Statistical Mechanics
and
Molecular Dynamics

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

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Thermodynamic ensemble properties:

Static equilibrium properties:
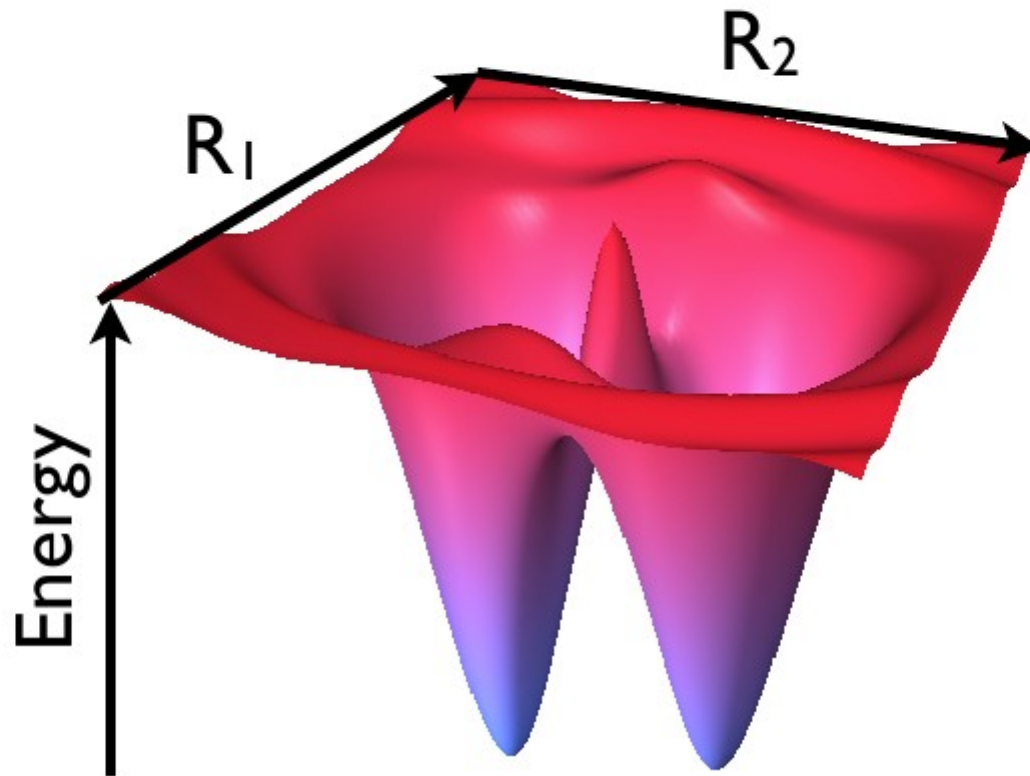
Partition Function

Hamiltonian

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

Dynamic properties $\langle A(0)B(t) \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; e^{-\mathcal{H}/k_B T} A(p(0), R(0)) B(p(t), R(t))$
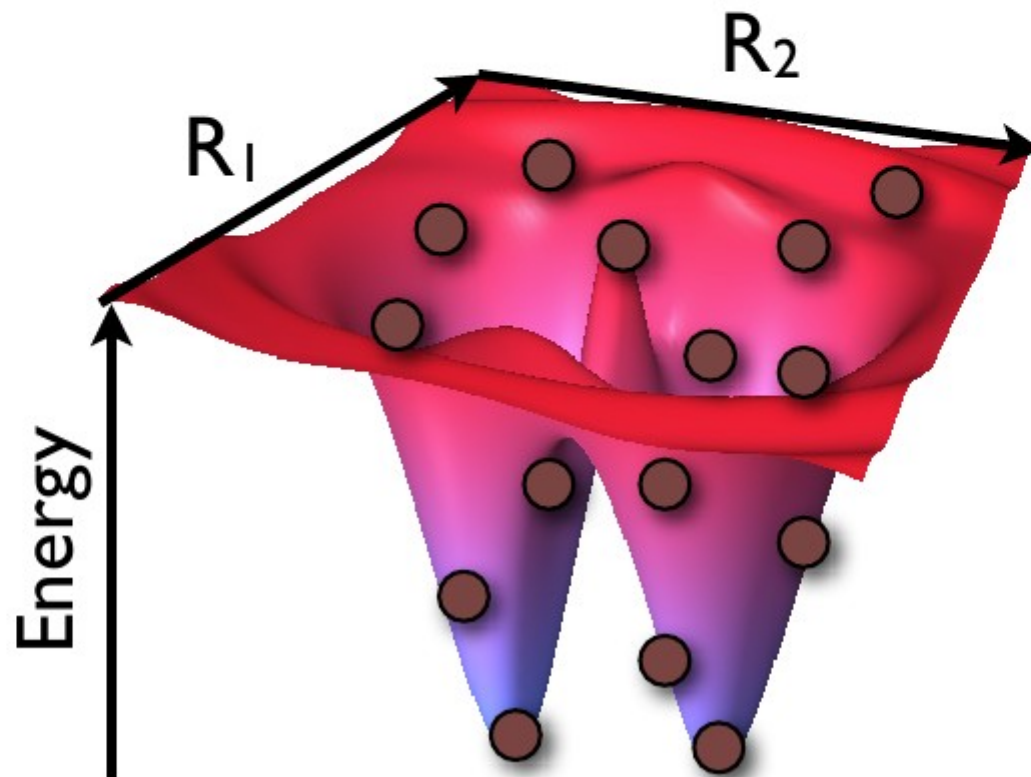
Ensemble averages:
possibility of directly sampling via **Metropolis Monte Carlo** algorithms

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

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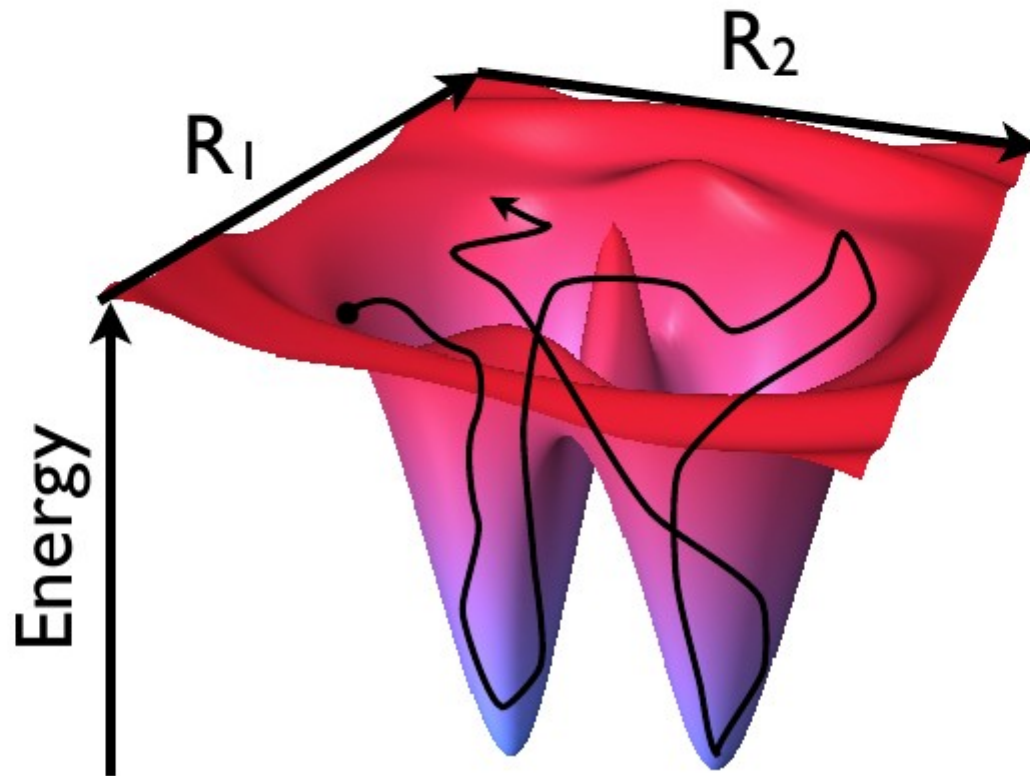
Why statistical sampling?

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

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

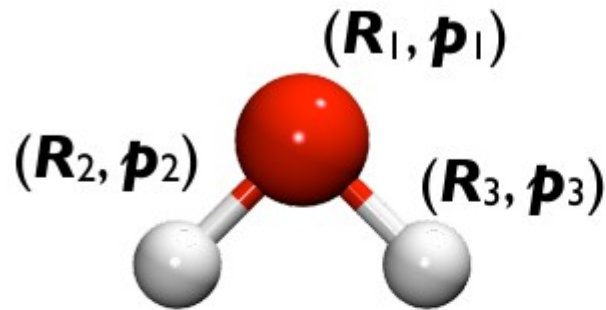$$\langle A(0)B(t) \rangle = \frac{1}{T} \int_0^T dt' A(t')B(t + t')$$

Ergodicity?

