Surface conduction

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Abstract

This paper deals with the dynamics of liquids, water in particular, at hard surfaces. The stacking of the first adjacent molecules leads to a thin layer which upon shear appears phenomenologically stagnant. Electrokinetic phenomena are particularly suited to study such layers. We shall show how surface conduction studies contribute to the understanding of the dynamics of stagnant layers.

1. Introduction

At interfaces the molecular density profile $\rho(z)$ of a liquid differs from that in the bulk. This distribution obeys different laws between soft and hard adjacent phases. For the former systems, with the liquid–vapour interface as the paradigm, $\rho(z)$ decreases gradually from its average bulk value $\langle\rho\rangle$ to its value p/kT in the vapour. According to recent insight $\rho(z)$ obeys a hyperbolic tangent law. Surface rheology and surface light scattering reveal the absence of an excess surface excess viscosity, provided these surfaces are completely free of adsorbates.

In the present contribution liquids near hard walls will be discussed. At such interfaces $\rho(z)$ passes through a few oscillations. Phenomenologically it is observed that a very thin liquid layer remains stagnant when the liquid is sheared with respect to the solid. The thickness of such layers corresponds to a few molecular diameters. The phenomenon is generic: it is found both for hydrophilic and hydrophobic surfaces. Most likely it is a general property of the adjacent fluid. Probably it is related to the oscillations of $\rho(z)$.

Hydrodynamically such thin layers are esoteric. For instance, in Poiseuille flow the bulk of the transport takes place through the heart of the capillary lumen; absence of flow in a few molecular layers near the inner capillary wall does not count quantitatively. In extremely narrow capillaries the occurrence of a stagnant layer does count, but then other complications arise.

However, electrokinetic phenomena do offer this information. Electrokinetic phenomena involve tangential motion of a liquid with respect to a charged wall. The countercharges are distributed in a more or less diffuse layer with a relatively large fraction inside the stagnant layer. Not surprisingly the final outcome of the process is sensitive to the thickness and dynamics of the stagnant layer.

Excess conduction in such layers is a relevant phenomenon and therefore the *surface conductivity* is a central characteristic; this will now be addressed. Anticipating the following,

there are no reasons to assume that the presence of charges significantly affects the properties of adjacent liquids.

2. Electrokinetics and the stagnant layer

All electrokinetic phenomena have in common that they involve tangential movement of a liquid with respect to a charged surface. In the various electrokinetic techniques different driving forces are applied and different (second-order) quantities measured. Well known is *electrophoresis*: charged particles move under the influence of an applied electric field E, the electrophoretic mobility u is measured, with $v = uE$, where v is the electrophoretic velocity. In electrophoresis the liquid is stationary whereas the solid moves. The reverse situation (solid stationary, liquid moves) can be created with porous plugs through which the fluid percolates. *Electro-osmosis* is the flow of liquid as a result of an applied field and *streaming potentials* are created as a result of an applied pressure difference. The measurable quantities are the electro-osmotic volume flow Q_{eo} and the streaming potential, E_{str}, respectively. There are more such techniques, which essentially give the same information; this follows from Onsager's reciprocal relations. Electrokinetics can also be carried out in oscillatory fields; *dielectric spectroscopy* is the most familiar example. By this technique the complex dielectric permittivity $\varepsilon_0 \hat{\varepsilon}(\omega)$ is measured as a function of frequency. For a review of all of this, see [1].

The central quantity in electrokinetics is the *electrokinetic* or *zeta-potential* ζ, which can be related to the electrokinetic charge density σ^{ek}. For a double layer that is relatively flat ($\kappa a \gg 1$ where κ^{-1} is the Debye length) the relation is

$$\sigma^{ek} = -(8\varepsilon_0 \varepsilon c RT)^{1/2} \sinh(zF\zeta/2RT) \tag{1}$$

where c is the electrolyte concentration and where R, T and F have their usual meanings. Below we shall restrict ourselves to geometrics (particle size a, capillary radius a) for which $\kappa a \gg 1$.

