

Generalized Ensembles: Multicanonical Simulations

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Multicanonical Ensemble

One of the questions which ought to be addressed before performing a large scale computer simulation is “What are suitable weight factors for the problem at hand?” So far we used the Boltzmann weights as this appears natural for simulating the Gibbs ensemble. However, a broader view of the issue is appropriate.

Conventional canonical simulations can by re-weighting techniques only be extrapolated to a vicinity of this temperature. For multicanonical simulations this is different. A single simulation allows to obtain equilibrium properties of the Gibbs ensemble over a range of temperatures. Of particular interest are two situations for which canonical simulations do not provide the appropriate implementation of importance sampling:

1. The physically important configurations are rare in the canonical ensemble.
2. A rugged free energy landscape makes the physically important configurations difficult to reach.

Multicanonical simulations sample, in an appropriate energy range, with an **approximation** to the weights

$$\hat{w}_{mu}(k) = w_{mu}(E^{(k)}) = e^{-b(E^{(k)}) E^{(k)} + a(E^{(k)})} = \frac{1}{n(E^{(k)})}$$

where $n(E)$ is the spectral density. The function $b(E)$ defines the **inverse microcanonical temperature** and $a(E)$ the **dimensionless, microcanonical free energy**. The function $b(E)$ has a relatively smooth dependence on its arguments, which makes it a useful quantity when dealing with the weight factors. The multicanonical method requires **two steps**:

1. Obtain a **working estimate** the weights. Working estimate means that the approximation has to be good enough so that the simulation covers the desired energy or temperature range.
2. Perform a Markov chain MC simulation with the **fixed** weights. The thus generated configurations constitute the **multicanonical ensemble**.

How to get the Weights?

To get the weights is at the heart of the method (and a stumbling block for beginners). Some approaches used are listed in the following:

1. Overlapping constrained (microcanonical) MC simulations. Potential problem: ergodicity.
2. **Finite Size Scaling (FSS) Estimates.** Best when it works! Problem: There may be no FSS theory or the prediction may be so inaccurate that the initial simulation will not cover the target region.
3. General Purpose Recursions. Problem: Tend to deteriorate with increasing lattice size (large lattices).

Multicanonical Recursion (A variant of Berg, J. Stat. Phys. 82 (1996) 323.)

Multicanonical parameterization of the weights (ϵ smallest stepsize):

$$w(a) = e^{-S(E_a)} = e^{-b(E_a) E_a + a(E_a)},$$

where $b(E) = [S(E + \epsilon) - S(E)] / \epsilon$ and
 $a(E - \epsilon) = a(E) + [b(E - \epsilon) - b(E)] E$.

Recursion:

$$b^{n+1}(E) = b^n(E) + \hat{g}_0^n(E) [\ln H^n(E + \epsilon) - \ln H^n(E)] / \epsilon$$

$$\begin{aligned} \hat{g}_0^n(E) &= g_0^n(E) / [g^n(E) + \hat{g}_0^n(E)], \\ g_0^n(E) &= H^n(E + \epsilon) H^n(E) / [H^n(E + \epsilon) + H^n(E)], \\ g^{n+1}(E) &= g^n(E) + g_0^n(E), \quad g^0(E) = 0. \end{aligned}$$

ANIMATION: 2d 10-state 80×80 Potts model (Iterations of 100 sweeps each).

F. Wang and Landau: Update are performed with estimators $g(E)$ of the density of states

$$p(E_1 \rightarrow E_2) = \min \left[\frac{g(E_1)}{g(E_2)}, 1 \right] .$$

Each time an energy level is visited, they update the estimator

$$g(E) \rightarrow g(E) f$$

where, initially, $g(E) = 1$ and $f = f_0 = e^1$. Once the desired energy range is covered, the factor f is refined:

$$f_1 = \sqrt{f}, \quad f_{n+1} = \sqrt{f_n}$$

until some small value like $f = e^{-8} = 1.00000001$ is reached.

Afterwards the usual, MUCA production runs may be carried out.

Example Runs ($2d$ Ising and Potts models)

Ising model on a 20×20 lattice: The multicanonical recursion is run in the range

$$n_{\min} = 400 \leq i_{\text{act}} \leq 800 = n_{\max} .$$

The recursion is terminated after a number of so called tunneling events. A **tunneling event** is defined as an updating process which finds its way from

$$i_{\text{act}} = n_{\min} \quad \text{to} \quad i_{\text{act}} = n_{\max} \quad \text{and back} .$$

This notation comes from applications to first order phase transitions. An alternative notation for tunneling event is **random walk cycle**. For most applications 10 tunneling events lead to acceptable weights.

For an example run of the Ising model we find the requested 10 tunneling events after 787 recursions and 64,138 sweeps (assignment a0501_01, see assignment a0501_02 for the $2d$ 10-state Potts model).

Performance

If the multicanonical weighting would remove all relevant free energy barriers, the behavior of the updating process would become that of a free **random walk**. Therefore, the theoretically optimal performance for the second part of the multicanonical simulation is

$$\tau_{\text{tun}} \sim V^2 . \quad (1)$$

Recent work about first order transitions by Neuhaus and Hager shows that the multicanonical procedure removes only the leading free energy barrier, while at least one subleading barrier causes still a residual supercritical slowing down. Up to certain medium sized lattices the behavior $V^{2+\epsilon}$ gives a rather good effective description. For large lattices supercritical slowing down of the form

$$\tau_{\text{tun}} \sim \exp(+\text{const } L^{d-1}) \quad (2)$$

dominates again. The slowing down of the weight recursion with the volume size is expected to be even (slightly) worse than that of the second part of the simulation.

