Ab initio based Multiscale Methods

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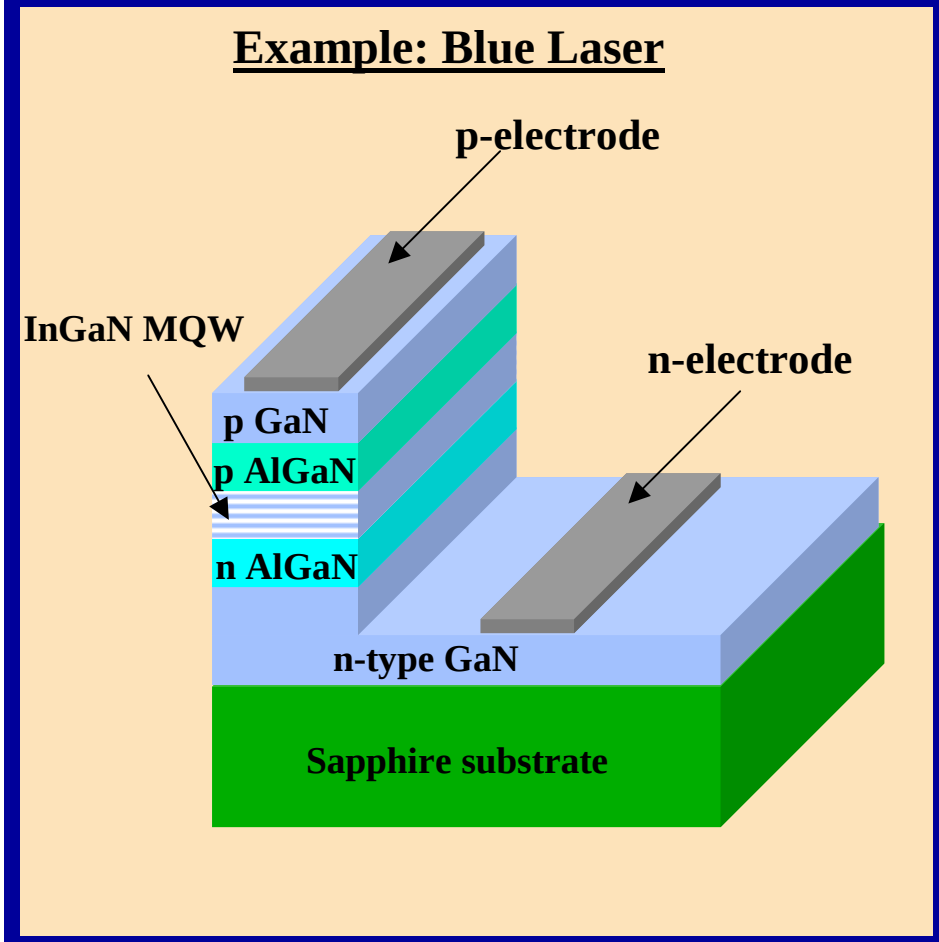
Example: Blue Laser



Challenges:

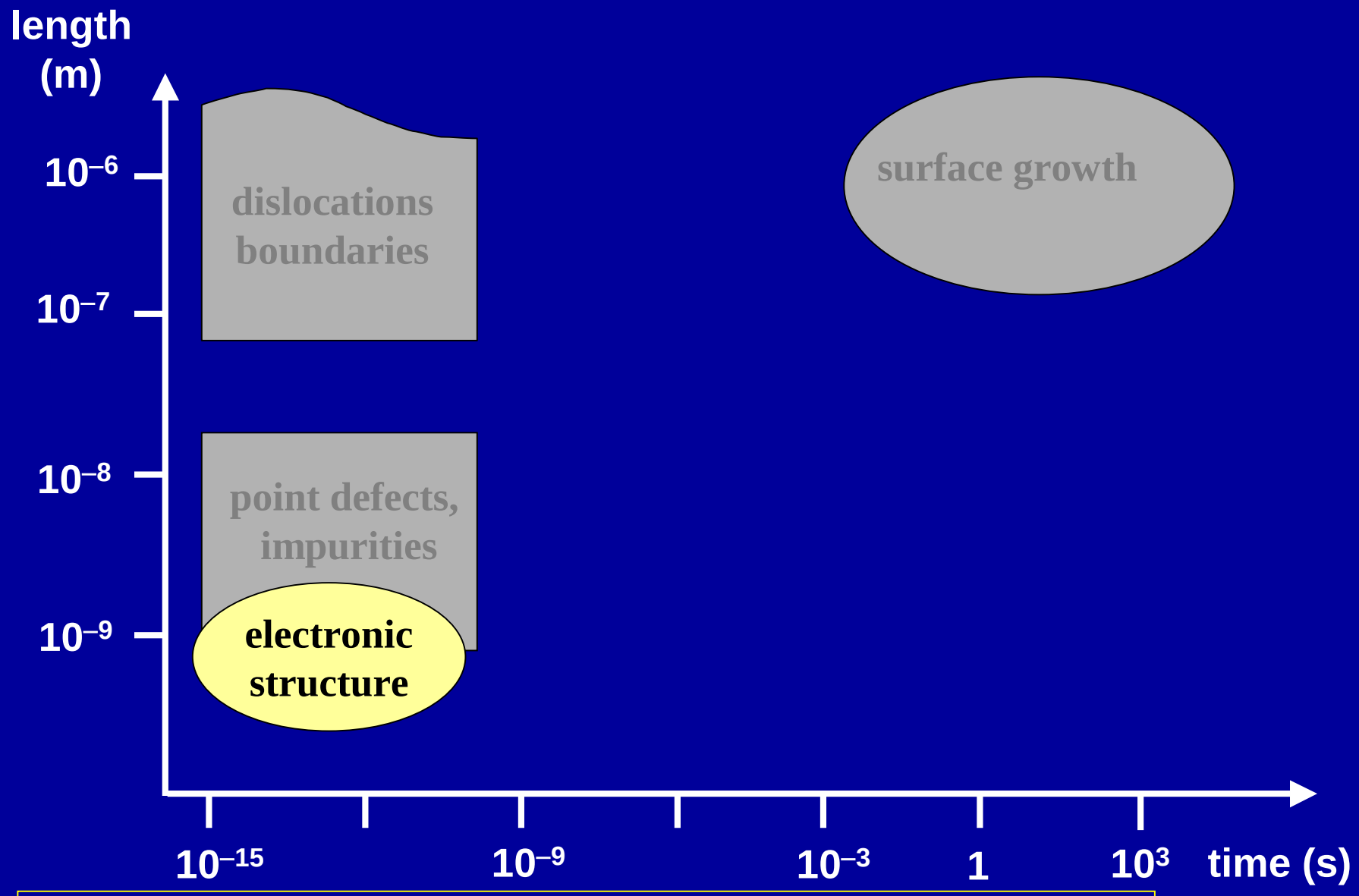
- Interfaces
- Dislocations/Grain Boundaries
- Alloys
- Formation of nanostructures (intentional/unintentional)
- Growth optimization

Simulations:

- compute properties of above structures
- compute synthesis (crystal growth)

S. Nakamura et al., Jpn. J. Appl. Phys. 35, L217 (1996).

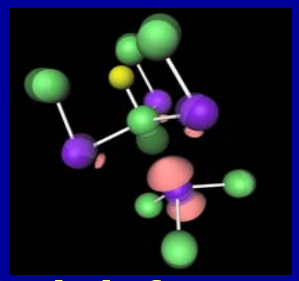
Scaling Problem in Modeling



How to simulate across length and time scales?

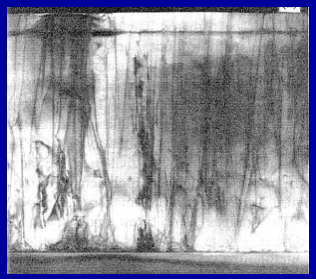
Outline

- Motivation: Multi-scale simulation methods
- Point Defects: Impurities



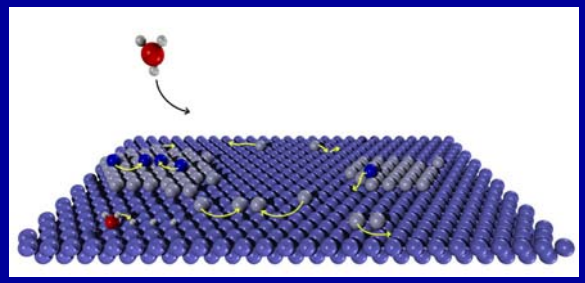
  - charge states
  - atomic geometry
  - formation energy/concentrations

- Extended defects: Dislocations

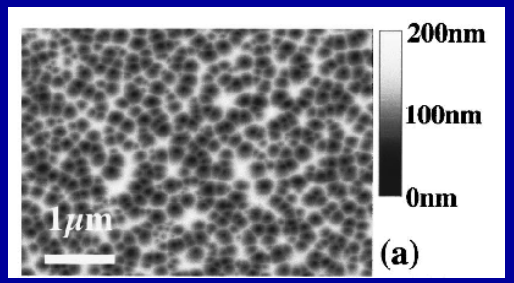


  - electronic structure
  - atomic geometry/stoichiometry
  - energetics/stability

- Crystal growth

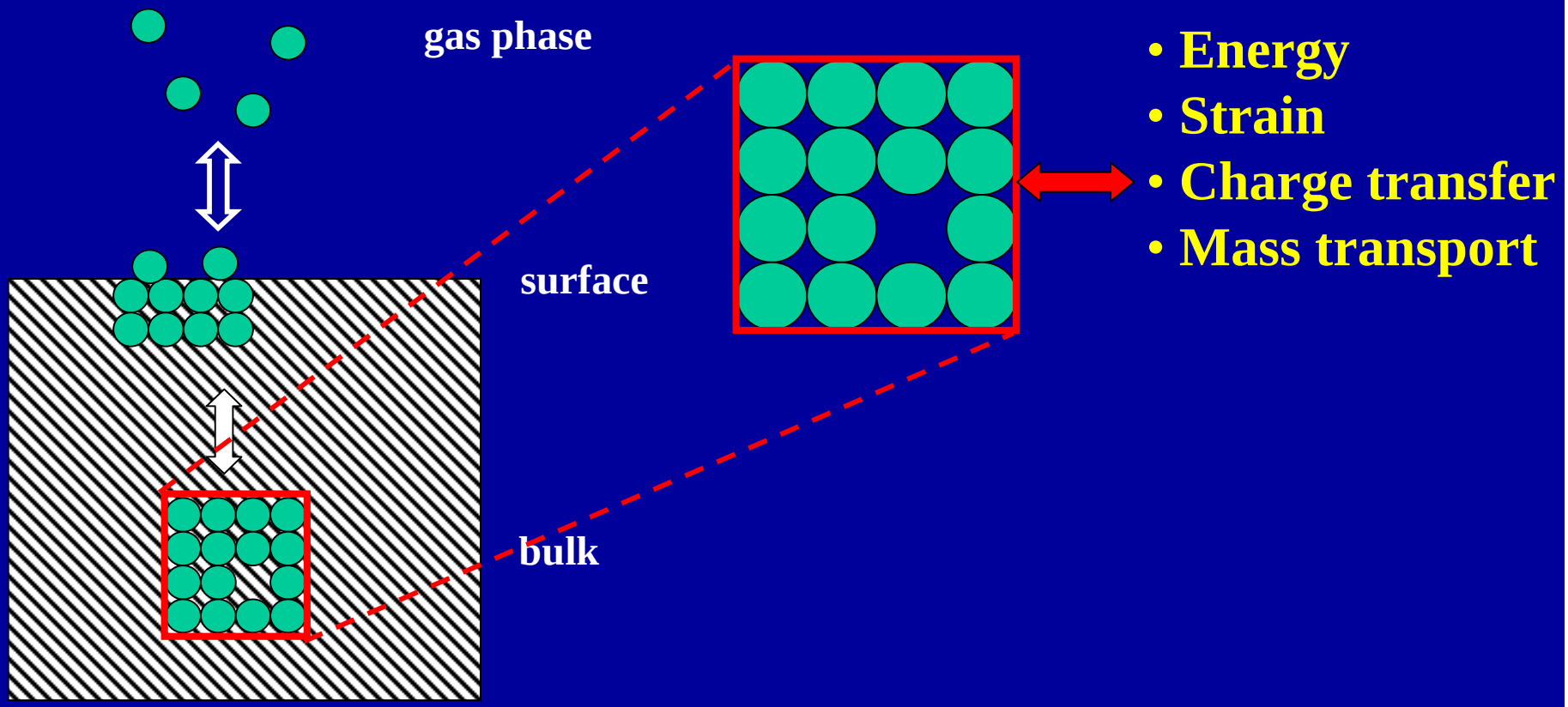


atomic scale



mesoscopic scale

Key Concepts of Multiscale Methods



Idea:

1. Partition total system into regions containing the relevant microscopic structures
2. Calculate all relevant properties + interaction parameters for these regions (DFT)
3. Connect the regions based on the calculated interaction parameters

How to Describe the Different Types of Interactions

Energy

⇒Thermostats (Lars Ismer)

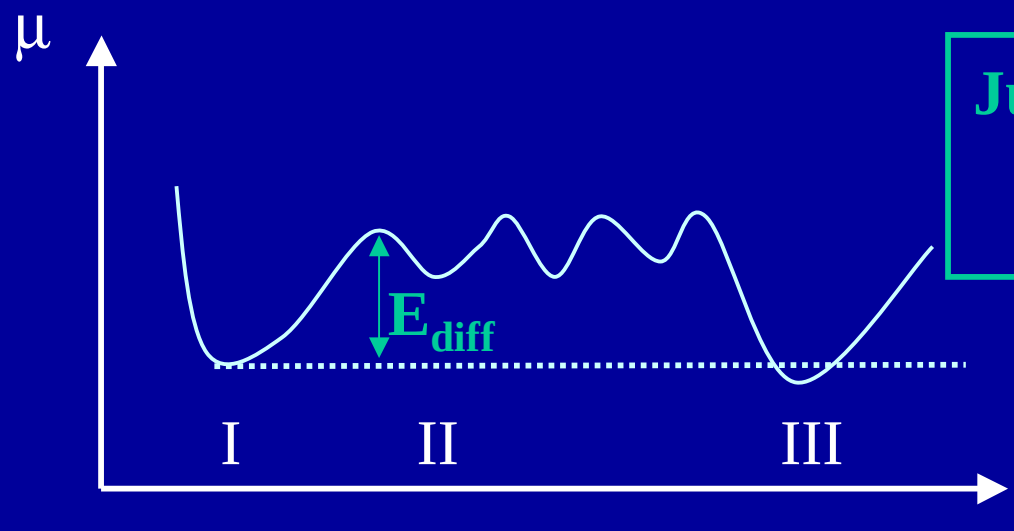
Strain

⇒ Approximated microscopic models/continuum theory

Particle transfer (electrons, atoms, defects)

⇒Thermodynamic equilibrium (→ chemical potentials)

⇒ Kinetics (→ energy barriers, transition state theory)

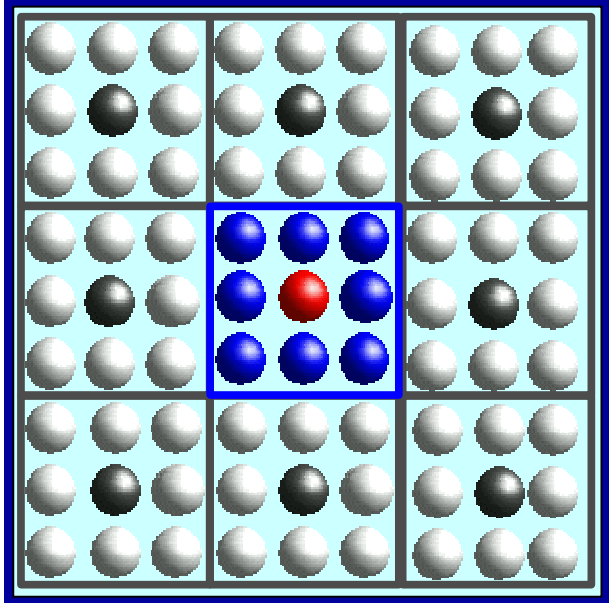


Jump rate:

$$w_{I \to II} = v_0 \exp(-E_{diff}/k_B T)$$

Convergence aspects for defect calculations

Periodic boundary conditions



⇒ interaction across cell boundaries:

elastic:
- strain fields

electrostatic:
- monopoles
- multipoles

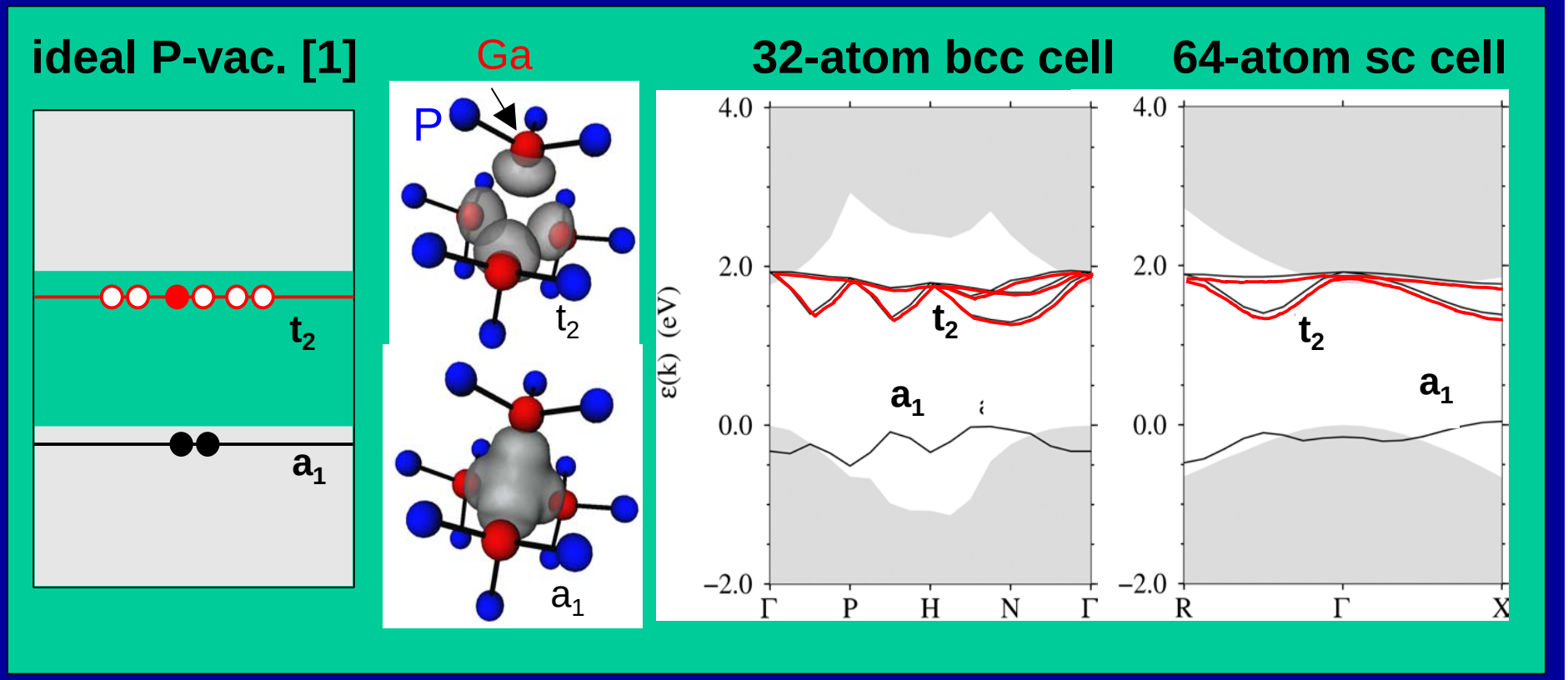
long ranged
$1/R^n$

electronic:
- overlap of wave functions
- dispersion of defect states

- Artificial interaction across cell boundaries → have to be removed
- Increase cell size → all physical quantities converge
- Error estimation and reduction for 'small' cells is crucial!

Electronic effects (I)

Example: Neutral GaP P-Vacancy:

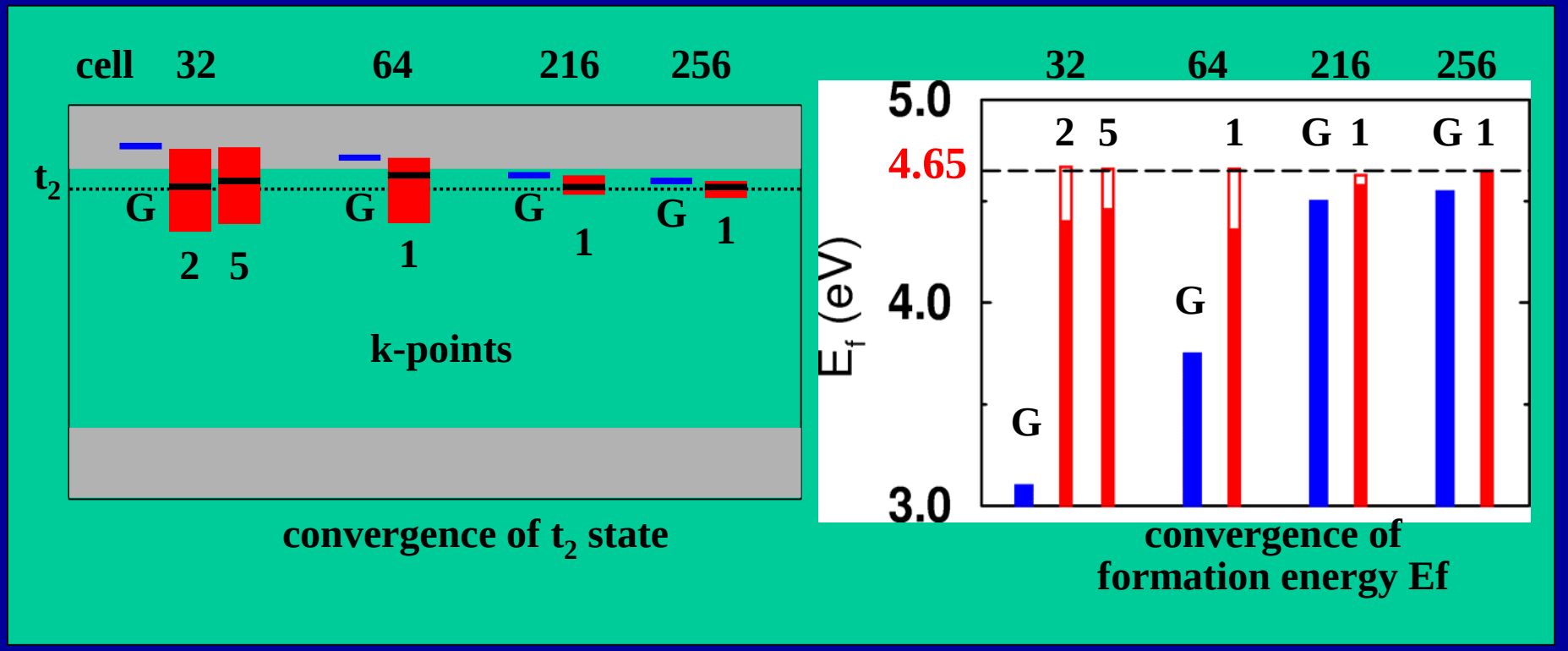


- large dispersion due to defect-defect interaction
- unphysical splitting of degenerate t_2 defect state

