Thermal osmosis in membranes

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Aim of the Project

- ✓ Study the transport of gaseous components and heat across a membrane
  - → reveal molecular mechanisms of rate-limiting processes and factors that influence the selectivity of gas adsorption in membranes

- ✓ As a model membrane is used a pure siliceous zeolite membrane (silicalite).

- ✓ The method that is used is the non-equilibrium molecular dynamics (NEMD) simulation.

Introduction : zeolites

Zeolites :

crystalline microporous aluminosilicates with periodic arrangements of cages and channels of nanometer dimensions.

Properties :

- ion-exchange properties
- sorption capacity
- shape selectivity
- catalytic properties
- …

→ determined by the structures

Applications :

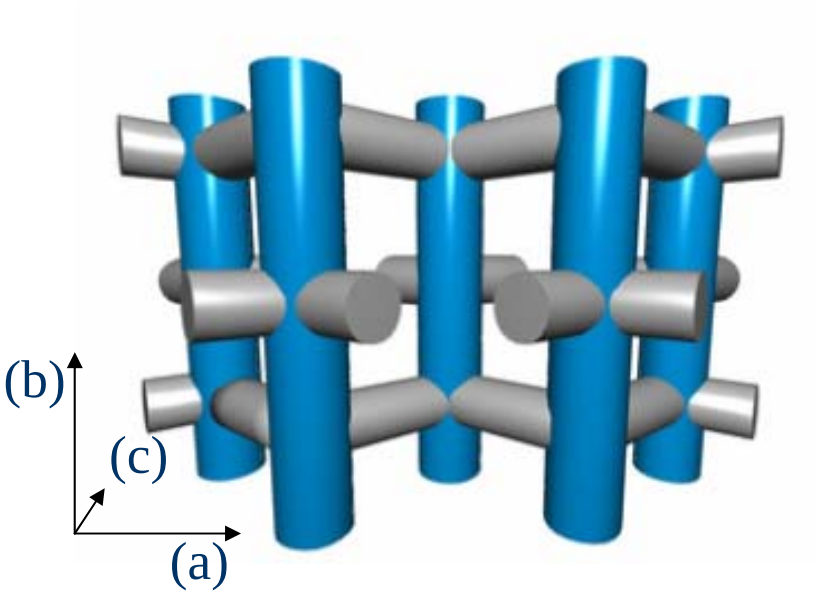
- purification
- adsorption
- catalytic cracking
- catalytic reforming
- fine chemicals synthesis
- …

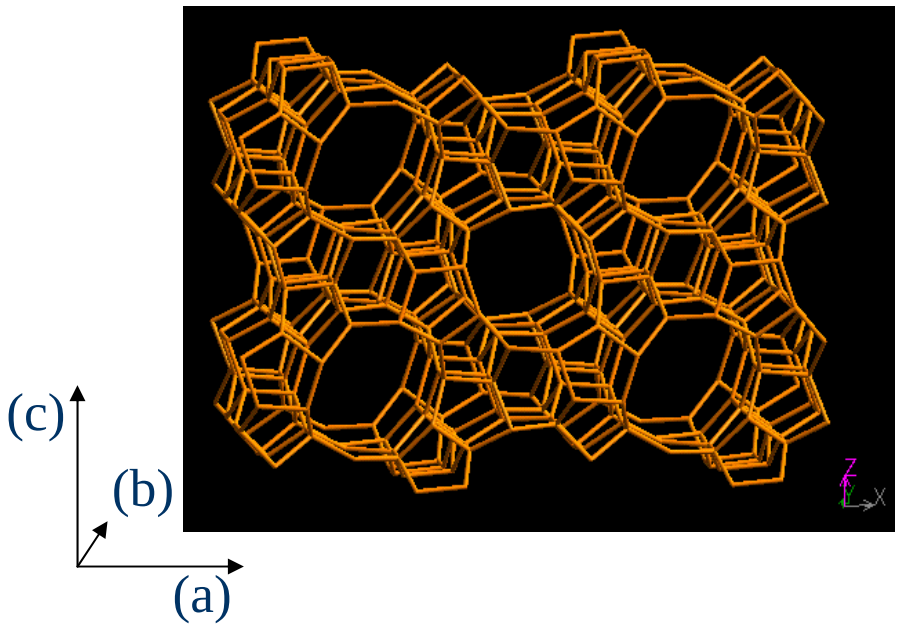
Introduction: silicalite

Silicalite :

pure siliceous MFI zeolite ($[SiO_2]_{96}$ per unit cell) characterized by interconnected zig-zag and straight channels of a nominal pore size ~ 0.6 nm, running along the (a) and (b) directions, respectively

→ Medium pore size: useful for separation processes.





