Mapping equilibrium and non-equilibrium entropy landscapes : the path-sampling approach

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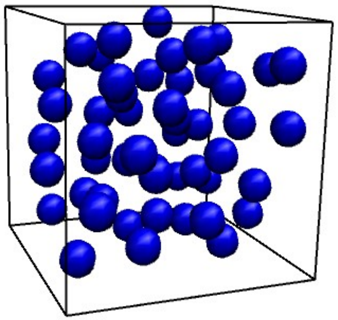
Introduction

- Statistical mechanics in ensembles of paths rather than of states
  - Transition-path sampling implicitely computes entropies
    - « migration » entropies, Sinai-Kolmogorov entropy
- Extentions to compute entropies in various contexts
  - Adequate to compute non-equilibrium entropies
  - Efficicient in rugged energy landscapes
  - Built-in diagnosing tools in methods based on non-equilibrium work theorems

Non-equilibrium and equilibrium entropy



- N particle system
  state $\chi = (\mathbf{r}, \mathbf{p})$ with hamiltonian $\mathrm{H}(\mathbf{r}, \mathbf{p})$

- définition of ensemble : phase space + associated probabilities

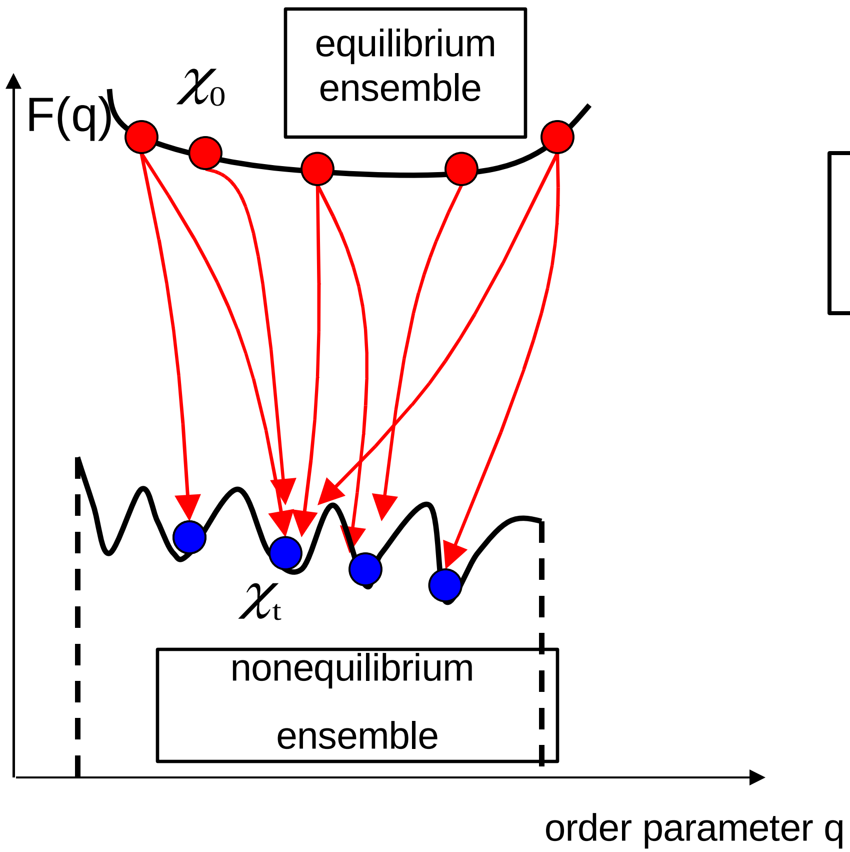
- entropy $S_t^{neq} = -\int \rho^{neq}(\chi, t) \ln \rho^{neq}(\chi, t) \mathrm{d}\chi$

- equilibrium :Boltzmann $\rho^{eq}(\chi) = \exp\left[-\beta H(\chi) + F\right]$

$$S^{eq} = -\int \rho^{eq}(\chi) \ln \rho^{eq}(\chi) \mathrm{d}\chi = \int \rho^{eq}(\chi)\left[\beta H(\chi) - \beta F\right] \mathrm{d}\chi = \beta \langle H \rangle - \beta F$$

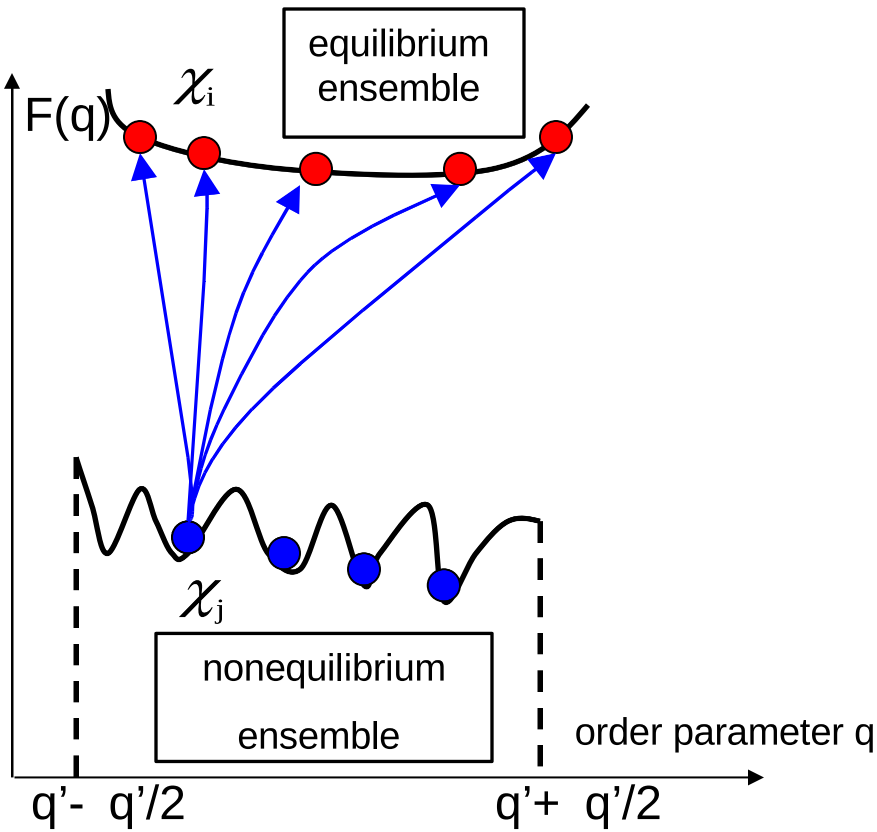
$$\beta F = -\ln \int \exp\left[-\beta H(\chi)\right] \mathrm{d}\chi = -\ln Z$$

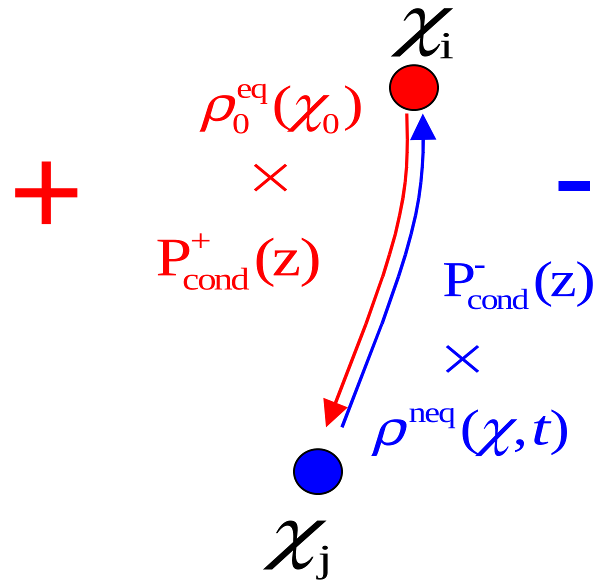
Nonequilibrium Entropy



$$\rho^{neq}\left(\chi,t\right) = \int_{z\in\,(\chi\ t)} \rho^{eq}\left(\chi_0\right)\mathrm{P}^{+}_{\mathrm{cond}}(z)\mathrm{D}z$$

