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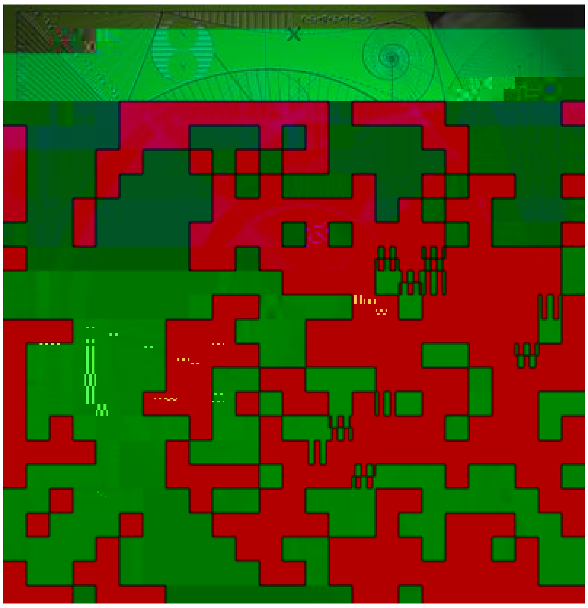

Liquid flow over a substrate structured by seeded nanoparticles.

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Abstract

Recent experiments have demonstrated that nanoparticles which sparsely distributed over a solid substrate can substantially change the flow conditions at the solid surface in the presence of slip. Inspired by these observations, the flow past tiny particles seeded on

Consider experimental results in [18] in more detail. The flow measurements of hexadecane at the initially molecularly smooth sapphire surfaces, covered with PDMS oligomer layer, have shown finite slip length λ approaching $\lambda \simeq 250 \pm 50$ nm. Then the same measurements have been taken on the surface modified with seeded small particles of $25-30$ nm size. Remarkably, strong effect has been already observed with only 2% of the substrate area covered by the particles, i.e. when the average distance between the particles is about 180 nm. The slip length has shown a perceptible decline to $\lambda \simeq 150 \pm 50$ nm, whilst the average distance between the particles was still much greater than the particle size. Further increase of the area covered by the particles to just 5% was sufficient to decrease the observed slip length to $\lambda \simeq 50 \pm 50$ nm and thus, within the accuracy of measurements, to restore the no-slip condition. This effect has no satisfactory theoretical explanation so far, and one might assume that the particles were able to disturb the flow at the boundary on a length scale large compared to their own size. In order to identify the mechanisms of the phenomenon and bearing in mind that, as shown in [19], the effects of slip and the surface-tension gradients are coupled in the interfacial layer, we consider the interfacial dynamics as it could be affected by the presence of seeded particles. We will show that even a single seeded particle will disturb the interfacial layer and create surface tension gradients. This effect, generated by the seeded particles, is expected to be similar to the well-known Marangoni phenomenon, first discovered for the surface tension gradients induced by the gradients of surface temperature [20].

The mathematical model that we use here is based on the interface formation theory developed earlier, [2], coupled with the effect of surface slip. In the case of a liquid consisting of spherical molecules, this effect, studied microscopically, has been shown to be sufficient to produce surface slip exceeding 30 molecular diameters, [21, 22]. To simplify the problem, consider a steady two-dimensional Stokes flow (in the vicinity of the substrate, one almost always has flows with negligible inertia) of an incompressible Newtonian liquid of constant density ρ and viscosity μ over a smooth solid surface with just one particle (with similar to the substrate physical properties) seeded on the surface. We note, however, that, geometrically, the three-dimensional analogue of the two-dimensional particle introduced here would be a lattice of threads lying on the surface normal to the direction of the flow. On the one hand, this simplification will allow us to obtain readily observed analytical results; on the other hand, this case is sufficiently representative to study the main features of the phenomenon.

The flow velocity $\mathbf{u}$ and pressure p in the bulk satisfy the Navier-Stokes (NS) equations,

$$\nabla \cdot \mathbf{u} = 0, \quad \nabla p = \mu \nabla^2 \mathbf{u}. \tag{1}$$

substrate, (Fig.1), one has:

$$\frac{\partial u_x}{\partial y} = S_0, \quad u_y = 0, \quad y \to \infty. \tag{2}$$

Boundary condition on the solid surface are given by [2]:

$$\mathbf{v}^s \cdot \mathbf{n} = 0, \tag{3}$$

$$\mu \mathbf{n} \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^*] \cdot (\mathbf{I} - \mathbf{nn}) + \tfrac{1}{2} \nabla \sigma = \beta(\mathbf{u} - \mathbf{u}^-) \cdot (\mathbf{I} - \mathbf{nn}), \tag{4}$$

$$\rho \mathbf{u} \cdot \mathbf{n} = (\rho^s - \rho^s_e)\tau^{-1}, \tag{5}$$

$$\nabla \cdot (\rho^s \mathbf{v}^s) = -(\rho^s - \rho^s_e)\tau^{-1}, \tag{6}$$

$$\mathbf{v}^s \cdot (\mathbf{I} - \mathbf{nn}) = \tfrac{1}{2}(\mathbf{u} + \mathbf{u}^-) \cdot (\mathbf{I} - \mathbf{nn}) + \alpha \nabla \sigma. \tag{7}$$

