Statistical Mechanics and Molecular Dynamics

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

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Why statistical sampling?

Thermodynamic ensemble properties:

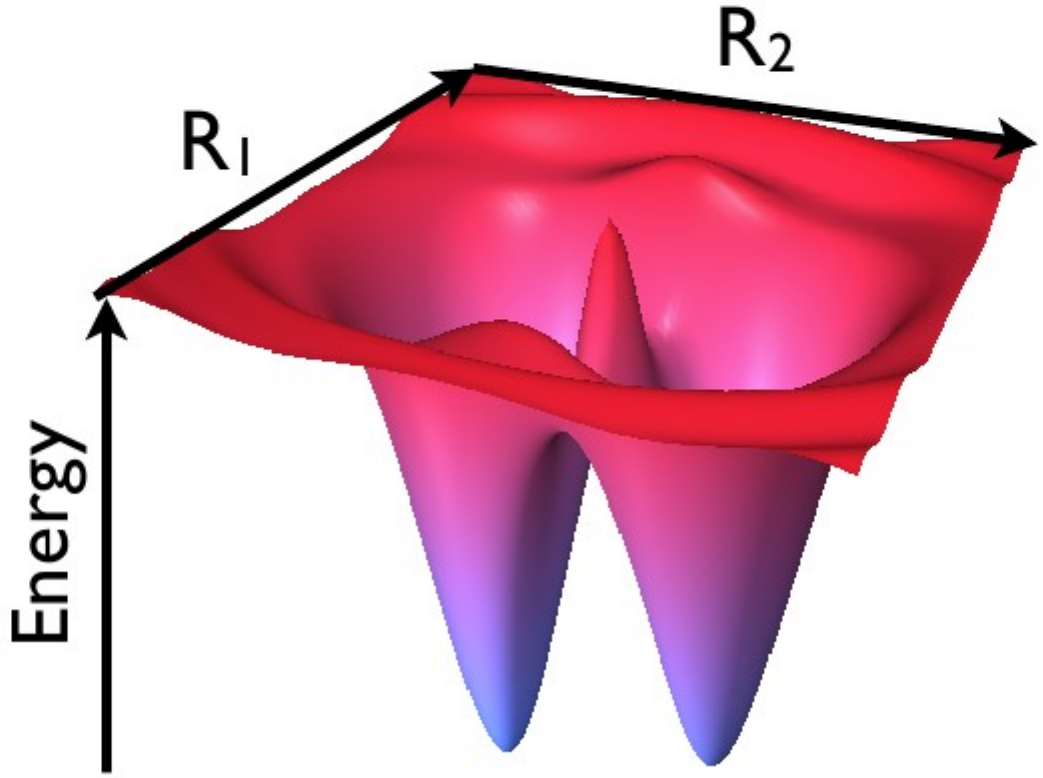
Static equilibrium properties:

Partition Function

Hamiltonian

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

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

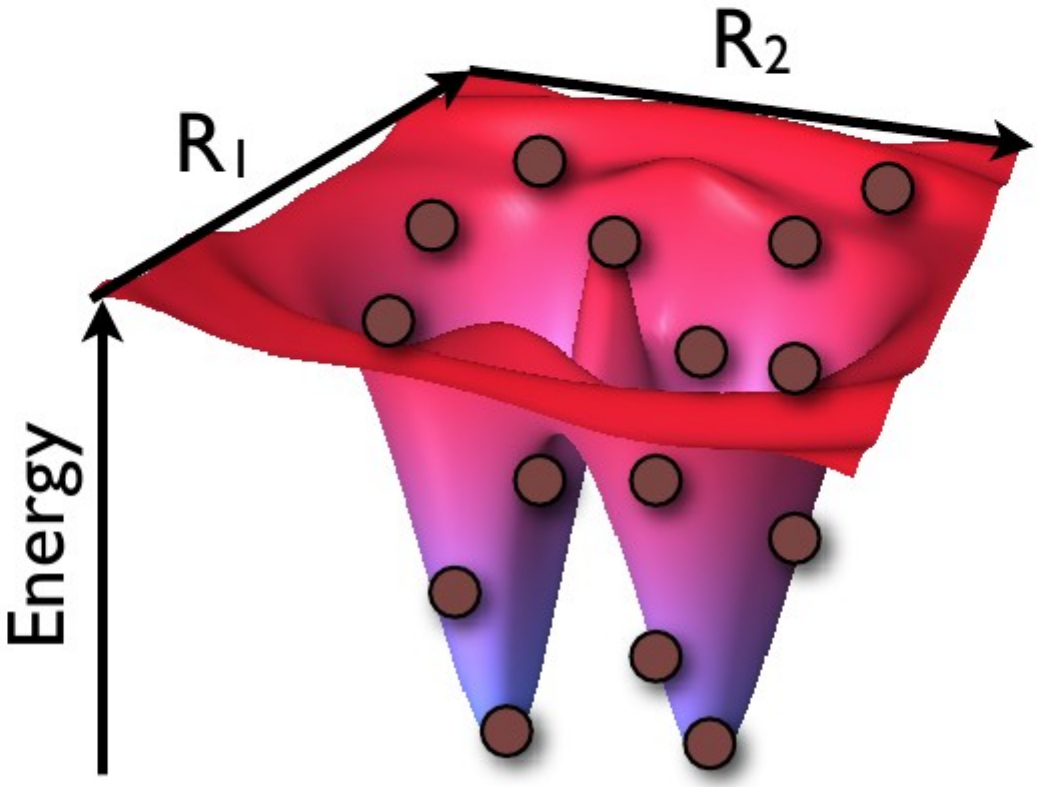


Why statistical sampling?

Ensemble averages:
possibility of directly sampling via **Metropolis Monte Carlo** algorithms

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

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

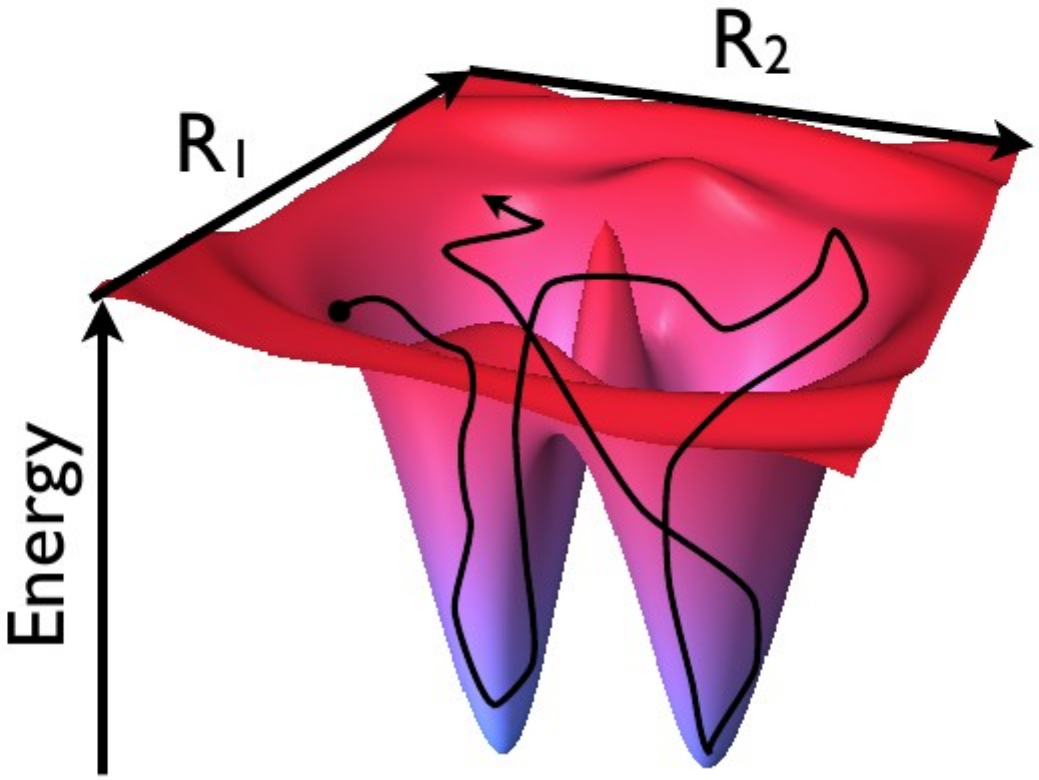


Why statistical sampling?

Ergodic assumption/hypothesis : ensemble averages equal to time averages: possibility of sampling via time evokution of the system (Molecular Dynamics)

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

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



Ergodicity?

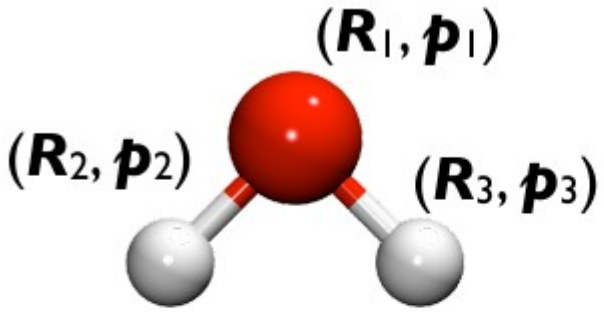
$$A(q(\boldsymbol{r}^N);\boldsymbol{r}^N(0),\boldsymbol{p}^N(0),t) \rightarrow \overline{A(q)} = \lim_{t\rightarrow\infty}\frac{1}{t}\int_0^t \mathrm{d}t' A(q,t')$$

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

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

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

Molecular dynamics: the basic idea



1. Assign initial $\boldsymbol{R}$ (position) and $\boldsymbol{p}$ (momenta)

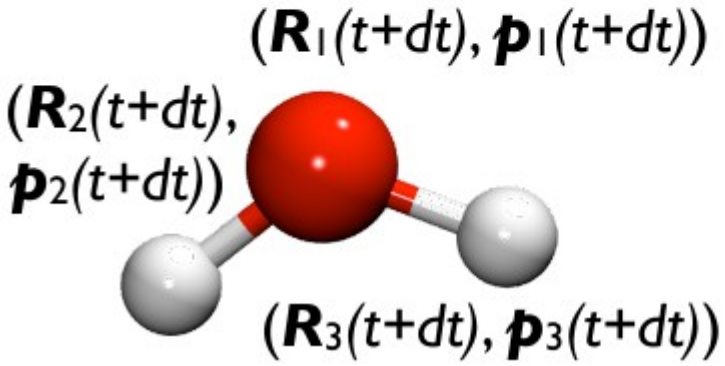
2. Evolve (numerically) Newton's equations of motion for a finite time increment