Scientific importance of the project (1)

The dynamic behaviour of alkanes inside zeolite micropores is important in determining its catalytic and separating properties.

Different experimental techniques to calculate D :

- ✓ Macroscopic methods (gravimetric and manometric)
  → Transport diffusion (Fick's law)
- ✓ Microscopic methods (PFG-NMR and QENS)
  → Self diffusion (Einstain relation)

Until recently the literature has agreed that intra-crystalline diffusion was the rate limiting process

But discrepancies between the results from different techniques suggest that this explanation may be too simple

Scientific importance of the project (2)

The Department of Chemistry has extended the theory of non-equilibrium processes to surface transport phenomena which predicts :

- ✓ excess resistivities to the transport of mass and heat across the surface
- ✓ large coupling effects between them

⇨ Important role in zeolite gas adsorption

MD simulations is an important tool for studying sorbates in zeolites:

- ✓ both the equilibrium and the dynamical behaviour can be studied
- ✓ allows to get insight into the microscopic mechanism of the process

This useful technique will be used to learn more about gas-membrane interface transports.

Program for the PhD

The plan of the project will focus on the following points:

- ✓ Use NEMD simulations to analyze the adsorption of hydrocarbons on a zeolite membrane
- ✓ Develop equations of gas transport and adsorption that are capable of including thermal effects
- ✓ Test these equations on a well defined model system
- ✓ Application to new systems

The simulations

Adsorption of n-butane on a silicalite membrane

Semi-infinite membrane with the external surfaces perpendicular to y direction (= direction of straight channels), in contact with 250 molecules of n-butane.

1) **Fixed temperature at the boundaries in y direction**

   To mimic the real uptake-experiments

   → analysis of the adsorption process

2) **Constant temperature (everywhere and at any time)**

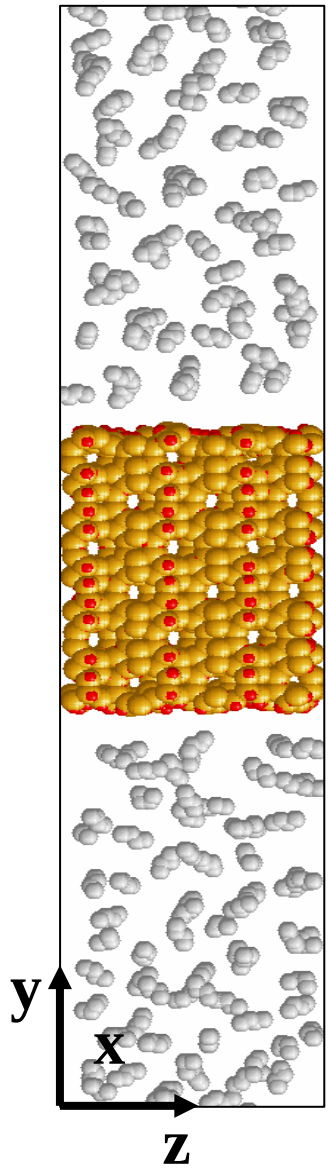
   To mimic the end state of the experiments

