

On Slippage Induced by Surface Diffusion

F. BALDONI

*Magneti Marelli Ltd., Research and Development Division
San Salvo, Chieti, 66050, Italy*

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Abstract. The mechanism of surface diffusion is taken at the basis of the phenomenon of slippage of the contact line of a liquid film. With the aid of the condition of continuity of the traction vectors at the solid-liquid interface, we obtained an evolution equation for the velocity of the fluid particles at the wall which shows a marked resemblance with Millikan's equation for the slippage coefficient of gases and reduces, in the limit of small surface diffusivity, to the classical Stokes-Einstein model. The influence of surface roughness is explicitly taken into account and, among other results, cases of absence of slip caused by the attachment of the liquid film to the solid surface and of slippage solely induced by surface roughness are found. Finally, the effect of the surface deformation upon the surface velocity of the fluid particles is examined in some detail.

Key words: continuum mechanics, thin films, wetting, slip boundary condition.

1. Introduction

Evidence of the limitations of the famous no-slip condition adopted in classical Fluid Mechanics can be traced back to the formulation of the condition itself which arose as a possible answer to a long-standing problem. The principles of mechanics say nothing about the behaviour of the velocity at the boundary between two different media: they just state that the traction vector must be continuous. When one medium is a fluid and the other is a gas, the usual assumption that everywhere in the gas the viscous effects are small and that the stress tensor coincides with the atmospheric pressure seems to give good results and is taken at the basis of the whole class of free-surface problems. When one medium is fluid and the other is solid, no conjecture about the stress field in the latter can be easily formulated and, as such, the continuity of the traction vectors at the interface ceases to be an applicable condition, since one term in it (the traction field in the solid) remains unknown. The no-slip condition was then proposed as a replacement to that "lost" condition but no proof that the absence of slippage implies continuity in the traction vectors at the interface (and vice-versa) has ever been provided. An example of a class of problems where such proof is certainly needed comes from the field of phase transformations where a detailed description of the solidification process requires the computation of the velocity field in the liquid phase and of the deformation field in the solid. The continuity of the traction vectors at the solid-liquid interface and the absence of slippage are both fully applicable conditions despite the fact that only one of them can be chosen. Clearly, unless one condition follows directly from the other or some criterium of choice is provided, the final results of the computation will be (more or less significantly) different.

Although the no-slip condition has proved to be valid when moderate pressures and low surface stresses are involved, its range of validity has never been clearly assessed and is the subject of some controversy. It is well known, for instance, that in high altitude aerodynamics such condition is no longer true [1] and some evidences regarding its inappropriateness came from the mixture theory as well.

In more recent times, a relatively new context, where the failure of the no-slip condition has been suggested, is the wetting of a solid by a thin liquid film. Huh and Scriven [2] showed that the adoption of this condition would result in an infinite tangential stress at the line of contact between the liquid and the solid surface and ironically concluded that “ not even Heracles could sink a solid ”. In an attempt to remove such singularity, Dussan [3] applied different types of slip-conditions next to the contact line which reduced to the classical no-slip at some distance from it. However, no definite indication regarding what condition could efficiently replace the absence of slippage arises from her results. Recently [4] it has been proved that even an infinitesimal degree of slippage is able to remove the contact singularity existing in the Stokes-Einstein model of surface diffusion and since an infinitesimal amount of slippage could be hardly distinguished from no slippage at all, such possibility cannot be dismissed as a simple mathematical device tailored for the removal of the singularity itself. Hence, while slip at solid surfaces has often been invoked to resolve the fluid-solid contact singularities (see also the review article of O’Neil [5]), very little is actually known about the explicit form that the function describing such slippage should eventually take.

The interest in the understanding of the behaviour of liquid particles next to solid surfaces is not limited, furthermore, to the classical theory of Newtonian fluids. A long standing issue in non-Newtonian Fluid Mechanics is, in fact, the chronic lack of boundary conditions needed for the closure (and hence for the mathematical solvability) of the equation of motion. Even if marked differences in the behaviour of Newtonian and non-Newtonian liquids next to solid surfaces has been frequently observed [6, 7] the unspoken hope is that a better understanding of such behaviour for the simpler class of Newtonian fluids could offer some insight into the surface physics of the more complex class of polymeric liquids. We remark, moreover, that the study of thin liquid films next to solid surfaces is, to some extent, a non-conventional hydrodynamical problem. When a liquid film (that we may imagine to be approximately 100 microns thick) wets a solid surface, several microscopic effects come into play. On the one hand, the intermolecular forces between the liquid and the solid surface become increasingly important, while, on the other, the unavoidable roughness of the solid surface becomes relevant, thus introducing several factors that in classical Fluid Mechanics are easily ruled out as physically inessential.

