Slip and friction of liquid flow over solid surfaces
On the validity of the no slip condition in hydrodynamic systems
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1 Slip and friction in liquid flow over solid surfaces

When a solid body slides over the horizontal surface of another, a force must be applied in order to maintain the motion. The reaction force, which seems to put a brake on the sliding motion, is found to be proportional to the normal force, i.e. the weight, of the sliding body. The ratio of these two forces appears to be more or less constant and equal to $\mu$, the coefficient of friction. Friction is an almost universal fact of life and a complicated physical phenomenon. In fact, for a long time, it has been one of the most important problems in physics from a practical point of view. Only in the USA, friction has an estimated cost of about 6% of the American gross national product, i.e. about $420 billion annually. Friction, by creating heat, is decreasing the efficiency of processes and creates surface damages, i.e. wear, leading to a shorter lifetime of equipment. However, friction is not just a nuisance. We indeed need it to play the violin or drive a car. So, in some cases, one wants to maximize the friction rather than to minimize it.

Three experimental observations summarize the properties of the friction coefficient [1].

1. The friction coefficient is independent of the load (Amonton’s first law).

2. The friction coefficient is independent of the apparent contact area (Amonton’s second law).

3. The friction coefficient is independent of the sliding velocity (Coulomb’s law).

But these laws are not fundamental laws of physics. The friction coefficient is found to depend, among other parameters, on the surface roughness of the materials, on the contact area of the microscopic asperities of the sliding surfaces and on the interaction between the atoms or the molecules of the materials. If the two solids do adhere to each other by some kind of surface forces, there will be a finite additional friction force. Even in microgravity conditions, friction between sliding body remains, i.e. in the absence of a weight. The friction force at the sliding surface is then described by a combination of
ordinary friction and a term $F_0$, which is describing the interfacial properties to resist to
the applied external forces, e.g. by deformation (see fig. 1.1.a, page 7). The total force $F$
becomes

$$F = \mu(N_0 + N) = F_0 + \mu N \quad (1.1)$$

$F_0$ is a constant force, arising from the attractive van der Waals interactions between
the two surfaces. $N$ is the normal force (load) and $\mu$ the friction coefficient.

What is fundamental about the friction phenomenon is the dissipation of adhesion
energy at the sliding surface and the dissipation of kinetic energy at the surface of the
sliding body. These energy losses are evidenced at the sliding surface by an increase in
temperature: heat is released to the environment. The dissipation of energy in a natural
process is a consequence of thermodynamics’ Second Law.

The necessity of considering dissipation mechanisms in friction models was already
pointed out by Leslie [2] in 1804. Without dissipation the relative motion of the sliding
bodies should continue indefinitely, as a consequence from Newton’s laws of frictionless
motion. Following up on this idea Tomlinson [3] in 1929 suggested a kinetic model for
the dissipation in a sliding contact. Particles, coupled by springs, which represent the
chemical bonds in the solid, collide at the sliding surface and dissipate the directional
impulse during the collision into the random molecular vibrations of the lattice atoms.

Lord Rayleigh [4] at the end of the 19th century effectively introduced the concept
of a dissipation function $\Phi$ in the description of flow in viscous fluids. In an analogy
with friction of sliding solids he assumed friction between infinitesimally thin layers of a
viscous fluid with different velocities. Integrating over experimental laminar flow patterns,
he discovered that all the characteristic velocity profiles in steady flows, for example the
well-known Poiseuille profile for a flow between solid surfaces, represent an optimum in
$\Phi$. The velocity patterns in steady viscous flow have the smallest possible internal energy
dissipation that is compatible with the boundary conditions in the system. Rayleigh’s
result of minimum dissipation is an early example of the thermodynamical principle of
minimum entropy production. This theorem is the general principle that describes the
steady states of natural processes. In its modern form it was formulated by Prigogine
[5]. In this thesis we shall consider dissipation phenomena and entropy production in this
thermodynamic fashion. That opens the opportunity for a comprehensive description
of the mechanism in dissipative processes like friction and flow. The thermodynamics
of irreversible processes also suggests that friction can be coupled with other transport
phenomena in the same system.

Natural processes follow the principle of minimum entropy production. Liquid flows
and electrical currents, indicated as fluxes “$J$” in the equation 1.2, are good examples.
The fluxes are driven by well-defined forces $X$ like pressure gradients and applied elec-
tric potentials. Dissipative processes and the relations between them are quantitatively
described in sets of phenomenological equations,

\[
\begin{align*}
J_1 &= L_{11}X_1 + L_{12}X_2 + ... \\
J_2 &= L_{21}X_1 + L_{22}X_2 + ... \\
J_3 &= ......etc
\end{align*}
\]  

(1.2)

In small deviations from equilibrium it can be proven that the conductivity coefficients
$L$ will be independent of the driving force $X$ (the linear case). The dimensions of the
individual fluxes $J_i$ and of the corresponding driving forces $X_i$ are chosen in such a way
that the products $J_iX_i$ have the dimension of an entropy production $dS/dt$. Then, the
total entropy production for the set of coupled dissipative processes in a system will be
the sum of the terms $J_iX_i$ in the set of the phenomenological equations. With constant
boundary conditions for the flow process, a steady state is achieved, which consists of the
coupled processes giving minimum total entropy production. In every steady state, $dS/dt$
must be at the minimum for the imposed boundary conditions on $J$ or $X$.

The diagonal coupling coefficients $L_{ii}$ in the phenomenological equations are material
properties. They represent the observed conductivities, for heat flow like in Fourier’s law,
for electric current like in Ohm’s law... Cross-coefficients $L_{ij}$ describe the phenomena
because of coupled processes. An example is electro-osmosis where an applied electrical
potential $X_j$ causes a liquid flow $J_i$, in addition to the expected electric current $J_j$. Of
course, this coupled process contributes to the overall entropy production. If we should ignore coupled hydrodynamic (electroosmotic) flow \( J_i \) it seems that the extra contribution of a term \( L_{ij} X_j \) adds to the conductivity of the liquid in the porous system, but this is, in fact, an oversight. The fundamental symmetry between cross-coefficients is expressed by the Onsager’s reciprocal relations [6], \( L_{ij} = L_{ji} \), which appear in experiments as a universal law for coupled flux/forces combinations.

Together with the required minimum entropy production, the reciprocal relations describe the natural responses of a system to externally applied forces or fluxes. They indicate the power dissipation in the individual mechanisms, which contribute to the fluxes in the overall process. The system itself is always characterized by its material properties, summarized in the conductivity coefficients \( L \).

We shall concentrate in this thesis on the dissipative processes in a flowing viscous liquid, which moves over a solid surface because of an applied pressure gradient. In addition to the internal friction within the fluid as the origin of dissipation in a Poiseuille pattern, friction at the solid liquid interface could also exist. This dissipation mechanism could then be described with a friction coefficient \( \mu \) for the liquid material, which is sheared over the interface by the drag force of the flowing fluid. In principle, the two dissipation effects, in the fluid and at the interface, are additive. They are contained in the overall conductivity \( L \) and thus in the entropy production of the flow. However, the possibility of slip along the interface is often neglected in hydrodynamic models. Without further argumentation, a no slip boundary condition at the solid-liquid interface, i.e. infinite friction, is then assumed at the solid boundary. This no slip condition was originally introduced by Stokes [7] as a description of solid-liquid boundaries in the mathematical solution of the Navier-Stokes equation, for a flow velocity \( \vec{v} \) in a liquid of density \( \rho \) under the influence of applied stresses \( \vec{\tau} \) and exchange of impulse \( \vec{\Psi} \) between the elements of the liquid.

\[
\rho \frac{D\vec{v}}{Dt} = \nabla \cdot \vec{\tau} + \rho \nabla \cdot \vec{\Psi}
\]  

(1.3)

With such a boundary condition, he could obtain the Poiseuille velocity pattern. This
velocity profile gives, as Lord Rayleigh discovered for the linearised regime, the smallest entropy dissipation for a given flow rate. Allowing slip at the interface implies an extra possibility for friction and dissipative losses in the system. The combination of a Poiseuille flow in the bulk and slip at the interface could, mathematically, result in a smaller overall dissipation compared to the amount of lost work when the total flux was either a plug flow or a pure Poiseuille flow. Then, the expected response would be a combined profile of liquid velocities that gives minimum entropy production. Slip at the solid-liquid interface, i.e. a plug flow in addition to a parabolic Poiseuille profile, has the effect of smaller velocity gradients in the bulk. In a capillary tube, such a flux would still be proportional with the applied driving force but, overall, it would be larger than expected for viscous flow without slip at the solid boundaries.

From a chemical engineering point of view, slip is nothing but a mechanical transport mechanism along an interface. This mechanism can be affected by the chemical constitution of the fluid, with additives, which adsorb in the interface. Considering that the mobility of these molecules in these adsorbed layers allows interfacial motion, Timmerman [8] developed a Dynamic Detergency Model. She suggested that detergent action in laundering must be explained from the nano-mechanical motion of adsorbed layers, which are dragged over the interface by the shear of the flowing liquid.

More often, however, friction at the interface is not wanted. Small friction coefficients are desirable in order to reduce wear at a given sliding velocity. Lubricants are indeed used for that purpose in many technological processes. The deliberate use of such additives aims to reduce the overall dissipation, lower the friction and obtain more flux, $J$, for the imposed value (a boundary condition!) of the driving force $X$. Lubricants can lower the friction and the wear of two sliding bodies by redistributing fractions of the dissipative process between the bulk of materials and an interfacial mechanism. In this way, they alter the total flow conductivity $L_{11}$.

In practice, all surfaces are covered by layers of oxide or grease. The bare surface layer may occasionally have a similar influence on sliding friction as a deliberately added
surfactant. It might be interesting to note that most sliding contacts are, therefore, lubricated anyway.

Let us ask why should a viscous oil be a good lubricant? At first sight the higher viscosity of the oil would give more dissipation - upon shearing the emulsion between solid surfaces. It would indeed, but that is not the point. The higher viscosity prevents the oil to be squeezed out from between the two surfaces. Without the oil film present, there would be a direct contact between the two surfaces. The viscous liquid layers prevent this. In such a lubricated contact, the solid surfaces will remain separated by a relatively thick layer of liquid. All the motion and consequently all the dissipation during the approach of solid surfaces will occur inside this layer. That sort of a lubrication regime is called hydrodynamic lubrication.

Flow patterns in this regime were described by Trijssenaar in her study [9] to explain emulsion lubrication for the cold rolling of steel. Indeed, all the motion, the flow patterns and the dissipation are inside the lubricant liquid. In such an oil in water emulsion, the flow will concentrate the emulsion drops near the shearing interfaces. As a result the overall dissipation is reduced with the help of the dissipative flow patterns in the lubricant, the surface being covered by an almost pure layer of oil.

On the other hand, if the viscosity of the lubricant emulsion is too low for the rate of sliding, this protective mechanism will break down. Instead of being dragged into the narrow contact, the fluid is squeezed out and direct contact is occurring between the two surfaces. This second regime is an example of boundary lubrication. It is characterized by a much higher sliding friction that remains almost independent of the shear velocity. The figure 1.1b is illustrating these two types of lubrication.
Within the hydrodynamic lubrication regime, friction forces can be calculated from the Navier-Stokes equation, that is, by calculating the dissipation in the liquid that is sheared between the two surfaces. This type of lubrication is nowadays fairly well understood. In contrast, the role of additives - which is essential in boundary lubrication - is very difficult to analyze. In this regime, the rate of dissipation involves processes like slip, directly at the shearing interface, in which direct interactions between the solids and the adsorbed molecules of lubricant are of greatest importance. It is these layers of lubricant that can introduce the very special slip effects at solid/liquid interfaces under shear, which are found with detergent action and with other dynamic properties of surfactants.

Although the work in this thesis was originally aimed at a better understanding of the surfactant properties, which are relevant in the Dynamic Detergency Model, we do not want the work to be restricted to this particular application. Combining the thermodynamics of liquid flow, and allowing lubrication by interfacial processes, we aim for results of a more general interest. We shall discuss lubrication and demonstrate why added lubricants can be applied to relax the no slip boundary condition for viscous liquid flow over a solid surface. Thermodynamic driving forces will create slip in such a dynamic system, even in a solid/liquid interface, and in any case where the slip effect reduces the total amount of dissipated energy, i.e. lost work, during the process. It will be a specific
aspect of the dynamics of motion that should be taken into account.

Mathematically, slip at solid interfaces has been described by means of a "slip length" \( \lambda \). The idea is that, because of the slip, the diameter of a capillary "seems" wider than it really is. More of the viscous liquid flows through a restriction than would, without the slip effect, correspond to the applied hydrostatic pressure gradient. The difference between the real radius \( R \) of a capillary, and its effective hydrodynamic radius \((R + \lambda)\) by definition), is the slip length. In this model the dissipation that is, in reality, caused by slip in the interface, is attributed to an excess internal friction inside a virtual, extra layer of the viscous fluid of thickness \( \lambda \).

We have studied the nature of slip effects both theoretically and in experiments with different lubricated model systems. We also have investigated how the liquid flow in a capillary couples with other fluxes, like with electrical currents, and how this coupling can affect the slip length in such systems. The outcome demonstrates the importance of specific surface effects in lubricated flows. It also suggests new measuring methods for their quantitative determination and how apparatus can be designed for that purpose.

Our model for friction does account for the experimentally observed properties of the slip length in thermodynamic terms. That is a step forward. It illustrates the importance of slip, friction and lubrication as dissipative mechanisms in the flow of viscous liquids over solid surfaces.

References


2 Slip phenomena and entropy production

The entropy production in a flow is obtained by adding the products of the different fluxes in the system multiplied with their corresponding driving forces. In the simple case of a purely Newtonian liquid flow $J_1$ the relevant driving force $X_1$ is the pressure gradient in the fluid. The conductivity $L_{11}$ is determined by several factors: the geometry of the system, e.g. flow through in a narrow cylindrical pore, the flow regime (laminar at low Reynolds numbers, which is implicitly the case in small pores), and the viscosity $\eta$ of the liquid. In a steady state flow, the work done by the applied external forces, e.g. by the pressure gradient, is completely dissipated by the friction forces in the liquid and at the capillary walls. The flow conductivity $L_{11}$ describes, through the phenomenological equations (see equation 1.2), how the total flux depends on the externally applied force $X_1$. Internal friction in a viscous liquid and interfacial friction at a capillary wall are separate contributions to the dissipation in the flow. Their respective effects $L_{11a}$ and $L_{11b}$ add up to the effective conductivity $L_{11} = L_{11a} + L_{11b}$.

The cause of the internal energy dissipation inside the liquid is the momentum exchange $\vec{v} \cdot \vec{\Psi}$ between liquid elements with different velocities. For energy dissipation at a solid surface the molecules in the liquid must move relative to the wall, which is thought to be an immovable elastic solid. For dissipation by friction at solid-liquid interfaces there must be enough mobility of these molecules to give an observable effect on the conductivity $L_{11}$. In that case, the liquid must move in the interface with a finite slip velocity.

In physics, thermodynamic and molecular considerations of this type are normally lumped together in the friction coefficient $\mu$. One might describe $\mu$ as some sort of 2D interfacial viscosity or, for a chemical audience, as the parameter that accounts for the intermolecular interactions between the liquid and the wall material. Such views imply fundamental aspects in $\mu$. But these underlying fundamentals are always obscured by important variables, like the presence of irregular asperities in any real interface. Only in a perfectly flat interface the friction factor $\mu$ and the corresponding intrinsic friction force
F could be completely determined by the intermolecular interaction, eq. 1.1, and not by other factors.

