Waste-Recycling Monte Carlo and the calculation of free energies

Manuel Athènes, C.-M. Marinica

Service de Recherches de Metallurgie Physique, CEA Saclay

Gilles Adjanor, *EDF-R&D les Renardières*

Florent Calvo, *Université de Lyon*

Waste-recycling Monte Carlo

Goal : reducing the statistical variance of the estimator in Markov Chain Monte Carlo techniques based on the Metropolis algorithm

How? by including information within the estimator about the states that have been sampled but rejected.

Ceperley, Chester and Kalos, Phys. Rev.1977,
Frenkel, PNAS 2004,
Delmas &Jourdain, J. Applied Probab. 2009.

Outline

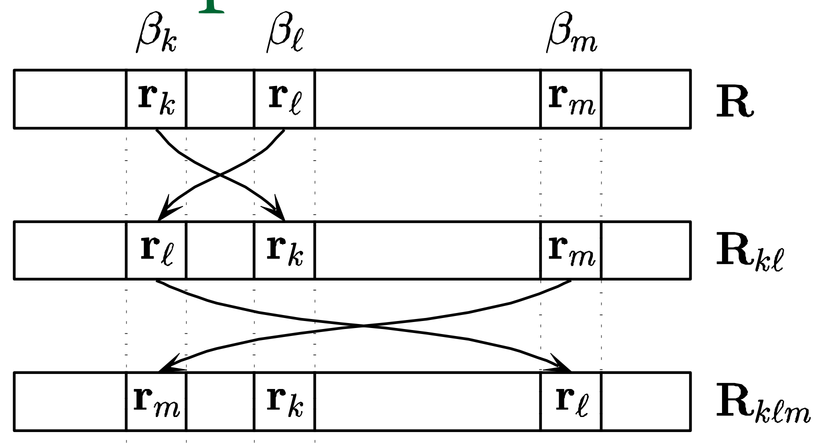
I-Conditional expectations

- Speeding-up of parallel tempering with configuration bias (col. F. Calvo)
- Control variate problem & optimal estimator (Delmas&Jourdain)
  - Applications : Ising systems and realistic FeCr system (col. G. Adjanor)
- Free energy reconstruction from steered molecular dynamics
  - Vacancy in Iron, Structural transitions in LJ_{38} cluster (col. C. Marinica)

II-Posterior conditional expectations

- Combination of waste-recycling and multistate Bennett acceptance ratio method

Parallel replica simulations



Exchanges between replicas

monoproposal

multiproposal

$$\alpha\left(\mathbf{R}\rightarrow\mathbf{R}_{kl}\right)=\frac{1}{I}$$

Esselink, Loyens, Smit, PRE 1995

$$\alpha\left(\mathbf{R}\rightarrow\mathbf{R}_{kl}\right)=\frac{\rho\left(\mathbf{R}_{kl}\right)}{\sum\rho\left(\mathbf{R}_{ki}\right)}$$

$$acc\left(\mathbf{R}\rightarrow\mathbf{R}_{kl}\right)=\min\left(1,\frac{\rho\left(\mathbf{R}_{kl}\right)}{\rho\left(\mathbf{R}\right)}\right)$$

$$acc\left(\mathbf{R}\rightarrow\mathbf{R}_{kl}\right)=\min\left(1,\frac{\sum\rho\left(\mathbf{R}_{klm}\right)}{\sum\rho\left(\mathbf{R}_{kl}\right)}\right)$$