Nonequilibrium Entropy



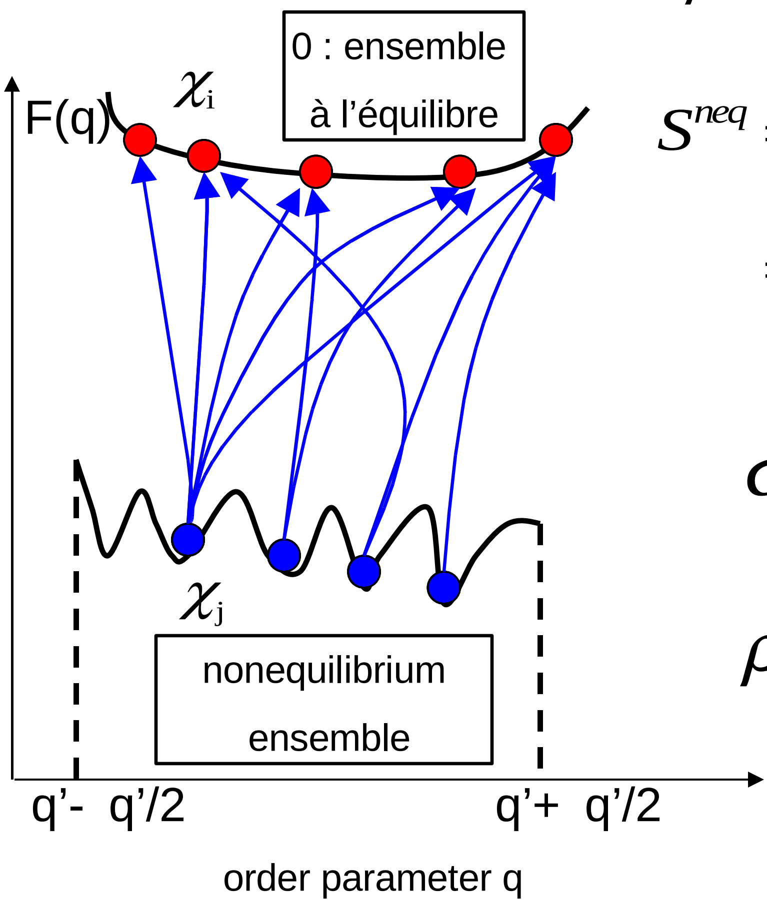


$$\rho^{neq}(\chi,t)=\frac{\int_{z\in(\chi)}\rho_0^{eq}(\chi_0)\,P^+_{cond}(z)Dz}{\int_{z\in(\chi)}P^-_{cond}(z)Dz}$$

$$=\left\langle \rho_0^{eq}(\chi)\,\frac{P^+_{cond}(z)}{P^-_{cond}(z)}\right\rangle_{\chi,R}$$

$$=\left\langle \exp\left[-\beta H(\chi)+\beta F-\beta Q\right]\right\rangle_{\chi,R}$$

Nonequilibrium Entropy



$$\rho^{neq}(\chi,\tau) = \left\langle \exp\left[-\beta H(\chi_0) + \beta F - \beta Q\right]\right\rangle_{\chi_j,R}$$

$$S^{neq} = -\int \rho^{neq}(\chi,\tau)\ln\rho^{neq}(\chi,\tau)\,d\chi$$

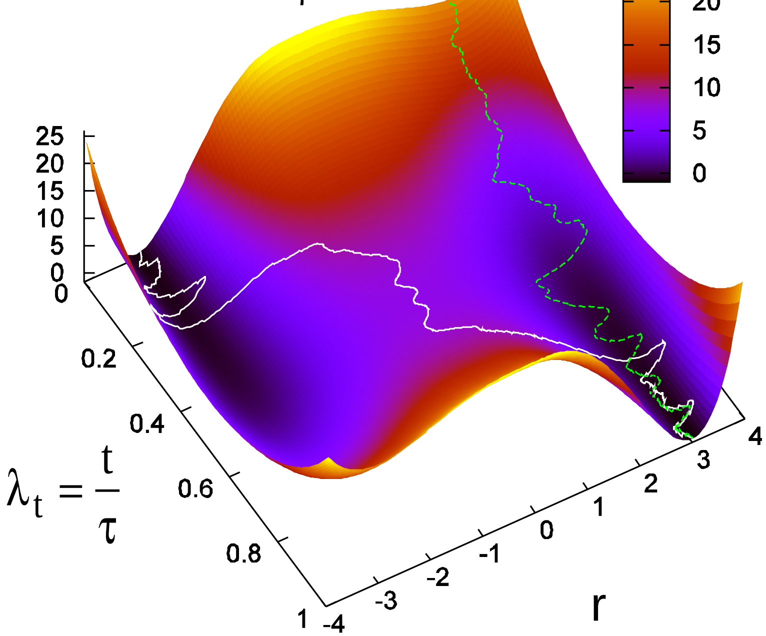
$$= -\left\langle \ln\left\langle \exp\left[-\beta H(\chi_0) + \beta F - \beta Q\right]\right\rangle_{\chi,R}\right\rangle_{neq}$$

$$\sigma_\theta = \theta\beta\left[H(\chi_0) - F_\beta + Q\right] - \ln \bar{P}_{\mathrm{cond}}$$

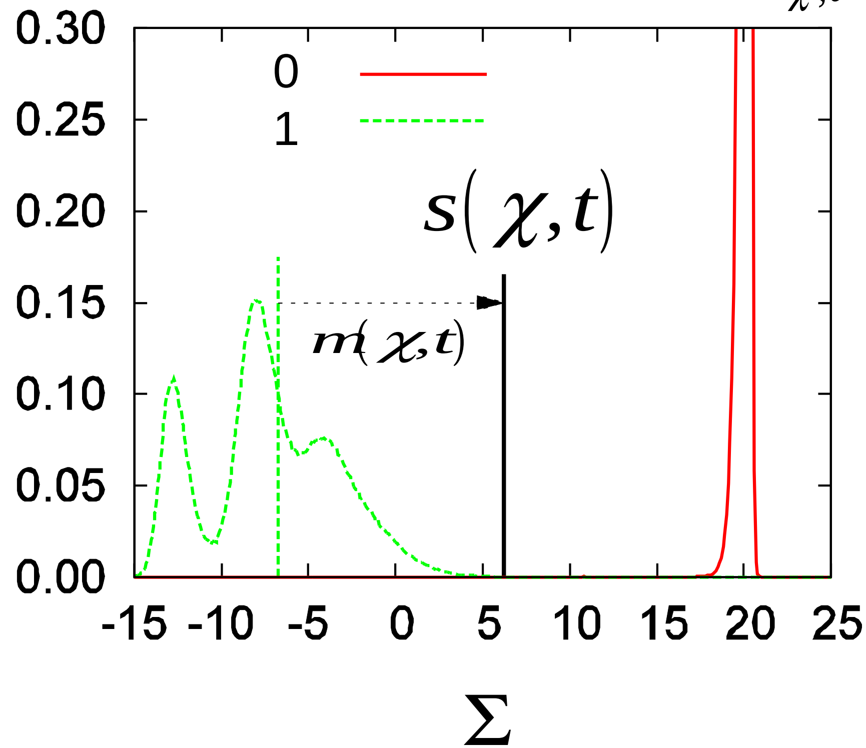
$$\rho^{neq}(\chi,t) = \left\langle \exp\left[-\sigma_1(z) + \sigma_0(z)\right]\right\rangle_{\chi,0}$$

Space-time thermodynamic perturbation

$s_\lambda(r) = \beta V(r) - \beta F_\beta$



$$\left\langle \delta\left(\sigma_1(z) - \sigma_0(z) - \Sigma\right)\right\rangle_{\chi,\theta}$$



$$s(\chi,t) = -\ln\left\langle \exp\left[-\sigma_1(z) + \sigma_0(z)\right]\right\rangle_{\chi,0}$$

Space-time thermodynamic integrations

Method 1

$$\sigma_\theta = \theta\sigma_1 + (1-\theta)\sigma_0$$

$$S^{neq}_{t=\tau} = -\left\langle \ln \left\langle \exp[-\sigma_1 + \sigma_0] \right\rangle_0 \right\rangle_{t=\tau} = -\left\langle \ln \frac{\int \exp[-\sigma_{\theta=1}]\,\mathrm{Dz}}{\int \exp[-\sigma_{\theta=0}]\,\mathrm{Dz}} \right\rangle_{t=\tau}$$

$$= -\left\langle \int_0^1 d\theta \cdot \partial_\theta \ln \int \exp[-\sigma_\theta]\,\mathrm{Dz} \right\rangle_{t=\tau} = \int_0^1 \mathrm{d}\theta \left\langle \left\langle \partial_\theta \sigma_\theta \right\rangle_\chi \right\rangle_{t=\tau}$$

Method 2

$$= \left[\left\langle \theta \left\langle \partial_\theta \sigma_\theta \right\rangle_\chi \right\rangle_{t=\tau} \right]_0^1 - \int_0^1 \theta d\theta \left\langle -\mathrm{var}_\chi \left(\partial_\theta \sigma_\theta \right) \right\rangle_{t=\tau}$$