2.1 A direct observation on slip flow

Tolstoi [1] and also Churaev [2] have investigated slip at solid-liquid interfaces. With different liquids, such as water and mercury, Churaev measured the dependence of the flux through narrow capillaries on the applied pressures. Some of the liquids, like water, would wet the internal interface with a glass capillary. Others, like mercury, would not. For all the liquids in his experiment Churaev knew the viscosity \( \eta \) under the experimental conditions. And his objective was to study whether wetting affects the flow conductivity \( L_{11} \) in a capillary.

Using the capillaries as viscometers, Churaev made the assumption that wetting liquids would stream through a capillary in a Poiseuille flow. By assuming this, he implicitly introduced the no-slip condition for these combinations of wetting materials and neglected the possibility of dissipation in the solid-liquid interface. Without further complications the diameter of the capillaries can then be calibrated for wetting fluids of known viscosity. Using this as the experimental capillary diameter, and always assuming the no-slip condition at the capillary walls, it should be possible to predict the flux of any liquid, wetting or non-wetting, at a given pressure gradient. But with the non-wetting liquids, Churaev’s experimental observations suggested a discrepancy between results and expectations. Fluxes of non-wetting liquid through the calibrated capillaries would always be larger than expected. In the phenomenological equations one would find \( L_{11} > L_{11a} \).

The conductivity for non-wetting liquids of well known viscosity in a capillary viscometer is always larger than the predicted value for a Poiseuille flow. The magnitude of the neglected friction term \( L_{11b} \) is not an inherent property of the liquid. It depends on wettability of the capillary walls, i.e. on the strength of the interactions between molecules of the liquid and of the capillary walls. That was what he observed.

Churaev [2] explained this in terms of variable density profiles in liquids near the
interfaces because of the "wetting" interactions. The "rarefied" liquid in a non-wetting
interface would have a smaller shear viscosity. This would allow the flow to apparently slip
over the capillary walls, the rarefied layer acting as a lubricant with properties different
from the viscous fluid. Later on, we shall call such a flow, in which internal dissipation is
combined with friction at the interfaces, a flow regime with surface response.

The model of a slip length $\lambda$, which describes the slip effect in liquid flow, had already
been formulated and applied by Tolstoi [1] to this kind of problem. Churaev [2] and de
Gennes [3] used it in a modified form to account for their observations. Of course, the
model had to account for the total dissipation that is measured in the system. It does so
by adding up the internal viscous dissipation with the interfacial friction.

The slip effect is the wall shear stress exerted by the surface flow velocity $v_S$.

$$\tau_w = \mu v_S$$

(2.1)

$\mu$ is the friction coefficient. It relates the stress $\tau_w$ to the slip velocity.

By continuity, in every fluid element, the stress must be equal to the stress, which is
exerted by the flow of liquid. Therefore, $\tau_w$ can be written,

$$\tau_w = \eta_0 \left. \frac{\partial v}{\partial r} \right|_{r=R}$$

(2.2)

for the stress in the solid liquid interface at $r = R$.

In the formalism of a "slip length", Tolstoi introduced the notion of an "apparent"
layer of the viscous liquid with a thickness $\lambda$ at $r > R$. The virtual flow in this thin liquid
layer produces the extra dissipation, which is observed because of the slip between the
real liquid and the real capillary wall. The amount of internal dissipation in this outer
layer of liquid is relatively large, because the velocity gradients of the Poiseuille profile
are the steepest in this region.

The fluid, subject to a pressure gradient $-\partial p/\partial z$ in a capillary of radius $R$, will develop
a velocity profile $v(r)$. The profile is obtained by integrating eq.2.2 and using eq.2.1 for
boundary conditions.

$$v(r) = -\frac{\partial p}{\partial z} \frac{1}{4\eta_0} \left( R^2 - r^2 + \frac{2\eta_0 R}{\mu} \right)$$

(2.3)
Assuming a zero velocity at \( r = R + \lambda \), instead of a slip velocity, one finds

\[ \lambda = \frac{\eta_0}{\mu} - \frac{\lambda^2}{2R} \approx \frac{\eta_0}{\mu} \]  

(2.4)

If the steep, parabolic velocity profile is linearized between \( R \) and \( R + \lambda \) under the assumption that \( \lambda \ll R \), we do obtain the expression 2.4.

The outcome of eq.2.4 shows that the slip length should, in fact, be interpreted differently: it represents the ratio of two dissipative quantities \( \mu \) and \( \eta \), which are properties of the chosen materials in the experimental system.

Inserting eq.2.4 into eq.2.3 and integrating over the radius, the total flow rates becomes,

\[ J = \frac{\pi R^4}{8\eta_0} \left( 1 + \frac{4\lambda}{R} \right) \frac{-\partial p}{\partial z} \]

(2.5)

In a capillary of radius \( R \), a Poiseuille profile without slip adds up with the slip velocity of the liquid relative to the solid pore walls. The total flux is a superposition of a Poiseuille flow in the bulk of the viscous liquid and a plug flow with friction at the pore walls. With increasing radius, i.e. with \( \lambda \ll R \), the slip contribution is becoming more and more difficult to observe separately, because the ratio \( 4\lambda/R \) in eq.2.5 tends towards zero.

Let us now consider the dissipation for a pure Poiseuille flow, with no-slip boundary condition, and for an ideal plug flow, with slip at the solid surface. In steady state conditions the dissipation in the Poiseuille mode (in \( Jm^{-1}K^{-1} \)) is:

\[ \frac{\sigma_P}{z} = \frac{\pi R^4}{8\eta_0} \left( -\frac{\partial p}{\partial z} \right)^2 = \frac{J^2_P}{L_{11,P}} \]

(2.6)

whereas it is,

\[ \frac{\sigma_{PF}}{z} = \frac{\pi R^3}{2\mu} \left( -\frac{\partial p}{\partial z} \right)^2 = \frac{J^2_{PF}}{L_{11,PF}} \]

(2.7)

for a pure plug flow without velocity gradients in the liquid.

In both these expressions \( z \) is the length of the capillary and \( L_{11} \), the coefficient that were introduced in the phenomenological equations 1.1. Depending of the values of \( \mu \) and \( \eta \), the flow can be Poiseuille flow or lubricated slip, following the regime that yields to minimum entropy production.
Now let us consider the equations 2.6 and 2.7 and investigate which of the two describes the larger effect. The ratio of the entropy productions for a given flow for the Poiseuille profile over the plug flow profile gives the dimensionless quantity,

\[
\frac{\sigma_P}{\sigma_{PF}} = \frac{L_{11,PF}}{L_{11,P}} = \frac{4\eta_0}{R^* \mu} = \frac{R^*}{R}
\]

In other words, there exists a capillary radius \( R^* = \frac{4\eta_0}{\mu} \approx 4\lambda \) where the entropy production of a Poiseuille flow, eq.2.5, and of a plug flow, eq.2.6, are the same for a simple flow. In capillaries with \( R > R^* \), the preferred flow mode will be the Poiseuille flow profile. In narrower capillaries, i.e. \( R < R^* \), as encountered in colloids or nanotechnological applications, a pure plug flow will be the predominant mode (see Appendix A for further details).

In Churaev’s investigations, the values for \( L, R \) and \( T \) were experimentally fixed. The variables \( \mu \) and \( \eta \) depended on the chosen liquids and capillaries. Based on these variables and on the applied pressure, the profile having the smaller entropy production should become predominant in the flow through the capillary, provided that \( z/R \) is large enough.

With a non-wetting liquid, the effective 2D viscosity near the interface was low. In these systems \( \mu \) is then relatively small compared to the corresponding viscosity \( \eta \) of the liquid. This parameter combination should cause considerable slip, in relatively wide capillaries. With wetting liquid, it is generally accepted that the flow will obey the no-slip condition. The intermolecular interactions between the liquid and the wall are comparable to those inside the liquid itself for a wetting interface. This is the accepted explanation for wetting in general. The value of \( \mu \) is high with wetting fluids and then it is difficult to move the liquid in the interface. Interaction between the fluid and the solid surface gives a smaller value for the apparent radius \( R \) with the same liquid viscosities. In such situation, slip in a liquid without a lubricant can only be observed with very small radii.

The concept of a critical radius \( R^* \) is based purely on thermodynamic considerations. In the next chapters, in a Newtonian spirit, we specifically address slip in relation to surface forces for a given flow geometry. In eq.2.1, slip is a function of the wall shear
stress, which varies only with the pressure gradient or with the capillary radius. It is important to realize that $R^*$ is a reference length, which compares the advantages of a real Poiseuille flow with an ideal plug flow in terms of the magnitude of the dissipation. As such, $R^*$ is a valuable indicator length scale in experiments on the observation of slip.

In experimental situations, with determining materials properties $\eta$ and $\mu$, viscous flow will choose the mechanism presenting the smallest dissipation. But the optimum is when plug flow and Poiseuille flow are superimposed. This is a regime that differs from the two simple flow profiles that are compared in $R^*$. We shall refer to this combined flow mode as the "surface response regime". The net flow in this regime is larger than pure Poiseuille flow at the same applied pressure, because the dissipation of the kinetic energy is less.

Should one assume, instead, that there must always be a pure Poiseuille flow, without slip, then this assumption makes the capillary radius seem larger. The extra width is the slip length $\lambda$. Dissipation due to the friction in the interface is then accounted for as internal friction in the hypothetical velocity gradients, which are projected out of the real velocity profile in the liquid into the virtual flow profile between $R$ and $R + \lambda$.

![Figure 2.1: flow profile in presence of slip. The apparent extra flow from the Poiseuille law with stick boundaries is quantified using an experimental parameter $\lambda$.](image)
This flow mode is characterized by smaller velocity gradients compared to the Poiseuille pattern up to the capillary of radius R and, at the wall, a slip velocity. This sliding velocity \( v_s \) and the friction coefficient produce the equivalent amount of dissipation as the velocity gradients would give in the viscous liquid when it would fill a wider capillary radius extending between \( r = R \) and \( r = R + \lambda \). In the total conductivity slip flow and Poiseuille flow have their own contribution (\( L_{11a} \) and \( L_{11b} \) respectively). The fluxes add up to a total, which exceeds either of the two "pure" flow regimes.

2.2 Slip as surface excess mobility and its role in interfacial rheology

Rheology is the experimental branch of science that studies dissipation. For internal friction, the viscosity of a liquid is measured by shearing a fluid sample and recording the resulting stress. Rheologists study the properties of a liquid medium and they usually neglect the interfacial region effects, which are of interest in this thesis. They choose geometries in their measuring equipment so that bulk effects are predominant.

In practice, an interface has a thickness and in this volume, comprised between the liquid and the solid bulk phases, the properties are gradually changing as travelling from one phase to the other. Scientists, like Slattery [4], have attempted to directly characterize the rheological properties of the interfacial region by designing interfacial rheometers. In such equipment, the interface is directly stressed by a solid mobile component. Liquid-liquid and liquid-air interfaces can then be characterized. With such mobile interfaces, the measuring position is realized with force sensors. This calibration technique is allowed because the solid stressing device can penetrate the two bulk phases. This is not the case at solid-liquid interfaces. For that reason, a description in term of excess quantities is an ingenuous idea.

In discussions on slip at the solid-liquid interface, it can implicitly be assumed that there is some sort of Gibbs’ dividing plane, located at the pore surface. All the bulk properties of the liquid and the solid are retained up to the surface. All deviations will
then be attributed to mobility and friction in this plane. Using a momentum balance, Tolstoi introduced the idea of a slip length to describe the excess of interfacial dissipation. The whole dissipation can then be accounted for by an overall conductivity $L_{xx}$ split in two components: one for the bulk and the other for dividing plane.

In what follows, we take one step backward. Instead of describing the interfacial region with excess quantities condensed into one plane, we will discuss the molecular structure of the interfacial region in its microscopic detail. The slip length will then be linked with the viscous properties of this region. In that perspective, the excess of momentum, which is quantified by an "interfacial viscosity", is now distributed in a given molecular volume. The description of the viscosity profile in this region by a continuous function should again lead to one single observable phenomenological coefficient $L_{xx}$.

Viscoelastic materials are often encountered in interfaces, e.g. with adsorbed layers of surfactants or with proteins. But, before presenting our experimental approach to deal with such chemically defined solid-liquid interfaces, let’s first describe a methodology that can be applied with liquid-liquid or liquid-air interfaces to measure the rheological data when such a layer is present.

In the real world, the interfacial region is a 3D volume, comprised between two bulk phases. The rheological quantities of interest are constants in the bulk phases. But a gradual change of these properties is expected upon approaching the interface. The profiles of change are totally unknown. Gibbs [5] did postulate that the interface is a two-dimensional plane and assigned all surface properties, which differs from those in the bulk as excess properties to that plane.

Following up on this idea, Boussinesq [6] derived an expression which does relate the stress to the strain rate in an interface. Scriven [7] combined the rheological properties of the interface into a two dimensional Navier-Stokes equation, which gave a constitutive equation [8], [9].

$$\tau^{(s)} = \sigma \vec{I}_s + \vec{S}^s = \left[ \sigma + (\kappa^s - \eta^s) \nabla_s \cdot \vec{v}^s \right] \vec{I}_s + \eta^s \vec{D}^s$$

(2.9)
where $\kappa$ and $\eta$ are respectively the dilatational and the shear viscosity. $\nabla_s$ is the surface gradient and $v^s$ the surface velocity. $\vec{D}^s = \vec{\nabla}_s v^s \cdot \vec{I}_s + \vec{I}_s \cdot (\vec{\nabla}_s v^s)^T$ is the surface interfacial rate of deformation tensor. $\sigma$ is the 2 dimensional thermodynamic tension that can be defined under special circumstances as the interfacial tension.

This equation is the two-dimensional analogue of the constitutive equation for bulk fluid, $\sigma I_s$ and $S^s$ being respectively the two dimensional stress tensor and the extra viscous stress tensor.

After having defined a constitutive equation for the interface, this region must be coupled with the adjacent bulk phases. This is usually done by considering the Boussinesq number:

$$Bo = \frac{\eta_s}{\eta_{\text{bulk}} R}$$

In $Bo$, the parameter $R$ has the dimension of a length. It is a characteristic distance of the flow geometry like the radius of a capillary. $Bo$ characterizes the ratio of the interfacial viscosity $\eta_s$ over the bulk viscosity $\eta$ [10].

At this point, we may introduce this concept into $\Phi$, the dissipation function in a flowing liquid at an interface, as was studied by Lord Rayleigh. At high Boussinesq numbers, most of the dissipation is occurring in the interfacial flow. In that case, the rest of the dissipation, in the two adjacent bulk phases, becomes negligible. In fact, the interface is now treated as an isolated two-dimensional fluid. Such an interface can still exchange heat and momentum with the bulk phases but it is kept in equilibrium with the bulk volumes by these transport phenomena. The entropy production $dS/dt$ in these transport processes is then equal to the entropy, which is produced by the friction in the interface.

### 2.3 Interfaces and slip length at constant stress

In the three-dimensional model for an interface there is a profile of mechanical properties, which relates the concept of a slip length $\lambda$ to the reduced interfacial viscosity $\eta_s$. In that
respect, the bulk flow field still extends to the solid boundaries. A second flow field $v^{ex}$, which describes the interfacial flow influence, is superimposed.

Throughout this thesis, apparent slip velocities were determined without any assumption on the presence of substances in the interfacial region. We are now specifically addressing this point and consider "lubricated slip" in adsorbed layers of surfactants or proteins that are adsorbed at the solid surface, and not "true slip" where molecules of a pure liquid are sliding over the solid surface. The 3D interfacial region is now, chemically, defined by its unique properties as an adsorption layer. We shall assume that the no-slip condition can be applied at the borders of this surface layer with both bulk phases. All slip phenomena will occur inside the thin interfacial region with the special chemical composition that is fixed by an adsorption equilibrium between the interfacial region and the bulk phases.

