Ab initio statistical mechanics

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Extending the scale

Potential Energy Surface: $E\{R_i\}$

(3N → 1) dimensions

Length (m)

$E$

$\{R_i\}$

$10^{-9}$

$10^{-6}$

$10^{-3}$

Thermodynamics: $p, T, V, N, \text{some } q$

continuum

Macroscopic regime

average over all processes

more processes

thermodynamic regime

interplay among processes

few atoms

elementary processes

more details

Mesoscopic regime

$10^{-15}$

$10^{-9}$

$10^{-3}$

$1$ Time (s)
Extending the scale

Potential energy surface → Free-energy method → Free-energy surface \((T,\{q_i\})\)

PES can be from:
- \textit{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 $\exp\left(-\frac{\Delta F}{kT}\right)$
• Selectivity: eliminate or at least reduce the undesired products
Entropy?

\[ S(E) = k_B \ln \Omega(E) \]

Density of states \( \Omega(E) = \int dQ \delta(U(Q) - E) \)

**I principle:**
\[ dU = \delta W + \delta Q \]

**I + II principle, reversible transformations:**
\[ dU = \sum_i X_i d\tau_i + T dS \]

E.g.: \(-PdV\)  
Everything we do not know: lack of information
Free energy: one quantity, many definitions

\begin{align*}
F &= -k_B T \ln Z \\
\beta F &= -\ln Z
\end{align*}

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

Classical statistics (for nuclei):

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

\[ \Lambda = \frac{\hbar}{\sqrt{2\pi mk_B T}} \]
Thermodynamics

\[ F = E - TS \]

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

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

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

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

Probabilistic interpretation of free energy

\[
\int dQ \delta(U(Q) - E)
\]
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:

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

$$\mathcal{P}_\Phi(\xi) = \frac{d\xi}{Z} = \frac{d\xi}{Z} e^{-\beta F_\Phi(\xi)}$$
Statistical mechanics, quantities derived from $Z$

**Average energy:**

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

**Heat capacity:**

\[
N C_V = \frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial E}{\partial \beta}
= -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left( \frac{\sum_n E_n e^{-\beta E_n}}{Z} \right)
= -\frac{1}{k_B T^2} \left[ \frac{(\sum_n E_n e^{-\beta E_n})^2}{Z^2} - \frac{\sum_n E_n^2 e^{-\beta E_n}}{Z} \right]
= \frac{1}{k_B T^2} \left( \langle E^2 \rangle - \langle E \rangle^2 \right)
= \frac{\sigma_E^2}{k_B T^2}
\]
Evaluation of pressure

\[ L = V^{1/3} \]
\[ r_i = L s_i \]

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

\[ P = k_B T \left. \frac{\partial \ln Z}{\partial V} \right|^{T,N} = k_B T \frac{\partial \ln V^N}{\partial V} + k_B T \frac{\partial}{\partial V} \ln \int_0^1 \cdots \int_0^1 dS^N e^{-\beta U} \]

\[ P = \frac{N k_B T}{V} - \left\langle \frac{1}{3V} \sum_i r_i \frac{\partial U}{\partial r_i} \right\rangle = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_i r_i f_i \right\rangle \]
Ensemble averages on discrete machines

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

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

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

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

But:

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

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

One cannot converge such a quantity!

... but one cannot measure it, either

\[ Z_{\text{ideal gas}} = \frac{V^N}{\Lambda^{3N} N!} \]
Computational 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}
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How are free energies measured experimentally?

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

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

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

\( V_0 \to \infty : \text{ideal gas} \)
Let us assume a mixed Hamiltonian: $U = (1 - \lambda)U_0 + \lambda U_1$

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

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

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

How to choose the reference?
Case study: phase diagram of pure carbon

Road map:

• Calculation of change of 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)
Case study: phase diagram of pure carbon

Reference phases
Solid(s): Einstein solid

\[ U^E = \frac{\alpha}{2} \sum_{i=1}^{N} (r_i - r_{i,0})^2 \]

\( \alpha \)? Maximum resemblance of harmonic and “real” potential

\[ \frac{3}{\beta \alpha} = \left\langle \frac{1}{N} \sum_{i=1}^{N} (r_i - r_{i,0})^2 \right\rangle \]
Case study: phase diagram of pure carbon

Reference phases
Liquid: Lennard Jones

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

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

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

How to choose \( \sigma, \varepsilon \)?
Maximum resemblance between LJ liquid and “real”:
alignment radial distribution function peaks
Case study: $\lambda$-ensemble sampling and integration

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

$P(\rho) = a + b\rho + c\rho^2 \quad \rightarrow \quad \beta \mu(\rho) = \frac{\beta F^{\Xi}}{N} + \beta \left[ \frac{a}{\rho^{\Xi}} + b \ln \frac{\rho}{\rho^{\Xi}} + b + c \left( 2\rho - \rho^{\Xi} \right) \right]$
Case study: equating Gibbs free energies