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

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

Molecular dynamics and thermodynamic ensembles

Microcanonical (NVE) ensemble: Number of particles, Volume, and total Energy are conserved

Natural ensemble for MD (the Hamiltonian is conserved)

Canonical (NVT): Number of particles, Volume, and Temperature are conserved

System in contact with a heat bath (discussed in few slides)

Isothermic-Isobaric ensemble (NPT): Number of particles, Pressure, and Temperature are conserved

"Computer experiment": equilibrate system and measure

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:

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

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

Verlet algorithm
compute position in next and previous time steps

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

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

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

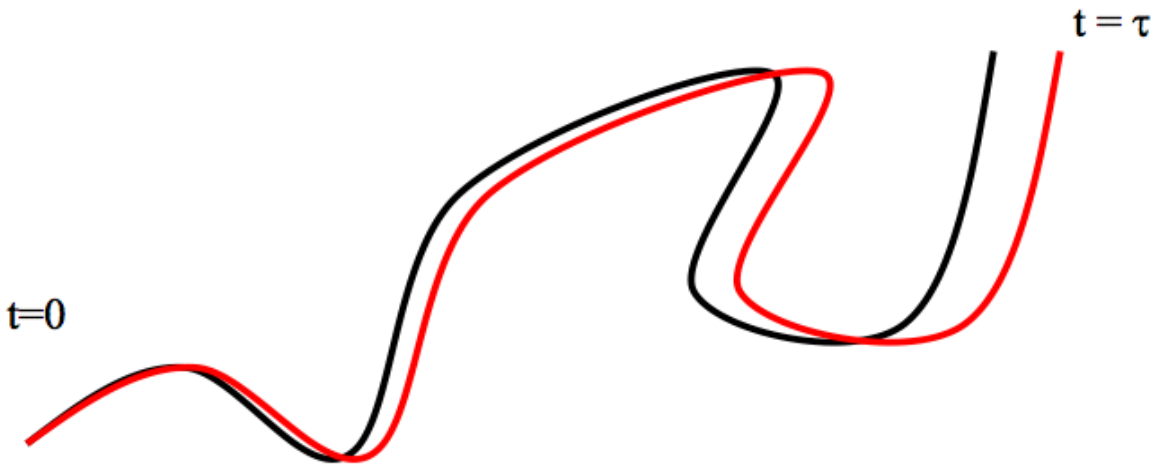
Or $$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + \ddot{x}(t)\Delta t^2$$

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

Molecular chaos

Dynamics of “well-behaved” classical many-body system is chaotic.
Consequence: Trajectories that differ very slightly in their initial conditions diverge exponentially (“Lyapunov instability”)



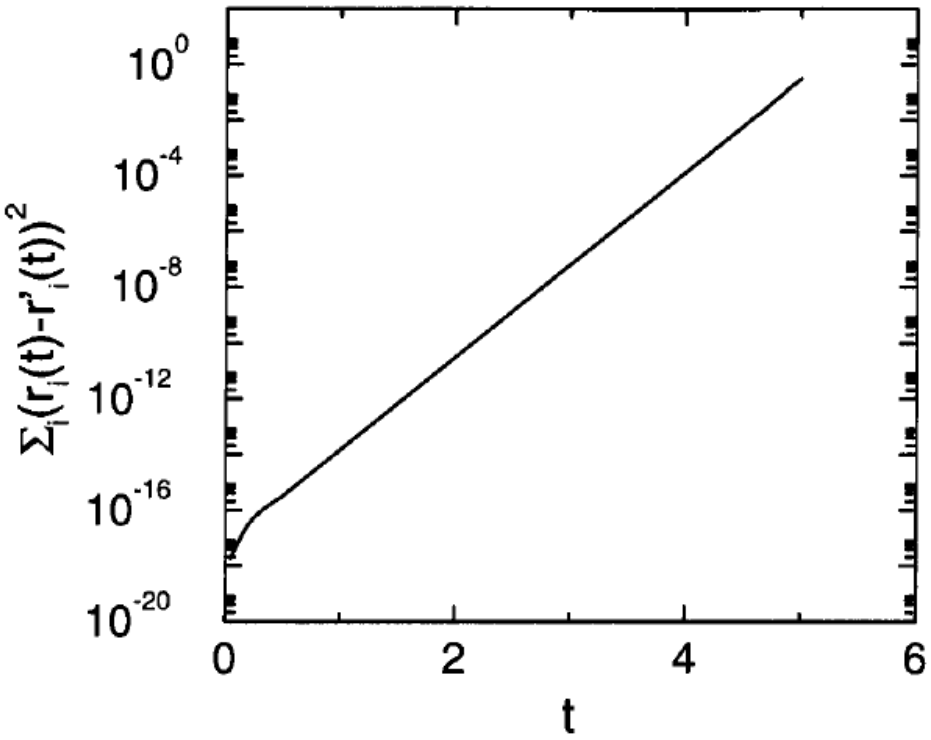
Chaos

$$\mathbf{r}(t) = f\left[\mathbf{r}^N(0), \mathbf{p}^N(0); t\right]$$

$$\mathbf{r}'(t) = f\left[\mathbf{r}^N(0), \mathbf{p}^N(0) + \epsilon; t\right]$$

$$|\Delta\mathbf{r}(t)| \sim \epsilon \exp(\lambda t)$$

$$\epsilon \sim \Delta_{max} \exp(-\lambda t_{max})$$



Why should anyone believe in Molecular Dynamics simulations ???

Chaos

Why should anyone believe in Molecular Dynamics simulations ???

Answers:

1. Good MD algorithms (e.g. Verlet) can also be considered as good (*NVE*!) Monte Carlo algorithm – they therefore yield reliable STATIC properties ("Hybrid Monte Carlo")

2. What is the point of simulating dynamics, if we cannot trust the resulting time-evolution???

3. All is well (probably), because of... The Shadow Theorem.

Shadow trajectory

Shadow theorem (hypothesis)

• For any realistic many-body system, the shadow theorem is merely a hypothesis.

• It basically states that good algorithms generate numerical trajectories that are “close to” a REAL trajectory of the many-body system.

• Question: Does the Verlet algorithm indeed generate “shadow” trajectories?

• In practice, it follows an Hamiltonian, depending on the timestep, $\tilde{\mathcal{H}}(\mathrm{x}, \Delta t)$ which is close to the real Hamiltonian $\mathcal{H}(\mathrm{x})$, in the sense that for $\Delta t \rightarrow 0$ $\tilde{\mathcal{H}}(\mathrm{x}, \Delta t)$ converges to $\mathcal{H}(\mathrm{x})$

• Take a different look at the problem.

– Do not discretize NEWTON's equation of motion…

– …but discretize the ACTION

Shadow trajectory

Lagrangian Classical mechanics

- Newton:

$$F(x,t) = m\ddot{x}$$

- Lagrange (variational formulation of classical mechanics):

– Consider a system that is at a point r_0 at time 0 and at point r_t at time t, then the system follows a trajectory $r(t)$ such that:

$$S = \int_{t_b}^{t_e} dt\,[\mathcal{K} - \mathcal{U}]$$

is an extremum.

Reminder: Lagrangian formulation

$$\mathcal{L}(\dot{r}, r) = K(\dot{r}) - U(r) = \frac{m\dot{r}^2}{2} - U(r)$$

$$\frac{\partial \mathcal{L}}{\partial \dot{r}} = \frac{\partial K}{\partial \dot{r}} = p \qquad \frac{\partial \mathcal{L}}{\partial r} = -\frac{\partial U}{\partial r} = F$$

$$p = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial \dot{r}} \qquad \dot{p} = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial r}$$

Shadow trajectory

Lagrangian

For example, if we use Cartesian coordinates:

$$\mathcal{L}(r(t)) = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{r}_i^2 - U(r_1, r_2, \ldots r_N)$$

Consider the "true" path R(t), with $R(0)=r_0$ and $R(t)=r_t$.
Now, consider a path close to the true path:

$$r(t') = R(t') + \delta r(t')$$

Then the action S is an extremum if

$$\frac{\partial S}{\partial r(t')} = 0 \text{ for all } t$$

What does this mean?

Shadow trajectory

Discretized action

$$S_{cont} = \int_{t_0}^{t_1} dt\mathcal{L}(t)$$

$$S_{disc} = \Delta t \sum_{i=0}^{i_{max}} \mathcal{L}(t_i) \qquad \mathcal{L}(t_i) = K(t_i) - U(t_i)$$

For a one dimensional system this becomes

$$\mathcal{L}(t_i)\Delta t = \frac{1}{2} m \Delta t \frac{(x_{i+1} - x_i)^2}{\Delta t^2} - U(x_i)\Delta t$$

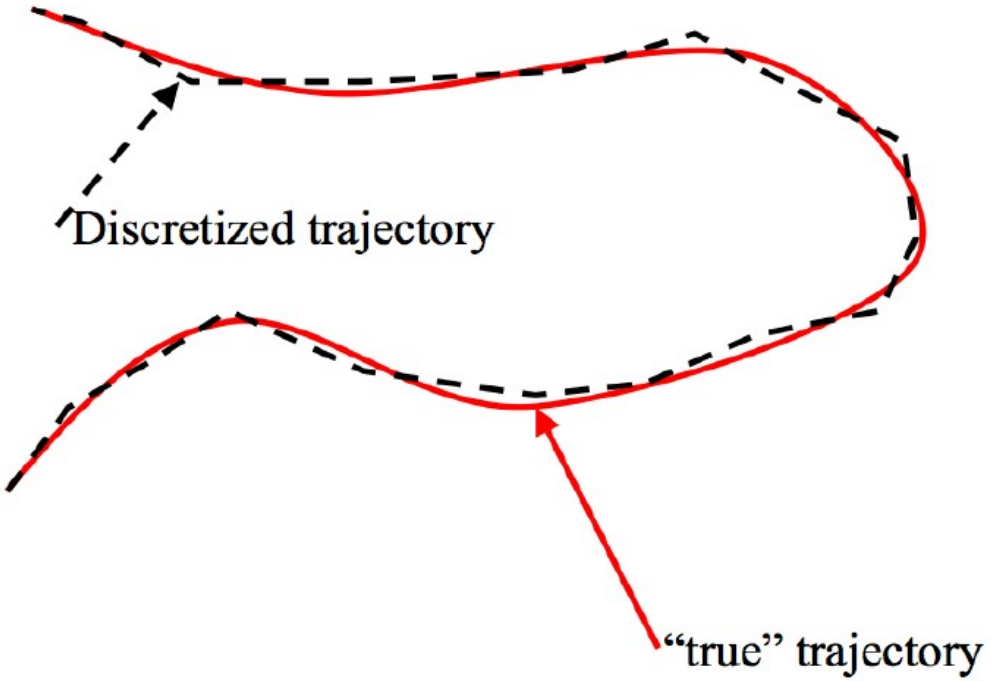
$$S_{disc} = \sum_{i=1}^{i_{max}} \left[\frac{m(x_{i+1} - x_i)^2}{2\Delta t} - U(x_i)\Delta t \right]$$

Shadow trajectory

Minimize the action
Now do the standard thing: Find the extremum for small variations in the path, i.e. for small variations in all xi.

$$\frac{\partial S_{disc}}{\partial x_i} = 0 \text{ for all } i$$

This will generate a discretized trajectory that starts at time t_0 at X_0, and ends at time t at X_t.