Assuming a Newtonian bulk fluid of viscosity $\eta_0$, the flow properties are perfectly known everywhere within a straight cylindrical pipe of length $z$ and radius $R$. We will now consider slip as a Gibbs interfacial excess flow. Due to the presence of an adsorbed layer of thickness $\delta$, variations in viscosity and hence, in velocity, are expected at the interface. We can explicitly consider such deviations in the velocity field as,

$$v(r) = \overline{v}_0(r) + \overline{v}^{ex}(r)$$ (2.11)

where $\overline{v}_0$ is the bulk flow field found using the no-slip condition and $\overline{v}^{ex}$, an excess velocity field that describes deviations from this behavior.

From the Navier-Stokes equation for the bulk phases, one can express the field derivative of the excess velocity field $\partial v^{ex}/dr$ by substituting $\overline{v}(r)$ from eq.2.11,

$$\frac{\partial v^{ex}}{\partial r} = \frac{-r}{2} \left( \frac{1}{\eta(r)} - \frac{1}{\eta_0} \right) \frac{-\partial p}{\partial z}$$ (2.12)

In this expression, $\eta(r)$ is an effective viscosity, which includes the net effects of the interfacial properties. This viscosity $\eta$ is thus describing local deviations and accordingly, it is position dependent. Far from the interface, $\eta(r)$ tends towards the bulk viscosity, $\eta_0$, and the local flow profiles will then correspond to those in the Newtonian flow. Integrating
2.12 between 0 and \( r \) yields

\[
v_{ex}(r) = \int_0^r \frac{-r}{2} \left( \frac{1}{\eta (r)} - \frac{1}{\eta_0} \right) dr \frac{-\partial p}{\partial z} + v_{ex}(0) = I(r) \frac{-\partial p}{\partial z} + v_{ex}(0)
\]  

(2.13)

This brings out \( v_{ex}(0) \) as the slip velocity. By applying the no-slip boundary condition \( v(R) = v_0(R) = v_{ex}(r) = 0 \) for the flow field, \( v_{ex}(0) \) is given by

\[
v_{ex}(0) = -I(R) \frac{-\partial p}{\partial z}
\]  

(2.14)

The function \( I \) is dependent on the interfacial rheological properties. Far from the interface, the excess velocity is becoming constant, its derivative being zero. The total velocity field can be represented as shown schematically in figure 2.2.

Figure 2.2: Velocity profile for a Poiseuille flow and a excess flow. Far from the interface, the viscosity is equal to the expected bulk viscosity and the function \( I(r) \) is zero. The apparent slip velocity is then equal to \( I(R) \) up to the centerline times the pressure gradient. Within the interfacial region, precise knowledge of the function \( I(r) \) is required to express the velocity field explicitly. This unknown velocity profile within the interface is expressed on the graph with a question mark.

By substituting eq.2.13 into eq.2.11 and integrating by parts, one obtains the overall flow rate \( J \),

\[
J = \left[ \frac{\pi R^4}{8\eta_0} + \frac{\pi}{2} \int_0^R r^3 \left( \frac{1}{\eta (r)} - \frac{1}{\eta_0} \right) dr \right] \frac{-\partial p}{\partial z}
\]  

(2.15)
In this expression, \( \eta \) is position dependent. We must find its profile as a function of \( r \).

Far from the interface, \( \eta = \eta_0 \). Comparing this expression with eq.2.5, one obtains for the slip length \( \lambda \) in the flow through the capillary,

\[
\frac{\lambda}{R} = \int_0^1 x^3 \left( \frac{\eta_0}{\eta(xR)} - 1 \right) dx
\]

(2.16)

where a change of variable was realized, writing \( x = r/R \).

Consider the interface as a three dimensional region of thickness \( \delta \) and a transition in the viscosity at \( R - \delta \) from the bulk value to \( \eta \), which differs significantly from \( \eta_0 \). The slip length is then a function of both the interfacial thickness \( \delta \) and of the interfacial viscosity \( \eta \).

\[
\frac{\lambda}{R} = \int_{1 - \frac{\delta}{R}}^{1} x^3 \left( \frac{\eta_0}{\eta(xR)} - 1 \right) dx
\]

(2.17)

Further assuming constant viscosities \( \eta \) and \( \eta_0 \), we obtain the relation

\[
\lambda = \delta \left( \frac{\eta_0}{\eta} - 1 \right)
\]

(2.18)

In the following chapter, we will experimentally consider slip with an oscillating flow rate.

References


3 Oscillating flows

3.1 Complex mechanical properties

Surfactant molecules and proteins adsorbed at liquid-liquid and liquid-air interfaces are very often viscoelastic. Considering this possibility at solid-liquid interfaces, the effective viscosity $\eta$ should become frequency dependent. Formally, this can be written as $\eta = \eta' - i\eta''$. Inserting such a complex viscoelastic quantity into equation 2.17 gives:

$$\lambda = \frac{\lambda'}{R} + i \frac{\lambda''}{R} = \int_{1-\delta/\eta}^{1} x^3 \left( \frac{\eta_0 \eta'}{\eta^2 + \eta''^2} - 1 \right) dx + i \int_{1-\delta/\eta}^{1} x^3 \frac{\eta_0 \eta''}{\eta^2 + \eta''^2} dx$$

(3.1)

In this expression, $\lambda = 0$ when $\eta = \eta_0$. The flow is Poiseuille-like up to the pore wall with the usual no-slip boundary condition applies. The condition $\eta > \eta_0$ corresponds to the no-slip boundary layer being displaced inwards, into the liquid. The transition from $\eta$ to $\eta_0$ occurs at $r = R - \delta$. In that case, there is an adsorbed layer of thickness $\delta$ that does not yield under the hydrodynamic surface stress, which derives from the liquid flow. But adsorbed layers of surfactant or proteins at liquid-air and liquid-liquid interfaces are viscoelastic. The rheological properties depend on the interfacial stress. The determination of these properties in interfacial structures is an essential factor in many technological applications, such as boundary lubrication or detergency. In the general case, the viscosity $\eta$ is the complex quantity $\eta = \eta' - i\eta''$. It expresses terms for the viscous dissipation as well as for elasticity, i.e. for energy storage in the material. Eq.2.17 shows that $\lambda$ must then be a complex quantity too. To verify this assumption, a pulsating flow must be applied to a surfactant solution that flows through a laser-etched membrane.

3.2 Experiments with complex interfacial viscosity in pulsating flow

The experiments with single capillaries, like those by Tolstoi and Churaev, are difficult. Experimental difficulties are eliminated however by using a large number of capillaries in parallel, like in a thin perforated membrane between vessels with different pressures.
The Isopore VCTP- membrane from Millipore is a 10 μm thick film of polycarbonate with straight and parallel pores of 0.1 μm diameter. The pore size distribution is very narrow and is the equivalent of a bundle of narrow parallel capillaries. The polycarbonate has been made hydrophilic with a coating of PVP (poly-vinylpyrrolidone) coating.

To investigate the complex nature of interfacial properties involving a slip length, we adsorb Sodium Dodecyl Sulfate (SDS) molecules at the pore walls in such a membrane. In this experiments, we used a solution at 5 times the critical micellar concentration (CMC). Applying a pulsating flow, evidence for an elastic component of the interfacial region will be detected as a variable phase angle shift between the applied pulsating flow rate and the resulting measured pressures.

To obtain these results, a stable constant flow is applied and then, an oscillation is superimposed to the flow rate. A direct observable consequence is a decrease in the mean pressure needed for the same average flow as illustrated in figure 3.1. Such an observation could only be done at lower flow rates.

![Figure 3.1: At low shear stress, the addition of oscillations to the flow rate leads to flow enhancement. For the same average imposed flow rate, the resulting pressure gradient is decreasing. This behavior is characteristic of a viscoelastic material.](image-url)
For more quantitative evaluations, we shall consider a capillary of radius R and length z with a solution of viscosity $\eta_0$ subject to a pulsating flow of frequency $\omega$ imposed by a syringe pump. The flow field and the pressure are described by the equations 2.20 for the liquid velocity in the pore and the gradient in the pressure respectively:

$$v = v_0 + \hat{v} e^{i\omega t}$$

$$P = P_0 + \hat{P} e^{i\omega t+\phi} = P_0 + \hat{P} e^{i\omega t}$$

$P = -\partial p/\partial z$ is the pressure gradient over the capillary. The amplitude of periodical flow rate and pressure variations are, respectively, written as $\hat{J}$ and $\hat{P}$. $\phi$ is the phase angle between the flow rate $J$ and the pressure gradient $\hat{P}$ where $\hat{P} = \hat{P} e^{i\phi}$. In these periodic terms, the Navier-Stokes equation is written,

$$\rho \frac{D\vec{v}}{Dt} = \rho \frac{\partial \vec{v}}{\partial t} = P + \eta \nabla \cdot \vec{v}$$

subject to the boundary conditions,

$$\left. \frac{\partial v}{\partial r} \right|_{r=0} = 0$$

$$v(R) = \lambda \left. \frac{\partial v}{\partial r} \right|_{r=R}$$

Inserting eq.3.2 into eq.3.3, one separates the frequency dependent and independent components. The latter allows the determination of the stationary velocity profile $v_0$ and, by integration, one obtains the background value of the average flow rate $J_0$,

$$v_0(r) = \left[ \left( \frac{R^2 - r^2}{4\eta} \right) + \frac{2\lambda R}{4\eta} \right] P_0$$

$$J_0 = \frac{\pi R^4}{8\eta} \left( 1 + \frac{4\lambda}{R} \right) P_0$$

This flow rate is obtained experimentally and is plotted as a function of the average pressure in the flow diagram of figure 3.2.
Figure 3.2: Average flow rate versus average pressure. Two regimes can be observed. In the lower pressure region, elastic effects are thought to be predominant. This flow diagram is characterized by two distinctively different regions, which differ in the overall flow conductivity through the same membrane.

The superimposed, time dependent part of the Navier-Stokes equation leads to the expression,

\[ i\omega \hat{v} = \hat{P} + \frac{\eta}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \hat{v}}{\partial r} \right) \]  

(3.6)

with the boundary equations

\[ \frac{\partial \hat{v}}{\partial r} \bigg|_{r=0} = 0 \]  

(3.7)

\[ \hat{v}(R) = \lambda \frac{\partial \hat{v}}{\partial r} \bigg|_{r=R} \]

Rearranging eq.3.6 leads to the expression

\[ r^2 \frac{\partial^2 \hat{v}}{\partial r^2} + r \frac{\partial \hat{v}}{\partial r} - k^2 r^2 \left( \hat{v} - \frac{\hat{P}}{i\omega \rho} \right) = 0 \]  

(3.8)

The substitution of \( W = \hat{v} - \frac{\hat{P}}{i\omega \rho} \) and \( z = kr \), with \( k^2 = \omega \rho / \eta \) brings this equation
into the standard form for the modified Bessel function. The solution is written as

\[ \hat{v} = \frac{\widehat{P'}}{i\omega \rho} + AI_0(kr) + BK_0(kr) \] (3.9)

where \( I_0 \) and \( K_0 \) are the modified Bessel functions of zeroth order and of the first and second kind respectively. The constants \( A \) and \( B \) are obtained from the boundary equations and we find:

\[ \hat{v} = \frac{\widehat{P'}}{i\omega \rho} \left( 1 - \frac{I_0(kr)}{I_0(kr) - \lambda I_1(kr)} \right) \] (3.10)

for the relation between the periodic velocity \( \hat{v} \) and the periodic pressure gradient \( \widehat{P'} \). \( I_1 \) is the modified Bessel function of first order and of the first kind.

The Bessel functions are known to converge very rapidly because of the presence of factorial terms in the denominators. This behavior is accentuated at low frequencies. Since the product \( kR \) is small, we expand the Bessel functions up to the second order. The oscillating part of the flow field can then be described with a similar profile as found in a stationary flow,

\[ \hat{v}(r) = \left[ \left( \frac{R^2}{4\eta} - \frac{r^2}{4\eta} \right) + \frac{\lambda R^2}{2\eta} \right] \widehat{P'} \] (3.11)

\[ \hat{J} = \frac{\pi R^4}{8\eta} (1 + \frac{4\lambda}{R}) \widehat{P} e^{i\phi} \]

But in these time dependent expressions, there is a phase shift \( \phi \) between the oscillating flow and the pressure gradient that is generating by it. The amplitude ratio \( \hat{J}/\widehat{P} \) is allowing to express the tangent of the phase shift as a function of \( \lambda' \) and \( \lambda'' \),

\[ \tan \phi = \frac{4\lambda}{R} \frac{\lambda}{1 + \frac{4\lambda}{R}} \] (3.12)

In the figure 3.3, we have plotted \( \tan \phi \) against the average flow rate.
This is characteristic behavior for a shear thinning, viscoelastic substance. The viscous losses decrease when the internal shear in the material is increased. This behavior leads in practice to fluids systems with apparent yield stress, Bingham fluids. The experiment illustrates this viscoelastic behavior in the adsorbed surfactant layer in a combination with the completely Newtonian flow of the bulk of the liquid. That the results depend on the periodicity of the oscillations indicates that the adsorbed surfactant layer is more elastic with higher frequencies. The parameter $\eta^*$ can be described as a storage modulus. For viscoelastic materials, it usually has a constant value over a certain frequency region and, after a transition zone, it should reach another plateau. Here, the transition seems to occur at an average flow rate around 2ml/min.

Figure 3.3: $\tan \phi$ is found to decrease with the average flow rate, i.e. with the wall shear stress.
Figure 3.4: Ratio of the oscillating conductance $\frac{\tilde{J}}{\tilde{P}}$ over the stationary conductance $J_0/P_0$.

Dividing the flow rate by the pressure is equivalent to define the ability of the fluid to flow with a phenomenological coefficient $L_{11}$. The conductances $L_{11}$ in the oscillatory regime and in the stationary state can be compared. Their ratio is presented in figure 3.4 versus the average flow rate. For higher flow rates, i.e. for higher shear stresses, the ratios of conductance $L_{11}$ are tending towards unity. The bulk conductance is thus becoming equal to the interfacial one. The elastic structure at the interface is thus breaking up at higher surface stresses. At low stress, the conductance to flow is lower than for the stationary flow rate. That means that below the transition point, the interface is acting as a brake. There is more elastic resistance at the interface than in the bulk. This would suggest that the effective interfacial viscosity is higher than the bulk viscosity. Or, the adsorbed layer in the interface is behaving as elastic matter. The 3D interface is deforming at low flow rates of the solutions, but not flowing with it.

These results are, indeed, complex from an experimental point of view. The frequency dependence is illustrating the presence of a relaxation mechanism or of a spectrum of
relaxation effects. In classical rheology, time-dependent flows show hysteresis in their rheograms. The classical and physical explanation for the time dependence is a competition between structuration and destructuration of the fluid. Extending this model to our interface, composed of adsorbed surfactant molecules, a dynamic equilibrium is created within the interface. This leads to the viscoelastic behavior, which come to the fore in the oscillation experiments.

Experiments realized on time-dependent fluids are very sensitive and require a lot of precautions. In fact, a rheological history is already given to the layer of surfactant during its formation. We are not aware of any experimental work that specifically addressed this point, even though theoretical considerations were given to it by Sagis [1]. The next chapters describe our observation on the viscoelastic interfaces. When these are exposed to constant flow rates, or shear stresses, they will relax to a steady state and, by applying this protocol, the time dependence vanishes from the model.

These preliminary experiments and these results warrant further investigations. For individual surfactant layers, it seems possible to determine the frequency domain of relevance and to characterize it. The dissipative slip length $\lambda'$ can be related to the loss modulus of the interfacial region. In rheology, the loss modulus is known to have a maximum at a given frequency with viscoelastic materials.

