FHI-aims Tutorial Series 2021

Ab initio thermodynamics: Replica-Exchange Grand-Canonical Method

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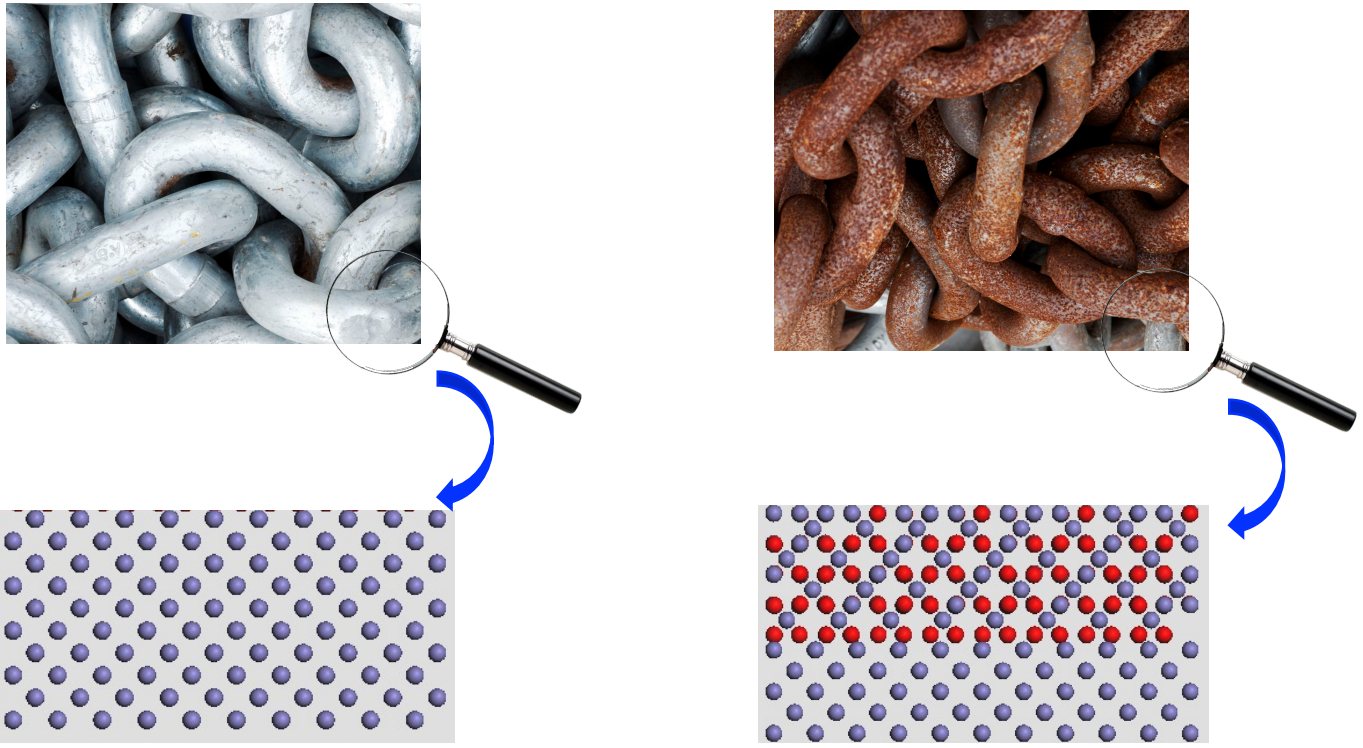
The problem to be addressed

Macroscopic regime



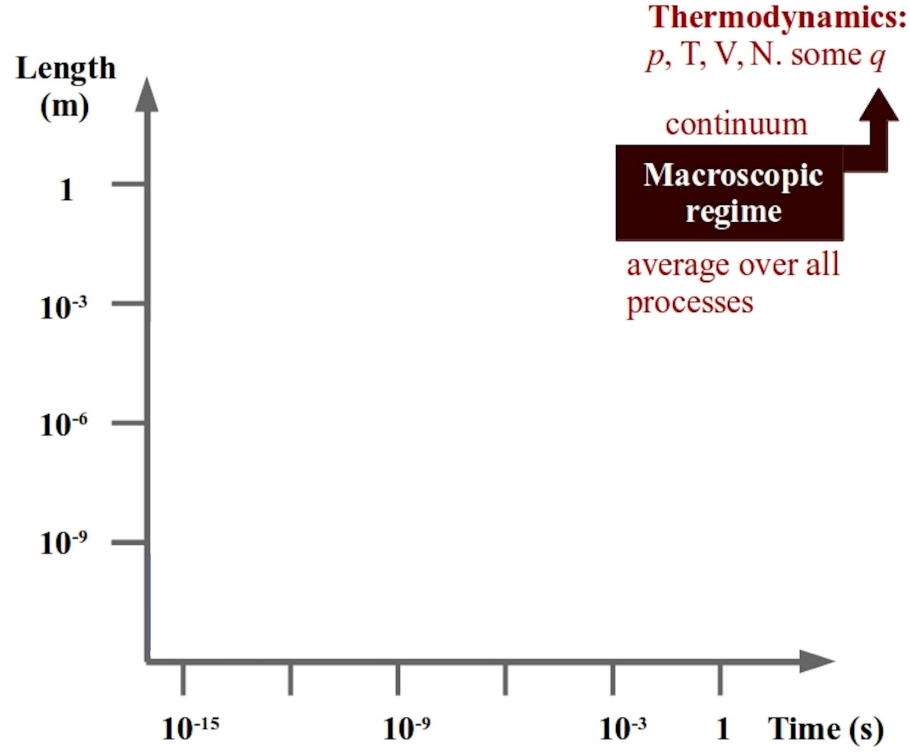
Atomistic level

***Ab initio* thermodynamics:**

- ***Ab initio* atomistic thermodynamics (aiAT)**
- **Replica-Exchange Grand-Canonical method (REGC)**
- **Computational hydrogen electrode (CHE)**

Thermodynamics

Thermodynamics studies macroscopic systems i.e. composed of a large number of particles



Thermodynamic equilibrium

Thermodynamic potentials

Internal energy $U = \int \left(TdS - pdV + \sum_i \mu_i dN_i \right)$

Enthalpy $H = U + pV$

Helmholtz free energy $F = U - TS$

Gibbs free energy $G = U + pV - TS$

Bridge between microscopic and macroscopic

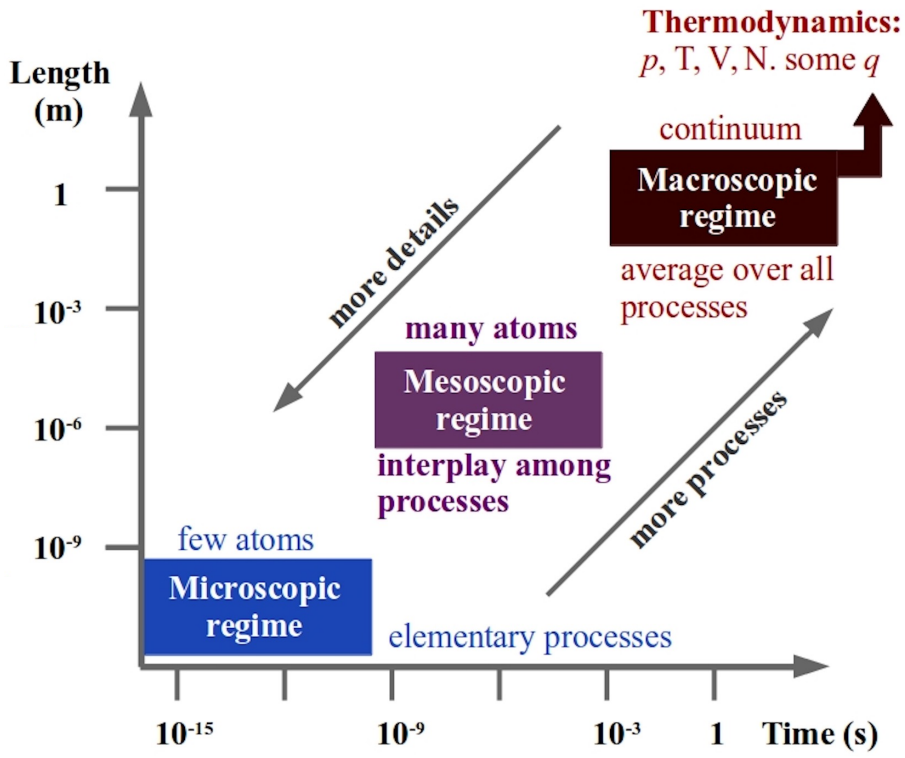
$$S = k_B \ln \Omega$$

Ω : **Number of microstates in a given macrostate**

This is only a postulate but it works:

1> in equilibrium $\Omega \longrightarrow$ **max,** $S \longrightarrow$ **max**

2> Ω **is multiplicative,** S **is additive**



Bridge between microscopic and macroscopic

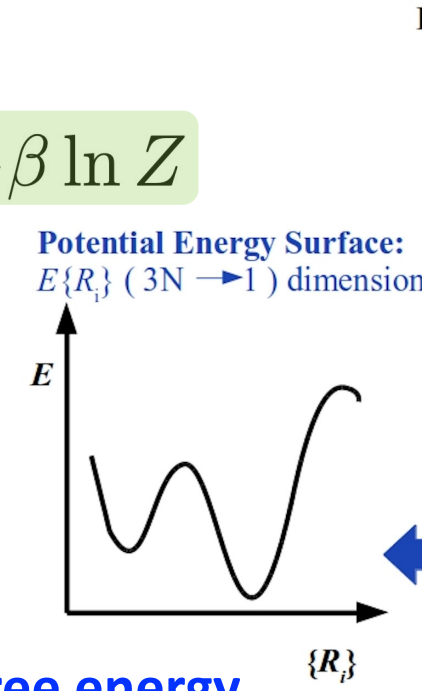
$$S = k_B \ln \Omega$$

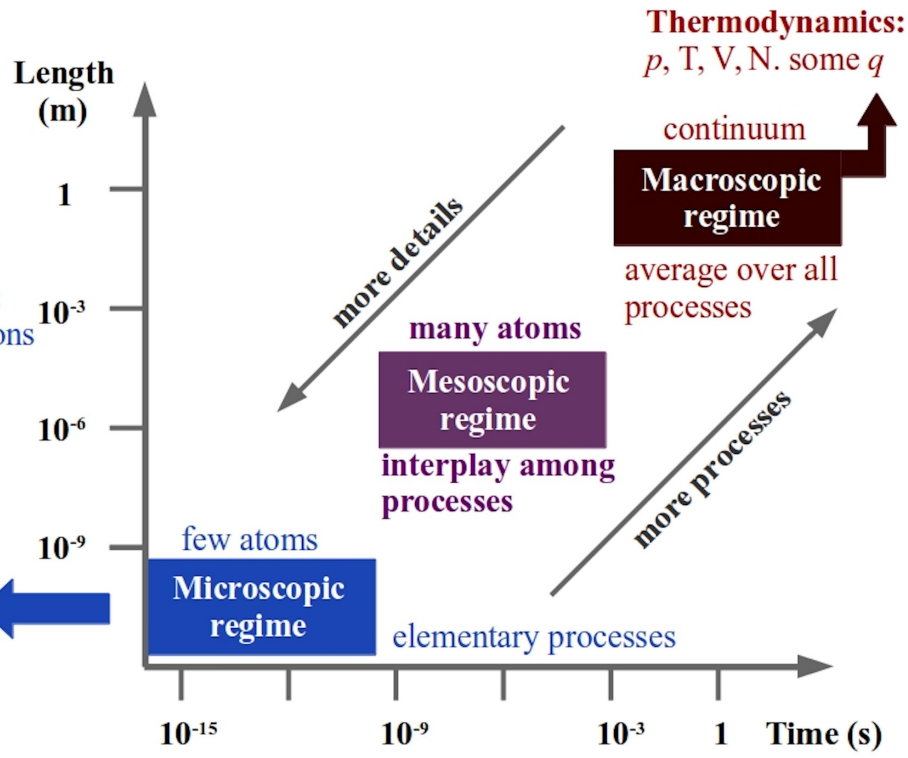
$$F = -k_B T \ln Z = -\beta \ln Z$$

Classical statistics for nuclei

$$Z = \frac{1}{\Lambda^{3N} N!} \int dR e^{-\beta U(R)}$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$





Probabilistic interpretation of free energy

$$P(E) = \rho(E) dE = \frac{dE}{Z} \Omega(E) e^{-\beta E} = \frac{dE}{Z} e^{-\beta E + \ln \Omega}$$

$$= \frac{dE}{Z} e^{-\beta (E - TS)} = \frac{dE}{Z} e^{-\beta F(E)}$$

$$\frac{P(E1)}{P(E2)} = e^{-\beta \left[F(E1) - F(E2) \right]}$$

Ab initio atomistic Thermodynamics: ideal gas $pV = Nk_BT$

$$Z = \frac{1}{N!} z^N \qquad z = z^{\text{trans}} z^{\text{rot}} z^{\text{vib}} z^{\text{el}} z^{\text{conf}} z^{\text{nucl}}$$

Translational:

$$z^{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V$$

Particle mass

Rotational:

$$z^{\text{rot}} = 8\pi^2 \left(\frac{2\pi k_B T}{h^2}\right)^{\frac{3}{2}} (I_A I_B I_C)^{\frac{1}{2}}$$

Non-linear molecules

Rotational inertia of a rigid molecule

$$z^{\text{rot}} = \frac{8\pi^2 I_A k_B T}{h^2}$$

linear molecules

Vibrational:

$$z^{\text{vib}} = \prod \left[e^{-\frac{h\nu_i}{2k_BT}} \left(1 - e^{-\frac{h\nu_i}{2k_BT}}\right)^{-1} \right]$$

Vibrational frequencies
Harmonic oscillator

Statistical Mechanics, D. A. McQuarrie, University Science Books, 2000

Electronic:

$$z^{\mathrm{el}} = \sum (2s_i + 1) e^{-\frac{E_i}{k_B T}} \approx (2s_0 + 1) e^{-\frac{E_0}{k_B T}}$$

Conformational:

$$z^{\mathrm{conf}} = \frac{1}{\sigma}$$

Symmetry number

Polyatomic molecules

$\sigma = N$

Symmetry operations

Diatomic molecules

$\sigma = 1$ **heteroatomic**

$\sigma = 2$ **homoatomic**

Nulei:

In most practical cases, we can neglect the interaction between nuclear spins

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

$$\begin{aligned}\mu(T,p) = &- k_{\mathrm{B}} T \ln\left[\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} (k_{\mathrm{B}} T)^{\frac{5}{2}}\right] + k_{\mathrm{B}} T \ln p \\ &- k_{\mathrm{B}} T \ln\left(\frac{8\pi^2 I_{\mathrm{A}} k_{\mathrm{B}} T}{\sigma h^2}\right) - k_{\mathrm{k_B}} T \ln(2s_0 + 1) \\ &+ E^{\mathrm{DFT}} + \frac{hv}{2} + k_{\mathrm{B}} T \ln\left(1 - e^{-\frac{hv}{k_{\mathrm{B}} T}}\right)\end{aligned}$$

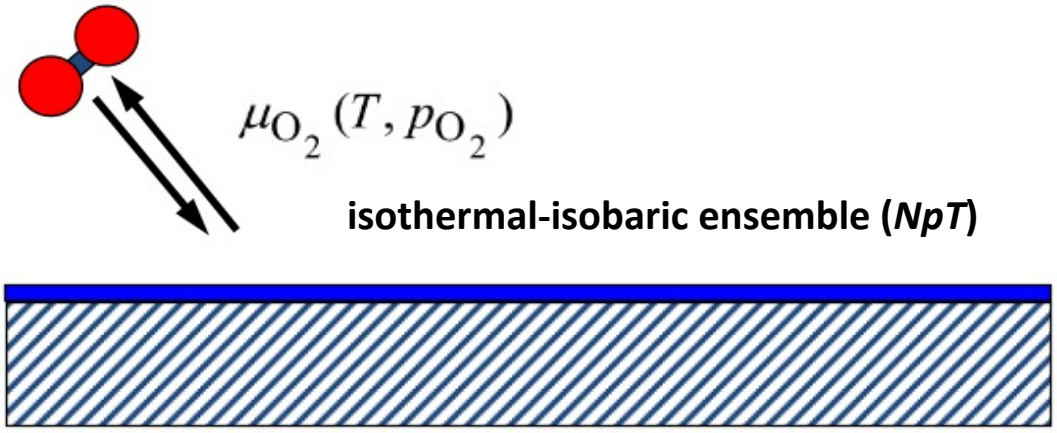
Relation between *T*, *p* and μ

$$pV = Nk_BT$$

$$\mu(T,p) = \Delta\mu(T,p)$$
$$- k_{\mathrm{B}}T\ln\left[\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}(k_{\mathrm{B}}T)^{\frac{5}{2}}\right] + k_{\mathrm{B}}T\ln p$$
$$- k_{\mathrm{B}}T\ln\left(\frac{8\pi^2 I_{\mathrm{A}} k_{\mathrm{B}}T}{\sigma h^2}\right) - k_{\mathrm{k_B}}T\ln(2s_0+1)$$
$$+ E^{\mathrm{DFT}} + \frac{h\nu}{2} + k_{\mathrm{B}}T\ln\left(1 - e^{-\frac{h\nu}{k_{\mathrm{B}}T}}\right)$$

JANAF Thermochemical tables, D.R. Stull, H. Prophet. US National Bureau of Standards, Washington DC, 1971

Ab initio atomistic thermodynamics (aiAT)



isothermal-isobaric ensemble (*NpT*)

The Gibbs free energy of adsorption

$$\Delta G^{\mathrm{ad}}(T, p_{\mathrm{O}_2}) = G^{\mathrm{surf}} - G^{\mathrm{clean}} - N\mu_{\mathrm{O}}(T, p_{\mathrm{O}_2})$$

[1] Statistical Mechanics, D. A. McQuarrie, (2000)
[2] Weinert and Scheffler, Mater. Sci. Forum 25 (1986)
[3] Reuter and Scheffler Phys. Rev. B 65 (2001)

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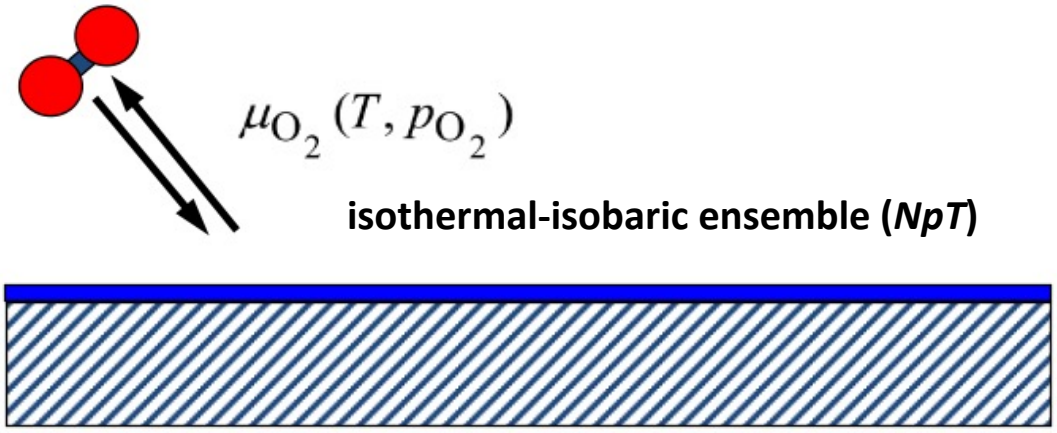

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From partition function Q

Gibbs free energy $G(T,p) = -k_{\mathrm{B}}T \ln Q + pV$

For ideal gas

$$Q = \frac{1}{N!}q^N \qquad q = q^{\mathrm{trans}} q^{\mathrm{rot}} q^{\mathrm{vib}} q^{\mathrm{el}} q^{\mathrm{conf}} q^{\mathrm{nucl}}$$