In the present work we will derive and discuss an equation governing the slippage of the fluid particles in contact with a solid surface, whose range of validity is confined to the class of wetting problems (thin films). In the next Section we will set at the basis of the phenomenon of slippage the mechanism of surface diffusion, due to the gradient of the surface chemical potential and to the intermolecular forces exerted by the solid surface on the thin liquid film. In Section 3 we use the classical jump conditions which in Fluid Mechanics hold at a surface separating two media, in conjunction with the basic equation of surface diffusion to obtain, in the two dimensional case, an inhomogeneous differential equation for the (unknown) difference between the tangential velocity of the fluid particles and of the solid surface. This equation includes, as special cases, the Stokes-Einstein equation of surface diffusion, but the phenomenon is also shown to depend explicitly upon the roughness and the deformation of the solid surface. In Section 4 we solve some subcases of the general equation previously derived and recover, on the one hand, the results obtained by Ruchenstein [8] and by Smart [9] while, on the other, we find cases of slippage purely induced by the curvature of the surface and cases of absence of slippage caused by the “pinning” of the liquid film to the solid. Section 5 is devoted to a discussion of the effect of surface deformation upon slippage where it is shown, in particular, that any gradient of deformation on the solid can cause slippage

of the fluid particles. The comparison of our results with the classical equation of Millikan is discussed in the last Section. Needless to say, the tacit assumption of the present work is that the characteristic lengthscale of the wetting problem under examination (thickness of the film) falls into the range of a continuum description of the phenomenon.

2. The Equation of Surface Diffusion

A parametric representation of a regular surface $\mathcal{S}(\tau)$ of class C^2 in \mathcal{E}^2 is given by

$$\mathcal{S}(\tau) : \mathbf{x} = \varphi(s, \tau),$$

where s is the parameter of the surface (arclength) and τ is the time. We introduce the tangent vector

$$\mathbf{t} = \frac{\partial \varphi}{\partial s},$$

and the unit normal \mathbf{n} such that $\mathbf{n} \cdot \mathbf{t} = 0$. The tangent and the normal to the surface are, in the plane case, related to each other by the Frenet formulas for which

$$\begin{aligned} \frac{\partial \mathbf{t}}{\partial s} &= K \mathbf{n}, \\ \frac{\partial \mathbf{n}}{\partial s} &= -K \mathbf{t}, \end{aligned} \quad (1)$$

where K is the curvature of $\mathcal{S}(\tau)$. The jump of a function f across $\mathcal{S}(\tau)$ is defined as

$$[f] = f^l(\tau, \varphi) - f^s(\tau, \varphi) = \lim_{\mathbf{x} \rightarrow \varphi^+} f(\tau, \mathbf{x}) - \lim_{\mathbf{x} \rightarrow \varphi^-} f(\tau, \mathbf{x}), \quad (2)$$

and, in a similar way, the average $\langle f \rangle = (f^l + f^s)/2$. Central to the theory of singular surfaces is the notion of condition of compatibility [10] which states that the jump (average) of the gradient of a function f and the surface gradient of the jump (average) are related through

$$[\nabla f] = \frac{\partial [f]}{\partial s} \mathbf{t} + \left[\frac{\partial f}{\partial n} \right] \mathbf{n}. \quad (3)$$

It can be easily checked that the jump of the product of two functions f and g obeys the following identity

$$[fg] = [f]\langle g \rangle + \langle f \rangle [g]. \quad (4)$$

Consider a domain $\Omega(\tau)$ divided into two subdomains $\Omega_l(\tau)$ and $\Omega_s(\tau)$ by a surface $\mathcal{S}(\tau)$ and denote with μ , θ , ρ , p and \mathbf{u} the chemical potential, the temperature, the density, the pressure and the velocity of a generic particle in the two subdomains. In $\Omega_l(\tau)$ (which has the shape of a thin layer of decreasing thickness) are present particles of some component (say A) while the component B is in the subdomain $\Omega_s(\tau)$ (which, for a perfectly flat interface, would coincide with the lower half space). As the thickness of $\Omega_l(\tau)$ decreases, its outer boundary will become closer and closer to $\mathcal{S}(\tau)$ until it will intersect the surface along a common line. We place the origin of the arclength s of $\mathcal{S}(\tau)$ at some distance d from this line of intersection chosen in such a way that for $s \geq 0$ a continuum description of the phenomenon still holds. The points $s = -d$ and $s = 0$ will then denote the positions of the *microscopic* and of the

macroscopic contact line and the considerations which follow will always refer to the latter, never to the former.

