Atomistic Simulation Centre

ma per seguir virtute e canoscenza
SISSA

PLUMED

The heart of the matter

Gareth Tribello
Massimiliano Bonomi
Carlo Camilloni
Giovanni Bussi

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http://www.plumed.org

The equation

Probability

$$F(\mathbf{s}) = -k_B T \ln P(\mathbf{s})$$

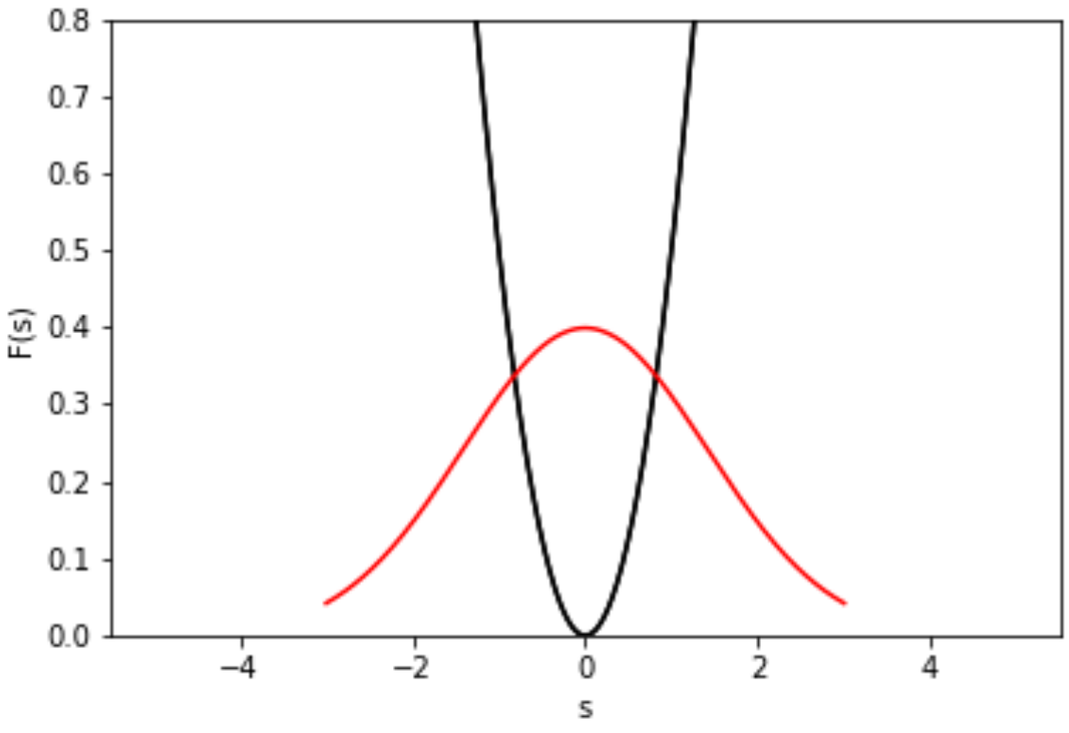
Free energy

Temperature

Undergraduate (classical) statistical mechanics

$$F(\mathbf{s}) = -k_B T \ln P(\mathbf{s})$$

$$F(s) - F(a) = \cancel{F'(a)}^{\,0}(s-a) + \frac{F''(a)}{2!}(s-a)^2 + \dots$$