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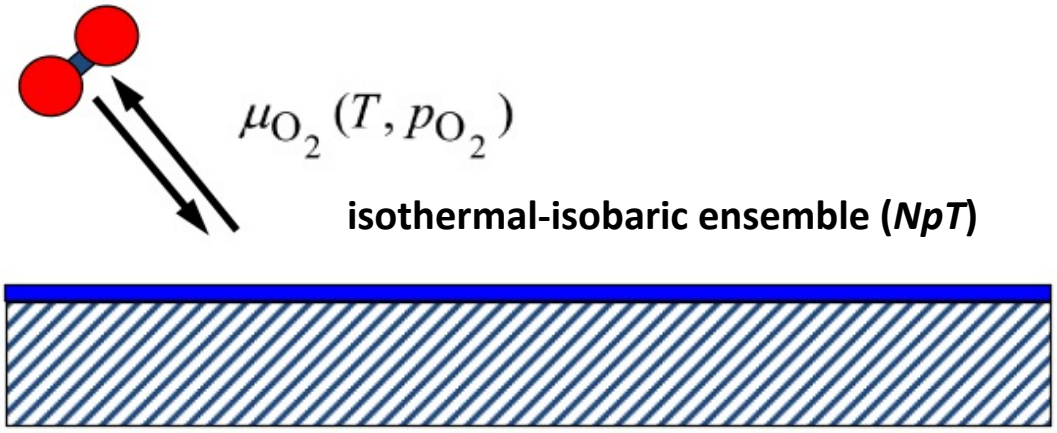

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$$G(T,p) = E^{\mathrm{total}} + F^{\mathrm{trans}} + F^{\mathrm{rot}} + F^{\mathrm{vib}} + F^{\mathrm{conf}} + pV$$

E^{total} → **DFT**

F^{trans}, F^{rot} } **discarded for solids**

F^{vib} → **canceled out or treated at harmonic approximation**

F^{conf} → **neglected**

pV → **neglected**

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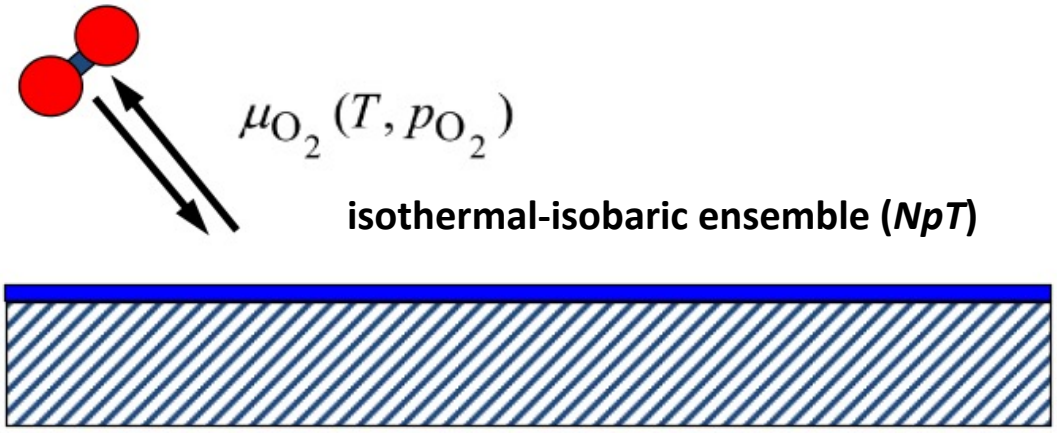

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An unbiased sampling of the configurational and compositional space

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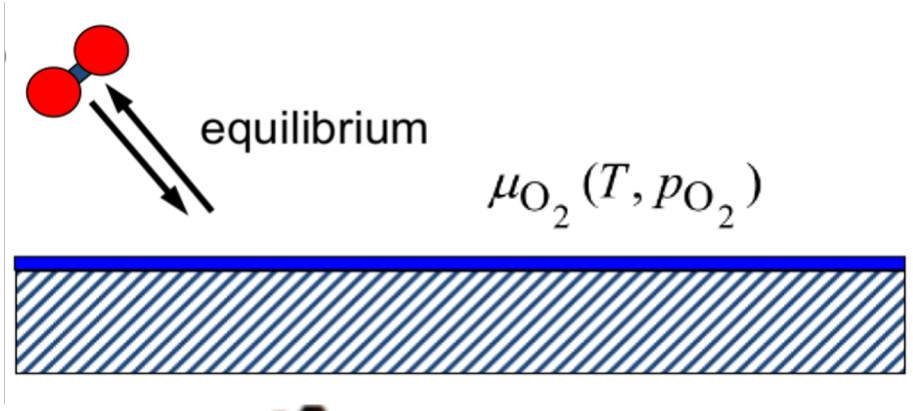
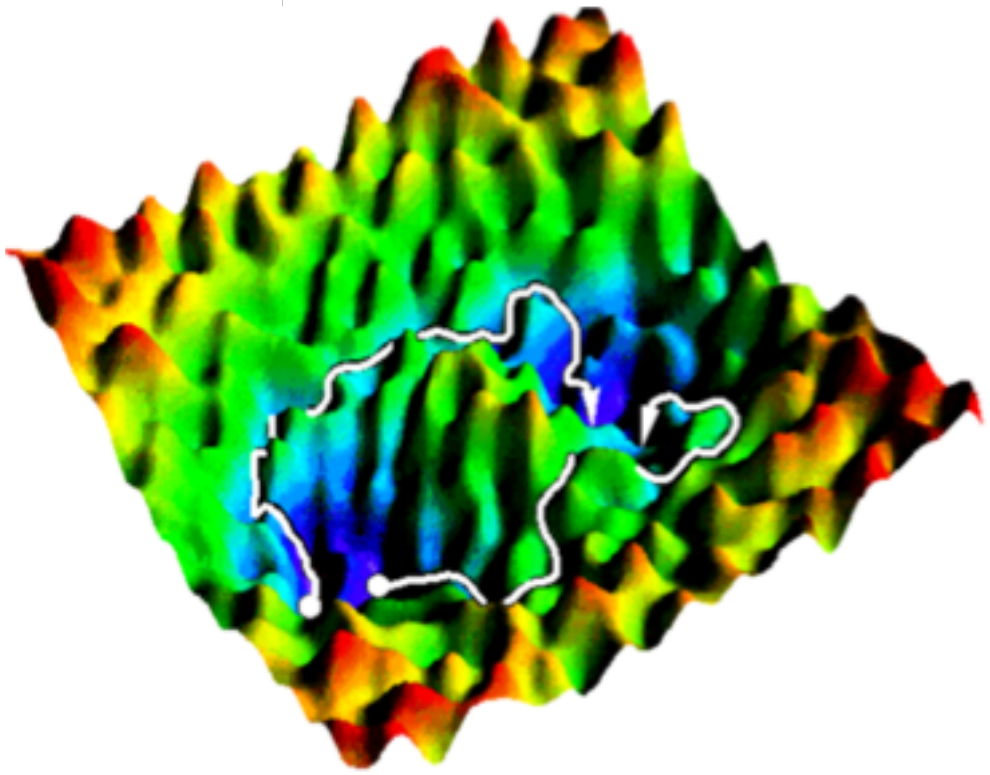
An effective sampling in phase space

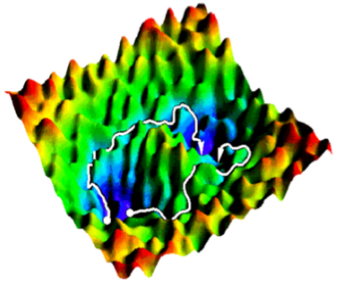


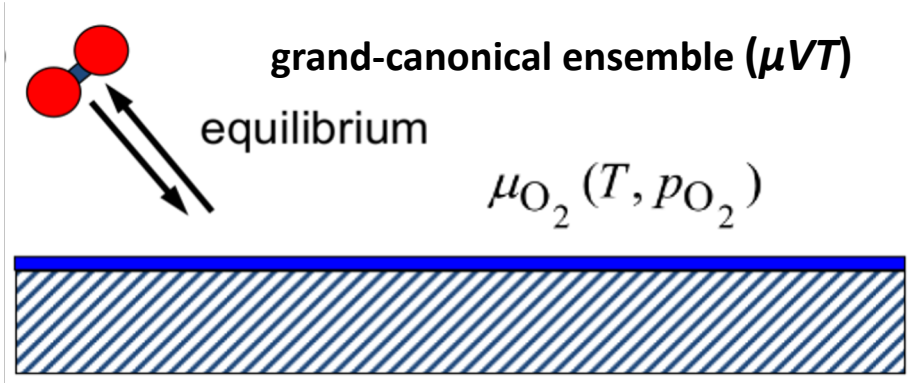


- Numerous minima
- Large free-energy barriers
- Slow-diffusion issues

An effective sampling in phase space: Replica-Exchange Grand-Canonical

- **Slow-diffusion issues**



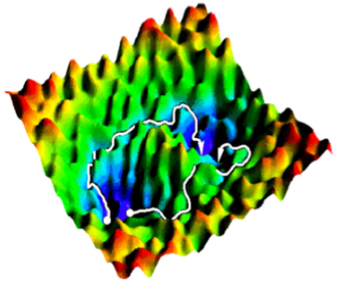


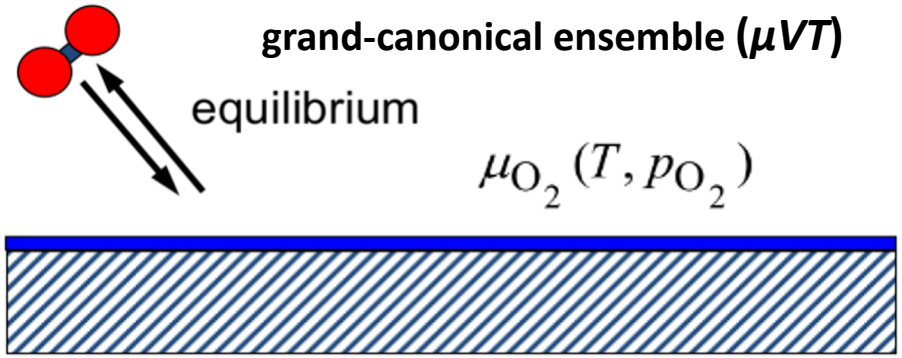
- ✓ **Statistical average over adsorption/desorption processes**
- ✓ **Generation of possible defects by atoms' insertion or removal**
- ✓ **Circumventing dissociation barrier**
- ✓ **Straightforward extension to multi-component systems**

Frenkel, D.; Smit, B. Understanding Molecular Simulation: From Algorithms to Applications; Academic Press: San Diego, 2002.

An effective sampling in phase space: Replica-Exchange Grand-Canonical

- **Slow-diffusion issues**





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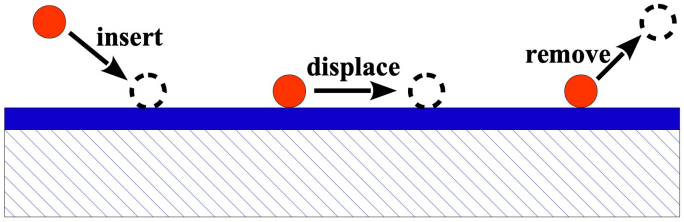
Realization of the Markov chain



Probability density $\mathcal{N}_{\mu,V,T}(\boldsymbol{R};N) \propto \frac{e^{(\beta\mu N)}V^N}{\Lambda^{3N}N!}e^{[-\beta E(\boldsymbol{R};N)]}$

$$P_{(N\to N+1)} = \min\left[1, \frac{V}{\Lambda^3(N+1)}e^{-\beta[\mu - E_{N+1} - E_N]}\right]$$

$$P_{(N\to N-1)} = \min\left[1, \frac{\Lambda^3 N}{V}e^{-\beta[\mu + E_{N-1} - E_N]}\right]$$

$$P_{(\boldsymbol{r}\to\boldsymbol{r}+\Delta\boldsymbol{r})} = \min\left[1, e^{-\beta[E(\boldsymbol{r}+\Delta\boldsymbol{r},\boldsymbol{r}^{N-1}) - E(\boldsymbol{r},\boldsymbol{r}^{N-1})]}\right]$$

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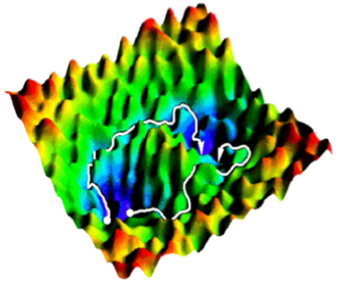
An effective sampling in phase space: Replica-Exchange Grand-Canonical

- Numerous minima
- Large free-energy barriers



✓ Adding bias to Hamiltonian:

metadynamics
umbrella samling
accelerated molecular dynamics

} appropriate collective variables
convergence criterion

✓ A generalized ensemble:

simulated tempering
multicanonical sampling

} Not priori known probability
weight factor

parallel tempering (replica exchange) → Known weight factor

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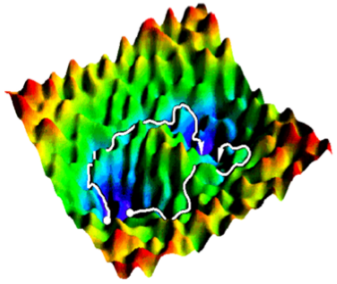
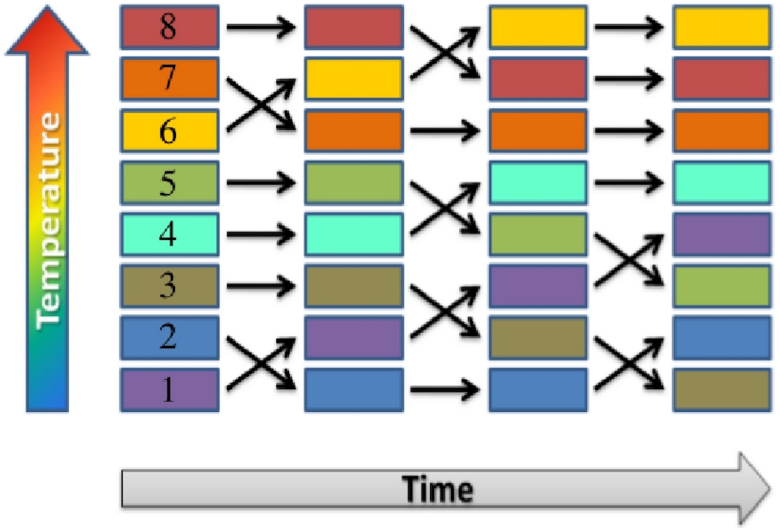




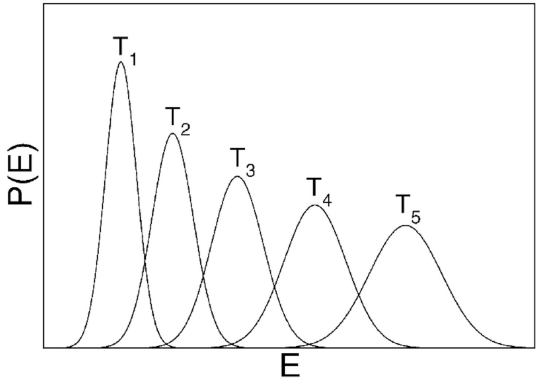
Low T: thoroughly sampling in the local minimas

High T: jumpimg between minimas (basins)

Partition function of extended *NVT* ensembles

$$Q_{\text{extended canonical}} = \prod_{l=1}^{L} \frac{1}{\Lambda_l^{3N} N!} \int d\boldsymbol{R}\, e^{-\beta_l E(\boldsymbol{R};N)}$$

$$P_{[\beta_i \to \beta_j]} = \min\left[1, e^{[-(\beta_j-\beta_i)(E(\boldsymbol{R}_i)-E(\boldsymbol{R}_j)]}\right]$$



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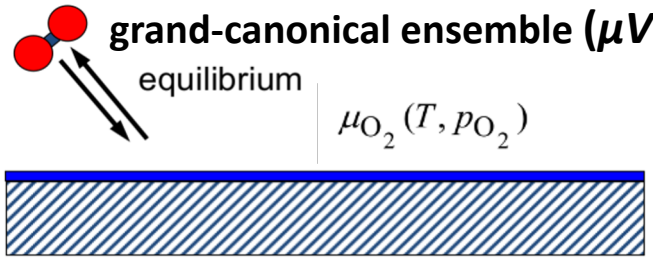
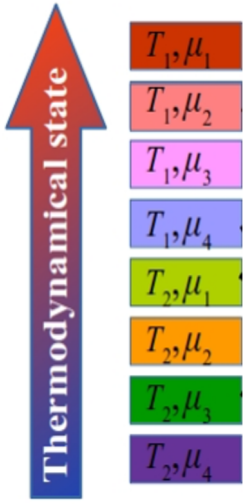
An effective sampling in phase space: Replica-Exchange Grand-Canonical



- ✓ Statistical average over adsorption/desorption processes
- ✓ Generation of possible defects by atoms' insertion or removal
- ✓ Circumventing dissociation barrier
- ✓ Kinetic barrier
- ✓ Straightforward extension to multi-component systems
- ✓ REGC coupled with molecular dynamics or monte carlo



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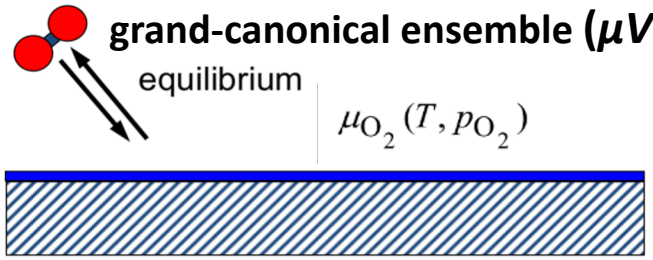

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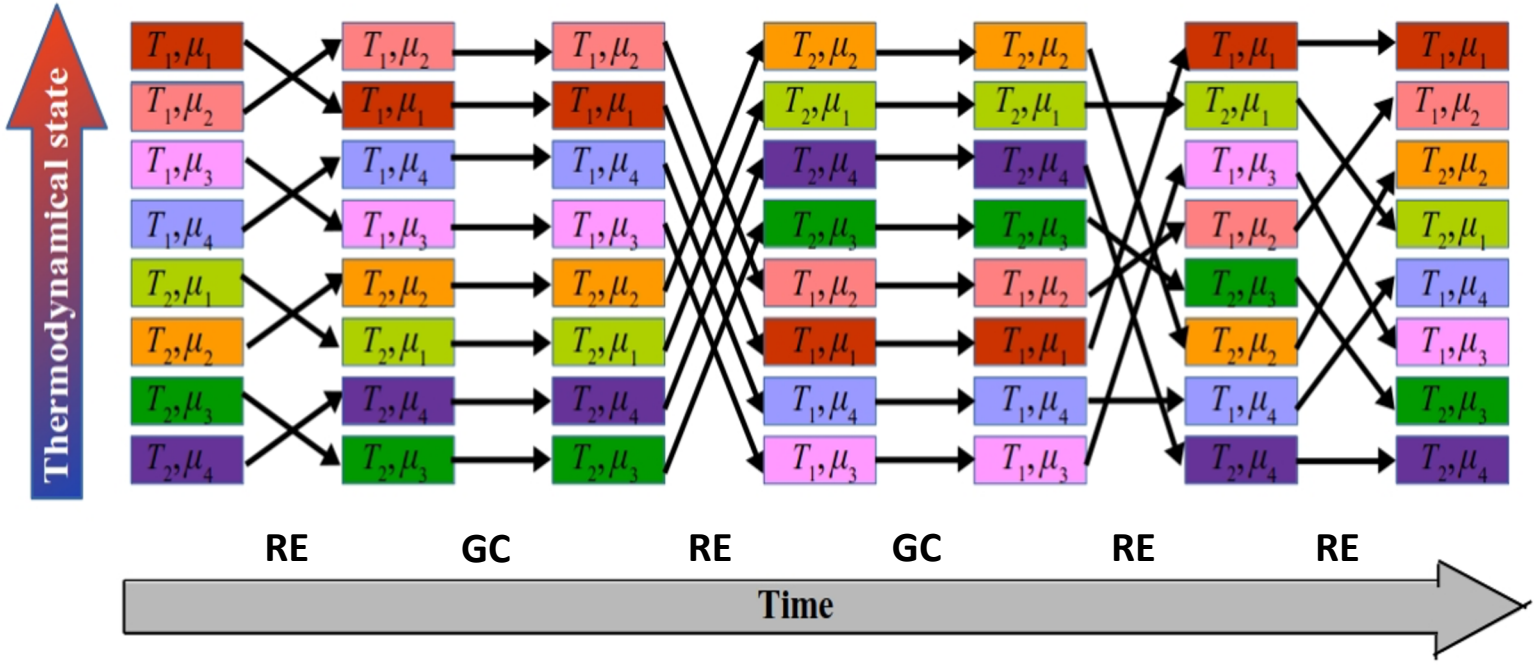