At zero frequency, the loss modulus is zero. The storage modulus is at its maximum value. Experiments of this type should enable a scientist to demonstrate a maximum value and the dynamic response of $\lambda'$ at a given frequency and relate these observations to the lubricant action of the adsorbed surface layers.

References

4 A transition between hydrodynamic regimes

4.1 Membrane experiments

Experiments with single capillaries, like those by Tolstoi [1] and by Churaev [2], are difficult because very high pressures must be applied over long capillaries $L$. With long capillaries, the pressure gradients remain small and the "high stress" regime experimentally inaccessible. However, these difficulties are eliminated by using a large number of capillaries in parallel, like in a thin perforated membrane between two vessels with different pressure.

The Isopore VCTP- membrane from Millipore is such a perforated membrane. It is a 10 $\mu$m thick film of polycarbonate in which pores have been made by laser etching. The pores that are obtained via this technique are straight and parallel, with a uniform diameter of 0.1$\mu$m. The membrane porosity is 4%. The pore size distribution is very narrow with a variation coefficient of 1%. The material is made hydrophilic with a PVP (poly-vinylpyrrolidone) coating. The manufacturer guarantees the membrane to withstand pressures up to 2 bars without deformation.

4.2 The mathematical model

To model the liquid flow in a membrane with narrow pores, we shall use a mathematical description that was introduced by Albano et al [3]. It gives the momentum transfer at the surface of a solid body in a viscous liquid. We have rewritten Albano’s equations in a more condensed way as,

$$
\left( \frac{\sqrt{1}}{1} - \hat{n} \hat{n} \right) \bullet \left( \eta \nabla \cdot - 2 \lambda \text{sym} \left[ \eta \nabla \cdot v \right] \bullet \hat{n} \right) \bigg|_{r=R} = 0
$$

(4.1)

where the symbol $\hat{n}$ stands for the unit vector normal to the surface. Eq.4.1 states that the boundary fluid velocity is proportional to the tangential component of the shear stress at the boundary, i.e. the Stokes’ friction law. $\left( \frac{\sqrt{1}}{1} - \hat{n} \hat{n} \right)$ is the dyadic operator. It allows to only consider the "surface" component of the pressure tensor $\eta \nabla \cdot v$.
Just like in chapter 2, the slip length $\lambda$ is related to the friction coefficient $\mu$ as,

$$\lambda = \frac{\eta}{2\mu} \quad (4.2)$$

The factor "2" is introduced here for symmetry reasons: to simplify the calculations about the symmetrical part of the surface force balance in terms of a slip length.

For high friction, i.e. $\mu = \infty$, the slip length is infinitesimally small and the no slip boundary condition applies. For finite friction coefficients or slip lengths $\mu$, or $\lambda$, there is some degree of slip, with energy dissipation at the interface.

The description of an incompressible Newtonian fluid flow in a capillary of radius $R$ starts with the solution of the Navier-Stokes equation and produces the velocity profile:

$$v(r) = -\frac{1}{4\eta} P \left( r^2 - 2\lambda R - R^2 \right) \quad (4.3)$$

with $P$ the pressure gradient in the capillary.

For capillary radii $R >> R^* = 4\lambda$ (see eq.2.8), the extrapolated velocity vanishes at an imaginary wall, located at $r = R + \lambda$. This is how the concept of a slip length $\lambda$ was in introduced in [4]. In many cases, $R >> R^*$ and, as predicted, the flow is in a Poiseuille mode. High shear wall stresses are still possible in systems with big radius. From purely mechanical considerations, slip is most likely present then, even though it is totally unobservable in flow experiments. Indeed, the $\lambda R$-term is becoming too small, compared to $R^2$, to be noticed at all. For a given set of forces and forces, slip will become a significant effect with capillary radii around $R \approx R^*$, when $\lambda$ and $R$ become commensurate. In some limiting cases, where $R << R^*$, (i.e. in the plug flow regime) a more accurate expression in terms of $\lambda$ requires the $\lambda^2$ term.

Integrating the expression 4.3 over the radius, one gets the flow rate $J$,

$$J = \frac{\pi R^4}{8\eta} P \left[ 1 + \frac{4\lambda}{R} \right] = J_{v,0} \left( 1 + \frac{4\lambda}{R} \right) \quad (4.4)$$

Expressing $J$ as an average velocity, i.e. dividing the flux by the cross sectional area of the capillary, gives Churaev’s expression [2] for flow with slip at the capillary walls.

The Albano’s equation 4.1 is equivalent to the equations for slip flow presented by de Gennes [4]. Even though the eq.4.1 seems more complex, this formulation allows an
easier introduction of other forces than friction into the problem of a liquid sliding over a solid surface. We shall use this option in the next chapter. Albano’s interfacial equation, just like the Navier-Stokes equation for the bulk itself, is a force balance. Assuming the surface to be in thermal and mechanical exchange (equilibrium) with the bulk, forces in the solution must either be balanced in the interface by some elastic reaction force or lead to friction because of an excess mobility in the interfacial area.

4.3 A model experiment: flow of surfactant solutions through narrow pores

Armed with the mathematical model of eq. 4.1, 4.3 and 4.4 we set out to investigate this concept experimentally, again using the Isopore membrane as a collection of monodisperse parallel capillaries.

We have studied the flow of surfactant solutions through such a perforated membrane. During its transport, adsorption of surfactant molecules is taking place at the solid-liquid interface and allows selectively established, chemically well-defined surface properties. At surfactant concentrations above the CMC, the structure and the density of the adsorbed layer is in equilibrium with the micellar solution. It will then behave like a separate surface phase and not change very much when the concentration of the surfactant solution is changed. Mechanical properties of the viscoelastic adsorption layer are then expected to be independent of the concentration too. The adsorbed surfactant layer is soft, condensed, viscoelastic matter, like any liquid crystalline mesophase of ordered molecules.

Accurate flow rates through the membrane are imposed by a syringe pump Postnova PN1610 in the pressure range of 0 to 20 Bar. The pressure drop across the membrane, which results from the imposed flow, is measured by a Bronckhorst pressure transmitter P-506C-FAC-22V. The accuracy of this device is ±0.5%.

Both the pressure transmitter and the pump are connected to a computer. The program controls the pump and allows simultaneous recordings of \( J \) and \( P \). Pressure readings are averaged over 100 values (measured each 5s) and showed deviations less than 1%. Pres-
sure gradients \( P \) are expressed in terms of measured pressure \( p \) over actual membrane thickness \( l \).

The experiments are carried out with the Newtonian, wetting, solvent water to establish a reference state, and with solutions of sodium dodecyl sulfate (SDS). The solution concentrations were all above the critical micellization concentration. Crystalline sodium dodecyl sulfate (SDS), commercially available from Fisher Scientific, was used as the surfactant. The CMC of this substance is at 2.3g/l.

The viscosities are measured using three capillaries of radius 0.24, 0.46 and 0.36mm, respectively. Within experimental error, viscosities are found to be the same in the three capillary viscometers for a given concentration. The flow of the surfactant solutions varied linearly with the pressure for smaller and for bigger pore diameters in test membranes, 0.05\( \mu m \) and 0.2\( \mu m \) respectively. In the measurements, we used membranes with pore diameters of 0.1\( \mu m \). We conclude that the solutions are Newtonian. These data are summarized in the table 4.1.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (*CMC)</th>
<th>Relative Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>1</td>
<td>0.978 ± 0.008</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.057 ± 0.009</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1.088 ± 0.006</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.151 ± 0.007</td>
</tr>
</tbody>
</table>

**Table 4.1:** Relative viscosity \( \eta/\eta_w \) for various surfactant at various concentrations.

The structure and the mechanical properties of the adsorbed layers in the interface are an unknown variable. We expect that they will depend on the type of surfactant, the properties of the solvent and the polarity of the membrane material. With adsorbed SDS molecules in a polar interface it is anticipated that a bilayer of surfactant molecules will dominate the complex mechanical properties of the solid-liquid interface at the pore walls in the membrane. We shall treat these adsorbed layers like before, as a 3D interface. The interfacial layer is wetting the pore walls and it is, itself, wetted by the solution. Therefore,
it shall be assumed that all the slip phenomena occur inside the interfacial layers and that there is no slip at all between that layer and either the solid or the solution.

At the start of each experiment the membrane was flushed at high flow rates with pure, doubly distilled water. After that, the investigated surfactant solution was admitted and pumped through the membrane. Flow rates were increased step-wise from lower to higher values and back again. The resulting pressures across the membrane were recorded, so that the flow conductivity $L_{11}$ could be obtained as a function of the flow rate in the pores. Fouling of the membrane during the experiment was largely avoided by recycling the surfactant solution after it had passed through the membrane.

A characteristic example of the results, which were obtained upon applying this protocol, is given in figure 4.1. The test solutions of this diagram contain different concentrations of the anionic surfactant SDS.

![Figure 4.1](image)

**Figure 4.1:** Flow rate of surfactant solutions through a nanopore membrane versus applied pressure gradient for some SDS concentrations: 0, 1x and 2x, 5x and 7x CMC. The drawn lines are a linear fit according to eq.4.4.
The concentration C=0 sets the reference state for the membrane and calibrates the flow diagrams. At a relatively low surfactant concentration, C=1 or 2 CMC, the pressure across the membrane varied in a linear fashion with the imposed flow rates. This is the expected behavior. The proportionality of the flux with its driving force is predicted by Poiseuille’s law for Newtonian liquids like pure water (assuming that there is no slip at the pore walls!). Up to a certain flow rate the more concentrated solutions flow in an analogous mode. But upwards from a critical value of the flow rate or of the pressure, the conductivity $L_{11}$ of the pores in the membranes increases. With the concentrations of 5, 7 and 10 CMC, there is an unexpectedly high flow rate of the surfactant solution in relation to the pressure across the membrane, which is caused by the flow of liquid through the pores. We attribute these conductivity changes to a transition from a regime of simple Poiseuille flow to the ”surface response” regime, where the adsorbed layer of surfactant molecules in the solid-liquid interface yields to friction forces and begin to slide over the interface. There is a critical value of the pressure and the flow rate, where the admicellar layer of adsorbed surfactant between the solid and the liquid begins to move along the pore walls in slip.

The adsorbed surfactant bilayer (admicelle) is a viscoelastic interfacial structure. At the lower shear rates as well as at lower surfactant concentrations, the same SDS bilayers seem to remain immobile. They are sheared by the streaming liquid but they do not flow under these conditions. The 3D interfacial layer now behaves as a structured elastic material. Some energy is stored in its strained structure, but then there is no dissipation of energy from the slip at the interface. A gradient in the local surfactant concentrations may be an aspect of this elasticity. If surfactant is dragged along the interfaces with the liquid flow its concentration in the admicelle must be replenished by adsorption from the solution. At lowly concentrations, the replenishing rate may be limited by and too small for complete restoration of the equilibrium in the adsorbed surfactant layer. In such a case, there will be a Marangoni force contributing to the elasticity, which counteracts the slipping motion. But when the solutions become more concentrated, the interface can
flow in response to the stress that the liquid exerts at the pore walls and overcome the
elastic strength of the admicellar bilayer.

We shall describe this regime, with measurable slip in the interface, as the "surface
response" mode of the flow. As the shear stress increases the interface can no longer
oppose the externally applied drag forces. The mobility of the molecules in the adsorbed
surfactant layers becomes apparent and the interface begins to respond and yield to
momentum transfer accompanied by friction. In the next chapter we shall introduce
a cut-off vector to account for the transition from the no-slip Poiseuille regime to the
surface response regime that is characterized by mobility and friction in the solid-liquid
interfaces.

The mathematical representation, which we have developed, has no built-in non-
linearities. It can therefore not completely describe a transition between two regimes,
and link the Poiseuille equation, which is adequate for flow at low shear stresses, to the
surface response regime at the higher pressures and flow rates. As a description of the
transition we introduce a Heaviside function \( \theta \) in expression 4.4 of our mathematical model
and write for the flux,

\[
J = \frac{\pi R^4}{8\eta} N \left[ P + \frac{4\lambda}{R} (P - P_c) \theta (P - P_c) \right]
\]

Below the critical pressure across the membrane the flow is obeying the no slip condi-
tion at the interfaces with the solid pore walls. However, above this critical value, which
was clearly observed in the experiments of fig.3.1b and c, there is a slip length \( \lambda \) and
the extra slip term contributes to the overall flux of liquid through the pores. The two
contributions are additive but the value of their sum is still under control of the principle
of minimum entropy production which determines the partitioning between the two diss-
ipation mechanisms. The predetermined constant flux of the viscous liquid \( J \) is imposed
by the pumping device as a boundary condition and generates the pressure gradient \( P \)
across the membrane as the response for \( L_{11} = L_{11a} + L_{11b} \).

The description of the transition with the Heaviside function is purely a mathematical
device, and probably not very representative of what is really happening. The flow is not
expected to jump from one regime to another. One could describe our observations in
term of critical shear stresses for the transition and of the slip lengths that are determined
by the dissipation mechanisms in the regime with surface response. We did derive the
virtual slip length $\lambda$ from our experimental data above the transition point. We are
then, in fact, describing the slip velocity in an interfacial region with the adsorbed layer
of surfactant layers, and the friction coefficient caused by that interface under the slip
conditions. The adsorbed surfactant layer behaves as a thin, viscoelastic lubricant, with
the characteristics of wetting both water and the (poly-vinylpyrrolidone) solid membrane
material.

Slip inside the surfactant layer is seen as a contribution to the flux that is driven
by one and the same pressure gradient $P$. It can then be observed as the larger flow of
the liquid at the same applied pressure, because with slip the pores appear to have a
slightly wider radius $R+\lambda$, instead of the calibrated value $R$ for wetting liquids. The flow
representations are illustrated in figure 2.1.

Even though they remain within the range of experimental errors, the measured data
indicate that the slopes in the flow diagrams, i.e. the slip length, tend to decrease slightly
with increasing surfactant concentrations above the transition, in the surface response
regime. Keeping in mind the relation between the slip length and the friction force, a
constant value of $\lambda$ was expected for constant, concentration independent properties of the
adsorbed layers. And, when the concentration of surfactant is increased, the transition
itself is seen to shift to higher shear stresses. An explanation for observations like these
could be that other driving forces ($X_2, X_3,...$ see eq. 1.2) are active in addition to the
applied pressure $X_1$. These forces could affect the flux $J_1$ through cross-effects and depend
on the solution concentrations. We shall investigate this proposition in the following
chapter of this thesis.

According to eq.4.5, slip can only be observed if the ratio $\lambda/R$ is experimentally
accessible, i.e. if the capillary radius $R$ is small enough. In that case the slip contribution
to the total flow can be measured. On the other hand, the wall stress $\tau_w = -R/2. dP/dl,$
which is necessary at the solid boundary to start the slipping, will be directly dependent on the pore size. A smaller pore radius must be compensated by an increase in the pressure gradient, while staying within the pressure-operating window. For this kind of membrane, that window lies between 0 and 2 bars.

In figure 4.2, the entropy production $dS/dt = JP$ is plotted as a function of the flow rate. In these graphs, we introduced experimental results, i.e. a slip length of 8 nm, a pore radius of 50 nm and a pore number of $9.2 \times 10^9$ into eq.4.5. The entropy production for a pure Poiseuille flow can then be plotted and also compared with the graph for the surface response regime. The Heaviside function is the discrimination factor between the two plots. It is taken 0 for the Poiseuille configuration and 1 for the surface response.