Integration by part

$$= S_{t=0} + \beta \langle Q \rangle + \int_0^1 \theta d\theta \left\langle \mathrm{var}\left(\partial_\theta \sigma_\theta \right) \right\rangle_{t=\tau}$$

Method 3

Implies second law

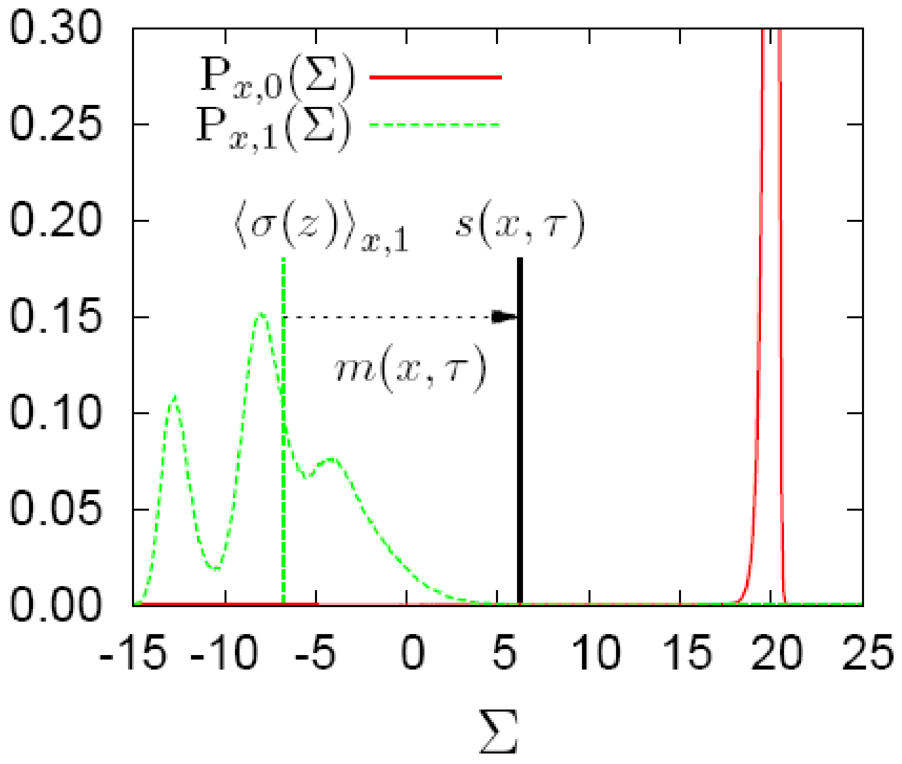
Analogy with equilibrium thermodynamics

$$S_\tau^{total} - S_0^{total} = S_t^{neq} - S_0 - \beta\langle Q\rangle$$

$$= \int_0^1 \theta d\theta \left\langle \mathrm{var}\left(\partial_\theta \sigma_\theta\right)\right\rangle_{\chi_t}$$

$$S_{\beta_1}^{eq} - S_{\beta_0}^{eq} = \int_{\beta_0}^{\beta_1} \beta d\beta\, \mathrm{var}\left(\partial_\beta\left(\beta H\right)\right)$$

$$m(\chi, t) = \int_0^1 \theta d\theta\, \mathrm{var}_{\chi_t}\left(\partial_\theta \sigma_\theta\right)$$



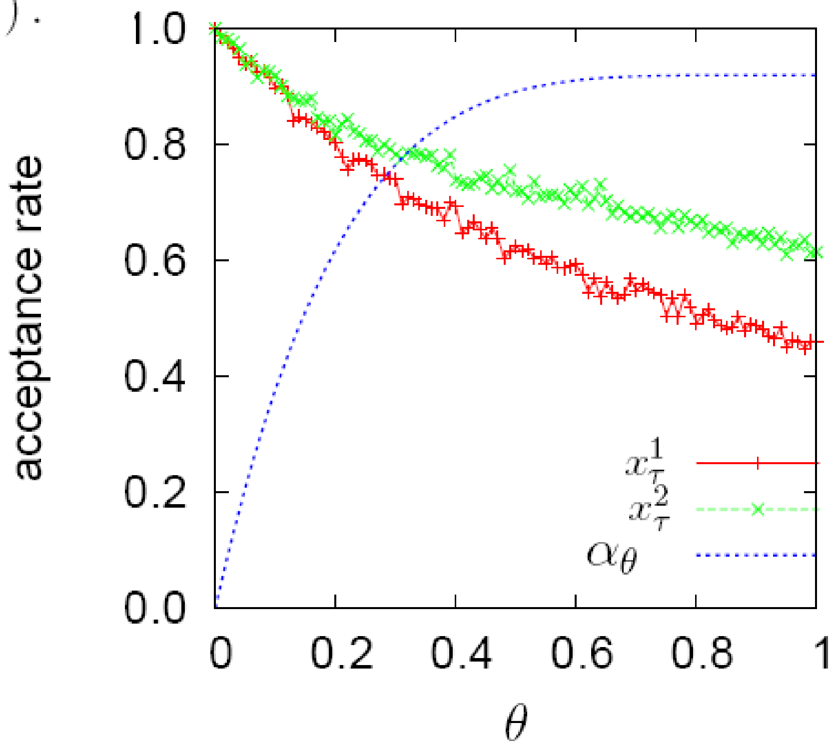
Brownian tube proposal

$$\tilde{\boldsymbol{\xi}}_\ell^- = \alpha_\theta \boldsymbol{\xi}_\ell^- + \sqrt{1-\alpha_\theta^2}\mathrm{R}_\ell,$$

$$\frac{\exp\left[-\sigma_\theta(\tilde{z})\right] \mathrm{P}_{\mathrm{gen}}(\tilde{\boldsymbol{\xi}}_\ell^- \to \boldsymbol{\xi}_\ell^-)}{\exp\left[-\sigma_\theta(z)\right] \mathrm{P}_{\mathrm{gen}}(\boldsymbol{\xi}_\ell^- \to \tilde{\boldsymbol{\xi}}_\ell^-)} = \frac{\exp\left[-\theta\sigma(\tilde{z})\right]}{\exp\left[-\theta\sigma(z)\right]},$$

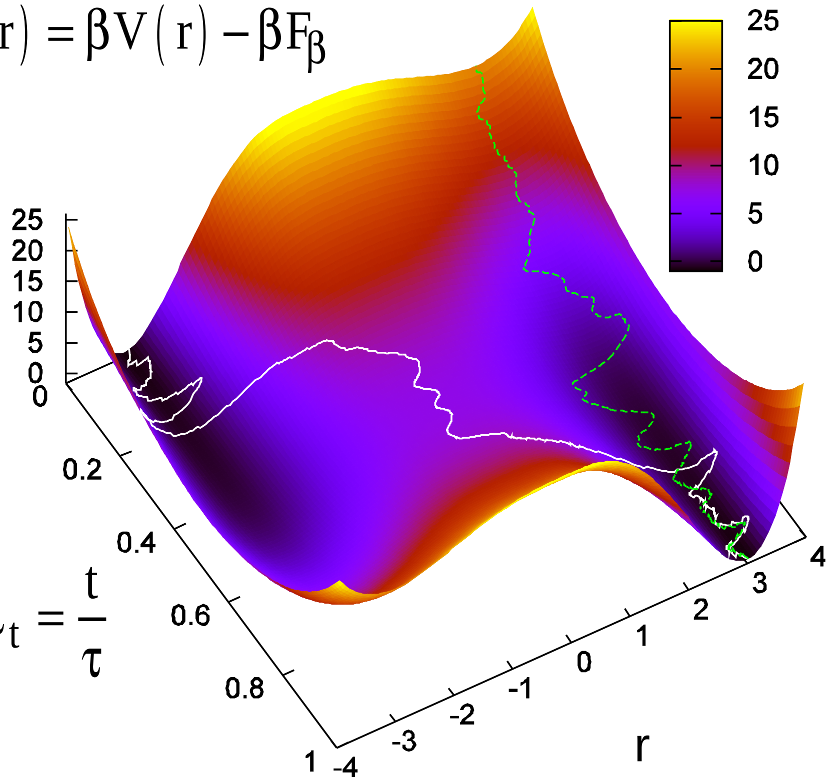
$$\mathrm{P}_{\mathrm{acc}}(\tilde{z}) = \min\left(1 \exp\left[-\theta\left(\sigma(\tilde{z}) - \sigma(z)\right)\right]\right).$$