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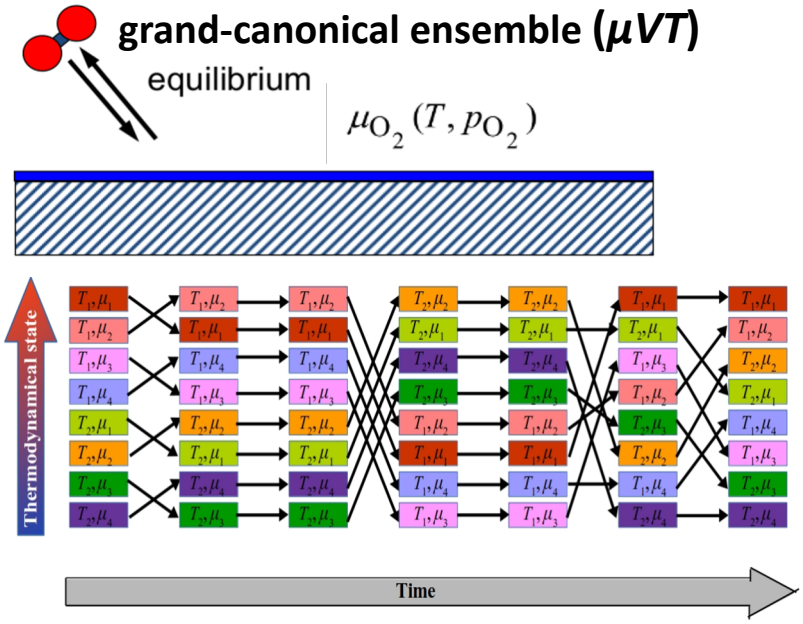

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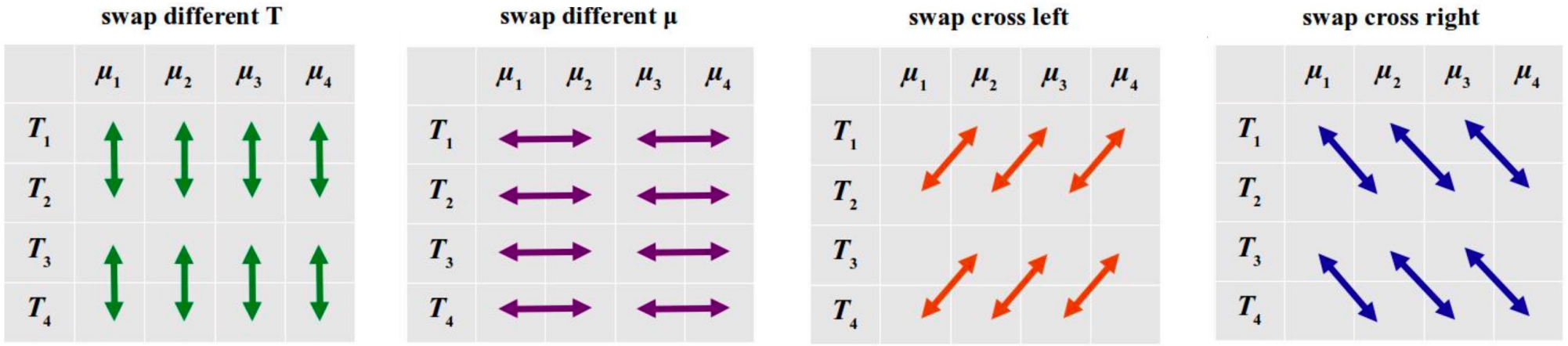
2D schematic of REGC



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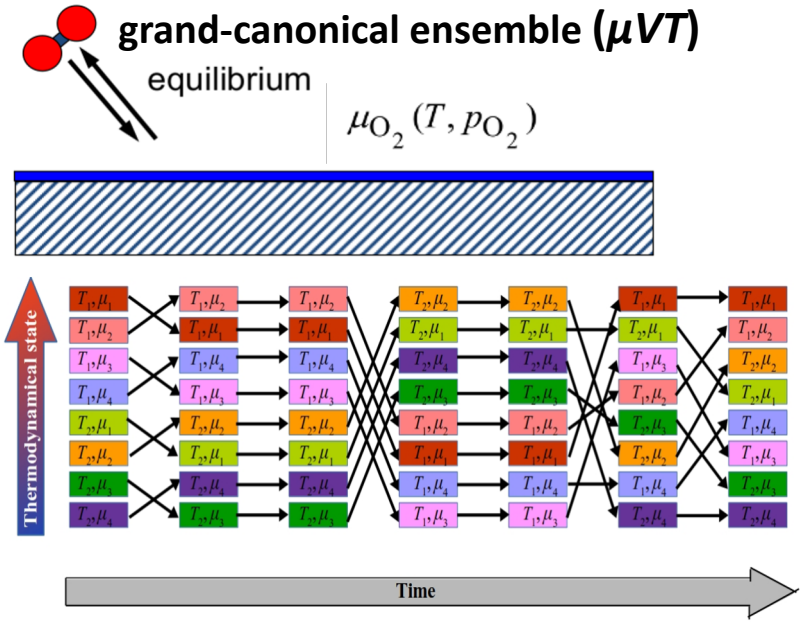

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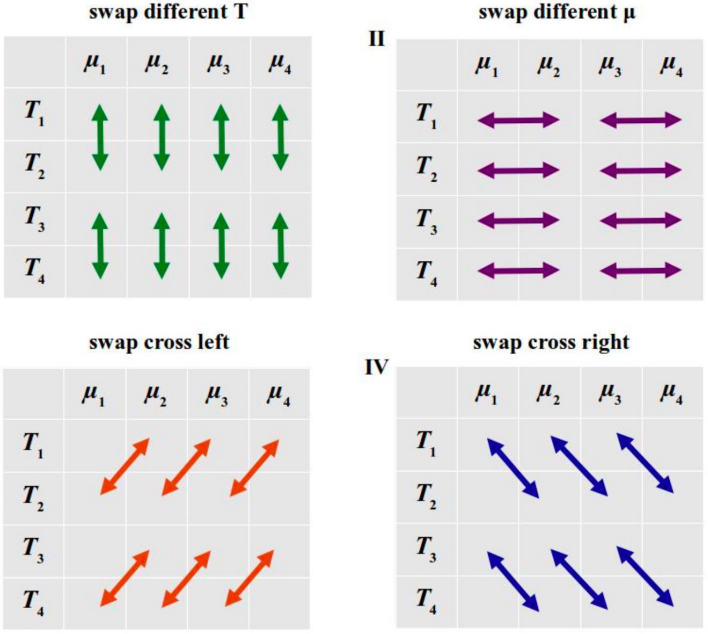


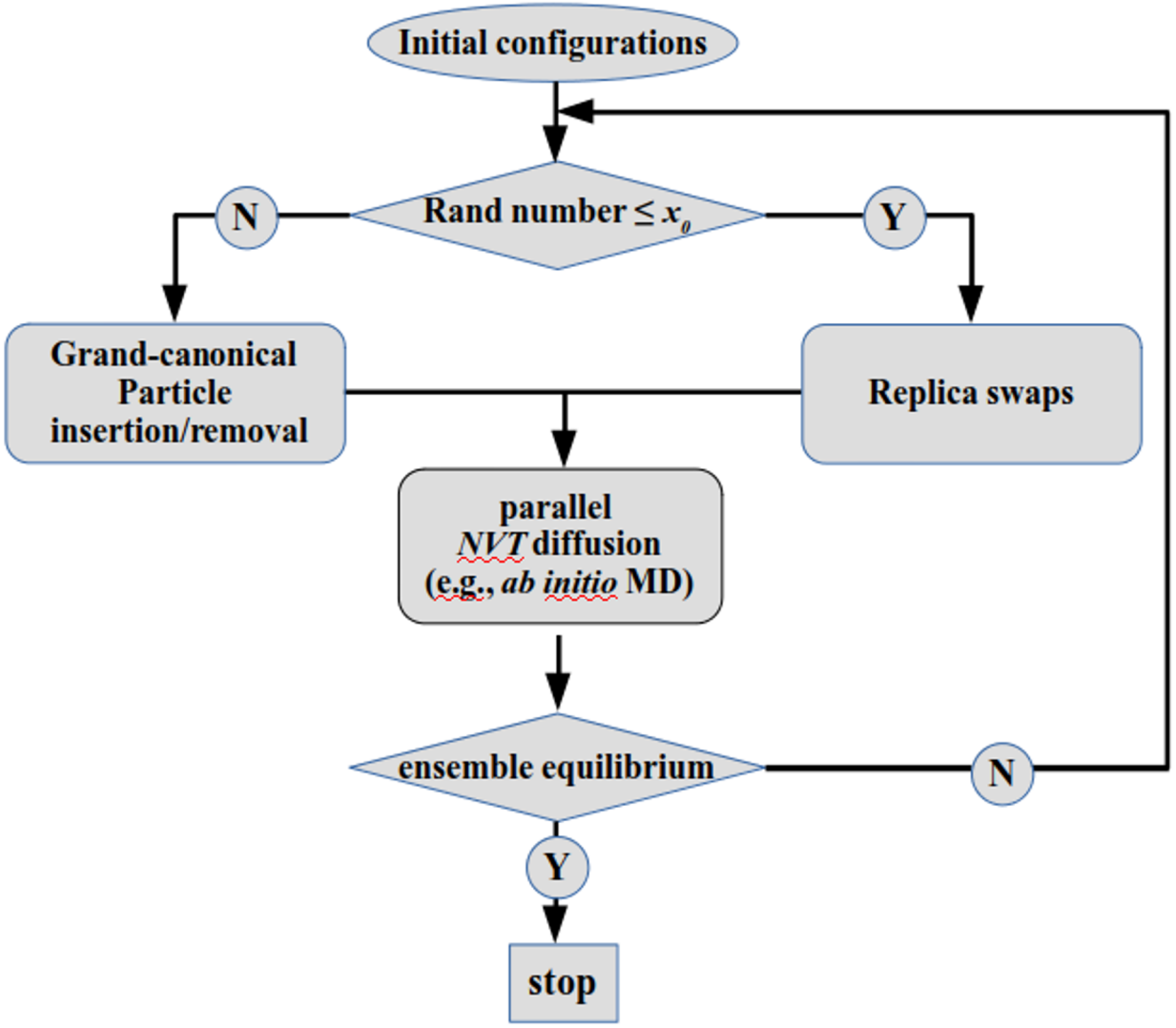
Partition function of extended *μVT* ensembles

$$Q_{\text{extended}} = \prod_{l=1}^{L} \prod_{m=1}^{M} \frac{e^{\beta_l \mu_m N_{l,m}} V^{N_{l,m}}}{\Lambda_l^{3N_{l,m}} N_{l,m}!} \int d\boldsymbol{R}\, e^{-\beta_l E(\boldsymbol{R};N_{l,m})}$$

$$P_{[(\beta_l,\mu_m,\boldsymbol{R}_i)(\beta_k,\mu_o,\boldsymbol{R}_j)\to(\beta_l,\mu_m,\boldsymbol{R}_j)(\beta_k,\mu_o,\boldsymbol{R}_i)]} =$$

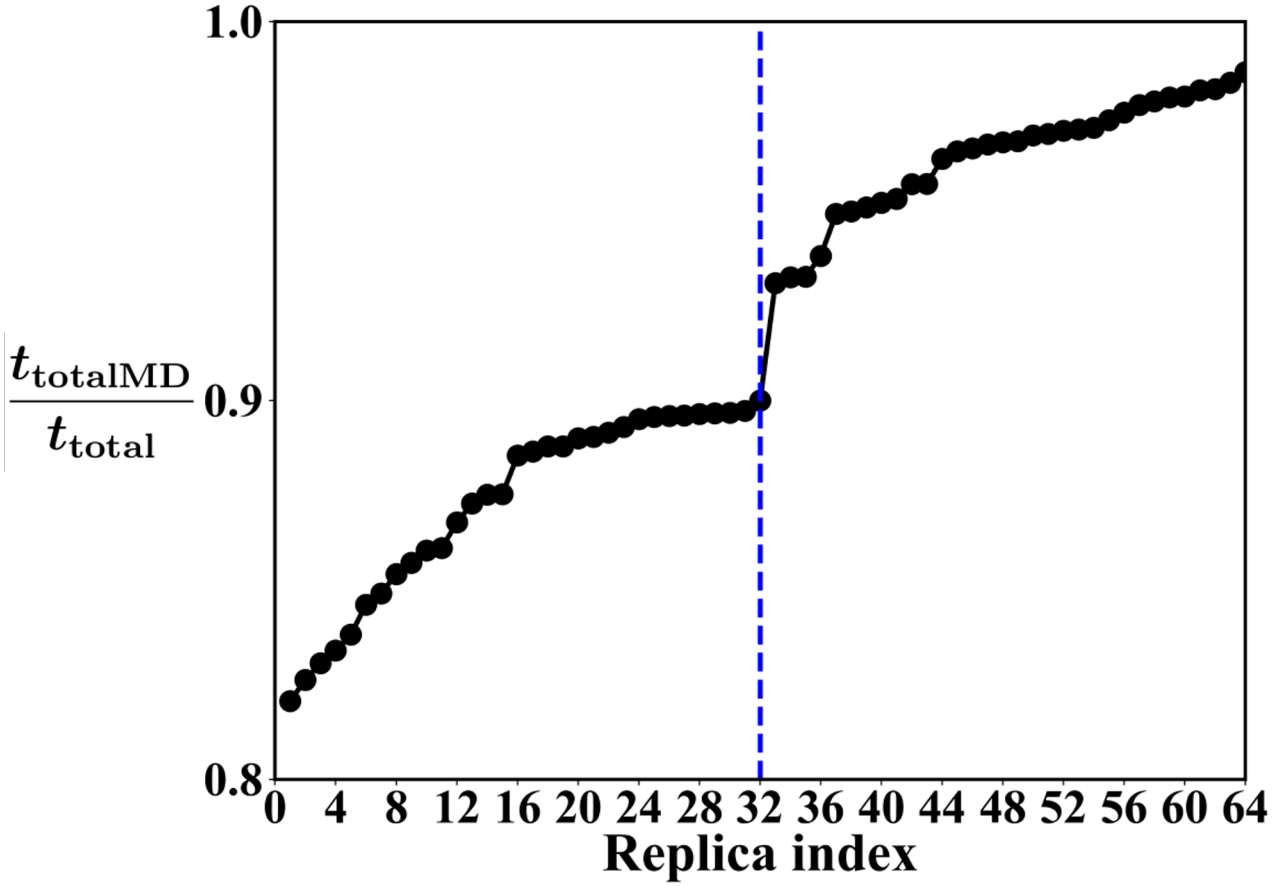
$$\min\left[1, \left(\frac{\beta_l}{\beta_k}\right)^{\frac{3}{2}(N_{l,m}-N_{k,o})} \times e^{[-(\beta_l-\beta_k)(E(\boldsymbol{R}_j)-E(\boldsymbol{R}_i)+(\beta_l\mu_m-\beta_k\mu_o)(N_{l.m}-N_{k,o})]}\right]$$

Replica-Exchange Grand-Canonical Scheme



Zhou, Scheffler and Ghiringhelli, Phys. Rev. B 100, (2019)
https://gitlab.com/zhouyuanyuan/fhi-panda
Shirts and Chodera, J. Chem. Phys. 12 (2008)

Scalability of REGC with FHI-aims



A REGCMD simulation of Si(100) system with 64 replicas.
This was performed on 10 240 cores (160 core for the MD run of every replica)

Free energy from probabilities: a posteriori

Free energy

$$F_i(\mu,T) = -k_{\mathrm{B}}T \ln P_i(\mu,T)$$

probability

$$= -k_{\mathrm{B}}T \ln \frac{\int_\Gamma d\boldsymbol{R}\, \chi_i(\boldsymbol{R})\, q(\boldsymbol{R};\mu,\beta)}{\int_\Gamma d\boldsymbol{R}\, q(\boldsymbol{R};\mu,\beta)}$$

$$\beta = 1/k_{\mathrm{B}}T$$

Ensemble average

$$\langle A(\boldsymbol{R})\rangle_{\mu,\beta,i} = \frac{\int_\Gamma d\boldsymbol{R}\, \chi_i(\boldsymbol{R})\, A(\boldsymbol{R})\, q(\boldsymbol{R};\mu,\beta)}{\int_\Gamma d\boldsymbol{R}\, q(\boldsymbol{R};\mu,\beta)}$$

partition function

$$c(\mu,\beta)$$

Free energy from probabilities: a posteriori

Free energy $F_i(\mu, T) = -k_B T \ln P_i(\mu, T)$ **probability**

$$= -k_B T \ln \frac{\int_\Gamma d\boldsymbol{R}\, \chi_i(\boldsymbol{R})\, q(\boldsymbol{R}; \mu, \beta)}{\int_\Gamma d\boldsymbol{R}\, q(\boldsymbol{R}; \mu, \beta)}$$

$$\beta = 1/k_B T$$

Ensemble average $\langle A(\boldsymbol{R})\rangle_{\mu,\beta,i} = \frac{\int_\Gamma d\boldsymbol{R}\, \chi_i(\boldsymbol{R})\, A(\boldsymbol{R})\, q(\boldsymbol{R}; \mu, \beta)}{\int_\Gamma d\boldsymbol{R}\, q(\boldsymbol{R}; \mu, \beta)}$

partition function $c(\mu, \beta)$

Reduced potential function for the GC ensemble $U(\boldsymbol{R}; \mu, \beta) = \beta[E(\boldsymbol{R}) - \mu N(\boldsymbol{R})]$

Grand-canonical density function $q(\boldsymbol{R}; \mu, \beta) = \exp[-U(\boldsymbol{R}; \mu, \beta)]$

Multistate Bennett acceptance ratio (MBAR) approach estimates $c(\mu, \beta)$

$$\hat{c}_{l,m} = \sum_{i=1}^{\Omega_{l,m}} \frac{q(\boldsymbol{R}_{i,l,m}; \mu_m, \beta_l)}{\sum_{l=1}^{L}\sum_{m=1}^{M} \Omega_{l,m} \hat{c}_{l,m}^{-1} q(\boldsymbol{R}_{i,l,m}; \mu_m, \beta_l)}$$

***L* × *M* thermodynamic states in REGC simulation**

$$\langle A(\boldsymbol{R})\rangle_{\mu,\beta,i} = \sum_{n=1}^{\Omega_i} \frac{A(\boldsymbol{R}_n)\, c_{\mu,\beta}^{-1}\, q(\boldsymbol{R}_n; \mu, \beta)}{\sum_{l,m} \Omega_{l,m,i} c_{\mu_m,\beta_l}^{-1} q(\boldsymbol{R}_{l,m,i}; \mu_m, \beta_l)}$$

in the MBAR formalism

Zhou, Scheffler and Ghiringhelli, Phys. Rev. B 100, (2019)
https://gitlab.com/zhouyuanyuan/fhi-panda
Shirts and Chodera, J. Chem. Phys. 12 (2008)

Free energy from probabilities: a posteriori

Free energy $F_i(\mu,T) = -k_{\mathrm{B}}T \ln P_i(\mu,T)$ **probability**

$$= -k_{\mathrm{B}}T \ln \frac{\int_\Gamma d\boldsymbol{R}\, \chi_i(\boldsymbol{R})\, q(\boldsymbol{R};\mu,\beta)}{\int_\Gamma d\boldsymbol{R}\, q(\boldsymbol{R};\mu,\beta)}$$

$$\beta = 1/k_{\mathrm{B}}T$$

Ensemble average $\langle A(\boldsymbol{R})\rangle_{\mu,\beta,i} = \frac{\int_\Gamma d\boldsymbol{R}\, \chi_i(\boldsymbol{R})\, A(\boldsymbol{R})\, q(\boldsymbol{R};\mu,\beta)}{\int_\Gamma d\boldsymbol{R}\, q(\boldsymbol{R};\mu,\beta)} \stackrel{?}{=} \frac{\sum A_i e^{-\beta U_i}}{\sum e^{-\beta U_i}} = \sum_i A_i P_i$

