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Clarke, N., Gibbons, N. and Long, D.R. (2020) Diffusio-osmosis and wetting on solid surfaces: a unified description based on a virtual work principle. *Soft Matter*, 16 (14). pp. 3485-3497. ISSN: 1744-683X

<https://doi.org/10.1039/c9sm02118c>

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Diffusio-osmosis and wetting on solid surfaces: a unified description based on a virtual work principle.

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(Dated: March 9, 2020)

Abstract

In order to account for diffusio-osmosis, Derjaguin proposed long ago that there is an excess pressure confined within a layer of typically a few nanometers in the vicinity of a solid surface immersed in a liquid and resulting from the interaction between the liquid and the surface. In the presence of a composition gradient in the liquid a confined pressure gradient parallel to the surface is therefore responsible for the diffusio-osmotic flow. This picture appears in contradiction with the contact theorem of colloidal science according to which such excess pressure does not exist. We propose a theoretical description for calculating hydrodynamic flows in inhomogeneous liquids in the vicinity of solid interfaces which is consistent with the contact theorem. This approach is based on a Gibbs free energy and a virtual work principle for calculating the driving forces in the liquid due to inhomogeneous composition along a capillary and to the interaction with the solid interfaces. Our approach allows to show that the physics at play is the same in wetting or in diffusio-osmosis experiments, as one can go continuously from the latter to the former by making composition gradients sharper. We obtain an explicit expression for the diffusio-osmotic mobility which depends on the Gibbs free energy density in the vicinity of the interface and its dependence on the solute concentration in the liquid beyond the interfacial region, and which is inversely proportionnal to the liquid viscosity.

I. INTRODUCTION

The most simple description of hydrodynamic motion is provided by the Stokes equation which is valid when inertial effects are negligible, in the so-called low Reynolds number limit [1]. Even if this is the most simple limit of the Navier Stokes equation, this equation covers a broad range of phenomena and embodies a wealth of various physical situations. It is the relevant equation for polymer dynamics for describing Rouse relaxation or Zimm relaxation which takes into account long-ranges hydrodynamic interactions [2]. Stokes equations are used also for describing the motion of electrically charged particles under the application of an external electric field [3]. This motion is called electrophoresis. The same equations allow for describing the hydrodynamic flow created in a capillary when an electric field is applied [3]. The electric field exerts a force in the vicinity of the capillary, where the liquid is electrically charged within the so-called Debye layer. This force pulls the liquids in the vicinity of the capillary and a so-called plug flow is created: velocity gradients are non zero within a few Debye length and beyond the hydrodynamic flow is uniform. If the capillary surface is uniformly charged and if the liquid is also homogeneous, no pressure is created by the applied electric field. When the surface is non-uniformly charged, a pressure gradient appears on larger scale and a so-called Poiseuille flow superimposes to the plug flow [4]. Stokes equations are relevant also for describing wetting phenomena [5, 6]. A central issue of wetting is describing how a droplet spreads on a surface in order to reduce the interfacial energy which is the driving force of the effect. The reverse process, dewetting, is how a liquid recedes when it has been forcefully spread on a surface. These processes are described by Stokes equations in the presence of pulling forces resulting from surface tension imbalances at the triple line between the substrate, the liquid and the atmosphere or between the substrate and the two liquids when one considers a droplet imbedded in another liquid for instance.

Wetting or dewetting are a particular example of so-called “force-free” motions [7]. This name is given to motions which take place without the presence of an external applied field, contrary to the case of electrophoresis or electroosmosis where the driving force is an externally applied electric field. In the case of wetting or dewetting, the evolution and the motion are driven by internal forces. Other examples of “force-free” motions include

diffusiophoresis where a solid particle moves in a liquid which has a gradient of composition, or thermophoresis where a solid particle moves in a liquid with a temperature gradient [3]. Other kinds of so-called force-free motions may include spinodal decomposition in blends, in particular in polymer blends where phase separation processes result in motions without the presence of an applied field [8, 9].

Frequently, each of these phenomena are described in their particular way. Spinodal decomposition is described by the Cahn-Hilliard equation and its subsequent extensions: a gradient of chemical potential results in diffusion and possibly also in convection. The wetting dynamics of a droplet is described as a result of the imbalance of capillary forces at the triple line, which induces a Poiseuille-like Stokes flow in the droplet. Diffusiophoresis is described by the Derjaguin model [3, 10–14]. These authors assume that interfacial forces between the solid surface and the liquid, which have a range of up to a few tens of nanometers, create a local pressure in the vicinity of the interface. A gradient of composition along a capillary results in a gradient of pressure due to the interaction between the liquid and the solid interface. This gradient of pressure in the vicinity of the solid interface creates a diffusio-osmotic flow. This flow is a plug flow if the composition gradient in the vicinity of the interface is constant along the capillary. Calculating the pressure gradient requires a detailed description of forces on a local scale between the solute and the interface, including ionized charges in its vicinity when the interface becomes ionized. This description is complex and cannot be checked directly experimentally, except by measuring the diffusio-osmotic mobility which is the very effect that one aims at calculating. In any case, the Derjaguin picture used for describing diffusio-osmosis appears in contradiction with the well established contact theorem of colloidal science [15–19], a consequence of which is that the pressure between two plates immersed in a liquid is uniform between the two plates. The pressure becomes equal to the atmospheric pressure (if we assume that the system is equilibrated under the atmospheric pressure) when the distance between the two plates is larger than a few tens of nanometers, depending on the range of the interactions. In particular, the interfacial interactions between a single plate and the liquid does not result in the presence of an excess pressure in the vicinity of the solid surface. The pressure in that case is uniform and equal to the pressure under which the system is at thermodynamic equilibrium.

There is thus a need to reconcile what is known in colloidal science as regards to the equilibrium state in the vicinity of colloidal surfaces, the interaction between colloids on the one hand, and the description of the physics of diffusio-osmosis. The description of the latter, in its present state, is in contradiction with the former. We solve this problem by introducing a mesoscopic description of Stokes flow in inhomogeneous solutions and in the presence of solid interfaces as a relaxation process towards thermodynamic equilibrium in a way that is consistent with the Onsager general formulation. This description is based on a variational principle which relates the Gibbs free energy of the considered system to the driving forces in Stokes equation. This variational principle was introduced by Doi and Onuki [20]. This variational principle is directly linked to the fact that the Stokes equations are Onsager-like equations [1, 21] which drive the evolution of the system in out-of-equilibrium conditions and which relate linearly the fluxes to the thermodynamic forces. This description allows for describing convection in inhomogeneous liquids and flow in the presence of solid interfaces in situations corresponding either to wetting or dewetting or diffusio-osmosis. In particular there is no need for a confined pressure field in the vicinity of solid surfaces for creating diffusio-osmosis flows. Our description allows for a common formalism regarding wetting or diffusio-osmosis as relaxation processes towards thermodynamic equilibrium. The physics at play is the same in both types of experiments, as one can go continuously from the latter to the former by making the composition gradient sharper.

II. DERJAGUIN'S TREATMENT OF DIFFUSIO-OSMOSIS

Derjaguin considered the case of a solution bounded by a solid surface. The volume fraction of the solute is denoted by ψ . In the vicinity of the surface, there is an interaction potential Φ which decays with the distance z from the surface. This interaction potential exerts a body force due to the solute concentration which is given by $\mathbf{f}_{ext} = -\psi \nabla \Phi$ which we assume to be oriented in the direction opposite to the normal to the surface. The Stokes equations read [1]:

$$\begin{aligned} -\nabla p + \nabla \cdot \eta (\nabla \mathbf{v} + \nabla \mathbf{v}^+) - \psi \nabla \Phi &= 0 \\ \nabla \cdot \mathbf{v} &= 0 \end{aligned} \tag{1}$$

where η is the viscosity, p is the pressure and \mathbf{v} is the velocity field. The flow velocity is zero in the z -direction and is parallel to the interface. Let us suppose that the gradient of solute volume fraction is in the x -direction, and a decreasing function of x for being specific. By considering Eq.1 in the z -direction, one obtains then

$$\frac{-\partial p}{\partial z} - \psi \frac{\partial \Phi(z)}{\partial z} = 0$$