The chemical potentials of the components A and B next to the surface are, in general, constant except next to the contact line where the concentration of the component A is expected to decrease (as a consequence of the thinning of the layer) to reach a minimum at $s = 0$ where the thickness of the film tends to zero. Under such conditions a diffusion process will set up tending to equilibrate the difference in the surface chemical potentials of the two components. An additional mechanism is provided by the forced diffusion arising from the difference in the body force \mathbf{F} that each component experiences [11]. Apart from the effect of gravity, particles of each component immediately next to the interface are subject to an attractive force (van der Waals force) generated by the presence of the other component, whose intensity can be roughly said to depend, among other factors, upon the difference in the masses M^s and M^l contained in a thin region (Gibbs domain) with midsurface $\mathcal{S}(\tau)$ and thickness $2r_c$. When the total mass of each component in this layer is comparable in magnitude with the other this force field is usually negligible. It increases however, as the difference $|M^s - M^l|$ becomes larger and larger, as it is expected to happen next to the contact line.

The overall effect of these diffusion phenomena will result in a tendency, for the particles of both constituents next to the surface, to move with respect to each other with different velocities whose magnitude will clearly depend, upon the nature of the single constituents. We will then summarize these concepts by saying that the difference in the particles velocities on $\mathcal{S}(\tau)$ (the velocity jump) can be expressed as

$$[\rho\mathbf{u}] = \mathcal{F} \left\{ \left[\rho \nabla \left(\frac{\mu}{\theta} \right) \right], [\mathbf{F}] \right\}, \quad (5)$$

where \mathcal{F} is an arbitrary functional of the argument. The requirement of indifference to the reference system implies that, if \mathbf{Q} is any time-dependent orthogonal transformation (rotation) then

$$\mathbf{Q}[\rho\mathbf{u}] = \mathcal{F} \left\{ \mathbf{Q} \left[\rho \nabla \left(\frac{\mu}{\theta} \right) \right], \mathbf{Q}[\mathbf{F}] \right\}. \quad (6)$$

A function that obeys such a transformation rule is an isotropic function. We then apply the available representation theorems [12] to find

$$[\rho\mathbf{u}] = \alpha_1 \left[\rho \nabla \left(\frac{\mu}{\theta} \right) \right] + \alpha_2 [\mathbf{F}], \quad (7)$$

where α_1 and α_2 depend, in general, upon s , τ and upon various scalar combinations of $[\mathbf{F}]$ and of the jump in the gradient of μ/θ . We now restrict our attention to the case in which the body force, the gradients of the chemical potential and of the temperature are small (in some suitable norm). The α 's then depend solely upon s and τ and eq.(7) becomes the counterpart, for interfaces, of the Ficksian law of diffusion classically formulated for bulk phases [13]. By analogy we set $\alpha_1 = -D_s$, $\alpha_2 = D_f$ and take the scalar product of eq.(7) with \mathbf{t} . Then, for $\mu = \mu(p, \theta)$ eq.(7) gives

$$[\rho\mathbf{u}] \cdot \mathbf{t} = -D_s \left[\frac{\rho}{\theta} \frac{\partial \mu}{\partial p} \nabla p + \left(\frac{\rho}{\theta} \frac{\partial \mu}{\partial \theta} - \frac{\rho \mu}{\theta^2} \right) \nabla \theta \right] \cdot \mathbf{t} + D_f [\mathbf{F}] \cdot \mathbf{t}. \quad (8)$$

With the aid of basic thermodynamic identities we rewrite eq.(8) as

$$[\rho\mathbf{u}] \cdot \mathbf{t} = -D_s \left[\frac{1}{\theta} \nabla p - \frac{\rho}{\theta^2} (\eta \theta + \mu) \nabla \theta \right] \cdot \mathbf{t} + D_f [\mathbf{F}] \cdot \mathbf{t}, \quad (9)$$

where η is the entropy. Since the temperature θ is continuous across $\mathcal{S}(\tau)$ we set $\langle \theta \rangle = \theta_s$ in eq.(9) and find

$$[\rho \mathbf{u}] \cdot \mathbf{t} = -\frac{D_s}{\theta_s} \frac{\partial [p]}{\partial s} + D_s \frac{[\rho \epsilon + p]}{\theta_s^2} \frac{\partial \theta_s}{\partial s} + D_f [\mathbf{F}] \cdot \mathbf{t}, \quad (10)$$

where ϵ is the internal energy and where the identity

$$\eta \theta + \mu = \epsilon + \frac{p}{\rho},$$

has been used. In the steady state case that we will consider next the jump of an arbitrary variable across the interface will only depend upon the arclength parameter s and not upon time.

