Modelling Materials at Realistic Temperatures and Pressures

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Materials Modelling

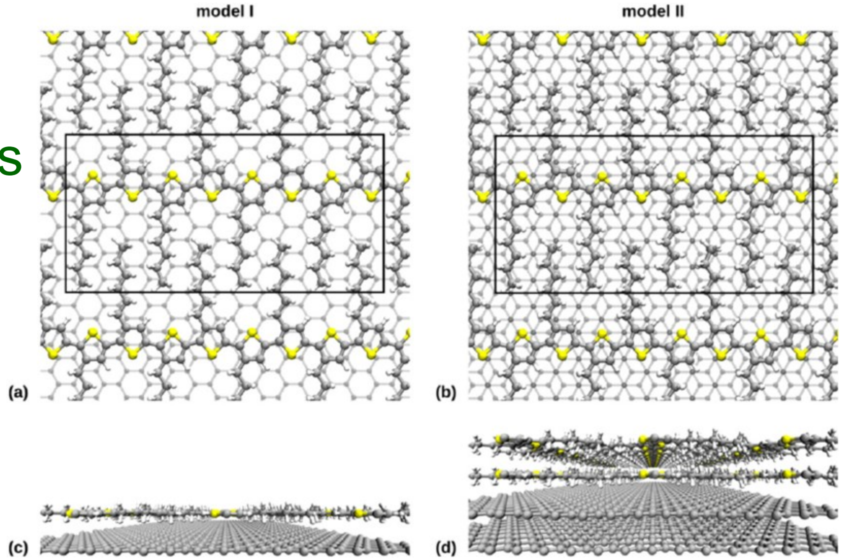
Macroscopic (continuum) models

Example: Diffusion equation

$$\frac{\partial \phi(\boldsymbol{r},t)}{\partial t} = \sum_{i=1}^{3}\sum_{j=1}^{3}\frac{\partial}{\partial x_i}\left(D_{ij}(\phi,\boldsymbol{r})\frac{\partial \phi(\boldsymbol{r},t)}{\partial x_j}\right)$$

parameters

Atomistic models

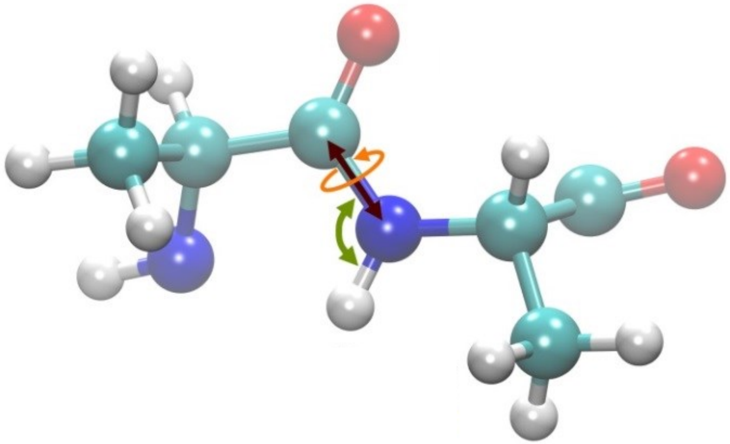


10 orders of magnitude in spatial scale,

15-18 orders of magnitude in time scale

Atomistic Modelling

Potential energy surface (PES): $E(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, \ldots), -\frac{\partial E}{\partial \mathrm{R}_i}, \ldots$



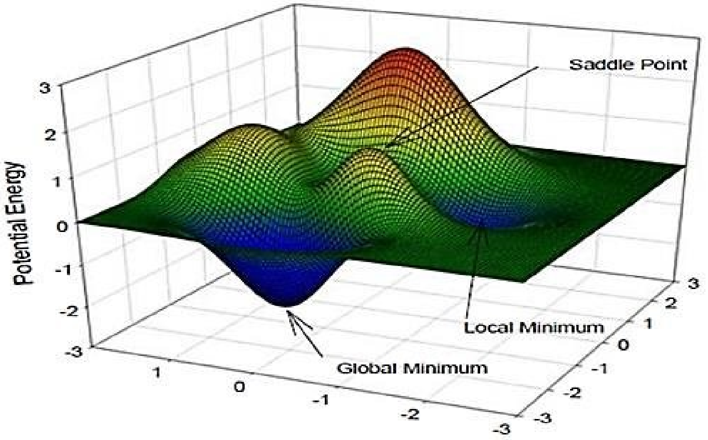
Empirical force fields:

$$E(R_1, \ldots) = \sum_{ij} \frac{k_{ij}}{2} \left(l_{ij} - l_{0,ij}\right)^2 + \sum_{ij} \frac{q_i q_j}{|R_i - R_j|} + \ldots$$

parameters - ?

no electronic properties (electronic levels, conductivity, etc.)

Can be very accurate - but only for a small part of PES



Many-body Quantum Mechanics

$$i\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

non-relativistic Schrödinger equation (otherwise need Dirac equations)

$\Psi\left(\{\mathbf{r}_i\},\{\sigma_i\},t\right)$ – wave function, depends on spatial ($\mathbf{r}_i$) and spin (σ_i) coordinates of particles, and time *t*

Hamiltonian operator

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \frac{\partial^2}{\partial \mathbf{r}_i{}^2}}_{\textbf{kinetic energy}} + \underbrace{U(\mathbf{r}_i,\sigma_i,t)}_{\textbf{potential energy}}$$

$$U(\{\mathbf{r}_i\},\{\sigma_i\},t) = \frac{1}{2}\sum_{i\neq j}\frac{Q_iQ_j}{\left|\mathbf{r}_i-\mathbf{r}_j\right|} + V^{ext}\left(\{\mathbf{r}_i\},t\right) + \sum_i C(\mathbf{r}_i,t)\left(\hat{\mathbf{L}}\cdot\sigma_i\right)$$

Thermodynamics

- **Why thermodynamics for materials?**

  A material is a collection of a large number of particles -- statistics starts to play a significant role at finite T

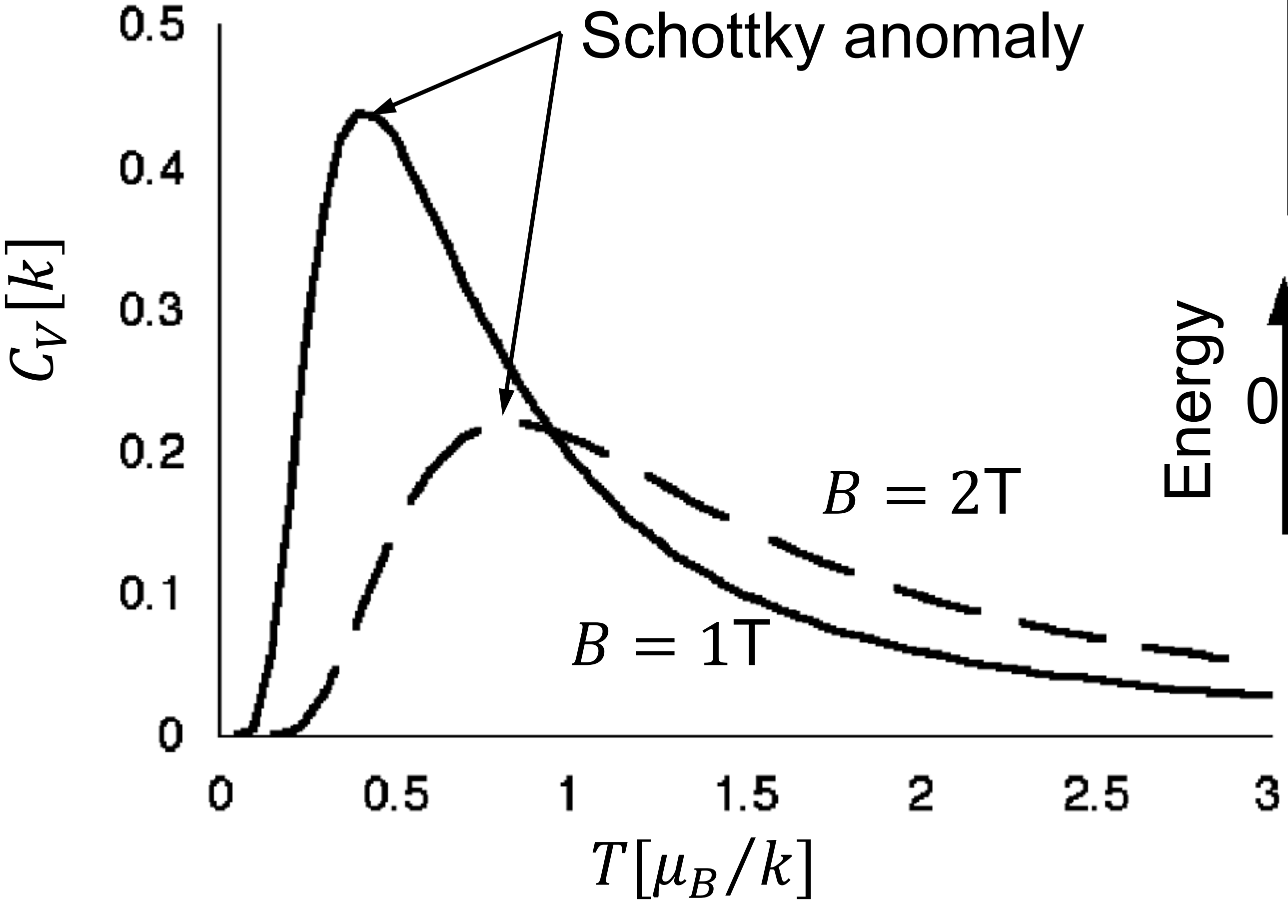
  Thermodynamics determines defect concentrations and phase transformations, and influences magnetic properties, surface reactions, and crystal growth (the latter two are controlled by *kinetics*)

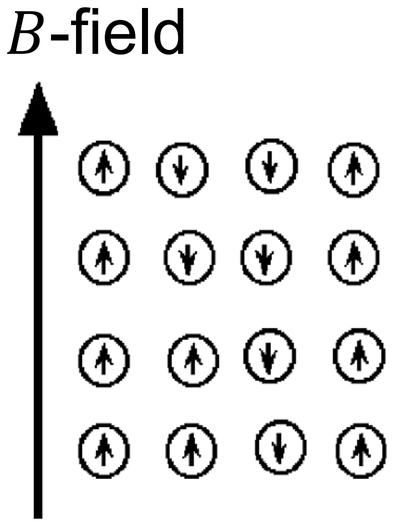
  There is always a particle exchange between the material and its environment at finite T

