PARALLEL TEMPERING: From Spin Glasses to Proteins.

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http://www.unex.es/fisteor/juan/juan_talks.html

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Plan of the Talk

- Monte Carlo Methods in Science.

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Monte Carlo Methods

- Goal: We want to generate samples of a known probability distribution (measure) π (e.g. the Gibbs distribution in Statistical Physics).
- We define a Markov Process which generates a sequence of samples $X_t \to X_{t+1}$ (the transitions are stat. indep.). More precisely we need:
  - The space of states: S.
  - The initial distribution: $P(X_0 = X) = \alpha_x$.
  - The transition probability matrix: $P = \{p_{xy}\} = \{p(x \to y)\}$, $x, y \in S$, satisfying: $p_{xy} \geq 0$ and $\sum_y p_{xy} = 1$.
- The Markov process is given by:

$$P(X_{t+1} = y | X_t = x) = p_{xy} \text{ for all } x \in S.$$

Monte Carlo Methods

How to design a dynamical Monte Carlo Method for generating samples from π?
It suffices to provide a transition probability with two properties:

- (A) Irreducibility. For each pair $x, y \in S$, there exists and $n \geq 0$ for which $p^{(n)}(x, y) > 0$. Where $p^{(n)}(x, y) \equiv P(X_{t+n} = y | X_t = x)$.
- (B) Stationarity of π. For each $y \in S$, $\sum_x \pi_x p_{xy} = \pi_y$. [Balance]

Instead of (B), we can use the following stronger condition:

- (B') For each pair $x, y \in S$, $\pi_x p_{xy} = \pi_y p_{yx}$. [Detailed Balance]

Monte Carlo Methods: Autocorrelation times

- We define $\{f_t\} = \{f(X_t)\}$. The mean is

$$\mu_f \equiv \langle f_t \rangle_\pi = \langle f_t \rangle = \sum_x \pi_x f(x)$$

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$$C_{ff}(t) \equiv \langle f_{s+t} f_s \rangle - \mu_f^2$$

- The normalized autocorrelation function is defined as

$$\rho_{ff}(t) \equiv C_{ff}(t)/C_{ff}(0)$$

Monte Carlo Methods: Autocorrelation times

- Typically $\rho_{ff}(t)$ decays exponentially for large t: $\exp(-t/\tau)$. So, one can define the exponential autocorrelation time:

$$\tau_{\mathrm{exp},f} = \limsup_{t\to\infty} \frac{t}{-\log|\rho_{ff}(t)|}$$

- And, the biggest exponential autocorrelation time (associated with the slowest mode)

$$\tau_{\mathrm{exp}} = \sup_{f} \tau_{\mathrm{exp},f}$$

- The integrated correlation time is defined as

$$\tau_{\mathrm{int},f} \equiv \frac{1}{2}\sum_{t=-\infty}^{\infty} \rho_{ff}(t) = \frac{1}{2}\sum_{t=1}^{\infty} \rho_{ff}(t)$$

