CENTRE D'ÉLABORATION DE MATÉRIAUX ET D'ÉTUDES STRUCTURALES

cnrs

UNIVERSITÉ TOULOUSE III PAUL SABATIER

CALMIP

THERMAL MASS TRANSPORT MECHANISM OF AN ADATOM ON A CRYSTALLINE SURFACE

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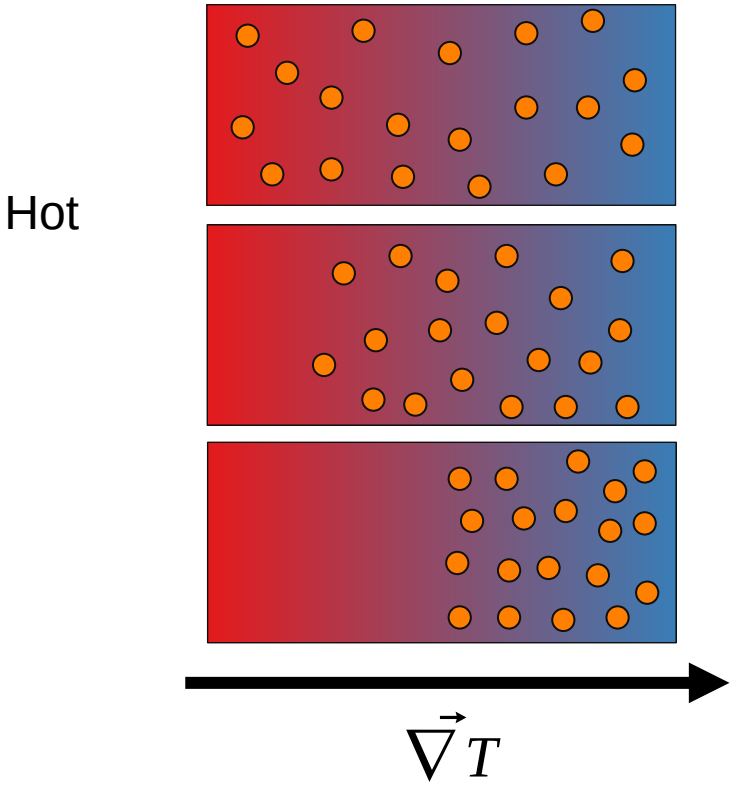
CEMES-CNRS (UPR-8011)

09/11/2023

THERMOMIGRATION: DEFINITION

Thermomigration: diffusion of particles subjected to a thermal gradient



→ Density current along the thermal gradient

→ Displacement of particles towards the cold side

THERMOMIGRATION: BACKGROUND

Liquids → Ludwig(1856) and Soret(1879) ✓

Gases → Tyndall(1870) and Strutt(1882) ✓

Solids → Pfann (1955) and Huttington (1968) ✓

Surfaces → Less studied ✗

Recent experiments (growth [1, 2], transport [3,4]) involving surface thermomigration

[1] Xie, et al. Controlled growth of single-crystalline metal nanowires via thermomigration across a nanoscale junction. Nat Commun 10, 4478 (2019).
[2] Samarao, et al. Temperature Compensation of Silicon Resonators via Degenerate Doping. IEEE Transactions on Electron Devices. 59. 1 – 4. (2010).
[3] Barreiro, et al. Subnanometer motion of cargoes driven by thermal gradients along carbon nanotubes. Science. 320, 5877 :775-8. (2008)
[4] Leroy, et al. Determination of the Thermomigration Force on Adatoms. Phys. Rev. Lett.,131, 116202(2023)

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I THERMOMIGRATION: TOOLS

Applied thermal gradients to surfaces:

➡ In materials, the transport of heat can be provided by :

→ Propagation of electrons → Metals

→ Propagation of phonons → Semiconductors and insulators

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THERMOMIGRATION: TOOLS

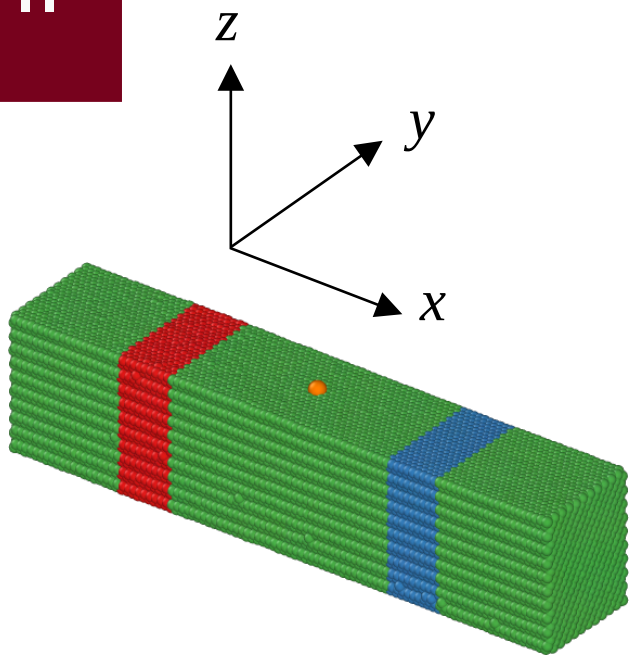
Applied thermal gradients to surfaces:

→ In materials, the transport of heat can be provided by :

Objective: To understand the thermomigration of an atom or a cluster on a crystalline surface in the presence of a thermal gradient

