Thermal Marangoni effects, thermodiffusion, and thermo-osmosis in slit pores

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Abstract

I will present some recent results from molecular dynamics simulations of thermodiffusion and thermos-osmosis in porous media, including results for the thermal Marangoni effect, also called thermo-capillary convection. When a temperature gradient is applied to a fluid mixture in a porous medium, thermo-capillary convection, thermodiffusion, and thermos-osmosis may occur simultaneously. We investigate how the processes couple and why thermo-capillary convection must be considered in measurements of Soret effects in porous media.

The flux equations for a binary fluid mixture in a porous medium may be expressed as[

$$J_q' = L_{qq}\nabla\left(\frac{1}{T}\right) - L_{qV}\frac{1}{T}\nabla P - L_{qD}\frac{x_1}{T}\nabla\mu_{1,c} \quad (1a)$$

$$J_V = L_{Vq}\nabla\left(\frac{1}{T}\right) - L_{VV}\frac{1}{T}\nabla P - L_{VD}\frac{x_1}{T}\nabla\mu_{1,c} \quad (1b)$$

$$J_D = L_{Dq}\nabla\left(\frac{1}{T}\right) - L_{DV}\frac{1}{T}\nabla P - L_{DD}\frac{x_1}{T}\nabla\mu_{1,c} \quad (1c)$$

where J_q' is the measurable heat flux and J_V and J_D are the volume flux and diffusion flux, respectively, defined as

$$J_V = J_1 V_1 + J_2 V_2 \quad (2a)$$

$$J_D = \frac{J_1}{x_1} - \frac{J_2}{x_2} \quad (2b)$$

were J_i is the mass flux, V_i the partial molar volume, and x_i the mole fraction of component i, respectively. Furthermore, the L-coefficients are the Onsager coefficients, P is pressure, T is temperature, and $\mu_{1,c}$ is the compositional contribution to the chemical potential from component 1.

Two examples of the system layout for a one-component fluid of Lennard-Jones/spline particles is shown in Figure 1 (top). Non-equilibrium molecular dynamics (NEMD) simulations were done with the LAMMPS software. Temperature gradients were established by heating the parts of the "hot fluid" and cooling parts of the "cold fluid". The particle momenta of the left and right boundaries of the MD box were set to zero in order to ensure zero net mass fluxes in x-direction. The temperature gradients were the only external forces on the system.
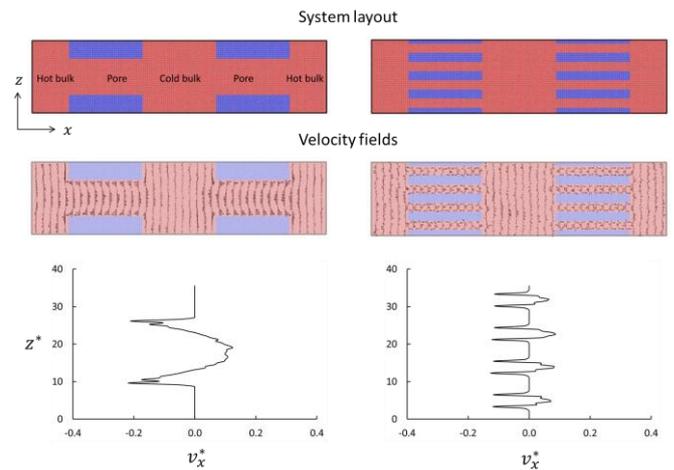

Figure 1. Top: Side view of two slit pore configurations used in this work, one wide pore (left) and four narrow pores (right). The blue regions are pore walls of Lennard-Jones/spline particles in a solid state. The red regions contain the same type of particles in a one-component liquid state. A temperature gradient is set up in the fluid between the hot and cold bulk compartments. Middle: Convective flow fields in the pores as illustrated by the velocity vectors. The velocity is towards the hot bulk along the walls and in the opposite direction in the pore centers. Bottom: x-components of the fluid velocity in the left pores as function of z.

Result for the case shown in Figure 1 include the velocity profiles in the bottom panel of the figure. The wide pore has a distinct flow pattern with creep flow along the walls in the direction of high temperature. A consequence of the zero net mass flow is that the fluid is forced in the opposite direction in the center of the pore. The four pores show the same feature, but the narrower channels restrict fluid back-flow. The consequence is that pressure builds up in the hot bulk regions, which is the thermo-osmotic effect.

References

A. Katchalsky, P.F. Curran, *Nonequilibrium Thermodynamics in Biophysics* (Harvard University Press, Cambridge, 1975)
I. Wold and B. Hafskjold, Int. J. Thermophys, **20**, (1999) 847–856
R. Hannaoui, G. Galliero, D. Ameur, C. Boned, Chem. Phys. **389** (2011) 53–57
R. Hannaoui, G. Galliero, H. Hoang, C. Boned, J. Chem. Phys. 139 (2013) 114704
R. Ganti, Y. Liu, and D. Frenkel, Phys. Rev. Lett., **119**, (2017) 038002
L. Fu, S. Merabia, and L. Joly, Phys. Rev. Lett. **119** (2017) 214501
W.Q. Chen, M. Sedighi, and A. P. Jivkov, Nanoscale, **13** (2021) 1696

M. T. Rauter, S. K. Schnell, B. Hafskjold and S. Kjelstrup, Phys. Chem. Chem. Phys. **23** (2021) 12988
W.Q. Chen, M. Sedighi, and A. P. Jivkov, Nanoscale, **13** (2021) 1696
O. Galteland, D. Bedeaux, and S. Kjelstrup, Nanomaterials, **11** (2021) 165
P. Anzini, Z. Filiberti, A. Parola, Phys. Rev. E **106**, 024116 (2022)
B. Hafskjold, D. Bedeaux, S. Kjelstrup, and Ø. Wilhelmsen, Eur. Phys. J. E (2022) 45:41