A Statistical Approach to Thermo-Osmosis

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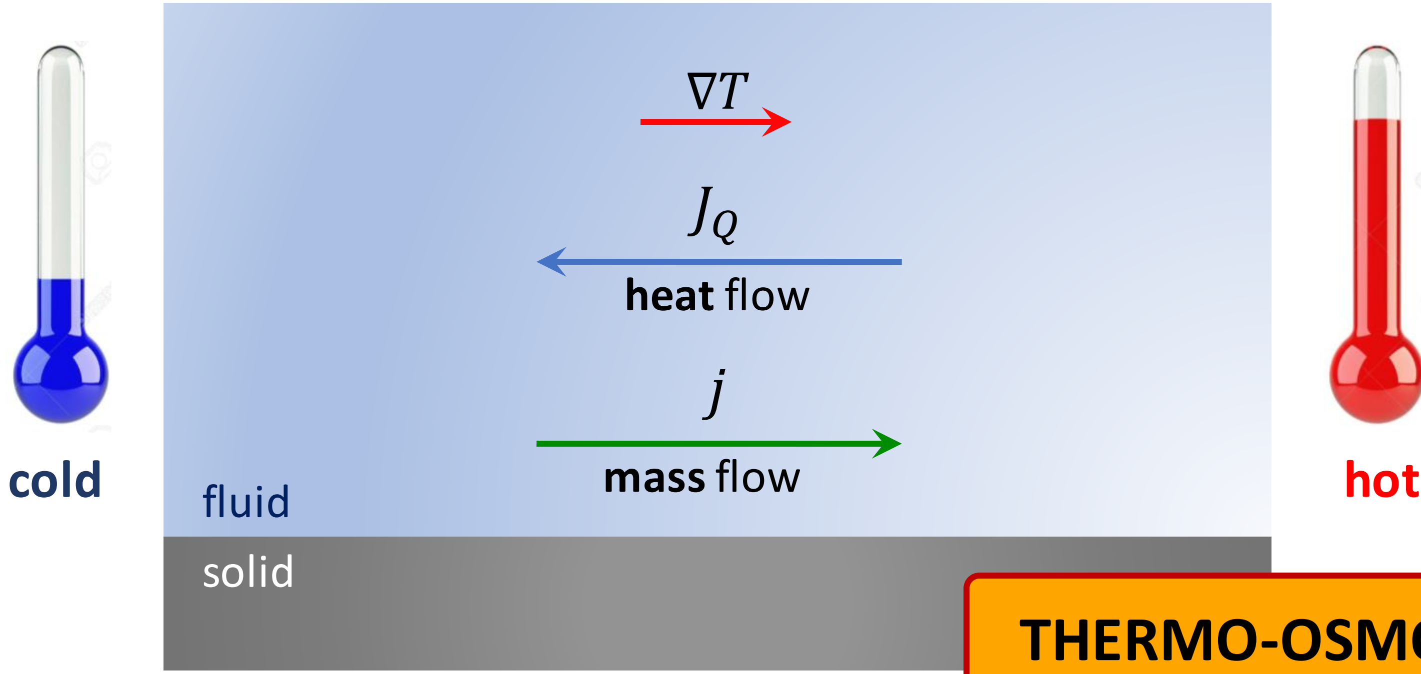
Fluids in thermal gradients

A ***bulk fluid*** placed in a temperature gradient reaches a steady state characterized by