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

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

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

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

Molecular dynamics: the basic idea

$(R_1, \boldsymbol{p}_1)$

$(R_2, \boldsymbol{p}_2)$
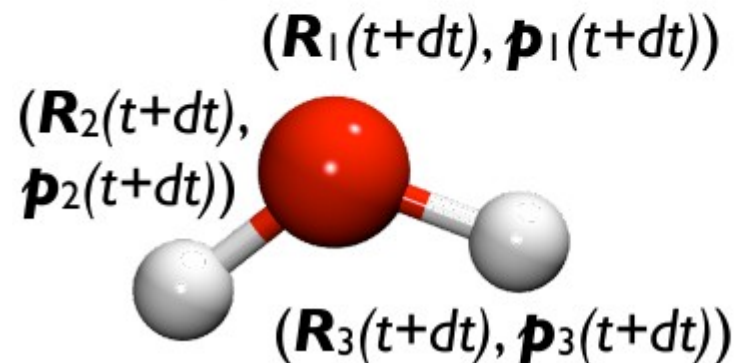
$(R_3, \boldsymbol{p}_3)$

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

$(R_1(t+dt), \boldsymbol{p}_1(t+dt))$

$(R_2(t+dt), \boldsymbol{p}_2(t+dt))$

$(R_3(t+dt), \boldsymbol{p}_3(t+dt))$

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

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

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

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

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

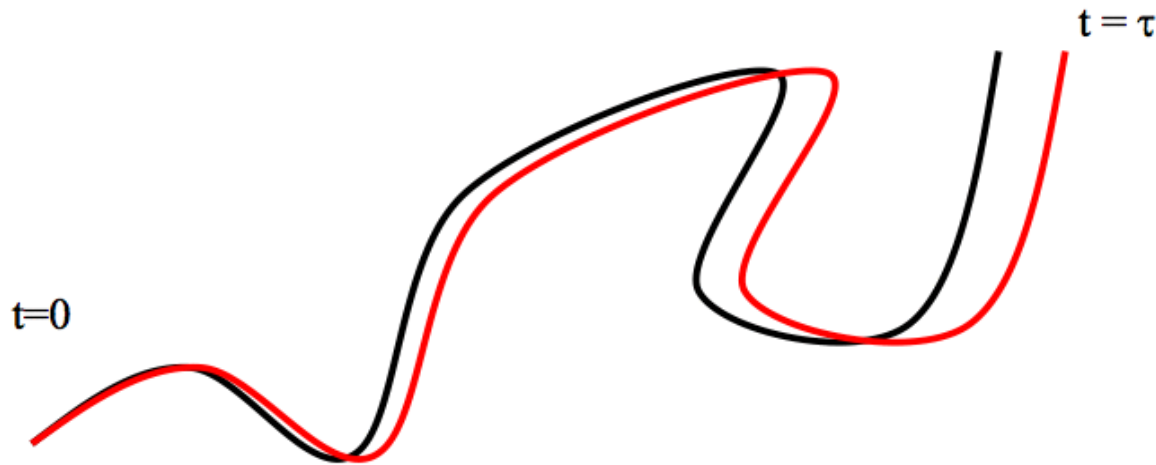Or $$x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \ddot{x}(t)\Delta t^2$$

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???

Molecular chaos

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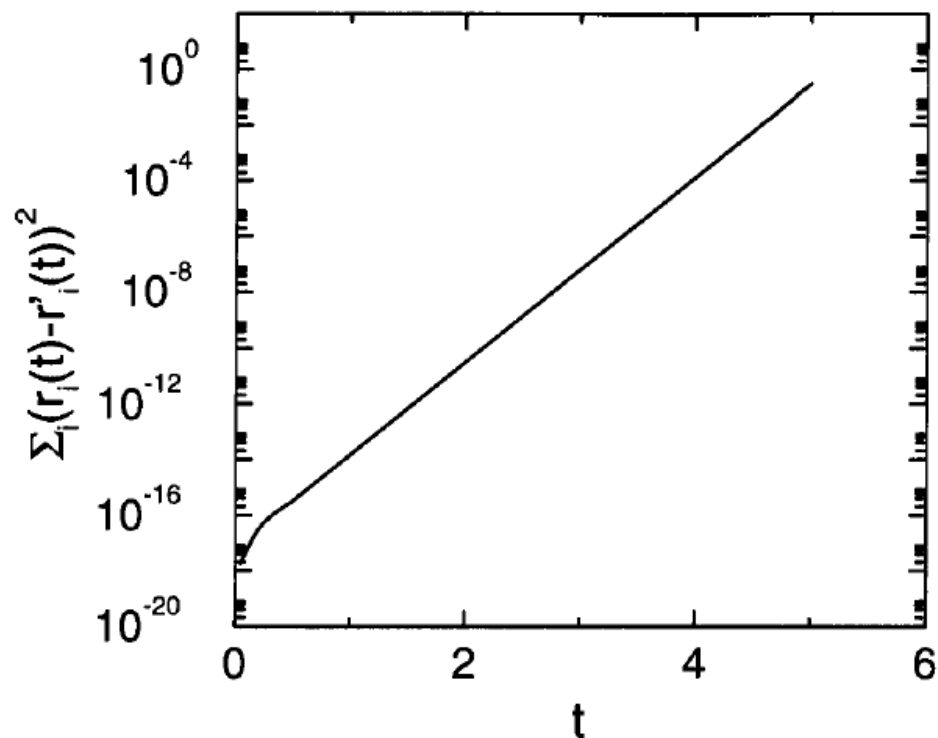conditions diverge exponentially ("Lyapunov instability")

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

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

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

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

Why should anyone believe in Molecular Dynamics simulations ???

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 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, $\tilde{\mathcal{H}}(\mathbf{x}, \Delta t)$ which is close to the real Hamiltonian $\mathcal{H}(\mathbf{x})$, in the sense that for $\Delta t \rightarrow 0$ $\tilde{\mathcal{H}}(\mathbf{x}, \Delta t)$ converges to $\mathcal{H}(\mathbf{x})$

• Take a different look at the problem.

– Do not discretize NEWTON's equation of motion…

– …but discretize the ACTION

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.

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

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

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

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

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

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

For a one dimensional system this becomes

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

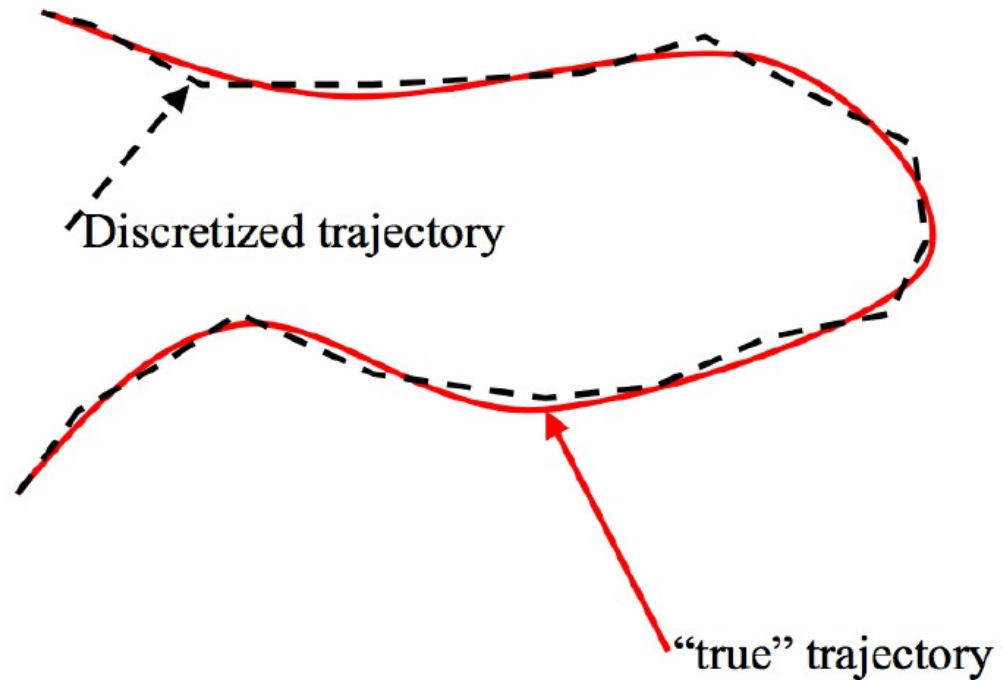$$S_{disc} = \sum_{i=1}^{i_{max}} \left[\frac{m(x_{i+1} - x_i)^2}{2\Delta t} - U(x_i)\Delta t \right]$$

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.