Tools: theoretical study with molecular dynamics simulation

II MODEL

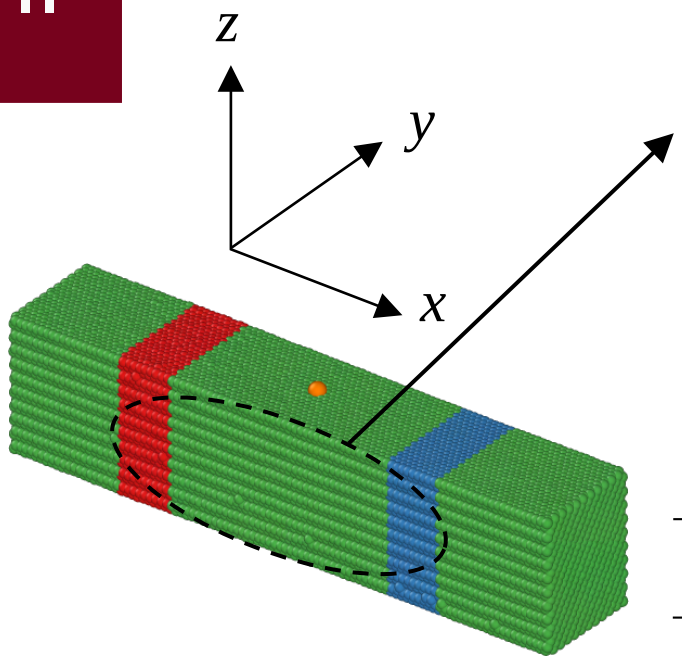


Schematic of the simulation box

- Face-centered cubic crystal (FCC)
- Adatom on the (1,1,1) surface
- Atomic interactions → Lennard-Jones potential
  → reduced Lennard-Jones units
- Periodic conditions in x and y directions
- Hot and cold regions (Nosé-Hoover thermostats)

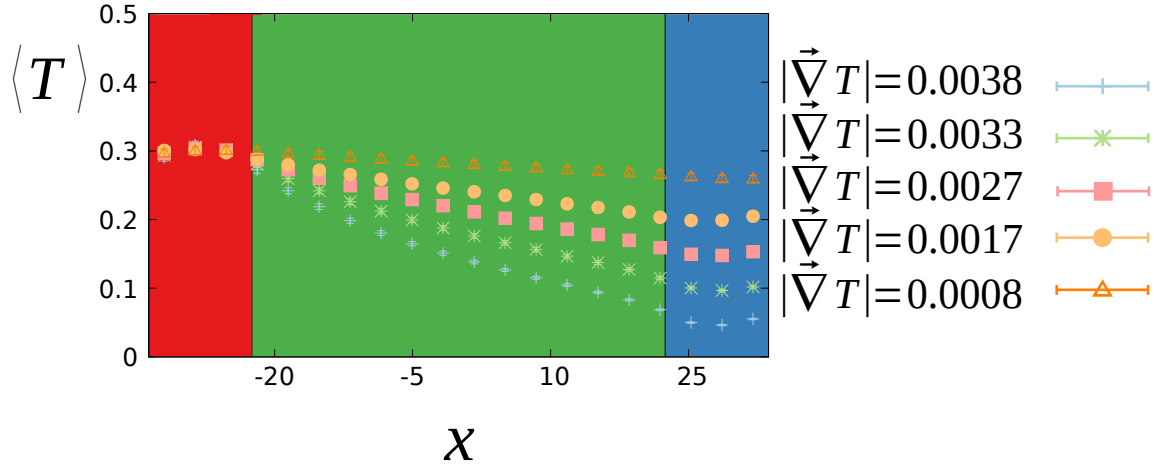
II

MODEL



Schematic of the simulation box

→ Substrate in the steady state



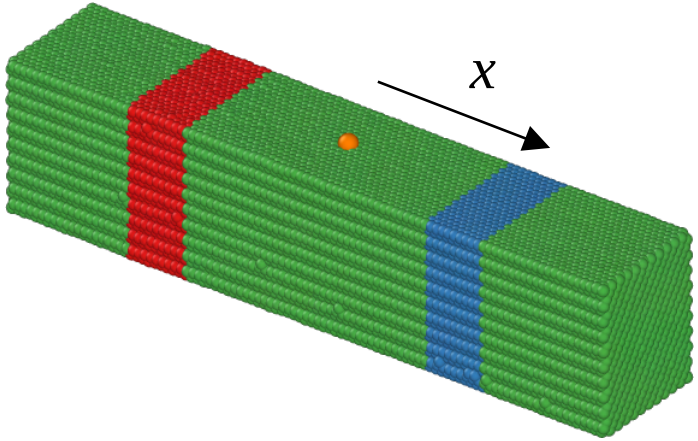
→ For the lowest gradients, the profile is linear.

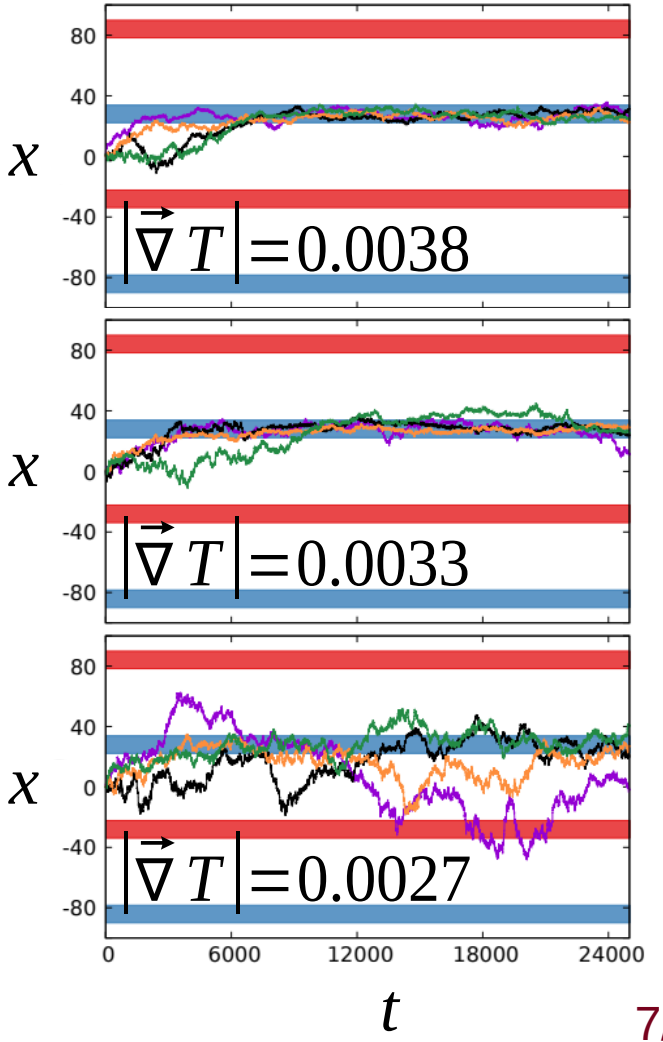
→ For the highest gradients, the profile is non-linear.

