

Compositional Gradients

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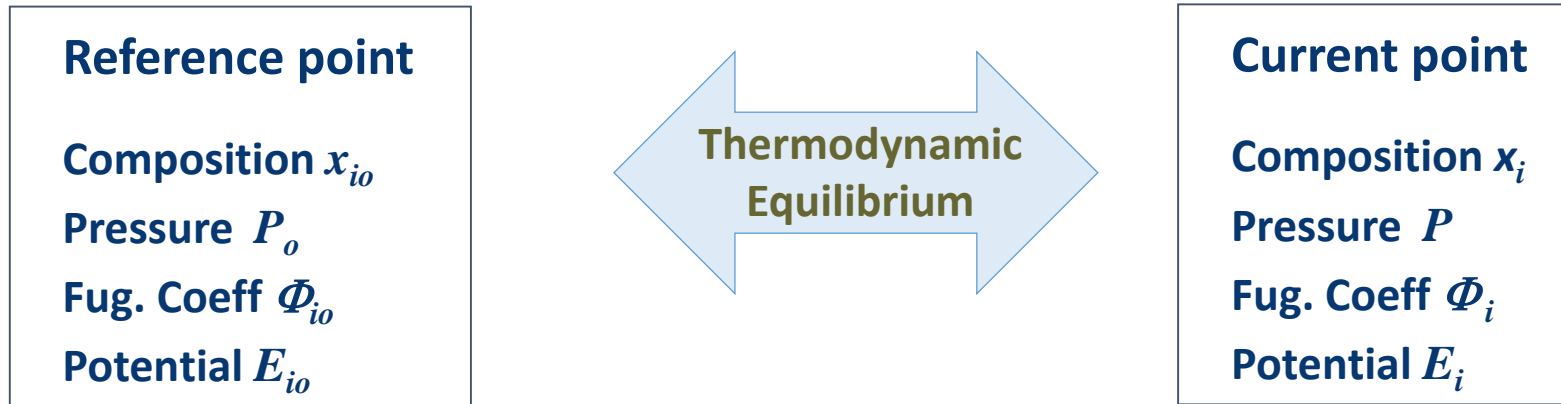


Context

- The initial state of a petroleum reservoir must be established prior to any development plan.
- Compositional gradients are mainly a consequence of gravity and **thermal gradient**.
- Impact on Oil and Gas accumulations can be huge and the development scenario is very sensitive to initial state of reservoirs.
- In most cases, **stationary state** is achieved on geological time scale (MYs) but the reservoir is an open system and light components (CO₂, CH₄...) diffuse continuously through the reservoir.


CURRENT INDUSTRIAL PRACTICES

Generic formulation for Geosciences: **isothermal case, no flux**



$$\ln\left(\frac{x_i}{x_i^o}\right) + \ln\left(\frac{P}{P^o}\right) + \ln\left(\frac{\varphi_i}{\varphi_i^o}\right) - \frac{E_i - E_i^o}{RT} = 0$$

$\sum_i x_i = 1$


EOS

CURRENT INDUSTRIAL PRACTICES

Extension to temperature gradient case (no flux), current formulation:

$$\ln\left(\frac{x_i}{x_i^o}\right) + \ln\left(\frac{P}{P^o}\right) + \ln\left(\frac{\varphi_i}{\varphi_i^o}\right) + \underbrace{\left(T - T^o\right) \frac{\partial \ln(\varphi_i)}{\partial T}}_{\text{This term compensate the temperature impact on fugacities}} - \underbrace{\frac{Q_i}{RT^o} \ln\left(\frac{T}{T^o}\right)}_{Q_i \text{ molar heat of transport (Thermodiffusion factors)} } = 0$$

Available today in commercial software with various correlations for Q_i

Closure equation $\sum_i x_i = 1$ imply constraints on Q_i

Predictive tools are necessary because of the lack (and the cost) of reliable samples from the field
But available software can be misused ! **Q_i are not tuning parameters**

Compositional gradients

The Lesson of Tall Trees

Maximum height of the trees on earth?

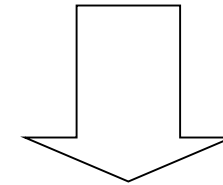


P far below 0 atm

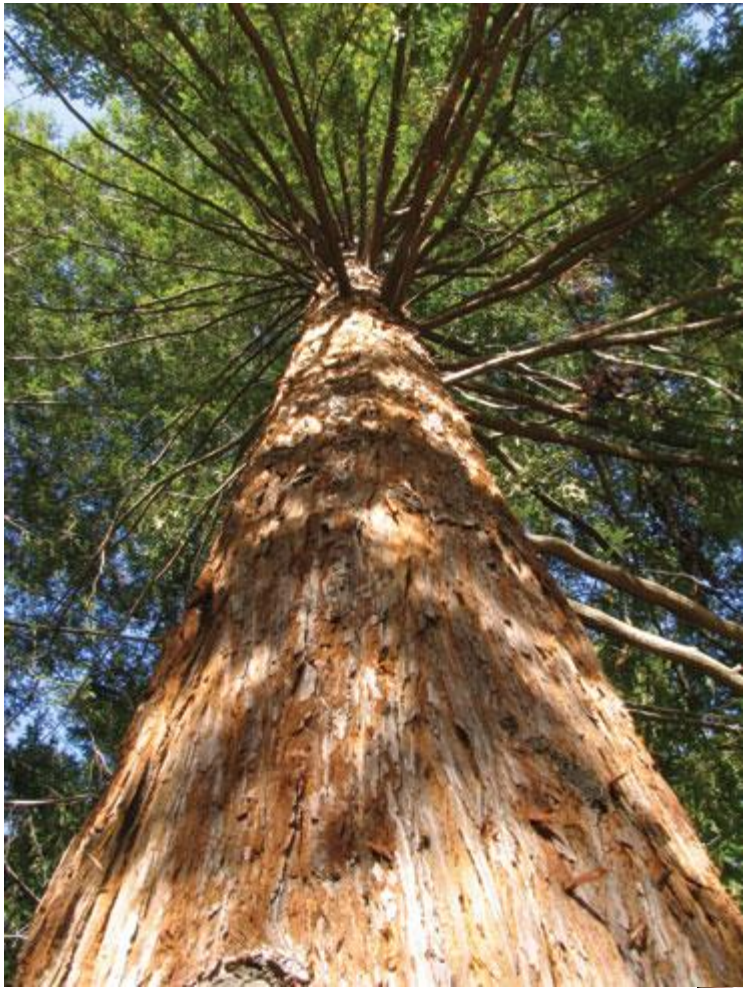
$$\nabla_z P = \rho g - \frac{\mu}{k} \rho U$$

$P = 1 \text{ atm } \pm \varepsilon$

Negative pressure are metastable and could only subsist for very short period of time in complex system



Tall trees do not exist on earth



Hopefully tall trees
actually exist on earth

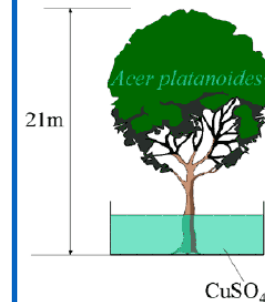


How water is transported in trees: a brief history

- 300 years ago, the analogy with blood circulation prevailed
- Main step in 1727 Stephen Hales proposed a unidirectional flow
- Many disputes on the conducting elements until second half of 19th century: “Vitalists” against “Physicists”
- Disputes ended with the Strasburger’s demonstration in 1880: dead woody stems readily suck the solution up
- In 1914 Dixon wrote his book “Transpiration and the ascent of sap in plants”, a reference for the cohesion-tension theory (CTT)
- During the last decades, many debates on cavitation, CTT in question => the Multi-Force hypothesis.
- Recent work on thin film disjoining pressure help understanding sap ascent and recovery after embolism

But one of these forces is missing: the temperature gradient

Strasburger experiment



- 30 liters/14 days
- wood impregnated up to 20 m

Experiments

Stems of living trees killed by heat or poison taken up in solution

Conclusions

- Involvement of living cells excluded
- Physical forces of an unknown nature are active (but not barometric pressure or root pressure)

Dixon experiment



With this experiment, Dixon convincingly showed that a leafy branch subjected to a pressure of 3 atmospheres was nevertheless able to draw up water from an external vessel (beneath the pressure chamber) at atmospheric pressure.

