From *ab initio* molecular dynamics to statistical mechanics

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Density functional theory and beyond:
Computational materials science for real materials

Held at the Abdus Salam International Centre for Theoretical Physics (ICTP)
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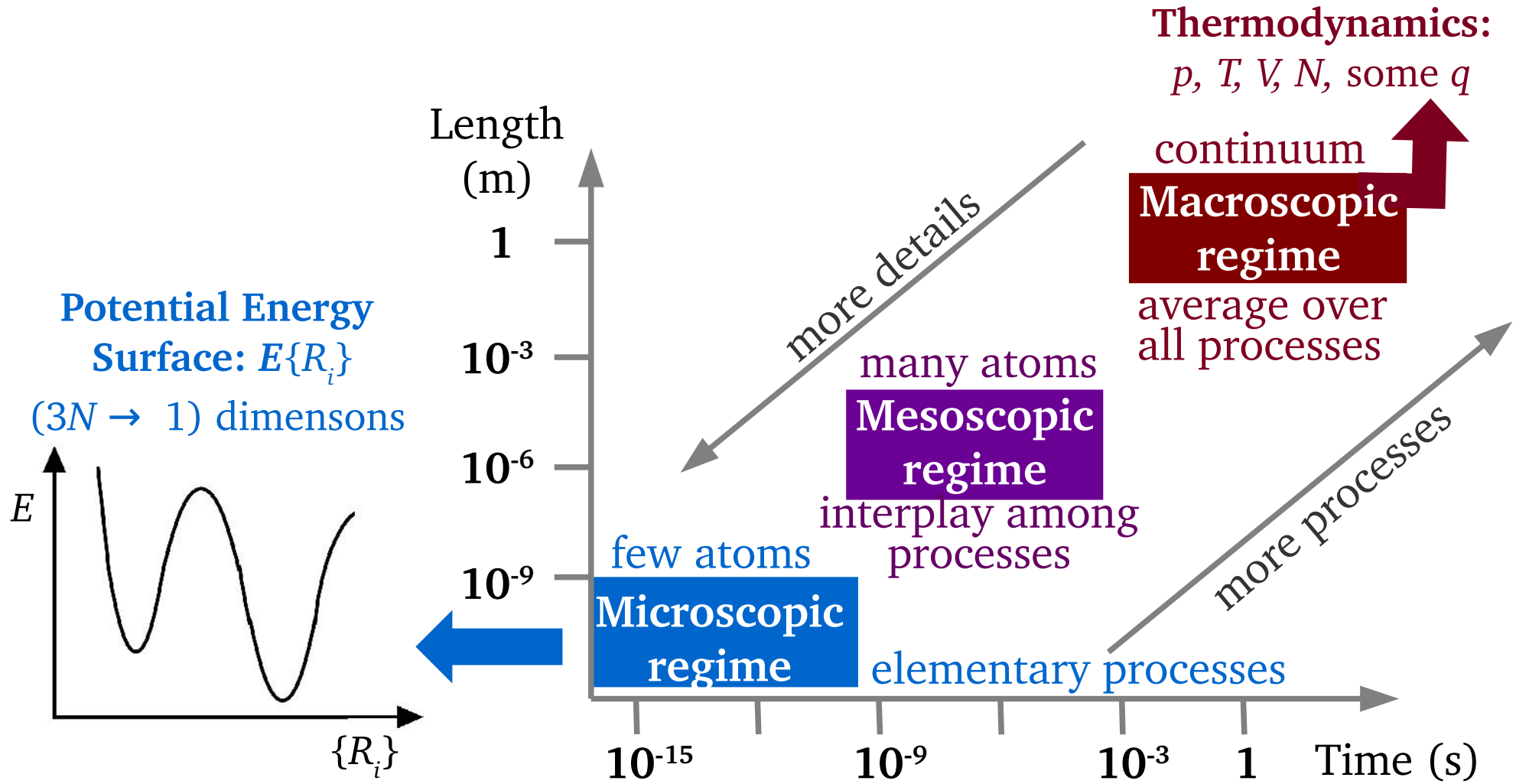
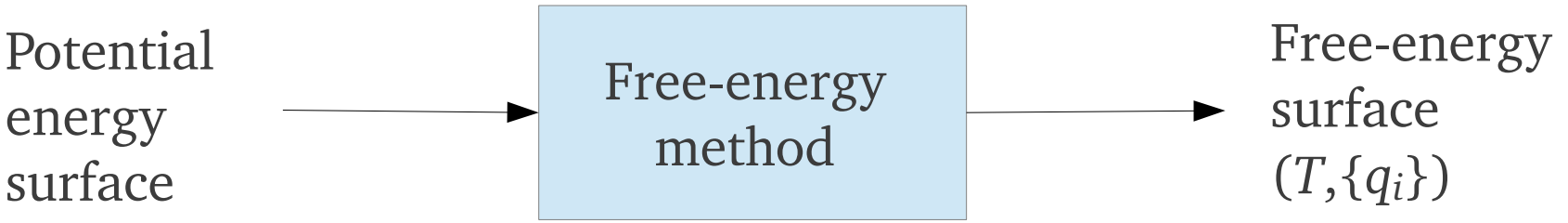
Extending the scale



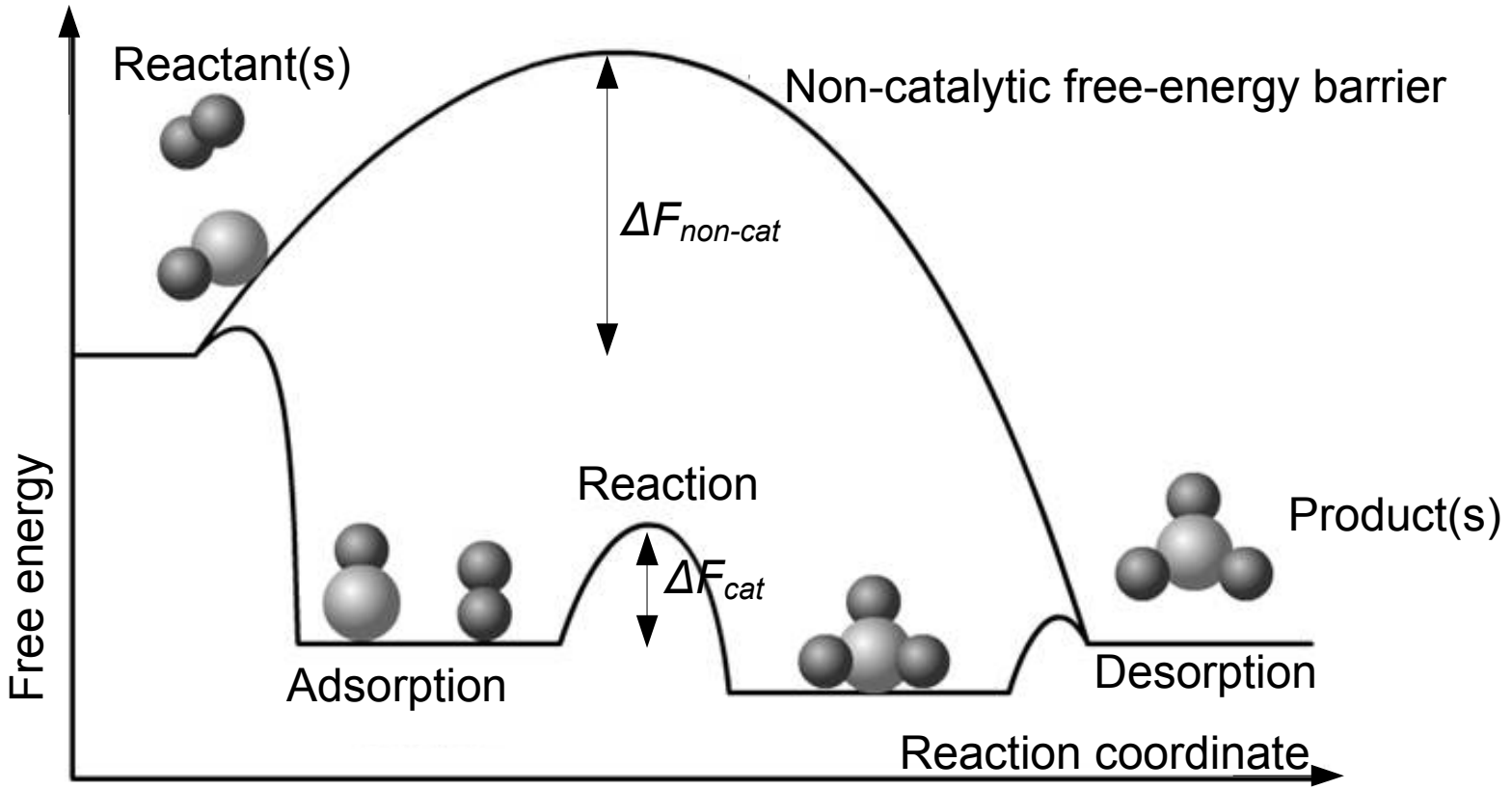
Extending the scale



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

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

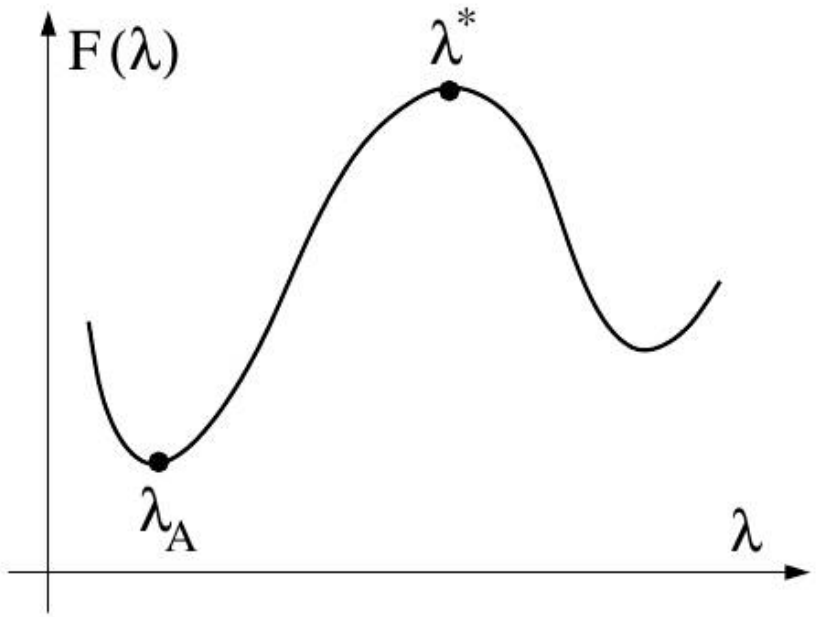
Transition rates from free energy

kinetic prefactor

$$k_{AB}^{TST} = \langle \dot{\lambda}\theta(\dot{\lambda})\rangle_{\lambda=\lambda^*} \frac{e^{-\beta F(\lambda^*)}}{\int_{-\infty}^{\lambda^*} e^{-\beta F(\lambda')} d\lambda'}$$

$$\backsimeq \langle \dot{\lambda}\theta(\dot{\lambda})\rangle_{\lambda=\lambda^*} e^{-\beta(F(\lambda^*)-F(\lambda_A))}$$

$$= \langle \dot{\lambda}\theta(\dot{\lambda})\rangle_{\lambda=\lambda^*} e^{-\beta \Delta F}$$



harmonic TST

$$k_{AB}^{hTST} = \frac{\prod_i^N \nu_i^A}{\prod_i^{N-1} \nu_i^*} e^{-\beta(E^*-E^A)}$$

If $\lambda(r) = r_1$ (one of the Cartesian coordinates), then: $\dot{\lambda} = v_1$

Entropy?

$$S(E) = k_{\mathrm{B}} \ln \Omega(E) \quad \text{density of states} \quad \Omega(E) = \int d\mathbb{Q}\delta(U(\mathbb{Q}) - E)$$

I principle:

$$dU = \delta W + \delta Q$$

I + II principle, reversible transformations:

$$dU = \sum_i X_i dr_i + TdS$$

E.g.: $-PdV$

Everything we do not know:
lack of information

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.