→ Substrate leaves the domain of validity of Fourier's law

III

STUDY OF TRAJECTORIES





- The adatom moves towards the cold region
- Competition between the drift induced by the thermal gradient and the diffusion
- The weaker the gradient, the weaker the drift

We intend to decorrelate the drift induced by the thermal gradient and diffusion.

IV THERMODYNAMIC POTENTIAL

hypothesis: the adatom is in local thermodynamic equilibrium

→ Probability of presence of the adatom is driven by : $p(x_0) \propto e^{-\frac{A(x_0)}{T(x_0)}}$

Thermodynamic potential $\Phi(x_0) = \frac{A(x_0)}{T(x_0)}$ → Not directly computable

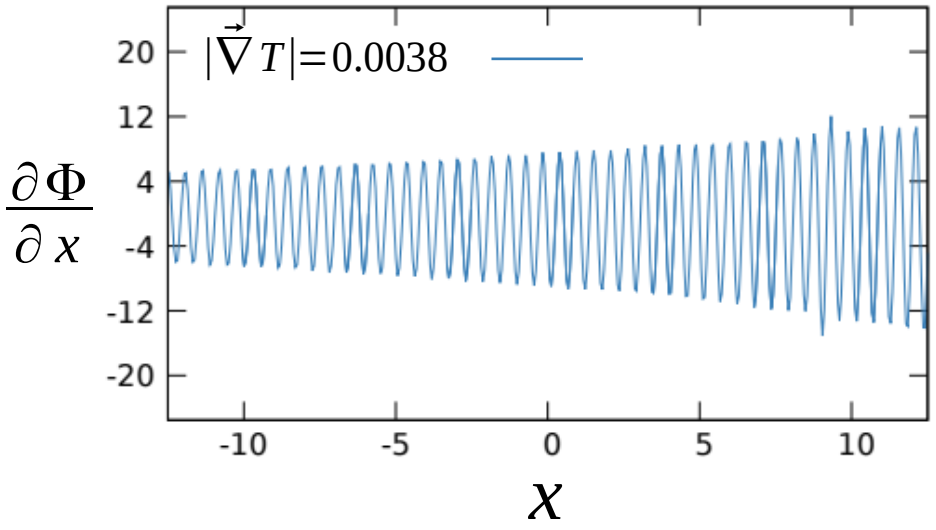
$$\frac{\partial(\Phi(x_0))}{\partial x} = -\left\langle \frac{Fx_{adatom \Leftarrow substrate}}{T(x_0)} \right\rangle - \left\langle \frac{\frac{Ep_{adatom \Leftrightarrow substrate}(x_0, y, z)}{2} + Ec_{adatom}(vx, vy, vz)}{T(x_0)^2} \frac{\partial T(x_0)}{\partial x} \right\rangle$$

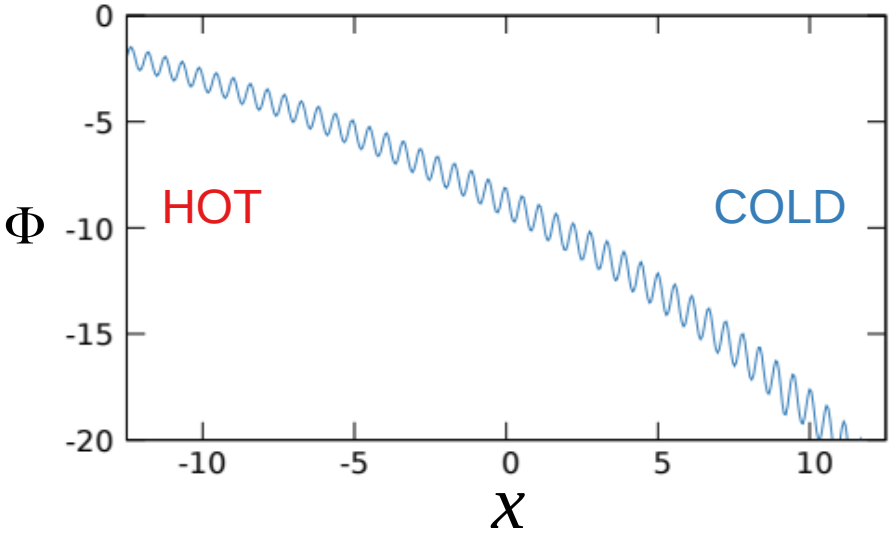
T	Temperature
Ep	Potential energy
Ek	Kinetic energy
F	Force

→ Generalization of thermodynamics integration for of a system subjected to a thermal gradient