Over the decades it transpired that only a part of the double layer is electrokinetically 'active'. For those systems, in which, besides ζ or σ^{ek}, the *surface potential* ψ^0, or the *surface charge* σ^0, are also available it was found that usually $|\sigma^{ek}| < |\sigma^0|$ and $|\zeta| < |\psi^0|$. Sometimes the surface and electrokinetic quantities even bear opposite signs. This difference is commonly attributed to the presence of the stagnant layer, mentioned above. The underlying idea is that ions in this layer do not contribute to electrokinetics because the layer is hydrodynamically immobile.

Static double layers are electroneutral, meaning that the surface charge σ^0 is exactly compensated by the countercharge. The latter consists of two parts, one in the stagnant layer, σ^i and one in the 'electrokinetically active' part, σ^{ek}. In a formula,

$$\sigma^0 + \sigma^i + \sigma^{ek} = 0. \tag{2}$$

Experience has shown that the electrokinetically active part satisfactorily coincides with the diffuse part of the double layer. Part of the evidence stems from colloid stability studies, demonstrating a close correlation between stability and ζ, but not with ψ^0. The implication is that

$$\sigma^{ek} \approx \psi^d \tag{3}$$

where ψ^d is the potential of the diffuse part of the double layer. It is the diffuse part of the countercharge which controls colloid interaction. By the same argument, σ^i more or less coincides with the non-diffuse, or Stern, part of the double layer. When we know σ^{ek} from electrokinetics and σ^0 (say, from titration of surface groups), (2) can be used to obtain σ^i. Often σ^{ek} is much less than σ^0, so errors made in σ^{ek} do not significantly propagate in σ^i.
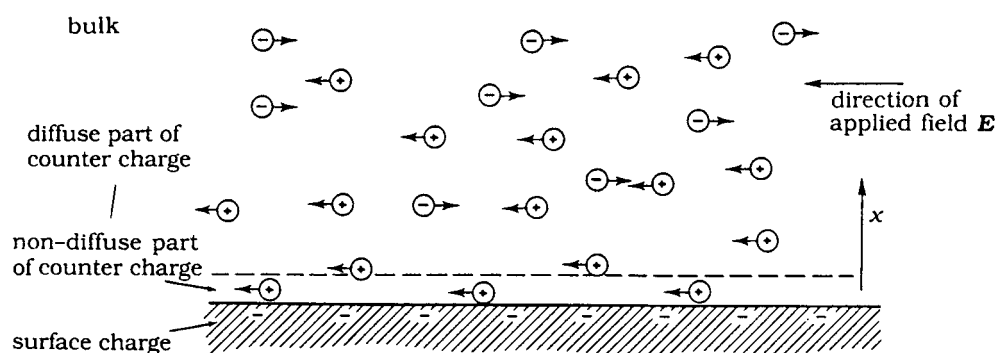
Figure 1. Visualization of surface conduction in a flat electric double layer. Discussion in the text.

A problem of principle is whether the above balances and equalities also apply for double layers in an external field, which leads to *polarization*. Basically this perturbation has to be accounted for, but quantitatively this effect is so small that it can be neglected, leading to the now generally accepted notion of *local equilibrium*, which is heeded in all modern electrokinetic theories [2, 3]. In fact, accounting for surface conduction is quantitatively a much more pressing issue.

3. Surface conduction

As electric double layers carry excess ionic charges, charged interfaces have an excess tangential conductivity. For the interpretation of electrokinetic phenomena this conductivity is relevant because it governs the field lines around the (polarized) particle (or between particles in a plug) and the resulting ion fluxes. We shall use the symbols K^σ and K^L for the surface and bulk conductivity, respectively. The units are [S] and [S] [m]$^{-1}$, respectively. The fraction of the total conductivity that is governed by the surfaces is given by the dimensionless *Dukhin number Du*, defined as

$$Du \equiv K^\sigma / a K^L. \tag{4}$$

The trend is that Du increases with decreasing electrolyte concentration.

