# Liquid-vapour interface transfer coefficients of a two-component mixture

**I. Inzoli[1,2], Signe Kjelstrup[1,3], Dick Bedeaux[1,3], Jean-Marc Simon[4]**

jmsimon@u-bourgogne.fr

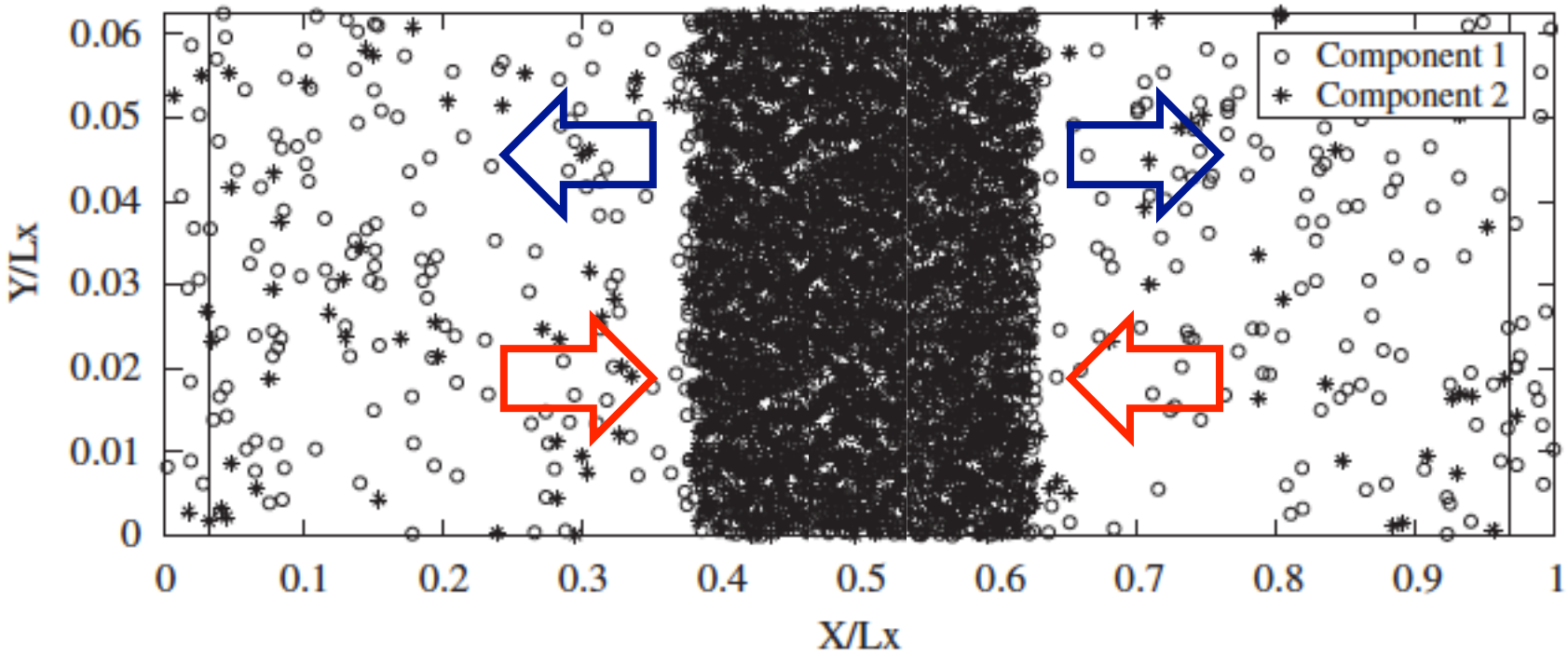
*1- Department of Chemistry, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway.*

2- ARAMCO

3-*Process and Energy Laboratory Delft University of Technology, 2628CA Delft, The Netherlands*

*4- Laboratoire interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne, F-21078 Dijon Cedex, France*

# Transport of heat and mass from liquid to vapour or vapour to liquid

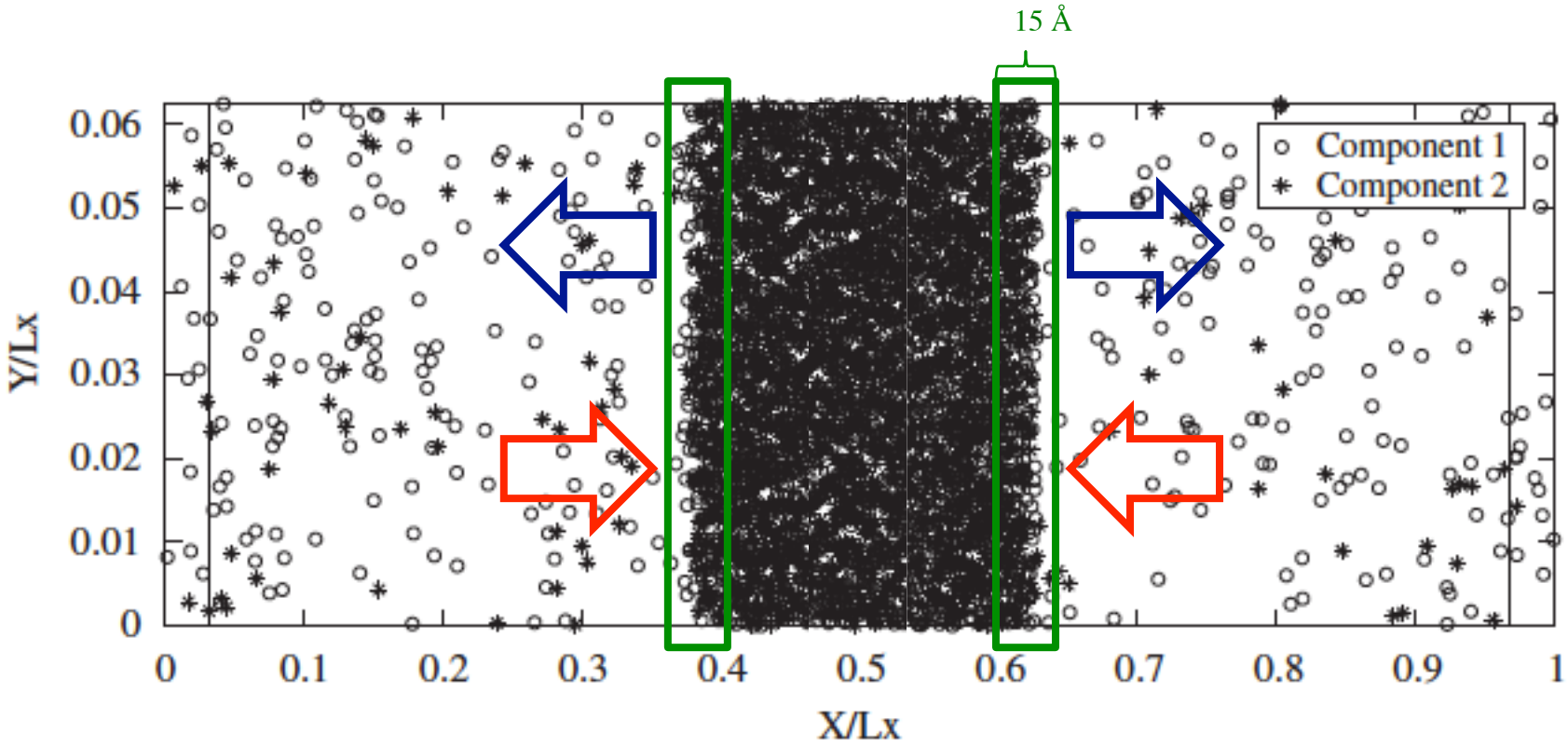



Evaporation/condensation; Heat exchanger

=> Nature (sea, sweat,…)

=> Industry (distillation, …)

# Transport of heat and mass from liquid to vapour or vapour to liquid

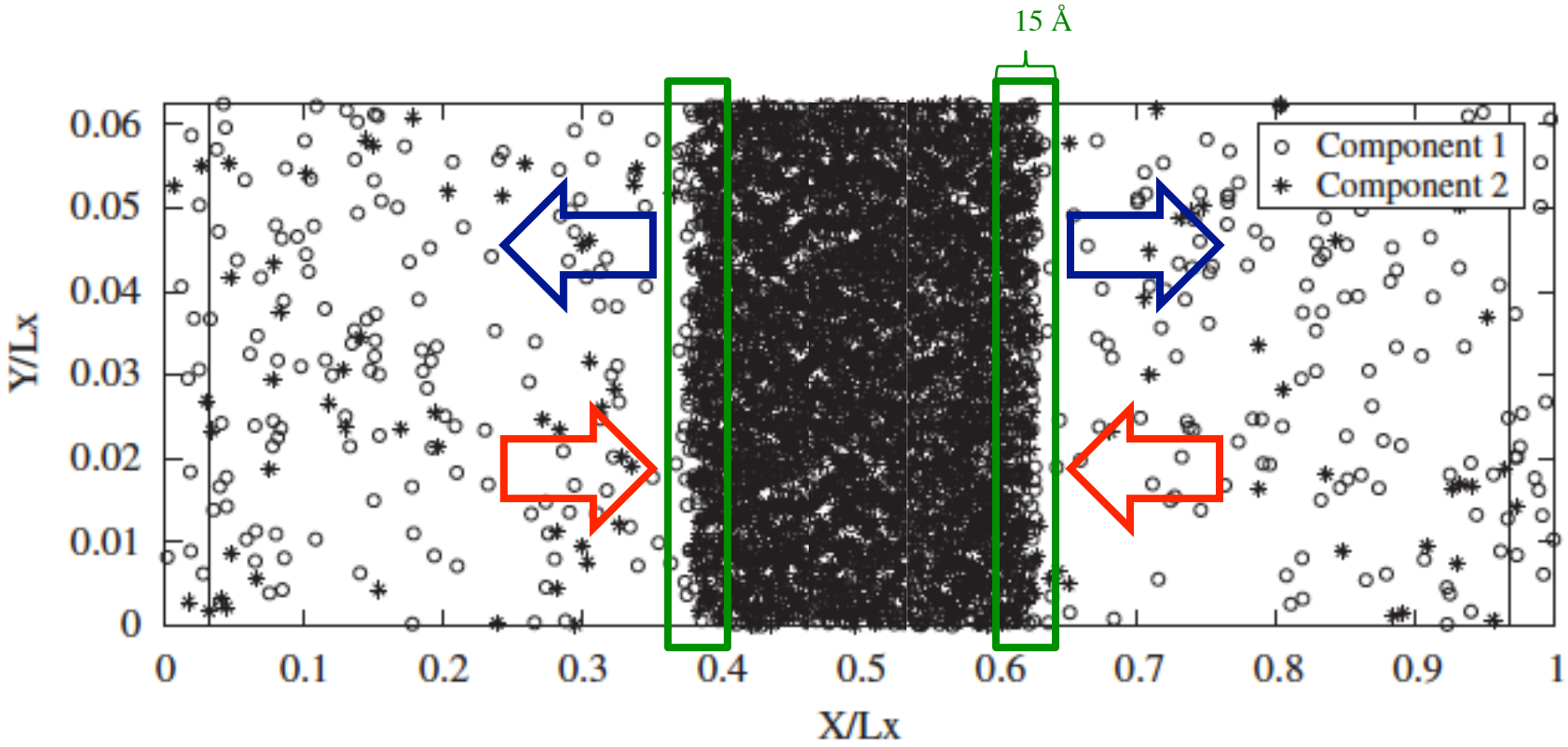



Surface effects:

-State of the surface?

-Transfer coefficients?

# Transport of heat and mass from liquid to vapour or vapour to liquid




Molecular dynamics simulations of a binary mixture with flat surface

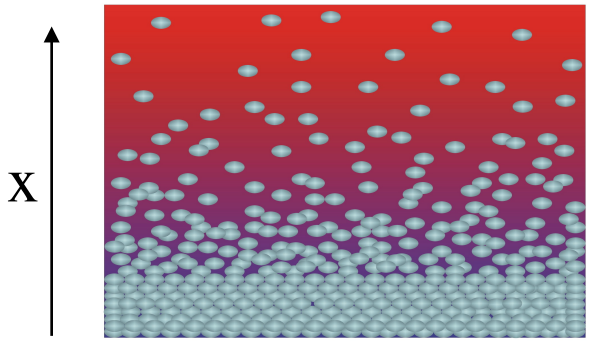
=> Numerical experiments

# Outline

- ✓ NET+integral relations
- ✓ MD simulation
- ✓ Equilibrium results
- ✓ Out of equilibrium results
- ✓ Transfer coefficients
- ✓ Non-isothermal adsorption in zeolites
- ✓ Conclusion

# Non-equilibrium thermodynamics of heterogeneous systems

**Signe Kjelstrup and Dick Bedeaux**: "Non-equilibrium thermodynamics of heterogeneous systems", Series on Advances in Statistical Mechanics, Vol. 16, 2008 World Scientific, Singapore.




Entropy production: σ

$$\sigma^{tot} = \int \sigma^{g} dx + \int \sigma^{l} dx + \sigma^{s}$$

# Entropy production:

$$\sigma^{bulk}(x) = J_q^{'}(x).\nabla\left[\frac{1}{T(x)}\right] + J(x).\left[\frac{\nabla_T \mu(x)}{T(x)}\right]$$

$$\sigma^{s} = J_q^{'l}\left[\frac{1}{T^l} - \frac{1}{T^s}\right] + J_q^{'g}\left[\frac{1}{T^s} - \frac{1}{T^g}\right] - J\left[\frac{\mu^l\left(T^s\right) - \mu^g\left(T^s\right)}{T^s}\right]$$

$J, \quad J_i$ Mass flux and mass flux of species i

$J_q^{'}, \quad J_q^{'l}, \quad J_q^{'g}$ Measurable heat flux in the bulk, on the liquid side of the surface, on the gas side of the surface,

$\mu^l(T^s), \quad \mu^g(T^s)$ Chemical potential at the surface temperature

Based on the validity of the local equilibrium hypothesis

# Entropy production:

$$\sigma^{bulk}(x) = J_q^{'}(x).\nabla\left[\frac{1}{T(x)}\right] + J(x).\left[\frac{\nabla_T \mu(x)}{T(x)}\right]$$

$$\sigma^s = J_q^{'l}\left[\frac{1}{T^l} - \frac{1}{T^s}\right] + J_q^{'g}\left[\frac{1}{T^s} - \frac{1}{T^g}\right] - J\left[\frac{\mu^l(T^s) - \mu^g(T^s)}{T^s}\right]$$

**Under stationary state**: $J = cst, \quad J_u = cst = J_q^{'} + Jh$

$$J_q^{'g} = J_q^{'l} - J\Delta_{vap}H$$

Liquid reference

$$\sigma^s = J_q^{'l}X_q + JX_\mu^l$$

$$X_q = \frac{1}{T^l} - \frac{1}{T^g}$$

$$X_\mu^l = -\left[\frac{\mu^l(T^g) - \mu^g(T^g)}{T^g}\right]$$

Gas reference

$$\sigma^s = J_q^{'g}X_q + JX_\mu^g$$

$$X_q = \frac{1}{T^l} - \frac{1}{T^g}$$

$$X_\mu^l = -\left[\frac{\mu^l(T^l) - \mu^g(T^l)}{T^l}\right]$$

# Surface transfer coefficients

*Interface film resistivities (R)*

Liquid reference

$$X_q = R^{s,l}_{qq} J'^{l}_{q} + R^{s,l}_{q\mu} J$$

$$X^{l}_{\mu} = R^{s,l}_{\mu q} J'^{l}_{q} + R^{s,l}_{\mu\mu} J$$

$$R^{s,l}_{q\mu} = R^{s,l}_{\mu q}$$

Gas reference

$$X_q = R^{s,g}_{qq} J'^{g}_{q} + R^{s,g}_{q\mu} J$$

$$X^{g}_{\mu} = R^{s,g}_{\mu q} J'^{g}_{q} + R^{s,g}_{\mu\mu} J$$

$$R^{s,g}_{q\mu} = R^{s,g}_{\mu q}$$

Direct coefficients: $R^{s,l}_{qq}, R^{s,l}_{\mu\mu}, R^{s,g}_{qq}, R^{s,g}_{\mu\mu}$ Heat and mass resistivities

Coupling coefficients: $R^{s,l}_{q\mu}, R^{s,l}_{\mu q}, R^{s,g}_{q\mu}, R^{s,g}_{\mu q}$ Thermal diffusion process