Sap ascent

Trees operate close to equilibrium conditions

Different mechanisms are involved for sap ascent:

- Osmotic pressure (roots)
- Thin liquid film dynamics (Xylem)
- Evaporation (leaves)
- Exchange between Xylem flow (low sugar x) and Phloem (high sugar x)

At night sap ascent stops the tree is at equilibrium

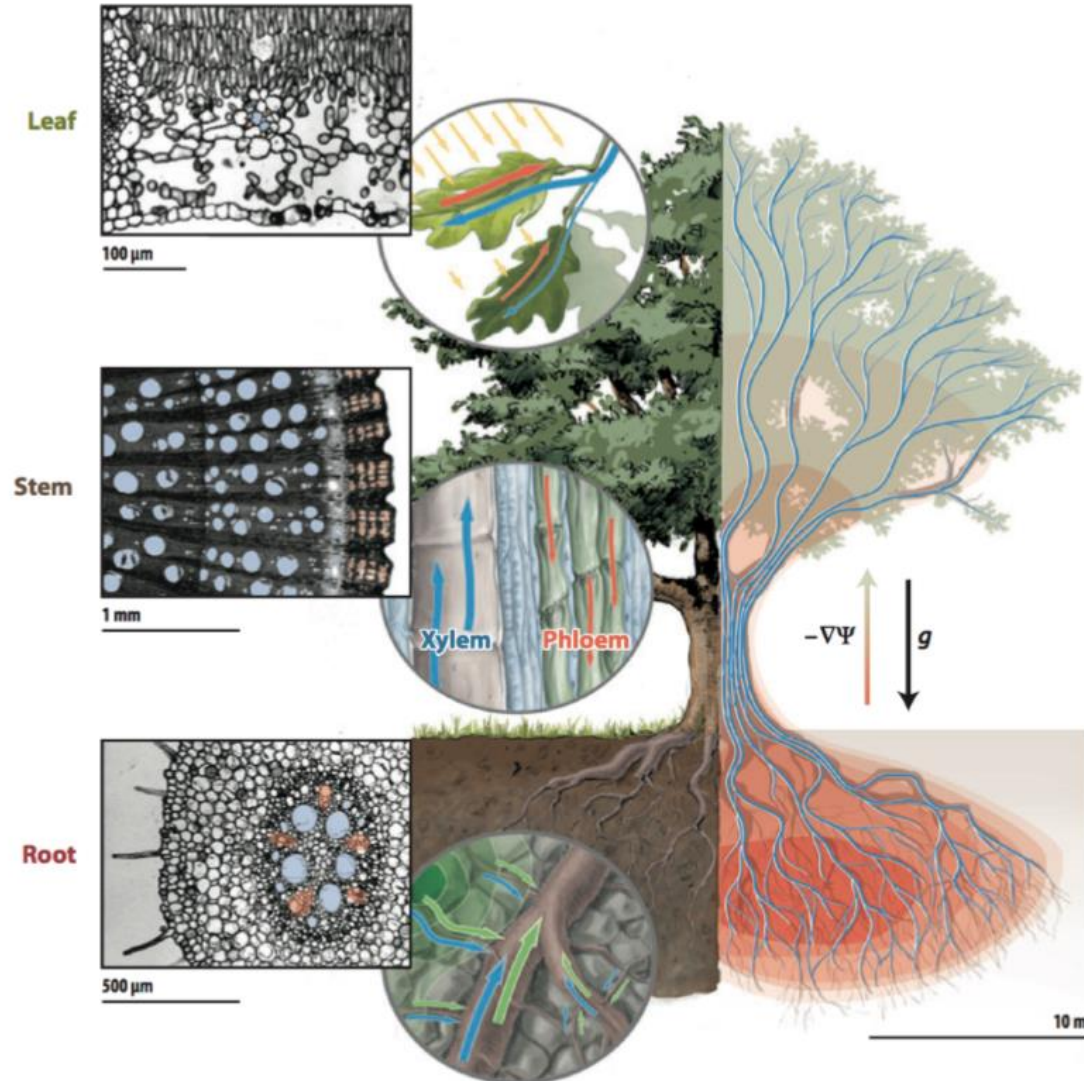
At midday:

Typical sap velocity : 2cm/minute

Typical xylem permeability : 1 darcy

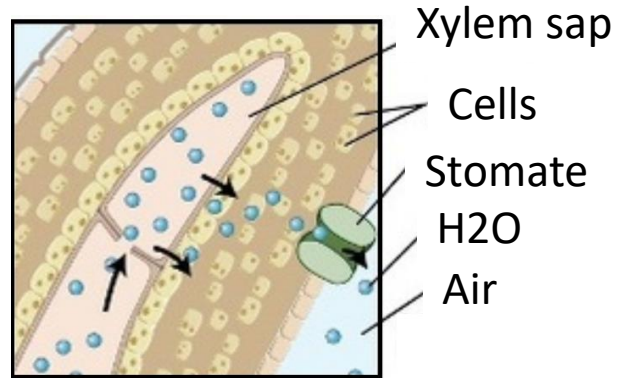
=> Grad $P = 3 \text{ bar/m}$

=> Pressure far below cavitation threshold



Importance of thermal gradient

Leaf

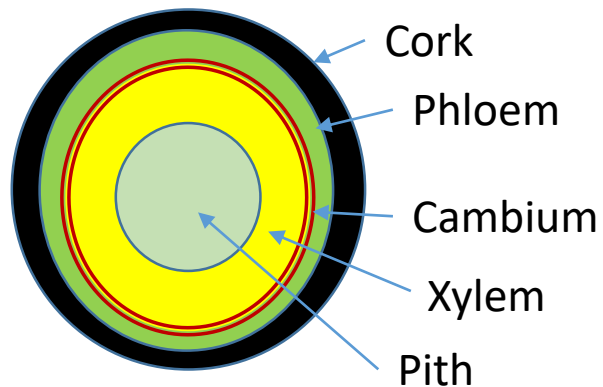
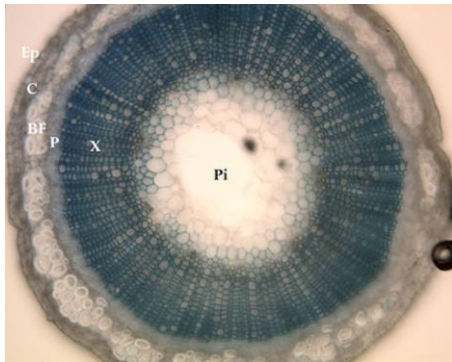


- CO₂/H₂O exchange through stomates
- Pressure gradient between Xylem and air

Trees wonderfully use all the laws of physics of interest for our industry.

1 km² of forest produces 300 000 tons /year of H₂O from the soil with solar energy only

Stem



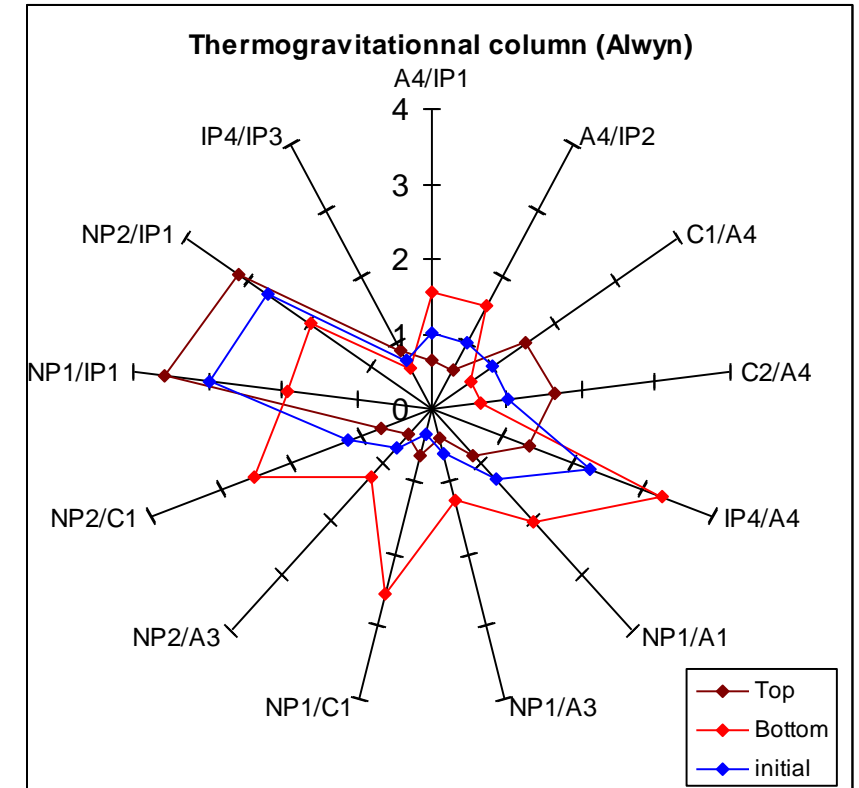
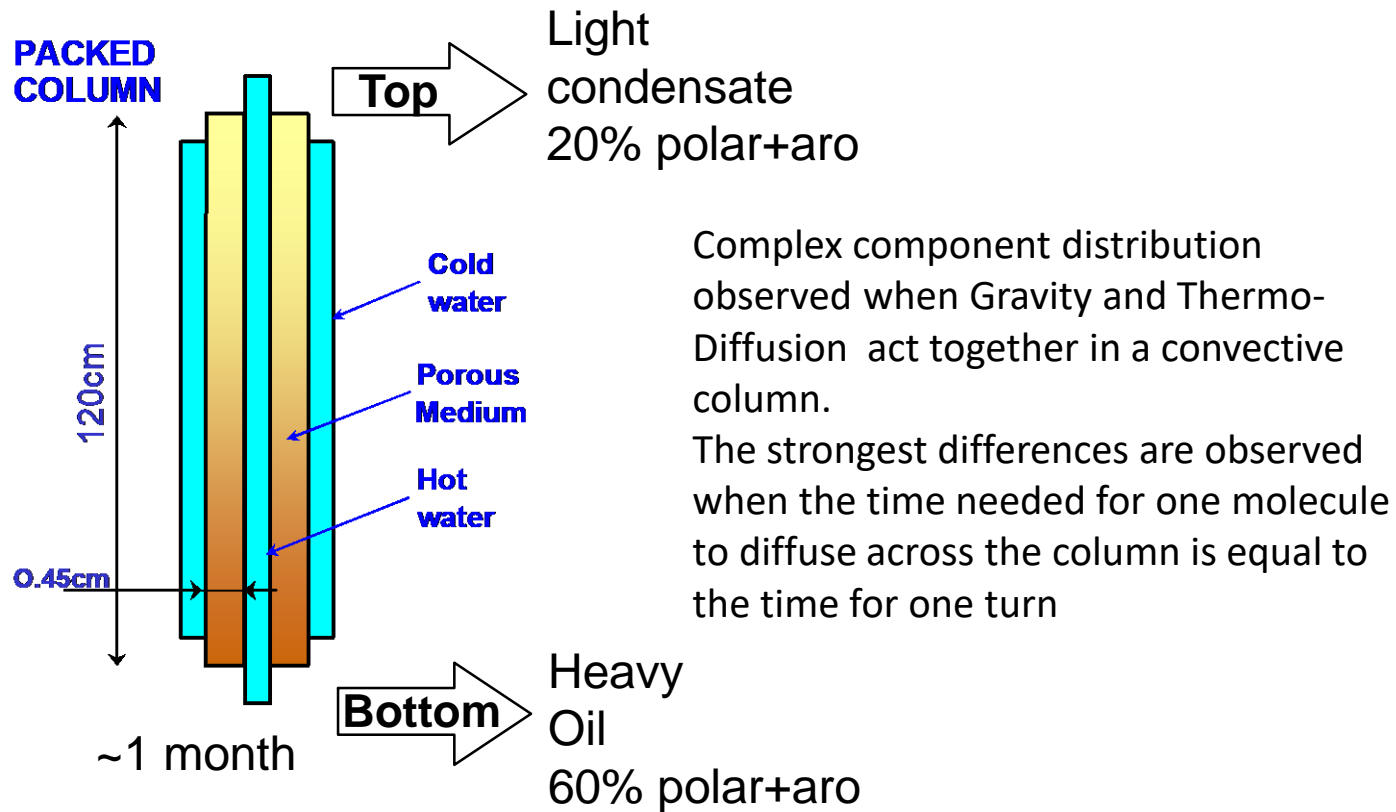
- Water exchange Xylem ↔ Phloem through Cambium
- Recovery after xylem embolism