G. Schwarz, PhD thesis

Electronic effects (II)

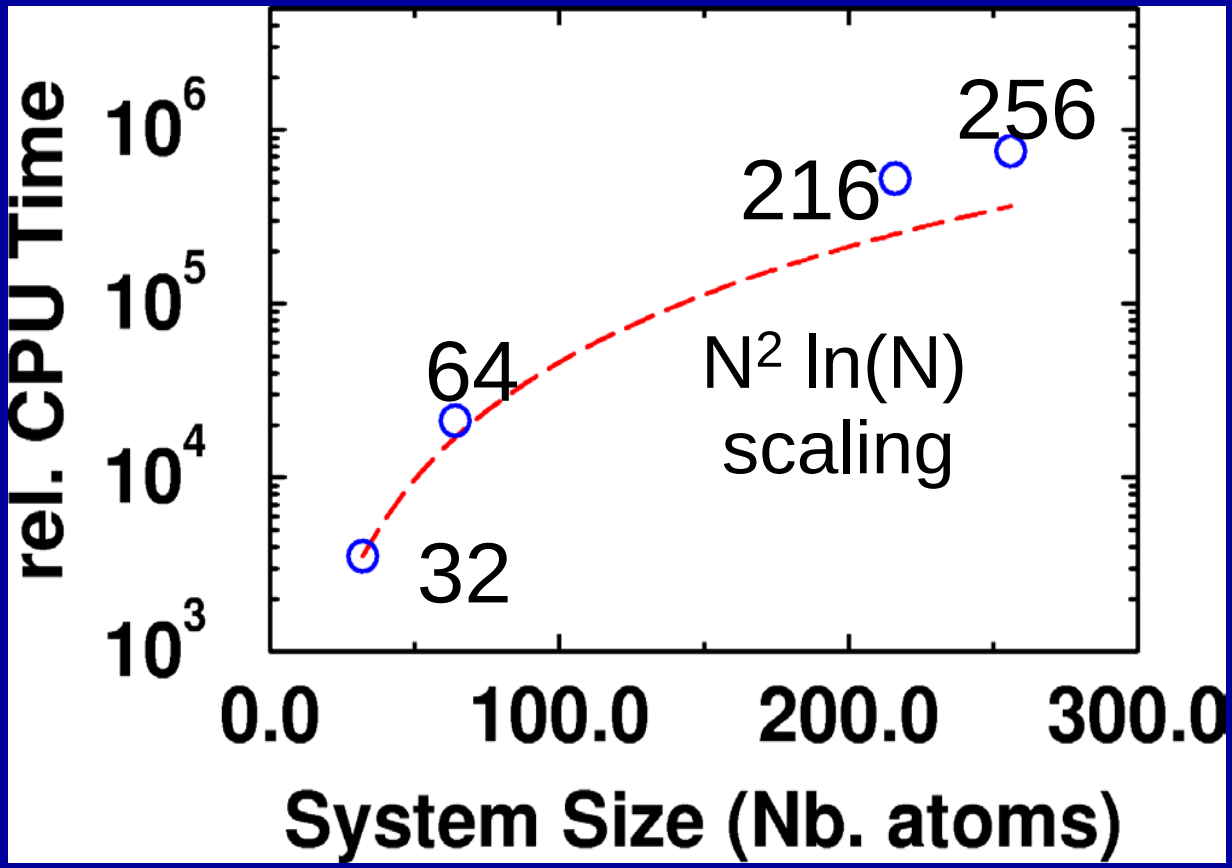
Convergence Tests: Cell Size and k-Points
Example: Neutral Ideal GaP P-Vacancy



- slow convergence of defect state and energy at the Γ point
- average over special k-points converges significantly faster (error < 0.02eV)

Relative CPU Time Consumption

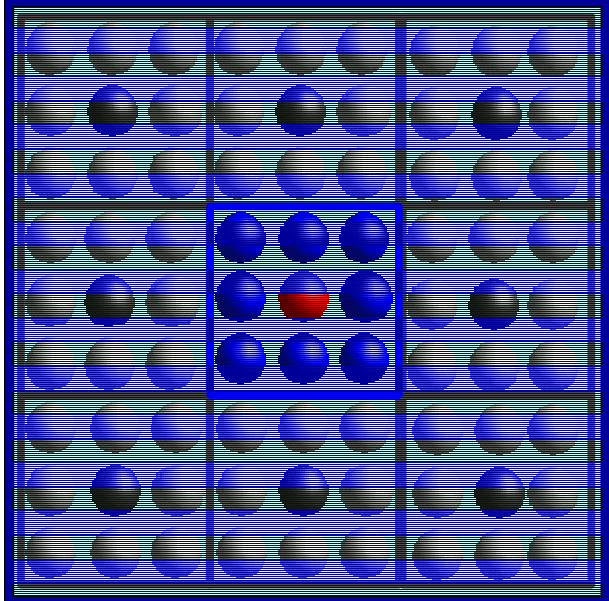
Example: Neutral GaP P-Vacancy



By a proper treatment of defects in supercells more than two orders of magnitude in CPU time can be saved!

Convergence aspects for defect calculations

Periodic boundary conditions



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✓

- Artificial interaction across cell boundaries → have to be removed
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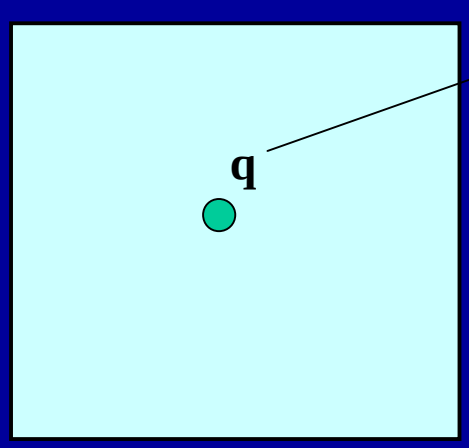
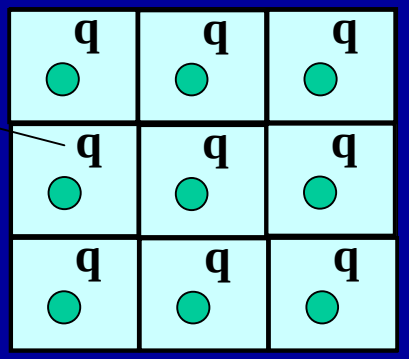
Calculating charged defects

Charged defect in an infinite cell



electron reservoir

Charged defect in a supercell



asymptotic behavior:

$$V \propto \frac{q}{\varepsilon\varepsilon_0 r}$$

screened Coulomb potential

electrostatic potential

$$V^{Hartree} \propto \frac{\rho(G)}{|G|^2}$$

$$\rho(G=0) = \int_{\Omega} \rho(\vec{r})d\vec{r}$$

For non-neutral systems the G=0 component of the potential diverges ($V^{Hartree}$ ill defined!)

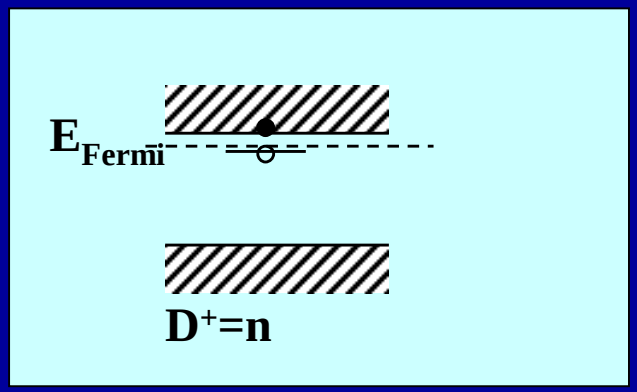
⇒ supercell must be always charge neutral!

Charge compensation

How to realize a charge neutral supercell?

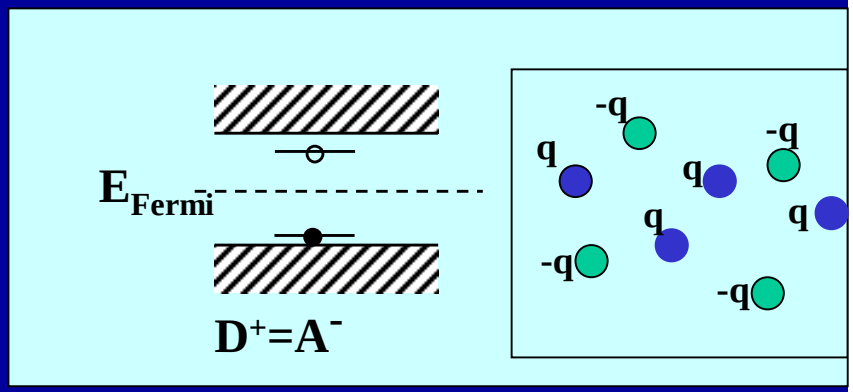
⇒ Look at nature!

Example: Donor



Transfer electron from donor level to bottom of conduction band

delocalized state



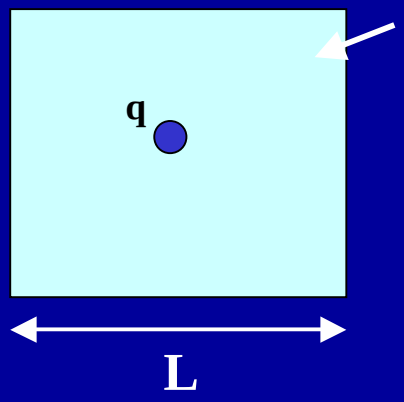
Transfer electron from donor to acceptor level

statistically homogeneous distribution

First approximation: constant background [set $V^{Hartree}(G=0) = 0$]