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

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

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

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

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

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

Statistical mechanics: free energy as a probabilistic concept

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

Let's introduce:

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

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

Formal definition of a free energy:

$$\Phi : F_\Phi(\xi) = -k_B T \ln Z_\Phi(\xi) \qquad \mathcal{P}_\Phi(\xi) = \frac{d\xi}{Z} = \frac{d\xi}{Z} e^{-\beta F_\Phi(\xi)}$$

Statistical mechanics, quantities derived from Z

Average energy:

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

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

Heat capacity:

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

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

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

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

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

Statistical mechanics, quantities derived from Z

Evaluation of pressure

$$L = V^{1/3}$$
$$r_i = L s_i$$

$$Z = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\boldsymbol{r}^N e^{-\beta U(\boldsymbol{r}^N)} = \frac{V^N}{\Lambda^{3N} N!} \int_0^1 \cdots \int_0^1 \mathrm{d}\boldsymbol{s}^N e^{-\beta U(\boldsymbol{s}^N, L)}$$

$$P = k_B T \frac{\partial \ln Z}{\partial V}\bigg|^{T,N} = k_B T \frac{\partial \ln V^N}{\partial V} + k_B T \frac{\partial}{\partial V} \ln \int_0^1 \cdot\cdot \int_0^1 dS^N e^{-\beta U}$$

$$P = \frac{N k_B T}{V} - \left\langle \frac{1}{3V} \sum_i r_i \frac{\partial U}{\partial r_i} \right\rangle = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_i r_i f_i \right\rangle$$

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?

$$A(q(\boldsymbol{r}^N);\boldsymbol{r}^N(0),\boldsymbol{p}^N(0),t) \rightarrow \overline{A(q)} = \lim_{t\rightarrow\infty}\frac{1}{t}\int_0^t \mathrm{d}t' A(q,t')$$

$$= \frac{\sum_{\text{initial conditions}}\left(\lim_{t\rightarrow\infty}\frac{1}{t}\int_0^t \mathrm{d}t' A(q(\boldsymbol{r}^N);\boldsymbol{r}^N(0),\boldsymbol{p}^N(0),t')\right)}{\text{number of initial conditions}}$$

$$\left[\frac{\sum_{\text{initial conditions}} f\left(\mathbf{r}^N(0),\mathbf{p}^N(0)\right)}{\text{number of initial conditions}} \rightarrow \frac{\int_E f\left(\mathbf{r}^N(0),\mathbf{p}^N(0)\right)}{\Omega(N,V,E)}\right]$$

$$= \lim_{t\rightarrow\infty}\frac{1}{t}\int_0^t \mathrm{d}t' \left\langle A(q(\boldsymbol{r}^N);\boldsymbol{r}^N(0),\boldsymbol{p}^N(0),t)\right\rangle_{NVE} = \left\langle A(q)\right\rangle_{NVE}$$

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

Theoretical 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

- Evaluation: Parallel (over densities) or >>> Serial <<<

Free energy: “physical”-path thermodynamic integration

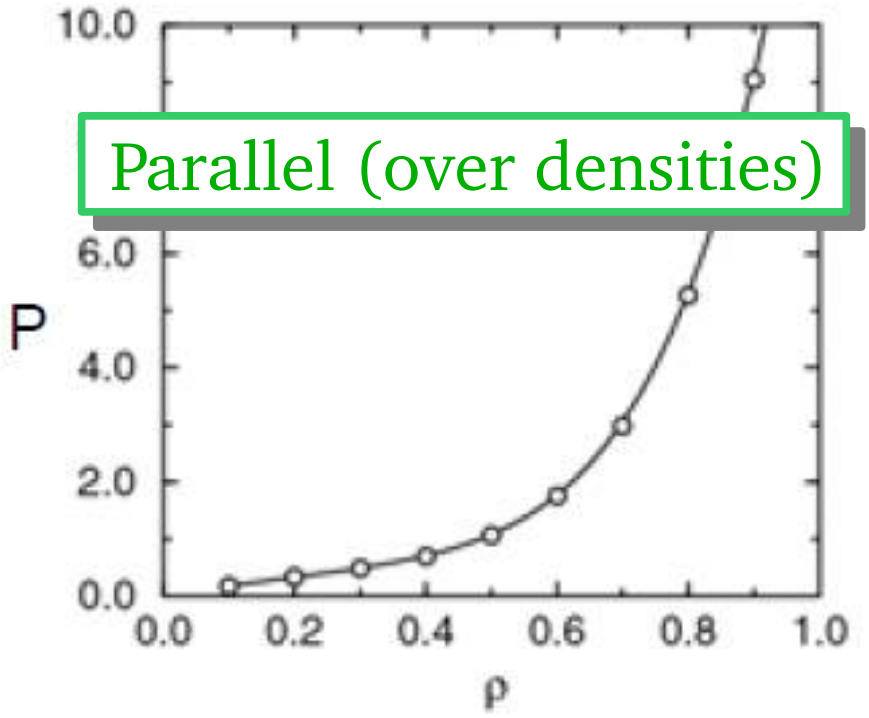
How are free energies measured experimentally?

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

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

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

$V_0 \to \infty$: ideal gas



Free energy: “unphysical”-path thermodynamic integration

Let us assume a mixed potential: $U = (1-\lambda)U_0 + \lambda U_1$

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

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

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

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

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)

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

Case study: phase diagram of pure carbon

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

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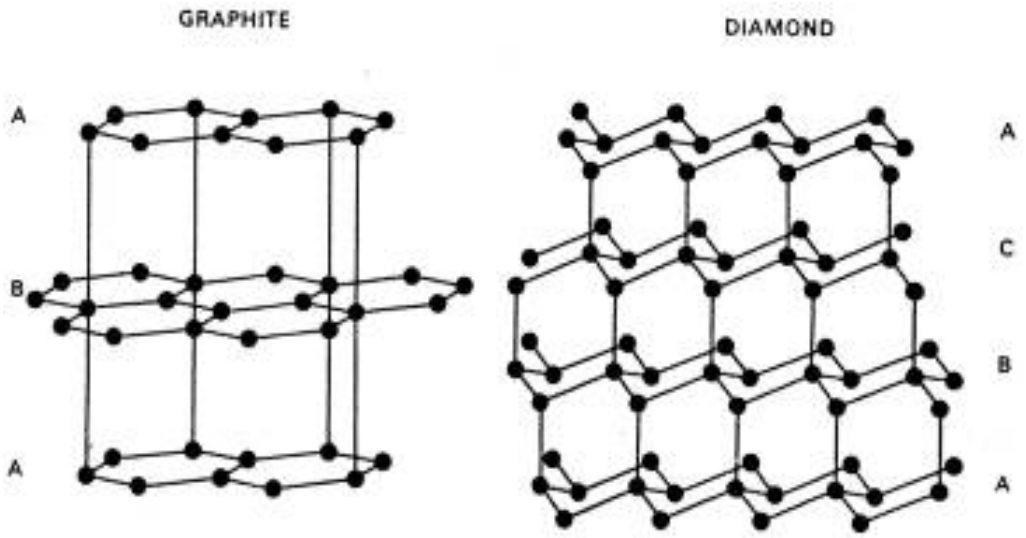
\end{aligned}
$$



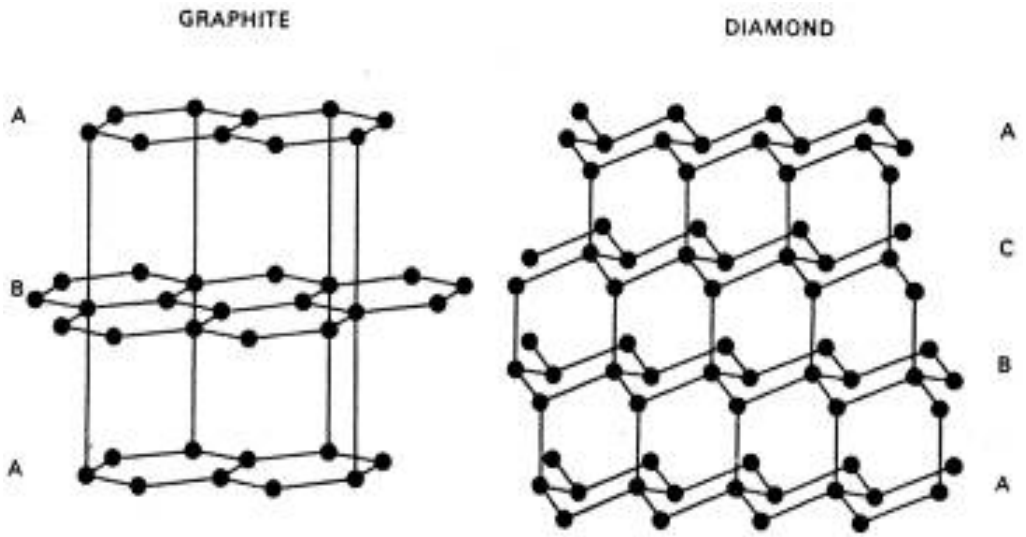
Case study: phase diagram of pure carbon

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

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

Reference phases
Liquid: Lennard Jones

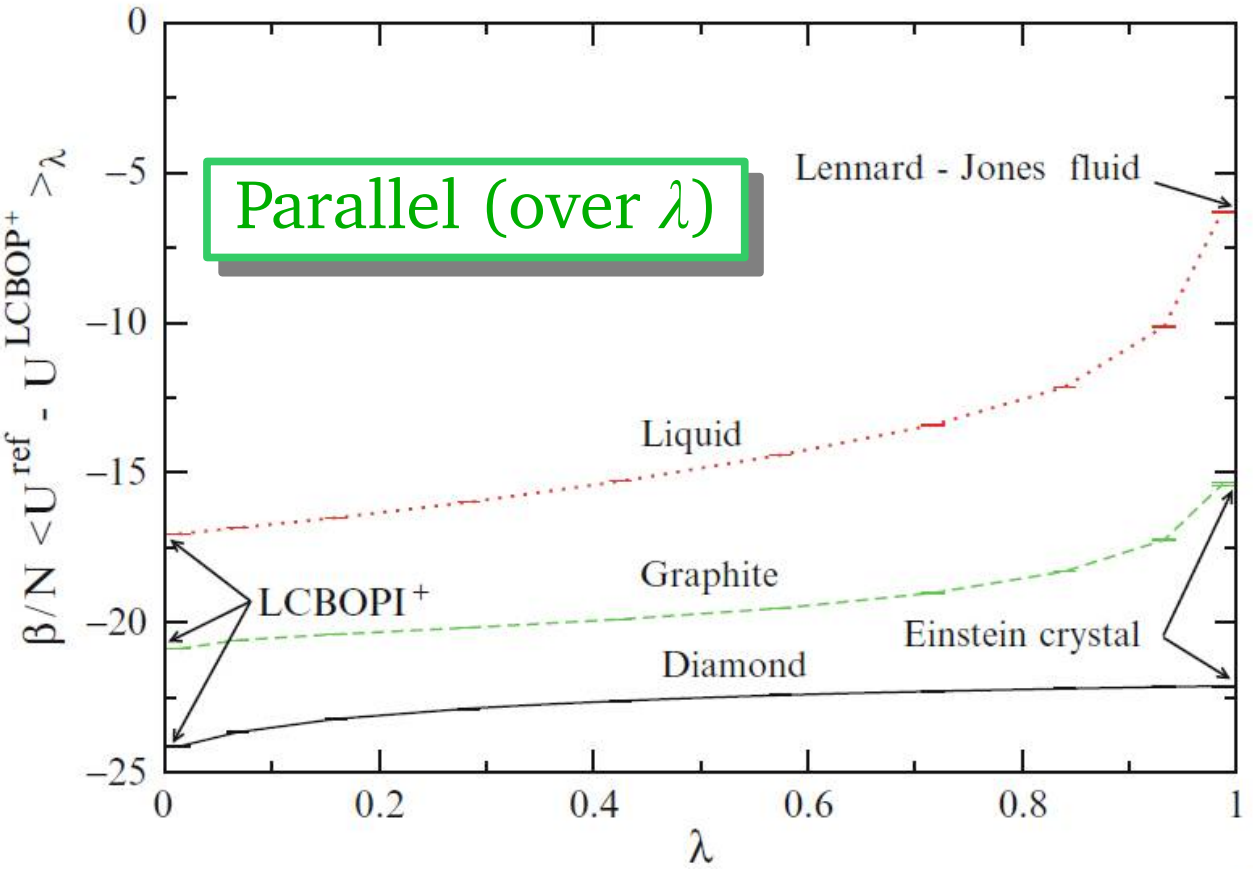
$$U^{LJ} = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

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

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

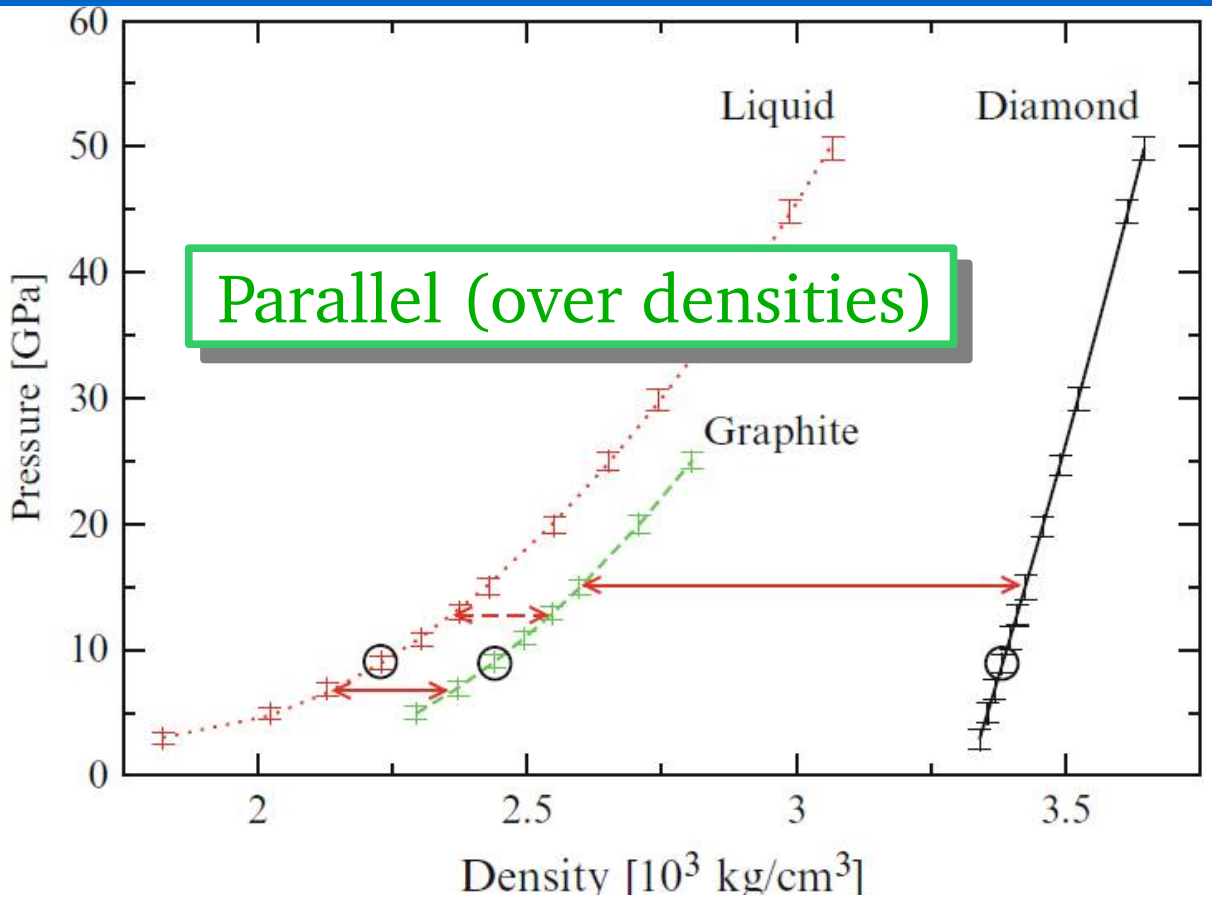
How to choose σ, ε ?
Maximum resemblance between
LJ liquid and “real”:
alignment radial distribution function peaks