Compositional gradient in a thermal field

Our attempt to get reliable Q_i values

Measuring Soret Coefficients

An old story, starting point in Toulouse J. Schott PhD (1973) followed by P. Costeseque PhD (1982)
 "Thermo-Diffusion-Gravitational column"



Experiments performed on Alwyn and Oseberg stock tank oil

Dedicated Meetings

Initiated by ELF-AQUITAINE and Toulouse University

- MT1 (Toulouse, France, 1994)
- IMT2 (Pau, France, 1996)
- IMT3 (Mons, Belgium, 1998)
- IMT4 (Bayreuth, Germany, 2000)
- IMT5 (Lyngby, Denmark, 2002)
- IMT6 (Varenna, Italy, 2004)
- IMT7 (San Sebastian, Spain, 2006)
- IMT8 (Bonn, Germany, 2008)
- IMT9 (Toulouse, France, 2010)
- IMT10 (Brussels, Belgium, 2012)
- IMT11 (Bayonne, France, 2014)
- IMT12 (Madrid, Spain, 2016)
- IMT13 (London, UK, 2018)
- IMT14 (Trondheim, Norway, 2020)*

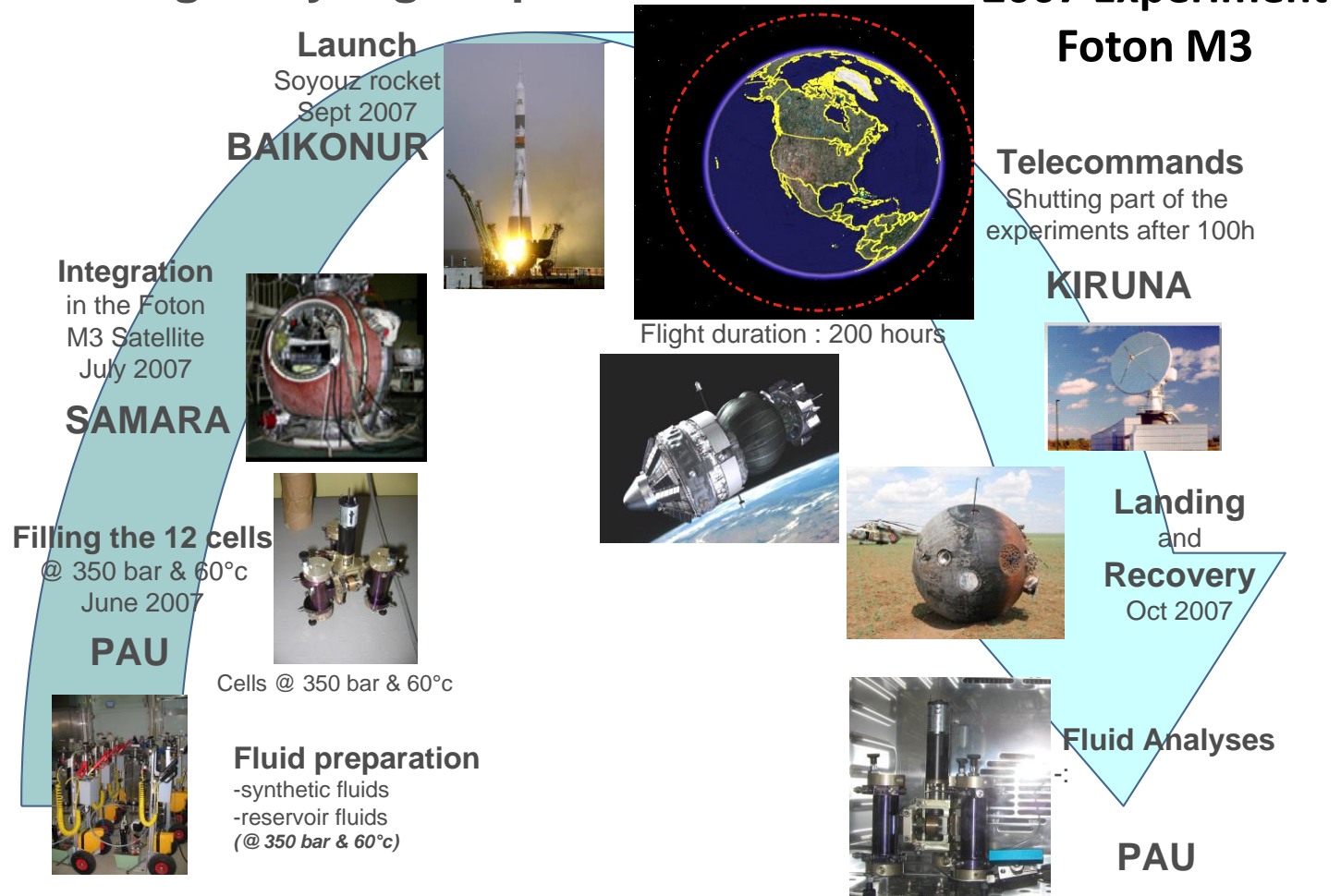
13th International Meeting on Thermodiffusion



- Theoretical, experimental and numerical methods to investigate thermodiffusion in binary, ternary and multicomponent mixtures
- Non equilibrium thermodynamics of fluids under thermal stress
- Non-equilibrium fluctuations in thermally inhomogeneous fluids
- Macromolecular solutions, airborne particles, colloidal suspensions, and biological fluids: the thermophoresis case
- Thermodiffusion in porous media and enhanced oil recovery
- Soret-driven hydrodynamic instabilities and convective patterns
- Thermodiffusion effects in crystal growth and polymer processing
- Thermodiffusion in microgravity
- Thermodiffusion in biological transport
- Applications of thermal diffusion

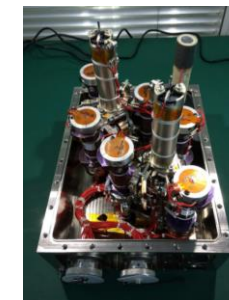
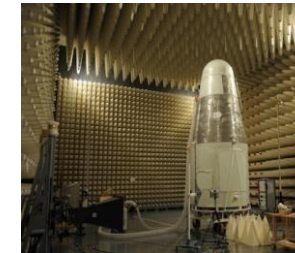
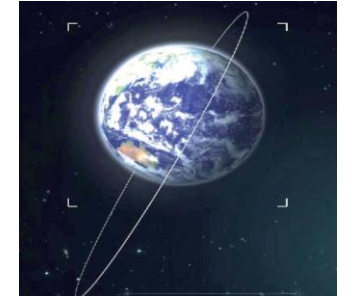
Microgravity experiments (SCCO project with ESA)