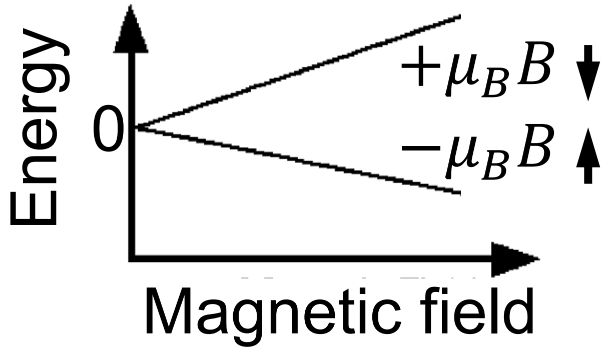
Thermodynamics

- **Example: Spins**

  Heat capacity of a paramagnet

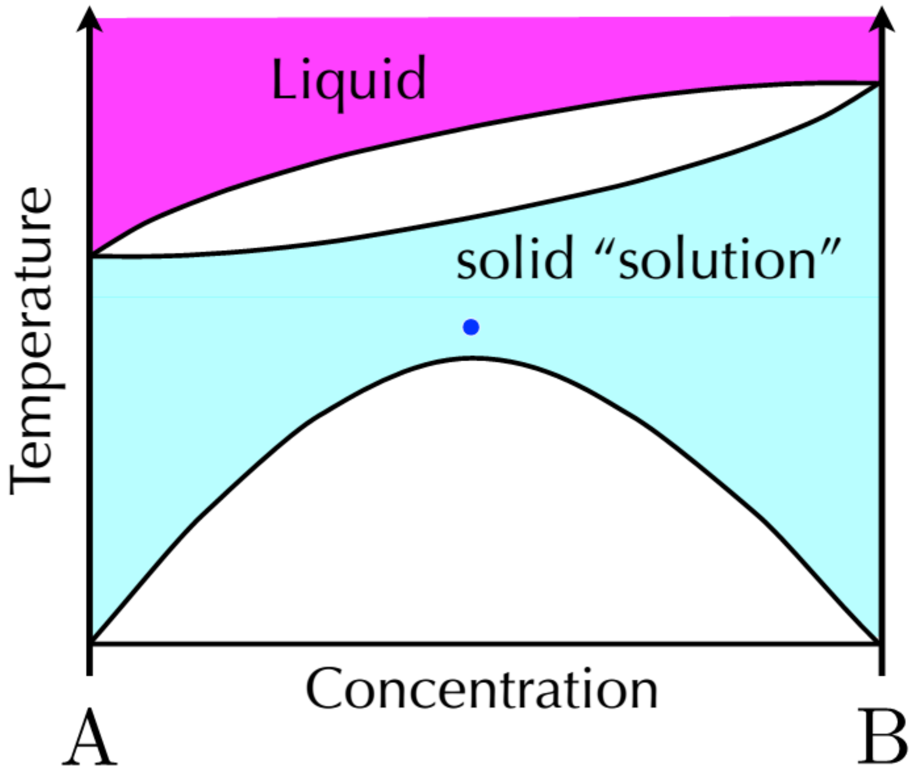






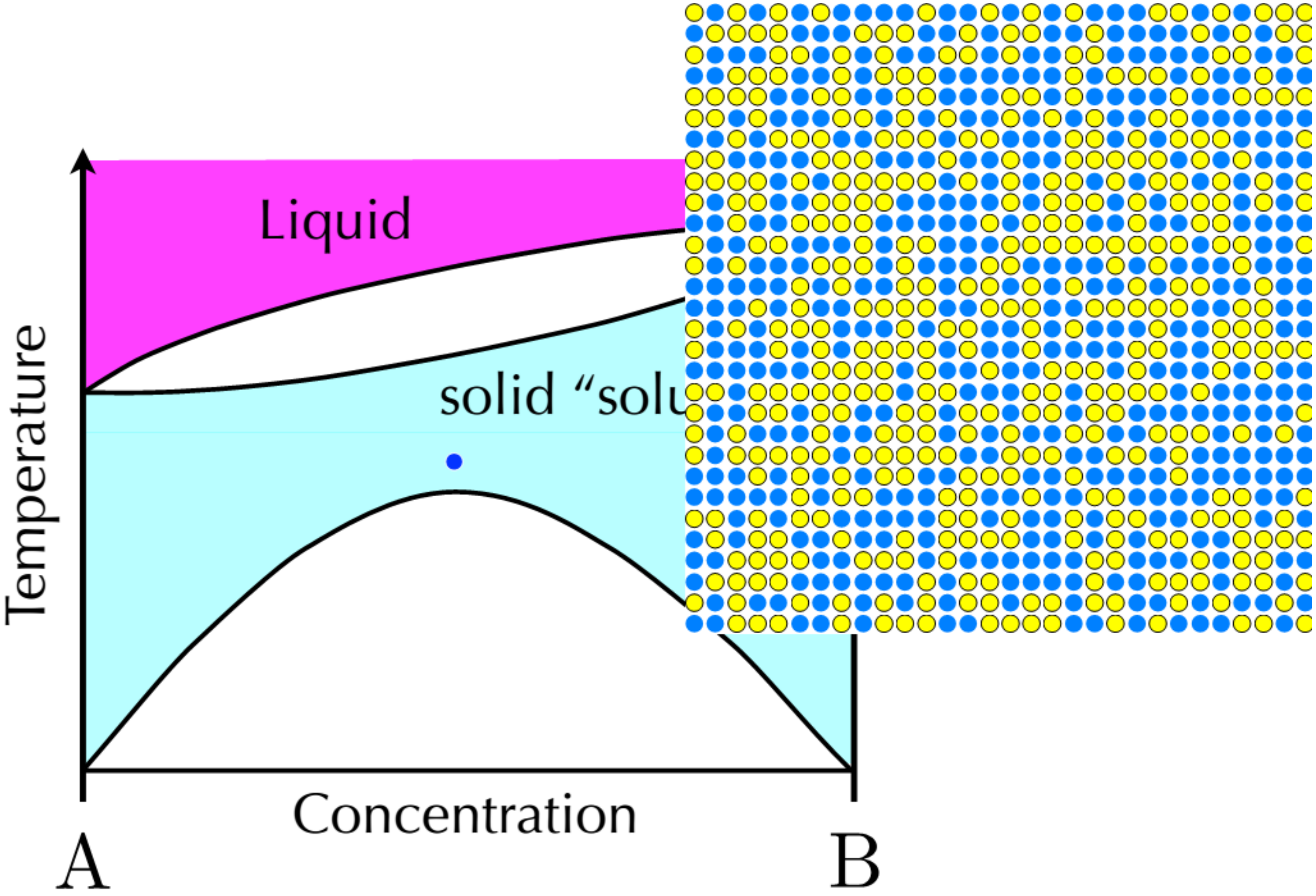
Alloys

- **Example: alloy phase diagrams**



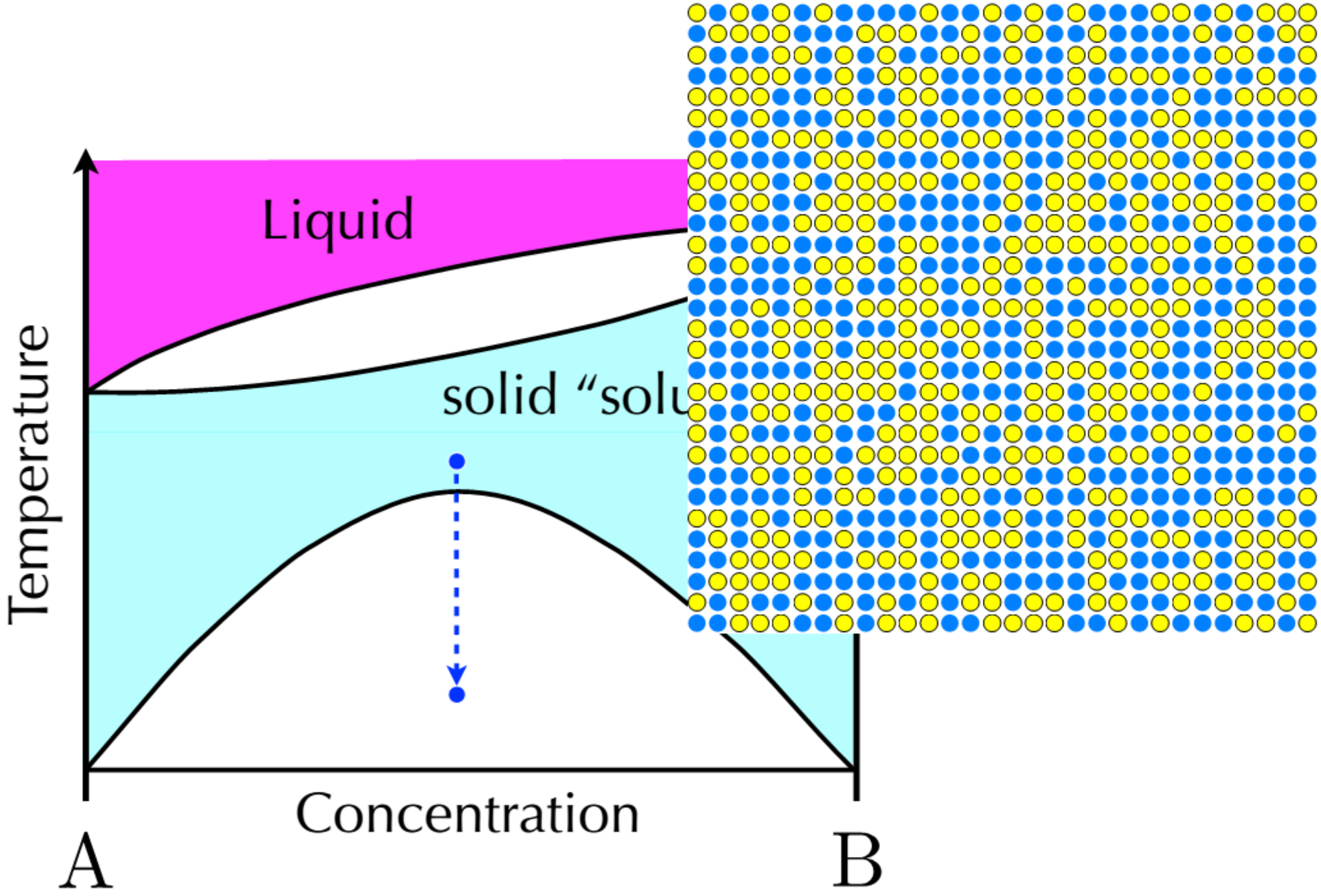
Alloys

- Example: alloy phase diagrams



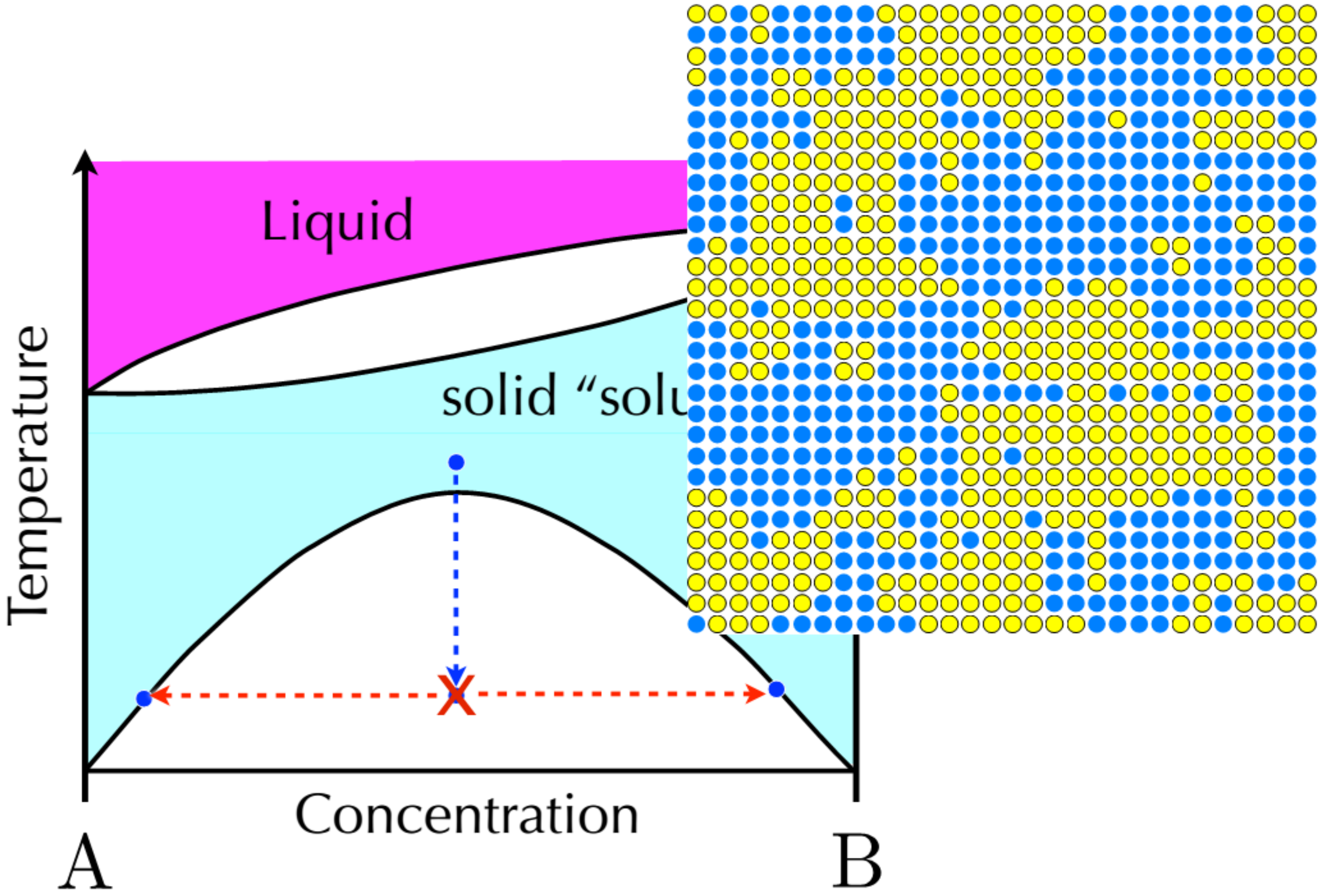
Alloys

- **Example: alloy phase diagrams**



Alloys

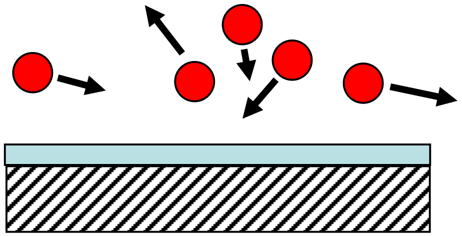
- **Example: alloy phase diagrams**



Surfaces

- **Example**

  Consider a metal surface in an oxygen atmosphere



$$\nu = \frac{p}{\sqrt{2\pi m k T}}$$

For T = 300 K, p = 1 atm → $\nu \sim 10^{8}$ site^{-1} s^{-1}

→ **Requires $p \leq 10^{-12}$ atm to keep a "clean" surface clean; surface can also lose atoms**

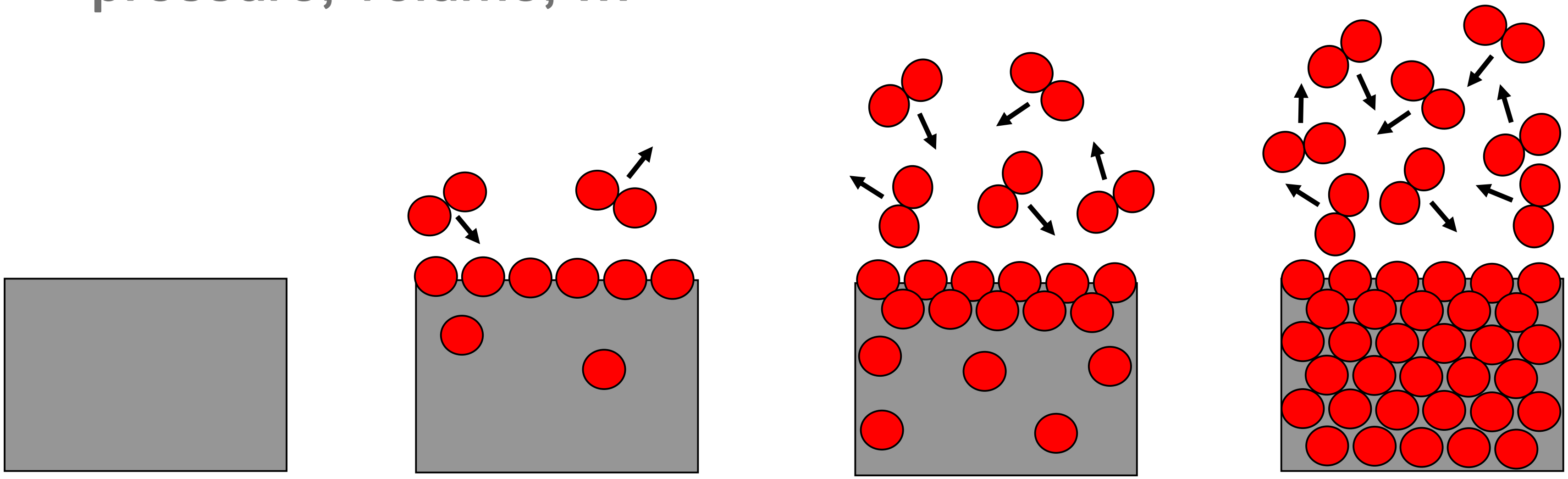
Adsorption will take place until the equilibrium is reached

Surfaces

- **Example**

  Consider a metal surface in an oxygen atmosphere

  The point of equilibrium depends on temperature, pressure, volume, …



Thermodynamics

❒ Thermodynamic potentials

Internal energy $U(S,V,\{N\})$

Enthalpy $H(S,p,\{N\}) = U + pV$

Helmholtz free energy $F(T,V,\{N\}) = U - TS$

Gibbs free energy $G(T,p,\{N\}) = U - TS + pV$

Grand potential $\Omega(T,p,\{\mu\}) = U - TS - \sum_i N_i\mu_i$

Gibbs free energy 2 $G\left(T,p,\{N_{i\neq j}\},\mu_j\right) = G - N_j\mu_j$

Energy balance equation

$$dU = TdS - pdV + \sum_i \mu_i dN_i$$

with chemical potentials

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V} = \left(\frac{\partial H}{\partial N_i}\right)_{S,p} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V} = \left(\frac{\partial G}{\partial N_i}\right)_{T,p}$$

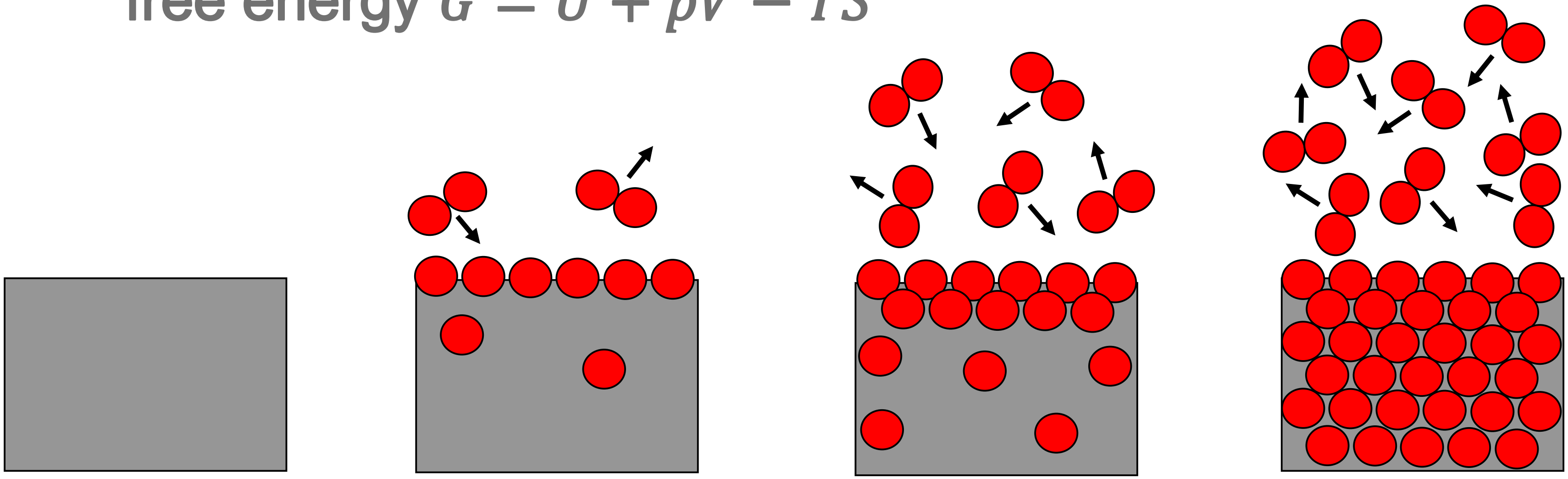
Thermodynamics

❒ Reaching the equilibrium

At constant T a system minimizes its free energy ($-TS$), not the internal energy U

If also volume V is constant, the energy minimized is the Helmholtz free energy $F = U - TS$

If (T, p) are constant, the energy minimized is the Gibbs free energy $G = U + pV - TS$



Thermodynamics

- **Statistical thermodynamics**

$$S = k \log W$$

W - number of *microstates* for a given *macrostate*

This is “only” a postulate - but it works!

Why it should work: (i) in equilibrium $W \to \max$, so that $S \to \max$; (ii) S is additive, but W is multiplicative

Thermodynamics

- **Statistical thermodynamics**

Let us consider a system that can be in one of states i with energy E_i

At a given T, the probability of the system to be in state i is $P_i = \frac{e^{-E_i/kT}}{Z}$, $Z = \sum_i e^{-E_i/kT}$, $\sum_i P_i = 1$

What are the average values of entropy and thermodynamic potentials?