Case study: λ–ensemble sampling and integration



$$F^{\Xi} = F^{\mathrm{ref}} + \Delta F^{\mathrm{ref}\to\Xi} = F^{\mathrm{ref}} + \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda = F^{\mathrm{ref}} + \int_0^1 \mathrm{d}\lambda \left\langle U^{\mathrm{ref}} - U^{\Xi} \right\rangle_\lambda$$

Case study: integration of $P(\rho)$ equations of state

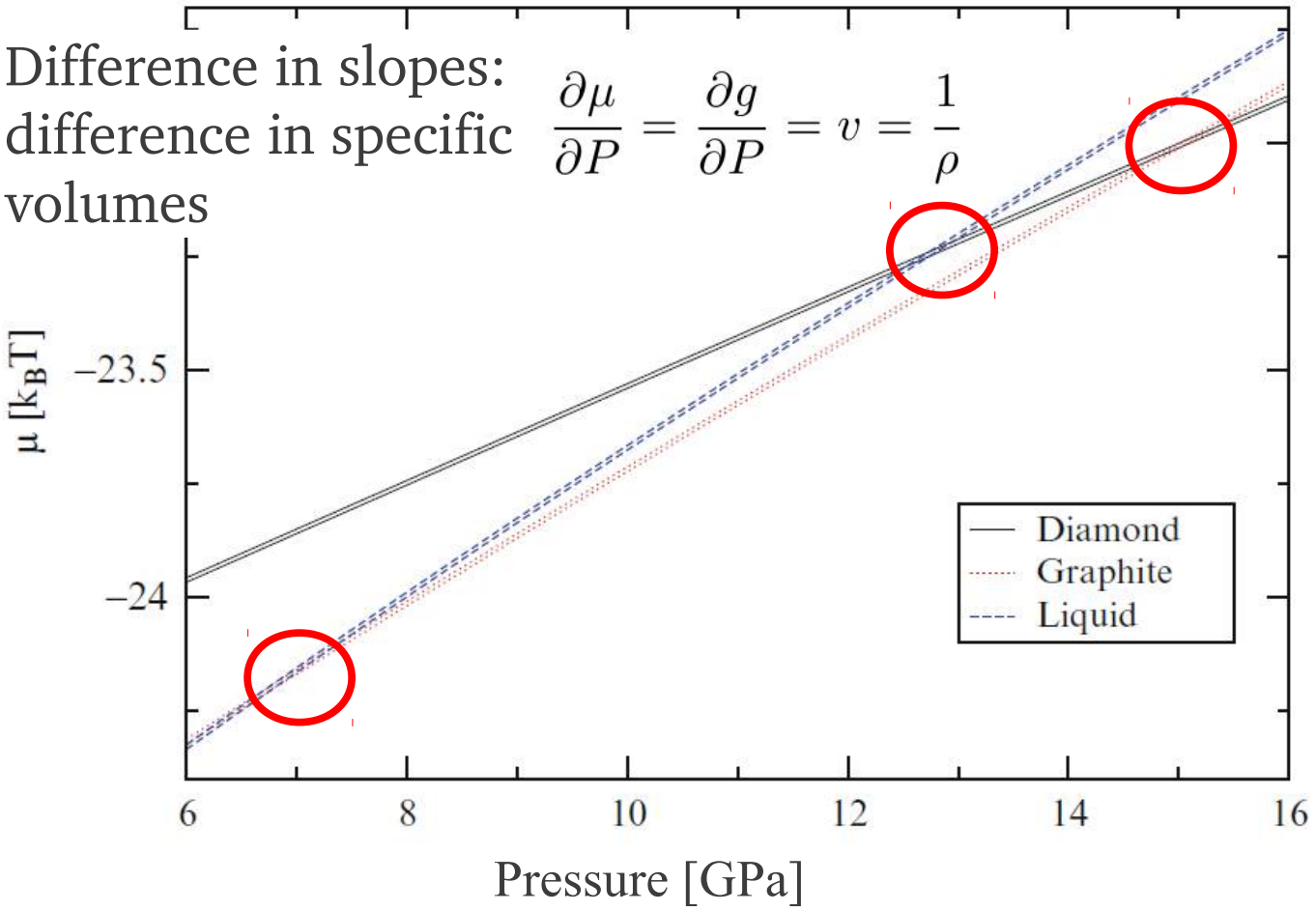


$$P(\rho) = a + b\rho + c\rho^2 \longrightarrow \beta\mu(\rho) = \frac{\beta F^{\Xi}}{N} + \beta\left[\frac{a}{\rho^{\Xi}} + b\ln\frac{\rho}{\rho^{\Xi}} + b + c\left(2\rho - \rho^{\Xi}\right)\right]$$

Case study: equating Gibbs free energies

Difference in slopes: difference in specific volumes

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



And then: Gibbs-Duhem integration

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

$T\Delta s$

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

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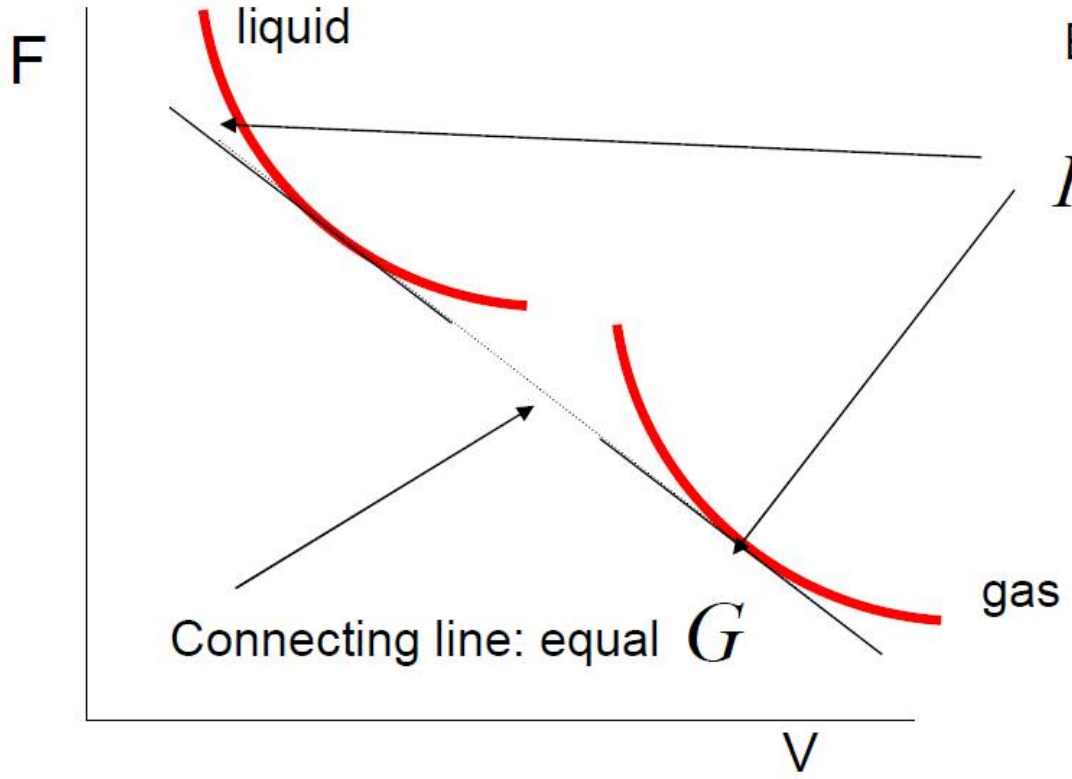
Alternative method for finding phase coexistence via $F(V)$