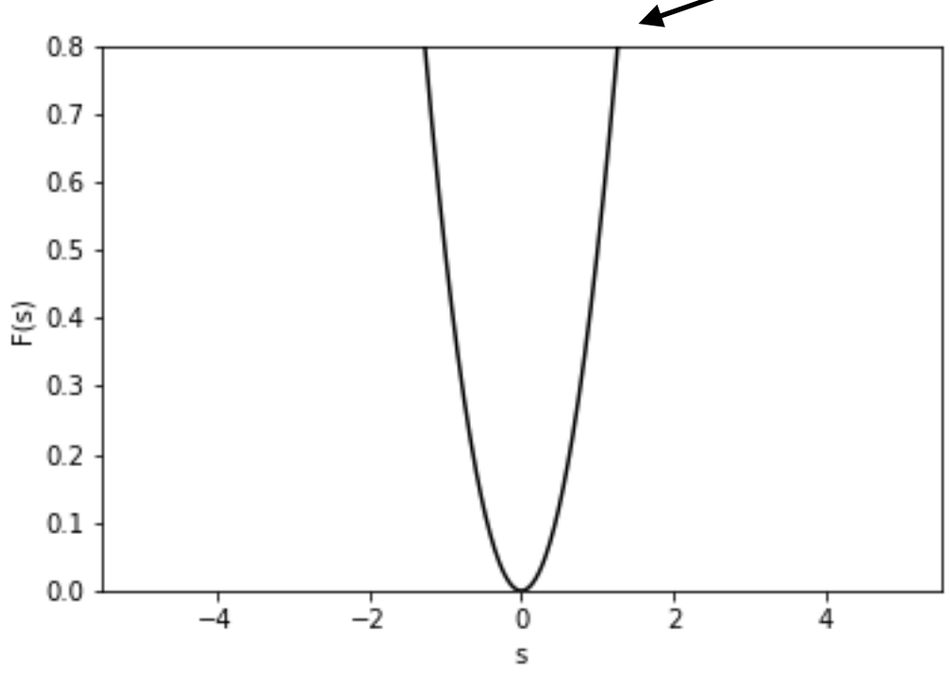


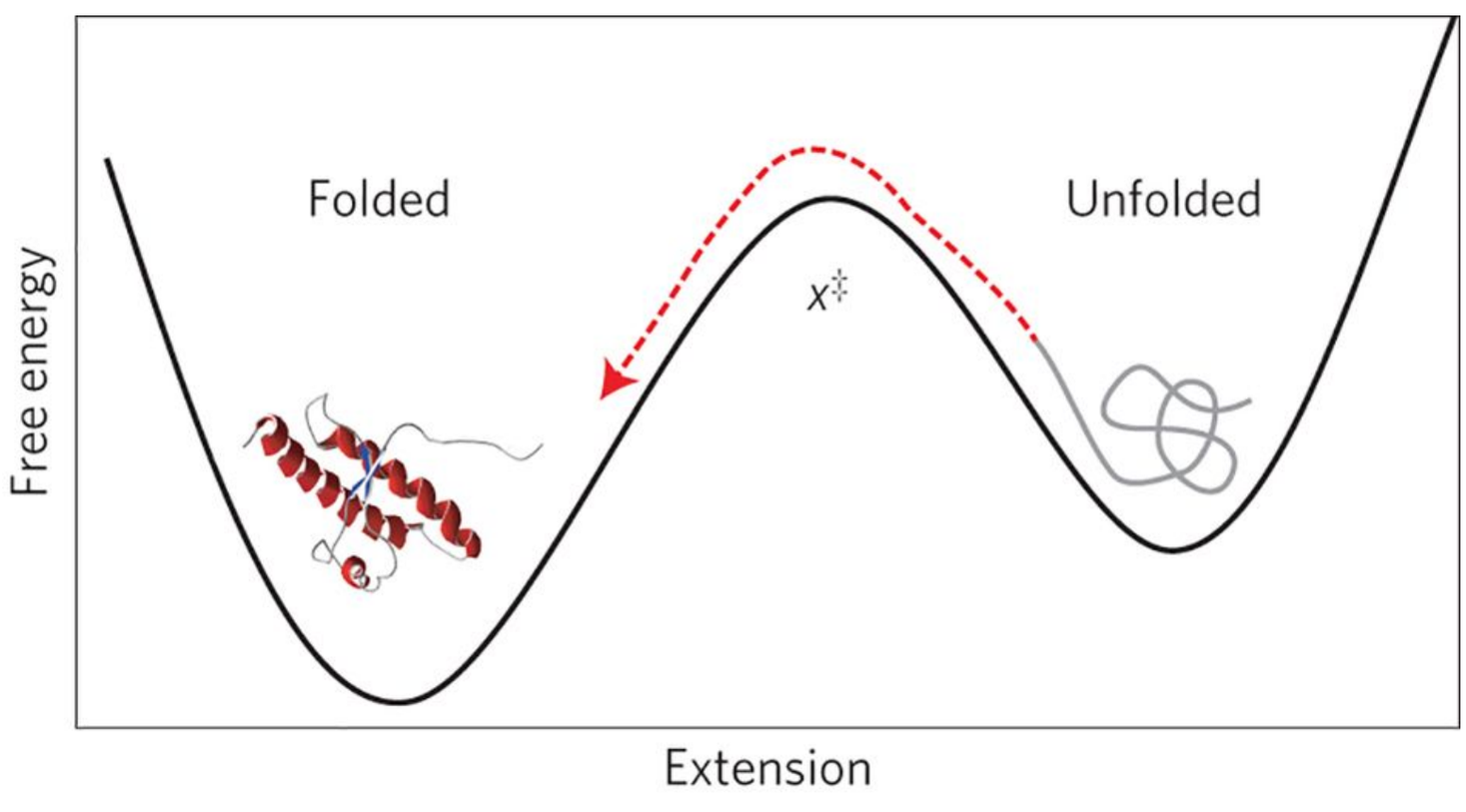
What we use MD to investigate

$$P(s) \propto \exp\left(-\frac{F''(a)(s-a)^2}{2k_B T}\right)$$

Why we care about anharmonic effects

$$F(s) - F(a) = F'(a)(s-a) + \frac{F''(a)}{2!}(s-a)^2 + \ldots$$





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The reaction free energy is an integral

reactants $\xrightarrow{\Delta F}$ products

reactants

ΔF

products

$$\int_{\text{reactants}}^{\text{products}} F'(x)\mathrm{d}x$$