By integrating between the current z -position and far from the solid surface, one obtains an expression for the pressure term :

$$p(x, z) = -\psi(x)\Phi(z) + p_0 \quad (2)$$

where p_0 is the atmospheric pressure under which the system is equilibrated (in the absence of solute concentration gradient). This pressure field is confined within a layer corresponding to the range of the potential interaction, which may be a few nanometers and up to a few tens of nanometers, depending on the nature of the interactions and the Debye layer of the solution as regard to ionic interactions. We see that this pressure field is present even in the absence of a gradient of solute concentration, provided the solute concentration is different from zero. If one considers a high volume fraction of solute, *e.g.* 1%, and if the interaction potential is 0.1 eV per molecular volume at the surface, the pressure is of order 10^7 Pa and decays to the atmospheric pressure under which the system is equilibrated. If the interface we consider is that of a capillary with diameter a few micrometers or more which connects two reservoirs, one with a high solute concentration and the other one without solute, a concentration gradient establishes along the capillary in the vicinity of its surface. The surface of the latter can be considered as flat if the diameter is much larger than the range of the potential Φ which we assume. Then, the pressure gradient is described by Eq.2 and Eq.1 becomes:

$$\frac{\partial \psi(x)}{\partial x} \Phi(z) + \eta \frac{\partial^2 v_x}{\partial z^2} = 0 \quad (3)$$

Let us assume that Φ is given by

$$\Phi(z) = \Phi(0) \exp\left(\frac{-z}{\lambda}\right)$$

This equation allows to calculate the flow velocity profile

$$v_x(z) = \frac{\lambda^2}{\eta} \frac{\partial \psi(x)}{\partial x} \Phi(0) \left(\exp\left(\frac{-z}{\lambda}\right) - 1 \right) \quad (4)$$

Eq. 4 represents a so-called plug-flow observed in diffusio-osmosis experiments and also in electro-osmosis for instance [4]. This is a standard behavior when forces act on the liquid only within a thin layer in the vicinity of a solid surface, as it is a case for the considered diffusio-osmotic flow. The driving force in Derjaguin's picture is the pressure field in the vicinity of the capillary wall.

However, the term $p(x, y)$ is difficult to interpret. Even in the absence of a concentration gradient, it corresponds to a local pressure that can be of typical order of magnitude 10^6 - 10^7 Pa. This pressure should be maximal at the very interface between the solid and the liquid and decay towards the atmospheric pressure at a distance corresponding to the range of the interaction potential $\Phi(z)$. As mentioned above, this picture is in contradiction with the current understanding regarding interactions between colloidal particles in solutions, or regarding the thermodynamical state of a liquid in the vicinity of a colloidal particle at thermodynamic equilibrium. For instance, if one considers two parallel plates in an electrolyte solution [17], the Poisson-Boltzmann model predicts that the repulsive pressure between the two plates is homogeneous in the volume bounded by these two plates and is given by

$$P(z, D) = k_B T \rho_0(D) + p_0$$

where k_B is the Boltzmann constant, T is the temperature, D is the distance between the two plates, $\rho_0(D)$ the counterion density mid-way between the plates and z the coordinate in the direction normal to the plates. In particular the pressure is uniform and decays to zero when the plates are separated by a distance larger than the range of the molecular interactions, which are typically of order a few nanometers up to a few tens of nanometers. In a capillary for which the diameter is larger than a micrometer, this pressure is uniform and equal to the atmospheric pressure p_0 . This result is known as the so-called contact theorem [15, 17, 18] and is exact, beyond the Poisson-Boltzmann approach and regardless of the nature of the interactions.

The presence of a layer with a pressure larger than the atmospheric pressure under which the system is equilibrated raises indeed some questions. The first one is the meaning of the grand-canonical equilibrium under an imposed pressure (*e.g.* atmospheric pressure p_0) if some regions of the considered system have a higher pressure than the nominal pressure

p_0 as a result of the interactions between parts of the systems. For instance, the thin layer with a higher pressure in Derjaguin's picture should relax by slightly expanding to decrease the pressure towards p_0 , thereby reducing the Gibbs free energy of the system. The very presence of this thin layer with a higher pressure seems to contradict the very concept of thermodynamic equilibrium under an imposed pressure.

Our point of view is that Derjaguin's calculation takes into account only a part of the stress tensor, corresponding to molecular interaction between the long-ranged interaction between the solid surface and the solute. However, this is not correct. When one considers the thermodynamics of dielectric media one does not consider separately the stress associated to intermolecular interactions and the stress of the electric field itself. One considers only the whole. This is the meaning of the equilibrium condition discussed in Landau and Lifshitz [22], for which the field and the density of the sample relax together to build the thermodynamic equilibrium. It is explicitly stated that there is no body force in the dielectric. On the contrary, in Derjaguin's picture, the interaction between the solid surface and the liquid are treated as external body forces acting on the liquid. In a dielectric, all forces on a elementary volume are transmitted through the boundaries by the local stress tensor σ which satisfies thus the condition [22] :

$$\nabla \cdot \sigma = 0 \tag{5}$$

Derjaguin's force violates this condition by introducing a body force. The thermodynamic equilibrium is described by minimizing the contribution of all the interactions, that of the field and the intermolecular forces that cannot be considered separately. This is what makes necessary the introduction of the polarizability of a material. This is the case for instance when one considers the electro-striction effect in a dielectric. The body force of the Derjaguin's treatment of the diffusio-osmosis is only a part of the interaction. One cannot consider that only a part of the local stress tensor acts on the liquid without taking into account all the contributions to the stress tensor. And when one take all the contributions, the pressure is that under which the system is equilibrated, that is the atmospheric pressure p_0 . As a consequence, the Derjaguin's picture breaks down for describing diffusio-osmosis.

One needs to propose another approach for explaining the diffusio-osmotic effect consistently with what is known regarding the equilibrium thermodynamics of liquids in the

vicinity of colloids.

III. HYDRODYNAMICS

We introduce in this section a formalism for Stokes equations in out-of-equilibrium liquids, such as inhomogeneous ones, based on a virtual work principle. It allows to obtain equations which describe the Stokes flow as a relaxation process towards thermodynamic equilibrium. In the following we use a non-specified Gibbs free energy. It is made dimensionless by considering the Gibbs free energy per monomer, by dividing the physical Gibbs free energy by the thermal energy, and by setting as unit length scale the monomer length or the molecular size in simple liquids. In an out-of-equilibrium situation, one can calculate the stress as a driving force in a liquid according to a principle of virtual work. The total Gibbs free energy is given by

$$G = \int g(\psi(\mathbf{r}), \nabla\psi(\mathbf{r}))d^3\mathbf{r}$$

g is the density of Gibbs free energy. It is a function of ψ and $\nabla\psi$. The dependance of g on $\nabla\psi$ allows for taking into account the finite range of the interactions. Following Doi and Onuki [20], let us consider a virtual displacement in the liquid so that \mathbf{r} is changed into $\mathbf{r} + \delta\mathbf{r}$. The quantities ψ and $\nabla\psi$ are varied by an amount

$$\begin{aligned}\delta\psi &= -\delta\mathbf{r}\cdot\nabla\psi; \\ \delta\nabla\psi &= \nabla\delta\psi\end{aligned}\tag{6}$$

The density of Gibbs free energy may be assumed to be the sum of two contributions :

$$g(\psi, \nabla\psi) = g^{(0)}(\psi) + g^{(1)}(\nabla\psi)$$

Then the variation of Gibbs free energy is given by :

$$\delta G = \int \delta g(\mathbf{r})d^3\mathbf{r} = \int \left(\frac{dg^{(0)}}{d\psi}\delta\psi + \frac{dg^{(1)}}{d\nabla\psi}\cdot\delta\nabla\psi \right) d^3\mathbf{r}$$

By substituting Eq.6 in the previous equation, and by integrating by parts the second term, one obtains:

$$\delta G = \int -\delta\mathbf{r}\cdot\nabla\psi \left(\frac{dg^{(0)}}{d\psi} - \left(\nabla\cdot\frac{dg^{(1)}}{d\nabla\psi} \right) \right) d^3\mathbf{r}\tag{7}$$

We assume that the term

$$\frac{dg^{(1)}}{d\nabla\psi}\delta\mathbf{r}\cdot\nabla\psi$$

is zero on the boundaries. This is the case if the flow we consider is zero at the boundaries, or if the fluid is homogeneous at these boundaries. If this is not the case, an additional contribution at the boundaries should be added. The stress is related to the variation of Gibbs free energy by :

$$\delta G = - \int \delta \mathbf{r} \cdot \nabla \cdot \boldsymbol{\sigma} d^3 \mathbf{r} \quad (8)$$

One obtains thus an expression for the hydrodynamic stress:

$$\nabla \cdot \boldsymbol{\sigma} = \left(\frac{dg^{(0)}}{d\psi} - \nabla \cdot \frac{dg^{(1)}}{d\nabla\psi} \right) \nabla\psi = \mu \nabla\psi$$

One may introduce the quantities

$$\begin{aligned} \mu^{(0)} &= \frac{dg^{(0)}}{d\psi} \\ \mu^{(1)} &= \frac{dg^{(1)}}{d\psi} \end{aligned}$$

$\mu^{(0)}$ is the usual chemical potential. $\mu^{(1)}$ is a functional derivative which contains the contribution in $\nabla\psi$ to the Gibbs free energy. This is this term which gives rise to surface tension in inhomogeneous liquids. The force term resulting from thermodynamic forces has to be included into the Stokes equation for describing hydrodynamic flow in out of equilibrium conditions. An explicit expression for μ is given in Appendix A for a specific Gibbs free energy.