Ergodic hypothesis: average over time is equal to the average over ensemble - holds if all states are equiprobable (for most realistic systems)

Thermodynamics

- **Statistical thermodynamics**

  Consider the ensemble of N replicas of the system - let us count microstates of this ensemble

  A microstate describes which replicas are in which state, while a macrostate describes how many replicas are in each state; thus: $W = \frac{N!}{N_1!(N-N_1)!}\frac{(N-N_1)!}{N_2!(N-N_1-N_2)!}\ldots = \frac{N!}{N_1!N_2!\ldots}$ where N_1, N_2,… are the numbers of the replicas in state 1, 2,…

$$N_i = NP_i = N\frac{e^{-E_i/kT}}{Z},\ \tilde{S} = k\ln W = k\ln(N!) - k\sum_i \ln(N_i!)$$

Z - canonical *partition function*

Use Stirling's formula: $\ln(N!) \approx N\ln N - N$

Thermodynamics

- **Statistical thermodynamics**

$$\tilde{S} = k\ln W = Nk\ln Z + \frac{N}{TZ}\sum_i E_i e^{-E_i/kT}$$

Internal energy, by definition: $\tilde{U} = \frac{N}{Z}\sum_i E_i e^{-E_i/kT} = \frac{NkT^2}{Z}\frac{\partial Z}{\partial T}$

$$U = \frac{\tilde{U}}{N} = \frac{kT^2}{Z}\frac{\partial Z}{\partial T} = kT^2\frac{\partial \ln Z}{\partial T}$$

$$S = \frac{\tilde{S}}{N} = \frac{k\ln W}{N} = k\ln Z + \frac{U}{T} = k\ln Z + kT\frac{\partial \ln Z}{\partial T}$$

$$F = U - TS = -kT\ln Z$$

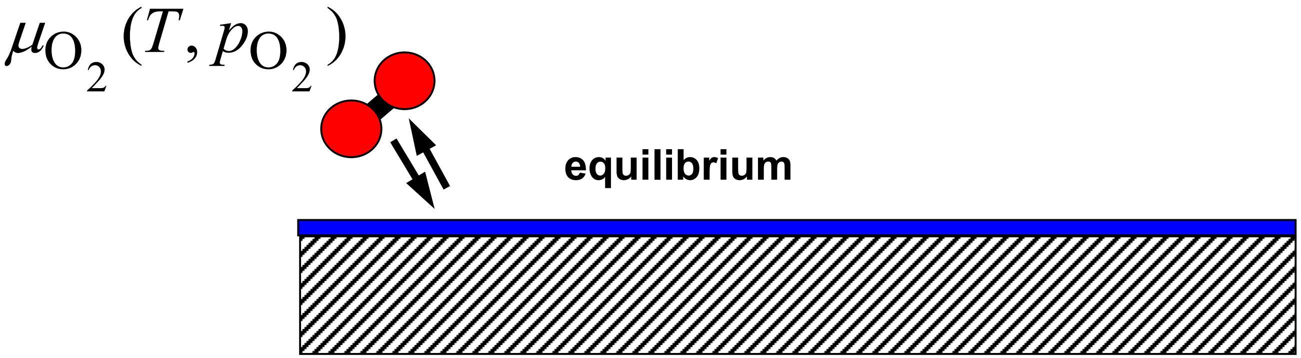
$$G = F + pV = -kT\ln Z + pV$$

$$\mu(T,p) = \left(\frac{\partial G}{\partial N}\right)_{T,p} = \frac{\partial}{\partial N}(-kT\ln Z + pV)_{T,p}$$

Thermodynamics

❐ Statistical thermodynamics

Practical example: surface free energy



Change in Gibbs free energy upon addition of O to the surface: $\Delta G = G_{surf}(N_O + 1) - \left(G_{surf}(N_O) + \frac{1}{2}\mu_{O_2}\right)$

since $\mu_O = \frac{1}{2}\mu_{O_2}$

Goal - find surface composition that minimizes G at given T, p

Thermodynamics

- **Statistical thermodynamics**

Practical example: surface free energy

$$\Delta\gamma(N_O,T,p)=\frac{1}{A}\left[G_{surf}(N_O,T,p)-G_{surf}\left(N_O^{ref},T,p\right)-\mu_O\left(N_O-N_O^{ref}\right)\right]\rightarrow\min_{N_O}$$

where A is the surface area, N_O^{ref} is the number of O atoms in the reference system

$$G_{surf}(N_O)-G_{surf}\left(N_O^{ref}\right)=\Delta E_{surf}+\Delta U_{vib}-T\Delta S_{vib}-T\Delta S_{conf}+p\Delta V$$

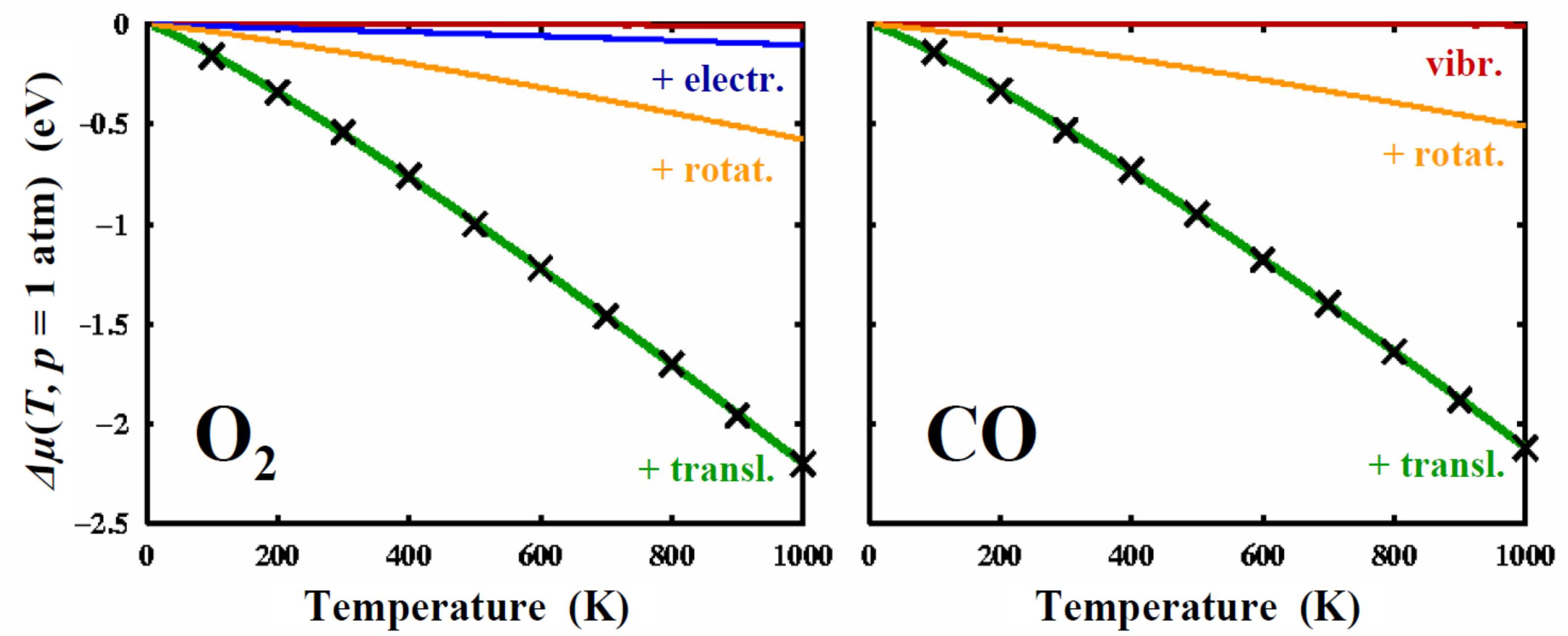
$\mu_O(T,p)$ - ?

In thermodynamic equilibrium, μ is the same everywhere (gas, surface, bulk) - can calculate μ in gas

Thermodynamics

❐ Ab initio atomistic thermodynamics

It is convenient to define a reference for $\mu(T,p)$ **:** $\mu(T,p) = E_0 + \Delta\mu(T,p)$

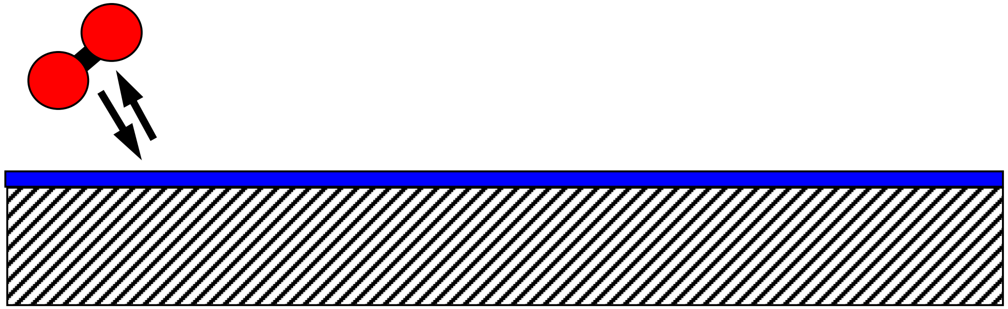


Alternatively: $\Delta\mu(T,p) = \Delta\mu(T,p^{\mathrm{O}}) + k_{\mathrm{B}}T\ln(p/p^{\mathrm{O}})$

and $\Delta\mu(T,p^{\mathrm{O}} = 1\ \mathrm{atm})$ **from thermochemical tables (e.g., JANAF)**

Thermodynamics

- ***Ab initio* atomistic thermodynamics**



$$\Delta\gamma(N_O,T,p) = \frac{1}{A}\left[\Delta E_{surf} + \Delta U_{vib} - T\Delta S_{vib} - T\Delta S_{conf} + p\Delta V - \mu_O \Delta N_O\right]$$

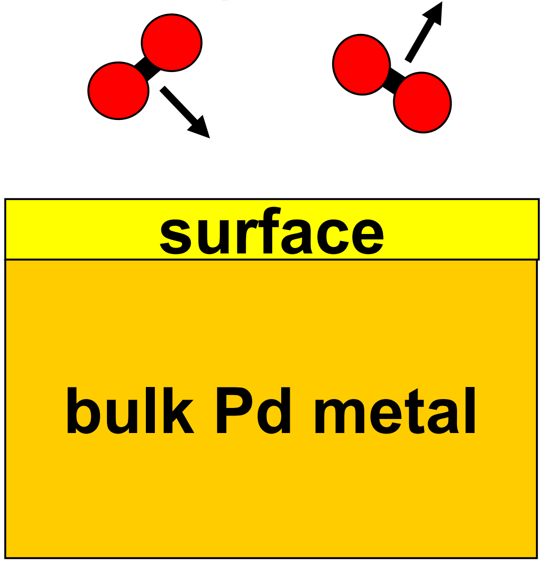
electronic structure calculations

$\Delta F_{vib}(T,V) = V\int_0^\infty f(T,\omega)\left(\sigma(\omega) - \sigma_{ref}(\omega)\right)d\omega$, $\sigma(\omega)$ - phonon density of states, $f(T,\omega) = \frac{\hbar\omega}{2} + kT\ln\left(1 - e^{-\hbar\omega/kT}\right)$

Thermodynamics

- ***Ab initio* atomistic thermodynamics**

Example: Metal surface in contact with O_2 gas



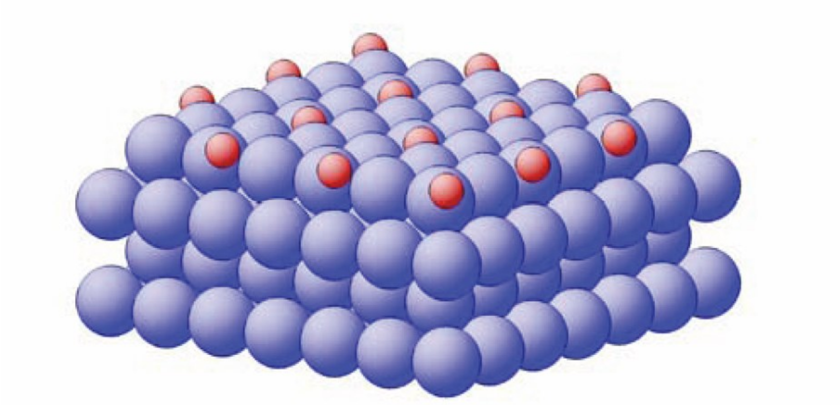
Reservoir: $\mu_O(T, p_{O_2})$ from ideal gas, $N_O^{ref} = 0$ (bare metal surface is the reference system), $\frac{1}{2}E_{O_2}$ is the reference for the chemical potential of O: $\mu_O = \Delta\mu_O + \frac{1}{2}E_{O_2}$

Neglect for now ΔF_{vib} and $T\Delta S_{conf}$

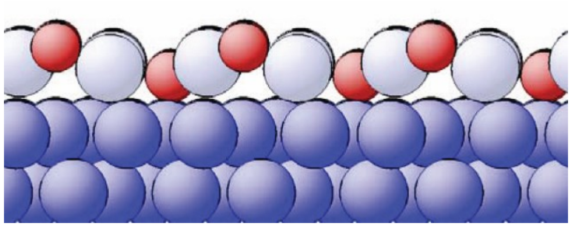
$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A}\left[E_{surf}(N_O) - E_{surf}(0) - N_O \frac{1}{2} E_{O_2}\right] - \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2})$$

Example: Pd(100)

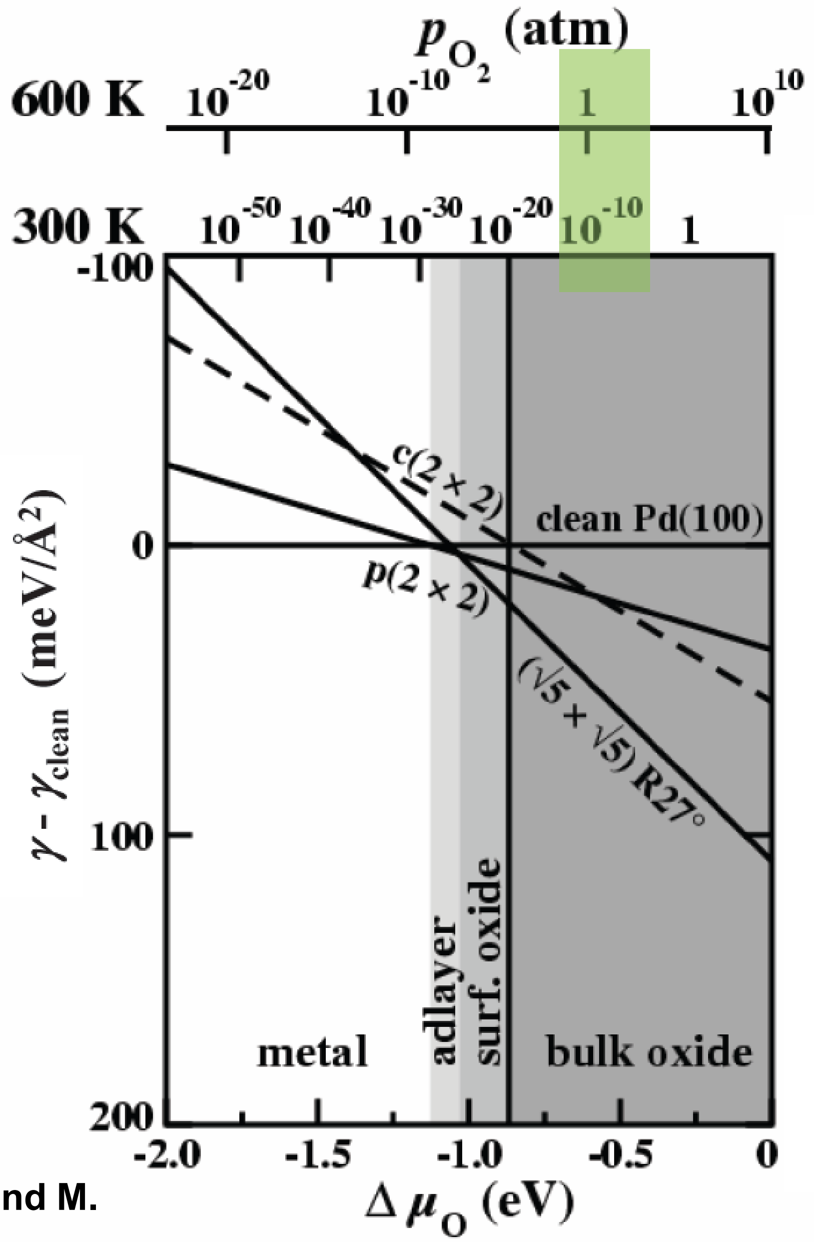
$$\Delta\gamma(T,p_{O_2}) = \frac{1}{A}\Delta E_{surf}(N_O) - \frac{1}{A}N_O\Delta\mu_O(T,p_{O_2})$$



***p*(2x2) O/Pd(100)**

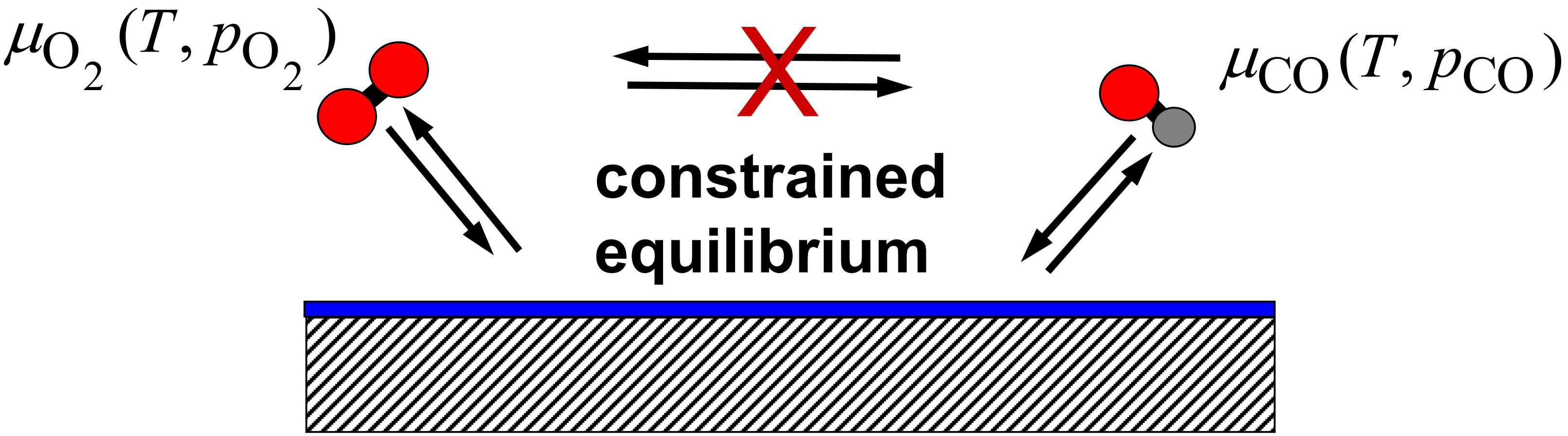


(√5x√5)*R*27° PdO(101)/Pd(100)