In connection with our theme it makes sense to split K^σ and Du into two parts

$$Du = Du^d + Du^i = K^{\sigma d} / a k^L + K^{\sigma i} / a K^L \tag{5}$$

where the superscripts d and i stand for the diffuse and non-diffuse parts of the double layer, respectively. In connection with (3) we identify $K^{\sigma i}$ as the surface conductivity in the stagnant layer, which is the most interesting contribution of the sum

$$K^\sigma = K^{\sigma i} + K^{\sigma d}. \tag{6}$$

Figure 1 illustrates the phenomenon of surface conduction and the contributions of the diffuse and non-diffuse parts. In the diffuse part two ionic species contribute, their relative roles being determined by the transference number. Moreover, in this part the liquid as a whole can also move by electro-osmosis. In the stagnant layer counterions dominate; below we shall assume that co-ions are completely absent here. In this layer there is no electro-osmosis.

In electrokinetics surface conduction plays a dual role. (i) It helps to suppress polarization and (ii) depending on Du, it promotes or inhibits the concentration of the field lines of an external field, and hence it can affect the driving force for polarization. Factors (i) and (ii)

work out differently in different electrokinetic phenomena, and this is the basis for one of the experimental approaches to assess Du, and hence K^σ.

For $K^{\sigma d}$ theory is available which goes back to Bikerman [4, 5]. His result can be rewritten to become

$$K^{\sigma d} = \frac{2F^2 z^2 c}{RT\kappa} \left[D_+(e^{-zF\zeta/2RT} - 1)\left(1 + \frac{3m_+}{z^2}\right) + D_-(e^{zF\zeta/2RT} - 1)\left(1 + \frac{3m_-}{z^2}\right) \right] \qquad (7)$$

in which

$$m_\pm = \left(\frac{RT}{F}\right)^2 \frac{2\varepsilon_0 \varepsilon}{3\eta D_+} \qquad (8)$$

is a dimensionless parameter, indicating the relative contribution of electro-osmosis to $K^{\sigma d}$. For aqueous solutions at room temperature $m \approx 0.15$. Theories [2, 3, 6, 7] are all based on solution of the equations of motion in the double layer (with certain boundary conditions depending on the problem at hand) and hence automatically account for electro-osmosis and surface conduction in the diffuse part of the double layer. In fact, these theories contain expressions for Du^d. The diffusion constants D_+ and D_-, occurring in (7) and (8), are taken to be identical to those in the bulk, the argument being that the diffuse part is so far from the surface proper that the structural alterations of the adjacent liquid are not felt any more.

More recently, after the insight that $K^{\sigma i}$ is not negligible had been winning ground, theories for $K^{\sigma i}$ were also developed [8–10]. Modelling this quantity is more demanding than it is for $K^{\sigma d}$; among other things assumptions have to be made about numbers of ions in that layer ('adsorption isotherms'), their distributions and friction coefficients. Electro-osmosis does not occur in this layer because the liquid is stagnant. Below we shall present a simplified analysis, assuming that the stagnant layer contains only one type of ion (the counterion, subindex i) with only one tangential mobility, u_i^i. In that approximation simply

$$K^{\sigma i} = \sigma^i u_i^i. \qquad (9)$$

We shall use u_i^i as a dynamic characteristic of the adjacent liquid in the range where density oscillations occur. This defines our following steps:

(i) How can the total surface conductivity K^σ be measured?
(ii) How do we use (6) and (7) to establish u_i^i?
(iii) By how much does u_i^i differ from its bulk value u_i^L? As we shall show, over the past years much progress has been made in this line of investigation.

4. Measuring K^σ

A number of methods are nowadays available to establish K^σ. Five of these will be discussed.