Shadow trajectory

$$\frac{\partial S_{disc}}{\partial x_i} = \frac{\partial}{\partial x_i} \sum_{i=1}^{i_{max}} \left[\frac{m(x_{i+1} - x_i)^2}{2\Delta t} - U(x_i)\Delta t \right]$$

$$x_{i+1} = 2x_i - x_{i-1} + \frac{\Delta t^2}{m} F(x_i)$$

- which is the Verlet algorithm!
- The Verlet algorithm generates a trajectory that satisfies the boundary conditions of a REAL trajectory – both at the beginning and at the endpoint.
- Hence, if we are interested in statistical information about the dynamics (e.g. time-correlation functions, transport coefficients, power spectra...)

...then a “good” MD algorithm (e.g. Verlet) is fine.

First principle Molecular Dynamics

Forces come from an ab initio potential V
(via Hellmann-Feynman theorem, including Pulay terms, etc.)

Possible flavors in the ground state:

- Born-Oppenheimer MD
- Car-Parrinello MD

Including excited states:

- Ehrenfest MD
- Surface hopping MD

Time scales: hundreds of picoseconds to nanoseconds for hundred of atoms

First principle MD in practice: Car Parrinello approach

Extended Lagrangian: add (fictitious) degrees of freedom for the electrons in the Lagrangian and solve coupled equations of motion

$$\mathcal{L} = \frac{1}{2}\left[\sum_I M_I \dot{\mathbf{R}}_I^2 + \mu \sum_i \int d\mathbf{r} |\dot{\phi}_i(\mathbf{r},t)|^2\right] - V(\phi, \phi^*, \mathbf{R}) + 2\lambda_{ij}\left[\int d\mathbf{r}\phi_i^*(\mathbf{r},t)\phi_j(\mathbf{r},t) - \delta_{ij}\right]$$

Lagrange multipliers

Fictitious electron mass

Kohn-Sham orbitals

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I V(\phi, \phi^*; \mathbf{R})$$

$$\mu\ddot{\phi}_i = -\frac{1}{2}\frac{\delta V(\phi, \phi^*; \mathbf{R})}{\delta \phi_i^*} + \sum_j \phi_j \lambda_{ji}$$

Electrons “follow” nuclei: avoids self-consistent calculation at every time step

Adiabatic separation: fictitious mass of the electrons need to be very (but not too..) small => small time step

(First principle) MD: beyond the basics

Simulating conditions that are experimentally accessible:
Control temperature and/or pressure, number of particles, other external fields

Including quantum nature of the nuclei
(see Mariana Rossi's talk on Friday)

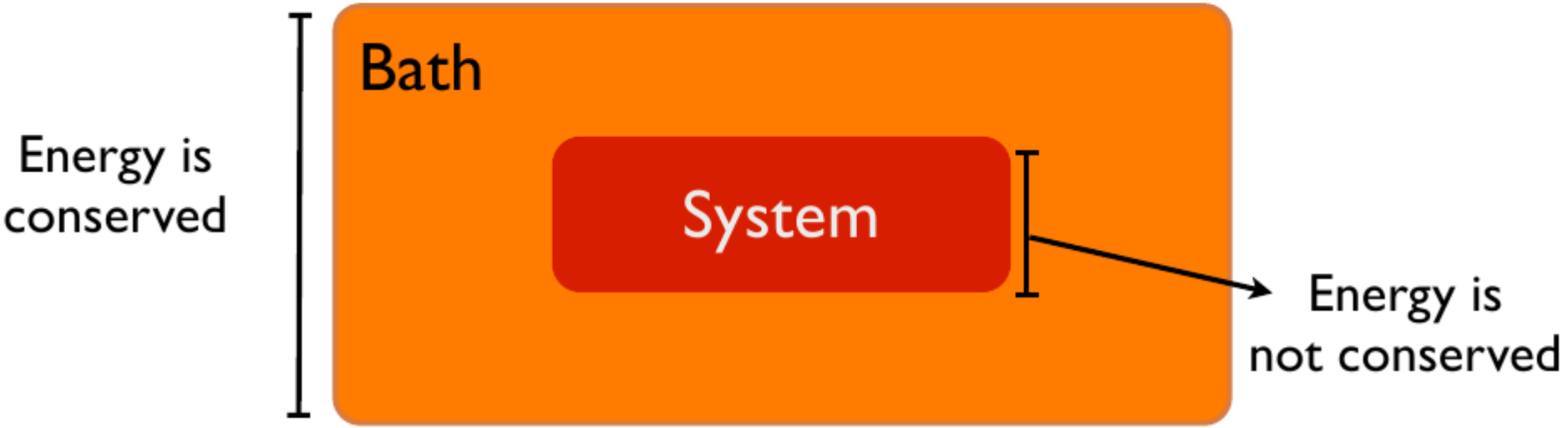
Enhanced sampling of potential energy surfaces

Sampling the canonical ensemble: thermostats

The basic idea: coupling the system to a heath bath (acts as a thermostat)

Interesting because:

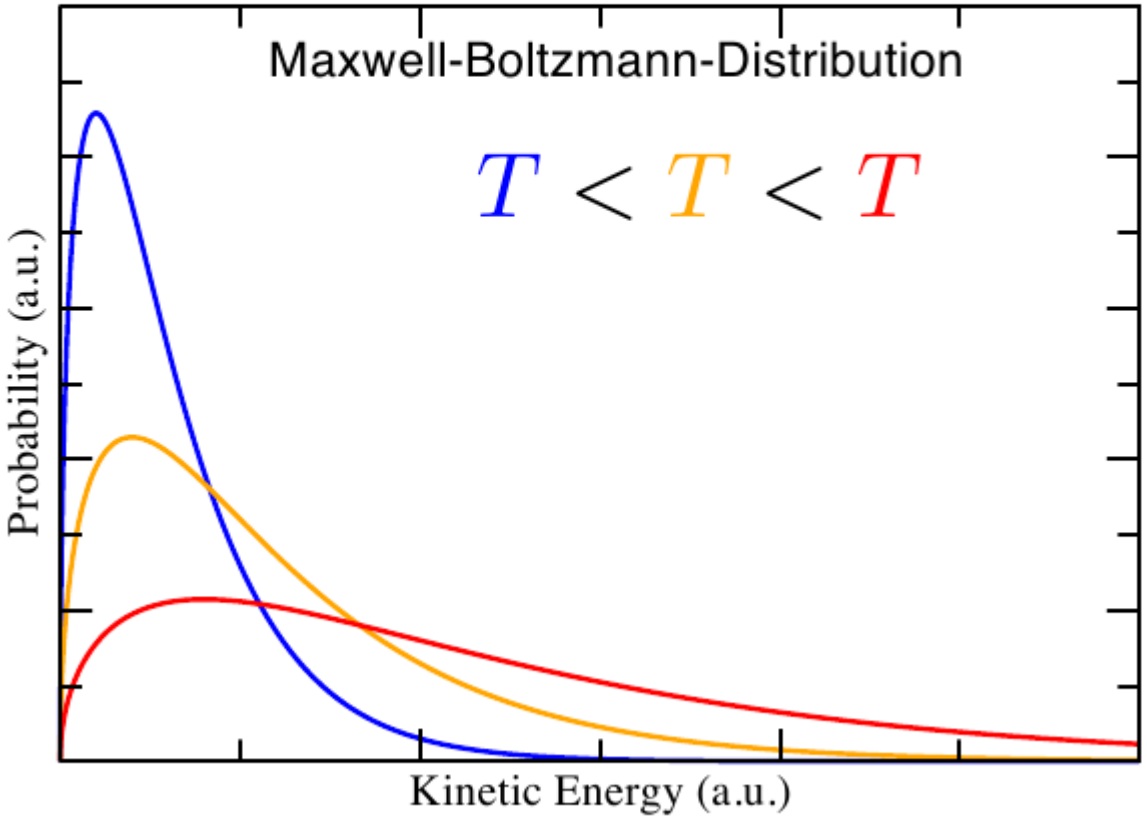
- Experimental sets up are usually at constant temperature
- Favors better modeling of conformational changes



Sampling the canonical ensemble: thermostats

Probability distribution of the kinetic energy:

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



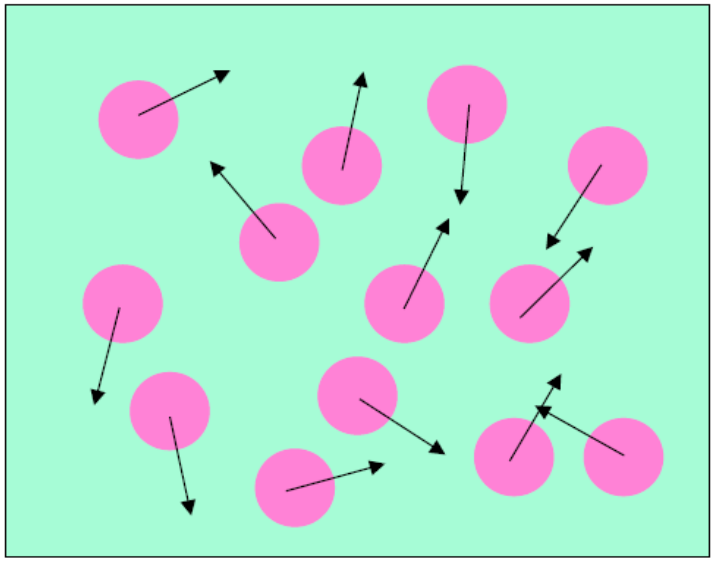
kinetic energy: $p^2/2M$

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

# of particles

Stochastic thermostat: Andersen

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



- After collision the particle is give a new Velocity

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

- The probabilities to collide are uncorrelated (Poisson distribution)

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

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

Deterministic thermostat: Nosé Hoover

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

Extended Lagrangian approach, leading to extended Hamiltonian (conserved):

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

Original system — Fictitious Oscillator

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

- Known possible ergodicity problem: system may be stuck in a subset of the phase space

Possible solution: Nosé-Hoover chains: attach a second fictitious oscillator to the first, then a third to the second, and so on. The effect is of randomizing the action of the heath bath

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).