# Surface transfer coefficients

$$X_q = R^{s,l}_{qq} J'^{l}_{q} + R^{s,l}_{q\mu} J$$

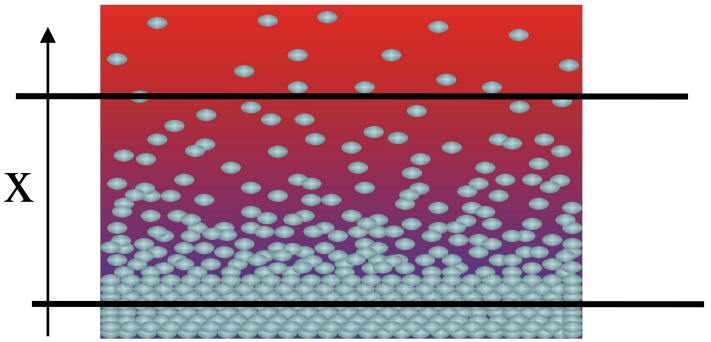
$$X^{l}_{\mu} = R^{s,l}_{\mu q} J'^{l}_{q} + R^{s,l}_{\mu\mu} J$$

$$R^{s,l}_{q\mu} = R^{s,l}_{\mu q}$$

Resistivities can be calculated without knowing the details inside the surface, but knowing the thermodynamic properties of the gas and liquid in contact with the surface

$$X_q = \frac{1}{T^l} - \frac{1}{T^g}$$

$$X^{l}_{\mu} = -\left[\frac{\mu^l(T^g) - \mu^g(T^g)}{T^g}\right]$$



# Surface transfer coefficients

$$X_q = R^{s,l}_{qq} J^{'l}_q + R^{s,l}_{q\mu} J$$

$$X^l_\mu = R^{s,l}_{\mu q} J^{'l}_q + R^{s,l}_{\mu\mu} J$$

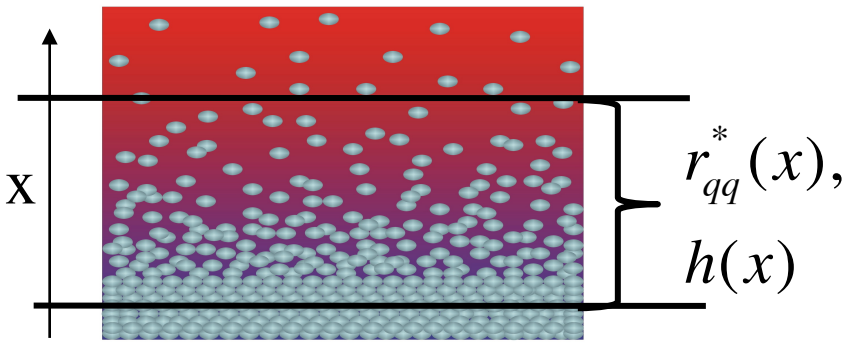
$$R^{s,l}_{q\mu} = R^{s,l}_{\mu q}$$

Integral relations

$$R^s_{qq} = \int_g^l r^*_{qq}(x)dx = \frac{1}{\lambda^s \left(T^s\right)^2}$$

$$R^{s,l}_{q\mu} = \int_g^l r^*_{qq}(x)\left[h(l) - h(x)\right]dx$$

$$R^{s,l}_{\mu\mu} = \int_g^l r^*_{qq}(x)\left[h(l) - h(x)\right]^2 dx$$




$$r^*_{qq}(x) = \left[\nabla_x \frac{1}{T(x)} \Big/ J^{'}_q(x)\right]_{J=0}$$

# Heats of transfer

$$J_q^{'l} = \frac{X_q}{R_{qq}^{s,l}} + q^{*s,l} J$$

$$q^{*s,l} = \left( \frac{J_q^{'l}}{J} \right)_{T^l = T^g} = -\frac{R_{q\mu}^{s,l}}{R_{qq}^{s,l}}$$

$$J_u = J_q^{'l} + h^l J = \frac{X_q}{R_{qq}^{s,l}} + \left( q^{*s,l} + h^l \right) J$$

The magnitude of $q^*$ reflects the strength of the coupling between heat and mass transfer. It can be very large in evaporation processes, although it is often neglected.

# Force-Flux relations for binary systems

$$J_u = J_q^{'l} + h_1^l J_1 + h_2^l J_2$$

Measurable heat flux reference from the **liquid side**: $J_q^{'l}$

$$\Delta_{g,l}\frac{1}{T} = R_{qq}^{s,l} J_q^{'l} + R_{q1}^{s,l} J_1 + R_{q2}^{s,l} J_2$$

$$-\frac{\Delta_{g,l}\mu_1^l(T^g)}{T^g} = R_{1q}^{s,l} J_q^{'l} + R_{11}^{s,l} J_1 + R_{12}^{s,l} J_2$$

$$-\frac{\Delta_{g,l}\mu_2^l(T^g)}{T^g} = R_{2q}^{s,l} J_q^{'l} + R_{21}^{s,l} J_1 + R_{22}^{s,l} J_2$$

$$J_u = J_q^{'g} + h_1^g J_1 + h_2^g J_2$$

Measurable heat flux reference from the **vapour side**: $J_q^{'g}$

$$\Delta_{g,l}\frac{1}{T} = R_{qq}^{s,g} J_q^{'g} + R_{q1}^{s,g} J_1 + R_{q2}^{s,g} J_2$$

$$-\frac{\Delta_{g,l}\mu_1(T^l)}{T^l} = R_{1q}^{s,g} J_q^{'g} + R_{11}^{s,g} J_1 + R_{12}^{s,g} J_2$$

$$-\frac{\Delta_{g,l}\mu_2(T^l)}{T^l} = R_{2q}^{s,g} J_q^{'g} + R_{21}^{s,g} J_1 + R_{22}^{s,g} J_2$$

Direct resistances: $R_{qq}^s, R_{11}^s, R_{22}^s$ Coupling resistances: $R_{iq}^s = R_{qi}^s, R_{12}^s = R_{21}^s$

Based on the validity of the local equilibrium hypothesis

To verify that the extension of NET to surface is valid

=> Square gradient models and classical density functional theory

$\Rightarrow$ Molecular dynamics (non-equilibrium) on

* Liquid vapour interfaces of pure atomic or molecular compounds (argon like particles, n-octane)
* Liquid vapour of mixtures of atomic species
* molecules in contact with solids and porous system

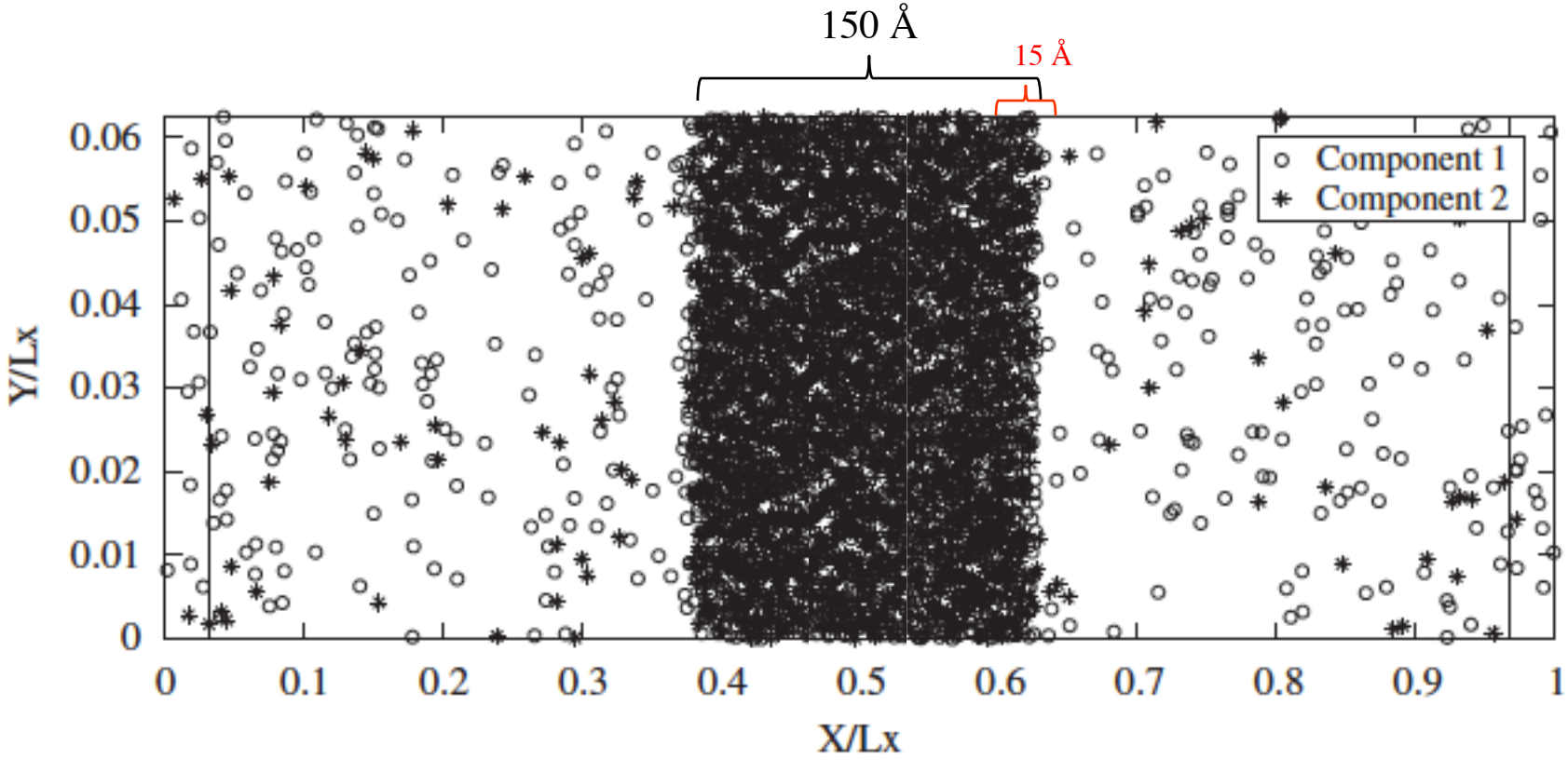
*Important for the evaporation/condensation model (efficiency of distillation column), adsorption/desorption, catalytic reaction, …*

**For one component systems:**

* Large excess of heat and mass surface resistances

* Large coupling effects between transport of heat and mass at interfaces

* Non-equilibrium thermodynamics is well adapted to the description of transport properties across surface.

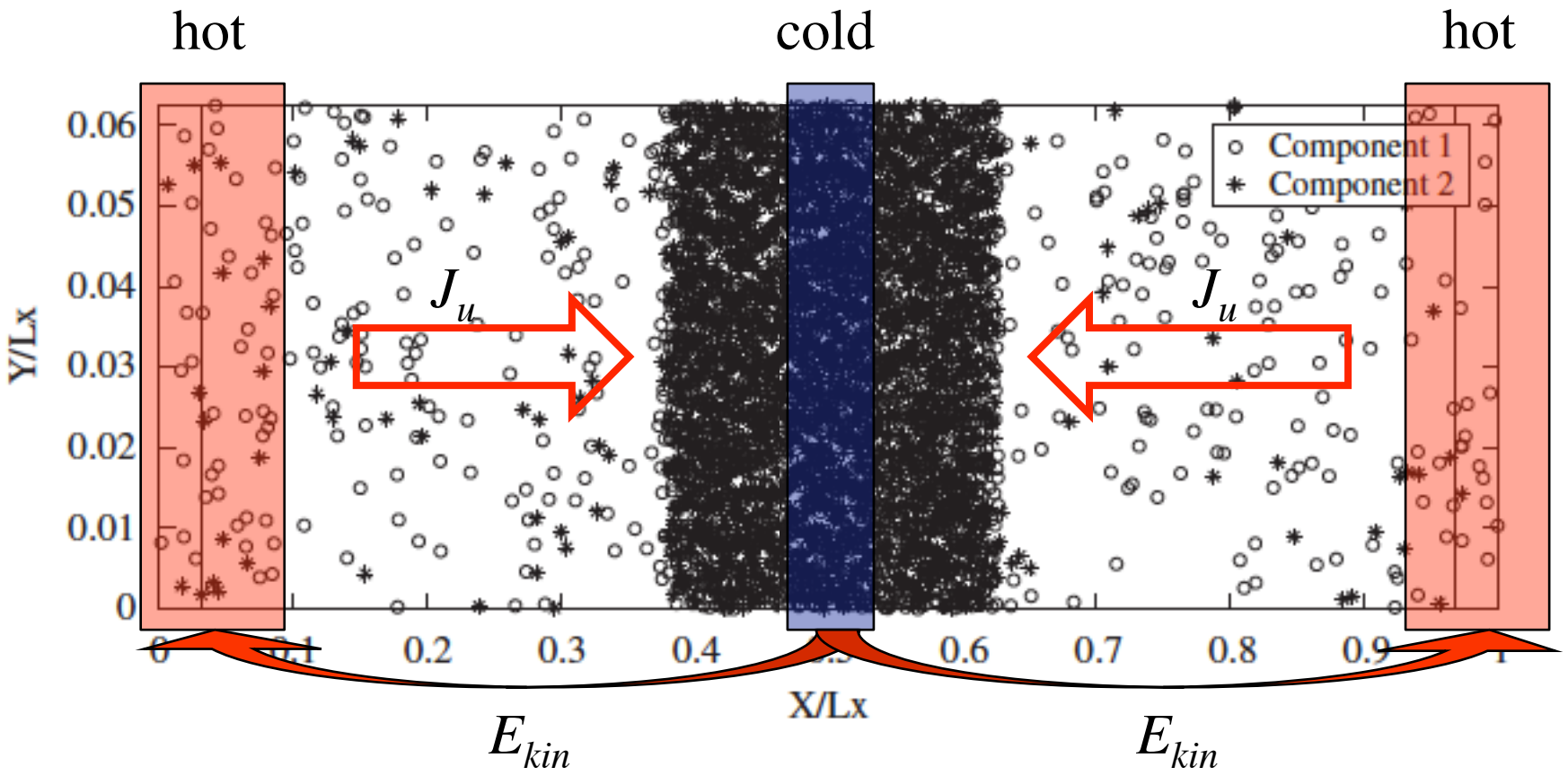



Lennard-Jones particles (spline potential $r_c=2.5\sigma_1$)

- Component 1: argon-like, $\sigma_1=3.42$ Å, $\varepsilon_1/k_B=124$ K
- Component 2 : $m_2=m_1$, $\sigma_2=\sigma_1$, $\varepsilon_2=\varepsilon_{12}=0.8\,\varepsilon_1$

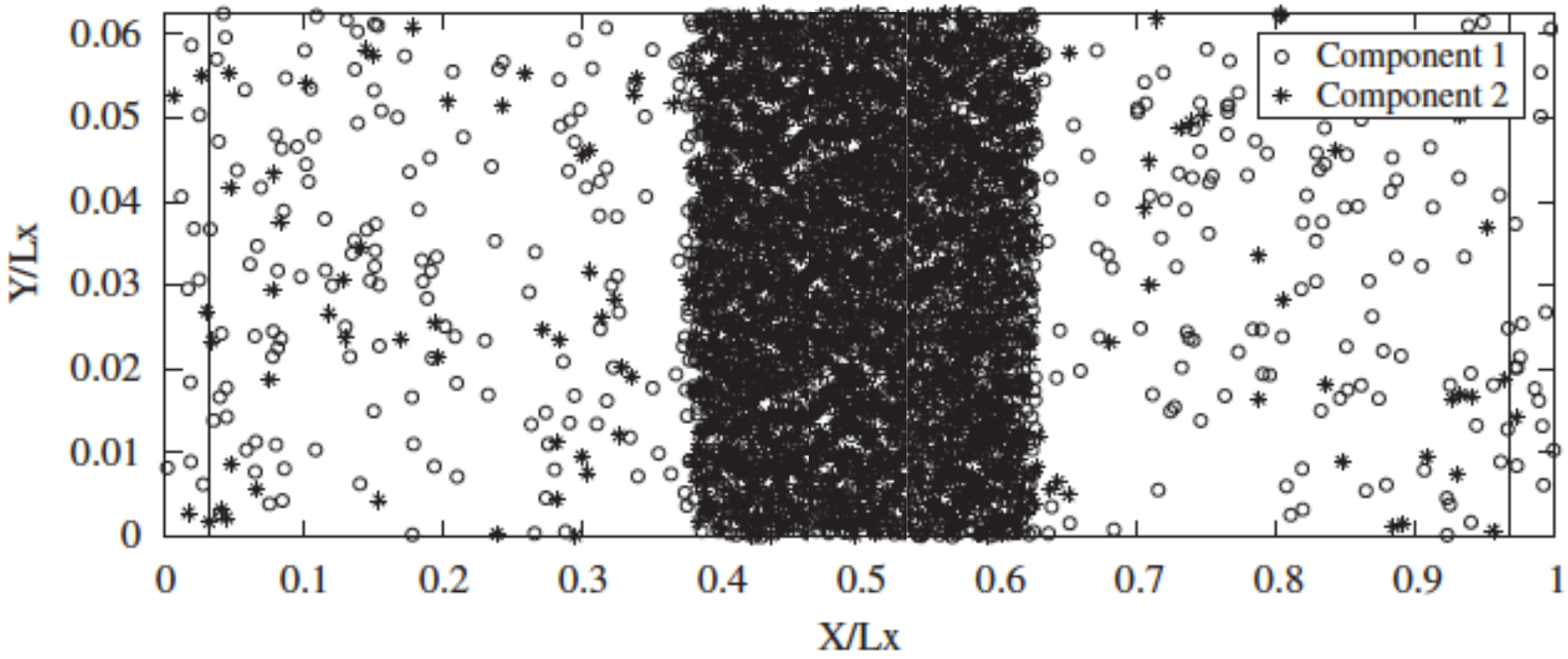
- Simulations at different temperatures (60-105 K) and mole fractions (0-1)