M. Todorova *et al.*, Surf. Sci. 541, 101 (2003); K. Reuter and M. Scheffler, Appl. Phys. A 78, 793 (2004)

First-principles atomistic thermodynamics: constrained equilibria



$\mu_{\mathrm{O}_2}(T, p_{\mathrm{O}_2})$

$\mu_{\mathrm{CO}}(T, p_{\mathrm{CO}})$

constrained equilibrium

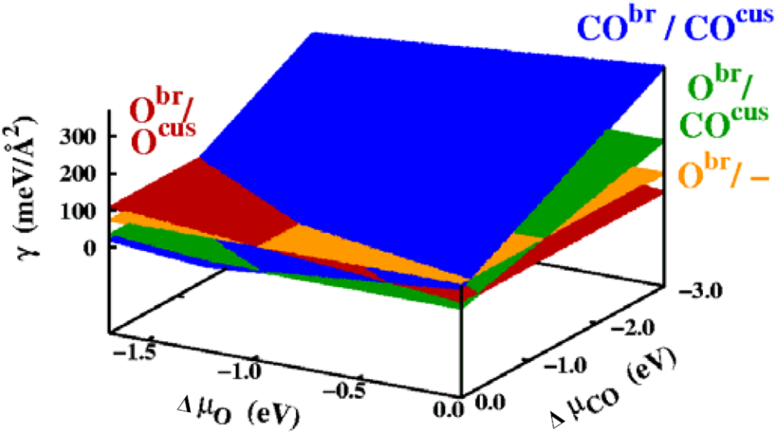
$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A}\left[E_{surf}(N_O, N_{CO}) - E_{surf}^{ref} - N_O \frac{1}{2} E_{O_2} - N_{CO} E_{CO}\right]$$

$$- \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2}) - \frac{1}{A} N_{CO} \Delta\mu_{CO}(T, p_{CO})$$

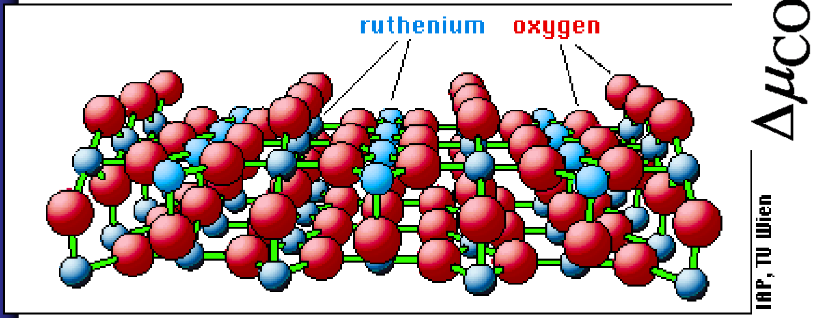
C.M. Weinert and M. Scheffler, Mater. Sci. Forum 10-12, 25 (1986); E. Kaxiras *et al.*, Phys. Rev. B 35, 9625 (1987);

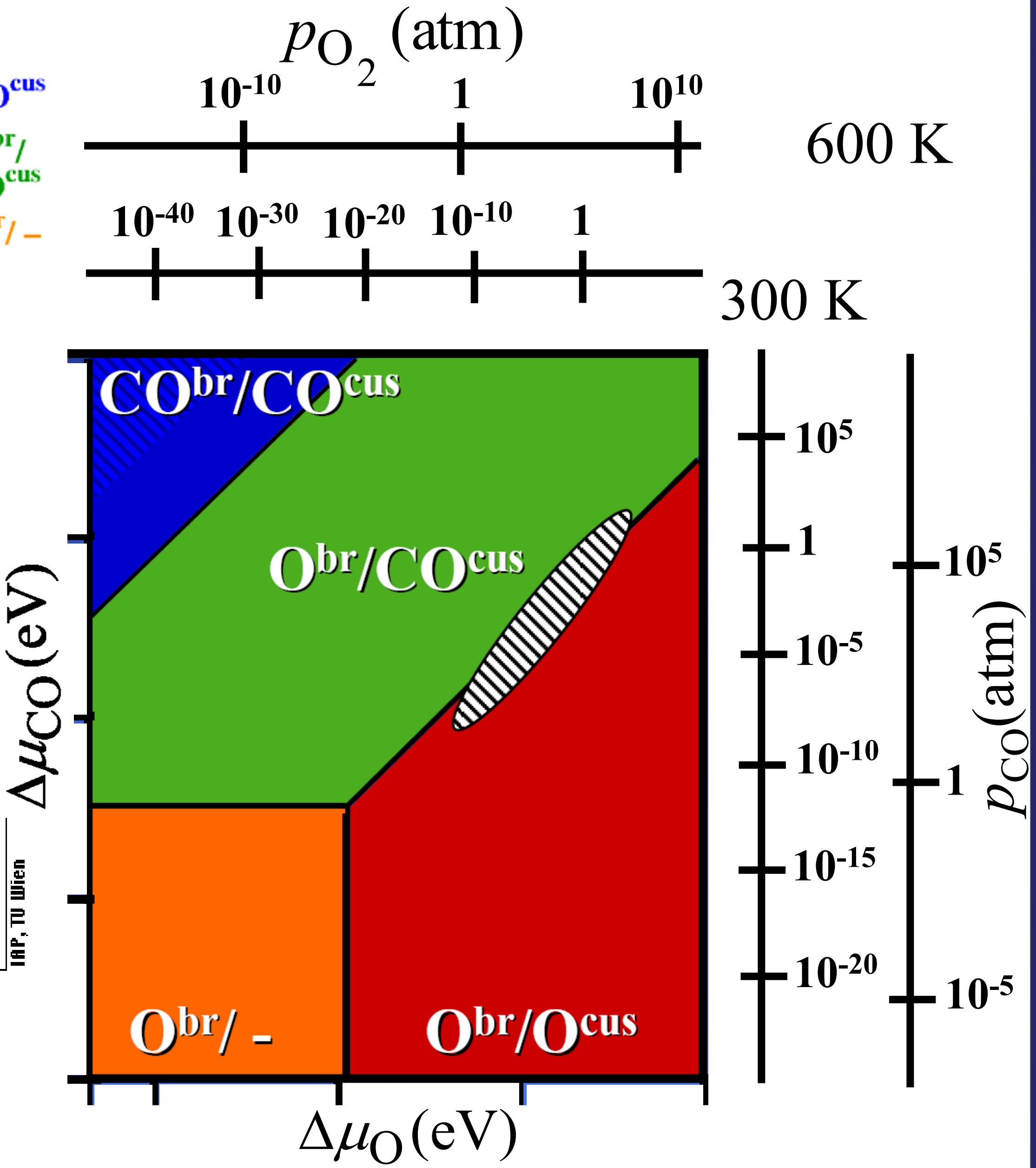
K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2001); Phys. Rev. B 68. 045407 (2003)

Surface phase diagrams



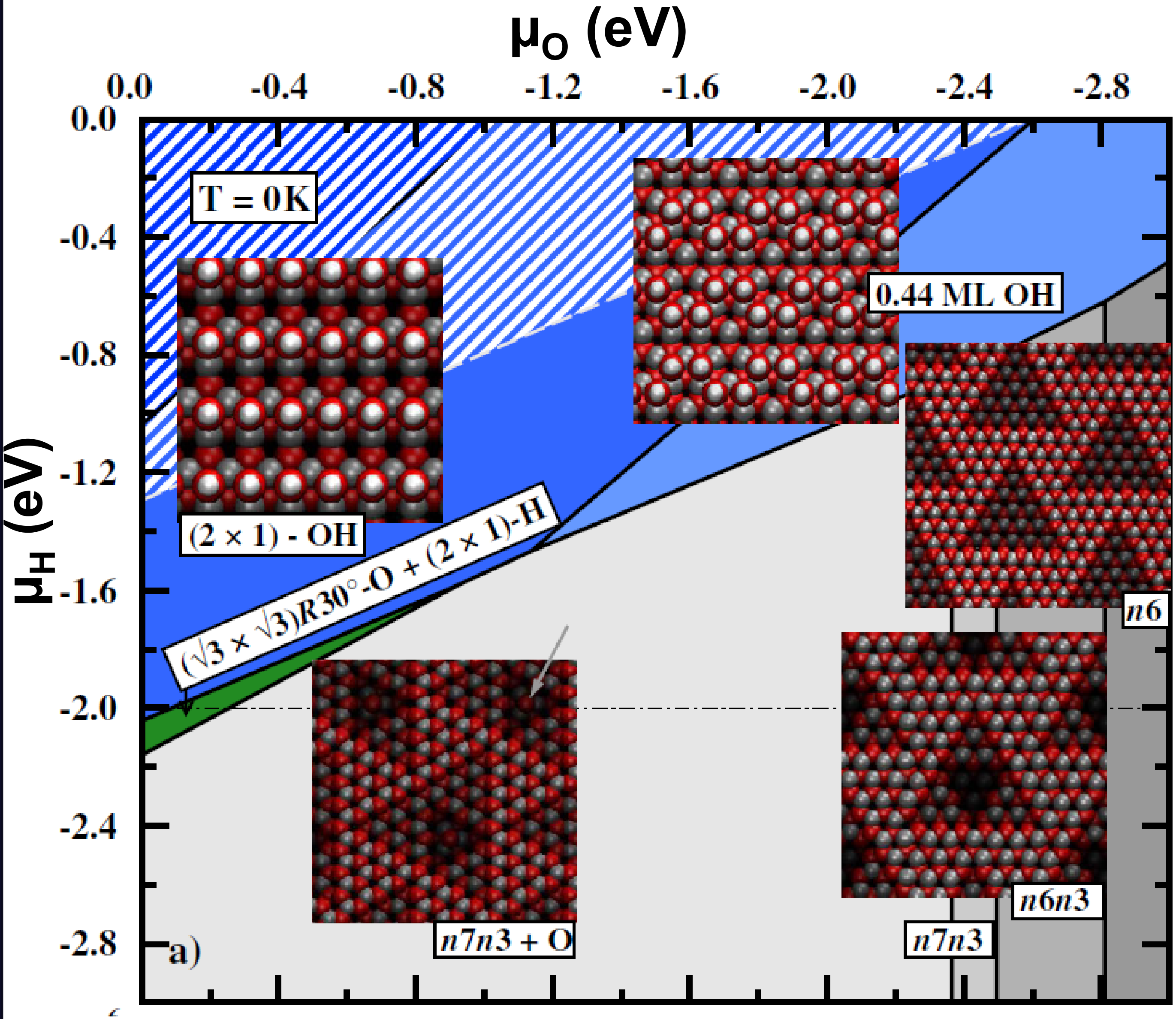
CO oxidation on $RuO_2(110)$





K. Reuter and M. Scheffler,
Phys. Rev. Lett. 90, 046103 (2003)

When vibrations do matter

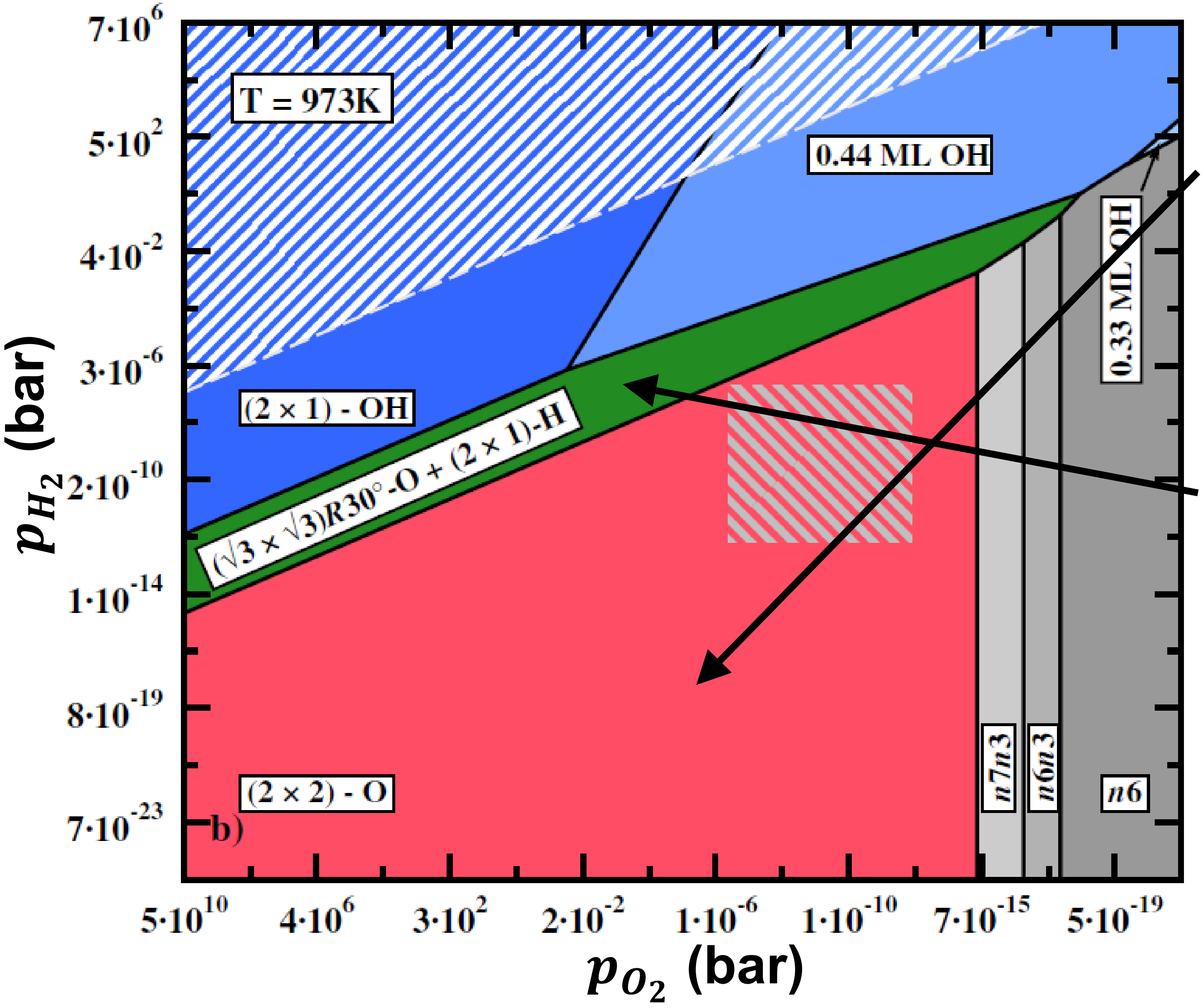


ZnO (0001) surface phase diagram in H_2O-O_2 atmosphere – no vibrations

No structure with (2x2) periodicity as seen at the ZnO(0001) surface annealed in a dry oxygen atmosphere (containing at maximum 2 ppm water)

M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer, PRL **103**, 065502 (2009)

When vibrations do matter



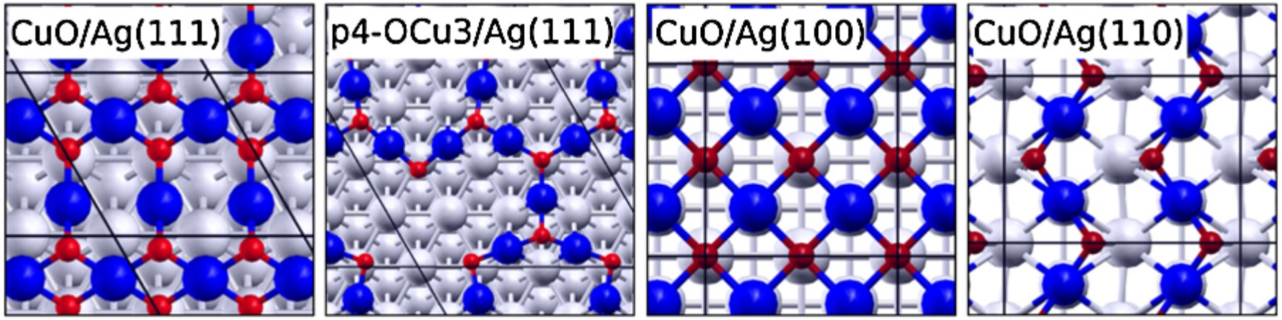
A (2x2)-O adlayer structure is stabilized by vibrational entropy effects