Micro gravity flight operations



ELGIN reservoir Fluid and synthetic mixtures

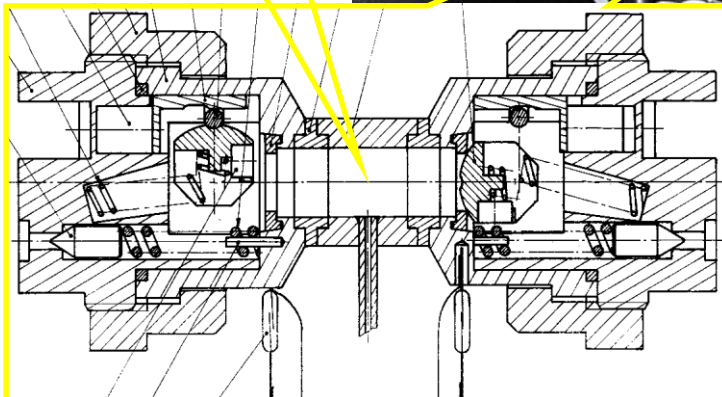
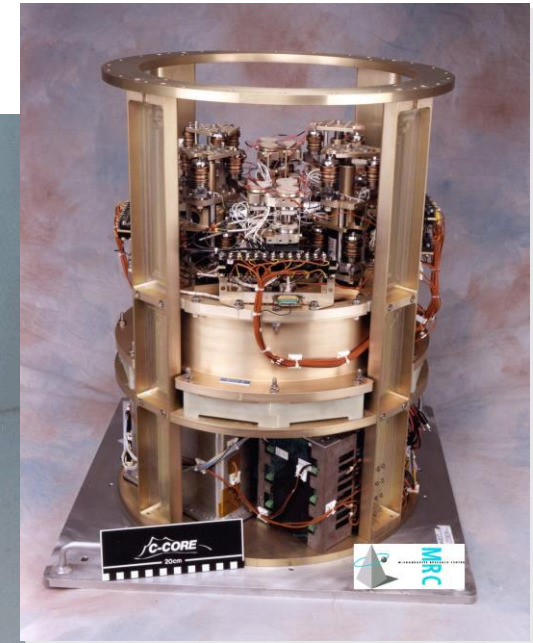
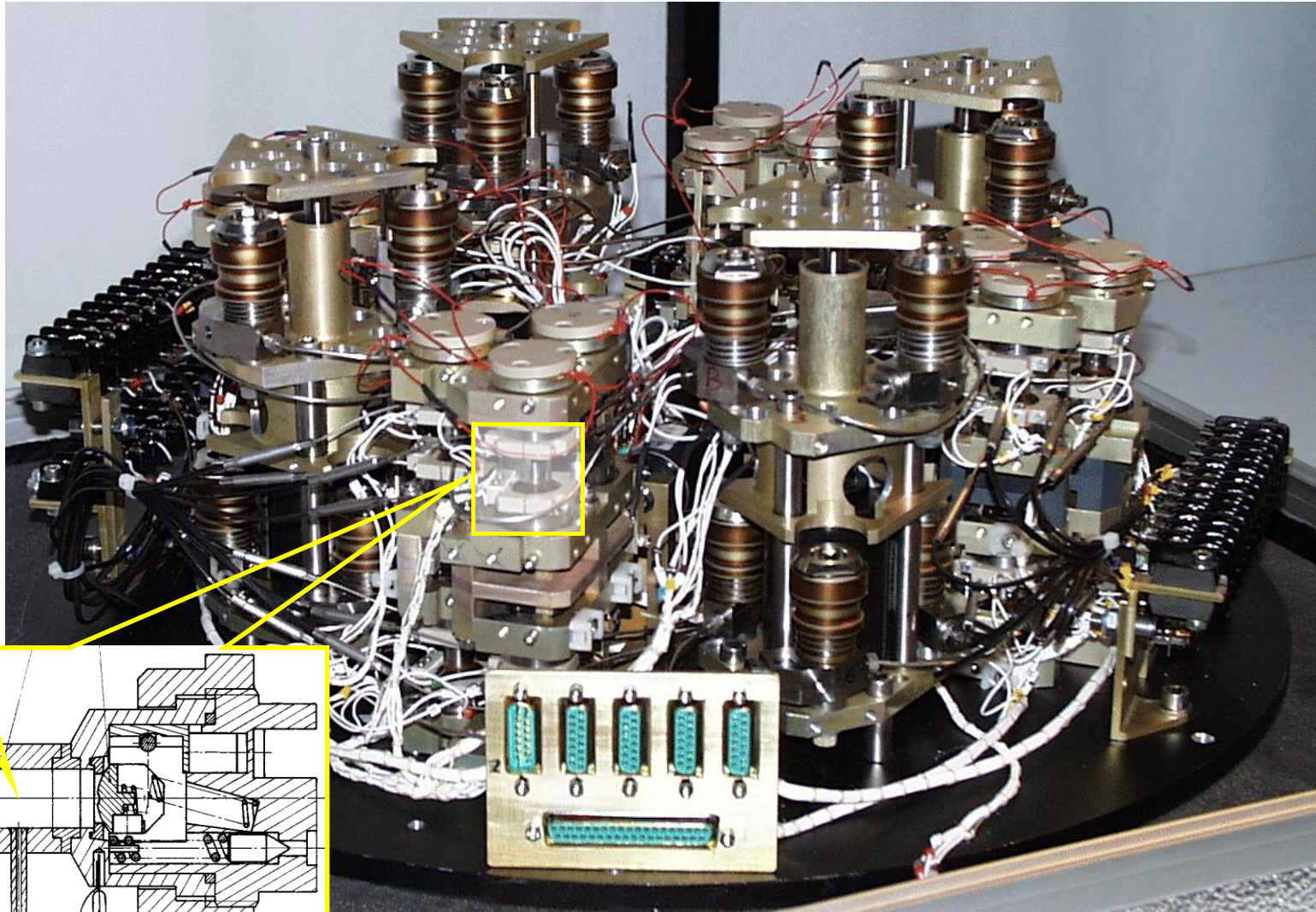
2016 Experiment Shijian-10



Synthetic HC mixtures

Initial SCCO Cell design

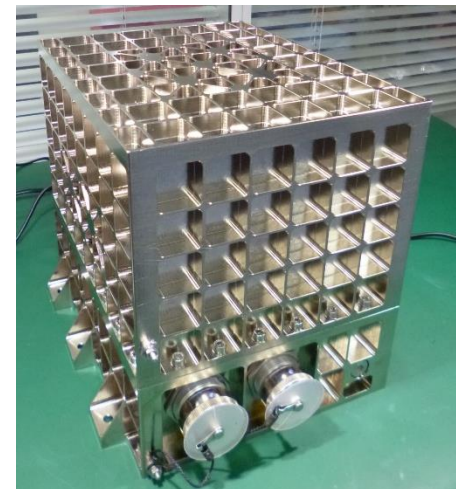
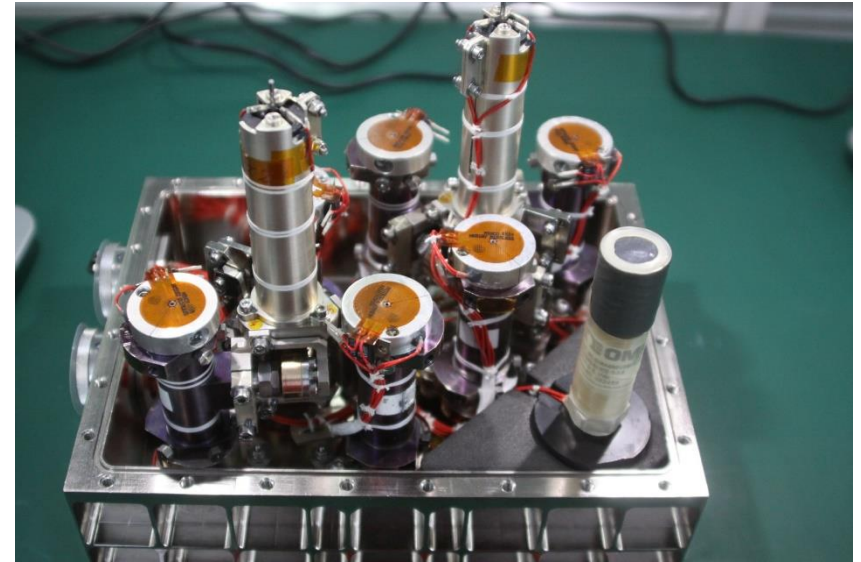
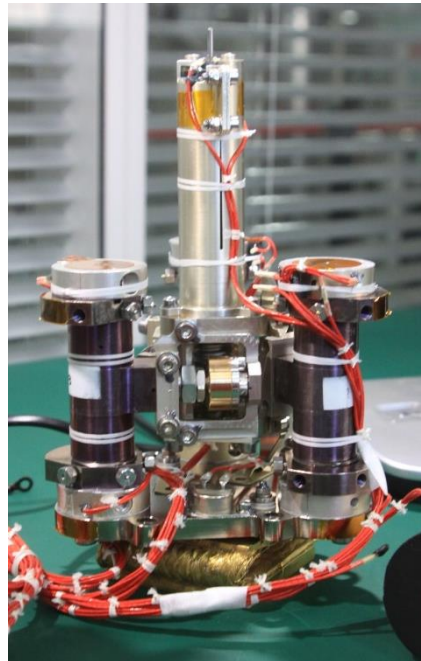
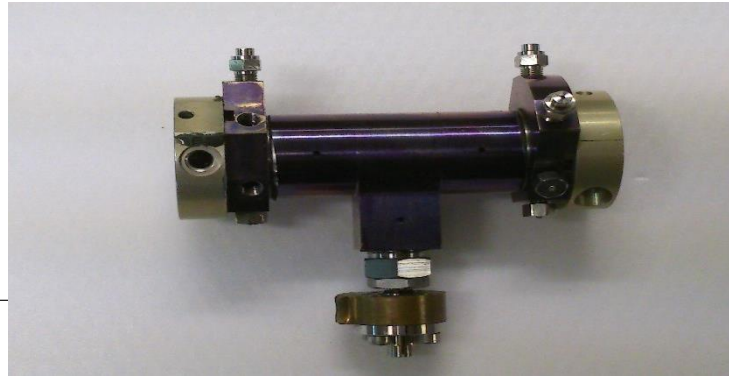
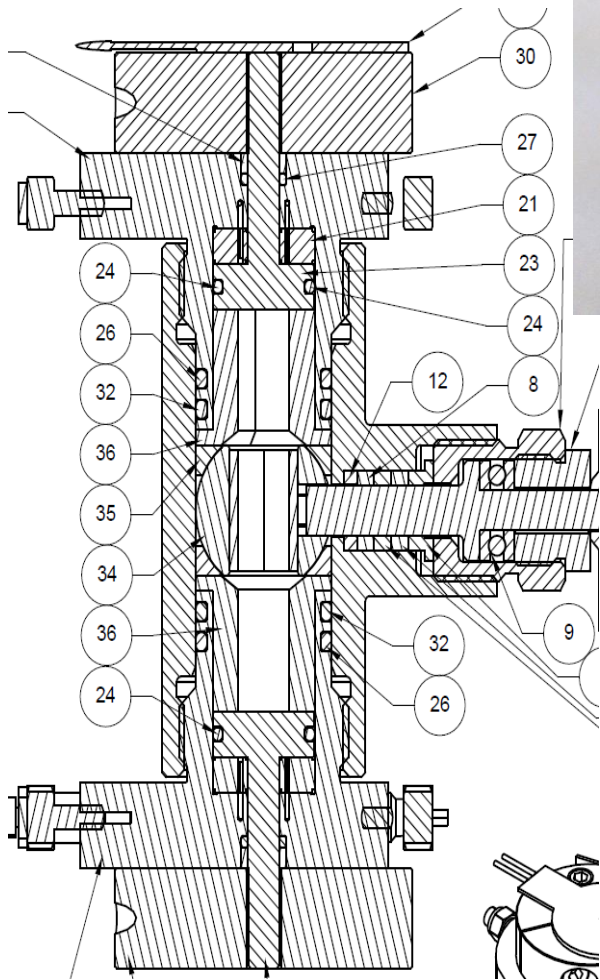
**Reservoir
fluid
350 bar
55/65°C**