Heat flow but no mass flux

But confining surfaces make the difference

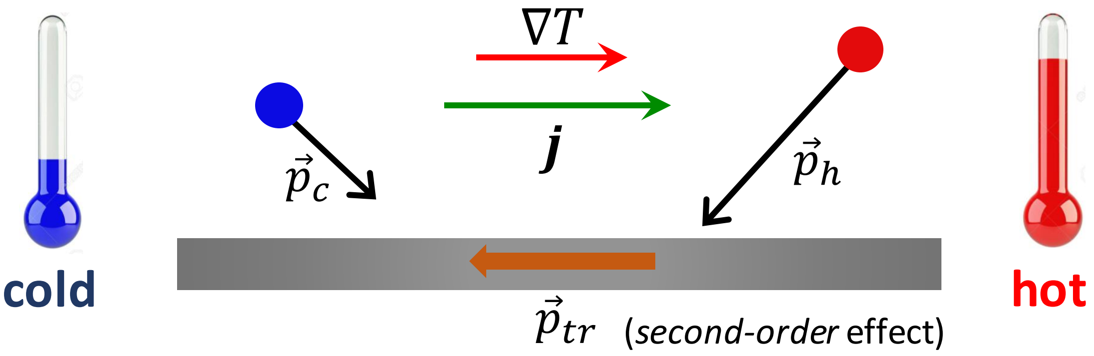


THERMO-OSMOSIS

Gases: *Physical Picture*

- ✓ The study of thermo-osmosis in gases began in the ***late 1800***, when ***Maxwell*** and ***Reynolds*** started an intense debate about the ***radiometer***

- ✓ Thermo-osmosis critically depends on ***particle-surface interaction***



momentum loss during the collision is necessary

The gas is set into motion in the ***direction of the thermal gradient***

- ✓ By means of ***kinetic theories*** Maxwell predicted the slip velocity

$$\boxed{v_\infty = \frac{3}{4}\frac{\eta}{\rho}\frac{\nabla T}{T}}$$

Phil. Trans. Royal Soc. (1879)

Liquids: *Derjaguin's Approach*

11.4. THERMO-OSMOSIS, THE MECHANOCALORIC EFFECT, AND THERMOPHORESIS

The phenomenon of thermo-osmosis, defined as the flow of a liquid, driven by a temperature gradient, through capillaries or porous bodies, appears because the specific enthalpy of the liquid in boundary layers and thin pores differs by ΔH from the bulk value. The theory of thermo-osmosis and other thermokinetic phenomena was developed in [46] on the basis of nonequilibrium thermodynamics.

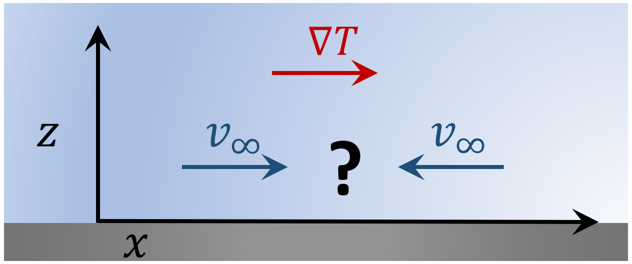
46. B. V. Derjaguin and G. P. Sidorenkov, Dokl. Akad. Nauk SSSR, 32, 622 (1941).

B. V. Derjaguin

$$\boxed{v_\infty = -\frac{1}{\eta}\int_0^\infty \mathrm{d}z\, z\, \Delta h(z)\, \frac{\nabla T}{T}}$$

$$\begin{aligned}\Delta h(z) &= h(z) - h_b \\ &= T\left.\frac{\partial p_\mathrm{T}(z)}{\partial T}\right|_{\beta\mu} - h_b\end{aligned}$$

(Local Equilibrium)