3. The Slippage Equation

Consider now a thin liquid layer (Ω_l) placed on a solid surface (Ω_s) under isothermal conditions. The solid, with uniform density ρ_o , is at rest such that eq.(10) becomes

$$\rho^l u_t^l = -\frac{D_s}{\theta_s} \frac{d(p^l - p^s)}{ds} + D_f F_t^l, \quad (11)$$

where the body force experienced by the solid particles has been considered entirely negligible. Across the surface \mathcal{S} the following conditions hold

$$\mathbf{u}^l \cdot \mathbf{n} = 0, \quad (12)$$

$$(p^l - p^s) \mathbf{n} - \mathbf{T}_e^l \mathbf{n} + \mathbf{T}_e^s \mathbf{n} = \sigma K \mathbf{n} + \frac{d\sigma}{ds} \mathbf{t}, \quad (13)$$

where $\mathbf{T} = -p\mathbf{1} + \mathbf{T}_e$ is the Cauchy stress tensor, σ is the surface tension and K is the mean curvature. The scalar product of eq.(13) with \mathbf{n} gives

$$p^l - p^s - \mathbf{T}_e^l \mathbf{n} \cdot \mathbf{n} + \mathbf{T}_e^s \mathbf{n} \cdot \mathbf{n} = \sigma K. \quad (14)$$

When the fluid in Ω_l is linearly viscous (Newtonian) and the solid in Ω_s is linearly elastic the stress tensors are given by

$$\begin{aligned} \mathbf{T} &= (-p + \lambda \nabla \cdot \mathbf{u}) \mathbf{1} + \frac{\delta}{2} (\nabla \mathbf{u} + \nabla \mathbf{u}^T) & \text{in } \Omega_l, \\ \mathbf{T} &= -p\mathbf{1} + \alpha (\nabla \mathbf{f} + \nabla \mathbf{f}^T) & \text{in } \Omega_s, \end{aligned} \quad (15)$$

where δ and λ are the viscosities, α is the shear modulus. $\mathbf{f} = \mathbf{x} - \mathbf{X}$ is the deformation vector of the solid, \mathbf{x} and \mathbf{X} are the position vectors of a generic particle of the solid in the deformed and in the undeformed configuration. By substituting eq.(15) into eq.(14) and after some lengthy algebra we obtain

$$p^l - p^s - \tilde{\nu}^l \rho^l \left(\frac{\partial \mathbf{u}}{\partial n} \right)^l \cdot \mathbf{n} + \alpha \left(\frac{\partial \mathbf{f}}{\partial n} \right)^s \cdot \mathbf{n} = \sigma K, \quad (16)$$

where $\tilde{\nu}^l = (\lambda^l + \delta^l) / \rho^l$.

The equation of conservation of mass in Ω_l states that

$$\nabla \cdot (\rho \mathbf{u}) = 0. \quad (17)$$

The limit of the gradient of $\rho \mathbf{u}$ as it approaches \mathcal{S} from the right is given by

$$\lim_{\mathbf{x} \rightarrow \varphi^+} \nabla(\rho \mathbf{u}) = \frac{d(\rho^l \mathbf{u}^l)}{ds} \otimes \mathbf{t} + \left(\frac{\partial}{\partial n}(\rho \mathbf{u}) \right)^l \otimes \mathbf{n}. \quad (18)$$

We take the trace of both sides of eq.(18) and use the limit for $\mathbf{x} \rightarrow \varphi^+$ of eq.(17) to find

$$\left\{ \frac{d}{ds}(\rho^l \mathbf{u}^l) \right\} \cdot \mathbf{t} + \left(\frac{\partial}{\partial n}(\rho \mathbf{u}) \right)^l \cdot \mathbf{n} = 0. \quad (19)$$

We then apply the Frenet formulas to the first term in eq.(19) and use the no-inflow condition eq.(12) to obtain

$$\frac{d(\rho^l u_t^l)}{ds} = -\rho^l \left(\frac{\partial \mathbf{u}}{\partial n} \right)^l \cdot \mathbf{n}. \quad (20)$$

Since in Ω_s the density is constant, the equation of conservation of mass reads

$$\nabla \cdot \mathbf{f} = 0.$$

Following the same procedure as before we find

$$\frac{df_t^s}{ds} - K f_n^s = - \left(\frac{\partial \mathbf{f}}{\partial n} \right)^s \cdot \mathbf{n}. \quad (21)$$

With the aid of eqs.(20) and (21), eq.(16) becomes

$$p^l - p^s = \sigma K - \tilde{\nu}^l \frac{d(\rho^l u_t^l)}{ds} + \alpha \left(\frac{df_t^s}{ds} - K f_n^s \right). \quad (22)$$