(i) *From the radius dependence of streaming potentials in cylindrical pores.* This is the oldest approach, dating back to the 1930s. During those years it had not yet been established that ζ-potentials do not depend on the curvature of the surface (as long as $\kappa a \gg 1$). A good approximation (the so-called Helmholtz–Smoluchowski model) for the streaming potential is

$$E_{str} = \frac{\varepsilon_0 \varepsilon \zeta \Delta p}{\eta(K^L + 2K^\sigma/a)} = \frac{\varepsilon_0 \varepsilon \zeta \Delta p}{\eta K^L(1 + 2Du)}. \qquad (10)$$

The sum of the bulk and the surface conductivities appears in the denominator because the higher this sum is, the stronger the counterconduction, which tends to reduce the potential difference across the capillary. Du depends on the radius, and so does E_{str}.

In earlier measurements the necessity of including K^σ was not realized, leading to ζ-potentials that were a-dependent and too low. Once the role of surface conduction was recognized [11, 12], ζ was found to be insensitive to a. Moreover, K^σ could be established by performing measurements in capillaries differing only with respect to their radii: a plot of $\varepsilon_0 \varepsilon \Delta p / E_{str} \eta$ as a function of a^{-1} should give a straight line with intercept K^L/ζ and slope $2K^\sigma/\zeta$. This method is not very accurate.

Notwithstanding the lack of precision in the data, available around 1950, one thing became clear; for many systems K^σ (exp) appeared to exceed $K^{\sigma d}$. In some cases the difference is a factor of 10 or 100. Overbeek [13] summarized the data then available. At that time experiments were carried out only with glass or glasslike materials (quartz, silica), which may have porous surfaces. Nowadays we know that the phenomenon is more general and caused by the $K^{\sigma i}$ term in (6).

(ii) *From harmonization of ζ-potentials obtained by different techniques.* As ζ-potentials are characteristics for given charged surfaces under fixed conditions (pH, salt concentration, temperature etc) different electrokinetic methods, using the required interpretation, should result in identical ζ-values. In a number of cases, in which such different experiments were available, this was not observed. For instance, ζ-potentials obtained from electrophoresis or streaming potentials were systematically lower than those from dielectric spectroscopy, even if the advanced electrokinetic theories [2, 3] were used for the interpretation. However, although these theories do include surface conduction, they do so only in the diffuse part. Hence, K^σ is underestimated. It follows from the underlying techniques whether this underestimation leads to a lowering or an increase of the measured quantity, so it works through in different directions in different techniques. Kijlstra [14] realized that this difference could be used to obtain the proper K^σ-values as those for which the computed ζ-potentials are method independent. Essentially, in this approach $K^{\sigma i}$ acts as an adjustable parameter.

(iii) *Direct measurement from the conductivity of plugs.* This is a rather direct method, originally proposed and elaborated by Minor *et al* [15]. The conductivity K(plug) is measured as a function of the bulk conductivity K^L, which, in turn, is monitored by adjusting the electrolyte concentration. Except for the low K^L region, where salt exclusion from the plug by the Donnan mechanism counts, the relationship is linear. Extrapolation to $K^L \rightarrow 0$ gives rise to a non-zero intercept which is attributed to surface conduction. For a plug of volume fraction φ O'Brien and Perrins [16] derived

$$K(\text{plug}) = [1 + 3\varphi f(Du = 0)]K^L - \frac{6\varphi f(Du = 0)}{a} K^\sigma \tag{11}$$

for the linear part. The way in which the field lines and stream lines go from particle to particle is determined by the Dukhin number and quantified by the function f, given by the authors. Numerically, for close-packed dielectric spheres and $\kappa a \gg 1$ $f(Du = 0) = -0.4$. The equation is redundant, since the product $\varphi f(Du = 0)$ can be obtained both from the slope and from the intercept. In our experiments we took φ as an unknown, computed this quantity from (11) and found it to agree very well with its directly determined value. So there is an intrinsic control of the consistency of the equation possible, and eventually K^σ is obtained.

(iv) *From improved electrokinetic theories.* The standard theories [2, 3] can be extended to include conduction inside the stagnant layer. Essentially this requires re-writing these theories with differing boundary conditions. A number of such elaborations are now available, including work by Mangelsdorf and White [9, 10], Grosse *et al* [17], Rosen *et al* [8] and Barchini *et al* [18]. These theories differ with respect to assumptions about the

ion adsorption mechanisms in the inner layer. Barchini's work also involved experiments on dielectric spectroscopy of phospholipid vesicles and aimed at finding that pair of Du^i and Du^d values that optimally matched the experimental $\varepsilon(\omega)$ spectra.