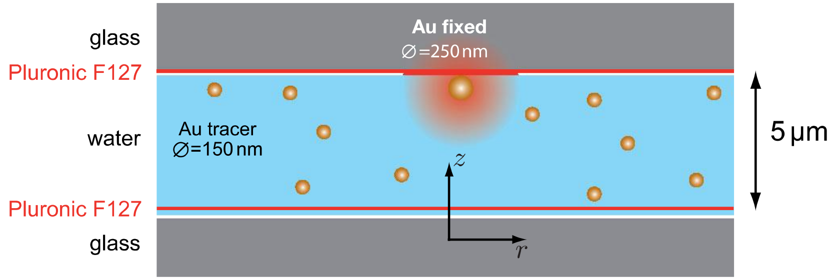


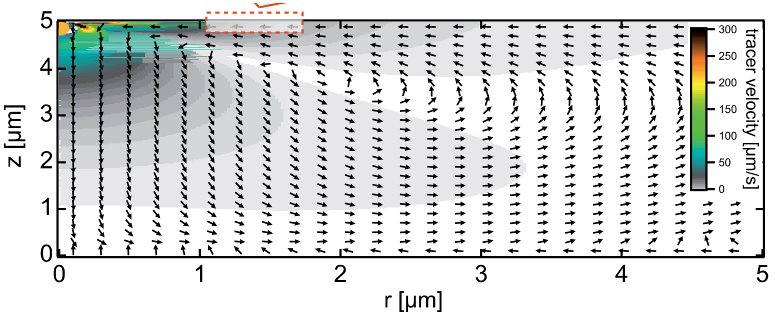
both $h(z)$ and $p_\mathrm{T}(z)$ are *ill-defined* quantities

†Churaev, ***Derjaguin*** and Muller – *Surface forces* (1987)

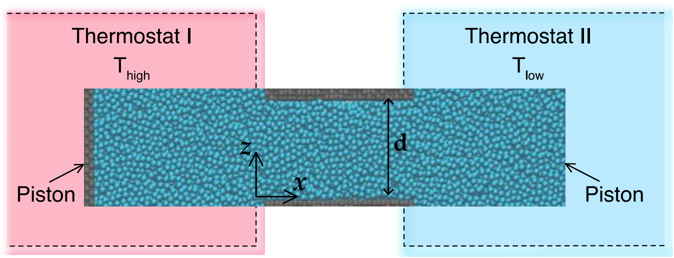
Liquids: *Experiments and Simulations*

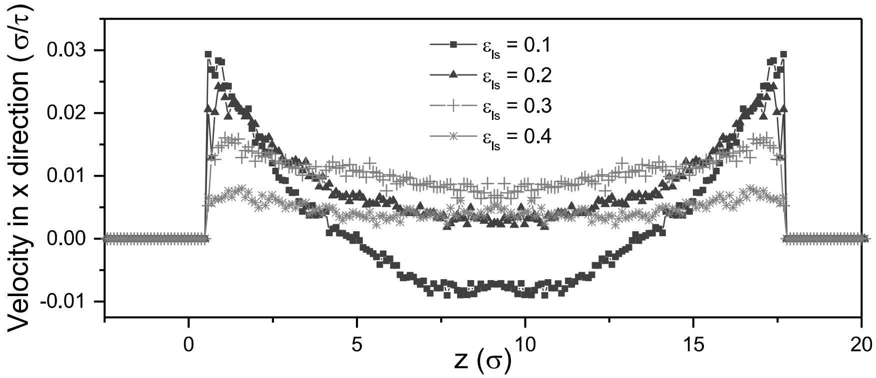
- ✓ Many experiments in ***membranes***
- ✓ First ***microscale observation*** of thermo-osmosis ‡





- ✓ MD ***simulation*** of the thermo-osmotic flow †





‡ Bregulla, Wurger, Chichos et al. – *PRL* **116** (2016), 188303

† Fu, Merabia, Joly – *PRL* **119** (2017), 214501

Summary

Thermo-osmosis has been theoretically investigated for a long time

BUT…

Gases

- The theoretical approach is based on ***kinetic equations***
- Good agreement with experiments
- The effect is driven by the specificity of ***the atom-surface scattering***
- The relevant length-scale is the ***mean free path***