Monte Carlo Methods: Autocorrelation times

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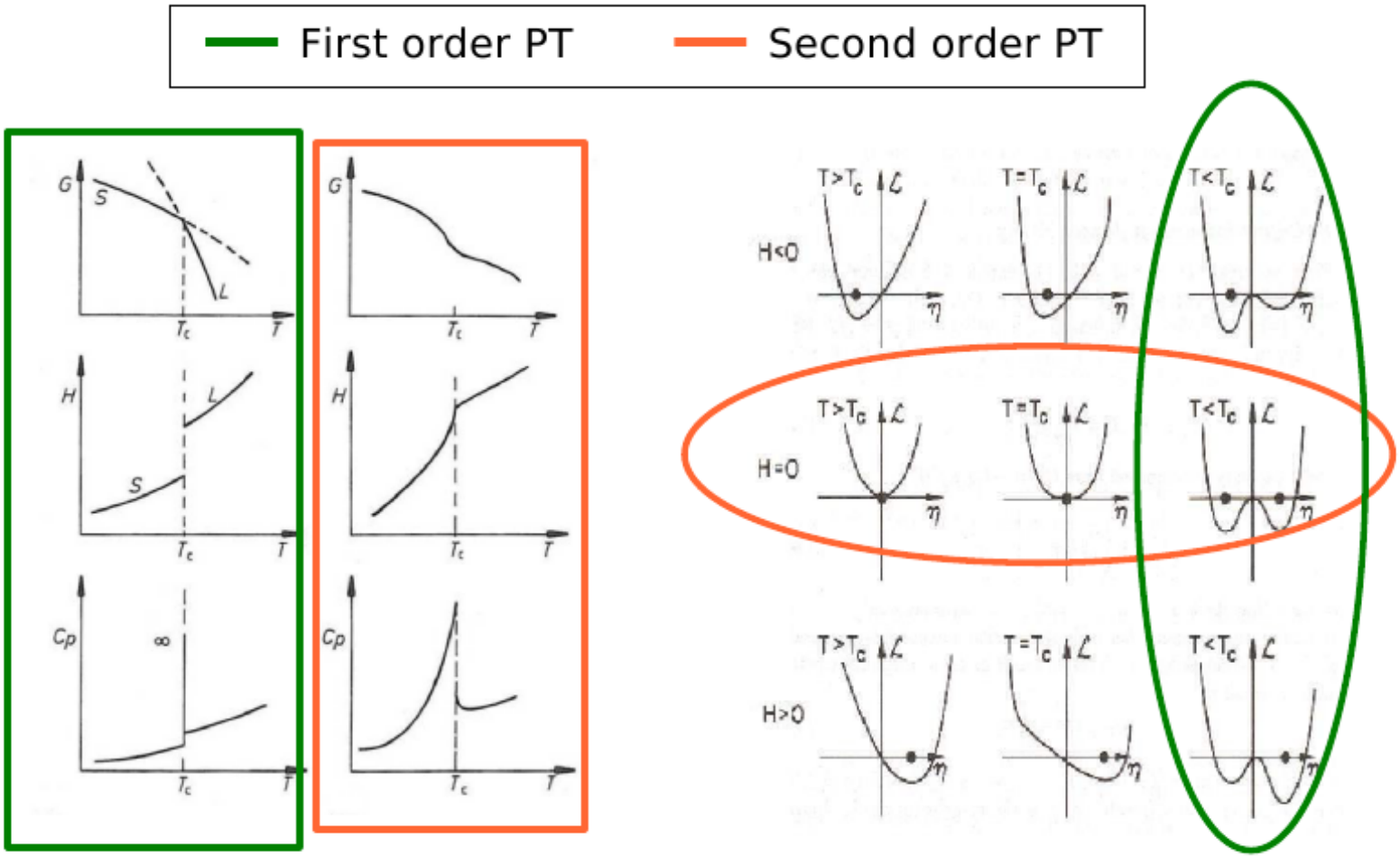
  - The mean, $\bar{f}$, of a given observable, f, in a Monte Carlo simulation is:

$$\bar{f} \equiv \frac{1}{n} \sum_{i=1}^{n} f_t$$

  - and its associated error:

$$\mathrm{var}(\bar{f}) \simeq \frac{1}{n}(2\tau_{\mathrm{int},f}) C_{ff}(0)$$

Phase Transitions



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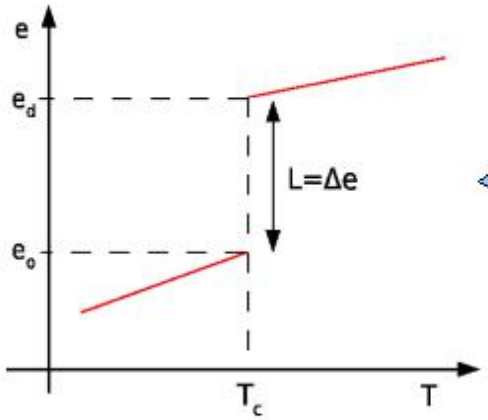