![Figure 4.2: entropy production versus flow rate for slip and stick boundary conditions. The plain lines are representing the most favorable boundary condition.](image)

The surface response regime, in which a linear and a quadratic contribution add up, is flatter than the flow profile in a pure Poiseuille regime. Therefore, the entropy production in the surface response regime is larger for the small flow rates but lower at larger flow rates or pressure gradients. This causes the intersection point of the plots and a transition between the two alternatives for a flow regime at a sharp critical value for the flow rate,
Recalling the observations of transition points in figure 4.1, the curves for the entropy production of the two regimes must indeed intersect at two points, one at the origin, when no fluxes are observed at all so the entropy production is zero in both regimes, and another at the transition. Only considering the two straight lines in the flow diagrams, we can anticipate the transition in the entropy production profile. This transition is occurring when the shear stress that is applied to the interface is high enough to put the admicelle into motion. In the experimental conditions, this critical pressure represents a switch from a Poiseuille regime to a surface response regime at the flow rate where the entropy production of the two regimes is equal and \( R = R^* \).

The Heaviside function, originally introduced for an easier mathematical description is in fact describing an experimental property. The physical flow \( J_1 \), described in this mathematical model, is indeed selecting the configuration leading to the lesser dissipation, i.e. the highest thermodynamic efficiency. From the flow diagrams \( J = f(P) \) (fig 4.1), it can be seen that above the transition, the force required to obtain a given total flux of liquid, is less for the surface response regime than for Poiseuille. The separate contributions \( L_{11a} \), i.e. pure Poiseuille, and \( L_{11b} \), i.e. the slip effect, of the flow are thus clearly distinguished in the figure 4.3 and the transition between the two regimes can be understood as a result of minimization in the entropy production.

If we express the flow rates with the phenomenological equations, the slip length \( \lambda \) is simply obtained from the ratio of the experimental slopes for the Poiseuille and for the surface response regime, which is according to eq.4.4, found by the factor \((1 + 4\lambda/R)\). This gives values for the slip lengths \( \lambda \), which are 7.3nm, 9.8nm and 6.5nm for the concentrations of 5, 7 and 10 CMC. It can be concluded that the slip length in these systems is of this order of magnitude under the given experimental conditions.

At the end of this chapter we conclude, like Timmerman did before us on the basis of her experiments with detergents, that the no slip condition at the interface between a solid and a viscous flow is not always a valid assumption. Slip can be experimentally observed
and the effects can be quantified by studying the flow in membranes or capillaries. It seems that an adsorbed surfactant layer does determine slip and lubrication properties in the system that we have investigated. It turns out to be a fruitful simplification where these properties are described in terms of a 3D interfacial region with clearly viscoelastic properties.

Summarizing the observations up to this point elucidates what happens. Beyond a critical shear stress in the interface the flow enters into a "surface response" regime where deviations from the Poiseuille law becomes noticeable in small pores and capillaries. Thermodynamics of the flow allows a flow regime that consists of superimposed plug flow to the Poiseuille profile. The dissipation of kinetic energy is split between these two contributions on the basis of minimum entropy production. The ratio between the friction factor $\mu$ at the interface and the bulk viscosity $\eta_0$ in the fluid determines the transition conditions from purely viscous flow to the surface response regime.

Alternative model descriptions for slip between a liquid and a solid are available in the literature. The slip length $\lambda$ is itself such a concept. Models, which use $\lambda$ instead of the ratio $\eta_0/\mu$, give a phenomenological description of slip phenomena but they introduce non-physical model parameters like $\lambda$ in the analysis. The only reason for such idea is the conservative desire to maintain the no slip condition as a universal assumption in computing viscous flow over solid surfaces.

In this chapter, we have addressed slip in two different ways. One of them was pure thermodynamics, considering fluxes with driving forces. This approach led to the determination of a theoretical radius $R^*$, as a cross-over point between two regimes with flow conductivity coefficients $L_{11,a}$ and $L_{11,b}$. The second is based on transfer of momentum at the surface. Such a model would be more appropriate to describe dynamic phenomena like a Marangoni effect, which implies a transport of surfactant from the bulk to regenerate the moving interface. If the interfacial velocity gradients are high enough, the Marangoni effect will be switched on, acting as a brake.

Effects of this kind can, themselves, be considered as a contribution to the elasticity
in the interfacial layer. Consequently, the onset of slip is depending not only on the thermodynamic state of the whole system, but also on assorted kinetic properties in the bulk of the solution. The choice of a radius $R$ in a way, which favors slip is a necessary conditions for the experiments, but not a sufficient one.

To conclude, such interfacial flow, or slip, is expected to manifest itself in viscous flow through porous media, flow in colloidal systems and, in particular, the transport phenomena in nano-technological processes; that is, with geometries that have characteristic radii $R$ smaller than the theoretical value $R^*$, an intrinsic property of the system.

References


5 Slip boundary condition and electrokinetics

Starting with the Navier-Stokes equation we have distinguished between the bulk forces that make a Newtonian liquid flow and the surface forces that are exerted on the liquid by the friction of the solid surfaces as the flowing liquid moves over it. A surface flow effect and bulk flow will always be superimposed in the motion of the liquid in such a way that the entropy production in the flow has the smallest value that is compatible with the flow conditions. In the phenomenological equations the two contributions add up in the overall flow conductivity $L_{11}$, the proportionality factor between the applied flow rate $J_1$ and the pressure gradient $X_1$.

The relation between the force that is exerted by the surface and its effect on the flow rates must be related by a dissipation coefficient, just like the viscosity of the liquid relates the bulk flow with the pressure gradients in the liquid. Since such a surface viscosity coefficient is a-priori an unknown quantity in the theory, it is customary to introduce a slip length $\lambda$, which we have interpreted here as a measure of the dissipative surface effect in the liquid flow.

Having discovered the transition in the flow of surfactant solutions, from the no slip Poiseuille regime of the flow to a surface response regime, where the streaming liquid slips over the solid surfaces because a critical shear stress has been exceeded, we shall have to investigate whether and how this transition of the flow regime is affected by the mechanism of processes that are thermodynamically coupled with the flow. One possible mechanism of this kind was the Marangoni elasticity of the bilayer [1], [2] but many other types of forces are involved in the elastic strength of the interface, as follows from eq.1.1. Our purpose in this investigation is to extend the scheme of phenomenological equations and bring these other driving forces into the play.

As our target we shall focus on one of these possibly relevant forces: the electrical driving force $X_2$. Effects of this force on the flow are usually referred to as “electrokinetic phenomena” or as “electroviscous effect”, because the apparent viscosity seems higher than expected. A lower flow is observed for a given pressure gradient $P$, then would
follow from the experimental viscosity of the bulk liquid and the geometry of the barrier that obstruct the flow. Electric potential differences in the flowing liquid lead to an electric back-current through the conducting liquid (Ohm’s law), but there are also other measurable electrokinetic phenomena, like electroosmosis. Electroosmosis is the extra flow of liquid, because of an applied electric potential. Thus the flow \( J_1 \) is not only produced by a hydrostatic pressure gradient, but it is also coupled to a force \( X_2 \) by the phenomenological coefficient \( L_{12} \), (as described in the phenomenological equation 1.2).

These electrical surface effects introduce phenomenological coefficients \( L_{12} \) and coupled processes in every description of the liquid flow through capillaries, membranes and porous materials. Including the influence of electrical potential differences on the liquid flow \( J_1 \) we obtain the complete phenomenological equation \( J_1 = J = L_{11}X_1 + L_{12}X_2 \) for the flow of liquid. Conversely, the electrical current \( J_2 = i = L_{21}X_1 + L_{22}X_2 \) is the response of the capillary with the liquid when an electric potential gradient \( X_2 \) is present in it. The Onsager reciprocal relations predict that the coefficients \( L_{12} \) and \( L_{21} \) are equal in a system, which has coupled electric current and liquid flow rate.

The total entropy production \( dS/dt = J_1X_1 + J_2X_2 \) in such a system indicates that electrical effects can considerably reduce the net flow, as if they did actually increase the viscosity of the liquid. In many of these cases, it is not really the viscosity of the liquid that is altered by the electric potential but the net flow, which is the response to an applied pressure gradient. This becomes clear when the thermodynamics of electroosmosis is considered.

5.1 Thermodynamics of electroosmosis

The application of a pressure gradient \( P \) in a capillary leads to the creation of a velocity profile in the liquid that can be found using a Poiseuille velocity profile and extrapolate this to the capillary wall. Such velocity profile is the result of balancing the viscous drag force with the pressure force within a cylindrical element. And, if an electrical double layer is present at the interface, which extends up to a distance \( d \) into the liquid where
there is discernible motion because of the flow, a stationary state of the electrical current will be attained when the transport of charge by convection, $L_{21}P$, is equal to the back transport by conduction $L_{22}E$.

Since the solution must remain electroneutral at both ends of the capillary, the net current must be zero and one can write,

$$\frac{L_{21}}{L_{22}} = -\left(\frac{E}{P}\right)_{i=0} = \left(\frac{J}{E}\right)_{P=0} \quad (5.1)$$

Such expressions are known as the Saxen’s relations. They are based on the Onsager reciprocity theorem.

In his lecture notes at MIT, Overbeek [3] stated that such relations established within irreversible thermodynamics are "absolutely general relationship, which cannot be invalidated by complications such as surface conductance, tortuosity...".

However, in this classical derivation, only one dissipation mechanism is introduced a-priori. In the previous chapter, we described in addition to the bulk viscous dissipation a friction between a moving liquid over a solid surface. We shall later on test the "absolute" validity of the Saxen’s relation when a system is undergoing a transition from one dissipation mechanism to another. In that case, a non-linearity in the flow system comes about, which creates the condition for the transition. This reveals itself in observations like the change of the transition point with the surfactant concentration.

### 5.2 The kinetic model for electroosmosis

A kinetic model for electroosmosis is obtained by considering the structure of electrical double layers at the interface between a liquid and a solid capillary wall. Such an interface will be charged either by ionization of surface groups or by adsorption of "potential determining" ions that are dissolved in the liquid. Because of this adsorption the solid acquires a surface charge, which is balanced by an equally large space charge in the liquid. This space charge is partly due to counter-ions that are attracted by the charged surface and partly to the desorption of ions with the same charge sign as the solid. A fraction of the counter-ions can be bound chemically in the interface and form a Stern or Helmholtz
layer. The rest of them form a diffuse ionic atmosphere, which extends into the liquid over a distance of the order of the Debye length $d = \kappa^{-1}$.

Under the influence of an applied pressure gradient, the liquid will flow past the surface, thereby dragging along the diffuse layer of charge carriers. In the fluid, dissolved molecules or ions cannot be separated from their charge. They contribute both to the mass transport and to the electrical current in the system. The electric currents have to be included in the thermodynamic analysis as extra fluxes $J_2 = i$, with the electric potential $E$ as the corresponding driving forces $X_2 = E$. The entropy production in such system will then be $dS/dt = J_1X_1 + J_2X_2$. This phenomenological equation indicates, that in a porous material with electrical double layers, the transport of an amount of liquid requires more applied pressure than without electrically charged pore walls - like under the zero point of charge condition.

The phenomenological equations do not specify a model for electrokinetic phenomena, or a boundary condition for a flow regime. As long as fluxes and forces are proportional thermodynamics predicts quantitative coupling between the observed phenomena, as in the Saxen’s relations. This can create an interesting working hypothesis. In the previous chapter we have discovered the new surface response regime for liquid flow, where a flowing liquid begins to slip over a surface after a critical shear stress at the surface has been exceeded. In the surface response regime the measured overall conductivity $L_{11}$ of the flow is larger than in the no-slip Poiseuille regime. The Saxen’s relations then predict that the "anomalous" ionic conductivity in the surface response regime must also differ from $L_{22}$ for the same liquid in Poiseuille flow. Anomalous electrical conductivity is the consequence of slip in the interface between a solid wall and a flowing liquid.

5.3 Electrokinetic forces

In order to verify this hypothesis we shall first develop a kinetic model and analyze electrokinetic phenomena in the surface response regime. We shall begin by including the effect of electrical forces in the Navier-Stokes equation, which generally describes the
velocities in a fluid under the influence of applied forces. With the no slip condition at the solid surface this would lead to the expression 4.2 of the velocity field under the influence of the driving forces P and E,

\[ v = \frac{P}{\eta} \left( R^2 - r^2 \right) - \frac{\varepsilon E}{4\pi \eta} \left[ \zeta - \phi(r) \right] \quad (5.2) \]

\( P \) is the pressure gradient, \( R \) the pore radius, \( \eta \) the bulk viscosity, and \( E \) the axial electric field. The total electric potential is the sum of the streaming potential and the potential \( \phi \) due to the surface charge,

\[ \phi_t = -EZ + \phi(r) \quad (5.3) \]

For the electrical potential \( \phi(R) \) at the interface, we shall take the experimental zeta potential \( \zeta = \phi(R) \). As in ref.[4], integrating the velocity profile, eq.5.2, over the radius, one obtains the flow rate and the electric current density,

\[ j_v = 2\pi \int_0^R r v(r) \, dr = l_{11,0}P + l_{12,0}E \quad (5.4) \]

\[ i = 2\pi \int_0^R r i_\pm(r) \, dr = l_{21,0}P + l_{22,0}E \]

with the coefficients,

| \( l_{11,0} \) | \( \frac{\pi R^4}{8\eta_0} \) | \( \frac{\pi R^4}{8\eta_0} \) |
| \( l_{12,0} = l_{21,0} \) | \( -\frac{\varepsilon R^2}{4\eta_0} \zeta (1 - G) \) | \( -\frac{\varepsilon R^2}{4\eta} \zeta \left( 1 - \frac{2}{\kappa R} I_1(\kappa R) \right) \) |
| \( l_{22,0} \) | \[2\pi e n_0 \int_0^R r \sum \chi_\pm \exp \left( \frac{\mp e \phi}{kT} \right) \, dr\] \[+\frac{\varepsilon^2}{8\pi \eta} \int_0^R r \left( \frac{d\phi}{dr} \right)^2 \, dr\] | \[\pi R^2 e n_0 (\chi_+ + \chi_-)\] \[+\pi R^2 \frac{e^2 n_0}{kT} \zeta (\chi_- - \chi_+) G\] |

**Table 5.1:** Phenomenological coefficients for no-slip flow in the presence of electrokinetic effect [4].

where \( \chi_\pm \) are the electric mobilities of the ions. For simplicity, we have chosen a 1-1 electrolyte. \( G \) is a function of the radial potential [4] given by

\[ G = \frac{2}{R^2 \zeta} \int_0^R r \phi(r) \, dr \quad (5.5) \]
For low surface potentials, $\zeta \lesssim 25 \text{mV}$, the exponential terms in $l_{II}$ can be expanded up to the first order. A simpler expression for the potential $\phi$ is obtained [5],

$$
\phi = \zeta \frac{I_0(\kappa r)}{I_0(\kappa R)}
$$

(5.6)

where $I_0$ is the zero order modified Bessel function of the first kind and $\kappa$ the inverse Debye screening length. The function $G$ is then given by,

$$
G = \frac{2}{\kappa R} \frac{I_1(\kappa R)}{I_0(\kappa R)}
$$

(5.7)

with $I_1$, the first order modified Bessel function of the first kind.

Hence, to quantify the electrokinetic effects one would, in addition to the pore radius and the Debye length, only need the effective surface charge at the plane of shear or the $\zeta$-potential.

### 5.4 Electrokinetic effects in the surface response (slip) regime

Zukoski and Saville [6, 7, 8] have suggested that the zeta potential in itself is insufficient to describe all the observed electrokinetic phenomena. They suggested the presence of additional transport of charge in the Stern layer. But that layer is generally assumed to be hydrodynamically immobile, [9], so that there should be a case of "anomalous" surface conduction.