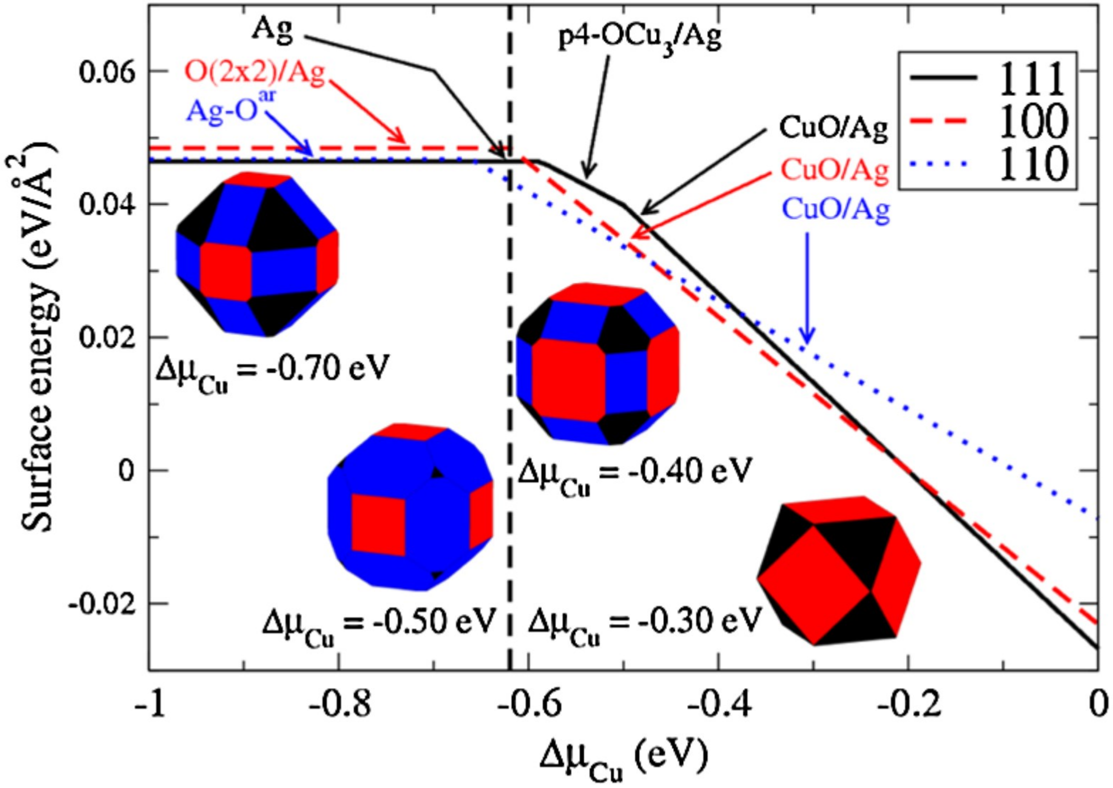
Observed at “humid” conditions

M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer, PRL **103**, 065502 (2009)

Thermodynamics of nanoparticles

Ag-Cu nanoparticles in O atmosphere





The shape and surface composition of the particles depends on the conditions

S. Piccinin *et al*., Phys. Rev. Lett. **104**, 035503 (2010)

Thermodynamics of Defects

- **Very small concentrations of defects can significantly alter materials properties**

50 ppm Fe

Small concentration of Fe impurities are visible by naked eye in intrinsically transparent MgO

Si semiconductors contain 10^{-9}-10^{-3} intentional impurities per atom

“My precious!”: Perfect defected gems

$Cr:Al_2O_3$

$V:Al_2O_3$

$Fe:Al_2O_3$

$Fe:Al_2O_3$

Impurities are responsible for the color of sapphire and many other precious stones

Typical concentrations: 100-10000 ppm

$Fe,Ti:Al_2O_3$

When imperfections are useful

Tailoring defect properties has a tremendous potential for designing novel functional materials in many areas of technology (electronics, optics, catalysis, photocatalysis, thermoelectrics, optoelectronics, spintronics, etc.)

↓

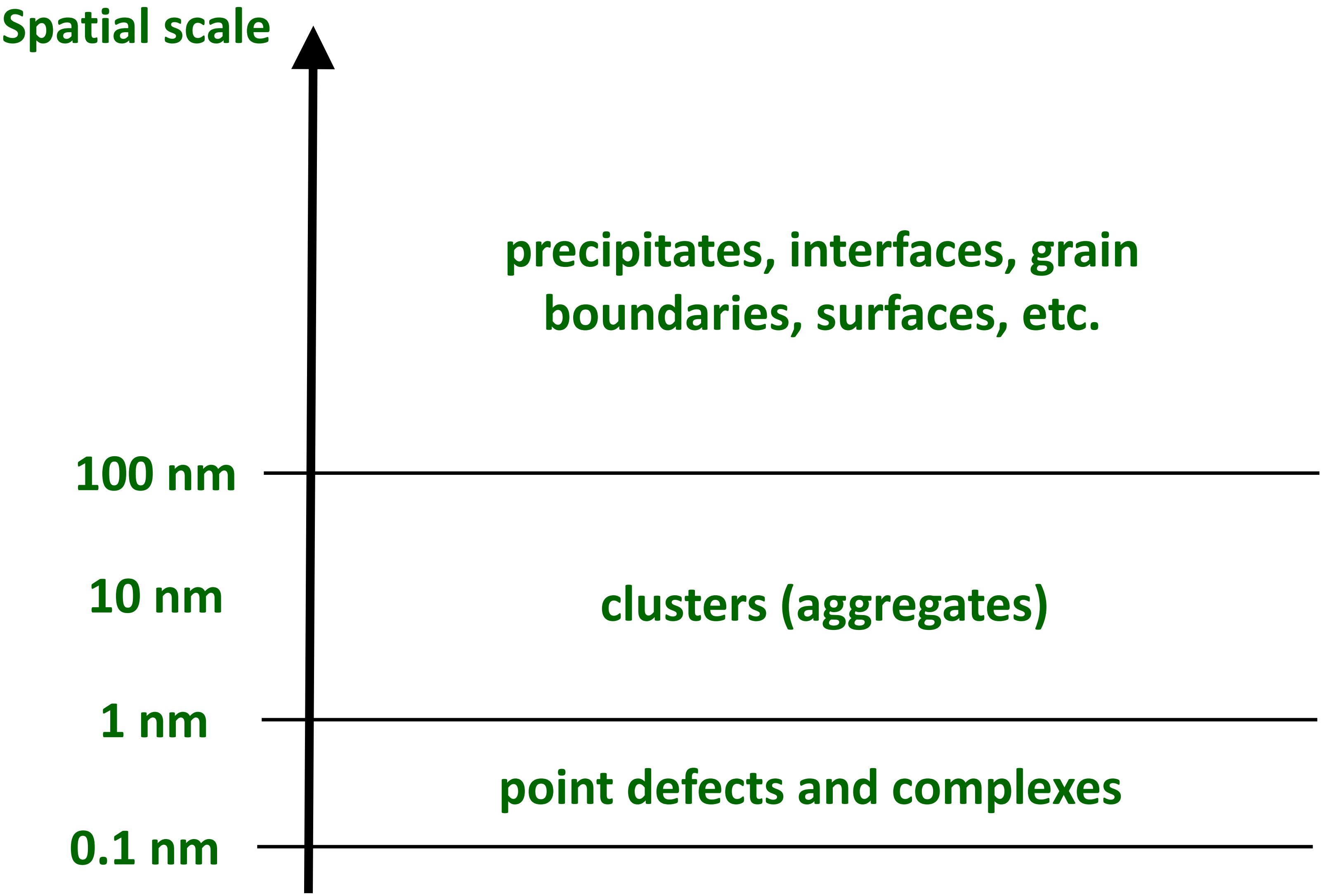
Understanding the electronic and atomic structure of defects is of great importance

The “invisible agent”

“…The problem is that defects are often elusive species, highly diluted, and therefore difficult to detect. It is as if one wanted to identify all the men with a beard among the population of Europe from a satellite which is a few hundreds of kilometers away from the earth surface: the task is difficult, and it is easy to get confused.” (G. Pacchioni, ChemPhysChem **4**, 1041 (2003))

In fact, the situation is even more complex: The nature and concentration of defects depend on temperature, pressure, and charge-carrier doping

Larger-scale symmetry breaking



Spatial scale

precipitates, interfaces, grain boundaries, surfaces, etc.

100 nm

10 nm

clusters (aggregates)

1 nm

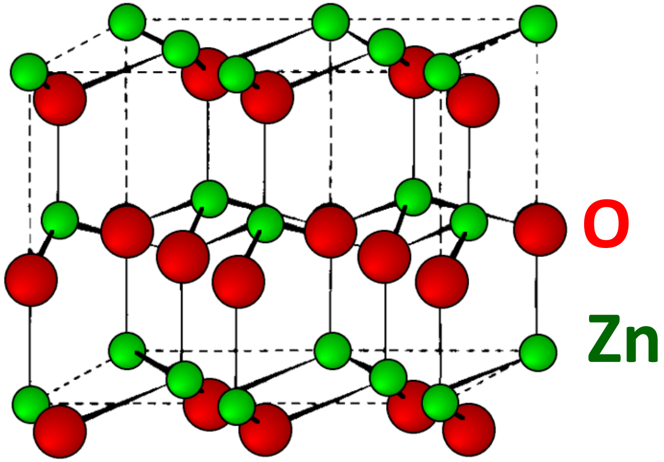
point defects and complexes

0.1 nm

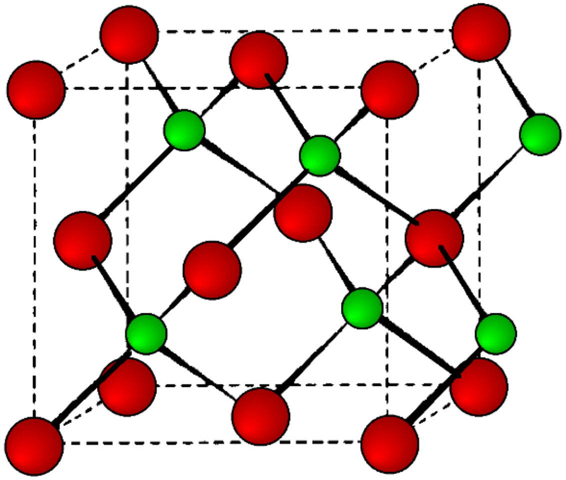
Nanometer-size defects are building blocks for the larger defects

Why oxides are semiconductors?

ZnO – example of a very promising functional material



wurtzite (stable)

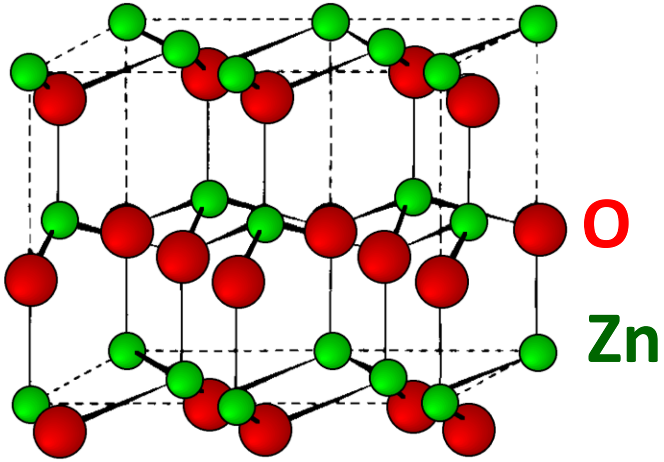


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

Band gap ~3.3 eV (direct), but (almost?) exclusively *n*-type semiconductor

Why oxides are semiconductors?

ZnO – example of a very promising functional material



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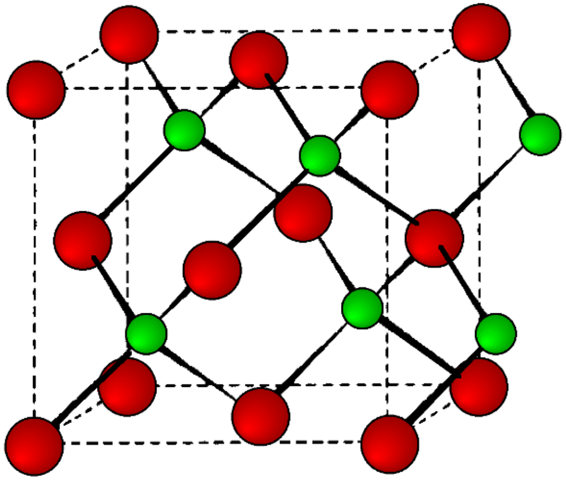
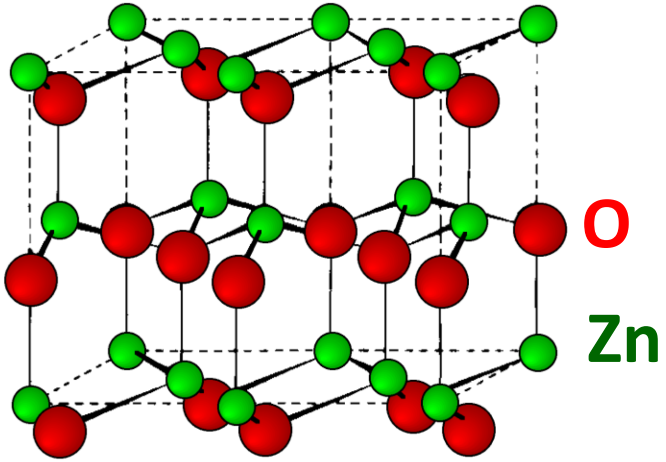


zinkblende (can be obtained by growth on substrates with cubic lattice structure)

Can be used for blue/UV LED/lasers, and, in contrast to GaN, is available as large bulk single crystals

Why oxides are semiconductors?

ZnO –example of a very promising functional material



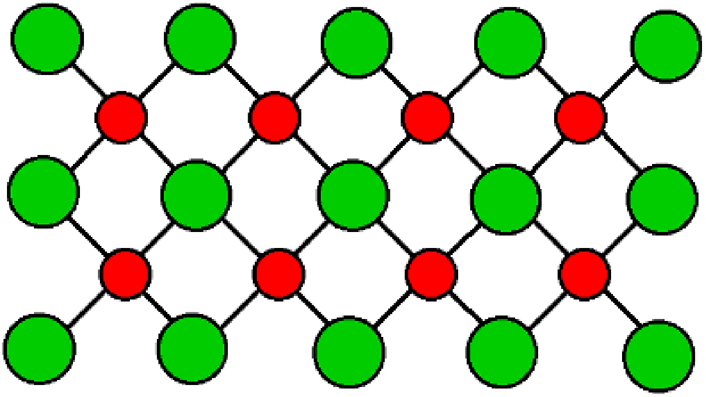
wurtzite (stable)

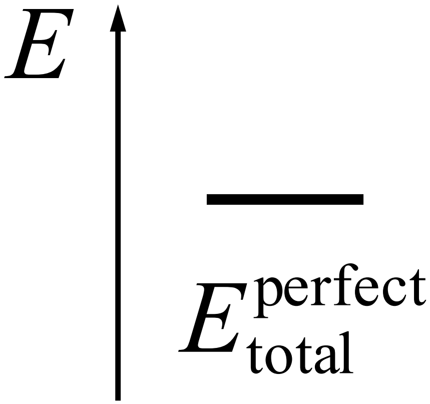
There is no consensus on the nature of *n*-type conductivity, and whether reliable *p*-type doping is possible. However, there is hope (GaN story repeats itself):

"…native point defects cannot explain the often-observed *n*-type conductivity, but the latter is likely to be caused by the incorporation of impurities during growth or annealing."