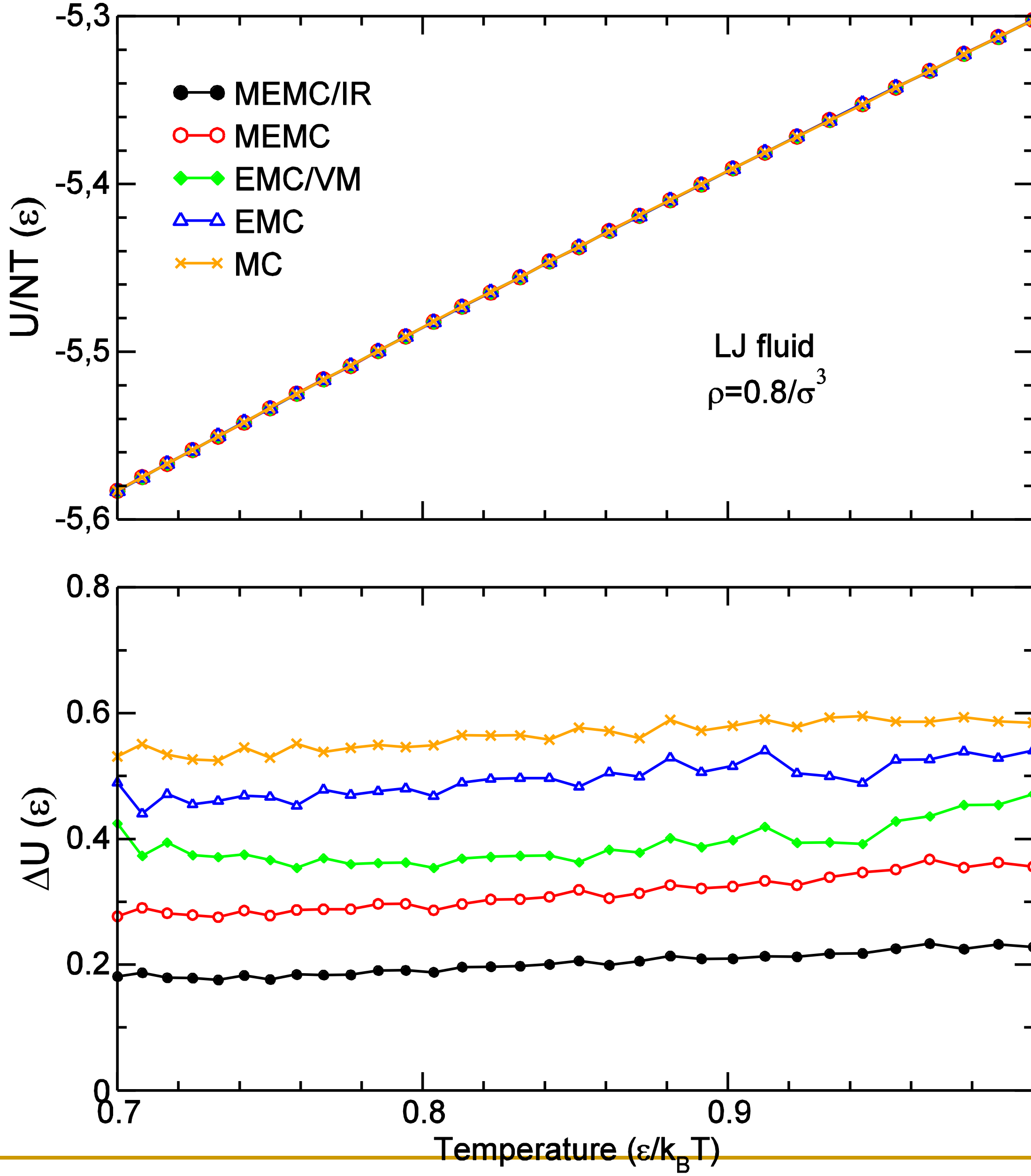
LJ fluid

$$E_{ij}(r) = \frac{\varepsilon}{4}\left(r^{-12} - r^{-6}\right)$$

$$U\left(\mathrm{r}^{\mathrm{N}}\right) = \sum_{i>j} E_{ij}(r)$$

Colluza, Frenkel
PhysChemPhys 2005

Athenes, Calvo
PhysChemPhys 2008

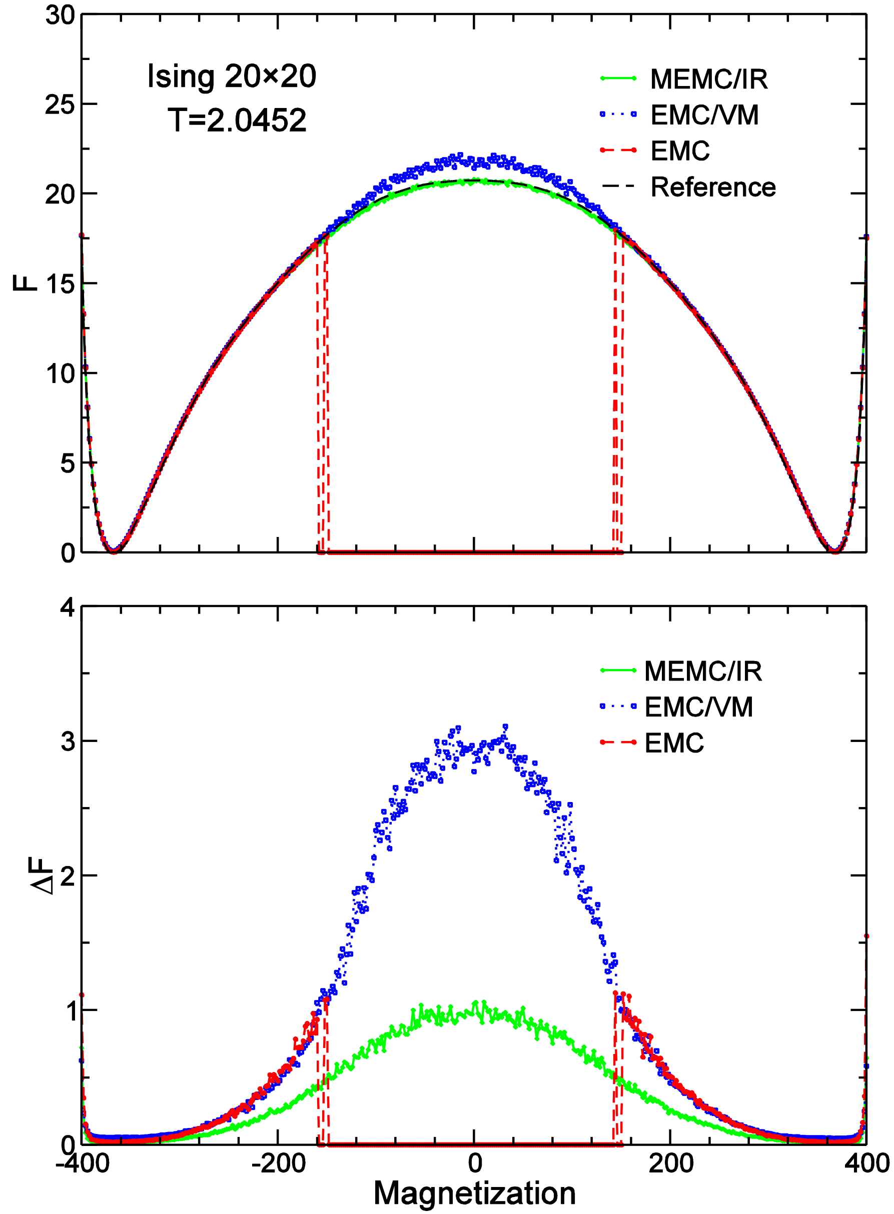


Ferromagnetic system

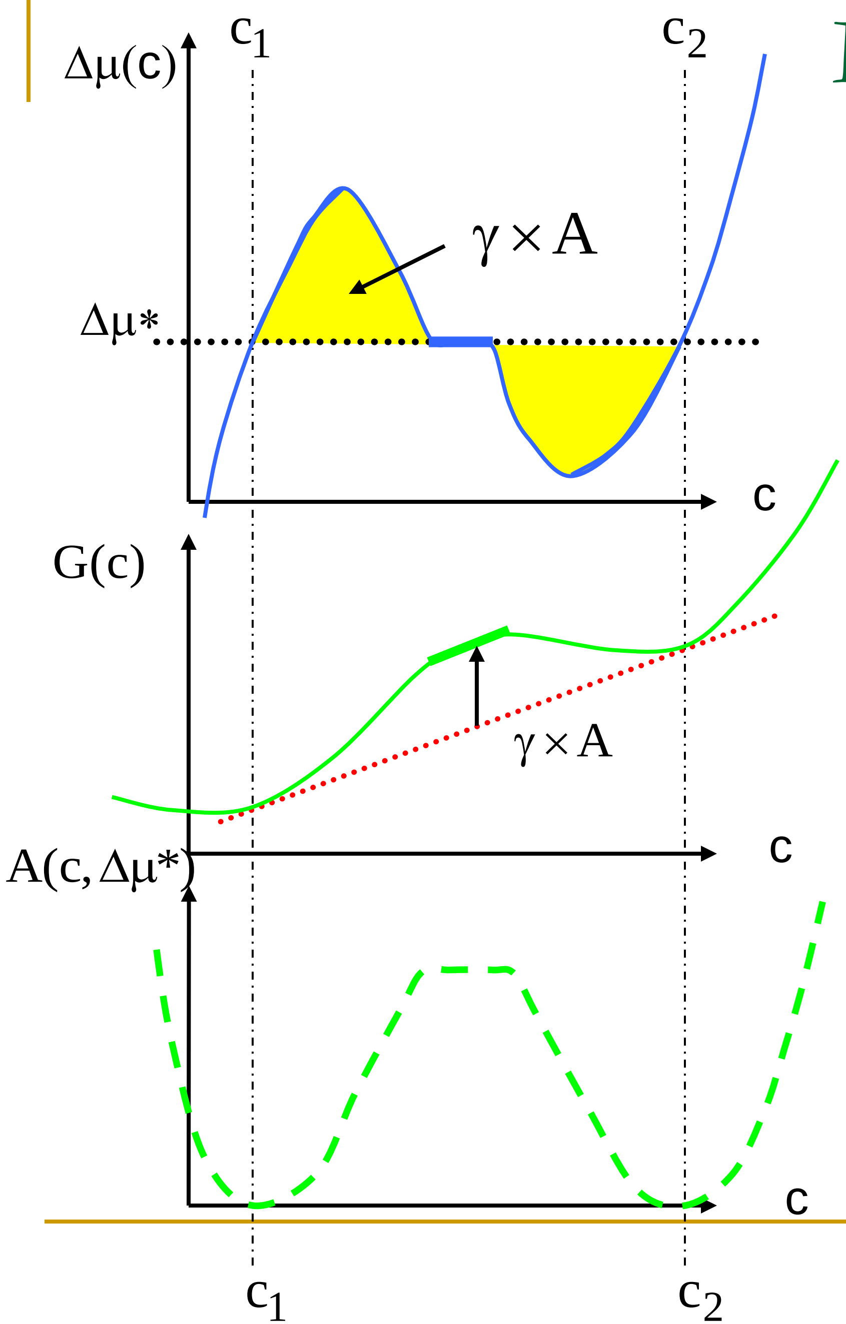
$$E_{ij}(\uparrow\uparrow) = E_{ij}(\downarrow\downarrow) < E_{ij}(\uparrow\downarrow)$$

$$F(M) = -kT \ln p(M)$$

$$p(M_i) = \left\langle h_{M_i \pm \Delta M_i} \right\rangle$$



Maxwell construction



$$\frac{\partial G(c)}{\partial c} = \Delta\mu(c)$$

$$\int_{c_1}^{c_2} \left(\Delta\mu(c) - \Delta\mu^*\right) dc = 0$$

$$\Updownarrow$$

$$G(c_2) - G(c_1) = \left(c_2 - c_1\right)\Delta\mu^*$$

$$A(c, \Delta\mu^*) = -kT \ln \sum_{conf} h_c(conf)$$

$$h_c(conf) = \delta\left(\frac{N^{Cr}}{N^{Cr} + N^{Fe}} - c\right)$$

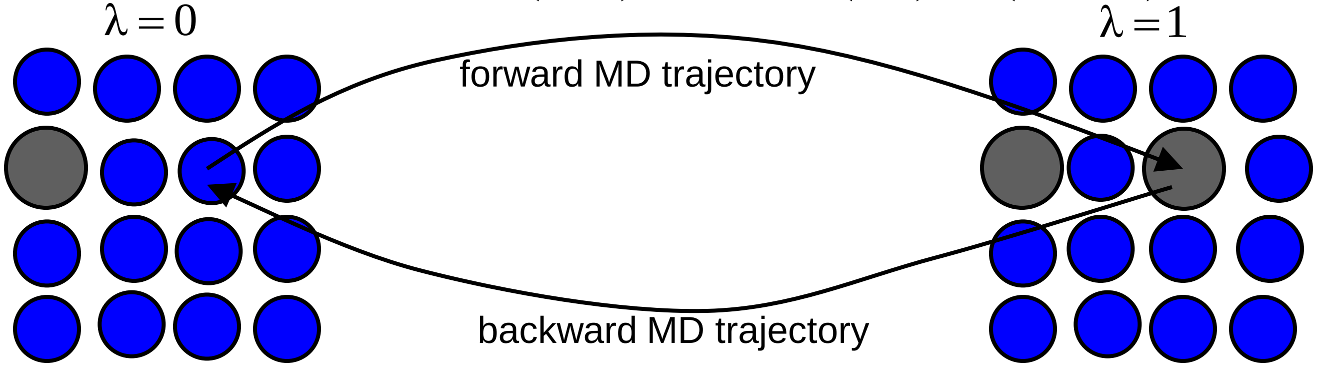
Estimation of chemical potential differences

Gradual transmutation of a Fe atom into Cr atom

Reference system 0: nFe - (m-n)Cr

Target system 1: (n-1)Fe - (m-n+1)Cr

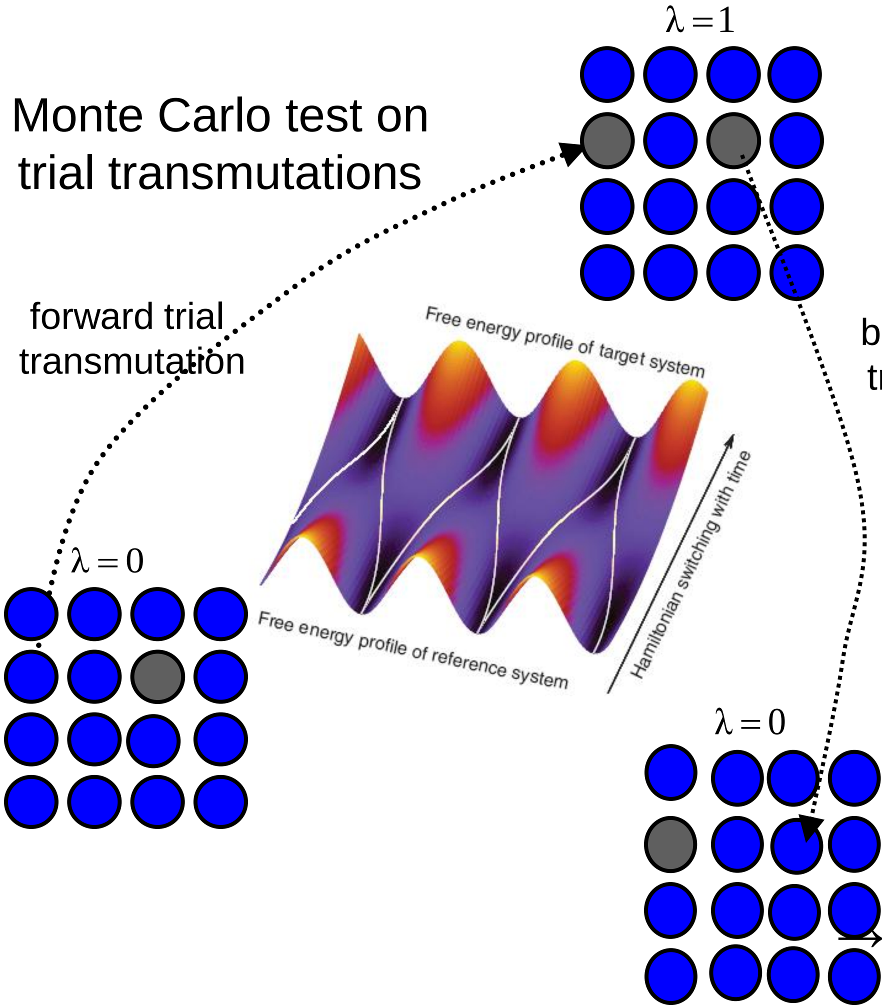
$$H_\lambda = (1-\lambda)\, H_{nFe,(m-n)Cr} + \lambda\, H_{(n-1)Fe,(m-n+1)Cr}$$



$$\exp(-\beta\Delta\mu^{ex}) = \exp(-\beta\Delta G) = \left\langle \exp(-\beta W) \right\rangle_{0\to 1} = \frac{1}{\left\langle \exp(+\beta W) \right\rangle_{1\to 0}}$$