Compensation by constant background

Problem: Slow convergence with supercell size



total charge of background: -q

$$\Delta E = -\frac{q^2 \alpha}{2\epsilon L}$$
$$\alpha = 2.84$$

Electrostatic interaction between charged defects in neighboring supercells:

$$E \propto \frac{q^2}{\varepsilon L}$$

ε bulk dielectric constant

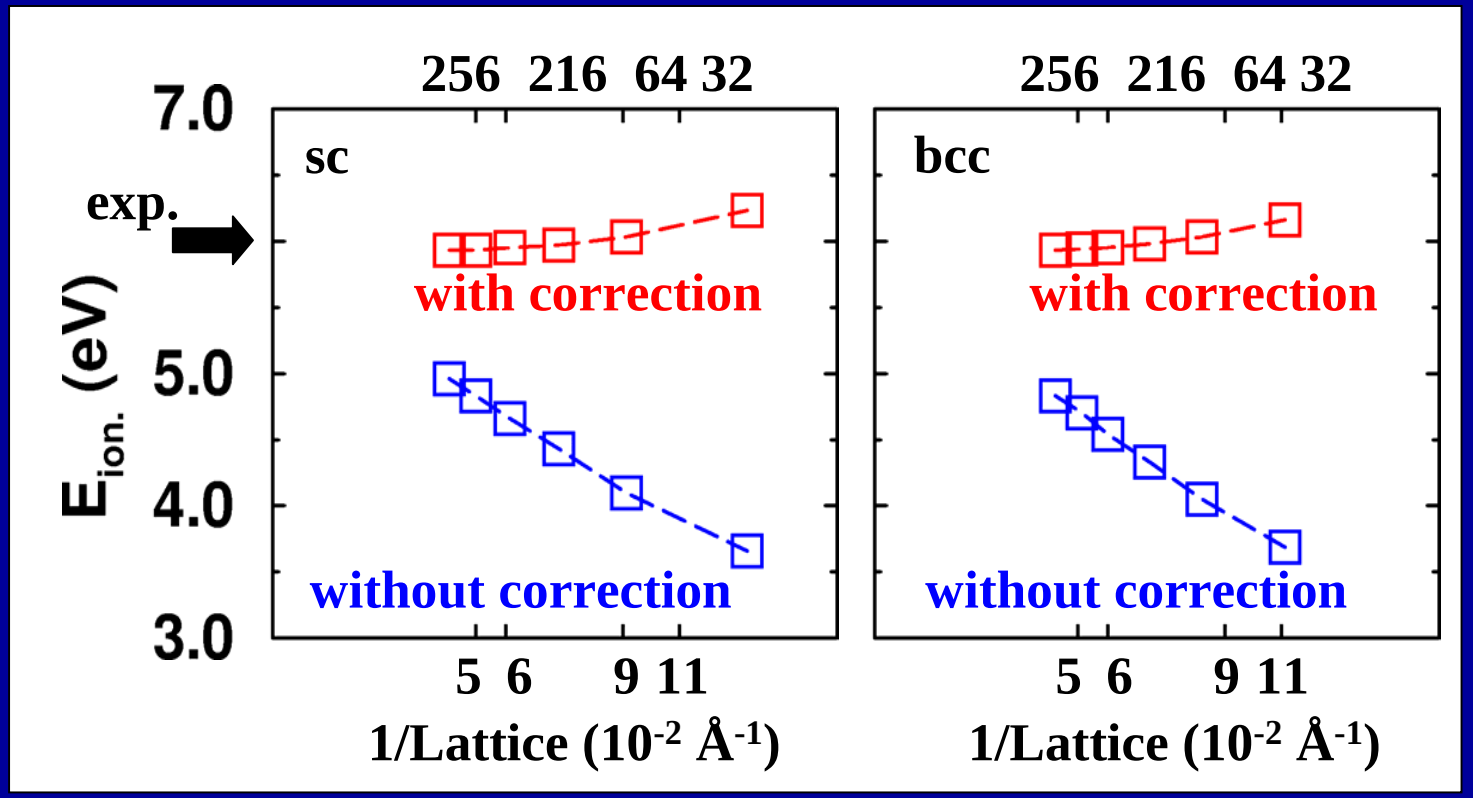
Defect-defect interaction vanishes asymptotically like 1/L!

Suggestion (Ref. [1]): Correct explicitly for this error
⇒ subtract it from total energy

[1] G. Makov and M. C. Payne, Phys. Rev. B 51, 4014 (1995).

Example: First ionization energy of an atom

System: Ga Atom in Cubic Cells

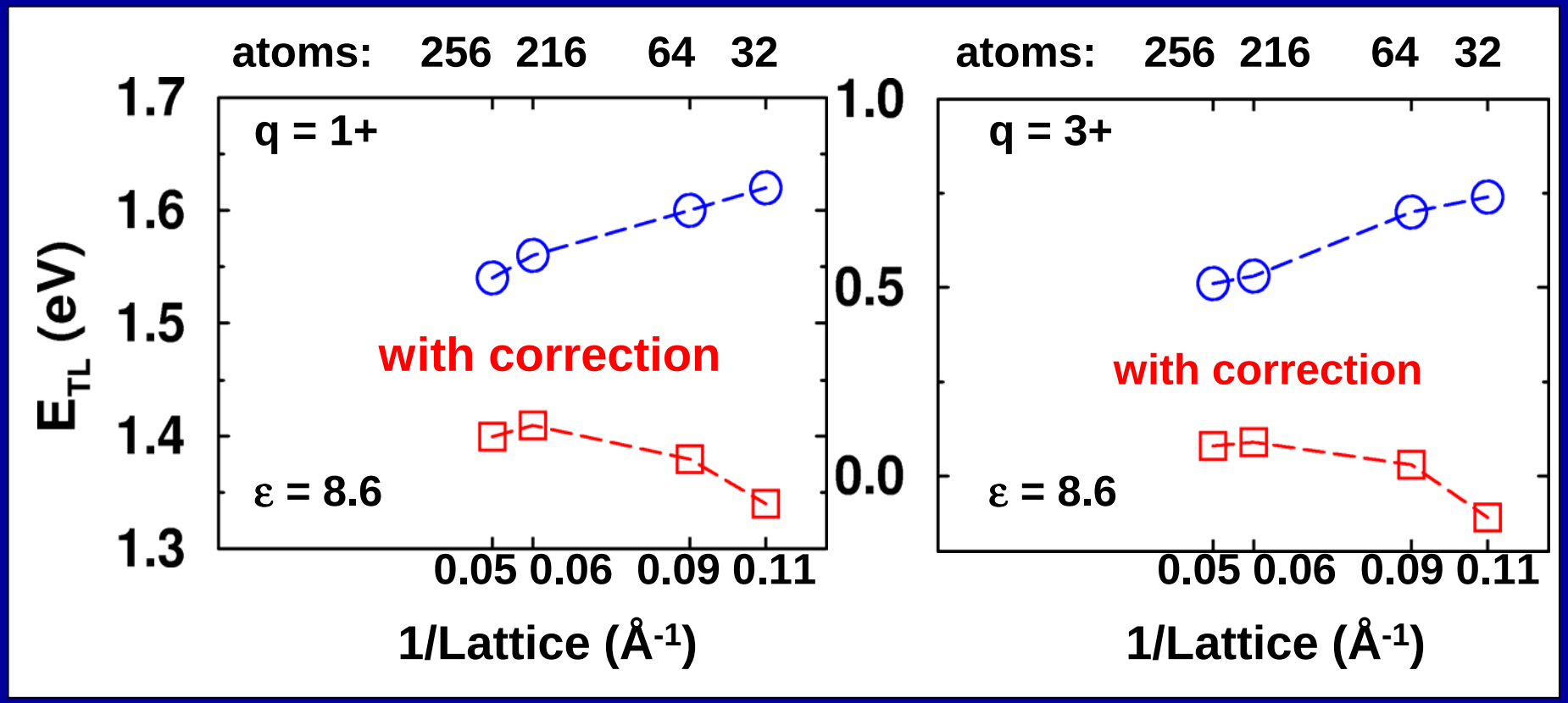


Makov/Payne correction significantly improves convergence with respect to supercell size for this system!

G. Schwarz, PhD thesis

Example: Positively Charged Vacancy

Charge Transfer Level ETL for 1+ and 3+



Makov/Payne correction overestimates the error!
Problem: bulk dielectric constant not appropriate
$\Rightarrow$ enhanced screening around defect

Thermodynamic potentials

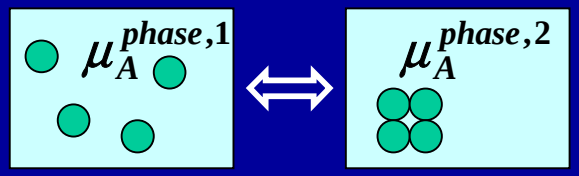
Key quantity:

Partition function: $$Z(V,T) = \sum_i e^{-E_i / k_B T}$$

Free energy*: $$F(V,T) = -k_B T \ln\{Z(V,T)\}$$

Gibbs Free energy: $$G(p,T) = F(V,T) + pV$$

Chemical potential: $$\mu_A = \left(\frac{\partial G(A^n)}{\partial n} \right)_{T,p}$$



Phase 1 Phase 2

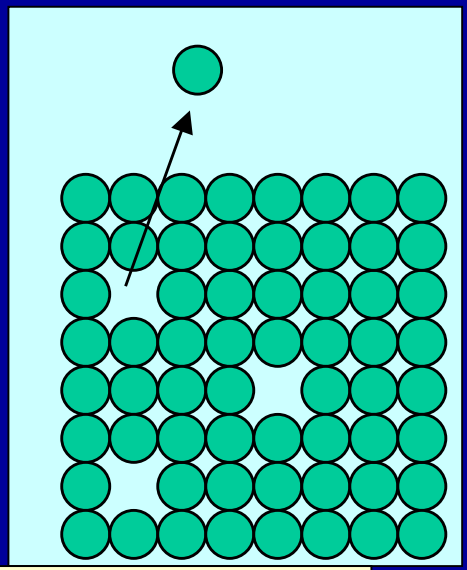
*From E_{tot} + dynamical matrix
Implemented in SFHIngX

Example: Point defects

Free energy: $F = U - TS$

For isolated defects: $U = nE_D$

- n: **number of defects**
- E_D: **formation energy of an isolated defect**



Configurational entropy:

$$S^{config} = k_B \ln W \qquad \text{with} \quad W = \frac{N(N-1)\ldots(N-n-1)}{n!} = \frac{N!}{(N-n)!\,n!}$$

Minimize free energy:

$$\left(\frac{\partial F}{\partial n}\right)_T = E_S - k_B T \ln\frac{N-n}{n} = 0$$

➡ **Defect concentration:**

$$n = N \exp\left(-\frac{E_D}{kT}\right)$$

Defect Formation energy

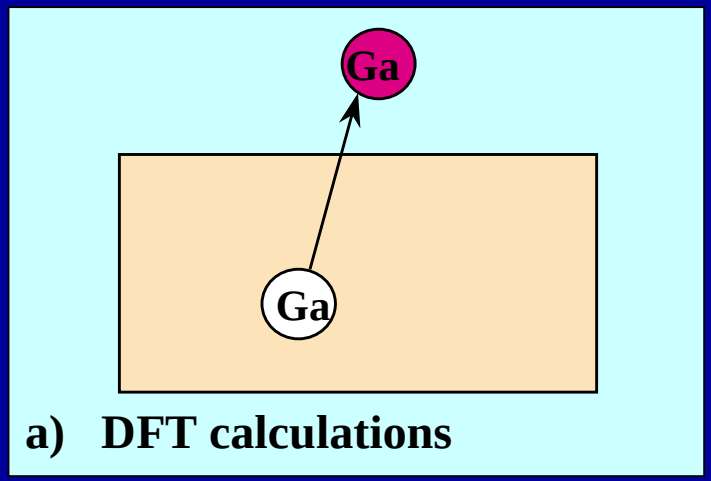
Defect concentration:

$$n_{Defekt} = N_{sites} \exp\left(-\frac{E_D}{kT}\right)$$

How can we calculate formation energy E_D?

Note: To create a defect the number of atoms in the system may change!

Example: Creation of a vacancy in GaN (two steps)



a) DFT calculations

Ga atom gains energy μ_{Ga}

b) Thermodynamics

$$E_D(GaN:V_{\mathrm{Ga}}^q) = E_{tot}\left(GaN:V_{\mathrm{Ga}}^q\right) + \mu_{\mathrm{Ga}} + qE_{\mathrm{Fermi}}$$

Chemical Potentials

Specific value of the chemical potentials depends on the environment!