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

The target temperature follows a stochastic differential equation:

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

Temperature rescaling

White noise

- Very successful thermostat, weakly dependent on relaxation time τ
- A conserved pseudo-Hamiltonian is defined

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

Vanilla MD: what can it be useful for

– Average structure / static properties at finite temperature

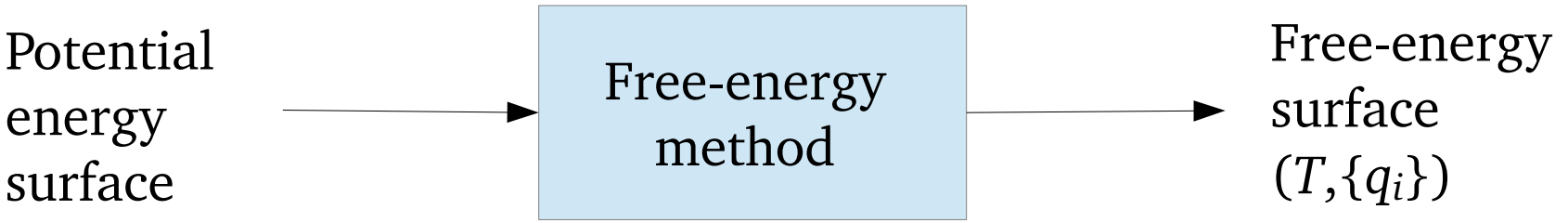
– **Vibrations (IR,** Raman **spectroscopy)**
see Mariana Rossi's talk on Friday

– NMR spectroscopy

– Transport properties

– For realistic **processes**, phase transitions: enhanced sampling

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)

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:

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

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

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

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

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

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

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 or >>> Serial <<<

Free energy: “physical”-path thermodynamic integration

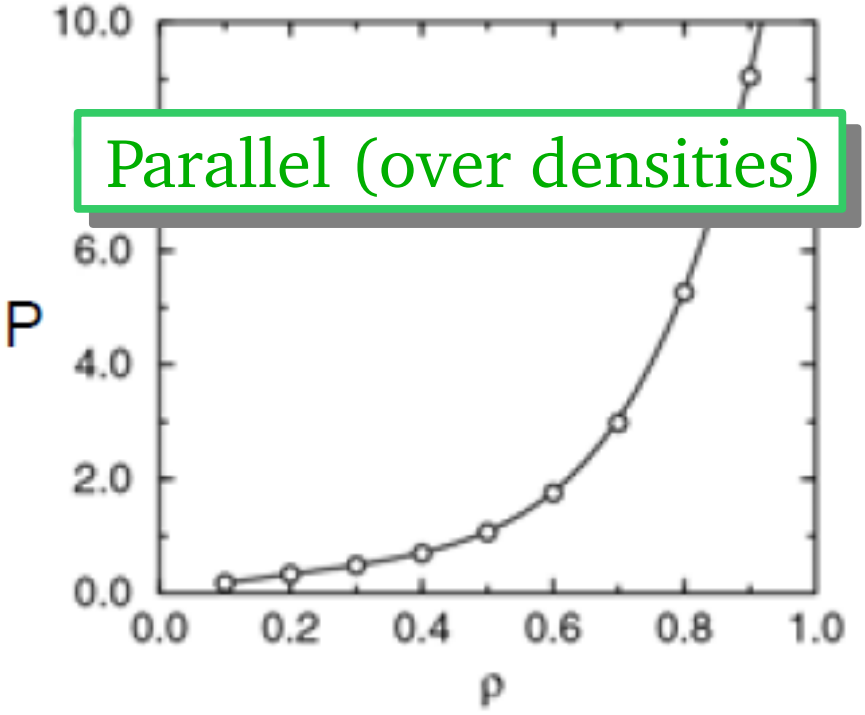
How are free energies measured experimentally?

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

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

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

$V_0 \to \infty$: 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 Helmholtz 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

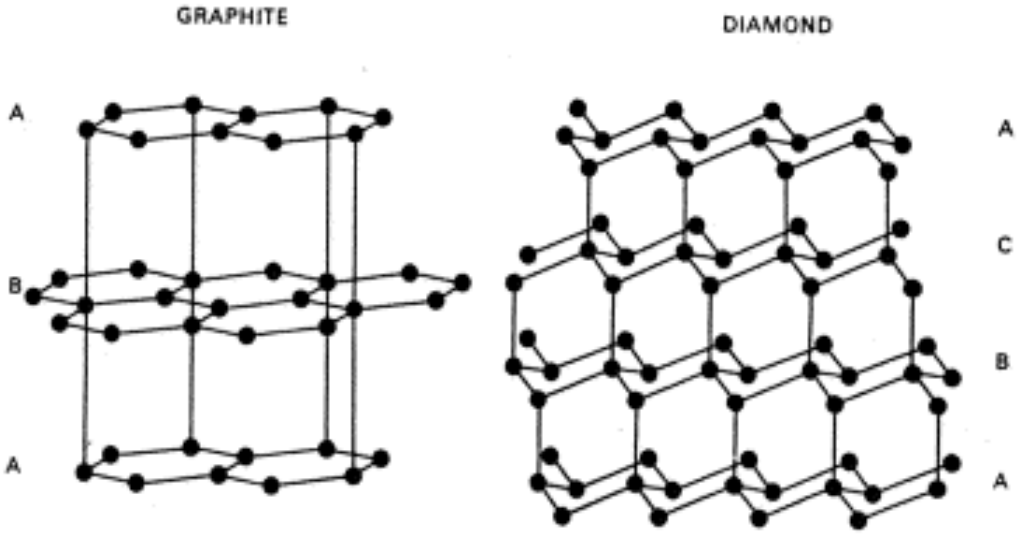
Considered phases: diamond, graphite, and liquid(s)

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

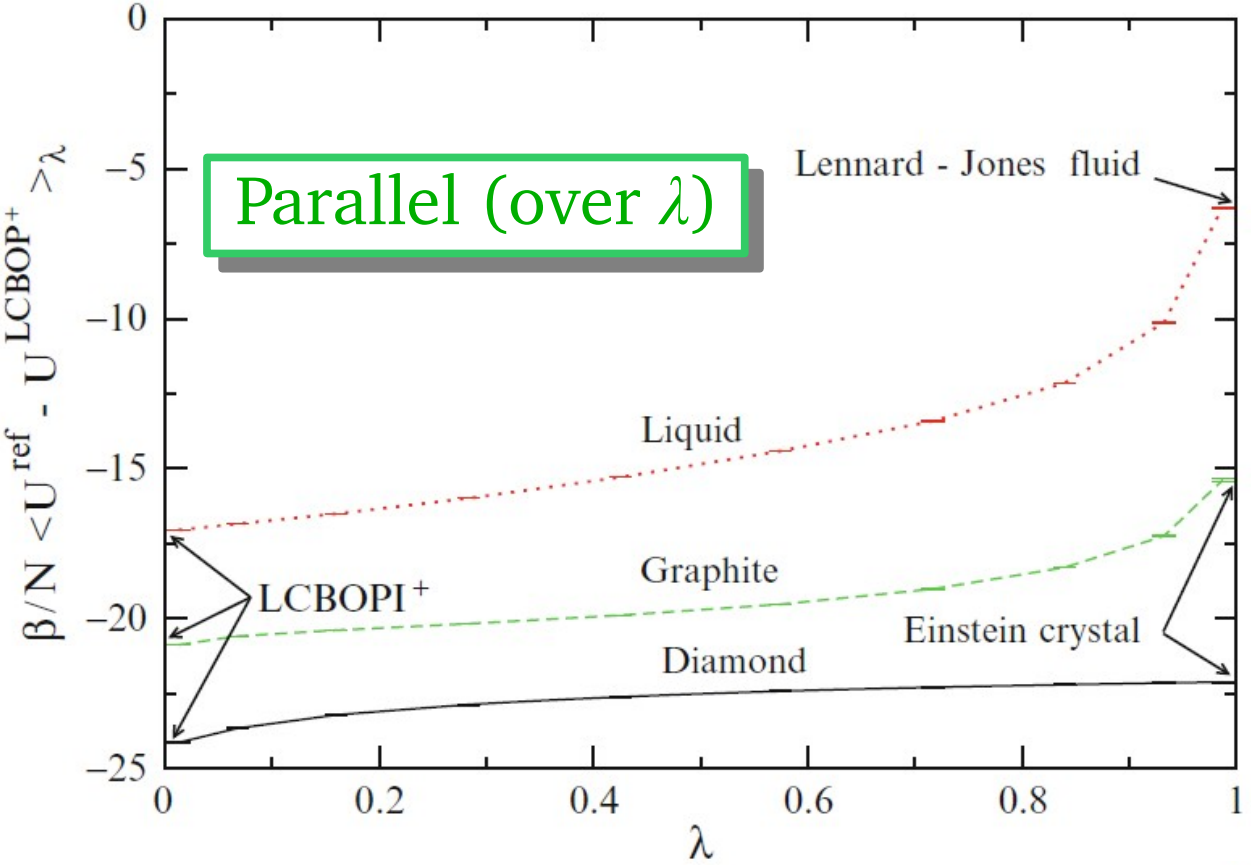
Case study: phase diagram of pure carbon