C. Jarzynski PRL (1997), G. E. Crooks, J. Stat. Phys. (1998)

Exploration of alloy configurations: path sampling



Acceptance rate $\propto \exp\left(\pm\frac{\beta}{2}\Delta W\right)$

Measurement of chemical potential difference

$$\exp(-\beta\Delta\mu^{ex}) = \frac{\left\langle \exp\left(-\frac{\beta}{2}W\right)\right\rangle_{1/2}}{\left\langle \exp\left(+\frac{\beta}{2}W\right)\right\rangle_{1/2}}$$

G. Adjanor, M. Athènes, J. Rodgers, J. Chem. Phys. 2011

Metropolis estimator

$$J_N^0(f) = \frac{1}{N}\sum_{n=1}^{N} f_n \approx \langle f \rangle \qquad f_n = \exp\left(\pm\frac{\beta}{2}W_n\right)$$

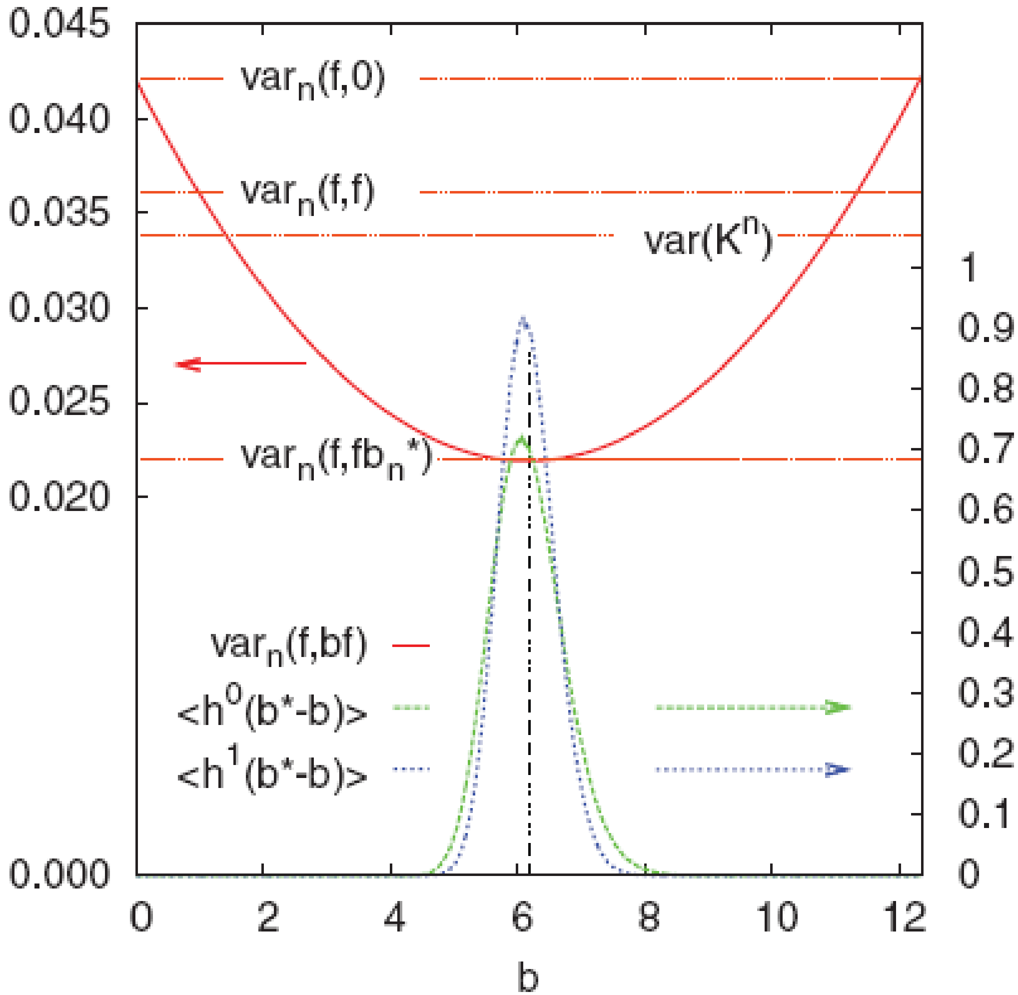
Waste-recycling estimator (Frenkel, PNAS 2004)

$$J_N^{WR}(f) = \frac{1}{N}\sum_{n=1}^{N} f_n\left(1-p_n^{acc}\right) + \tilde{f}_n p_n^{acc} \qquad \tilde{f}_n = \exp\left(\pm\frac{\beta}{2}\tilde{W}_n\right)$$

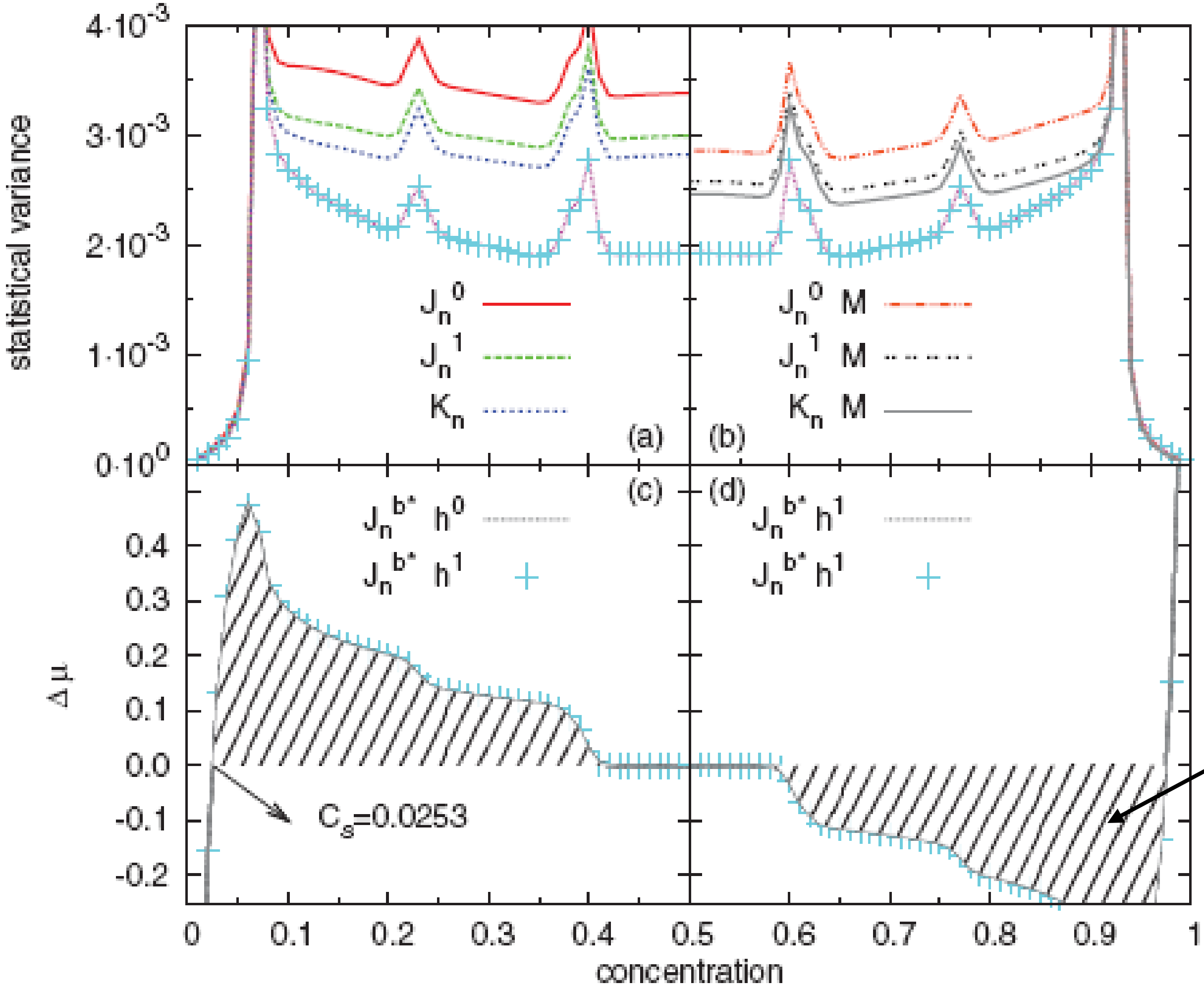
Optimal estimator (Delmas & Jourdain, J. Appl. Probab. 2009)

$$J_N^{b*}(f) = \left(1-b*\right)J_N^0(f) + b*J_N^1(f) \qquad b* = 1/\mathrm{corr}\left(f_n, f_{n+1}\right)$$

Assessement of optimal estimator in a BCC Ising-like binary system



Statistical variances and chemical potentials

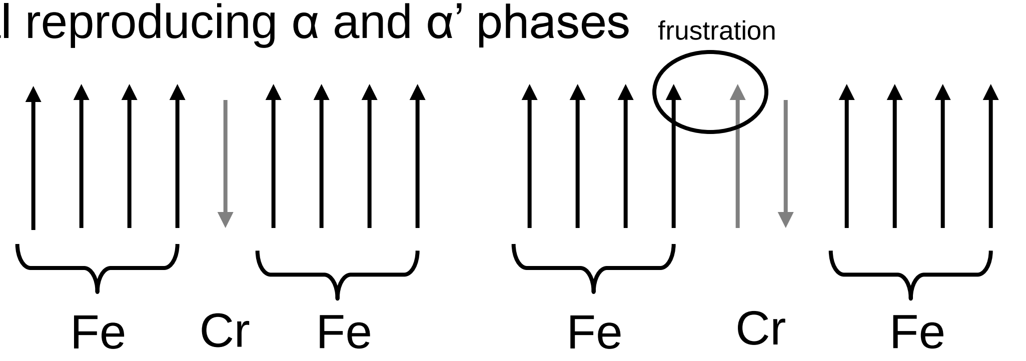


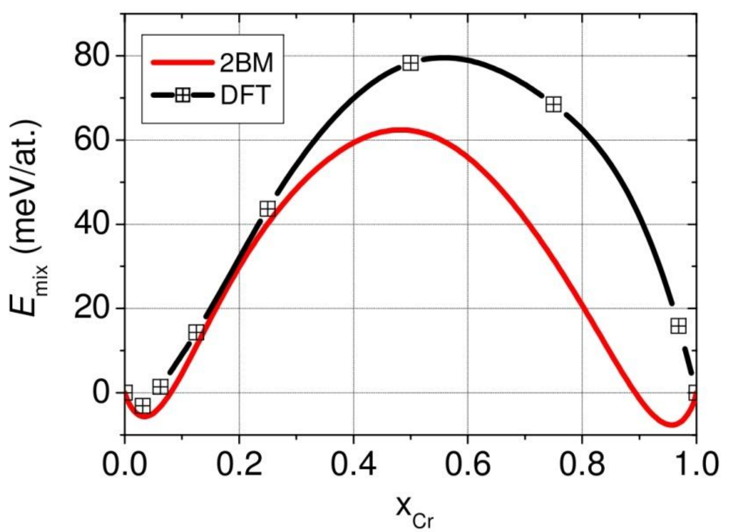
$$\gamma \times A$$

G. Adjanor, M. Athènes, J. Rodgers, J. Chem. Phys. 2011

Empirical potential used:

two-band model (2BM) (P. Olsson et al.Phys. Rev. B 2005)
EAM potential reproducing α and α’ phases