derivative of a thermodynamic potential

The reaction coordinate

Thermodynamics: http://gtribello.github.io/mathNET/AMA40041-overview.html

The free energy

Environment

Momentum of everything else

$$U(\text{env}) = \frac{1}{2}\sum_{i=1}^{M}\frac{1}{m_i}\sum_{\alpha=1}^{3}p_{i\alpha}^2$$

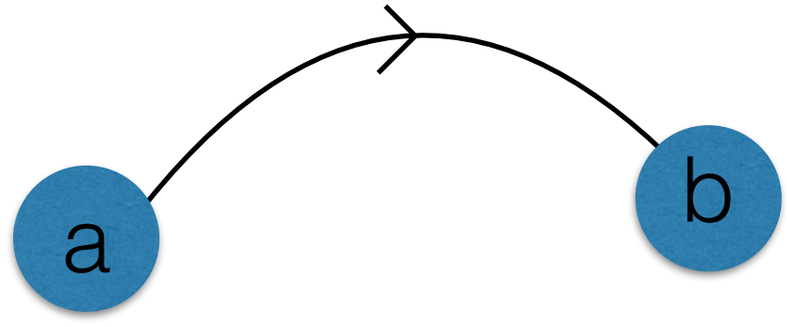
$$\Big\| \quad V(x)$$

System

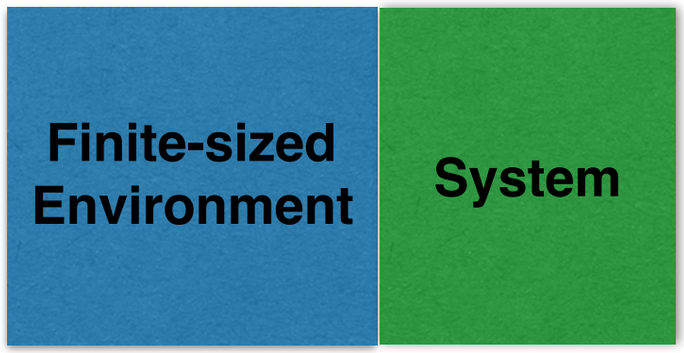
momentum of
atoms in system

$$U(\text{system}) = \frac{1}{2}\sum_{i=1}^{N}\frac{1}{m_i}\sum_{\alpha=1}^{3}p_{i\alpha}^2$$