⇒ variables, which can be experimentally controlled
(via T, p, fluxes and flux ratio)

But: Boundary conditions are well defined and can be calculated

Example: Ga vacancy in GaN

Boundary conditions:

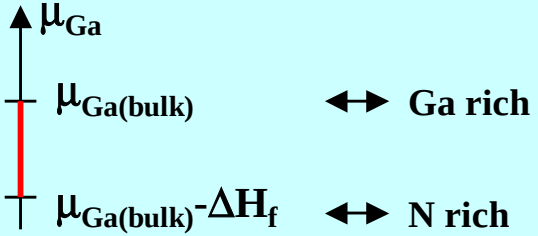
$\mu_{Ga} < \mu_{Ga(bulk)}$

$\mu_{N} < \mu_{N(molecule)}$

$\mu_{Ga} + \mu_{N} = \mu_{GaN(bulk)}$

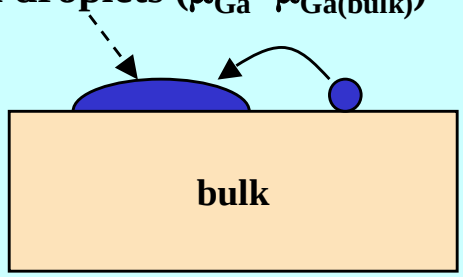
$\mu_{Ga(bulk)} + \mu_{N(molecule)} = \mu_{GaN(bulk)} + \Delta H_f$

$\mu_{Ga(bulk)} - \Delta H_f < \mu_{Ga} < \mu_{Ga(bulk)}$



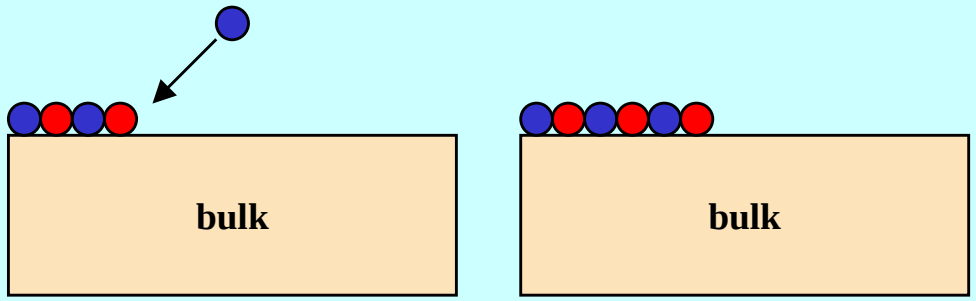
Interpretation:

Ga droplets ($\mu_{Ga}=\mu_{Ga(bulk)}$)



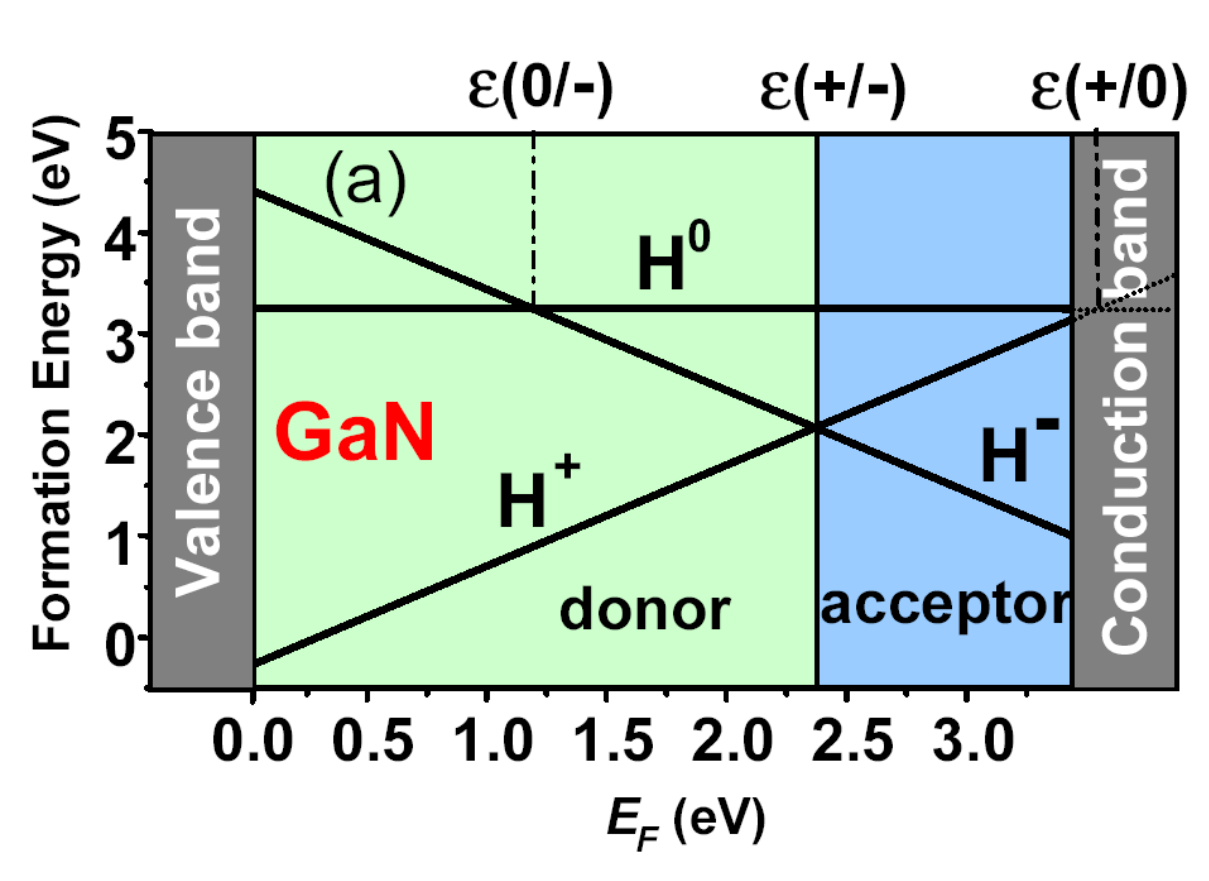
Ga rich

Incorporation at a Kink ($\mu_{Ga}=\mu_{Ga(bulk)}- \Delta H_f$)



N rich

Example: H in GaN



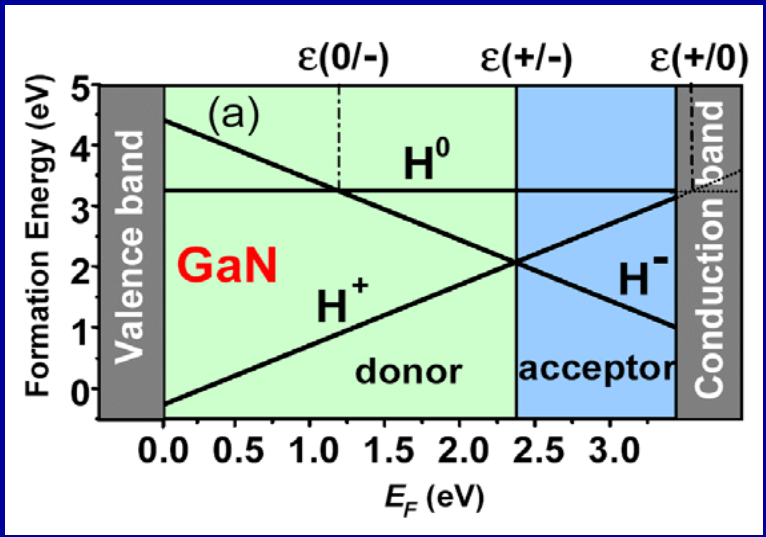
$$E_f(GaN:H^q) = E_{tot}(GaN:H^q) - \mu_H + qE_F$$

Electric behavior of hydrogen in GaN can be identified!

J. Neugebauer and C. Van de Walle, Phys. Rev. Lett. 75, 4452 (1995)

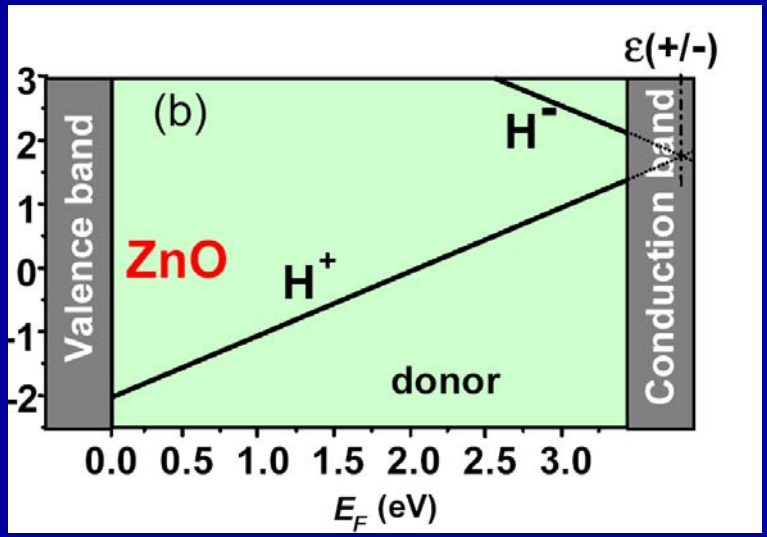
Explore Chemical Trends

GaN



compensating center

ZnO

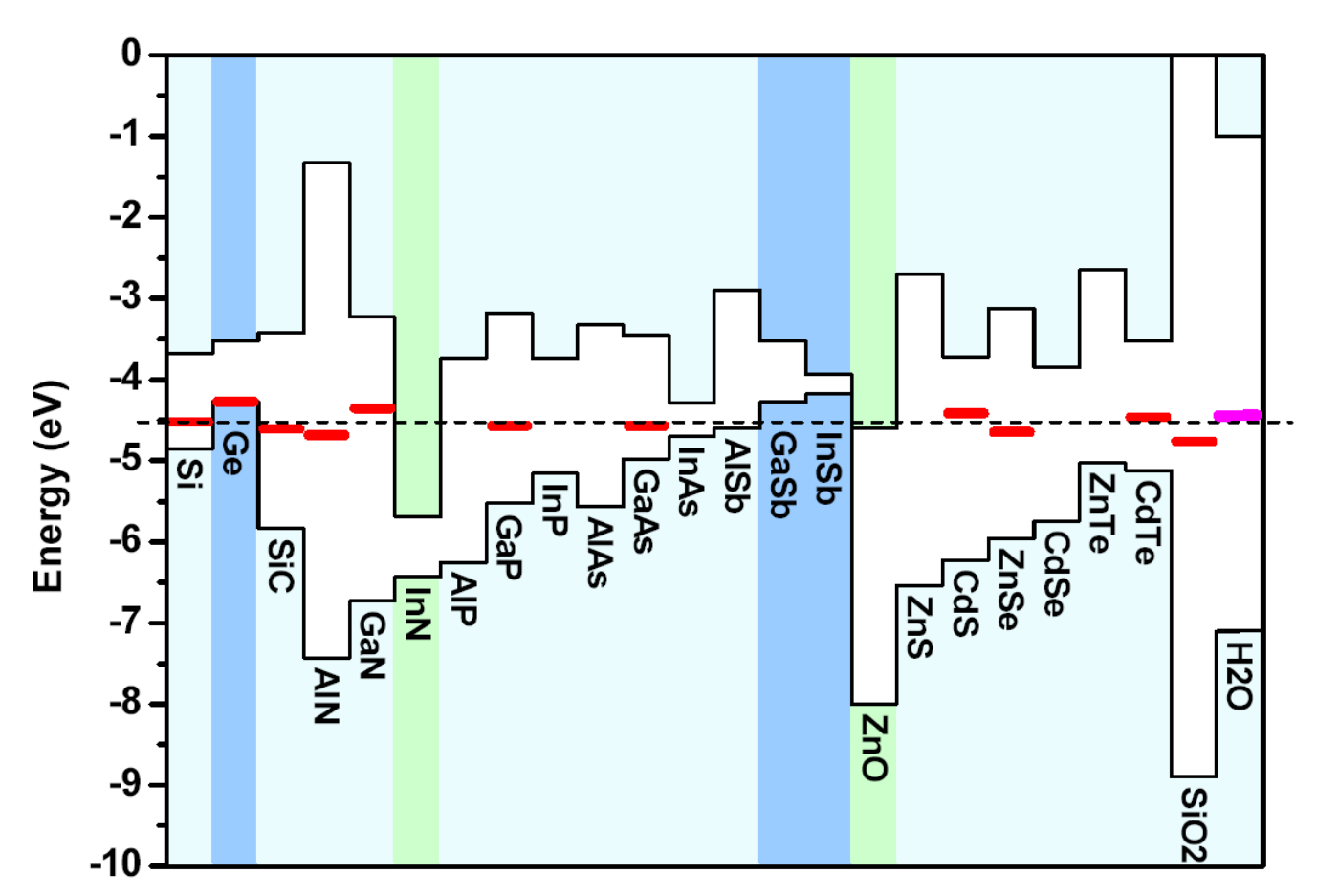


donor impurity

Hydrogen exhibits very different behavior!