(Olsson et al.2005, Phys. Rev. B

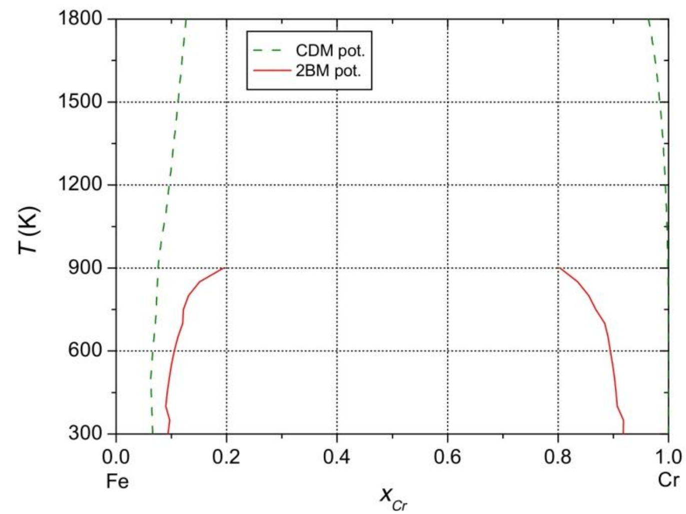
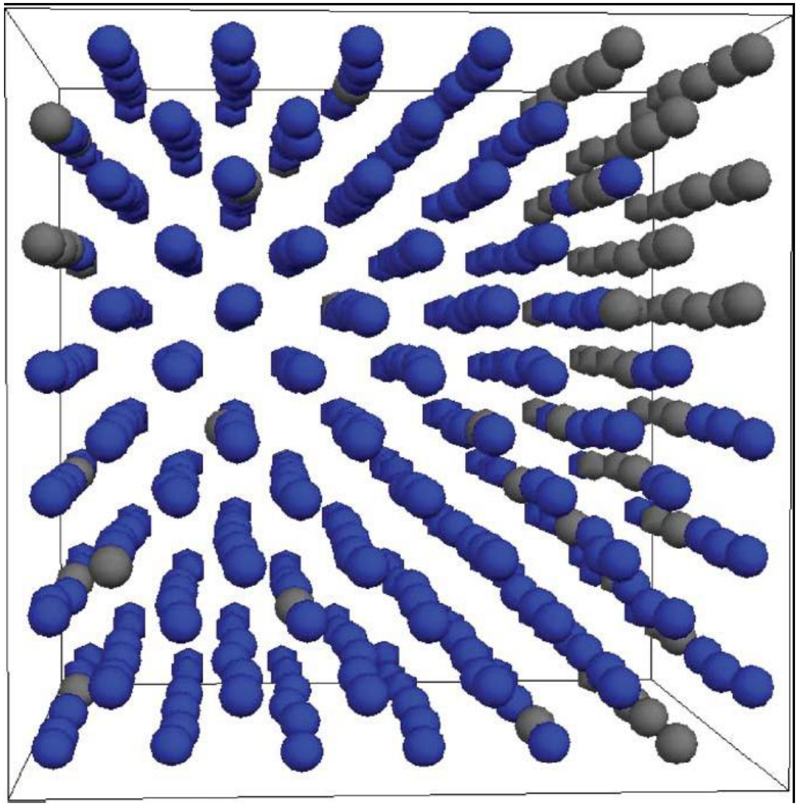


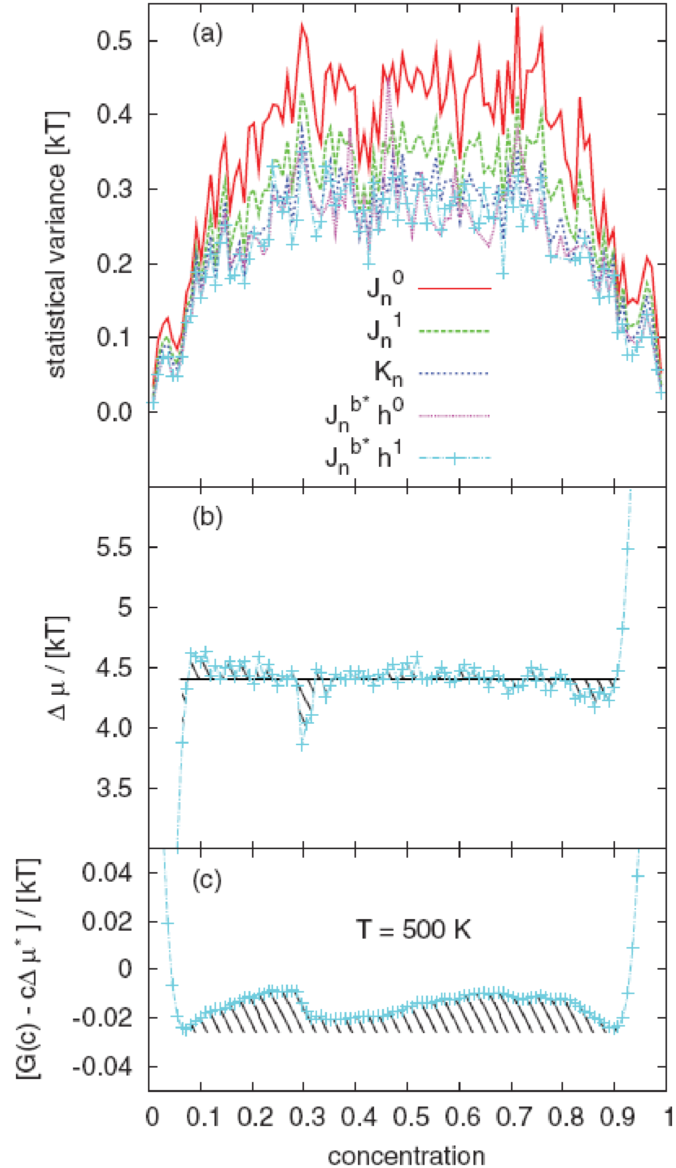
fig :G. Bonny et al., J. Nucl. Mat. 2008)