$$\sigma = \gamma(\rho^s_0 - \rho^s). \tag{8}$$

Here $\sigma = \gamma(\rho^s_0 - \rho^s)$ is the surface tension in the interfacial layer which is modelled as a two-dimensional 'surface phase'; ρ^s is the surface density in this phase (mass per unit area) and $\mathbf{v}^s$ is the velocity with which it is transported along the interface; $\mathbf{u}^-$ is the velocity on the *solid*-facing side of the liquid-solid interfacial layer (Fig.1); α, β, γ, τ, ρ^s_e and ρ^s_0 are phenomenological material constants; $\mathbf{n}$ is the normal vector pointing in the liquid, $\mathbf{I}$ is the metric tensor; the tensor $(\mathbf{I} - \mathbf{nn})$ singles out the tangential projection of a vector; an asterisk marking a second-rank tensor indicates its transposition.

It should be emphasized here, that the above formulation can only be employed for lyophilic or, possibly, for intermediate liquid-solid combinations. In the opposite case of lyophobic combinations, the flow at the boundary may be conditioned by the trapped bubbles and the nature of the boundary conditions will be different.

The problem formulation should

and

$$\left(\frac{\mu}{\beta} + \frac{\mu}{\beta_s}\right)\frac{\partial u_{\|}}{\partial n} = u_{\|}.$$

Identifying the slip length measured in experiments with

$$\lambda = \frac{\mu}{\beta} + \frac{\mu}{\beta_s},$$

we arrive at the form of the standard Navier boundary condition

$$\lambda\frac{\partial u_{\|}}{\partial n} = u_{\|}.$$

So, in equilibrium situations, the contributions from apparent and *surface* slip collapse into one parameter, the measurable slip length λ, so that it appears that surface slip is not directly observable. From this point of view, the [illegible]

$$u_x = \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) - \frac{1}{2Ca}\frac{\partial \rho^s}{\partial x}\left(\frac{1+2\delta_s}{1+\delta_s}\right), \tag{13}$$

$$\epsilon\, u_y = Q(\rho^s - 1), \tag{14}$$

$$\epsilon \frac{\partial \rho^s v^s}{\partial x} = 1 - \rho^s, \tag{15}$$

$$2v^s = u_x + \frac{\delta_s}{1+\delta_s}\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) - \frac{1}{Ca}\frac{\partial \rho^s}{\partial x}\left(\frac{2+\delta_s}{1+\delta_s}\right). \tag{16}$$

To complete the

Matching asymptotic expansions in all three regions, one can obtain, in the leading order, at the boundary $y = 0$,

$$\rho^s(x) = 1 \mp \epsilon\, \xi_0\, C_\delta \exp(-\xi_0 |x|), \tag{20}$$

$$v^s(x) = v_0^s - C_\delta \exp(-\xi_0 |x|), \tag{21}$$

$$u_x(x, 0) = 1 - \frac{2 + 4\delta_s}{5 + 4\delta_s}\, C_\delta \exp(-\xi_0 |x|), \tag{22}$$

$$u_y(x, 0) = \mp Q\, \xi_0\, C_\delta \exp(-\xi_0 |x|), \tag{23}$$

where

$$\xi_0^2 = \frac{Ca}{\epsilon} \frac{1 + \delta_s}{\frac{5}{4} + \delta_s}, \quad v_0^s = \frac{1}{2}\left(1 + \frac{\delta_s}{1 + \delta_s}\right), \quad C_\delta = v_0^s - \bar{V}_0, \tag{24}$$

and the upper sign is for $x > 0$. Note, that to obtain the simplest and readily observable analytic expressions, we have neglected contributions proportional to $Q << 1$ in the coefficients of the asymptotic solution (20)–(22) and used a simplifying assumption that numerically parameter $\xi_0^2 << 1$.

param-

The mechanism of this effect in both cases is the same. While the seeded particle directly affects only the surface velocity, via the condition $v^s(0) = \bar{V}_0$, this disturbs the equilibrium

Now, slip measurements on patterned substrates provide an alternative and unique method of direct measurements of this fundamental parameter.

The analysis can be easily generalised to the case of [illegible] particles located at points x_k, $k = 1...N$. The asymptotic [illegible] similar to (20)-(22), of the flow field at the boundary between each pair of the particles located, say, at x_1 and x_2, is given by

$$u_x(x, 0) = 1 - (A \exp(-\xi_0 x) + B \exp(\xi_0 x)) \frac{2 + 4\delta_s}{5 + 4\delta_s}, \tag{26}$$

$$A = B \exp(\xi_0 (x_1 + x_2)),$$

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Figure 1: Definition sketch for the problem.

Figure 3: Distributions of the tangential component of the bulk velocity on the [illegible] side of the interfacial [illegible] u_τ along the substrate at different values of parameter δ_s and the distance between the particles Δx distributed uniformly; (a) $|\Delta x| = 3$, (b) $|\Delta x| = 30$, (c) $|\Delta x| = 300$. The seeded particles are located at $x_i, \quad i = 1...5$. For all curves $l_0 = 10$ and $\bar{V}_0 = 0$; (1) $\delta_s = 0.1$, (2) $\delta_s = 1$, (3) $\delta_s = 10$; the distance x along the substrate is scaled with the slip length λ and u_τ is scaled with the undisturbed value