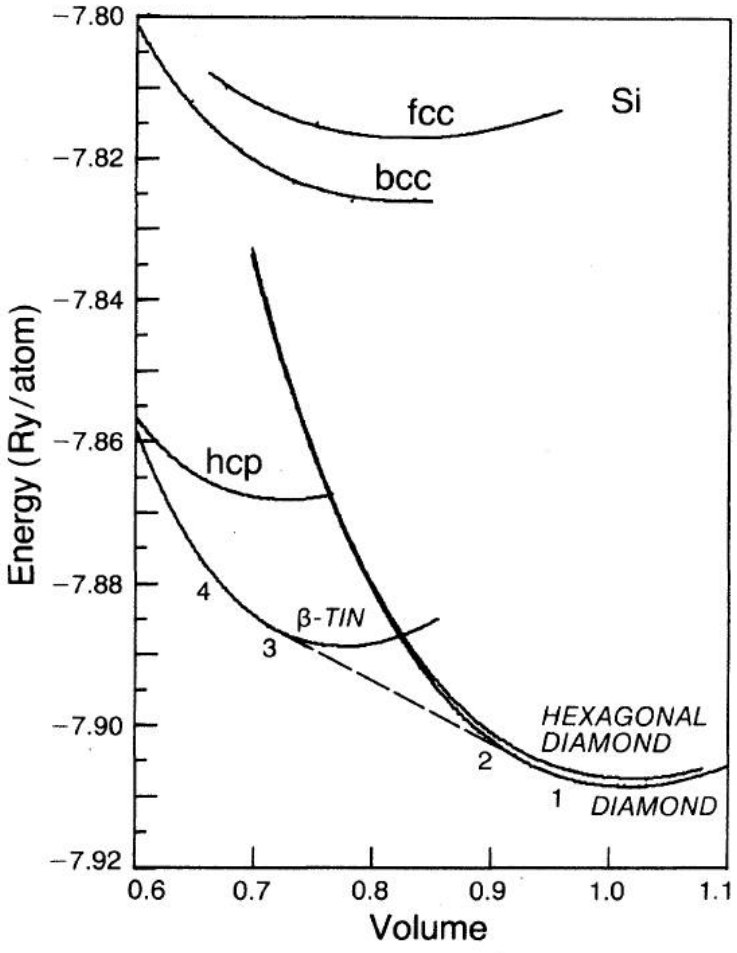
Common tangent construction



Equal tangents

$$P = -\left(\frac{\partial F}{\partial V}\right)_{n,T}$$

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

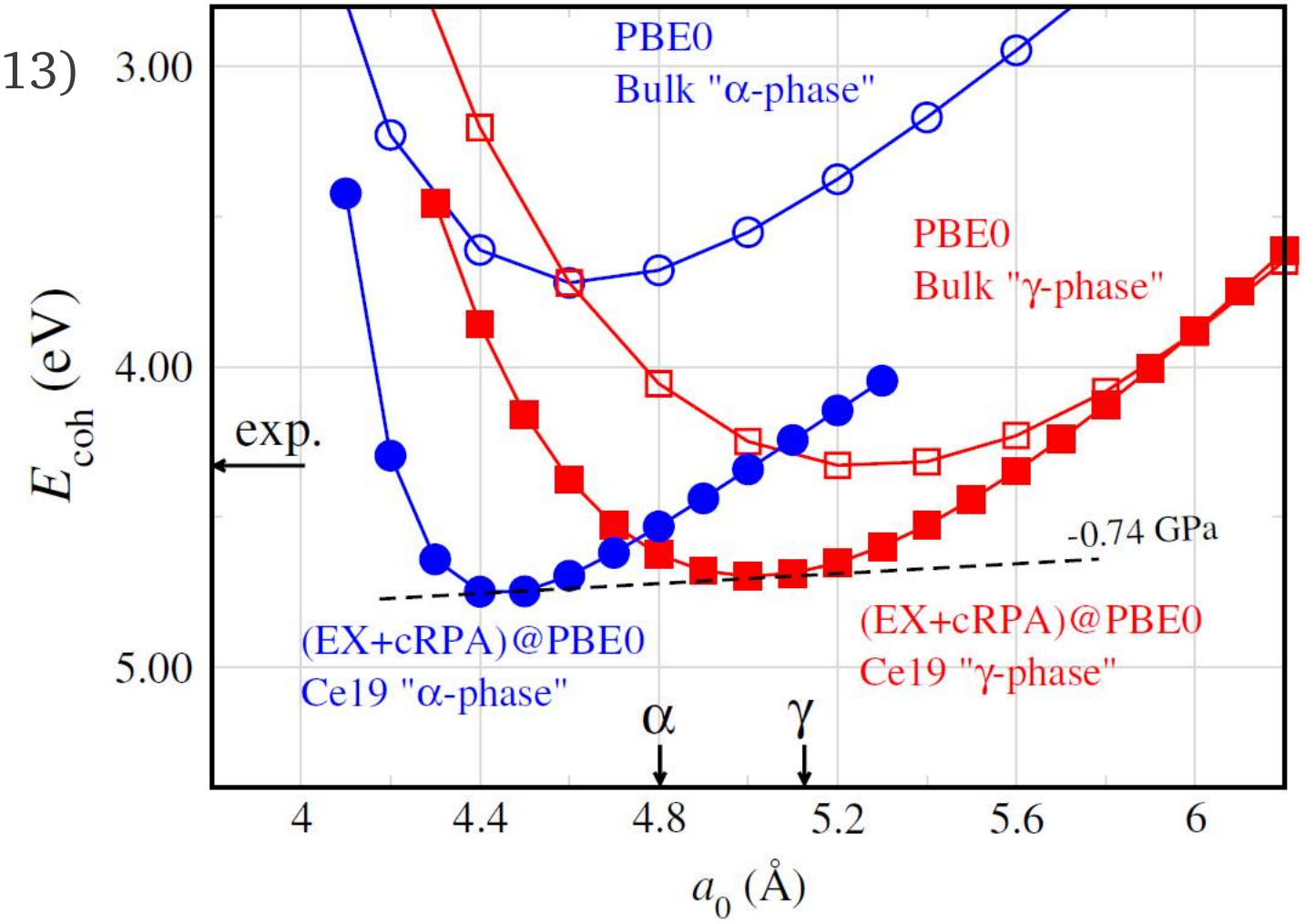


Yin and Cohen, PRL 1980
DFT with LDA functional

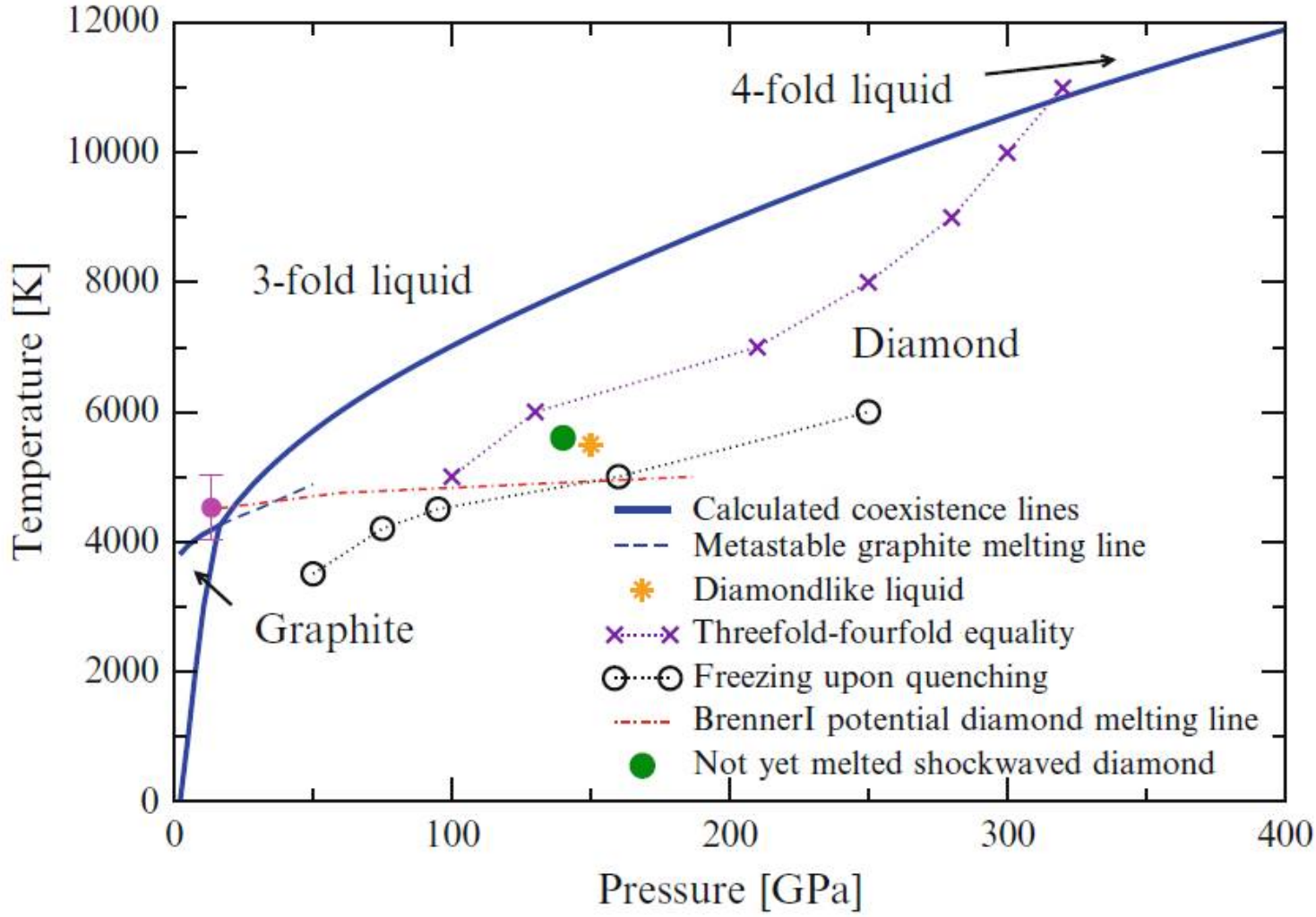
	$V_t{}^d$	$V_t{}^\beta$	$V_t{}^\beta / V_t{}^d$	P_t (kbar)
Calculation	0.928	0.718	0.774	99
Experiment[a]	0.918	0.710	0.773	125
Deviation	1.1%	1.1%	0.1%	−20%

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

Casadei *et al.* PRL (2013)



Carbon phase diagram



LMG *et al.* PRL 2005

Sparing CPU time: adiabatic switch

Start again from two systems:

$$H_0 = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \qquad H_1(\lambda) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \lambda U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$F_0(T_0) = -k_B T_0 \ln\left[\int_V d^{3N} r \exp(-U_0/k_B T_0)\right] + 3Nk_B T_0 \ln\Lambda(T_0)$$

$$F_1(T_0, \lambda) = -k_B T_0 \ln\left[\int_V d^{3N} r \exp(-U_0/k_B T)\right] + 3Nk_B T_0 \ln\Lambda(T_0)$$

$$\frac{U_1}{k_B T_0} = \frac{\lambda U_0}{k_B T_0} = \frac{U_0}{k_B T}$$

$$T = \frac{T_0}{\lambda}$$

$$\frac{F_0(T)}{T} = \frac{F_1(T_0, \lambda)}{T_0} + \frac{3}{2} N k_B \ln\frac{T_0}{T}$$

Sparing CPU time: adiabatic switch

$$\frac{F_0(T)}{T} = \frac{F_1(T_0,\lambda)}{T_0} + \frac{3}{2}Nk_B \ln\frac{T_0}{T}$$

time ?!?

reversible?

$$\Delta F_1(\lambda(t),\lambda(0)) = \int_0^t dt' \frac{d\lambda}{dt}\bigg|_{t'} U_0(\mathbf{r}_1(t'),\ldots,\mathbf{r}_N(t')) \equiv W(t)$$

$$\frac{F_0(T(t))}{T(t)} = \frac{F_0(T(0))}{T(0)} + \frac{W(t)}{T_0} - \frac{3}{2}Nk_B \ln\frac{T(t)}{T(0)} \qquad \begin{aligned} T(t) &= T_0/\lambda(t) \\ T(0) &= T_0/\lambda(0) \end{aligned}$$

Sparing CPU time: adiabatic switch

$$\frac{F_0(T(t))}{T(t)} =$$

$$= \frac{F_0(T(0))}{T(0)} + \frac{W(t)}{T_0} - \frac{3}{2} N k_B \ln \frac{T(t)}{T(0)}$$

$$T(t) = T_0/\lambda(t)$$

$$T(0) = T_0/\lambda(0)$$

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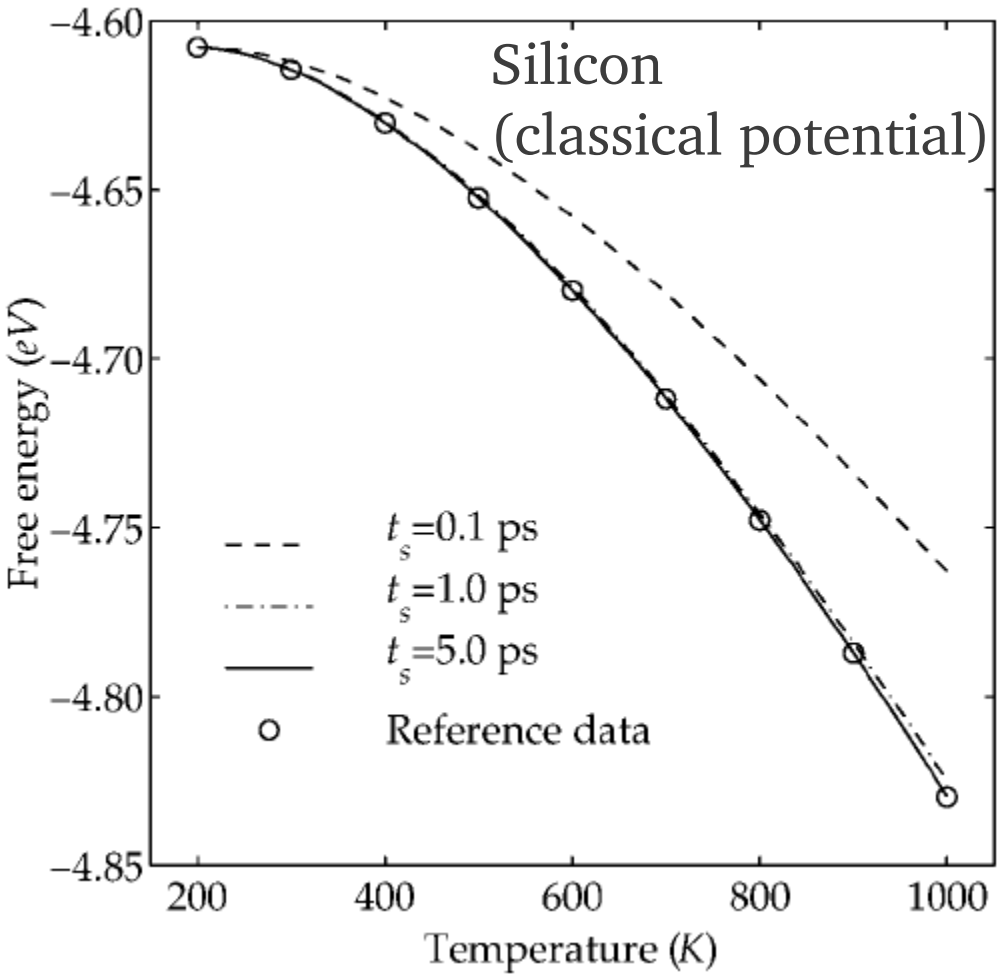
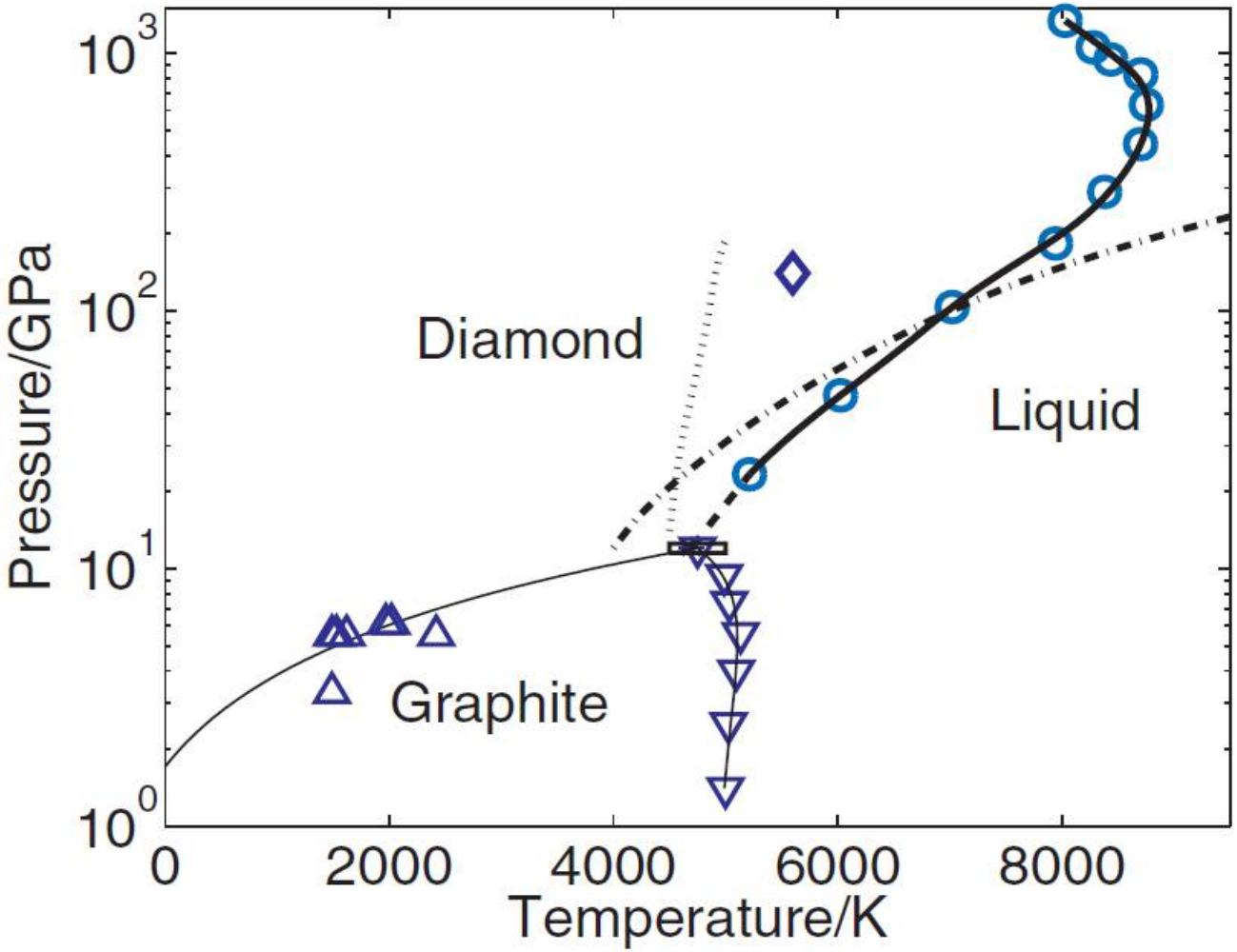


Ab initio diamond melting line



Wang *et al.* PRL **95**, 185701 (2005)

Beyond equilibrium: Jarzynski theorem

$$W_{\mathcal{AB}} = \langle \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0) \rangle_{\mathcal{A}} = \frac{C_N}{Z_{\mathcal{A}}(N,V,T)} \int \mathrm{dx}_0 \, \mathrm{e}^{-\beta \mathcal{H}_{\mathcal{A}}(\mathrm{x}_0)} \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)$$