CDM potential : A. Caro et al

Calculations in FeCr

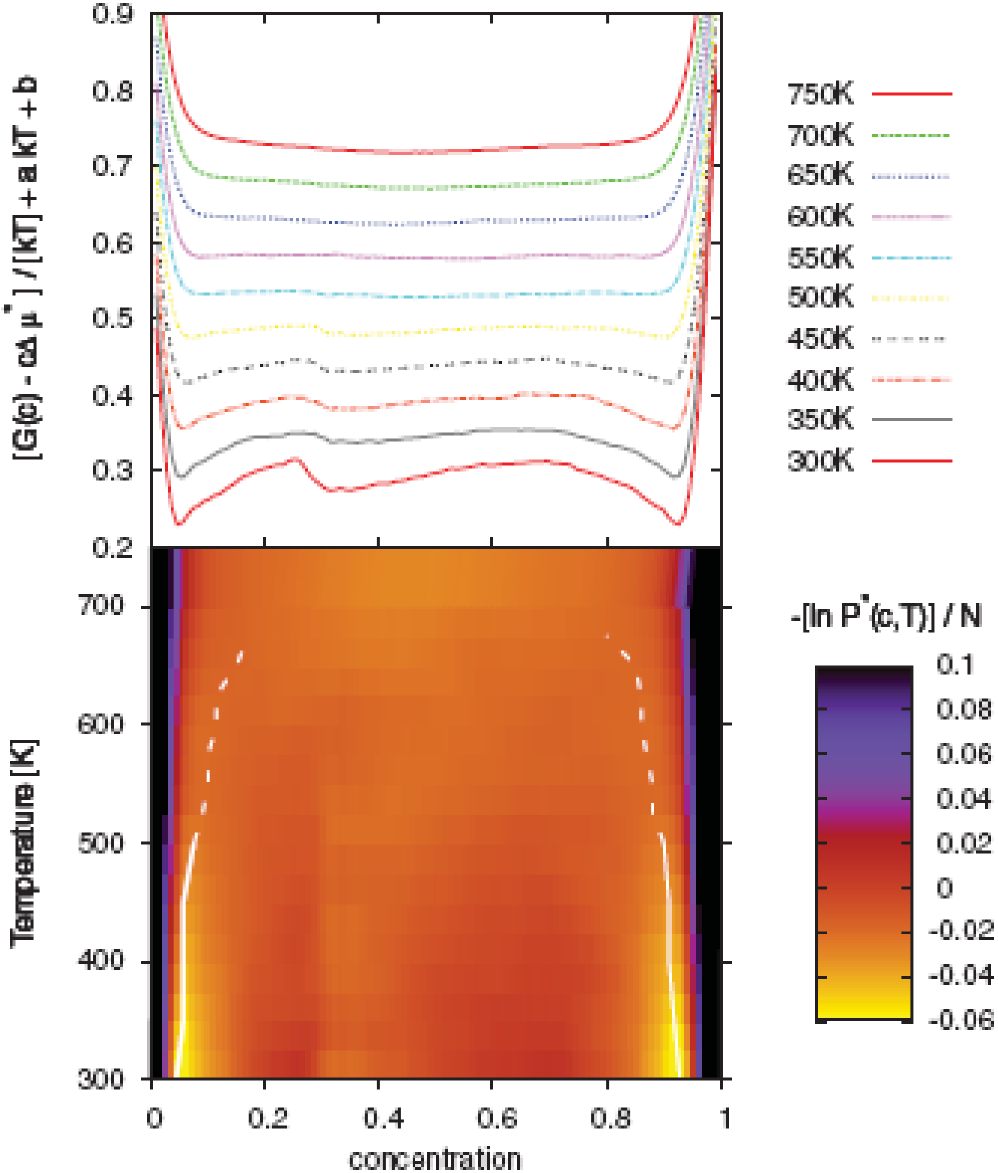


432 atoms



G. Adjanor, M. Athènes, J. Rodgers, J. Chem. Phys. 2011

Equilibrium phase diagram of FeCr



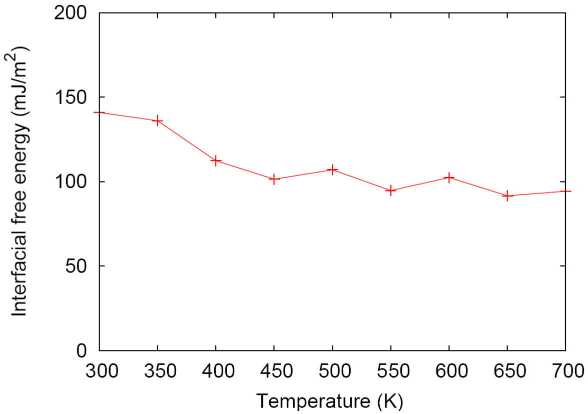
432 atoms:
Strong finite size effects

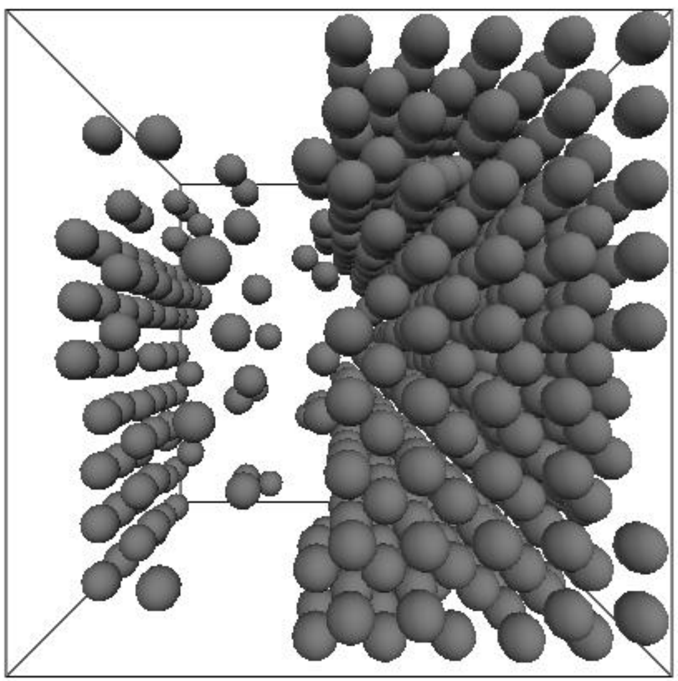
G. Adjanor, et al.
J. Chem. Phys. 2011

Interfacial free energy

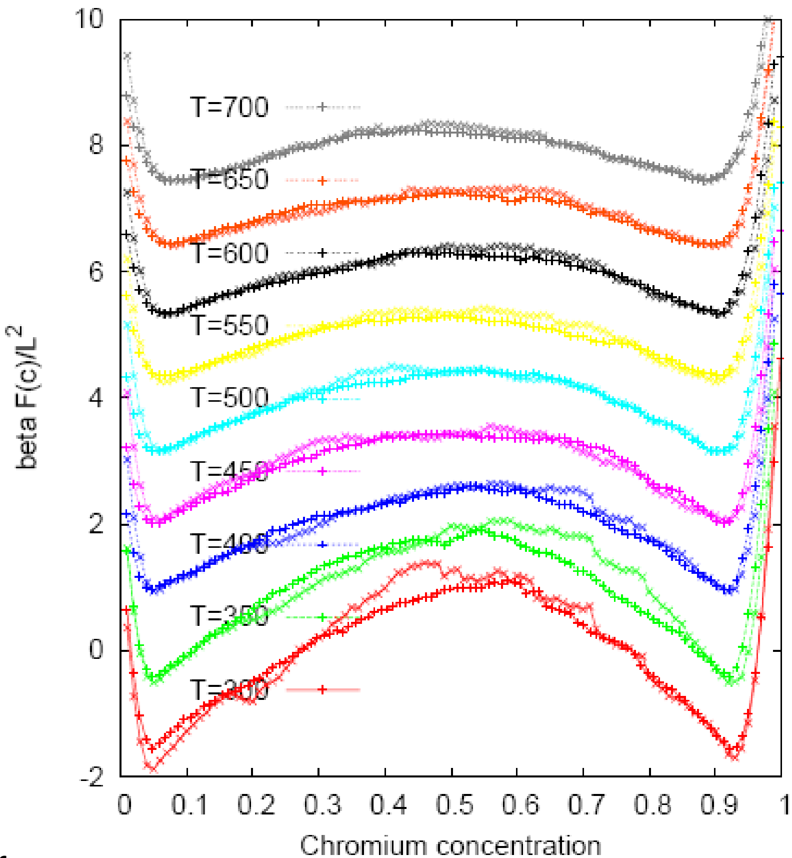
1456 & 2000 atoms

γ





51at.% Cr
1456 atoms
T=300K

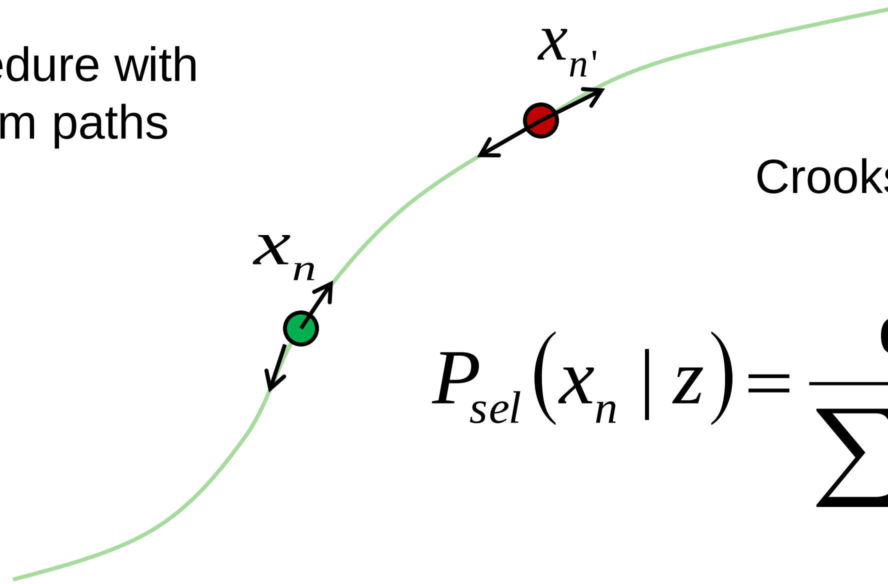


CDM potential
B. Sadigh & P. Erhart,
cond-mat.mtrl-sci 2011

Waste-recycling & steered molecular dynamics

$$P_{sel}(x_n \mid z)P_{cond}(z \mid x_{n'})P(x_{n'}) = P_{sel}(x_{n'} \mid z)P_{cond}(z \mid x_n)P(x_n)$$

Shooting procedure with nonequilibrium paths



Crooks work theorem

$$P_{sel}(x_n \mid z) = \frac{\exp[-\beta W_n]}{\sum_{\ell}^{N} \exp[-\beta W_\ell]}$$

Summary of Monte Carlo algorithm

1. Run the following sampler
   1. Proposed states in generated nonequilibrium path
   2. Select new state using posterior conditional probability

2. Evaluate average with estimator

$$\langle A \rangle = \frac{1}{M} \sum_{m=1}^{M} \frac{\sum_{n=0}^{N} A(r_{n|m}) \exp\left[-\beta W_{n|m}\right]}{\sum_{n=0}^{N} \exp\left[-\beta W_{n|m}\right]}$$

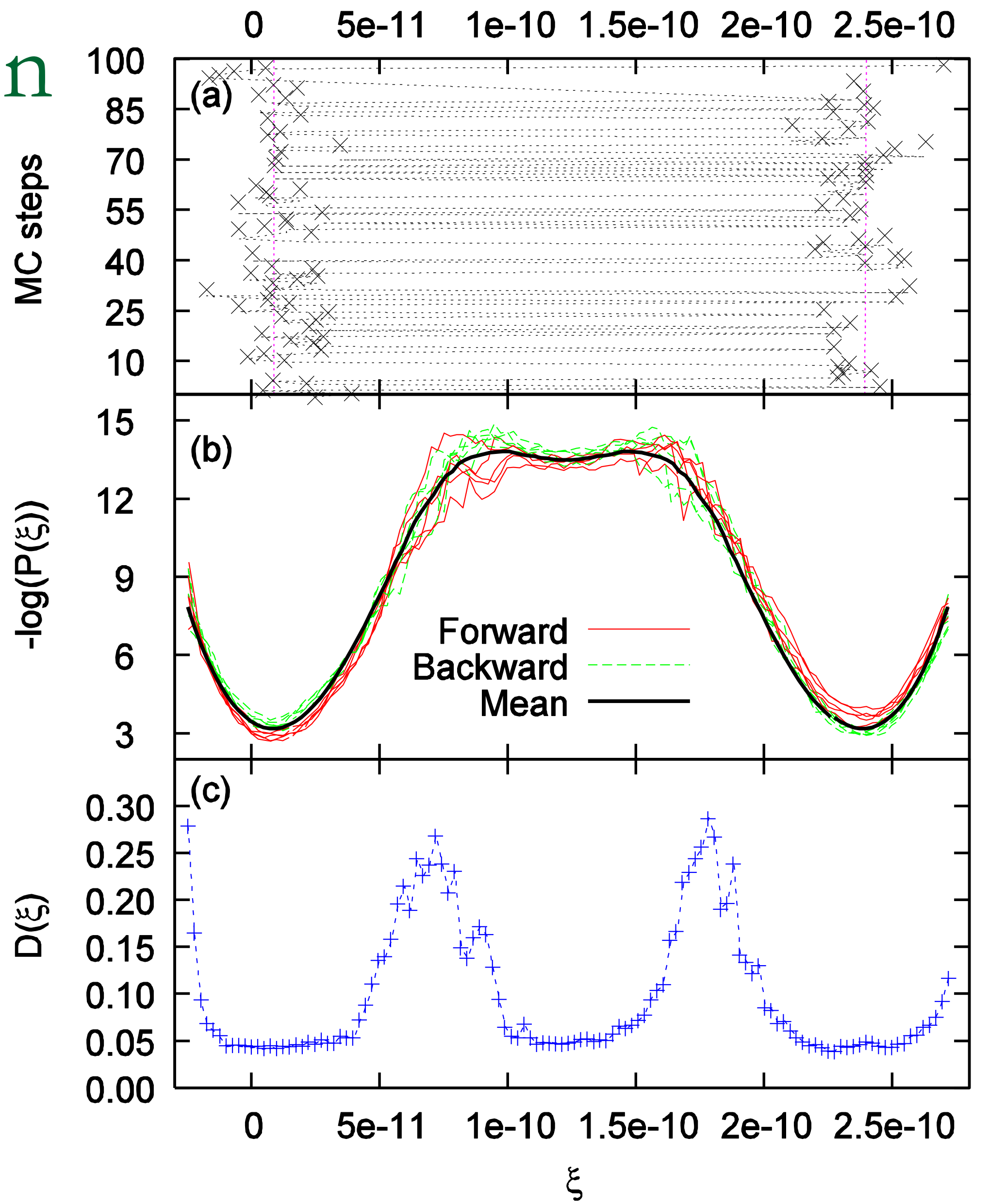
Vacancy migration in α–Fe

- Mendelev potential
- α–Fe structure (bcc)
- Single additional steering variable
- Harmonic spring on nearest vacancy neighbor