Reduced potential function for the GC ensemble $U(\boldsymbol{R};\mu,\beta) = [E(\boldsymbol{R}) - \mu N(\boldsymbol{R})]$

Grand-canonical density function $q(\boldsymbol{R};\mu,\beta) = \exp[-U(\boldsymbol{R};\mu,\beta)]$

Ergodic hypothesis: ensemble average equal to time average

$$\langle E\rangle = \frac{\sum_i E(\mathbf{R}_i;\mu,\beta) e^{-\beta U(\mathbf{R}_i;\mu,\beta)}}{c(\mu,\beta)}$$

$$NC_v = \frac{\partial\langle E\rangle}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial E}{\partial \beta} = -\frac{1}{k_B T^2}\frac{\partial}{\partial\beta}\left(\frac{\sum_i E_i e^{-\beta U_i}}{c(\mu,\beta)}\right)$$

$$= -\frac{1}{k_B T^2}\left[\frac{\left(\sum_i E_i e^{-\beta U_i}\right)^2}{c^2(\mu,\beta)} - \frac{\sum_i E_i^2 e^{-\beta U_i}}{c(\mu,\beta)}\right]$$

$$= \frac{1}{k_B T^2}\left(\langle E^2\rangle - \langle E\rangle^2\right)$$

Zhou, Scheffler and Ghiringhelli, Phys. Rev. B 100, (2019)
https://gitlab.com/zhouyuanyuan/fhi-panda
Shirts and Chodera, J. Chem. Phys. 12 (2008)

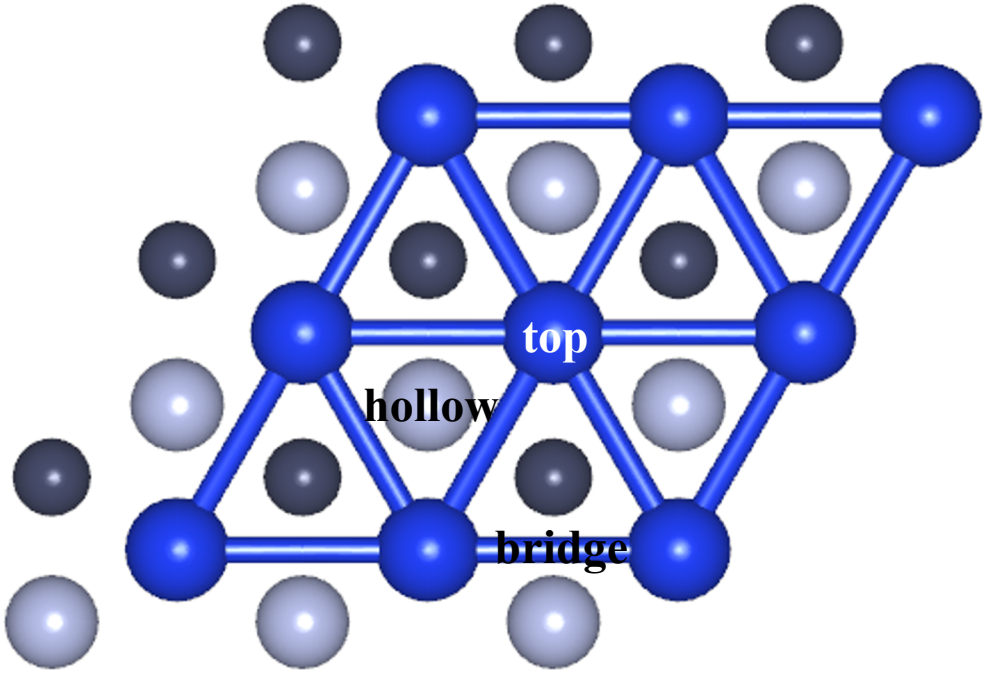
Results

Proof of concept: Two-component Lennard-Jones surface

Application: Si(100) surface in contact with D_2 reactive atmosphere at *ab initio* level

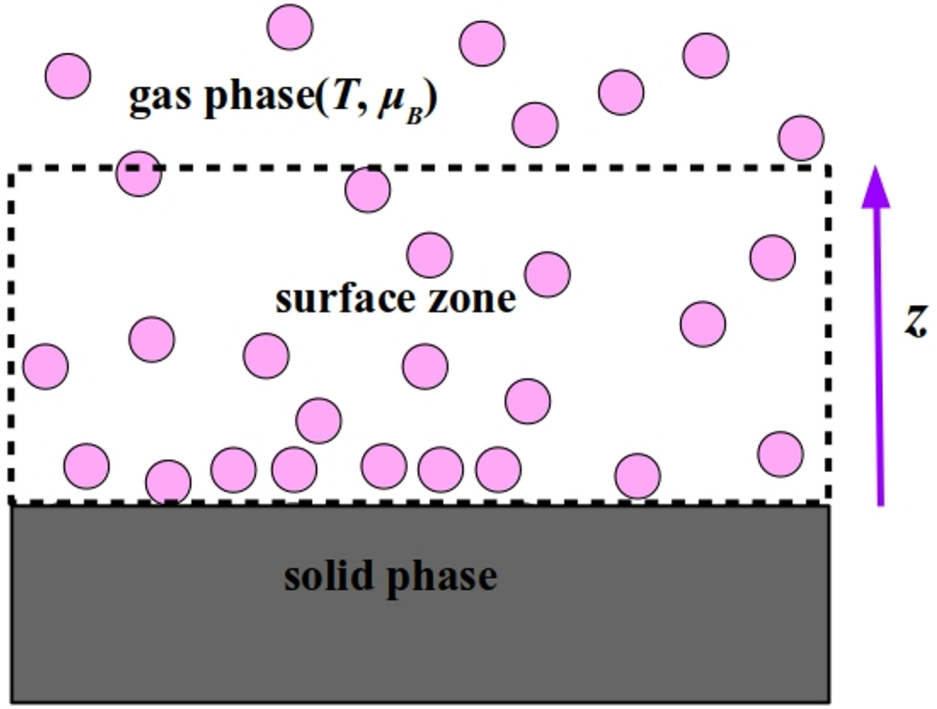
Two-component Lennard-Jones surface

Top view



fcc(111)

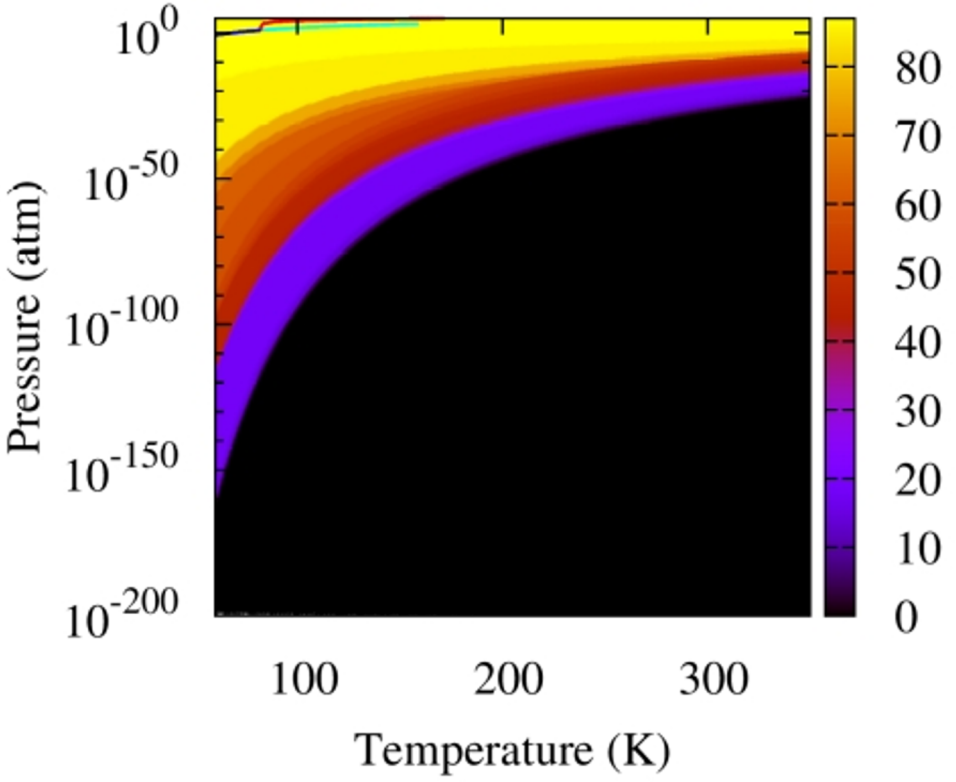
Side view



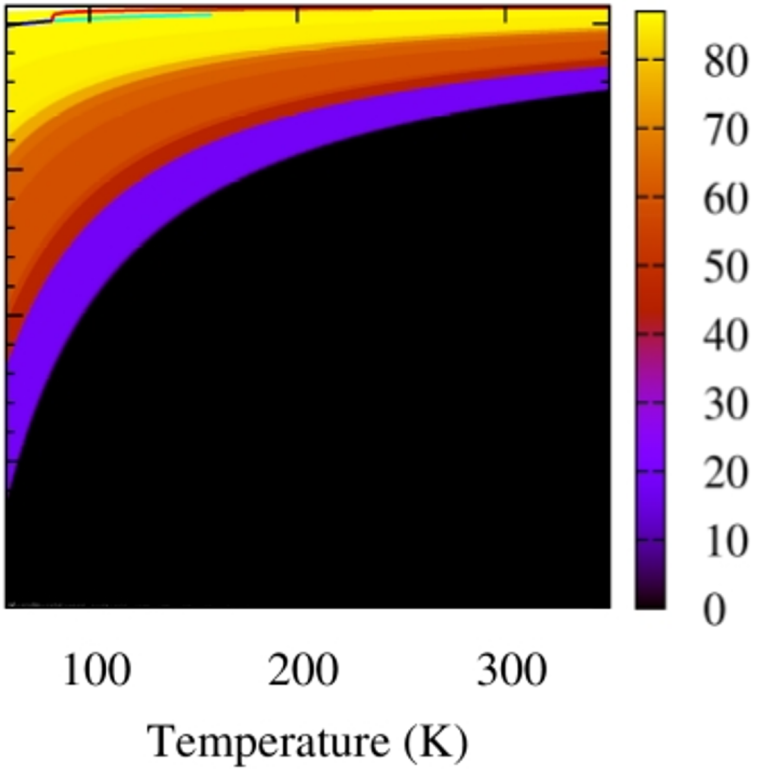
REGC: 10 temperatures and 16 chemical potentials

Two-component Lennard-Jones surface

REGC+ MBAR



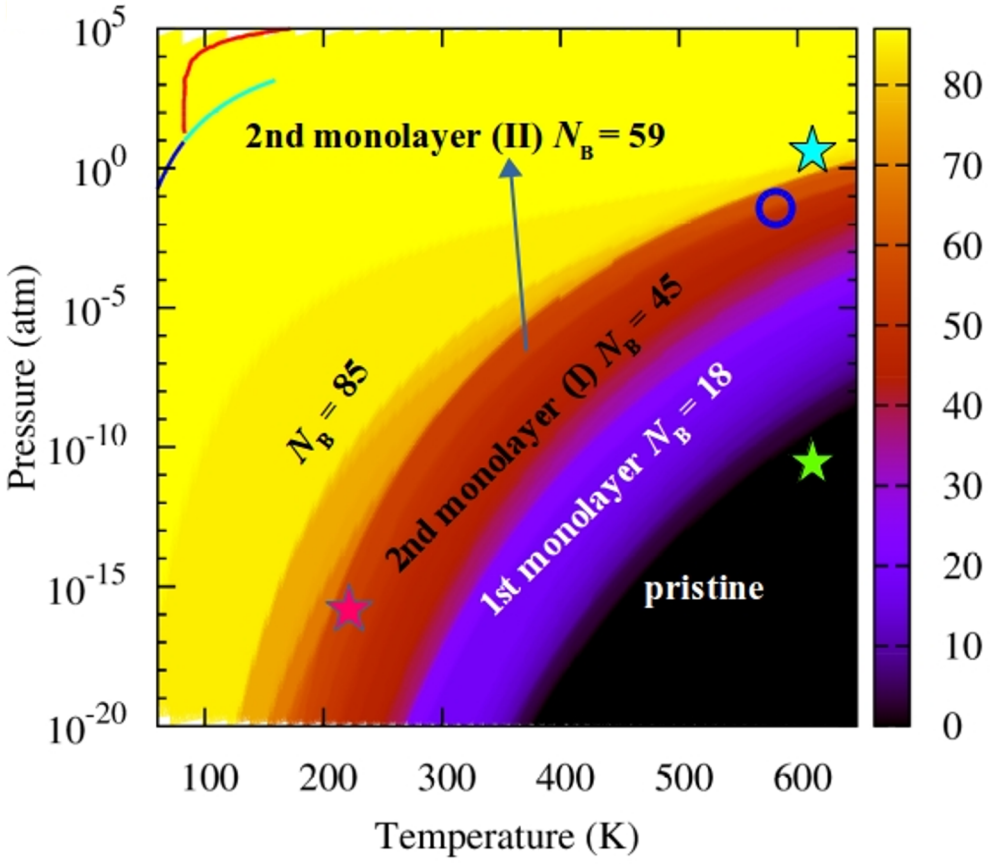
REGC(minimum-energy-structures) +aiAT



$$\mu(p, T) = k_{\mathrm{B}} T \ln(p/p_0)$$

Two-component Lennard-Jones surface

REGC+ MBAR



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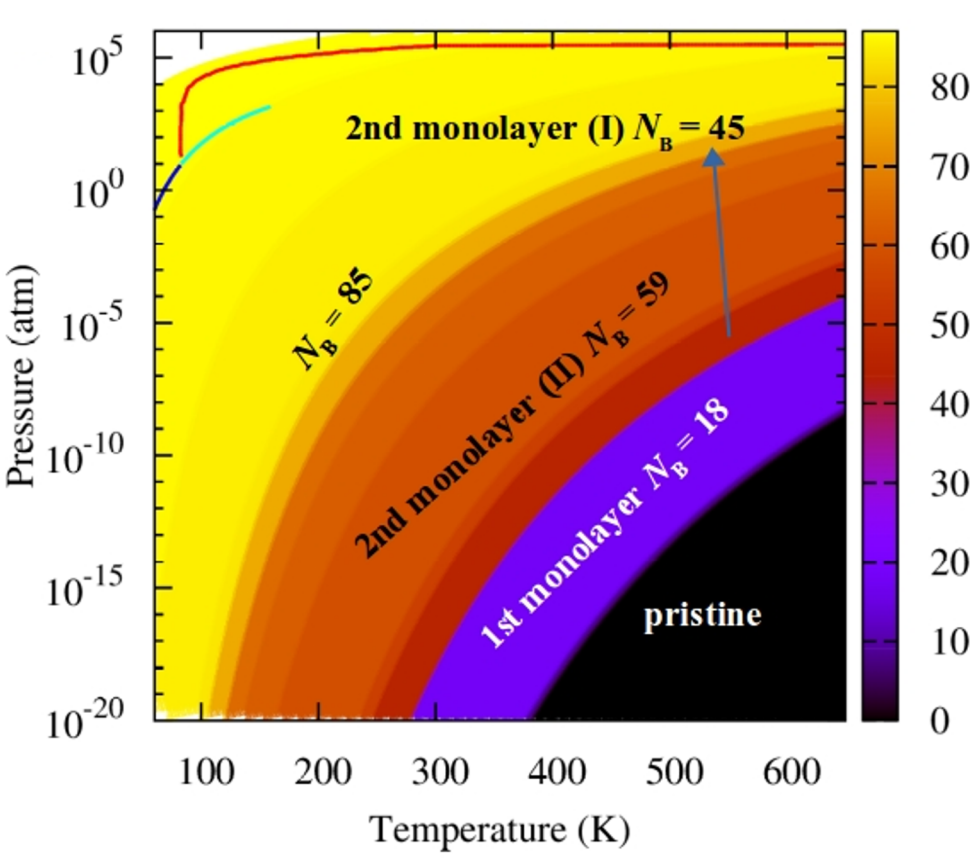
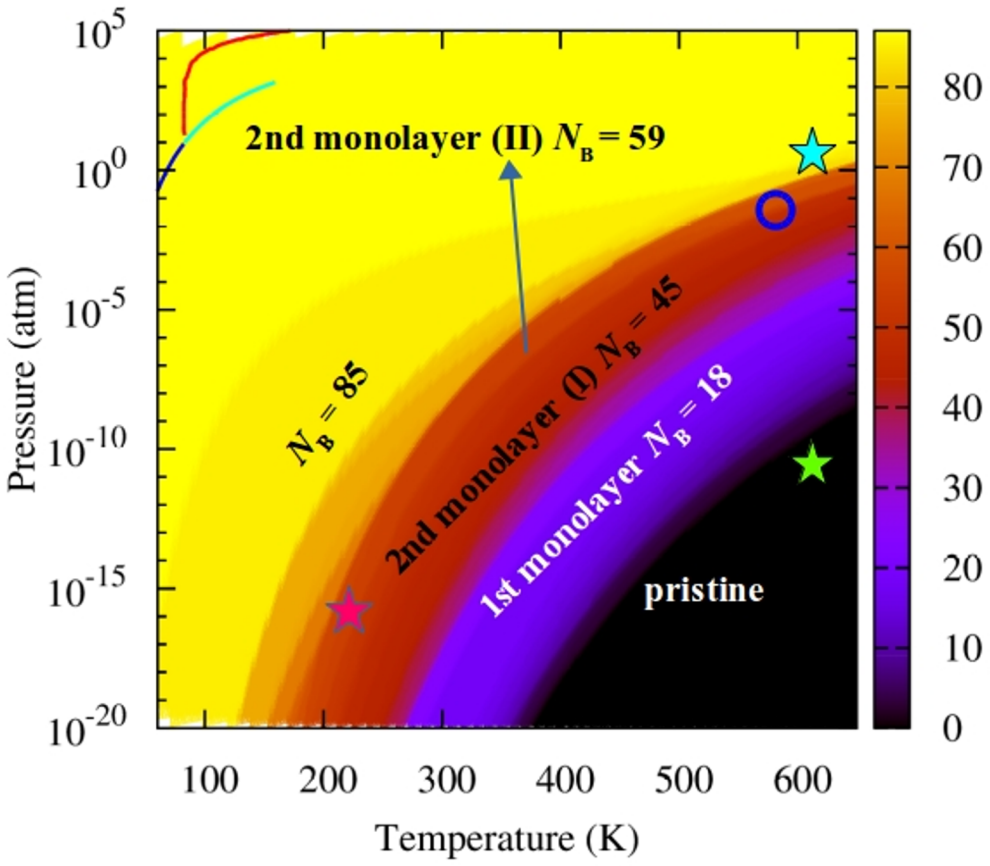
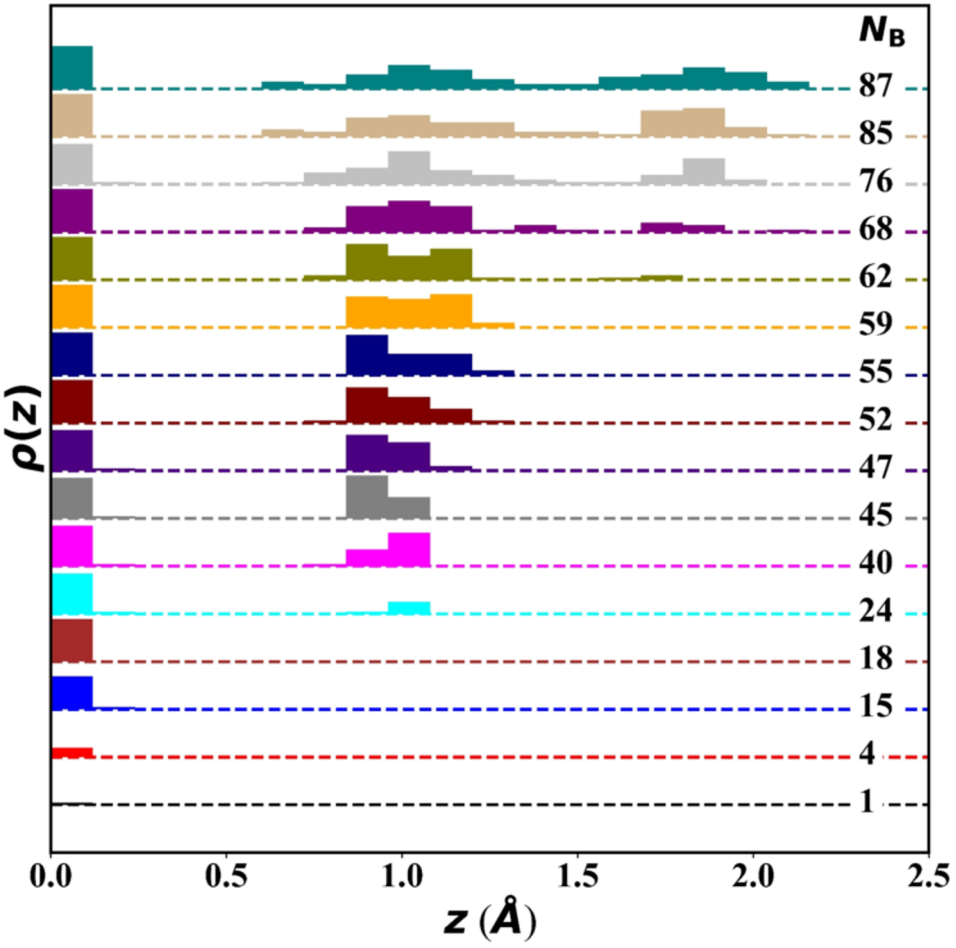