We can now substitute eq.(22) into eq.(11) to find

$$\tilde{\nu}^l \frac{d^2}{ds^2}(\rho^l u_t^l) - \frac{\theta_s}{D_s} \rho^l u_t^l = \frac{d}{ds} \left(\sigma K + \alpha \frac{df_t^s}{ds} - \alpha K f_n^s \right) - \frac{D_f \theta_s}{D_s} F_t^l, \quad (23)$$

where, for sake of simplicity, the kinematic viscosity of the liquid and the shear modulus of the solid have been considered constant. Let us introduce the following non-dimensional quantities

$$u_t = \frac{u_t^l}{u_o} \quad \rho = \frac{\rho^l}{\rho_o} \quad \hat{s} = \frac{s}{s_o} \quad \aleph = K s_o \quad f_{t,n} = \frac{f_{t,n}^s}{L}, \quad (24)$$

$$F = \frac{F_t^l}{\bar{F}_t} \quad \delta_s = \frac{D_s}{D_s} \quad \delta_f = \frac{D_f}{D_f} \quad \Sigma = \frac{\sigma}{\bar{\sigma}}, \quad (25)$$

where s_o is a characteristic length of the problem and the overbar means average over \mathcal{S} . Let

$$A = \frac{\alpha L}{\rho_o u_o \tilde{\nu}^l} \quad B = \frac{\overline{D_f \theta_s s_o^2 \bar{F}_t}}{D_s \rho_o u_o \tilde{\nu}^l} \quad C = \frac{\bar{\sigma}}{\rho_o u_o \tilde{\nu}^l} \quad D = \frac{s_o^2 \theta_s}{D_s \tilde{\nu}^l}, \quad (26)$$

and

$$\rho u_t = w ,$$

where $w(s)$ has the meaning of a slippage function. Then, with the aid of eqs.(24), (25) and (26), eq.(23) becomes

$$\frac{d^2 w(s)}{ds^2} - \mathcal{D} \frac{w(s)}{\delta_s(s)} = \frac{d}{ds} \left(\mathcal{C} \Sigma(s) \mathfrak{N}(s) + \mathcal{A} \frac{df_t(s)}{ds} - \mathcal{A} \mathfrak{N}(s) f_n(s) \right) - \mathcal{B} \frac{\delta_f(s)}{\delta_s(s)} F(s) . \quad (27)$$

where we have dropped the superscript hat on the non-dimensional arclength. Eq.(27) is our main result and shows clearly that, even for the simplest models of fluid and solid behaviour, the slippage will depend upon surface diffusion, curvature, intermolecular forces and upon the deformation of the solid surface. However, eq.(27) is far too general for practical purposes and its full exploitation strongly depends upon a detailed knowledge of the various coefficients, knowledge that can only be achieved through experiments. In addition, its range of validity is limited by the basic assumption that the fluid in Ω_l is Newtonian. The constitutive equation of a polymeric liquid would have given additional terms (contained in the traction vector $\mathbf{T}^l \mathbf{n}$) that would have sensibly changed the resulting equation hence reflecting the differences between the behaviour of Newtonian and non-Newtonian liquids next to solid surfaces, differences widely documented in the experimental literature [14].

4. Some Asymptotic Solutions and Slippage Induced by Surface Roughness

We will now consider separately some subcases of eq.(27) chosen in such a way that the influence of the various effects upon slippage can be better appreciated. For the time being we will disregard the effect of deformation which will be treated more extensively in the next Section. When \mathcal{A} is negligible and the surface is completely flat eq.(27) becomes

$$\frac{d^2 w}{ds^2} - \mathcal{D} \frac{w(s)}{\delta_s(s)} = -\mathcal{B} \frac{\delta_f(s)}{\delta_s(s)} F(s) . \quad (28)$$

Since we expect that the slippage will disappear as s increases (that is, as the film thickness grows) we require

$$\lim_{s \rightarrow \infty} w(s) = 0 . \quad (29)$$

First of all, when $\mathcal{B} \approx 0$ (that is, negligible intermolecular forces) and $\delta_s(s)$ varies slowly with the arclength, a solution of eq.(28) can be obtained with the aid of the Liouville-Green (WKB) approximation. In this case

$$\frac{w(s)}{\delta_s(s)^{1/4}} = \frac{w(0)}{\delta_s(0)^{1/4}} \exp \left\{ -\mathcal{D}^{1/2} \int_0^s \frac{ds'}{\delta_s(s')^{1/2}} \right\} , \quad (30)$$

showing an exponential decay in the slippage for non zero values of δ_s while in the limiting case of zero diffusivity at the contact line the no-slip condition is recovered. A case in which \mathcal{B} is not negligible happens when $\tilde{v}_l = O(\varepsilon)$, $\varepsilon \ll 1$. Then from eq.(26) it follows that $(\mathcal{D}, \mathcal{B}) = O(\varepsilon^{-1})$ and eq.(28) gives a singular perturbation problem whose outer solution is given by

$$w(s) = \mathcal{M} \delta_f(s) F(s) , \quad \mathcal{M} = \frac{\overline{D}_f \overline{F}_t}{\rho_o u_o} , \quad (31)$$