$$h_\xi = \frac{\sum_{n=0}^{N} h_\xi(\xi_n)\exp[-\beta W_n]}{\sum_{n=0}^{N} \exp[-\beta W_n]}$$

$$P(\xi) = \langle h_\xi \rangle$$

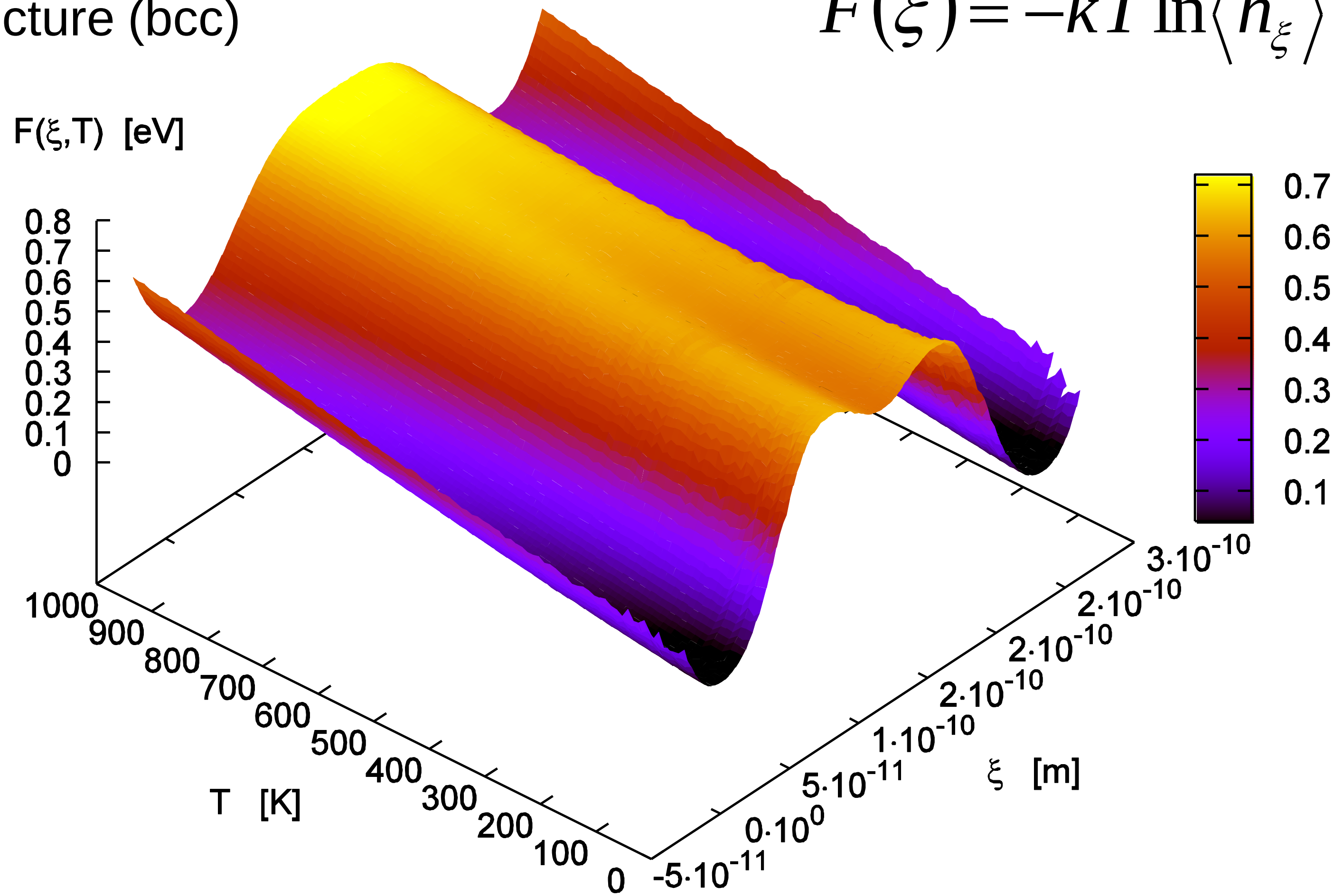
$$D(\xi) = -\langle \ln h_\xi \rangle$$



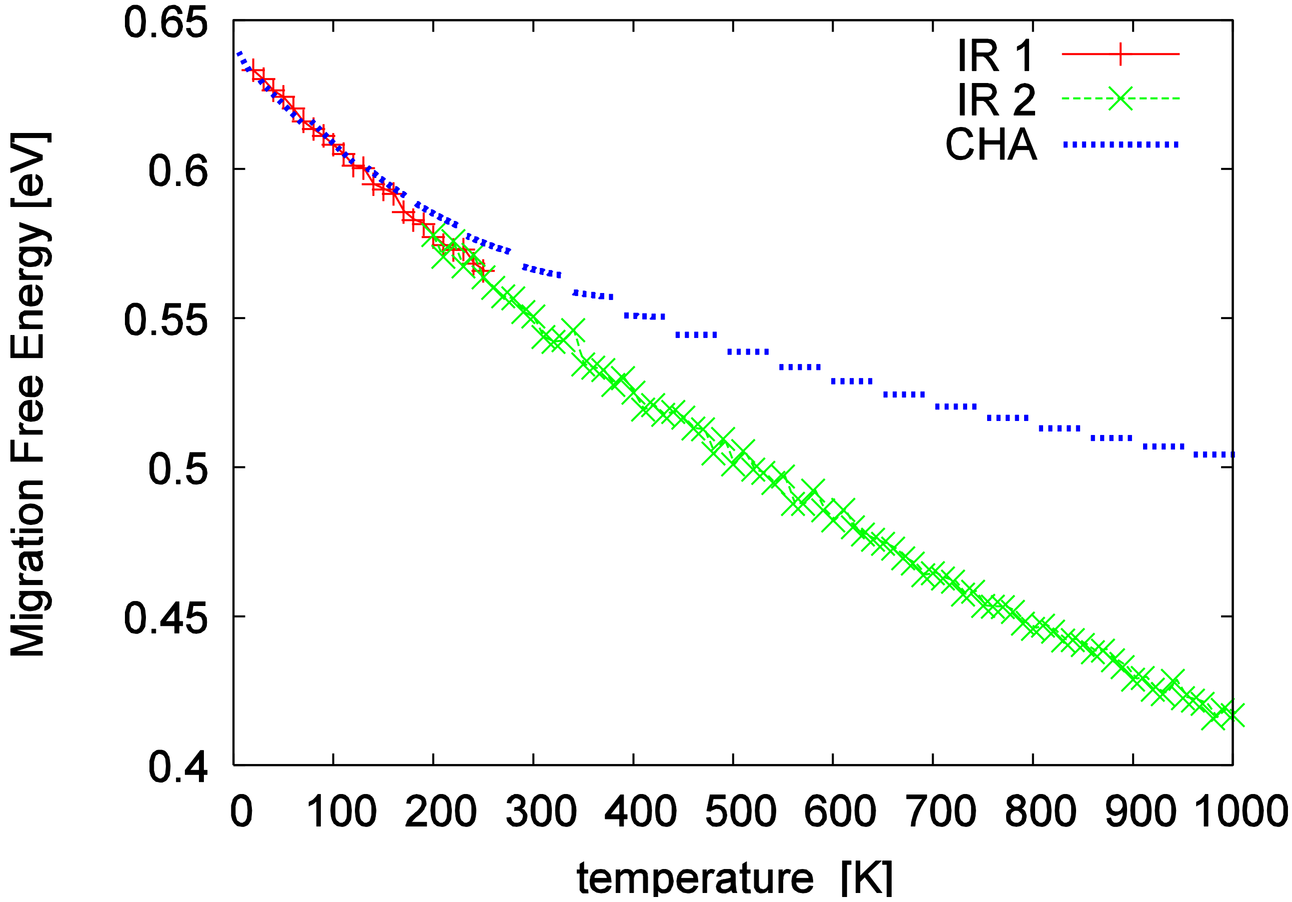
Vacancy migration in α–Fe

- Mendelev potential
- α–Fe structure (bcc)

$$F(\xi) = -kT \ln\langle h_\xi \rangle$$



Comparison with classical harmonic approximation



Intermezzo: the 38-atom cluster « LJ_{38} »

orientational order parameter Q_4

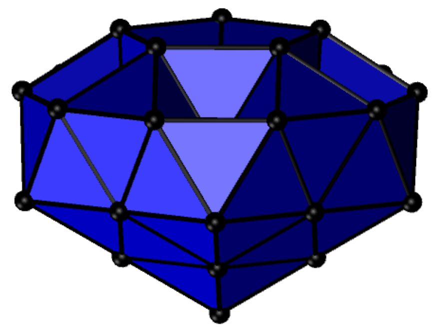
liquid structures (desordered)

$4\cdot10^{-2} \leq Q_4 \leq 9\cdot10^{-2}$

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

incomplete icosahedron (fivefold symmetry)

E=-173,252 ε [r.u.]