Both viscosity and surface charge distribution have to be included, as such, in our analysis of the surface response regime. Formally, a slip velocity $v(R)$ can easily be added in eq.5.2 by writing:

$$
v = \frac{P}{4\eta} (R^2 - r^2) - \frac{\varepsilon E}{4\pi \eta} [\zeta - \phi(r)] + v(R)
$$

(5.8)

Its value can be determined by solving the generalized boundary condition, as in eq.4.1,

$$
(1 - \hat{n} \cdot \hat{n}) \cdot (\eta \nabla \cdot \tau - 2\lambda \text{sym}(\tau) - \frac{\tau}{\tau}) \cdot \hat{n} \bigg|_{r=R} = 0
$$

(5.9)

where $\hat{n}$ is the normal unit vector, $\tau$ the viscous pressure tensor, $\frac{\tau}{\tau}$ the Maxwell tensor [10] with $T_{zr} = \varepsilon/4\pi.(E_r E_z - \delta_{zr} E_\theta E_\theta/2)$. This boundary condition involves two
parameters, a slip length $\lambda$ and a surface stress response $\overrightarrow{\tau}$. We model the surface with a stick to slip transition, i.e. the applied surface stress is balanced up to a certain limiting value $\overrightarrow{\tau}_c$. Beyond that yield value, slip is observed. The resulting slip velocity is given by the expression:

$$v(R) = \frac{\lambda}{\eta} \left[ \frac{R}{2} P + \frac{\varepsilon}{4\pi} \frac{\partial \phi}{\partial r} \bigg|_{r=R} E - \tau_c \right] \theta \left[ \frac{R}{2} P + \frac{\varepsilon}{4\pi} \frac{\partial \phi}{\partial r} \bigg|_{r=R} E - \overrightarrow{\tau}_c \right],$$  \hspace{1cm} (5.10)

where we have again used the Heaviside function to describe the stick to slip transition.

Allowing for slip at the interface, the phenomenological equations 5.4 must be rewritten as,

$$j_v = 2\pi \int_0^R r v(r) dr = l_{11} P + l_{21} E + k_V$$ \hspace{1cm} (5.11)
$$i = 2\pi \int_0^R r i_x(r) dr = l_{21} P + l_{22} E + k_I$$

with the coefficients,

<table>
<thead>
<tr>
<th></th>
<th>general form</th>
<th>linear approximation</th>
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<tbody>
<tr>
<td>$\frac{l_{11}}{l_{11,0}}$</td>
<td>$1 + 4 \frac{\lambda}{R}$</td>
<td>$1 + 4 \frac{\lambda}{R}$</td>
</tr>
<tr>
<td>$\frac{l_{12}}{l_{12,0}} = \frac{l_{21}}{l_{21,0}}$</td>
<td>$1 - \lambda \frac{\zeta'}{\zeta(1 - G)}$</td>
<td>$1 - \lambda R \frac{\kappa^2 G}{2(1 - G)}$</td>
</tr>
<tr>
<td>$l_{22}$</td>
<td>$l_{11,0} - \lambda R \frac{\varepsilon^2}{8\pi \eta_0} (\zeta')^2$</td>
<td>$l_{11,0} - \lambda R \frac{\varepsilon^2 \kappa^2}{8\pi \eta_0} \left( \frac{I_1(\kappa R)}{I_0(\kappa R)} \right)^2 \zeta'^2$</td>
</tr>
<tr>
<td>$\frac{k_V}{\lambda}$</td>
<td>$- \frac{\pi R^3}{2\eta_0} P_c - \frac{\varepsilon R^2}{4\eta_0} \zeta' E_c$</td>
<td>$- \frac{\pi R^3}{2\eta_0} P_c - \frac{\varepsilon R^2}{4\eta_0} \kappa \zeta' I_1(\kappa R) I_0(\kappa R) E_c$</td>
</tr>
<tr>
<td>$\frac{k_I}{\lambda}$</td>
<td>$- \frac{\varepsilon R^2}{4\eta_0} \zeta' P_c + R \frac{\varepsilon^2}{8\pi \eta_0} (\zeta')^2 E_c$</td>
<td>$- \frac{\varepsilon R^2}{4\eta_0} \kappa \zeta' \left( \frac{I_1(\kappa R)}{I_0(\kappa R)} \right)^2 (\zeta')^2 E_c$</td>
</tr>
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| Table 5.2: Phenomenological coefficients in the slip regime |

in which we have written $\zeta'$ as a shorthand symbol for $\partial \phi / \partial r \bigg|_{r=R}$.

In this flow model for the surface response regime, the forces describing the transition have been split arbitrarily into two components: a pressure gradient and an electric field under the critical set of conditions for the transition. The two are related by symmetry considerations. In any case, it is the sum of the two contributions, which is relevant for the onset of the slip regime.

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Independent of the flow regime, the set of linear flux-force equations must satisfy the Onsager symmetry relation for the cross-coefficients which describe the electrokinetic effects, $L_{ij} = L_{ji}$. As a consequence, the ratio of the streaming current $i$ with the volumetric flux of the liquid $J$ is equal to the applied pressure gradient $P$ divided by the streaming potential $E$. Since $\frac{E}{P} = -L_{12}/L_{22}$ (Saxen’s relation) it is clear, that a slip contribution to $L_{11}$ or $L_{22}$ in the surface response regime, will also affect the cross-coefficients $L_{12}$ and $L_{21}$. When we substitute the set of equations 5.11, which were obtained by using the Heaviside function in these thermodynamic expressions, we do obtain relations which describe the streaming potential and the electroosmotic flow by

$$
\left( \frac{E}{P} \right)_{i=0} = -\frac{l_{21}}{l_{22}} + \frac{k_I}{l_{22}} \frac{1}{P} \\
\left( \frac{J_v}{i} \right)_{P=0} = -\frac{l_{21}}{l_{22}} \left( 1 + \frac{k_V}{l_{21}} \frac{1}{E} \right)
$$

It is clear that these expressions do not generally obey the Onsager symmetry requirement at the stick-slip transition itself. The Onsager principle only holds for linear force-flux relations not far from equilibrium. It appears that beyond the transition, the pressure gradient $P$ and the electric field $E$ become sufficiently large, and then the Saxen relation is satisfied again for this new, linear, system with viscoelastic interface.

Another method to restore the Saxen symmetry could be to introduce the slip effects of the surface response regime in the values of the coefficients $L$. This can be done for $L_{22}$ in the same way as in the previous sections, where slip was made explicit as separate contributions in $L_{11}$. An alternative strategy would consist in replacing the fluxes $J$ by $J - k_V$ and $i$ by $i - k_I$. From a mathematical point of view, this corresponds to a change of the frame of reference at the transition point. Doing so, we exclude from the experimental fluxes the processes needed to activate the system into a new and more efficient flow mode. The generalized fluxes, which are obtained by these operations will, again, obey the pertinent Saxen relations [11].

Generally speaking, for Saxen’s relations to apply, the system must fulfil two condi-
tions:

- the force-flux relations must be linear
- the fluxes must become zero when the forces are extrapolated to zero.

We shall not elaborate further on this aspect here, but discuss the experimental observations on electrokinetic effects in the flow conductivity of liquids through capillaries and porous systems. The pertinent phenomena, which have been described in the literature, imply changes of slope for electrokinetic variables, like the streaming potential, as a function of the applied pressure gradients. These electric phenomena were referred to as "anomalous surface conduction". They would be anomalous if there were no correlation with slip effects in the flow of liquids through the same pores, like were described in chapter 4.

5.6 An example: electrokinetic effects in water flows through porous plugs

As a start for the study of anomalous surface conduction, we analyzed a comprehensive set of electrokinetic data, measured by Gonzales-Cabalero and Las Nieves [12] for several ion exchange membranes. In their article, extensive data sets are presented on electroosmotic flow as graphs, which show how volumetric flow depend on applied electric potentials. These graphs do show the partially linear, but broken flow curves, which are indicative of anomalous surface conduction, see fig.5.1.
The way in which the streaming potential depends on applied pressure does not exhibit this feature. We have examined this case as a possible manifestation of an electrokinetic effect in the transition from sticking to slip behavior in the interface.

At small Reynolds number, the electroosmotic equations for a cylindrical pore can be applied to flows through porous plugs, if the plugs can be modelled as an ensemble of identical cylindrical pores [13]. The coefficients in the data set under study differ in two trivial ways from the coefficients in tables 5.1 and 5.2. First, Gonzales-Caballero et al used the pressure difference and the electric potential rather than their gradients. Second, the reported coefficients $L_{12}$ hold for a membrane plug and hence constitute the response of the whole ensemble of pores. The ratio between the reported coefficients, written by $L$, and those derived in our analysis, written $l$, is therefore constant. $L/l = N/h$, with $N$ the number of pores and $h$ the pore length.

The values for the conductivity below the transition point are reported in [12]. But values for the coefficients above the transition must be obtained from their figures. The
surface potential of the plug was sufficiently low, so that a linearized approximation can be applied. In ref. [12] the specific conductivity of the water was of the order of $10^{-6}\Omega\text{m}^{-1}$. This value is too inaccurate for calculating double layer thicknesses.

Instead, we applied a minimization procedure to obtain the Debye length $\kappa^{-1}$ and the related coefficients above the transition. From the graphs $J_{P=0} = f(E)$, we can obtain the coefficients $L_{12,0}$ and $L_{12}$. Using the table 5.2, with a linearized exponential term, the slip length $\lambda$ under the influence of externally applied electrical forces can then be expressed as,

$$\lambda = \left(1 - \frac{L_{12}}{L_{12,0}}\right) \frac{1 - G}{G} \frac{2}{\kappa^2 R},$$

(5.13)

where the coefficients $L_{ij}$ are experimentally measured and given in ref.[12].

From the experimental data in ref.[12] we also estimate the limiting surface stress at the transition. The results are given in table 5.3 and illustrated in figure 5.1.

<table>
<thead>
<tr>
<th>No</th>
<th>C ($\mu\Omega.m^{-1}$)</th>
<th>Radius (µm)</th>
<th>Zeta potential (mV)</th>
<th>$\lambda$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Computed</td>
<td>Experimental</td>
<td>Computed</td>
</tr>
<tr>
<td>2</td>
<td>9.5</td>
<td>2.0</td>
<td>1.68</td>
<td>-15.7</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>1.9</td>
<td>1.91</td>
<td>-10.7</td>
</tr>
<tr>
<td>5</td>
<td>3.2</td>
<td>2.8</td>
<td>2.23</td>
<td>-9.0</td>
</tr>
<tr>
<td>6</td>
<td>0.3</td>
<td>1.6</td>
<td>1.47</td>
<td>-8.3</td>
</tr>
<tr>
<td>7</td>
<td>0.2</td>
<td>3.0</td>
<td>3.02</td>
<td>-10.9</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
<td>1.0</td>
<td>2.20</td>
<td>-28.4</td>
</tr>
<tr>
<td>9</td>
<td>9.5</td>
<td>1.6</td>
<td>1.09</td>
<td>-2.9</td>
</tr>
<tr>
<td>10</td>
<td>0.4</td>
<td>1.1</td>
<td>2.57</td>
<td>-26.2</td>
</tr>
</tbody>
</table>

Table 5.3: the first column identifies the membranes as in [12]. Computed results of $R$ and $\zeta$ and experimental data are found in good agreement. Zeta potentials are calculated to check the quality of the iteration process.

In this data set, the measured slip length shows a clear correlation with the surface potential, see fig.5.2 below. Again, this is, by definition, the slip length $\lambda = \eta/\mu$. The applied stress at the interface is parallel to the surface and to the slip velocity, as in eq.5.9.
The surface potential $\zeta$ constitutes a measure for the attraction between the space charge in the liquid and the surface where the counter charges are residing. The trend observed in fig. 5.2 could then be interpreted as a verification of Amonton’s law: friction is proportional to the normal force, which is in this case of electrical nature.

**Figure 5.2:** (a) Critical shear stress and (b) slip length as a function of the zeta potential.

In figure 5.2 the limiting surface stress and the slip length above the transition are given as a function of surface potential $\zeta$.

The limiting surface stress itself, fig. 5.2a, is hardly dependent on the zeta potential. It is of the order of 7 kPa. Unfortunately, the underlying data do not allow more accurate reading of the yield stresses. Therefore the data are scattering considerably. Calculating the relative contributions of the viscous and electric forces to the surface stress, we find
that the electric contribution $E_c$ was negligible in these experiments. The yield stress of the viscoelastic surface material extrapolates to a value between 5 and 10 kPa.

Amonton’s rules would suggest, that the critical shear stress and the slip length should correlate. If we consider the electric potential as a normal force to the surface, the ions will be more attracted by the surface with higher zeta potential, yielding in a smaller slip effect. The former is an elastic property, related to the structure of the interface. The latter is a viscous response when the interface is set in motion by the drag force which is exerted by the liquid flow. It appears in this data set that there could be some dependence on electrical surface properties in the onset of the slip motion at the transition (fig5.2b).

An indication for this idea is, that Barrat et al [14], using a Lennard-Jones potential in a Monte Carlo simulation, found that the larger the surface charge, and hence the higher the surface potential, the more difficult the onset of slip will be in a model liquid that moves over a solid surface.

In the experimental setting which has been chosen by Gonzales-Caballero et al.[12], it is the charges at the surface of the pores, which are strongly interacting with the ions in the electric double layer. At equilibrium, these interactions only manifest themselves in the distribution of ions in the solution. But under flow conditions, these interactions affect the elastic response below the limiting surface stress and the friction above the limiting surface stress. Even if the pores themselves should still be too large to notice these surface effects in the viscous flow properties, it is the electrokinetic cross effects, which betray the slip. That they are much more sensitive to slip is demonstrated here: in the total conductivities, the surface and bulk effect add up in the flows $J_1$ and $J_2$.

The surface response model includes slip in the liquid at a solid interface. It is an alternative to three ”non-slip” models, which were proposed by Dukhin and van de Ven [9] for the electrokinetic characterization of polydisperse particles.

Their first electrokinetic model is the classical approach, which we have used to describe flow in the absence of slip at low shear in the interface. The second model, arbitrarily, assumes that the mobility of the ions varies strongly with their distance from
the particle surface. The third model introduces the notion of anomalous surface conductivity. Its objective was all along, to deal with the breaks in the response curves which authors like Gonzales-Caballero and De Las Nieves [12] had observed. But in this third model, Dukhin and van de Ven relates the anomalous surface conductivity to a transition in the ion conductivity of the chemisorbed counterions in the Stern layer. In their model, this transition should occur when the applied fields and stresses at the interface increase beyond a critical level.

The third model resembles the surface response model. But it addresses the electrical conductivity rather than the flow rate of the liquid in the interface. In this third model of Dukhin and van de Ven, the enhanced ionic mobility above the transition would lead to extra electroosmotic flows as a response to higher applied pressure gradient. The Ohmic conductance $I/E$ should increase for larger applied forces, and so should the electroosmotic flow. However, the experiments tell the opposite. A negative effect is found: the electrical surface effect produces a net decrease of the liquid flow. This is what our surface response regime, with its electrical interactions affecting the transition to slip flow, correctly predicts.

Therefore, concluding our analysis of the experimental data obtained by Gonzales-Caballero and De Las Nieves, we suggest that electrokinetic data, as surface phenomena, are a sensitive monitor for the inherent slip effects on general flow behavior. The so-called anomalous surface conduction that many authors have been assuming to describe experimental electrokinetic results can very well be accounted for by the slip of a flowing liquid over the surface of the pore walls in solid obstructions.

References


6 Surfactant flow through a membrane

Our own experiments on the effects of electric fields affecting liquid flow were performed as in chapter 4. Solutions of ionic and non-ionic surfactants were pumped through narrow pores in thin polymer membranes to study the effect of the electrokinetic phenomena in the pores on the transition to a surface response regime.

In figure 6.2, we have represented the experimental flow diagrams for several surfactant solutions. In chapter 3 the method is described for obtaining such diagrams. Solutions of different surfactants and a range of concentrations between 1 and 10 CMC were selected in order to obtain variable electrokinetic effects that could interfere with a supposedly constant liquid flow resistance.