(v) *From (the difference between the isoelectric and) isoconductive points*, for which the idea stems from Verbich *et al* [19]. The charge of a colloidal particle can be affected by changing the pH, the nature and concentration of electrolytes. By changing these variables, or one of these, a state an be reached where $\zeta = 0$, i.e. the *isoelectric point (i.e.p.)*. At the i.e.p. the surface charge is usually non-zero, so isoelectricity requires σ^i to be equal to $-\sigma^0$. Adding charged particles to an electrolyte solution of given composition and pH can either decrease or increase the conductivity, depending on the balance between the dielectric interior and the conductive outer shell. When these two contributions exactly balance each other the particles are said to be at their *isoconductive point (i.c.p.)*. Addition of such particles has no consequences for the conductivity of the system. From the i.c.p., K^σ can be evaluated; when the i.e.p. is also available u_i^i can be obtained. Note that at the i.e.p. $K^{\sigma d} = 0$, so that there $K = K^{\sigma i}$.

In conclusion, a variety of procedures is now available to obtain surface conductivities K^σ. In principle, $K^{\sigma d}$ can be subtracted, using (6)–(8), to find $K^{\sigma i}$. This subtraction is not entirely straightforward because computation of $K^{\sigma d}$ requires knowledge of ζ, which can only be obtained if surface conduction is duly accounted for, so some iteration or alternative procedures are required. We repeat the earlier finding that in many systems $K^{\sigma i} \gg K^{\sigma d}$; in those cases the procedure is reliable.

Having in this way established $K^{\sigma i}$, (9) can be used to find the tangential mobility u_i^i of counterions in the adjacent liquid layer.

5. Tangential mobilities in, and other properties of, stagnant liquid layers

We are now in a position to make an inventory of the electrokinetic information available for liquids adjacent to charged hard walls (i.e. for the thin hydrodynamically stagnant layers).

(1) Stagnant layers are observed both on hard hydrophilic surfaces (such as silica, quartz, inorganic metallic oxides) and on hard hydrophobic surfaces (silver iodide, polystyrene latices). This is in line with the earlier conclusion that we are dealing with a typical feature of liquids near hard surfaces rather than with a liquid–surface interaction phenomenon.

(2) For amphoteric surfaces stagnant layers are observed both on the positive and the negative side. It is logical to interpolate and conclude that they also exist at the point of zero charge, except that in that state electrokinetics cannot be invoked to prove its presence.

(3) No longer can electrokinetics be used to verify the presence of stagnant layers in apolar liquids adjacent to hard surfaces, because in such media the potential decay $d\psi/dz$ is too low to give rise to a measurable difference between ζ and ψ^0. However, in view of the foregoing there is no reason for assuming such layers to be absent in these systems.

(4) There is no reason for postulating stagnant layers at solid–vapour interfaces because at such boundaries the molecular stacking is not oscillatory but rather obeys a tanh-profile. Moreover electrokinetic experiments with unstabilized air bubbles are extremely difficult, and when the surfaces are stabilized by surfactants Marangoni-effects are created. However, the statement is confirmed by the absence of any surface-excess viscosity inferred from surface rheology and surface light scattering experiments.

The conclusion so far is that the existence of hydrodynamically stagnant layers is a real phenomenon, which has its roots in the (oscillatory) stacking of liquid molecules against a hard wall. What remains is the issue of tangential mobility of counterions embedded in it. In the

Table 1. Mobility ratios R between the tangential mobility of counterions in the stagnant layer u_i^i and the corresponding value in bulk, u_i^L. Different experimental methods and different ways of interpretation.