February 12-14, 2019

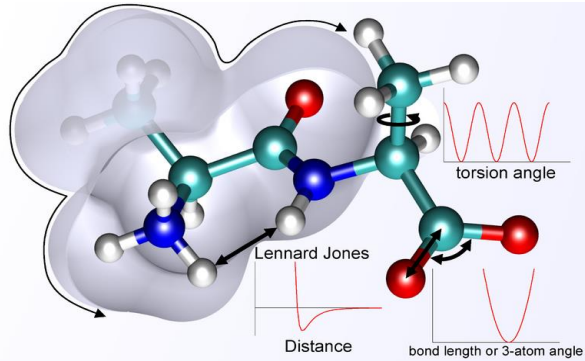
SPE Workshop "Complex Reservoir Fluids"

Final SCCO Cell design



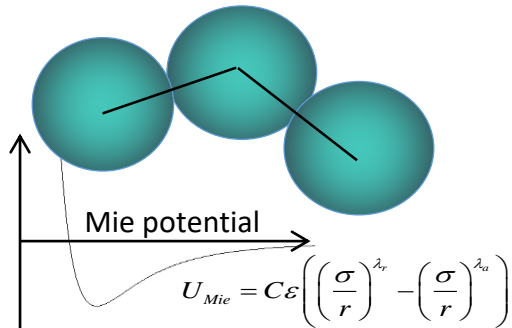
NEMD SIMULATIONS

Detailed molecular model

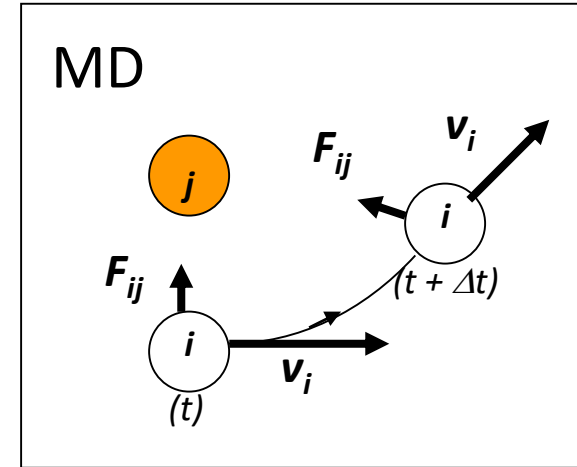


Produced quasi-experimental data
 Applicable only to well-characterized system
 Hours/days computer time

Coarse Grained model



Compatible with engineering requirement
 Questionable when used outside fitting domain



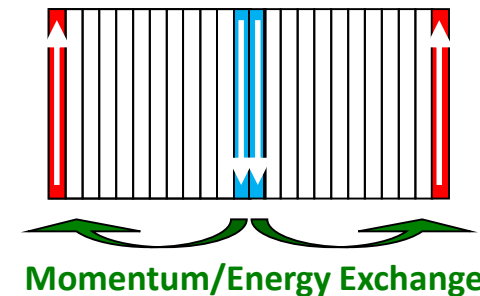
Newton's Equation + interaction potentials

$$\sum_j \vec{F}_{ij} = m_i \frac{d\vec{v}_i}{dt} \quad \vec{F}_{ij} = -\frac{\partial V}{\partial \vec{r}_{ij}} \hat{r}_{ij}$$

New position at $t + \Delta t$

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + (\Delta t)\vec{v}_i(t) + \frac{1}{2}(\Delta t)^2 \frac{\vec{F}_i(t)}{m_i}$$

Transport properties from NEMD

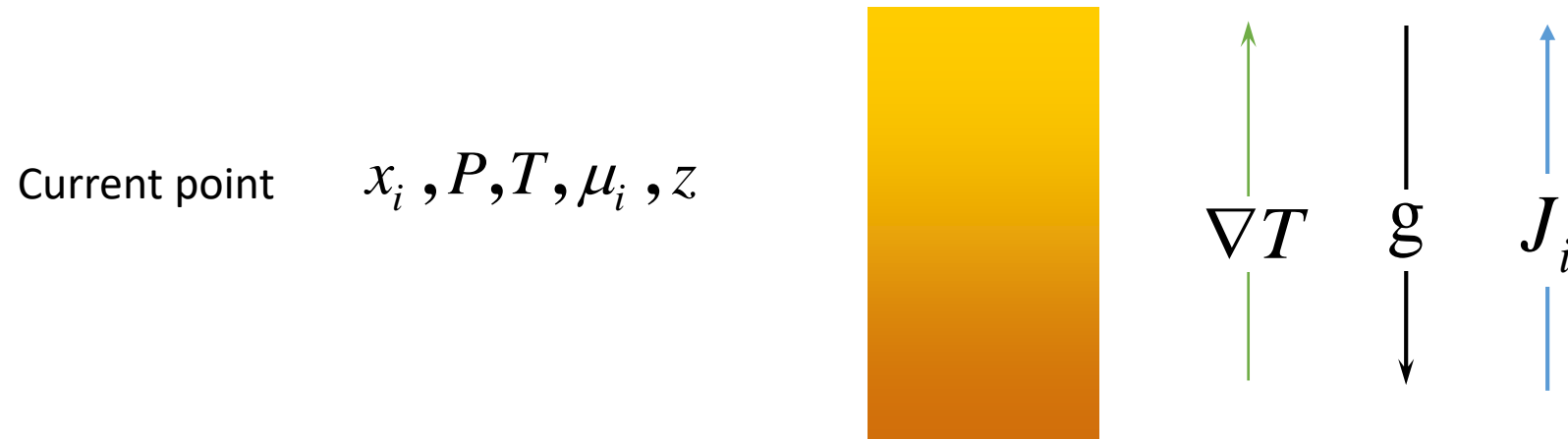


Compositional gradient in a thermal field

Linking up Pressure, Chemical Potential and Thermal Gradients
(Accepted in EPJE)

MAIN HYPOTHESES

Compositional gradient in a reservoir fluid column :



- The average fluid velocity is low enough to allow linearization of the fluid transport equation
- The local equilibrium hypothesis is valid in the fluid phase
- The fluid phase is homogeneous
- The transport and conservation equations can be homogenized in a simple manner regarding thermodynamic variables and properties
- Maintained diffusion fluxes conditions at stationary state

ONSAGER RECIPROCAL RELATIONS

Monophasic multicomponent mass transfer

Advection + Thermodiffusion + Chemical Diffusion

$$\mathbf{J}_i = -n_i L_p \left(\frac{V \nabla P - M \mathbf{g}}{T} \right) + n_i L_{iq} \nabla \left(\frac{1}{T} \right) + n_i L_{ii} \nabla \left(-\frac{\mu_i^t}{T} \right)$$