Crystalline sodium dodecyl sulfate (SDS), commercially available from Fisher Scientific, and crystalline cetyltrimethylammonium bromide (CTMA), commercially available from Acros Organics, were dissolved in doubly distilled water. Solutions of a non-ionic surfactant, Triton X-100 (TX100), pure from Serva, have been prepared by dilution. Concentrations are given in units of the critical micelle concentration (CMC), specific to each surfactant.

CMC values were determined by measuring the change of interfacial tension with respect to the surfactant concentration. They were 2.3 g/l, 0.23 g/l and 0.11 g/l, respectively, for SDS, CTMA and TX100.

Viscosities were measured as already described in the previous chapter for SDS solutions. All solutions were Newtonian and the viscosities for the different concentrations are given in the table 6.1.
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>concentration (*CMC)</th>
<th>Relative viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>1</td>
<td>0.978 ± 0.008</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.057 ± 0.009</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1.088 ± 0.006</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.151 ± 0.007</td>
</tr>
<tr>
<td>CTMA</td>
<td>2</td>
<td>0.994 ± 0.007</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.999 ± 0.008</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.010 ± 0.010</td>
</tr>
<tr>
<td>TX100</td>
<td>5</td>
<td>1.010 ± 0.050</td>
</tr>
</tbody>
</table>

**Table 6.1:** Relative viscosity $\eta/\eta_w$ for various surfactant at various concentrations.

The structure and the mechanical properties of the adsorbed layers at the pore walls are unknown variables for the different surfactants. We expect that they will depend on the shape of the molecules, the polydispersity, the properties of the solvent and the polarity of the membrane material. With SDS adsorbed in a polar interface, there is a bilayer of surfactant molecules. CTMA and TX100 will form analogous layers (admicelles) of adsorbed surfactant in which the hydrophobic moieties of the molecules constitute apolar, alkane-like bilayers inside the admicelle.

The SDS is an anionic surfactant with a CMC of 2.3g/l. It has monovalent Na-counterions in the electric double layer and in the solution. CTMA is a cationic surfactant with 0.23g/l CMC and bromide counterions, Triton X100 is a non-ionic surfactant with CMC=0.1g/l.

When surfactant solutions were pumped through the membranes, the flow rates were varied up to higher values and down again afterwards. The resulting pressures were recorded. The results are given in fig.6.1.
Figure 6.1a: Experimental SDS flow-pressure curves. These curves are plotted by averaging of all the obtained results. Not corrected for different viscosities of the solutions.

Figure 6.1b: Experimental flow-pressure curves for CTMA. The curves are averaged curve characteristics not corrected for solutions viscosities.
Figure 6.1c: Experimental flow-pressure results for TX100. With higher concentrations, one obtains a non-Newtonian response for a Newtonian bulk fluid.

The underlying picture in these experiments is that pore walls in the membrane are covered with bilayer admicelles of adsorbed surfactant. These admicelles are a viscoelastic liquid crystalline material and their mechanical properties as in the chapters 2 and 3. The slip in the interfacial region is assumed to be between the alkane tails in the inner part of the admicelle. In that case, this should give comparable friction coefficients in the plane of shear when the hydrophobic tails of the different surfactants molecules are chemically comparable - like with SDS, CTMA and TX100. It is the counter-ions that differ in mobility and concentration. This varies the streaming potentials. The charge of the adsorbed surfactant layers determines sign and magnitude of the zeta potentials of the pore walls. The electrokinetic effects are proportional with the zeta potential.

The membranes in these experiments were all of the same type of Isopore polycarbonate membranes (already described in chapter 3). In our membrane experiments we have used the expression $L_{xx} = Nl_{xx}$ to relate the overall membrane conductivities $L$ to the conductivity $l$ of individual pores and the number $N$ of parallel pores through the membrane.

In the calculations, data on the experimental flow conductivity, like those with the CTMA in fig.6.1b, must still be corrected for the viscosities of the individual solutions. In case of the high concentrations of the TX100, around 10 times the CMC, the measured
effect appear to not vary linearly even though the solution itself is still known to be Newtonian at such concentration. To obtain a value for $\lambda = f(\dot{\gamma})$, the only way to relate the slip length to the slope of the curves is to use the tangent of the plot.

To maintain electroneutrality, the net current must be zero, which leads to an expression for the electric potential across the membrane. Inserting Saxen’s relations, eq.5.12, into eq. 5.11 for the flow in presence of a streaming potential, we can express the flow rate with no-slip as well as with slip boundary conditions as a function of only a single driving force: the pressure gradient across the membrane.

With the no slip boundary condition, the velocity profile is given by Poiseuille flow. The flow rate through the membrane in the presence of an electrokinetic effect reads,

$$J = \left( L_{11,0} - \frac{L_{12,0}}{L_{22,0}} \right) P = a_1 P$$

(6.1)

In $a_1$, we write the experimental slope of the flow diagram in the low shear stress regime. Adding the slip flow of the surface response regime (i.e. describing the situation above the critical transition) gives,

$$J = \left( L_{11} - \frac{L_{12}^2}{L_{22}} \right) P + \left( k_V - \frac{k_I}{L_{22}} \right) = a_2 P + b$$

(6.2)

In this expression, $a_2$ is the experimental slope and $b$ the extrapolated flow rate at $P=0$.

In these expressions the conductivity $L_{11}$ is not only changed by a transition between regimes with different boundary conditions but also because of "electroviscous" corrections. The electric field, driving the electrokinetics, is related to the applied pressure gradients by the Saxen relations.

As before, the experimental diagrams of fig. 6.1 reveal the discontinuities, which we have interpreted as the transition to the surface response regime.

Plotting the flow rate as a function of the pressure we calculated slip length values.

As a result of these calculations, ignoring electrokinetic effect and assuming a slip length to account for the extra flow we obtain the values of $\lambda$ for the different surfactant concentrations, which are given in table 6.2 under the heading "Hydrodynamic model A".

The procedure for this calculation, which was also used in chapter 4, is given in the Appendix B. Flow rates are expressed with the equations 6.1 and 6.2 and phenomenological
coefficients $L_{22}$ and $L_{12}$ of the electrokinetic processes are set to zero. The slope $a_1$ is then somewhat smaller than the theoretical value that would follow from the viscosities and the radius of the pores. Above the transition the slip length is derived from the ratio of the experimental "Poiseuille" and "Surface Response" slopes,

$$\frac{a_2}{a_1} = 1 + 4 \frac{\lambda}{R}$$

(6.3)

In the hydrodynamic model A, $a_1 = l_{11,0}$ and $a_2 = l_{11}$.

In the model, which takes electroviscous effect into account, the slip at the interface takes over above the transition from the slope $a_1$ to the steeper slope $a_2$. The slopes $a_1$ and $a_2$ are expressed via Saxen’s relations by

$$\frac{a_1}{N} = l_{11,0} - \frac{l_{12,0}^2}{l_{22,0}}$$

$$\frac{a_2}{N} = l_{11} - \frac{l_{12}^2}{l_{22}}$$

(6.4)

In the zero point of charge, the zeta potential is zero. The effects of $l_{12,0}$, $l_{12}$, $l_{22,0}$ and $l_{22}$ are then negligible. But in table 5.1, there is an implicit relation between the slope $a_1$ and the zeta potential, which determines the difference between $a_1$ values with and without considering electrokinetic effects. Since the electrostatic density along a cross-sectional pore area, including the pore wall, must be equal to zero, in the case of a plug flow no charge accumulation will occur at the capillary end and the resulting electroosmotic field will be equal to zero, i.e. $a_2/N = l_{11}$. Rewriting the slope ratio, as in 6.4 and expressing the slip length $\lambda$, one finds,

$$\lambda = \left( \frac{a_2 - a_1 R}{a_1} \frac{R}{4} \right) - \frac{a_2 l_{12,0}^2 R}{a_1 l_{22,0}^2} \frac{1}{l_{11,0}}$$

(6.5)

The first term between brackets is recognized as the slip length calculated by a-priori neglecting electrostatic effects. The second term describes the lowering of the flux $J_1$ by coupled electrokinetic processes.

Now, let us consider what happens at the transition from $a_1$ to $a_2$. Above the transition, there is slip in the adsorbed surfactant layer, so that both the anions in the surface
and the cationic counter-ions are dragged through the capillary together. There is no net charge transport then and the electrokinetic streaming potential collapses. Above the transition, the flow of the liquid is hardly interfered with by electrokinetic effects.

But below the transition, the surface charge is buried in the elastic admicelle, whereas the counter-ions are transported by convection in the liquid flow. Now, there is a viscoelastic effect as described by the second term in eq.6.5. At the transition, from a regime in which $\lambda = 0$ (the no-slip condition and a slope $a_1$) to the regime in which there is slip but only a small electrokinetic effect, the two terms in eq.6.5 must have been of equal size. As long as the electrokinetic effect dominates, the admicelle behaves as an elastic solid, but when the shear stress at the surface exceeds this effect the surfactant layer begins to flow and the electrokinetic effect collapses. That this happens for different flow rates at different concentrations for the same surfactant could be an indication that, again, the electrokinetic effect is a more sensitive monitor of slip in the interface than the flow of liquid through a capillary itself.

Increasing concentrations of the adsorbed surfactants would normally imply increasing zeta potentials and increased attraction between the surface charge and the counter-ions. This would constitute an electric load force which affects the slip coefficient at the interface according to Amonton’s first law, described in the chapter 1 and given in the eq.1.1.

Acting on this kind of an assumption, one could attempt to calculate the zeta potentials which are effective at the transition point to keep the surfactant layer from flowing. Equation 6.5 describes the slip length. The value of $\lambda$ reduces to zero at the transition from the plug flow to the Poiseuille regime. The hydrodynamic contribution (the first term in eq.6.5) is then equal to the electrokinetically determined second term. This second term contains the zeta potential of the surface in its parameters $l_{11,0}$ and $l_{21,0}$, as mentioned in the table 5.1.

Using eq.6.3, the slope $a_1$ leads to an implicit expression

$$\left(l_{11,0} \frac{a_1}{N}\right) l_{22,0} = l_{12,0}^2$$

for the zeta potential $\zeta$ that can be obtained by fully expressing these coefficients. The
results of such calculations are presented in table 6.2 for the different surfactant concentrations.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (*CMC)</th>
<th>(\zeta(mV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>5</td>
<td>(-15.4 \pm 0.8)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>(-18.3 \pm 0.9)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>(-22.3 \pm 1.2)</td>
</tr>
<tr>
<td>CTMA</td>
<td>2</td>
<td>(12.2 \pm 0.6)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>(19 \pm 1)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>(26.1 \pm 1.3)</td>
</tr>
<tr>
<td>TX100</td>
<td>5</td>
<td>(ND)</td>
</tr>
</tbody>
</table>

**Table 6.2:** *Zeta potential calculated using eq.6.6.*

In the calculation of the zeta potential, we have neglected the micellar and free surfactant contribution to the conductivity. The results are in accordance with the assumption of low potentials and we obtain reasonable value for the zeta potentials themselves. The increase in the calculated zeta potentials can be seen as an indication that the mechanical strength of the viscoelastic surface, which is reflected in the change of the transition points to higher surface stresses when the concentration is increased, could indeed be related to the electrokinetic effects in the regime without slip below the transition.

In table 6.3, we have expressed the zeta potential, at the critical transition, calculated as described above (Electrostatic model B), and the slip length above the transition which are obtained with the hydrodynamic model A. The combination of these two sets of values does indeed give negligible values for the slip length at the transition, which was the underlying assumption for the electrostatic model.
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>SDS</th>
<th>CTMA</th>
<th>TX100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative concentration</td>
<td>5</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Hydodynamic model (A)</td>
<td>λ (nm)</td>
<td>7.3 ± 3.7</td>
<td>9.8 ± 3.8</td>
</tr>
<tr>
<td>Electrostatic model (B)</td>
<td>ζ (V)</td>
<td>-15.4 ± 0.8</td>
<td>-18.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>λ (nm)</td>
<td>0.29 ± 0.03</td>
<td>0.29 ± 0.03</td>
</tr>
</tbody>
</table>

Table 6.3: slip lengths for SDS, CTMA and TX100 at various concentrations.
To summarize what we have learned about slip at the solid interface, we can state that the slip length \( \lambda \) is some excess quantity, which describes dissipation mechanisms at interfaces. The more complete the force-flux relations, the more complex the combination of effects becomes which can affect the flow. This is what is described theoretically in the phenomenological equations for a liquid flow \( J_1 \). It seems that the dependence of the slip length on the force field can give information on the structure, mechanical, electrical or molecular of the interfacial region. In the case of adsorbed layers of ionic surfactants, it seems that the slip length and the transition to the response surface regime will be zeta potential dependent. The free energy of the double layer, i.e. the attraction between oppositely charged surfaces and their counter-ions is a factor which can affect the transition from the no slip Poiseuille regime to the surface response regime in which a flowing liquid does indeed slip along solid surfaces.

References


7 Thesis

As has become customary in our laboratory, we shall attempt to condense the main conclusions of this dissertation into the form of statements which are better known as theses. With each of these statements, we give a condensed version of the reasoning behind it, which is also found in the dissertation in a more extended, and sometimes dispersed fashion.

1) Above a certain applied shear stress, the admicelle structure will be modified in such a way that the adsorbed surfactant begins to flow over a solid surface, thereby violating the no slip condition.

The observation of a phase shift between an applied flow rate and a resulting pressure gradient is characteristic of a viscoelastic material. Since the solutions that were studied in this thesis are Newtonian, these viscoelastic properties were attributed to the adsorbed admicelle. The variations in the hydrodynamic flow conductivity are related to the viscous, and elastic interfacial properties. To fully describe the system, the slip length must describe a complex viscosity, the slip length must be written as a complex quantity.

2) The yield value of an adsorbed admicelle with ionic surfactants is dependent on the zeta potential, because electrokinetic effects must be incorporated in the effective yield strength of the soft condensed matter of the admicelle.

In this thesis, the transition was analyzed in term of force balance and thus characterized as the sum of two interdependent terms, a maximum pressure gradient and a maximum induced electric field (electroosmotic potential).

The intensity of the electric field is directly proportional to the zeta potential that
ionizes the liquid in its neighborhood. The net effect of such potential is to organize the liquid in an electric double layer by exerting on the ions an attractive force. An analogy was made with the macroscopic Amonton’s law of friction. The higher the zeta potential, the higher the friction at the surface and so, the lower the interfacial motion. Indeed analyzing table 6.2 with figures 6.1, the onset of the slip regime is found to shift toward higher wall shear stresses with increasing zeta potential.

3) An adsorbed admicelle is a viscoelastic material with a complex viscosity. Surface rheology can then be executed by oscillatory measurements in order to define the loss angle $\phi$ between the applied flow rates and the response of the materials in a interfacial region.

When applying an oscillating flow of SDS through a membrane, a phase angle difference was found. For significant phase differences, a flow enhancement was observed, the required pressure gradient to flow a given amount of liquid in a given time decreases with oscillations. Such results have already been observed with bulk viscoelastic solutions. With increasing wall shear stress (i.e. flow rates), the interfacial region loses its structure and the phase angle shift tends towards 0, a pure Newtonian behavior that defines the slip regime.

4) For each capillary, there is a radius $R = R^*$, so that for $R < R^*$, a Newtonian liquid will flow through the capillary as a plug, whereas there is Poiseuille flow for $R > R^*$.

