Ab initio statistical mechanics and molecular dynamics

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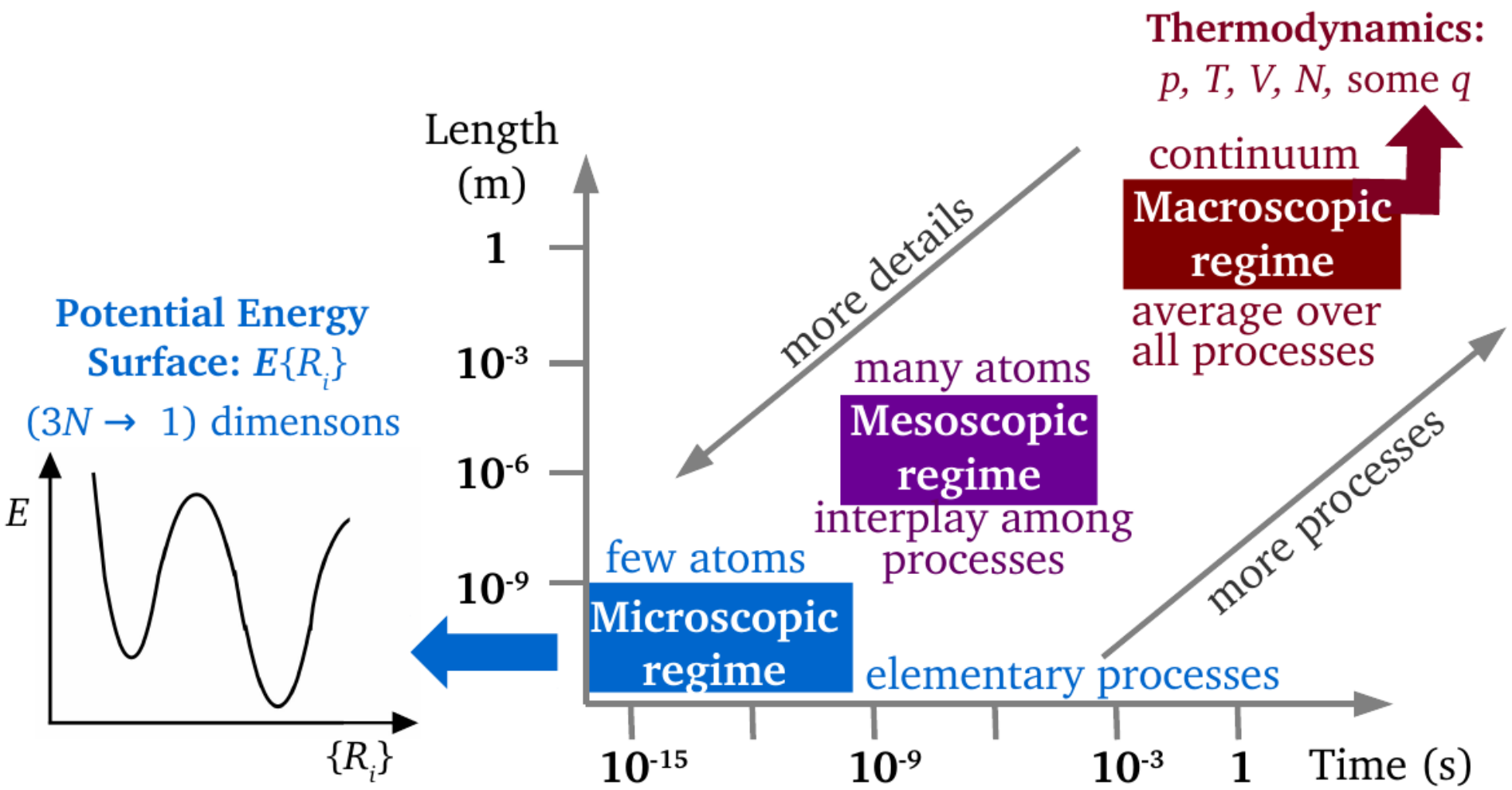
Hands-On DFT and Beyond:
High-throughput screening and big-data analytics,
towards exascale computational materials science
University of Barcelona, Spain, August 26th to September 6th, 2019

Extending the scale



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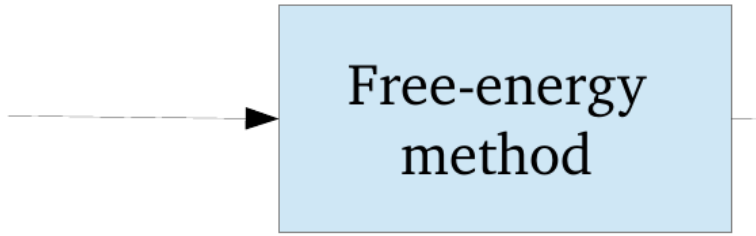

Free-energy surface $(T, \{q_i\})$

"Interesting" coordinates
Reaction coordinate(s)
Collective variables

PES can be from:
- *Ab initio*
- Classical force field
- Toy models

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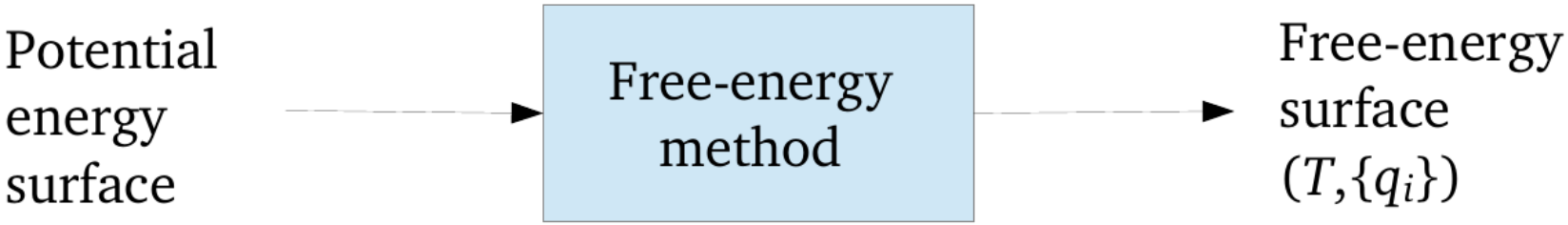

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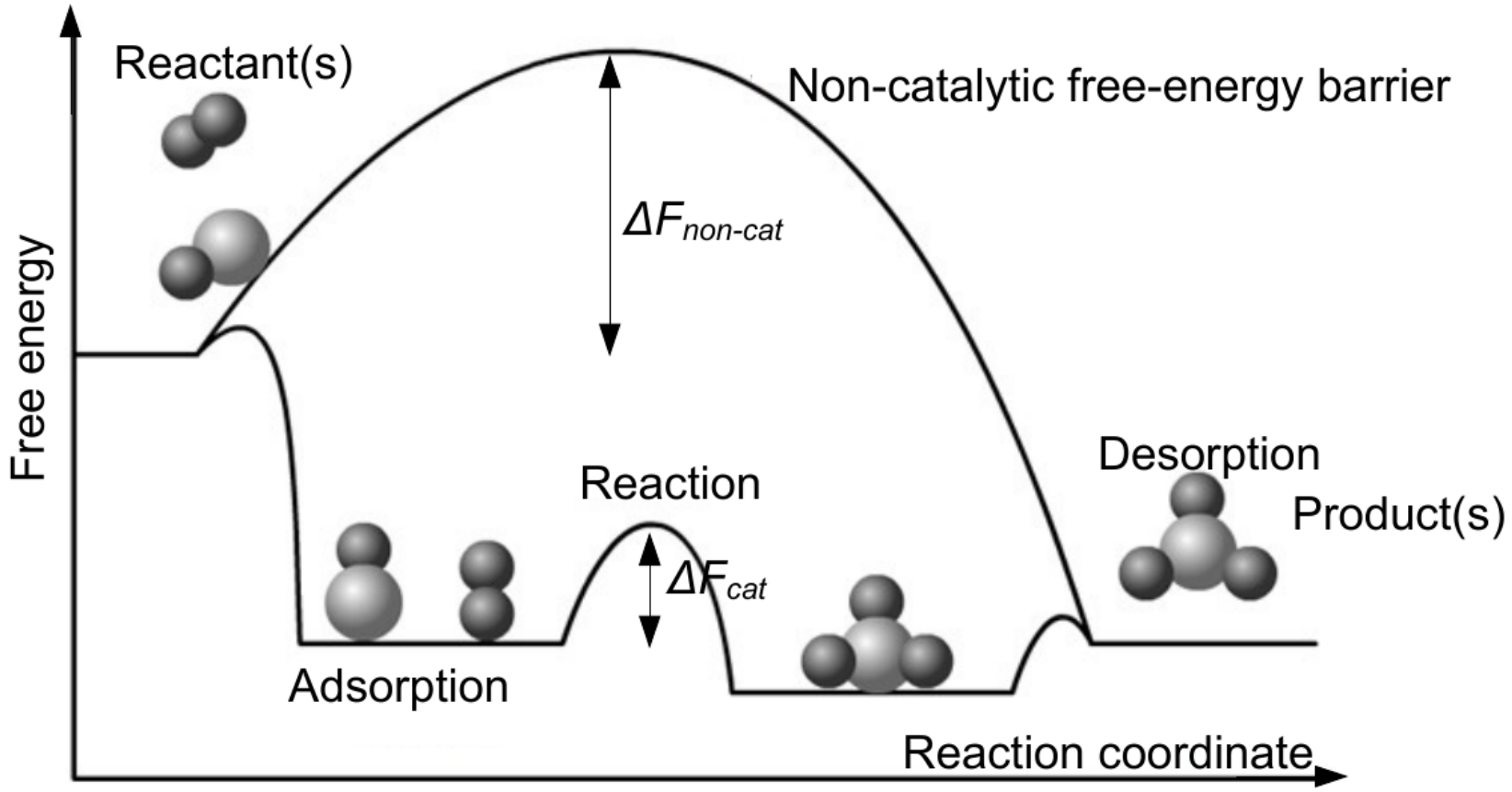
Why free energy? Nature at equilibrium minimizes free-energy, not energy
- (extended) phase equilibria ($\mu_\alpha = \mu_\beta = \ldots$)
- relative population of competing structures (nanoscale) $\mathcal{P}(A) \propto e^{-\beta E_A}$
- rate of processes (via Transition State Theory)

Chemical energy conversion: catalysis



Issues:

- Reaction rate: proportional to *exp (- ΔF / kT)*
- Selectivity: eliminate or at least reduce the undesired products

Free energy: one quantity, many definitions

- Fundamental statistical mechanics ↔ thermodynamics link

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

$$Z = \frac{1}{N! h^{3N}} \int d\mathbb{P} d\mathbb{Q} e^{-\beta \mathcal{H}(\mathbb{P},\mathbb{Q})}$$

Classical statistics (for nuclei):

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

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

Free energy: one quantity, many definitions

Thermodynamics

$$F = E - TS$$

if we can calculate E and write analytically on approximation for S for our system, we use this expression. Example: *ab initio* atomistic thermodynamics

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Thermodynamic Integration

$$\frac{\partial (\beta F)}{\partial \beta} = \langle E \rangle_{NVT}$$

or similar derivatives that yield measurable quantities (in a computer simulation): one can estimate the free energy by integrating such relations. This is the class of the so called thermodynamic-integration methods.

Free energy: one quantity, many definitions

Probabilistic interpretation of free energy

$$\int d\mathbb{Q}\delta(U(\mathbb{Q}) - E)$$

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

$$\frac{1}{\Lambda^{3N} N!}\int d\mathbb{Q}e^{-\beta U(\mathbb{Q})}$$

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

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$$\frac{\mathcal{P}(E_1)}{\mathcal{P}(E_2)} = e^{-\beta[F(E_1)-F(E_2)]}$$

Statistical mechanics: free energy as a probabilistic concept

What is energy? A mapping from 3N coordinates into one scalar $\mathbb{R}^{3N} \rightarrow \mathbb{R}$

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Let's introduce:

$\Phi : \mathbb{R}^{3N} \rightarrow \mathbb{R}$ so that:

$$\mathcal{P}_{\Phi}(\xi) = \frac{d\xi}{Z} \int e^{-\beta U(\vec{Q})} \delta(\Phi(\vec{Q}) - \xi) d\vec{Q} = d\xi \frac{Z_{\Phi}(\xi)}{Z}$$

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Formal definition of a free energy:

$$\Phi : F_\Phi(\xi) = -k_B T \ln Z_\Phi(\xi)$$

$$\mathcal{P}_\Phi(\xi) = \frac{d\xi}{Z} = \frac{d\xi}{Z} e^{-\beta F_\Phi(\xi)}$$

Statistical mechanics, quantities derived from Z

Average energy:

$$\langle E \rangle = \sum_n E_n P_n \qquad P_n = \frac{e^{-\beta E_n}}{Z} \qquad \sum_n P_n = 1$$

$$\langle E \rangle = \frac{\sum_n E_n e^{-\beta E_n}}{Z} = \frac{\frac{\partial Z}{\partial \beta}}{Z} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial (\beta F)}{\partial \beta}$$

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Heat capacity:

$$NC_V = \frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial E}{\partial \beta}$$

$$= -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left(\frac{\sum_n E_n e^{-\beta E_n}}{Z} \right)$$

$$= -\frac{1}{k_B T^2} \left[\frac{(\sum_n E_n e^{-\beta e_n})^2}{Z^2} - \frac{\sum_n E_n^2 e^{-\beta E_n}}{Z} \right]$$

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

$$= \frac{\sigma_E^2}{k_B T^2}$$

Ensemble averages on discrete machines

$$\langle A \rangle = \frac{\int d\mathbb{Q} A(\mathbb{Q}) e^{-\beta U(\mathbb{Q})}}{\int d\mathbb{Q} e^{-\beta U(\mathbb{Q})}} = \frac{\int d\mathbb{Q} A(\mathbb{Q}) e^{-\beta U(\mathbb{Q})}}{Z}$$

$$\stackrel{?}{=} \frac{\sum A_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \frac{1}{M} \sum_{n=0}^{M} A_n$$

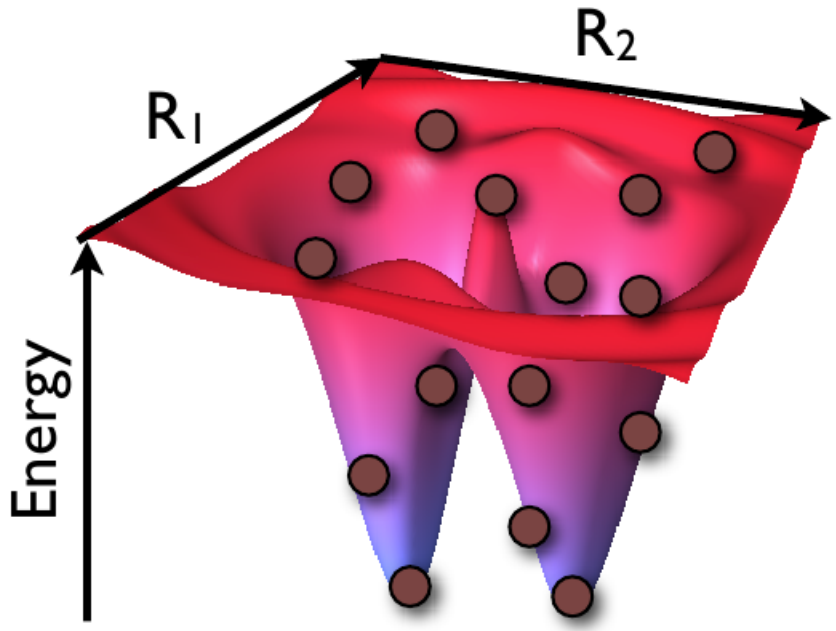
If ***canonical*** and ***ergodic*** sampling is performed

Ergodicity

Ergodic hypothesis: ensemble average equal to time average

$$\langle A \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; \mathrm{e}^{-\mathcal{H}/k_B T} A(p,R)$$

$$\langle A(0)B(t) \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; \mathrm{e}^{-\mathcal{H}/k_B T} A(p(0),R(0))B(p(t),R(t))$$

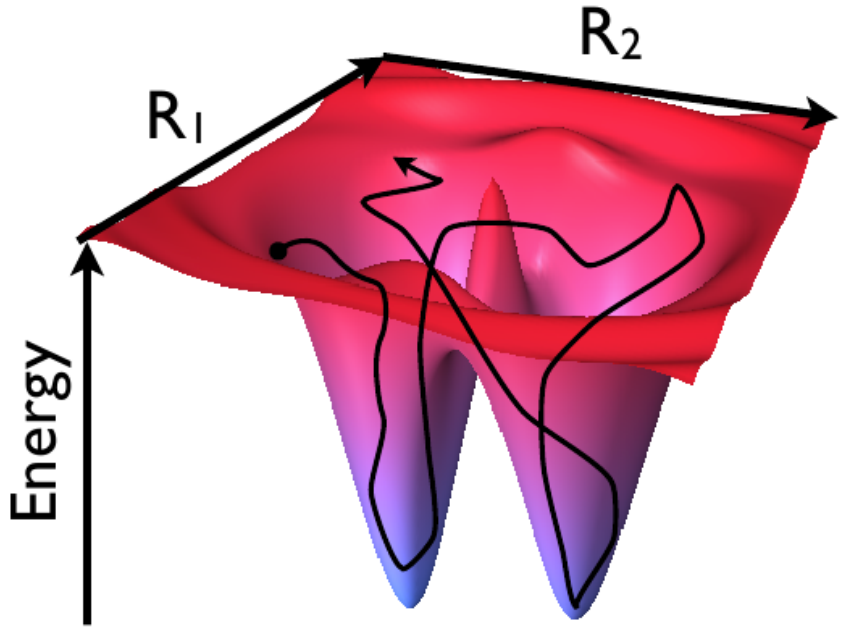


Ergodicity

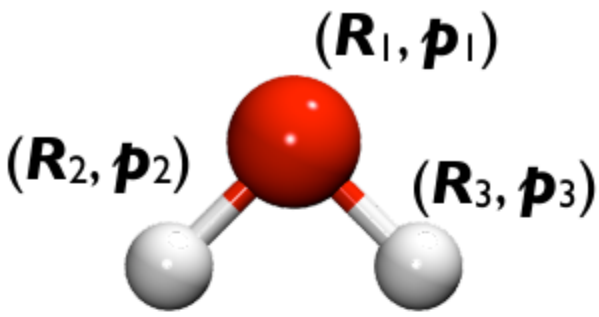
Ergodic hypothesis: ensemble average equal to time average

$$\langle A \rangle = \frac{1}{T} \int_0^T dt' A(p(t'), R(t'))$$

$$\langle A(0)B(t) \rangle = \frac{1}{T} \int_0^T dt' A(t')B(t+t')$$



NVE Molecular dynamics, the basic loop



1. Assign initial ***R*** (positions) and ***p*** (momenta)

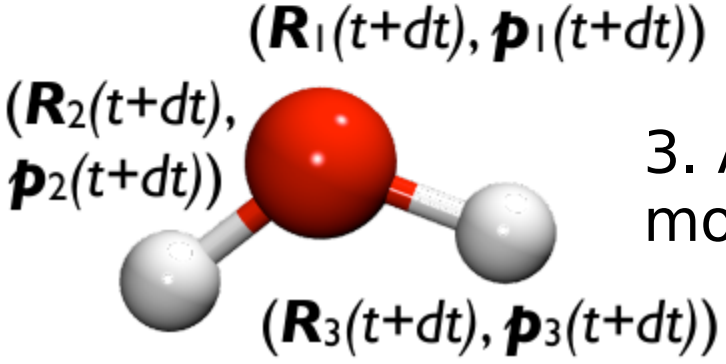
2. Evolve (numerically) Newton's equations of motion for a discrete time increment (requires evaluation of the forces)

$$\mathcal{H}(\mathbf{R}, \mathbf{p}) = \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R})$$

Potential

$$\dot{\mathbf{p}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} = -\nabla_I V(\mathbf{R}) \rightarrow M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I \qquad \dot{\mathbf{R}}_I = \mathbf{p}_I / M_I$$

Force



3. Assign new positions and momenta

Numerical integration

This is an N-body problem, which can only be solved numerically (except in very special cases) at least in principle.

One (always) starts from a Taylor expansion:

$$x(t+\Delta t) = x(t) + \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 + \frac{1}{6}\dddot{x}(t)\Delta t^3 + \dots$$

Naïve implementation: truncation of Taylor expansion

$$x(t+\Delta t) = x(t) + \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2$$

Wrong!
The naive “forward Euler” algorithm

- is not time reversible
- does not conserve volume in phase space
- suffers from energy drift

Better approach: “Verlet” algorithm

Verlet algorithm

compute position in next and previous time steps

$$x(t+\Delta t) = x(t) + \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 + \frac{1}{6}\dddot{x}(t)\Delta t^3 + \frac{1}{24}\ddddot{x}(t)\Delta t^4 ...$$

$$x(t-\Delta t) = x(t) - \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 - \frac{1}{6}\dddot{x}(t)\Delta t^3 + \frac{1}{24}\ddddot{x}(t)\Delta t^4 ...$$

$$x(t+\Delta t) + x(t-\Delta t) = 2x(t) + \ddot{x}(t)\Delta t^2 + \mathcal{O}(\Delta t^4) ...$$

Or

$$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + \ddot{x}(t)\Delta t^2$$

Verlet algorithm:
– is time reversible
– does conserve volume in phase space, i.e., it is “symplectic” (conservation of “action element” $dp \wedge dq$)
– does not suffer from energy drift
...but is it a good algorithm?
i.e. does it predict the time evolution of the system correctly?

Chaos and shadow theorem

For a given Hamiltonian, trajectories diverge quickly for arbitrarily small perturbations of the initial conditions. (Lyapunov instability, chaos)

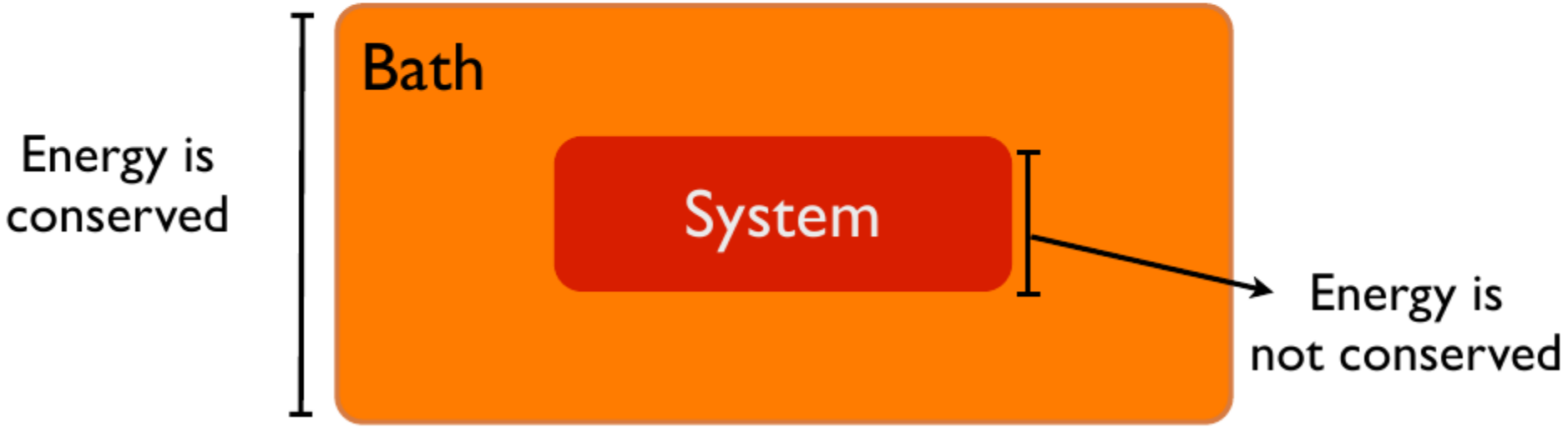
Never ever believe in the significance of a single MD trajectory

Single trajectories are realistic, if we fix initial and final conditions.
Shadow theorem: discrete trajectories are arbitrarily close to the real (infinite precision, analytic) trajectory with the same initial and final conditions for discrete time step going to zero.

