 \right) \left( 1 - \frac{5H^2}{12\Lambda^2} \right) + \ln 2,$$

but when $H/\Lambda$ is large, it follows from (40) that

$$\zeta \simeq 2 \ln \left( \frac{\Lambda_D}{\ell} \right) + \left( \frac{\Lambda}{\ell} \right)^2 + \frac{2\Lambda}{H} \ln 2 - 1 \quad (50)$$

It can be seen that Eqs. (49) and (50) provide an excellent fit to our numerical data. At larger concentrations, $c_\infty \geq c_\infty^*$, $\psi_H$ is small, and substituting (A7) into Eqs. (17) and (19) for small and large $H/\Lambda$ we derive

$$\zeta \approx \left( \frac{\Lambda_D}{\ell} \right)^2 \left( 1 - \frac{1}{8} \left( \frac{H}{\Lambda} \right)^2 \right) + \left( \frac{H}{\ell} \right)^2 \left( 1 - \frac{5}{12} \left( \frac{H}{\Lambda} \right)^2 \right), \quad (51)$$

$$\zeta \approx \left( \frac{\Lambda_D}{\ell} \right)^2 \left( \frac{1}{2} + \frac{\Lambda}{H} \right) + \left( \frac{\Lambda}{\ell} \right)^2 \quad (52)$$

The calculations from Eqs. (51) and (52) are also included in Fig. 8 and we see that the agreement with numerical data is again extremely good.

For the film of $\ell = 30$ nm, when $\Lambda/H$ is large, the variation of $\zeta$ in the low salt regime, $c_\infty \leq c_\infty^*$, is described by Eq. (54) that can be transformed to

$$\zeta \approx 2 \arcsinh \left( \frac{\Lambda_D H}{2\ell^2} \right) - \frac{H^2}{3\Lambda^2 \ell^2} \quad (53)$$

As already discussed in Sec. III B 1, in this case even at the infinite Brinkman length the zeta potential exceeds $\psi_H$ but very slightly (see also the lower curve in Fig. 9). This is, of course, confirmed by numerical calculations of $\zeta$ as the function of $c_\infty$ (not shown). Subtracting Eq. (47) from (53) we find $\zeta - \psi_H \leq (H/\ell)^2$, which is small. If $\Lambda/H$ is small, $\zeta$ is described by

$$\zeta \approx 2 \arcsinh \left( \frac{\Lambda_D H}{2\ell^2} \right) - \left( \frac{\Lambda}{H} \right)^2 \left( 1 - \frac{\Lambda}{H} \right), \quad (54)$$

which can be easily obtained from (36). Finally, when $c_\infty \geq c_\infty^*$, Eqs. (51) and (52) are, of course, valid.

VI. CONCLUDING REMARKS

We have presented a theory of surface and zeta potentials of non-thick porous coatings, i.e. those of a thickness $H$ comparable or smaller than that of the inner diffuse layer, of a finite hydrodynamic permeability. Our mean-field theory led to a number of asymptotic approximations, which are both simple and very accurate, and can easily be used to predict or to interpret $\psi_H$ and $\zeta$ in different regimes, including situations when non-linear electrostatic effects become significant.

The main results of our work can be summarized as follows. We have introduced an electrostatic length scale $\ell \propto g^{-1/2}$ and demonstrated that depending on its value two different scenarios occur. In the high salt concentration regimes, $\ell > \Lambda_D \propto c_\infty^{-1/2}$, the non-thick porous films are weakly charged and their electrostatic properties can be described by linearized equations. These films effectively behave either as thin or thick depending on the value of $H/\Lambda_D$. At low salt, $\ell < \Lambda_D$, the non-thick films are highly charged, and their effective (dimensionless electrostatic) thickness is set by $H/\ell$. When the latter is small, the film behaves effectively as thin, and when large, as thick. The highly charged films generally possess a high surface potential, which growth with increasing $H/\ell$. We have also stressed the connection between the zeta potential and the Brinkman length, which is a characteristics of the hydrodynamic permeability of the porous film. Interestingly, the Brinkman length contribution to $\zeta$ permits to augment it compared to $\psi_H$ only if $(H/\ell)^2$ is large, i.e. when films are quasi-thick.