A transport process moves an unit amount of liquid from one side of the capillary to the other in a specified time. The question whether the flow regime will plug flow or Poiseuille flow is decided by the conductivity for the liquid flow in these two modes. For plug flow,
the flow rate $J$ is given by:

$$J = \frac{\pi R^3 R^*}{8\eta} P$$

and for Poiseuille flow:

$$J = \frac{\pi R^4}{8\eta} P$$

In our problem the question is asked which of the two flow regimes will have the smallest entropy production. This depends on the radius of the capillary. For $R = R^* = 4\frac{2}{\pi}$, the entropy production is equal for the equal $J$ in the two cases. But for smaller radii $R < R^*$, the smallest entropy production is with plug flow, whereas it is the smallest for Poiseuille flow if $R > R^*$. This implies that the no slip condition is violated in systems with characteristic dimensions below some inherent value, like in colloids and nanotechnological devices.
Appendix A

A critical radius $R^*$
Appendix A

In equation 2.8, two transport mechanisms are compared assuming a given flow rate. We propose in this appendix to explain why such result is found. In a second part, we will introduce the concept of a critical shear stress, $\tau^*$, a concept that is used in chapter 2, page 14. Such parameter is then described as a cut-off tensor (surface response regime).

Appendix A1: Description of discrepancy

The minimum entropy production is achieved with the process that uses the least energy to realize a given work with given conditions. To compare the various possible processes, one has to compare their entropy production for a given production, i.e. the same flow in the two cases.

\[
J_P = \frac{\pi R^4 - \frac{\partial p}{\partial l}}{8\eta_0} = L_{11,P} \frac{-\partial p}{\partial l} \tag{A1}
\]

\[
J_{PF} = \frac{\pi R^4 R^* - \frac{\partial p}{\partial l}}{8\eta_0} = L_{11,PF} \frac{-\partial p}{\partial l}
\]

Let’s consider the case where $R > R^*$. For a given pressure gradient, the most efficient transport mechanism is the one that gives the higher flow rate. The Poiseuille flow is preferred for $R > R^*$, but plug flow is dominant for $R < R^*$.

Appendix A2: a chemical engineer approach

Once the unit operation installed, a chemical engineer will deal with forces and the geometry of its system is now a fix property. His goal is then to provide a given flux with a given pressure, or driving force. In fact, the Navier-Stokes equation itself is a force balance. We will now introduce a critical wall shear stress $\tau^* = \frac{R^* - \frac{\partial p}{\partial l}}{2}$ for which slip is observed. Equations A1 rewrites,

\[
J_P = \frac{-\pi R^3}{4\eta_0} \left( \frac{-R}{2} \frac{-\partial p}{\partial l} \right)_P = \frac{-\pi R^3}{4\eta_0} \tau_{w,P} \tag{A4}
\]

\[
J_{PF} = \frac{-\pi R^3}{4\eta_0} \left( \frac{-R^*}{2} \frac{-\partial p}{\partial l} \right)_{PF} = \frac{-\pi R^3}{4\eta_0} \tau_{w,PF}
\]
For a given flow rate, if one varies the radius, the pressure gradient will vary too but with a different order of magnitude.

\[
\left. \frac{-\partial p}{\partial l} \right|_P = \frac{8\eta_0}{\pi R^4} J \\
\left. \frac{-\partial p}{\partial l} \right|_{PF} = \frac{8\eta_0}{\pi R^3 R^*} J
\]

(A5)

From A4, for a given flow, the pressure gradient tends toward zero with increasing radius. This means that, for a given flux, the wall shear stress is decreasing with increasing radius. When \( \tau_w \) is smaller than \( \tau^* \), the stress acting at the solid-liquid interface is not big enough to break the molecular interaction, a no-slip condition should be applied, the preferred mechanism is a Poiseuille flow.

In fact, the only consideration of the radius is not sufficient to determine a-priori whether or not slip can be observed. As chemical engineers, we will prefer the Newtonian approach based on force analysis.

In the case where the radius is decided and fixed, the only degree of freedom left to the experimentalist is to observe the evolution of the flow rate as a function of the pressure, or vice versa.
9 Appendix B

Hydrodynamic or electrostatic model
Appendix B

We discuss in this appendix the difference between the hydrodynamic model A, in which only viscous forces are present in the bulk, with the electrostatic model B where both an electric field and a viscous force is intervening in the flow field expression. These two models are independent and excluding each other. We consider in this thesis and in this appendix the error than can be done if one neglects significant electrostatic forces.

Appendix B1: the pure hydrodynamic model

As written on page 59, the pure hydrodynamic case should be considered when no charge distribution is present. By example, if the experimental conditions are such that the point of zero charge of the surface is reached, an electric double layer will not develop. In absence of double layer, the electroosmotic field will be equal to zero, there is no charge accumulation at the ends of the capillary.

The slopes before and after the stick-slip transition can then be written as,

\[
\begin{align*}
\frac{a_1}{N} &= \frac{J}{P} = \frac{\pi R^4}{8 \eta_0} = l_{11,0} \\
\frac{a_2}{N} &= \frac{J}{P} = \frac{\pi R^4}{8 \eta_0} + \lambda \frac{\pi R^3}{8 \eta_0} = l_{11}
\end{align*}
\]

where N is the pore number of the membrane. Dividing by N yields to consider the flow of liquid within one single pore.

By dividing the slopes, a very simple and attractive expression is found for the determination of \( \lambda \).

\[
\frac{a_2}{a_1} = \frac{l_{11}}{l_{11,0}} = 1 + 4 \frac{\lambda}{R}
\]

\[
\lambda = \frac{a_2 - a_1 R}{a_1 \frac{R}{4}}
\]

The only pre-requisite knowledge concerns the pore radius R of the membrane to obtain the slip length. The presence of an electroviscous effect singularly complicates the determination of \( \lambda \).
Appendix B2: electrostatic case

If the membrane properties are known, one can easily estimate the slope \( a_1 \) that should be experimentally observed in the case described in appendix B1, see eq.B1. A lower experimental value than expected is a sign of extra forces that put a brake on the system. In many cases, such deviations are observed in narrow capillaries and are attributed to the presence of an electroosmotic effect, see chapter 5.1.

The slopes \( a_1 \) and \( a_2 \) are then expressed, using the Saxen’s relations, see chapter 5.5 as,

\[
\frac{a_1}{N} = l_{11,0} - \frac{l_{12,0}^2}{l_{22,0}} \\
\frac{a_2}{N} = l_{11} - \frac{l_{12}^2}{l_{22}}
\]

(B3)

In the zero point of charge, the zeta potential is zero. \( l_{12,0}, l_{12}, l_{22,0} \) and \( l_{22} \) are then equal to zero.

Using the table 5.1, a relation between the slope \( a_1 \) and the zeta potential is found. This approach requires the full knowledge of the pore membrane (radius \( R \) and pore number \( N \)).

To explain the mistake that is done by neglecting the electroosmotic effect when significant, we shall now consider a limiting case\(^1\), the Poiseuille flow becomes plug flow from a certain value of the shear stress.

Since the electrostatic density along a cross-sectional pore area, including the pore wall, must be equal to zero, in the case of a plug flow no charge accumulation will occur at the capillary end and the resulting electroosmotic field will be equal to zero, i.e. \( a_2/N = l_{11} \). Rewriting the slope ratio, as in B2 and expressing the slip length \( \lambda \), one finds,

\[
\lambda = \left( \frac{a_2 - a_1}{a_1} \frac{R}{4} \right) - \frac{a_2 l_{12,0}^2 R}{a_1 l_{22,0} l_{11,0} 4}
\]

\(^1\)The real situation, where the Poiseuille profile undergoes a transition towards a sum of plug flow and Poiseuille, is treated in the thesis, chapter 5.
where the first term between brackets is recognized as the slip length calculated by a-priori neglecting electrostatic effects. In agreement with table 5.5, the slip length is over-estimated if one uses the hydrodynamic model when the electrostatic one applies.
10 Symbols used in this thesis

Latin alphabet:

\[ E, E_c \]  electric field and critical electric field gradient \( (V\ m^{-1}) \)
\[ F \]  force \( (N) \)
\[ J \]  flow rate \( (m^3\ s^{-1}) \)
\[ N \]  load \( (N) \)
\[ l, L_{xx} \]  phenomenological coefficients, conductance
\[ N \]  pore number contained in a membrane
\[ \hat{n} \]  normal unit vector to a surface
\[ P, P_c \]  pressure and critical pressure gradient \( (N\ m^{-3}) \)
\[ R \]  pore radius \( (m) \)
\[ R^* \]  thermodynamical transition radius \( (m) \)
\[ \frac{dS}{dt} \]  entropy production \( (JK^{-1}) \)
\[ v_s \]  slip velocity \( (m\ s^{-1}) \)

Greek alphabet

\[ \phi \]  electric potential \( (V) \)
\[ \Phi \]  dissipation function, \( \Phi = T \dot{S} \) \( (J) \)
\[ \Psi \]  force \( (N) \)
\[ \eta_0 \]  bulk viscosity \( (N\ s\ m^{-2}) \)
\[ \kappa \]  Debye length \( (m^{-1}) \)
\[ \lambda \]  slip length \( (m) \)
\[ \mu \]  friction coefficient \( (N\ s\ m^{-3}) \)
\[ \rho \]  density \( (kg\ m^{-3}) \)
\[ \overrightarrow{\tau} \]  shear stress tensor
\[ \tau_w \]  wall shear stress \( (N\ m^{-2}) \)
\[ \chi \]  ionic conductivity \( (S\ m^{-2}) \)
\[ \zeta \]  zeta potential \( (V) \)
Summary

In the first chapter a review is presented of the existing ideas on surfactant dynamics, and irreversible thermodynamics is introduced as a tool of reference for different models. The two examples of lubrication and detergency are used to survey the implications of specific boundary conditions in dissipative processes.

The second chapter gives a review of some published results and reinterprets those in terms of entropy production. The concept of a critical capillary radius, for which liquid flow with slip in the interface would be the thermodynamically favoured mode is discussed. This discussion leads to a new interpretation of the slip length: as a measure for the interfacial viscosity.

To investigate this concept, Newtonian surfactant solutions are subjected to oscillating flow through a membrane. Phase differences between the flows and their driving forces are recorded as a function of the stress. The observations are attributed to the complexity of the pore/solution interface, where surfactant adsorption is taking place. The experiment indicates viscoelastic interfacial behaviour. With low shear stress as the driving force surface elasticity is predominant and the no slip boundary condition applies for the flow pattern. At higher stresses, surface motion is allowed.

In the fourth chapter an expression is worked out for the momentum transfer from the bulk of a flowing liquid to the interface. This equation allows the calculation of the slip length as a function of the relevant driving forces. Two linear regimes are observed in flows through a membrane of surfactant solutions with different concentrations. The difference between these two regimes is described in terms of a stick to slip transition.

In the following chapter, the mathematical description is extended to consider both the stick to slip transition and the effect of coupled hydrodynamic and electroosmotic flows. This extended model is then applied to, as yet, unexplained observations of regime transitions in the electroosmotic flow through porous plugs. It follows from the analysis that the slip length (i.e. the interfacial viscosity) should depend on surface forces, which are characterized by the zeta potential.
In the sixth chapter our mathematical models are applied to describe the flow of various surfactants at different concentrations through porous membranes. A definition of the deceivingly simple concept of a slip length as the sum of interfacial effects is suggested. These effects can then be lumped together in a new interfacial excess function for the fluid flow over a solid surface (the viscoelastic interfacial flow). A description in terms of a (complex) interfacial viscosity is preferred over the concept of a slip length.

The last chapter summarizes our results in succinct statements about the physical chemistry of surfactant solutions, which flow over solid pore walls of membranes, textiles and sorbent materials.
Samenvatting

In het eerste hoofdstuk wordt de thermodynamica van irreversibele processen geïntroduceerd als een methode om experimentele waarnemingen te correleren. De twee voorbeelden van smering en detergentie worden gebruikt om de implicaties te illustreren als de randvoorwaarden voor dissipatieve processen er op worden toegepast.

In het tweede hoofdstuk worden enkele waarnemingen uit de literatuur ge(her)-interpreteerd in termen van entropieproduktie. Het concept van een kritieke straal $R^*$, zodat voor $R < R^*$ het slip-effect aan de vaste wanden de thermodynamisch meest gunstige randconditie oplevert voor het snelheidsprofiel van een stromende vloeistof in een capillair, wordt besproken. Het hoofdstuk wordt afgesloten met een nieuwe interpretatie van de "slip length" als een oppervlakteviscositeit.


Het vierde hoofdstuk begint met een uitdrukking voor de impulsoverdracht van de bulk oplossing naar het oppervlak. Met deze vergelijking is de "slip length" te berekenen als functie van allerlei relevante krachten. Als deze analyse toegepast wordt op de stroming van surfactant oplossingen met diverse concentraties door een membraan blijken er daarbij twee lineaire regimes te worden waargenomen. De overgang daar tussen wordt geïnterpreteerd als een "stick to slip" transitie.

In het volgende hoofdstuk is de beschrijving zo uitgebreid dat zowel de hydrodynamische overgang als een electroosmotische stroom kunnen worden meegenomen. Dit uitgebreidere model wordt dan toegepast op (tot nu toe onverklaarde) waarnemingen over
de electroosmostroom in een poreuze prop. Hierbij blijkt de berekende "slip length"
afhankelijk van oppervlaktekrachten die samenhangen met de zeta potentiaal.

In het zesde hoofdstuk passen we ons wiskundige model toe op onze eigen metingen
aan de stroom door poreuze membranen van diverse surfactant oplossingen bij verschillende concentraties. Een beschrijving van de "slip length" als een som van verschillende bijdragen (mechanismen) wordt voorgesteld. Samen leveren zij een nieuwe excesgrootheid (de viscoelastische oppervlaktestroming) op die kan worden toegekend aan het grensvlak tussen een vaste wand en een stromende vloeistof.

Het laatste hoofdstuk vat onze resultaten samen in bondige stellingen over de fysische chemie van surfactantoplossingen die over de vaste poriewanden van membranen, textielle weefsels en andere poreuze sorbentia gepompt worden.
Curriculum Vitae

Christophe Cheikh was born on May 8, 1974 in Colmar (France). After a technical degree in chemistry, in Strasbourg (1993-1995), he studied chemistry in the "Ecole Nationale Superieure de Chimie de Mulhouse" that he left in the last year to complete his diploma in the "Denmark Technical University" in Copenhagen.

As an engineer in chemistry, he wanted to work with surfactants and he followed a one-year specialization degree. He obtained his "DESS en chimie de formulation" in Lille (1999) before to sign up for a PhD position in Sept.2000 in the Laboratory of Physical Chemistry in Delft. This thesis is the result of his investigations on the flow behavior of surfactant solutions under shear flows.
Acknowledgements

With this thesis, another page of my life is turning but before moving on, I want to thank those who contributed to this work and to my own intellectual and social development.

First of all, I want to thank Ger. Since my background was not mathematics oriented, I quickly met my limits. I worked hard to push them a bit further everyday but without you, this thesis would only be a bunch of true but not proven ideas. You tried to teach me how to be rigorous. At least, I hope you managed partially. At the end of my PhD, you equally convinced me to apply oscillating flow fields. With this brilliant idea, I almost wish a PhD contract would be five years long.

I also want to thank Prof Frens. Not only for this amazing amount of energy that you use to help me in the redaction of this thesis, too short in your opinion, but also for the interesting discussions we had. I was almost surprised at the end that we could agree on the experimental results. To summarize what I learnt with you, I will refer to Kekule who dreamed the structure of benzene. He said, "Let us learn to dream gentlemen, and then perhaps, we shall learn the truth".

To summarize the influence of these two mentors, one was telling me "look at the horizon, there is your goal" and the other one was saying, "anywhere you go, make one step after another". I think I still did not choose between the two of you.

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I have now to leave you. The future is waiting for me, a future with Janneke. Farewell!!!
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