# Non-equilibrium molecular dynamics

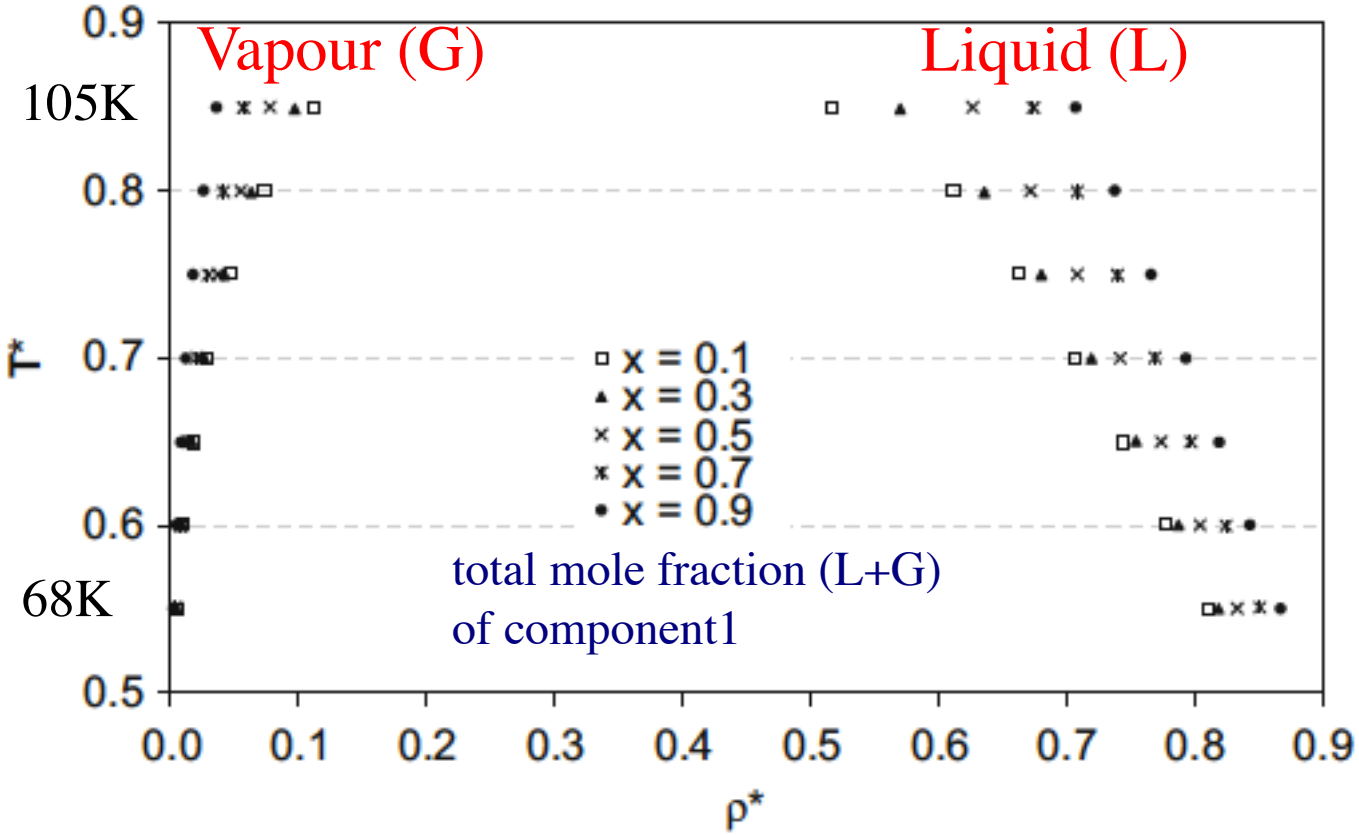



**Heat flow by exchange of kinetic energy**
**Stationary conditions**
Inzoli et al., Chem. Eng. Sc. **66**, 4533 (2011)

# Equilibrium MD

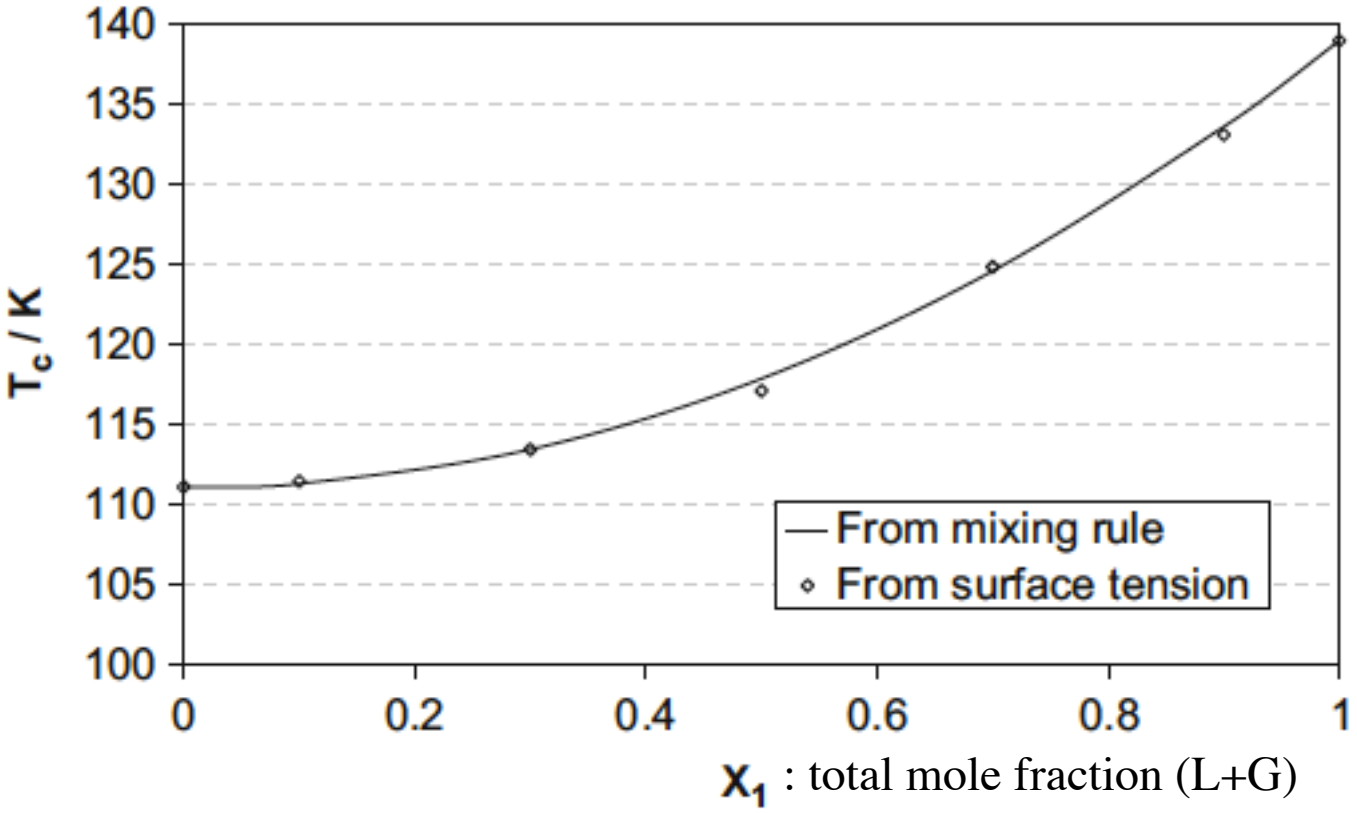


# Equilibrium results: liquid-vapour coexistence curve



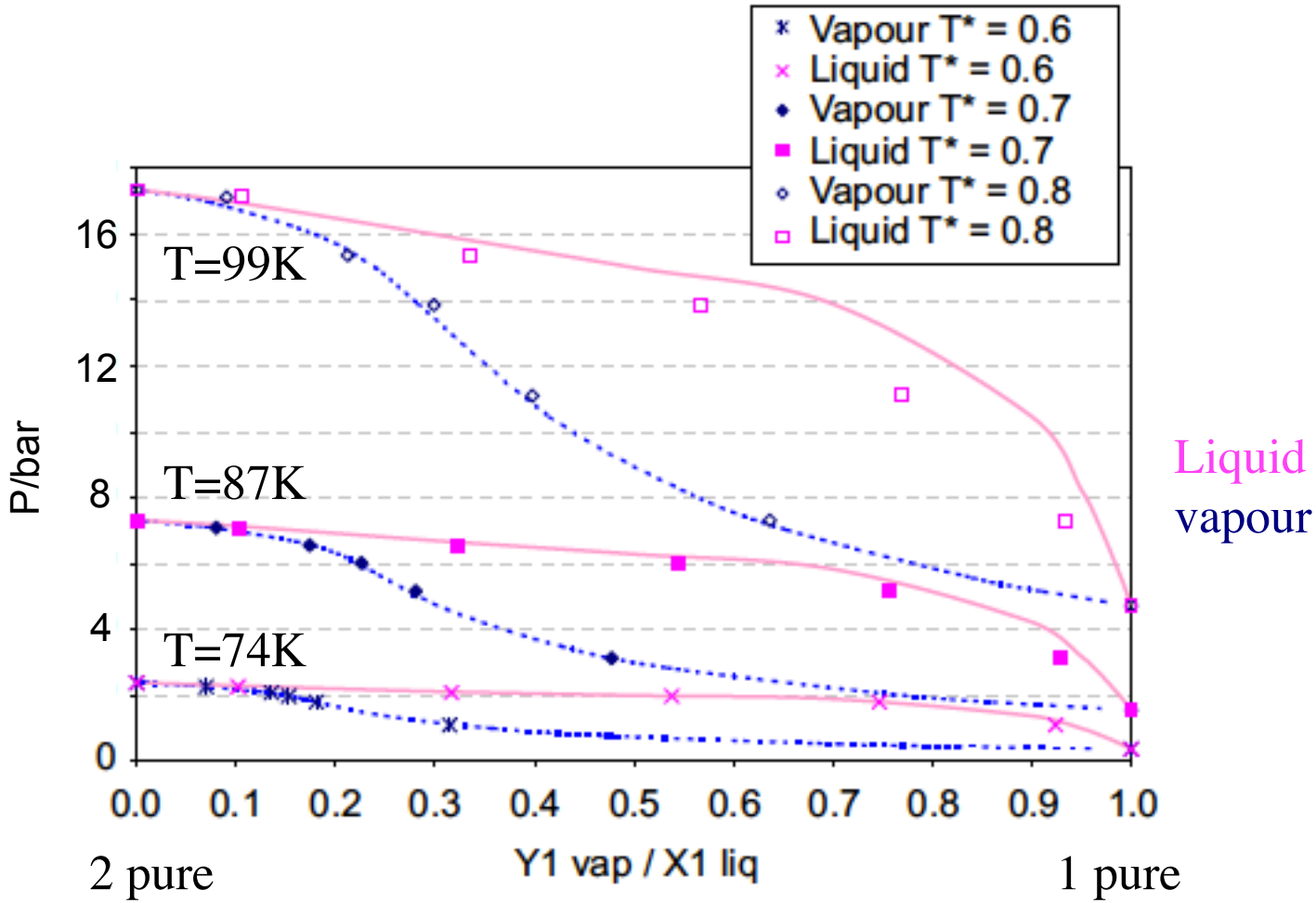

Inzoli et al., Chem. Eng. Sc. **65**, 4105 (2010)

# Equilibrium results: critical curve



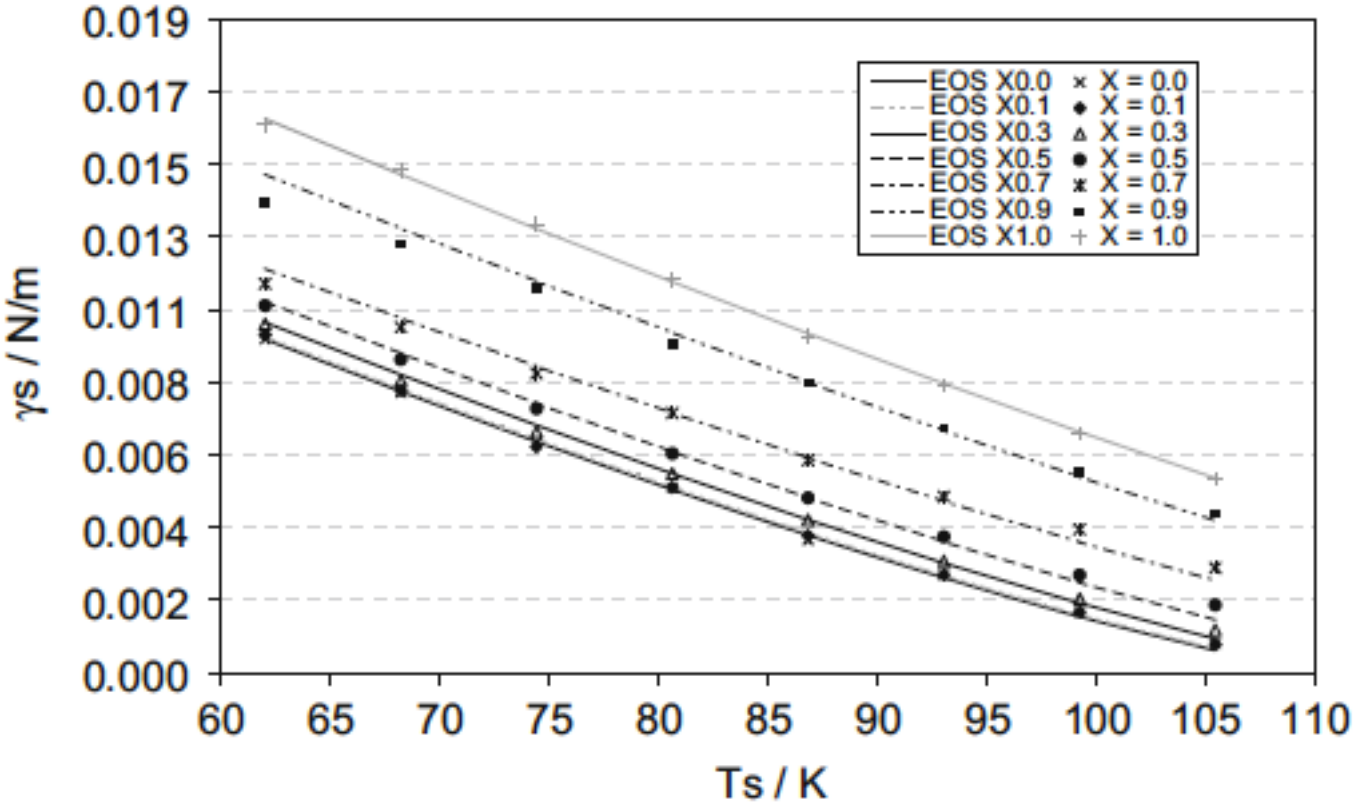

$$T_{C,X_1} = X_1 T_{C,1} + (1-X_1) T_{C,2} + K X_1 (1-X_1) \sqrt{T_{C,1} T_{C,2}}$$

