1 Adsorption Desorption equilibrium

1.1 A bit of theory

Let the system be a surface in interaction with a gaz that mean that the gaz can adsorbate and desorbate at the surface. We note r_A and r_D the adsorption and desorption rate of gaz respectively and θ the fractional surface coverage of gaz. Moreover we consider that are no interaction between the molecule of gaz adsorbate on a surface. That mean each molecule adsorpbate on the surface can be treated independently of his environement. To solve the time evolution of our system we begin from master equation (1) :

$$\frac{\partial P(\sigma,\, t)}{\partial t} = \sum_{\sigma'} W(\sigma' \to \sigma)P(\sigma',\, t) - W(\sigma \to \sigma')P(\sigma,\, t) \tag{1}$$

1. We will consider that the state σ is the surface coverage of gaz θ and the transition $W(\theta' \to \theta)$ is represented by the rate r_A and $W(\theta \to \theta')$ by r_D. Knowing that the adsorption rate is associate at uncover part of the surface $1 - \theta$ and the desorption rate at coverage part of the surface θ, rewrite the eq. (1) like a variation in time of coverage surface $\frac{\partial \theta}{\partial t}$ as function of r_A, r_D and θ.

2. At the steady state the left term of eq. 1 vanishing. Write θ as function of r_A and r_D at equilibrium between gaz and surface.

3. Now integrate the equation wrote in question 1. and write the fractional coverage of surface $\theta(t)$ as function of r_A, r_D and t. Find K and G in the equation:

$$\theta(t) = K.(1 - e^{G.t})$$

1.2 Go now in the KMC code

We will compile the exercie file Ex01.f90 or Ex01.c (as you want) like a shared library. The makefile is already write for a source directory positioned in parent forlder (../src). The program work with an input file (input_KMC.dat) to define the system and an event file (lib_event.dat) which contain the event information. We will define in "input_KMC.dat" the general parameters of our system.

1. Define a system in 2 dimensions with key word "system_dimension"

2. Define a square of 128x128 with "nsite_x" and "nsite_y"

3. Define "bound_condition" p p f, that mean periodic, periodic, no periodic

4. Define "init_config" : none

5. Define "algorithm" BKL

6. Define "node_prop" 2, the number of state of each node (0 or 1)

7. Define the number of properties you want compute "calc_properties"

8. Number of step with "step"

9. The frequence of write the result "freq_write"

10. Define the dynamic library with "shared_lib"

System Implementation

In the first step we will give directly the rate r_A and r_D to the code to make a connection with the equation derived previously. In the second part we will introduce the thermodynamic point of view with the flux of particule gaz of the surface and the desorption mechanism.

1. In the file "lib_event.dat" you can define the event. First you declare the number of event by key word "Number_of_event" and the number of event in the same line.

2. For each event you must give: "index of event" "initial state" "final state" "prefactor" "rate". In this case the value of rate of each event will be stored in array ebarrier. You can modify the event parameter in your user file exo_1.f90 (or exo_1.c) in routine read_event(struct kmc_type).

3. In the routine "event_rate_calc(struct kmc_type)" you must write the part of code which identify the possible event, compute and store the rate in array ptr_event_rate(ievent) for each site. Moreover you will store the total rate of each site in array ptr_rate(isite)

4. In the routine "analyse(struct kmc_type)" you will define the propertie of the system that you want mesure. You can define the number of properties you want in the input file "input_KMC.dat" with the key word "calc_properties". Here you define one or more if you want. So in the routine analyse you compute the fractional coverage of the surface θ as a number of site $== 1$ in your system.

5. Now compile your dynamic library. If the kMC code is already compiled you can execute the command "run" in the Makefile of your exercie. it will copy the executable (KMC.x) and after ./KMC.x input_KMC.dat.

6. Let run for 40000 step and write the result each 1000 step.

You can see the program run and write some information about the simulation as the "Step", "Time", "Rand_rate" and 'Rand_time". Moreover you can see one column more that represente the propertie that you have compute with routine "analyse". The program write automatically the result in the file "fort.100". So you can see the time evolution of the fractional coverage of the surface as function of time with gnuplot for instance. So in gnuplot:

1. Plot the fractional coverage of the surface as function of time

2. Plot in the same graph the fractional coverage of the surface and the function $\theta(t)$ that you have found previously.

3. If the two courve doesn't correspond... back at the begining of the section...

Optimisation

May be you have noticed that at each step the algorithm compute the rate of all the system while only one site of the system change its state. So you can recompute the rate of this specific site and let quiet the rest of the system. To do that you save the index of the site when you select and use this index in the next step to compute only one rate. Try to do that....

For this may be you must define a global variable in the header in language C or in a module in fortran.

Time Versus System's size

In this system the random time is connected with the system's size. To see that run 3 differents size of our system: 50x50, 128X128 and 528x528. Comment the time and coverage between the three size of the system.

Introducing a bit of physic

At this step we have see that our simulation provide an solution of the detailed balanced which is an importante condition to model in right way the physical phenomenum. Now we introduce the thermodynamic point of view. Considering an atomic gaz of hydrogen (H) and surface (100) of Nickel (Ni(100)). The adsorption depend on the pressure and temperature of gaz by the flux of atome which touch the surface. We have the equation:

$$F = \sqrt{\frac{\mathcal{N}_a}{2\pi k_B}} . \frac{P.S}{\sqrt{M_H.T}} \qquad (2)$$

with $\mathcal{N}_a$ Avogadro number, k_B Boltzmann constant $(J.K)$, P the pressure of gaz (Pa), S the surface (m), M_H the hydrogen masse (kg) and T the temperature (K). Now we can compute the adsorption rate of an hydrogen on the Ni surface as $r_A = F.s$ where s is the sticking probability which will take at 1 to simplify the problem.

- To define the flux of particule on the surface we need a partial pressure and the masse of the particule on the gaz. You will add in read_event routine the instruction to read the "type of particule", the partial pressure of this element and it masse. This where the key word "partial_pressure" is read in event_file. You can help you reading the read_event routine. To differentiate adsorption and desorption event you can define an negative energy barrier at adsorption event.

- Also the cell parameter of Ni suface is 3 Å (10^{-10}m). So give the cell parameter in input file with the keyword "scale" to store the value in variable 'scale' in KMC structure. You will use this value to compute the good value of the flux. You can use the parameter 'ang' = 10^{-10} define in program.

The desorption rate depend on the bond strength between the hydrogen and the N_i at the surface. To compute we use the Transition state theory which describ this phenomenum as

$$r_D = \omega_{HN_i} . e^{-\frac{\Delta E}{k_B T}}$$

where $\omega_{HN_i} \sim 1.8\text{x}10^{-13}$ Hz represent the hydrogen vibration at the perpendicular direction of the surface and $\Delta E = 2.7\,eV$ represente the energy frees during the adsorption.