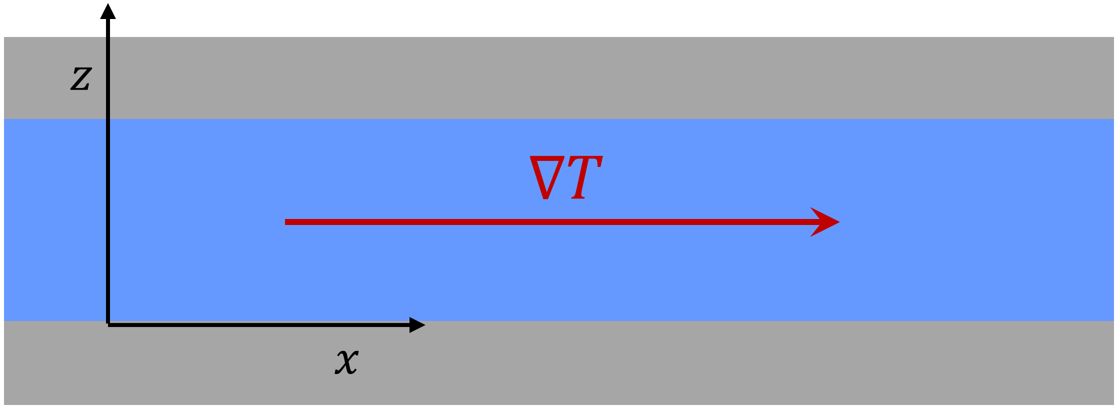
Liquids

- Derjaguin's theory is based on ***macroscopic irreversible thermodynamics***
- Very few experiments/simulations
- The effect is driven by the ***anisotropies of the pressure tensor*** near the surface
- The relevant length-scale is the ***correlation length***

Unified picture ?

STEP 0: *System and Method*

- ✓ We consider the ***simplest geometry:*** *infinite open channel*



- ✓ We impose a *thermal gradient* along the x-direction

- ✓ We restrict to the study of the ***stationary state***

Theoretical tool

Linear response theory *(Kubo-Mori)*

generalized to ***anisotropic environments***

STEP 1: *Stationary Averages*

Local Thermal Equilibrium

If the thermodynamic variables (e.g. ***temperature***) are *space dependent* the distribution function must be modified as:

$$\boxed{F^{LE} = \frac{1}{Z} e^{-\int \mathrm{d}\boldsymbol{r}\, \beta(\boldsymbol{r})\, \mathcal{E}(\boldsymbol{r})}}$$

temperature *field* local energy density

The occurrence of a thermal gradient induces $\boldsymbol{u}(\boldsymbol{r})$ **velocity *field***

$\mu(\boldsymbol{r})$ ***local chemical potential***

$$\mathcal{E}(\boldsymbol{r}) = H(\boldsymbol{r}) - \mathbf{j}(\boldsymbol{r}) \cdot \boldsymbol{u}(\boldsymbol{r}) - \mu(\boldsymbol{r})\, \rho(\boldsymbol{r})$$

Hamiltonian density

Momentum density $\sum_i \boldsymbol{p}_i \delta(\boldsymbol{r} - \boldsymbol{r}_i)$

Particle density $\sum_i m\, \delta(\boldsymbol{r} - \boldsymbol{r}_i)$

The distribution function depends on the five external fields: $\beta(\boldsymbol{r}), \boldsymbol{u}(\boldsymbol{r}), \mu(\boldsymbol{r})$

STEP 1: *Stationary Averages*

Linear Response Theory

The goal is to study the **stationary flow**: the *Local Thermal Equilibrium* distribution is ***not stationary!***

Hazime Mori[†] (1958): averages in ***stationary states*** expressed in terms of **dynamical correlations at equilibrium**

Example: *mass current* (planar geometry)

$$\langle j^x(z)\rangle = \rho_0(z)\, u^x(z) \longleftarrow \text{Local Thermal Equilibrium}$$

$$+\int_0^\infty \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \,\langle\, j^x(\boldsymbol{r},t')\, J_H^x(\boldsymbol{r}')\,\rangle_0\, \underline{\partial_{x'}\beta}(x') \qquad \text{coupling to } \textbf{\textit{energy}} \text{ flux}$$

$$-\int_0^\infty \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \,\big\langle\, j^x(\boldsymbol{r},t')\, J_j^{xz}(\boldsymbol{r}')\,\big\rangle_0\, \underline{\partial_{z'}[\beta u^x]}\,(z') \qquad \text{coupling to } \textbf{\textit{momentum}} \text{ flux}$$

$$-\int_0^\infty \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \,\langle\, j^x(\boldsymbol{r},t')\, j^x(\boldsymbol{r}')\,\rangle_0\, \underline{\partial_{x'}[\beta\mu]}\,(x') \qquad \text{coupling to } \textbf{\textit{mass}} \text{ flux}$$

According to LRT this expression is **exact** to linear order in $\partial_x\beta,\ u^x,\ \partial_x\mu$

[†] H. Mori, Phys. Rev. **112**, 1829 (1958)

STEP 2: *External Fields*

Conservation Laws

Linear response theory expresses averages in terms of correlations and **external fields**:

$\beta(\boldsymbol{r})$? $\boldsymbol{u}(\boldsymbol{r})$? $\mu(\boldsymbol{r})$?
unknown!