IV THERMODYNAMIC POTENTIAL

$$\Phi(x_0) = \frac{A(x_0)}{T(x_0)}$$





➡ Probability of presence is higher on the cold region than on the hot region $p(x_0) \propto e^{-\Phi(x_0)}$

IV THERMODYNAMIC POTENTIAL

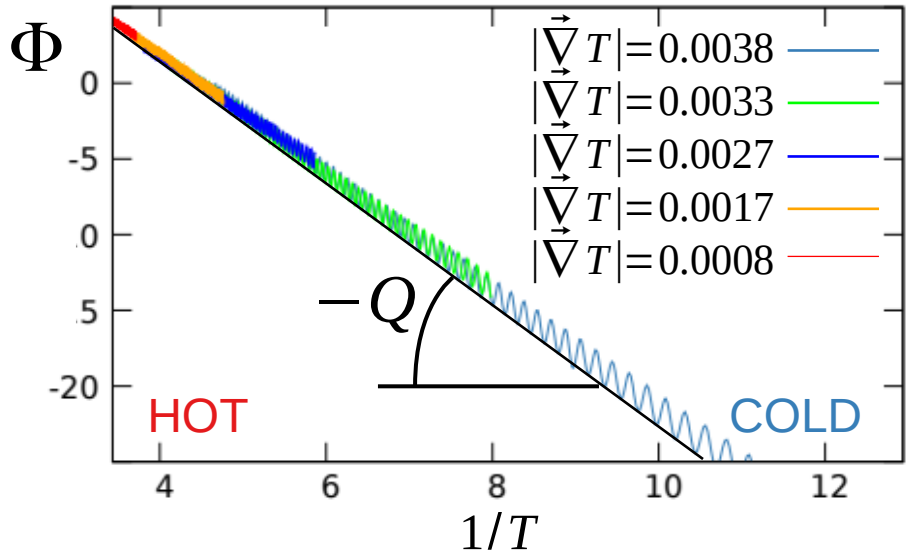
→ Φ depends on x

T depends on x

→ Plot Φ as function of $\frac{1}{T}$

$$\Phi(x_0)=\frac{A(x_0)}{T(x_0)}$$

→ Characterize Φ by the slope Q which passes through all the minimums



→ Slope Q does not depend on the gradient

→ Slope Q related to the response of the system to a thermal gradient that drives the adatom towards the cold region

Q → drift

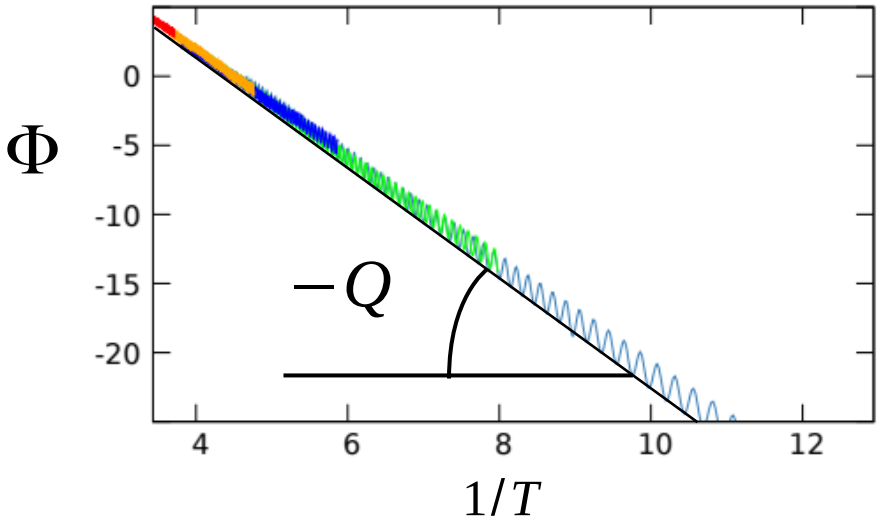
→ From the expression of $\frac{\partial \Phi}{\partial x}$, Q is related to the binding energy