which coincides with the Stokes-Einstein equation of surface diffusion [13]. When the body force F is derivable from an interaction potential $\Phi(s)$, a quantitative determination of the slippage velocity will depend upon the choice of a suitable intermolecular potential. When such a potential is substituted in eq.(31), it should allow the matching between eq.(31) and the inner solution of eq.(28) which gives the behaviour of the slippage velocity in the immediate proximity of the contact line. Hence, within the framework of our theory, for a flat solid surface and for small $\tilde{\nu}_l$, the Stokes-Einstein eq.(31) should be regarded as an *outer* solution for the slippage velocity, solution that holds outside a boundary layer of thickness $O(\tilde{\nu}_l^{1/2})$ from the contact line. It seems, in other words, that the slippage phenomenon is mainly governed by the interaction potential only at some distance from the contact line whereas, close to $s = 0$, it is substantially affected by the hydrodynamic flow. The general solution of the linearized slippage equation which satisfies the asymptotic condition eq.(29) is in fact

$$w(s) = c \times \exp\left(-s\sqrt{\frac{\mathcal{D}}{\delta_s(0)}}\right) + \mathcal{B} \frac{\delta_f(0)}{\delta_s(0)} \int_s^\infty \Phi(t) \cosh\left[(t-s)\sqrt{\frac{\mathcal{D}}{\delta_s(0)}}\right] dt, \quad (32)$$

where the first term on the right hand side of eq.(32) is dominant next to the contact line and the second term becomes more effective at some distance away from it.

The influence of the interface curvature upon slippage on the other hand can be better examined by linearizing the coefficients (26) in a neighborhood of the contact line and by considering the limit $\mathcal{D} \rightarrow 0$. Eq.(27), with the same assumption of negligible surface deformations, gives

$$\frac{dw}{ds} = \mathcal{C}\Sigma(0)\aleph(s) + c_1.$$

Since

$$\aleph = \frac{d\beta}{ds},$$

where β is the angle between the tangent of the interface and the x-axis we have

$$w(s) = \mathcal{C}\Sigma(0)\beta(s) + c_1s + c_2. \quad (33)$$

If the surface \mathcal{S} is given by the equation $y^s = h(x^s)$ then

$$\tan \beta = h'(x^s); \quad s = \int \left(1 + h'(x^s)^2\right)^{1/2} dx^s, \quad (34)$$

where a prime denotes differentiation with respect to x^s . Passing to the x^s -variable, eq.(33) becomes

$$w(x^s) = \mathcal{C}\Sigma(0) \arctan\{h'(x^s)\} + c_1 \int \left(1 + h'(x^s)^2\right)^{1/2} dx^s + c_2. \quad (35)$$

Now let

$$\lim_{x^s \rightarrow \infty} h'(x^s) = \lim_{x^s \rightarrow \infty} h''(x^s) = 0. \quad (36)$$

We are requiring, in other words, that asymptotically far from the contact line the surface roughness disappears. Then $c_1 = c_2 = 0$ and

$$w(x^s) = \mathcal{C}\Sigma(0) \arctan\{h'(x^s)\}. \quad (37)$$

Eq.(37) then gives an interesting result: in absence of surface diffusion if at the contact line the surface is absolutely flat ($h'(0) = 0$) then $w(0) = 0$ and the no-slip condition holds. In any other case even a minimum degree of surface roughness will generate some slippage in the fluid particles. This result is in agreement with the experiments of Smart [9] and Prokunin [15] where the removal of the no-slip condition was attributed to the effect of surface roughness.

5. No-Slip Caused by Film Pinning and Slippage Induced by Surface Deformation

Suppose now that the functions δ_s and δ_f are constant over S and let

$$\bar{\Sigma}(s) = C\Sigma(s) - \mathcal{A}f_n; \quad F(s) = -\frac{d\Phi(s)}{ds} .$$

Then, whenever

$$\frac{\delta_f}{\delta_s} \mathcal{B}\Phi(s) = -\bar{\Sigma}(s)\aleph(s) + \text{constant} , \tag{38}$$

eq.(27) admits a particular solution

$$w = 0; \quad f_t = 0;$$

while, from eq.(23)

$$p^l - p^s = (\sigma - \alpha f_n)\aleph .$$

In other words, in spite of the presence of a finite surface diffusivity δ_s , eq.(27) admits also the no-slip condition for every $s \in S$. When eq.(38) holds the intermolecular potential Φ is just responsible for the presence of surface tension at the solid-liquid interface and this implies a rather definite morphology for the surface next to the contact line. If the surface becomes flat as $s \rightarrow \infty$ the constant in eq.(38) is equal to zero and, with the aid of eq.(34) we find

$$\bar{\Sigma}\beta(s) = \mathcal{B}\frac{\delta_f}{\delta_s} \int_s^\infty \Phi(s')ds' . \tag{39}$$