G. Stoltz, J. Comp. Phys. 2007

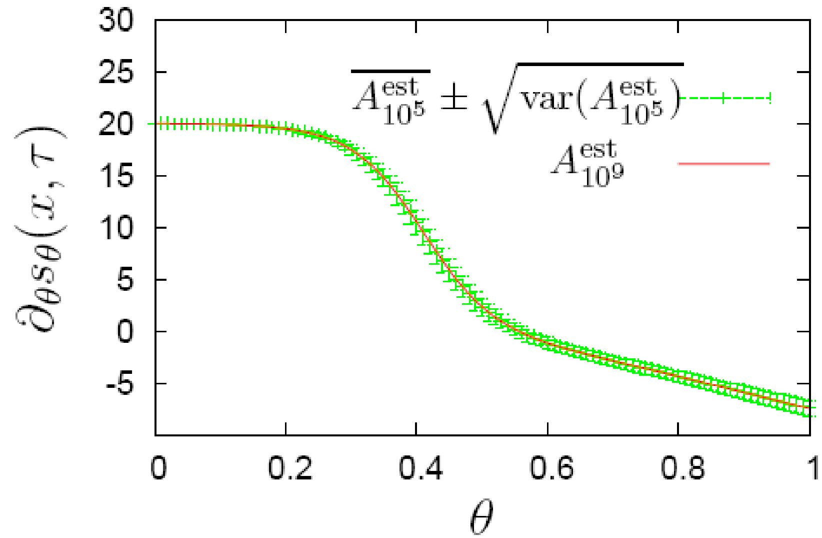


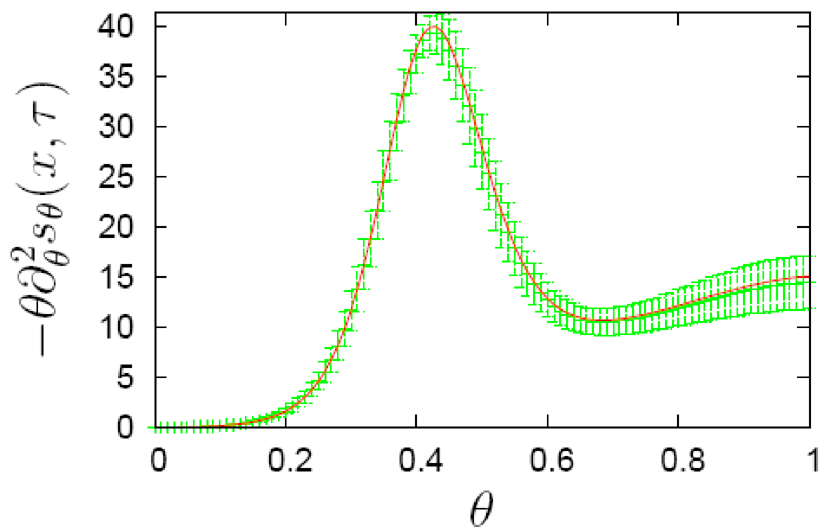
First and second moment integration

$$s_\lambda(r) = \beta V(r) - \beta F_\beta$$

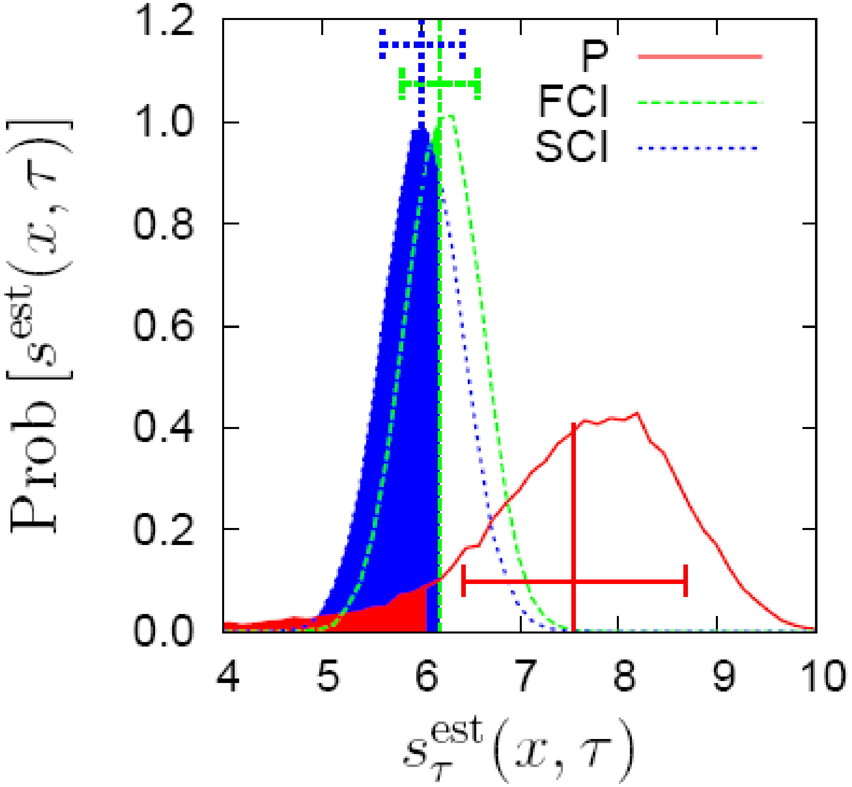


$$\lambda_t = \frac{t}{\tau}$$





Three path-sampling methods



$$S_{t=\tau}^{neq}$$

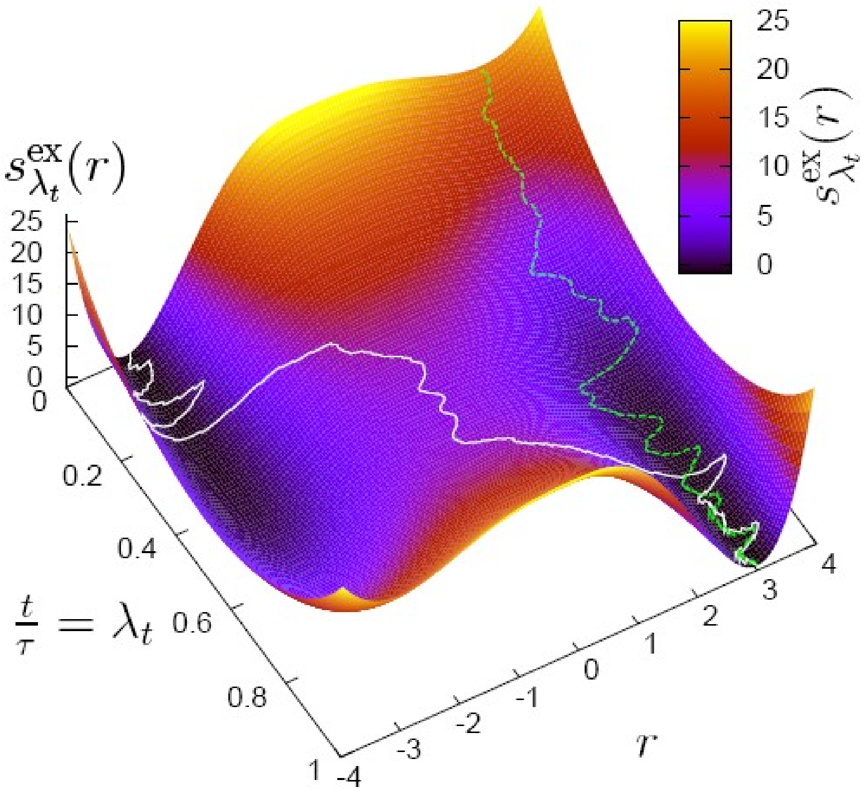
$$= -\left\langle \ln\left\langle \exp[-\Delta\varphi]\right\rangle_0 \right\rangle_{t=\tau}$$

$$= \int_0^1 d\alpha \left\langle \left\langle \Delta\varphi \right\rangle_\alpha \right\rangle_{t=\tau}$$