THERMODYNAMIC POTENTIAL

$$\Phi(x_0) = \frac{A(x_0)}{T(x_0)}$$

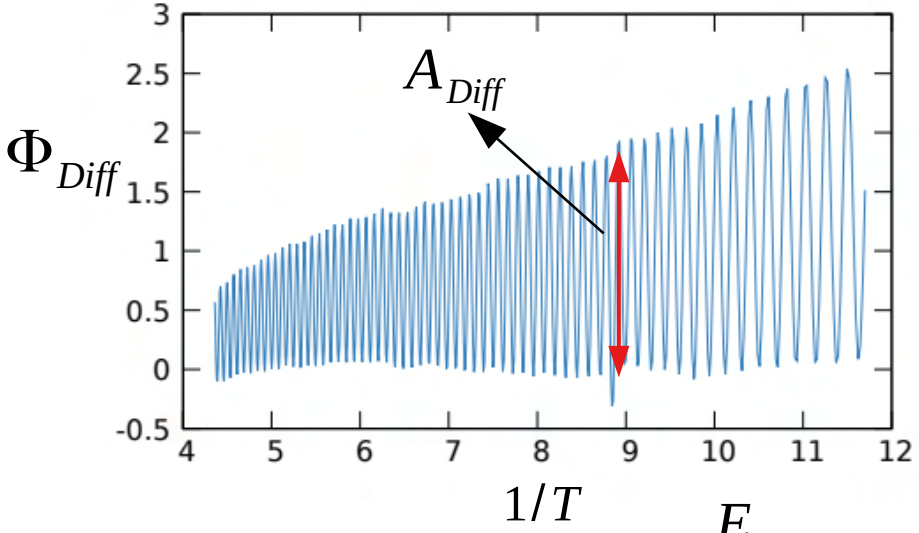
$$\Phi_{Diff} = \Phi + \frac{Q}{T}$$

Thermomigration



→ Slope Q

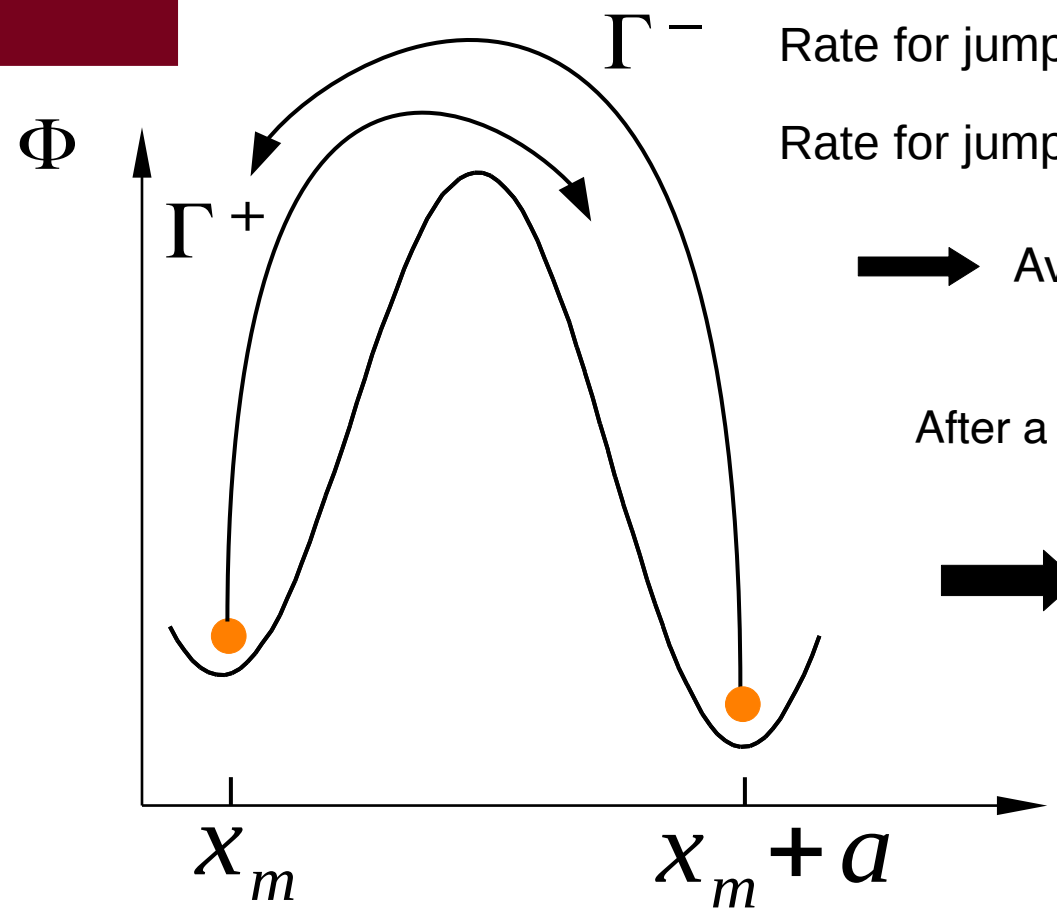
Diffusion



→ Amplitude $A_{Diff} \propto \frac{E_m}{T}$

→ Study the kinetics of the adatom with parameters Q and A_{Diff}

KINETIC OF THERMOMIGRATION



Rate for jump to the right $\Gamma^+ = \nu^+ e^{-[\Phi(xm+\frac{a}{2})-\Phi(x_m)]}$

Rate for jump to the left $\Gamma^- = \nu^- e^{-[\Phi(xm+\frac{a}{2})-\Phi(x_m+a)]}$

→ Average velocity of the adatom :

$$\langle v \rangle = a(\Gamma^+ - \Gamma^-)$$

After a Taylor expansion to the first order:

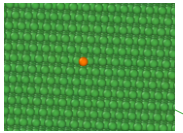
→

$$\langle v \rangle = -\frac{D(T)}{k_B} e^{-a\frac{(Q-E_m)}{2k_B T^2}\frac{\partial T}{\partial x}} \frac{Q}{k_B T^2}\frac{\partial T}{\partial x}$$

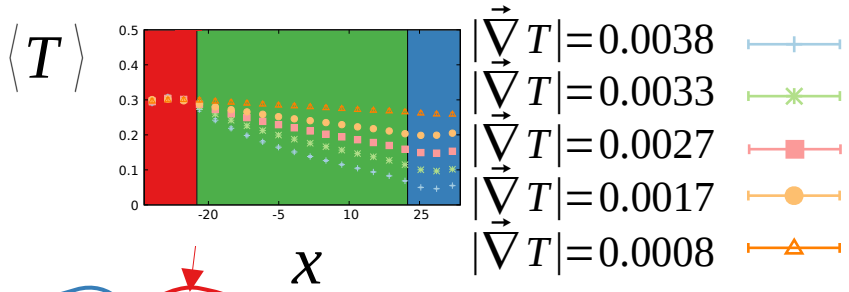
Diffusion coefficient : $D(T)$

KINETIC OF THERMOMIGRATION

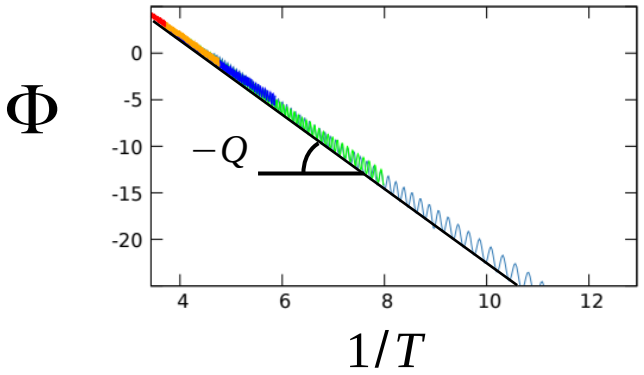
Mean square displacement on isothermal surfaces



