Velocity and temperature jumps at interfaces. A microscopic view, with consequences for microfluidics and heat transfer

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Why study interfacial transfers?

- Lubricated contacts
  (Mechanical and biomechanical interest; **first controlled studies at the nanoscale** by Tabor, Israelaschvili)

- Micro/Nano fluidics (biomedical analysis, chemical engineering)

- Heat transfer from nanoparticles or from nanostructured surfaces (nanofluids, hyperthermia, micro heat pipes)
Outline

- Interfacial constitutive equations
- Slip length
- Results for « ideal » surfaces
- Slip length on structured surfaces
- Electrokinetics
- Kapitsa length
- Thermal transport in « nanofluids »
- Critical flux around a nanoparticle
Hydrodynamic description of transport phenomena

1) **Bulk constitutive equations**: Navier Stokes, Fick, Fourier

\[ \vec{\phi}_i = L_{ij} \nabla \gamma_j \]

- \( \phi_i \) = flux of i
- \( \gamma_j \) = affinity (derivative of entropy) w.r.t. j
- \( L_{ij} \) = Onsager’s coefficient

**Physical property of the material, connected with statistical physics**

2) **Boundary conditions**: in textbooks, mathematical concept

\[ \Rightarrow \text{Replace with notion of interfacial constitutive relations} \]

**Physical property of the interface, connected with statistical physics**
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Interfacial constitutive equation for flow past a solid surface:

**the slip length** (Navier, Maxwell)

\[ \sigma_s = \lambda V_s = \eta \frac{\partial V}{\partial z} \]

Continuity of stress

\[ b = \frac{\eta}{\kappa} \quad \eta = \text{viscosity} \]
\[ \kappa = \text{friction} \]

**Macroscopic flow:** b is not measurable, b=0 is the usual “no slip boundary condition”

**Micro/nano-scale flows:** surface effects becomes dominant, even a small b could be important.

Finite slip, Poiseuille flow:

\[ V_s = b \frac{\partial V}{\partial z} \]

- Flow rate is increased
- Hydrodynamic dispersion and velocity gradients are reduced.

Also important for electrokinetic phenomena (see below)
Experimental tools: slip length

SFA (surface force apparatus)

AFM with colloidal probe

Optical methods::
PIV, fluorescence recovery after photobleaching (FRAP)

Drag reduction in capillaries (flow rate measurements)

Experiments often difficult – must be associated with numerical:theoretical studies

Churaev, JCSI 97, 574 (1984)
Craig & al, PRL 87, 054504 (2001)
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Some experimental results for ideal (?) surfaces

Contact angle $\theta$ (measure of solid liquid attraction)

Experiments are difficult; need for theory/simulation!
Simulation results IDEAL (atomically flat) surfaces

• Robbins-Thompson 1990: b at most equal to a few molecular sizes, depending on « commensurability » and liquid solid interaction strength

• Thompson Trojan 1996: boundary condition may become nonlinear at very high shear rates ($10^8$ Hz)

• Barrat Bocquet 1997: b can reach 50-100 molecular diameters under « nonwetting » conditions and low hydrostatic pressure
Linear response theory (L. Bocquet, JLB, PRL 1994)

Kubo formula:

\[ \kappa = \frac{S}{k_BT} \int_0^\infty dt \langle f_x(t) f_x(0) \rangle \]

\[ \kappa \leq \frac{S(q_0)}{D(q_0)} \int_0^\infty dz \rho(z) V_{FS}(z)^2 \]

\[ b \leq \frac{(k_BT)^2}{S(q_0) \sigma \int_0^\infty dz \rho(z) V_{FS}(z)^2} \]

- q_0 corrugation wavevector
- \( V(xyz) = V_0(z) + V_1(z)\{\cos(q_\parallel x) + \cos(q_\parallel y)\} \)
- S(q) response function
- Molecular quantity
- Depends on wetting properties
Water slippage versus contact angle: a quasi-universal relationship

David M. Huang,1, * Christian Sendner,2 Dominik Horinek,2 Roland R. Netz,2 and Lydéric Bocquet3,4.

(PRL 2008)

\[
\cos \theta = -1 + 2 \rho_s c_{FS}/\rho_F c_{FF}
\]

\[
b(\theta_c) \propto (\cos \theta_c + 1)^{-2}
\]

• Consistent with SFA experiments of Steinberger, Cottin-Bizonne, Charlaix, PRL 2007

• Two fluid description ?? « Vapor layer » (<nm) is much smaller than slip length

• slip length on atomically flat surfaces is at most of order 10-20nm !!
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Influence of roughness

Richardson (1975), Brenner
Fluid mechanics calculation – Roughness suppresses slip

Perfect slip locally – rough surface

But: combination of controlled roughness and dewetting effects can increase slip by creating a « superhydrophobic » situation.