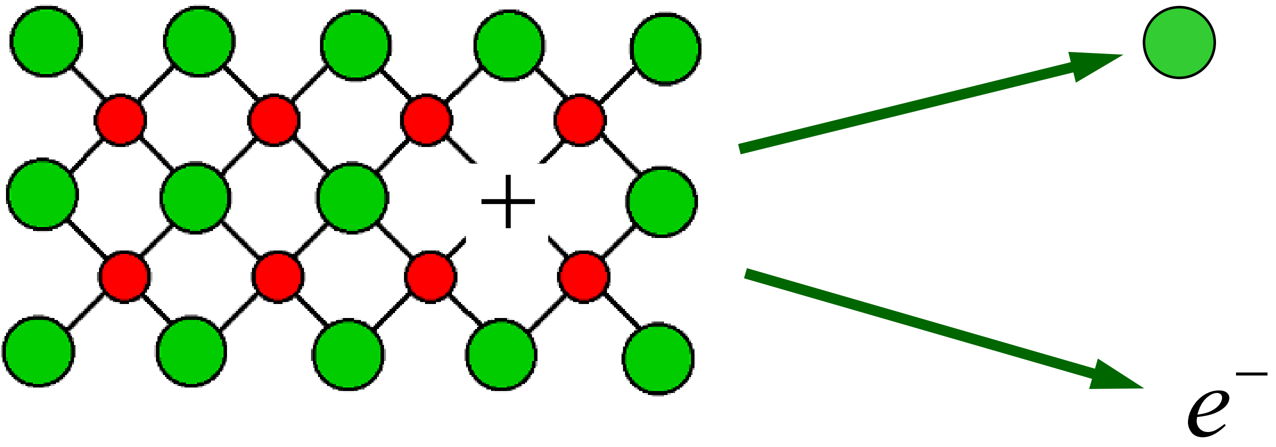
A. Janotti and C.G. van de Walle, Rep. Prog. Phys. **72**, 126501 (2009)

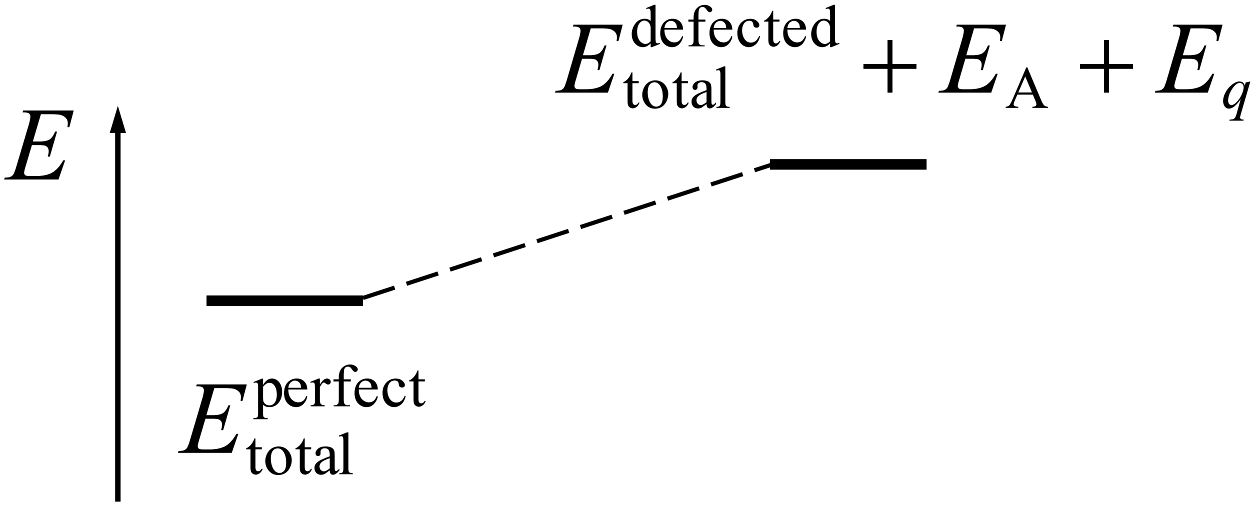
Defect formation energy (*T*=0)





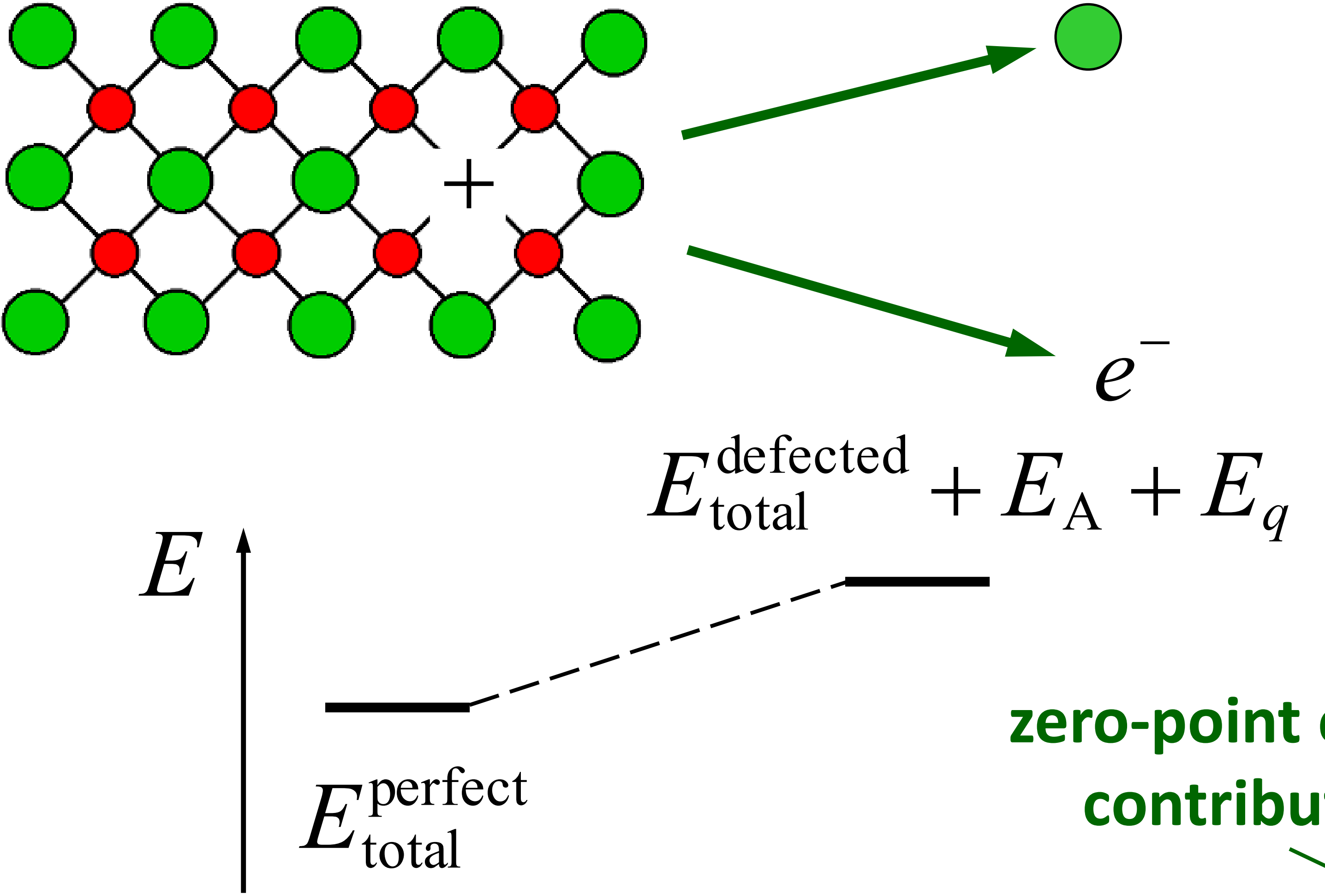
Defect formation energy (*T*=0)





$$\Delta E_f = E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q - E_{\text{total}}^{\text{perfect}}$$

Defect formation energy (*T*=0)



e^-

$$E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q$$

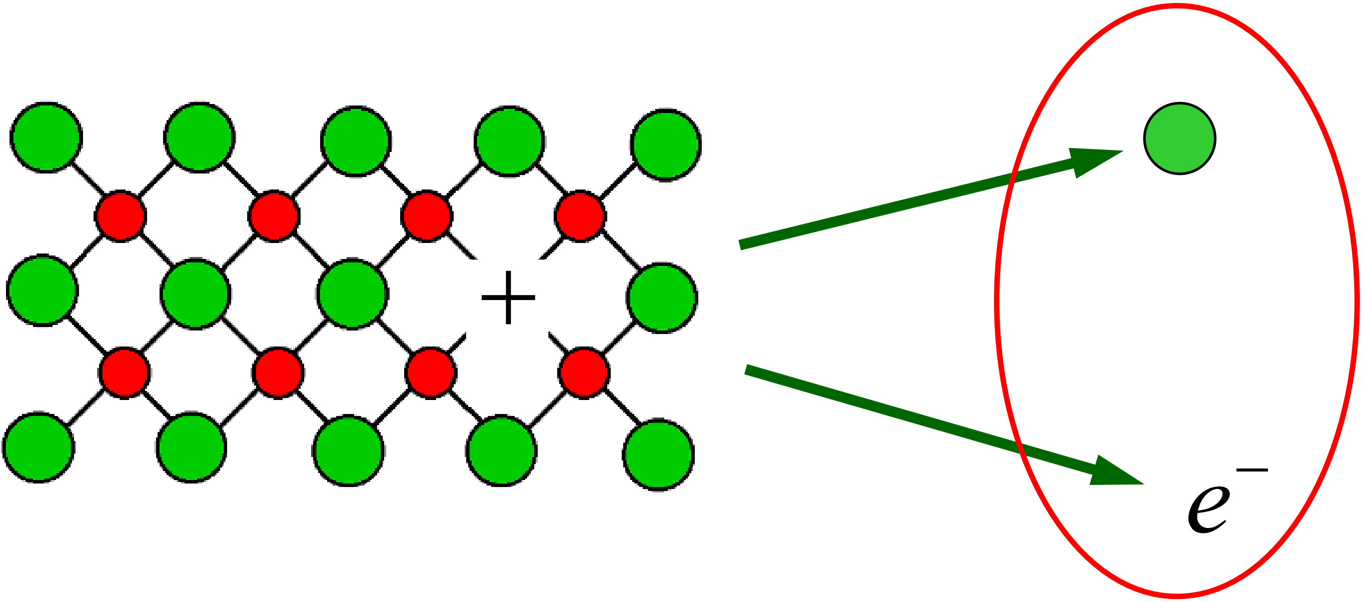
E

$$E_{\text{total}}^{\text{perfect}}$$

zero-point energy contribution

$$\Delta E_f = E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q - E_{\text{total}}^{\text{perfect}} + \Delta E_{\text{ZPE}}$$

Defect formation energy (*T*=0)



$$\Delta E_f = E_{\text{total}}^{\text{defected}} + \boxed{E_{\text{A}} + E_q} - E_{\text{total}}^{\text{perfect}} + \Delta E_{\text{ZPE}}$$

Formation energy depends on the final (initial) state of the removed (added) species

Defect formation energy (*T*=0)

$$\Delta E_f = E_{\text{total}}^{\text{defected}} + E_{\text{A}} + E_q - E_{\text{total}}^{\text{perfect}} + \Delta E_{\text{ZPE}}$$

Contributions to the formation energy:

1) Bond breaking/making
2) Atomic relaxation and polarization (screening)
3) Change in zero-point vibrational energy
4) Final/initial state of removed/added atoms and charges

Gibbs free energy of defect formation

T = 0:

$$\Delta E_f = E_{\mathrm{total}}^{\mathrm{defected}} + E_{\mathrm{A}} + E_q - E_{\mathrm{total}}^{\mathrm{perfect}} + \Delta E_{\mathrm{ZPE}}$$

$$\Downarrow$$

T > 0:

$$\Delta G_f(T,\{p\}) = G^{\mathrm{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\mu_e(T) - G^{\mathrm{perfect}}(T,\{p\})$$

Electronic chemical potential

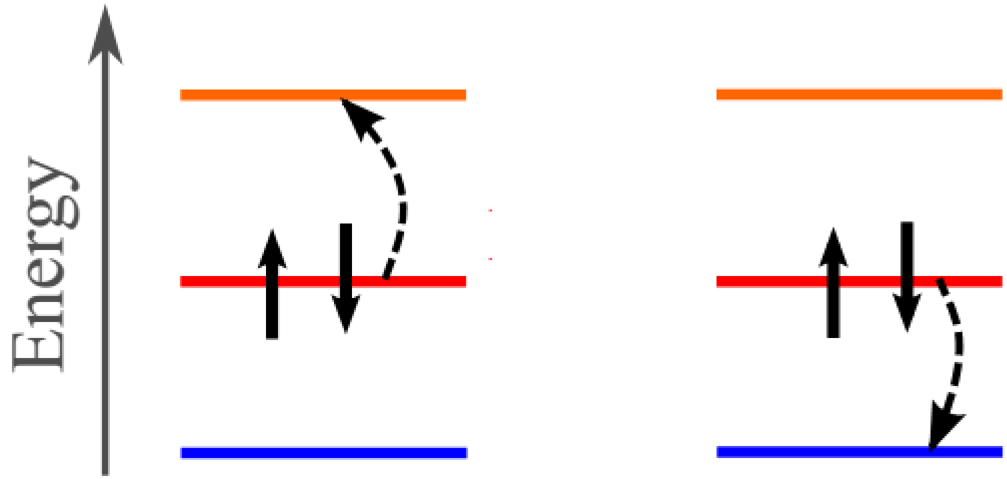
$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\boxed{\mu_e(T)} \\ - G^{\text{perfect}}(T,\{p\})$$

μ_e **is a property of the electronic reservoir**

In a doped system, μ_e is close to the Fermi level (the energy level separating occupied states from the empty states at $T = 0$)

Electronic chemical potential

$$\Delta G_f(T,\{p\}) = G^{\text{defected}}(T,\{p\}) - \sum_i \mu_i(T,p_i)\Delta N_i + q\boxed{\mu_e(T)} \\ - G^{\text{perfect}}(T,\{p\})$$



conduction band minimum (CBm)

defect level

valence band maximum (VBM)

***n*-doped**

μ_e **near CBm**

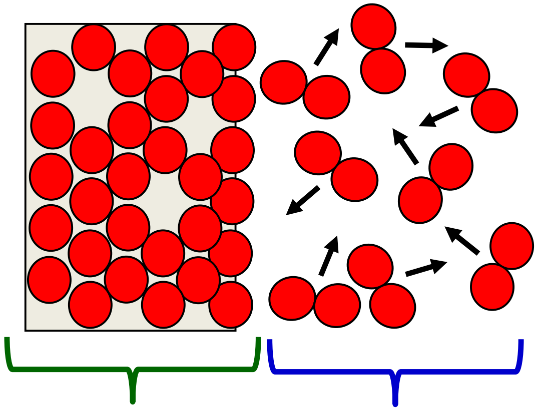
***p*-doped**

μ_e **near VBM**

The defects will charge when μ_e is below the defect level

Entropy

$$G = U + pV - TS$$



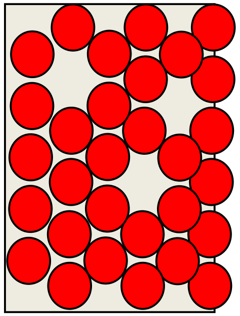
$$S = k \ln \Omega$$

Ω – number of microstates

1) Solid: vibrational entropy (phonons)
2) Solid: electronic entropy
3) Gas: vibrational, rotational, translational, etc. (part of μ_i)
4) Solid: defect disorder

Configurational entropy

$$G = [U + pV - T(S - S_{\text{config}})] - TS_{\text{config}} = \widetilde{G} - TS_{\text{config}}$$



N **equivalent defect sites in the sold**

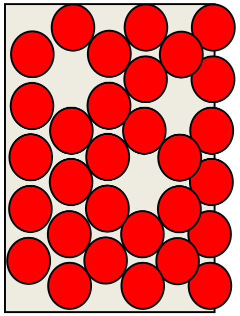
n **defects**

$$S = k\ln Z + kT\frac{\partial \ln Z}{\partial T},\ Z = \sum_i e^{-E_i/kT}$$

sum over different defect distributions

Configurational entropy

$$G=[U+pV-T(S-S_{\text{config}})]-TS_{\text{config}}=\widetilde{G}-TS_{\text{config}}$$



N **equivalent defect sites in the sold**

n **defects**

If defects do not interact: $S_{\text{config}}=k\ln\dfrac{N!}{n!(N-n)!}$

Stirling's formula:

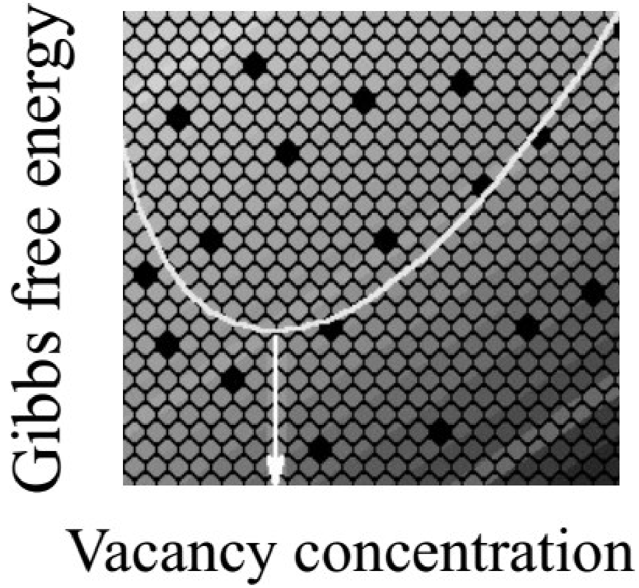
$$\ln(n!)=n(\ln n-1+\delta),\ n>>1,\ \delta\sim\frac{\ln(2\pi n)}{2n}$$

$$S_{\text{config}}\approx k\left[N\ln N-n\ln n-(N-n)\ln(N-n)\right]$$

Good approximation only on a macroscopic scale

Defect concentration

Minimize the free energy of the system with respect to the number of defects



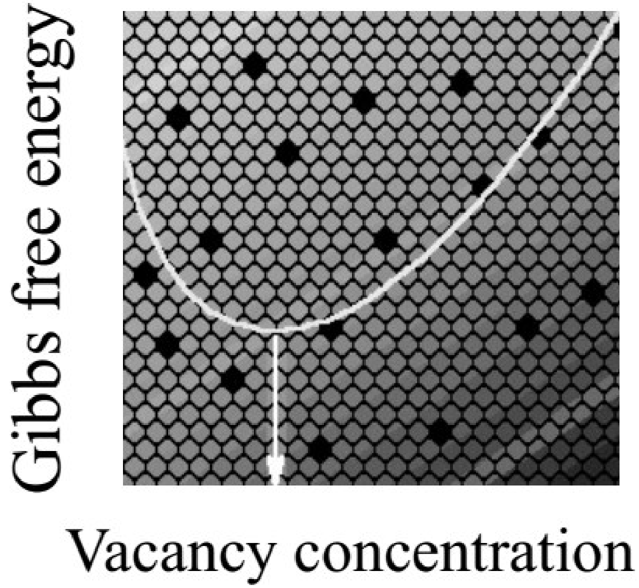
$$G(n) = \tilde{G}_0 + n\Delta G_f - TS_{\text{config}}(n)$$

$$S_{\text{config}} \approx k\left[N\ln N - n\ln n - (N-n)\ln(N-n)\right]$$

$$\frac{\partial G}{\partial n} = 0$$

Defect concentration

Minimize the free energy of the system with respect to the number of defects



$$G(n) = \tilde{G}_0 + n\Delta G_f - TS_{\text{config}}(n)$$

If defects do not interact:

$$\frac{n}{N} = \frac{1}{\exp\left(\Delta G_f / kT\right) + 1}$$

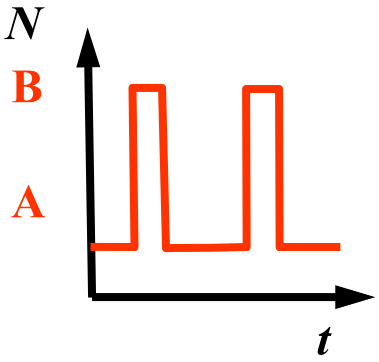
$$\frac{n}{N} << 1 \Leftrightarrow \exp\left(\Delta G_f / kT\right) >> 1$$