Temperature profil



$$\frac{dx}{dt} = -\frac{D(T)}{k_B} e^{-a\frac{(Q-E_m)}{2k_B T^2}\frac{\partial T}{\partial x}} \qquad \frac{Q}{k_B T^2}\frac{\partial T}{\partial x}$$



Thermodynamic potential

V

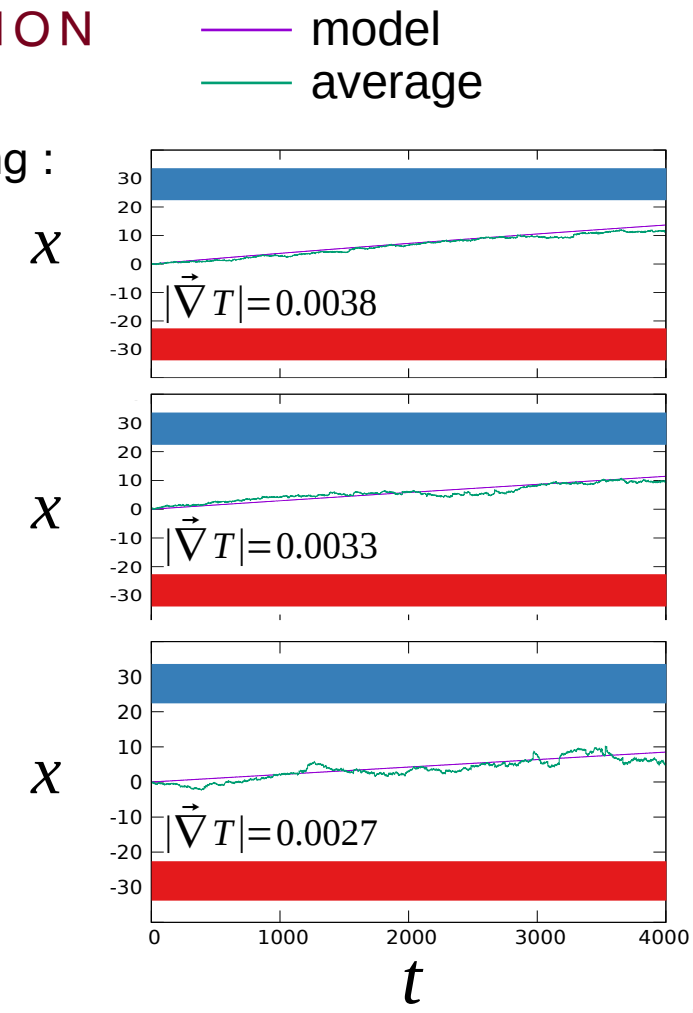
KINETIC OF THERMOMIGRATION

Application of our new model on the trajectories of thermomigrations by integrating :

$$\frac{dx}{dt} = -\frac{D(T)}{k_B} e^{-a\frac{(Q-E_m)}{2k_BT^2}\frac{\partial T}{\partial x}} \frac{Q}{k_B T^2}\frac{\partial T}{\partial x}$$

➡ Model in agreement with average molecular dynamics trajectories

➡ This agreement validates our approach and hypotheses



A. Roux and N. Combe. Phys. Rev. B 108, 115410, (2023)

VI

FROM ADATOMS TO CLUSTERS

Application of thermodynamic integration to a cluster subjected to a thermal gradient

Extension of thermodynamic integration scheme to clusters

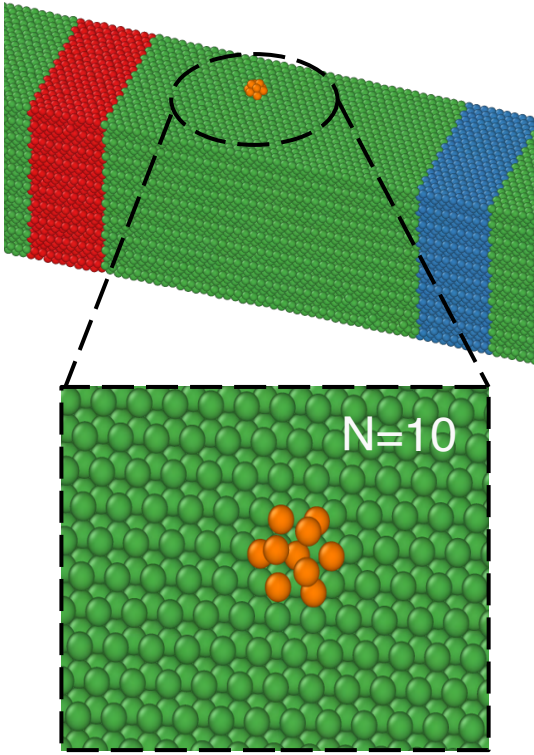
$$\frac{\partial(\Phi(x_0))}{\partial x} = -\left\langle \frac{Fx_{adatom \Leftarrow substrate}}{T(x_0)} \right\rangle - \left\langle \frac{\frac{Ep_{adatom \Leftrightarrow substrate}(x_0, y, z)}{2} + Ec_{adatom}(vx, vy, vz)}{T(x_0)^2} \frac{\partial T(x_0)}{\partial x} \right\rangle$$