Diagonal L_{ij}
for sake of simplicity

μ_i^t is the contribution of component "i" to the free energy of the fluid

Heat transfer

Conduction + Advection + Chemical Diffusion

$$\mathbf{J}_T = L_{qq} \nabla \left(\frac{1}{T} \right) - L_p H \left(\frac{V \nabla P - M \mathbf{g}}{T} \right) + \sum_i n_i h_i^* L_{ii} \nabla \left(-\frac{\mu_i^t}{T} \right)$$

h_i^* is the enthalpy of component "i" moving alone through a diffusion process

$$L_{iq} = h_i^* L_{ii}$$

LINK WITH THERMODYNAMIC QUANTITIES

Flux of component i

$$\mathbf{J}_i = -n_i L_p \left(\frac{V\nabla P - M \mathbf{g}}{T} \right) + n_i L_{ii} \left(h_i^* \nabla \left(\frac{1}{T} \right) + \nabla \left(-\frac{\mu_i^t}{T} \right) \right)$$

Total potential

$$\nabla \mu_i^t = \nabla \mu_i - M_i \mathbf{g}$$

Partial entropy

$$s_i = -\frac{\partial \mu_i}{\partial T}$$

Partial enthalpy

$$h_i = \mu_i - T \frac{\partial \mu_i}{\partial T}$$



$$\mathbf{J}_i = -n_i L_p \left(\frac{V\nabla P - M \mathbf{g}}{T} \right) + n_i L_{ii} \left((h_i^* - h_i) \nabla \left(\frac{1}{T} \right) - \frac{\nabla_T \mu_i^t}{T} \right)$$

h_i^* differs from h_i

The chemical potential is the same for the diffusing component at the boundary in and out the elementary volume: $\mu_i^* = \mu_i$

$$q_i = \frac{h_i - h_i^*}{T} = \frac{\mu_i - \mu_i^*}{T} + s_i - s_i^* = s_i - s_i^*$$

PRESSURE GRADIENT

Sum of reduced fluxes

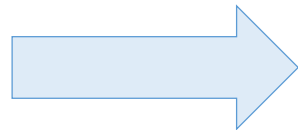
$$\frac{M}{\rho} \sum_i \frac{\mathbf{J}_i}{L_{ii}} = -\frac{L_p}{L_D} \left(\frac{V\nabla P - M \mathbf{g}}{T} \right) + \frac{Q}{T} \nabla T - \frac{1}{T} \sum_i x_i \nabla_T \mu_i^t$$

$$Q = \sum_i x_i (s_i - s_i^*) = S^{res} \qquad \frac{1}{L_D} = \sum_i \frac{x_i}{L_i}$$

Applying Gibbs-Duhem

$$\sum_i x_i \nabla_T \mu_i^t = \sum_i x_i \nabla \mu_i^t + S \nabla T = V \nabla P - M \mathbf{g}$$

Pressure gradient



$$\nabla P - \rho \mathbf{g} = \frac{\frac{\rho}{M} Q \nabla T - T \sum_i \frac{\mathbf{J}_i}{L_i}}{\frac{L_p}{L_D} + 1}$$

$\frac{L_p}{L_D}$ Overall Mobility / Diffusive Mobility

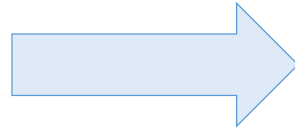
$$L_p = \frac{\rho}{M} T \frac{k}{\eta} \quad \longrightarrow \quad \frac{L_p}{L_D} = \frac{\rho}{M} T \frac{k}{\eta} \sum_i \frac{x_i}{L_i}$$

Transition occurs for k around 100nD

PRESSURE GRADIENT

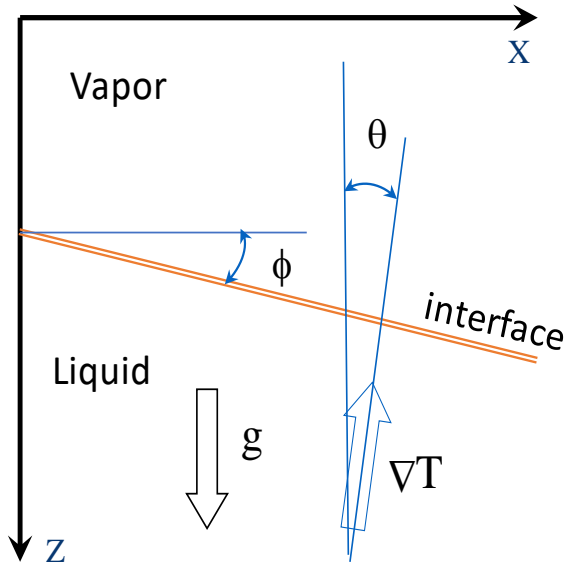
No flux, low permeability:

Pressure gradient



$$\nabla P - \rho \mathbf{g} = \frac{Q}{V} \nabla T$$

≡ **Clapeyron equation** along an interface if $Q=S_{res.}$ (Molar excess entropy)



Interface submitted to gravity and thermal gradient:

Tilt angle

$$\sin \varphi = \frac{\delta}{1 + \delta} \sin \theta$$

$$\delta = \frac{1}{(\rho_l - \rho_v)g} \left(\frac{\frac{Q_v}{V_v}}{1 + \frac{L_{pv}}{L_{Dv}}} - \frac{\frac{Q_l}{V_l}}{1 + \frac{L_{pl}}{L_{Dl}}} \right) \frac{dT}{dx}$$

CHEMICAL POTENTIAL GRADIENT

$$\nabla_T \mu_i = M_i \mathbf{g} + \underbrace{\left(q_i - \frac{L_p}{L_i} \left(\frac{Q}{\frac{L_p}{L_D} + 1} \right) \right)}_{\text{Thermodiffusion}} \nabla T - \frac{M}{\rho} T \underbrace{\left(\frac{J_i}{x_i L_i} - \frac{\sum_k \frac{L_p}{L_k} J_k}{L_i \left(\frac{L_p}{L_D} + 1 \right)} \right)}_{\text{External fluxes}}$$

No fluxes, High permeability => $\nabla_T \mu_i = M_i \mathbf{g} + \left(q_i - \frac{L_D}{L_i} Q \right) \nabla T$

Stationnary state = balance between q_i and $\frac{L_D}{L_i} Q$

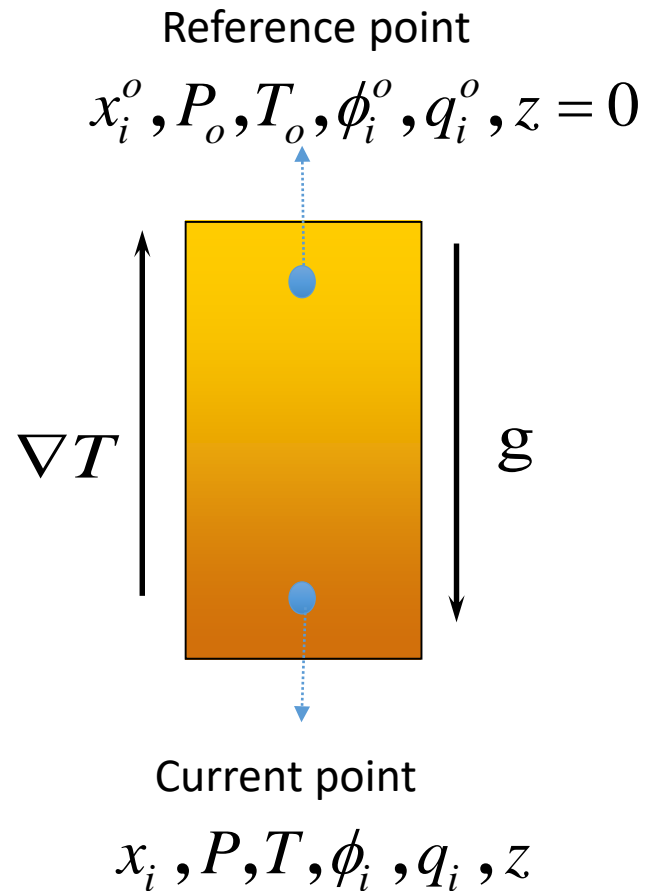
Statement:

s_i^* = ideal entropy at reference T and V conditions

$$q_i = s_i - s_i^* = s_i^{res} = -R \log \varphi_i - RT \frac{\partial \log \varphi_i}{\partial T} - R \log Z$$

COMPOSITIONAL GRADIENT

Compositional gradient in a fluid column :



Practical formulation for substitution algorithm

$$x_i = x_i^o \frac{\phi_i^o}{\phi_i} \frac{P_o}{P} e^{-\frac{M_i g \cdot z}{RT} + \left[\frac{q_i - \frac{L_D}{L_i} Q}{R} - T_o \frac{\partial(\ln(\phi_i^o))}{\partial T} \right] \left(1 - \frac{T}{T_o} \right)}$$

Application to a real field case

Reservoir conditions at -5525m : T= 87.5 C P = 641 bar

Modelling approach:

- Peng Robinson EOS modelling with detailed representation

- Lumping in 8 pseudo-components

- Building equivalent LJ chains coarse grained model

Simulation of the fluid column (-5325 to -5775m) by direct NEMD simulations and by PR-EOS using our proposed theory.