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

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



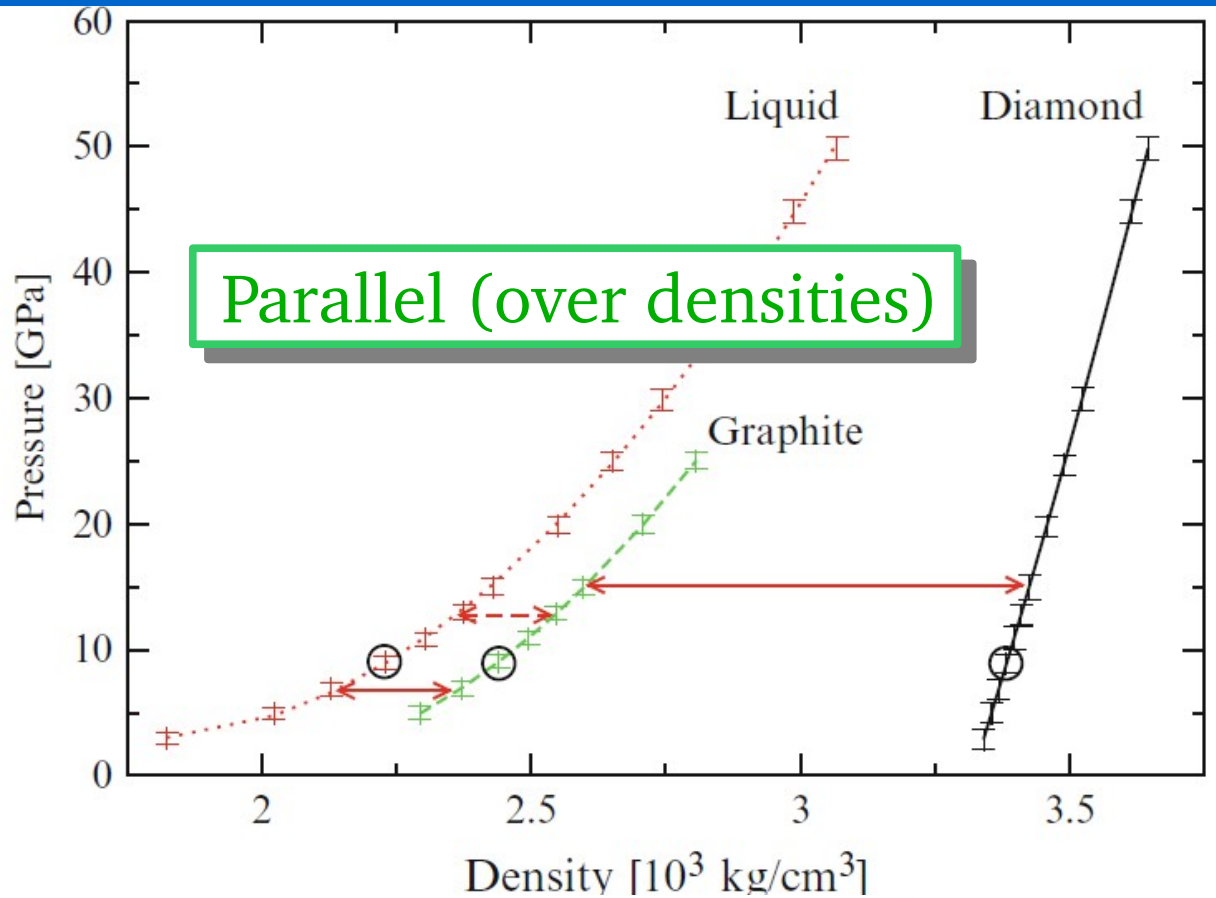
Case study: λ–ensemble sampling and integration



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

This gives the absolute Helmoltz F(T_0,V_0) for the three phases.
Here T_0 = 4000K

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



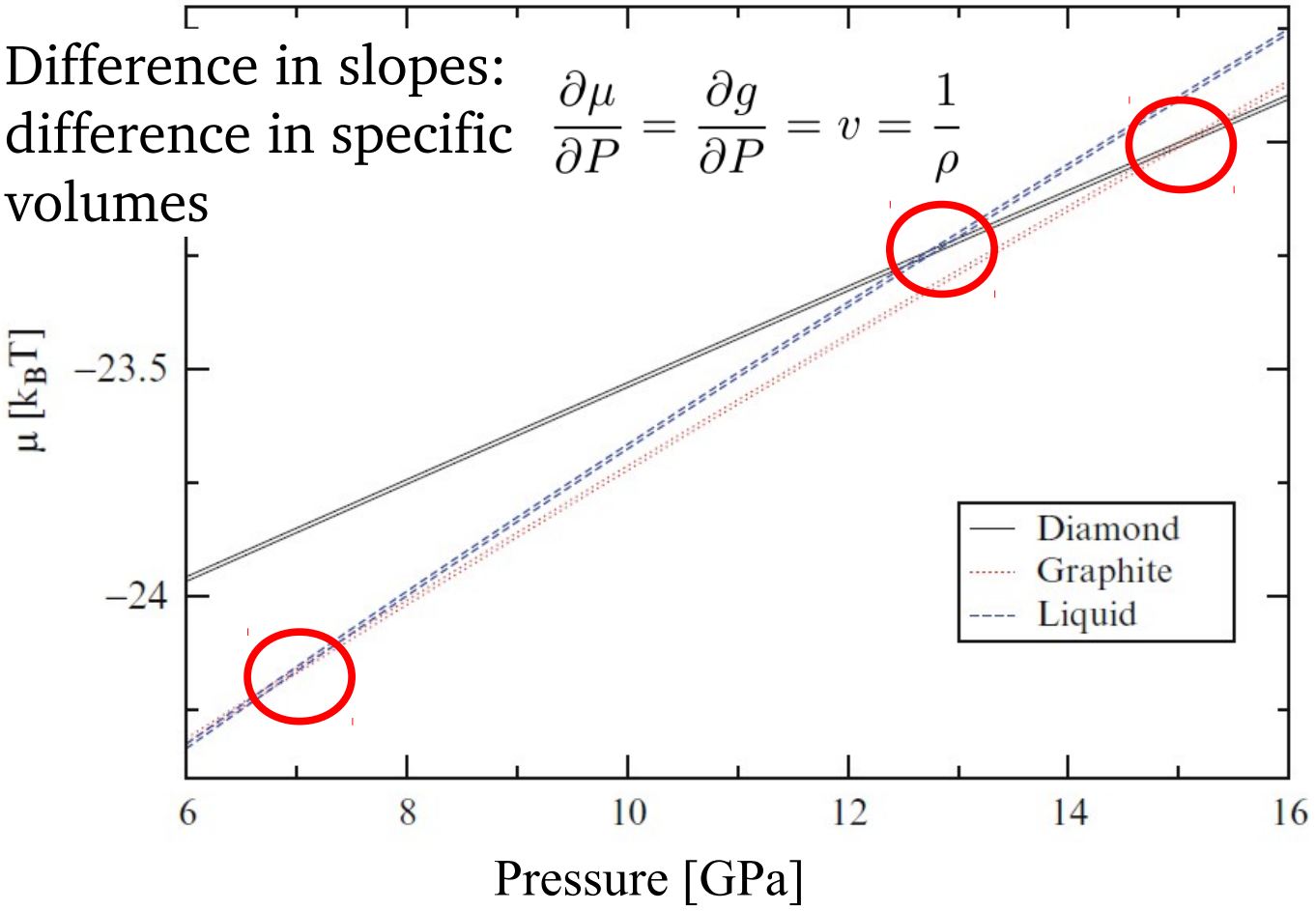
$$P(\rho) = a + b\rho + c\rho^2 \longrightarrow \beta\mu(\rho) = \frac{\beta F^{\Xi}}{N} + \beta\left[\frac{a}{\rho^{\Xi}} + b\ln\frac{\rho}{\rho^{\Xi}} + b + c\left(2\rho - \rho^{\Xi}\right)\right]$$