x_0 Position of the adatom

x_0 Center of mass of the cluster

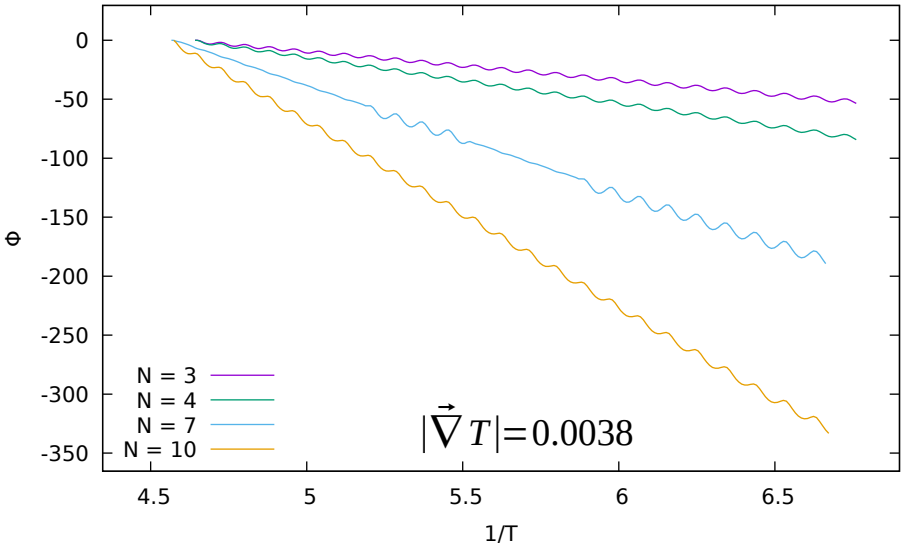
$$\frac{\partial(\Phi(x_0))}{\partial x} = -\left\langle \frac{Fx_{cluster \Leftarrow substrate}}{T(x_0)} \right\rangle - \left\langle \frac{Ep_{cluster \Leftrightarrow cluster}(x_0, y, z) + \frac{Ep_{cluster \Leftrightarrow substrate}(x_0, y, z)}{2} + Ec_{cluster}(vx, vy, vz)}{T(x_0)^2} \frac{\partial T(x_0)}{\partial x} \right\rangle$$

$$+\left\langle \frac{1}{T(x_0)^2} \frac{\partial T(x_0)}{\partial x} \sum_k^M \left[x_k{}' \frac{Fx_{k \Leftarrow substrate}}{2} + \sum_i^N x_i{}' \frac{Fx_{k \Leftarrow i}}{2} \right] \right\rangle + \left\langle \frac{\partial^2 \frac{1}{T}(x_0)}{\partial x^2} \sum_k^M x_k{}' \left[\frac{p_k^2}{2 m_k} + Ep_{k \Leftrightarrow substrate} \right] \right\rangle$$