Identification of an Universal Alignment

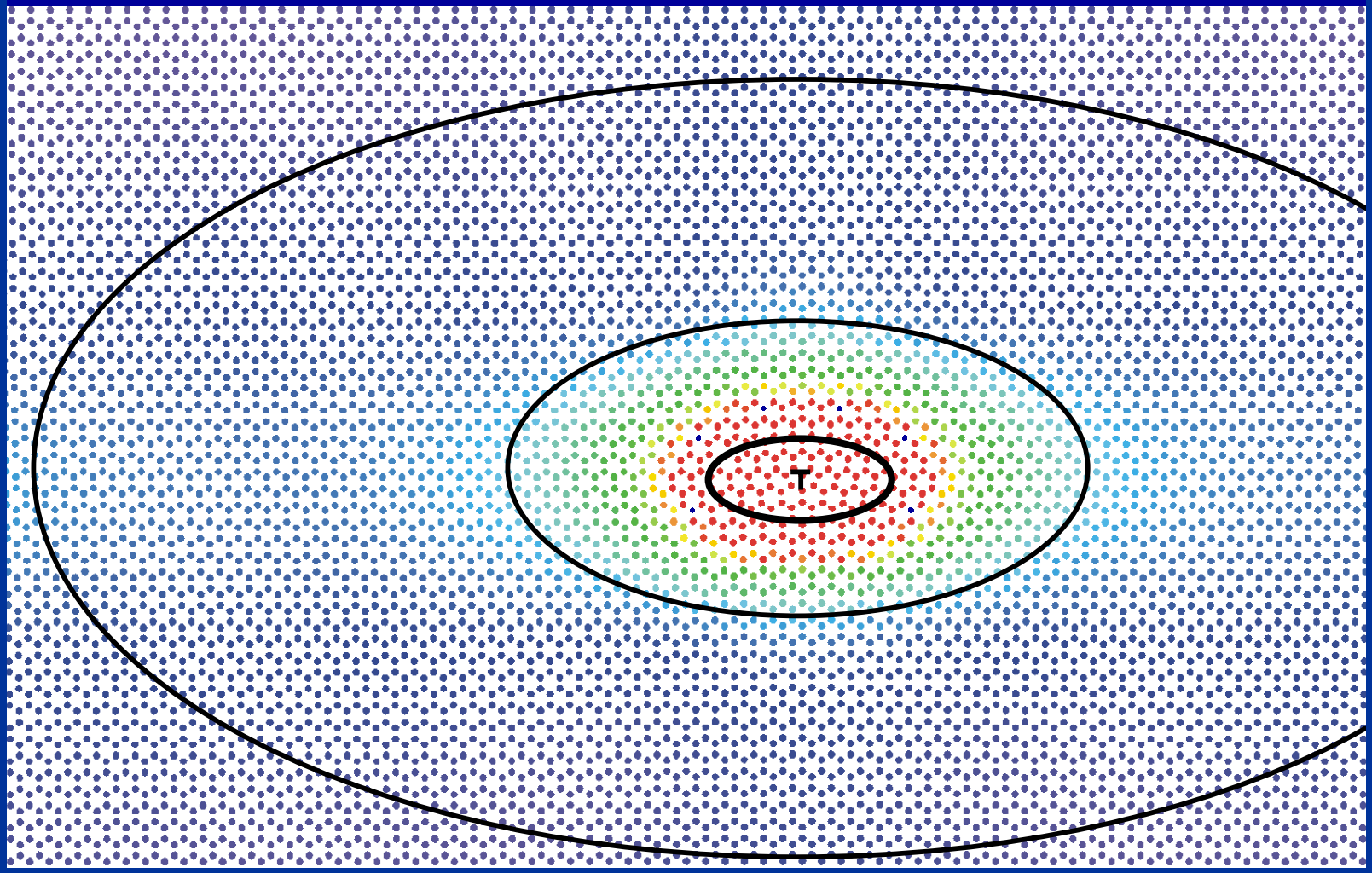
Position of the Hydrogen level:



Multiscale methods allow identification of hidden rules!

C.G. Van de Walle and J. Neugebauer, Nature 423, 626 (2003).

Scaling Problem



Zone I: broken bonds & large displacements ⇒ ab initio methods

Zone II: large displacements ⇒ empirical potentials

Zone III: small displacements

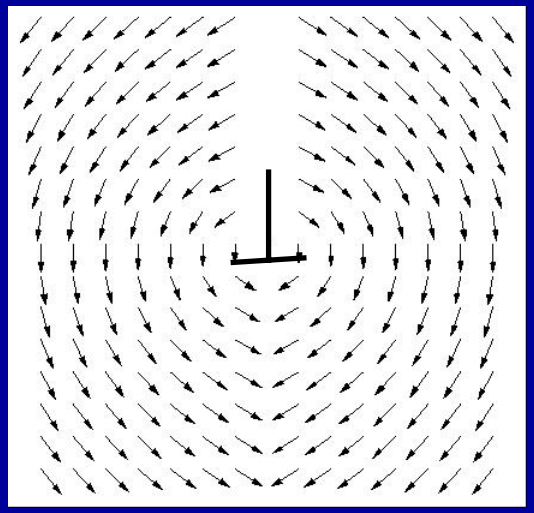
Step I: Linear Elastic Theory

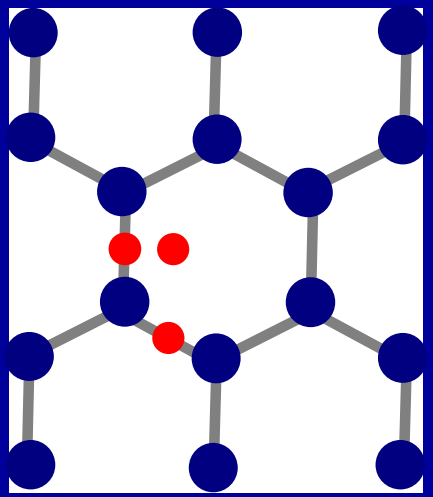
Displacement Field:[1,2]

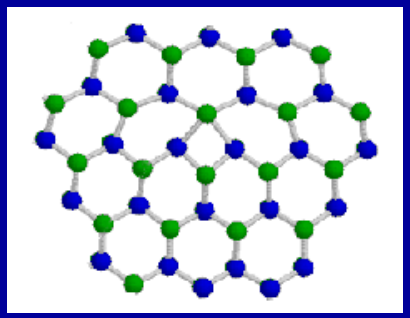
$$u_x(x,y) = \frac{b}{2\pi}\left(\tan^{-1}\left(\frac{y}{x}\right) + \frac{xy}{2(1-\nu)(x^2+y^2)}\right)$$

$$u_y(x,y) = -\frac{b}{2\pi}\left(\frac{1-2\nu}{4(1-\nu)}\ln(x^2+y^2) + \frac{x^2-y^2}{4(1-\nu)(x^2+y^2)}\right)$$

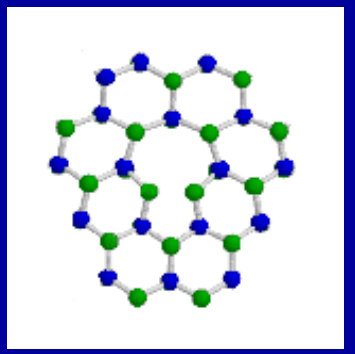
b: burger's vector
ν: Poisson's ratio



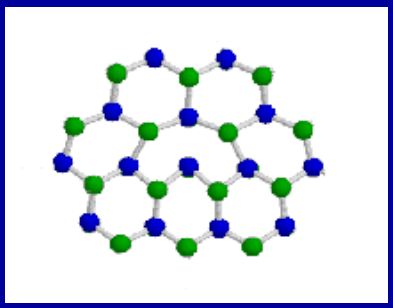




4 atom core



open core

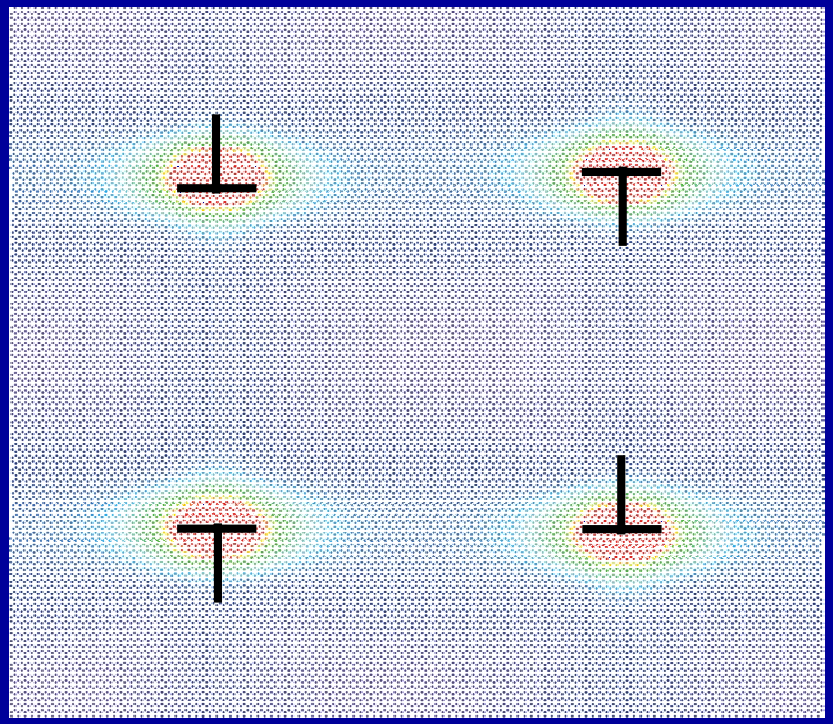


full core

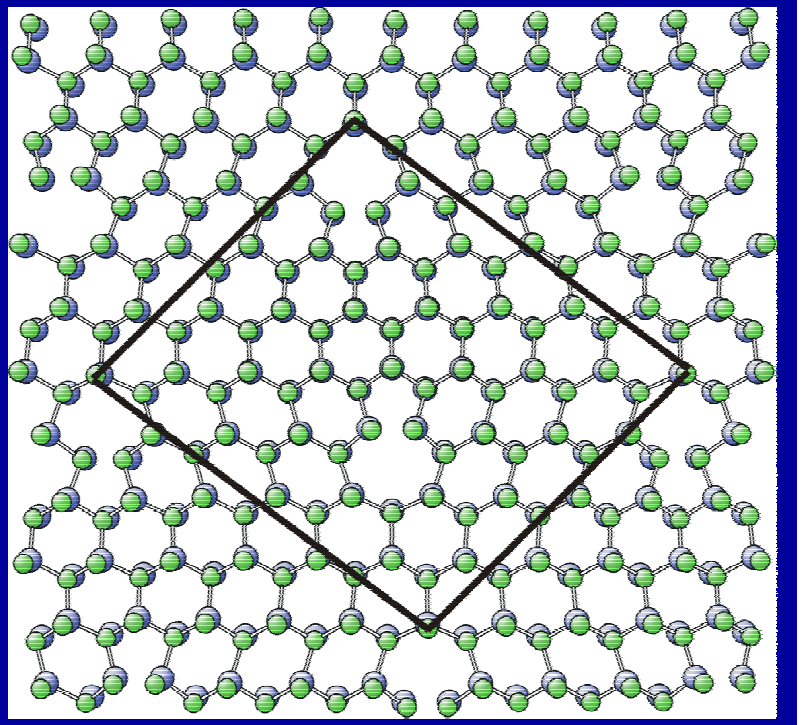
[1] J.P. Hirth & J. Lothe, *Theory of Dislocations* (Wiley, New York, 1982)
[2] M. Yu. Gutkin & E.C. Aifantis, Scripta Materiala **36**, 129 (1996)