The stress tensor introduced above, which we denote here $\boldsymbol{\sigma}_G$, allows for calculating the free energy release associated with a flow field \mathbf{v} . The Stokes equation allows for calculating the dissipation due to the flow. When a liquid is submitted to a body force \mathbf{f}_{ext} , the dissipated power P reads :

$$P = - \int d^3 r \nabla \cdot \boldsymbol{\sigma}_{Hydr} \cdot \mathbf{v} = \int \mathbf{f}_{ext} \cdot \mathbf{v} \quad (9)$$

When the forces are internal, the dissipation is equal to the opposite of the rate of release of free energy $\boldsymbol{\sigma}_G$, and the equations read

$$P = - \frac{dG}{dt} = \int \mathbf{v} \cdot \nabla \boldsymbol{\sigma}_G d^3 \mathbf{r} \quad (10)$$

One obtains then

$$\nabla \cdot \boldsymbol{\sigma}_{Hydr} + \nabla \cdot \boldsymbol{\sigma}_G = 0$$

This equation ensures that the relaxation towards equilibrium is consistent with Onsager theory. The fluxes ($\nabla \mathbf{v}$) are proportional to the thermodynamic forces $-\sigma_G$. The free energy release rate is equal to the dissipation rate and this equality is local. The basic equation regarding the hydrodynamic flow is therefore:

$$\begin{aligned} -\nabla p + \nabla \cdot \eta (\nabla \mathbf{v} + \nabla \mathbf{v}^+) + \mathbf{f}_{ext} + \mu \nabla \psi &= 0 \\ \nabla \cdot v &= 0 \end{aligned} \tag{11}$$

where we added a possible external force \mathbf{f}_{ext} which would drive the system out-of-equilibrium. The term $\mu \nabla \psi$ corresponds to internal forces.

IV. HYDRODYNAMICS AS A BRANCH OF OUT-OF-EQUILIBRIUM STATISTICAL PHYSICS

Navier-Stokes equations are described in *e.g.* *Landau and Lifshitz* [1] as a branch of out-of-equilibrium statistical physics. Out-of-equilibrium systems have been described by Onsager by introducing an out-of-equilibrium entropy. This entropy is smaller than that at equilibrium. This entropy is expressed as a function of coarse-grained variables (x_a). The derivative of the entropy according to each of these variables provides the thermodynamic forces X_a [1, 21, 23] :

$$X_a = -\frac{\partial S}{\partial x_a} \tag{12}$$

Then, the variables x_a relax towards equilibrium according to Onsager equations:

$$\frac{dx_a}{dt} = -\sum_b \gamma_{a,b} X_b \tag{13}$$

The matrix ($\gamma_{a,b}$) is symmetric positive definite. This equation describes how the entropy increases in order to reach the thermodynamic equilibrium at which it is maximum. The Navier-Stokes equation can be considered within the Onsager formalism. One needs to introduce an explicit spatial aspect to these equations. The entropy production reads then

$$\frac{dS}{dt} = - \int \sum_a X_a \dot{x}_a d^3 \mathbf{r} \tag{14}$$

From the expression of the entropy production derived from the Navier-Stokes equations, that are the conservation of momentum, the conservation of energy, the conservation of mass and of constituents, it is then possible to identify the thermodynamic forces X_a and the fluxes x_a [1]. The thermodynamic forces as derived from the Navier-Stokes equations appear as equal to the thermal gradient and to the chemical potential gradient.

As a consequence, the Navier-Stokes equations appear as the relaxation process for newtonian liquids when they are out of thermodynamical equilibrium and that their entropy is not at the maximum possible value. The relaxation processes as described in Landau and Lifshitz [1] or in De Groot and Mazur [21] are thermal and solute diffusion. No coupling between the out-of-equilibrium thermodynamical state and convection has been introduced.

As compared to these standard treatments, we make two changes:

a) First of all, instead of considering an out-of-equilibrium entropy S , we deal with an out-of-equilibrium Gibbs free energy for which similar approaches hold and are most frequently discussed in the context of the linear response theory [24, 25]. The reasons are the following. The general treatments by introducing an out-of-equilibrium entropy considers that small volume elements of the liquids can be considered as closed systems. Then, their internal state evolves by maximising their entropy. The Navier-Stokes equations allow for describing on longer time scales their exchange of energy and constituents with their neighbours by introducing energy and constituents laws conservation laws. When considering wetting or diffusio-osmosis problems, the full Navier-Stokes equations are not necessarily required. The small volume elements can be considered as thermostated. In that case, the relevant out-of-equilibrium function is the local excess of free energy. In addition, if the pressure can be considered as imposed, the relevant function is the local excess of Gibbs free energy. Instead of deriving the relaxation processes thanks to an entropy production, the relaxation processes are described by the release of an excess of Gibbs free energy [24, 25]. This is what is done for instance for considering relaxation processes in polymer rheology where the corresponding function is called the dynamical free energy by Doi and Edwards [2] and is essentially an excess of Gibbs free energy.

b) We do not consider solute diffusion, because it is either very fast in the direction normal to the considered solid surfaces, or too slow in the direction parallel to the solid surfaces that we consider. We do not consider either thermal diffusion because energy is not conserved in the canonical ensemble and is not conserved either in the Stokes equation. Energy is exchanged rapidly with the thermostat.

However, extension of the present theory for describing thermal diffusion and solute diffusion, following the lines presented in Landau and Lifshitz [1] is possible. Note that it is what has been done by Julicher and Prost [26] without discussing the effect of solute on convection or the effect of interfaces on the flow and how surface tension gradient come into play.

The entropy production function as calculated thanks to the Navier Stokes equation [1, 21] is of importance because it relates the relevant fluxes to the relevant thermodynamic forces and allow them to be identified in a way that is consistent with the general formalism of Onsager theory. We do the same as regards to convection, which has not been considered in this way to the best of our knowledge.

Starting from Eq.10 which has the general required form, we deduce that \mathbf{v} are the fluxes and that $\nabla\sigma_G = \mu\nabla\psi$ is the thermodynamic force. The general solution is

$$\mathbf{v} = \mathbf{M}\nabla.\sigma_G \quad (15)$$

where \mathbf{M} is a mobility tensor. The only solution for the flow which has the required symmetry, that is which is invariant by translation and rotation is that given by the Stokes equation [1]. Hence the flow is given by the solution of the Stokes equation 11.

V. HYDRODYNAMICS WITHOUT BOUNDARY CONDITIONS

Let us consider the Stokes equations in the presence of a chemical composition gradient in the unbounded 3D space. In the absence of short-ranged interactions, *i.e.* when there is no surface tension term, or gradient term in the free energy, a heterogeneous composition does not create any flow in an unbounded fluid. Indeed, in these conditions, the quantity μ is a function of ψ only and not on $\nabla\psi$. The corresponding driving force in Eq. 11 due to

composition gradient can be written as

$$\mu(\psi)\nabla\psi = \nabla g^{(0)}(\psi)$$

since we have

$$\frac{dg^{(0)}(\psi)}{d\psi} = \mu(\psi)$$

The Stokes equation reads then

$$\begin{aligned} -\nabla(p - g^{(0)}(\psi)) + \nabla.\eta(\nabla\mathbf{v} + \nabla\mathbf{v}^+) &= 0 \\ \nabla.v &= 0 \end{aligned} \tag{16}$$

From these two equations, one obtains the following equation:

$$\begin{aligned} -\nabla(p - g^{(0)}(\psi)) + \eta\Delta\mathbf{v} &= 0 \\ \Delta(p - g^{(0)}(\psi)) &= 0 \end{aligned}$$

where Δ is the laplacian operator. Given the boundary conditions of uniform pressure and solute concentration at infinity and of no flow at infinity, one obtains the following solution:

$$\begin{aligned} p - g^{(0)}(\psi) &= p_0; \\ \mathbf{v} &= 0 \end{aligned}$$

The physical pressure is the entire term $p - g^{(0)}(\psi)$ and is uniform. The quantity p is not the total pressure, it is just the Lagrange multiplier which ensures incompressibility of the flow. The term $\mu\nabla\psi$ which appears as a body force in the Stokes equation would result in a longitudinal flow with non zero divergence. This effect must be compensated to maintain the purely transverse nature of the flow. Without non-local interactions embodied with the $\nabla\psi$ dependence of the Gibbs free energy, non-homogeneous composition cannot create convection in an unbounded fluid. The relaxation towards equilibrium occurs entirely by diffusion. For instance, if we consider a salt gradient concentration in water, if there is no long range interaction and that the chemical potential depends only on the local concentration, such a gradient cannot create flow. In fact the local Lagrange multiplier p adjusts so that $p - g^{(0)}(\psi)$ is uniform and no flow takes place. This issue has been discussed with different arguments by Julicher and Prost [26].