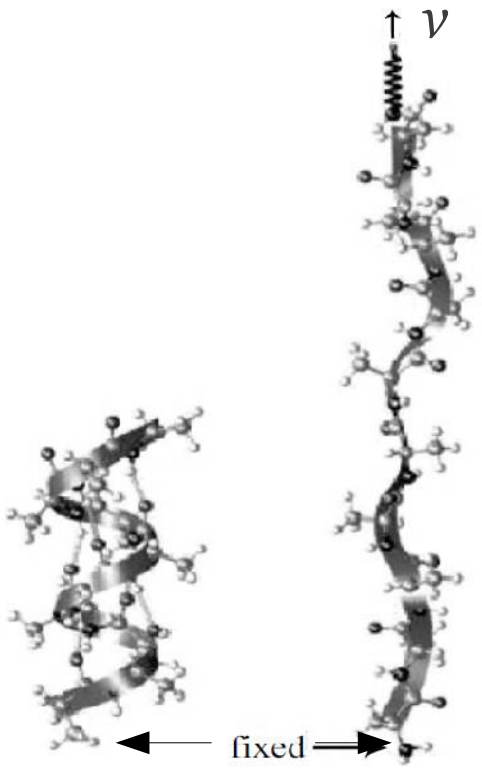
Clausius inequality:

$$\langle \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0) \rangle_{\mathcal{A}} \geq \Delta F_{\mathcal{AB}}$$

Jarzynski equality (1997!)

$$\mathrm{e}^{-\beta \Delta F_{\mathcal{AB}}} = \left\langle \mathrm{e}^{-\beta \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)} \right\rangle_{\mathcal{A}} = \frac{C_N}{Z_{\mathcal{A}}(N,V,T)} \int \mathrm{dx}_0 \, \mathrm{e}^{-\beta \mathcal{H}_{\mathcal{A}}(\mathrm{x}_0)} \mathrm{e}^{-\beta \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)}$$

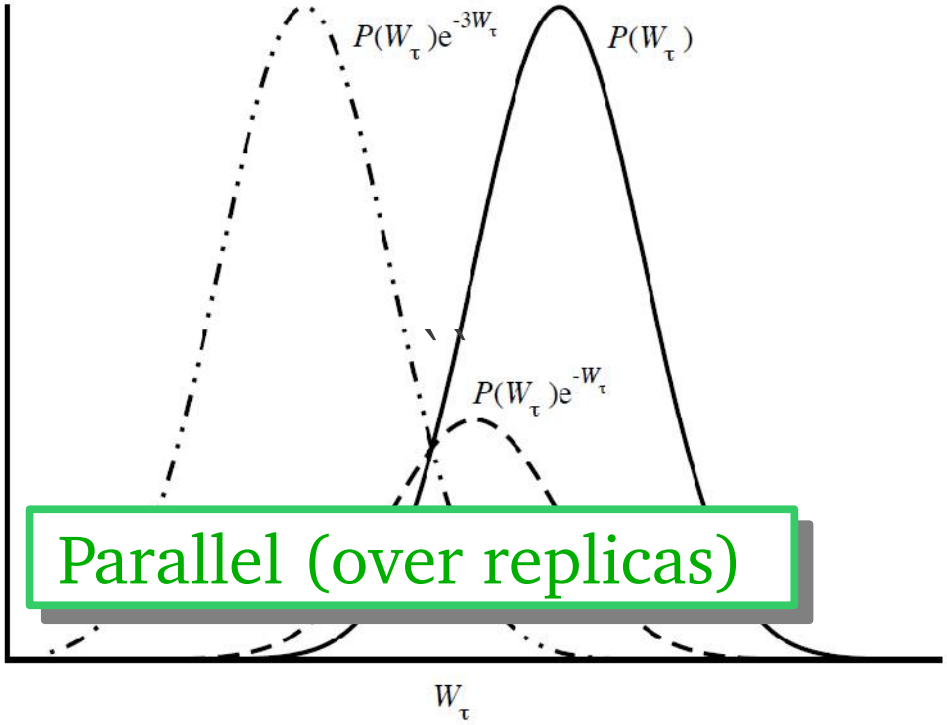
Jarzynski theorem: steered dynamics



$$U(\mathbf{r}_1, ..., \mathbf{r}_N, t) = U_0(\mathbf{r}_1, ..., \mathbf{r}_N) + \frac{1}{2}\kappa \left(|\mathbf{r}_1 - \mathbf{r}_N| - r_{\text{eq}} - vt\right)^2$$

$$\left\langle e^{-\beta W_\tau} \right\rangle = \int dW_\tau P(W_\tau) e^{-\beta W_\tau}$$

Inefficient because:



Parallel (over replicas)

Better estimated with the cumulant:

$$\ln \left\langle e^{-\beta W_\tau} \right\rangle \approx -\beta \langle W_\tau \rangle + \frac{\beta^2}{2} \left(\langle W_\tau^2 \rangle - \langle W_\tau \rangle^2 \right)$$

Summary of thermodynamic integrations

- Thermodynamic integration, from reference to state/system of interest along “physical” or “unphysical” paths
- Construction of accurate phase diagrams
- Speeding up: adiabatic switch
- Faster, non equilibrium: Jarzynski equality

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

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

$$\mathcal{P}_0(\Delta U) = \frac{\int d\boldsymbol{r}^N e^{-\beta U_0}\delta(U_1-U_0-\Delta U)}{\int d\boldsymbol{r}^N e^{-\beta U_0}}$$

$$\mathcal{P}_1(\Delta U) = \frac{\int d\boldsymbol{r}^N e^{-\beta U_1}\delta(U_1-U_0-\Delta U)}{\int d\boldsymbol{r}^N e^{-\beta U_1}}$$

$$\mathcal{P}_1(\Delta U) = \frac{\int d\boldsymbol{r}^N e^{-\beta(U_1-U_0)}e^{-\beta U_0}\delta(U_1-U_0-\Delta U)}{\int d\boldsymbol{r}^N e^{-\beta U_1}}$$

$e^{-\beta(U_1-U_0)}e^{-\beta U_0} \rightarrow 1$

Thermodynamic perturbation

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

$$\mathcal{P}_1(\Delta U) = \frac{\int d\boldsymbol{r}^N e^{-\beta(U_1-U_0)}e^{-\beta U_0}\delta(U_1-U_0-\Delta U)}{\int d\boldsymbol{r}^N e^{-\beta U_1}}$$

$$= \frac{Z_0}{Z_1}e^{-\beta\Delta U}\frac{\int d\boldsymbol{r}^N e^{-\beta U_0}\delta(U_1-U_0-\Delta U)}{Z_0}$$

$$= \frac{Z_0}{Z_1}e^{-\beta\Delta U}\mathcal{P}_0(\Delta U) = e^{\beta(\Delta F-\Delta U)}\mathcal{P}_0(\Delta U)$$

Thermodynamic perturbation

$$\mathcal{P}_1(\Delta U) = e^{\beta(\Delta F - \Delta U)}\mathcal{P}_0(\Delta U)$$

$$\ln \mathcal{P}_1(\Delta U) = \beta(\Delta F - \Delta U) + \ln \mathcal{P}_0(\Delta U)$$

$$\left.\begin{aligned} f_0(\Delta U) &\equiv \ln \mathcal{P}_0(\Delta U) - 0.5\beta\Delta U \\ f_1(\Delta U) &\equiv \ln \mathcal{P}_1(\Delta U) - 0.5\beta\Delta U \end{aligned}\right\} \beta\Delta F = f_1(\Delta U) - f_0(\Delta U)$$

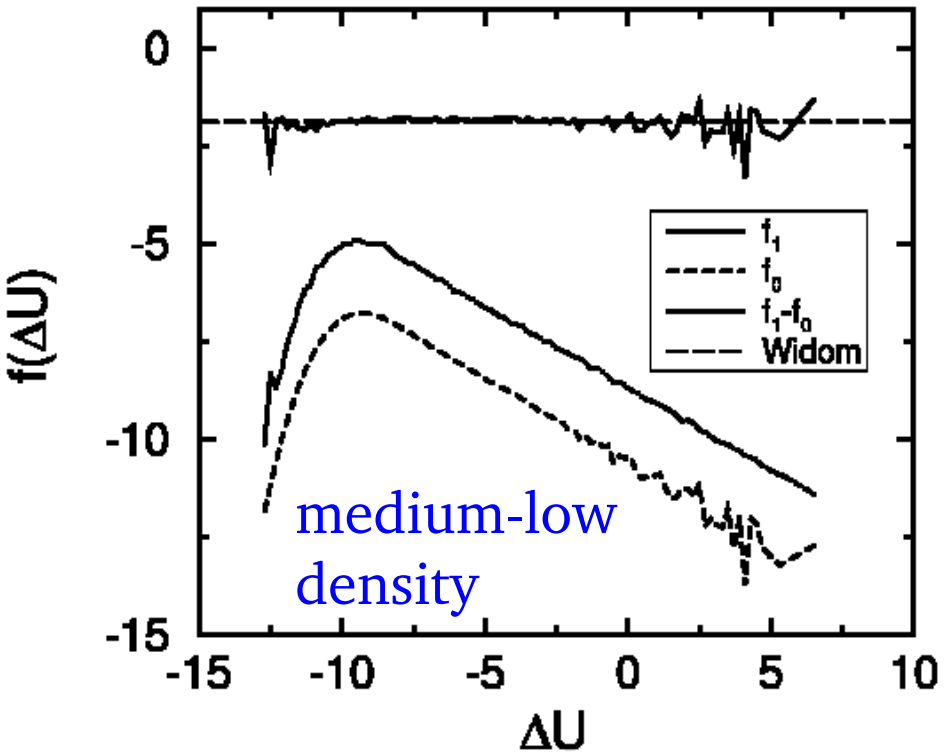
$$\left.\begin{aligned} f_0(\Delta U) &= C_0 + a\Delta U + b\Delta U^2 + c\Delta U^3 \\ f_1(\Delta U) &= C_1 + a\Delta U + b\Delta U^2 + c\Delta U^3 \end{aligned}\right\} \beta\Delta F = C_1 - C_0$$

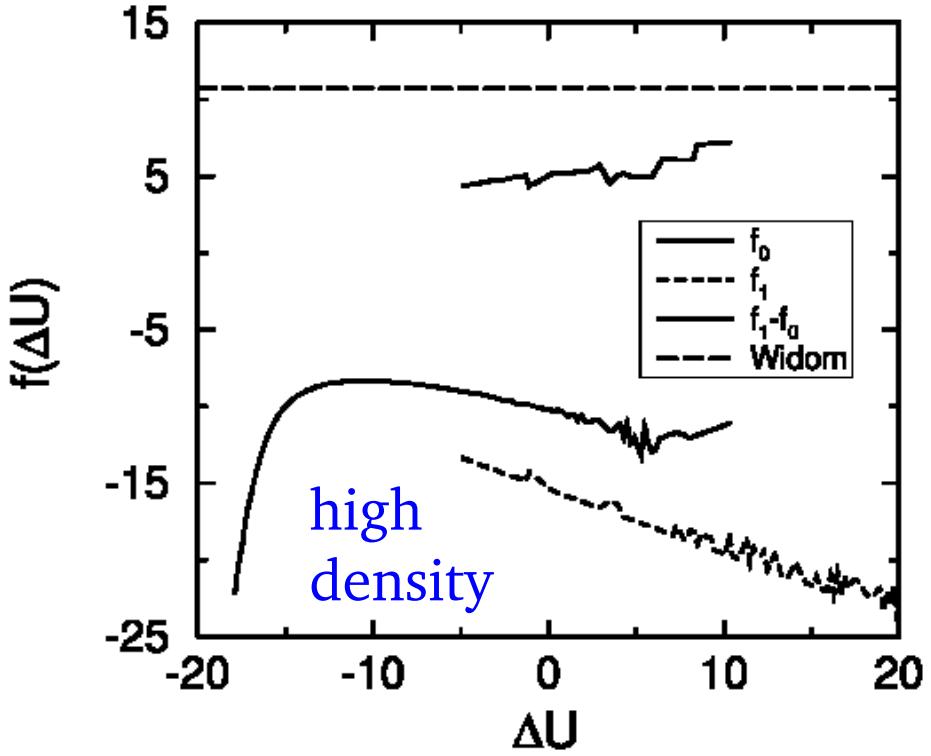
Parallel (over systems)

Thermodynamic perturbation

System 0: N-1 interacting particles, 1 ideal gas article

System 1: N interacting particles





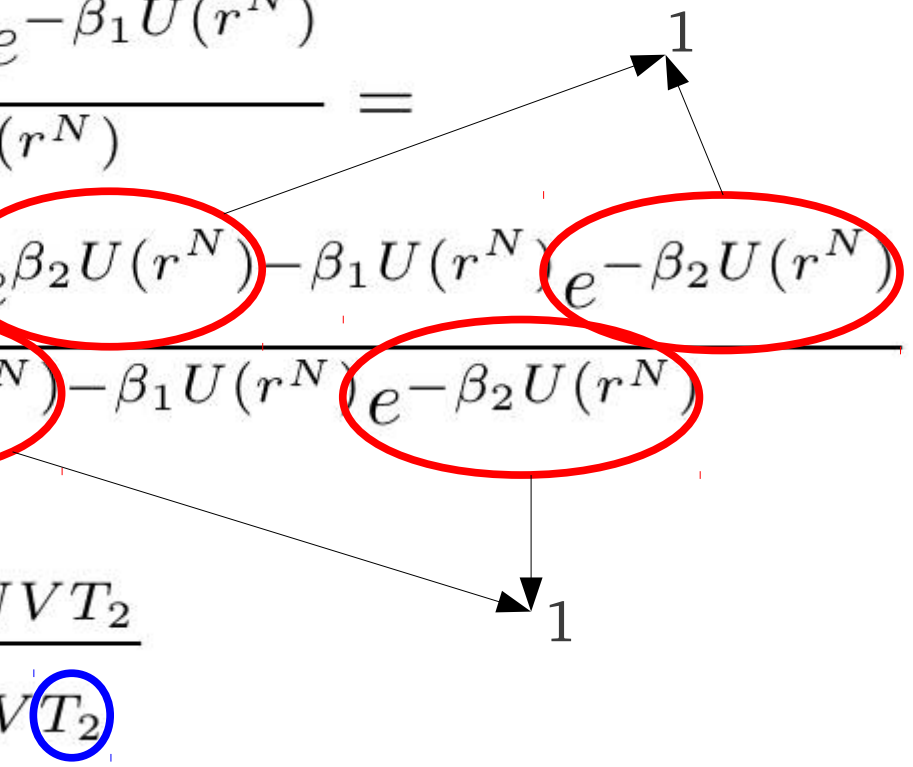
Question: How would you call $\beta\Delta F$ between these two systems?