Step II: Empirical Potentials

large scale



small scale



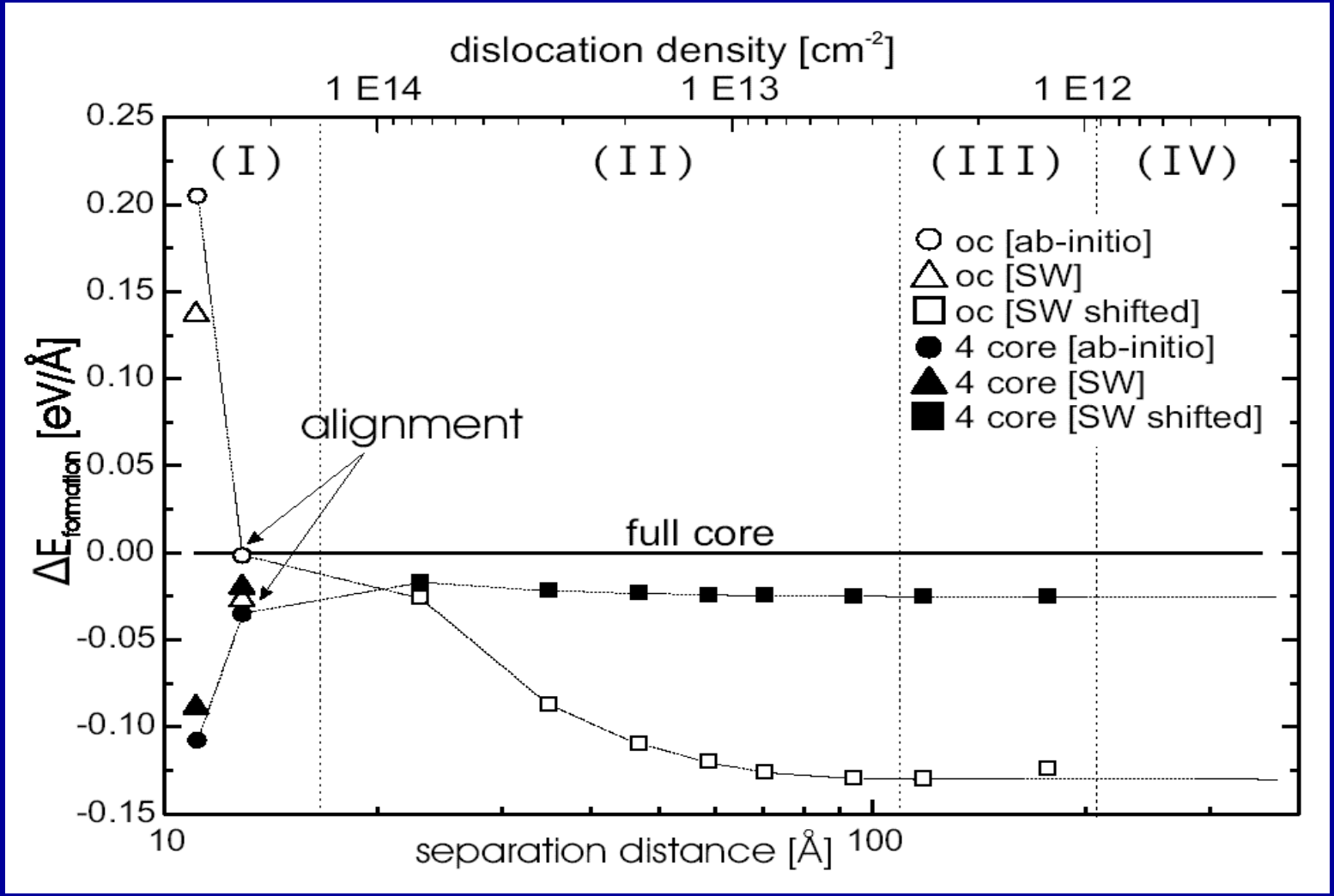
supercells with more than 10^5 atoms

⇒ Connect to continuum theory

supercells with ~10^2 atoms

⇒ Connect to ab initio calculations

Application: Energetics



L. Lymperakis and J. Neugebauer, to be published

Example: Crystal Growth

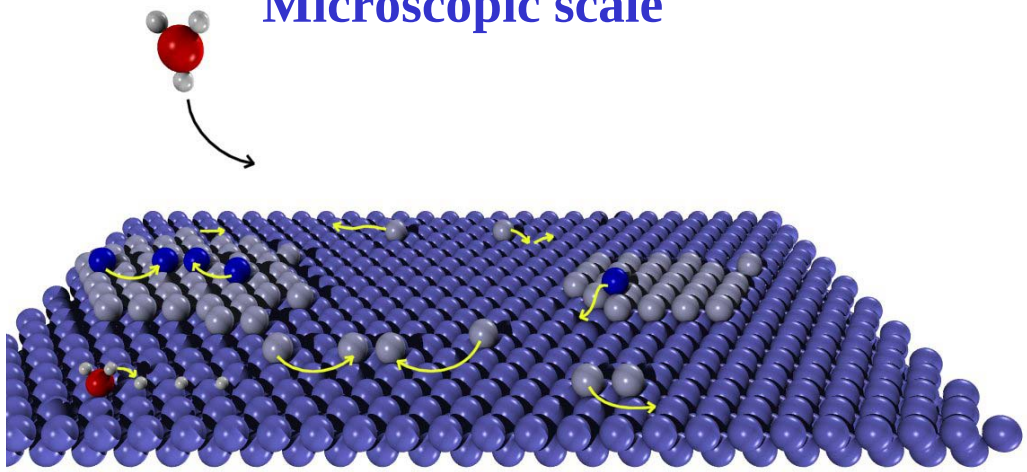
Length: 10^{-10} -10^{-9} m

Time: ~10^{-15} s

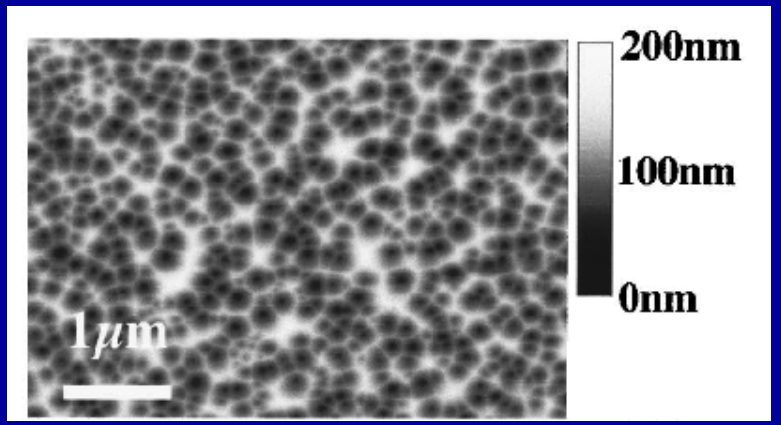
Length: 10^{-6} m

Time: 10^{0} s

Microscopic scale



Mesoscopic/macroscopic scale



Hierarchical Approach:

Electronic many particle system ✓

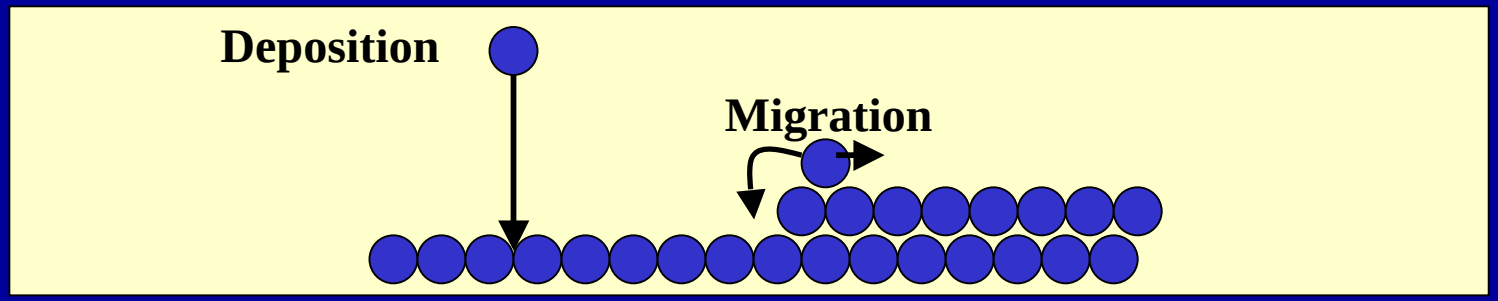
Atomic Interaction ✓

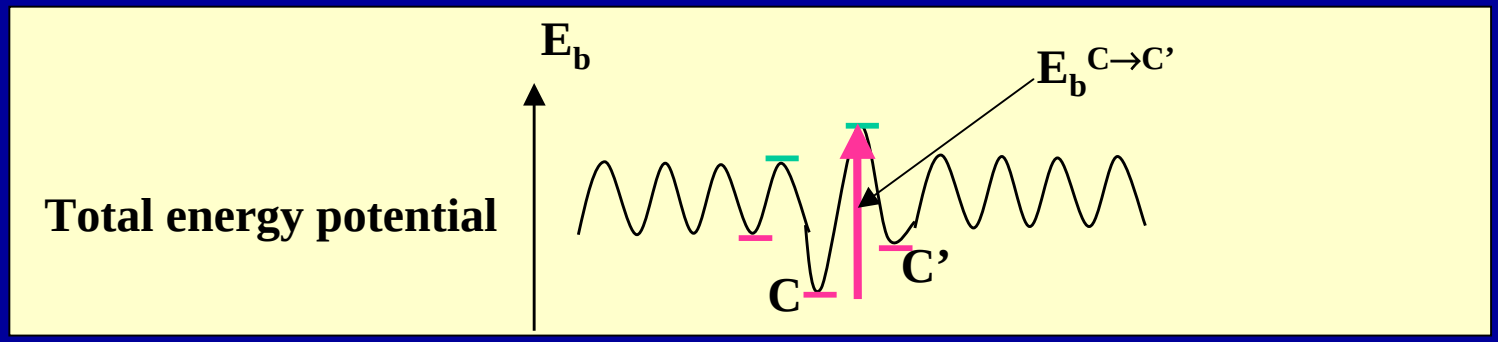
Atomic many particle system ?