This gives the absolute Gibbs G(T_0, p) for the three phases

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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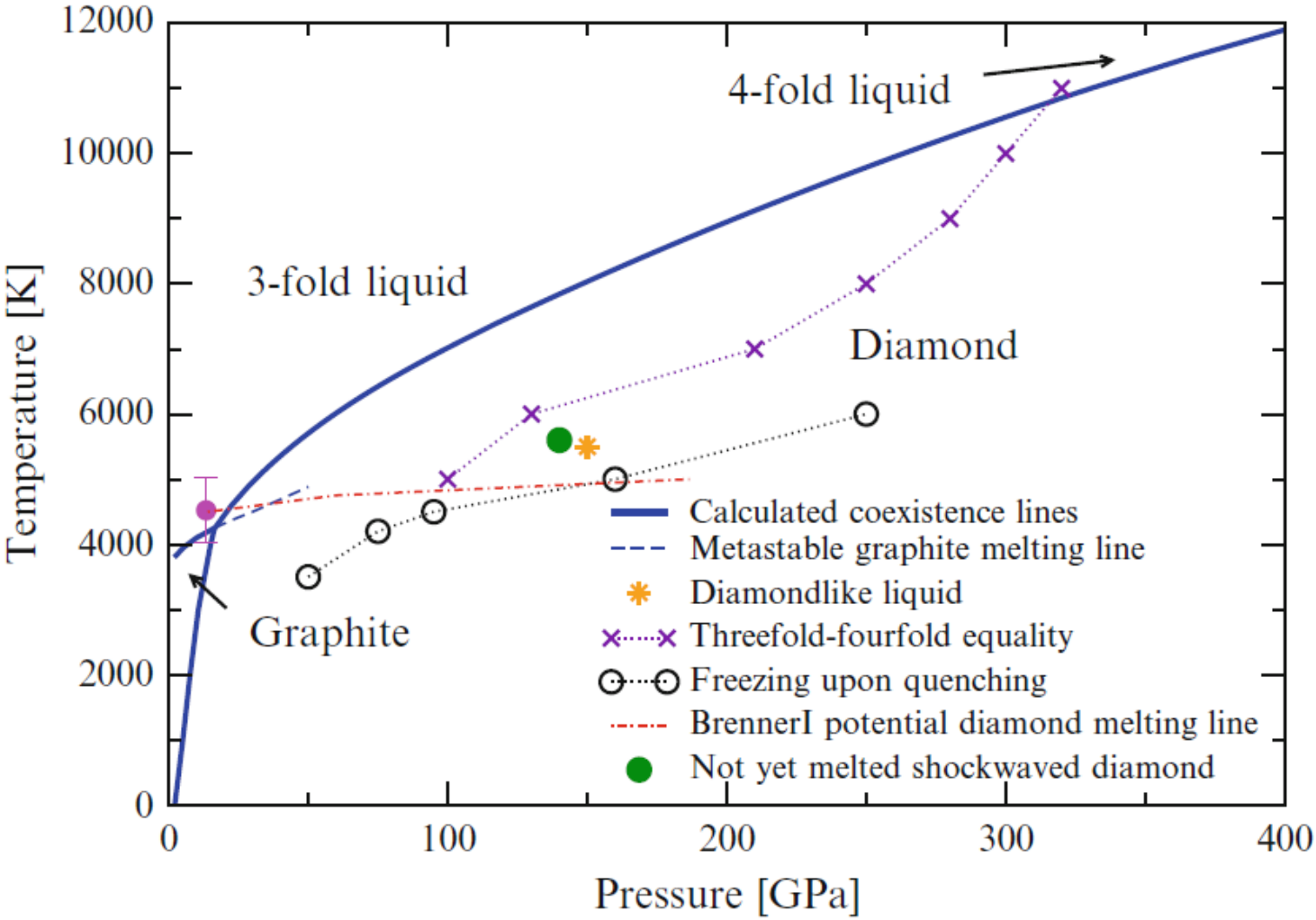
This gives three coexistence points at T_0

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

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

time ?!?

reversible?

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

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

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

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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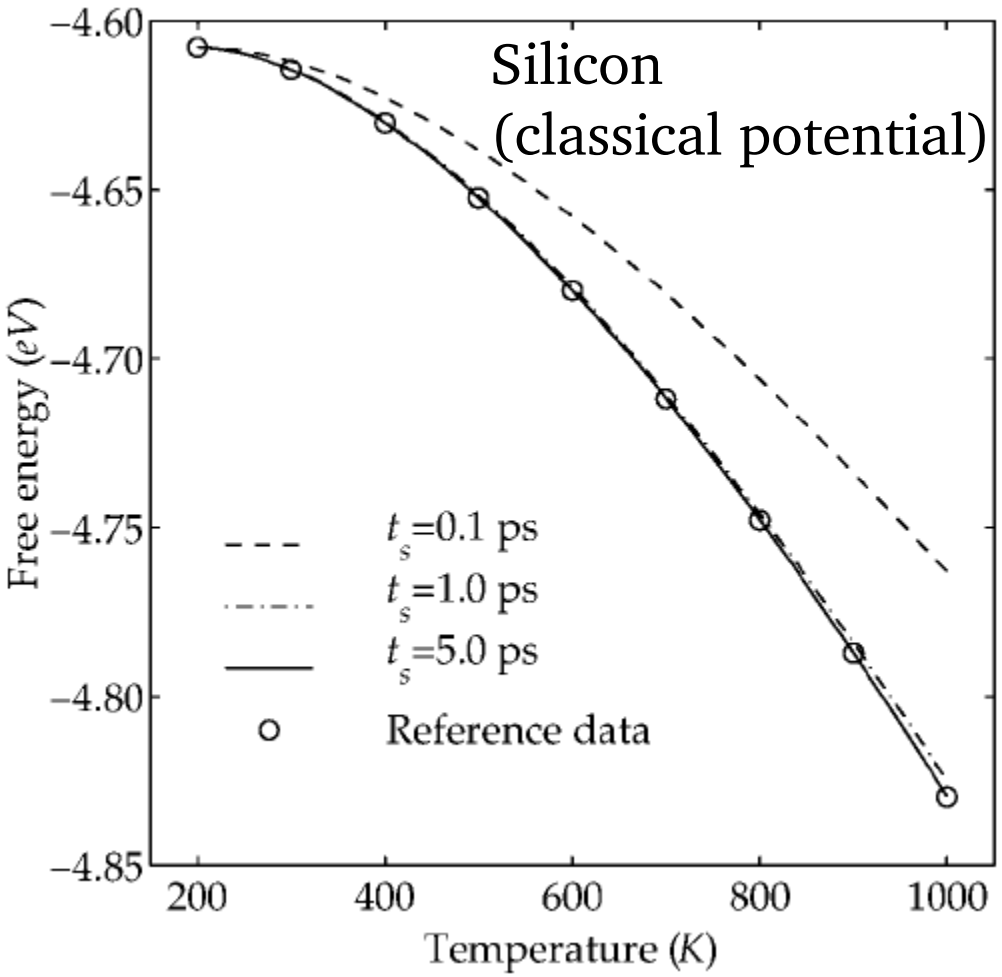
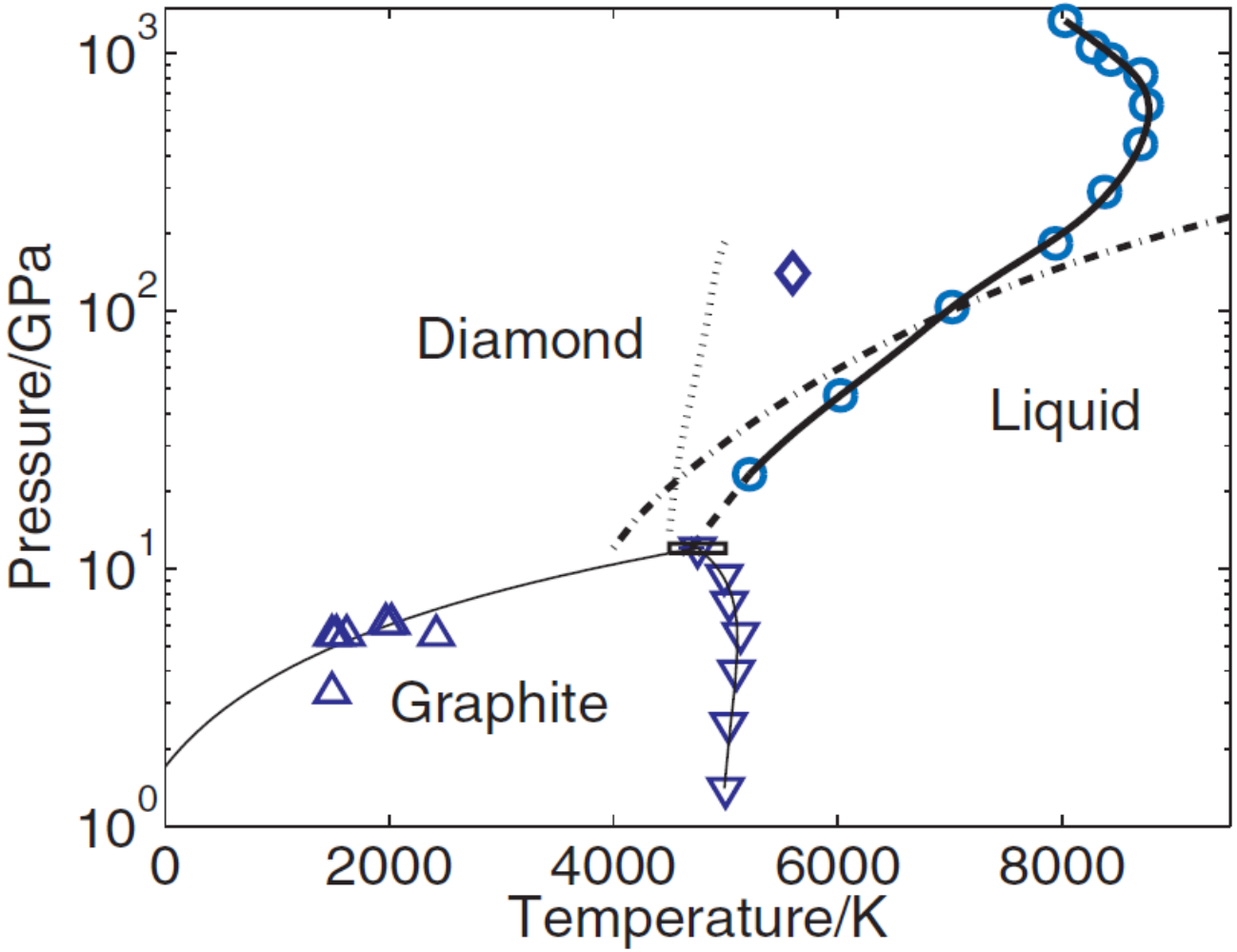


Ab initio diamond melting line



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

Beyond equilibrium: Jarzynski theorem

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

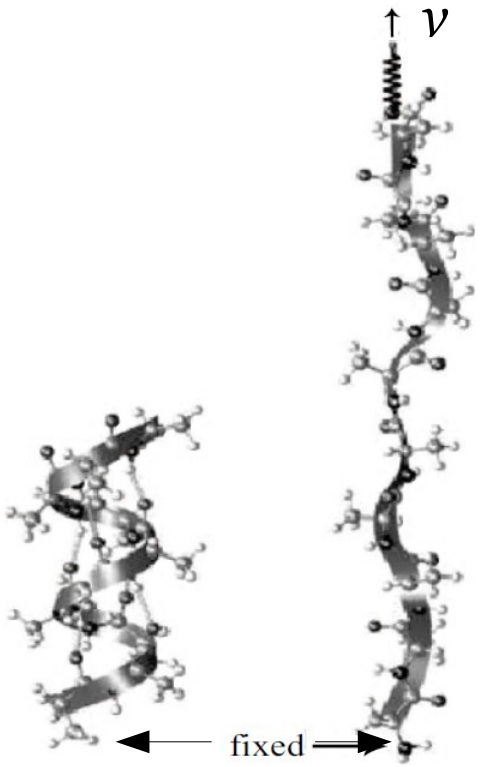
Clausius inequality:

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

Jarzynski equality (1997!)