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

And then: Gibbs-Duhem integration

\[
\frac{dP}{dT} = \frac{\Delta h}{T \Delta v}
\]

\[
\Delta h = \Delta u + P \Delta v
\]

>>> Serial <<<
Carbon phase diagram

LMG et al. PRL 2005
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

<table>
<thead>
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<th>$V_t^d$</th>
<th>$V_t^B$</th>
<th>$V_t^B/V_t^d$</th>
<th>$P_t$ (kbar)</th>
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<td>0.774</td>
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<td>Experiment$^a$</td>
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<td>Deviation</td>
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<td>1.1%</td>
<td>0.1%</td>
<td>-20%</td>
</tr>
</tbody>
</table>
Notable cases (at 0 K): Cerium (2013)

Casadei et al. PRL (2013)
Computational free-energy evaluation: the zoo

- Analytic: *ab initio* atomistic thermodynamics
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- Canonical sampling: thermodynamic perturbation
- Generalized sampling: biased sampling / biased dynamics
- Unbiased (canonical) sampling → re-weighting techniques
- Evaluation: Parallel or >>> Serial <<<
Thermodynamic perturbation

System 0: \( N, V, T, U_0 \)

Two systems:

System 1: \( N, V, T, U_1 \)

\[
Z_0 = \frac{V^N}{\Lambda^{3N} N!} \int d\mathbf{r}^N e^{-\beta U_0} \quad \quad Z_1 = \frac{V^N}{\Lambda^{3N} N!} \int d\mathbf{r}^N e^{-\beta U_1}
\]

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

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

If poor overlap: sequence of systems

\[
\beta \Delta F = -\sum \ln \langle e^{-\beta \Delta U_{\alpha,\alpha+1}} \rangle_\alpha
\]

Parallel (over systems)
Thermodynamic perturbation

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

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

\[ \mathcal{P}_1(\Delta U) = \frac{\int d\mathbf{r}^N e^{-\beta U_1} \delta(U_1 - U_0 - \Delta U)}{\int d\mathbf{r}^N e^{-\beta U_1}} \]
\[ \beta \Delta F = \beta F_1 - \beta F_0 = - \ln \frac{Z_1}{Z_0} = \frac{\int d\mathbf{r}^N e^{-\beta(U_1-U_0)} e^{-\beta U_0}}{\int d\mathbf{r}^N e^{-\beta U_0}} \]

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

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

\[= \frac{Z_0}{Z_1} e^{-\beta \Delta U} \mathcal{P}_0(\Delta U) = e^{\beta(\Delta F - \Delta U)} \mathcal{P}_0(\Delta U) \]
Thermodynamic perturbation

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

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

\[
\begin{align*}
  f_0(\Delta U) &\equiv \ln \mathcal{P}_0(\Delta U) - 0.5\beta \Delta U \\
  f_1(\Delta U) &\equiv \ln \mathcal{P}_1(\Delta U) - 0.5\beta \Delta U
\end{align*}
\]

\[ \beta \Delta F = f_1(\Delta U) - f_0(\Delta U) \]

\[
\begin{align*}
  f_0(\Delta U) &= C_0 + a\Delta U + b\Delta U^2 + c\Delta U^3 \\
  f_1(\Delta U) &= C_1 + a\Delta U + b\Delta U^2 + c\Delta U^3
\end{align*}
\]

\[ \beta \Delta F = C_1 - C_0 \]
Thermodynamic perturbation

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

System 1: N interacting particles
Thermodynamic perturbation: recycling data

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

\[
\langle A \rangle_{NVT_1} = \frac{\int d\mathbf{r}^N A\left(q\left(r^N\right)\right) e^{-\beta_1 U(r^N)}}{\int d\mathbf{r}^N e^{-\beta_1 U(r^N)}} =
\]

\[
= \frac{\int d\mathbf{r}^N A\left(q\left(r^N\right)\right) e^{\beta_2 U(r^N)} - \beta_1 U(r^N) e^{-\beta_2 U(r^N)}}{\int d\mathbf{r}^N e^{\beta_2 U(r^N)} - \beta_1 U(r^N) e^{-\beta_2 U(r^N)}} =
\]

\[
= \frac{\langle Ae^{(\beta_2 - \beta_1)U(r^N)} \rangle_{NVT_2}}{\langle e^{(\beta_2 - \beta_1)U(r^N)} \rangle_{NVT_2}}
\]
Thermodynamic perturbation: recycling data

\[ \langle A \rangle_{NVT_1} = \frac{\langle Ae^{(\beta_2 - \beta_1)U(r^N)} \rangle_{NVT_2}}{\langle e^{(\beta_2 - \beta_1)U(r^N)} \rangle_{NVT_2}} \]

Great, but...