Thermodynamic perturbation: recycling data

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

$$\langle A \rangle_{NVT_1} = \frac{\int \mathrm{d}\boldsymbol{r}^N A\left(\boldsymbol{q}\left(r^N\right)\right) e^{-\beta_1 U(r^N)}}{\int \mathrm{d}\boldsymbol{r}^N e^{-\beta_1 U(r^N)}} = \frac{\int \mathrm{d}\boldsymbol{r}^N A\left(\boldsymbol{q}\left(r^N\right)\right) e^{\beta_2 U(r^N) - \beta_1 U(r^N)} e^{-\beta_2 U(r^N)}}{\int \mathrm{d}\boldsymbol{r}^N e^{\beta_2 U(r^N) - \beta_1 U(r^N)} e^{-\beta_2 U(r^N)}} =$$

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

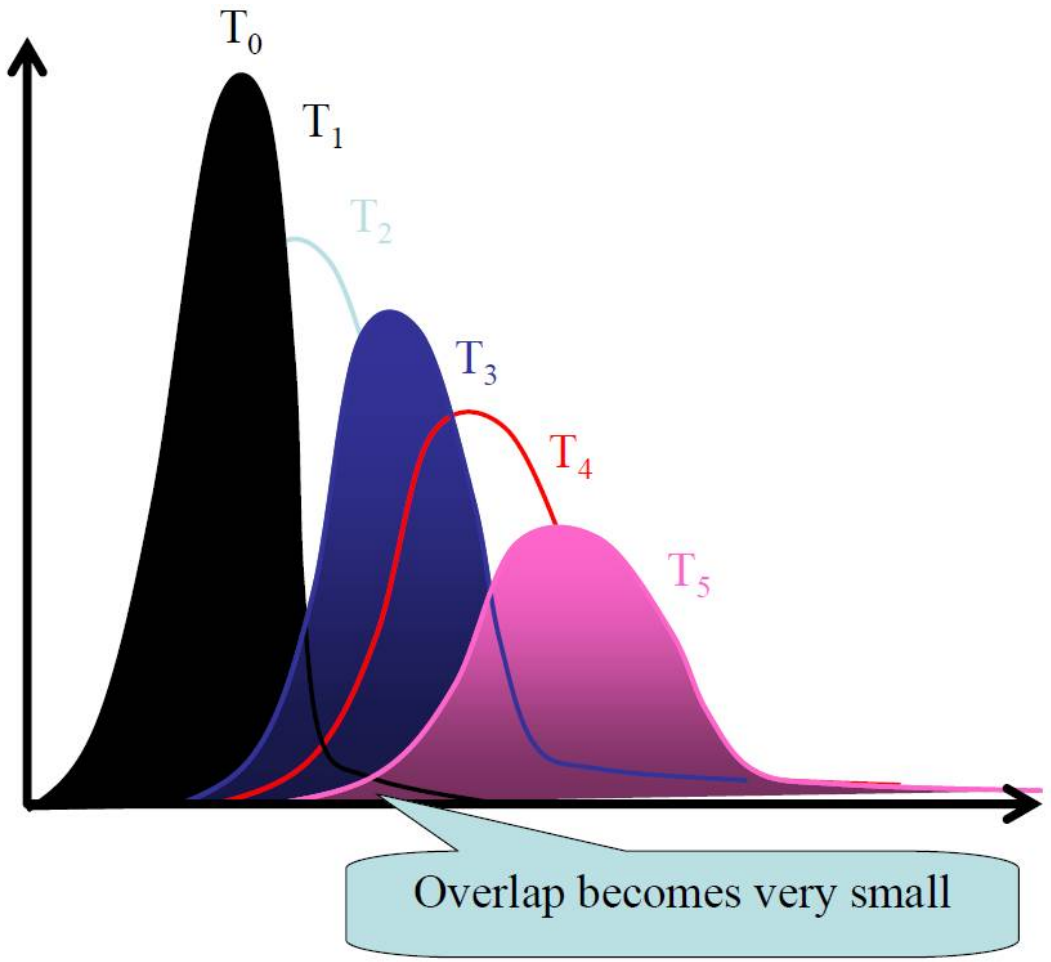


Non-Boltzmann sampling

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

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

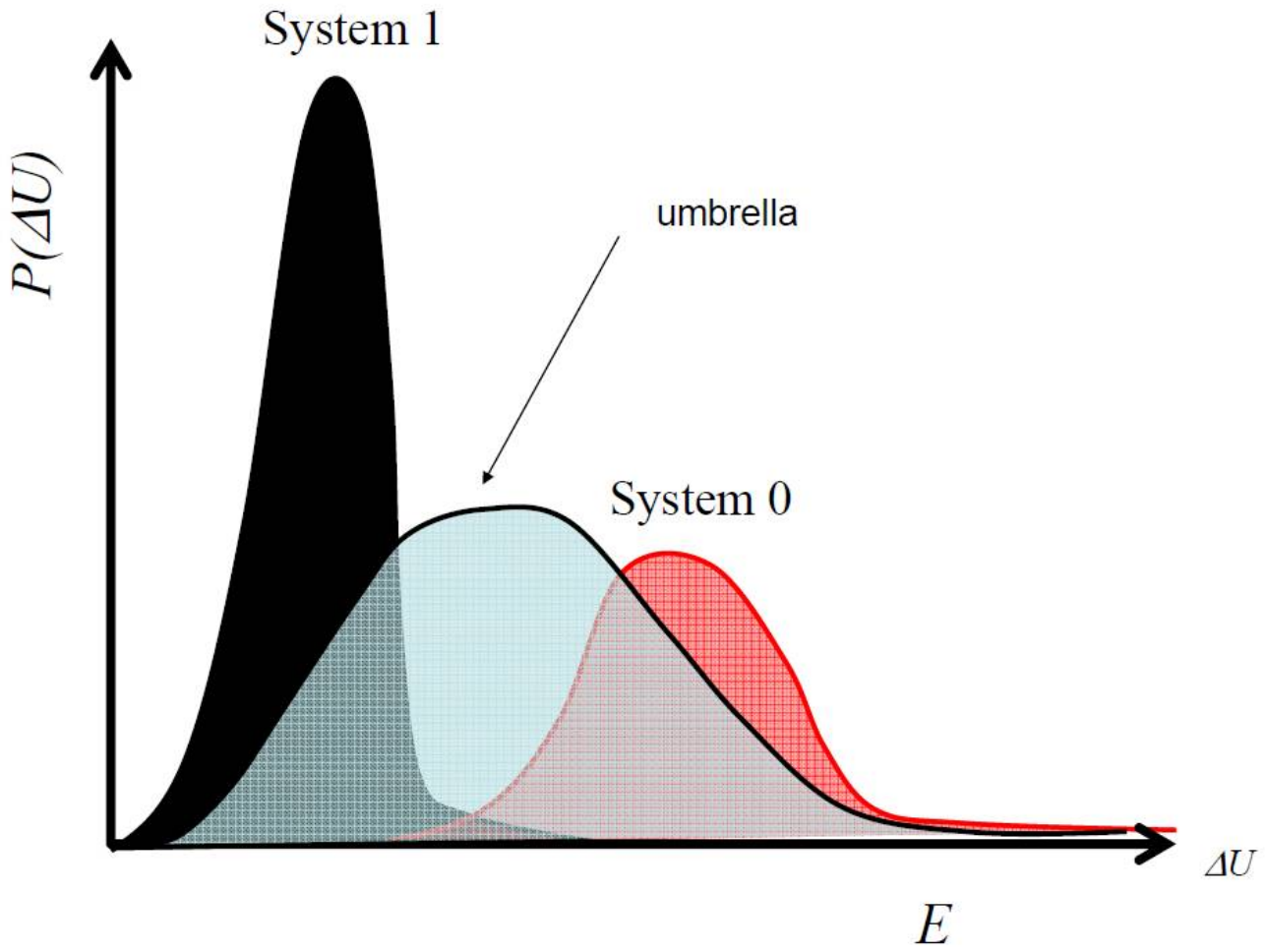
Great, but…



Umbrella sampling

$$\beta \Delta F =$$

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



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

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

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

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

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

Parallel
(over biasing potentials)

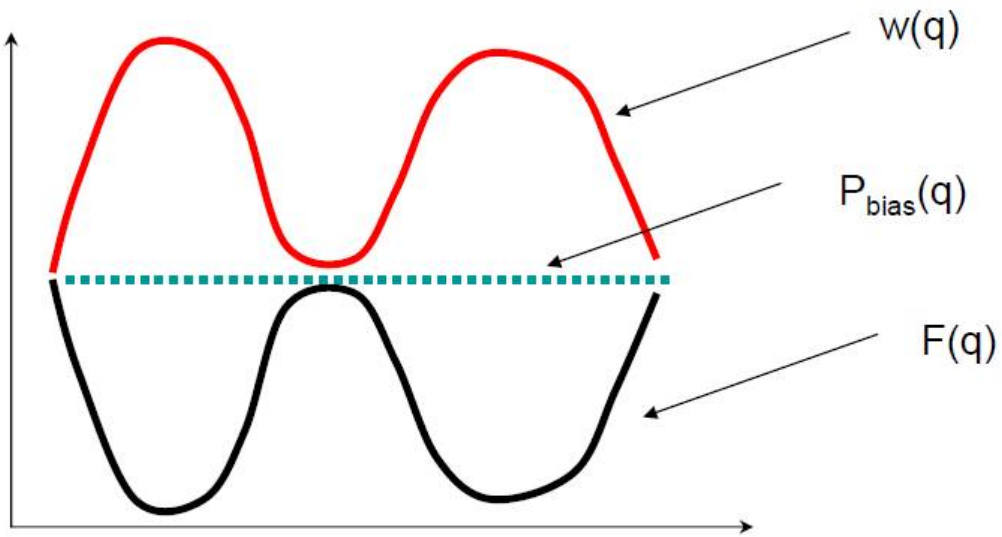
Umbrella sampling

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

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

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

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



Time dependent hamiltonian: Metadynamics

Alessandro Laio & Michele Parrinello, PNAS (2002)

- A method to “drive” chemical reactions using collective variables
- Add a small, repulsive potential at the present value of the reaction coordinate
- Free energy surface can be reconstructed after the simulation

Time dependent hamiltonian: Metadynamics

Algorithm

- Choose a set of collective variables, e. g. distances, coordination number, simulation cell parameters, . . .
  - $s_i = s_i\left(\{\mathbf{R}_I\}_{\text{subset}}\right)$
- Constraint these collective variables at a given point in s
  - $\mathcal{L} = \mathcal{T} - \mathcal{V} + \sum_i \lambda_i \left| s_i\left(\{\mathbf{R}_I\}_{\text{subset}}\right) - s_i^t \right|$
- Perform “metadynamics” in space of collective coordinates. . . (choice is crucial!)

Time dependent hamiltonian: Metadynamics

- *History dependent* potential:

– either in steps: “coarse grained dynamics”

$$V_G(x,t) = w \sum_{\substack{t' = \tau_G, 2\tau_G, \cdots \\ t' < t}} \exp\left(-\frac{\left(s\left(x\right) - s\left(t'\right)\right)^2}{2\delta s^2}\right)$$

– continuously: “smooth metadynamics”

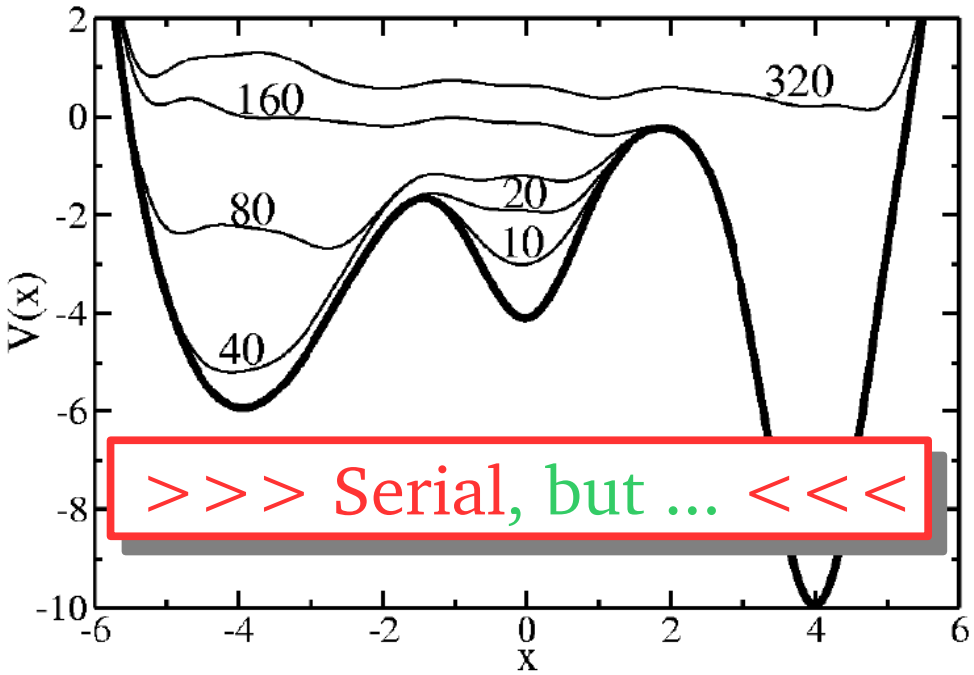
$$V\left(t, \mathrm{s}\right) = \int_{t'=0}^{t} \left|\dot{\mathrm{s}}\left(t'\right)\right| W\left(t'\right) \exp\left\{-\frac{\left[\mathrm{s} - \mathrm{s}\left(t'\right)\right]^2}{2\left(\Delta s^{\perp}\right)^2}\ \delta\left(\frac{\dot{\mathrm{s}}\left(t'\right)}{\left|\dot{\mathrm{s}}\left(t'\right)\right|} \cdot \left[\mathrm{s} - \mathrm{s}\left(t'\right)\right]\right)\right\} dt'$$