These fields are determined by the **physical boundary conditions**

The external fields are defined by the boundary conditions via the continuity equations

$$\cancel{\partial_t\langle\rho(\boldsymbol{r},t)\rangle} + \partial_x\langle j^x(\boldsymbol{r},t)\rangle = 0$$

mass conservation

$$\cancel{\partial_t\langle j^x(\boldsymbol{r},t)\rangle} + \partial_x\langle J_j^{xx}(\boldsymbol{r},t)\rangle + \partial_z\langle J_j^{xz}(\boldsymbol{r},t)\rangle = 0$$
$$\cancel{\partial_t\langle j^z(\boldsymbol{r},t)\rangle} + \partial_x\langle J_j^{xz}(\boldsymbol{r},t)\rangle + \partial_z\langle J_j^{zz}(\boldsymbol{r},t)\rangle = 0$$

momentum conservation

$$\cancel{\partial_t\langle H(\boldsymbol{r},t)\rangle} + \partial_x\langle J_H^x(\boldsymbol{r},t)\rangle = 0$$

energy conservation

stationary limit

STEP 3: *Velocity Profile*

- ✓ *Planar geometry:* non-trivial solutions for $u^x(z)$ with $\boxed{\partial_x \beta = \text{const}}$ $\boxed{\partial_x \mu = \text{const}}$
- ✓ The ***velocity profile*** follows from the solution of the continuity equation for $j^x(\boldsymbol{r})$:

$$\boxed{\int_0^h \mathrm{d}z' \, \mathcal{K}(z,z') \, \partial_{z'} u^x(z') = \partial_x \beta \, \mathcal{S}(z)}$$

$$\mathcal{K}(z,z') = \bar{\beta} \int_0^\infty \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}'_\perp \left\langle J_j^{xz}(\boldsymbol{r},t') \, J_j^{xz}(\boldsymbol{r}') \right\rangle_0$$

(*generalized viscosity*)

STATIC

DYNAMIC

$$\mathcal{S}(z) = \int_{h/2}^{z} \mathrm{d}z' \underbrace{\left.\frac{\partial p_\mathrm{T}(z')}{\partial \beta}\right|_p}_{\text{Anisotropy of the tangential pressure}} + \int \mathrm{d}\boldsymbol{r}' \, x' \underbrace{\left\langle J_j^{xz}(\boldsymbol{r}) \mathcal{P}(\boldsymbol{r}') \right\rangle_0}_{\text{Static correlation}} + \int_0^\infty \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \underbrace{\left\langle J_j^{xz}(\boldsymbol{r},t') \, J_Q^{x}(\boldsymbol{r}') \right\rangle_0}_{\text{Dynamical correlation function at equilibrium}}$$

Anisotropy of the ***tangential pressure***

Static correlation
$\mathcal{P}(\boldsymbol{r}) = h_m \rho(\boldsymbol{r}) - \mathcal{H}(\boldsymbol{r})$

Dynamical correlation function at *equilibrium*

In ***bulk***: $\mathcal{S}(z) = 0 \quad \Rightarrow \quad u^x(z) = 0$

Approximations: *Liquids*

✓ If we **assume** that in liquids

- ***static*** and ***dynamic correlations*** can be evaluated in bulk
- ***dynamic correlations*** are short-ranged

$$S(z) = \frac{\partial}{\partial \beta}\bigg|_p \int_{h/2}^{z} \mathrm{d}z'\, p_\mathrm{T}(z')$$