Due to ergodic assumption, we are reliably sampling ensemble averages

Sampling the canonical ensemble: thermostats

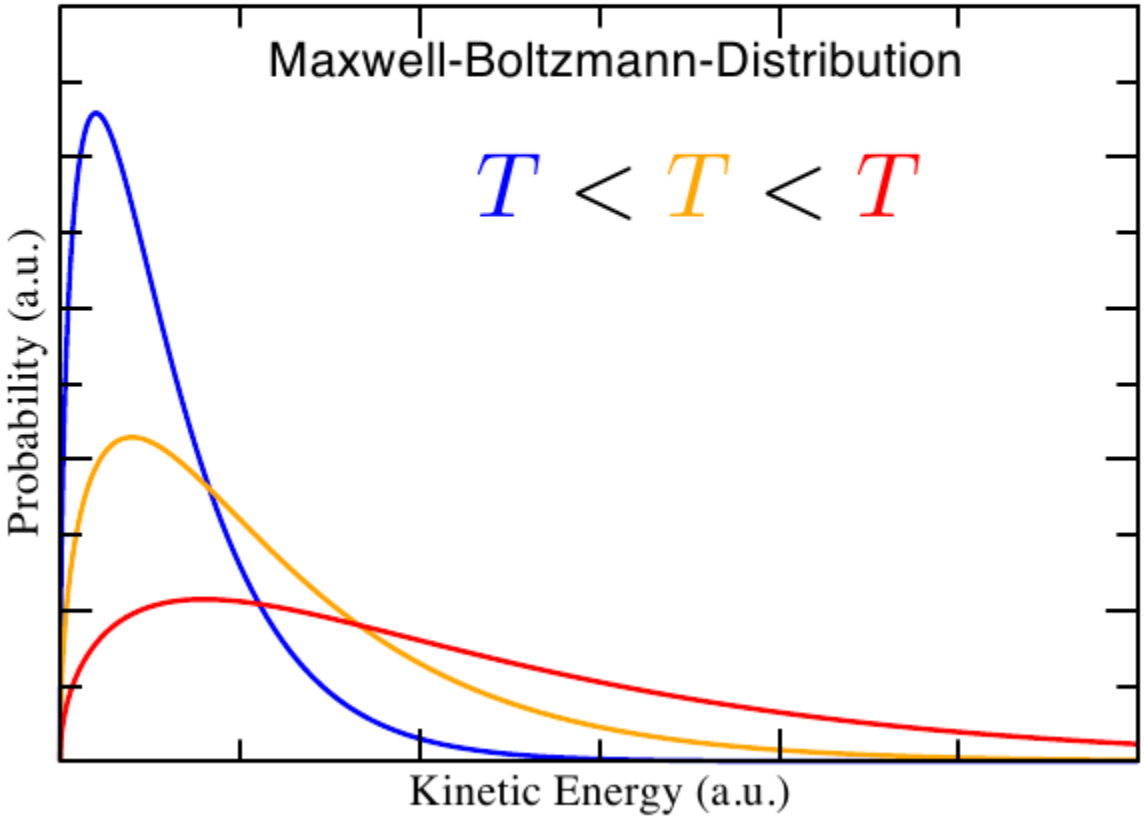
- The idea: couple the system to a thermostat (heat bath)
- Interesting because:
  - Experiments are usually done at constant temperature
  - Better modeling of conformational changes



Sampling the canonical ensemble: thermostats

Probability distribution of the kinetic energy:

$$P(E_{kin}) \propto \exp(-E_{kin}/k_B T)$$



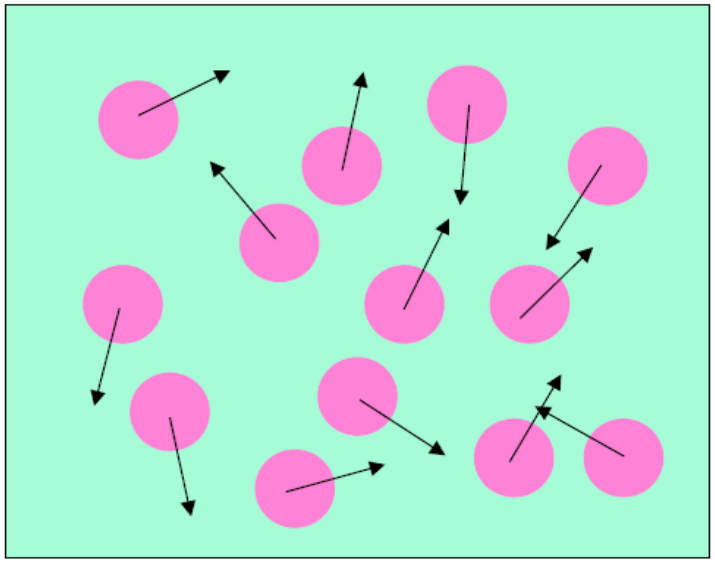
kinetic energy: $p^2/2M$

$$T = \frac{2\langle E_{kin} \rangle}{3N k_B}$$

# of particles

Stochastic thermostat: the Andersen thermostat

• Every particle has a fixed probability to
collide with the Andersen demon



• After collision the particle is give a new
Velocity

$$P(v) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left[-\beta m v^2/2\right]$$

$$P(t;\nu) = \nu \exp\left[-\nu t\right]$$

• The probabilities to collide are uncorrelated (Poisson distribution)

• Downside: momentum not conserved.
Fixed by Lowe-Andersen (2006)

Deterministic thermostat: the Nosé-Hoover

S. Nosé, *J. Chem. Phys.* **81**, 511 (1984) & W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).

Extended Hamiltonian (or Lagrangian):

$$\mathcal{H}_{NH} = \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R}) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta$$

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Original system — Fictitious Oscillator

- Momenta are damped by fictitious oscillator: $\dot{\mathbf{p}}_I = \mathbf{F}_I - \frac{p_\eta}{Q}\mathbf{p}_I$

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- Ergodicity problems - system may be stuck in a region of phase space
  - Possible solution: Nosé-Hoover chains
    Attach another fictitious oscillator to the first, and another to the second, and another to the third, ... (chain of fictitious oscillators)

Martyna, Klein, Tuckerman, *J. Chem. Phys.* **97**, 2635 (1992)

Stochastic velocity rescaling thermostat

G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).

Combine concepts from velocity rescaling (fast!) with concepts from stochastic thermostats (accurate!)

Target temperature follows a stochastic differential equation:

$$\frac{dT}{\bar{T}} = \left[1 - \frac{T(t)}{\bar{T}}\right]\frac{dt}{\tau} - 2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\xi(t)$$

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Temperature rescaling

White noise

- Very successful thermostat, weakly dependent on relaxation time τ
- Pseudo-Hamiltonian is conserved

Bussi, Parrinello, *Phys. Rev. E* **75**, 056707 (2007)

The problem of free energy sampling

$$\langle A \rangle = \frac{\int d\mathbb{Q} A(\mathbb{Q}) e^{-\beta U(\mathbb{Q})}}{\int d\mathbb{Q} e^{-\beta U(\mathbb{Q})}} = \frac{1}{M} \sum_{n=0}^{M} A_n$$

But:

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

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

One cannot converge such a quantity!

$$Z_{\text{ideal gas}} = \frac{V^N}{\Lambda^{3N} N!}$$

… but one cannot measure it, either

Computational free-energy evaluation: the zoo

- Analytic: *ab initio* atomistic thermodynamics

- Canonical sampling: thermodynamic integration

- Canonical sampling: thermodynamic perturbation

- Generalized sampling: biased sampling / biased dynamics

- Unbiased (canonical) sampling → re-weighting techniques

- Direct estimate of the density of energy states

+ Evaluation: Parallel or >>> Serial <<<

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Free energy: “physical”path thermodynamic integration

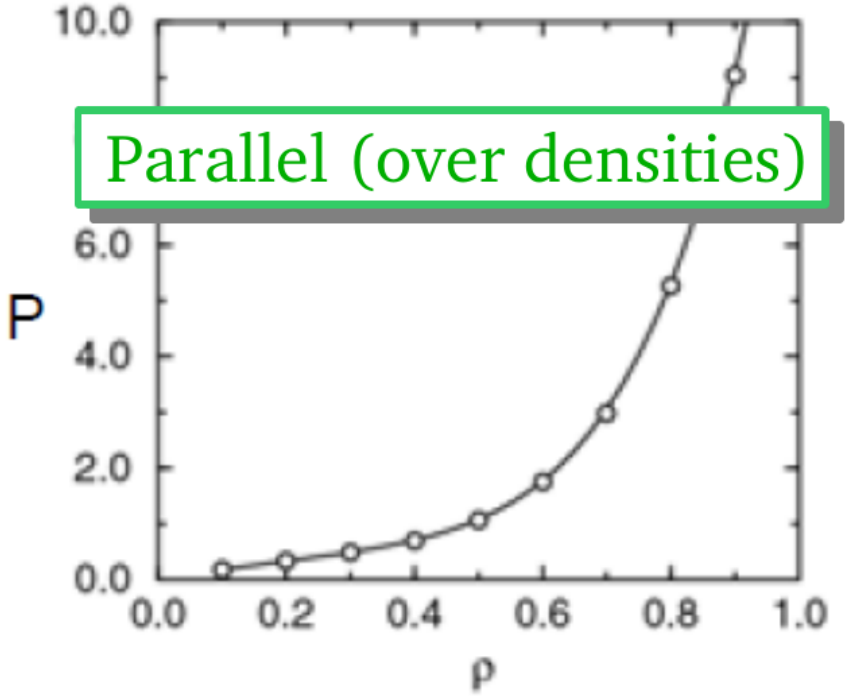
How are free energies measured experimentally?

$$\frac{\partial F}{\partial V} = -P$$

$$\frac{\partial(\beta F)}{\partial \beta} = E$$

$$F(V) = F(V_0) + \int_{V_0}^{V} dV(-P)$$

$V_0 \to \infty$: ideal gas



Free energy: “unphysical”path thermodynamic integration

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$$F_\lambda(N,V,T) = C - k_\mathrm{B}T \int d\boldsymbol{r}^N e^{-\beta((1-\lambda)U_0+\lambda U_1)}$$

$$\frac{\partial F_\lambda(N,V,T)}{\partial \lambda} = \frac{\int d\boldsymbol{r}^N (U_1-U_0) e^{-\beta((1-\lambda)U_0+\lambda U_1)}}{\int d\boldsymbol{r}^N e^{-\beta((1-\lambda)U_0+\lambda U_1)}} =$$

$$= \langle U_1 - U_0 \rangle_\lambda$$

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$$= \langle U_1 - U_0 \rangle_\lambda$$

$$F(N,V,T) = F_0(N,V,T) + \int_0^1 d\lambda \langle U_1 - U_0 \rangle_\lambda$$

How to choose the reference?

Case study: phase diagram of pure carbon

Road map:

- Calculation of change of Helmoltz free energy from chosen *reference state* to a particular (T,p) point, for *each* involved phase (what about overlooked phases?), by means of thermodynamics *integration*.

- Search for of all coexistence points at a given T between all pairs of phases, via *integration* of equations of state $P(\rho)$ and evaluation of crossing points (alternative: common tangent construction).

- Prolongation of coexistence line by Gibbs-Duhem *integration*

Case study: phase diagram of pure carbon

Considered phases: diamond, graphite, and liquid(s)

$$
\begin{aligned}
F^{\text{✠}} &= F^{\text{ref}} + \Delta F^{\text{ref}\rightarrow\text{✠}} \\
&= F^{\text{ref}} + \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda \\
&= F^{\text{ref}} + \int_0^1 \mathrm{d}\lambda \left\langle U^{\text{ref}} - U^{\text{✠}} \right\rangle_\lambda
\end{aligned}
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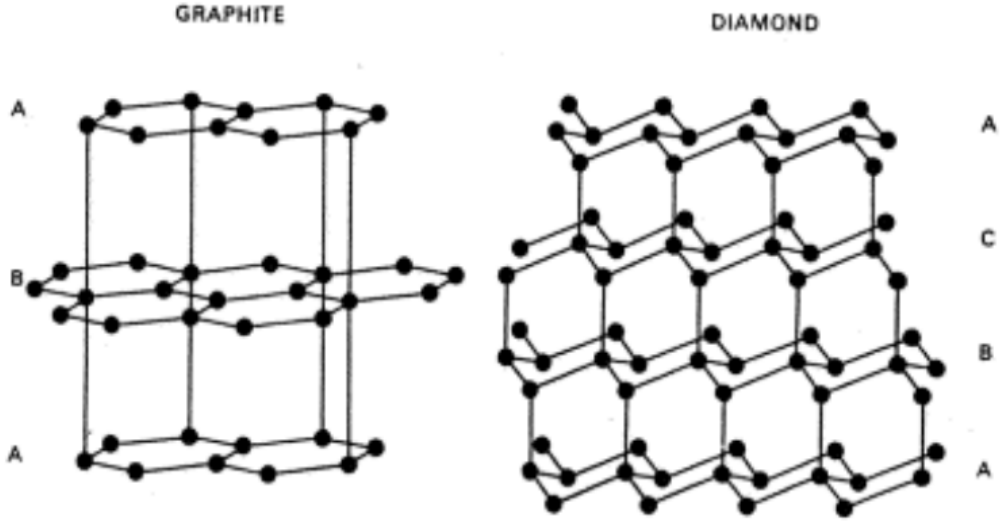


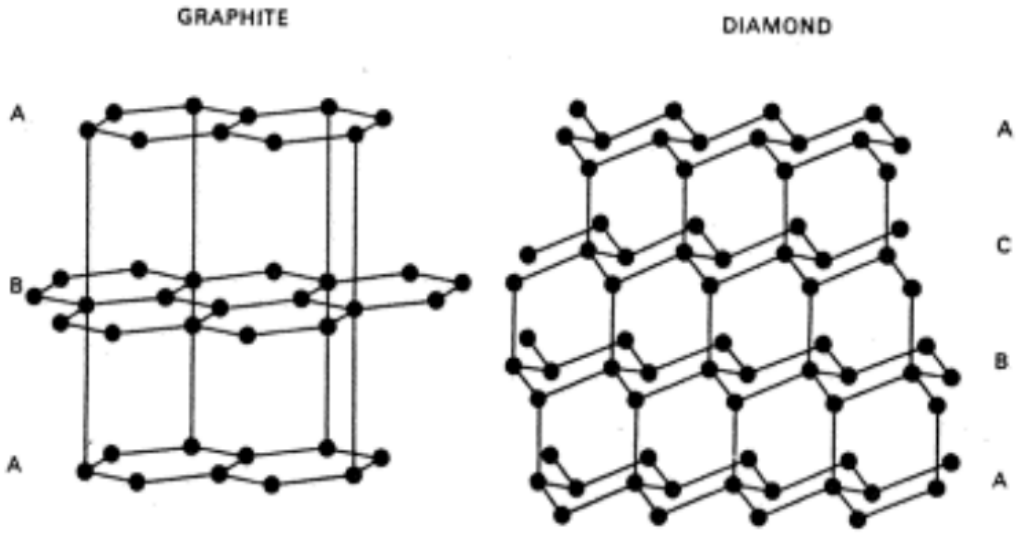
Case study: phase diagram of pure carbon

Reference phases
Solid(s): Einstein solid

$$U^E = \frac{\alpha}{2} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{i,0})^2$$

α? Maximum resemblance
of harmonic and "real" potential

$$\frac{3}{\beta\alpha} = \left\langle \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{i,0})^2 \right\rangle$$



Case study: phase diagram of pure carbon

Reference phases
Liquid: Lennard Jones

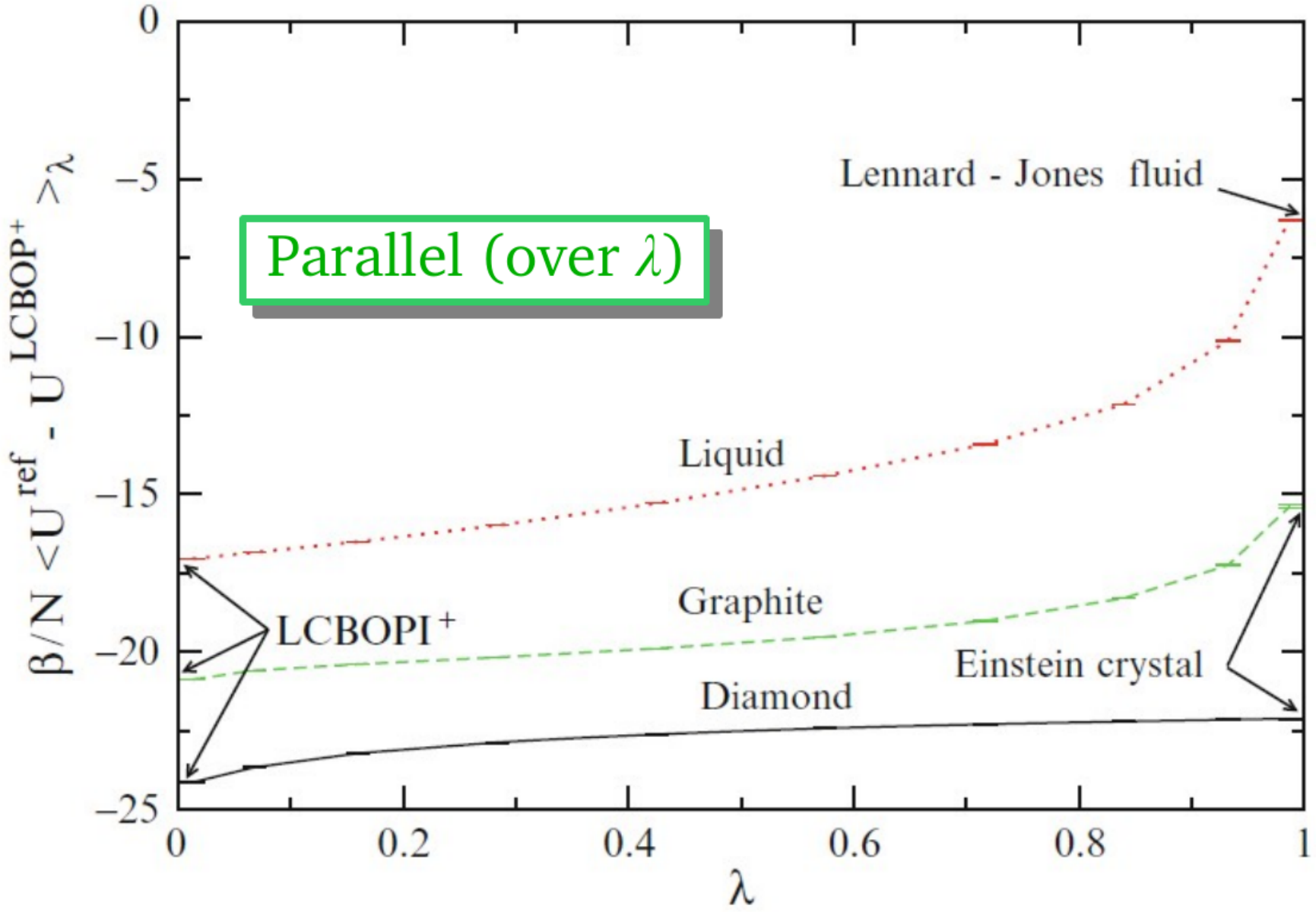
$$U^{LJ} = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

How to choose σ, ε ?
Maximum resemblance between
LJ liquid and "real":
alignment radial distribution function peaks

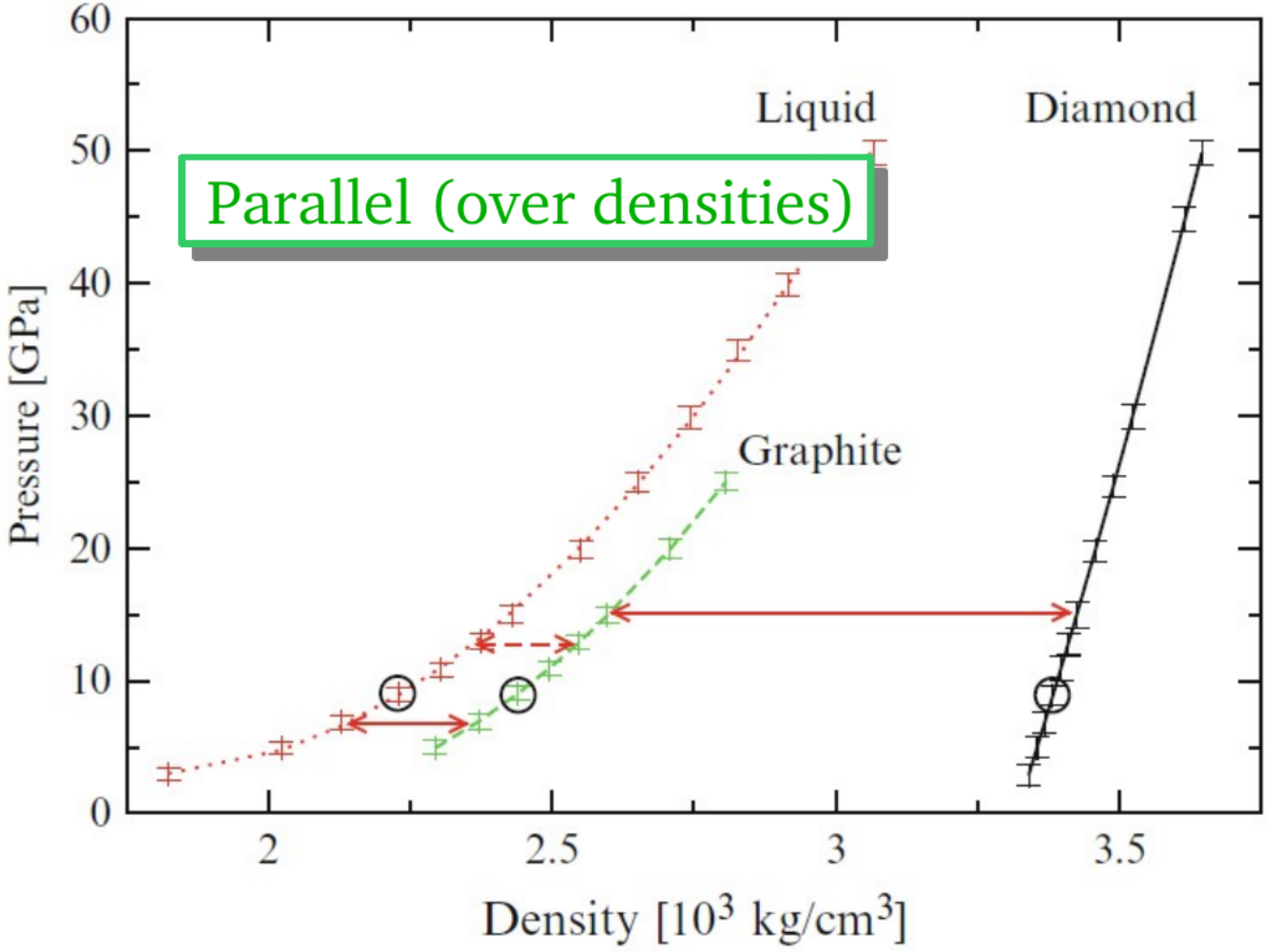
$$F^{\mathrm{ref}} = F^{\mathrm{LJ}} = F^{\mathrm{id}} + F^{\mathrm{ex}}_{\mathrm{LJ}}$$

$$\frac{\beta F^{\mathrm{id}}}{N} = 3\ln\Lambda + \ln\rho - 1 \qquad \Lambda = h/\sqrt{2\pi m k_B T}$$

Case study: λ–ensemble sampling and integration



Case study: integration of P(ρ) equations of state

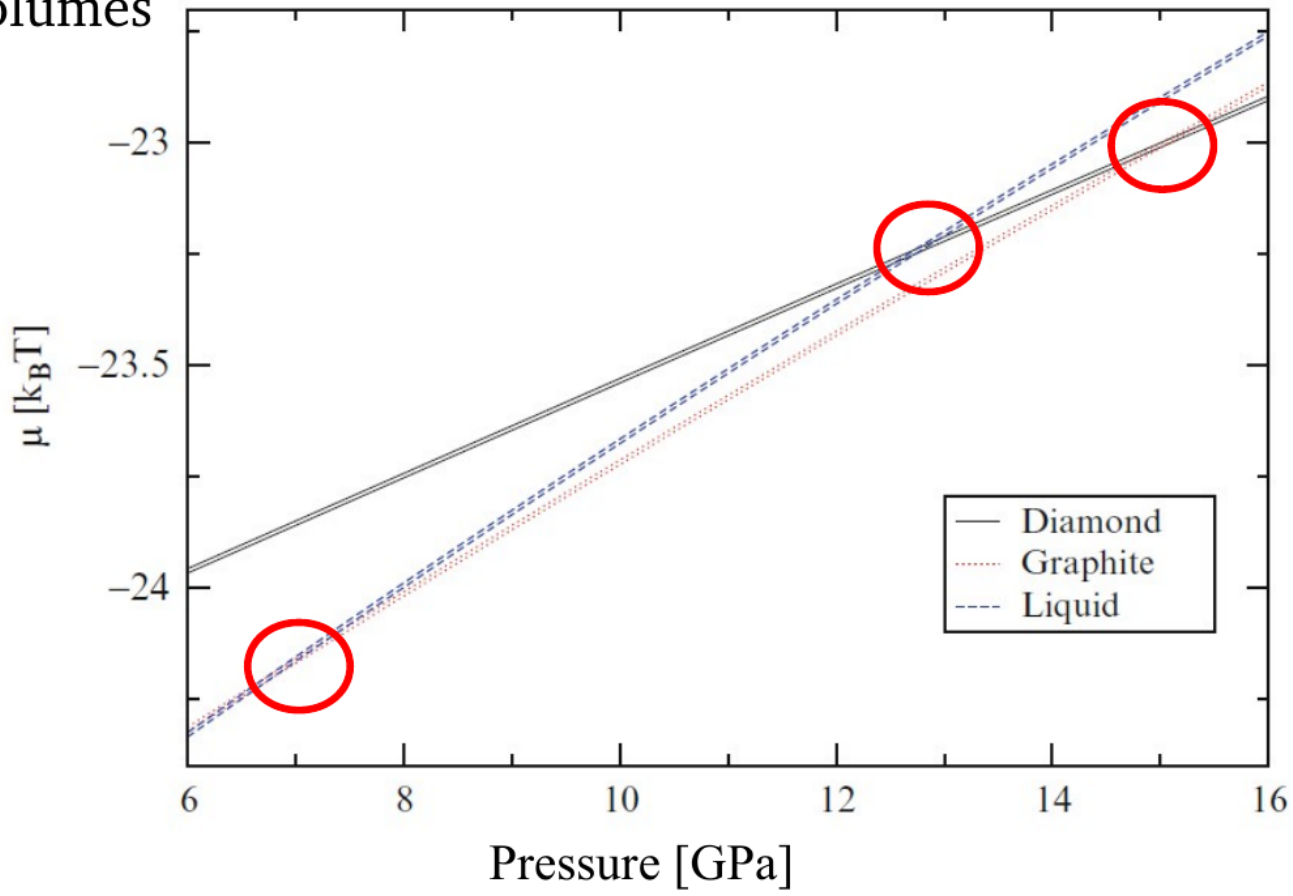


$$P(\rho) = a + b\rho + c\rho^2 \longrightarrow \beta\mu(\rho) = \frac{\beta F^{\Xi}}{N} + \beta\left[\frac{a}{\rho^{\Xi}} + b\ln\frac{\rho}{\rho^{\Xi}} + b + c\left(2\rho - \rho^{\Xi}\right)\right]$$

Case study: equating Gibbs free energies

Difference in slopes: difference in specific volumes

$$\frac{\partial \mu}{\partial P} = \frac{\partial g}{\partial P} = v = \frac{1}{\rho}$$



Case study: equating Gibbs free energies

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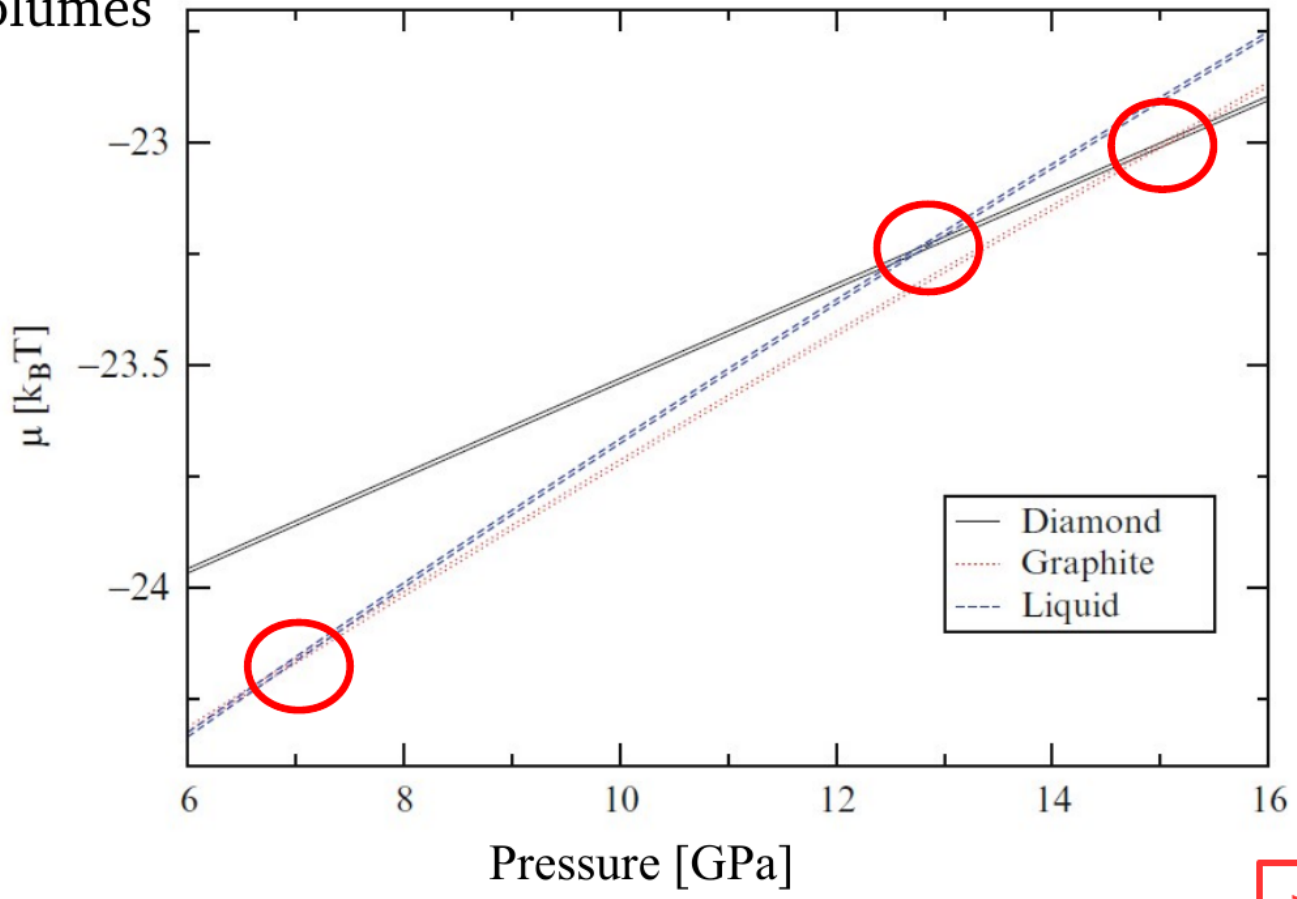