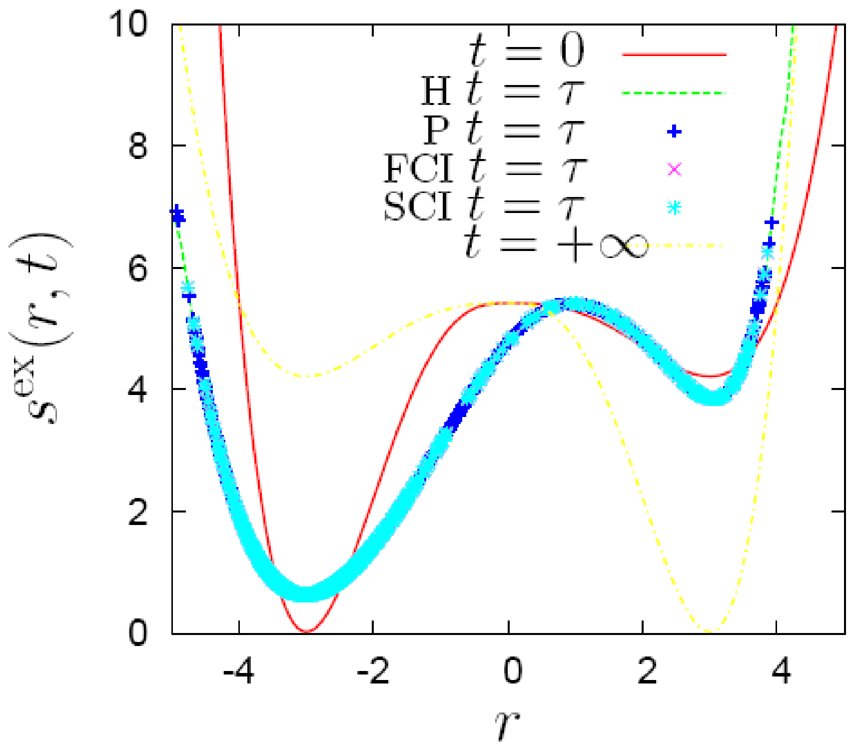
$$= S_{t=0} + \beta\langle Q\rangle + \int_0^1 \theta d\theta \left\langle \mathrm{var}_\theta\left(\Delta\varphi\right)\right\rangle_{t=\tau}$$

$$S^{eq}(\beta_1) \text{-} S^{eq}(\beta_0) = \int_{\beta_0}^{\beta_1} \beta d\beta \, \mathrm{var}_\beta(H)$$

Non-equilibrium entropy



Non-equilibrium entropy



Perspectives

N-particle system

Entropy at glass transition

Formalism for non-conservative dissipative systems

Free energy calculations in path ensembles

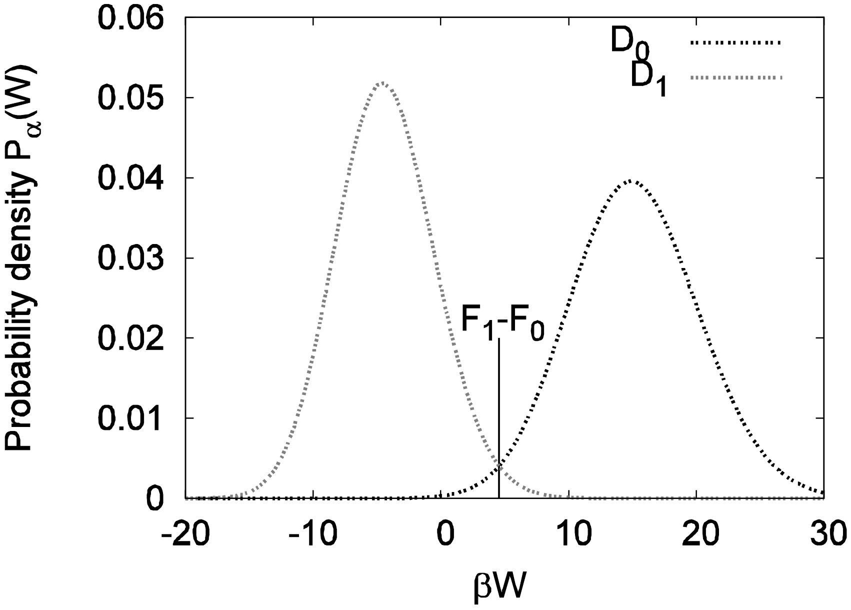
$$\tilde{Z}_0 = \frac{1}{h^{3N}N!}\int \mathrm{D}z N_0\left(\chi_i\right) \mathrm{P}^{+}_{\mathrm{cond}}\left(z\right)$$

$$\tilde{Z}_0 = \frac{1}{h^{3N}N!}\int \mathrm{d}\chi_i N_0\left(\chi_i\right) \int_{\Omega_i} \mathrm{D}z \mathrm{P}^{+}_{\mathrm{cond}}\left(z\right)$$

$$\tilde{Z}_0 = \frac{1}{h^{3N}N!}\int \mathrm{d}\chi_i N_0\left(\chi_i\right) = Z_0$$

$$\tilde{Z}_1 = Z_1 \qquad \exp\left[-\beta\Delta F\right] = \frac{\tilde{Z}_1}{\tilde{Z}_0}$$

Work distribution



Jarzynski's approach

$$\frac{\tilde{Z}_1}{\tilde{Z}_0} = \frac{\int \mathrm{Dz}\exp\left[-\frac{\beta}{2}\left(\tilde{U}+\tilde{W}\right)\right]}{\int \mathrm{Dz}\exp\left[-\frac{\beta}{2}\left(\tilde{U}-\tilde{W}\right)\right]}$$

$$\frac{\tilde{Z}_1}{\tilde{Z}_0} = \frac{\int \mathrm{Dz}\exp\left[-\beta\tilde{W}\right]\exp\left[-\frac{\beta}{2}\left(\tilde{U}-\tilde{W}\right)\right]}{\int \mathrm{Dz}\exp\left[-\frac{\beta}{2}\left(\tilde{U}-\tilde{W}\right)\right]}$$

$$\beta\left(F_1 - F_0\right) = -\ln\left\langle \exp\left[-\beta\tilde{W}\right]\right\rangle_0$$

$$= \ln\left\langle \exp\left[\beta\tilde{W}\right]\right\rangle_1$$

$$\frac{\tilde{Z}_1}{\tilde{Z}_0} = \frac{\tilde{Z}_\theta}{\tilde{Z}_\theta}\frac{\int \mathrm{Dz}\exp\left[\left(\theta-1\right)\beta\tilde{W}\right]K_\theta}{\int \mathrm{Dz}\exp\left[\theta\beta\tilde{W}\right]K_\theta}$$

Thermodynamic perturbation

$$F_1 - F_0 = -\frac{1}{\beta}\ln\frac{\left\langle \exp\left[\left(\theta-1\right)\beta\tilde{W}\right]\right\rangle_\theta}{\left\langle \exp\left[\theta\beta\tilde{W}\right]\right\rangle_\theta}$$

The 38-atom cluster « LJ_{38} »

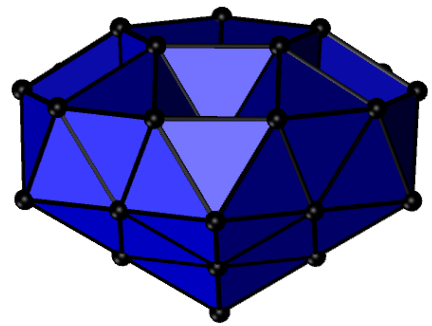
orientational order parameter Q_4

liquid structures (desordered)

$4 \cdot 10^{-2} \leq Q_4 \leq 9 \cdot 10^{-2}$

$T_{melt}=0.17$ (reduced units)

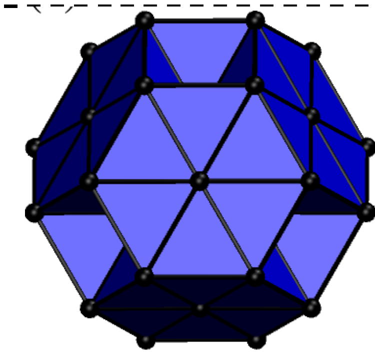
incomplete icosahedron (fivefold symmetry)
E=-173,252 ε€[r.u.]



$Q_4=4 \cdot 10^{-2}$

$T_{ss}=0.12$

truncated octahedron (fcc symmetry)
E=-173.928 ε [r.u.]