$$\mu(p, T) = k_B T \ln(p/p_0)$$

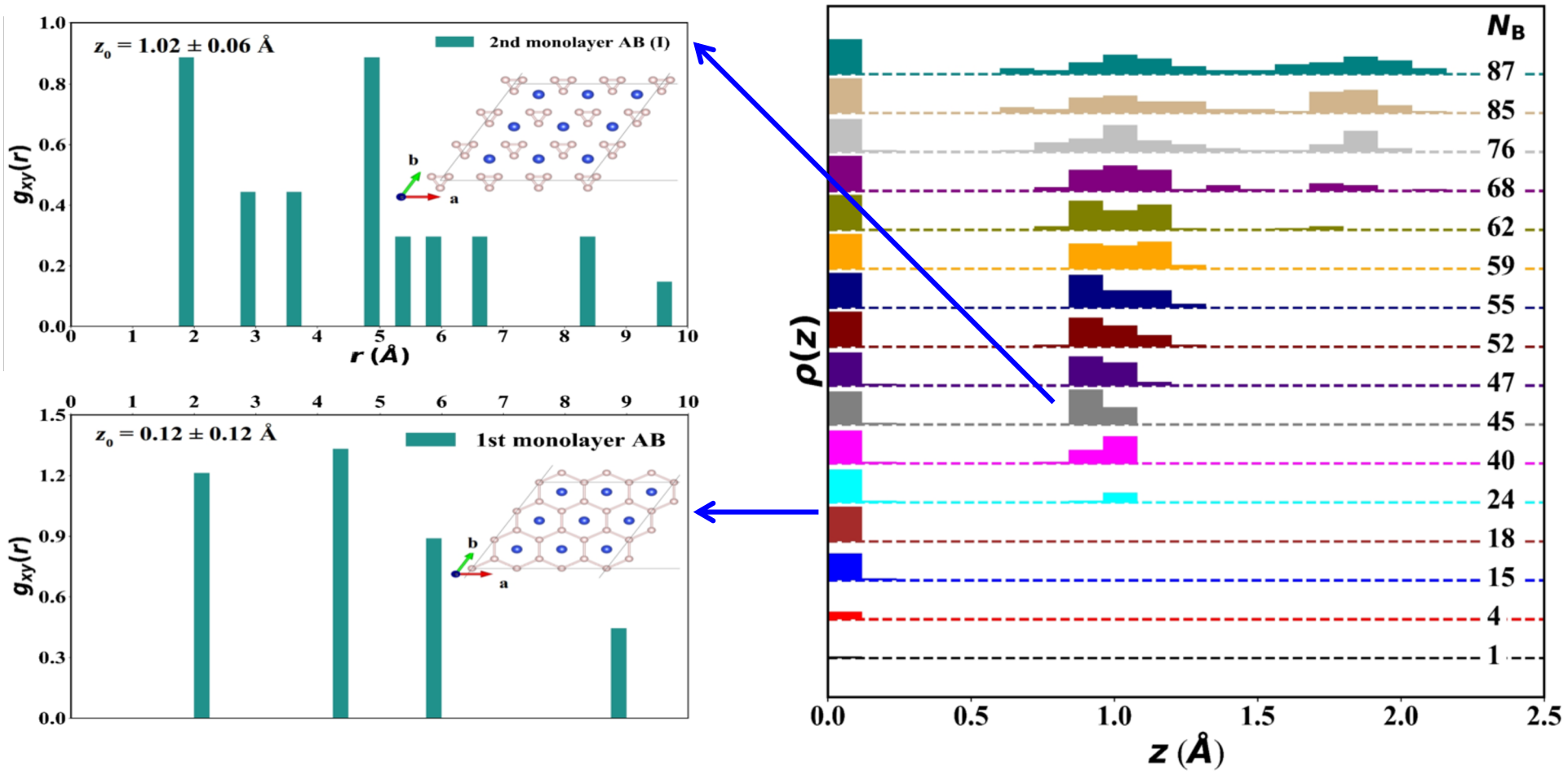
Two-component Lennard-Jones surface

REGC+ MBAR

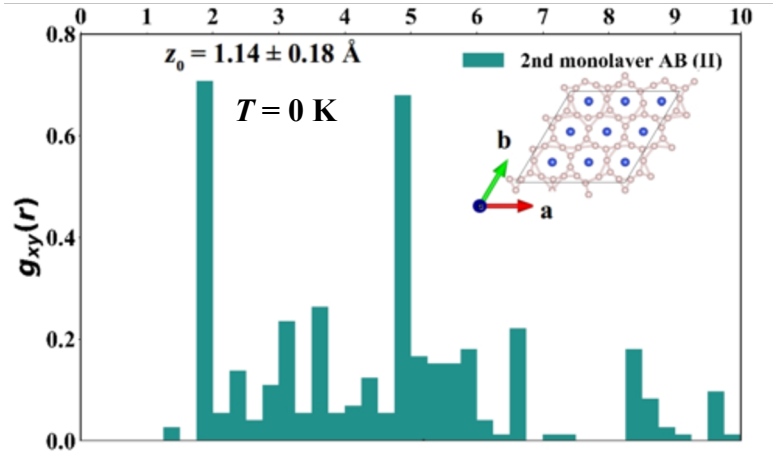


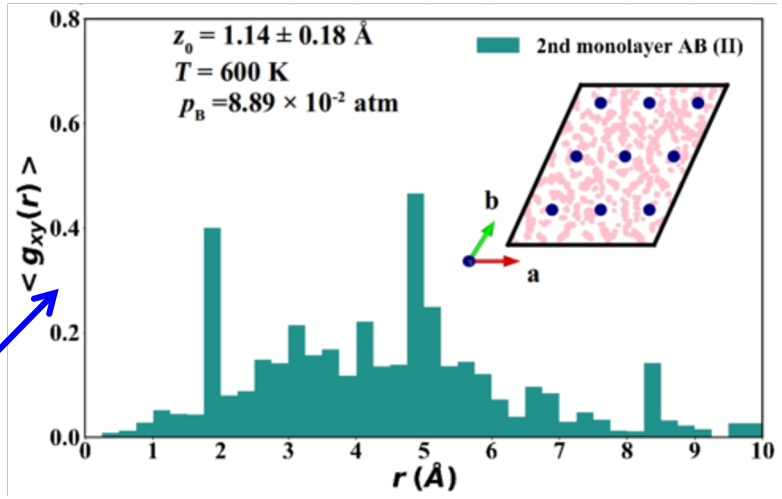


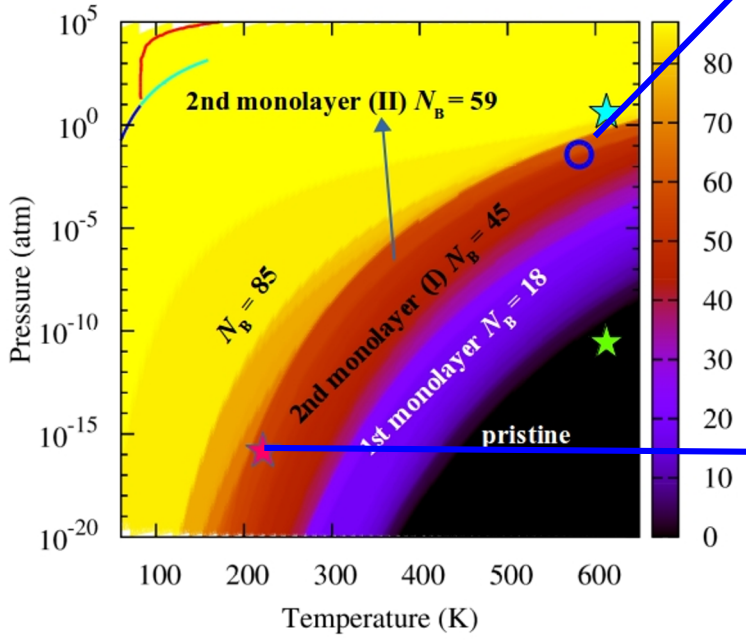
Two-component Lennard-Jones surface

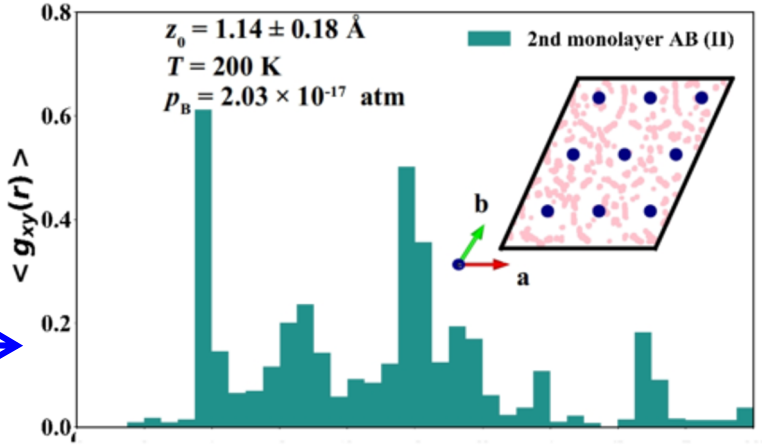


Two-component Lennard-Jones surface





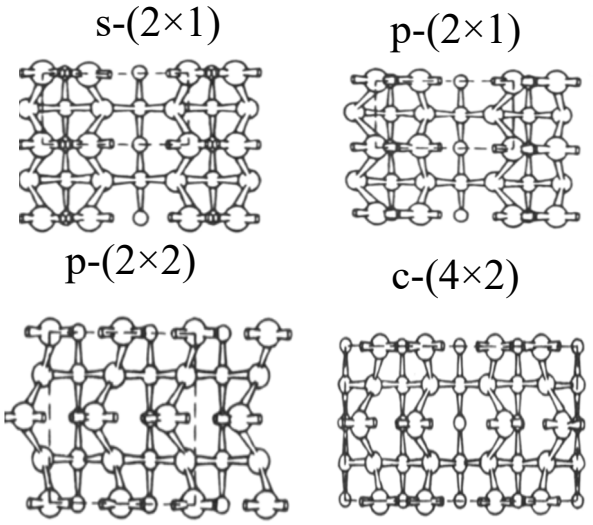




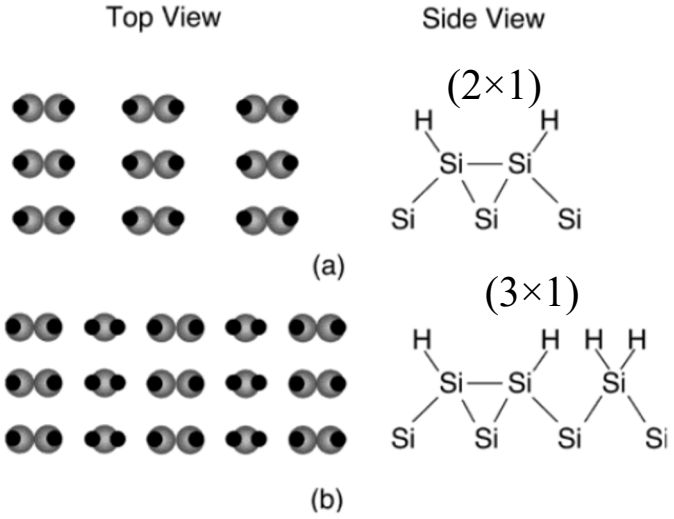
Zhou, Scheffler and Ghiringheli, Phys. Rev. B 100, (2019)

Si(100) surface in contact with D_2 reactive atmosphere at *ab initio* level

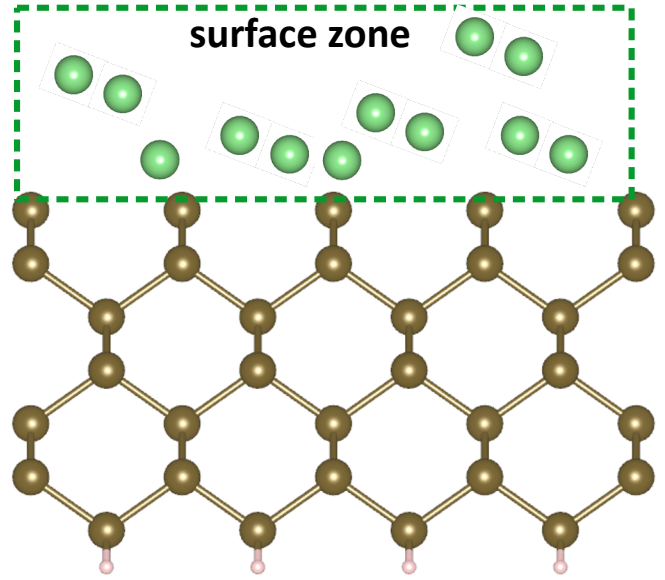
reconstruction



adsorption



Model systems: (4×4) and (3×3) supercell



***ab initio* molecular dynamics**

xc: PBE+vdW^{TS}

basis setting: light

stochastic velocity-rescaling thermostat

Using D_2 instead of H_2 during the simulation

[1] C.Manzano, et. al., Phys. Rev. B., 83, 201302 (2011)
[2] J. J. Boland, Adv. Phys., 42, 129 (1993)
[3] Chabal and Raghavachari, Phys. Rev. Lett 100, 1055 (1985)
[4] Blum, *et al*., Comput. Phys. Commun. 180, 2175 (2009)
[5] Perdew, *et al.,* Phys. Rev. Lett. 77, 3865 (2008)
[6] Tkatchenko, *et al*., Phys. Rev. Lett, 201, 073005 (2009)
[7] Bussi, *et al.*, J. Chem. Phys. 126, 014101 (2007)
[8] Zhou, *et al.,* unpublished

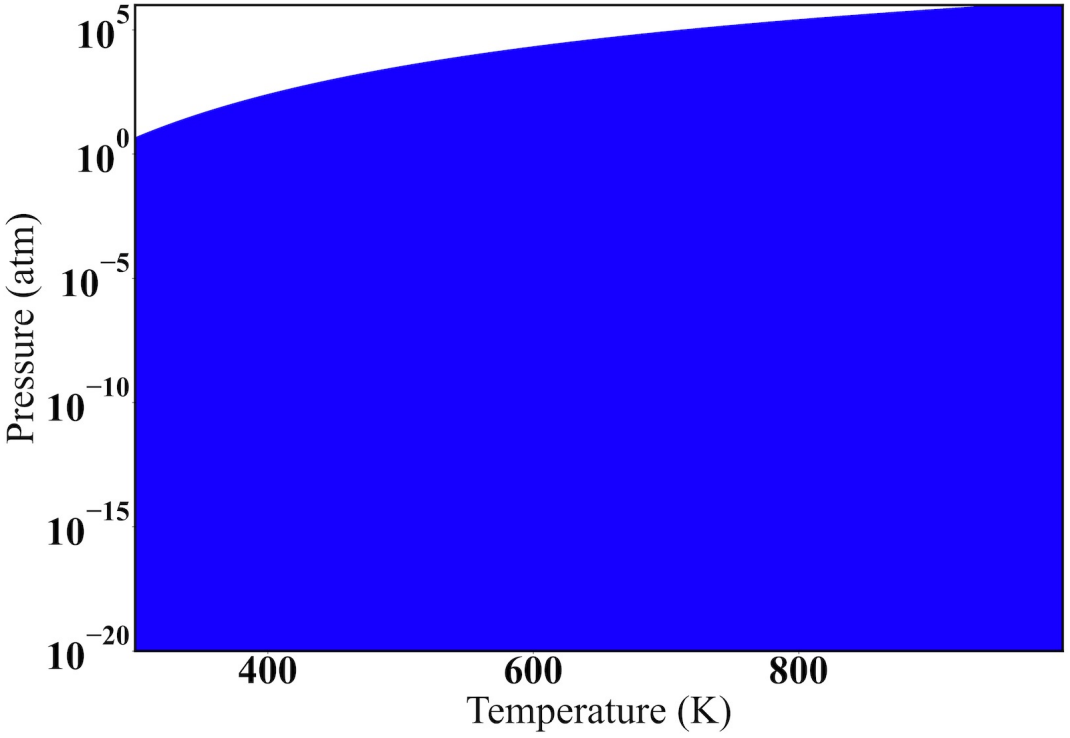
Quantitative calculation of *ab initio* phase boundaries

$$C_{v,\,(T,\,p_{\mathrm{H}_2})} = \frac{\langle E^2\rangle_{(T,\,p_{\mathrm{H}_2})} - \langle E\rangle^2_{(T,\,p_{\mathrm{H}_2})}}{k_B T^2}$$

$$\langle E\rangle_{\mu,\beta} = \sum_{n=1}^{\Omega} \frac{E(\boldsymbol{R}_n)\, c^{-1}_{\mu,\beta}\, q(\boldsymbol{R}_n;\mu,\beta)}{\sum_{l,m} \Omega_{l,m} c^{-1}_{\mu_m,\beta_l} q(\boldsymbol{R}_{l,m};\mu_m,\beta_l)}$$

in MBAR formalism

Every 1 K and 0.01 eV interval



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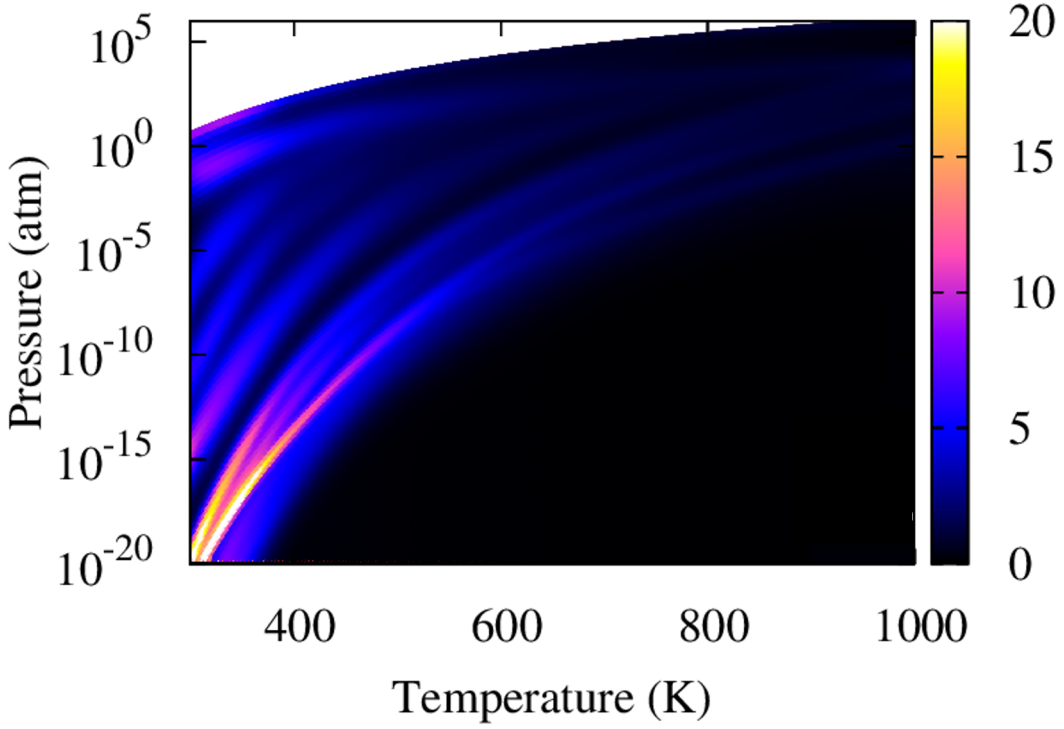