And then: Gibbs-Duhem integration

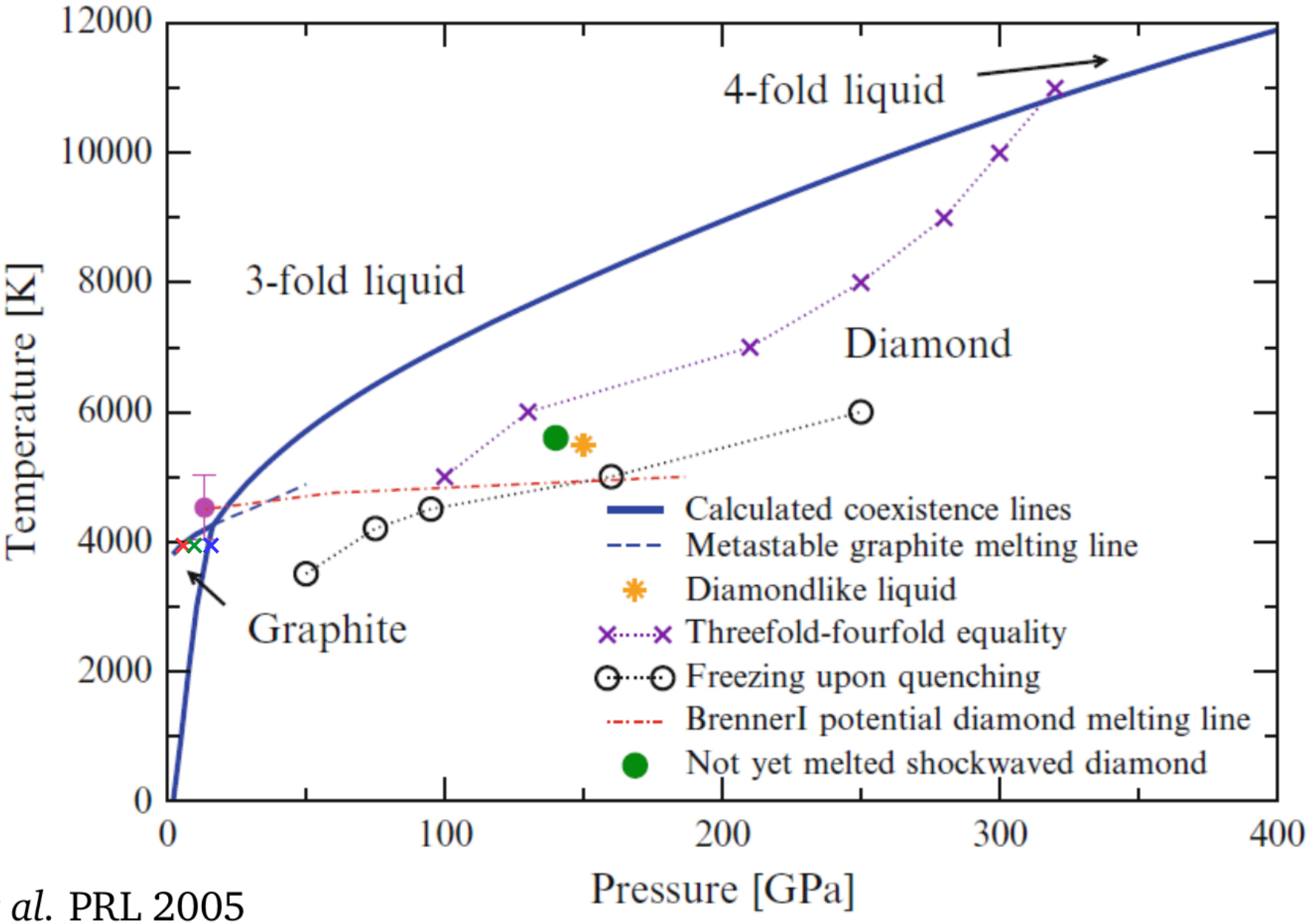
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta h}{T\,\Delta v}$$

$T\Delta s$

$$\Delta h = \Delta u + P\Delta v$$

>>> Serial <<<

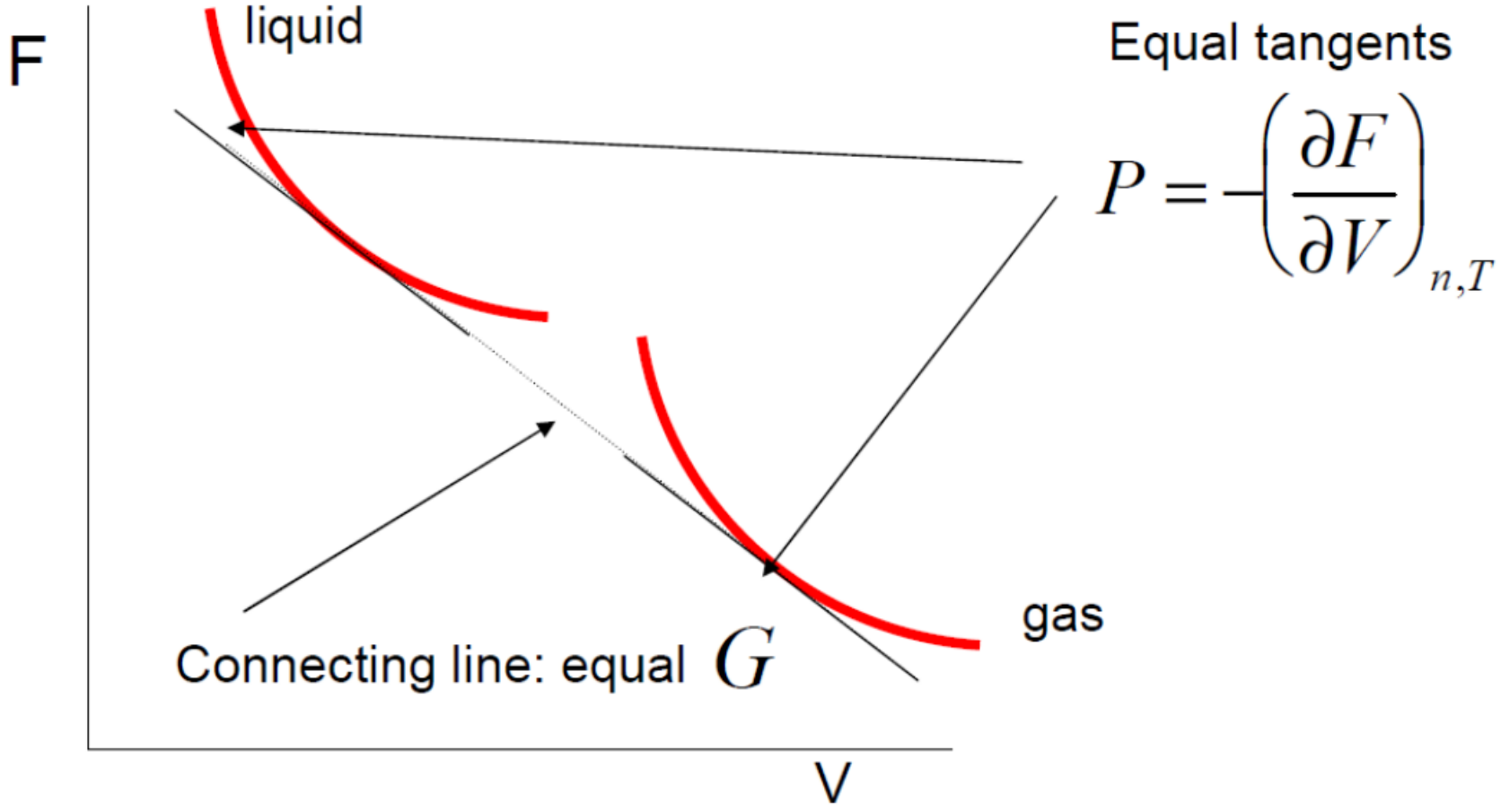
Carbon phase diagram



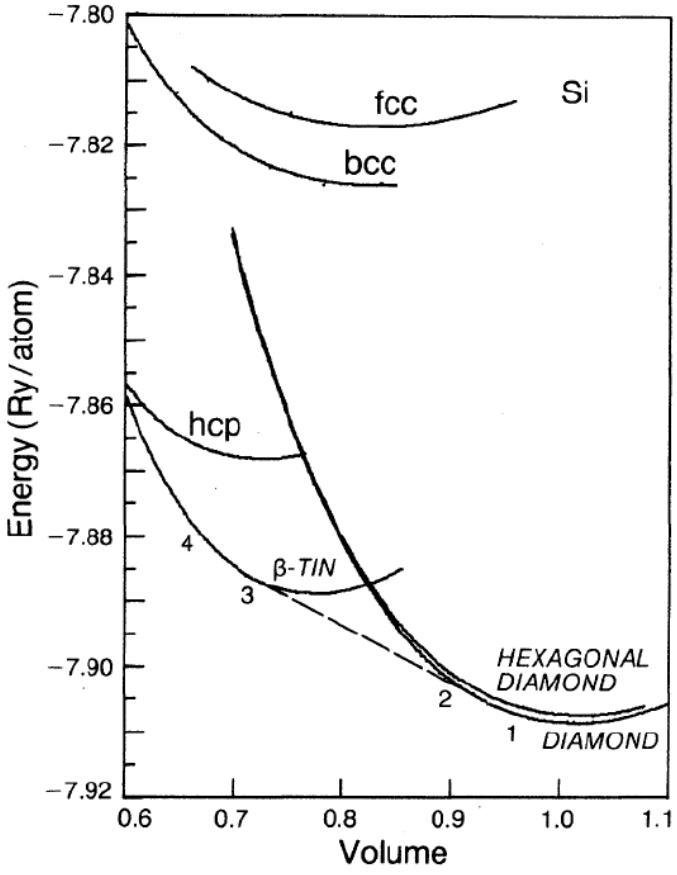
LMG *et al.* PRL 2005

Alternative method for finding phase coexistence via F(V)

Common tangent construction



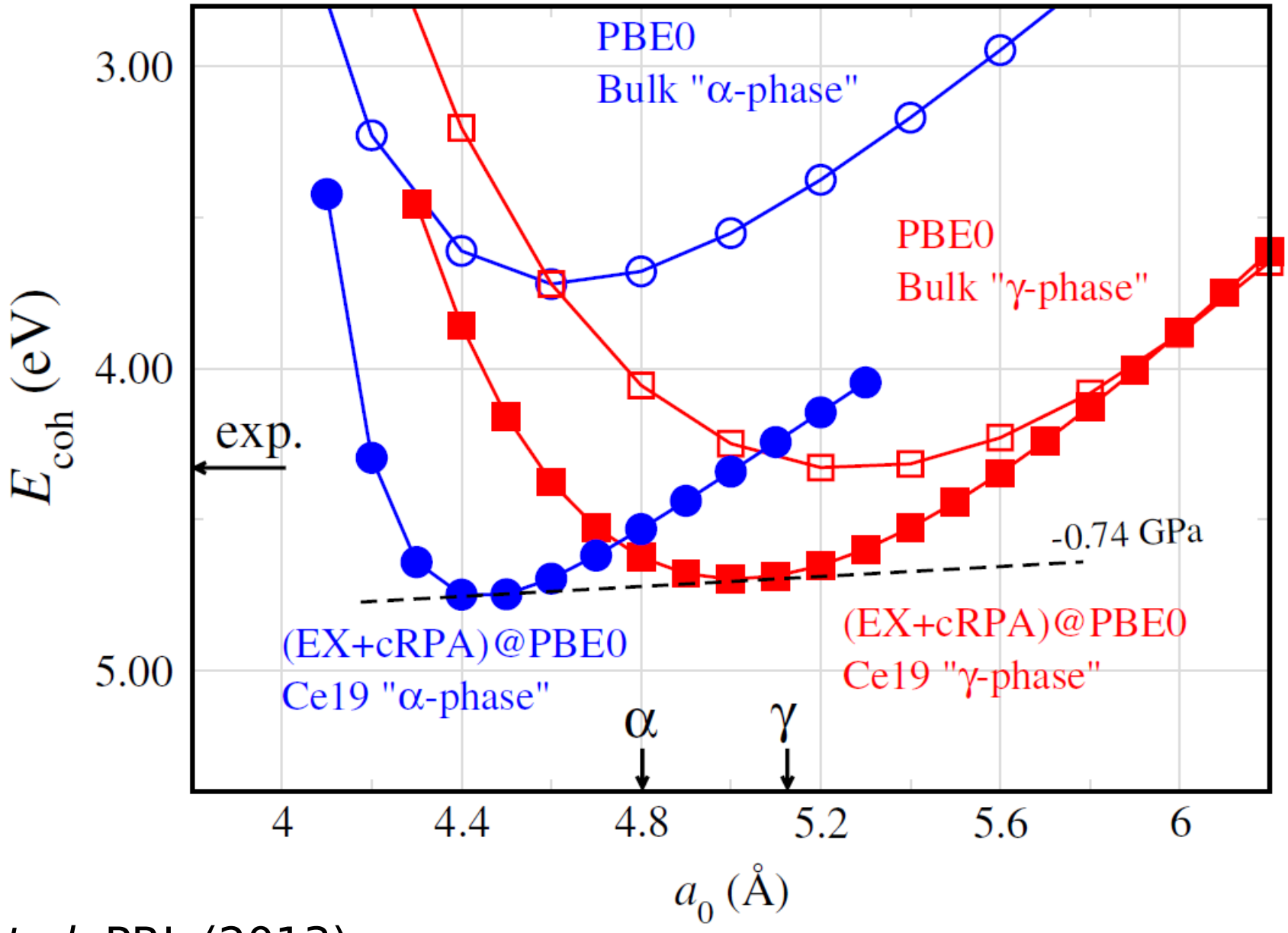
Notable cases (at 0 K): Silicon (1980)



Yin and Cohen, PRL 1980
DFT with LDA functional

	$V_t{}^d$	$V_t{}^\beta$	$V_t{}^\beta / V_t{}^d$	P_t (kbar)
Calculation	0.928	0.718	0.774	99
Experiment[a]	0.918	0.710	0.773	125
Deviation	1.1%	1.1%	0.1%	−20%

Notable cases (at 0 K): Cerium (2013)



Casadei *et al.* PRL (2013)

Computational free-energy evaluation: the zoo

- Analytic: *ab initio* atomistic thermodynamics

- Canonical sampling: thermodynamic integration

- Canonical sampling: thermodynamic perturbation

- Generalized sampling: biased sampling / biased dynamics

- Unbiased (canonical) sampling → re-weighting techniques

- Direct estimate of the density of energy states

+ Evaluation: Parallel or >>> Serial <<<

Thermodynamic perturbation

Two systems:

System 0: N, V, T, U_0

$$Z_0 = \frac{V^N}{\Lambda^{3N} N!} \int d\boldsymbol{r}^N e^{-\beta U_0}$$

System 1: N, V, T, U_1

$$Z_1 = \frac{V^N}{\Lambda^{3N} N!} \int d\boldsymbol{r}^N e^{-\beta U_1}$$

Thermodynamic perturbation

Two systems:

System 0: N, V, T, U_0 System 1: N, V, T, U_1

$$Z_0 = \frac{V^N}{\Lambda^{3N} N!} \int d\boldsymbol{r}^N e^{-\beta U_0} \qquad Z_1 = \frac{V^N}{\Lambda^{3N} N!} \int d\boldsymbol{r}^N e^{-\beta U_1}$$

$$\beta \Delta F = \beta F_1 - \beta F_0 = -\ln \frac{Z_1}{Z_0} = \frac{\int d\boldsymbol{r}^N e^{-\beta(U_1 - U_0)} e^{-\beta U_0}}{\int d\boldsymbol{r}^N e^{-\beta U_0}}$$

$$\boxed{\beta \Delta F = -\ln \langle e^{-\beta(U_1 - U_0)} \rangle_0} = -\ln \langle e^{-\beta \Delta U_{0,1}} \rangle_0$$

Thermodynamic perturbation

Two systems:

System 0: N, V, T, U_0 System 1: N, V, T, U_1

$$Z_0 = \frac{V^N}{\Lambda^{3N} N!} \int d\boldsymbol{r}^N e^{-\beta U_0} \qquad Z_1 = \frac{V^N}{\Lambda^{3N} N!} \int d\boldsymbol{r}^N e^{-\beta U_1}$$

$$\beta \Delta F = \beta F_1 - \beta F_0 = -\ln \frac{Z_1}{Z_0} = \frac{\int d\boldsymbol{r}^N e^{-\beta(U_1 - U_0)} e^{-\beta U_0}}{\int d\boldsymbol{r}^N e^{-\beta U_0}}$$

$$\beta \Delta F = -\ln \langle e^{-\beta(U_1 - U_0)} \rangle_0 = -\ln \langle e^{-\beta \Delta U_{0,1}} \rangle_0$$

If poor overlap: sequence of systems $\beta \Delta F = -\sum \ln \langle e^{-\beta \Delta U_{\alpha,\alpha+1}} \rangle_\alpha$

Parallel (over systems)

Thermodynamic perturbation: recycling data

Non-Boltzmann sampling,
or the pleasure of multiplying by 1 and see what happens

$$\langle A \rangle_{NVT_1} = \frac{\int \mathrm{d}\boldsymbol{r}^N A\left(\boldsymbol{q}\left(r^N\right)\right) e^{-\beta_1 U(r^N)}}{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta_1 U(r^N)}} =$$

$$= \frac{\int \mathrm{d}\boldsymbol{r}^N A\left(\boldsymbol{q}\left(r^N\right)\right) e^{\beta_2 U(r^N) - \beta_1 U(r^N)} e^{-\beta_2 U(r^N)}}{\int \mathrm{d}\boldsymbol{r}^N e^{\beta_2 U(r^N) - \beta_1 U(r^N)} e^{-\beta_2 U(r^N)}} =$$

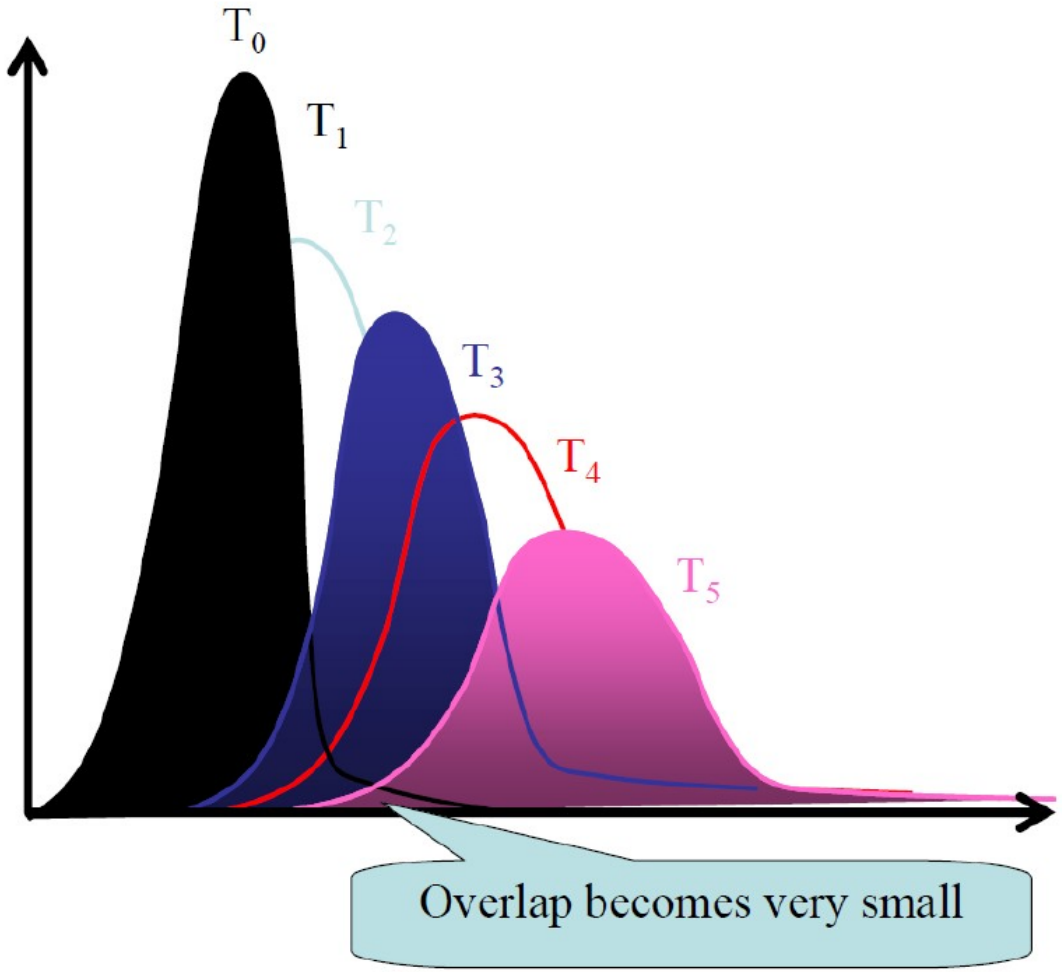
$$= \frac{\left\langle A e^{(\beta_2 - \beta_1) U(r^N)} \right\rangle_{NVT_2}}{\left\langle e^{(\beta_2 - \beta_1) U(r^N)} \right\rangle_{NVT_2}}$$

Thermodynamic perturbation: recycling data

$$\langle A \rangle_{NVT_1} =$$

$$= \frac{\left\langle A e^{(\beta_2 - \beta_1) U(r^N)} \right\rangle_{NVT_2}}{\left\langle e^{(\beta_2 - \beta_1) U(r^N)} \right\rangle_{NVT_2}}$$

Great, but...