Re-Weighting to the Canonical Ensemble

Given the multicanonical time series, where $i = 1, \dots, n$ labels the generated configurations. The formula

$$\overline{\mathcal{O}} = \frac{\sum_{i=1}^n \mathcal{O}^{(i)} \exp [-\beta E^{(i)} + b(E^{(i)}) E^{(i)} - a(E^{(i)})]}{\sum_{i=1}^n \exp [-\beta E^{(i)} + b(E^{(i)}) E^{(i)} - a(E^{(i)})]} .$$

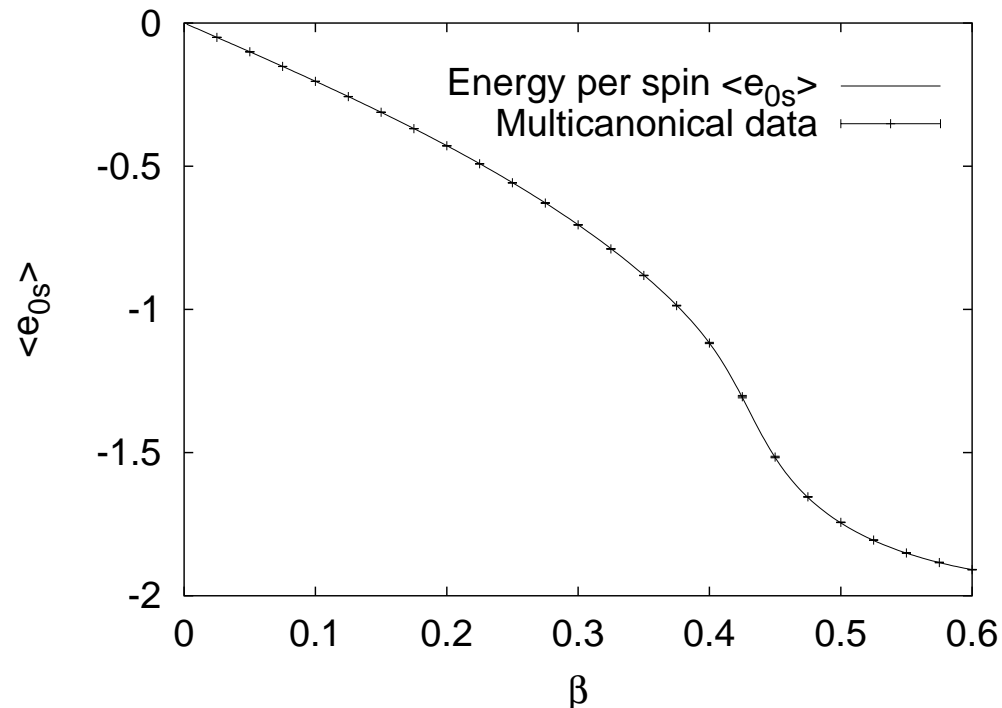
replaces the multicanonical weighting of the simulation by the Boltzmann factor. The denominator differs from the partition function Z by a constant factor which drops out (for discrete systems this simplifies for functions of the energy using histograms). The computer implementation of these equations requires care and a **Jackknife analysis with logarithmic coding** relying on the formula

$$\ln C = \max (\ln A, \ln B) + \ln \{1 + \exp [-|\ln A - \ln B|]\}$$

ought to be used.

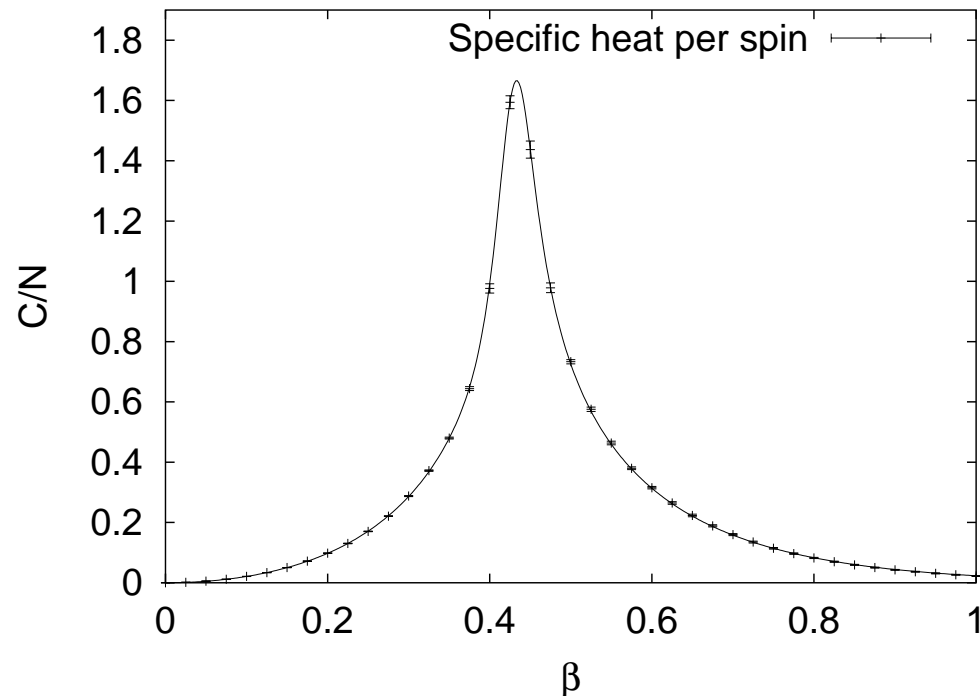
Energy and Specific Heat Calculation

We are now ready to produce multicanonical data for the energy per spin (with jackknife errors) of the $2d$ Ising model on a 20×20 lattice and compared them with the exact results of Ferdinand and Fisher (assignment a0501_03):

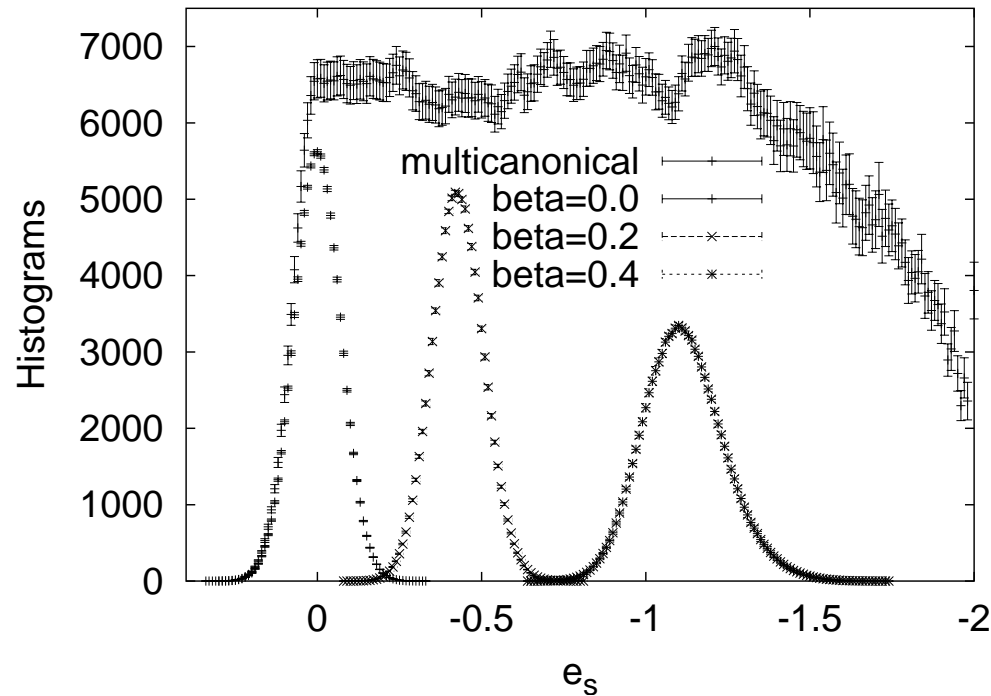


The same numerical data allow to calculate the **specific heat** defined by

$$C = \frac{d\hat{E}}{dT} = \beta^2 \left(\langle E^2 \rangle - \langle E \rangle^2 \right) .$$