On the other hand, the term $g^{(1)}$ contributes to convection flow in the presence of concentration gradients. The corresponding term is responsible for the surface tension between two different A-rich and B-rich domains [9, 27]. Thus, all the convection in such out-of-equilibrium systems is due to surface tension-like effects. All the contributions to convection come from the dependence on $\nabla\psi$ of the Gibbs free energy¹.

Finally, another way to see that $g^{(0)}$ contributions cannot give rise to convection is the following. Under an infinitesimal displacement, the new Gibbs free energy is given by :

$$G' = \int g(\mathbf{r})d^3\mathbf{r} = \int g^{(0)}(\psi(\mathbf{r} - \delta\mathbf{r}))d^3\mathbf{r}$$

One can consider the change of variable $\mathbf{r}' = \mathbf{r} - \delta\mathbf{r}$. Since the allowed displacements preserve the volume the corresponding Jacobian of the change of variable is 1. One has thus:

$$G' = \int g^{(0)}(\psi(\mathbf{r} - \delta\mathbf{r}))d^3\mathbf{r} = \int g^{(0)}(\psi(\mathbf{r}))d^3\mathbf{r}$$

Virtual displacements which preserve the volume cannot change the Gibbs free energy when the latter depends only on local variables. As a consequence, there can be no convection due to purely local contribution to the Gibbs free energy such as those corresponding to ideal solutions. One needs to introduce short-ranged interaction through concentration gradient contributions.

As a consequence, when there is no short-ranged interactions, the concentration evolves towards equilibrium only by diffusion or by an imposed convection, but composition gradients do not cause convection. In general, the complete evolution equation for the concentration is a convection-diffusion equation.

¹ It can be checked in Fourier space that the term $\mu^{(0)}$ gives contributions to the Stokes equation which are purely longitudinal which are cancelled by the pressure term p to ensure incompressibility. On the other hand, a $\mu^{(1)}$ term like $\Delta\psi$ gives rise to transverse contributions to the Stokes equation, thereby giving rise to convection.

VI. HYDRODYNAMICS IN THE PRESENCE OF AN INTERFACE

Having established the hydrodynamic equation in an unbounded fluid, we need to establish the equations in the presence of boundaries. These boundaries may be the wall of a capillary, or the surface of a particle. The boundary conditions must take into account two important physical effects. The first one is the interaction between the solid surface and the liquid. It is important to stress that these interactions have a finite range. Though small, this range is not zero and typically of order a few nanometers [3]. This is of fundamental importance as regard to wetting dynamics for instance. The physical origin of these interactions are van der Waals interactions, or ionic interactions for instance. It is not possible to describe properly wetting dynamics without taking into account this non-zero range of the interactions. The second feature that is of major importance for describing the flow of the liquid in the vicinity of a solid surface is the slipping length. The macroscopic description assumes a no-slip boundary condition for the flow. However, again, if one wants to describe and understand wetting dynamics, one needs to assume that there is a non-zero slipping length. This slipping length in the case of simple liquids as regard to wetting dynamics experiments may be assumed to be of order one nanometer [5]. A larger slipping length has been discussed in the literature, up to a few tens of nanometer [13] but the issue is still under debate [28].

For describing the effect of the interface on the hydrodynamic flow, we introduce an additional contribution to the Gibbs free energy density in the vicinity of an interface. We denote this contribution by $\Gamma(\psi, \mathbf{r})$, where ψ is the solute volume fraction in the liquid slightly beyond the interfacial region. The range of Γ is typically of few nanometers and up to a few tens of nanometers depending on the thickness of the interfacial layer. This is the contribution of the solid surface to the free energy of the liquid in its vicinity. The contribution of the interface to the Gibbs free energy reads

$$G_{Int} = \int \Gamma(\psi, \mathbf{r}) d^3\mathbf{r}$$

The quantity $\Gamma(\psi, \mathbf{r})$ must be understood in the following way: we assume that at some distance from the interface, the solute volume fraction ψ is imposed by the flow. Then, the interfacial layer equilibrates locally to assume a certain profile corresponding to the local

minimum of Gibbs free energy (such as that discussed in Appendix) given the specific nature of the interactions between the solute, the liquid and the solid surface and the imposed conditions ψ of solute concentration at a few correlation lengths from the solid surface [27]. This description relies on the following assumptions: the local equilibration is fast enough as compared to the flow; the concentration gradient imposed by the flow and parallel to the solid surface corresponds to a length scale much larger than the thickness of the interfacial region between the solid and the liquid; the bulk of the capillary acts as a reservoir for equilibrating the interfacial layer. The local equilibration is assured by a diffusion process which we assume thus to be faster on the scale of the interfacial layer than the disturbance caused by the flow.

Considering the same principle of virtual work in the vicinity of the boundary leads to the Stokes equation in the vicinity of a solid interface. Let us consider a virtual displacement in the liquid so that \mathbf{r} is changed into $\mathbf{r} + \delta\mathbf{r}$. The quantity ψ is varied by an amount

$$\delta\psi = -\delta\mathbf{r} \cdot \nabla\psi(\mathbf{r});$$

Then

$$\delta G_{Int} = \int -\delta\mathbf{r} \cdot \nabla\psi(\mathbf{r}) \frac{\partial\Gamma(\psi, \mathbf{r})}{\partial\psi} d^3\mathbf{r} \quad (17)$$

The derivative of Γ is calculated with respect to the imposed solute concentration beyond the interfacial layer. By adding the corresponding term in the Stokes equation, one obtains the Stokes equation in the presence of an interface:

$$-\nabla p(\mathbf{r}) + \nabla \cdot \eta (\nabla\mathbf{v}(\mathbf{r}) + \nabla\mathbf{v}^+(\mathbf{r})) + \mu(\mathbf{r})\nabla\psi(\mathbf{r}) + \frac{\partial\Gamma(\psi, \mathbf{r})}{\partial\psi} \nabla\psi(\mathbf{r}) = 0 \quad (18)$$

The total chemical potential is given by

$$\mu_{tot} = \mu + \frac{\partial\Gamma(\psi, \mathbf{r})}{\partial\psi} \quad (19)$$

The term μ contains all the contribution for the bulk, the second one contains the contribution which results from the interaction with the solid interface. The second term $\frac{d\Gamma(\psi)}{d\psi}$ is different from zero only in the vicinity of the interface. The variation of surface tension $\Delta\gamma(\psi)$ between the solid surface and the liquid with solute concentration ψ and the liquid

with solute concentration zero is given by

$$\Delta\gamma = \int_0^\infty (\Gamma(\psi, z) - \Gamma(0, z)) dz$$

One obtains then

$$\frac{d\gamma}{d\psi} = \int_0^\infty \frac{\partial\Gamma(\psi, z)}{\partial\psi} dz = \int_0^\infty \Psi(\psi, z) dz$$

where γ is the surface tension between the liquid and the solid. We have introduced

$$\Psi(\psi, z) = \frac{\partial\Gamma(\psi, z)}{\partial\psi}$$

A. Diffusio-osmosis without slipping length

Let us consider a capillary of sufficiently large diameter so that its surface can be considered locally flat. Let us suppose that the liquid has a uniform gradient of composition which induces a uniform gradient of surface tension between the liquid and the capillary along the x-direction. The normal to the flat surface is the local z-direction. Let us suppose that the bulk chemical potential μ in Eq.18 does not contain $\mu^{(1)}$ -like contributions. $\mu^{(0)}$ -like contributions cannot give rise to convection and can be discarded from the convection equations. The flow equation 18 reduces thus to

$$-\frac{\partial p}{\partial x} + \eta \frac{\partial^2 v_x}{\partial z^2} + \frac{\partial\psi}{\partial x} \frac{\partial\Gamma}{\partial\psi} = 0 \quad (20)$$

Let us assume that the gradient of concentration ψ is constant along the capillary as well as Ψ which is the contribution of the interfacial interactions to the local chemical potential. By taking the derivative of Eq.20 with respect to x and by using the incompressibility condition and the invariance by translation of the other terms, we deduce that the pressure p satisfies the following equation :

$$\frac{\partial^2 p}{\partial x^2} = 0$$

If the pressures at both extremities of the capillary are identical, *e.g.* the atmospheric pressure, we deduce from this equation that the pressure is uniform within the capillary and equal to the atmospheric pressure.

