

CFCAM Discussion Meeting

## **Simulation of systems under thermodynamic gradients**

***Tentative dates March 24-25, 2014***

***Université Pierre et Marie Curie (Paris)***

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## 1.1 Introduction and motivation

Materials out of equilibrium react to applied forces and develop fluxes that can be used to transport matter or energy. There exists a variety of means to drive a system out of equilibrium. In particular, electromechanical driving is a standard, and widely used procedure to manipulate matter due to the precise control on how to generate electric fields both in magnitude and spatial distribution, and also because generating pressure gradients is easy to implement in a lab thanks to gravity or mechanical forcing. Thermodynamical driving is also a relatively standard means of acting on a medium, e.g. by heating, or by a concentration gradient across semipermeable membranes or induced by localized chemical reactions. This variety of forcings affects physically different processes and hence its performance and control rely on the relevant transport mechanisms, which may depend on the scale at which the driving operates. At small scales, the effect that the driving forces have on the displacement of suspended particles, generically referred to as phoresis, plays a relevant role, and the mechanisms controlling them may vary.

Compared to the body of knowledge developed on electrochemical driving, that on the mechanisms associated to thermodynamical drivings is still insufficient. There is indeed a lack of understanding of the microscopic origin in some of the thermo- and diffusiophoretic processes that control particle motion, or of the relevant mechanism underlying cross thermodynamic effects, as e.g. Soret. In some cases thermodynamic transport is coupled to charge redistribution (induced by thermal inhomogeneities), giving rise to additional transport effects that are not well understood and/or described in macroscopic theories.

The understanding and control of thermodynamic driving forces does not only pose theoretical challenges; it also has potentially relevant applications. For example, osmosis and reverse osmosis play a relevant role in water desalination. The need of more efficient techniques to desalinate water require the understanding of how the efficiency of osmosis depends on the scale at which the relevant concentration fluxes develop. A similar situation is found with the need to develop more efficient and powerful batteries to cope with the energy challenges society is facing. The development of porous batteries requires a more thorough and clear understanding of the processes of matter transport at small scales and in heterogeneous environments, in particular how heat is dissipated. Systems which are out of chemical equilibrium and in which chemical reactions coupled to transport play an essential role, can be found everywhere, from all living systems to manufactured materials such as cement (in particular in the settling stage). In biological systems, the energy produced by chemical reactions is converted into forces and motion at different length scales. Synthetic materials that use the same principles and mimic the biological *active* matter are already being investigated and could open new frontiers in material science.

Therefore, the proposal for a discussion meeting focused on the fundamentals and applications of how matter reacts to thermodynamically applied gradients is timely. Since thermal and osmotic effects should be in principle simpler to understand from the microscopic point of view and have been the subject of more studies so far (at least for the former), the discussion meeting will be focussed on these two aspects. In addition, we will try to make the connection between the molecular and the macroscopic scale of continuous theories. Finally, we want to put these two aspects in the broader perspective of thermodynamic gradients by following the example of multi-scale approaches successfully developed in the case of electrochemical and mechanical forcing.

## 1.2 State of the art

The standard description of transport induced by thermodynamic gradients is based on Onsager's macroscopic thermodynamics of irreversible processes. In the linear response regime, the matrix which couples the chemical potential gradients to the fluxes of each species involves coefficients that are related to equilibrium fluctuations of microscopic quantities via Kubo relations [1]. This connection between equilibrium and non-equilibrium situations is exploited in simulations at various levels to determine transport coefficients of all kinds, such as viscosities or electrical conductivities [2].

Thermal conductivities can be determined in molecular simulations from both equilibrium simulations or under non-equilibrium conditions [3]. Particular care must be taken when using polarizable force fields in order to correctly account for the contribution of the "electronic" degrees of freedom [4]. Similarly, with coarse-grained and implicit-solvent models one should properly account for the contribution of the degrees of freedom that have been averaged out to the transport coefficient [5]. In addition, great care must be taken to account for finite size effects [6]. The non-equilibrium approach seems in principle simpler to deal with complex systems, in particular to determine Soret coefficients. Several strategies have been developed to simulate such situations, including simulations in which the system explicitly includes two regions associated with two different thermostats [7] or in which a constant heat-flux is imposed throughout the system [8]. Some technical difficulties associated with such simulations include heat exchange with the thermostat or the possibility to use periodic boundary conditions or, in the case of confined fluids, dissipation at the solid boundaries [9]. The Soret coefficients for mixtures have also been investigated by molecular simulations, in particular using the heat exchange method [10,11], by which it was possible to identify a pure chemical contribution to this effect [12]. The equilibrium or non-equilibrium approaches have already been exploited to determine the thermal conductivity in a variety of systems such as simple fluids [13], alkane mixtures [14], electrolyte solutions [15], molten salts [4]...