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

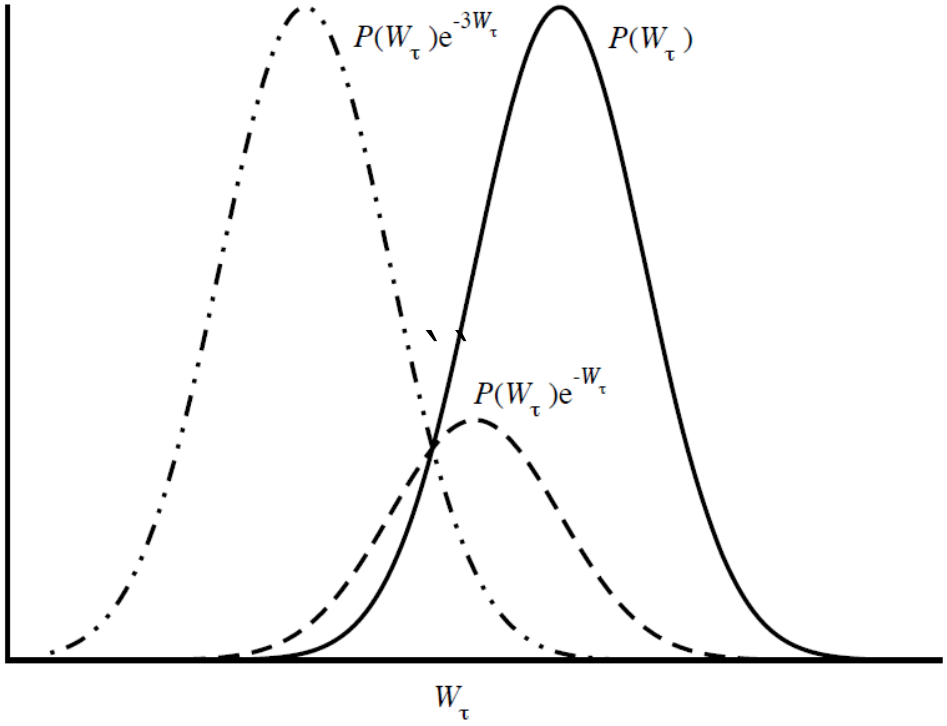
Jarzynski theorem: steered dynamics



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

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

Inefficient because:



Better estimated with the cumulant:

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

Parallel (over replicas)

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

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

System 1: N, V, T, U_1

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

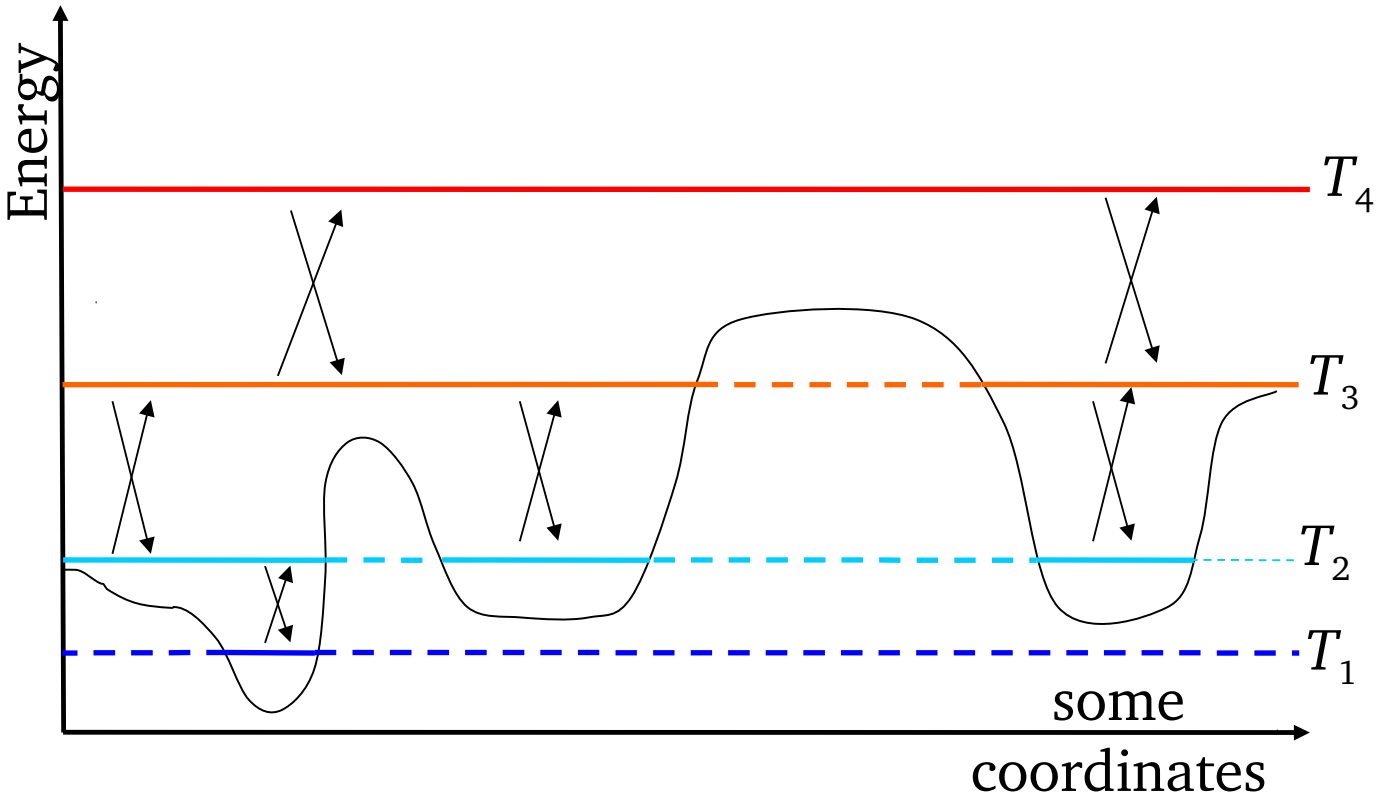
$$\beta \Delta F = \beta F_1 - \beta F_0 = -\ln \frac{Z_1}{Z_0} = \frac{\int d\boldsymbol{r}^N e^{-\beta (U_1 - U_0)} e^{-\beta U_0}}{\int d\boldsymbol{r}^N e^{-\beta U_0}}$$

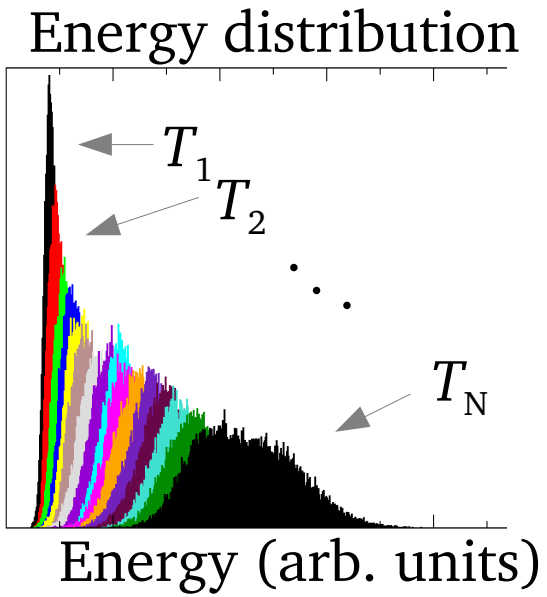
$$\beta \Delta F = -\ln \langle e^{-\beta (U_1 - U_0)} \rangle_0 = -\ln \langle e^{-\beta \Delta U_{0,1}} \rangle_0$$

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

Parallel (over systems)

Replica exchange: the concept

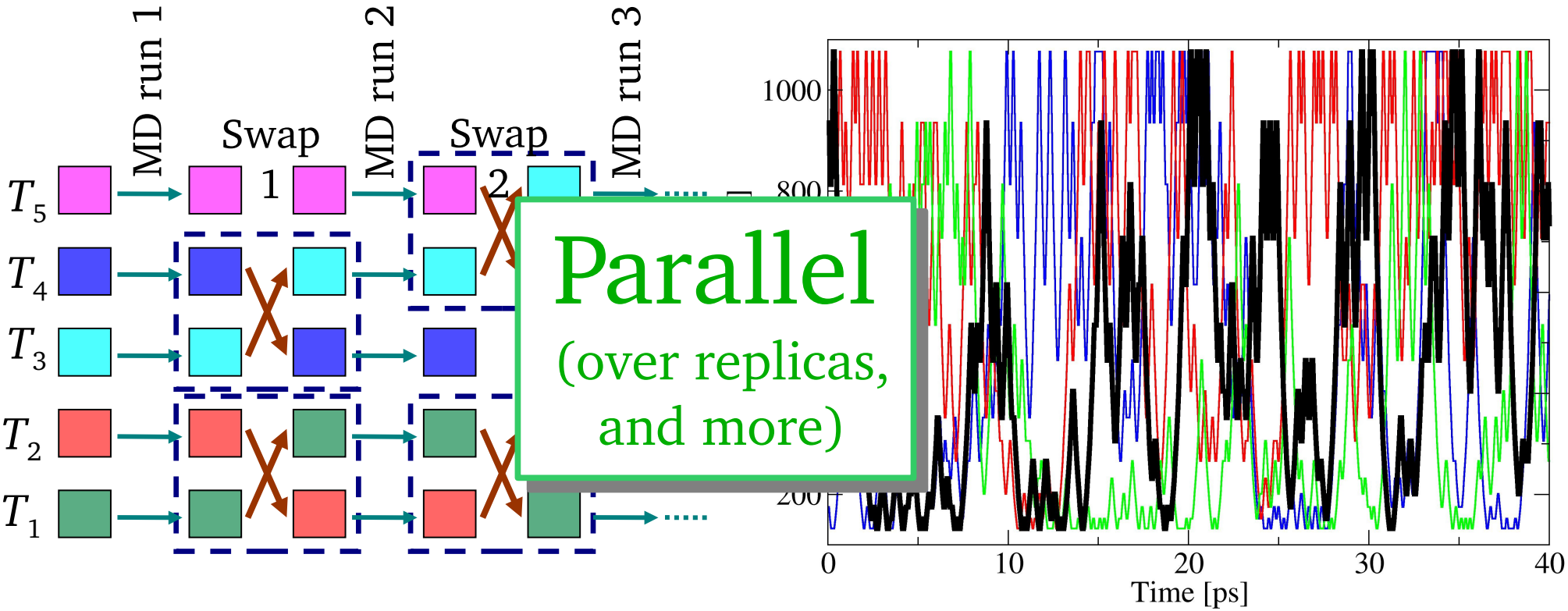




Exchange rule, ensuring canonical sampling at all temperatures:

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

Replica exchange: the implementation



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

Replica exchange: free energy?