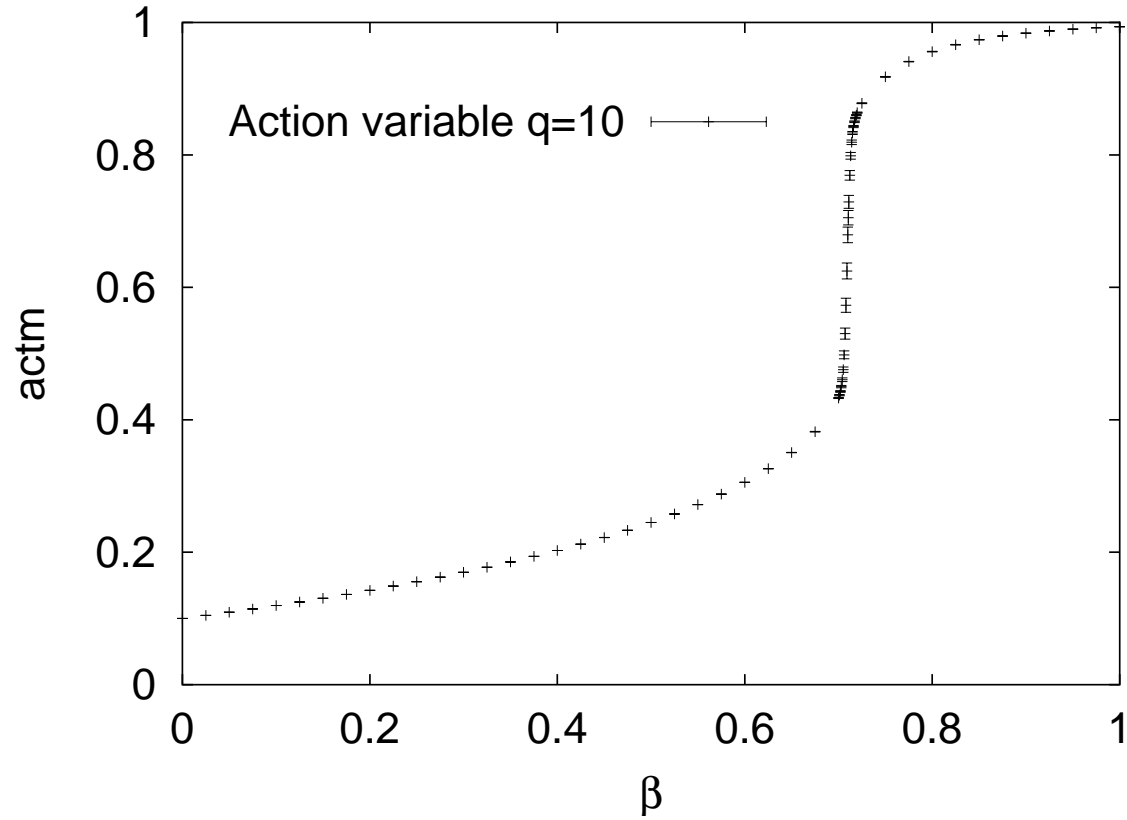


The energy histogram of the multicanonical simulation together its canonically re-weighted descendants at $\beta = 0$, $\beta = 0.2$ and $\beta = 0.4$ (assignment a0501_04):

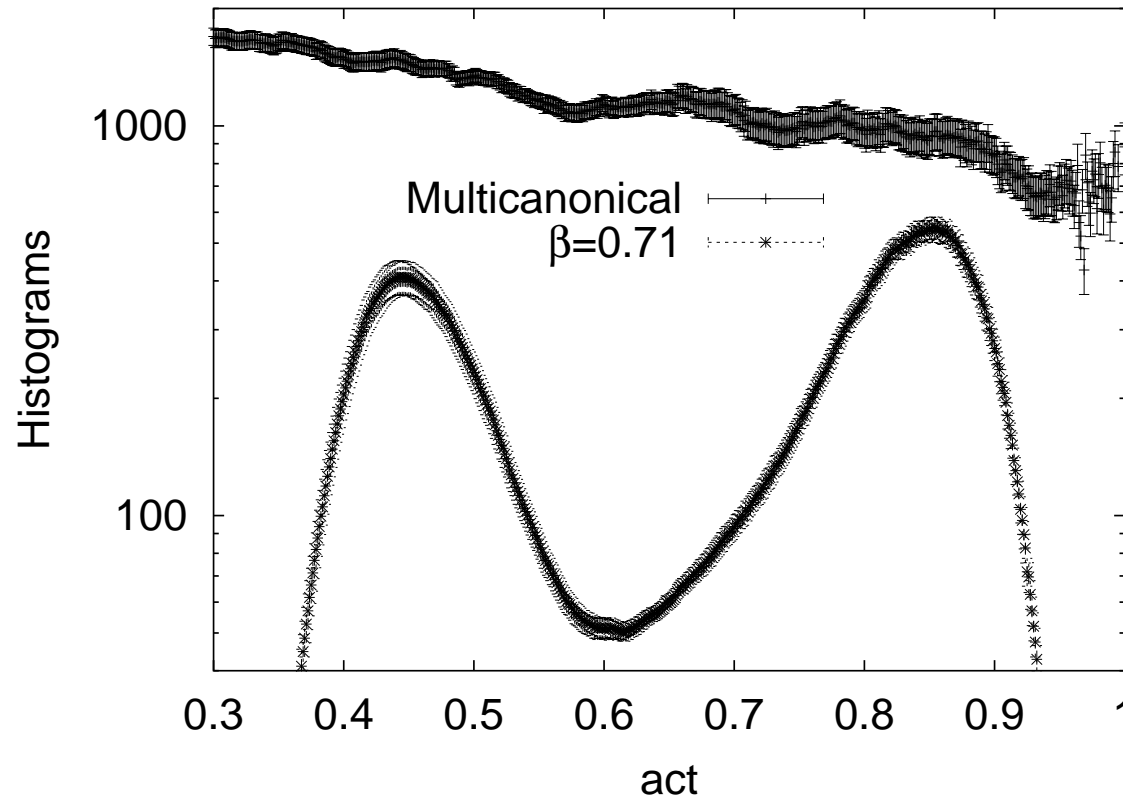


The normalization of the multicanonical histogram is adjusted so that it fits into the same figure with the three re-weighted histograms.