We adopt for $\Phi(s)$ the expression found by Ruchenstein [8] on the basis of a London-type potential for which

$$\Phi(s) = \frac{\Gamma(\psi; A_{LL}, A_{SL})}{s^3} ,$$

with

$$\Gamma(\psi; A_{LL}, A_{SL}) = \frac{\cos^3 \psi}{12\pi} [(A_{LL} - A_{SL})G(\psi) - A_{SL}G(\pi - \psi)] ,$$

$$G(\psi) = \csc^3 \psi + \tan^{-3} \psi + \frac{3}{2} \tan^{-1} \psi ,$$

where ψ is the angle of the liquid wedge and A_{LL} and A_{SL} are the Hamaker constants. Then

$$\bar{\Sigma}\beta(s) = \frac{\mathcal{B}\delta_f\Gamma(\psi; A_{LL}, A_{SL})}{2\delta_s s^2} . \tag{40}$$

It follows

$$\lim_{s \rightarrow 0} s^2 \beta(s) = \frac{\mathcal{B} \delta_f \Gamma(\psi; A_{LL}, A_{SL})}{2 \delta_s \bar{\Sigma}}, \quad (41)$$

that is $\beta(s) = O(s^{-2})$ and, by virtue of eq.(34), this implies

$$\lim_{x \rightarrow 0} h'(x) = \pi/2.$$

In other words, when the surface S forms at the contact line a step with a right angle the no-slip condition holds which seems to indicate that the liquid layer remains somehow pinned on such step. Whether or not such phenomenon really occurs is difficult to say, especially since, under such conditions, the rupture of the liquid film (excluded by the continuum nature of the present approach) may practically happen.

For what attains the slippage induced by surface deformation consider the limit $(\mathcal{D}, \mathcal{B}) \rightarrow 0$ of eq.(27). In this case we have

$$\frac{d^2 w}{ds^2} = \frac{d}{ds} \left(C \Sigma(s) \aleph(s) + \mathcal{A} \frac{df_t}{ds} - \mathcal{A} \aleph(s) f_n \right). \quad (42)$$

We integrate eq.(42) twice and use the condition of asymptotic flatness to find

$$w(s) = C \Sigma(s) \beta(s) + \mathcal{A} (f_t(s) - f_t^\infty) + \int_s^\infty \left(\mathcal{A} \aleph(s') f_n(s') - C \beta(s') \frac{d\Sigma}{ds'} \right) ds'. \quad (43)$$

Now

$$\mathbf{f} = \mathbf{x} - \mathbf{X} = (x^s - X) \mathbf{i} + (y^s - Y) \mathbf{j},$$

and we will denote with $y^s = h(x^s)$ and $Y = H(X)$ the equations of the surface in the deformed and in the undeformed configuration. It can then be shown that, in the limit of small displacements

$$\begin{aligned} f_t &= \frac{(x^s - X) + H'(h - H)}{\sqrt{1 + H'^2}}, \\ f_n &= \frac{-(x^s - X)H' + (h - H)}{\sqrt{1 + H'^2}}, \end{aligned} \quad (44)$$

with $x^s = x^s(X)$. We then use eqs.(44) and (34) in eq.(43) to obtain

$$\begin{aligned} w(X) &= C \Sigma(X) \arctan h'(X) + \mathcal{A} \left(\frac{(x^s - X) + (h - H)H'}{\sqrt{1 + H'^2}} - f_t^\infty \right) + \\ &+ \int_s^\infty \left(\mathcal{A} H'' \frac{(h - H) - H'(x^s - X')}{(1 + H'^2)^{3/2}} - C \arctan h'(X') \frac{d\Sigma}{dX'} \right) dX'. \end{aligned} \quad (45)$$

When the surface is completely flat eq.(45) gives

$$w(X) = \mathcal{A} \{ x^s(X) - X - f_t^\infty \}. \quad (46)$$

Hence, in absence of surface deformation eq.(46) reduces to

$$x^l(\tau, X) = x^l(0, X) = X,$$

and the fluid particle always remains at the same place. Otherwise any difference between the deformation of the solid surface next to the contact line and the deformation asymptotically far from it will generate some slippage between liquid and solid particles which could hardly be detected by any standard experiment.

6. Comparison with Millikan's Equation

The proper boundary condition for the phenomenon of a "slip flow" observed in high altitude aerodynamics were first investigated by Maxwell. Millikan simplified considerably Maxwell's treatment and obtained for the slippage velocity the following relation [16]

$$u_t^l = \omega \mathcal{T}^l \cdot \mathbf{t} + \frac{3\mu}{4\rho^l \theta_s} \frac{\partial \theta_s}{\partial s}, \tag{47}$$

where ω is a slip coefficient directly related to the air molecules reflected "diffusely", $\mathcal{T}^l = \mathbf{T}^l \mathbf{n}$ is the traction vector on the surface and the second term in eq.(47), which relates the slip velocity to the surface temperature gradient, takes the name of creep velocity. Let us consider eq.(10) when the lower solid is stationary, that is

$$u_t = -\frac{D_s}{\rho^l \theta_s} \frac{\partial [p]}{\partial s} + D_s \frac{[\rho \epsilon + p]}{\rho^l \theta_s^2} \frac{\partial \theta_s}{\partial s} + \frac{D_f}{\rho^l} [\mathbf{F}] \cdot \mathbf{t}. \tag{48}$$