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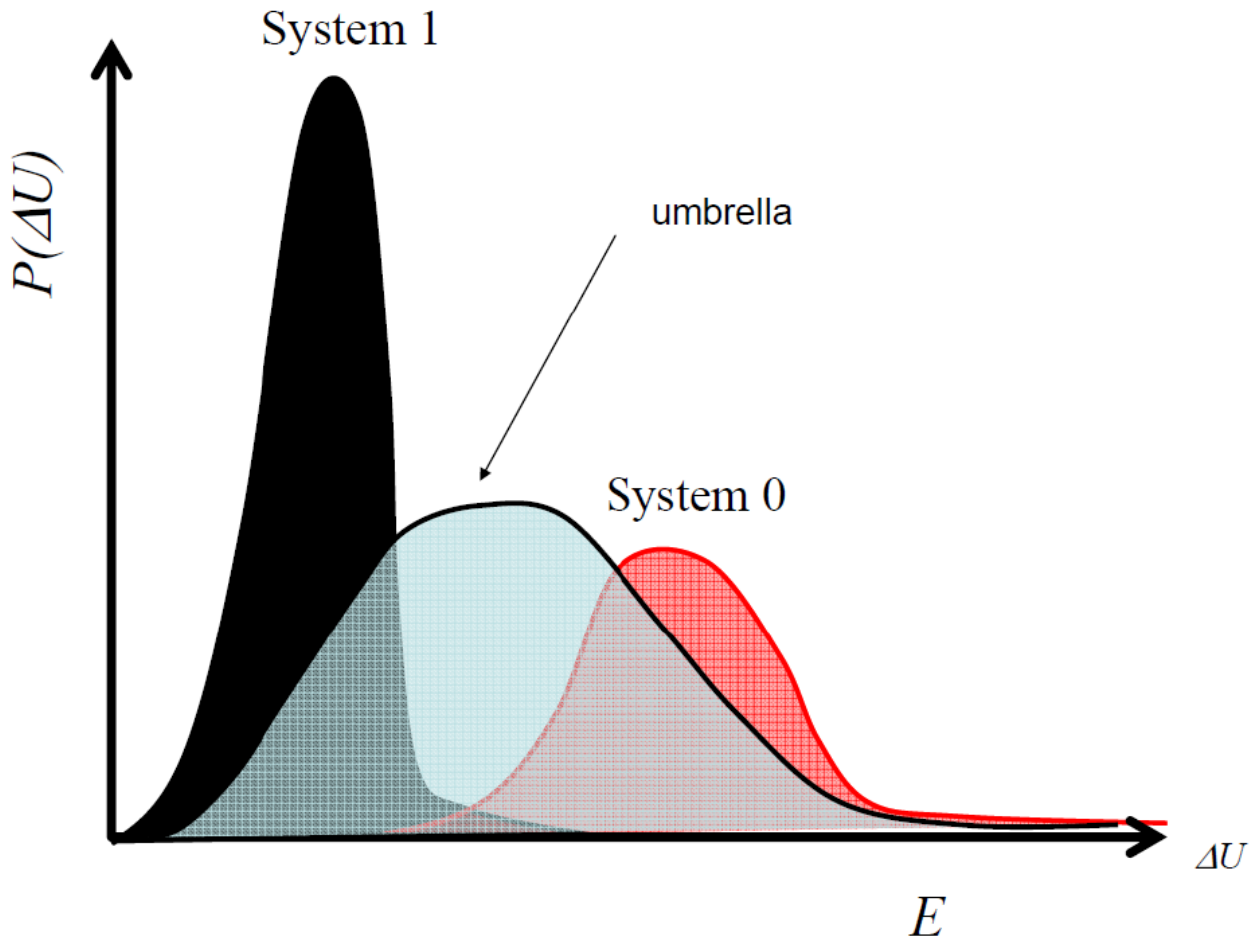
Umbrella sampling

$$\beta \Delta F = \\ = -\ln \langle e^{-\beta(U_1 - U_0)} \rangle_0$$



Umbrella sampling (multiplying by 1 few more times...)

$$\mathcal{P}(\boldsymbol{q}) = \frac{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U} \delta(\boldsymbol{q}'(\boldsymbol{r}^N) - \boldsymbol{q})}{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U}} =$$

Umbrella sampling (multiplying by 1 few more times...)

$$\mathcal{P}(\boldsymbol{q}) = \frac{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U} \delta(\boldsymbol{q}'(\boldsymbol{r}^N) - \boldsymbol{q})}{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U}} =$$

$$= \frac{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta (U + w(\boldsymbol{q}'))} e^{\beta w(\boldsymbol{q}')} \delta(\boldsymbol{q}'(\boldsymbol{r}^N) - \boldsymbol{q})}{\int d\boldsymbol{r}^N e^{-\beta (U + w(\boldsymbol{q}'))} e^{\beta w(\boldsymbol{q}')}} =$$

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$$\mathcal{P}(\boldsymbol{q}) = \frac{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U} \delta(\boldsymbol{q}'(\boldsymbol{r}^N) - \boldsymbol{q})}{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U}} =$$

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$$= \frac{Z_{U+w} e^{\beta w(\boldsymbol{q})} \int \mathrm{d}\boldsymbol{r}^N e^{-\beta (U + w(\boldsymbol{q}'))} \delta(\boldsymbol{q}'(\boldsymbol{r}^N) - \boldsymbol{q})}{Z_{U+w} \int \mathrm{d}\boldsymbol{r}^N e^{-\beta (U + w(\boldsymbol{q}'))} e^{\beta w(\boldsymbol{q}')}} =$$

Umbrella sampling (multiplying by 1 few more times...)

$$\mathcal{P}(\boldsymbol{q}) = \frac{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U} \delta(\boldsymbol{q}'(\boldsymbol{r}^N) - \boldsymbol{q})}{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U}} =$$

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$$= \frac{e^{\beta w(\boldsymbol{q})}}{\left\langle e^{\beta w(\boldsymbol{q})} \right\rangle_{U+w}} \mathcal{P}_{U+w}(\boldsymbol{q})$$

Umbrella sampling (multiplying by 1 few more times...)

$$\mathcal{P}(\boldsymbol{q}) = \frac{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U} \delta(\boldsymbol{q}'(\boldsymbol{r}^N) - \boldsymbol{q})}{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta U}} =$$

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Parallel
(over biasing potentials)

Umbrella sampling

$$\mathcal{P}(\boldsymbol{q}) = \frac{e^{\beta w(\boldsymbol{q})}}{\left\langle e^{\beta w(\boldsymbol{q})} \right\rangle_{U+w}} \mathcal{P}_{U+w}(\boldsymbol{q})$$

$$\beta F(\boldsymbol{q}) = -\ln \mathcal{P}(\boldsymbol{q}) = -\ln \mathcal{P}_{U+w}(\boldsymbol{q}) - \beta w(\boldsymbol{q}) + C$$

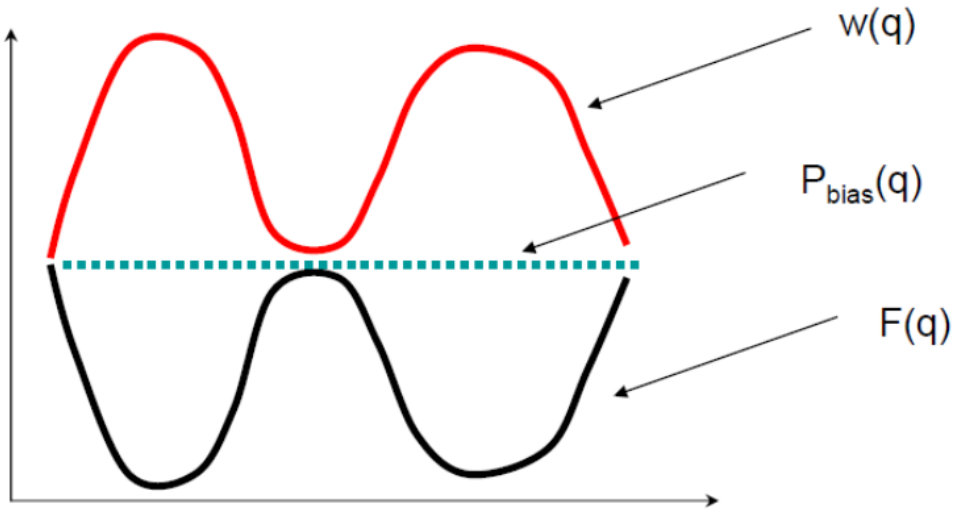
Umbrella sampling

$$\mathcal{P}(\boldsymbol{q}) = \frac{e^{\beta w(\boldsymbol{q})}}{\langle e^{\beta w(\boldsymbol{q})} \rangle_{U+w}} \mathcal{P}_{U+w}(\boldsymbol{q})$$

$$\beta F(\boldsymbol{q}) = -\ln \mathcal{P}(\boldsymbol{q}) = -\ln \mathcal{P}_{U+w}(\boldsymbol{q}) - \beta w(\boldsymbol{q}) + C$$

Best choice $w(\boldsymbol{q}) = -F(\boldsymbol{q})$

Not practical, $F(\boldsymbol{q})$ is what we want to calculate!



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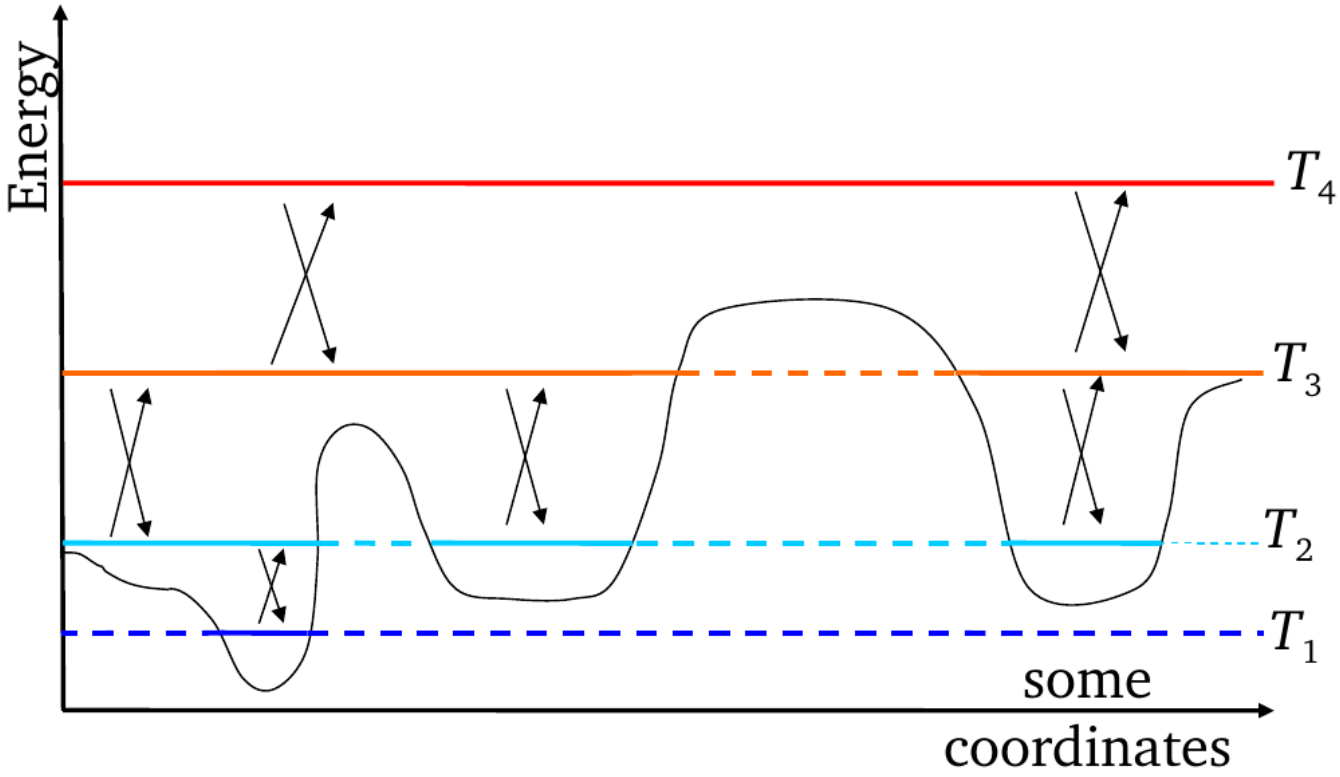
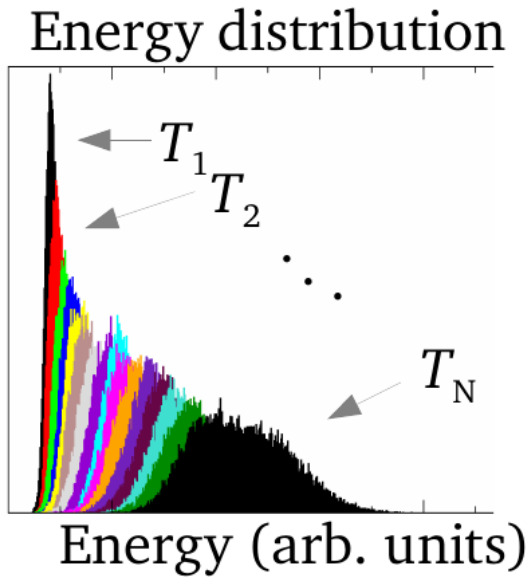
Parallel tempering: the concept

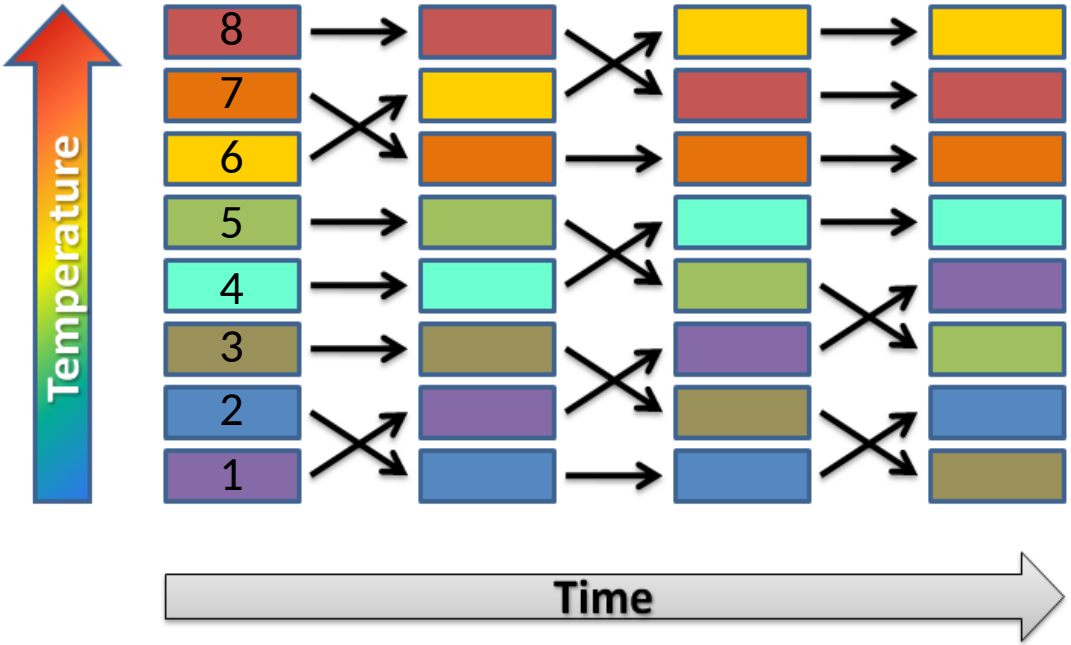




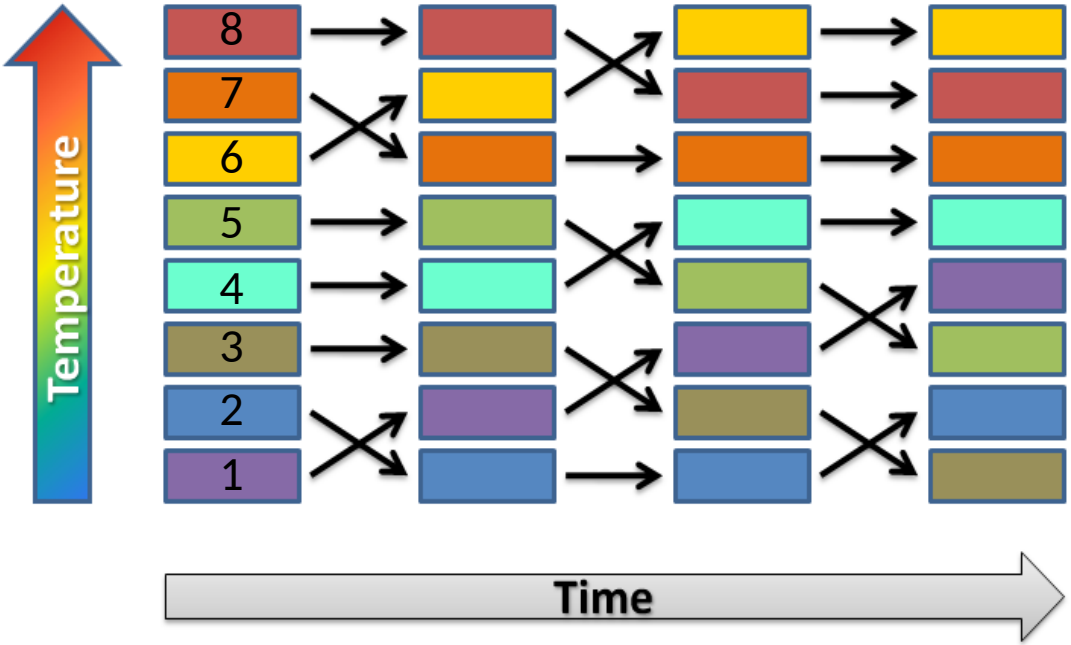
Exchange rule, ensuring canonical sampling at all temperatures:

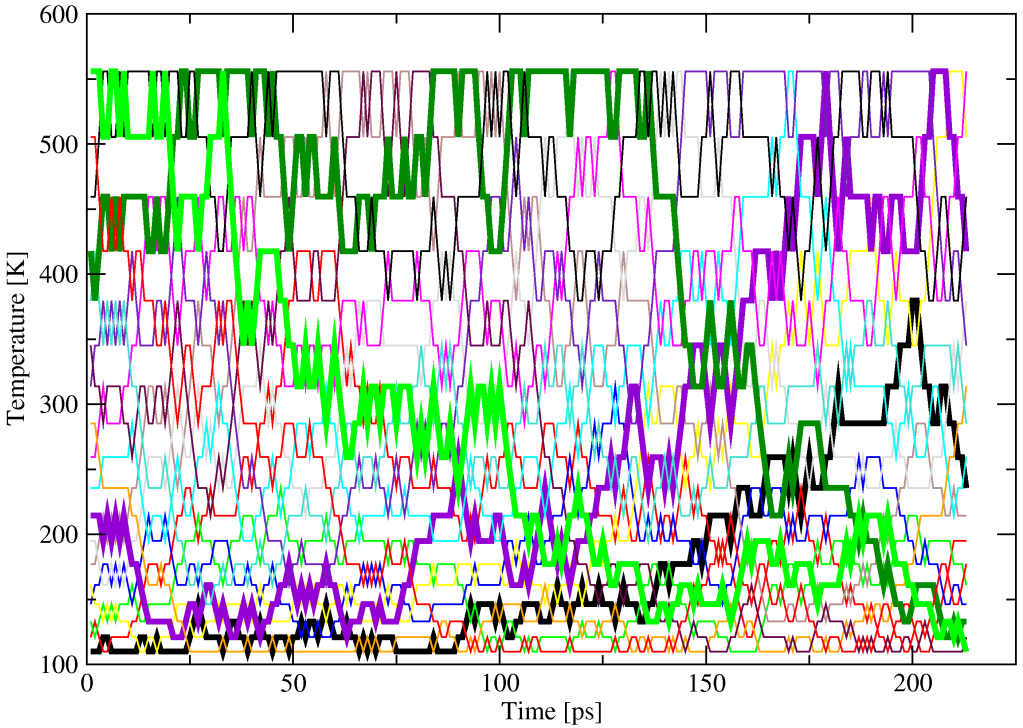
$$P_{exchange} = \min\left(1, \exp(-(\beta_i - \beta_j)(U_i - U_j))\right)$$

Parallel tempering: the implementation

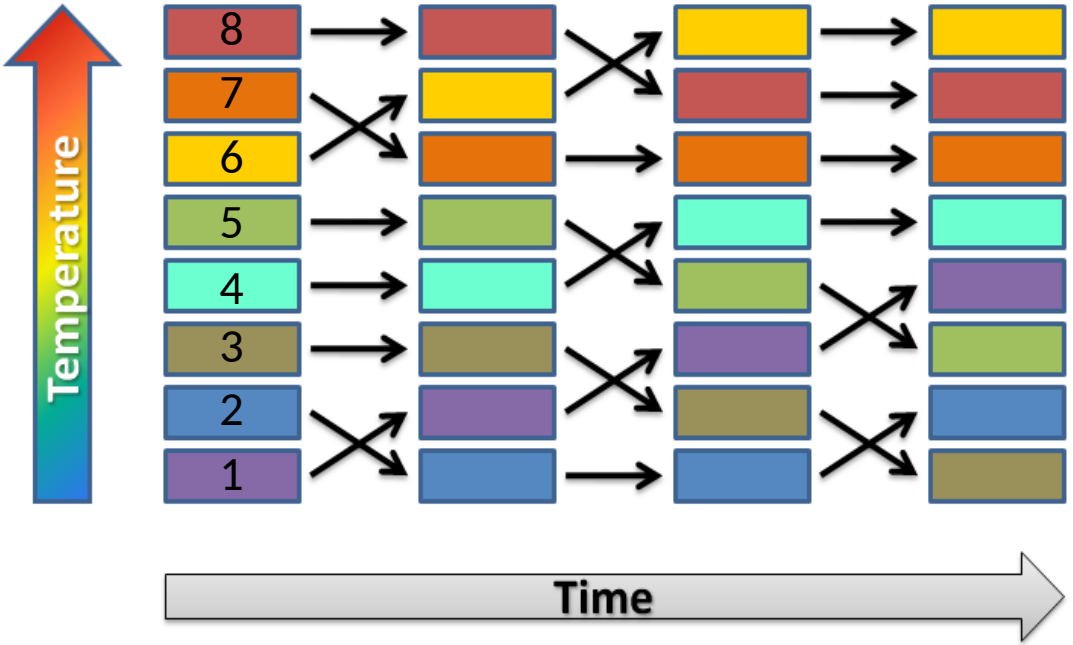


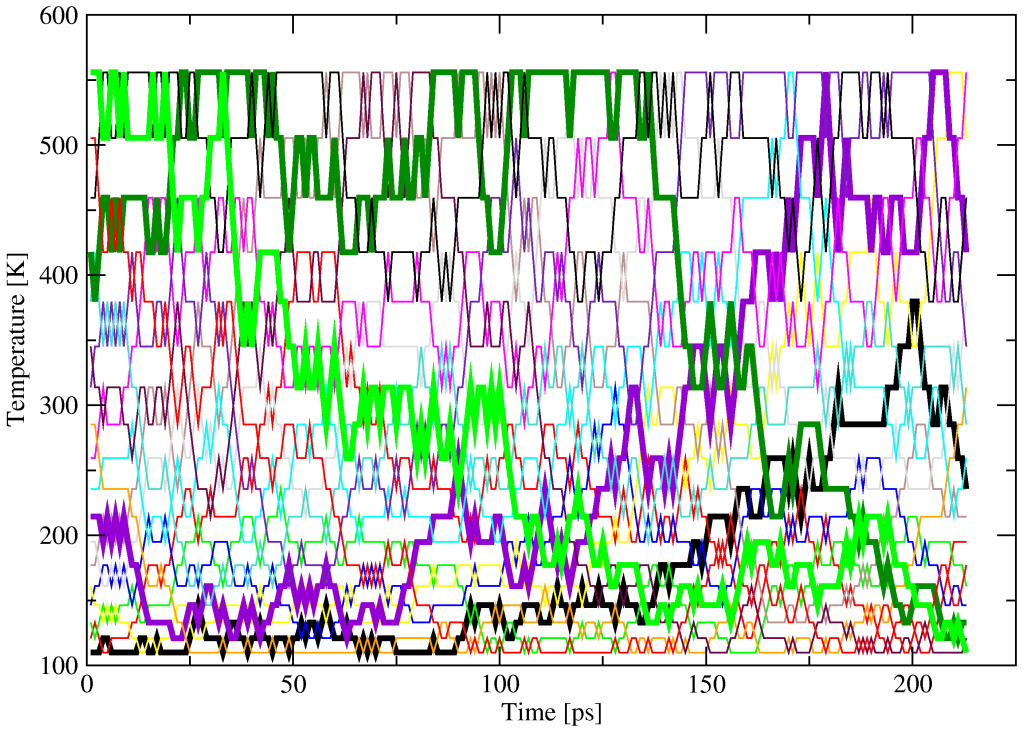
Parallel tempering: the implementation





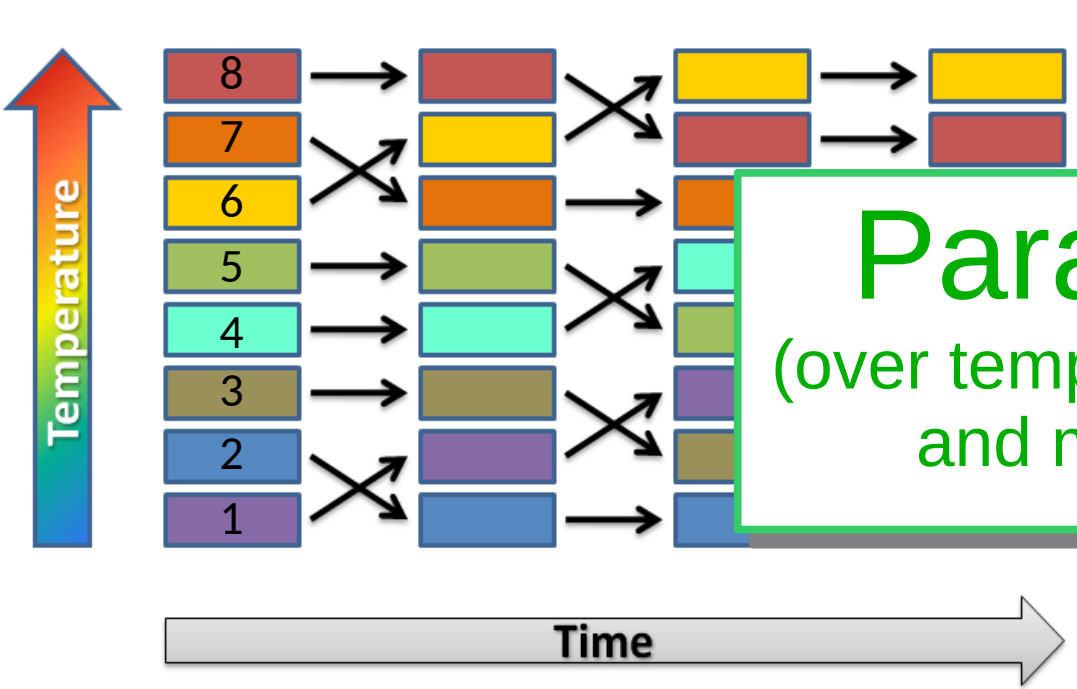
Parallel tempering: the implementation



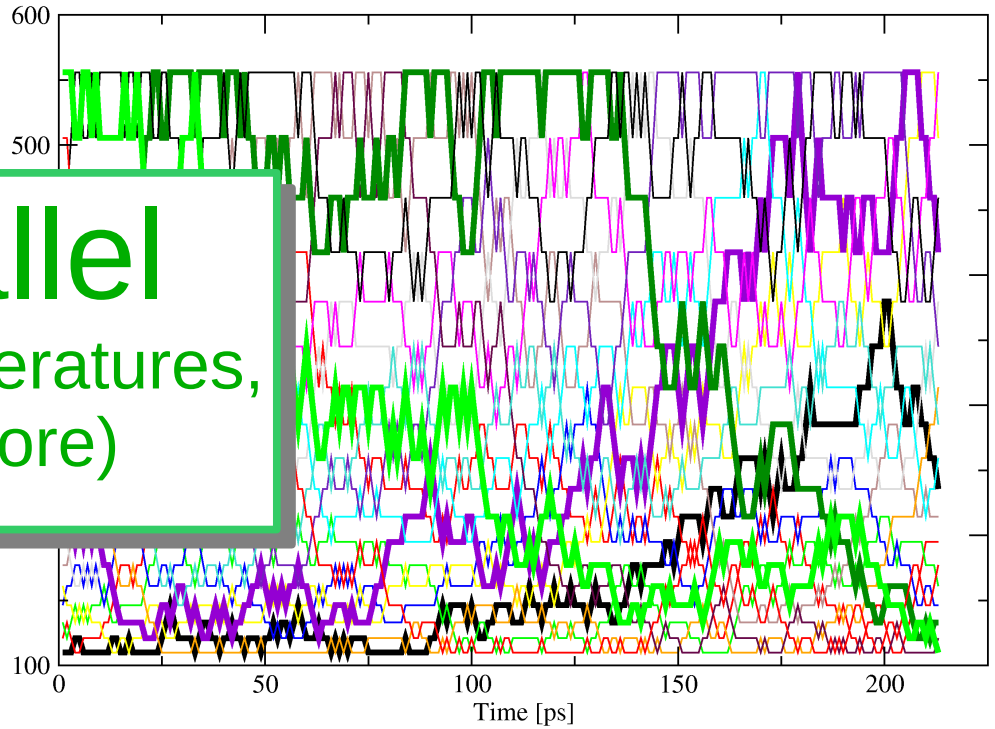


To be tuned for efficient sampling:
number of temperatures, list of temperatures, attempted swap frequency

Parallel tempering: the implementation



Parallel
(over temperatures, and more)



To be tuned for efficient sampling:
number of temperatures, list of temperatures, attempted swap frequency

Parallel tempering: free energy?

T-Weighted Histogram Analysis Method:

$$P_i(q) = \mathrm{e}^{\beta_i F_i} c_i(q) P_0(q)$$

$$c_i(q) = \mathrm{e}^{-(\beta_i - \beta_0)U(q)} \mathrm{e}^{-\beta_i V_i(q)}$$, in case: $H_i = H_0 + V_i(q)$

Parallel tempering: free energy?