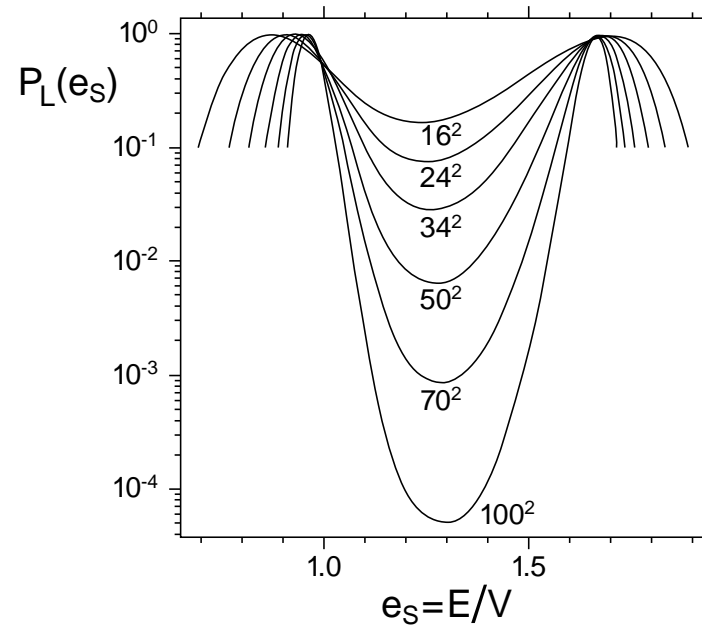
Similar data for the $2d$ 10-state Potts model, action variable act_m data (assignment a0501_05):