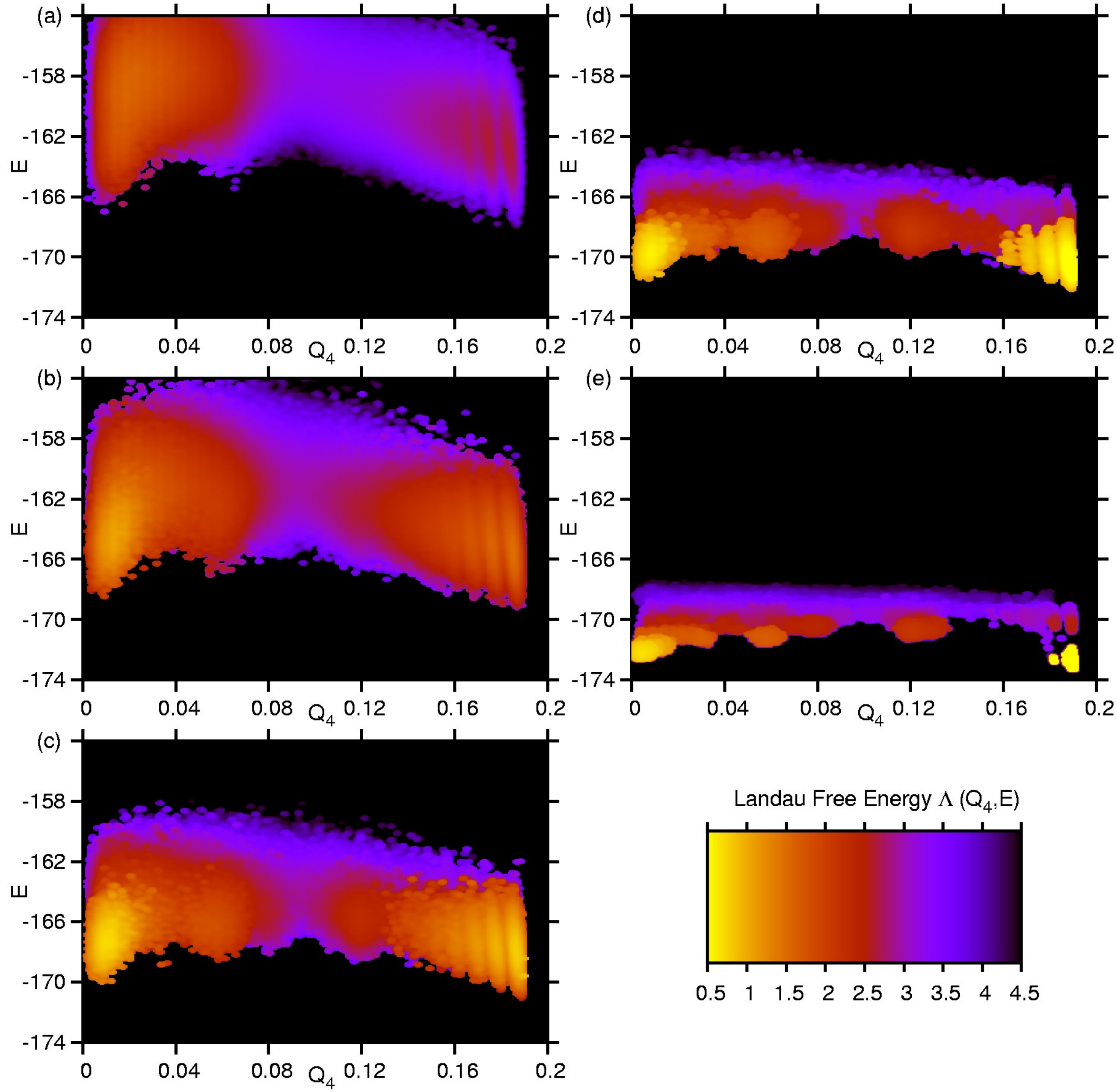
$Q_4=0.19$

T ↘

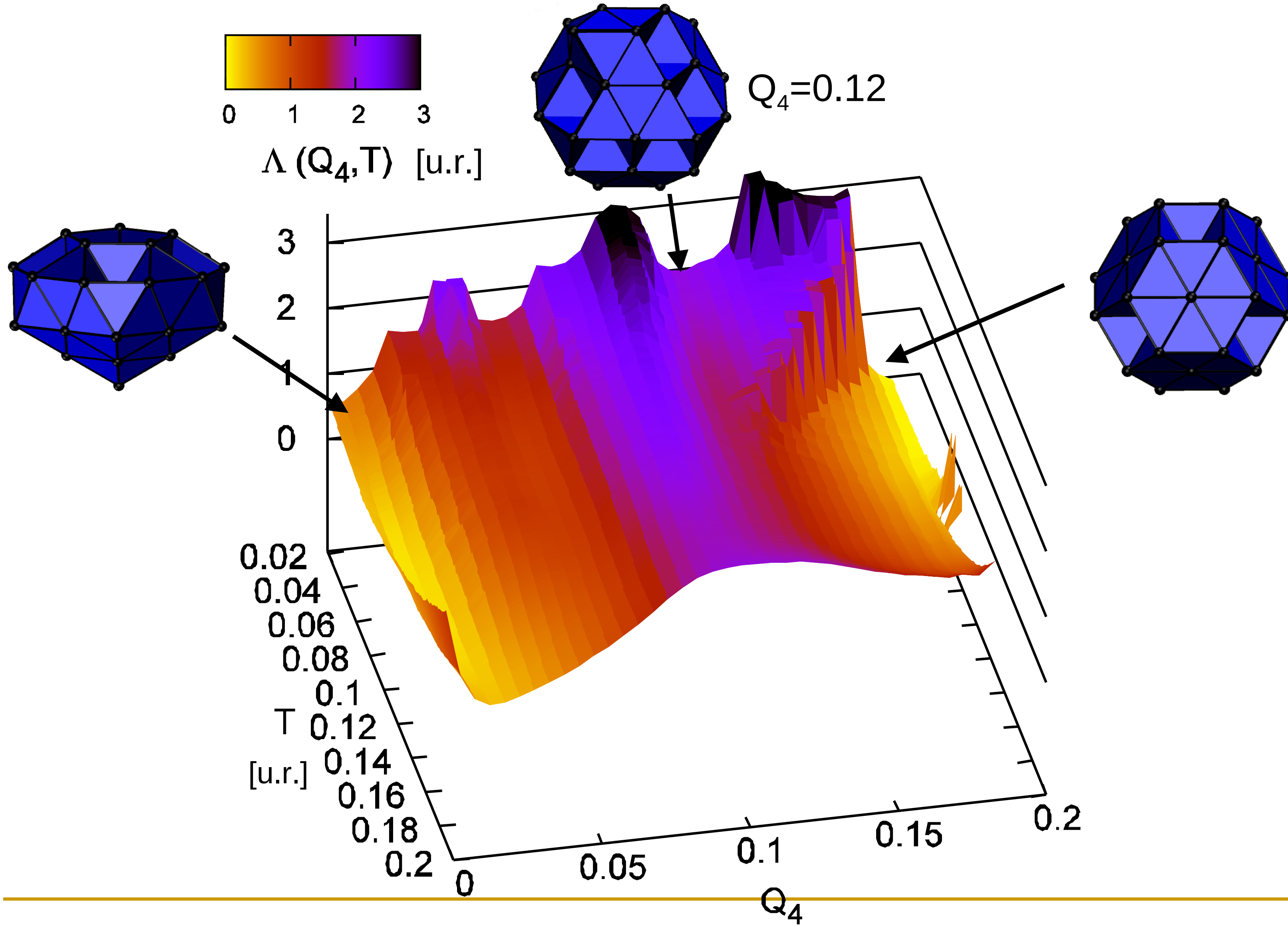
→ (Q_4) ?

