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:

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

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

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

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

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

\[ A(q(r^N); r^N(0), p^N(0), t) \rightarrow \overline{A(q)} = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' A(q, t') \]

\[ \sum_{\text{initial conditions}} \left( \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' A(q(r^N); r^N(0), p^N(0), t') \right) \]

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

\[ = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \left\langle A(q(r^N); r^N(0), p^N(0), t) \right\rangle_{\text{NVE}} = \left\langle A(q) \right\rangle_{\text{NVE}} \]
Molecular dynamics: the basic idea

1. Assign initial $R$ (position) and $p$ (momenta)

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

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

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

$$\dot{R}_I = \frac{p_I}{M_I}$$

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)

Isothermal-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:

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

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

compute position in next and previous time steps

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

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

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

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???
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”)

\[ t = 0 \]

\[ t = \tau \]
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, which is close to the real Hamiltonian $\mathcal{H}(x)$, in the sense that for $\Delta t \to 0$ converges to $\mathcal{H}(x)$

- 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:

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

is an extremum.
Reminder: Lagrangian formulation

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

\[ \frac{\partial \mathcal{L}}{\partial \dot{r}} = \frac{\partial K}{\partial \dot{r}} = p \]

\[ \frac{\partial \mathcal{L}}{\partial r} = -\frac{\partial U}{\partial r} = F \]

\[ p = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial \dot{r}} \]

\[ \dot{p} = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial r} \]
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?
Discretized action

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

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

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 $x_i$.

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

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

- "true" trajectory
- Discretized trajectory
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

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

Fictitious electron mass

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

Lagrange multipliers

Kohn-Sham orbitals

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

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 \(\Rightarrow\) 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
Sampling the canonical ensemble: thermostats

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

Interesting because:
- Experimental setups are usually at constant temperature
- Favors better modeling of conformational changes

Diagram:
- Bath: Energy is conserved
- System: Energy is not conserved
Sampling the canonical ensemble: thermostats

**Probability distribution of the kinetic energy:**

\[ P(E_{kin}) \propto \exp(-E_{kin}/k_BT) \]

\[ T < T < T \]

\[ T = \frac{2\langle E_{kin}\rangle}{3Nk_B} \]

# of particles
Stochastic thermostat: Andersen

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

- After collision the particle is given a new Velocity

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

- The probabilities to collide are uncorrelated (Poisson distribution)

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

Deterministic thermostat: Nosé Hoover


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

\[ H_{NH} = \sum_I \frac{p_I^2}{2M_I} + V(R) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta \]

- Original system
- Fictitious Oscillator

- Momenta are damped by a fictitious oscillator \( \dot{p}_I = F_I - \frac{p_\eta}{Q} p_I \)

- 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 heat bath

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

The target temperature follows a stochastic differential equation:

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

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

Potential energy surface → Free-energy method → 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 \( (\mu_\alpha = \mu_\beta = \ldots) \)
- relative population of competing structures (nanoscale) \( P(A) \propto e^{-\beta E_A} \)
- rate of processes (via Transition State Theory)
Fundamental statistical mechanics ↔ thermodynamics link

\[ F = -k_B T \ln Z \]
\[ \beta F = - \ln Z \]

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

Classical statistics (for nuclei):

\[ Z = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{Q} e^{-\beta U(\mathbf{Q})} \]
\[ \Lambda = \frac{\hbar}{\sqrt{2\pi mk_B T}} \]
Thermodynamics

\[ F = E - TS \]

if we can calculate \( E \) and write analytically on approximation for \( S \) for our system, we use this expression. Example: \( ab \text{ initio} \) 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

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

\[
\frac{1}{\Lambda^{3N} N!} \int dQ e^{-\beta U(Q)} = \frac{dE}{Z} e^{-\beta (E - TS)} = \frac{dE}{Z} e^{-\beta F(E)}
\]

\[
\frac{\mathcal{P}(E_1)}{\mathcal{P}(E_2)} = e^{-\beta [F(E_1) - F(E_2)]}
\]
What is energy? A mapping from 3N coordinates into one scalar $\mathbb{R}^{3N} \rightarrow \mathbb{R}$

Let's introduce:

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

so that:

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

Formal definition of a free energy:

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

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

$$\langle E \rangle = \sum_n E_n P_n$$

$$P_n = \frac{e^{-\beta E_n}}{Z}$$

$$\sum_n P_n = 1$$

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

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

\[ \langle A \rangle = \frac{\int d\mathcal{Q} A(\mathcal{Q}) e^{-\beta U(\mathcal{Q})}}{\int d\mathcal{Q} e^{-\beta U(\mathcal{Q})}} = \frac{\int d\mathcal{Q} A(\mathcal{Q}) e^{-\beta U(\mathcal{Q})}}{Z} \]

\[ \approx \frac{\sum A_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \frac{1}{M} \sum_{n=0}^{M} A_n \]

If *canonical* and *ergodic* sampling is performed
The problem of free energy sampling

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

But:

\[ \beta F = -\ln Z \]

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

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: \textit{ab initio} atomistic thermodynamics
- Canonical sampling: thermodynamic integration
- Canonical sampling: thermodynamic perturbation
- Generalized sampling: biased sampling / biased dynamics
- Unbiased (canonical) sampling $\rightarrow$ re-weighting techniques
- Evaluation: \textbf{Parallel} or \textbf{Serial}
How are free energies measured experimentally?

\[
\frac{\partial F}{\partial V} = -P
\]

\[
\frac{\partial (\beta F)}{\partial \beta} = E
\]

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

\[V_0 \to \infty: \text{ideal gas}\]
Free energy: “unphysical”-path thermodynamic integration