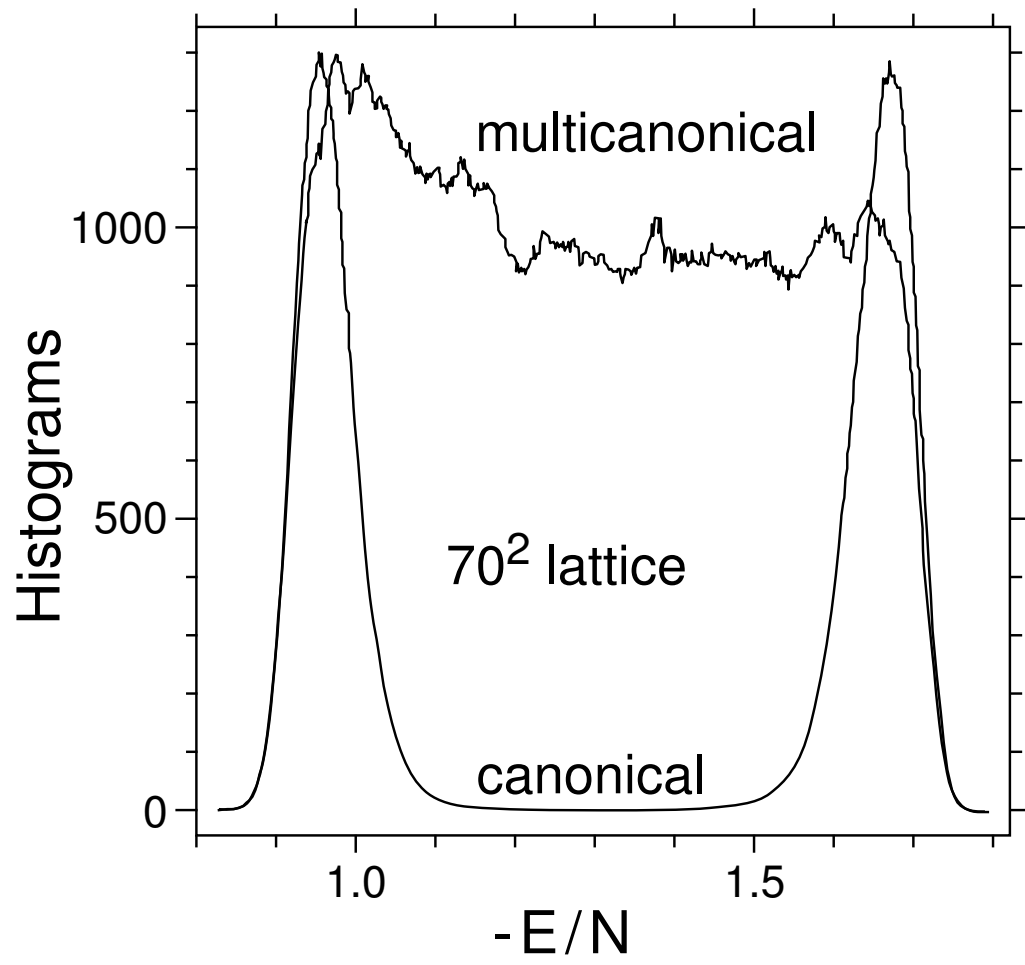


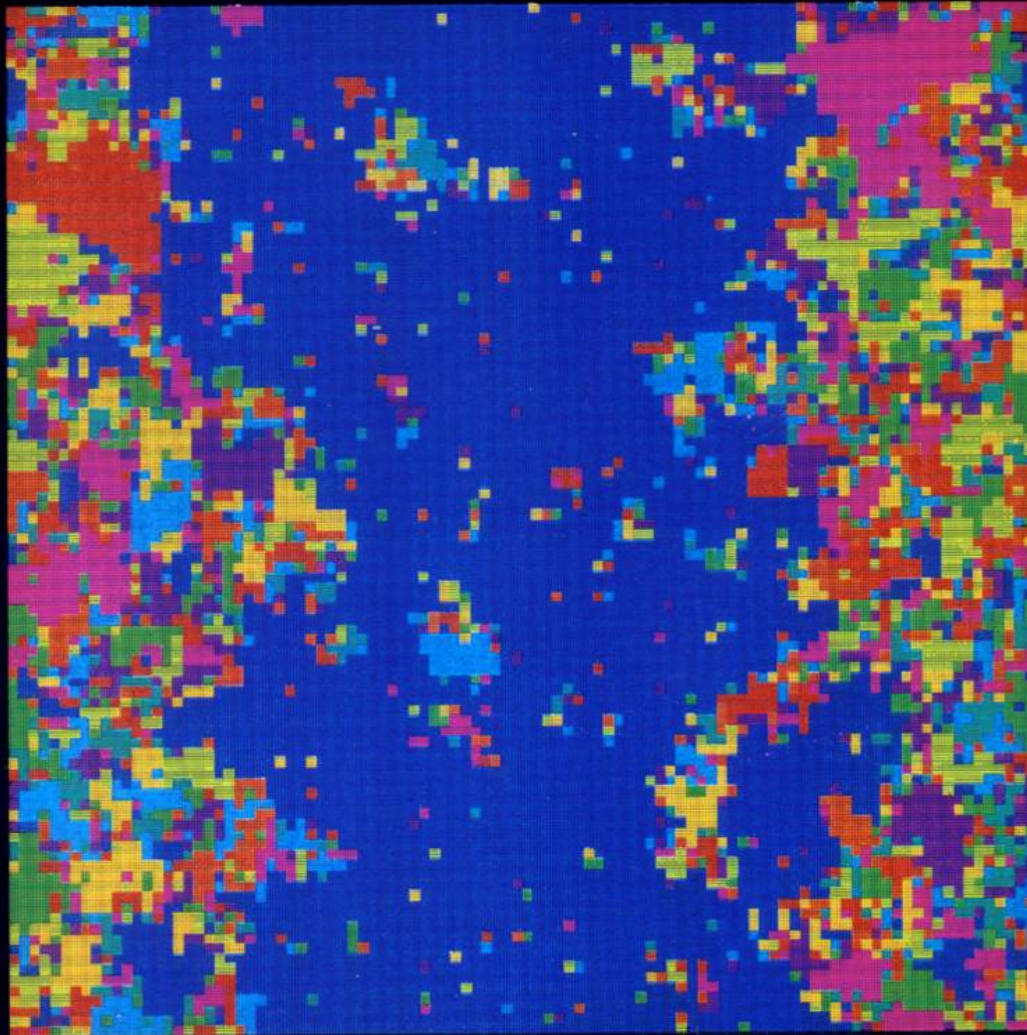
The canonically re-weighted histogram at $\beta = 0.71$ together with the multicanonical histogram using suitable normalizations (the ordinate is on a logarithmic scale):

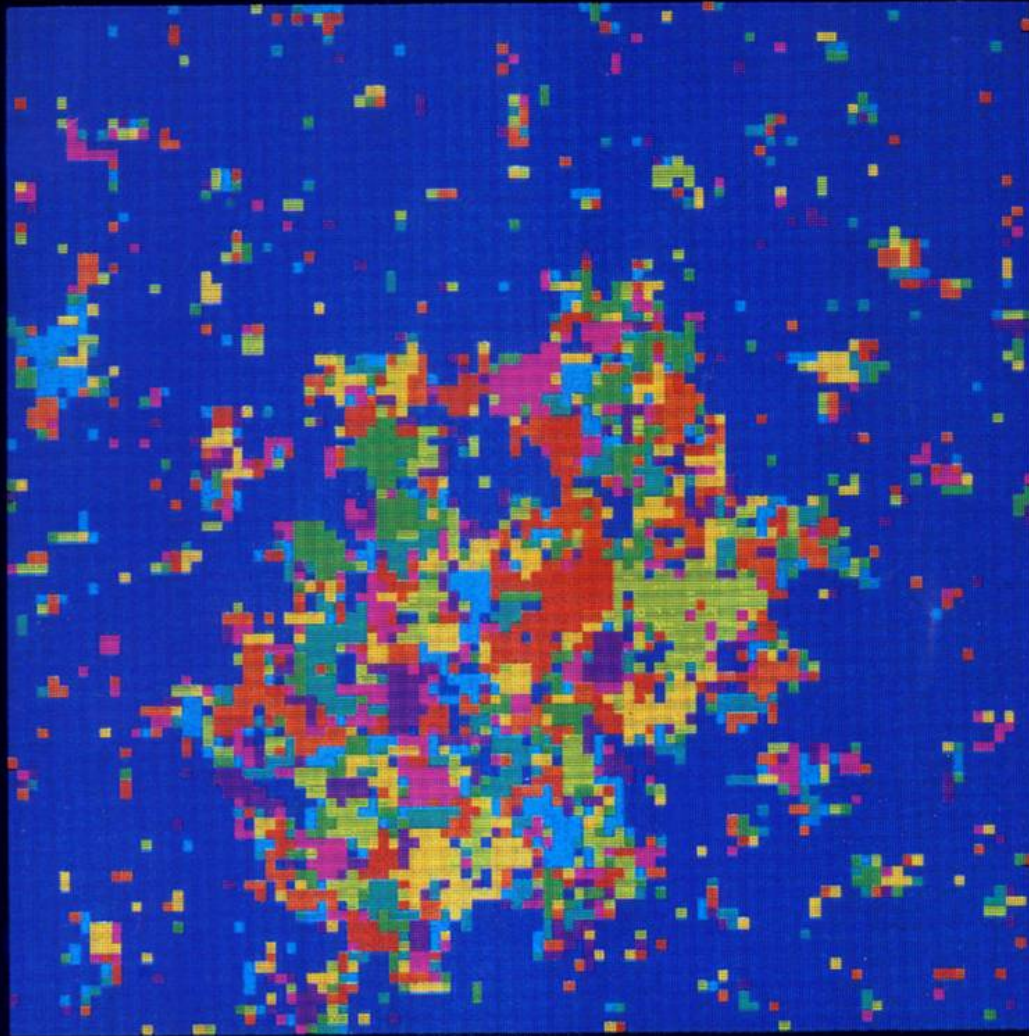


The multicanonical method allows to estimate the interface tension of the transition by following the minimum to maximum ratio over many orders of magnitude [Berg–Neuhaus, Phys. Rev. Lett. 68 (1992) 9]:









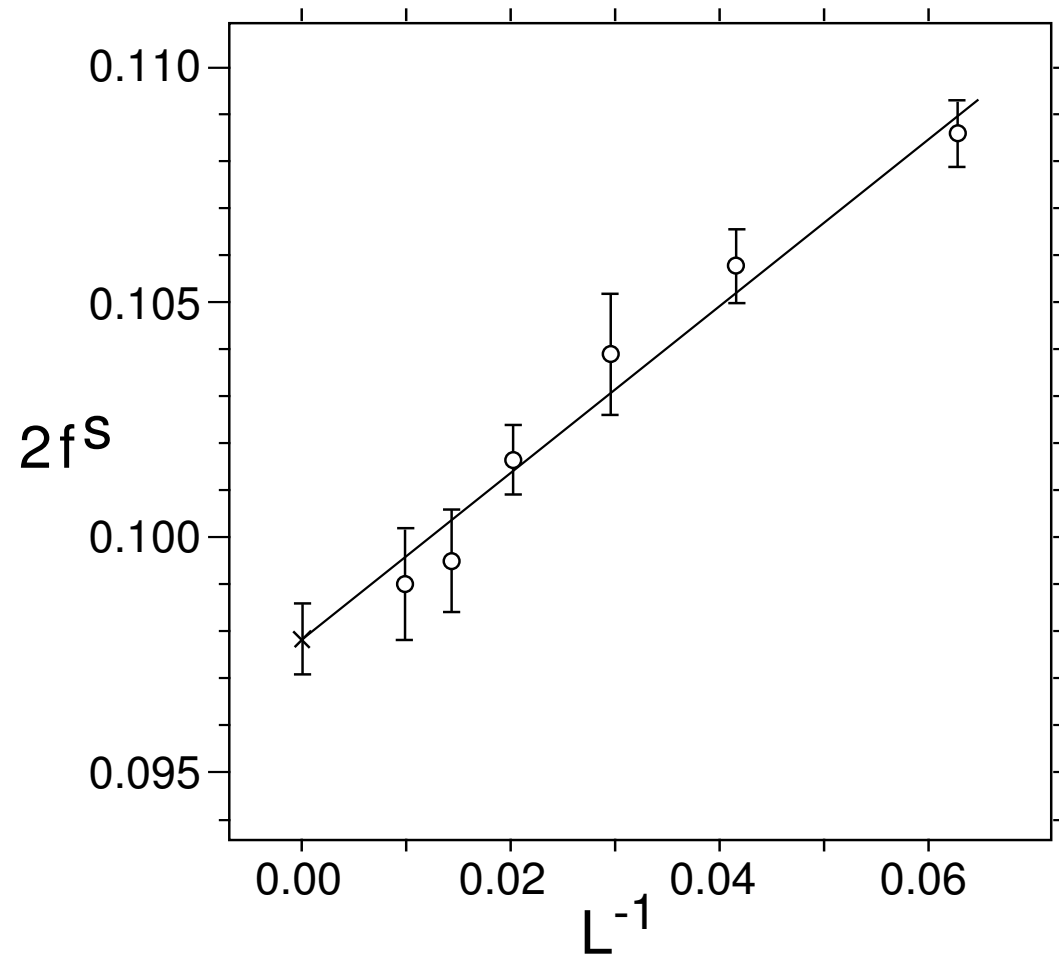


Figure 1: Interface tension fit (Berg and Neuhaus 1992).

Free Energy and Entropy Calculation

At $\beta = 0$ the Potts partition function is $Z = q^N$. Therefore, multicanonical simulations allow for proper normalization of the partition function, if $\beta = 0$ is included in the temperature range. The properly normalized partition function allows to calculate the **Helmholtz free energy**

$$F = -\beta^{-1} \ln(Z)$$

and the **entropy**

$$S = \frac{F - E}{T} = \beta (F - E)$$

of the canonical ensemble. Here E is the expectation value of the internal energy and the last equal sign holds because of our choice of units for the temperature. For the $2d$ Ising model as well as for the $2d$ 10-state Potts model, we show in the next figure multicanonical estimates of the free energy density per site

$$f = F/N .$$

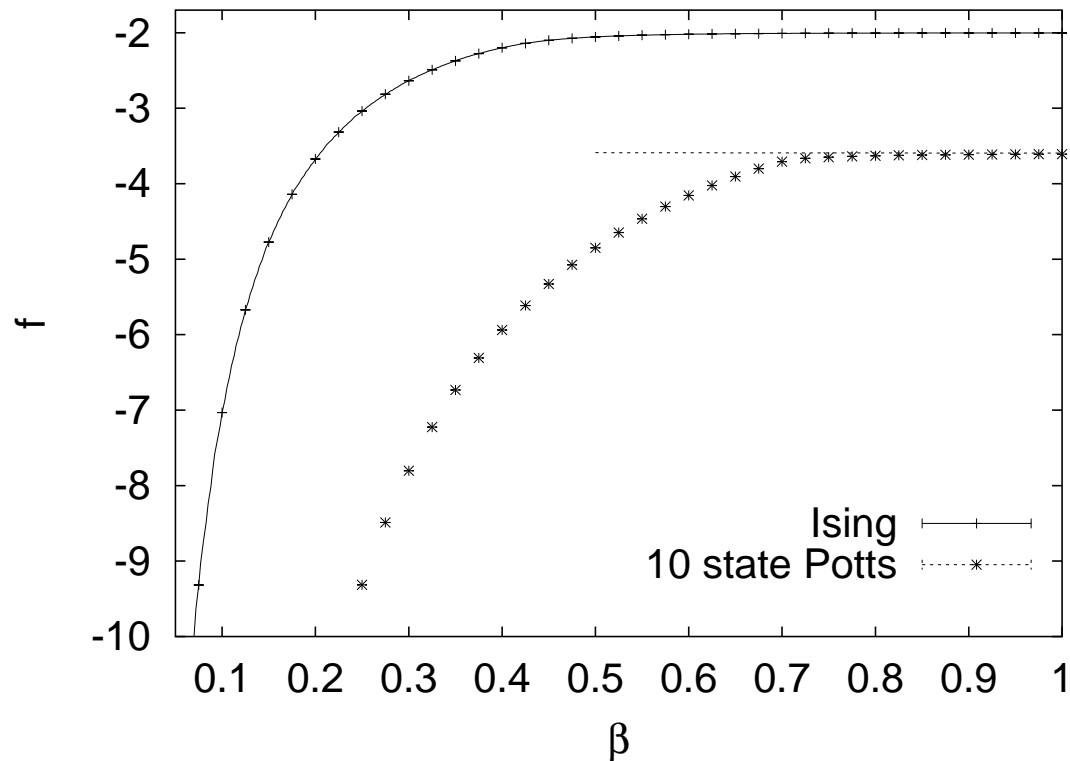


Figure 2: Free energies from multicanonical simulations of the Ising and 10-state Potts models on an 20×20 lattice (assignments a0501_03 and a0501_05). The full lines are the exact results of Ferdinand and Fischer for the Ising model and the asymptotic behavior $f_{\text{as}} = \frac{2d}{q} - 2d - \beta^{-1} \frac{\ln(q)}{N}$ for the 10-state Potts model.