# Equilibrium results: pressure-composition




Lines: Margules equation

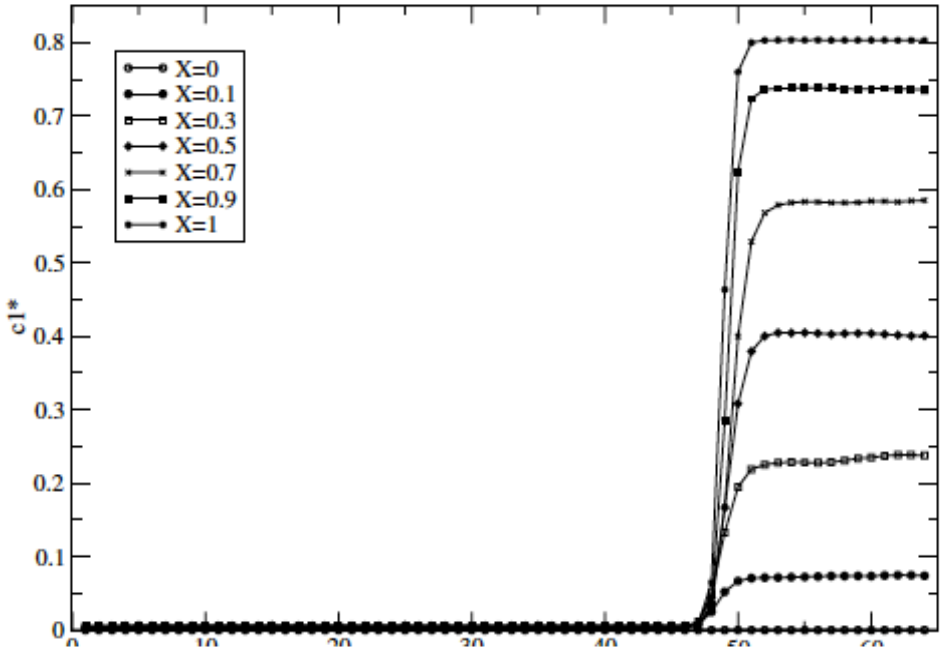
# Equilibrium results: surface tension



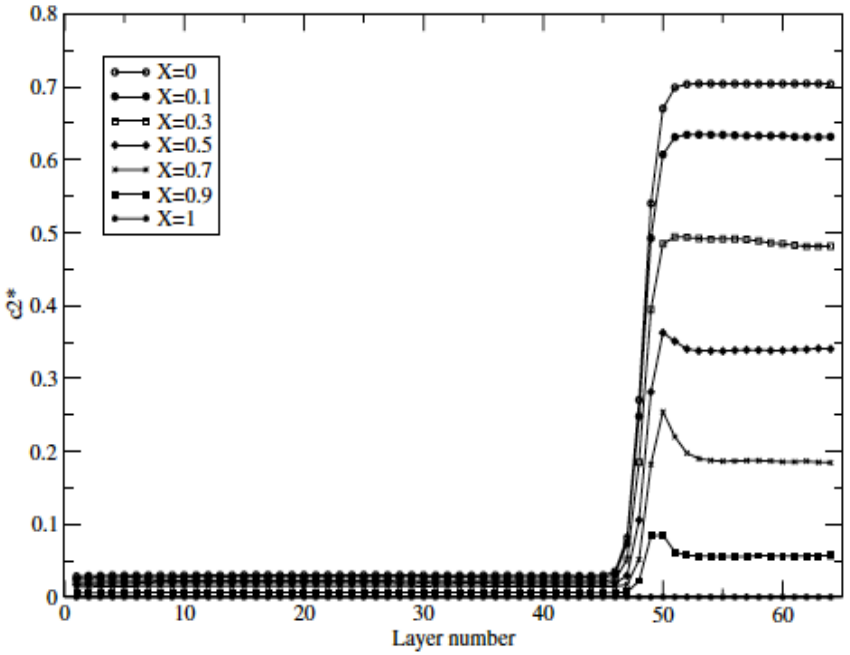

$$\gamma_s = \gamma_0 \left( \frac{T_C - T}{T_C} \right)^{2\nu}$$

EOS with the Universal constant, $\nu$ =0.63

# Equilibrium results: concentration profiles (T=87K)



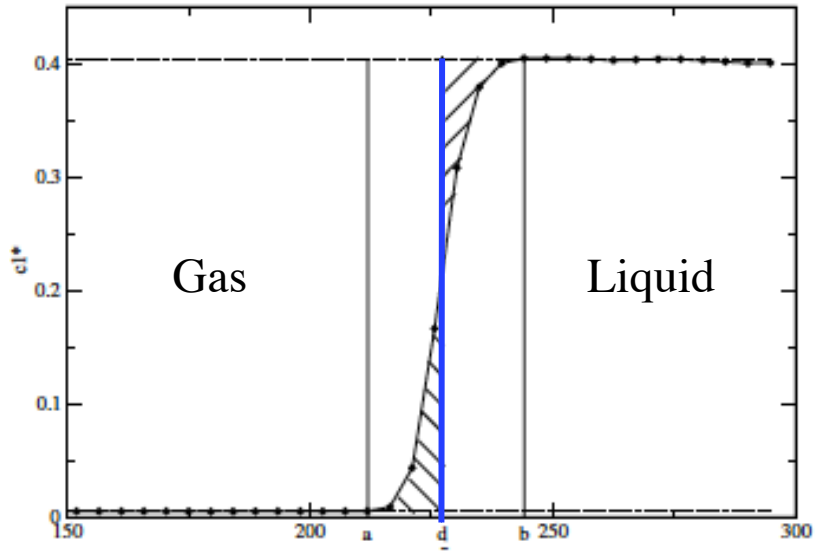

Component 1

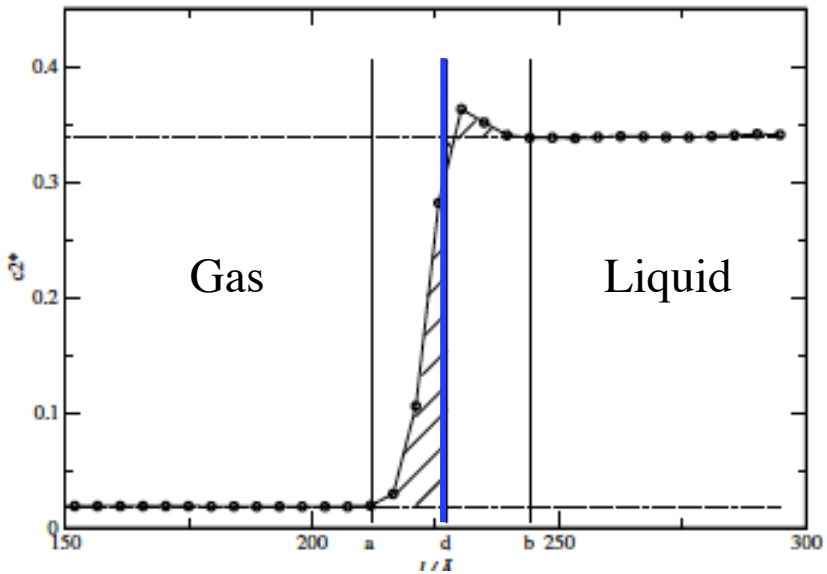



Component 2

# Equilibrium results: concentration profiles

Equimolar surface



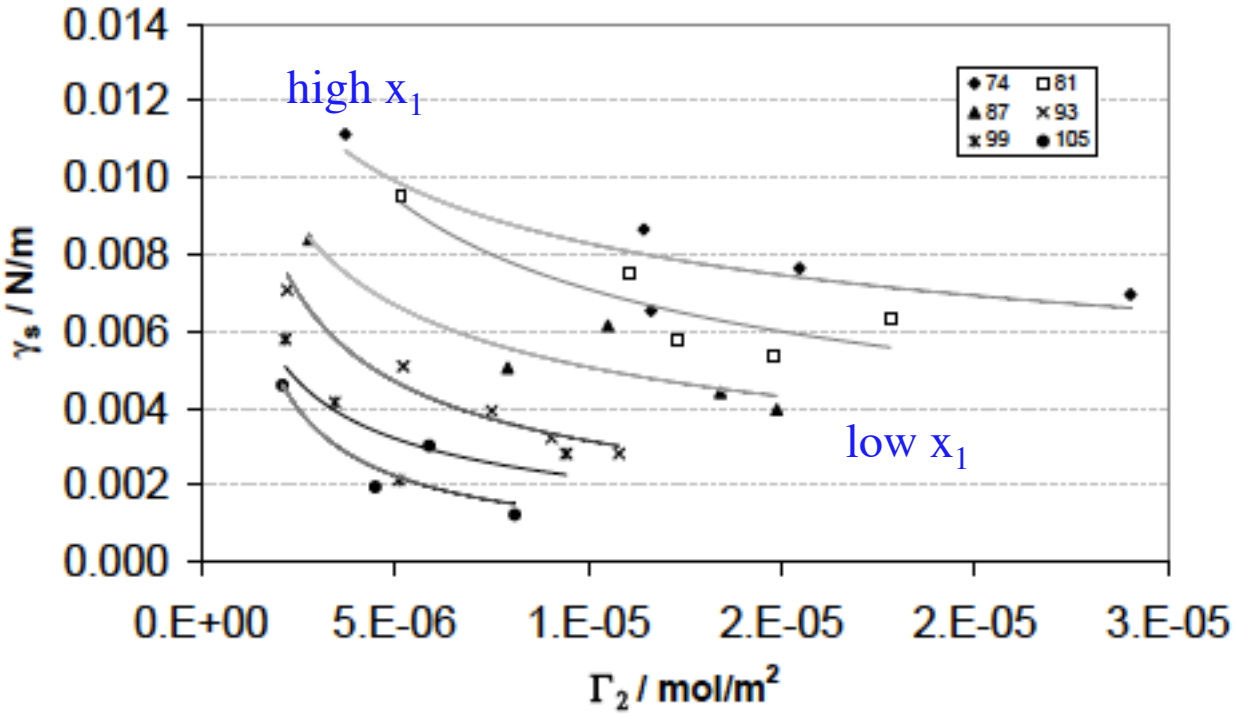




Component 1

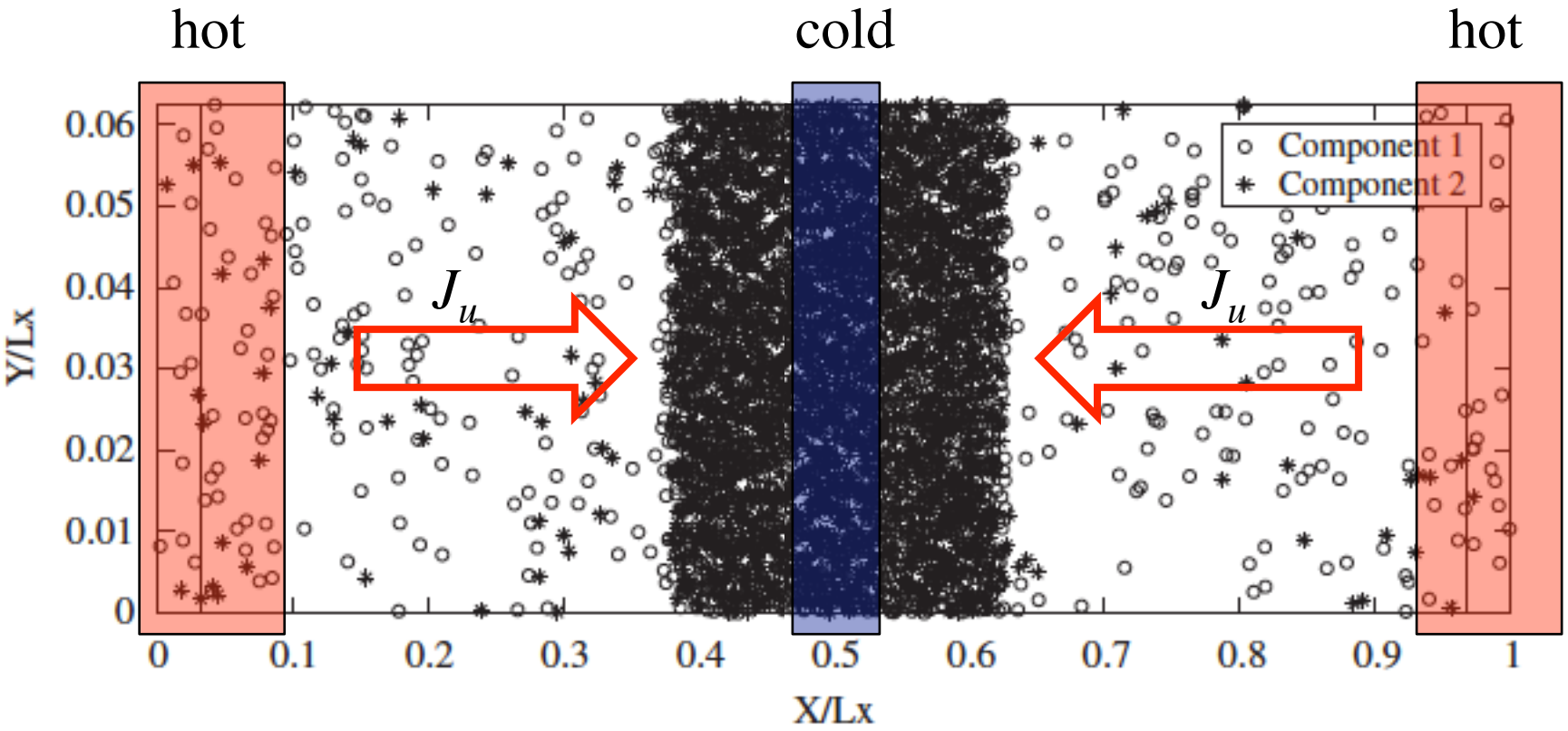
Component 2

$$\Gamma_{\mathrm{i}}(y,z) = \int_a^b \left[ c_{\mathrm{i}}(x,y,z) - c_{\mathrm{i}}^{\mathrm{g}}(a,y,z)\theta(d-x) - c_{\mathrm{A}}^{\mathrm{l}}(b,y,z)\theta(x-d) \right] dx$$

# Equilibrium results: excess concentration of component 2



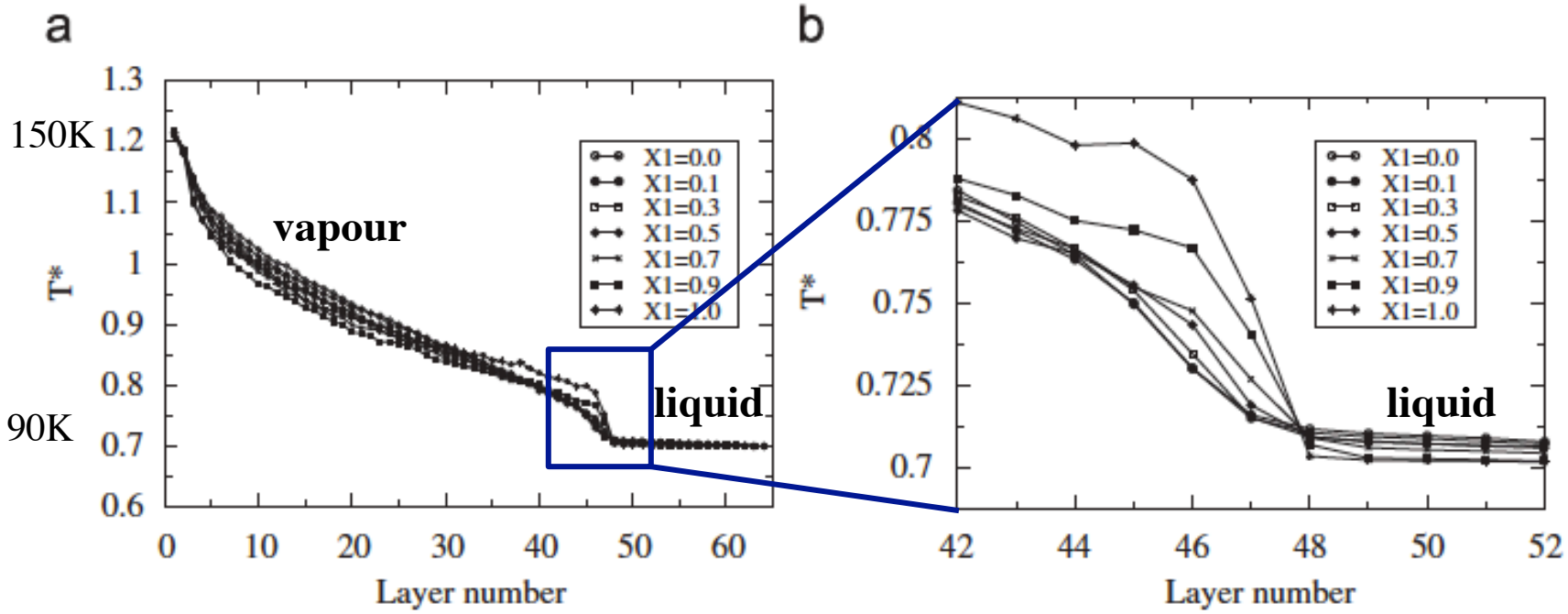
# Transport of heat and mass from liquid to vapour or vapour to liquid




Surface effects:
-resistance to heat and mass?
-State of the surface?

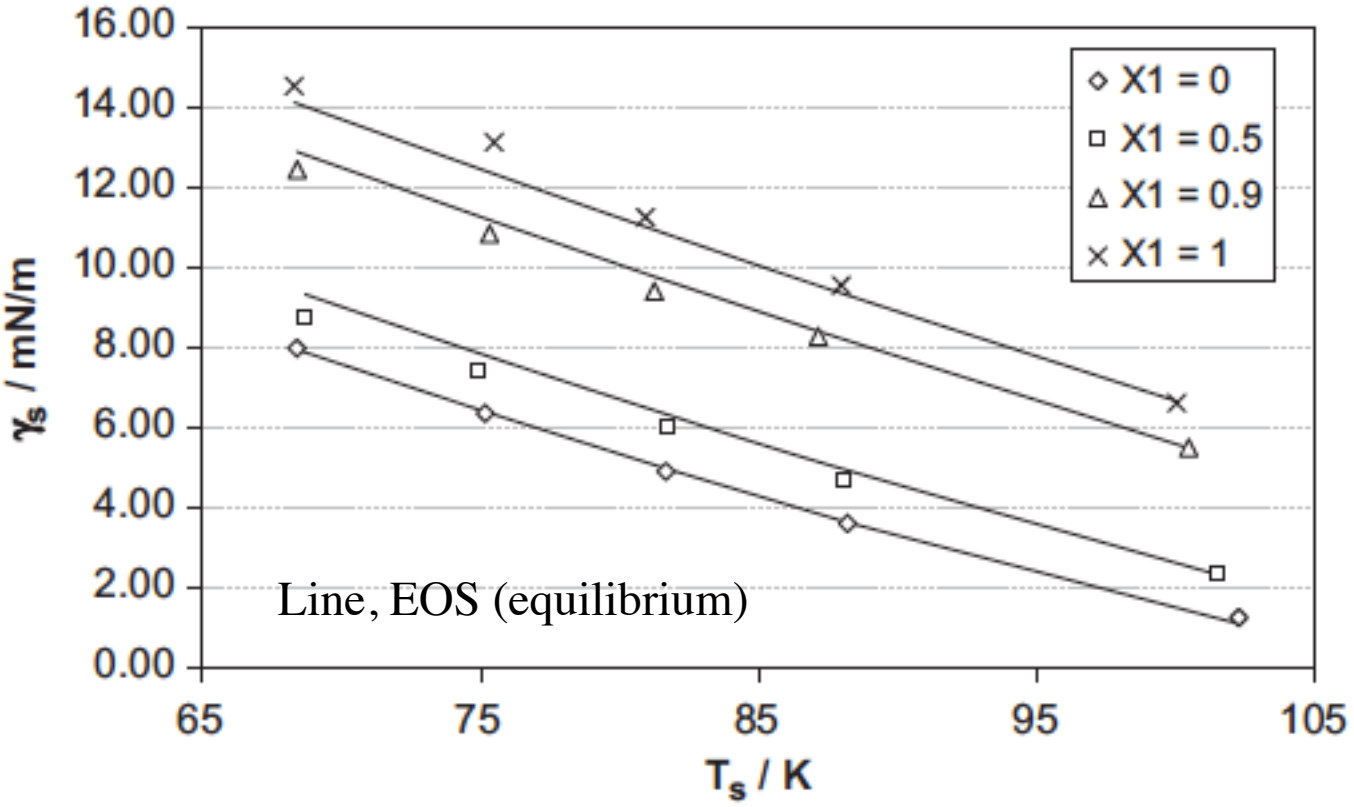
Non-equilibrium molecular dynamics simulations