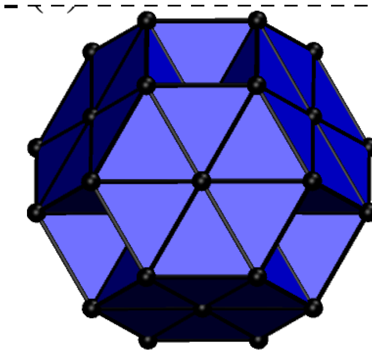


$Q_4=4\cdot10^{-2}$

$T_{ss}=0.12$

truncated octahedron (fcc symmetry)

E=-173.928 ε [r.u.]



$Q_4=0.19$

T ↘

$\rightarrow \Lambda(Q_4)$?

Autonomous steering with two additional coordinates

$$\xi_1(r) = Q_4(r) \rightarrow \xi_1^{add}$$
$$\xi_2(r) = E(r) \rightarrow \xi_2^{add}$$

TAMD,(Eric Vanden-Eijden)

$$\ddot{\xi}_j^{add} = -\frac{\mu_j}{m_j}\left(\frac{\partial E_\kappa}{\partial \xi_j^{add}} + \eta_j \dot{\xi}_j^{add}\right) + b_j\sqrt{2\frac{\mu_j}{m_j}\eta_j kT}$$

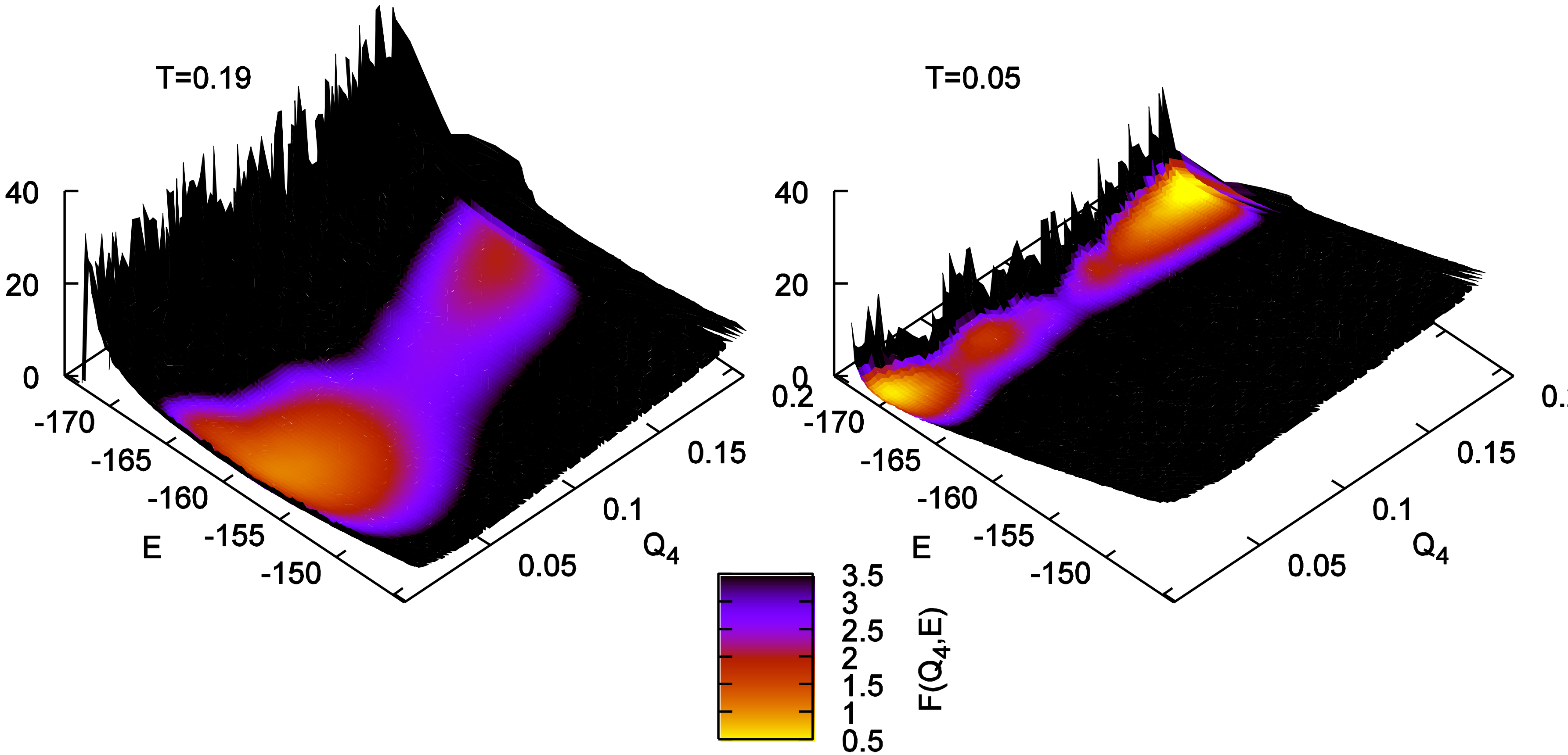
$$W(z) = \sum_j \int_0^\tau (1-\mu_j)\partial_{\xi_j^{add}} E_\kappa(r,\xi^{add})dt$$

$\mu_j = 0$ Non-autonomous steering

$0 < \mu_j < 1$ Autonomous steering out of equilibrium

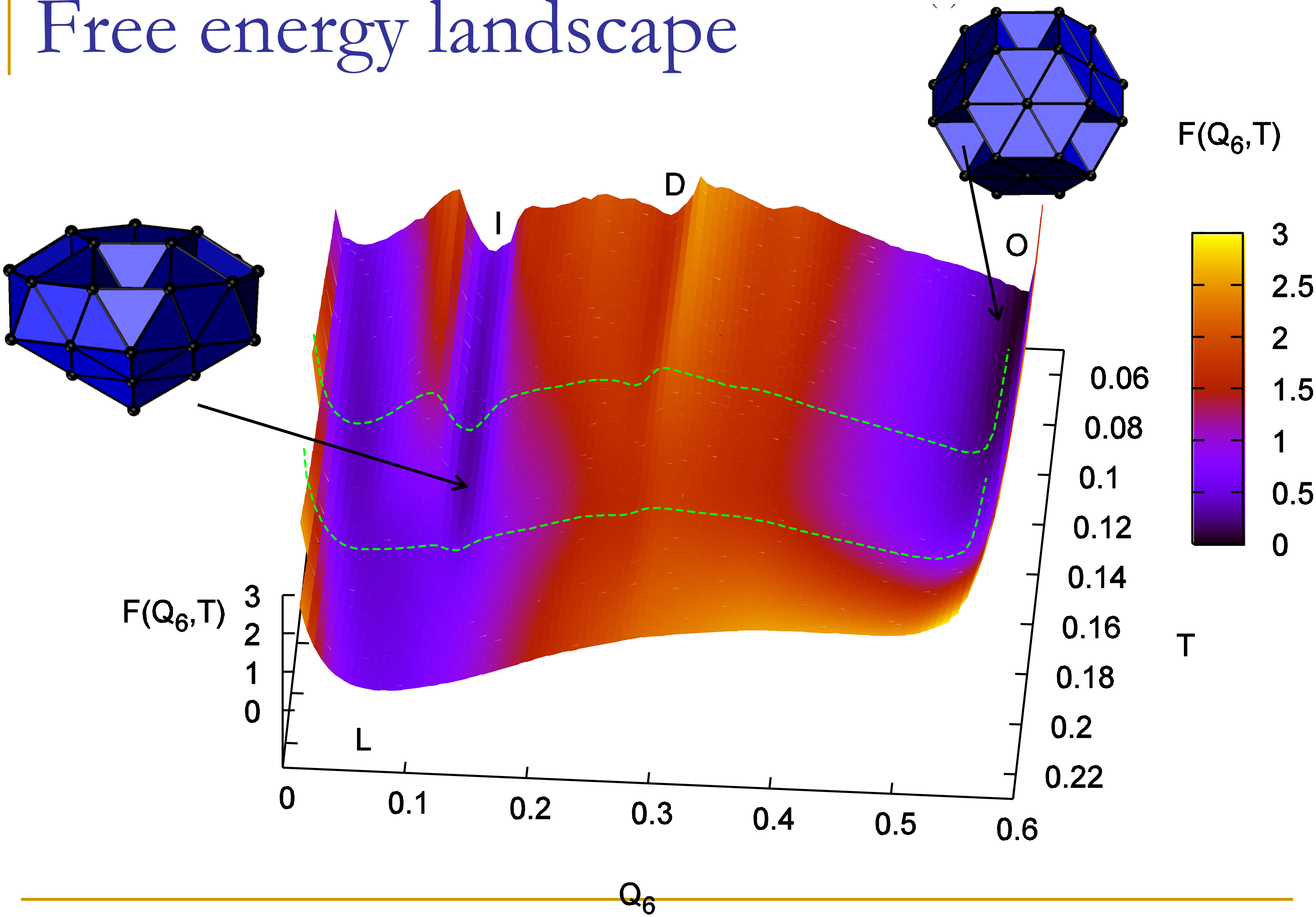
$\mu_j = 1$ Equilibrium case

Free energy contour plot $F_T(E, Q_4) = -kT \ln p(E, Q_4)$



$$p(E, Q_4) = \frac{1}{M} \sum_m \frac{\sum_n h_{E,Q_4}(r_{mn}) \exp[-\beta W_{mn}]}{\sum_n \exp[-\beta W_{mn}]}$$