Overlap becomes very small
Computational free-energy evaluation: the zoo

- Analytic: *ab initio* atomistic thermodynamics

- Canonical sampling: thermodynamic integration

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- Generalized sampling: biased sampling / biased dynamics

- Unbiased (canonical) sampling → re-weighting techniques

- Evaluation: Parallel or >>> Serial <<<
Umbrella sampling

\[ \beta \Delta F = - \ln \langle e^{-\beta (U_1 - U_0)} \rangle_0 \]
\[ \mathcal{P}(q) = \frac{\int d\mathbf{r}^N e^{-\beta U} \delta(q'(\mathbf{r}^N) - q)}{\int d\mathbf{r}^N e^{-\beta U}} = \]

\[ = \frac{\int d\mathbf{r}^N e^{-\beta(U+w(q'))} e^{\beta w(q')} \delta(q'(\mathbf{r}^N) - q)}{\int d\mathbf{r}^N e^{-\beta(U+w(q'))} e^{\beta w(q')}} = \]

\[ = \frac{Z_{U+w} e^{\beta w(q)} \int d\mathbf{r}^N e^{-\beta(U+w(q'))} \delta(q'(\mathbf{r}^N) - q)}{Z_{U+w} \int d\mathbf{r}^N e^{-\beta(U+w(q'))} e^{\beta w(q')}} = \]

\[ = \frac{e^{\beta w(q)}}{\langle e^{\beta w(q)} \rangle_{U+w}} \mathcal{P}_{U+w}(q) \]
Umbrella sampling (multiplying by 1 few more times...)

\[ \mathcal{P}(q) = \frac{\int d\mathbf{r}^N e^{-\beta U} \delta(q'(\mathbf{r}^N) - q)}{\int d\mathbf{r}^N e^{-\beta U}} = \]

\[ = \frac{\int d\mathbf{r}^N e^{-\beta (U + w(q'))} e^{\beta w(q')} \delta(q'(\mathbf{r}^N) - q)}{\int d\mathbf{r}^N e^{-\beta (U + w(q'))} e^{\beta w(q')}} = \]

\[ = \frac{Z_{U+w} e^{\beta w(q)} \int d\mathbf{r}^N e^{-\beta (U + w(q'))} \delta(q'(\mathbf{r}^N) - q)}{Z_{U+w} \int d\mathbf{r}^N e^{-\beta (U + w(q'))} e^{\beta w(q')}} = \]

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

Parallel (over biasing potentials)
Umbrella sampling

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

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

Best choice \[ w(q) = -F(q) \]

Not practical, \[ F(q) \] is what we want to calculate!
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Parallel tempering: the concept

Exchange rule, ensuring canonical sampling at all temperatures:

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

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

**T-Weighted Histogram Analysis Method:**

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

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

Iterative, self consistent solution of:

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

\[ \beta_i F_i = -\ln \left( \int dq \, c_i(q) P_0(q) \right) \]

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

$\text{Au}_4$: coexistence of several isomers

- $\alpha$: 0.00 eV
- $\alpha$: 0.04 eV
- $\times$: 0.36 eV

Potential Energy (eV)

- $\bullet$ 100—620 K
- $\bullet$ 100 K PT (100 ps)
- $\bullet$ 100 K serial (100 ps)
$\text{Au}_4$: coexistence of several isomers
Relative population of larger clusters: \(^{ Au_n }, 2D \) vs \( 3D \)

Free energy surface of \( Au_{10} \) shows multiple isomers above 100 K

B. Goldsmith and LMG unpublished
The Nested Sampling

Obtaining the partition function

\[ Z(N, V, \beta) = Z_m(N, \beta) \int dq \ e^{-\beta E(q)} \]

\[ = Z_m(N, \beta) \int dE \ \Omega(E) e^{-\beta E} \]

Consider cumulative density

\[ \chi(E) = \int_{-\infty}^{E} dE' \ \Omega(E') \]
The Nested Sampling: the main trick

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

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

Constrained uniform sampling

1. obtain \( K \) uniform samples such that \( E(q) < E_{\text{limit}} \)

2. compute median: \( E(\chi_1) = E_1, \chi_1 \approx \chi_0/2, E_{\text{limit}} \leftarrow E_1 \)

3. repeat...

\[
\chi_n \approx \chi_0 \alpha^n
\]

\[
\Omega(E_n) = \chi_0 (\alpha^{n-1} - \alpha^n)
\]

\[
Z = Z_m \int dE \Omega(E) e^{-\beta E}
\]

https://github.com/libAtoms/pymatnest (linked with LAMMPS), Csányi et al.
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- Generalized sampling: biased sampling / biased dynamics

- Unbiased (canonical) sampling (replica exchange, nested sampling)

- Evaluation: \textcolor{green}{Parallel} or \textcolor{red}{	extgreater	extgreater	extgreater Serial 	extless	extless	extless}