Overall we conclude that tuning fluid transport inside a nanometric non-thick coating can dramatically affect the whole response of the large system to an applied electric field. Such a tuning can be achieved modifying its internal structure and charge density, or by varying film thickness, or concentration of an external salt solution.

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AUTHOR’S CONTRIBUTION

E.F.S. developed numerical codes, performed computations, and prepared the figures. N.B. participated in theoretical calculations. O.I.V. designed and supervised the project, developed the theory, and wrote the manuscript.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available within the article.
Appendix A: The limit of low potentials

For completeness, in this Appendix we briefly discuss the case of low electrostatic potentials ($\psi \leq 1$), when Eq. (5) can be linearized to give

$$\psi_{i,o} = \kappa^2 \left[ \psi_{i,o} - \rho \Theta (H - z) \right]$$

(A1)

Note that this case has been considered before by Ohshima and Ohki [14]. Here we present a compact derivation of expressions for $\psi_i$ and $\psi_o$ in our (different) variables and complete the consideration by giving approximate expressions for $\Delta \psi$, $\mathcal{F}$. We also obtain an upper limit of $\zeta$.

Integrating Eq. (A1) with prescribed boundary conditions (see Sec. II) one can easily obtain

$$\psi_i = \cosh(\kappa z) (\psi_0 - \rho) + \rho, \quad \psi_o = \psi_s e^{-\kappa (z - H)}$$

(A2)

which leads to

$$\psi_0 = \rho \left( 1 - e^{-\kappa H} \right)$$

(A3)

$$\psi_s = \rho \sinh(\kappa H) e^{-\kappa H}$$

(A4)

It is then straightforward to obtain

$$\Delta \psi = \frac{\rho (1 - e^{-\kappa H})^2}{2},$$

(A5)

and

$$\mathcal{F} = 1 - e^{-\kappa H}$$

(A6)

We recall that these equations are valid at any $\kappa H$. At small $\kappa H$ they transform to Eq. (25), but at large $\kappa H$ they reduce to

$$\psi_0 \approx \rho, \quad \psi_s \approx \rho/2$$

(A7)

It is easy to verify that in fact the first equation of (A7) is valid already when $\kappa H \geq 5$, and the second when $\kappa H \geq 2$. In other words, they describe not only the thick films, but also valid for some non-thick ones that can be termed quasi-thick.

Interestingly, low potential films satisfying (A7) can potentially generate a high zeta-potential. Its upper achievable limit can be obtained using Eq. (3) and is given by

$$\zeta \approx \rho + \frac{\rho (\kappa H)^2}{2},$$

(A8)

The last equation coincides with that for weakly charged thick films [15]. Dividing (A8) by (A4) we conclude that for low potential thick and quasi-thick films $\zeta / \psi_s \approx 2 + (\kappa H)^2$. 