# Temperature profiles



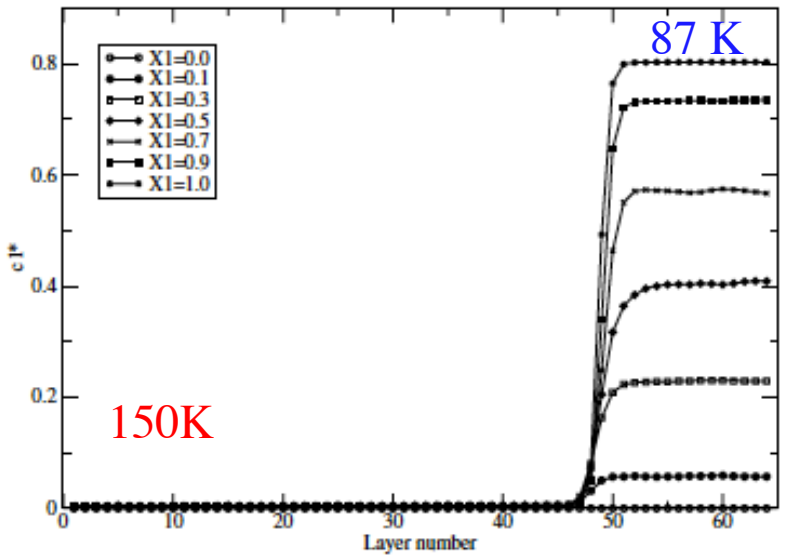

$$\frac{T^g - T^l}{l^s} \approx 0.5\ K/\text{Å}$$

# Surface tension

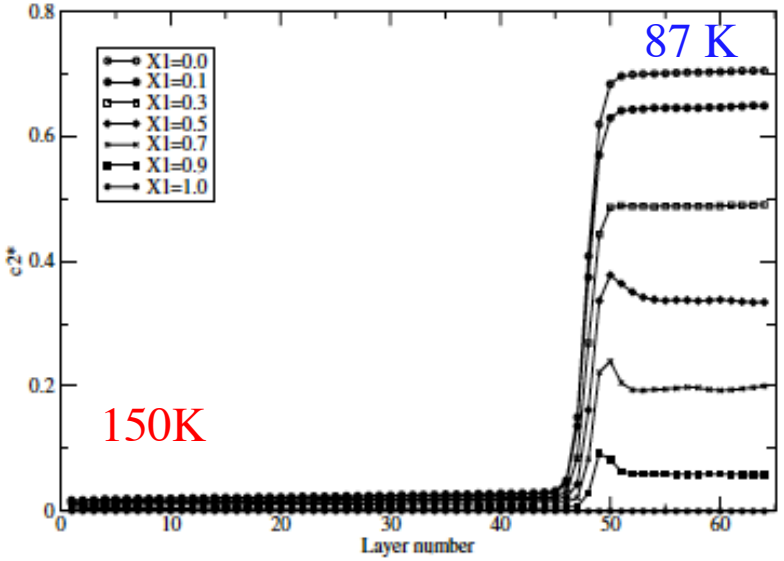



Local equilibrium assumption

# Concentration profiles

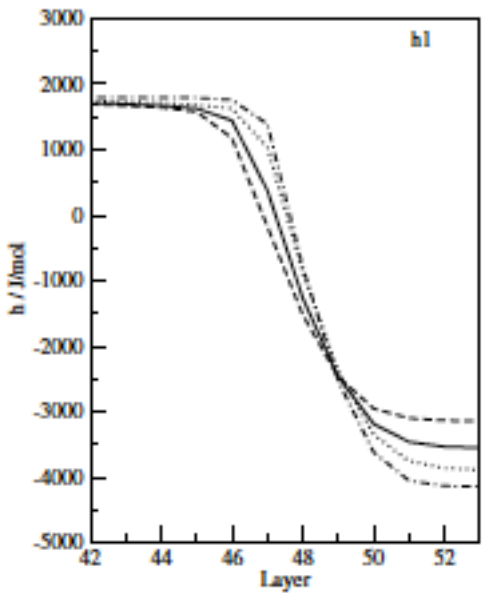


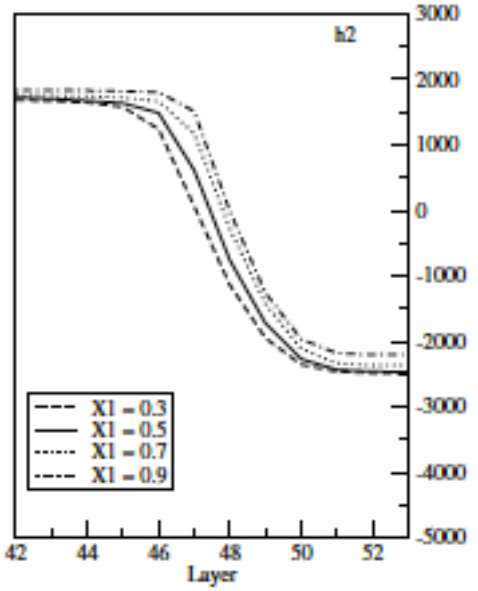

(a) Component 1




(b) Component 2

# Partial molar enthalpy profiles




Component 1

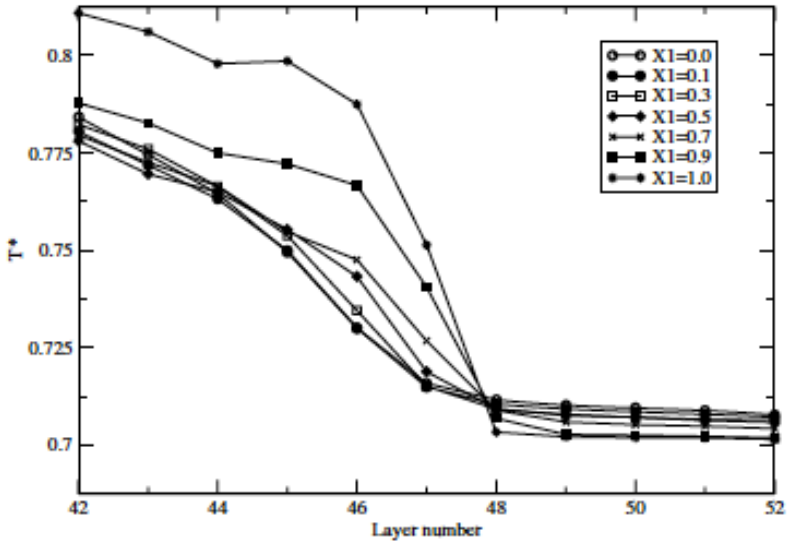
$\Delta_{vap} h_1 \approx 6 kJ/mol$

Component 2

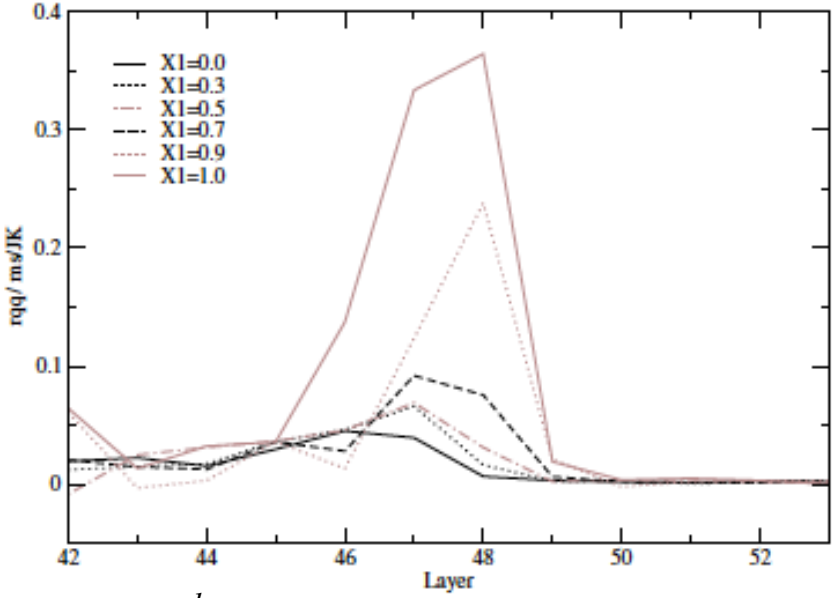
$\Delta_{vap} h_2 \approx 4 kJ/mol$

# Local resistivities to heat transfer

temperature




resistivities

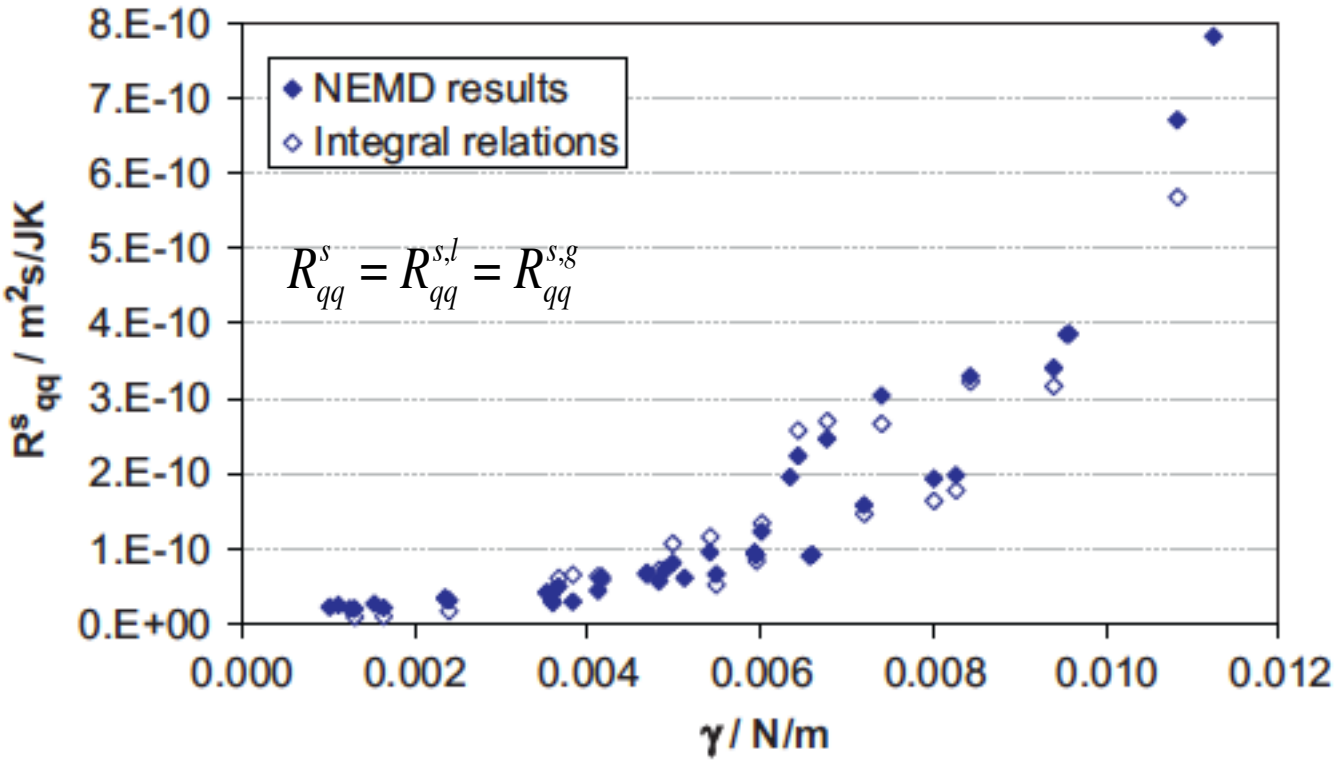



$$r^*_{qq}(x) = \left[ \nabla_x \frac{1}{T(x)} \Big/ J'_q(x) \right]_{J=0}$$

$$R^{s,l}_{q\mu} = \int_g^l r^*_{qq}(x)\left[h(l) - h(x)\right]dx$$

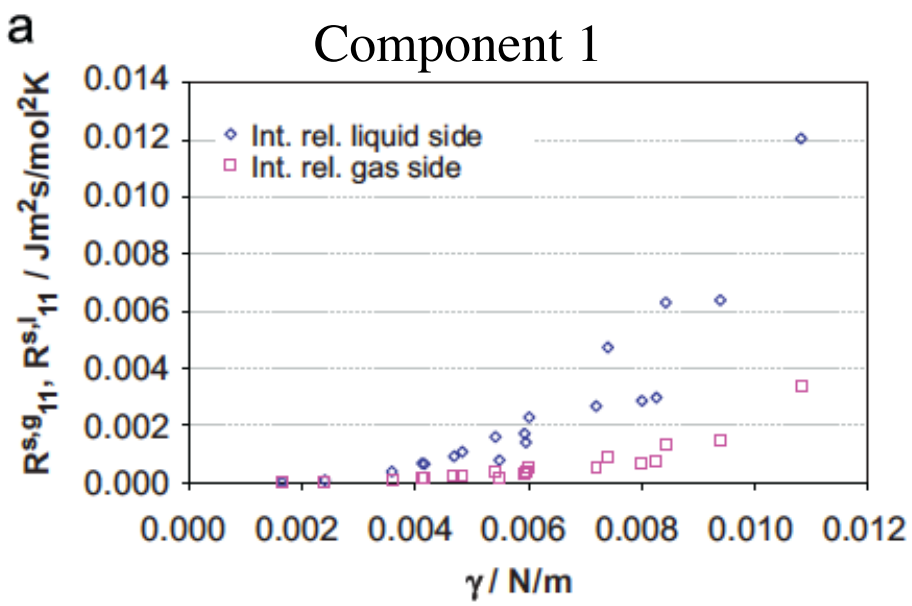
$$R^{s,l}_{\mu\mu} = \int_g^l r^*_{qq}(x)\left[h(l) - h(x)\right]^2 dx$$

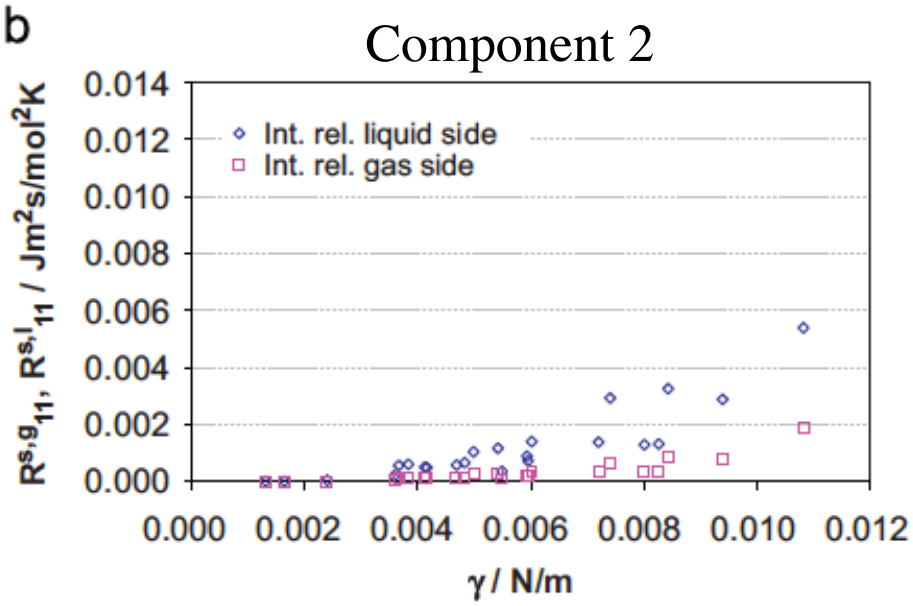
# Heat resistances




Integral relations: Glavatskiy et al. Phys. Rev. E **79**, 031608 (2009)