T-Weighted Histogram Analysis Method:

$$P_i(q) = \mathrm{e}^{\beta_i F_i} c_i(q) P_0(q)$$

$$c_i(q) = \mathrm{e}^{-(\beta_i - \beta_0)U(q)} \mathrm{e}^{-\beta_i V_i(q)} \text{ , in case: } H_i = H_0 + V_i(q)$$

Iterative, self consistent solution of:

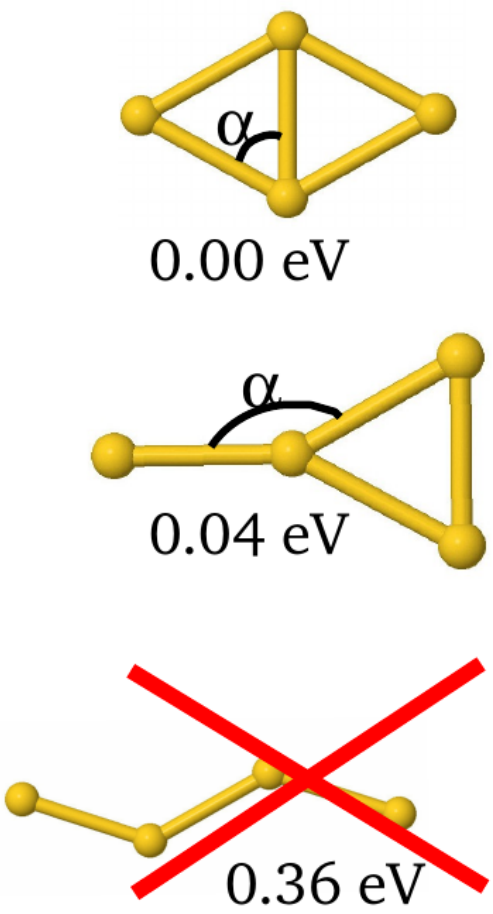
$$P_0(q) = \frac{\sum_{i=1}^{S} n_i(q)}{\sum_{i=1}^{S} N_i \mathrm{e}^{\beta_i F_i} c_i(q)}$$

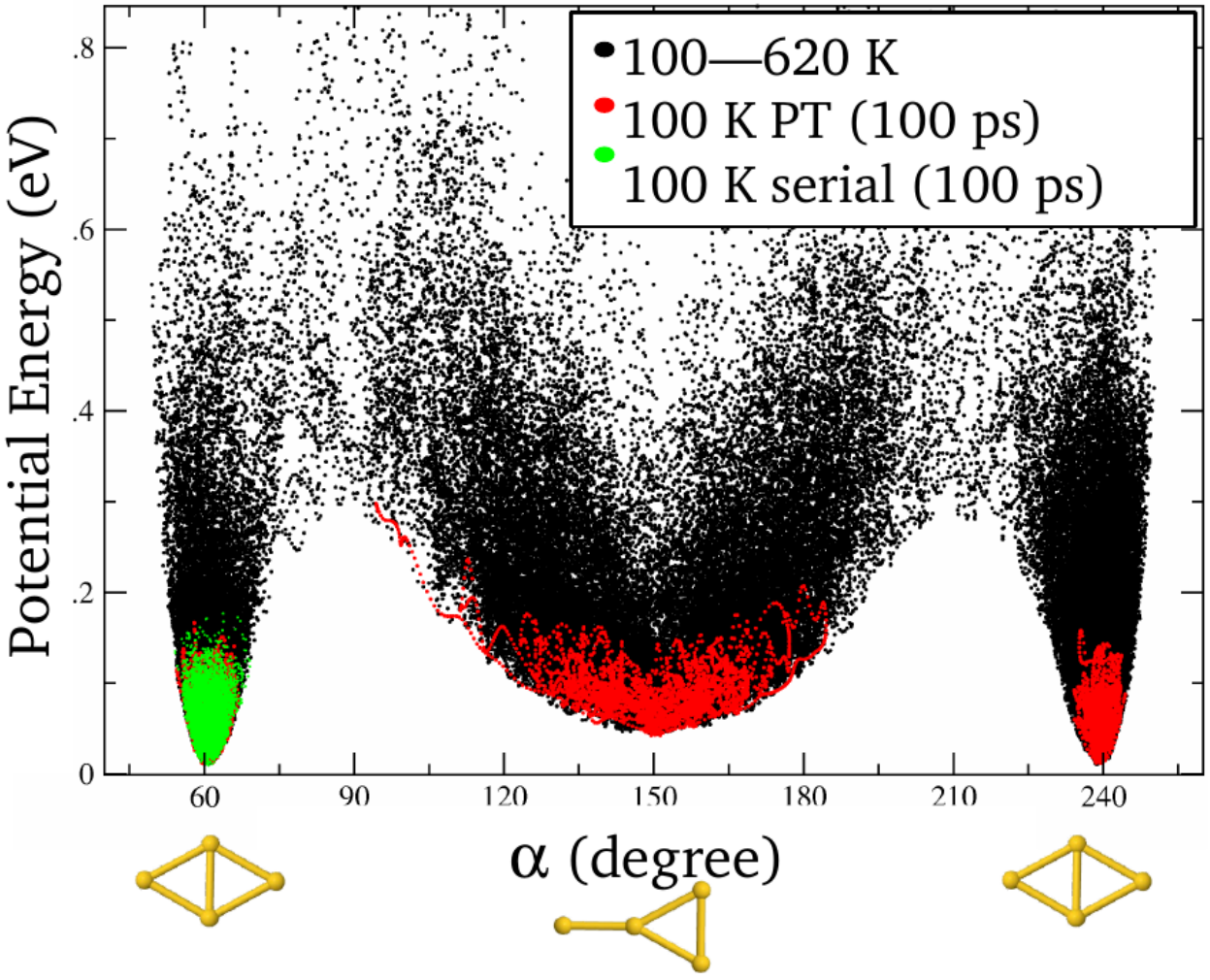
$$\beta_i F_i = -\ln \left(\int \mathrm{d}q \; c_i(q) P_0(q) \right)$$

IMPORTANT: "*q*" is a "post-production" (collective) variable

See also: J. Chodera *et al.*, J. Chem. Theory Comput. 3, 26 (2007)

Au_4: coexistence of several isomers





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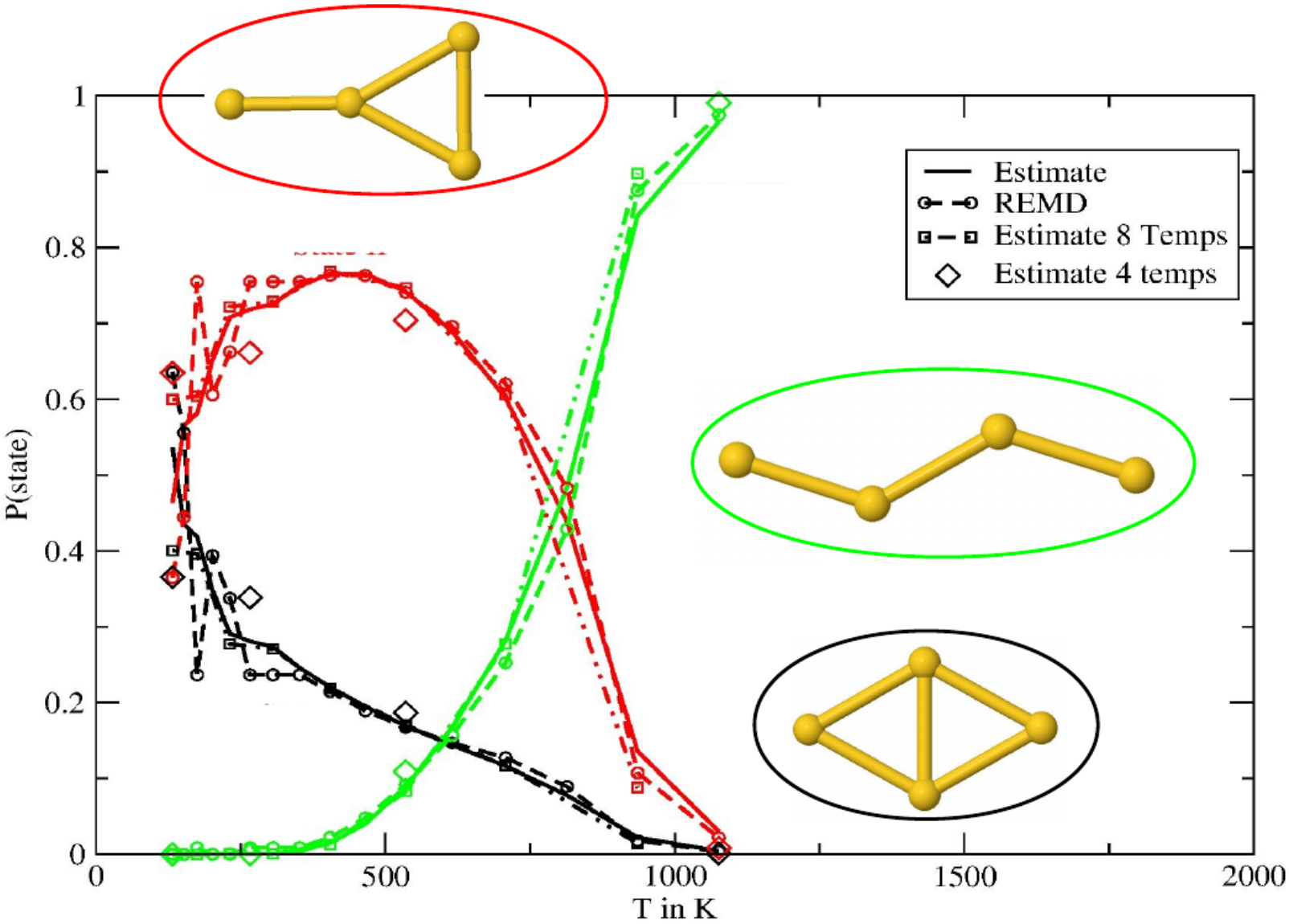
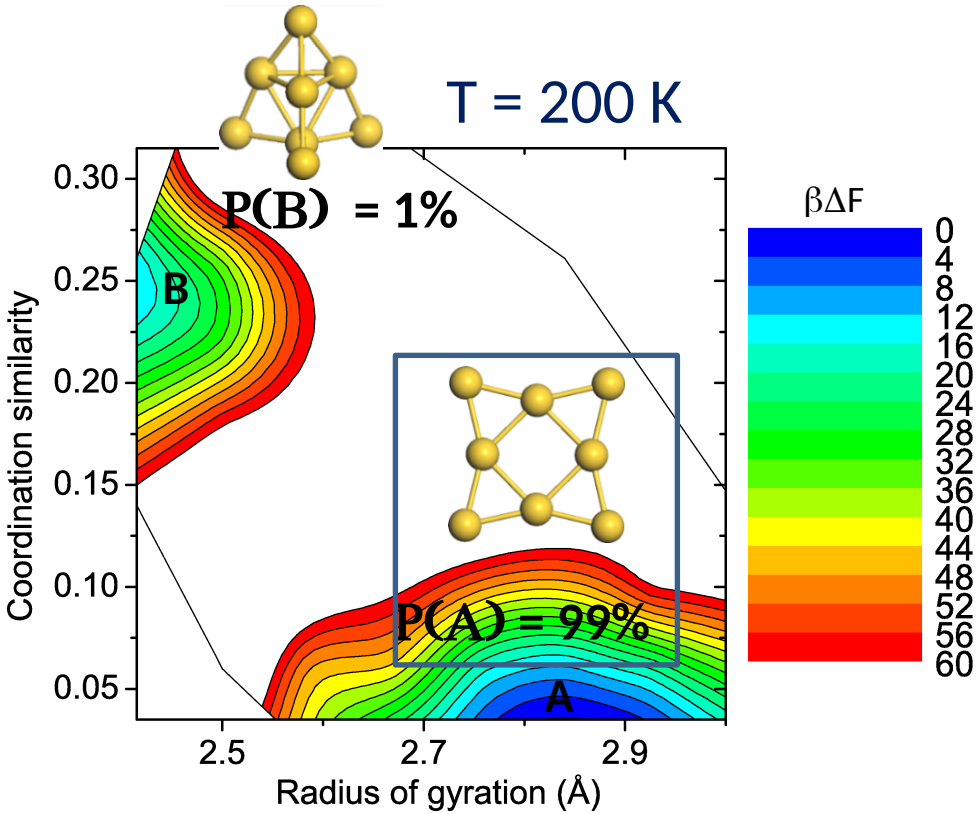
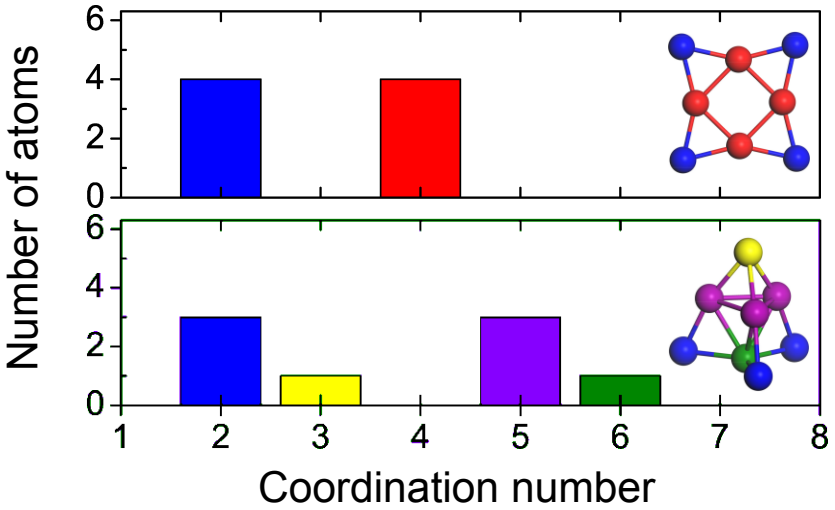


Au_8 free energy surface from replica-exchange MD



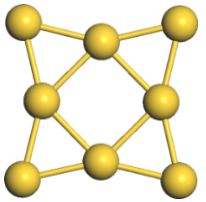


Mean relative bin error = 7.6%

Mean bin error = 1.1 k_BT = 19 meV

3 ns total per simulation

Boltzmann Probability, P



Structure experimentally assigned at 100 K

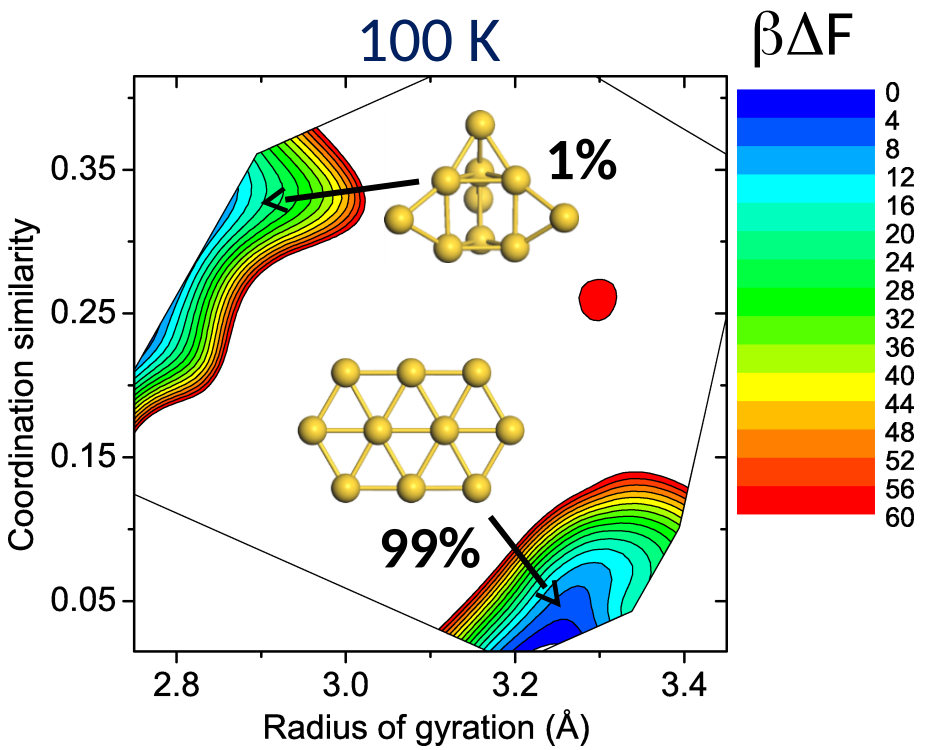
P. Gruene *et al Z. Phys. Chem.* 228, (2014)

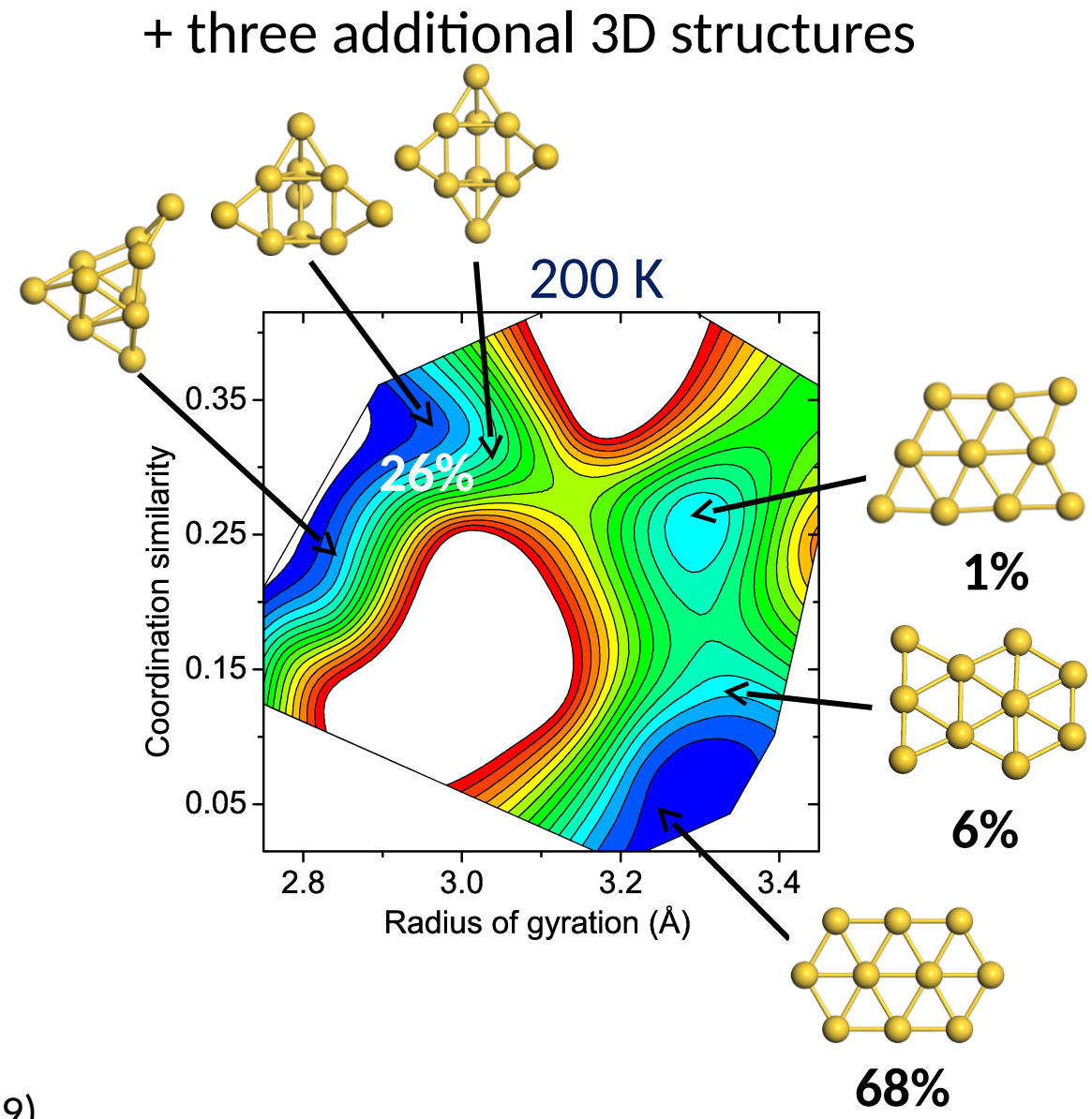
[1] *Multistate Bennett Acceptance Ratio:* M. R. Shirts and J. D. Chodera, *J. Chem. Phys*. 129, (2008)

[2] *Coordination similarity:* A. R. Oganov and M. Valle, *J. Chem. Phys.* 130, (2009)

[3] *Radius of gyration:* G. Santarossa *et al.*, *Phys. Rev. B.* 81, (2010)

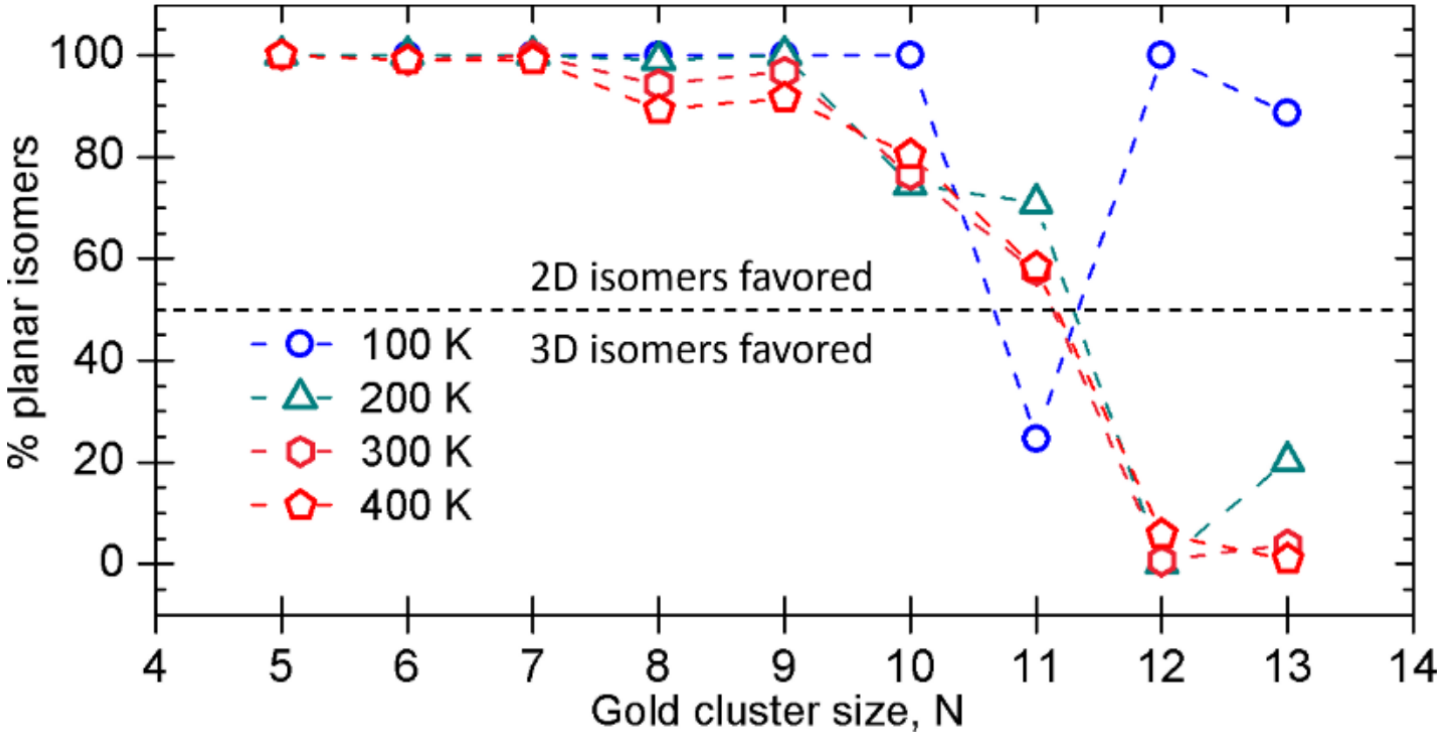
Free energy surface of Au_{10} displays multiple isomers above 100 K





Goldsmith, …, & LMG, Phys Rev Materials (2019)

The configurational entropy of 3D structures is typically larger compared to planar structures

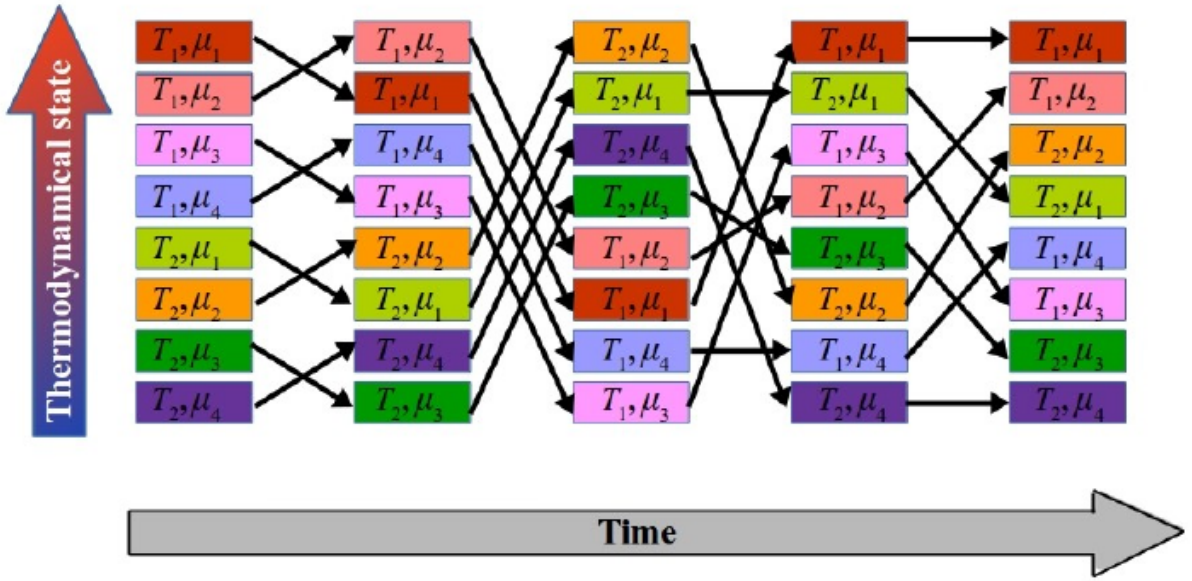


Au_{11} is exceptional case due to conformational entropy of planar structures

Typically fraction of 3D structures increases as size ↑ and temperature ↑

Goldsmith, …, & LMG, Phys Rev Materials (2019)