→ Identify stable surfaces

→ Identify kinetic pathways

The Master Equation





Transition probability:

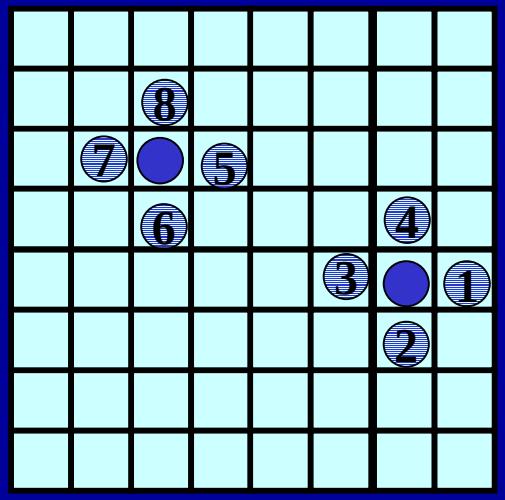
$$W_{C\rightarrow C'} = \Gamma_C e^{-E_b^{C\rightarrow C'}/K_B T}$$

Master Equation: $\partial P(C, t)/\partial t = \underbrace{-\Sigma_{C'} W(C\rightarrow C') P(C,t)}_{\text{Flux out}} + \underbrace{\Sigma_{C'} W(C'\rightarrow C) P(C',t)}_{\text{Flux in}}$

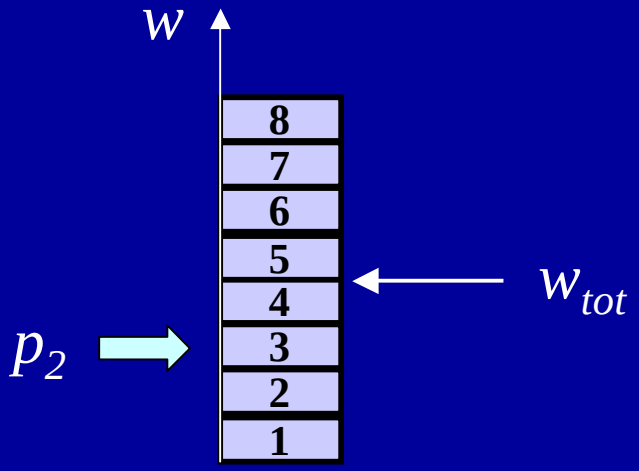
Solving the Master Equation: Kinetic Monte Carlo

Master Equation: $\partial P(C, t)/\partial t = -\Sigma_{C'} W(C \rightarrow C') P(C,t) + \Sigma_{C'} W(C' \rightarrow C) P(C',t)$

Example: Lattice gas



1. Build up probability vector:



2. Get time step:

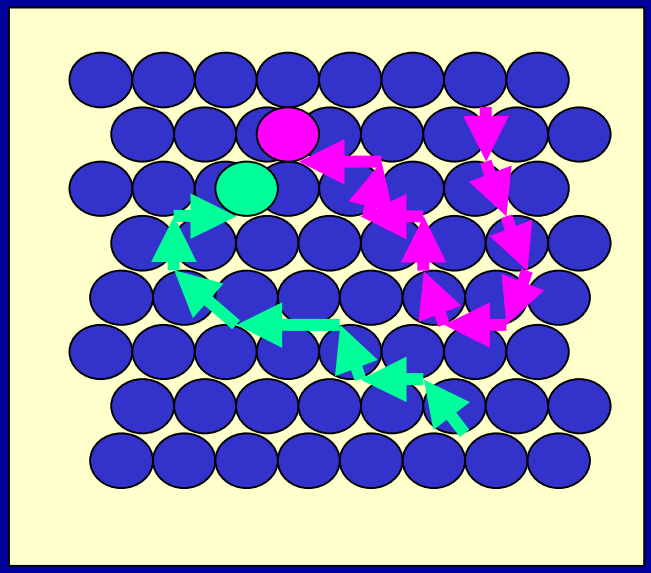
$$\Delta t = -\frac{\ln p_1}{w_{tot}}$$

3. Get event:

$$\frac{\ln w_i}{w_{tot}} \leq p_2 < \frac{\ln w_{i+1}}{w_{tot}}$$

Kinetic Monte Carlo Simulations

Conventional approach: Simulation of the process by KMC.



Temp. (K)	Diff. free path	Δt_{diff} (s)
500	30	$3.3*10^{-5}$
750	470	$2.1*10^{-6}$
1000	1800	$5.6*10^{-7}$
1150	60000	$1.7*10^{-8}$

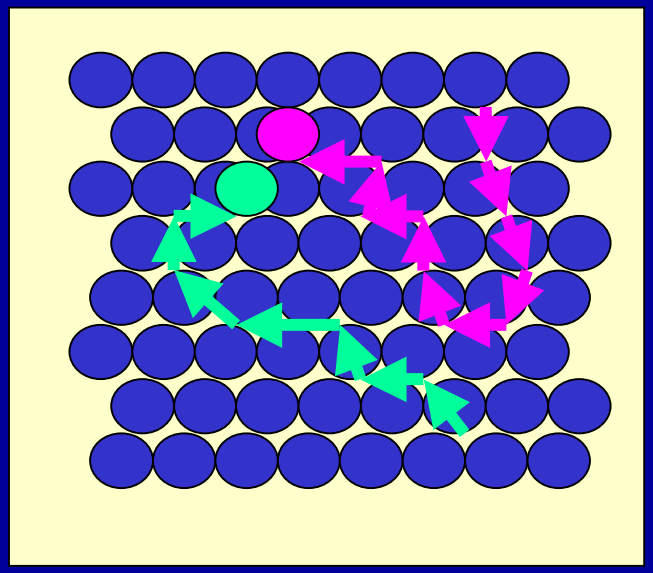
PROBLEM: Number of diffusion events is order of magnitudes larger than number of growth events!

Δt_s= average time for a change in the surface (nucleation, attachment)

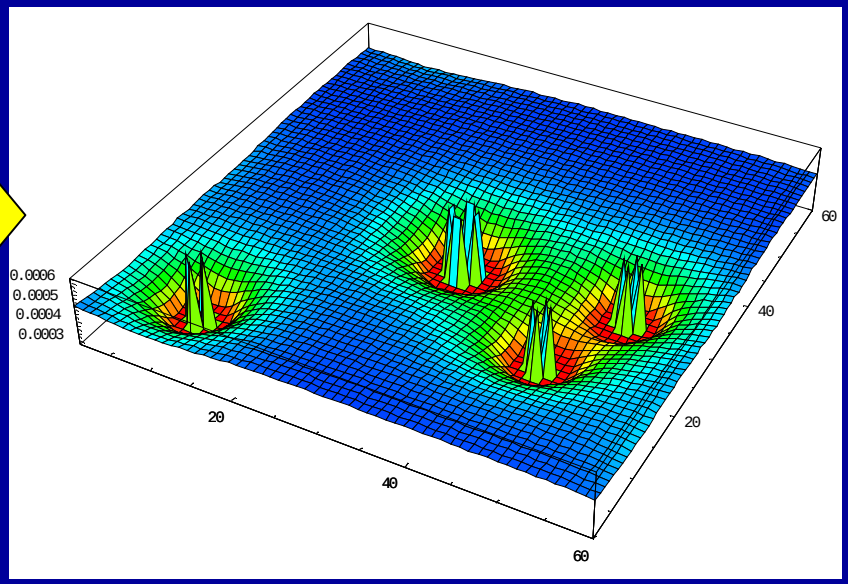
Δt_{ad}= average time for an adatom position change

$$\frac{\Delta t_s}{\Delta t_{ad}} \sim 10^3 .... 10^5$$

From Adatom Trajectories to Density



$P(x_1, x_2, ..., x_N, t)$



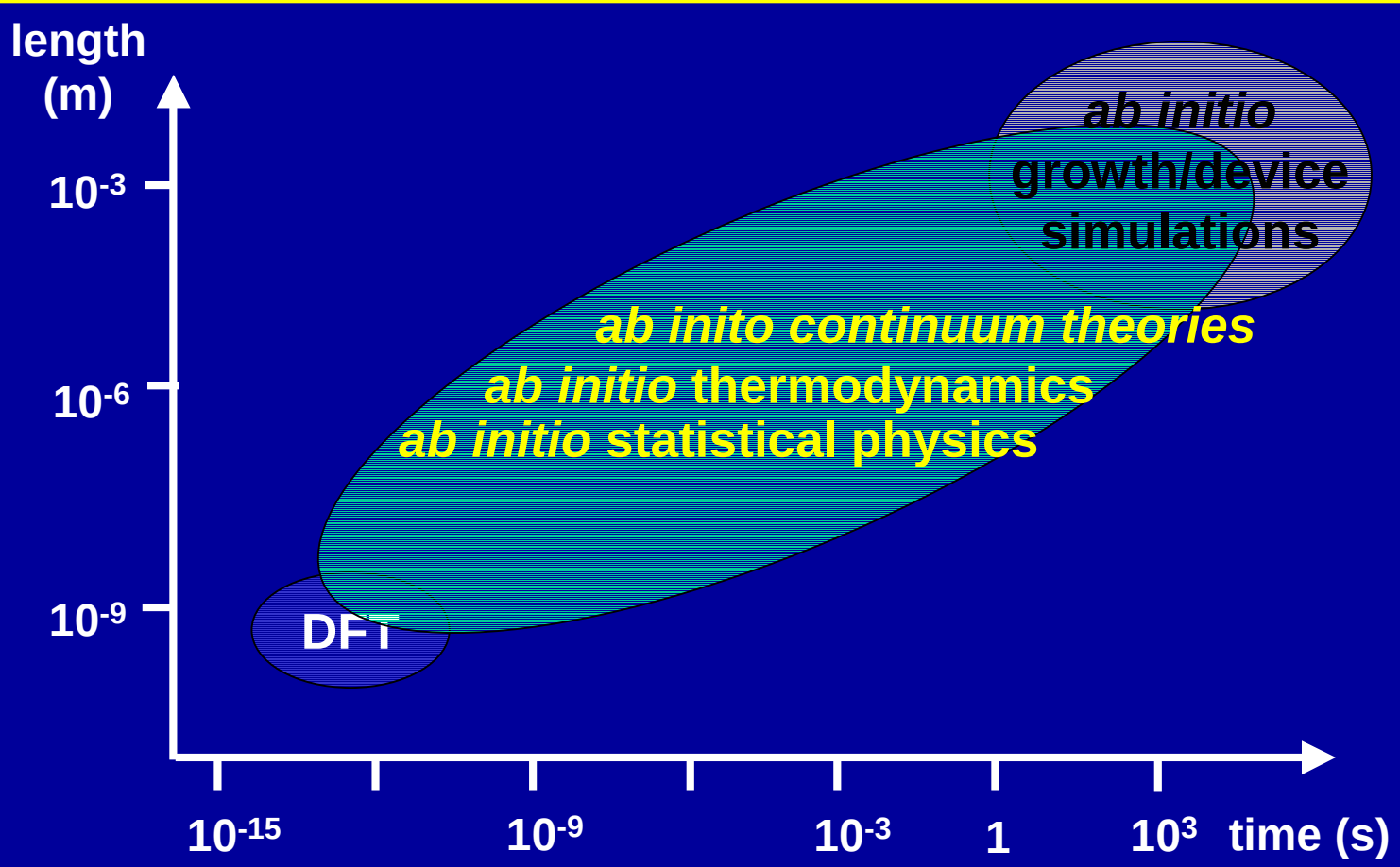
$\rho(x, t)$

Challenges:

- **Nucleation (requires in principle two particle density)**
- **Attachment**
- **Efficient calculation of the time evolution of the adatom density**
- **Numerical stability, statistical tests**
- **Connection to ab initio calculations (potential energy surface, diffusion paths)**

[1] L. Mandreoli, J. Neugebauer, R. Kunert, E. Scholl, subm. to PRB

Conclusions



Multiscale methods allow an accurate description of various aspects of materials science!