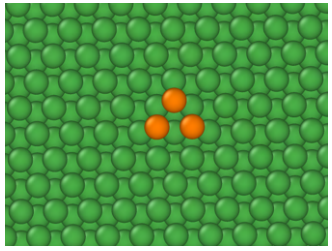


VI FROM ADATOMS TO CLUSTERS

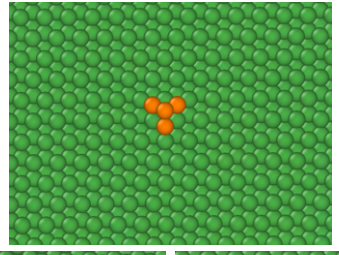
Thermodynamic integrations on cluster



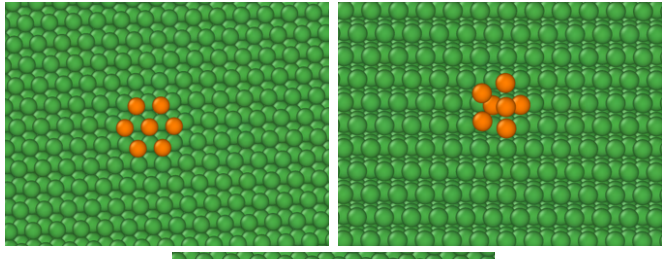
N=3



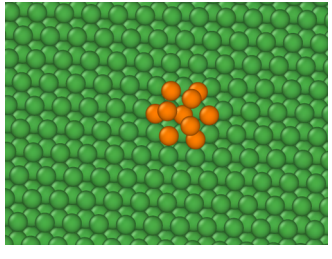
N=4



N=7



N=10



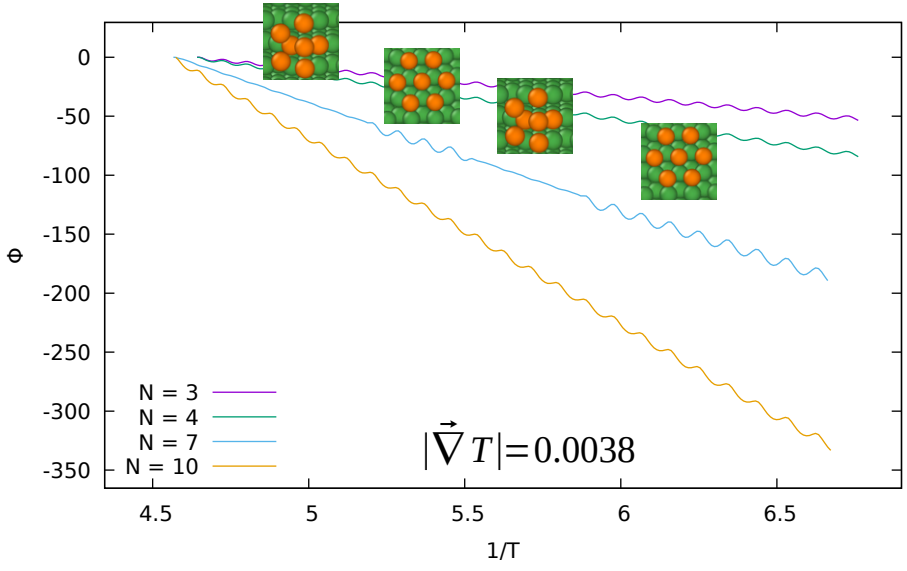
➡ effect of the size of the cluster

➡ effect of the conformation

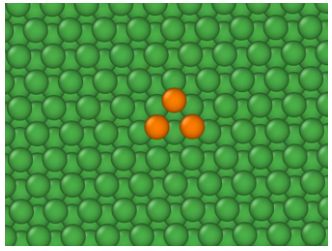
VI

FROM ADATOMS TO CLUSTERS

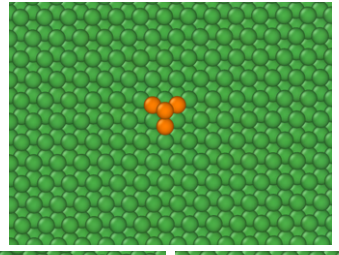
Thermodynamic integrations on cluster



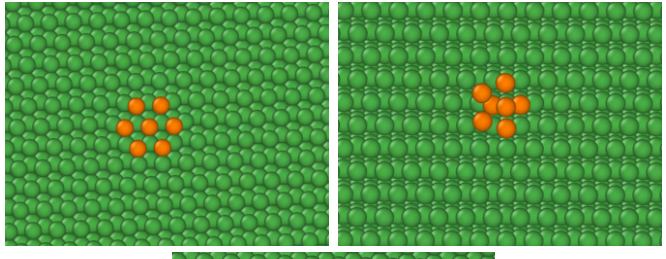
N=3



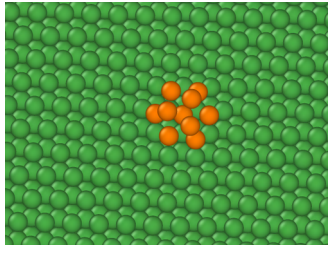
N=4



N=7



N=10



➡ effect of the size of the cluster

➡ effect of the conformation

Work in progress ...

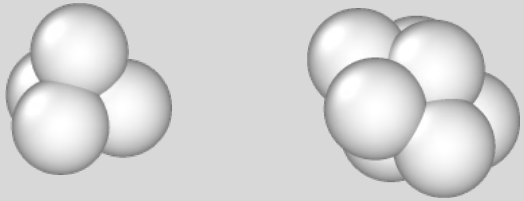
V

Conclusion

- Simulations and characterizations of thermomigration
- Generalization of thermodynamic integration to measure the thermodynamic potential
  - Drift
  - Diffusion
- Transition state theory in the case of a system subjected to a thermal gradient to deduce a drift velocity
- Preliminary results on clusters

Perspectives:

- Elastic effects on clusters thermomigration



Thank you for your attention !

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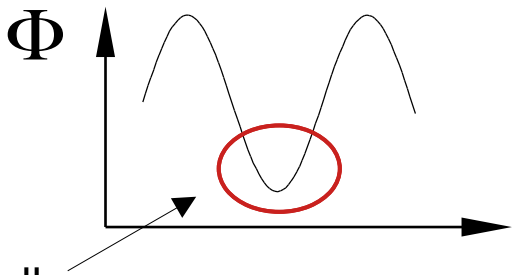
1 BINDING ENERGY



→ At the minima of a crystalline potential well

$V_0 > 0$ Binding energy

→ Harmonic approximation

→ potential energy of the adatom → $\langle Ep(x_0) \rangle = -V_0 + 2\frac{T(x_0)}{2}$

→ kinetic energy of the adatom → $\langle Ek(x_0) \rangle = \frac{3}{2} T(x_0)$

$$\frac{\partial(\Phi(x_0))}{\partial x} = \left\langle \frac{\frac{\partial Ep(x_0, y, z)}{\partial x}}{T(x_0)} \right\rangle - \left\langle \frac{\frac{1}{2} Ep(x_0, y, z) + Ec(vx, vy, vz)}{T(x_0)^2} \frac{\partial T(x_0)}{\partial x} \right\rangle$$

→ $$\Phi(x_0)_{min} = \frac{-V_0}{2T(x_0)} - 2\ln(T(x_0)) = \frac{-Q}{T(x_0)} - 2\ln(T(x_0))$$

2 ORDER OF MAGNITUDE

Lennard-Jones potential :

$$E_{LJ}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Lennard-Jones reduced units :

$$r^{+} = \frac{r}{\sigma} \qquad t^{+} = t\left(\frac{\epsilon}{m\sigma^{2}}\right)^{\frac{1}{2}}$$

$$T^{+} = \frac{T\,k_B}{\epsilon} \qquad E^{+} = \frac{E}{\epsilon}$$

Using copper's parameter :

$$\sigma_{Cu} = 0.2338\,nm$$
$$\epsilon_{Cu} = 0.4057\,eV$$
$$m_{Cu} = 105.4910^{-27}\,kg$$

$$\left|\vec{\nabla} T\right| = 0.0038 = 76.5\,K/nm \qquad Q = 1.9 = 0.77\,ev$$
$$\left|\vec{\nabla} T\right| = 0.0027 = 54.37\,K/nm \qquad E_m = 0.23 = 0.09\,ev$$
$$T_{HOT} = 0.3 = 1412.4\,K \qquad t = 25000 = 7.45\,ns$$
$$T_{COLD} = 0.05 = 235.4\,K \qquad Lx = 44.9 = 10.5\,nm$$

3

DIFFUSION

→ Trajectory on the surface is diffusive → No Lévy flights