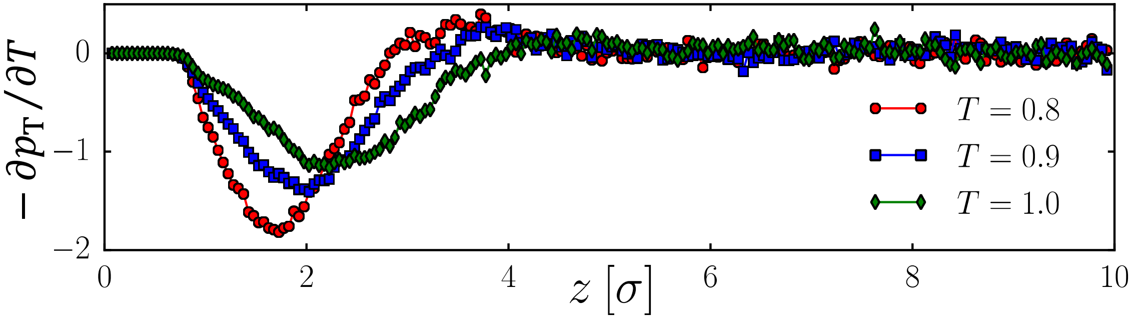
$$\mathrm{K}(z, z') = \eta\, \delta(z - z')$$

$$\boxed{u^x(z) = -\frac{\partial_x T}{\eta} \frac{\partial}{\partial T}\bigg|_p \int_0^{h/2} \mathrm{d}z'\, \mathrm{Min}(z, z')\, [p_\mathrm{T}(z') - p\,]}$$

Agreement with Derjaguin's approach

(based on nonequilibrium thermodynamics)

✓ It is possible to give a ***rough*** *estimate* of the slip velocity:



$$\boxed{u^x \approx 1\ \mu\mathrm{m/s}}$$

for $\partial_x T \sim 10\,\mathrm{deg/cm}$

Ganti, Liu and Frenkel, *PRL* **119**, 038002 (2017)

Approximations: *Gases*

In (*almost*) ***ideal gases*** the pressure tensor is **isotropic** also near the surface

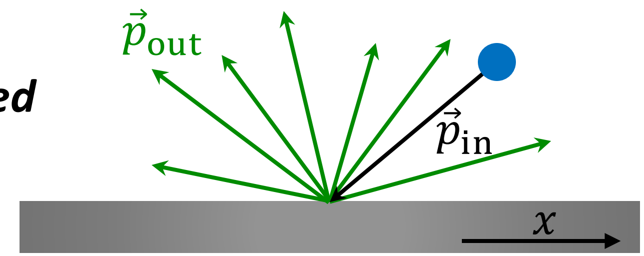
$$p_{\mathrm{T}} = p_{\mathrm{N}} = p \quad \longrightarrow \quad \left.\frac{\partial p_{\mathrm{T}}(z')}{\partial \beta}\right|_{p} = 0$$

The only source term comes from ***dynamical correlations*** at equilibrium

$$S(z) = \int_0^\infty \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \, \left\langle J_j^{xz}(\boldsymbol{r}, t') \, J_Q^{x}(\boldsymbol{r}') \right\rangle_0$$

Assuming that after the impact the x-component of the particle's momentum is ***completely uncorrelated***

(i.e. ***exchange*** of ***momentum*** with the surface)



$$\boxed{v_\infty = \frac{3}{4}\frac{\eta}{\rho}\frac{\partial_x T}{T}}$$

$$\boxed{u^x \approx 10 \ \mu\mathrm{m/s}}$$

(***parrallel*** to the gradient)

for $\partial_x T \sim 10\,\mathrm{deg/cm}$

$\mathrm{p} = p_{atm}$

Conclusions

- **Linear response theory** provides a natural framework for a *microscopic quantitative* description of the thermo-osmotic flow
- Our results are ***exact*** to the first order in the fields
- The emerging ***picture*** is ***more complex than expected*** on the basis of the existing approaches (*kinetic theory/irreversible thermodynamics*)
- The extent of the phenomenon depends on the behavior of ***dynamical correlations*** (transport coefficients) near the surface
- The ***scattering processes*** at the confining surface plays a key role, at least in the *rarefied limit*
- A quantitative investigation in liquids requires the evaluation of the tangential pressure. MD and DFT calculations are in progress

Thank You For Your Attention

P. Anzini, G. M. Colombo, Z. Filiberti, and A. Parola, *Phys. Rev. Lett.* **123**, 028002