Surface	Counterion	R	Ref.
Silica (Stöber)	K^+	0.96	[21]
Silica (Monosphere-100)	K^+	0.7	[20]
Silica (Monosphere-1000)	Mg^{2+}	0.7	[20]
Haematite	Cl^-	0.7	[21]
Poly(styrene sulphate) latex	H^+, Li^+, Na^+, K^+	0.85	[22]
Poly(styrene sulphate) latex + adsorbed PEO	H^+, Li^+, Na^+, K^+	∼0.6	[23]
Bacterial cell walls	Na^+	0.2–0.5	[24]
Liposome vesicles	Na^+	∼1.0	[18]
Liposome vesicles	Cs^+	∼1.0	[19, 25]
Liposome vesicles	Ca^{2+}, Cd^{2+}, Cu^{2+}	∼0.6	[25]
Liposome vesicles	Ca^{2+}	∼0.8	[19, 25]
Liposome vesicles	La^{3+}	∼0.07	[19, 25]

previous section it was shown that this mobility can be substantial. To render this quantitative, in table 1 a survey is given of the R values, defined as

$$R \equiv u_i^i / u_i^L. \tag{12}$$

These data represent a variety of systems, studied by a variety of techniques and interpreted along different lines. Hence, we may consider these as representative. Accepting a certain spread in the data, the following is concluded.

(1) For monovalent counterions R is close to unity. When it is not, there are reasons to account for the lowering; the monospheres are porous, so that ions may follow a tortuous path; this is also the case when polymers (like PEO) are adsorbed, and in bacterial cell walls. On haematite Cl^- ions bind specifically, impeding lateral motion.
(2) At given counterion valency there is no ion specificity. Even the proton has the same R as the alkali ions, although it is well known that the conduction mechanism of this ion is quite different.
(3) For bivalent counterions R is about two-thirds the value for $z = 1$.
(4) For the trivalent counterion La^{3+} $R \ll 1$.

The near-unity of R for monovalent counterions poses a quandary of sorts. It sounds like an absurdity that ions can move freely in a water layer that is phenomenologically 'frozen'. However, on closer reflection similar examples may be found. For instance, in three-dimensional gelatin gels the water is fully immobilized, although ions can diffuse in them virtually unimpeded. In this respect, stagnant layers behave like two-dimensional gels. In fact, the self-diffusion of water in such gels is not that much slower than in bulk water.

The distinction we are facing here is that ion movement is self-motion of individual charged particles, whereas in shear the viscosity reflects the *collective* motion of large collections of molecules.

Understanding of these phenomena on a molecular level has benefited from molecular dynamics (MD) simulations [26]. Although these simulations are still in progress, the first results confirm the picture developed above. The fact that, at least for monovalent counterions $R \approx 1$ is shown to result from short-circuiting of tangential motion in the stagnant layer via the diffuse part. So, some of the time bound counterions reside in a double layer part where they can move at bulk rates. For bivalent counterions jumps of the first layer may be more

difficult because the activation energy is larger; this may explain their lower R-value. At present we are studying this feature systematically by MD. Simulations also account for the difference between individual and collective tangential mobility. For the solvent the viscosity in the stagnant layer can be computed from

$$\eta = \frac{V}{kT} \int_0^\infty \langle \tau_{\alpha\beta}(t) - \tau_{\alpha\beta}(0) \rangle \, \mathrm{d}t \tag{13}$$

where the $\tau_{\alpha\beta}$ are pressure tensor components (α and β are two Cartesian components (x, y, z)). If from this viscosity (which is anisotropic) the tangential velocity of adjacent water molecules is computed, a value is found that is orders of magnitude lower than in bulk. So, in this way, a molecular footing is achieved for the notion of stagnancy in electrokinetics.

6. Conclusions

Interfacial regions between liquids and hard solids act as crossroads between liquid structure and electrokinetics. The region where the molecular density exhibits oscillations coincides with the layer that in electrokinetics is familiar as the 'stagnant' layer. Such layers contain a large fraction of the countercharge when the interfaces carry an electric double layer. Analysis of conduction in these layers therefore helps to clarify basic dynamic issues.

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