$\Lambda(Q_4\text{-}E)$

Q_4-Energy contour plots at decreasing temperatures



Free energy landscape of the LJ_{38} cluster



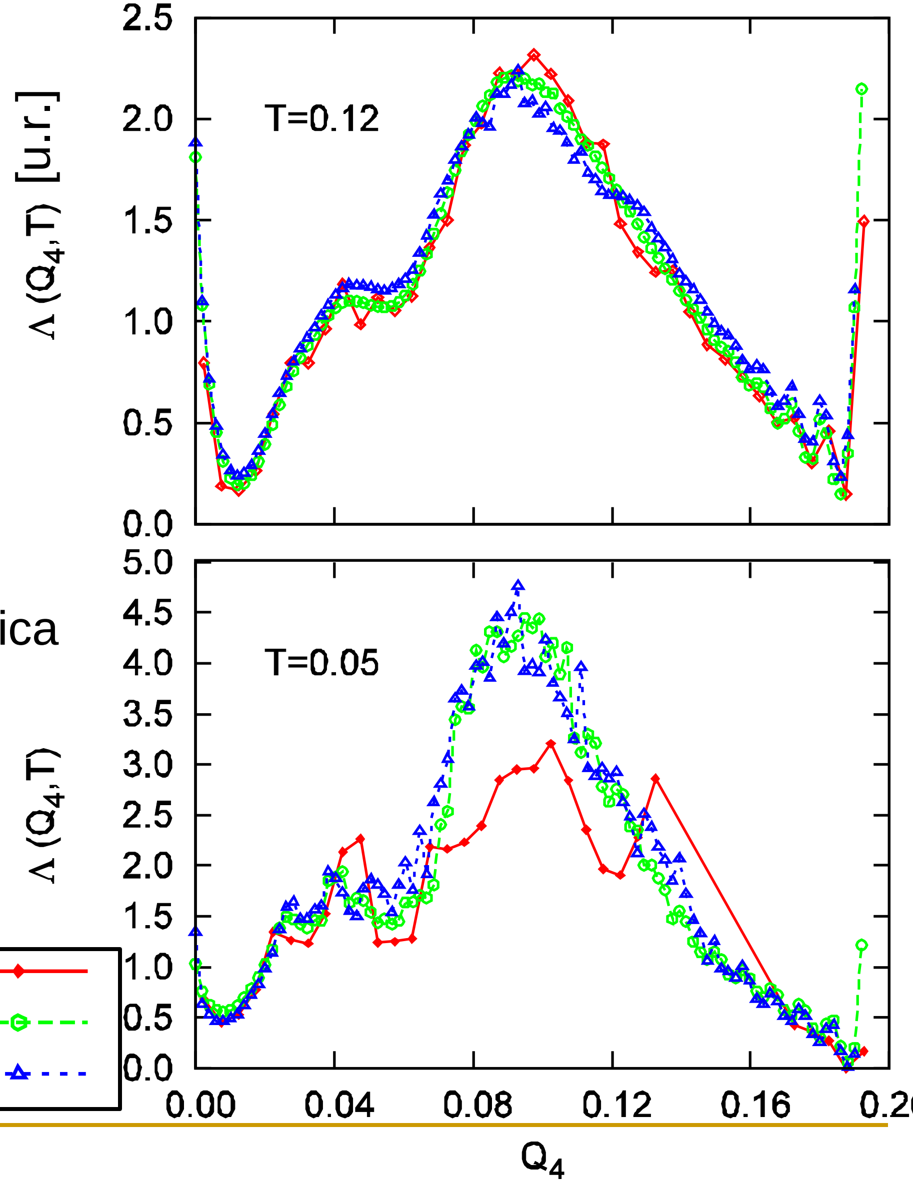
Comparison with state-sampling methods (F. Calvo)

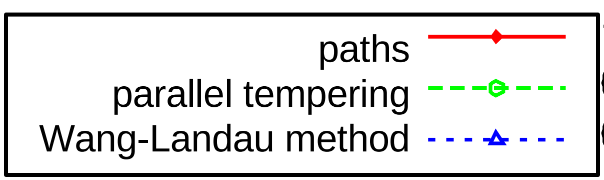
●Wang-Landau method:

auxiliary potential $\propto \ln(E)$

●parallel tempering :

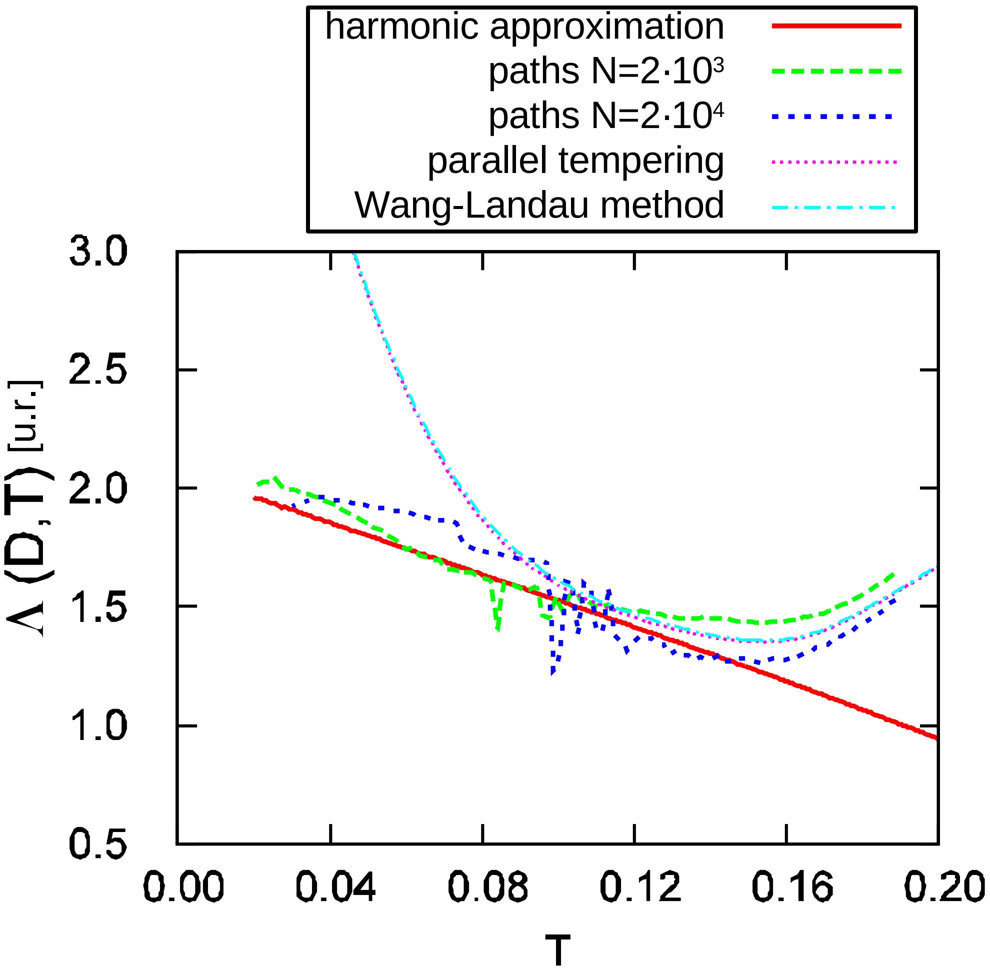
Monte-Carlo exchanges between N replica of the system at various temperatures





Comparison with harmonic superposition approximation

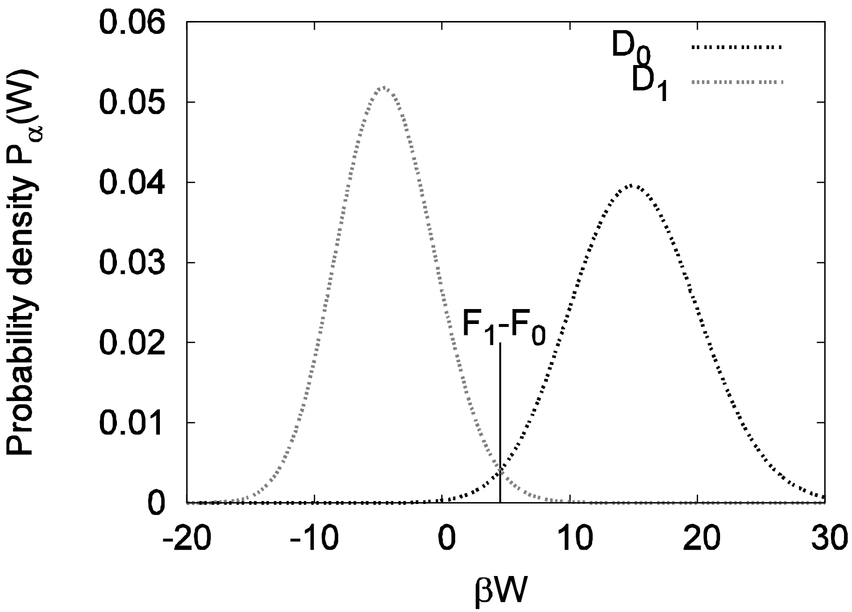
- harmonic superposition approximation in class D



→<u>validation of the path-sampling approach</u>

Adjanor, Athènes and Calvo, EPJB (2006)

Work distribution



Free energy computations: what is the optimal bias?

$$\beta\left(F_1 - F_0\right) = -\ln\left\langle \exp\left[-\beta\tilde{W}\right]\right\rangle_0$$