# Mass resistances

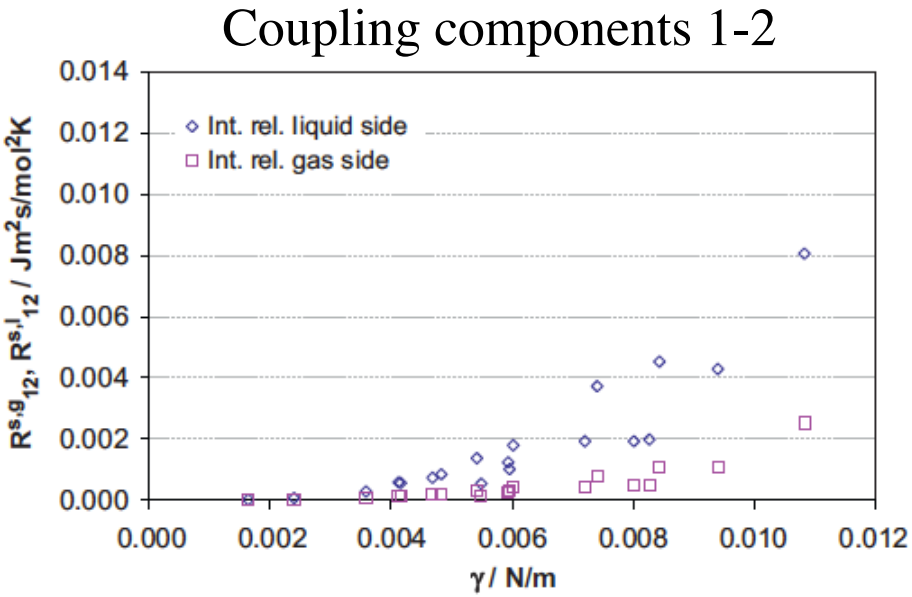


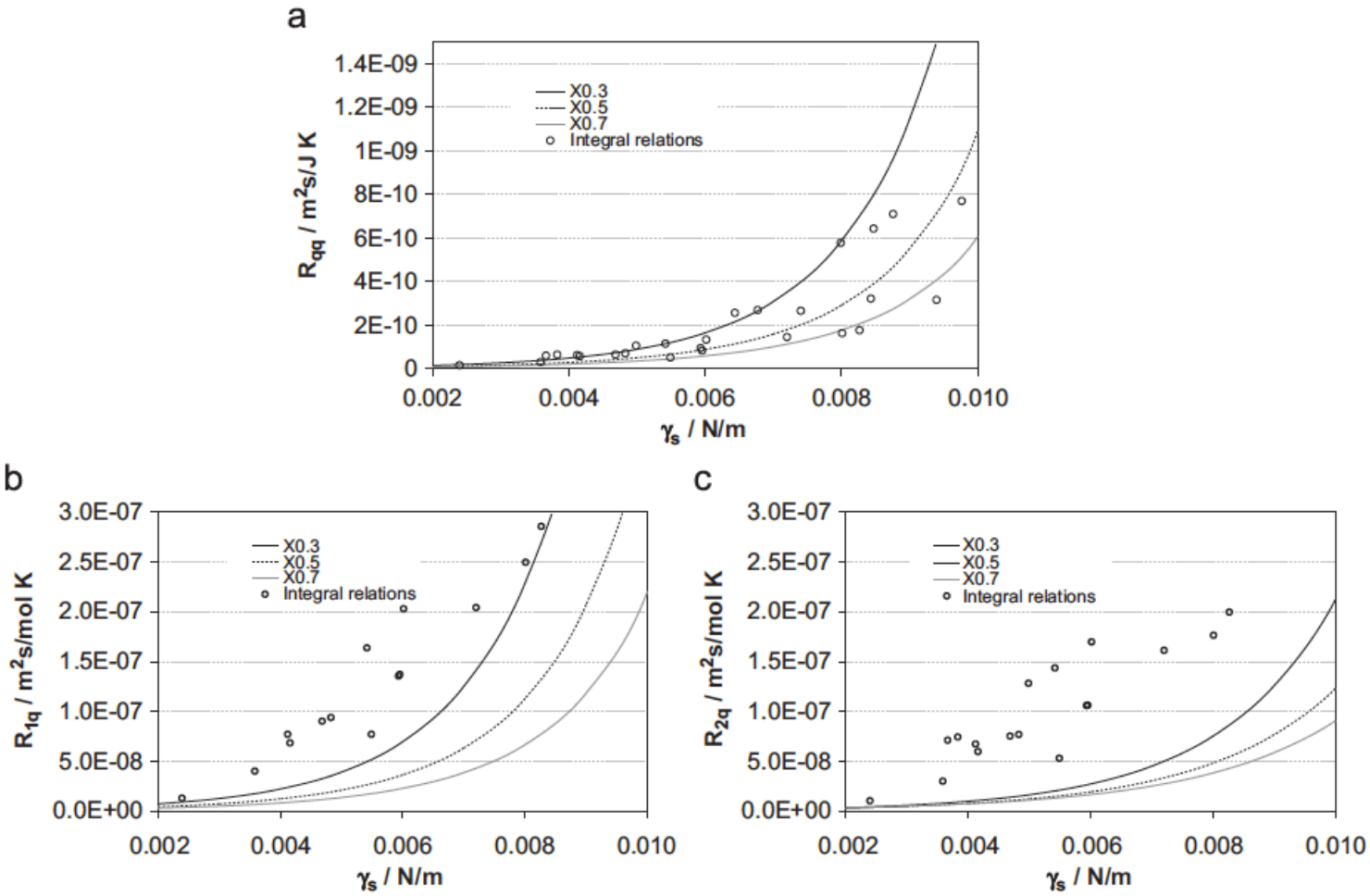

Blue: liquid side

Red: gas side

$$J_1 = -\left[\frac{\Delta_{g,l}\mu_1^l(T^g)}{T^g R_{11}^{s,l}}\right] - \left(\frac{R_{1q}^{s,l}}{R_{11}^{s,l}}\right) J_q^{'l} - \left(\frac{R_{12}^{s,l}}{R_{11}^{s,l}}\right) J_2$$

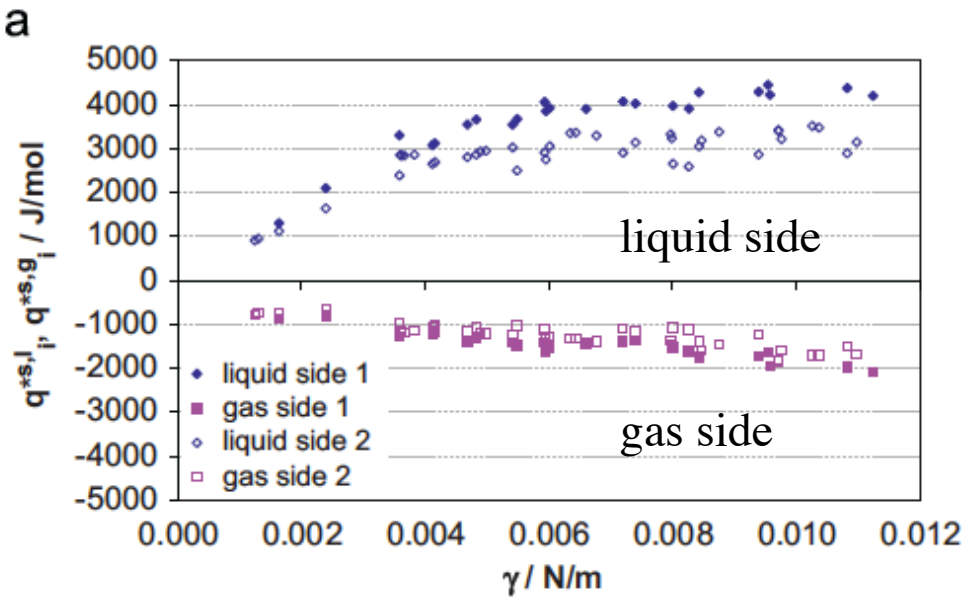


# Comparison with kinetic theory

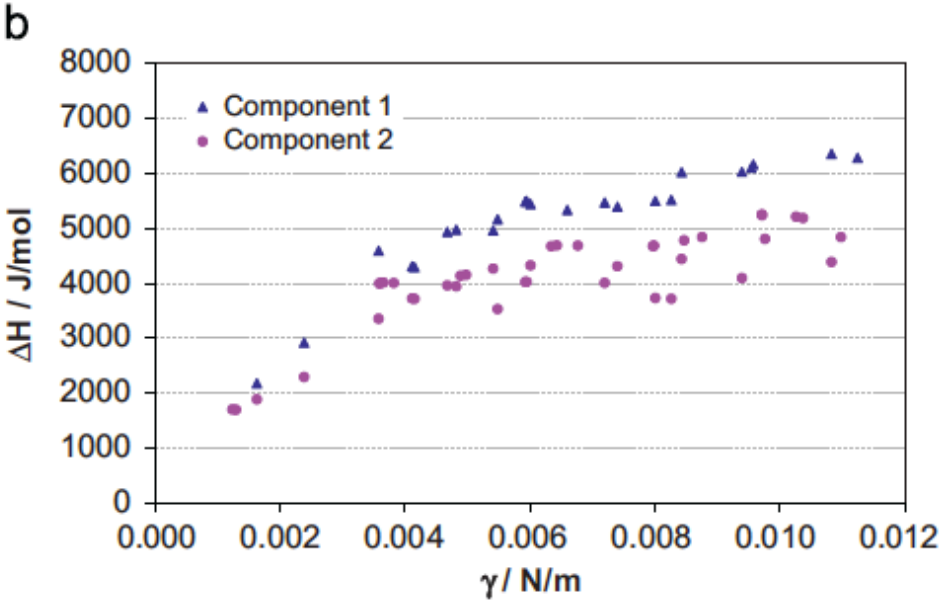


# Heat and mass coupling

Heat of transfer




Heat of evaporation




$$q_i^{*s,g} = \left(\frac{J_q^{'g}}{J_i}\right)_{\Delta_{g,l}T=J_j=0} = -\frac{R_{qi}^{s,g}}{R_{qq}^{s}}, \qquad J_q^{'l} = \frac{1}{R_{qq}^{s}}\nabla_{g,l}\frac{1}{T} + q_1^{*s,l}J_1 + q_2^{*s,l}J_2,$$

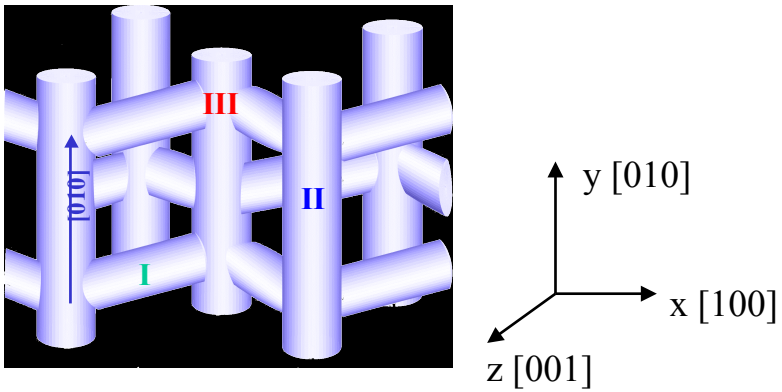
$$q_i^{*s,l} = \left(\frac{J_q^{'l}}{J_i}\right)_{\Delta_{g,l}T=J_j=0} = -\frac{R_{qi}^{s,l}}{R_{qq}^{s}} \qquad J_u = \frac{1}{R_{qq}^{s}}\nabla_{g,l}\frac{1}{T} + \left(h_1^l + q_1^{*s,l}\right)J_1 + \left(h_2^l + q_2^{*s,l}\right)J_2$$

**Influence of the coupling between heat and mass**
**On transient processus of evaporation condensation**

**Illustration adsorption of n-butane on the zeolite silicalite-1**

# Zeolite silicalite

-Zeolites are nanoporous crystals

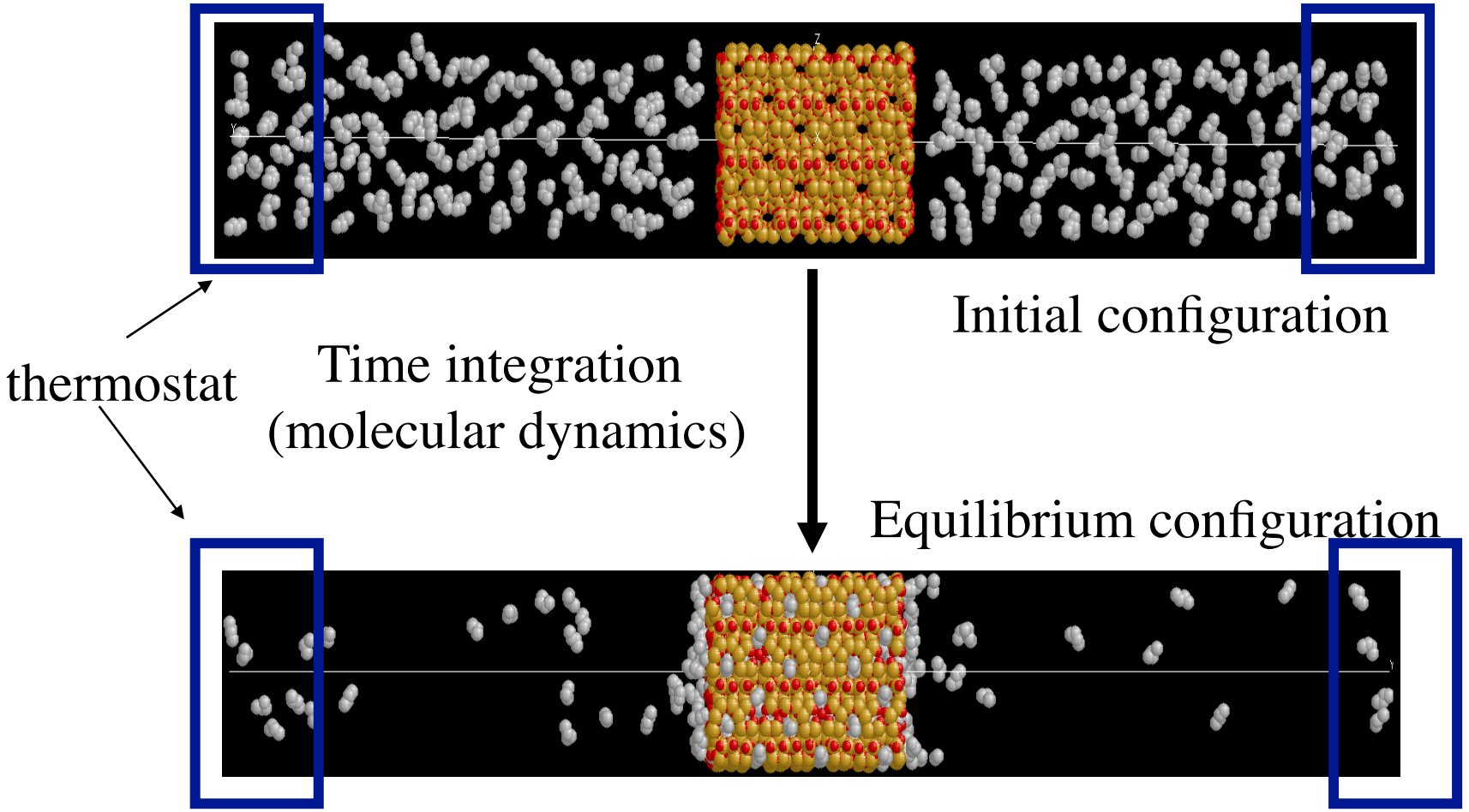



Silicalite, pure $SiO_2$
Crystals of micrometer size (0.5-50 μm).
MFI type, interconnected nanopores (Ø ≈ 5-6 Å).

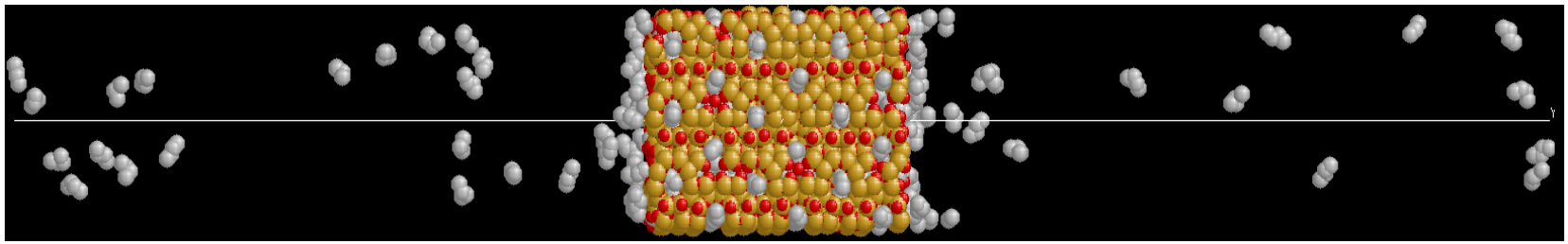
In the industry they are used as molecular sieves.