Entropy density $s = S/N$:

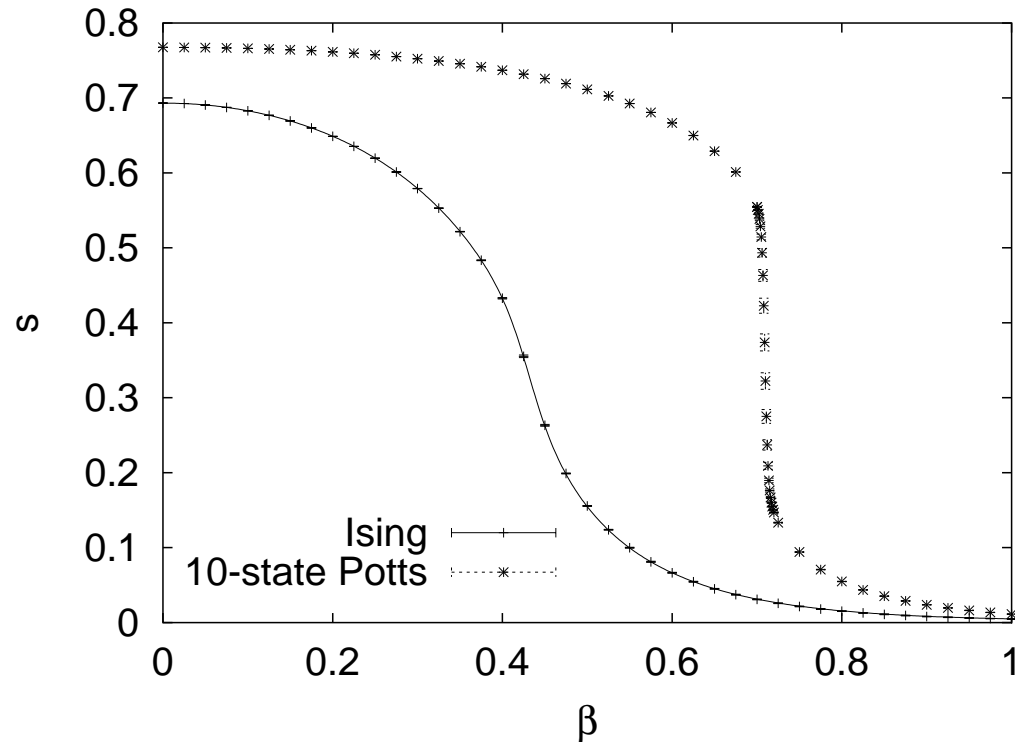


Figure 3: Entropies from multicanonical simulations of the Ising and 10-state Potts models on an 20×20 lattice (assignments a0501_03 and a0501_05). The full line is the exact result of Ferdinand and Fischer for the Ising model.

For the $2d$ Ising model one may also compare directly with the number of states using an algebraic computational method of Beale. One finds no real advantages over using other physical quantities.

Time series analysis

Typically, one prefers in continuous systems time series data over keeping histograms, because one avoids then dealing with the discretization errors. Even in discrete systems time series data are of importance, as one often wants to measure more physical quantities than just the energy. Then the RAM storage requirements may require to use a time series instead of histograms. To illustrate this point, we use the **Potts magnetization** (assignmentss a0501_08 and a0501_09).

For zero magnetic field, $H = 0$, the expectation value of the Potts magnetization on a finite lattice is simply

$$M_{q0} = \langle \delta_{q_i, q_0} \rangle = \frac{1}{q} ,$$

independently of the temperature. For the multicanonical simulation it is quite obvious that even at low temperatures each Potts state is visited with probability $1/q$. In contrast to this, the expectation value of the magnetization squared

$$M_{q0}^2 = q \left\langle \left(\frac{1}{N} \sum_{i=1}^N \delta_{q_i, q_0} \right)^2 \right\rangle$$

is a non-trivial quantity. At $\beta = 0$ its $N \rightarrow \infty$ value is $M_{q0}^2 = q(1/q)^2 = 1/q$, whereas it approaches 1 for $\beta \rightarrow \infty$. For $q = 2$ and $q = 10$ the next figure shows our numerical results and we see that the crossover of M_{q0}^2 from $1/q$ to 1 happens in the neighborhood of the critical temperature. A FSS analysis would reveal that, a singularity develops at β_c , which is in the derivative of M_{q0}^2 for the second order phase transitions ($q \leq 4$) and in M_{q0}^2 itself for the first order transitions ($q \geq 5$).

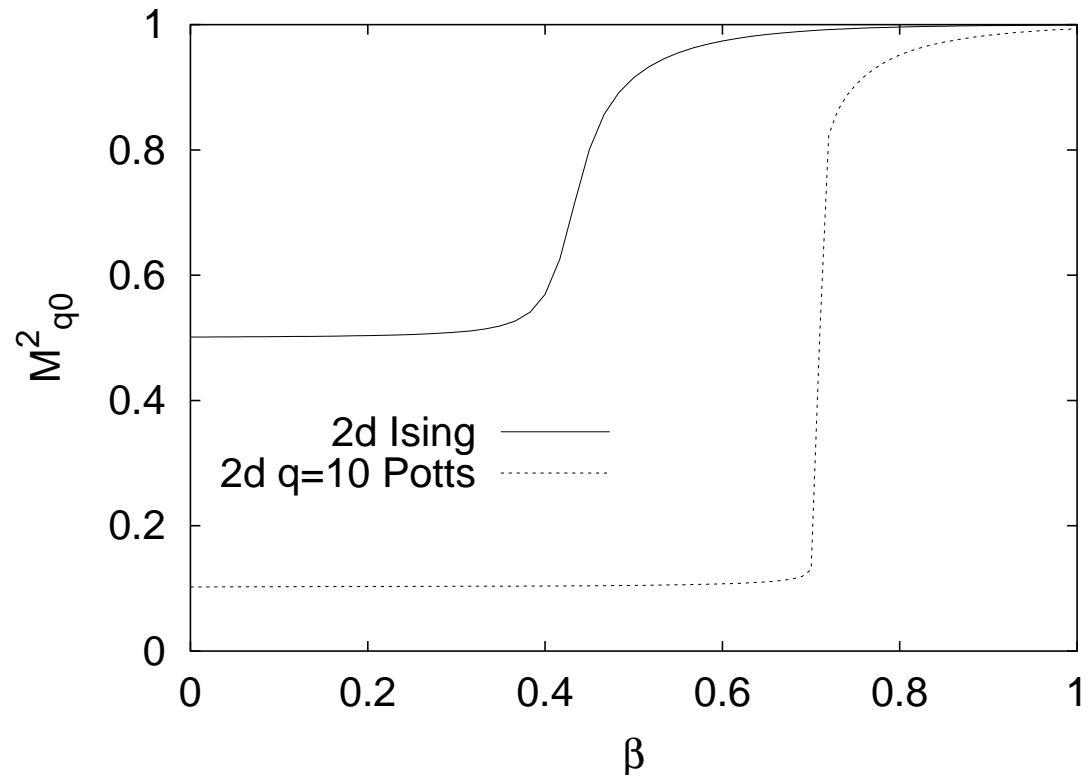


Figure 4: The Potts magnetization per lattice site squared for the $q = 2$ and $q = 10$ Potts models on an 20×20 lattice (assignments a0501_08 and a0501_09).