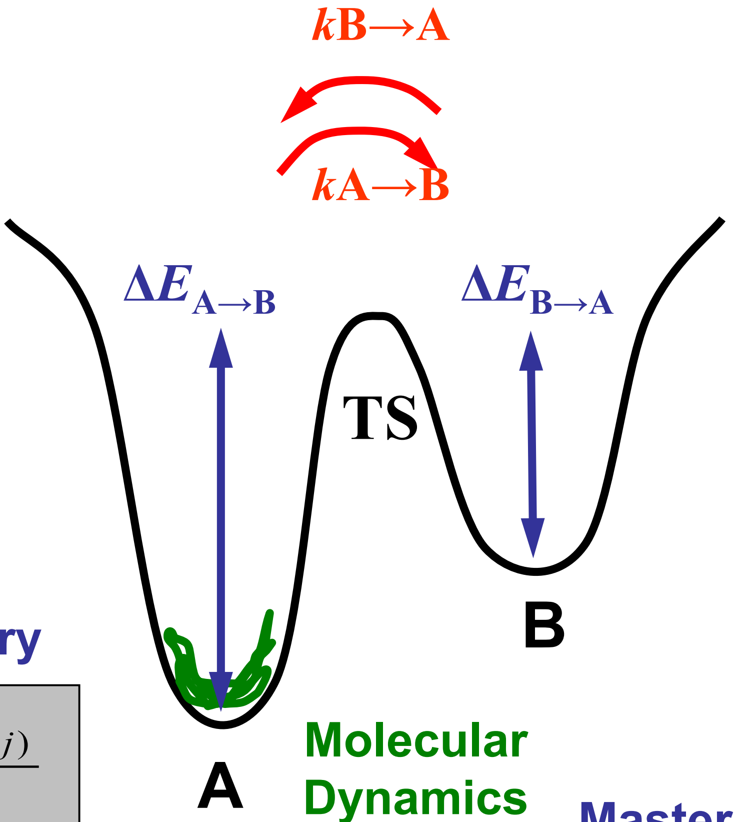
$$\frac{n}{N} \approx \exp\left(-\Delta G_f(T,p) / kT\right)$$

Kinetic Monte Carlo method

- ❒ **Reaction kinetics - kinetic MC (kMC)**

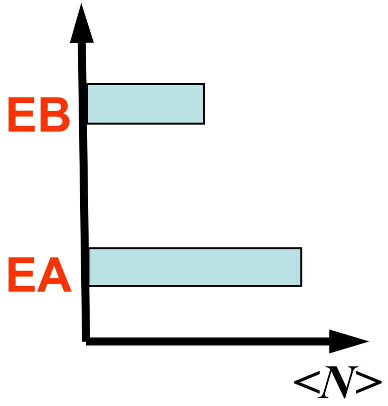
kinetic
Monte Carlo





Molecular
Dynamics

equilibrium
Monte Carlo



Transition State Theory

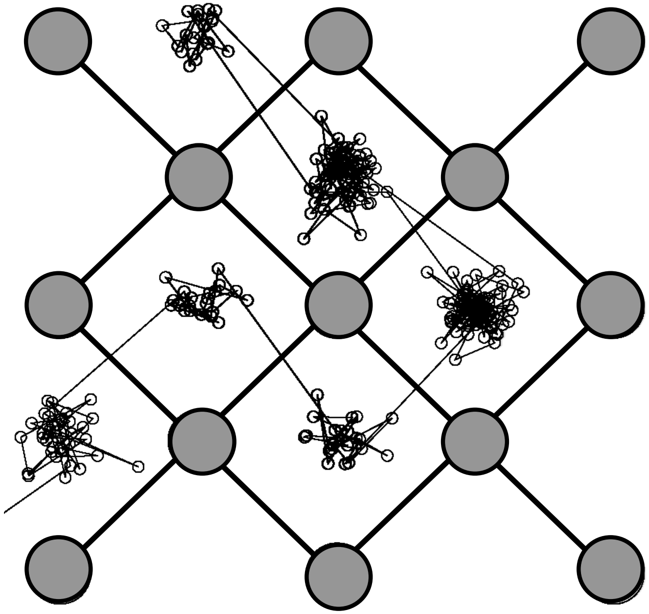
$$k_{i\to j} = \left(\frac{k_B T}{h}\right)\frac{Z_{TS(i\to j)}}{Z_i}$$
$$= \Gamma_o \exp\left(\frac{-\Delta E_{i\to j}}{k_B T}\right)$$

Master equation

$$\frac{dP_i(t)}{dt} = -\sum_j k_{i\to j}P_i(t) + \sum_j k_{j\to i}P_j(t)$$

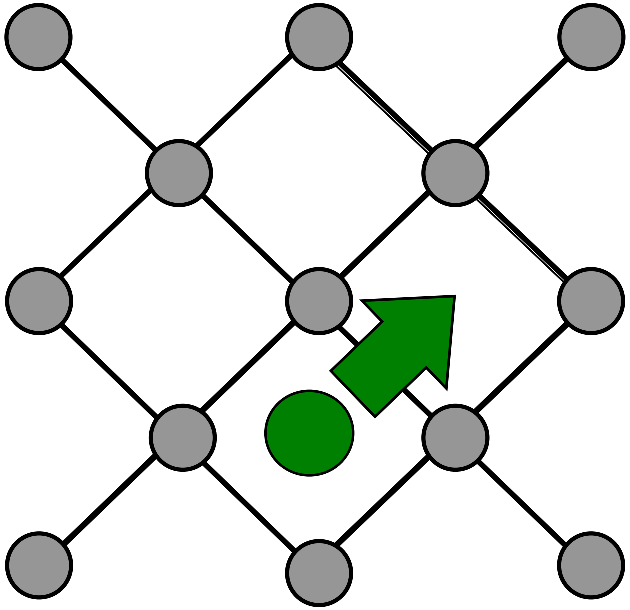
Kinetic Monte Carlo method

- **Reaction kinetics - kinetic MC (kMC)**



Molecular Dynamics:
the whole trajectory

***ab initio* MD:**
up to 50 ps



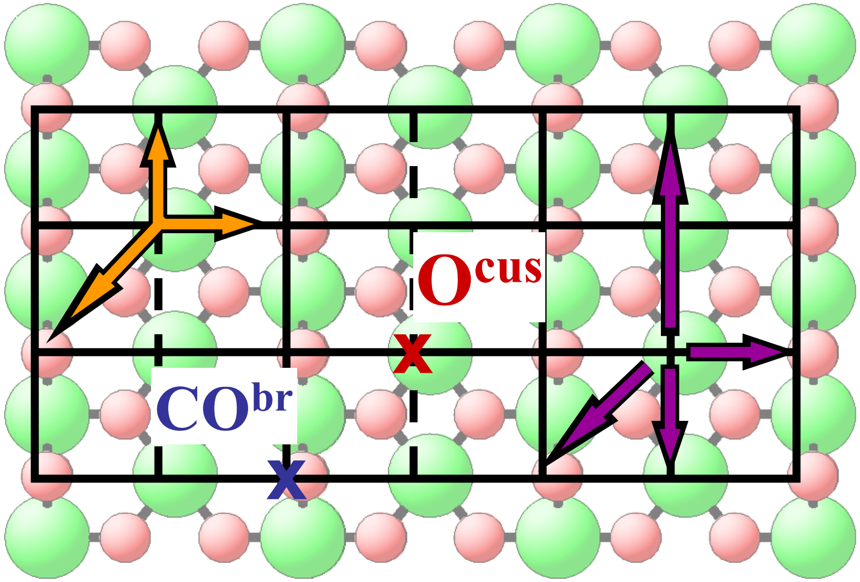
Kinetic Monte Carlo:
coarse-grained hops

***ab initio* kMC:**
up to minutes

Kinetic Monte Carlo method

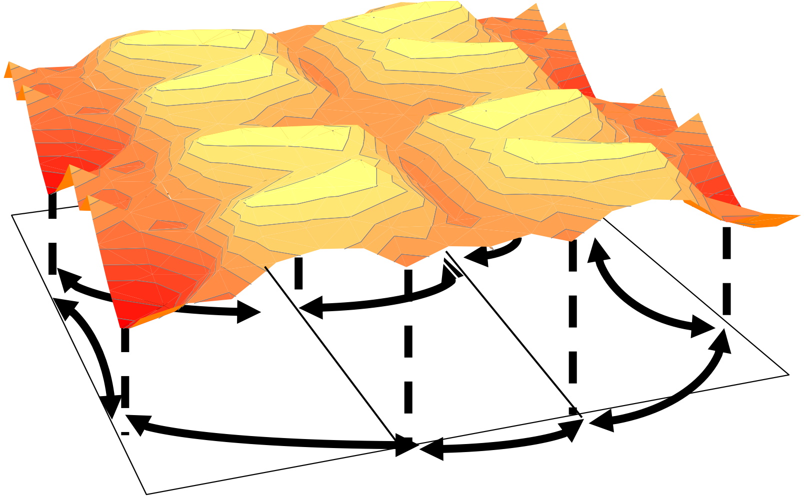
❒ Crucial ingredients of kMC

$$\frac{dP_i(t)}{dt} = -\sum_j k_{i\to j} P_i(t) + \sum_j k_{j\to i} P_j(t)$$



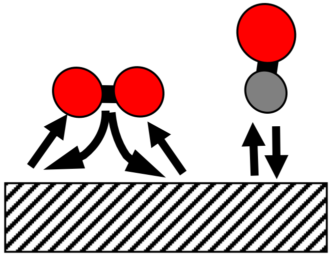
1) Elementary processes

Fixed process list vs. „on-the-fly“ kMC
Lattice vs. off-lattice kMC



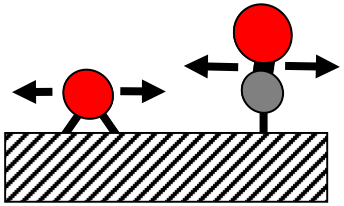
PES accuracy
Reaction rate theory

Kinetic Monte Carlo method

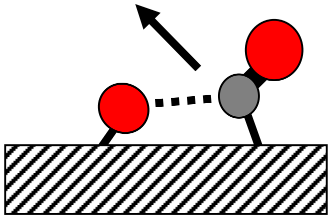


Adsorption: CO - unimolecular, O_2 – dissociative
no barrier
rate given by impingement $k \approx S_0 p / (2\pi m k_B T)$

Desorption: CO – 1st order, O_2 – 2nd order
out of DFT adsorption well (= barrier)
prefactor from detailed balance



Diffusion: hops to nearest neighbor sites
site and element specific
barrier from DFT (TST)
prefactor from DFT (hTST)



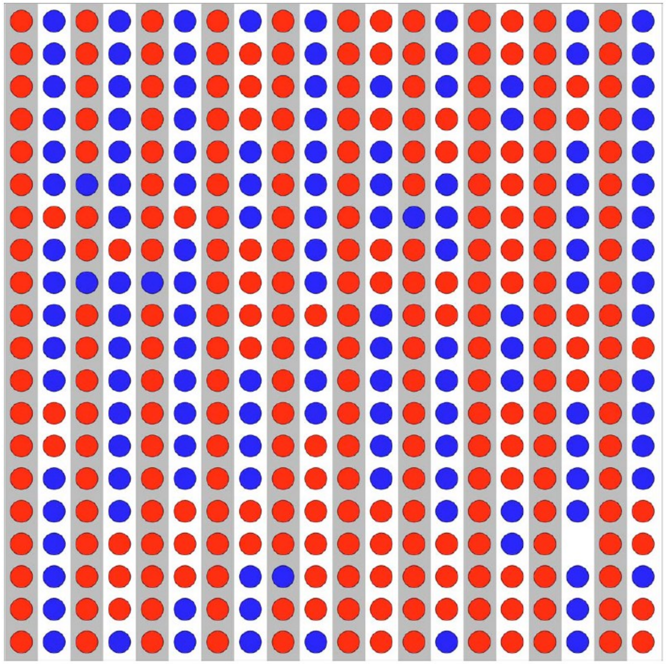
Reaction: site specific
immediate desorption, no readsorption
barrier from DFT (TST)
prefactor from detailed balance