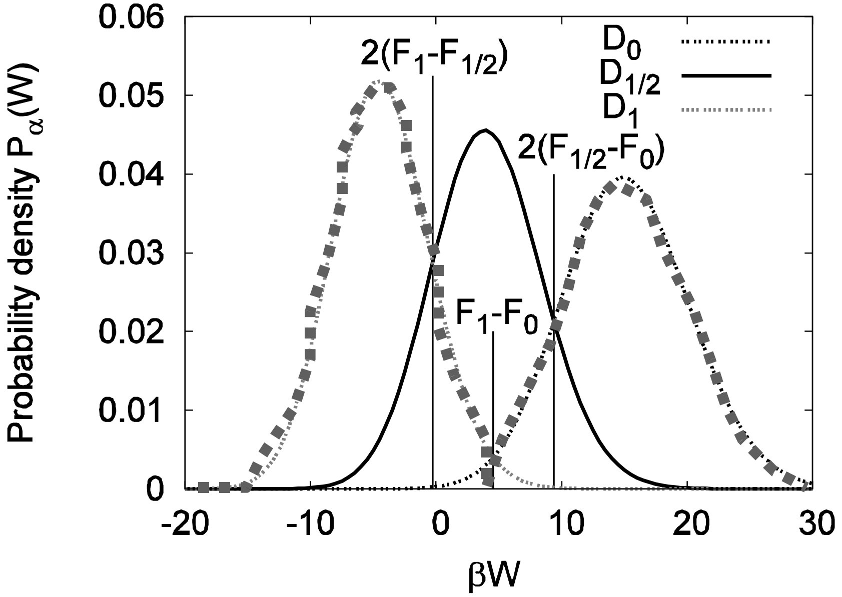
$$= \ln\left\langle \exp\left[\beta\tilde{W}\right]\right\rangle_1$$

$$\frac{\tilde{Q}_1}{\tilde{Q}_0} = \frac{\tilde{Q}_\theta}{\tilde{Q}_\theta}\frac{\int \mathrm{Dz}\exp\left[\left(\theta-1\right)\beta\tilde{W}\right]K_\theta}{\int \mathrm{Dz}\exp\left[\theta\beta\tilde{W}\right]K_\theta}$$

Thermodynamic perturbation

$$F_1 - F_0 = -\frac{1}{\beta}\ln\frac{\left\langle \exp\left[\left(\theta-1\right)\beta\tilde{W}\right]\right\rangle_\theta}{\left\langle \exp\left[\theta\beta\tilde{W}\right]\right\rangle_\theta}$$

Work distribution



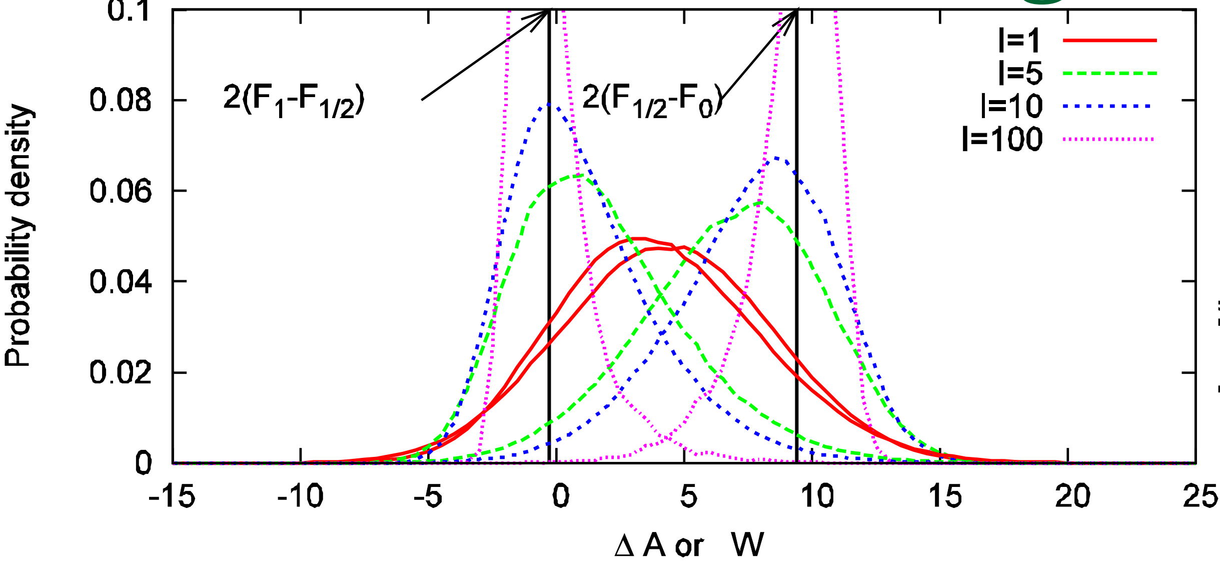
Athènes EPJB (2004),
Oberhofer, Geissler and Dellago JPCB(2005),
Adjanor and Athènes, JCP (2005)
Ytreberg, Zuckerman and Swendsen JCP(2006)
Lechner and Dellago J. Stat. Phys. (2007)

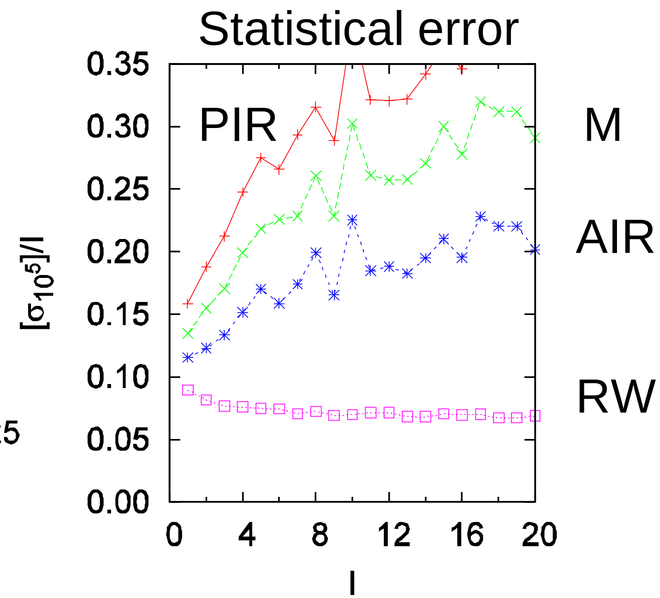
Optimal bias distribution

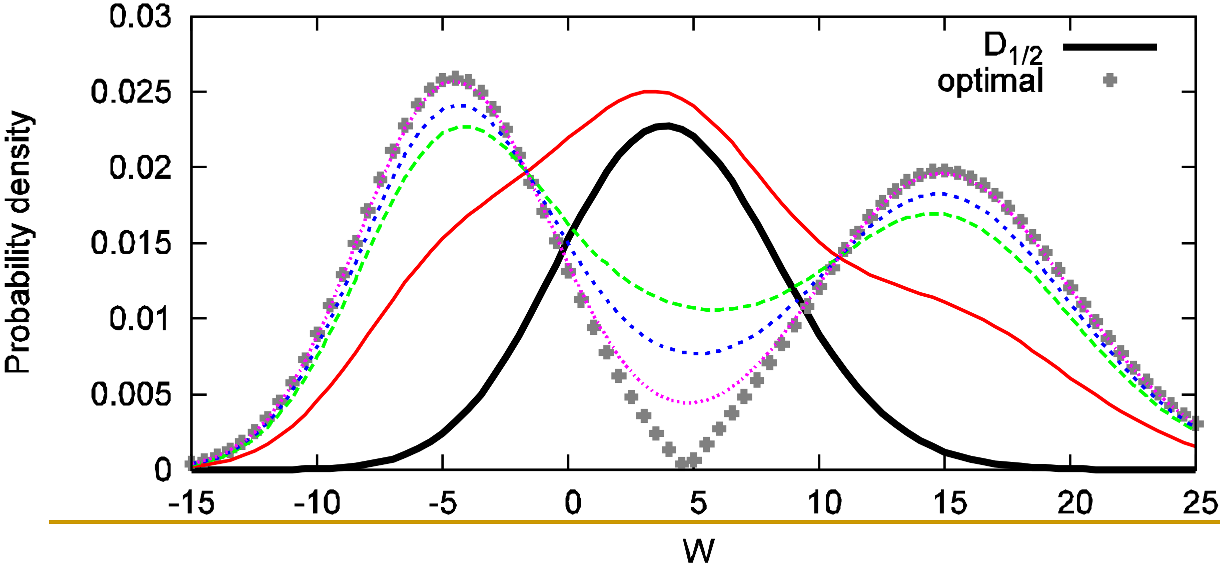
Oberhofer and Dellago (2007)

$$F_1 - F_0 = -\frac{1}{\beta} \ln \frac{\left\langle \exp\left[-\frac{1}{2}\beta \tilde{W}\right] \right\rangle_{\frac{1}{2}}}{\left\langle \exp\left[\frac{1}{2}\beta \tilde{W}\right] \right\rangle_{\frac{1}{2}}}$$

Information retrieving from the webs







Ceperley, Kalos, PRB (1977), Frenkel Boulougouris, JTCT (2005) Jourdain, Delmas (2007) Athènes, PRE (2002), EPJB (2007), Wu and Kofke (2005)