This equation allows to calculate the flow velocity profile

$$\frac{\partial v_x}{\partial z}(z) = \frac{-1}{\eta} \frac{\partial\psi}{\partial x} \left(\int_0^z \Psi(z') dz' - \int_0^\infty \Psi(z') dz' \right) = \frac{1}{\eta} \frac{\partial\psi}{\partial x} \int_z^\infty \Psi(z') dz' \quad (21)$$

We observe thus that the shear rate is a decreasing function of the distance to the interface and is zero at distances larger than the range of the thermodynamic perturbation of the liquid by the interface. One obtains

$$\frac{\partial v_x}{\partial z}(0) = \frac{1}{\eta} \frac{\partial \psi}{\partial x} \int_0^\infty \Psi(z') dz'$$

If we denote by a the range of Ψ , and assuming a no slip boundary condition at $z = 0$, one obtains that the velocity of the flow at a distance $z > a$ can be approximated by

$$v_x(z) \approx \frac{a}{\eta} \frac{\partial \psi}{\partial x} \int_0^\infty \Psi(z') dz'$$

The velocity field obtained by solving Eq.21 and assuming a no slip boundary condition at $z = 0$ is given by:

$$v_x(z) = \frac{1}{\eta} \frac{\partial \psi}{\partial x} \int_0^z \left(\int_{z'}^\infty \Psi(z'') dz'' \right) dz' \quad (22)$$

Equation 22 (together with Equation 18) is the main result of this article. It represents a so-called plug-flow observed also in electroosmosis for instance. This is a standard behavior when forces act on the liquid only within a thin layer in the vicinity of a solid surface, as it is a case for the considered diffusio-osmosis flow. We see that the flow velocity depends on the range of the interfacial forces a .

The term $\frac{\partial \psi}{\partial x} \frac{\partial \Gamma}{\partial \psi}$ in Eq. 20 represents a pulling force parallel to the interface. This term is analogous to the term ρE_∞ in electroosmosis [3, 4] where ρ is the density of charge in the vicinity of a solid surface which is non zero within the Debye layer, and E_∞ is the applied electric field in the direction parallel to the capillary. In the problem we consider here, the forces are internal and result from the interaction between the liquid and the solid. They appear as parallel to the surface: the surface pulls the liquid in order to reduce the Gibbs free energy of the liquid, taking into account the interaction between the solid and the liquid. These forces are tangential and do not result in the appearance of a confined pressure, nor are they the result of a preexisting confined pressure in the vicinity of the liquid-solid interface. As we discussed, the diffusio-osmotic flow is a so-called plug flow when the tangential force is constant. When this is not the case, one observes the superimposition of local plug flows and of a Poiseuille flow on larger scale. This situation has been discussed in the case of electroosmosis *e.g.* in reference [4].

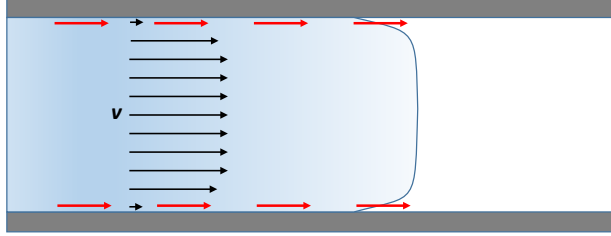


FIG. 1: Diffusion-osmosis flow. The driving force in Eq.20 appears as a tangential force in the liquid distributed within a distance a of the solid surface. This force, though purely internal to the system, is analogous to the force in electro-osmosis which is exerted within the Debye length.

Let us assume that $\Psi(z)$ is given by

$$\Psi(z) = \Psi(0) \exp\left(\frac{-z}{a}\right)$$

One obtains then

$$\frac{d\gamma}{d\psi} = a\Psi(0)$$

These equations allow to calculate the flow velocity profile

$$v_x(z) = \frac{a^2}{\eta} \frac{\partial\psi}{\partial x} \Psi(0) \left(1 - \exp\left(\frac{-z}{a}\right)\right)$$

The diffusio-osmotic velocity in the capillary is then given by

$$V = \frac{a^2}{\eta} \frac{\partial\psi}{\partial x} \Psi(0) = \frac{a}{\eta} \frac{\partial\psi}{\partial x} \frac{d\gamma}{d\psi}$$

The diffusio-osmotic mobility defined by $\mathbf{V} = \mu \nabla \psi$ is then given by

$$\mu_{chem}^{osm} = \frac{a}{\eta} \frac{d\gamma}{d\psi}$$

We obtain that the diffusio-osmotic mobility is proportional to the range of the interaction and to the derivative of the liquid-solid surface tension with respect to the solute concentration. When the gradient of solute concentration is zero, Eq.18 admits a no flow and uniform pressure solution (the atmospheric pressure p_0), contrarily to the description of diffusio-osmosis by the Derjaguin's model [3, 11, 14, 29], as can be seen by reference to 2. The fact that the diffusio-osmotic mobility is related to the gradient of surface tension has been recognized by many authors [29, 30]. However, the calculations by Ruckenstein or by Anderson et al derive from the Derjaguin's picture and rely on a confined pressure gradient as a driving force. Levich describes also the flow as due to surface tensions gradient for a liquid-liquid interface corresponding to a Marangoni effect [31] but this description cannot be extended to a solid-liquid interface which requires taking into account a description of the interfacial layer. Indeed, the effect of the structure and the perturbation of the density of Gibbs free energy on the hydrodynamic equation embodied in Equation 18 which leads to Equation 22 is not present in Levich's description. More recently, Marbach et al [14] and Liu et al [32] questions the role of the local pressure gradient and conclude that the osmotic flow is more probably related to the chemical potential gradient. Equations 18 and 22 provide an explicit dependence of the driving forces in the liquid and of the resulting diffusio-osmotic flow. This 3D driving force in the vicinity of the surface is, apart from a prefactor, the derivative of the local excess Gibbs energy density with respect to the imposed solute concentration beyond the interfacial layer. Our expression makes explicit the detailed nature of the interaction between the surface and the liquid which is responsible for the flow. Note that this is only the latter which is responsible for this effect since we have shown that local terms for the chemical potential such as $\ln c$ where c is the concentration, or any other term corresponding to a so-called ideal solution do not contribute to the flow.

It is important to note that the driving force that we obtain is $\mu \nabla \psi$ in Equation 11. Araki and Tanaka [33] introduced a similar Stokes equation but the driving force in their article is $-\psi \nabla \mu$. As regards to our derivation of the driving force, Araki and Tanaka's equation may be obtained by an additional integration by part following Equation 7, using the fact that $\nabla \cdot \delta \mathbf{r} = 0$ due to incompressibility. However, this integration by parts should

come with contributions at the boundaries which are :

$$-\psi \left(\frac{dg^{(0)}}{d\psi} - \left(\nabla \cdot \frac{dg^{(1)}}{d\nabla\psi} \right) + \Psi(\psi(x), z) \right) \delta \mathbf{r} \quad (23)$$

The contribution of this term is zero on the boundary corresponding to the solid interface since $\delta \mathbf{r}$ is zero there. But the contribution of this term is non zero in general. This is the case in particular if we consider diffusio-osmosis along a capillary which connects two reservoirs (1) and (2) of respective concentrations $\psi_1 > \psi_2$. The quantities related to $g^{(1)}$ in Eq.23 may be considered as zero at the boundaries because the reservoirs have a homogeneous concentration, but the two quantities $\psi \frac{dg^{(0)}}{d\psi}$ corresponding to the two reservoirs are different. The integration by parts which leads to this different driving force (as compared to $\mu \nabla \psi$) is unwarranted, except in the special case of periodic boundary conditions relevant to the application considered by Araki and Tanaka [33]. In this case the difference between $\mu \nabla \psi$ and $-\psi \nabla \mu$ is unimportant since the contributions at the boundaries cancel. An analogous term $\psi \nabla \mu$ has been considered also by Marbach et al [14] and by Liu et al [32], without specifying μ as regards to the interfacial interactions in the same way as we do though. If one uses this term as a driving force in the Stokes equation, one obtains a description very similar to that of Derjaguin since this term leads to the appearance of a confined pressure in the vicinity of the capillary, as shown in Appendix C. In principle this confined pressure should be cancelled by the effect of the boundary terms just mentioned which are absent though in all descriptions in the literature [3, 11, 14, 29, 32, 33]. As a consequence, the term $-\psi \nabla \mu$ cannot be considered as the local driving force in the Stokes equation [33]. We propose that the local driving force is $\mu \nabla \psi$.