Temperature-weighted Histogram Analysis Method:

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

Replica exchange: free energy?

Temperature-weighted Histogram Analysis Method:

Sampled probability

Re-weighting coefficients

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

Un-biased probability at temperature β_0

normalization

q is chosen *a posteriori*

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

Iterative, self consistent solution of:

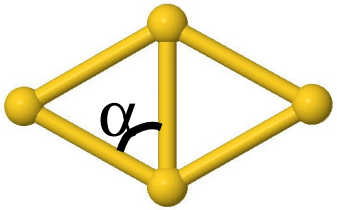
$$\begin{cases} P_0(q) = \dfrac{\sum_{i=1}^{S} n_i(q)}{\sum_{i=1}^{S} N_i \mathrm{e}^{\beta_i F_i} c_i(q)} \\ \beta_i F_i = -\ln\left(\int \mathrm{d}q \; c_i(q) P_0(q) \right) \end{cases}$$

# of observations of q in bin i

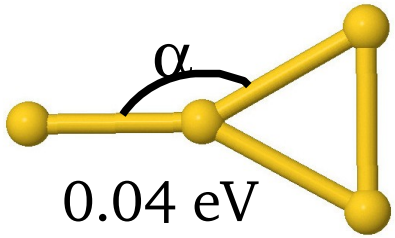
# of total observations in bin i

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

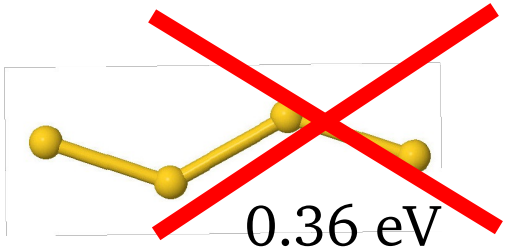
Au_4: coexistence of several isomers



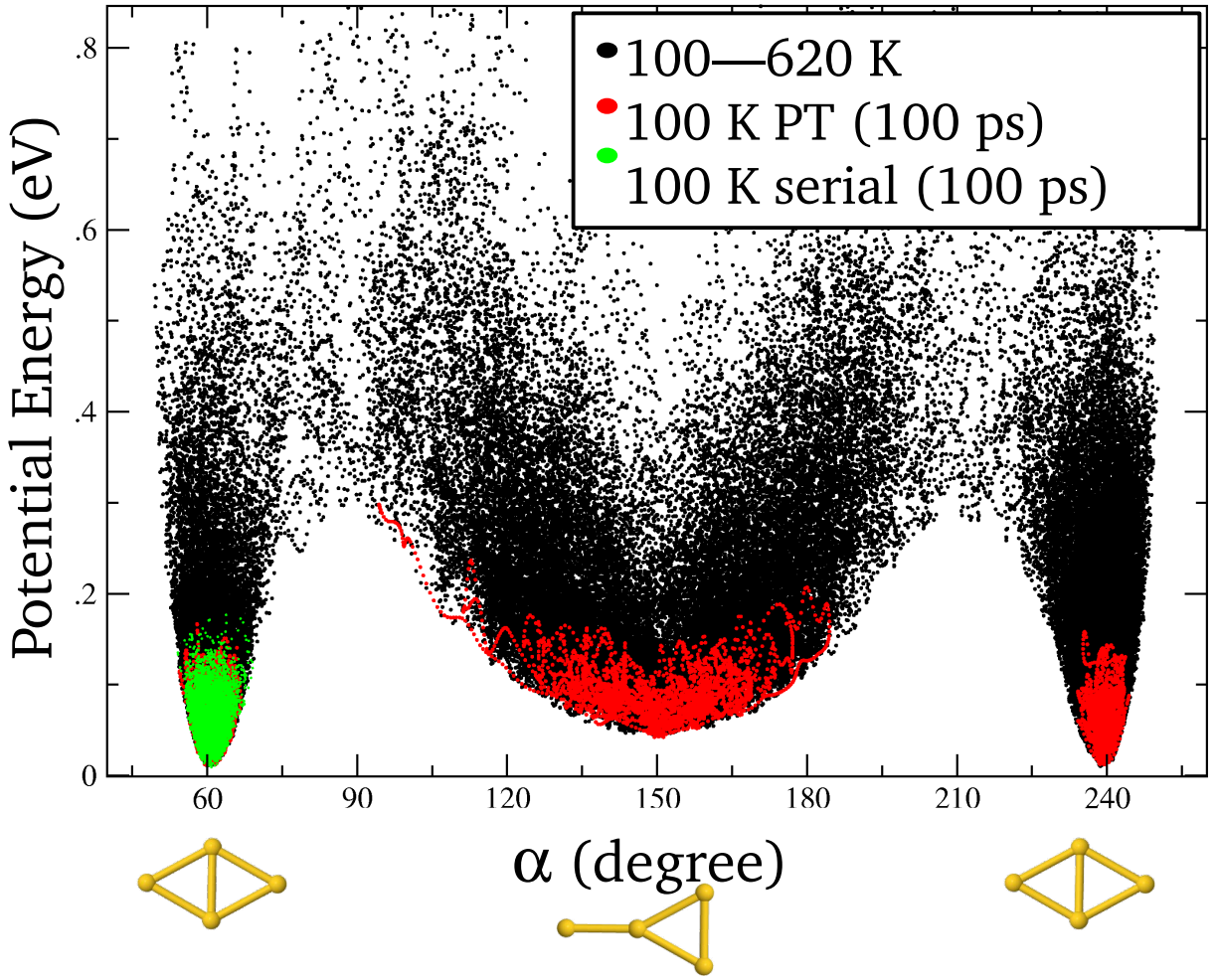
0.00 eV



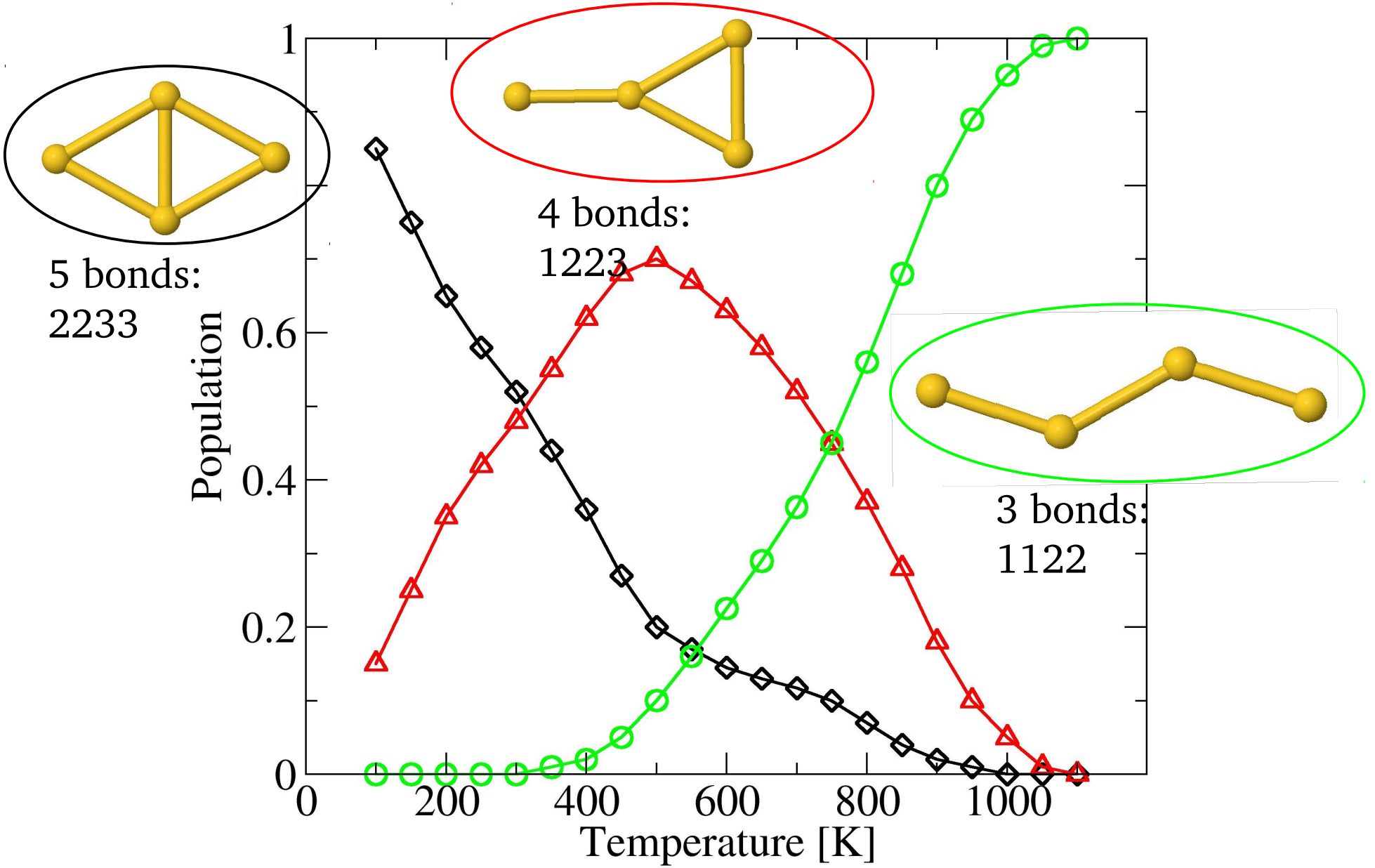
0.04 eV



0.36 eV



Au_4, relative population, coordination-based descriptor



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