D. Quéré et al; “Lotus leave” or “Fakir effect”
Simulation of a nonwetting pattern


Superhydrophobic (Cassie) state

« imbibited » state

Hydrophobic walls
\[ \theta = 140° \]

« Cassie Wenzel » transition between superhydrophobic state and imbibited state, controlled by pressure.
Flow past the patterned surface: Cassie-Wenzel transition
Modifies the slip length

\[ P_{\text{cap}} = \frac{-2\gamma_{LV} \cos \theta}{L - a} \]
Macroscopic description

(C. Barentin et al 2004; Lauga et Stone 2003; J.R. Philip 1972)

**Partial slip + complete slip, large scale pattern** \( b_1 \ll L \)

- \( L \) = spatial scale of the pattern
- \( a \) = lateral size of the posts
- \( \Phi_s = (a/L)^2 \) Area fraction of no-slip BC

Scaling argument:

- Force = (solid area) x viscosity x shear rate
- Shear rate = (slip velocity)/a
- Force = (total area) x (slip velocity) x (effective friction)

\[
B \sim \frac{a}{\Phi_s} \sim \frac{L}{\sqrt{\Phi_s}}
\]
How to design a strongly slippery surface?

For fixed working pressure (0.5 bars) size of the posts (a=100 nm), and value of $b_0$ (20 nm)

Compromise between

- Large $L$ to obtain large $B$
- $P_{cap} = \frac{\gamma}{L}$ large enough to prevent intrusion

$B \sim 500 \text{nm}$

for $P = 0.5 \text{bars}$

Realized for hydrophobic silicon microposts (Rothstein 2006), or carbon nanotube carpets (Bocquet et al 2006)
hydrophobic nanotubes « carpet » (C. Journet, S. Purcell, Lyon)

Contact angle 180 degrees

Effective slippage versus pattern: flow without resistance in micron size channel? (Joseph et al, PRL 2007)
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Slippage effects (even only 20nm) are important in electrokinetic phenomena (Joly et al, PRL 2004)

Electro-osmosis, ... are determined by the nanohydrodynamics at the scale of the Debye length
Physical mechanism

EK velocity results from the balance viscous stress versus electric driving force (Smoluchovski)

\[ \eta \cdot \frac{v_s}{\lambda_D + b} \approx Q \cdot E \]

\[ Q = -\varepsilon_d \cdot \frac{V_0}{\lambda_D} \]

\[ v_s = -\varepsilon_d \cdot \frac{1 + \frac{b}{\lambda_D}}{\eta} \cdot E \]

Zeta Potential \[ \approx V_0(1+b/\lambda_D) \]

The EK velocity is increased by a factor:

\[ 1 + \frac{b}{\lambda_D} \]
The ‘Zeta potential’ is not only a characteristic of the surface charge, but depends on the surface dynamics

\[ \zeta = V_0 \left( 1 + \frac{b}{\lambda_D} \right) \]

- Experimentally: large Zeta potential on hydrophobic surfaces: Teflon, silanized surfaces, … Schweiss et al., Langmuir 2001, etc.

- Direct experimental proof of the interplay between electrostatics and slippage? See Tabeling et al, PRL 2008
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INTERFACIAL HEAT TRANSPORT

- Micro heat pipes
- Evaporation, boiling
- Layered materials
- Nanofluids

Nanofluids for thermal transport

by Pavel Kebinski\textsuperscript{1}, Jeffrey A. Eastman\textsuperscript{2}, and David G. Cahill\textsuperscript{3}
Thermal contact resistance or Kapitsa resistance defined through

$$j_E \cdot n_{12} = \frac{1}{R_K} (T^{(1)} - T^{(2)}) = \frac{\delta T}{R_K},$$

Kapitsa length:

$$l_K = R_K \lambda$$

$l_K = \text{Thickness of material equivalent (thermally) to the interface}$
Analogy: hydrodynamic slip length ⇔ Kapitsa length

Energy ⇔ Momentum ;
Temperature ⇔ Velocity ;
Energy current ⇔ Stress

Kubo formula

\[
\frac{1}{R_K} = \frac{1}{S k_B T^2} \int_0^\infty dt (q(t)q(0)) .
\]


\[q(t) = \text{energy flux across interface, } S = \text{area}\]
Important in microelectronics (multilayered materials)

solid/solid interface: acoustic mismatch model

Phonons are partially reflected at the interface

Energy transmission:

\[ \alpha_{1 \rightarrow 2} = \frac{4Z_2Z_1}{(Z_1 + Z_2)^2} \]

\( Z_i \) = acoustic impedance of medium i

\( l_K \sim (\text{phonon mean free path}) \times \alpha_{1 \rightarrow 2} \)

See Swartz and Pohl, Rev. Mod. Phys. 1989
Kapitsa length at the liquid solid interface

Result from simulation (ideal surfaces):

- Kapitsa length and slip length have similar magnitudes

- Dependence of $l_K$ on wetting properties is also similar

J-L Barrat, F. Chiaruttini, Molecular Physics 2003

Keblinski et al, JCP 2003
Experimental tools for Kapitsa length:

Pump-probe, transient absorption experiments for nanoparticles in a fluid, or reflectivity at interfaces:
-heat particles (interface) with a « pump » laser pulse
-monitor cooling using absorption with the « probe » beam
Thermal Conductance of Hydrophilic and Hydrophobic Interfaces

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(Received 9 January 2006; published 8 May 2006)

interfaces measured to date is 50 MW m$^{-2}$ K$^{-1}$, with a Kapitza length, \( h = \Lambda/G = 12 \text{ nm} \). This large thermal resistance might be a significant factor modulating heat flow in biological systems as well as engineered systems.

smaller than water, then the thickness of this vapor layer must be less than \( \Delta h/30 = 0.25 \text{ nm} \), where \( \Delta h \) is the...
Order of magnitude from simulations and experiments for liquid/solid interface conductance:

Thermal conductance 100 MW m$^{-2}$ K$^{-1}$

Kapitsa length in the nanometer range, important for heat transfer from nanoparticles.
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• The puzzle of thermal transport in « nanofluids »
• Critical flux around a nanoparticle
• Large thermal conductivity increase (compared to effective medium theory) reported in some suspensions of nanoparticles
• No clear explanation
• Interfacial effects could be important in such suspensions
Effective medium theory

\[ \Delta T(r, \theta) = 0 \]

\[
\begin{align*}
T_1(r, \theta) &= Ar \cos \theta, \ 0 < r \leq r_0 \\
T_2(r, \theta) &= (Br + E/r^2) \cos \theta, \ r_0 < r \leq r_1 \\
T_{eff}(r, \theta) &= -gr \cos \theta, \ r_1 < r
\end{align*}
\]

Boundary conditions

\[
\begin{align*}
T_1(r_0, \theta) - T_2(r_0, \theta) &= -\lambda_1 \frac{\partial T_1}{\partial r}(r_0) R_K \\
\lambda_1 \frac{\partial T_1}{\partial r}(r_0) &= \lambda_2 \frac{\partial T_2}{\partial r}(r_0) \\
T_2(r_1, \theta) &= T_{eff}(r_1, \theta) \\
\lambda_2 \frac{\partial T_2}{\partial r}(r_1) &= \lambda_{eff} \frac{\partial T_{eff}}{\partial r}(r_1)
\end{align*}
\]
Simulation of heat transfer

Maxwell Garnett effective medium prediction (Nan et al, JAP 1997)

\[
\frac{\lambda_{\text{eff}}}{\lambda_l} = \left( \frac{\lambda_p}{\lambda_l} (1 + 2\alpha) + 2 \Phi \left( \frac{\lambda_p}{\lambda_l} (1 - \alpha) - 1 \right) \right)

\alpha = \left( \frac{\text{Kapitsa length}}{\text{Particle Radius}} \right)

Change RK using ratio between atom masses

M. Vladkov, JLB, Nanoletters 2006
Effective medium theory works well for a perfectly dispersed system. Explanations for NF conductivity found in the literature (Brownian motion, solid layer...) do not work.

Explanations of observed results: collective effects, clustering?
- Effective medium calculation (Nan et al, JAP 1997) also works for 2 aggregated particles (comparison with MD, Vladkov and JLB 2006)

- Extrapolate to effective medium calculation for a linear aggregate of particles:

10% volume fraction
Still another interpretation: high coupling between fluid and particle (Yip PRL 2007) and percolation of high conductivity layers (negative Kapitsa length ?)
Other modifications of heat transport in nanofluids (onset of nucleate boiling, critical heat flux) seem to be related to nanoparticle adsorption at the surface of the heater.
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Critical heat flux around a nanoparticle
(S. Merabia et al, PRE 2008, PNAS 2011)

Heat flux

Critical heat flux

\( \dot{q} \)

\( \Delta T \)

\( T_{coex} \)

« pool boiling » curve
Nanoparticle can sustain much higher fluxes than flat interface (Laplace pressure stabilisation of the film)

Patterned surfaces?
Melting and destruction of a gold nanoparticle in octane:
Conclusion

• Micro/nano patterning has rich and interesting consequences for transport phenomena across interfaces
• Experiments are difficult => need to combine with modeling at various scales
• Interesting perspectives: heat transfer, electro-diffusio osmosis phenomena
Kapitsa length at the liquid solid interface

- Lennard Jones fluids

\[ v_{ij}(r) = 4\epsilon \left( \frac{\sigma^{12}}{r^6} - c_{ij} \frac{\sigma^6}{r^6} \right) \]

Wetting properties controlled by \( c_{ij} \)

- equilibrium and nonequilibrium simulations
Nonequilibrium temperature profile – heat flux from the « thermostats » in each solid.

Equilibrium determination of $R_K$
Heat flux from the work done by fluid on solid

$$q(t) = \sum_{i \in \text{liquid}} \sum_{j \in \text{solid}} F_{ij} \cdot v_i.$$