Discretized trajectory

"true" 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

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

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

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

Probability distribution of the kinetic energy:

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

Maxwell-Boltzmann-Distribution

$$T < T < T$$
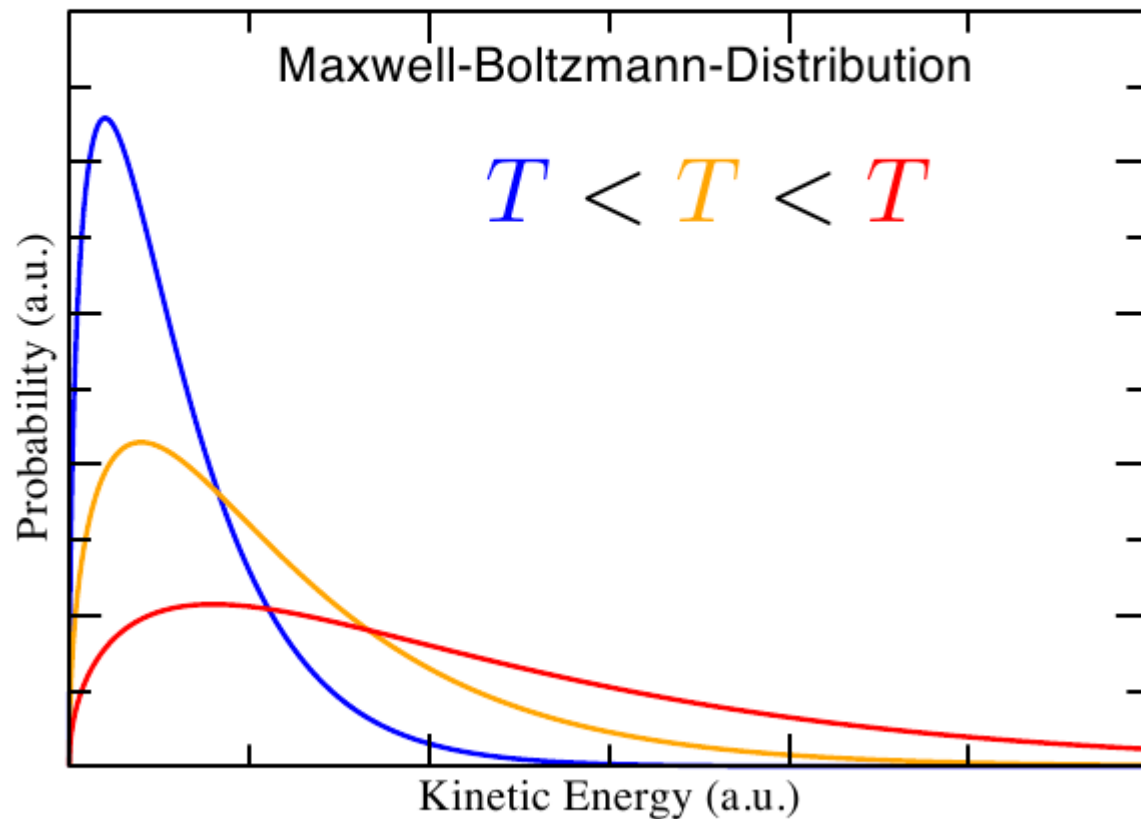
kinetic energy: $p^2/2M$

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

# 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

$$P(v) = \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp\left[-\beta m v^2 / 2 \right]$$
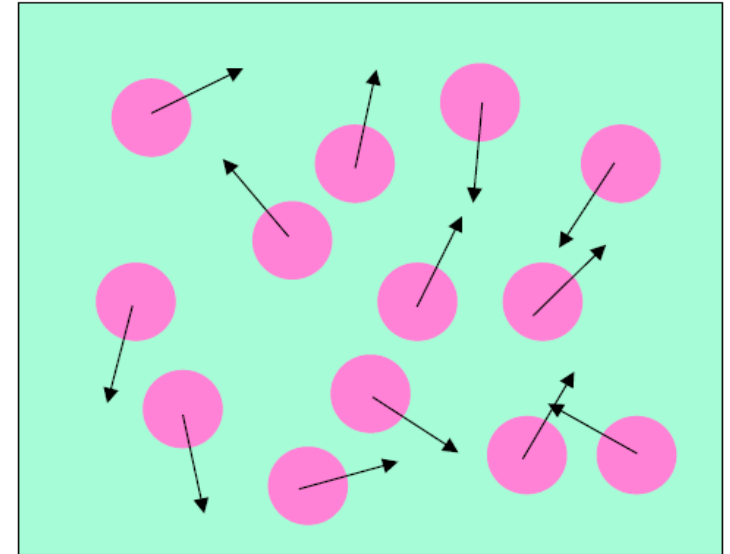
- The probabilities to collide are uncorrelated (Poisson distribution)

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

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

Deterministic thermostat: Nosé Hoover

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

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

<div style="text-align:center">Original system   Fictitious Oscillator</div>

- 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

Stochastic velocity rescaling thermostat

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

– 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

Potential energy surface $\longrightarrow$ [Free-energy method] $\longrightarrow$ Free-energy surface $(T,\{q_i\})$
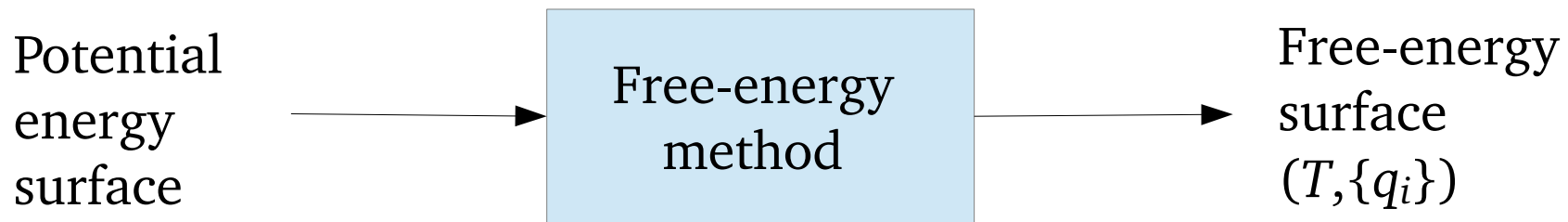
PES can be from:
- *Ab initio*
- Classical force field
- Toy models

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

- 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):

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

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

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.
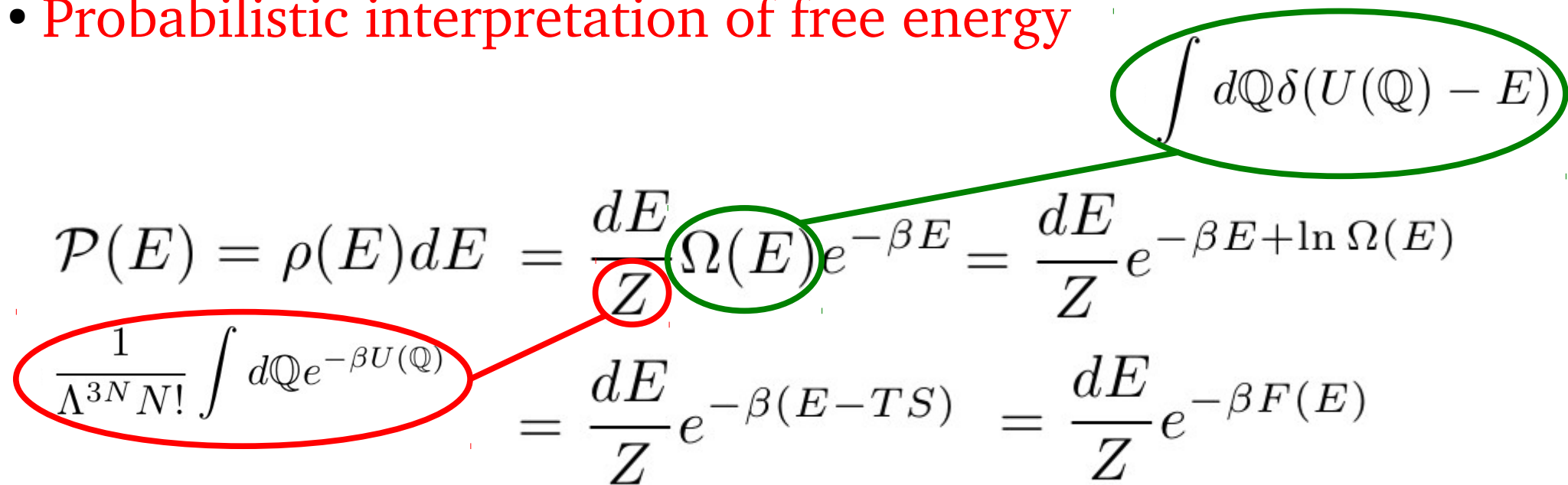
Thermodynamic Integration

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

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.

- Probabilistic interpretation of free energy

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

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

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

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

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:

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

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:

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

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

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

One cannot converge such a quantity!

… but one cannot measure it, either

- 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 <<<

How are free energies measured experimentally?