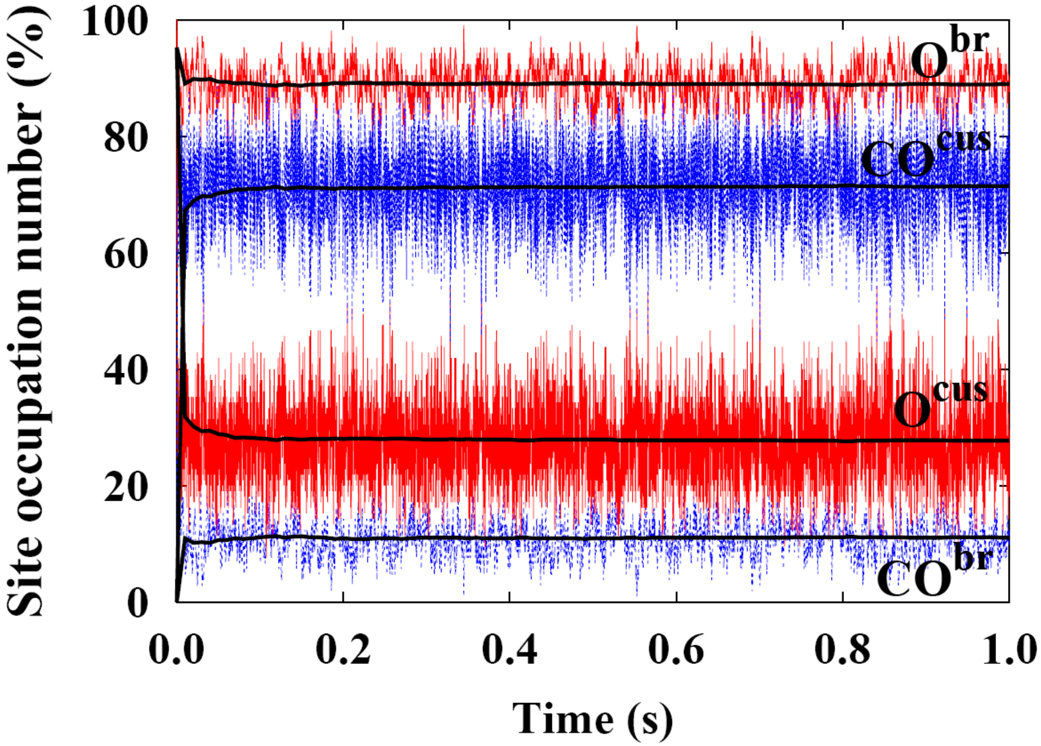
26 elementary processes considered

K. Reuter and M. Scheffler, Phys. Rev. B 73, 045433 (2006)

Kinetic Monte Carlo method

T = 600 K p_{O2} = 1 atm p_{CO} = 7 atm



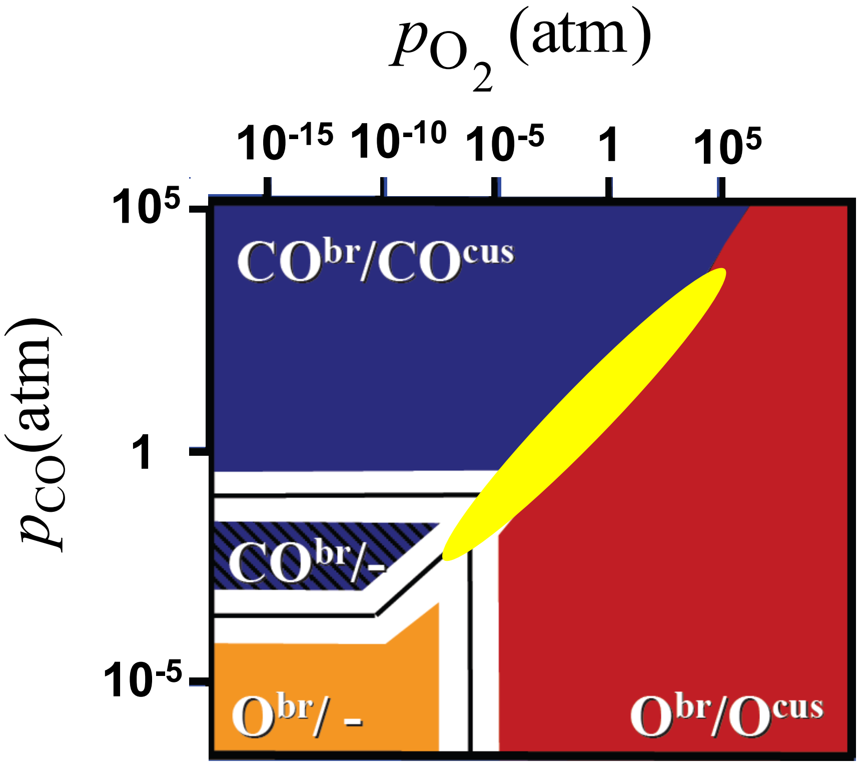


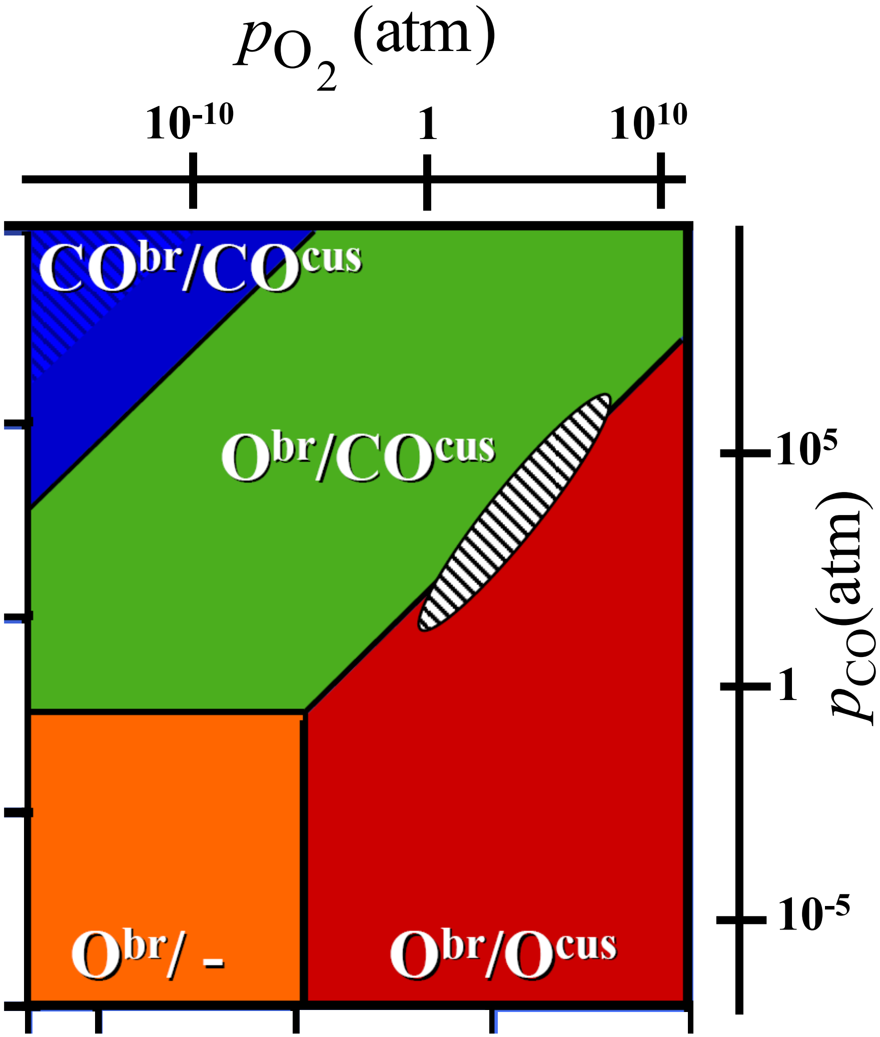
K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

K. Reuter, C. Stampfl, and M. Scheffler, Handbook of materials modeling, part A. Methods, p. 149, Springer, Berlin (2005)

Kinetic Monte Carlo method

- kMC phase diagrams

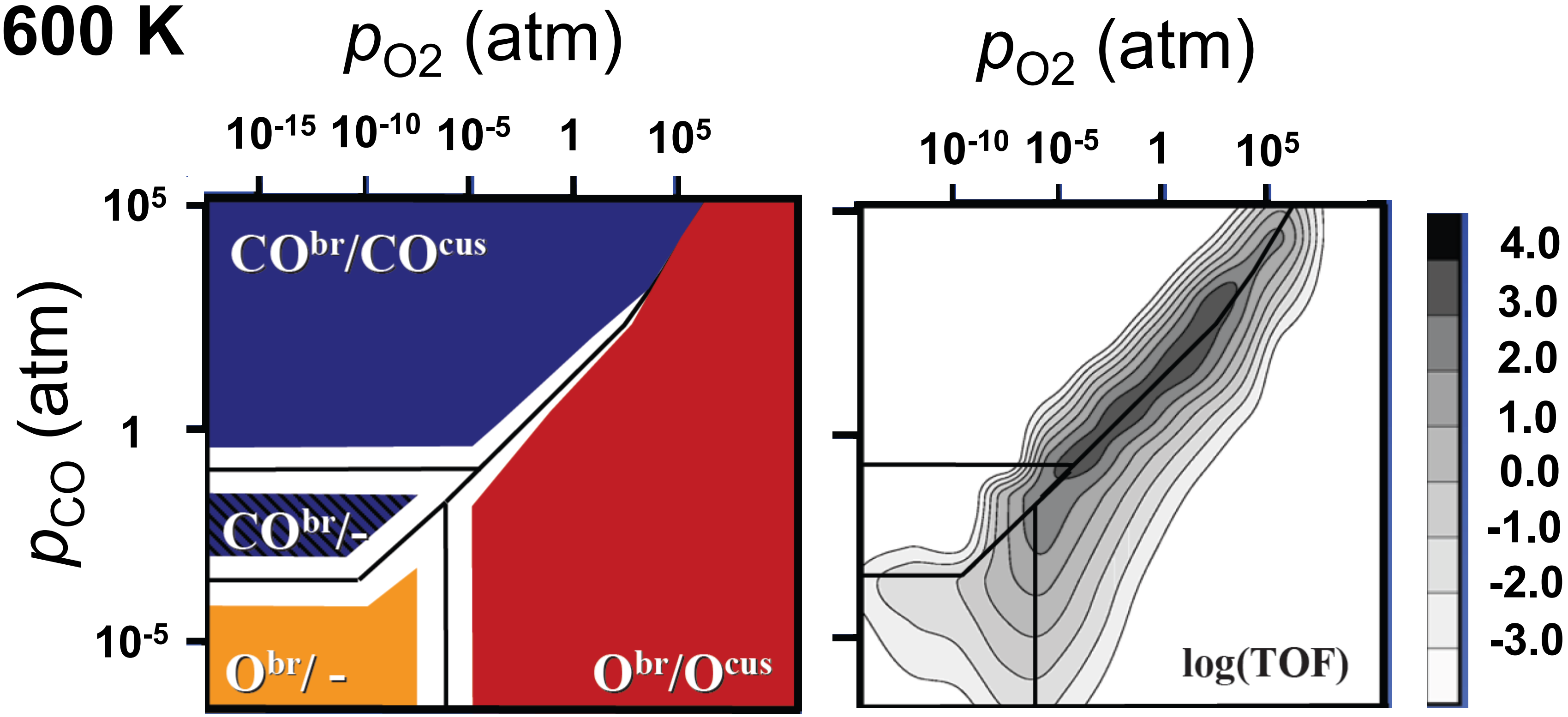




Kinetic Monte Carlo method

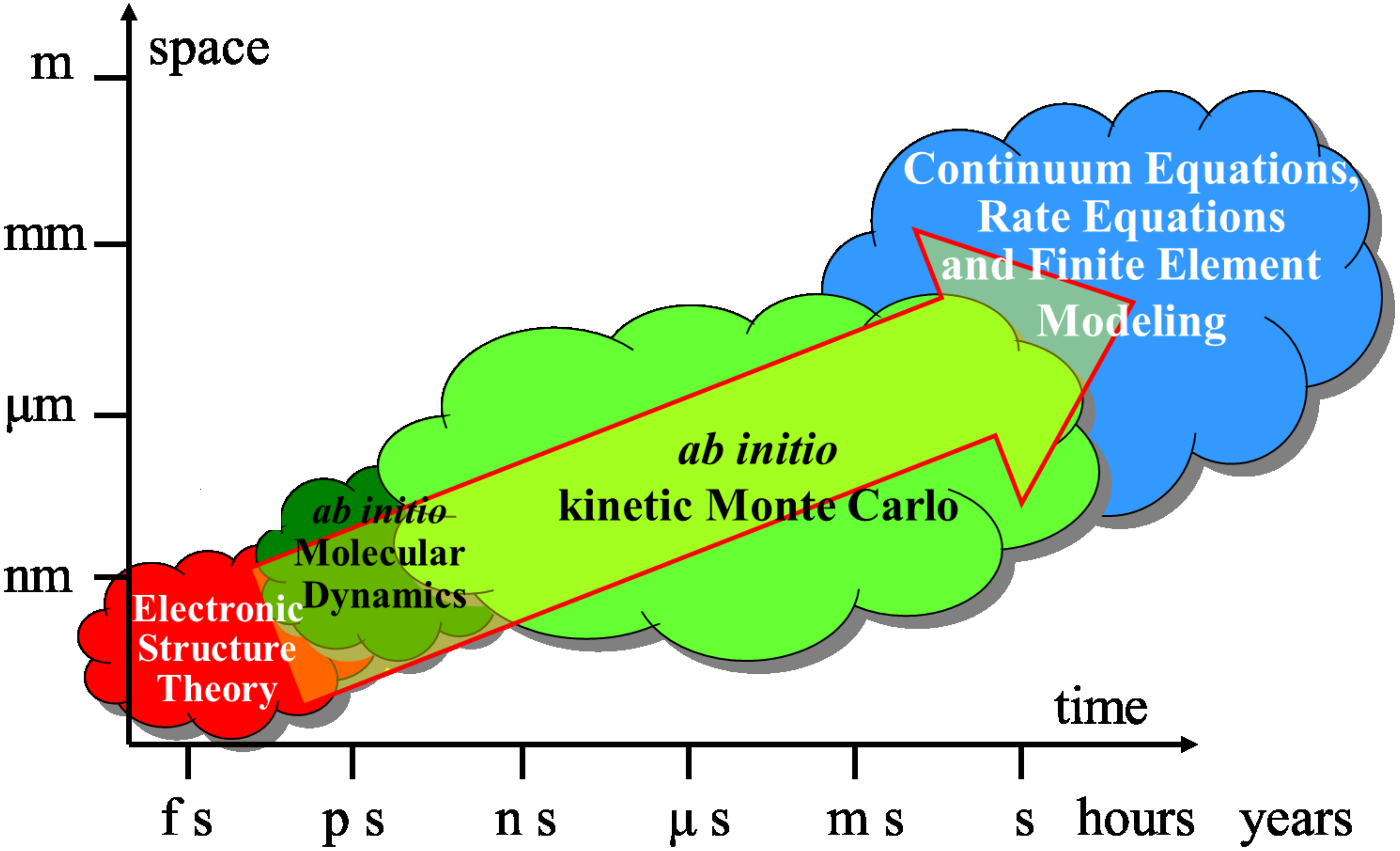
- (p_{O2}, p_{CO})-map of catalytic activity

600 K



K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

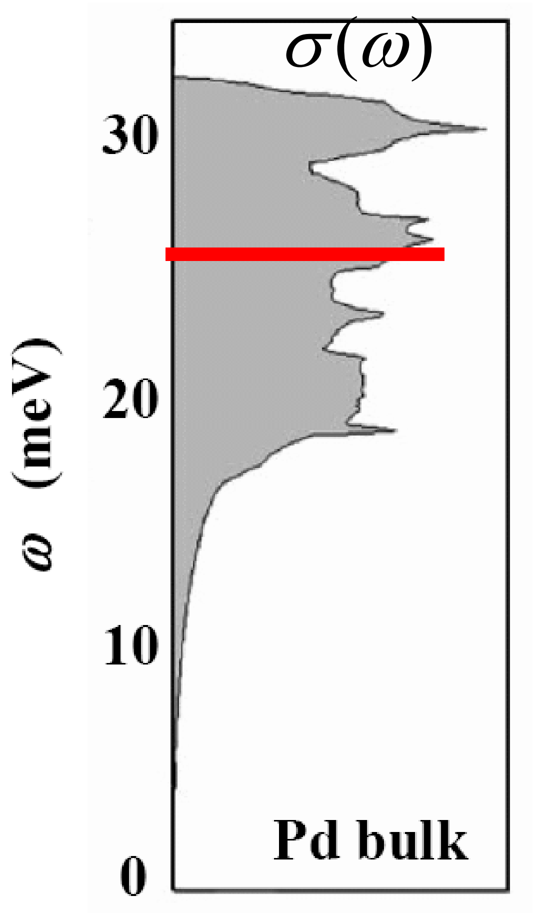
Multiscale Modelling



Thermodynamics

❒ *Ab initio* atomistic thermodynamics

Vibrational contributions to the surface free energy:



$$\Delta F_{vib}(T,V) = V \int_0^\infty f(T,\omega)\left(\sigma(\omega) - \right.$$

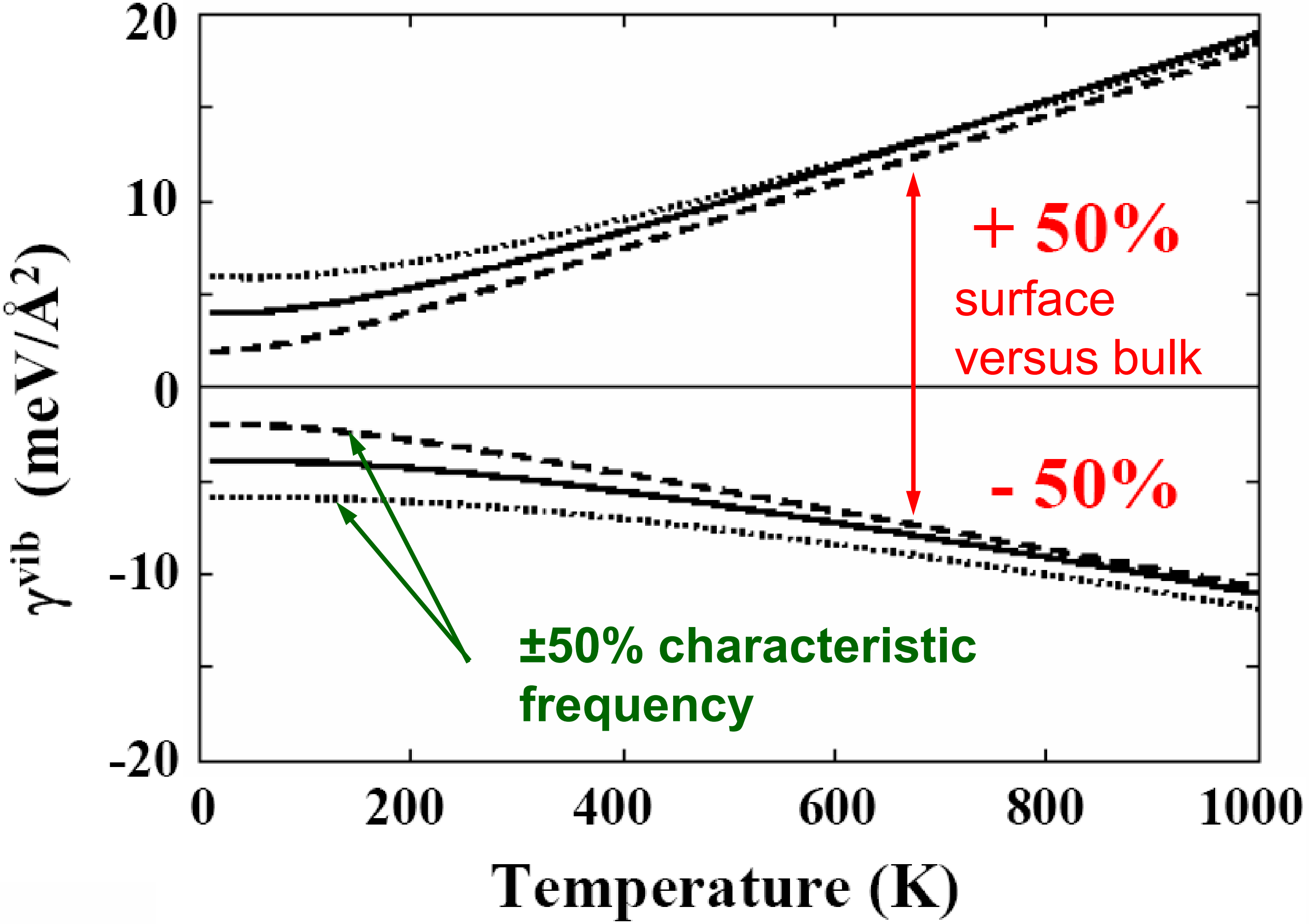
Only *changes* in vibrational free energy contribute to the surface free energy

Make estimate from simple models

e.g., Einstein model: $\sigma(\omega) = \delta(\omega - \langle\omega\rangle)$

$\langle\omega\rangle_{\mathrm{Pd}}$**(bulk) ~ 25 meV**

Surface-induced variations of substrate modes



< 10 meV/Å² for T = 600 K – in this case!!!

K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2001)