[1] M. von Smoluchowski, Handbuch der Elektrizität und des Magnetism. Vol. 2, edited by L. Graetz (Barth, J. A., Leipzig, 1921) pp. 366–428.
[2] O. I. Vinogradova, Int. J. Miner. Proc. 56, 31 (1999).
[3] V. M. Muller, I. P. Sergeeva, V. D. Sobolev, and N. V. Churaeva, Colloid J. USSR 48, 606 (1986).
[4] L. Joly, C. Ybert, E. Trizac, and L. Bocquet, Phys. Rev. Lett. 93, 257805 (2004).
[5] S. R. Maduar, A. V. Belyaev, V. Lobaskin, and O. I. Vinogradova, Phys. Rev. Lett. 114, 118301 (2015).
[6] E. F. Silkina, E. S. Asmolov, and O. I. Vinogradova, Phys. Chem. Chem. Phys. 21, 23036 (2019).
[7] O. I. Vinogradova and A. V. Belyaev, J. Phys.: Condens. Matter 23, 184104 (2011).
[8] S. S. Bahga, O. I. Vinogradova, and M. Z. Bazant, J. Fluid Mech. 644, 245 (2010).
[9] T. M. Squires, Phys. Fluids 20, 092105 (2008).
[10] A. V. Belyaev and O. I. Vinogradova, Phys. Rev. Lett. 107, 098301 (2011).
[11] G. S. Beavers and D. D. Joseph, J. Fluid Mech. 30, 197 (1967).
[12] J. L. Anderson, Annu. Rev. Fluid Mech. 21, 61 (1989).
[13] L. Bocquet and E. Charlaix, Chem. Soc. Rev. 39, 1073 (2010).
[14] H. Ohshima and S. Ohki, Biophys. J. 47, 673 (1985).
[15] O. I. Vinogradova, E. F. Silkina, N. Bag, and E. S. Asmolov, Phys. Fluids 32, 102105 (2020).
[16] M. Cohen Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsuchik, M. Urban, F. Winnik, S. Zauscher, I. Lizunov, and S. Minko, Nature Mater 9, 101 (2010).
[17] B. Chollet, M. Li, E. Martwong, B. Bresson, C. Fretigny, P. Tabeling, and Y. Tran, ACS Appl. Mater. Interfaces 8, 11729 (2016).
[18] M. Ballauf and O. Borisov, Current Opinion Colloid Interface Science 11, 316 (2006).
[19] O. I. Vinogradova, O. V. Lebedeva, K. Vasilev, H. Gong, J. Garcia-Turiel, and B. S. Kim, Biomacromolecules 6, 1495 (2005).
[20] A. van den Berg and M. Wessling, Nature 445, 12647 (2016).
[21] M. P. Pina, R. Mallada, M. Arruebo, M. Urban, F. Winnik, S. Minko, Nature Mater 9, 101 (2010).
[22] M. Lukatskaya, B. Dunn, and Y. Gogotsi, Nat Commun 7, 12647 (2016).
[23] E. Donath and V. Pastushenko, Bioelectrochem. Bioenergetics 6, 543 (1979).
[24] H. Ohshima and T. Kondo, J. Colloid Interface Sci. 135, 443 (1990).
[25] H. Ohshima, Adv. Colloid Interface Sci. 62, 189 (1995).
[26] E. F. Silkina, N. Bag, and O. I. Vinogradova, Phys. Rev. Fluids 5, 123701 (2020).
[27] J. F. L. Duval and H. P. van Leeuwen, Langmuir 20, 10324
(2004).
[28] J. F. L. Duval, Langmuir 21, 3247 (2005).
[29] H. Ohshima, Theory of colloid and interfacial electric phenomena (Elsevier, 2006).
[30] A. C. Barbati and B. J. Kirby, Soft Matter 8, 10598 (2012).
[31] L. P. Yezek and H. P. van Leeuwen, J. Colloid Interface Sci. 278, 243 (2004).
[32] V. D. Sobolev, A. N. Filippov, T. A. Vorob’eva, and I. P. Sergeeva, Colloid J. 79, 677 (2017).
[33] G. Chen and S. Das, J. Colloid Interface Sci. 445, 357 (2015).
[34] D. Andelman, “Soft Condensed Matter Physics in Molecular and Cell Biology,” (Taylor & Francis, New York, 2006) Chap. 6.
[35] J. N. Israelachvili, Intermolecular and Surface Forces, 3rd ed. (Academic Press, 2011).
[36] K. Z. Markov, in Heterogeneous Media, Modelling and Simulation, edited by K. Markov and L. Preziosi (Birkhauser Boston, 2000) Chap. 1, pp. 1–162.
[37] S. Torquato, Random Heterogeneous Materials: Microstructure and Macroscopic Properties (Springer, 2002).
[38] E. F. Silkina, T. Y. Molotilin, S. R. Maduar, and O. I. Vinogradova, Soft Matter 16, 929 (2020).
[39] G. Bader and U. Ascher, SIAM J. Sci. and Stat. Comput. 8, 483 (1987).
[40] M. Lorenzetti, E. Gongadze, M. Kulkarni, I. Junkar, and A. Iglič, Nanoscale Res. Lett. 11, 378 (2016).
[41] J. Irigoyen, V. B. Arekalyan, Z. Navoyan, J. Iturri, S. E. Moya, and E. Donath, Soft Matter 9, 11609 (2013).
[42] L. P. Yezek, J. F. M. Duval, and H. P. van Leeuwen, Langmuir 21, 6220 (2005).
[43] L. Braeken, B. Bettens, K. Boussu, P. Van der Meer, J. Cocquyt, J. Vermant, and B. Van der Bruggen, J. Membr. Sci. 279, 311 (2006).