The potential



System and Environment



$$E = V(\mathbf{x}) + K(\mathbf{p})$$

fixed — environment — system

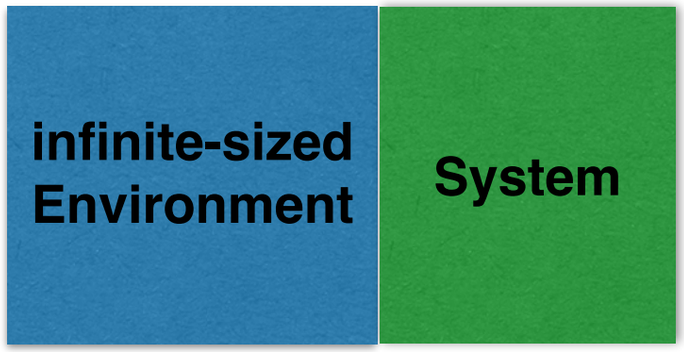
All extensive quantities for the universe are fixed

$$P(\xi) = \frac{\int\int\cdots\int \delta(V(\mathbf{x},\mathbf{p})-V)\delta(E(\mathbf{x},\mathbf{p})-E)\delta(\xi(\mathbf{x})-\xi)\mathrm{d}x_1\mathrm{d}x_1\ldots\mathrm{d}x_N\mathrm{d}p_1\mathrm{d}p_1\ldots\mathrm{d}x_N}{\int\int\cdots\int \delta(V(\mathbf{x},\mathbf{p})-V)\delta(E(\mathbf{x},\mathbf{p})-E)\mathrm{d}x_1\mathrm{d}x_1\ldots\mathrm{d}x_N\mathrm{d}p_1\mathrm{d}p_1\ldots\mathrm{d}x_N}$$

"count" — must have volume V — must have energy E — must have right cv — all micro states

Total number of states with energy E and volume V

System and Environment



Intensive variables for system are fixed

must be finite

$$\langle E \rangle = \int E(\mathbf{x},\mathbf{p}) P(\mathbf{x},\mathbf{p}) \mathrm{d}x_1 \mathrm{d}x_2 \ldots \mathrm{d}x_N \mathrm{d}p_1 \mathrm{d}p_2 \ldots \mathrm{d}p_N$$

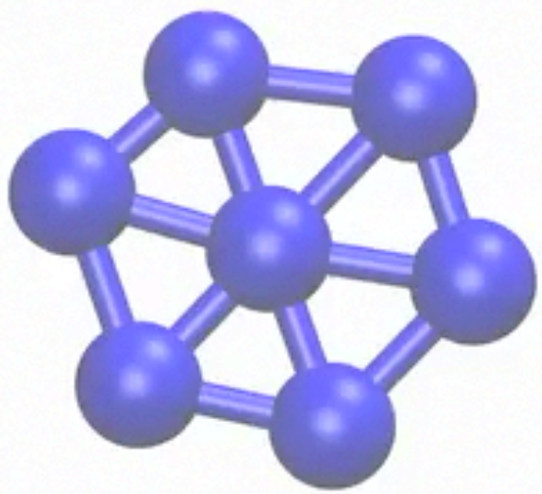
lots of maths*

The distribution sampled by molecular dynamics if we run with a (suitable) thermostat

$$P(\mathbf{x},\mathbf{p}) \propto e^{-\frac{E(\mathbf{x},\mathbf{p})}{k_B T}}$$

$$P(\xi) = \frac{\int\int\cdots\int \delta(V(\mathbf{x})-V)\delta(\xi(\mathbf{x})-\xi) e^{-\frac{E(\mathbf{x},\mathbf{p})}{k_B T}} \mathrm{d}x_1 \mathrm{d}x_2 \ldots \mathrm{d}x_N \mathrm{d}p_1 \mathrm{d}p_2 \ldots \mathrm{d}p_N}{\int\int\cdots\int \delta(V(\mathbf{x})-V) e^{-\frac{E(\mathbf{x},\mathbf{p})}{k_B T}} \mathrm{d}x_1 \mathrm{d}x_2 \ldots \mathrm{d}x_N \mathrm{d}p_1 \mathrm{d}p_2 \ldots \mathrm{d}p_N} \approx \frac{1}{T}\sum_{t=0}^{T} \Theta(|s(t)-s'|<\epsilon)$$

***See videos: http://gtribello.github.io/mathNET/AMA40043-understand.html**
http://gtribello.github.io/mathNET/AMA40042-understand.html