B. Diffusio-osmosis and slipping length

One can also describe these effects by taking into account a non-zero slipping length whereas the range of the interactions are zero, that is the effect of the interaction between the solid and the liquid are purely interfacial. The flow equation is given by Eq.20. We assume here that the interfacial perturbation due to the solid-liquid interface is non zero only at the interface and that the flow is characterized by a slipping length b [6]. If the interface is located at $z = 0$, Γ as a 3D function may be written as

$$\Gamma(\psi(\mathbf{r}), z) = \Gamma(\psi(x, y, 0))\delta(z)$$

where $\delta(z)$ is the Dirac function.

Then, Eq.20 can be solved by describing a virtual velocity profile for $z > -b$ whereas the solid-liquid interface is located at $z = 0$. The slipping length b is the length for which the flow, extrapolated in the negative z region cancels [6]. The flow is then described with a no-slip boundary condition at $z = -b$ and with pulling forces located at $z = 0$. One obtains then a plug like velocity profile where the velocity is uniform for $z > 0$ and is given by

$$v_x(z) = \frac{b}{\eta} \frac{\partial \psi}{\partial x} \frac{d\Gamma}{d\psi}$$

The diffusio-osmotic mobility defined by $\mathbf{V} = \mu \nabla c$ is given by

$$\mu_{chem}^{osm} = \frac{b}{\eta} \frac{d\Gamma}{d\psi}$$

We obtain here similar results as above where the range of the interaction a is replaced by a slipping length b . More details are given in Appendix B.

We see thus that the diffusio-osmotic mobility is proportional either to the slipping length or to the range of the interaction. To understand this effect, one needs to take into account that the tangential forces are exerted on the fluid at a different location where a no-slip boundary condition holds. The general result involves thus a combination of these two length scales as discussed *e.g.* in reference [13], though the interpretation of the origin of the effect is different.

C. Wetting

Wetting can also be described by using this formalism. Let us consider Eq.20. Wetting of a liquid A embedded within a liquid B on a solid surface corresponds to a situation of a sharp concentration gradient. One may assume that $\psi = 0$ on the right of the triple line in Figure 2, and $\psi = 1$ on the left corresponding to the spreading droplet. The term $\nabla \psi$ is essentially a Dirac δ function at the liquid A/liquid B interface. One may write thus $\nabla \psi = (\psi_B - \psi_A)\delta(x) \approx -\delta(x)$. The quantity $\frac{\partial \Gamma(\psi, z)}{\partial \psi}$ may be integrated along the direction z normal to the surface. It yields the quantity $d\gamma/d\psi$ which is equal to $\gamma_A - \gamma_B$, where γ_A is the surface tension of the pure solute with the solid surface and γ_B the surface tension

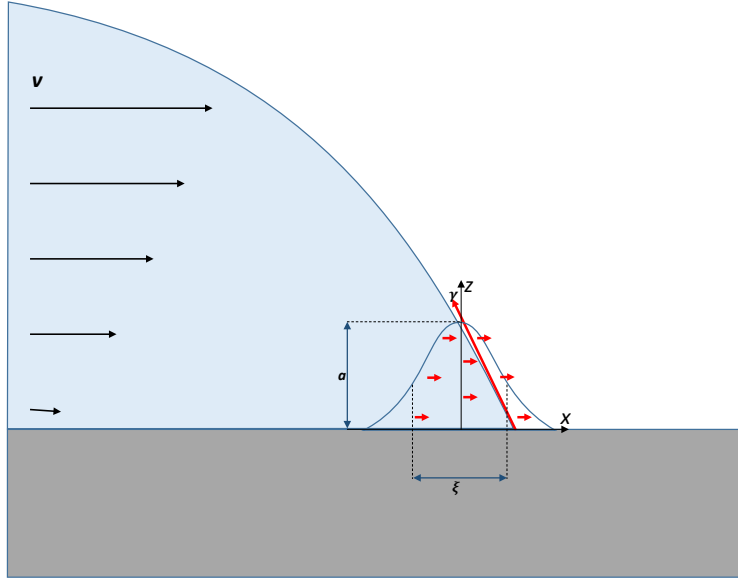


FIG. 2: The driving force term in Eq.20 is non zero in the vicinity of the liquid A-liquid B interface, corresponding to the surface tension between both liquids, and on the triple line where the contribution of the solid surface takes place. This contribution is a tangential body force in the liquid over a region indicated here of spatial extension a in the direction normal to the substrate and ξ in the direction parallel to the substrate. When integrated over the volume, it yields $\gamma_B - \gamma_A$.

of the pure liquid with the solid surface². Thus, when integrated over the small region of size a in the direction normal to the surface and of size ξ in the direction parallel to the surface (where ξ is the thickness of the liquid A-liquid B interface) where the pulling body force of Eq.18 is non zero, one obtains that the total pulling force due to the interaction with the solid substrate is equal to $\gamma_B - \gamma_A$. This is schematized in Figure 2. We recover thus the standard description of wetting when adding the contribution $\gamma_{A,B} \cos \theta$ due to the A-B surface tension provided by the third term of 18 where θ is the contact angle of the droplet with the solid substrate. This standard description may be obtained directly by a virtual work principle description of this problem in terms of interfacial free energy. As a consequence, the formalism introduced here allows for describing wetting or dewetting

² We have assumed a linear relation for γ as a function of ψ , which is consistent with the assumption made when deriving Eq.20. If this relation does not hold, one may modify Eq.20 without making this assumption. One obtains that the pulling force is indeed $\gamma_B - \gamma_A$

dynamics as a special case of diffusio-osmosis and to obtain the standard description of wetting in the literature [5, 6].

We emphasize that Equation 18 was derived by applying a principle of virtual work in the presence of an interface and with an arbitrary concentration gradient. This is the same principle of virtual work which is used in the literature in the context of wetting [5, 6], either for calculating the equilibrium Young contact angle or for calculating the kinetics of droplet spreading. For describing wetting, one considers indeed a virtual displacement of the contact line and calculate the release of interfacial free energy. When this release is zero to linear order, one obtains an equation for the Young contact angle. When this variation is not zero, the droplet spreads with a velocity such that the Stokes dissipation is equal to the release of interfacial free energy [5, 6]. These situations are particular cases that can be directly addressed within our model because it is based on the same principle of virtual work as wetting.

VII. DISCUSSION AND CONCLUSION

We have introduced a formalism which allows to describe diffusio-osmosis in a way which is consistent with the contact value theorem of colloidal science [15, 17–19]. According to this theorem, there is no excess pressure in the vicinity of a flat surface immersed in a liquid which would result from the interaction between the surface and the liquid, whereas it was assumed by Derjaguin that such a pressure is the cause for diffusio-osmotic flows. More recently, the relevance of the assumed pressure gradient as the cause of the diffusio-osmotic flow has been questioned by Marbach et al [14] and by Liu et al [32]. These authors conclude that the chemical potential gradient is probably a more relevant quantity. Our formalism provides an explicit expression for the driving force of the diffusio-osmotic flow confirming that this flow is not related to a local pressure gradient which, we argue in this manuscript, does not exist at all. Note that a pressure gradient arises on larger scale when the driving forces are not invariant by translation along the capillary. In this case Poiseuille-like flows superimpose to the plug-like flow in an analogous way to what has been described in the case of inhomogeneous electroosmosis [4].

Our formalism is based on a principle of virtual work which makes apparent that the

driving force is the consequence of an excess of Gibbs free energy release. This excess of Gibbs free energy as compared to an equilibrium situation is located in the vicinity of the solid-liquid interface. In the presence of a gradient of composition of the liquid along the capillary it gives rise to tangential body forces within the interfacial layer. In a coarse-grained picture, this excess of free energy may be related to a gradient of surface tension between the liquid and the solid. What is key in this picture is that the driving forces are purely transverse and have a spatial extension. They are not applied exactly where a no-slip boundary condition holds. The mobility is proportional either to the range of the interaction or to a slipping length and may be a combination of both in the general case. This formalism makes more apparent the physical nature of the driving force by which the excess of Gibbs free energy is released in a way which is consistent with the Onsager formalism. This formalism can also be applied for describing wetting and/or dewetting which appears as a limiting case of diffusio-osmotic flows with a sharp composition gradient between two different liquids. In wetting situations, our approach is consistent with the driving forces being the surface tensions between both liquids and between each of the liquids and the solid substrate. No reference is made to a possible high pressure confined region at the liquid/solid interfaces. Our point of view is that the standard picture for describing wetting is correct and that the Derjaguin's picture is not correct at this regard. The variational principle introduced by Doi and Onuki [20] and which we use in this context allows to propose a unified and consistent picture for describing wetting [5, 6] and diffusio-osmosis [3, 11, 12, 29] consistently with some key results of colloidal physics [15–19]. We will apply this formalism to calculate hydrodynamic flows in the context of wetting and/or dewetting situations in another manuscript.