Metadynamics: reconstruction of free-energy profile

The free energy surface can be reconstructed afterwards!

$$F(\mathbf{s}) = -k_B T \ln P((s)),\ P((s)) = \frac{1}{Q}\int_{s'} \exp\left[-E(\mathbf{s})/(k_B T)\right] \delta(\mathbf{s}-\mathbf{s}')\ d\mathbf{s}'$$

Slowly all the local minima are filled and $\lim_{t\to\infty} V(t,\mathbf{s}) + F(\mathbf{s}) = constant$



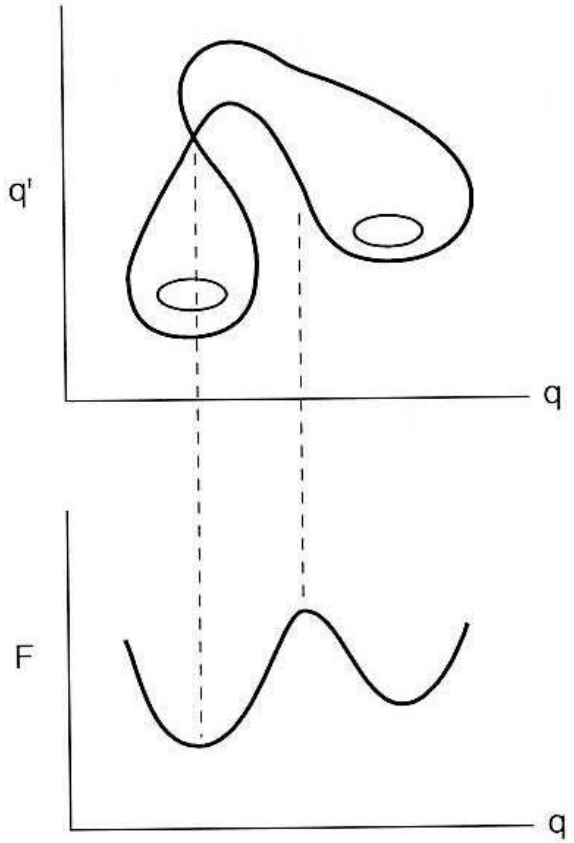
Metadynamics: pros and cons

Advantages:

- Can cope with high dimensionality
- Predictive, wide exploration of free energy surface (with lower resolution)

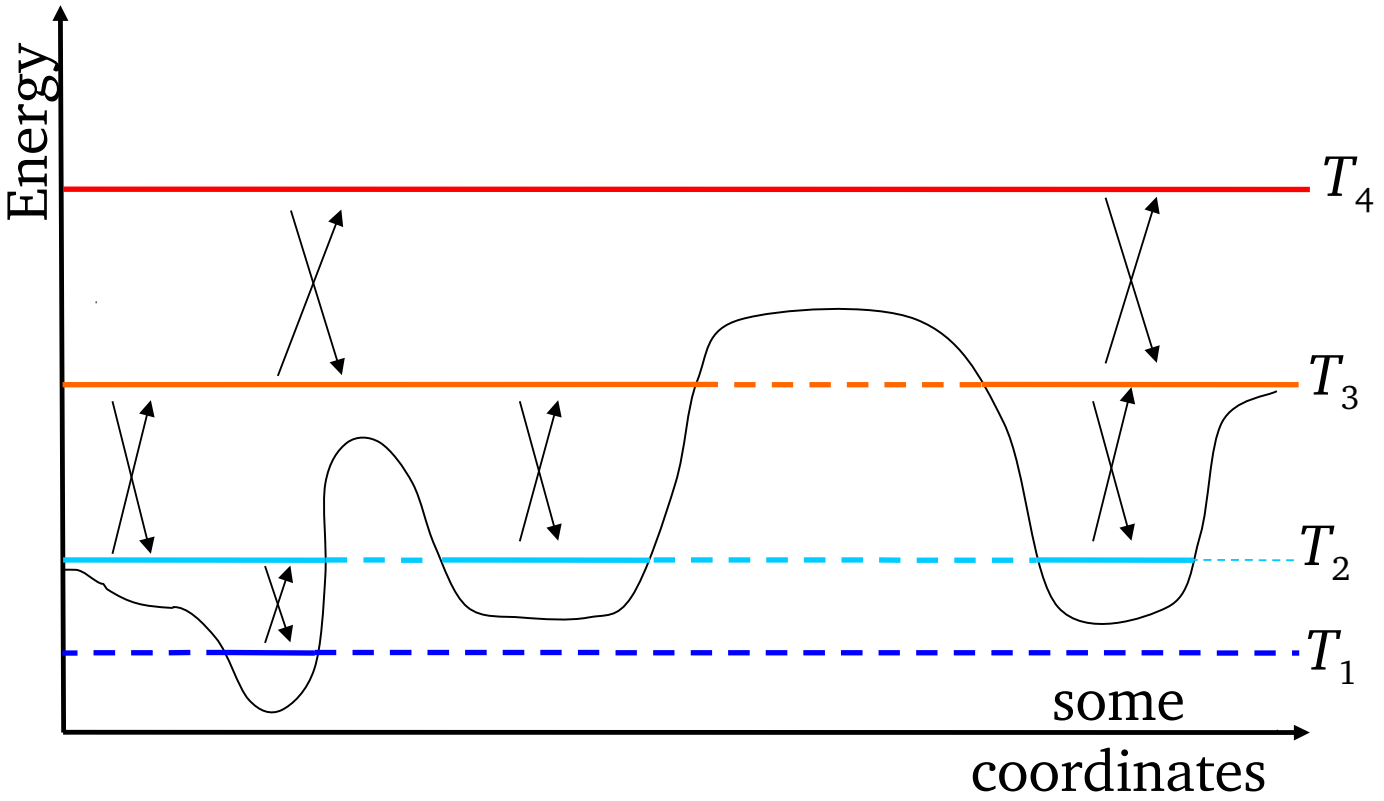
Disadvantages:

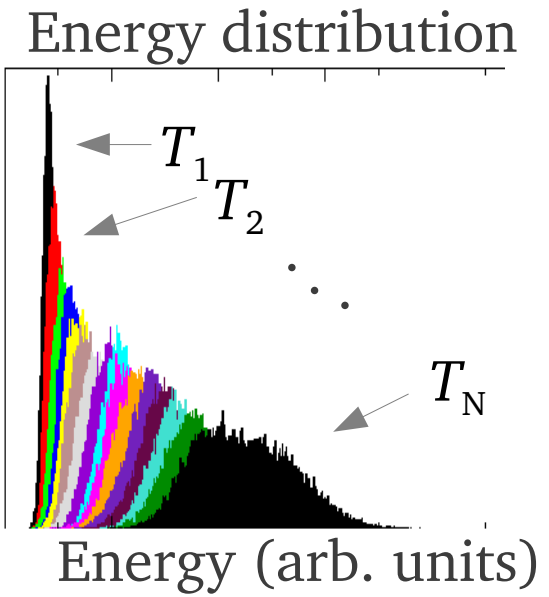
- Careful choice of the collective variables
- Inaccurate if a "slow" variable is forgotten (but this can be checked *a posteriori*)
- Choice of good (optimal) parameters (masses, coupling constants, . . .) not straightforward



- What happens if a single reaction coordinate is not enough? The low-energy path might not be captured

Parallel tempering: the concept

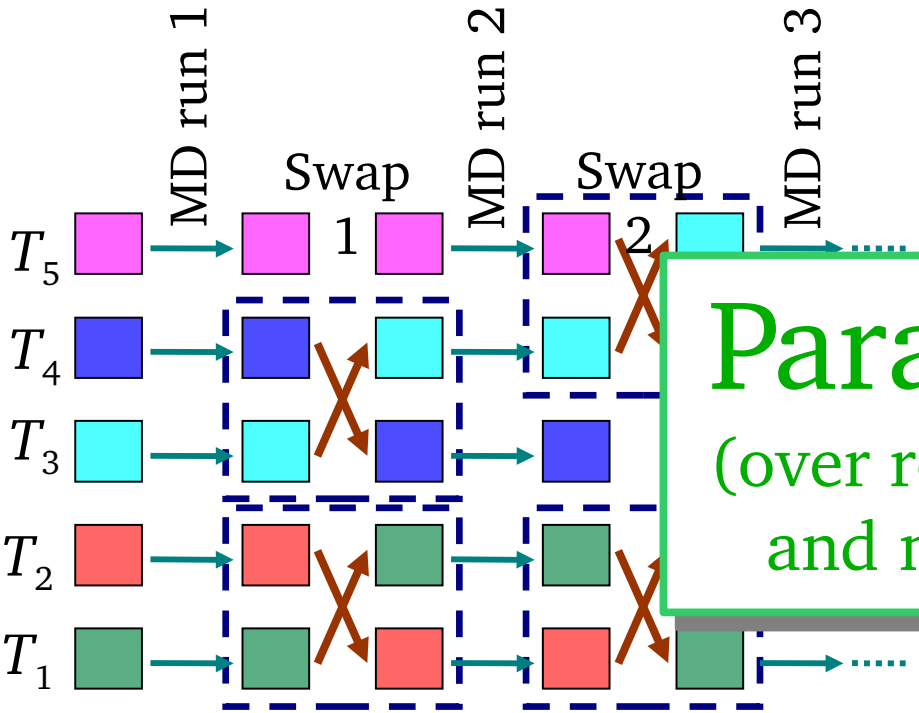




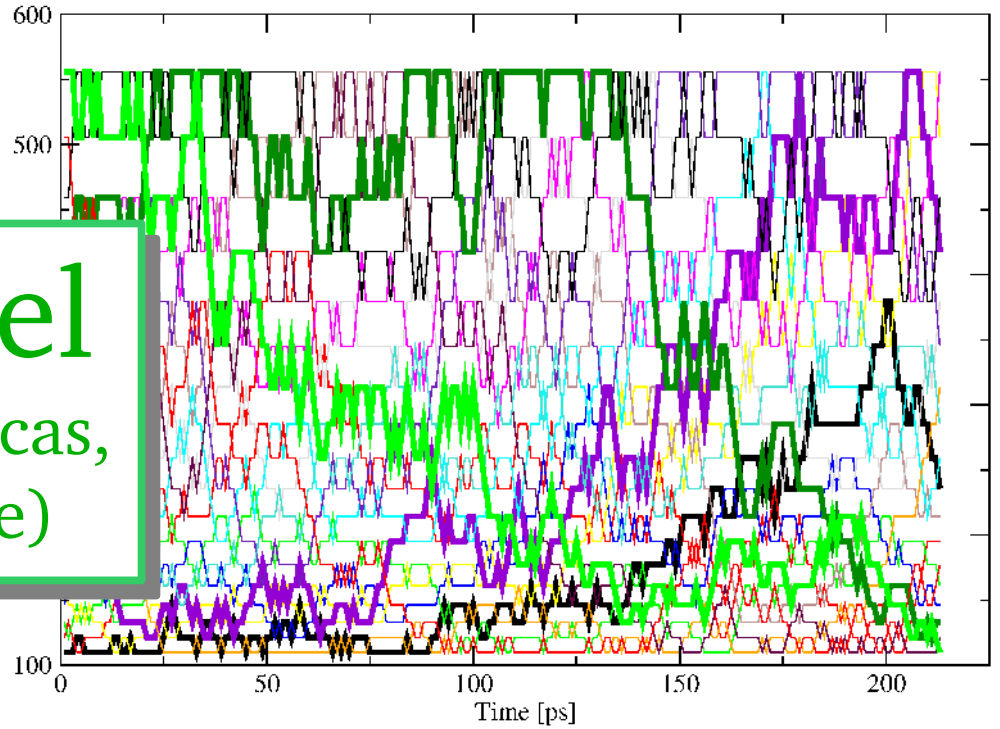
Exchange rule, ensuring canonical sampling at all temperatures:

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

Parallel tempering: the implementation



Parallel
(over replicas, 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: $H_i = H_0 + V_i(q)$

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

After parallel tempering: refinement of free energy

Umbrella Sampling (Weighted Histogram Analysis)

$$H_i = H_0 + V_i(q) = H_0 + \frac{k}{2}(q - q_{0,i})^2$$

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

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

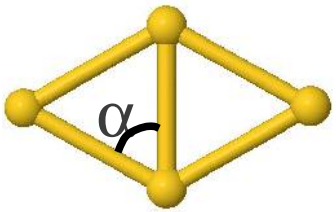
$$c_i(q) = \mathrm{e}^{-\beta_i V_i(q)}$$

More efficient: Replica Exchange Umbrella Sampling

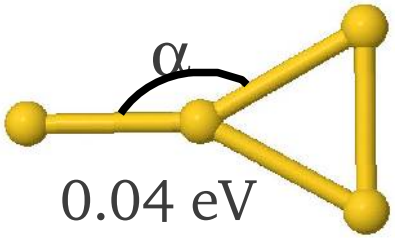
$$P_{exchange} = \min\left(1, \exp(-(V_{new} - V_{old})/k_B T)\right)$$

$$V_{old} = \frac{k_i}{2}(q_i - q_{0,i})^2 + \frac{k_j}{2}(q_j - q_{0,j})^2 \qquad V_{new} = \frac{k_i}{2}(q_j - q_{0,i})^2 + \frac{k_j}{2}(q_i - q_{0,j})^2$$