# Non-isothermal adsorption

The simulations mimic a real adsorption uptake experiment

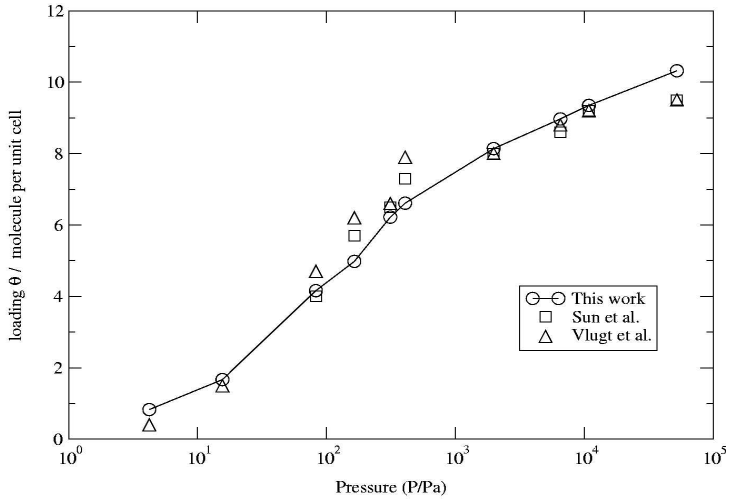


# Silicalite in contact with gas of n-butane



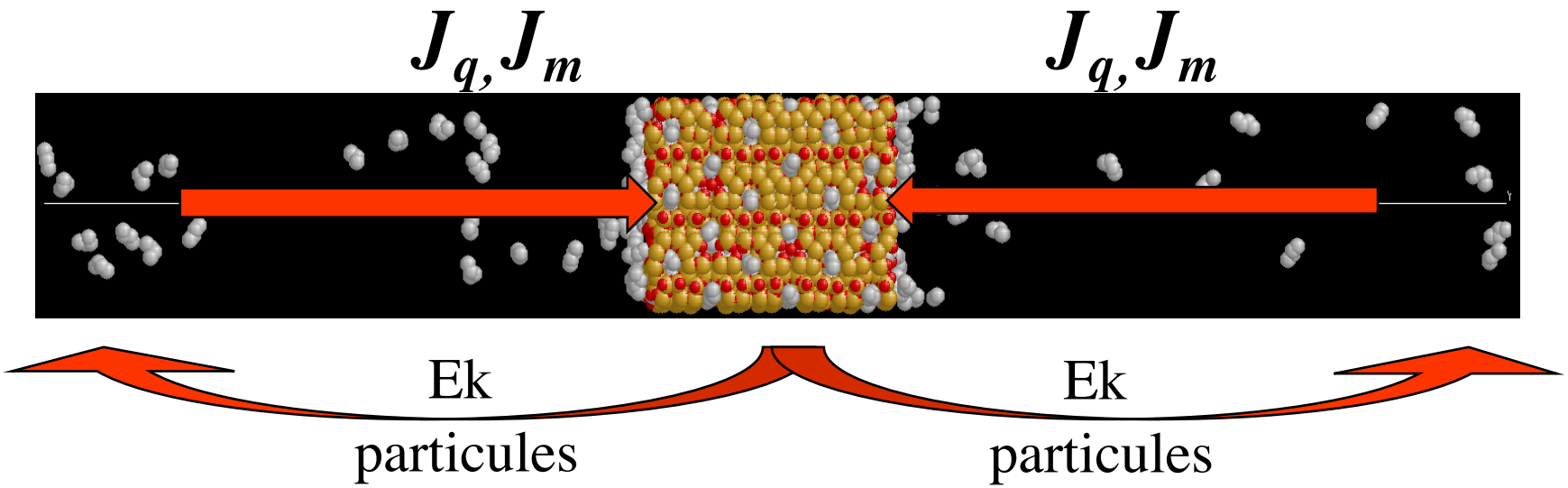
y

# Isotherms of adsorption at 300 K




$\Delta H_{ads} \approx -55$ kJ/mol

# HEAT AND MASS FLOWS APPLIED UNDER STATIONARY CONDITIONS




=> Large resistivity to heat and mass transfer

=> Large coupling between heat and mass flow

(q* close to heat of adsorption)

# Non-isothermal adsorption

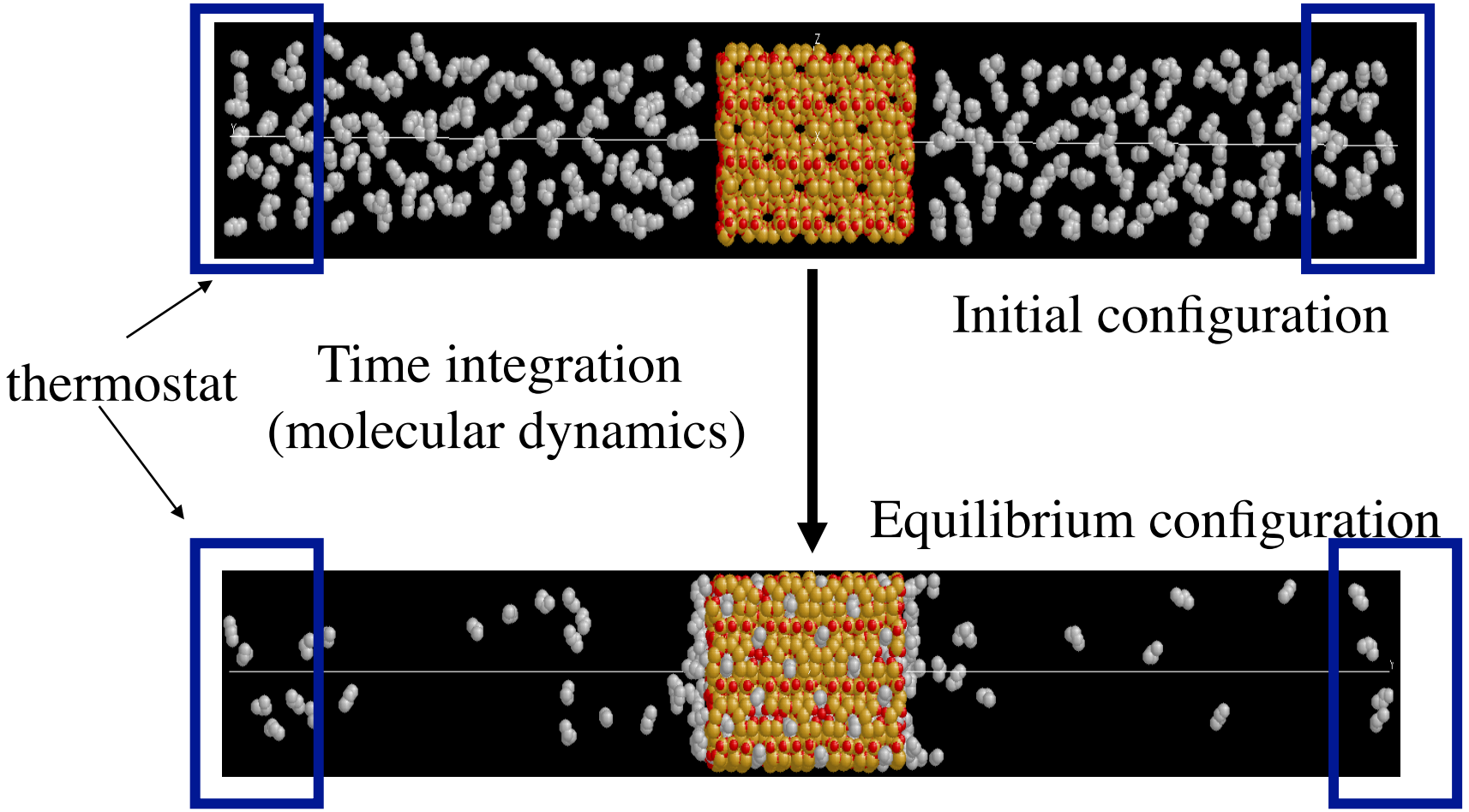
**D.M. Ruthven et al., Kinetics of non-isothermal sorption in molecular sieves crystal, AiChE, vol. 26, p16 (1980)**

-Adsorption is exothermic, $\Delta H_{ads} \approx$ -55 kJ/mol (n-butane) + high resistance to surface heat transfer => the zeolite temperature increases.

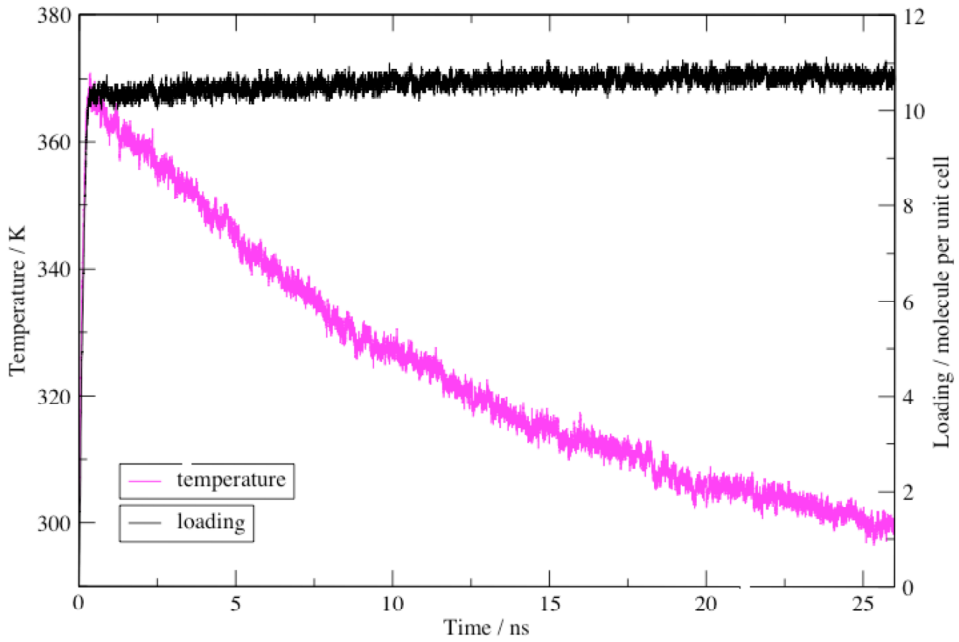
- If the diffusion coefficient is high, the release of the energy to the surrounding, to thermostat the zeolite, can govern the kinetics of adsorption.

# Non-isothermal adsorption

The simulations mimic a real adsorption uptake experiment



# Non-Isothermal Adsorption

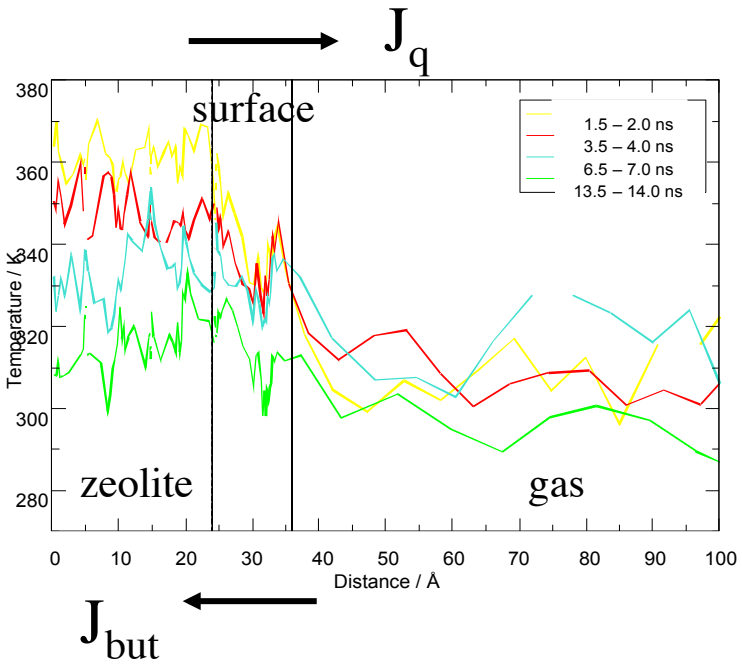


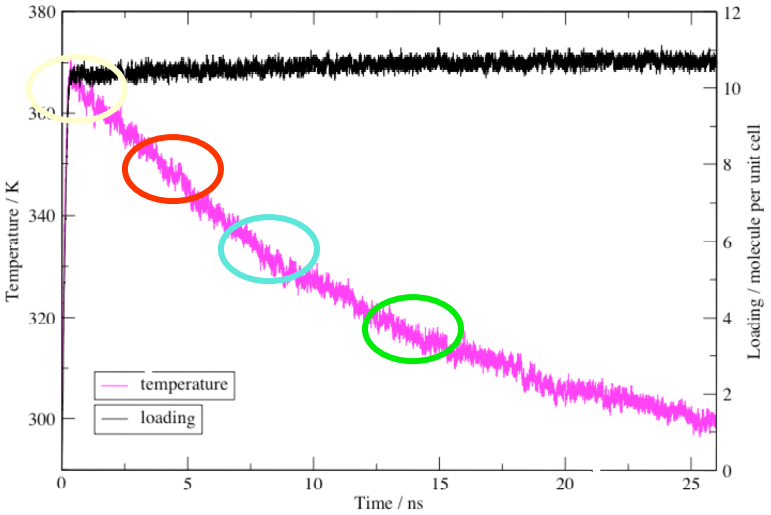

2 stages:

a) 1 ns the relaxation of the chemical potential (90% of the equilibrium loading)

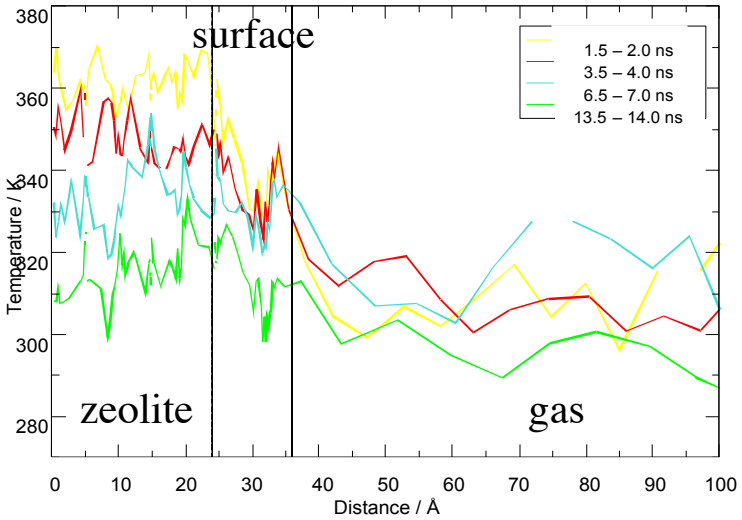
b) 25 ns the relaxation of the temperature (10% of the equilibrium loading)

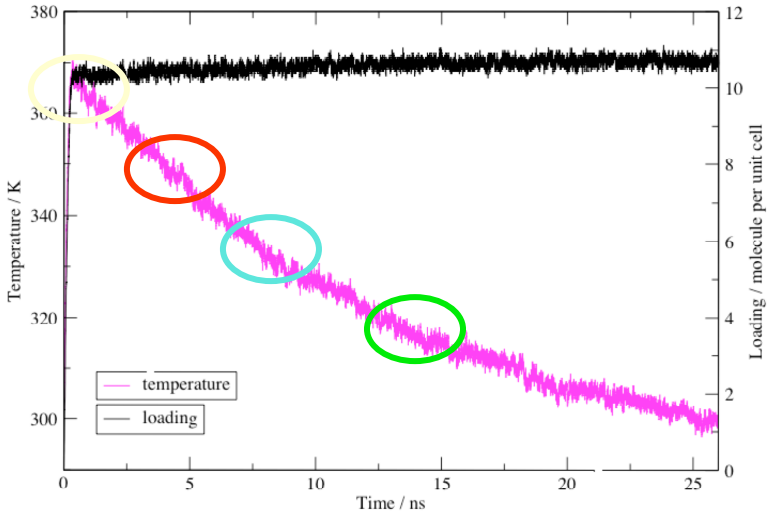
# Surface thermal resistance



# Surface thermal resistance




## Surface heat and mass fluxes

$$J_q = -\lambda^s \Delta T + q^* J_{but}$$

$$J_{but} = -\frac{c_b^2 q^*}{R_{\mu\mu} T^g T^s}\Delta T - \frac{c_b^2}{R_{\mu\mu} T^s}\Delta(\mu_b)_T$$

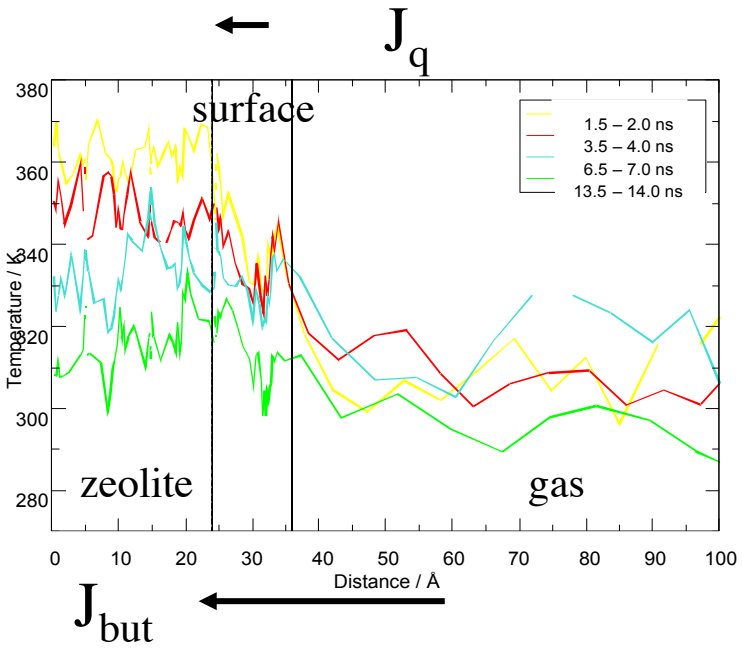
desorption ← adsorption

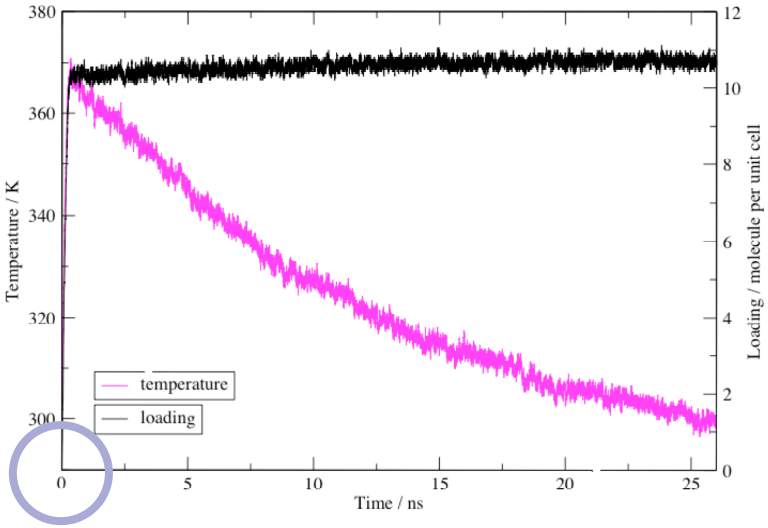
$$\Delta T = T^g - T^s \le 0, \quad \Delta(\mu_b)_T = \mu_b^g(T^s) - \mu_b^s(T^s) \ge 0$$