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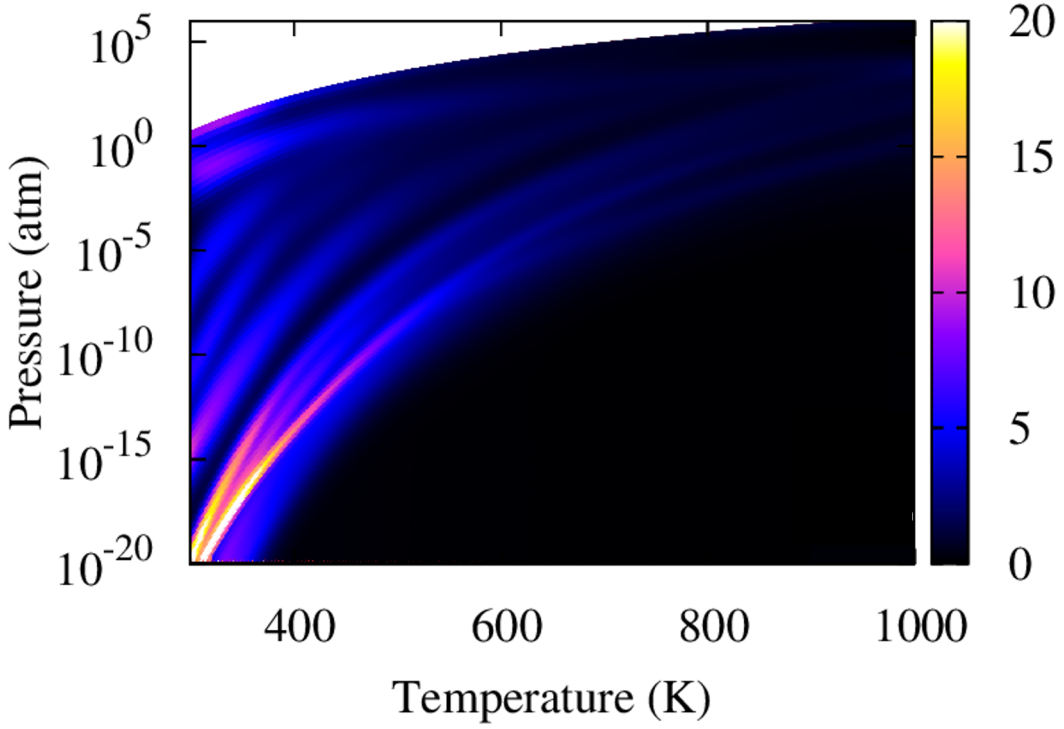
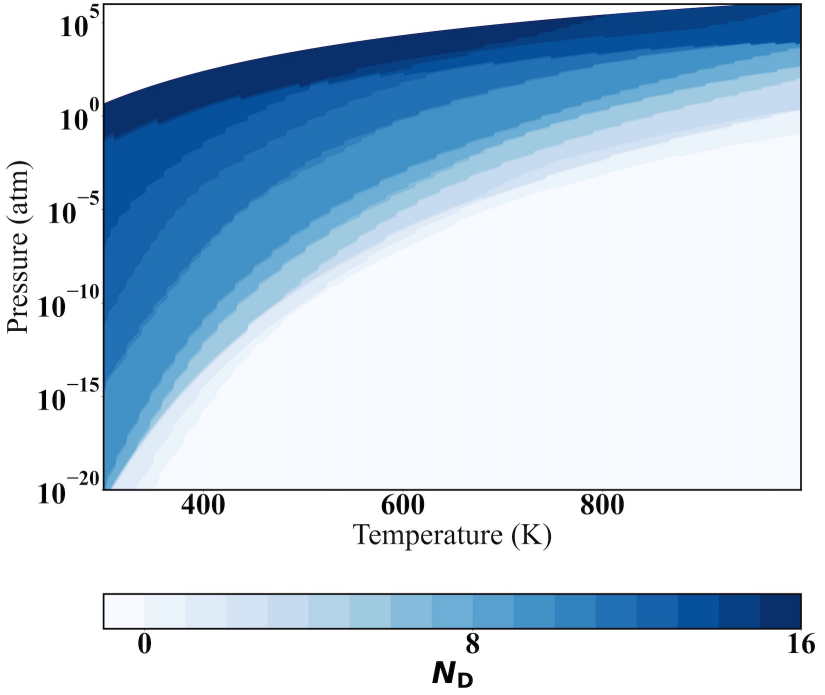
$$F_i(\mu,T) = -k_{\mathrm{B}}T \ln P_i(\mu,T)$$
$$= -k_{\mathrm{B}}T \ln \frac{\int_\Gamma d\boldsymbol{R}\, \chi_i(\boldsymbol{R})\, q(\boldsymbol{R};\mu,\beta)}{\int_\Gamma d\boldsymbol{R}\, q(\boldsymbol{R};\mu,\beta)}$$

$\chi_i(\boldsymbol{R})$: **number of chemisorbed D (N_{D})**





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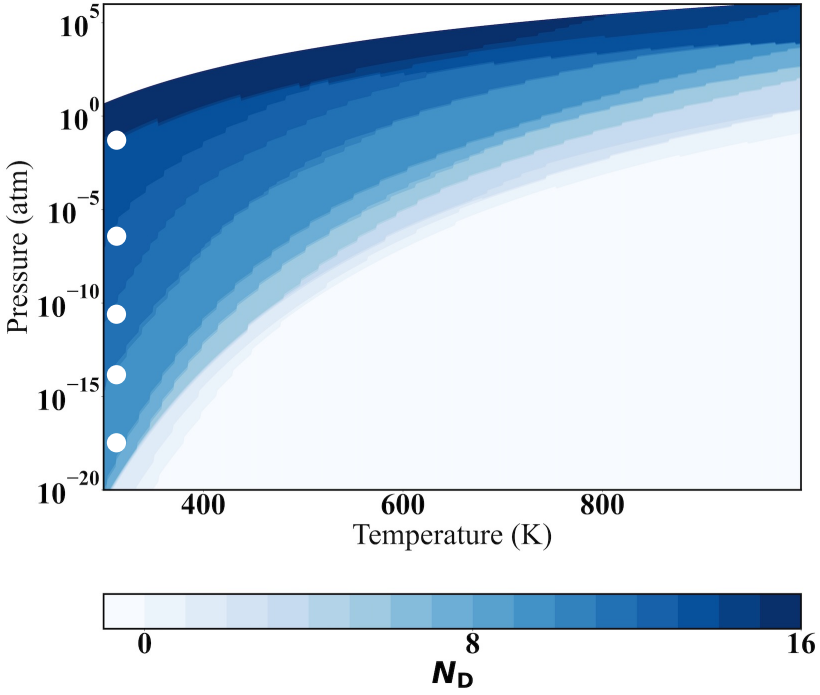

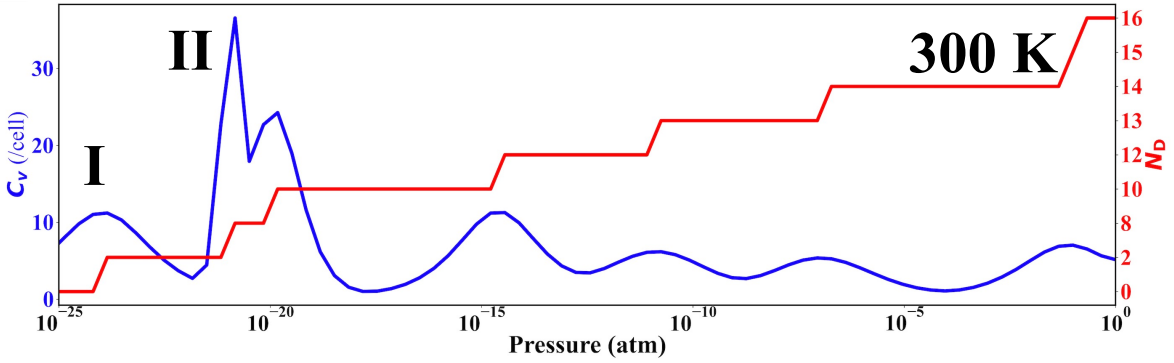

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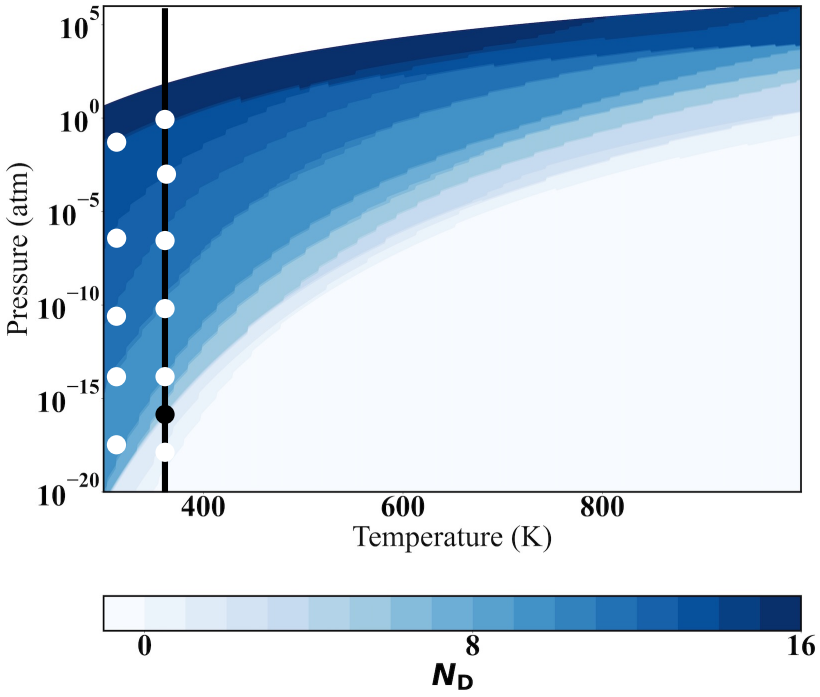

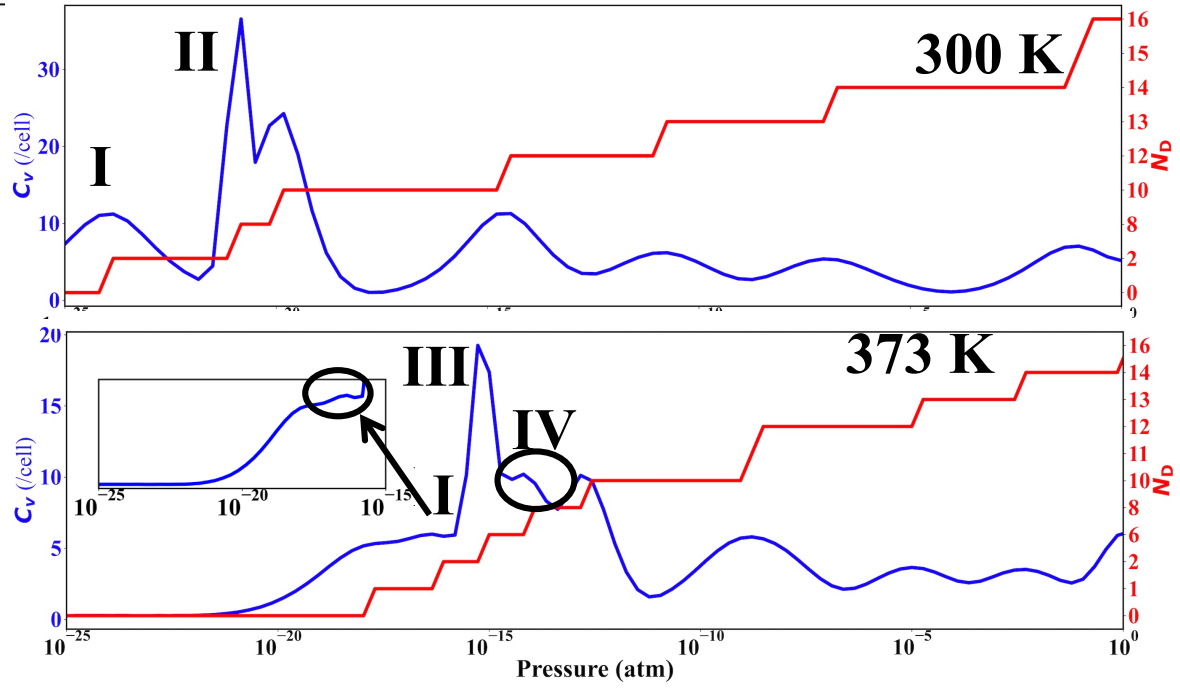

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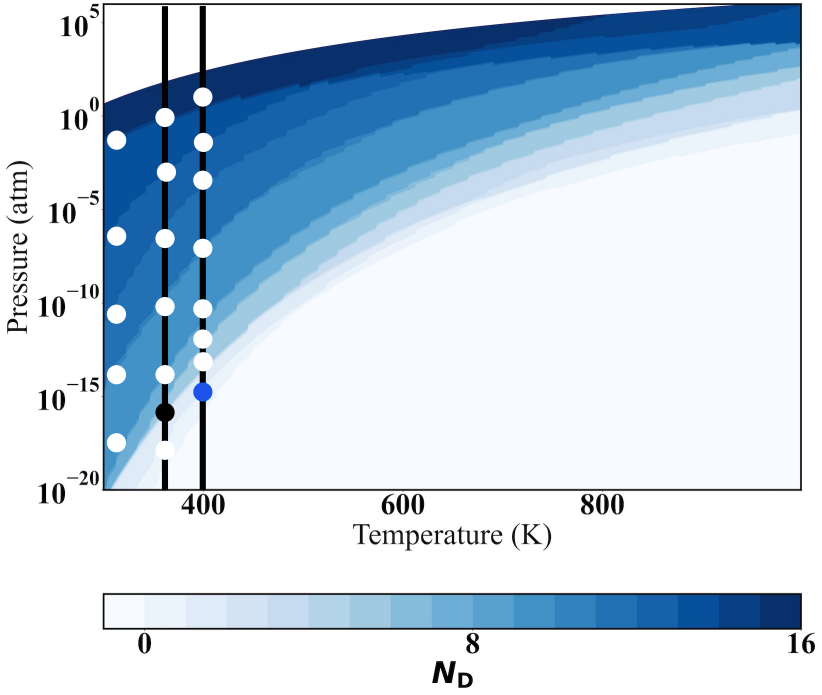
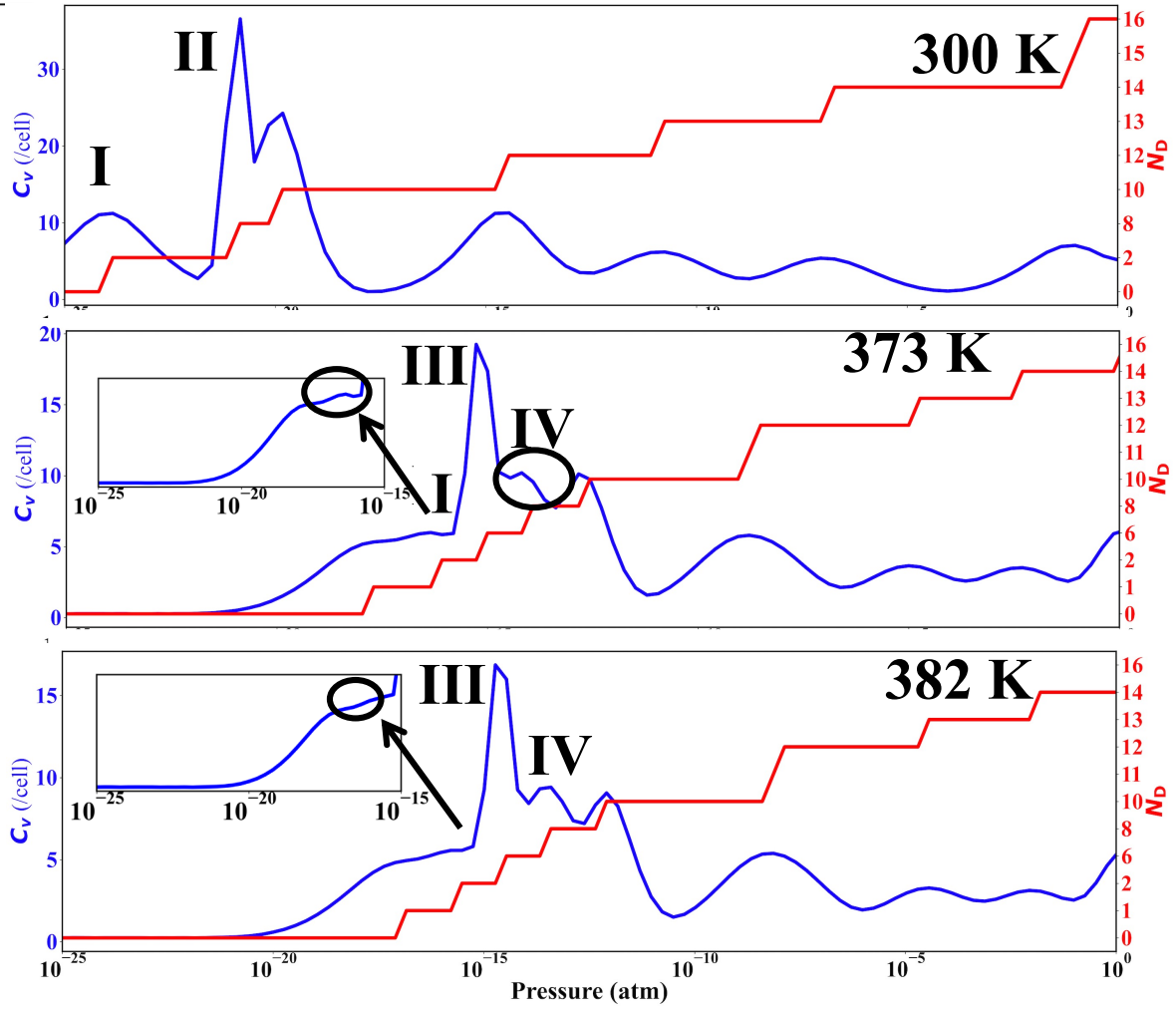
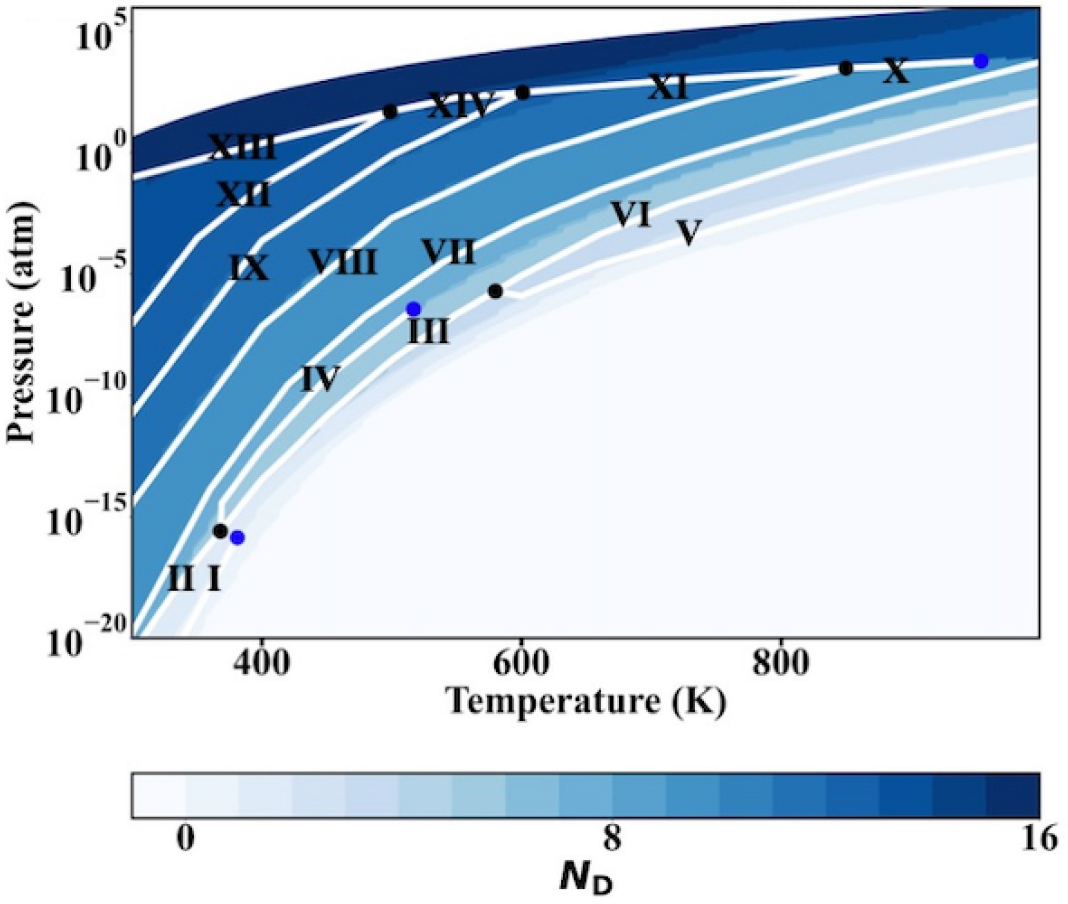