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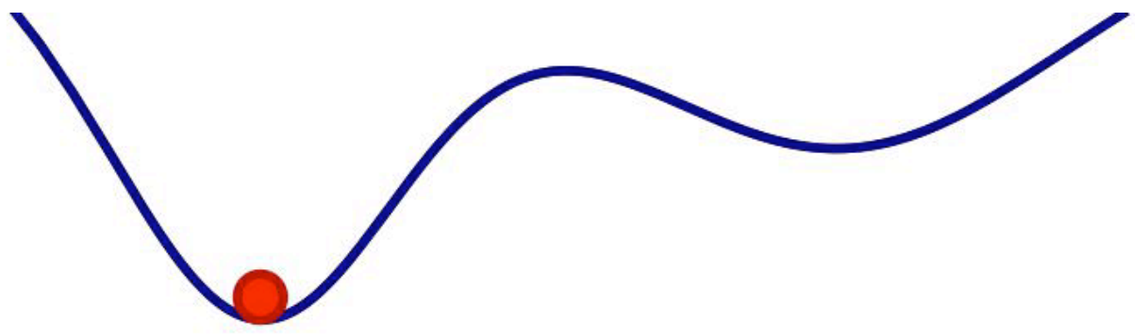
$$F(\mathbf{x}) = -k_B T \log[P(\mathbf{x})]$$

Non-ergodicity (life is a b*#ch)

Fast degree of freedom

Slow degree of freedom

$$V(\mathbf{x}, t) = \frac{1}{2} k(s(\mathbf{x}) - s'(t))^2$$



The equation

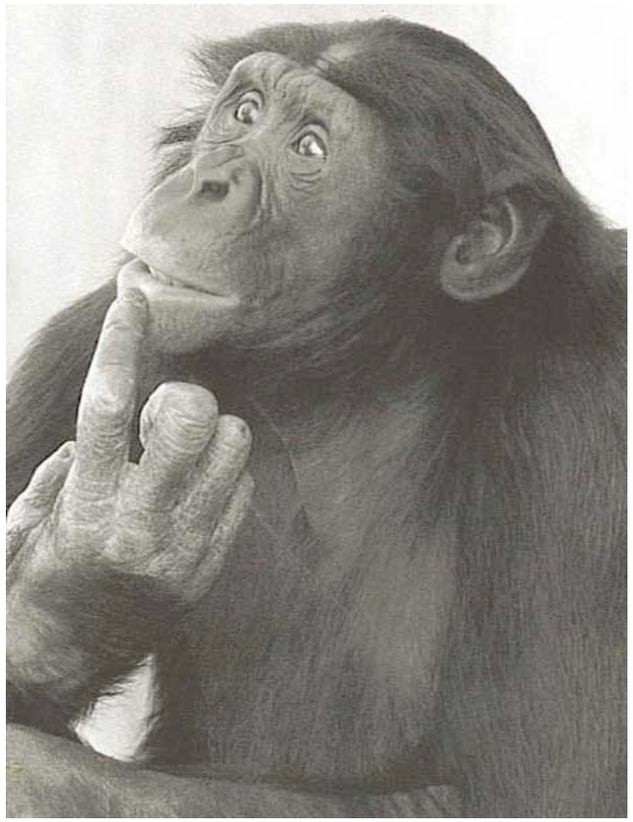
Probability

$$F(\mathbf{s}) = -k_B T \ln P(\mathbf{s})$$

Free energy

Temperature

The only question left



What collective variable should I use?

$$F(\mathbf{s}) = -k_B T \ln P(\mathbf{s})$$

More videos

Random variables:
http://gtribello.github.io/mathNET/SOR30121-understand.html

Central limit theorem:
http://gtribello.github.io/mathNET/SOR30121-understand.html

Markov chains:
http://gtribello.github.io/mathNET/SOR30123-understand.html
http://gtribello.github.io/mathNET/SOR30124-understand.html

Thermodynamics:
http://gtribello.github.io/mathNET/AMA40041-overview.html

Statistical Mechanics:
http://gtribello.github.io/mathNET/AMA40043-understand.html
http://gtribello.github.io/mathNET/AMA40042-understand.html