Note that our theory is not restricted to a particular Gibbs free energy. Regarding diffusio-osmosis or wetting we introduced a mesoscopic theory which describe them consistently, and also consistently with the contact value theorem. The theory presented here could be extended by taking into account other relaxation processes, such as thermal diffusion or solute diffusion in a way analogous to the approach described in references [21, 23].

VIII. APPENDIX

A. Free energy

In order to be specific, let us consider here the most simple Gibbs free energy that is used for describing spinodal decomposition in polymer blends for instance [9, 27]. Note that our approach is more general than this however. We consider a polymer blend made of two different polymers A and B of same molecular weight. We assume that the system may be considered as incompressible. The system may therefore be described by the variable $\psi = \psi_A - \bar{\psi}_A = 1 - \psi_B - 1 + \bar{\psi}_B = -\psi_B + \bar{\psi}_B$ where ψ_A and ψ_B are the volume fraction of component A and B respectively. One may consider the Gibbs free energy of the blend, as calculated for instance in reference [9, 27]. The typical order of magnitude of the Gibbs free energy of non polar liquids per monomer is of order the thermal energy T . As a consequence, G/T is of order one per monomer volume a^3 . If one chooses for unit length scale the monomer length, the dimensionless Gibbs free energy may be written as $G/T = \int d^3\mathbf{r}g(\psi)$ where the length scale has been made dimensionless and g is dimensionless of typical order of magnitude 1. A particularly frequent expression for the Gibbs free energy is given by

$$G = \int d^3\mathbf{r} \left(-\frac{\tau}{2}\psi^2 + \frac{u}{4}\psi^4 + \frac{K}{2}(\nabla\psi)^2 \right) \quad (24)$$

where the coefficients in the free energy term are all of order 1, except τ . τ which controls the miscibility of the two components may vary between a very low value, such as 10^{-3} (weak segregation) or 1 (strong segregation). This expression for the Gibbs free energy is valid close to the critical point. It may be extended by taking higher order terms in the expansion in powers of ψ . The surface tension A-rich and B-rich domains is $\Gamma \approx 1/\xi^3$, and the correlation length or the thickness of the interfacial regions is $\xi = \tau^{-1/2}$ (assuming $K = 1$ so that $\Gamma \approx \tau^{3/2}$). In physical units, the surface tension is then $\Gamma \sim T\tau^{3/2}/a^2$ and is thus of order $T/a^2 \sim 2 \times 10^{-2} \text{ J m}^{-2}$ in the case of strong segregation. In physical units, the correlation length is thus $\xi \sim a\tau^{-1/2}$. The corresponding dimensionless chemical potential (including gradient terms) reads

$$\mu = \frac{\delta G}{\delta\psi(\mathbf{r})} = -\tau\psi + u\psi^3 - K\Delta\psi = -\tau\psi + \psi^3 - \Delta\psi \quad (25)$$

where Δ is the Laplacian operator. The surface tension is entirely controlled by non-local contribution to the Gibbs free energy and is proportional to the parameter K which is

typically proportional to Ta^2 where T is the thermal energy and a one monomer length. This dimensionless free energy obtained by dividing the real free energy by T and by choosing as unit length the length of one monomer is a generic free energy able to describe non-polar liquid blends close to the critical point, but it is by no means the only possibility. It may be useful to include higher order terms in the expansion in order to better control the fluctuations of ψ and in particular to prevent negative values in numerical calculations. This is particularly required when describing systems in the strong segregation limit where the A-rich regions contain a very small fraction of B-polymer and the B-rich regions a very small fraction of A polymer.

B. Non-zero slipping length

We assume here that the interfacial perturbation due to the solid-liquid interface is non zero only at the interface. We assume also that the liquid slips at the interface, an effect characterized by a so-called slipping length b which is the extrapolated length at which the liquid velocity would be zero (see *e.g.* [6, 13]). If the interface is located at $z = 0$, Γ as a 3D function may be written as

$$\Gamma(\psi(\mathbf{r}), z) = \Gamma(\psi(x, y, 0))\delta(z) \quad (26)$$

where $\delta(z)$ is the Dirac function.

Let us assume that the gradient of concentration ψ is constant along the capillary as well as $d\Gamma/d\psi$. By taking the derivative of Eq.20 with respect to x and by using the incompressibility condition and the invariance by translation of the other terms, we deduce that the pressure p satisfies to the equation $\frac{\partial^2 p}{\partial x^2} = 0$. If the pressures at both extremities of the capillary are identical, *e.g.* the atmospheric pressure, we deduce from this equation that the pressure is constant and uniform within the capillary.

This equation allows to calculate the flow velocity profile. One has

$$\frac{\partial^2 v_x}{\partial z^2} = 0$$

when either $z > 0$ or $z < 0$ where the function Γ is zero. One obtains thus that $\frac{\partial v_x}{\partial z}$ is constant either for $z > 0$ or for $-b < z < 0$. The constant for $z > 0$ is zero by symmetry in

a capillary. The shear rate for $z < 0$ is constant also. By solving Equation 20 at $z = 0$, we obtain that

$$\frac{\partial v_x}{\partial z} = \frac{1}{\eta} \frac{\partial \psi}{\partial x} \frac{d\Gamma(x, y, 0)}{d\psi}$$

when $-b < z < 0$. By applying the no-slip boundary condition at $z = -b$, that is $v_x(z = -b) = 0$, one obtains the velocity profile:

$$v_x(z) = \frac{b}{\eta} \frac{\partial \psi}{\partial x} \frac{d\Gamma}{d\psi} \quad (27)$$

when $z > 0$ and

$$v_x(z) = \frac{(z+b)}{\eta} \frac{\partial \psi}{\partial x} \frac{d\Gamma}{d\psi} \quad (28)$$

when $-b < z < 0$. Equations 27 and 28 represent a plug-flow.

The diffusio-osmotic velocity in the capillary is then given by

$$V = \frac{b}{\eta} \frac{\partial \psi}{\partial x} \frac{d\Gamma}{d\psi}$$

whereas the diffusio-osmotic mobility defined by $\mathbf{V} = \mu \nabla c$ is given by

$$\mu_{chem}^{osm} = \frac{b}{\eta} \frac{d\Gamma}{d\psi}$$

This result had been proposed long ago by Ruckenstein [30], without the introduction of a Gibbs free energy and a virtual work principle. We obtain that the diffusio-osmosis mobility is proportional to the slipping length and to the derivative of the liquid-solid surface tension as regard to the solute concentration.

C. Araki and Tanaka Stokes equation

The Stokes equation is obtained by calculating the driving forces by using a principle of virtual work. A different Stokes equation as compared to Equation 18 may be obtained by integrating Equation 7 by part and by forgetting the boundary contributions. If we integrate also by part the contribution of the interface to the variation of the Gibbs energy given by Equation 17 and again do not consider the contributions at the boundaries, one obtains the

Stokes equation :

$$\begin{aligned}
-\nabla p(\mathbf{r}) + \nabla \cdot \eta (\nabla \mathbf{v}(\mathbf{r}) + \nabla \mathbf{v}^+(\mathbf{r})) - \psi(\mathbf{r}) \nabla \mu_{tot}(\mathbf{r}) &= 0 \\
\nabla \cdot \mathbf{v} &= 0
\end{aligned} \tag{29}$$

instead of Eq.18. The total chemical potential is given by Eq.19. Equation 30 differs by a term $\nabla(\psi \mu_{tot})$ from the Stokes equation Eq.18. They are equivalent if there is no contribution at the boundaries which is the case if one considers a 3D fluid problem with periodic boundary conditions for which both equations describe the same physics. But they are not equivalent in general. Apart from the definition of the chemical potential (in particular the term $-\psi(\mathbf{r}) \nabla \frac{\partial \Gamma(\psi, \mathbf{r})}{\partial \psi}$) this equation is similar to that discussed in references [14, 32, 33]. By focusing on the interfacial effects and neglecting $\mu = \mu^{(0)} + \mu^{(1)}$, the Stokes equation 30 becomes:

$$\begin{aligned}
-\nabla p + \nabla \cdot \eta (\nabla \mathbf{v} + \nabla \mathbf{v}^+) - \psi \nabla \frac{\partial \Gamma(\psi, \mathbf{r})}{\partial \psi} &= 0 \\
\nabla \cdot \mathbf{v} &= 0
\end{aligned} \tag{30}$$