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

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

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

$$V_0 \to \infty : \text{ideal gas}$$

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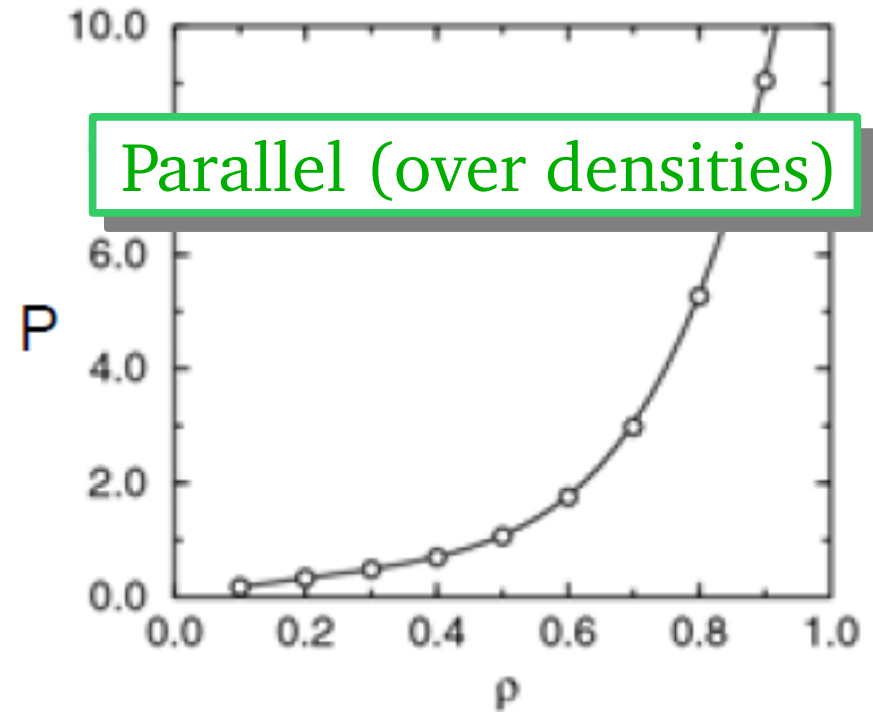
Let us assume a mixed potential: $U = (1 - \lambda)U_0 + \lambda U_1$

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

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

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

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

How to choose the reference?

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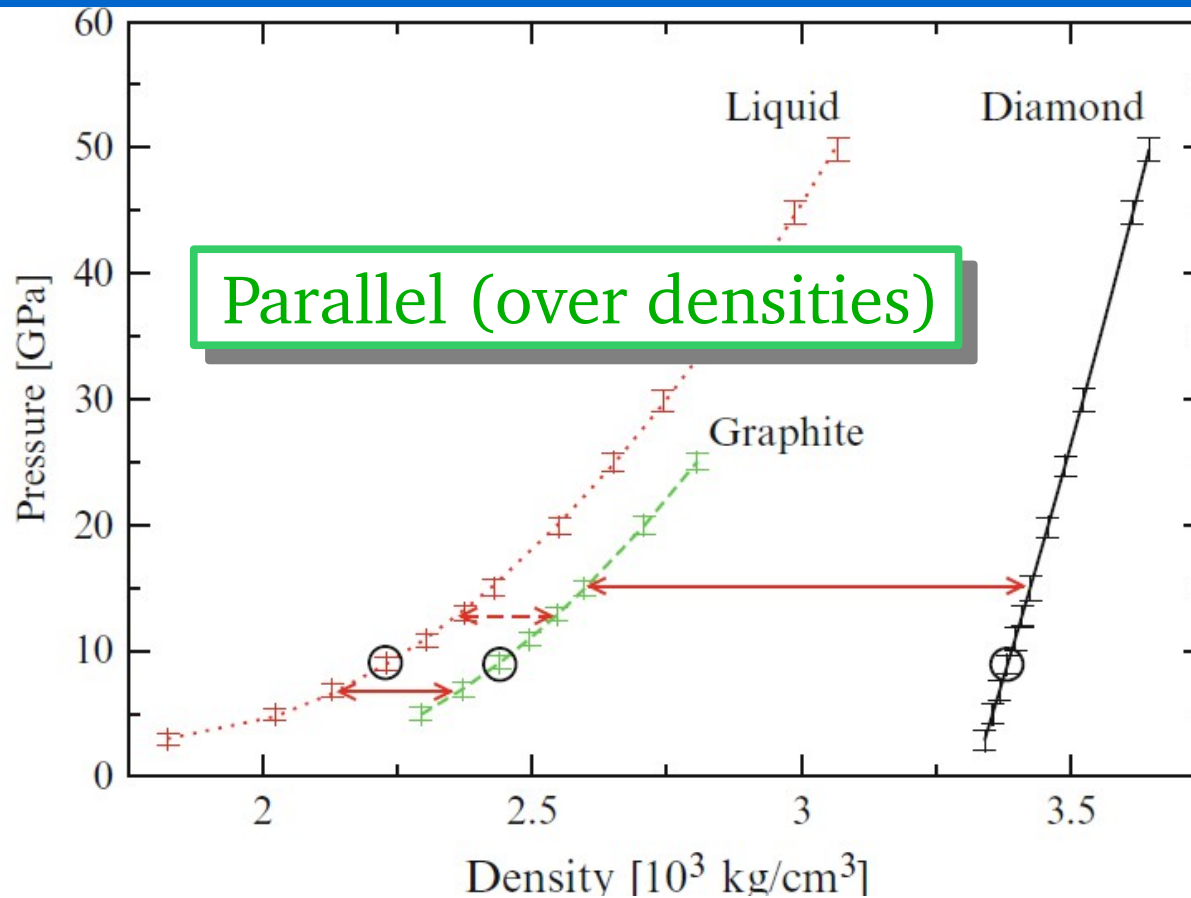
Considered phases: diamond, graphite, and liquid(s)

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

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GRAPHITE

DIAMOND

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

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

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

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

Difference in slopes: difference in specific volumes

$$\frac{\partial \mu}{\partial P} = \frac{\partial g}{\partial P} = v = \frac{1}{\rho}$$
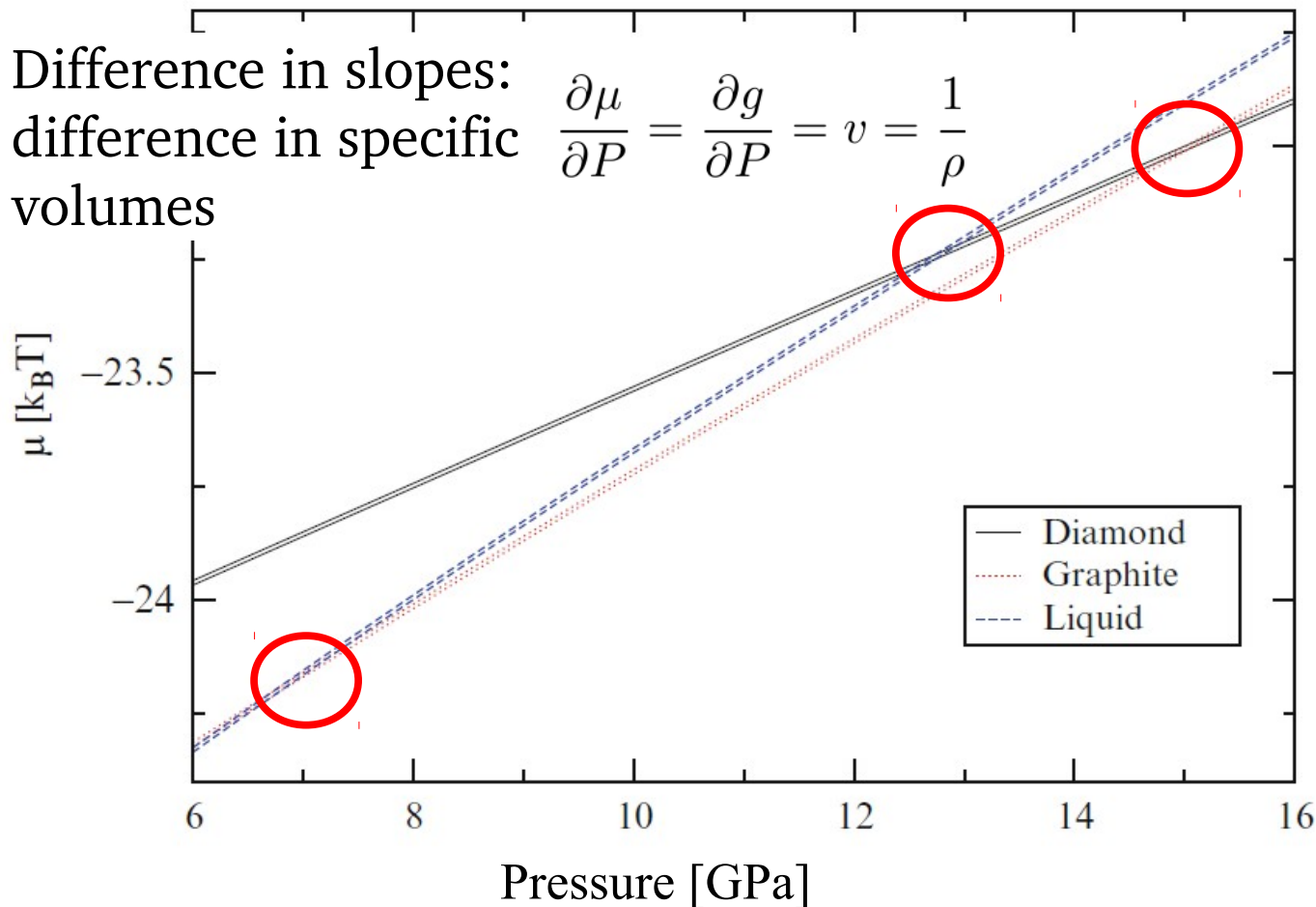
And then: Gibbs-Duhem integration