   → confirm the equilibrium situation of case (1) avoiding equilibration

3) **Constant total energy**

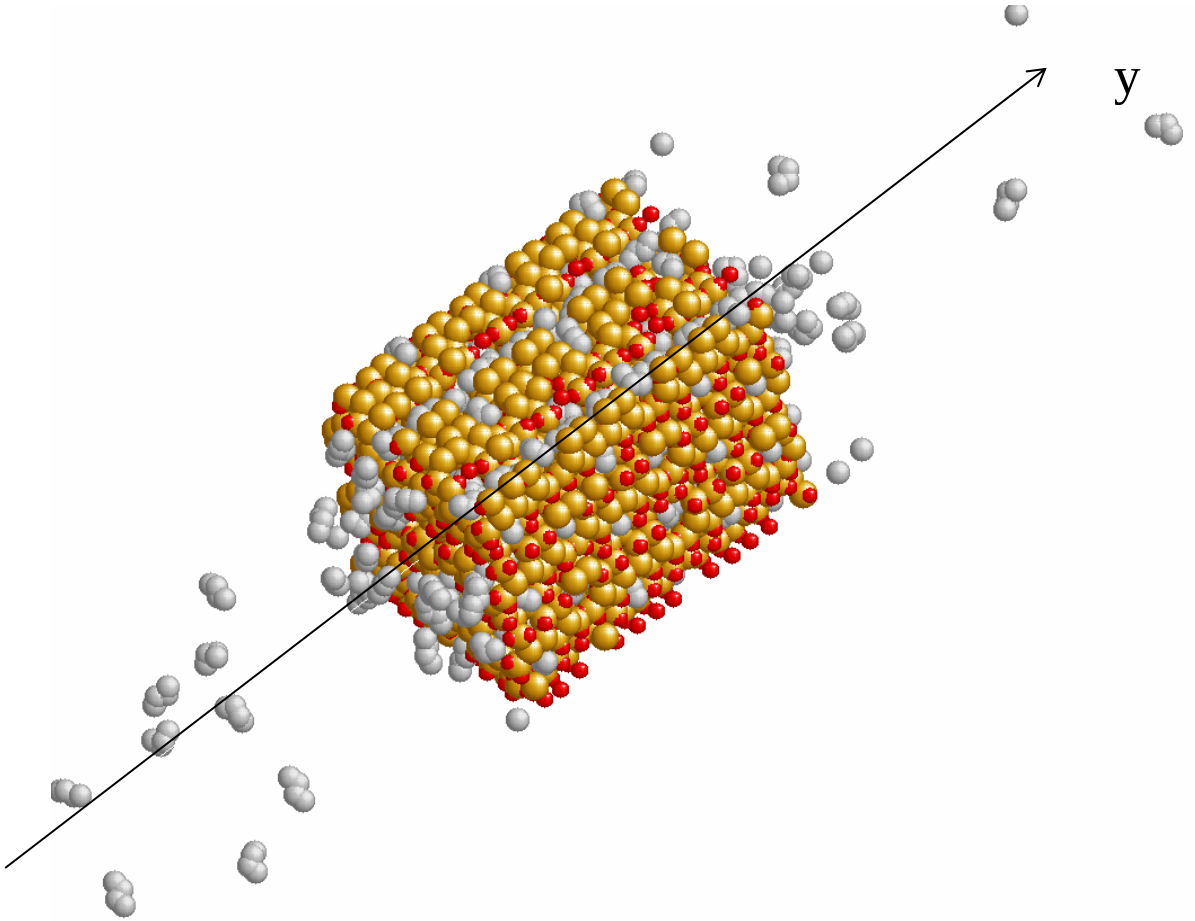
   System isolated and allowed to evolve in time.

   → differences compared to case (1)