Quantitative calculation of *ab initio* phase boundaries

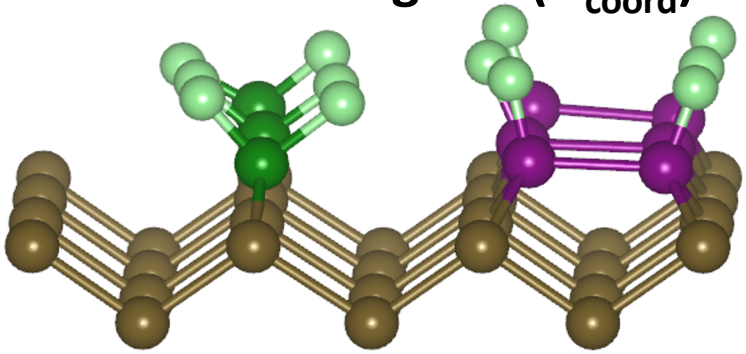


boundary	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
N_D	0	2	2	6	2	4	8	10	12	10	12	13	14
N_D	2	8	6	8	4	6	10	12	13	14	15	14	16

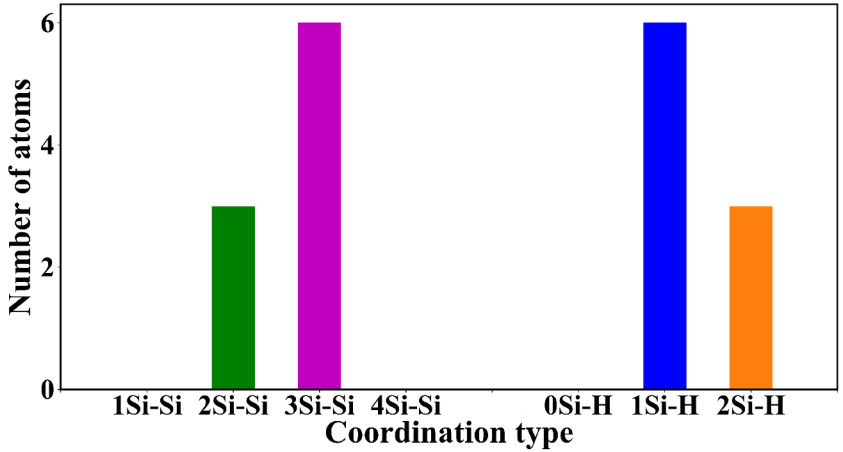
Descriptors for microstates

Number of chemisorbed hydrogen (N_D)

Coordination histogram (H_{coord})



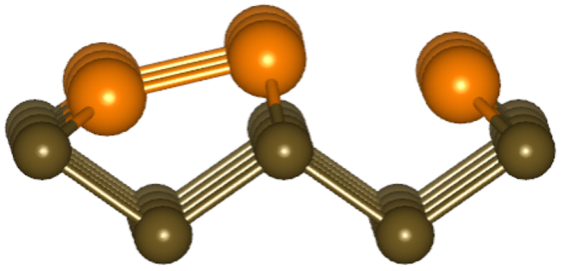
Si-Si bond length = 3.0 Å
Si-H bond length = 2.0 Å



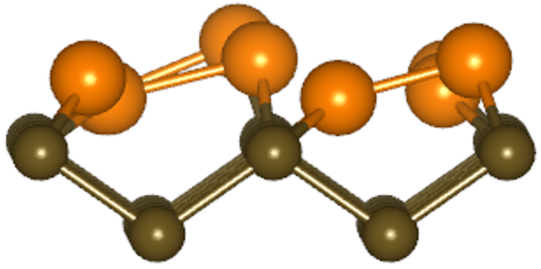
Coordination histogram is 0 3 6 0 0 0 6 3

Dimer type (κ_{dimer})

$\kappa_{dimer} = 0$

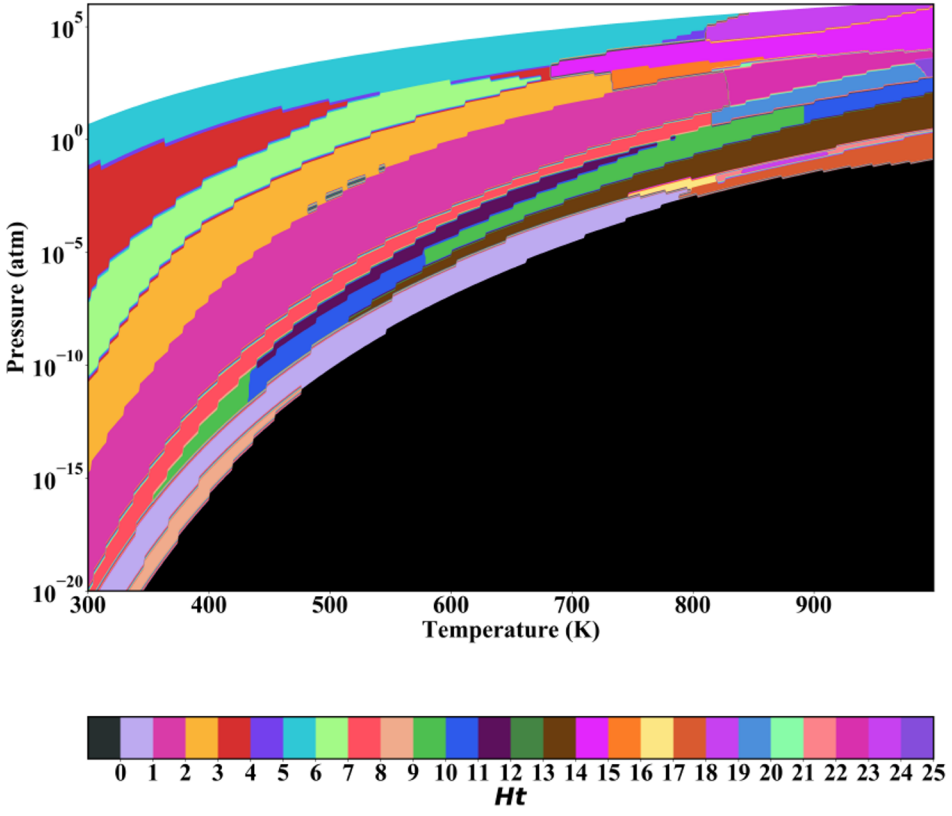


$\kappa_{dimer} = 1$

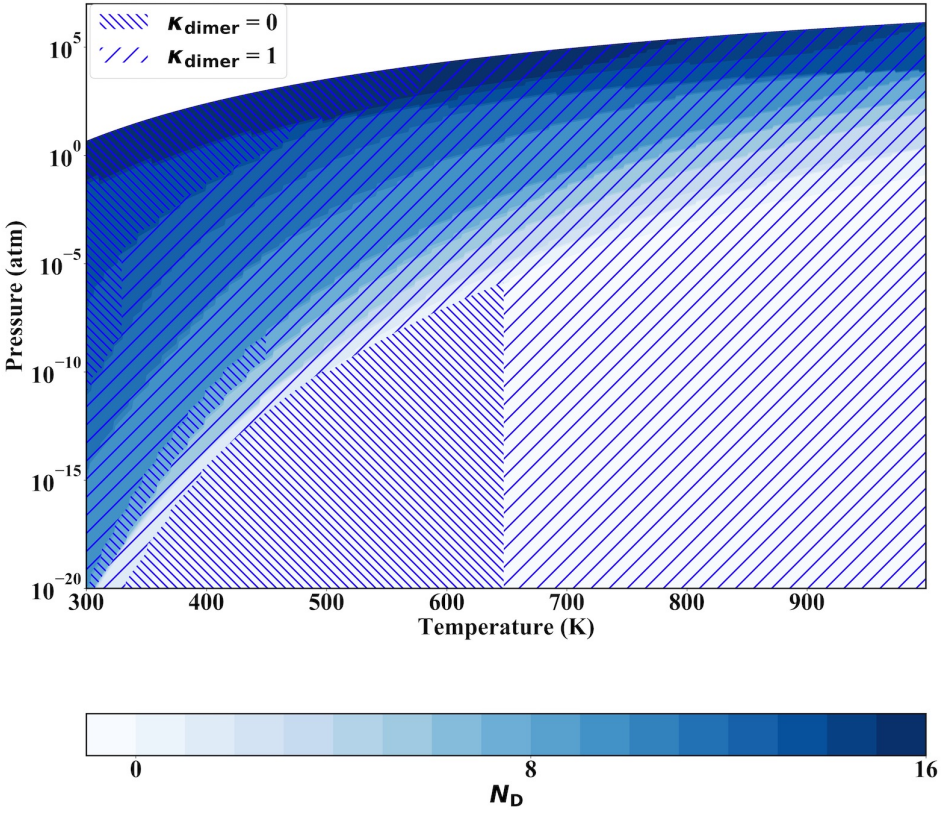


Structural descriptors

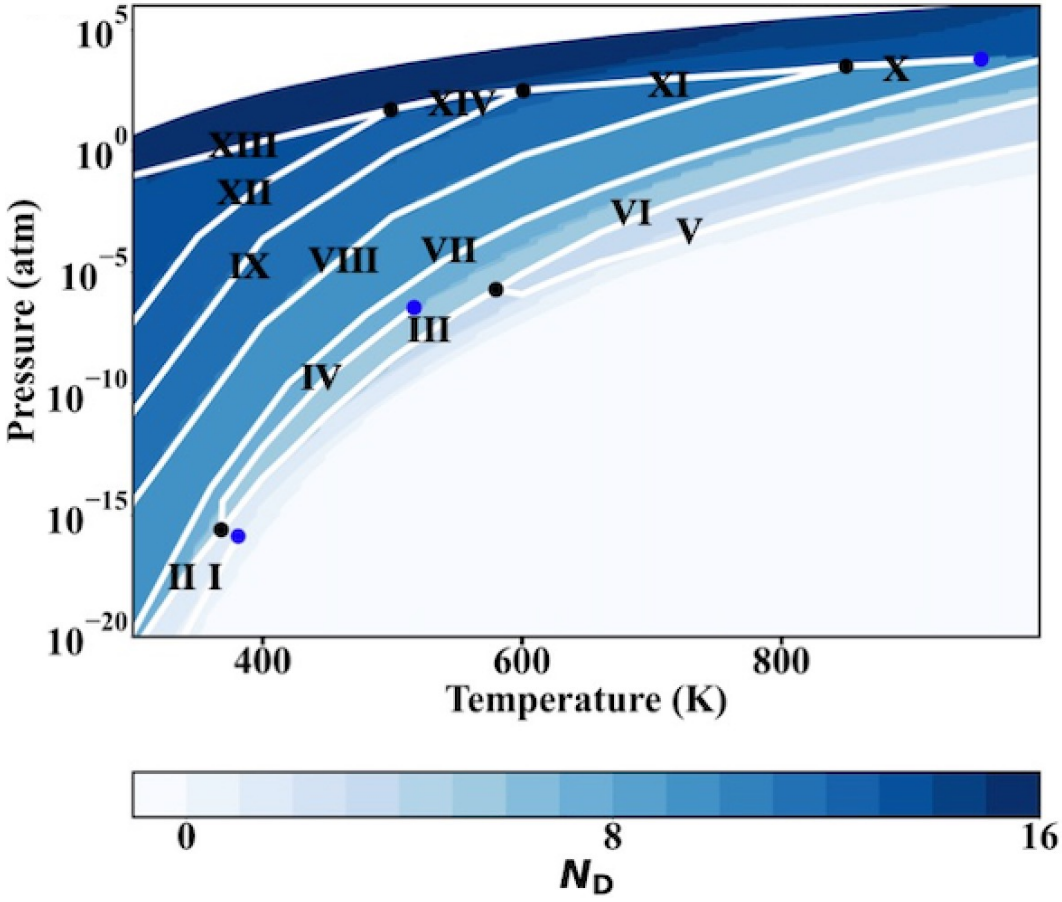
Coordination histogram (H_{coord})



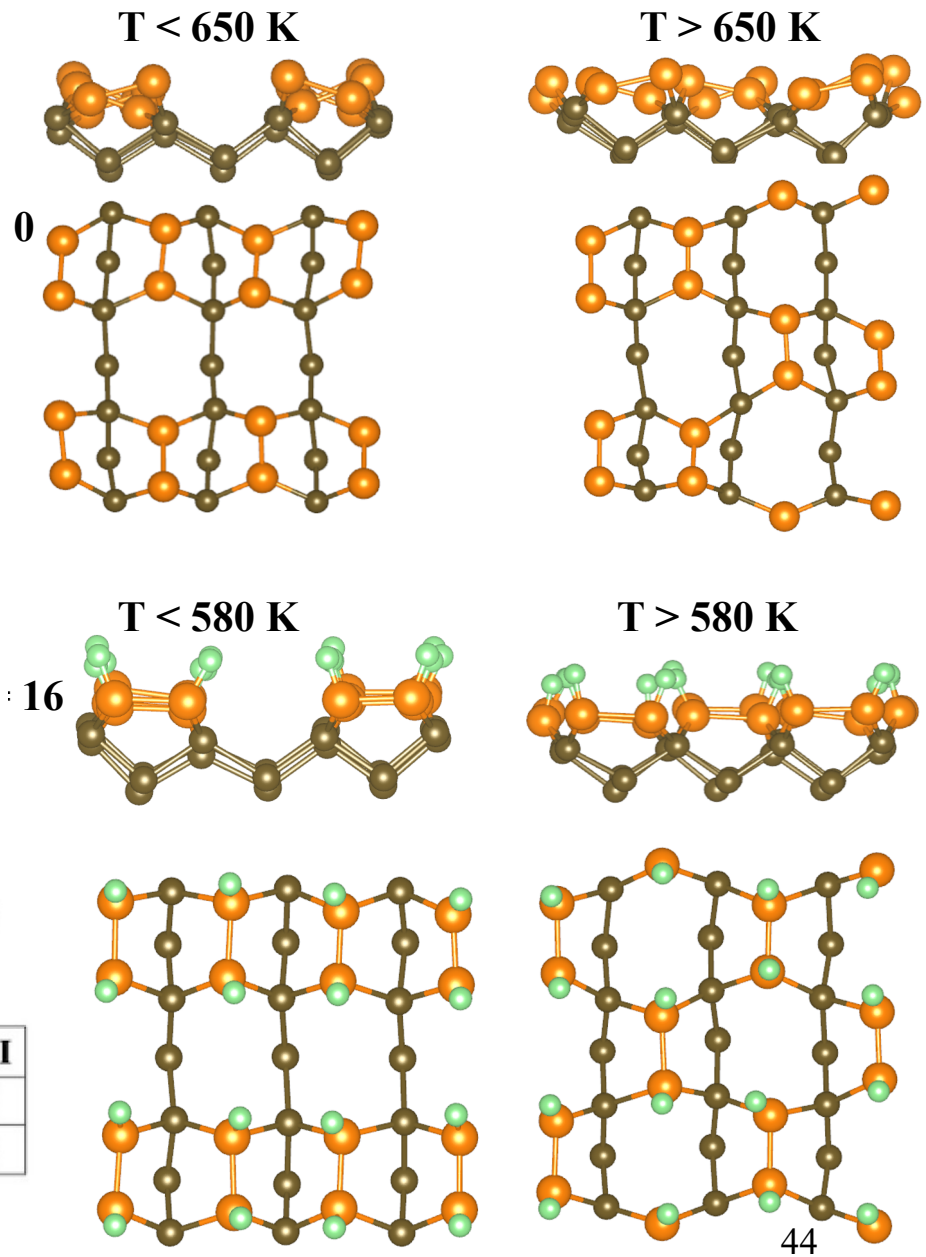
Dimer type (κ_{dimer})



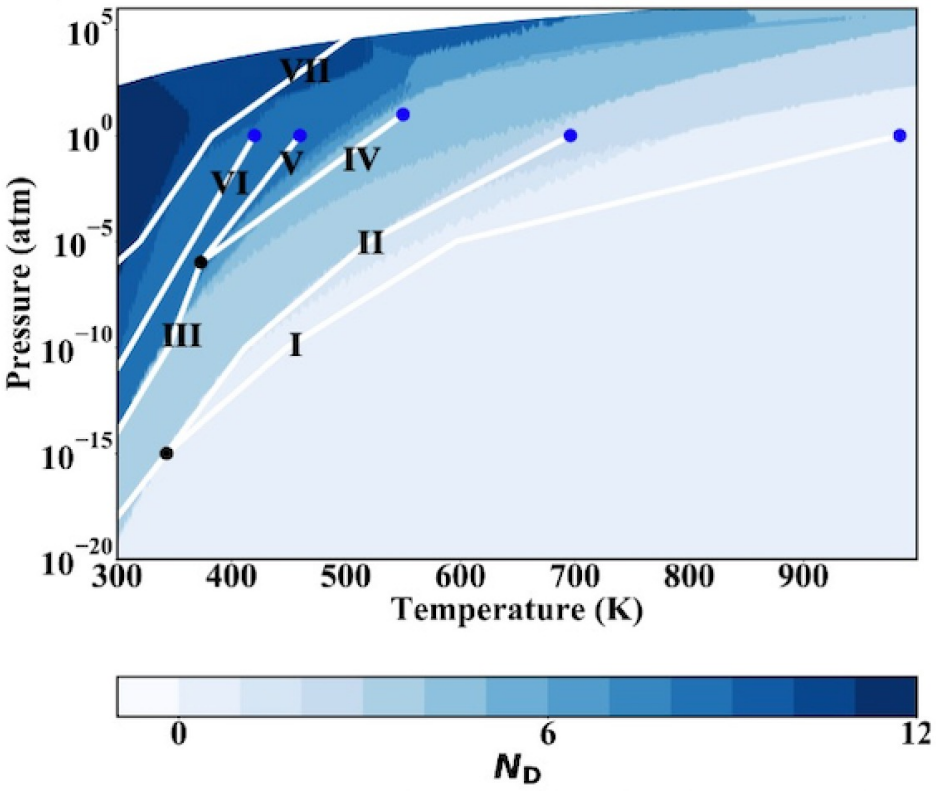
Si(100)-(4×4) surface in contact with D_2 reactive atmosphere at *ab initio* level



boundary	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
N_D	0	2	2	6	2	4	8	10	12	10	12	13	14
N_D	2	8	6	8	4	6	10	12	13	14	15	14	16