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

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

>>> Serial <<<

This gives three coexistence points at T_0

Carbon phase diagram
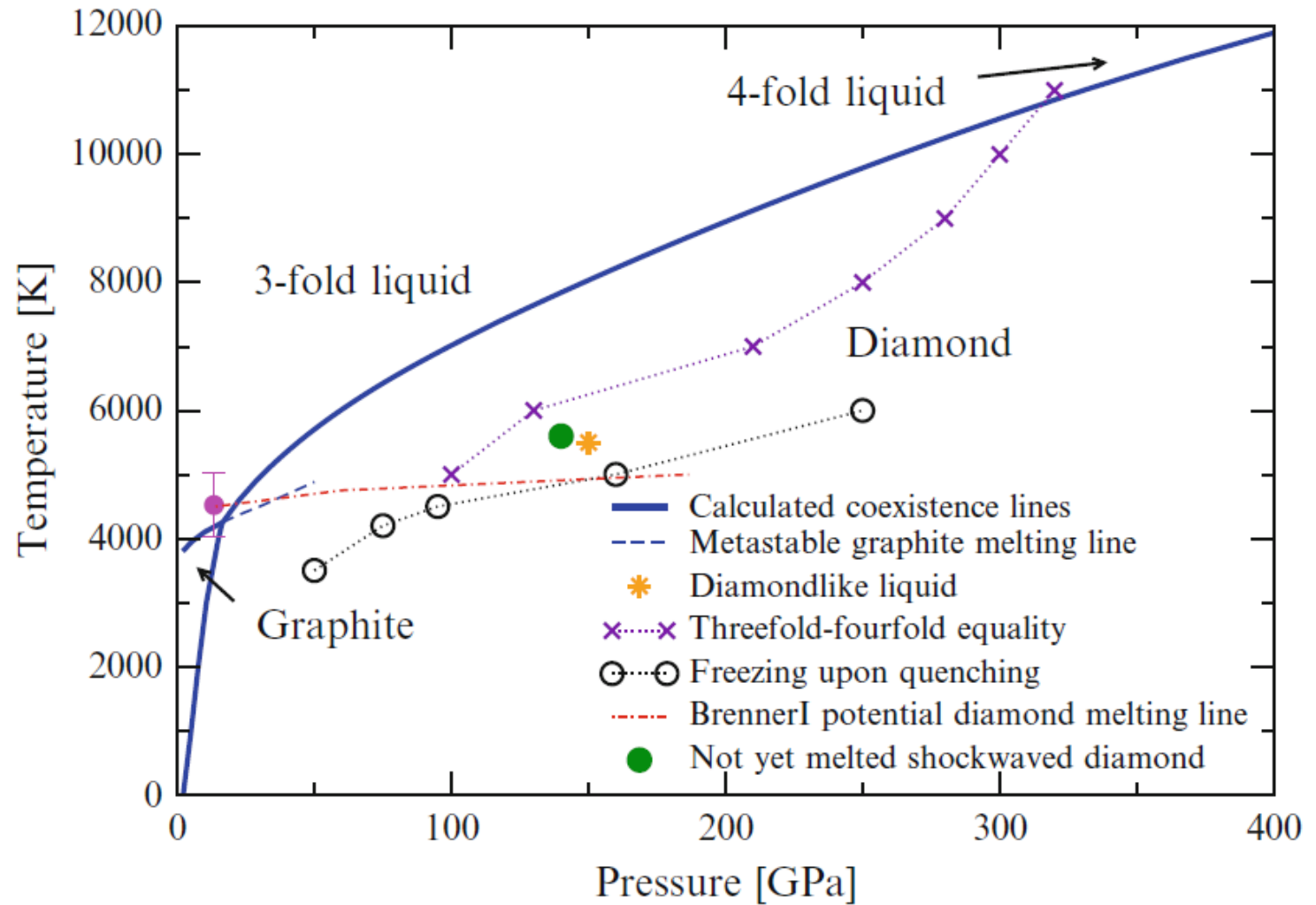
LMG *et al.* PRL 2005

Start again from two systems:

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

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

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

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

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

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

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

time ?!?

reversible?

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

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

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

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

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

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

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

> > > Serial < < <

Silicon (classical potential)

Free energy (eV) vs Temperature (K)

- - - t_s=0.1 ps
- · - · - t_s=1.0 ps
——— t_s=5.0 ps
○ Reference data
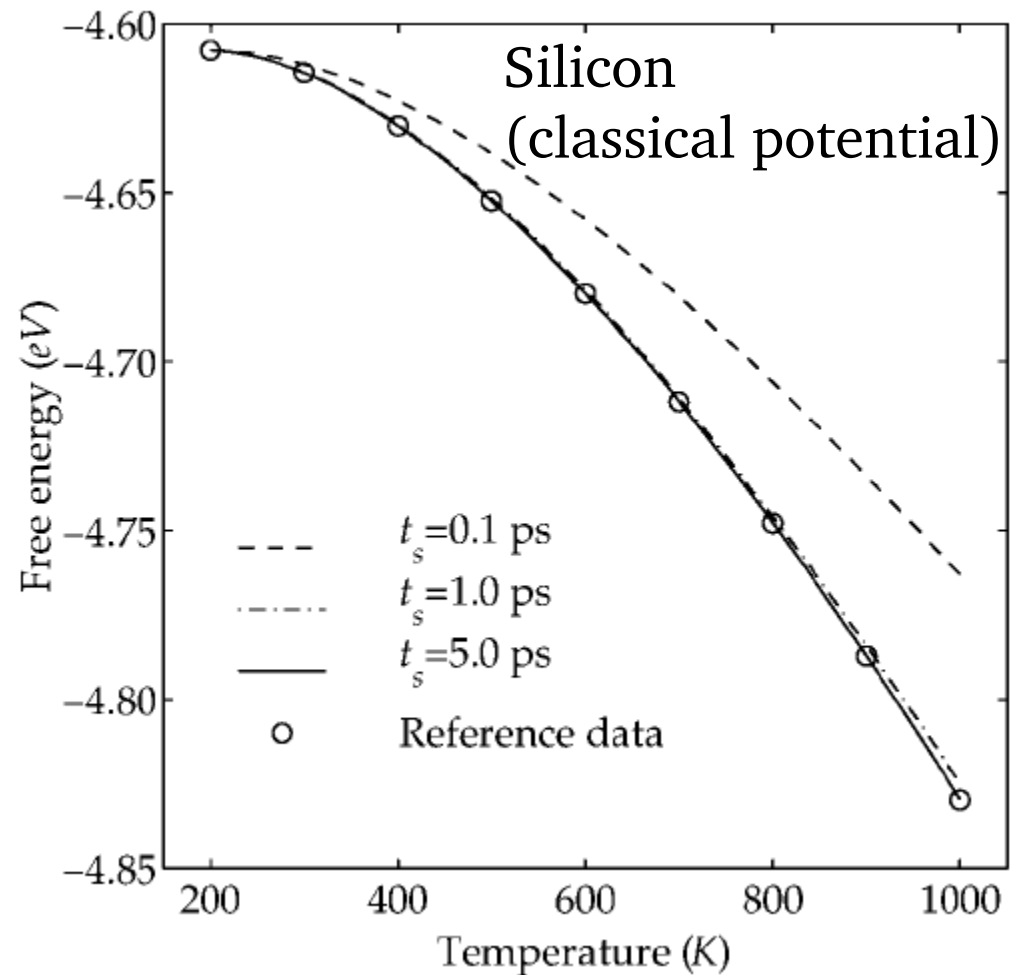
Ab initio diamond melting line
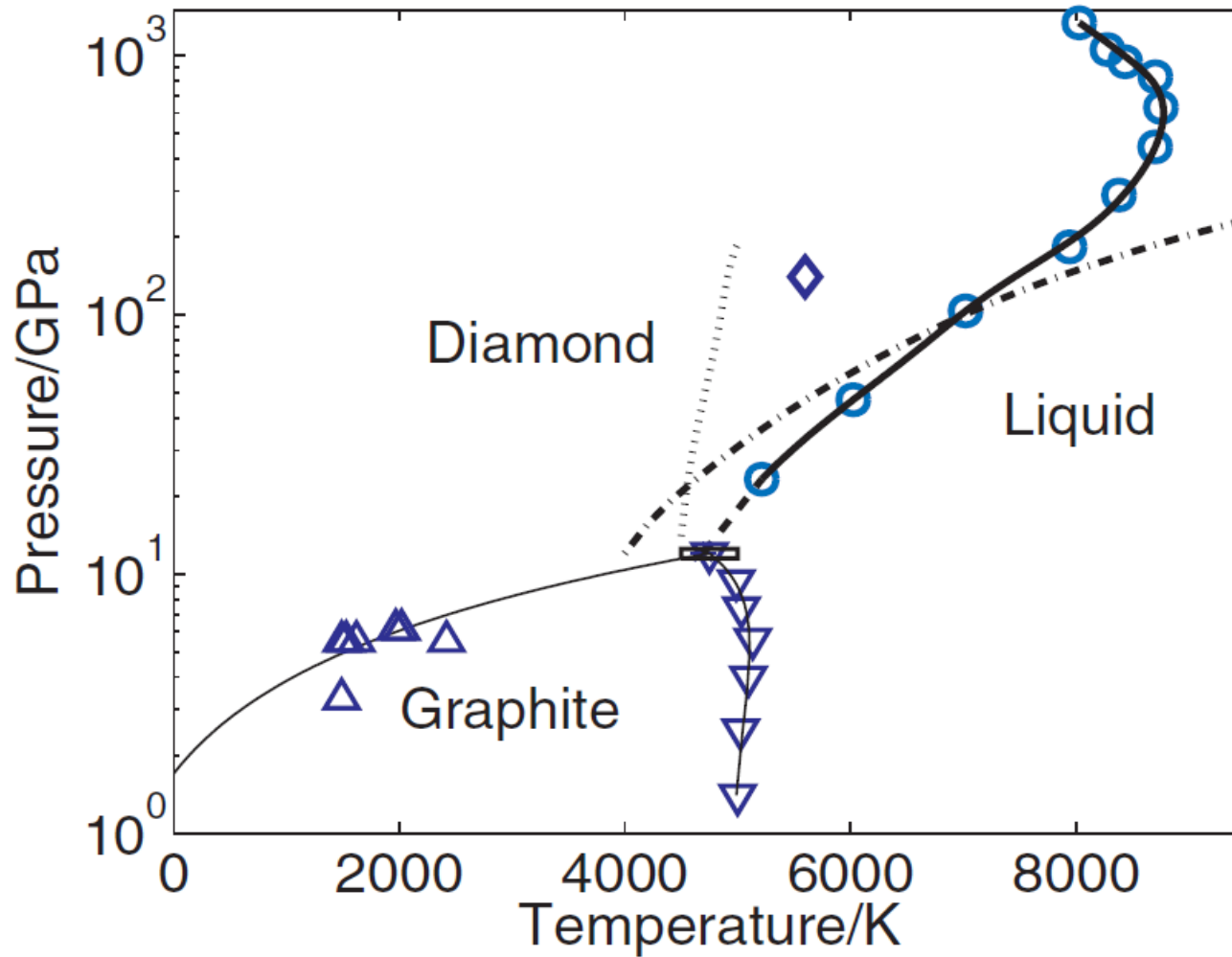
Wang *et al.* PRL **95**, 185701 (2005)