The microscopic simulation of osmotic pressure and osmotic flows has also attracted little attention compared to the high importance of this phenomenon. The osmotic

coefficients of solutions, e.g. electrolytes, can be obtained from direct molecular simulations [16] or, more efficiently, within a coarse-graining strategy whereby effective potentials are first determined from molecular simulations, then introduced in a second simulation or in an integral equation framework such as MSA or HNC [17,18]. Several studies of osmosis or reverse osmosis through membranes have been reported, such as model membranes [19], ZIFs [20] or functionalized carbon nanotubes [21]. Such simulations involve systems with explicit reservoirs of different compositions and under non-equilibrium conditions. The choice of proper boundary conditions in the direction of the flow is not without its difficulties, it is not always possible to maintain a steady state flow. In addition, the underlying microscopic mechanisms have only recently been investigated. A minimal model has been proposed, for which a virial-like relation of osmotic pressure could be derived [22]. The continuous description of osmotic flow through nanopores or of diffusio-phoresis involves the pressure gradient along a wall induced by a change in the solute profile in the direction perpendicular to the wall. Microscopic simulations should be able to confirm this mechanism, using in particular improved algorithms for the computation of local pressure [23].

Most of the modelling of thermophoresis and diffusio-osmosis of colloidal suspensions, as well as the interpretation of experiments of osmosis and reverse osmosis through nanopores is not based on simulation, but rather on continuous approaches. For example, recent experiments have allowed to measure the transport of electrolyte solutions through single nanotubes under the effect of pressure, potential and salt concentration gradients [24]. It was found that the osmotically induced electric currents generated by salinity gradients exceeded by two order of magnitude their pressure driven counterpart, and these results were discussed in the framework of continuous theories (at the Poisson-Boltzmann level). Diffusio-osmosis can also be modelled at this level, e.g. to account for the effect of hydrodynamic slip [25]. The effect of temperature gradients on suspensions of charged colloids can also be captured at this level, with various effects leading to the driving of the particles to the cold or warm region, depending on interfacial and solvent properties [26]. Recently, mesoscale simulations (SRD) were used to model and quantify the thermophoretic behaviour of a colloid [27] and a Lattice-Boltzmann scheme has been proposed to capture osmosis in addition to electro-osmotic effects [28]. In order to derive such continuous models, it is generally useful to start from molecular simulations - an approach that has proved very successful for hydrodynamic or electrokinetic transport. The use of molecular simulation to improve simple models has been much less explored in the context of thermal or osmotic transport [29].

Even if the present proposal focusses on thermal and osmotic effects, these are not the only types of thermodynamic gradients that are relevant and challenging to simulate. In particular, recent simulation schemes have been proposed to model chemically reacting systems such as cement [30]. In that case the reactions play an import role in the final structure of the material and consequently govern the mechanical properties. The possibility of temperature induced phase separation also raises interesting questions in the context of thermal gradients [31]. Another important class of systems which has recently received a lot of attention from the modelling community is that of active systems, where the underlying fluid generates motion without external forces, as a result of internal

driving mechanisms with free energy taken up and consumed at the level of each particle [32]. Finally, it would be interesting to discuss the connection with similar driving mechanisms for which multiscale strategies have been successfully developed in recent years, such as electrokinetic flows [33].