When the deformation of the surface is negligible, the jump condition (14) gives

$$[p] = \mathcal{T}^l \cdot \mathbf{n} + \sigma K. \tag{49}$$

We substitute eq.(49) in eq.(48) and use the Frenet formulas to find

$$u_t^l = \frac{D_s K}{\theta_s \rho^l} \mathcal{T}^l \cdot \mathbf{t} + D_s \frac{[\rho \epsilon + p]}{\rho^l \theta_s^2} \frac{\partial \theta_s}{\partial s} + \mathcal{G}, \tag{50}$$

where \mathcal{G} collects the remaining terms. Eqs.(47) and (50) share not only a direct proportionality between slippage velocity and tangential traction but also the presence of the creep velocity. This similarity is, however, quite surprising since eqs.(47) and (50) apply to different types of diffusion problems: the Knudsen free-molecule regime for the former and the viscous continuum regime for the latter. Such similarity, however, suggests a slippage coefficient for wetting problems given by

$$\omega = \frac{D_s K}{\rho^l \theta_s},$$

in which the curvature K is clearly the microscopic curvature of the surface; the surface roughness in other words. Hence, in Fluid Mechanical problems where the effect of surface roughness (or its characteristic lengthscale) can be considered negligible (the vast majority as a matter of fact) such slippage coefficient would vanish while problems in which the roughness of the surface is significant will admit a finite slippage.

7. Concluding Remarks

Slippage (that is, a finite relative velocity) between a solid and a fluid particle it is known to exist for a wide class of Fluid-Mechanical problems. The common denominator of this

class seems to be the fact that, due to the geometry or to the characteristic lengthscale of the problem, effects of surface concentration and intermolecular forces become increasingly important. When these effects are included in the problem of slippage of a thin liquid film on a solid surface, they can account for a finite slippage at the interface whose evolution in space is governed by the classical jump-conditions at the interface. The main results of the present work can be then summarized by saying that four effects seem to have a major impact upon the slippage phenomenon. In particular:

- Surface diffusion, due to inhomogeneities in the concentration of the solid and of the liquid particles next to the surface. This effect results in a tendency for the particles of one constituent to move with respect to the other in such a way as to re-equilibrate their distribution. This motion can either have a preferential direction or, due to the nature of the fluid motion just above the interface, an oscillatory behaviour whose stability properties will be the object of further investigations.
- Surface roughness which, in layman words, introduces the effect of the geometrical obstacles on the motion of the fluid particles. The results contained in Section 4 show, in particular, how the presence of a moderately rough surface can induce slippage at the interface probably (but this may need a rigorous proof) by generating a finite velocity gradient between particles that must overcome geometrical barriers of different height. When these obstacles become very steep however (microscopic walls), the kinetic energy of the particles seems to be insufficient to continue the motion, the slippage tends to zero and the phenomenon of “contact line pinning” present itself.
- Surface deformation gradients which, to a large extent, are the less tractable aspect of the problem. The motion of the fluid in the thin layer and in the bulk is structurally different, with different shear stresses at the wall. Since no solid is undeformable (perfectly rigid) the effect of different stresses applied by the fluid at different points on the solid results in an unequal deformation of the surface. Section 5 shows that fluid particles in contact with differently deformed surfaces behave differently and even if, intuitively, this effect can be classified as minor, it may be the basic feature that differentiates the behaviour of Newtonian and Non-Newtonian fluids next to solid walls (phenomenon of drag reduction).
- Intermolecular forces which, if negligible in the bulk liquid, become increasingly important with the thinning of the liquid layer. In this region the problem is complicated by the presence of a second interface (between liquid and air, which we did not address) with intermolecular forces of different intensity acting on it. The result is the presence of a region, inside the liquid layer but still far from the interfaces, where the forces acting on the solid-liquid and on the liquid-air interfaces are both present and which, for the static case, generate the so-called “Disjoining Pressure” introduced by Deryagin [6]. A fully dynamic case where all these effects are taken into account is, in our opinion, still far from being formulated. When, however, the presence of the liquid-air interface is neglected, the results of Section 5 with a simple London-type potential indicate that, immediately next to the contact line, these forces may strongly condition the overall phenomenon.

These four mechanisms certainly do not explain the slippage phenomenon in its full complexity but they are, we believe, the most important. Different problems may be heavily influenced by a single one of them and be less affected by the others, but the striking similarity with the phenomenon of “slip-flow” presented in Section 6 and well known by the aerodynamicists, suggests that a unified viewpoint for the treatment of the problem is indeed possible, thus

opening the way to a more rigorous formulation of boundary conditions of the modern Fluid Mechanics.

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