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

\[ F_\lambda(N, V, T) = C - k_B T \int d\mathbf{r}^N e^{-\beta((1-\lambda)U_0 + \lambda U_1)} \]

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

\[ = \langle U_1 - U_0 \rangle_\lambda \]

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

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)

\[
F^\Xi = F^{\text{ref}} + \Delta F^{\text{ref} \rightarrow ^\Xi} \\
= F^{\text{ref}} + \int_{\lambda = 0}^{\lambda = 1} d\lambda \left( \frac{\partial U_\lambda}{\partial \lambda} \right)_{\lambda} \\
= F^{\text{ref}} + \int_0^1 d\lambda \left( U^{\text{ref}} - U^\Xi \right)_{\lambda}
\]
Case study: phase diagram of pure carbon

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

\[
F^\Xi = F^{\text{ref}} + \Delta F^{\text{ref} \to \Xi} \\
= F^{\text{ref}} + \int_{\lambda=0}^{\lambda=1} d\lambda \left( \frac{\partial U_\lambda}{\partial \lambda} \right)_\lambda \\
= F^{\text{ref}} + \int_0^1 d\lambda \left( U^{\text{ref}} - U^\Xi \right)_\lambda
\]
This gives the absolute Helmholtz $F(T_0, V_0)$ for the three phases. Here $T_0 = 4000$K.
Case study: integration of $P(\rho)$ equations of state

Parallel (over densities)

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

This gives the absolute Gibbs $G(T_0, p)$ for the three phases
Case study: equating Gibbs free energies

Difference in slopes: \( \frac{\partial \mu}{\partial P} = \frac{\partial g}{\partial P} = v = \frac{1}{\rho} \)

And then:
Gibbs-Duhem integration
\[
\frac{dP}{dT} = \frac{\Delta h}{T \Delta v}
\]
\[
\Delta h = \Delta u + P \Delta v
\]

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:

\[ H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_0(r_1, \ldots, r_N) \quad H_1(\lambda) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \lambda U_0(r_1, \ldots, r_N) \]

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

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

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

\[ \frac{U_1}{k_B T_0} = \frac{\lambda U_0}{k_B T_0} = \frac{U_0}{k_B T} \]

\[ T = \frac{T_0}{\lambda} \]
Sparing CPU time: adiabatic switch

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

\[ \Delta F_1(\lambda(t), \lambda(0)) = \int_0^t dt' \frac{d\lambda}{dt} \bigg|_{t'} U_0(r_1(t'), \ldots, r_N(t')) \equiv W(t) \]

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

\[ T(t) = \frac{T_0}{\lambda(t)} \]

\[ T(0) = \frac{T_0}{\lambda(0)} \]
Sparing CPU time: adiabatic switch

\[ \frac{F_0(T(t))}{T(t)} = \]

\[ = \frac{F_0(T(0))}{T(0)} + \frac{W(t)}{T_0} - \frac{3}{2} Nk_B \ln \frac{T(t)}{T(0)} \]

\[ T(t) = T_0/\lambda(t) \]
\[ T(0) = T_0/\lambda(0) \]

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Ab initio diamond melting line

Wang et al. PRL 95, 185701 (2005)
Beyond equilibrium: Jarzynski theorem

\[ W_{AB} = \langle W_{AB}(x_0) \rangle_A = \frac{C_N}{Z_A(N, V, T)} \int dx_0 \ e^{-\beta H_A(x_0)} W_{AB}(x_0) \]

Clausius inequality:

\[ \langle W_{AB}(x_0) \rangle_A \geq \Delta F_{AB} \]

Jarzynski equality (1997!)

\[ e^{-\beta \Delta F_{AB}} = \langle e^{-\beta W_{AB}(x_0)} \rangle_A = \frac{C_N}{Z_A(N, V, T)} \int dx_0 \ e^{-\beta H_A(x_0)} e^{-\beta W_{AB}(x_0)} \]
Jarzynski theorem: steered dynamics

\[ U(r_1, \ldots, r_N, t) = U_0(r_1, \ldots, r_N) + \frac{1}{2} \kappa (|r_1 - r_N| - r_{eq} - vt)^2 \]

\[ \langle e^{-\beta W_\tau} \rangle = \int dW_\tau P(W_\tau) e^{-\beta W_\tau} \]

Inefficient because:

Better estimated with the cumulant:

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

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

System 0: $N, V, T, U_0$

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

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

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

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:

\[ P_{\text{exchange}} = \min \left( 1, \exp\left( - (\beta_i - \beta_j) (U_i - U_j) \right) \right) \]
Replica exchange: the implementation

Parallel (over replicas, and more)

To be tuned for efficient sampling:
number of temperatures, list of temperatures, attempted swap frequency
Replica exchange: free energy?

Temperature-weighted Histogram Analysis Method:

\[ P_i(q) = e^{\beta_i F_i} c_i(q) P_0(q) \]
Temperature-weighted Histogram Analysis Method:

Sampled probability

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

Re-weighting coefficients

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

Iterative, self consistent solution of:

\[
\begin{aligned}
P_0(q) &= \frac{\sum_{i=1}^{S} n_i(q)}{\sum_{i=1}^{S} N_i e^{\beta_i F_i} c_i(q)} \\
\beta_i F_i &= -\ln \left( \int dq \ c_i(q) P_0(q) \right)
\end{aligned}
\]

# 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

![Diagram showing potential energy landscape with different isomers and their energies: 0.00 eV, 0.04 eV, and 0.36 eV.](image)

- $\alpha$ (degree)
- Potential Energy (eV)
- 100—620 K
- 100 K PT (100 ps)
- 100 K serial (100 ps)
Au$_4$, relative population, coordination-based descriptor
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

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

See microtutorial !!!