### Bibliography

- [1] Kubo R, *J. Phys. Soc. Japan* **12**, 570 (1957).
- [2] Hansen JP and McDonald IR, *Theory of simple liquids* (Academic Press, London, 3rd Edition, 2006).
- [3] Heyes DM, March NH, *Phys. Chem. Liq.* **33**, 65 (1996)
- [4] Ohtori N, Salanne M, Madden PA, *J. Chem. Phys.* **130**, 104507 (2009)
- [5] Dahirel V, Jardat M, Dufrêche JF, Turq P, *J. Chem. Phys.* **131**, 234105 (2009)
- [6] Sellan DP, Landry ES, Turney JE, McGaughey AJH, Amon CH, *Phys. Rev. B* **81**, 214305 (2010)
- [7] Evans DJ, Morriss GP, *Statistical Mechanics of Nonequilibrium Liquids* (Academic Press, London, 1990).
- [8] Müller-Plathe F, *J. Chem. Phys.* **106**, 6082 (1997)
- [9] Hannaoui R, Galliero G, Ameer D, Boned C, *Chem. Phys.* **389**, 53 (2011)
- [10] Hafskjold B, Ikeshoji T, Ratkje SK, *Mol. Phys.* **80**, 1389 (1993)
- [11] Galliero G, *Fluid Phase Equilib.* **224**, 13 (2004)
- [12] Artola PA, Rousseau B, *Phys. Rev. Lett.* **98**, 125901 (2007)
- [13] Nieto-Draghi C, de Bruin, Pérez-Pellitero J, Bonet Avalos J, Mackie AD, *J. Chem. Phys.* **126**, 064509 (2007)
- [14] Simon JM, Dysthe DK, Fuchs AH, Rousseau B, *Fluid Phase Equilib.* **150**, 151 (1998)
- [15] Romer F, Wang ZL, Wiegand S, Bresme F, *J. Phys. Chem B*, **117**, 8209 (2013)
- [16] Kalcher I, Dzubiella J, *J. Chem. Phys.* **130**, 134507 (2009)
- [17] Molina JJ, Dufrêche JF, Salanne M, Bernard O, Turq P, *J. Chem. Phys.* **135**, 234509 (2011)
- [18] Molina JJ, Duvail M, Dufrêche JF, Guilbaud P, *J. Phys. Chem. B* **115**, 4329 (2011)
- [19] Murad S, Oder K, Lin J, *Mol. Phys.* **95**, 401 (1998)
- [20] Hu Z, Chen Y, Jiang J, *J. Chem. Phys.* **134**, 134705 (2011)
- [21] Chan WF, Chen HY, Surapathi A, Taylor MG, Shao X, Marad E, Johnson JK, *ACS Nano* **7**, 5308 (2013)
- [22] Lion TW, Allen RJ, *J. Chem. Phys.* **137**, 244991 (2012)
- [23] Lion TW, Allen RJ, *J. Phys Cond. Matt.* **24**, 284133 (2012)
- [24] Siria A, Poncharal P, Bianco AL, Fulcrand R, Blase X, Purcell ST, Bocquet L, *Nature* **494**, 455 (2013)
- [25] Ajdari A, Bocquet L, *Phys. Rev. Lett.* **96**, 186102 (2006)
- [26] Würger A, *Rep. Prog. Phys.* **73**, 126601 (2010)
- [27] Lüsebrink D, Yang M, Ripoll M, *J. Phys Cond. Matt.* **24**, 284132 (2012)
- [28] Obliger O, Duvail M, Jardat M, Coelho D, Békri S, Rotenberg B, *Phys. Rev. E* **88**, 013019 (2013)

- [29] Artola PA, Rousseau B, Galliero G, *J. Am. Chem. Soc.* **130**, 10963 (2008)
- [30] Masoero E, Del Gado E, Pellenq RJM, Ulm FJ, Yip S, *Phys. Rev. Lett.* **109**, 155503 (2012)
- [31] Warren P, Cates ME, Christenson HK, Higgins JS, Hinch EJ, Marrucci G, Frith WJ, McLeish TCB, Jones RB, Magerle R, *Phys. Trans. R. Soc. A* **361**, 804 (2003)
- [32] Golestanian R, Ramaswamy S, *Eur. Phys. J. E* **36**, 67 (2013)
- [33] Pagonabarraga I, Rotenberg B, Frenkel D, *Phys. Chem. Chem. Phys.* **12**, 9566 (2010)

### 1.3 Objectives

The first objective of the meeting is to identify and address the challenges related to the fundamental understanding and simulation of systems under thermodynamic gradients. In particular, the discussions will focus on the following aspects:

*a) How to simulate thermodynamic gradients and determine the corresponding transport coefficients ?*

- (i) Equilibrium vs non-equilibrium
- (ii) Technical aspects (size effects, etc)
- (iii) Non-equilibrium evolution with chemical reactivity
- (iv) How to describe these phenomena on the molecular and mesoscopic scales
- (v) Energy dissipation and entropy production

*b) Role of fluctuations, of confinement*

(i) From the fundamental point of view, what role do interfaces play? For example, it seems that an osmotic pressure gradient can generate flow only if an interface is present, not in the bulk.

(iii) From the simulation point of view, what should be done with the walls (in particular in terms of energy transfer, thermostats, etc) ?

(ii) For systems under confinement, fluctuations play a more important role than in the bulk. What is the impact of these fluctuations on the convergence of the computed properties?

A second objective is to encourage discussions between experimentalists and experts in simulation and theory on these topics. We have identified a tentative list of participants, reported below, with this in mind.

The third objective of this Discussion Meeting is to identify the most appropriate scope for a full CECAM proposal in 2014. We will dedicate a discussion round to this at the end of the meeting.

#### 1.4 Tentative list of participants

Not all these potential participants have been contacted yet (>20 names as we anticipate that not all of them will be available)

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## **2. Organization and financial support**

The Discussion Meeting will take place over 2 days. The proposed tentative dates might be reconsidered depending on the availability of the participants, but the meeting would be held during the weeks March 24-28 or April 7-11. We anticipate the following sessions, for half a day each:

- Thermal effects / microscopic scale
- Osmotic effects
- From the microscopic to the mesoscopic scale
- Other thermodynamic gradients: chemical reactivity, active fluids, ...

We ask CFCAM for  $4 \times 1500 = 6000$  € to cover the accommodation for all non-local participants, the coffee breaks and meeting dinner for all participants. If possible, we will also provide support to cover the travel cost of overseas participants.