Free energy landscape



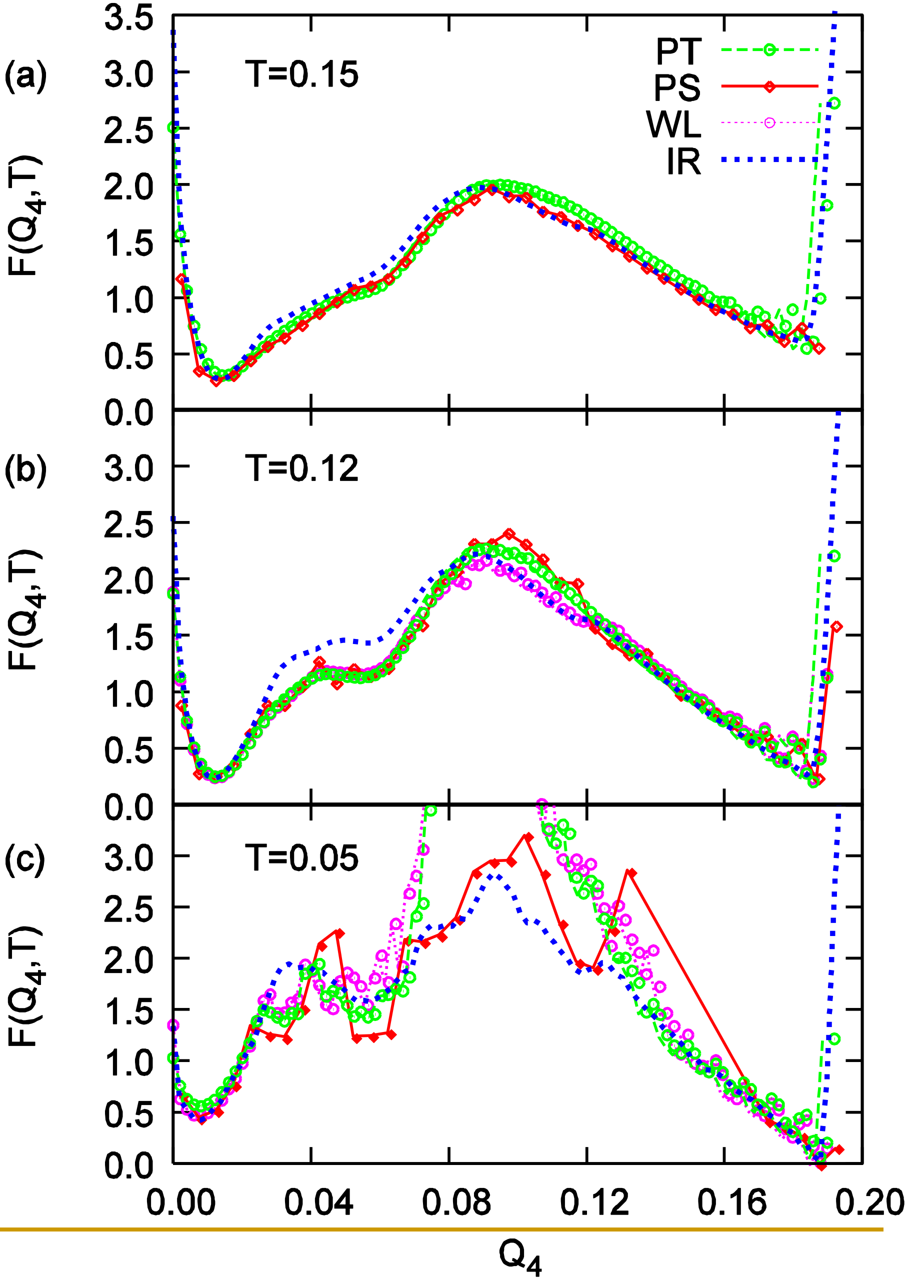
Comparative study

PT : Parallel tempering

PS : Path sampling

WL : Wang Landau

IR : Mutiple State Estimator



Reformulation of conditional expectations

$$\langle O \rangle_\alpha = \int O(z) P^\alpha(z) dz \qquad P^\alpha(z) \propto \exp[-s_\alpha(z)]$$

$$= \int O(z) P^\alpha_{\mathrm{cond}}(\zeta | z) P^\alpha(z) dz d\zeta$$

$$= \int \sum_{\ell=1}^{L} O(z_\ell) P^\alpha_{\mathrm{sel}}(z_\ell | \zeta) P^\alpha_{\mathrm{marg}}(\zeta) d\zeta$$

$$P^\alpha_{\mathrm{marg}}(\zeta) \propto \exp[-S_\alpha(\zeta)]$$

$$\overline{O}_\alpha = \sum_{\ell=1}^{L} O(z_\ell) P^\alpha_{sel}(z_\ell | \zeta)$$

Waste-recycling & multi-state Bennett acceptance ratio method

$$B_\alpha(O) = \sum_{m=1}^{M} \frac{O^m \exp\left[\hat{f}_\alpha - s_\alpha(z)\right]}{\sum_{k=1}^{K} \exp\left[\hat{f}_{\theta(k)} - s_{\theta(k)}(z)\right]}$$

$$B_\alpha^{WR}(O) = \sum_{m=1}^{M} \frac{\overline{O}_\alpha{}^m \exp\left[\hat{f}_\alpha - S_\alpha(\zeta)\right]}{\sum_{k=1}^{K} \exp\left[\hat{f}_{\theta(k)} - S_{\theta(k)}(\zeta)\right]}$$

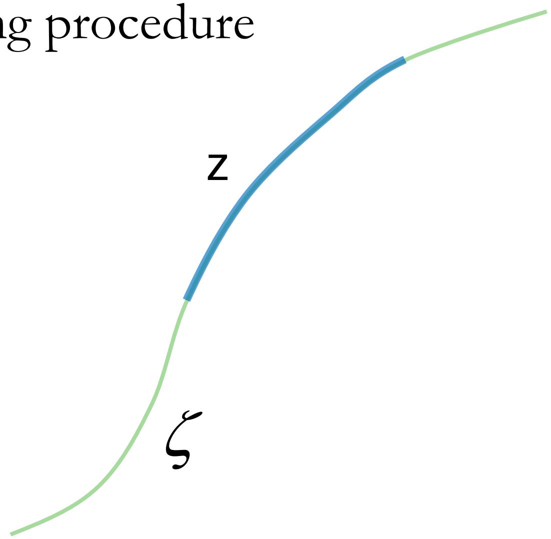
$$\overline{O}_\alpha = \sum_{\ell=1}^{L} O(z_\ell) P_{sel}^{\alpha}(z_\ell | \zeta)$$

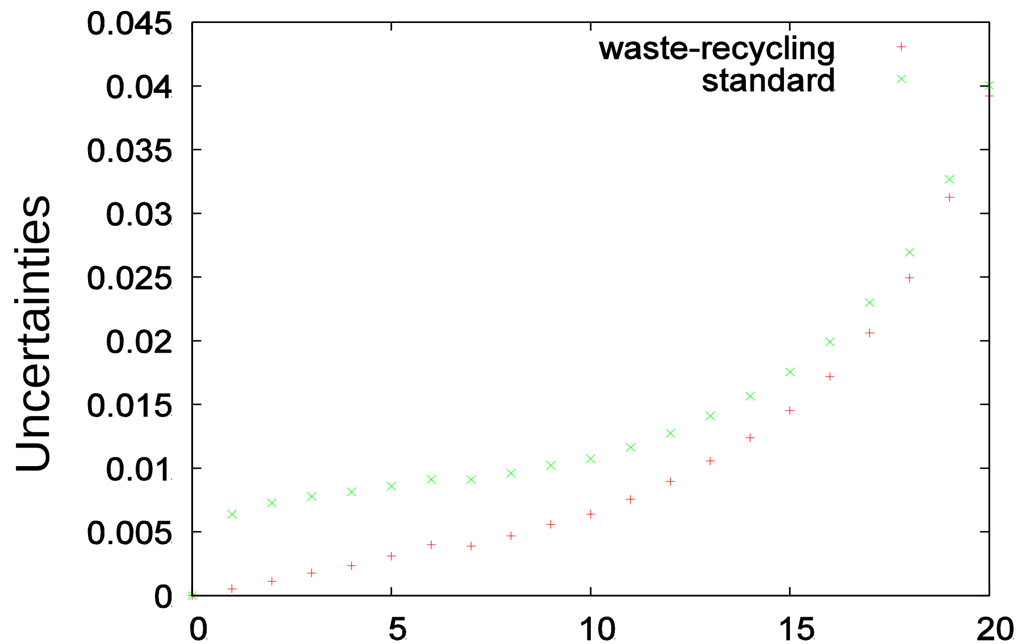
WR & MBAR

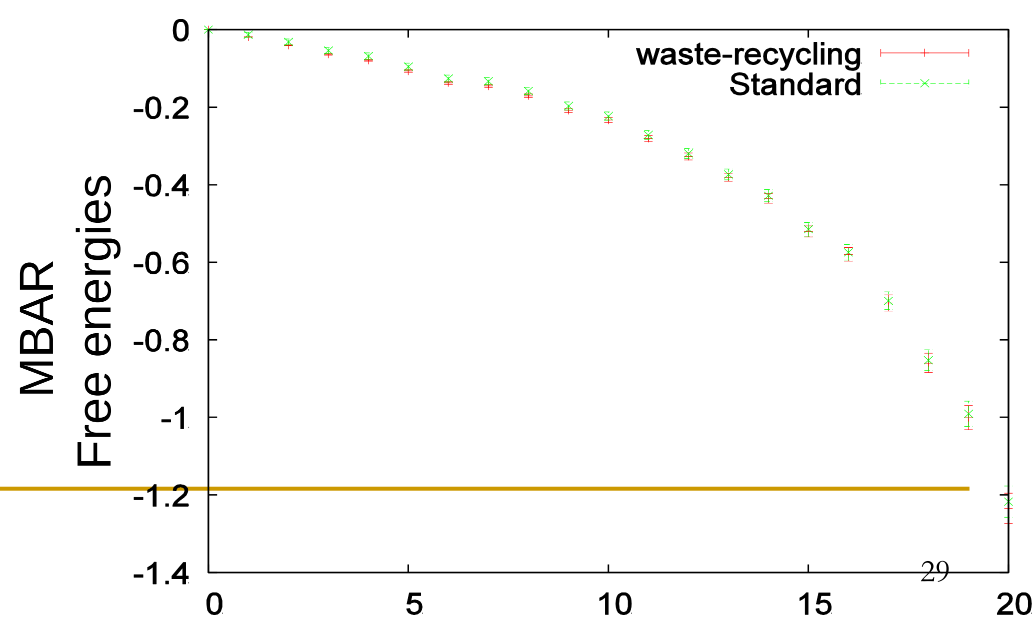
Transition path sampling simulations

Bias depends on eigenvalues of jacobian matrix

Shifting procedure







Summary

Two points of view to see waste-recycling estimators

1. Information of the unselected states is retrieved using a conditional expectation.

2. Information is infered from the posterior likelihood of states (paths) in the set of generated states (paths).

First approach is more general

- can be used in combination with existing methods
- rigorous mathematical analysis (Delmas and Jourdain)

Second approach can be used in combination with post-processing tools (MBAR). Open question: is variance reduction guaranteed?