The velocity is zero in the z-direction. One obtains then

$$\frac{-\partial p(x, z)}{\partial z} - \psi \frac{\partial \frac{\partial \Gamma(\psi, (x, z))}{\partial \psi}}{\partial z} = 0$$

By integrating between the current z-position and far from the solid surface, one obtains an expression for the pressure term :

$$p(x, z) = -\psi(x) \frac{\partial \Gamma(\psi(x), (x, z))}{\partial \psi} + p_0$$

which is the same as Equation 2 if we identify $\frac{\partial \Gamma(\psi(x), (x, z))}{\partial \psi} = \Psi(z)$. Equation 30 becomes then:

$$\frac{\partial \psi(x)}{\partial x} \frac{\partial \Gamma(\psi(x), (x, z))}{\partial \psi} + \eta \frac{\partial^2 v_x}{\partial z^2} = 0$$

which is the same as Equation 3. This equation yields the same flow field as Equation 20 but not the same pressure field. The pressure field $p(x, z)$ cannot be the real physical pressure since it is not possible to adjust its value at the boundaries of the capillary: we have a difficulty with the boundary conditions. This approach is that of Derjaguin as reported in [3, 11, 14]. Though the flow calculated likewise is the same as that calculated above, both points of view are difficult to reconcile. In any case, the pressure field obtained here

contradicts the contact value theorem [17].

Acknowledgments: NC and NG thank the EPSRC and Solvay (grant number ST/N504282/1) for financial support

- [1] L.D. Landau and E.M. Lifshitz. *Fluid Mechanics*. Elsevier, Amsterdam, 1987.
- [2] M. Doi and S. F. Edwards. *The Theory of Polymer Dynamics*. Oxford University Press, New York, 1986.
- [3] J. L. Anderson. Colloid transport by interfacial forces. *Ann. Rev. Fluid Mech.*, 21:61 – 99, 1989.
- [4] D. Long, H.A. Stone, and A. Ajdari. *Journal of Colloid Science*, 212:338–349, 1999.
- [5] P.-G. de Gennes. Wetting: statics and dynamics. *Review of Modern Physics*, 57:827 – 863, 1985.
- [6] P.-G. de Gennes, F. Brochard-Wyart, and D. Quéré. *Capillarity and Wetting Phenomena. Drops, Bubbles, Pearls, Waves*. Springer, New York, 2004.
- [7] H. A. Stone, A.D. Stroock, and A. Ajdari. Engineering flows in small devices: Microfluidics toward a lab-on-a-chip. *Ann. Rev. Fluid Mech.*, 36:381 – 411, 2004.
- [8] N. Clarke. Effect of shear flow on polymer blends. *Adv. Polym. Sci.*, 183:127 – 173, 2005.
- [9] J. W. Cahn and J. E. Hilliard. Free energy of a non-uniform system. 1. interfacial free energy. *J. Chem. Phys.*, 28:258 – 267, 1958.
- [10] J. L. Anderson and D. C. Prieve. Diffusiophoresis caused by gradients of strongly adsorbing solutes. *Langmuir*, 7:403 – 406, 1991.
- [11] B.V. Derjaguin, G.P. Sidorenkov, E.A. Zubaschenkov, and E.V. Kiseleva. Kinetic phenomena in boundary films of liquids. *Kolloidn. Zh.*, 9:335, 1947.
- [12] N.V. Churaev, B.V. Derjaguin, and V.M. Muller. *Surface Forces, chapter 11*. Springer Science + Business Media, New York, 1987.
- [13] A. Ajdari and L. Bocquet. Giant amplification of interfacially driven transport by hydrodynamic slip: Diffusio-osmosis and beyond. *Phys. Rev. Lett.*, 96:186102, 2006.
- [14] S. Marbach, H. Yoshida, and L. Bocquet. Osmotic and diffusio-osmotic flow generation at high solute concentration. i. mechanical approaches. *J. Chem. Phys.*, 146:194701, 2017.

- [15] D.C. Grahame. The electrical double layer and the theory of electrocapillarity. *Chemical Reviews*, 41(441-501), 1947.
- [16] V.A. Parsegian and D. Gingell. On the electrostatic interaction across a salt solution between two bodies bearing unequal charges. *Biophysical Journal*, 12(1192-1204), 1972.
- [17] J. Israelachvili. *Intermolecular and Surface Forces, chapter 12*. Academic Press, London, 1991.
- [18] D. Ben-Yaakov, D. Andelman, D. Harries, and R. Podgornik. Beyond standard poisson-boltzmann theory: ion-specific interactions in aqueous solutions. *J. Phys.: Condens. Matter*, 21(Article Number 424106), 2009.
- [19] R.M. Adar and D. Andelman. Osmotic pressure between arbitrarily charged planar surfaces: A revisited approach. *Eur. Phys. J. E*, 41(Article Number 11), 2018.
- [20] M. Doi and A. Onuki. Dynamic coupling between stress and composition in polymer solutions and blends. *J. Phys. II France*, 2:1631 – 1656, 1992.
- [21] S.R. de Groot, , and P. Mazur. *Non-Equilibrium Thermodynamics*. Dover, Mineola, 1984.
- [22] L.D. Landau and Lifshitz E.M. *Electrodynamics of Continuous Media*. Elsevier, Amsterdam, 1984.
- [23] L.D. Landau and Lifshitz E.M. *Statistical Physics, part 2*. Pergamon Press, New York, 1981.
- [24] N. Pottier. *Nonequilibrium Statistical Physics*. Oxford University Press, Oxford, 2010.
- [25] L.E. Reichl. *A Modern Course in Statistical Physics*. Edward Arnold, London, 1980.
- [26] F. Julicher and J. Prost. Generic theory of colloidal transport. *Eur. Phys. J. E*, 29:27 – 36, 2009.
- [27] S. A. Safran. *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes*. Addison-Wesley, New York, 1994.
- [28] E. Lauga, M. P. Brenner, and H. A. Stone. *Handbook of Experimental Fluid Dynamics*. Springer, New York, 2005.
- [29] J. L. Anderson, M.E. Lowell, and D.C. Prieve. Motion of a particle generated by chemical gradients part 1. non-electrolytes. *J. Fluid Mech.*, 117:107 – 121, 1982.
- [30] E. Ruckenstein. Can phoretic motions be treated as interfacial tension gradient driven phenomena ? *J. Colloid Interface Sci.*, 83:77 – 81, 1981.
- [31] V.G. Levich. *Physicochemical Hydrodynamics*. Prentice-Hall, Inc., Englewood Cliffs, N.J., 1962.

- [32] Y. Liu, R. Ganti, and D. Frenkel. Pressure gradients fail to predict diffusio-osmosis. *J. Phys.: Condens. Matter*, 30(Article Number 205002), 2018.
- [33] T. Araki and H. Tanaka. Wetting-induced depletion interaction between particles in a phase-separating liquid mixture. *Physical Review E*, 73:061506, 2006.

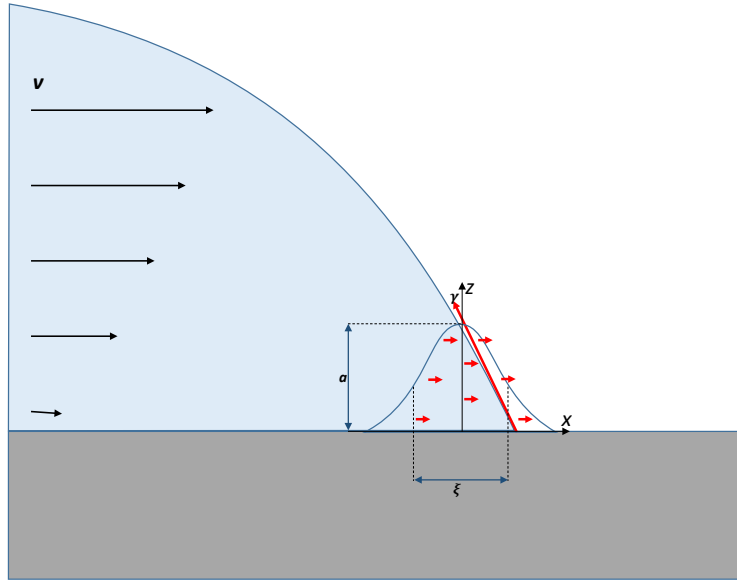


FIG. 3: Gradients of composition give rise to tangential forces which are responsible for diffusio-osmosis or wetting dynamics.

IX. FOR TABLE OF CONTENT