Beyond equilibrium: Jarzynski theorem

$$W_{AB} = \langle \mathcal{W}_{AB}(x_0) \rangle_A = \frac{C_N}{Z_A(N,V,T)} \int dx_0 \, e^{-\beta \mathcal{H}_A(x_0)} \mathcal{W}_{AB}(x_0)$$

Clausius inequality:

$$\langle \mathcal{W}_{AB}(x_0) \rangle_A \geq \Delta F_{AB}$$

Jarzynski equality (1997!)

$$e^{-\beta \Delta F_{AB}} = \left\langle e^{-\beta \mathcal{W}_{AB}(x_0)} \right\rangle_A = \frac{C_N}{Z_A(N,V,T)} \int dx_0 \, e^{-\beta \mathcal{H}_A(x_0)} e^{-\beta \mathcal{W}_{AB}(x_0)}$$
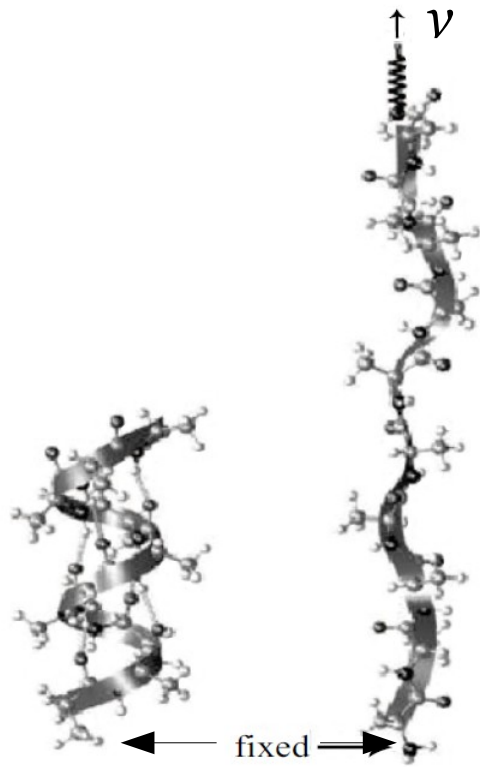
$$U(\mathbf{r}_1, ..., \mathbf{r}_N, t) = U_0(\mathbf{r}_1, ..., \mathbf{r}_N) + \frac{1}{2}\kappa \left(|\mathbf{r}_1 - \mathbf{r}_N| - r_{\text{eq}} - vt\right)^2$$

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

Inefficient because:
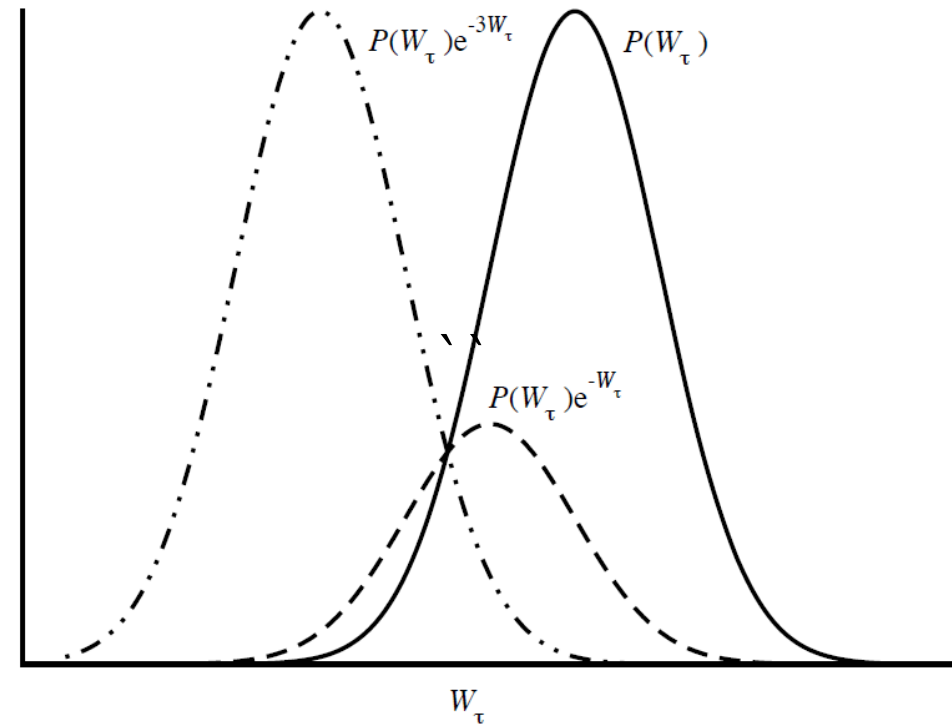
Better estimated with the cumulant:

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

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

System 1: N, V, T, U_1

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

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

$$\beta \Delta F = \beta F_1 - \beta F_0 = -\ln \frac{Z_1}{Z_0} = \frac{\int d\boldsymbol{r}^N e^{-\beta(U_1 - U_0)} e^{-\beta U_0}}{\int d\boldsymbol{r}^N e^{-\beta U_0}}$$
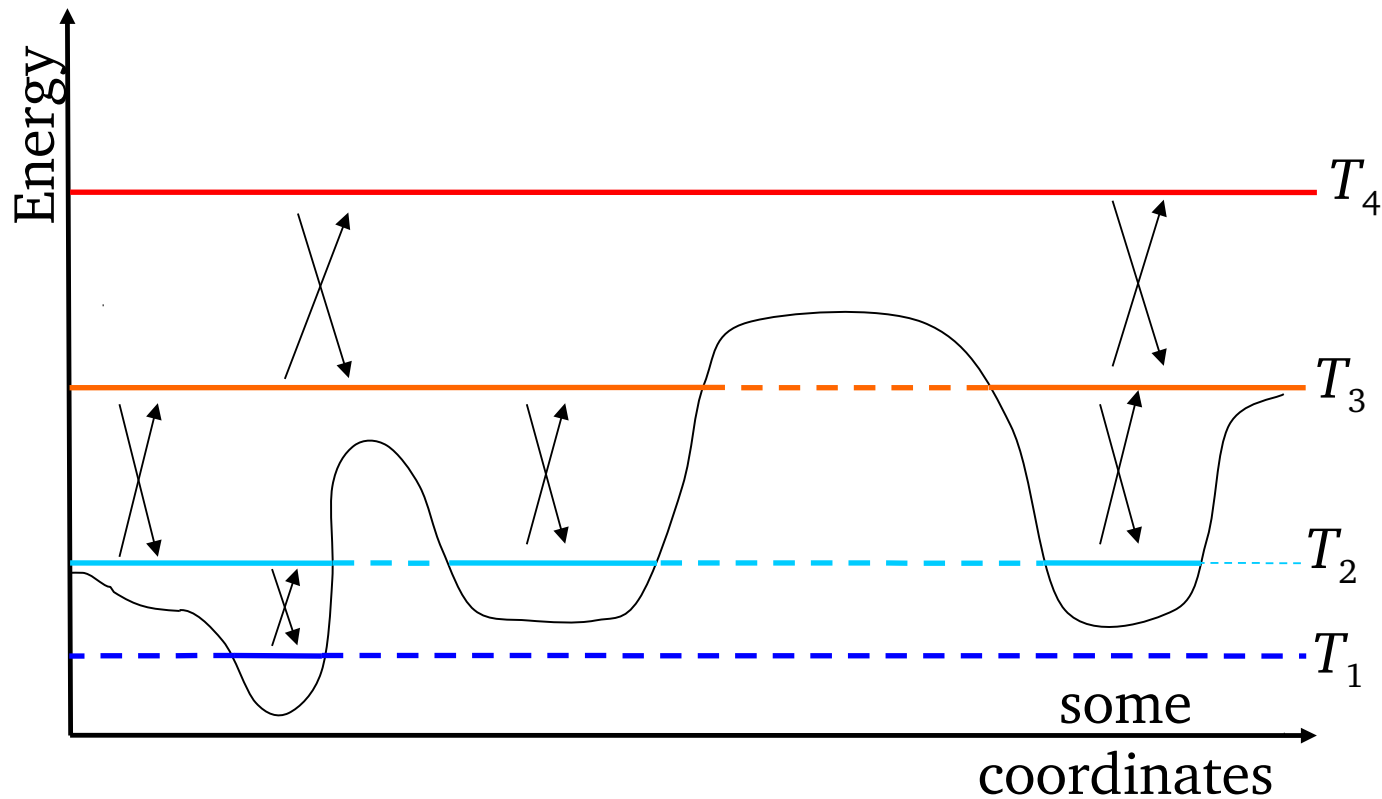
$$\beta \Delta F = -\ln \langle e^{-\beta(U_1 - U_0)} \rangle_0 = -\ln \langle e^{-\beta \Delta U_{0,1}} \rangle_0$$

If poor overlap: sequence of systems

$$\beta \Delta F = -\sum \ln \langle e^{-\beta \Delta U_{\alpha, \alpha+1}} \rangle_\alpha$$
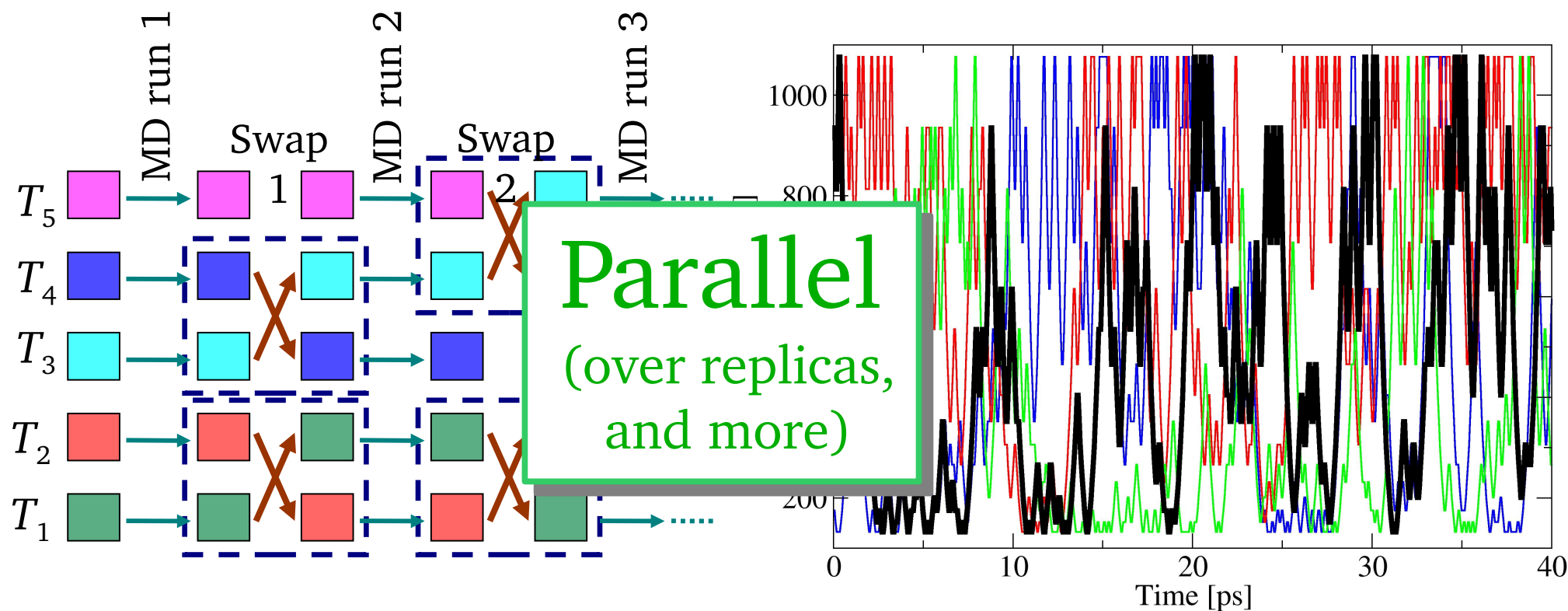
Parallel (over systems)

Replica exchange: the concept
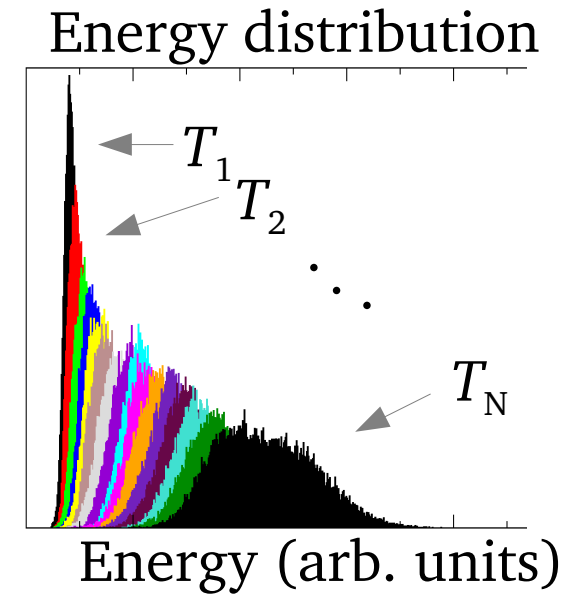
Exchange rule, ensuring canonical sampling at all temperatures:

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

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

Temperature-weighted Histogram Analysis Method:

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

Temperature-weighted Histogram Analysis Method:

Sampled probability → Re-weighting coefficients

→ Un-biased probability at temperature β_0

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

↘ normalization → q is chosen *a posteriori*

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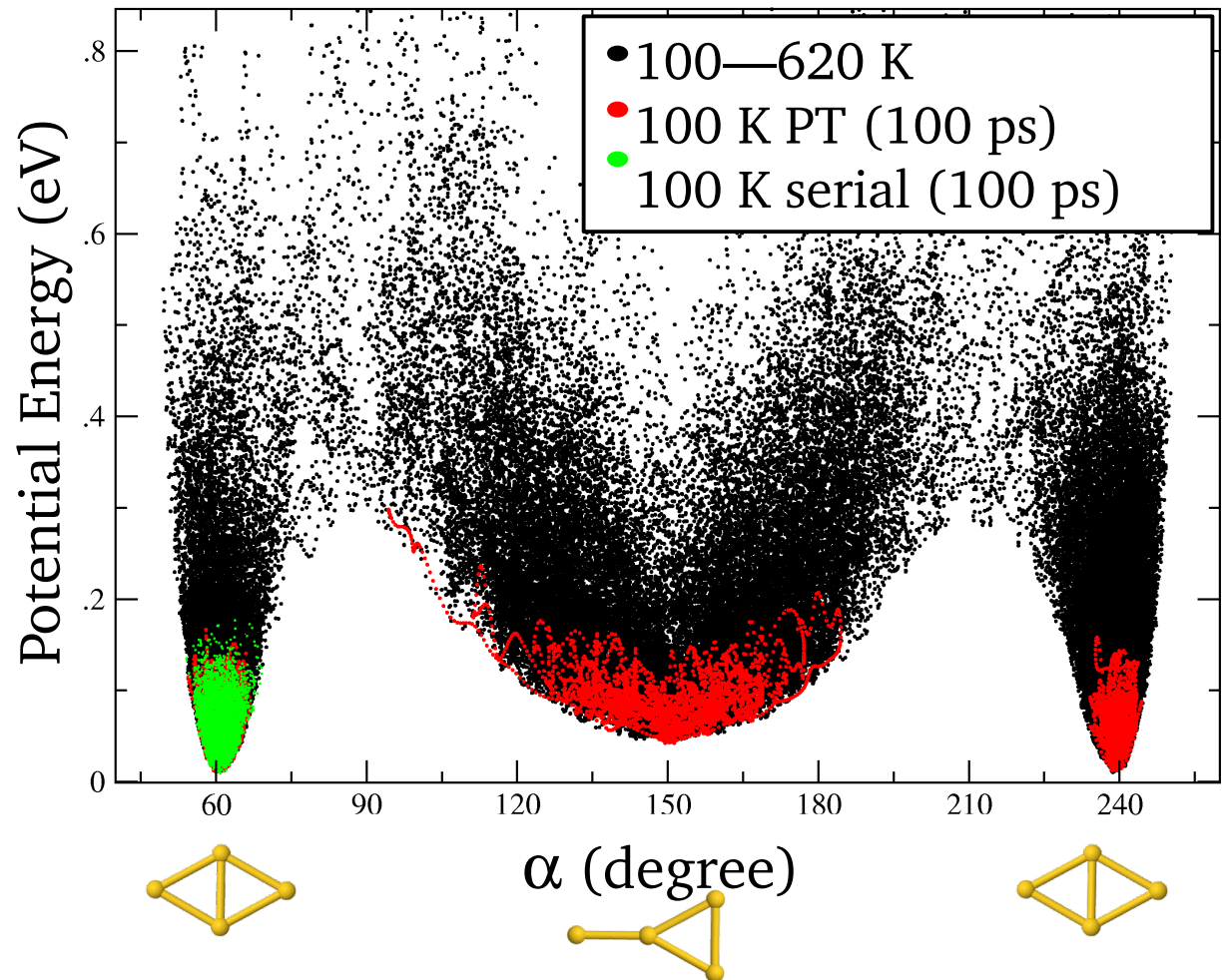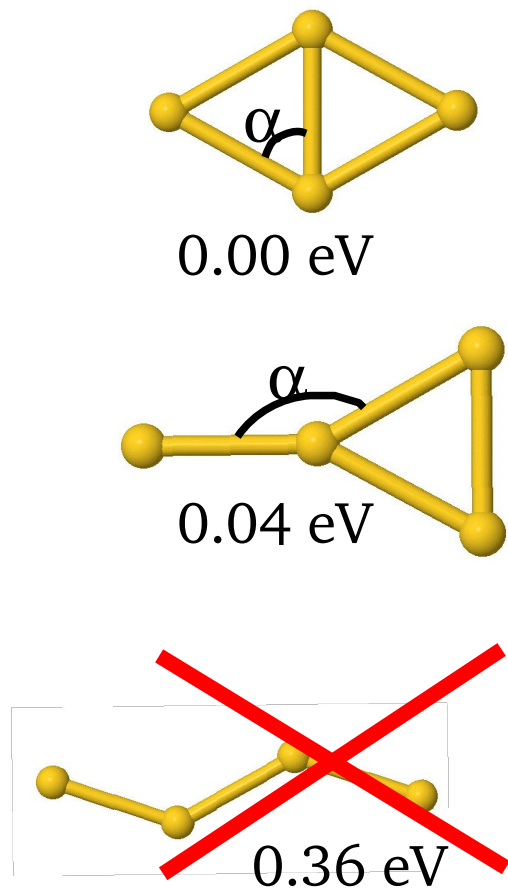
Iterative, self consistent solution of:

→ # of observations of q in bin i

$$\begin{cases} P_0(q) = \dfrac{\sum_{i=1}^{S} n_i(q)}{\sum_{i=1}^{S} N_i e^{\beta_i F_i} c_i(q)} \\[2em] \qquad\qquad \rightarrow \text{ \# of total observations in bin } i \\[1em] \beta_i F_i = -\ln\left(\int dq\ c_i(q) P_0(q)\right) \end{cases}$$

IMPORTANT: "q" is a "post-production" (collective) variable
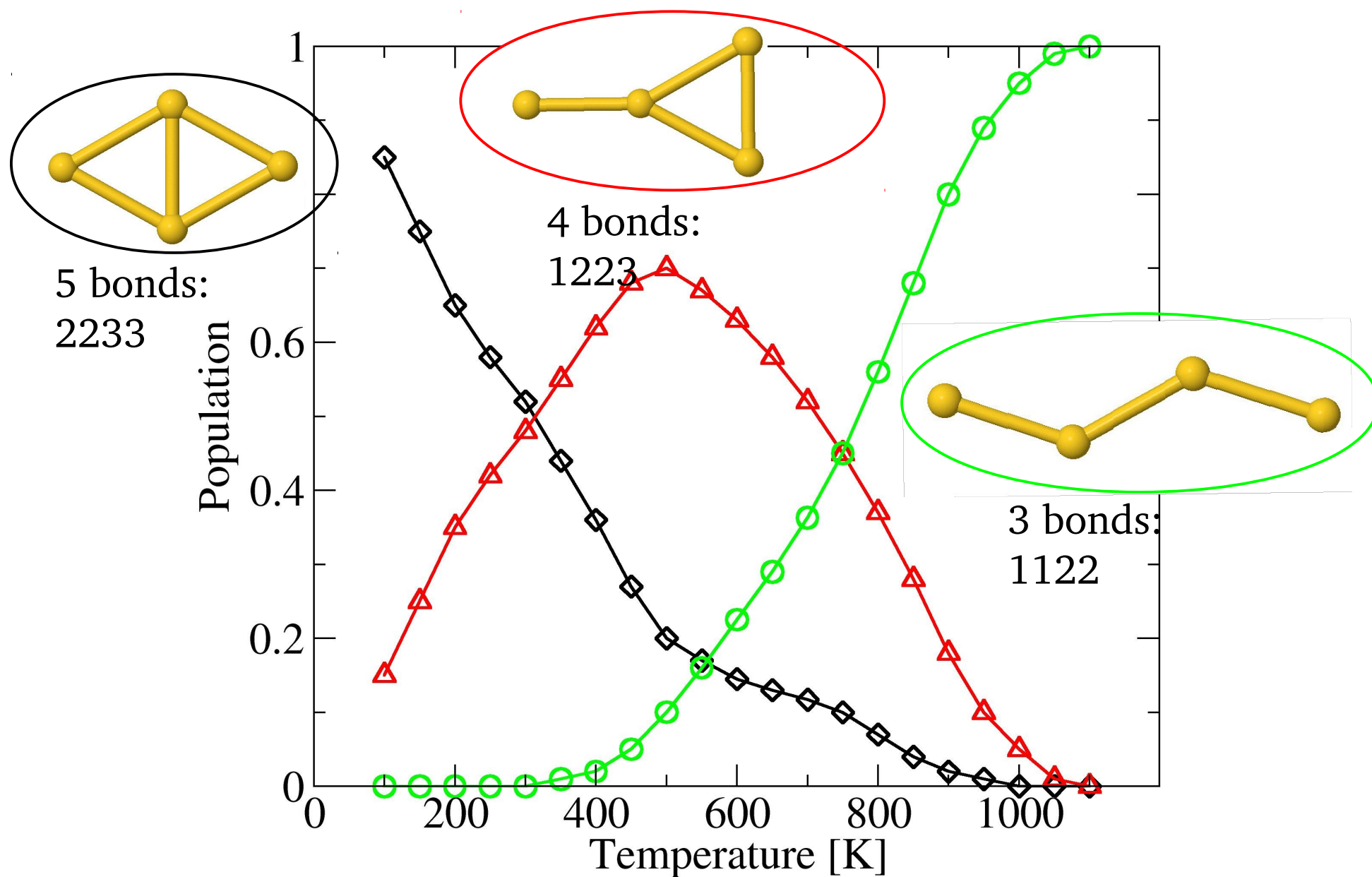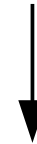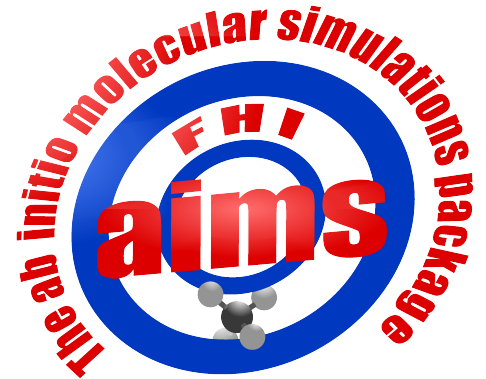
Free-energy methods: accessibility via FHI-aims

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