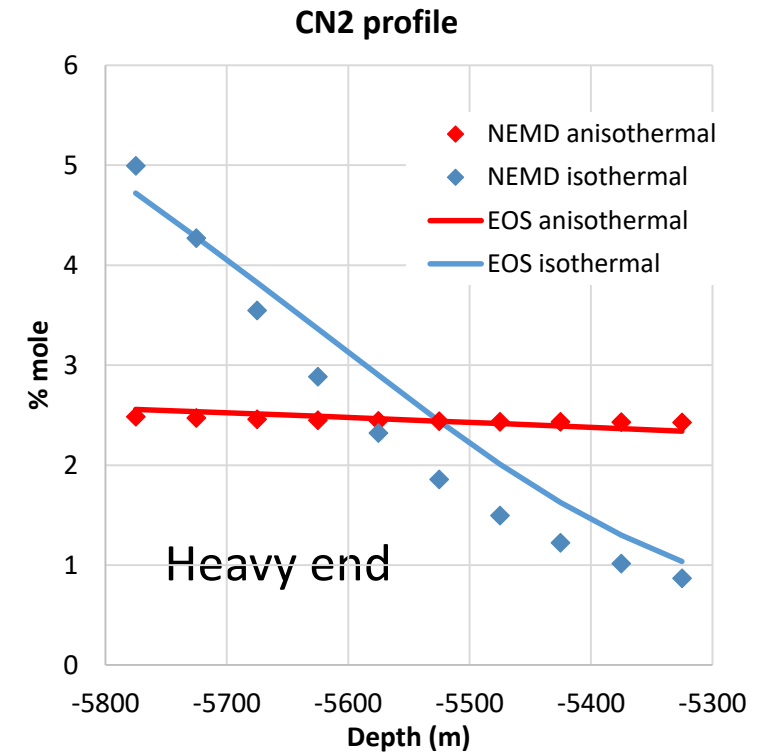
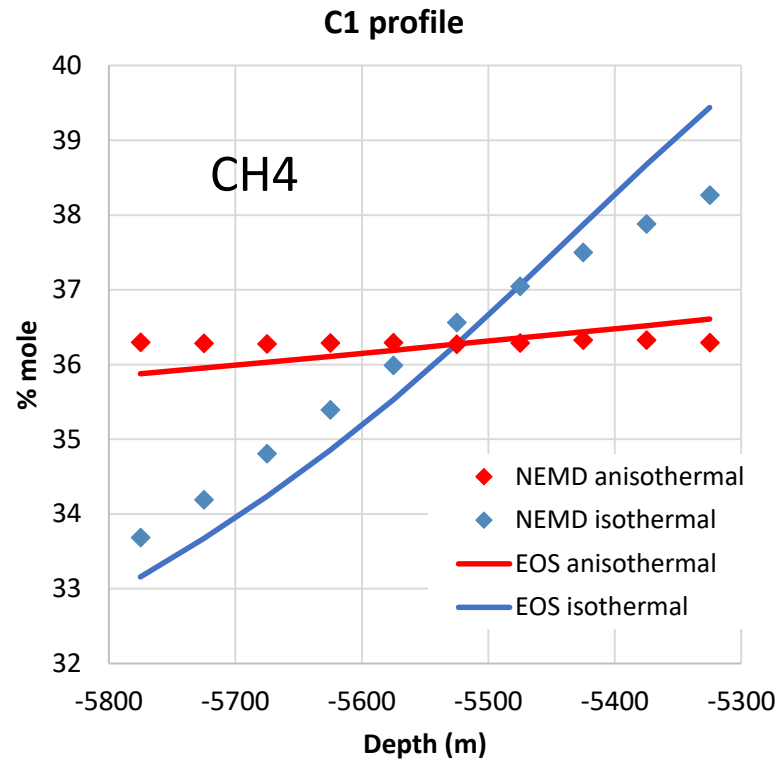
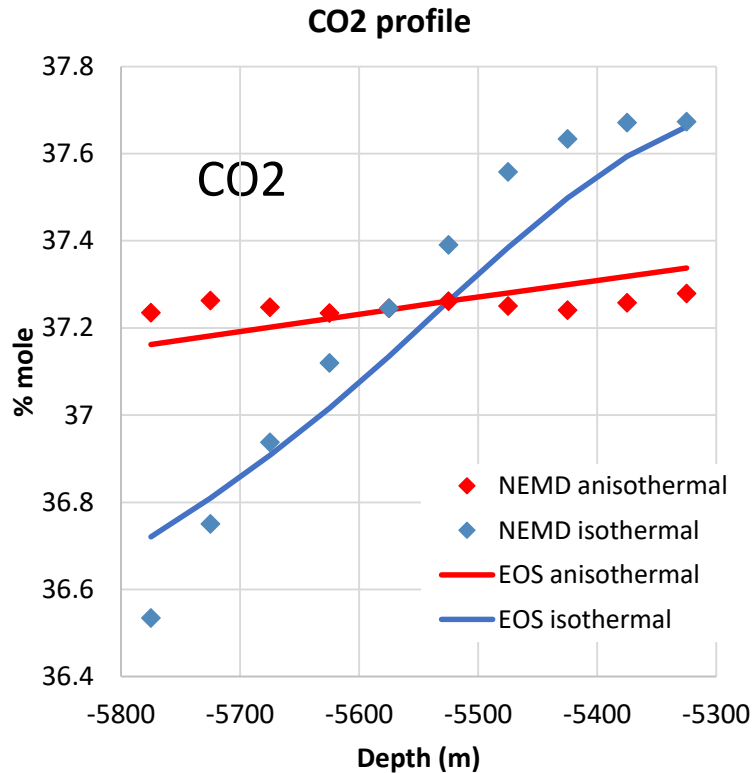
Component mobility proportional to $(T_c/P_c)^{-\tau}$

Very good match between PR-EOS results and NEMD results !

Results confirm field data (constant composition over the whole fluid column)

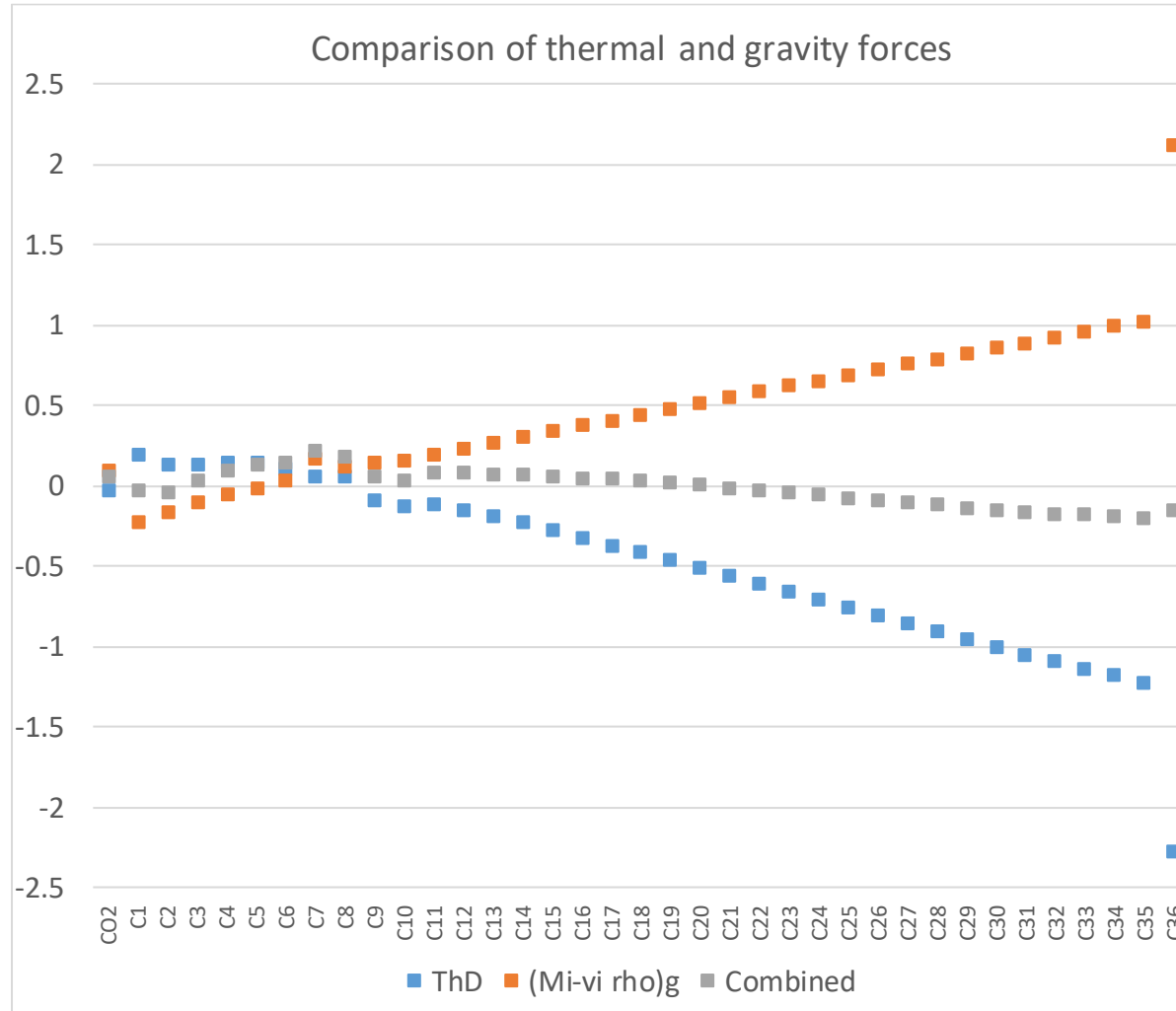
Application to a real field case

Component profile illustration



New wells/samples confirm these results obtained after the first well results.