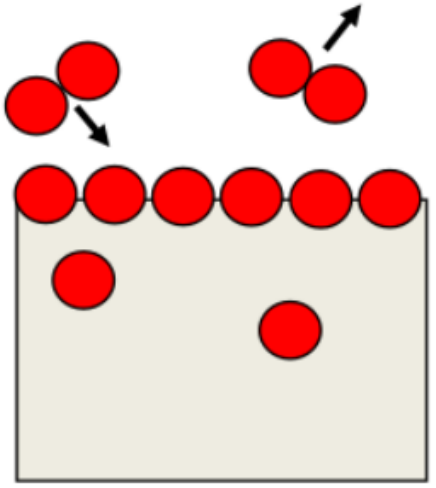
Replica-Exchange Grand-Canonical *ab initio* Molecular Dynamics



Replica-Exchange Grand-Canonical Molecular Dynamics (REGCMD)

Simulated in Grand-Canonical (μVT) ensemble

Overcome: ***kinetic trapping***
phase space diffusion



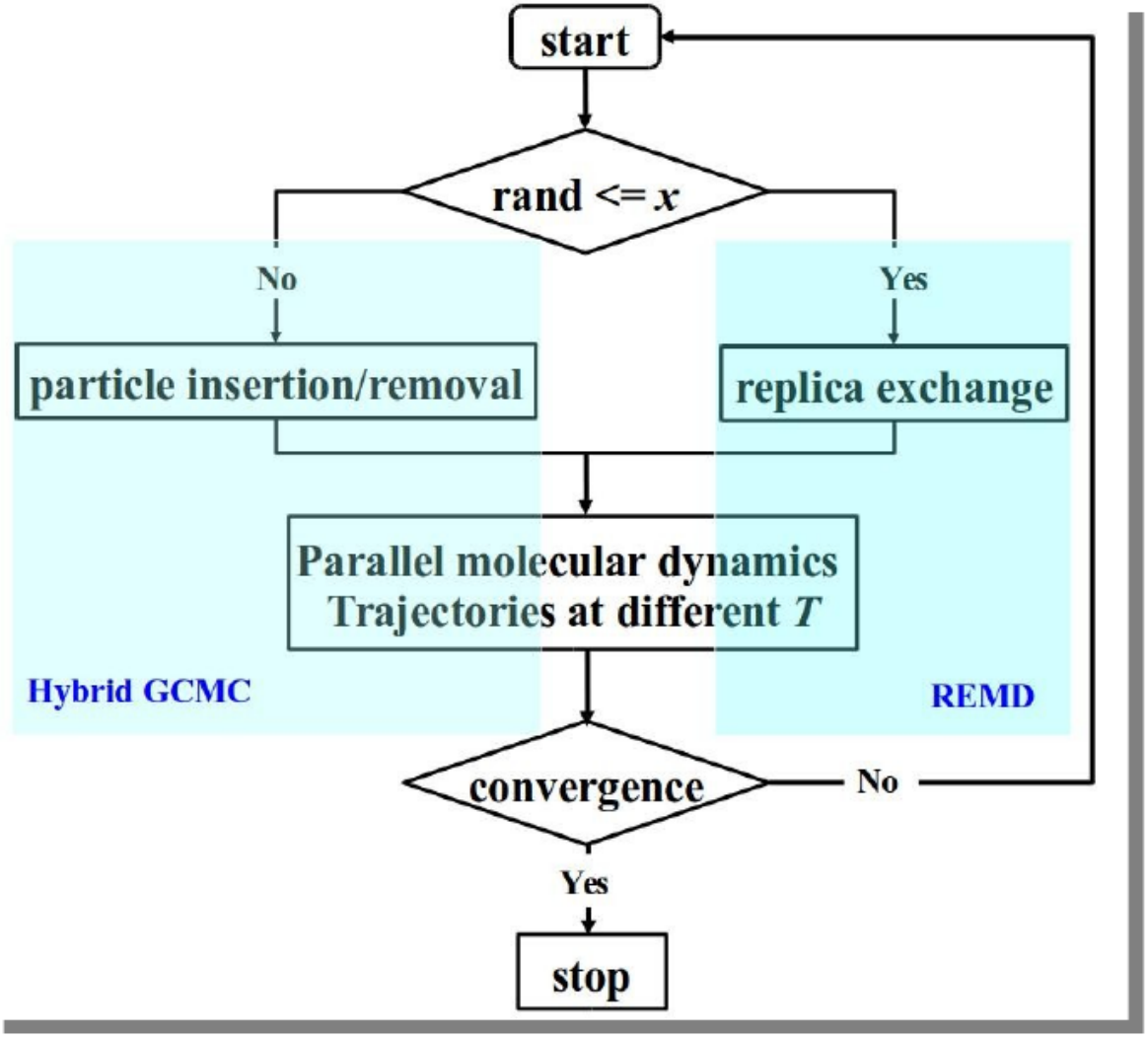
stable cluster structure

=

statistical average over adsorption and desorption processes

Open system ⟷ **Grand-Canonical ensemble (μVT)**

Replica-Exchange Grand-Canonical *ab initio* Molecular Dynamics



ab initio molecular dynamics
xc: PBE+vdW^{TS}
basis setting: light
stochastic velocity-rescaling thermostat

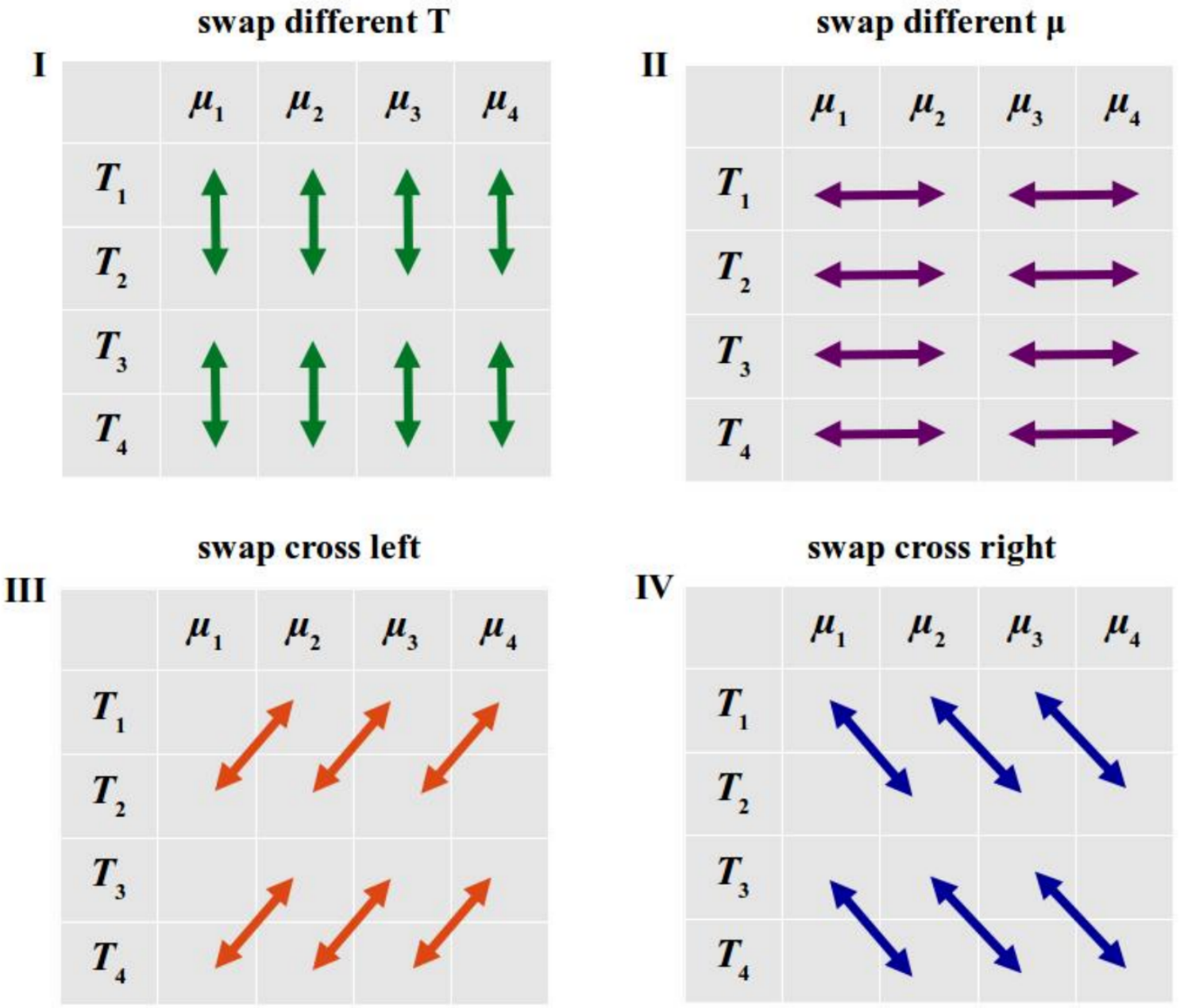
Electronic structure: PBE0

Gibbs free energy:
I *ab initio* atomistic Thermodynamics
(aT) $\Delta G_f = F_{TiMOn}(T) - F_{TiM}(T) - n\mu_O(T, p)$

II Multistate Bennett Acceptance Ratio (MBAR): partition function

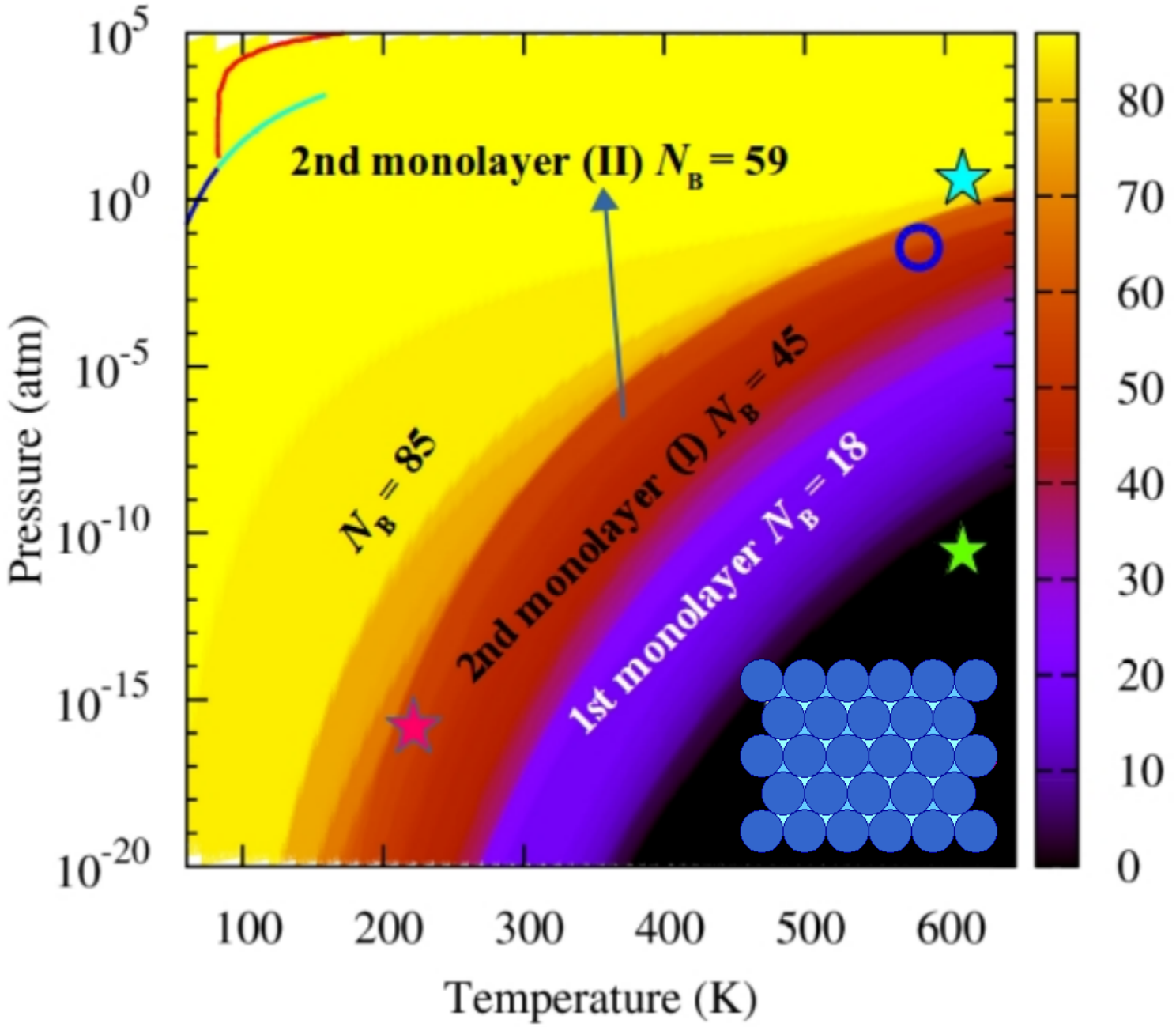
Zhou, Scheffler & LMG, submitted (2019)

Random walk in T, μ space



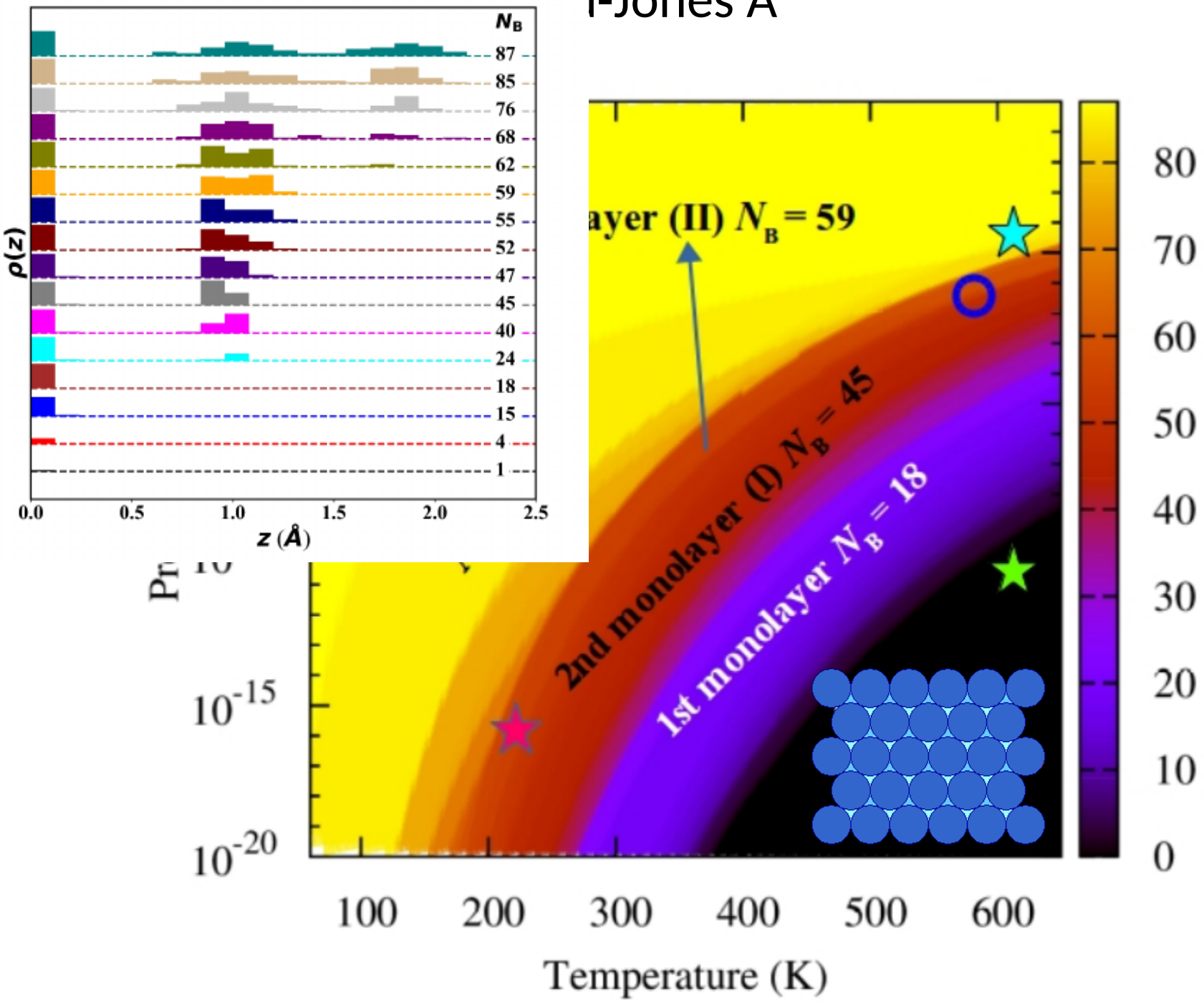
Zhou, Scheffler & LMG, submitted (2019)

Lennard-Jones B on Lennard-Jones A



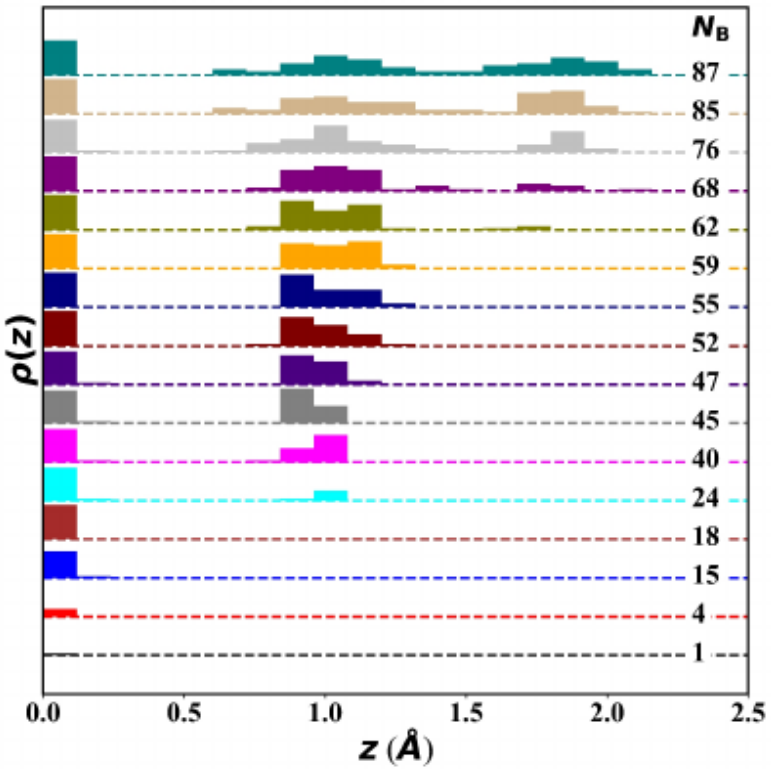
Zhou, Scheffler & LMG, submitted (2019)

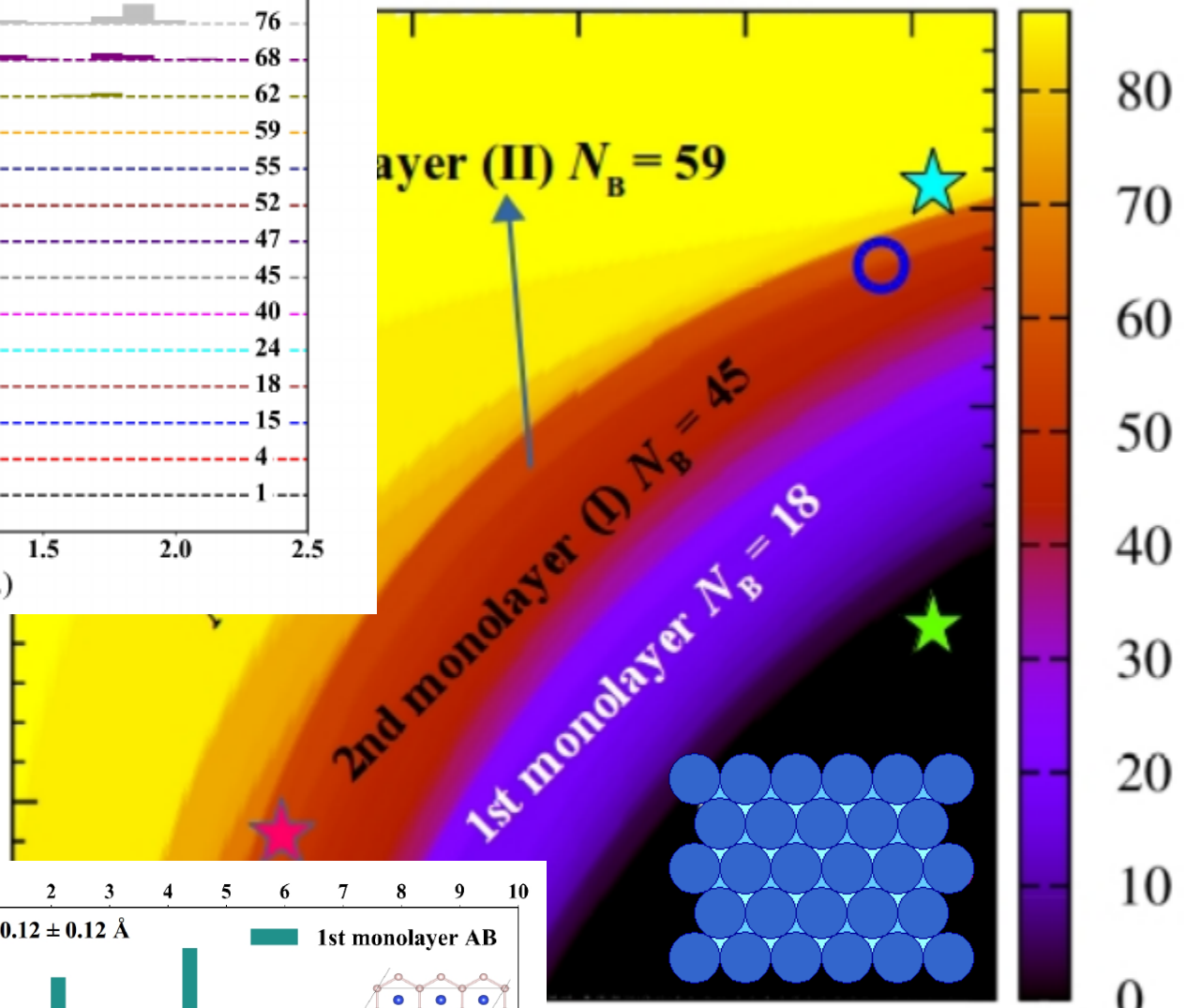
l-Jones A

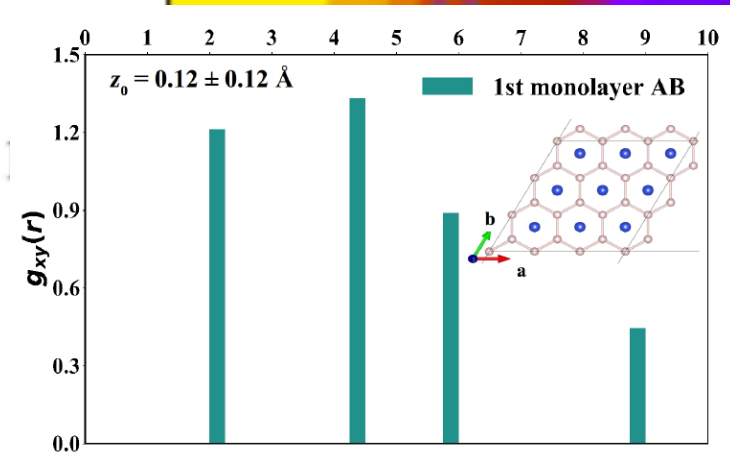


Zhou, Scheffler & LMG, submitted (2019)