$q^*$ = heat of transfer, $\lambda^s$ = heat conductivity

$R_{\mu\mu}$ = mass resistance

# Surface thermal resistance




Temperature profiles at different simulation times

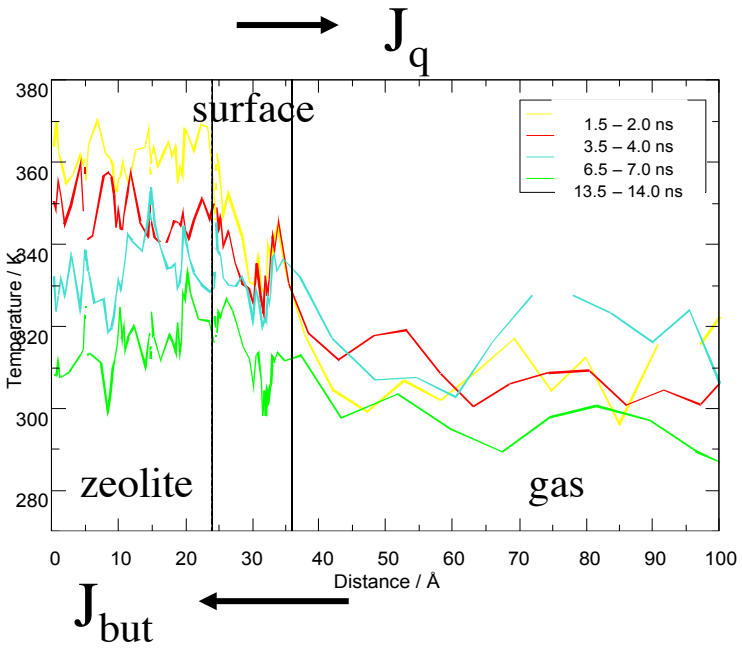
Initial situation

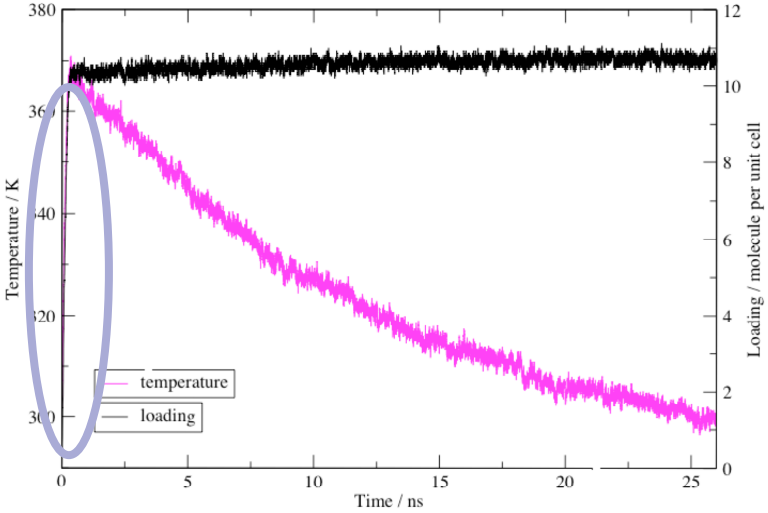
$$J_q = q^* J_{but}$$

$$J_{but} = -\frac{c_b^2}{R_{\mu\mu} T^s} \Delta(\mu_b)_T$$

$\Delta T = 0, \quad \Delta(\mu_b)_T$ large => $J_{but}$ large

# Surface thermal resistance




Temperature profiles at different simulation times

$$J_q \approx -\lambda^s \Delta T$$

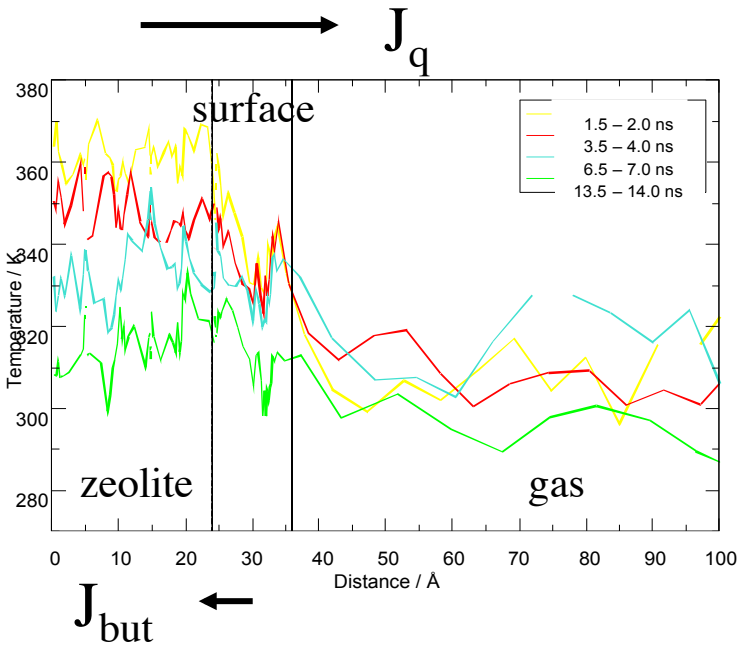
$$J_{but} = -\frac{c_b^2 q^*}{R_{\mu\mu} T^g T^s} \Delta T - \frac{c_b^2}{R_{\mu\mu} T^s} \Delta(\mu_b)_T$$

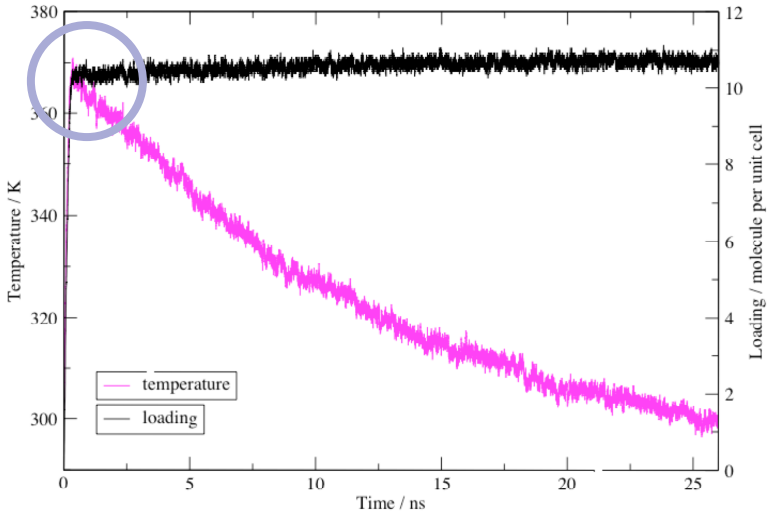
desorption adsorption

First stage 0-500 ps

$|\Delta T| \uparrow, \quad \Delta(\mu_b)_T \downarrow, |J_{but}| \downarrow$

# Surface thermal resistance




Temperature profiles at different simulation times

$$J_q \approx -\lambda^s \Delta T$$

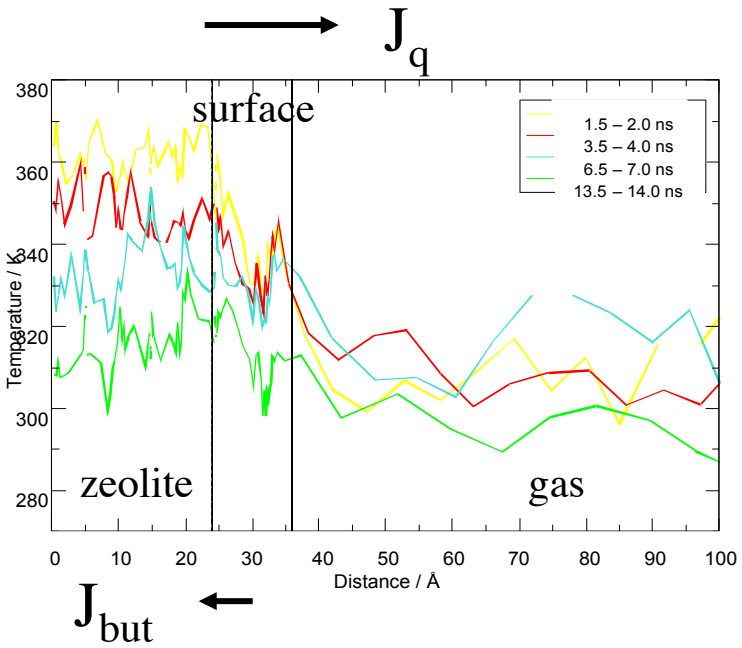
$$J_{but} = -\frac{c_b^2 q^*}{R_{\mu\mu} T^g T^s} \Delta T - \frac{c_b^2}{R_{\mu\mu} T^s} \Delta(\mu_b)_T \approx 0$$

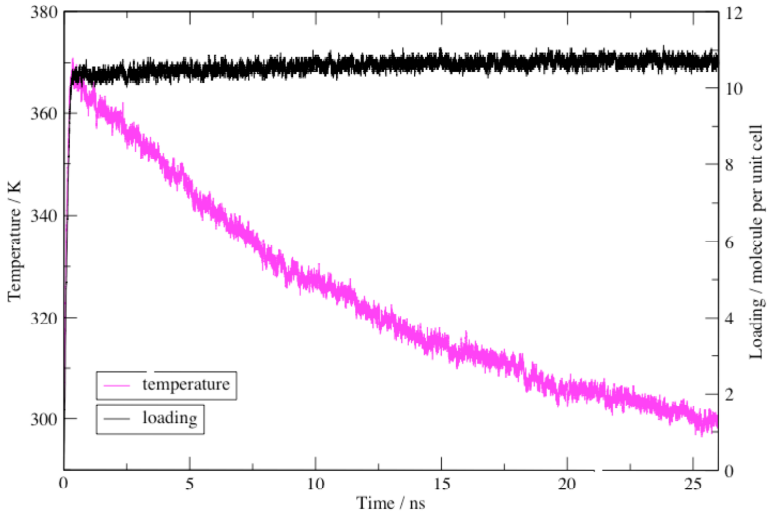
desorption ← adsorption

## Beginning second stage

$\Delta T$ large, $\Delta(\mu_b)_T$ small, $J_{but}$ small

# Surface thermal resistance




Temperature profiles at different simulation times

$$J_q \approx -\lambda^s \Delta T$$

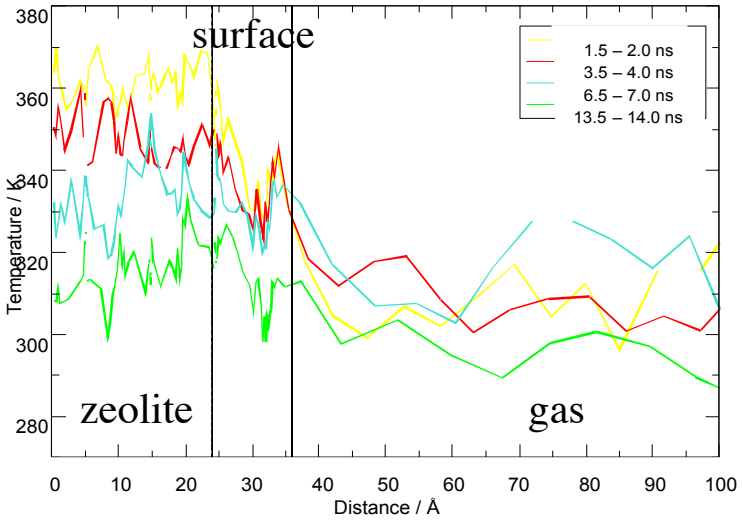
$$J_{but} = -\frac{c_b^2 q^*}{R_{\mu\mu} T^g T^s} \Delta T - \frac{c_b^2}{R_{\mu\mu} T^s} \Delta(\mu_b)_T$$

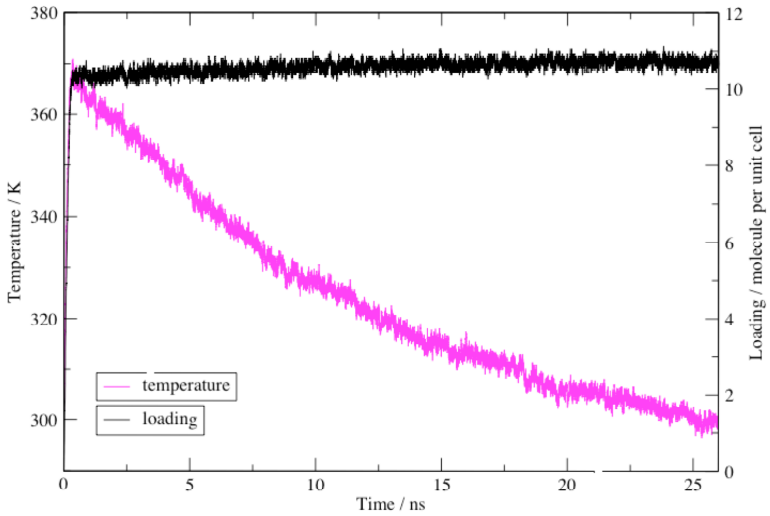
desorption adsorption

Second stage

$|\Delta T| \downarrow, \quad \Delta(\mu_b)_T \downarrow, J_{but}$ small

# Surface thermal resistance




Temperature profiles at different simulation times

$$J_q \approx -\lambda^s \Delta T$$

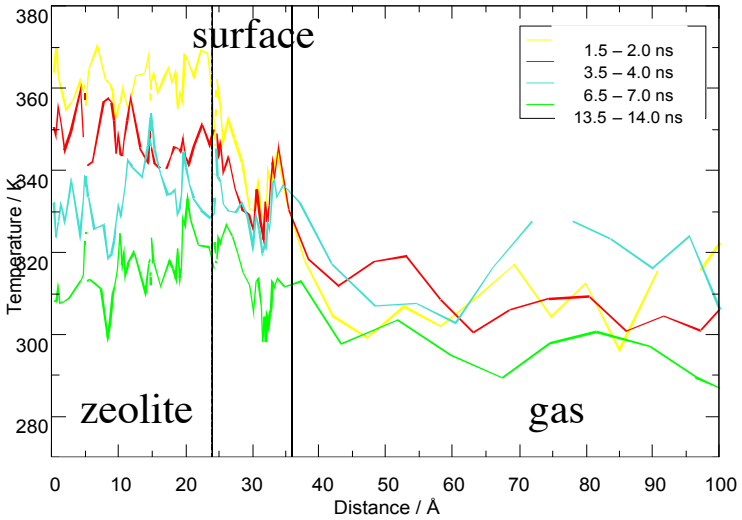
$$J_{but} = -\frac{c_b^2 q^*}{R_{\mu\mu} T^g T^s}\Delta T - \frac{c_b^2}{R_{\mu\mu} T^s}\Delta(\mu_b)_T$$

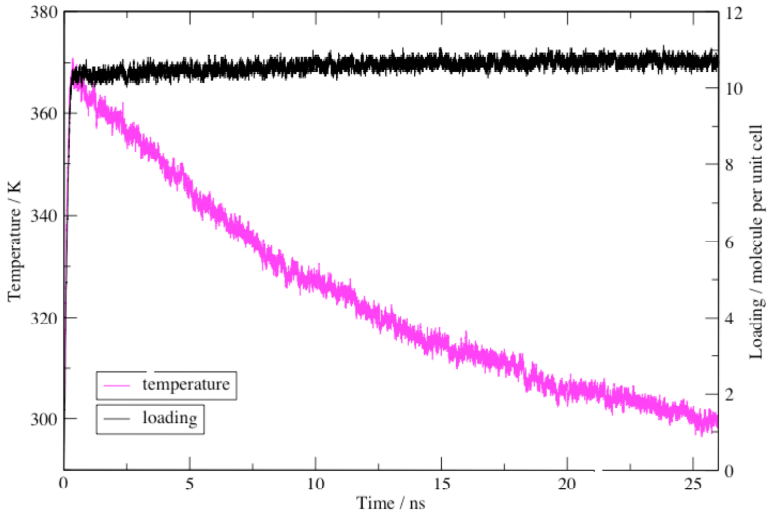
$$\lambda^s = 3.4\,10^{-4}\ \mathrm{W/Km}$$

$$C_v = 1500\mathrm{kJ/(Km^3)},\ \text{exp: } 1400\mathrm{kJ/(Km^3)}$$

$$\lambda(gas) \approx 10^{-2}\mathrm{W/Km},\ \lambda(zeo) = 1.5\ \mathrm{W/Km}$$

# Surface thermal resistance




Temperature profiles at different simulation times

$$J_q \approx -\lambda^s \Delta T$$

$$J_{but} = -\frac{c_b^2 q^*}{R_{\mu\mu} T^g T^s} \Delta T - \frac{c_b^2}{R_{\mu\mu} T^s} \Delta(\mu_b)_T$$

The non isothermal kinetics is governed by the thermal diffusion effects and thermal resistivity at surface

# Conclusion

-Molecular dynamics study of transport of mass and heat through liquid-vapour interface of binary Lennard-Jones systems and the non-isothermal adsorption  zeolite – n-butane system

-Local equilibrium hypothesis is valid for surfaces, non-equilibrium thermodynamics can be applied

-Larges resistances to heat and mass transfer at the surface, they increase with the surface tension

-Large coupling between the two components and between heat and mass transfer (heat of transfer)
$\Rightarrow$important to take into account to model evaporation/ condensation, adsorption/desorption processes