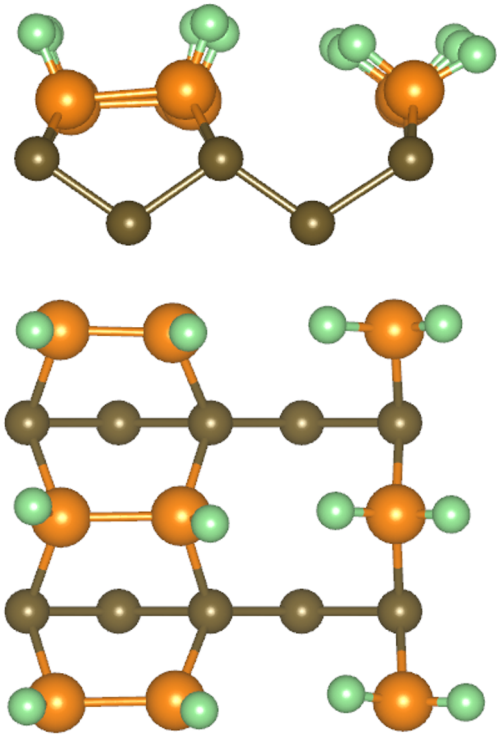


Si(100)-(3×3) surface in contact with D_2 reactive atmosphere at *ab initio* level



boundary	I	II	III	IV	V	VI	VII
N_H	0	2	4	4	7	9	10
N_H	1	4	9	7	9	10	12

$N_D = 12$ 380 K



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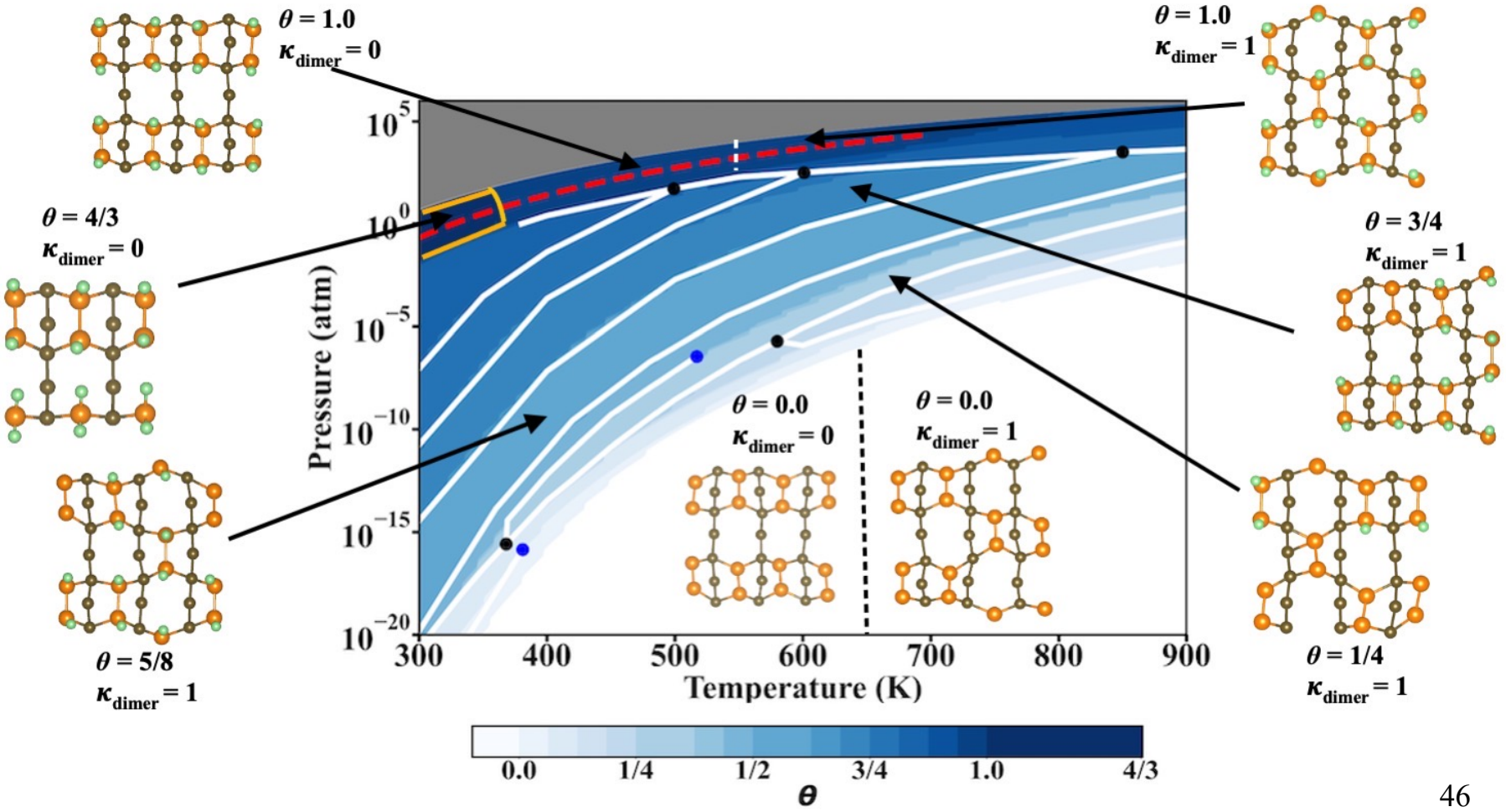
Si(100) surface in contact with D_2 reactive atmosphere at *ab initio* level

Reduced potential function for the GC ensemble $U(\boldsymbol{R};\mu,\beta) = \beta[E(\boldsymbol{R}) - \mu N(\boldsymbol{R})]$

$$U(\boldsymbol{R};\mu,\beta) = \beta\left[E(\boldsymbol{R}) - E_{\text{unrecon}}^{\text{supercell}} - \mu N_{\text{D}}(\boldsymbol{R})\right]/A^{\text{supercell}}$$

$E_{\text{unrecon}}^{\text{supercell}}$ **:the potential energy of the unreconstructed Si(100) surface**



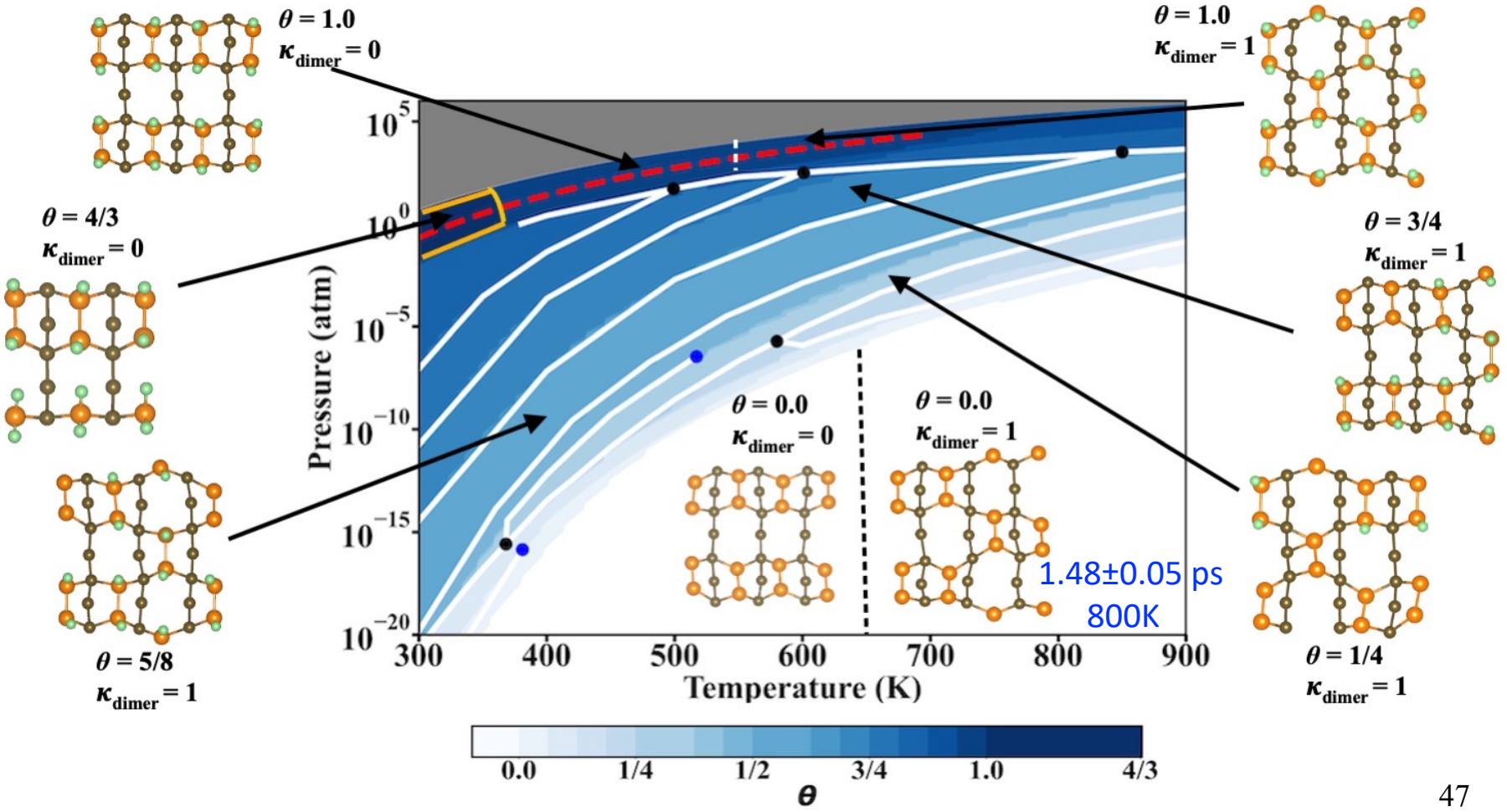
Si(100) surface in contact with D_2 reactive atmosphere at *ab initio* level

Reduced potential function for the GC ensemble $U(\boldsymbol{R};\mu,\beta)=\beta[E(\boldsymbol{R})-\mu N(\boldsymbol{R})]$

$$U(\boldsymbol{R};\mu,\beta)=\beta\left[E(\boldsymbol{R})-E_{\text{unrecon}}^{\text{supercell}}-\mu N_{\text{D}}(\boldsymbol{R})\right]/A^{\text{supercell}}$$

$E_{\text{unrecon}}^{\text{supercell}}$ **:the potential energy of the unreconstructed Si(100) surface**

Average bond lifetime: 1.63±0.06 ps, 800K



Adsorbed D slow the dynamics of dimer bonds

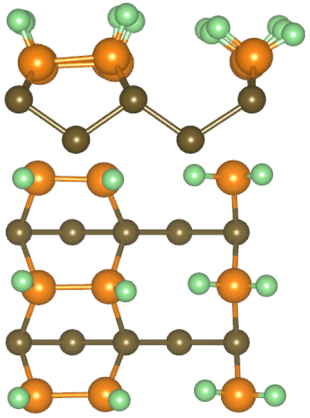
REGC@MBAR vs. aiAT@harmonic approximation

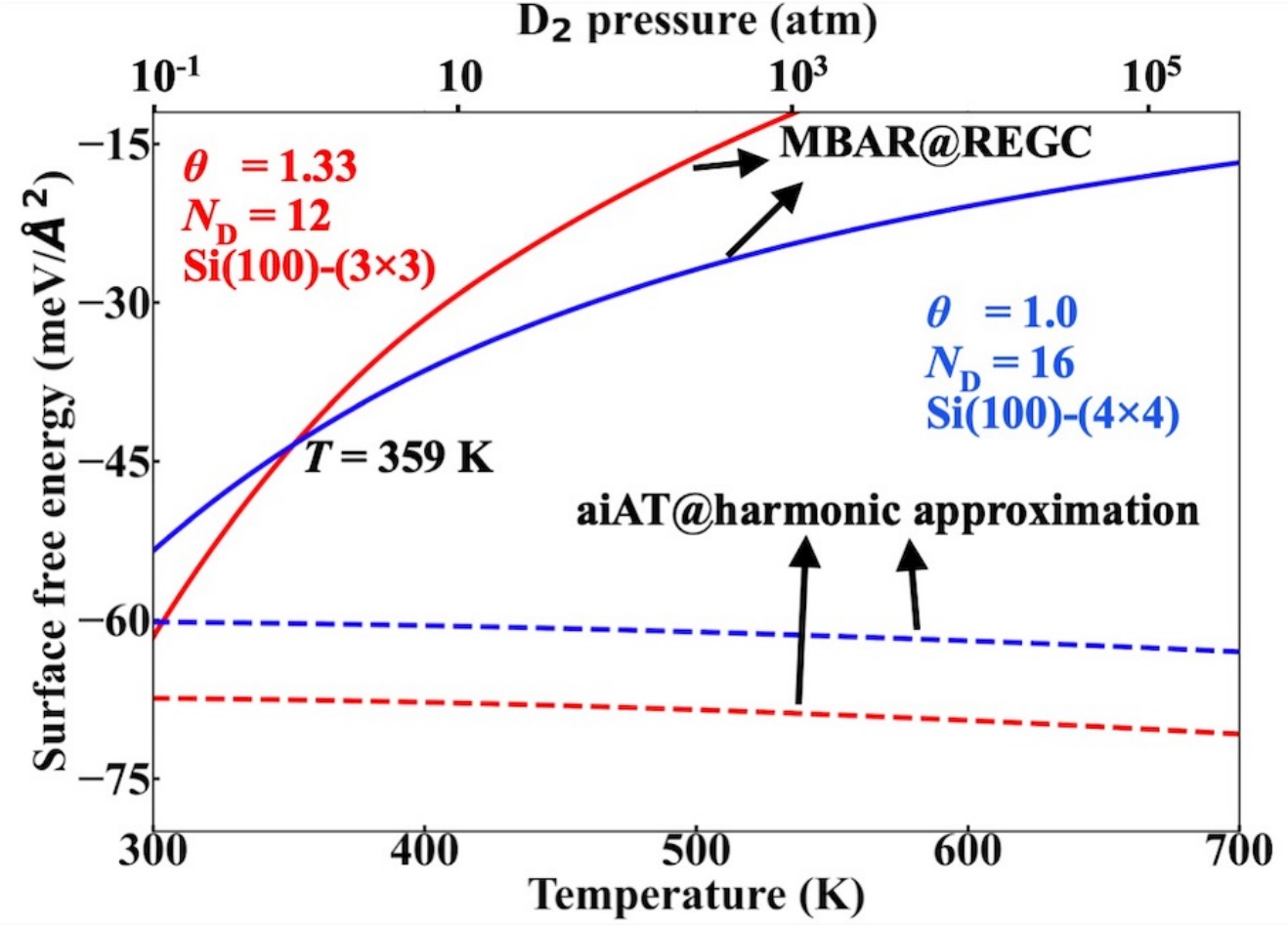
Reduced potential function for the GC ensemble $U(\boldsymbol{R};\mu,\beta)=\beta[E(\boldsymbol{R})-\mu N(\boldsymbol{R})]$

$$U(\boldsymbol{R};\mu,\beta)=\beta\left[E(\boldsymbol{R})-E^{\text{supercell}}_{\text{unrecon}}-\mu N_{\text{D}}(\boldsymbol{R})\right]/A^{\text{supercell}}$$

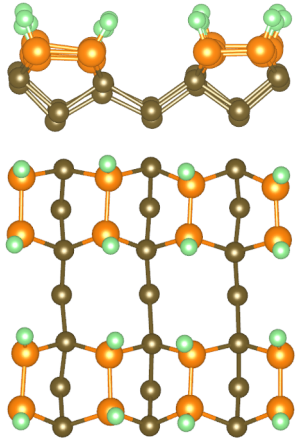
$E^{\text{supercell}}_{\text{unrecon}}$ **:the potential energy of the unreconstructed Si(100) surface**

3x1





2x1



Anharmonic contributions: dynamical restructuring of Si-Si dimers

Thermodynamic overpotential

Computational hydrogen electrode model

$$\Delta G_{\mathrm{ads}} = \Delta E_{\mathrm{ads}} + \Delta E_{\mathrm{ZPE}} - T\Delta S$$

Chemical potential of $\mathrm{H_2} \rightarrow 2(\mathrm{H^+} + \mathrm{e^-})$ is half of $\mathrm{H_2}$ when SHE is the reference potential

$\Delta G_{\mathrm{U}} = eU$ A bias effect of electron in the electrode

$\Delta G_{\mathrm{pH}} = -k_B T \ln[\mathrm{H^+}] = -k_B T \ln 10 \times pH$ pH effect

Solvent and dipole effect is neglected

$$\Delta G = \Delta E_{\mathrm{ads}} + \Delta E_{\mathrm{ZPE}} - T\Delta S - n\left(0.5G_{\mathrm{H_2}} - \Delta G_{\mathrm{U}} + \Delta G_{\mathrm{pH}}\right)$$

In an acid environment, O_2 reduction the associative mechanism

Elementary steps

$\mathrm{O_2(g)} + * \rightarrow \mathrm{O_2^*}$

$\mathrm{O_2^* + H^+ + e^- \rightarrow HOO^*}$

$\mathrm{HOO^* + H^+ + e^- \rightarrow O^* + H_2O(l)}$

$\mathrm{O^* + H^+ + e^- \rightarrow HO^*}$

$\mathrm{HO^* + H^+ + e^- \rightarrow H_2O(l) + *}$

Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard and Jonsson J. Phys, Chem, B. 108, 17886, (2004)

Thermodynamic overpotential

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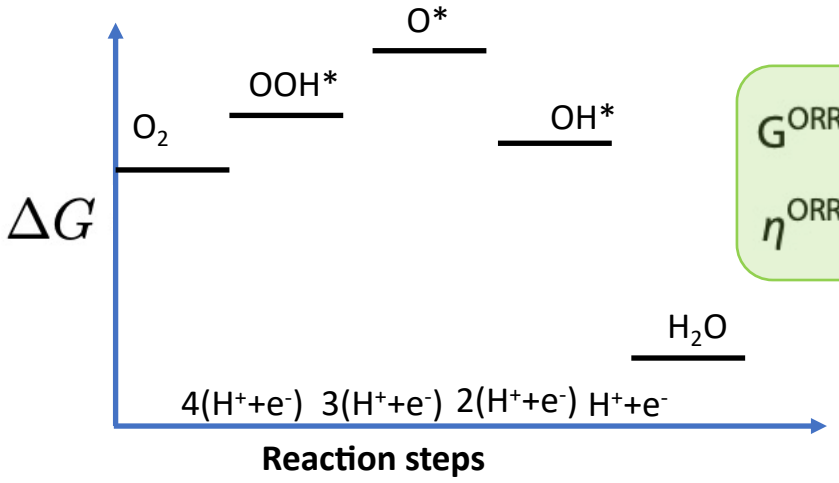

$G^{ORR} = \min\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}$

$\eta^{ORR} = |G^{ORR}|/e - 1.23\,V$

Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard and Jonsson J. Phys, Chem, B. 108, 17886, (2004)

Summary & outlook

***Ab initio* atomitic thermodynamics method:**

well-defined systems: screened structures

✓ F^{vib} **(quasi)-harmonic approaximation**

✓ F^{conf} **is negligible**

The Replica-Exchange Grand-Canonical *ab initio* Molecular Dynamics method:

✓ **to address surface composition and geometry at catalytic (*T*, *p*) condtions.**

to quantitatively determine *ab initio* phase boundaries.

✓ **to calculate *T*-*p* dependence of any (atom position dependent) observable.**

- ✗ Fixed volume
- ✗ Insertion directly into the lattice (lattice expansion/change)
- ✗ Kinetics of reactions: combined with methods e.g., Markov state models

Reference

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Computational hydrogen electrode

Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard and Jonsson J. Phys, Chem, B. 108, 17886, (2004)

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CAT·THEORY
Catalysis Theory Center DTU

Thank you for attention!