l-Jones A

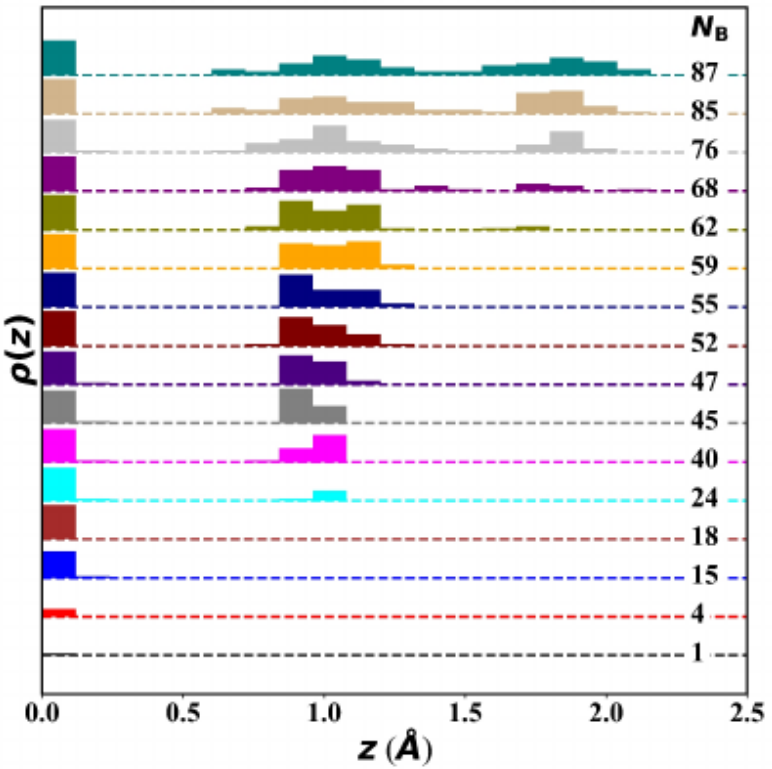


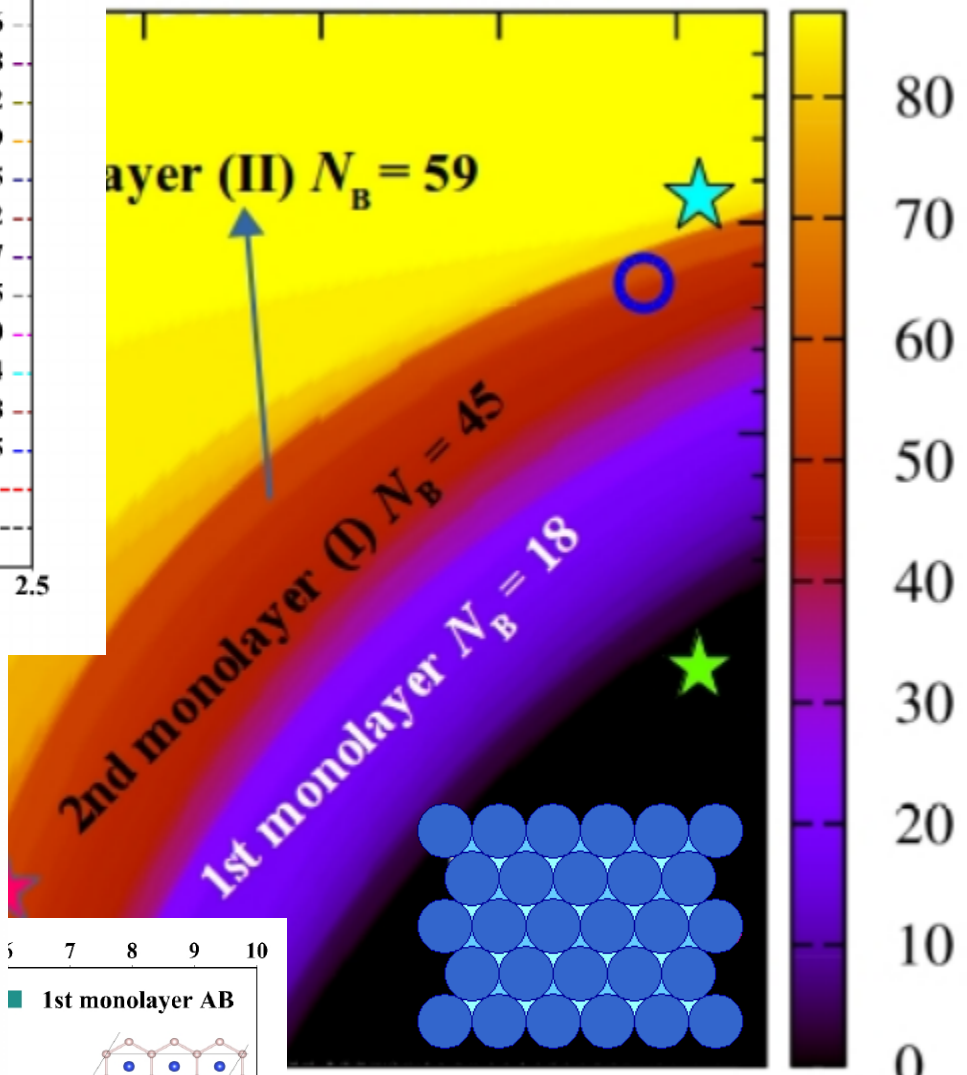


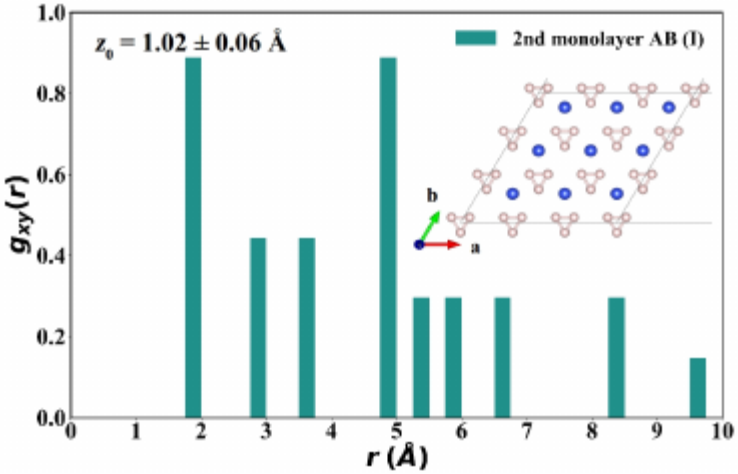


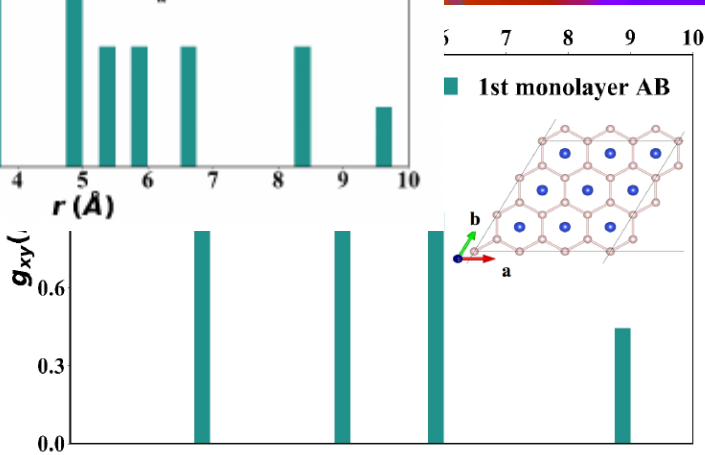
Zhou, Scheffler & LMG, submitted (2019)

l-Jones A



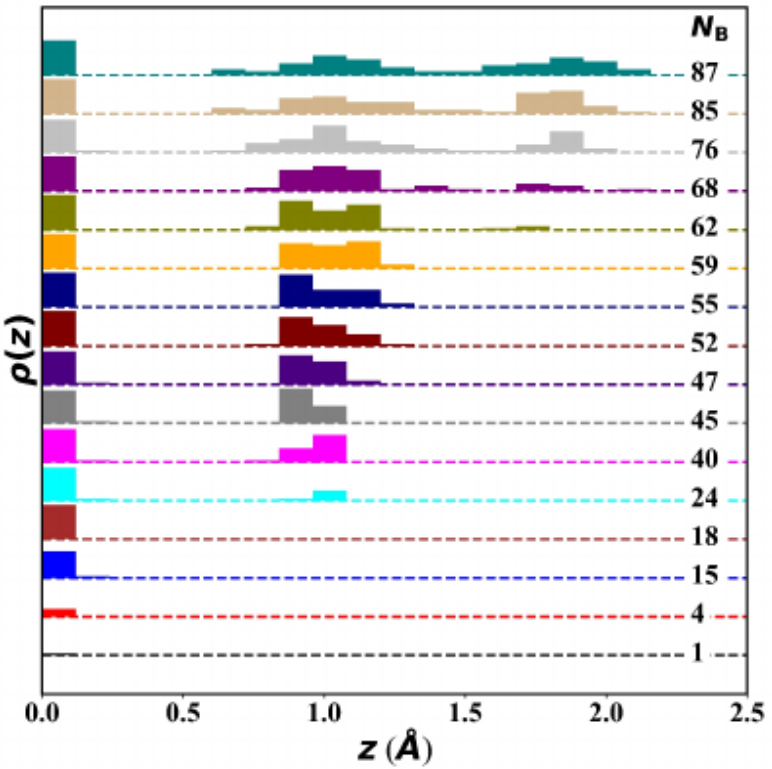


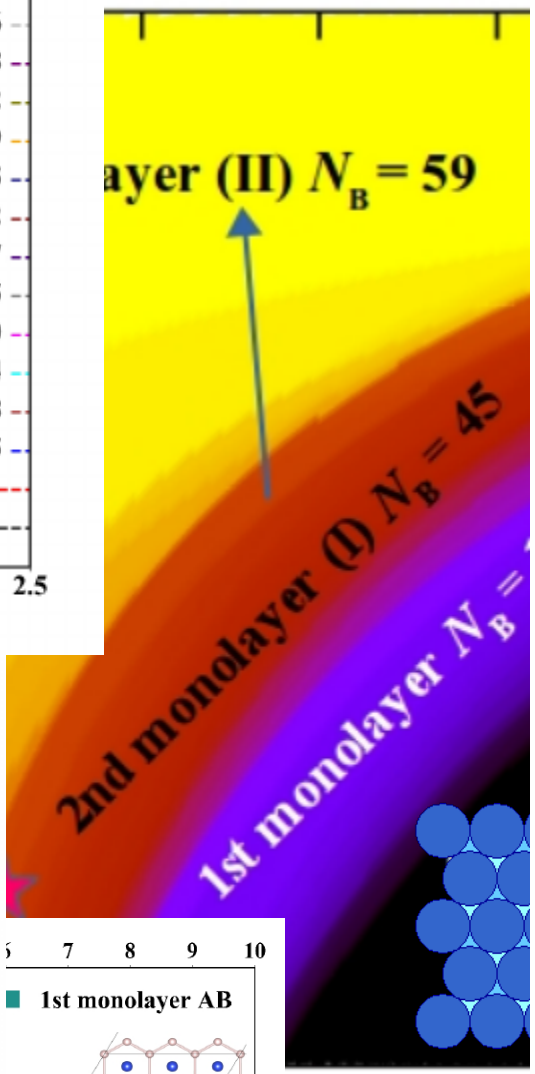


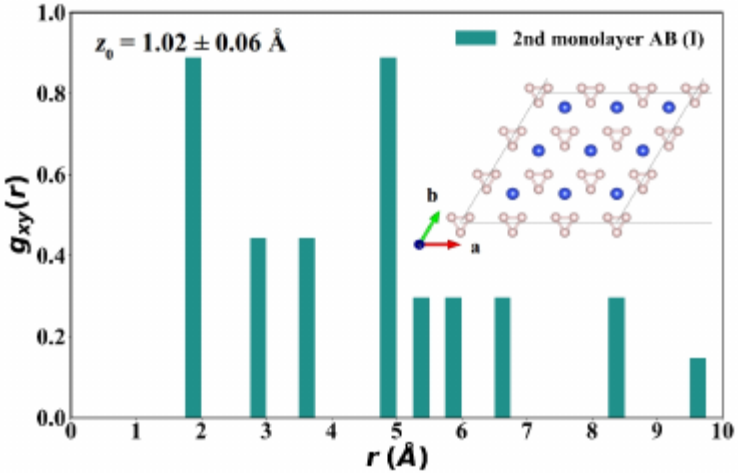


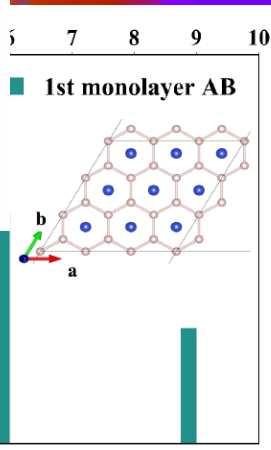
Zhou, Scheffler & LMG, submitted (2019)

l-Jones A



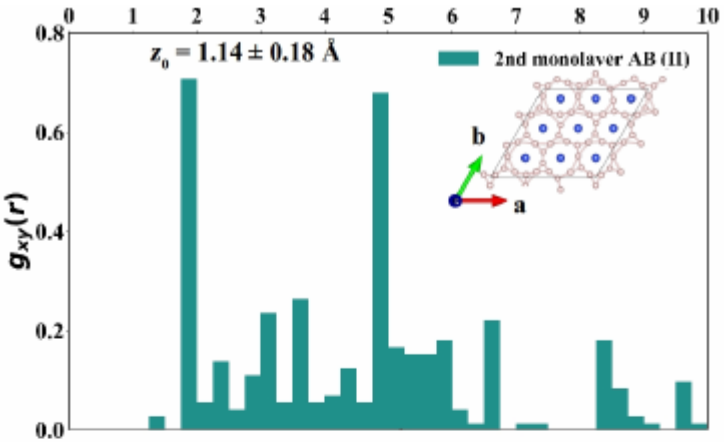


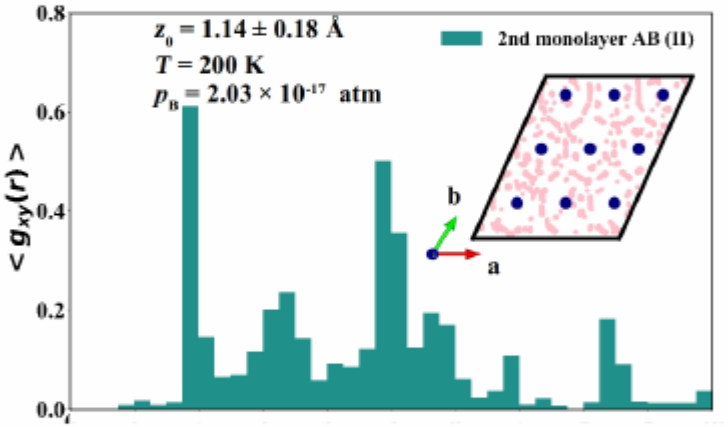


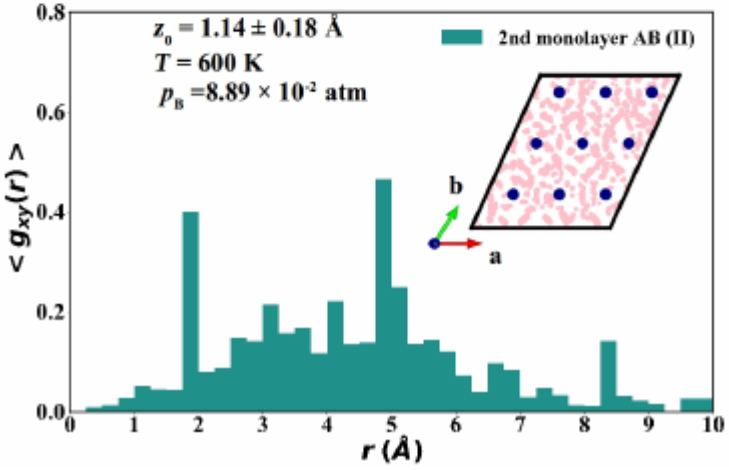


400 500

ıre (K)





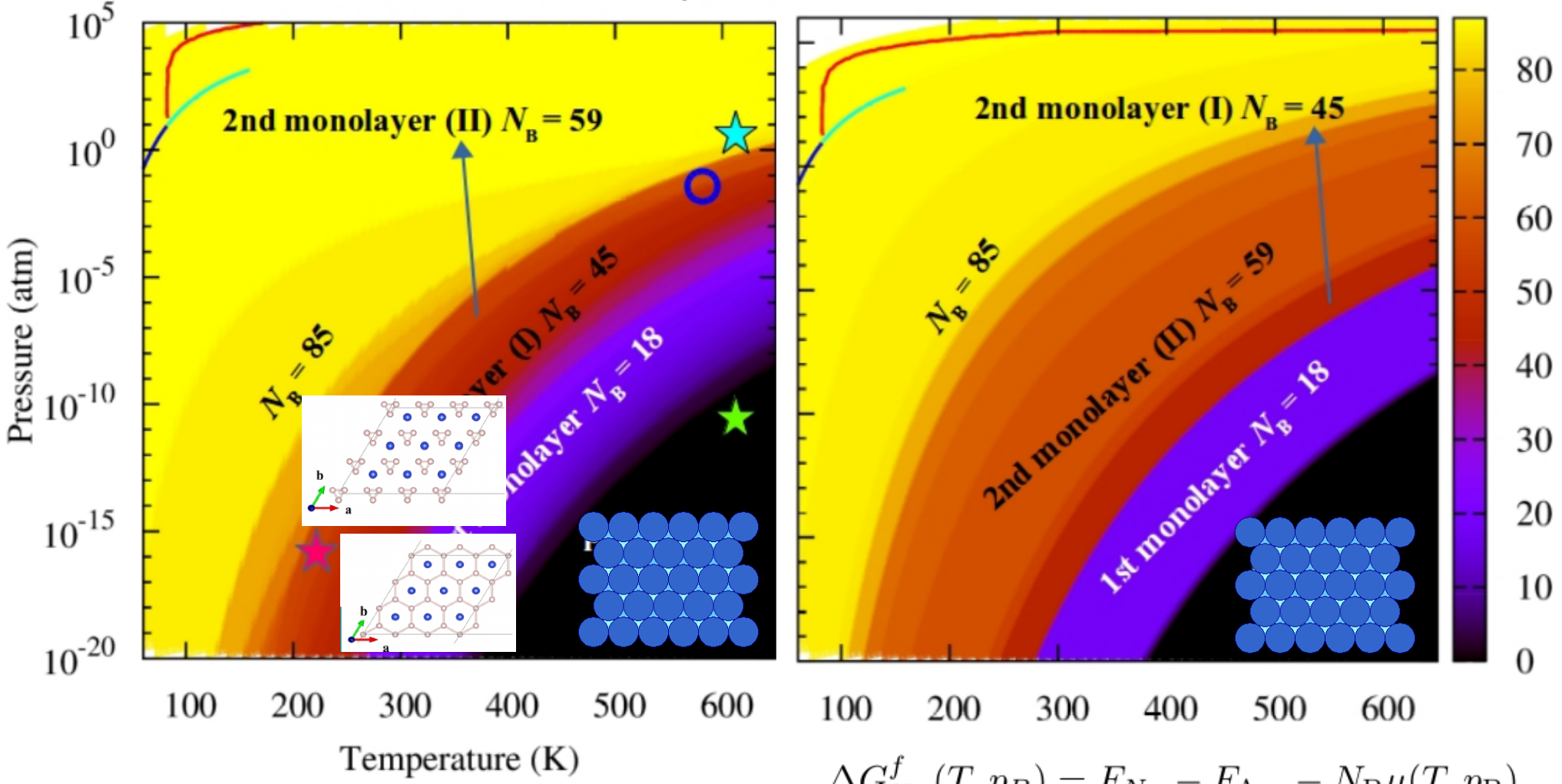


Zhou, Scheffler & LMG, submitted (2019)

Lennard-Jones B on Lennard-Jones A

Grand-canonical replica Exchange

Ab initio atomistic thermodynamics

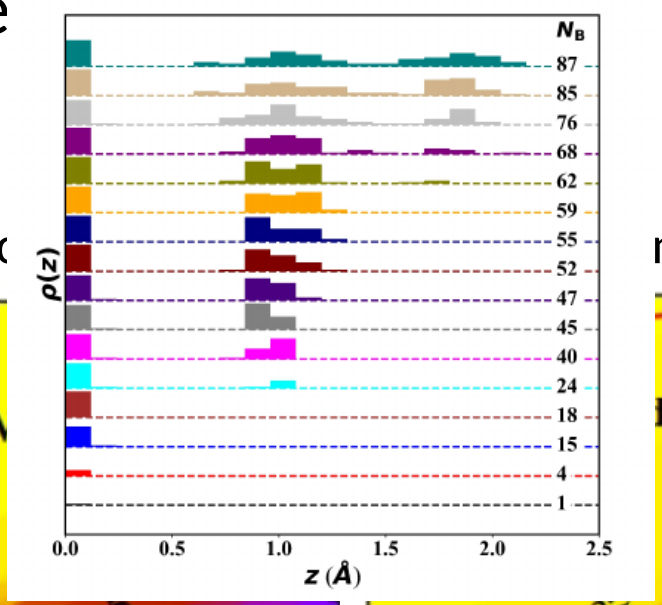


$$\Delta G^{f}_{N_{\mathrm{B}}}(T, p_B) = F_{N_{\mathrm{B}}} - F_{\mathrm{A}_{18}} - N_{\mathrm{B}}\mu(T, p_{\mathrm{B}})$$

Zhou, Scheffler & LMG, submitted (2019)

Lennard-Jones B on Le

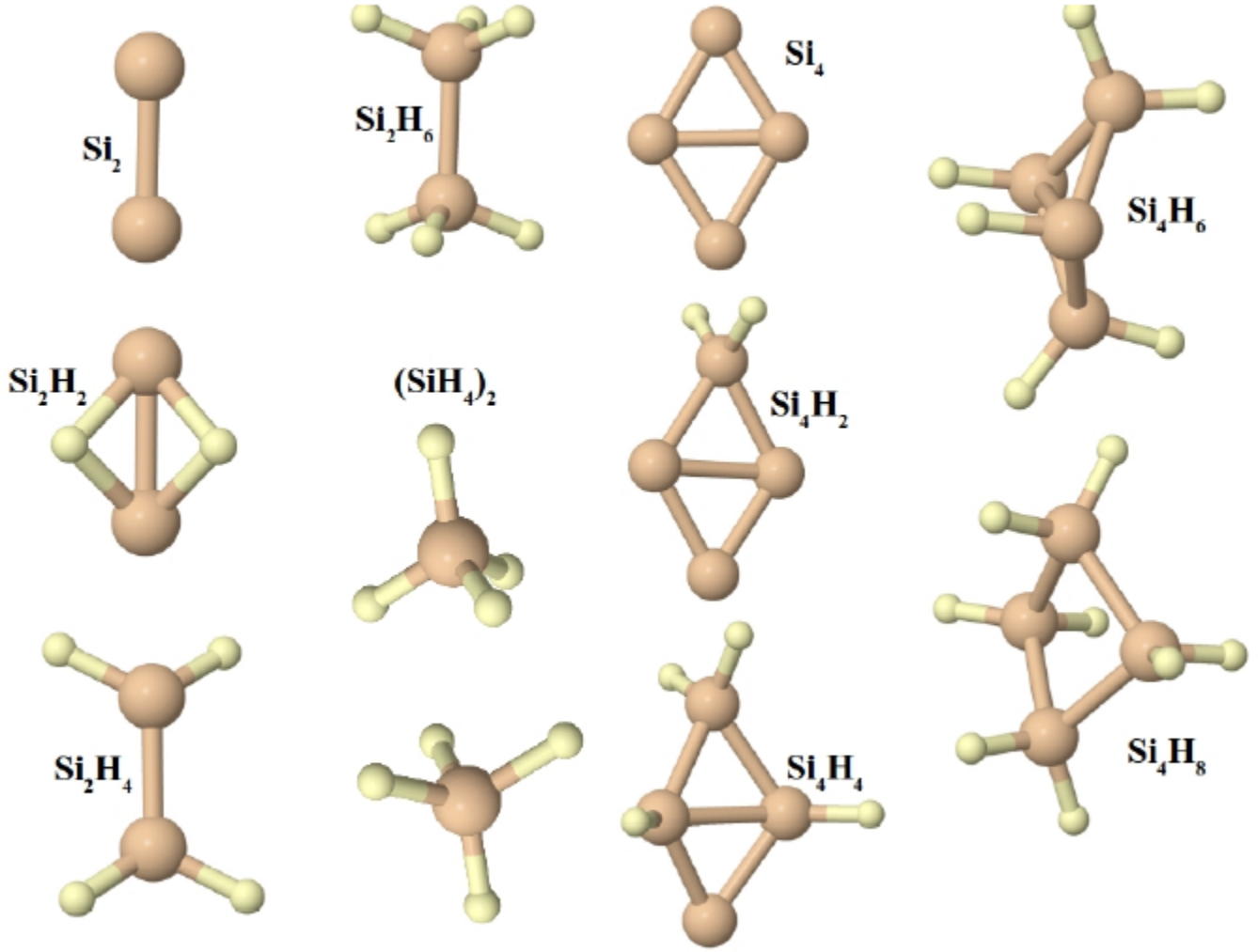
Grand-canonical replic mistic thermodynamics



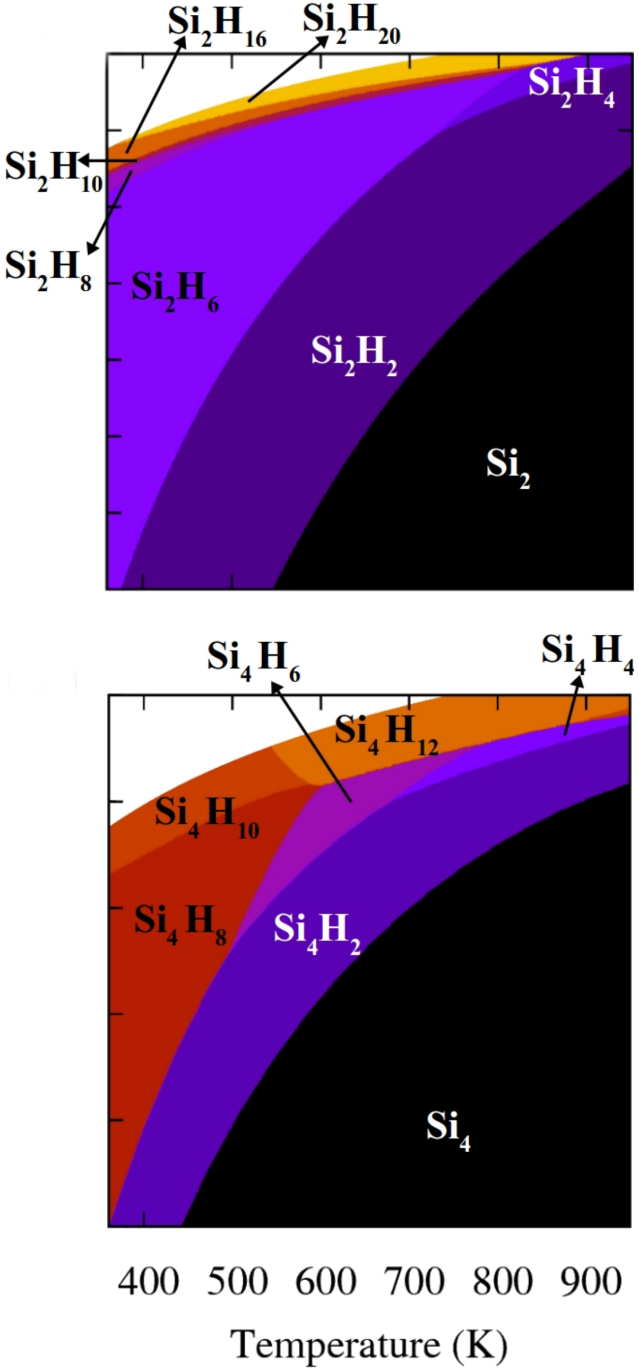
$$\Delta G^{f}_{N_{\mathrm{B}}}(T, p_B) = F_{N_{\mathrm{B}}} - F_{\mathrm{A}_{18}} - N_{\mathrm{B}}\mu(T, p_{\mathrm{B}})$$

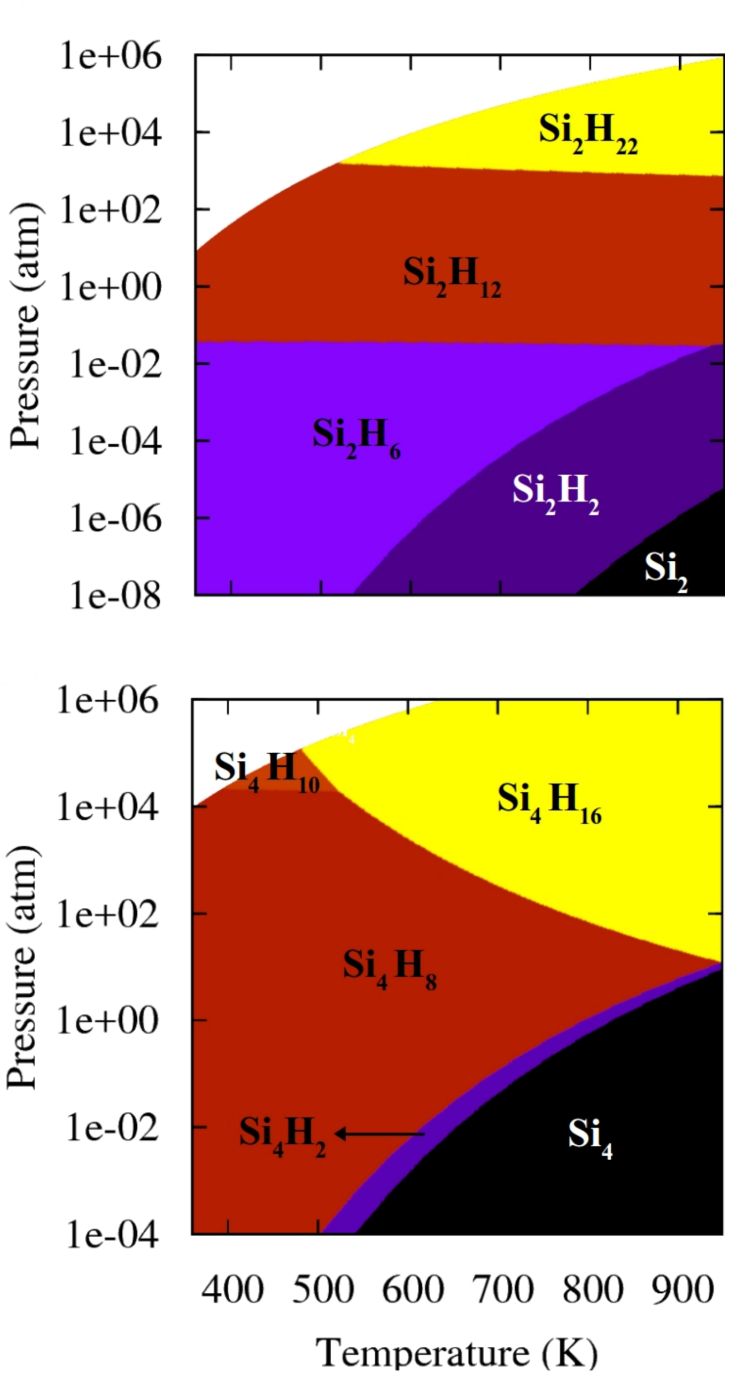
Zhou, Scheffler & LMG, submitted (2019)