Complex Systems with Rugged Free Energy Landscapes

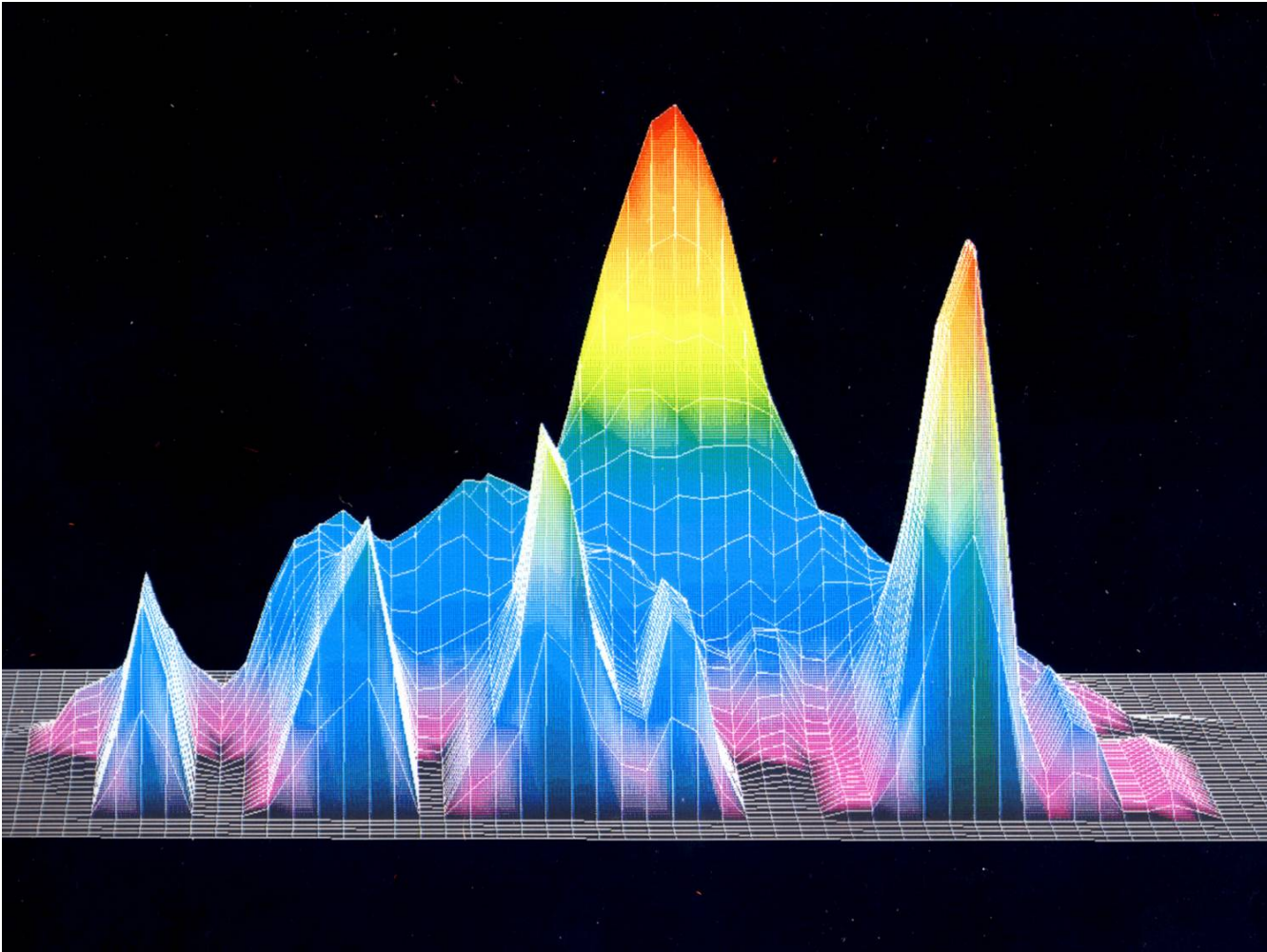
1. Spin Glasses

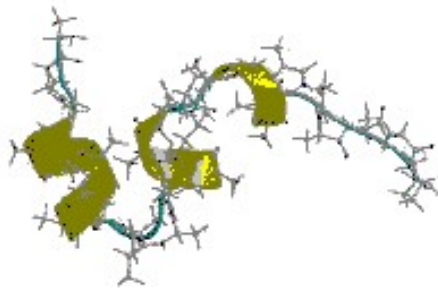
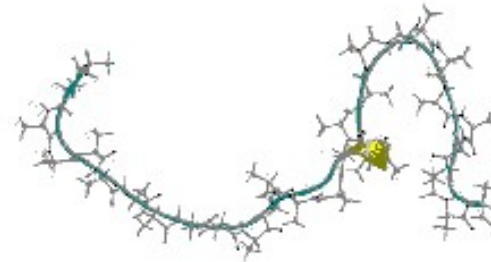
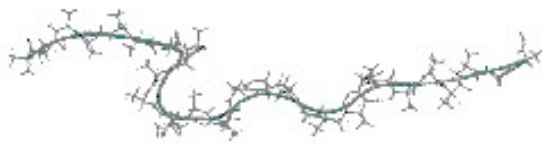
(first paper Berg-Celik, Phys. Rev. Lett. 69 (1992) 2292.)

2. Biomolecules

(first paper Hansmann-Okamoto, J. Comp. Chem. 14 (1993) 1333).

Basic Idea: Bridge free energy barriers through excursions into the disordered phase of the system.





Example configurations from a multicanonical simulation of poly-alanine (U. Hansmann and Y. Okamoto, J. Chem. Phys. 110 (1999) 1267).

Summary

- It is a strength of computer simulations that one can generate artificial (not realized by nature) ensembles, which enhance the probabilities of rare events one may be interested in, or speed up the dynamics.
- Nowadays **Generalized Ensembles** (umbrella, multicanonical, $1/k$, ...) have found many applications. Besides for first order phase transitions in particular for **Complex Systems** such as biomolecules, where they accelerate the dynamics.