Impact of fluid representation



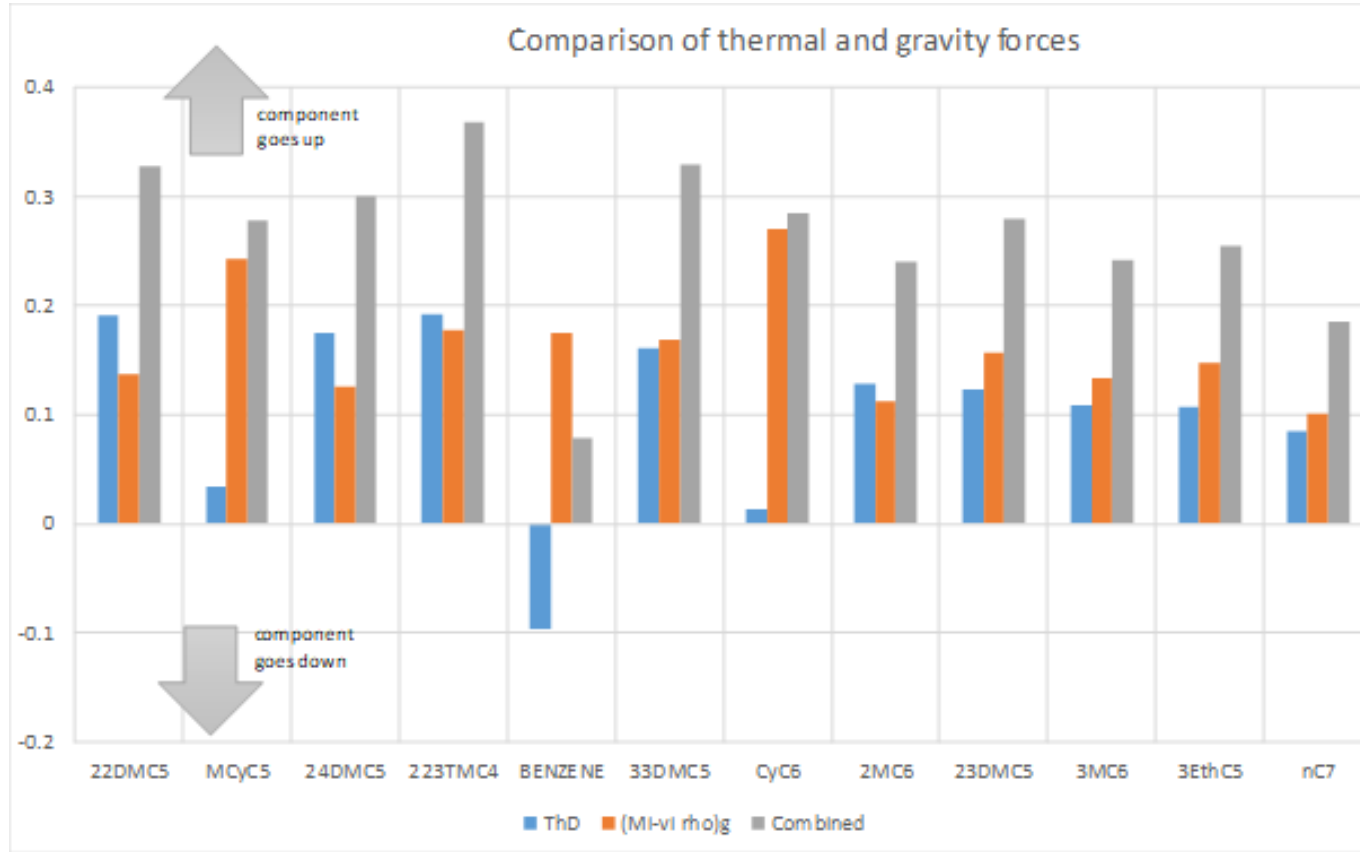
Gravity force
 $(M_i - \rho v_i)g$

Resulting force

Thermal force
 $(q_i - \frac{L_D}{L_i} Q) \nabla T$

Regular distribution
 \Rightarrow Keeping primary oil component distribution
 $X_n = \alpha X_{n-1}$

Impact of fluid representation



Gravity force

$$(M_i - \rho v_i)g$$

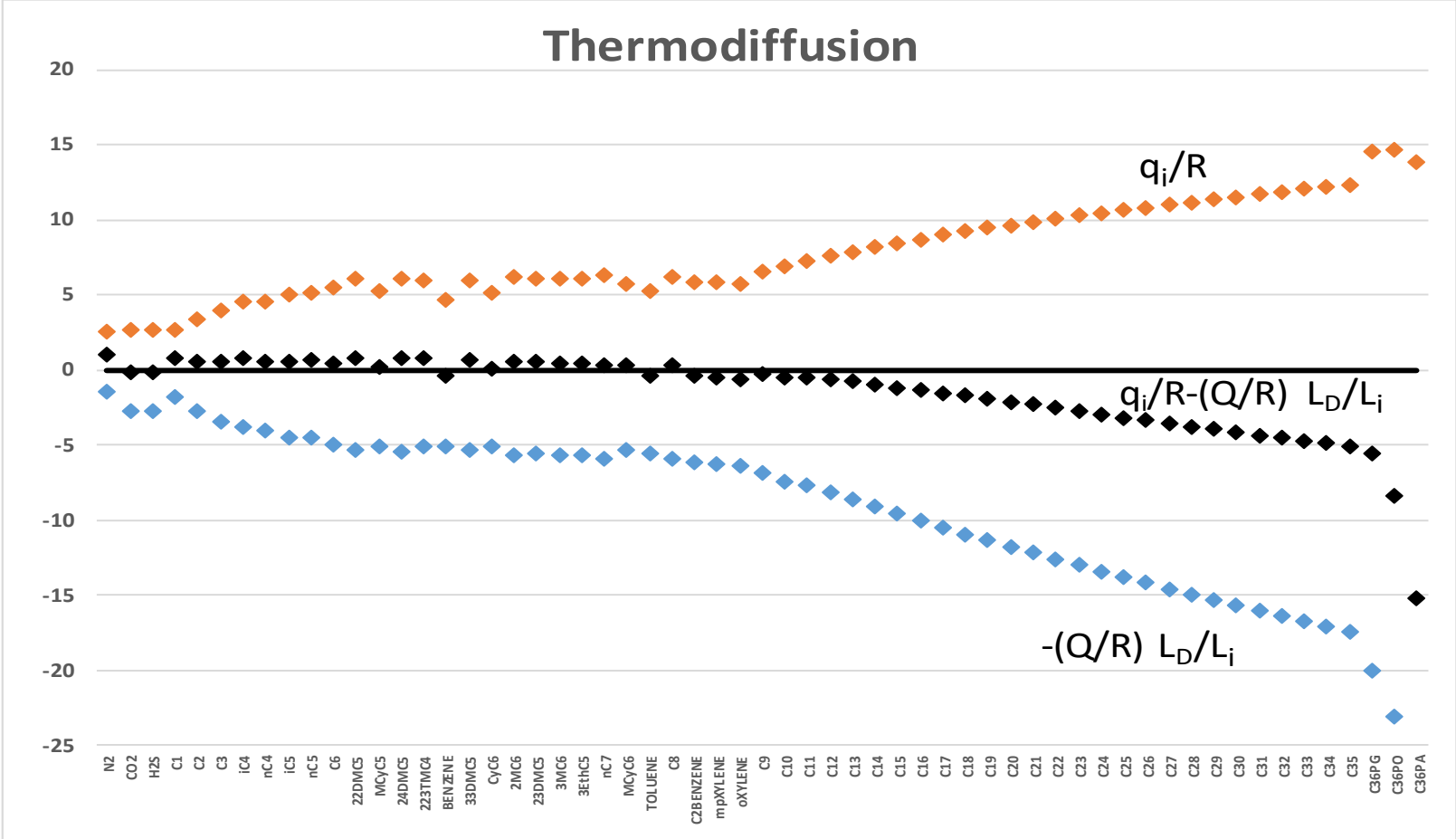
Thermal force

$$\left(q_i - \frac{L_D}{L_i} Q\right) \nabla T$$

Zooming C7 petroleum cuts

⇒ severe fractionation of aromatic components !

Impact of mobility ratio



Balance between the two terms $\left(q_i - \frac{L_D}{L_i} Q \right) \nabla T$

Conclusions

Accurate modelling of the Initial state of Oil&Gas reservoirs is an important step for petroleum engineers

EOS modelling is always compulsory, current practices require additional parameters to model the impact of thermal gradients:

Proposed model do not require any additional parameters !

Next steps

- On going validation on experimental and MD data
- Looking for « physical » explanation of $q_i = -s_i^{res}$
- Proposal for specific validation experiments

Thank you

Questions?