Results obtained so far

Adsorption of n-butane on a silicalite membrane

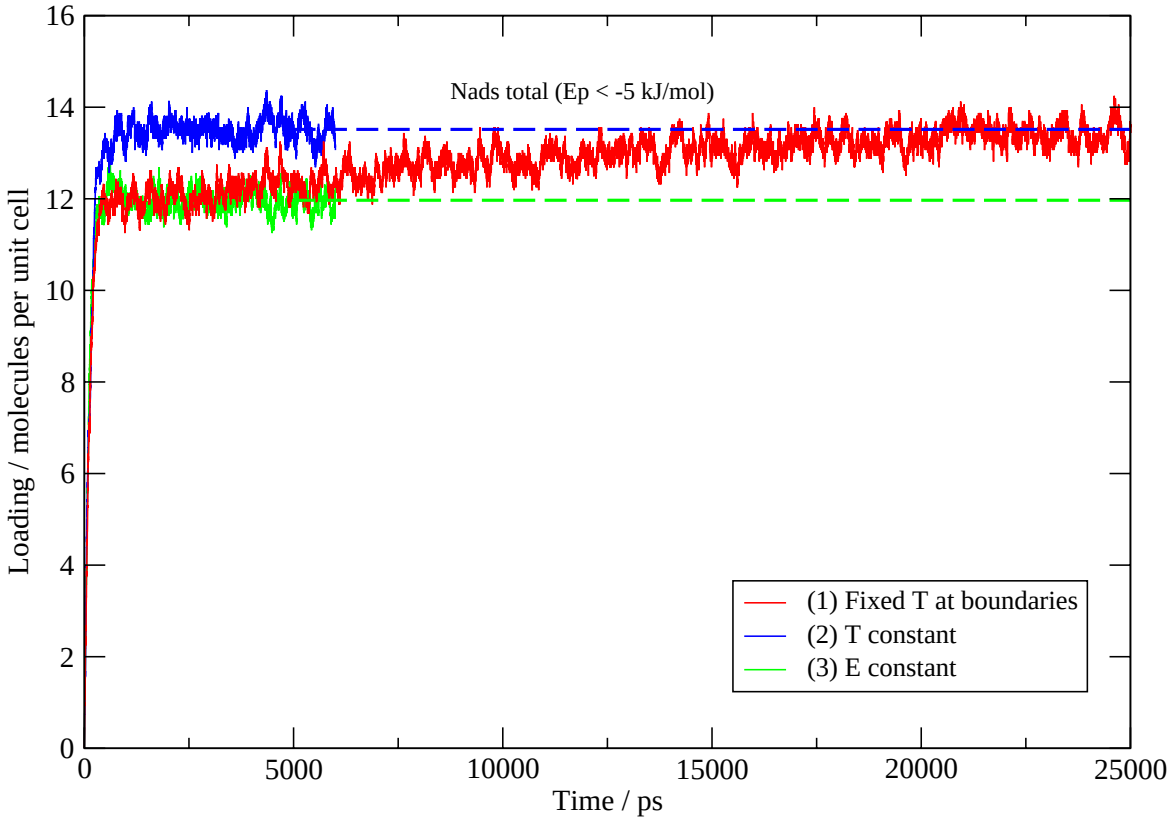


Results : Loading vs. Time

Two stages of the adsorption process:

1) Rapid stage where ~ 95% of the capacity is filled in ~ 200 ps

2) Slov

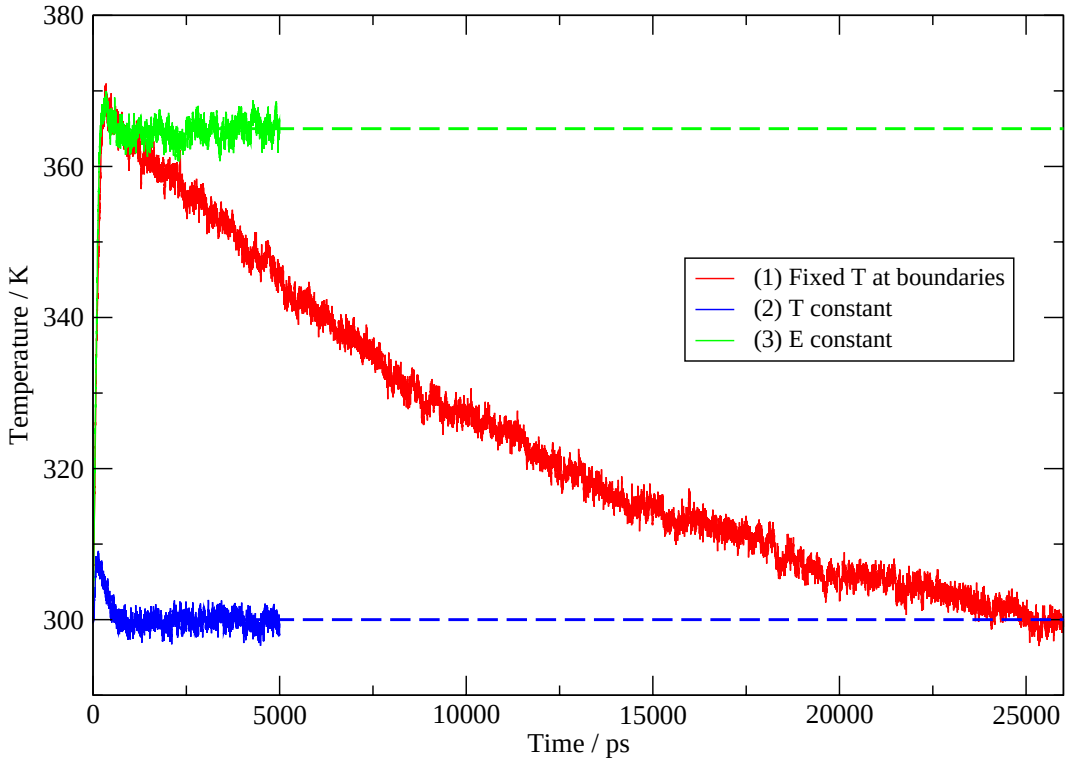


Results: Temperature vs. Time

Both stages of the adsorption process are non-isothermal :