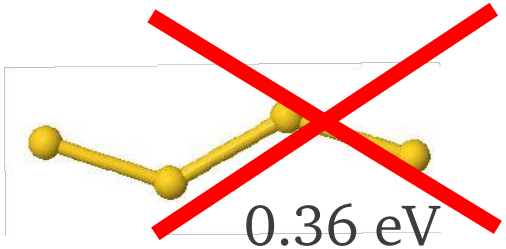
Au_4: coexistence of several isomers



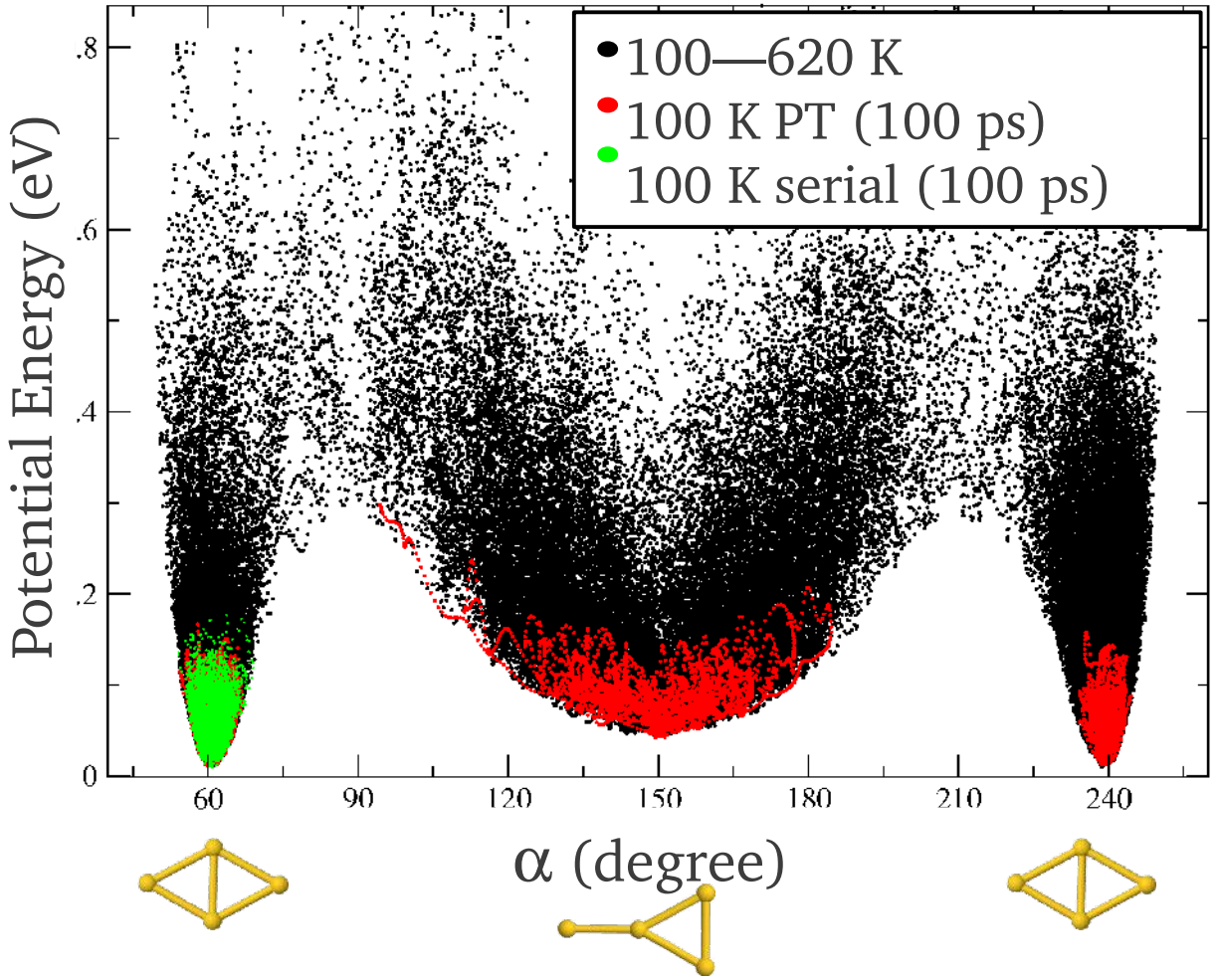
0.00 eV



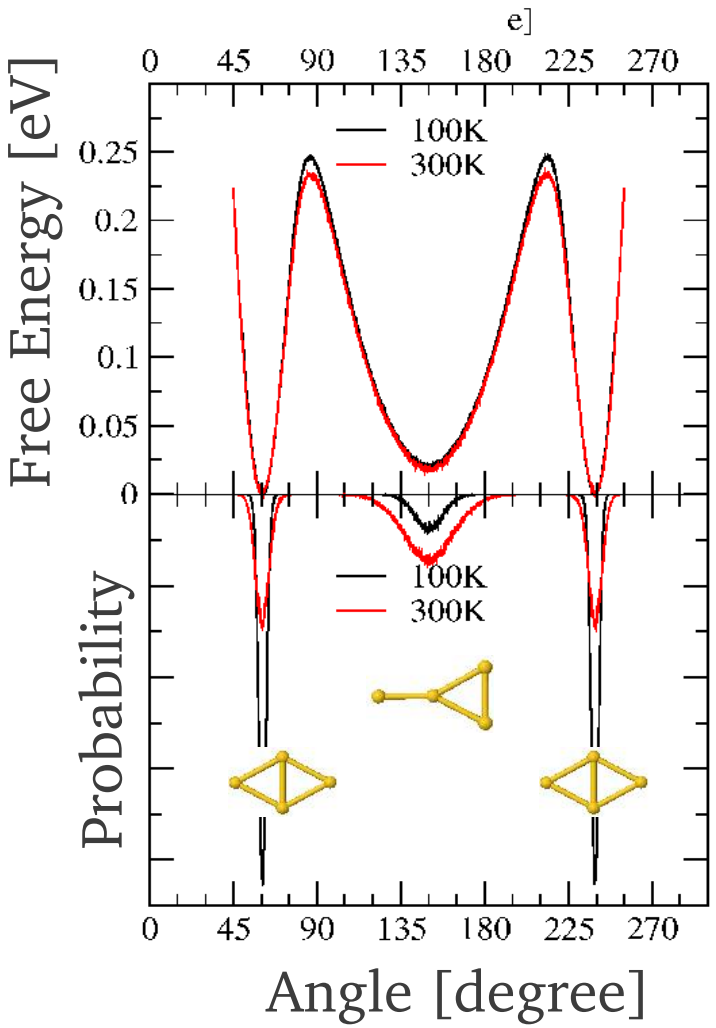
0.04 eV

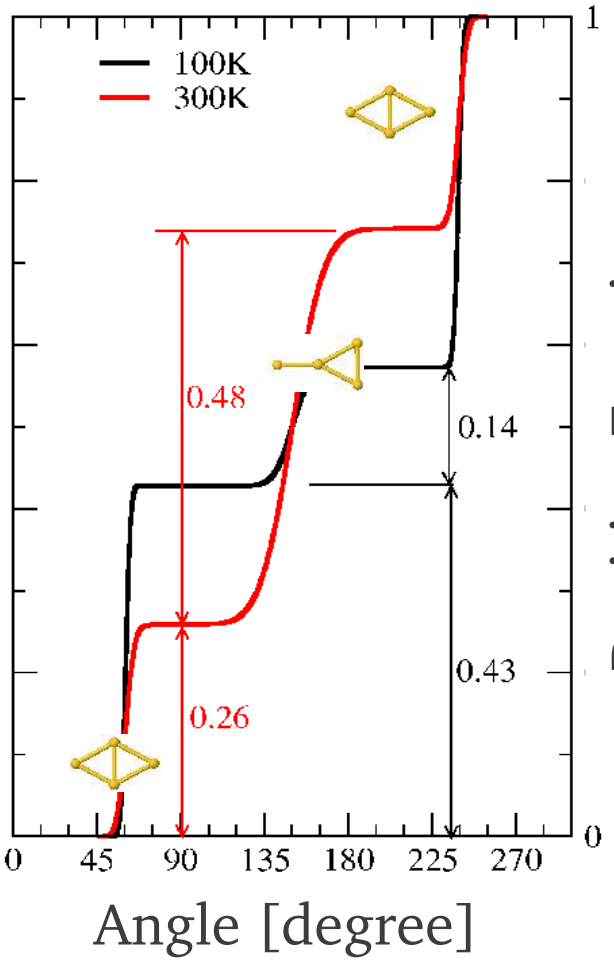


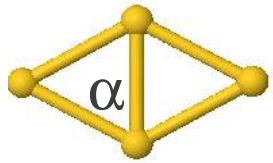
0.36 eV



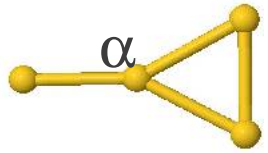
Au_4, relative population (T-WHAM)





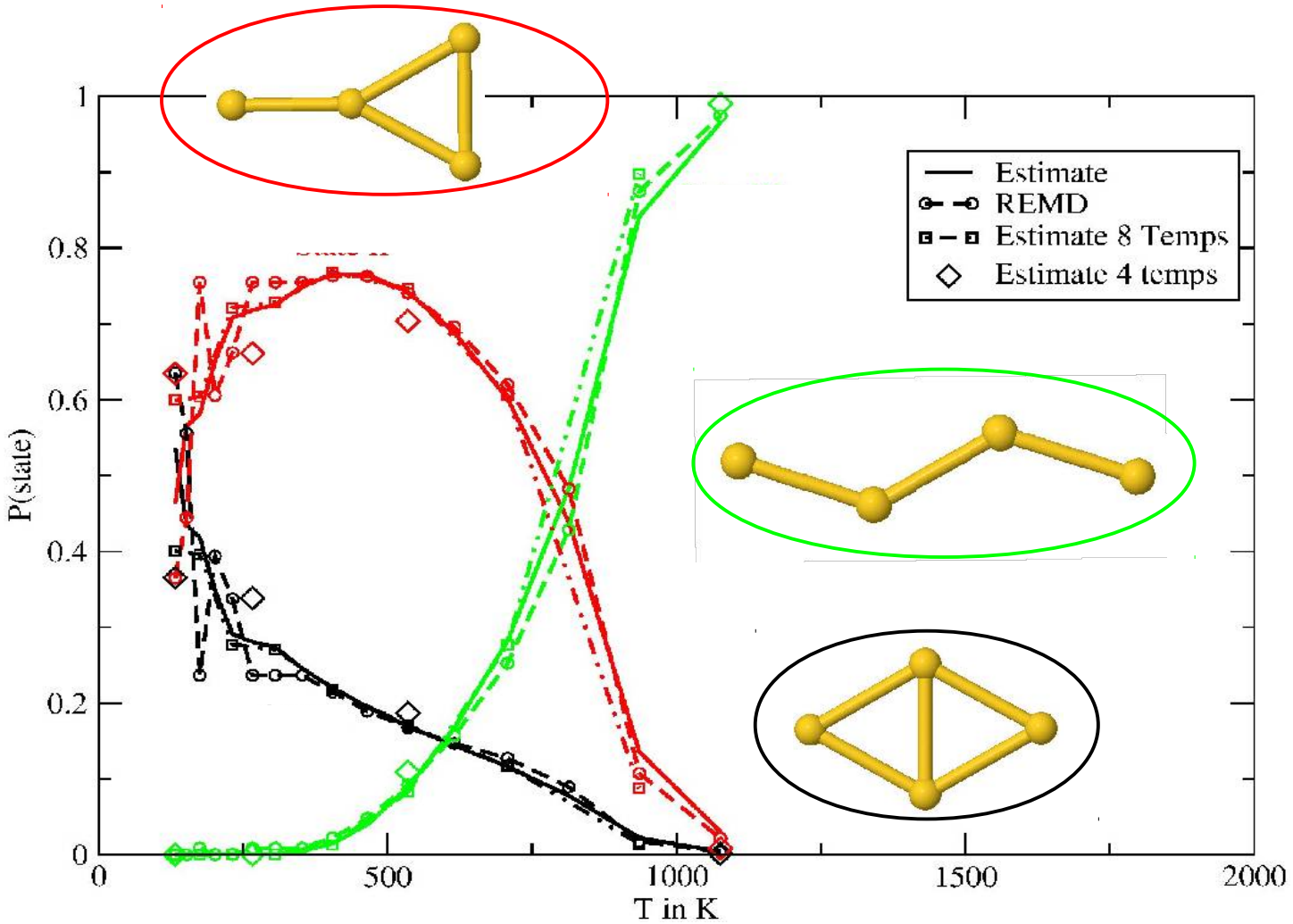


0.00 eV



0.04 eV
(PBE+vdW)

Au_4, relative population, coordination based descriptor



Final remarks

- We should be “afraid” of long *inherently serial* (force&energy) evaluations
- We should NOT be afraid of (shamefully) parallelizable, schemes, as computationally demanding as they can be

- Unbiased sampling (importance of not wasting anything)
- Reduction to relevant dimensions a posteriori

- Open system (grand-canonical ensemble) within MD framework?

Free-energy methods: accessibility via FHI-aims

Parallel tempering:
home tailored script-based implementation

Metadynamics, Umbrella Sampling, Steered Dynamics
external plug-in PLUMED
http://merlino.mi.infn.it/~plumed/PLUMED/Home.html

Replica-Exchange Umbrella Sampling
home tailored script + external plug-in PLUMED

See microtutorial !!!

Weighted Histogram Analysis Method
http://membrane.urmc.rochester.edu/Software/WHAM/WHAM.html