$Si_{2/4}H_x$



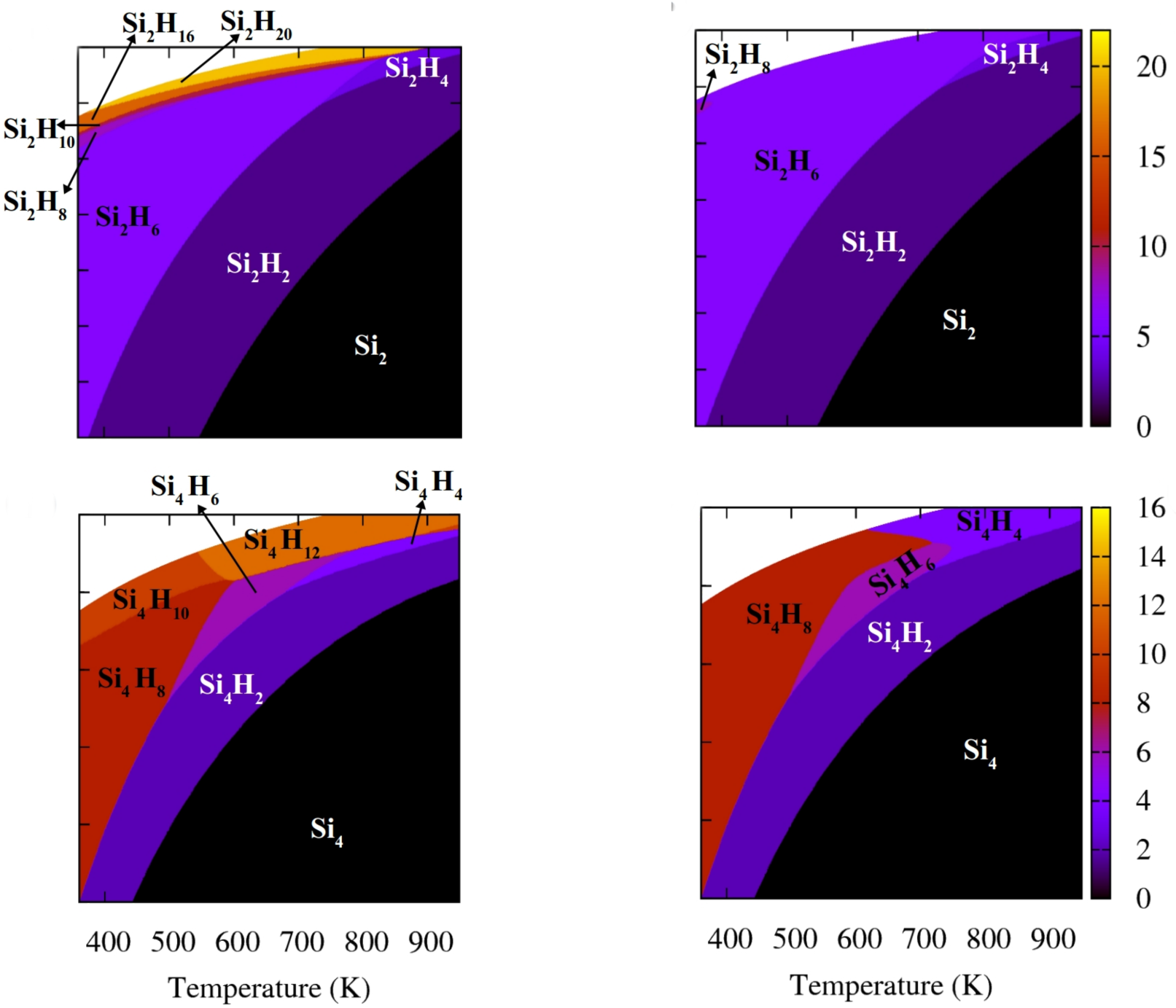
$Si_{2/4}H_x$: full-anharmonic vs harmonic free-energy (aiAT)





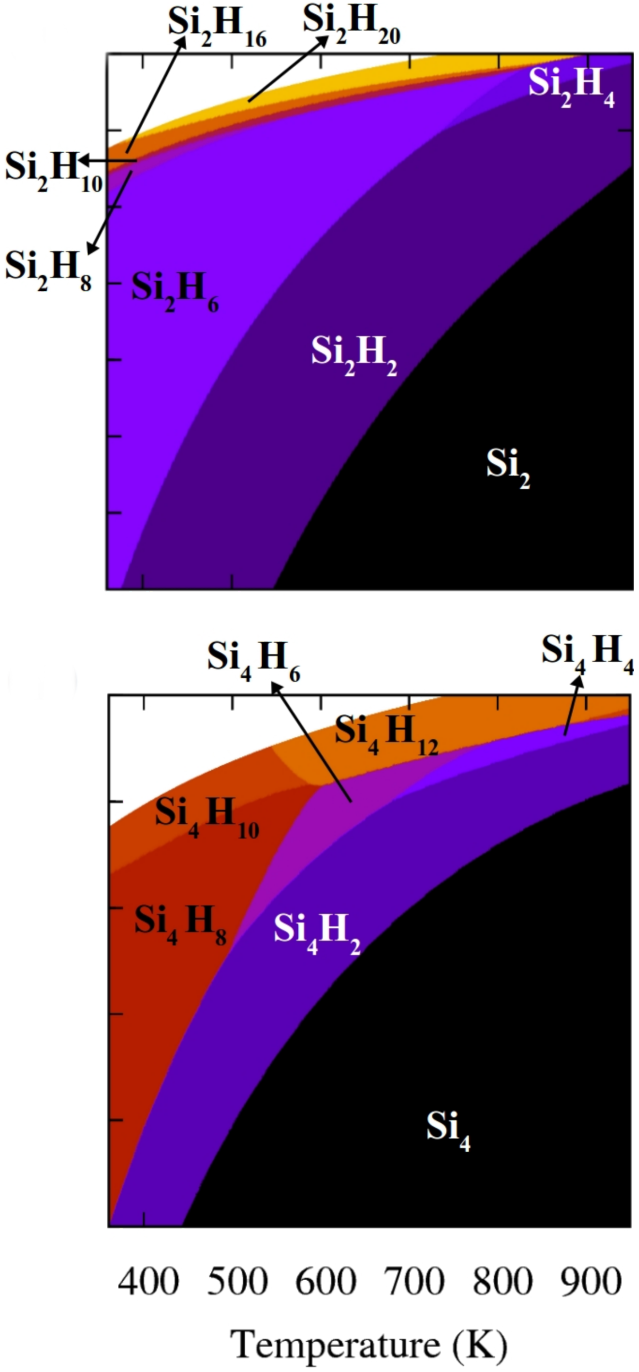
Zhou, Scheffler & LMG, submitted (2019)

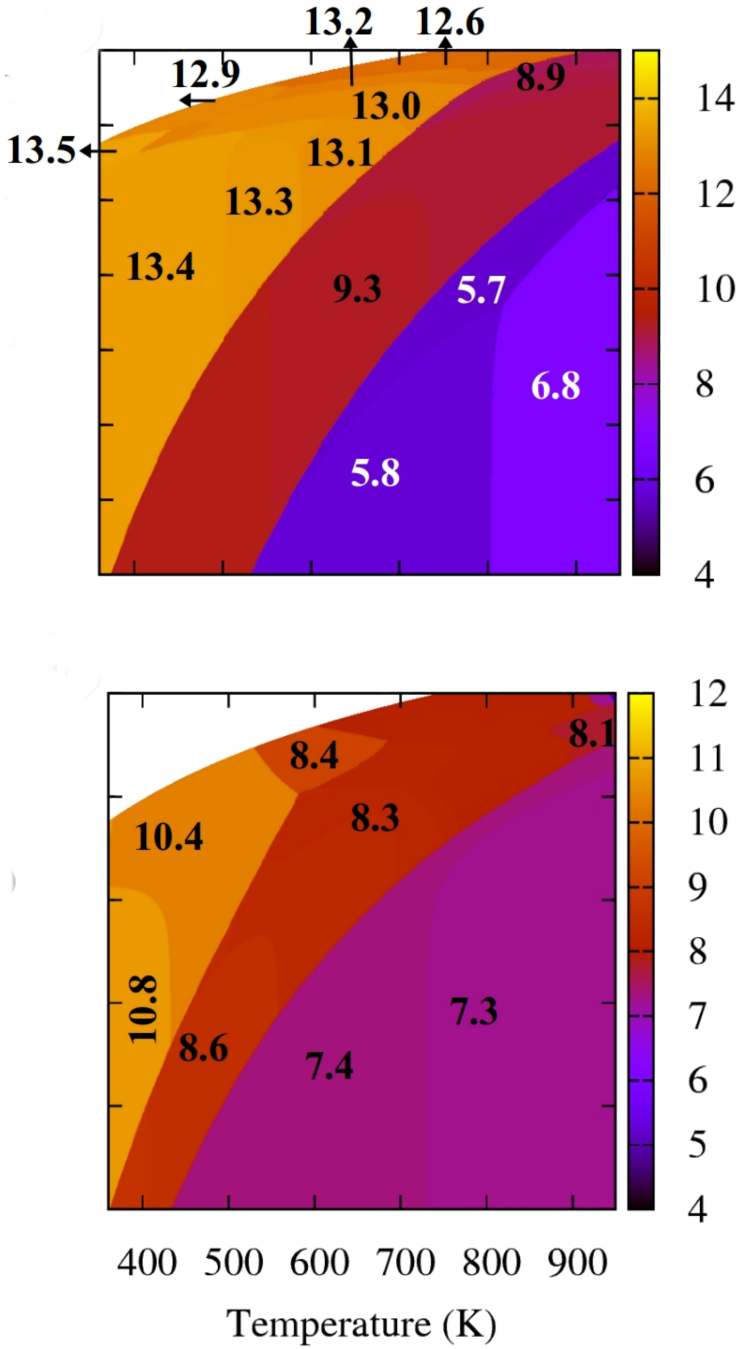
$Si_{2/4}H_x$: all-hydrogens vs chemisorbed-only phase diagrams



Zhou, Scheffler & LMG, submitted (2019)

$Si_{2/4}H_x$: phase diagram of HOMO-LUMO gap





Zhou, Scheffler & LMG, submitted (2019)

Computational free-energy evaluation: the zoo

- Analytic: *ab initio* atomistic thermodynamics

- Canonical sampling: thermodynamic integration

- Canonical sampling: thermodynamic perturbation

- Generalized sampling: biased sampling / biased dynamics

- Unbiased (canonical) sampling → re-weighting techniques

- Direct estimate of the density of energy states

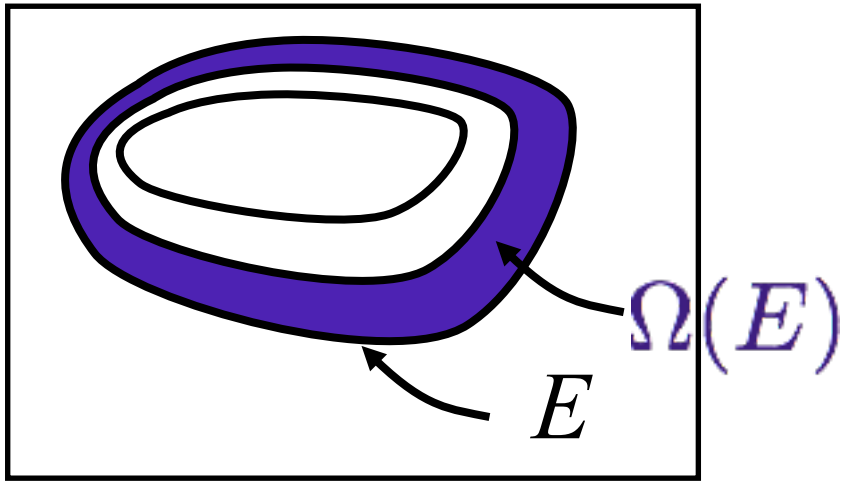
+ Evaluation: Parallel or >>> Serial <<<

The Nested Sampling

Obtaining the partition function

$$Z(N,V,\beta) = Z_{\mathrm{m}}(N,\beta)\int d\mathbf{q}\, e^{-\beta E(\mathbf{q})}$$

$$= Z_{\mathrm{m}}(N,\beta)\int dE\, \Omega(E) e^{-\beta E}$$

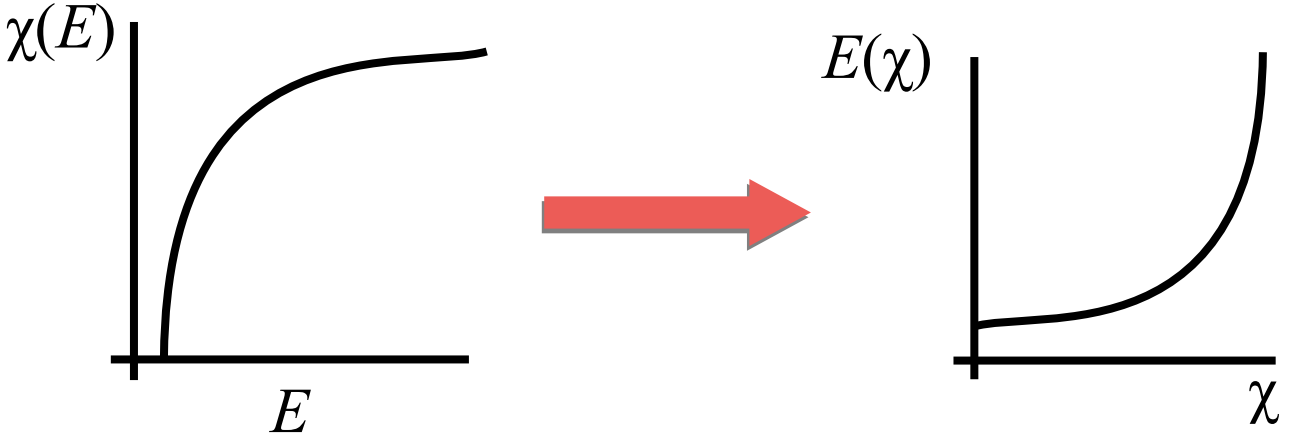


Consider cumulative density

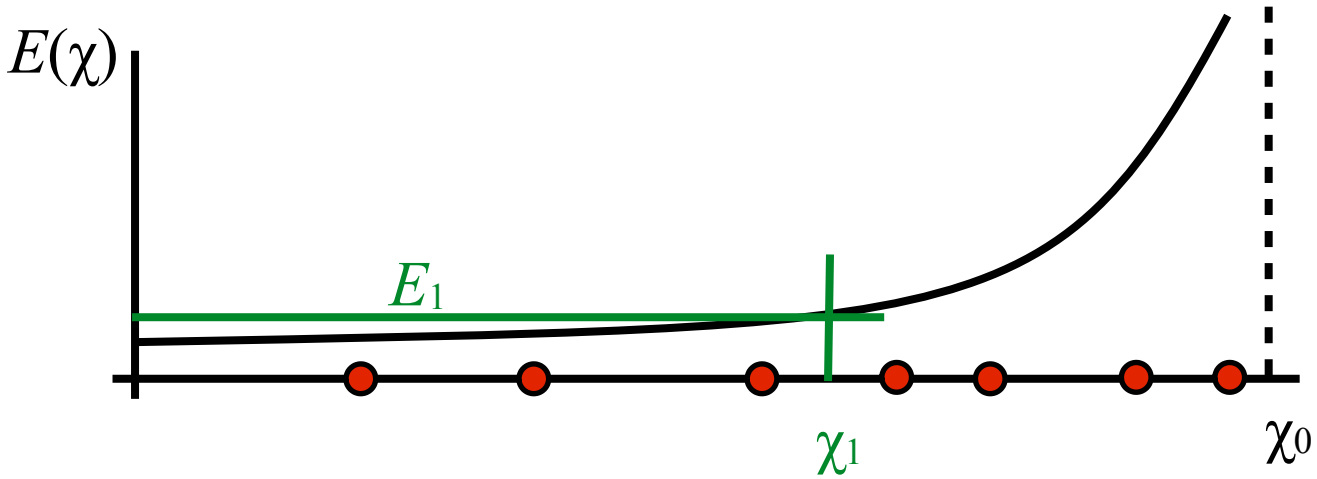
$$\chi(E) = \int_{-\infty}^{E} dE'\, \Omega(E')$$

The Nested Sampling: the main trick

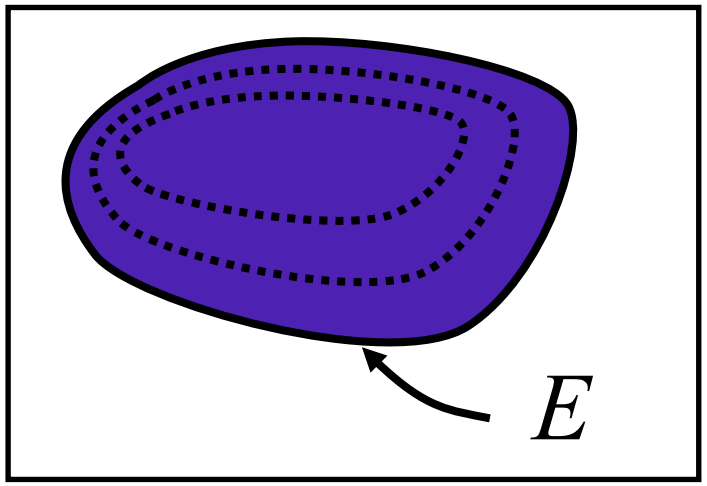
- Instead of $\chi(E)$, compute $E(\chi)$



- At $E = \infty$, we have an ideal gas, $\chi_0 = V^N$

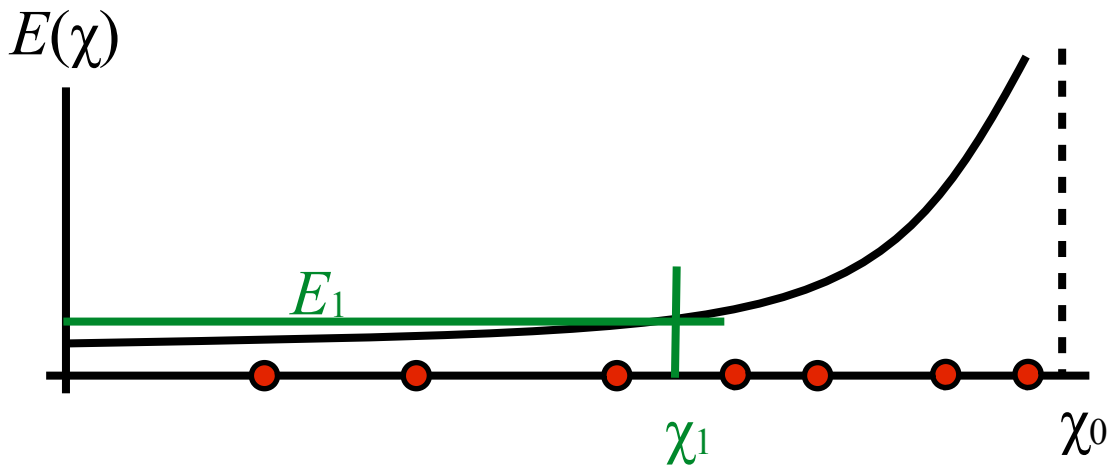


Constrained uniform sampling

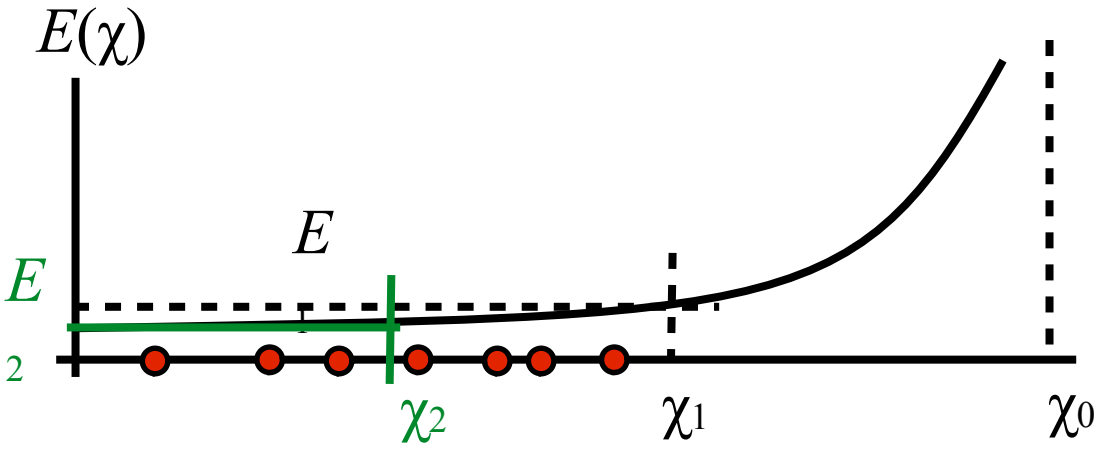


J. Skilling (2006) → G. Csányi (2011)

The Nested Sampling: the main trick



1. obtain K uniform samples such that $E(q) < E_{\text{limit}}$
2. compute median: $E(\chi_1) = E_1$, $\chi_1 \simeq \chi_0/2$, $E_{\text{limit}} \leftarrow E_1$
3. repeat...



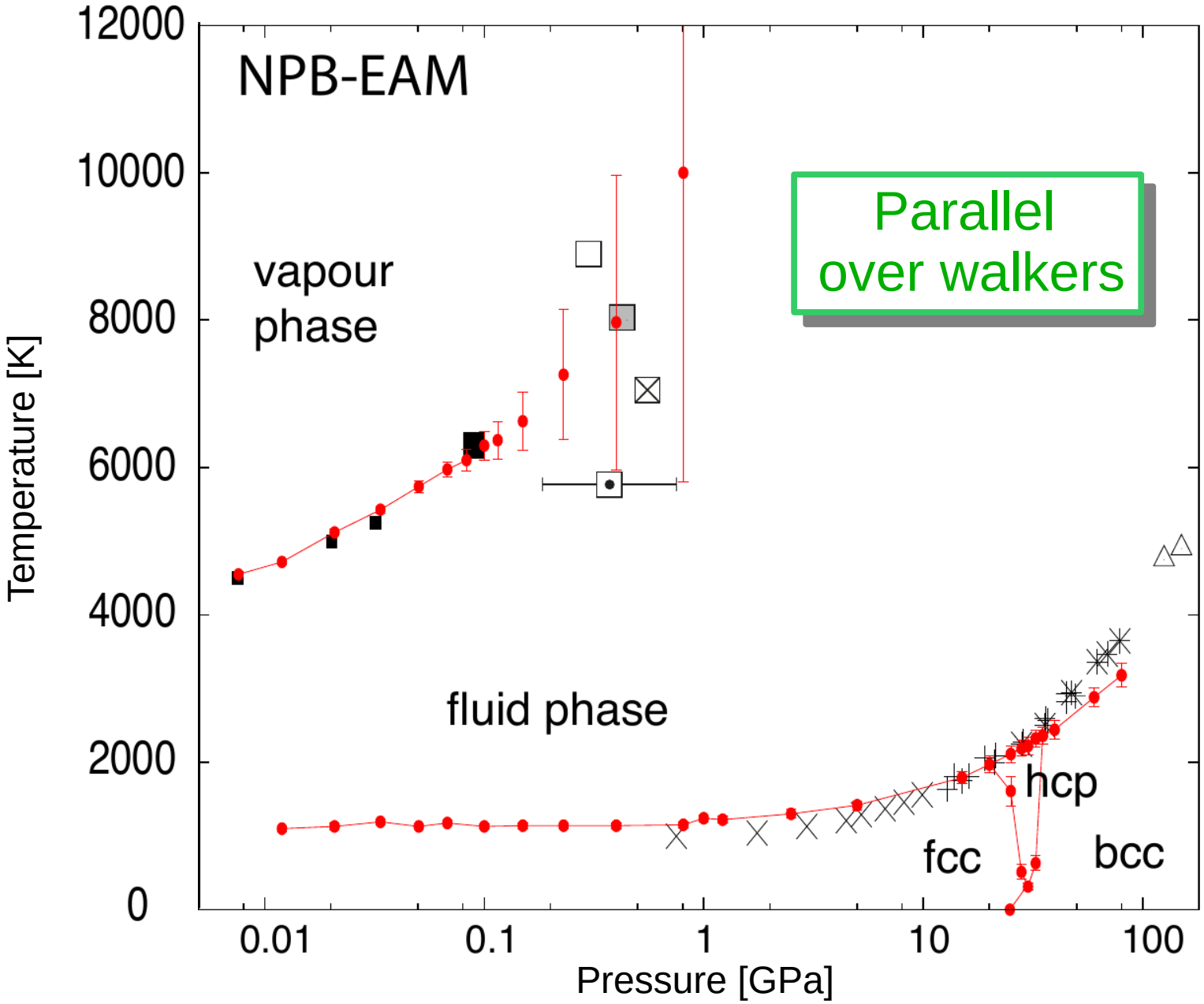
$$\chi_n \approx \chi_0 \alpha^n$$

$$\Omega(E_n) = \chi_0 \left(\alpha^{n-1} - \alpha^n\right)$$

$$Z = Z_{\text{m}} \int dE\, \Omega(E) e^{-\beta E}$$

https://github.com/libAtoms/pymatnest (linked with LAMMPS), Csányi *et al.*

The Nested Sampling: application to (EAM) Aluminum



R. Baldock, …, G. Csányi, PRB **93**, 174108 (2016)

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