1) Jump of 70 K of the temperature of the membrane caused by the heat released by the adsorption process.

2) Exponential-like decline of the temperature back to 300 K due to the fact that heat is driven out through the boundaries.



Results : Temperature vs. loading

Temperature perfectly linear in loading in both stages.

First stage:

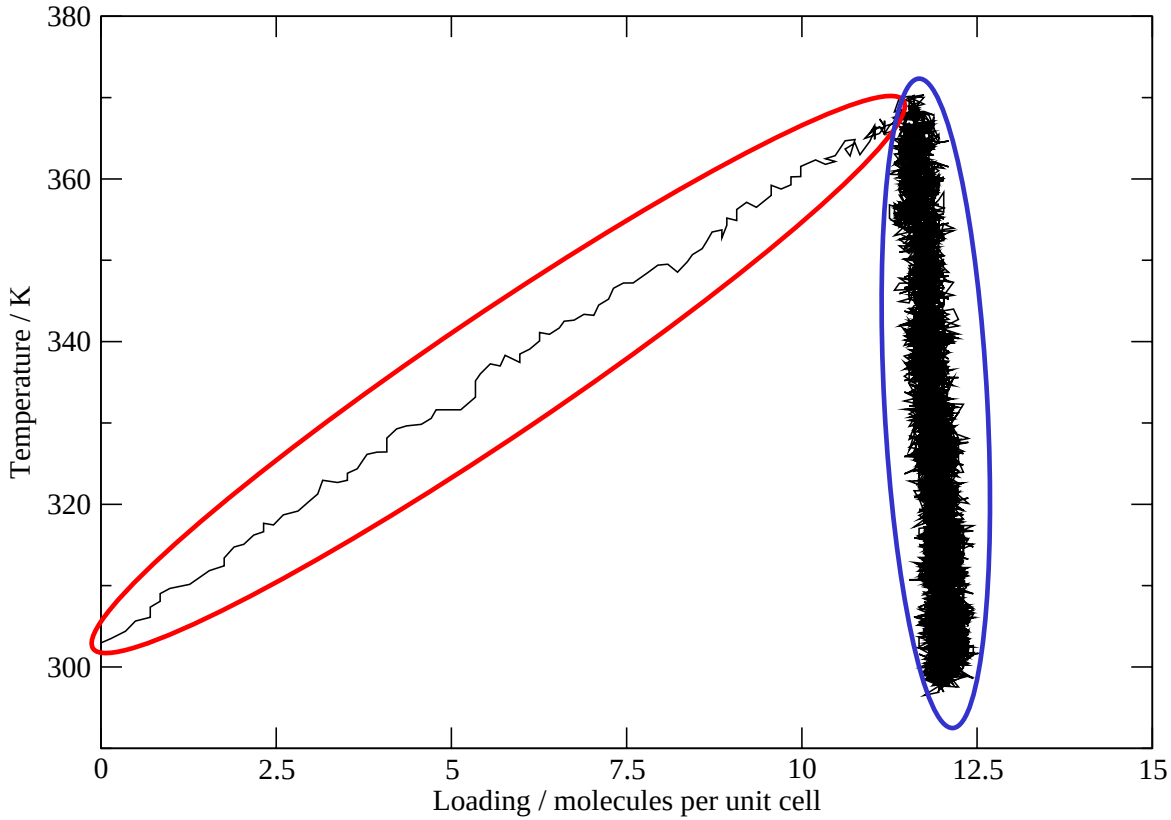
adsorption governed by a large chemical driving force.

Rapid increse in loading and in zeolite temperature (large enthalpy of adsorption)

Second stage:

thermal forces relaxes to zero while the adsorption slowly increases

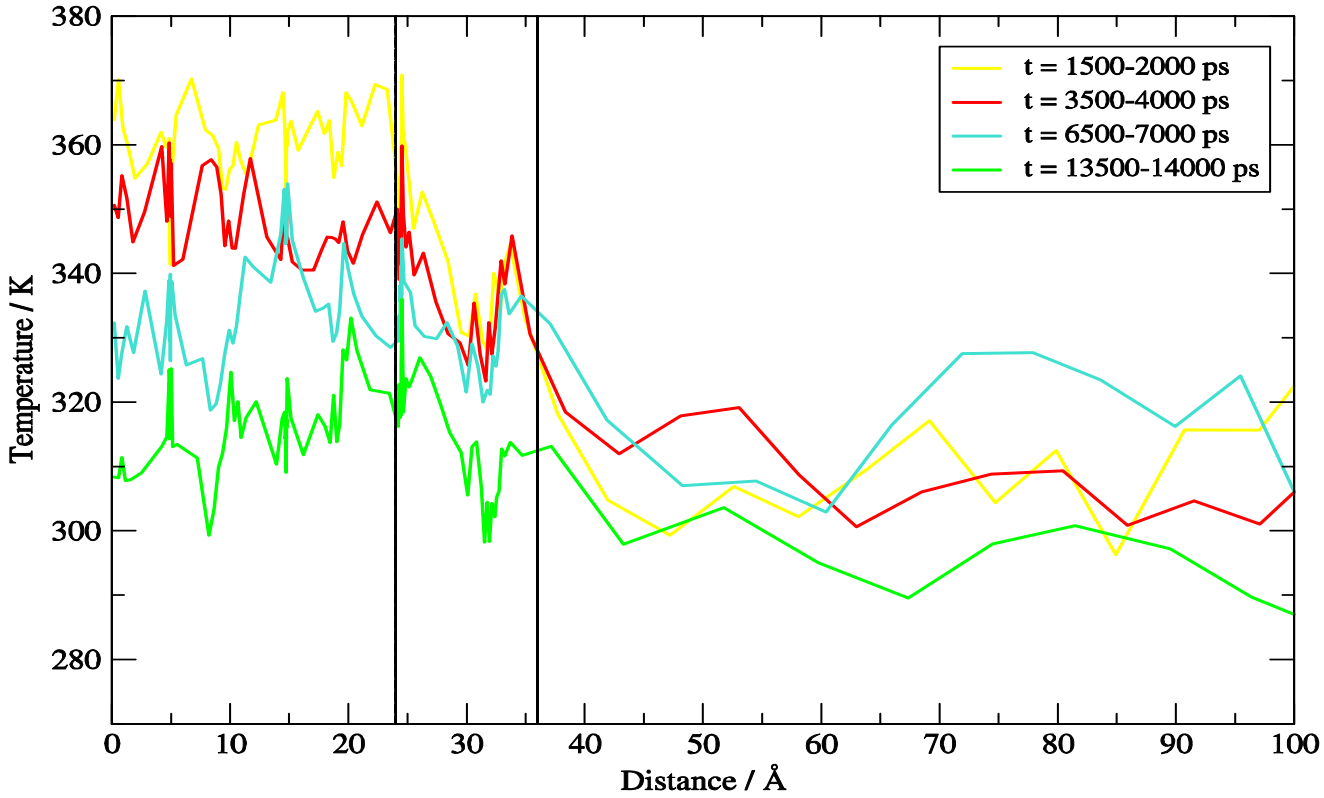
(additional uptake due to the reduction of the zeolite T)



Results : Temperature vs. Distance

Large gradients of temperature across the external surface of the crystal during the adsorption process

→ Large resistivity to heat transfer at the surface



Conclusions

- Adsorption is a two-step process : both steps are non-isothermal
- Butane flux is driven not only by the gradient of chemical potential but also by the thermal force which develops across the external surface
- The surface is rate-limiting to heat transfer

The presence of the thermal force can explain the discrepancy in D between equilibrium and non-equilibrium techniques

Including this force we can improve the understanding and the design of technologies for multi-components separation

Future plans

- Modify the MD code in order to:
  - ✓ Obtain the transport coefficients and the Onsager's resistivities
  - ✓ Analyse the coupling coefficients
- Apply the results to different systems

Thanks for your attention