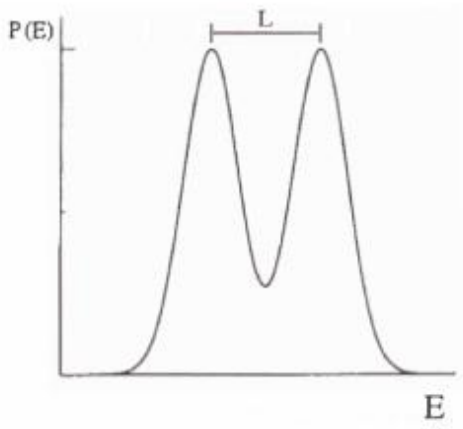

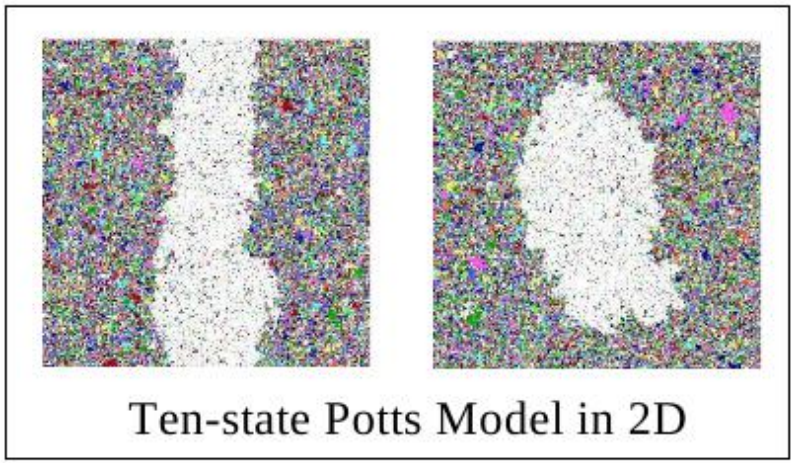

Ten-state Potts Model in 2D

Phase Transitions

- At criticality: $\tau \simeq (T - T_c)^{-\nu z}$.
- The correlation length scales as $\xi \simeq (T - T_c)^{-\nu}$. So,

$$\tau \simeq \xi^z \simeq L^z$$

Critical Slowing Down.

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Exponential Critical Slowing Down.

- In disordered models we will find free energy barriers growing as L^{θ}.

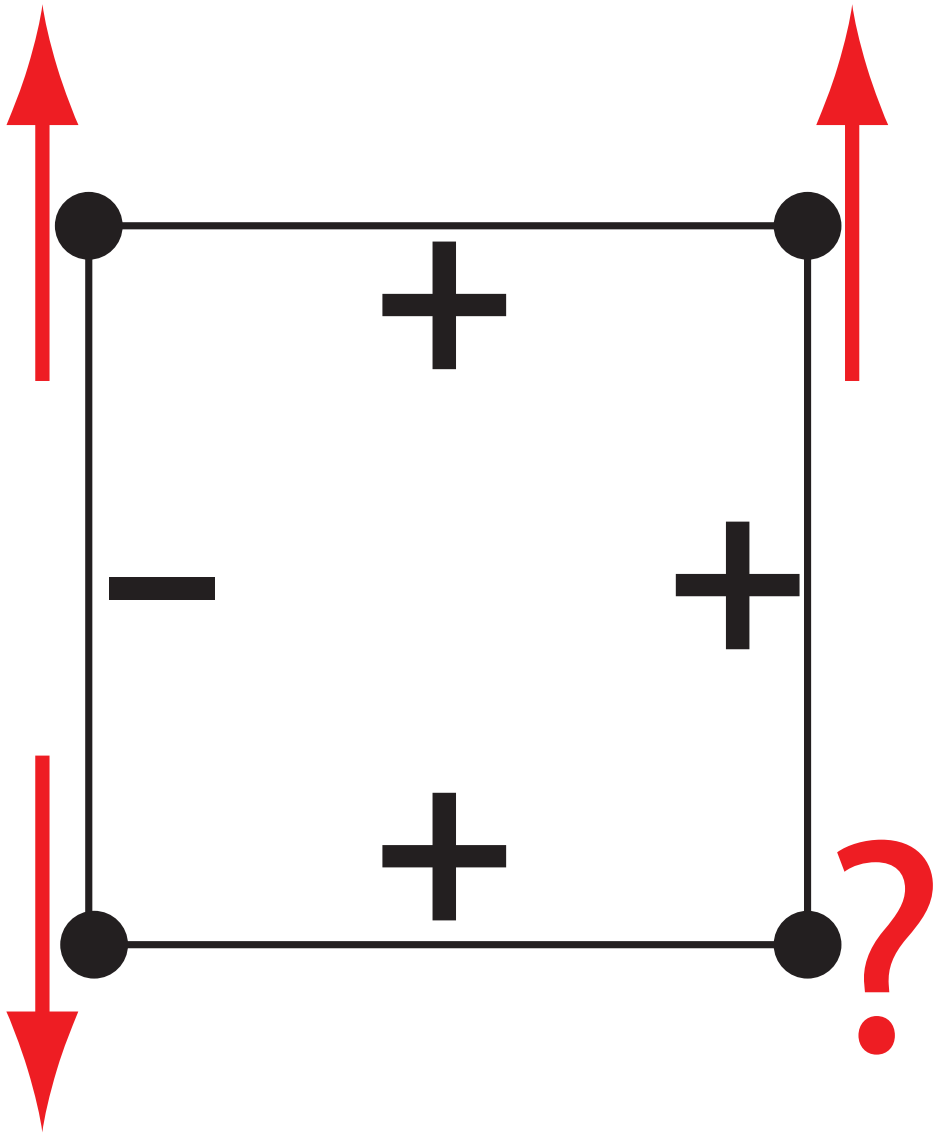
Spin glasses

- Materials with disorder and frustration.
- Quenched disorder (similar to the Born-Oppenheimer in Molecular Physics).
- Canonical Spin Glass: Metallic host (Cu) with magnetic impurities (Mn).
- RKKY interaction between magnetic moments: $J(r) \sim \frac{\cos(2k_F r)}{r^3}$.
- Role of anisotropy: Ag:Mn at 2.5% (Heisenberg like), $CdCr_{1.7}IN_{0.3}S_4$ (also Heisenberg like) and $Fe_{0.5}Mn_{0.5}TiO_3$ (Ising like).
- Edwards-Anderson Hamiltonian:

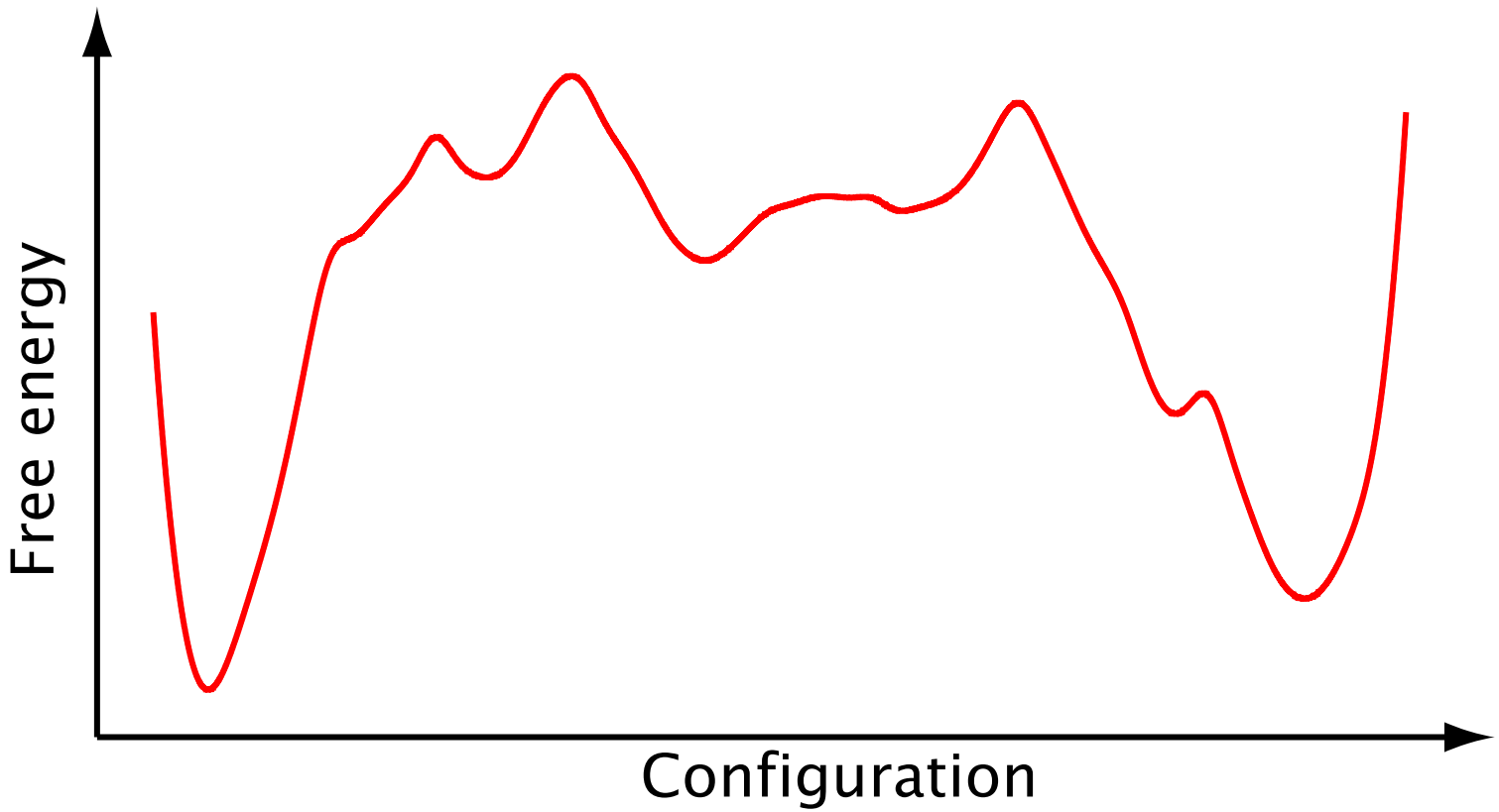
$$\mathcal{H} = -\sum_{<ij>} J_{ij}\sigma_i\sigma_j$$

  J_{ij} are random quenched variables with zero mean and unit variance, $\sigma = \pm 1$ are Ising spins.
- The order parameter is $q_{\mathrm{EA}} = \overline{\langle\sigma_i\rangle^2}$

Spin Glasses: Frustration



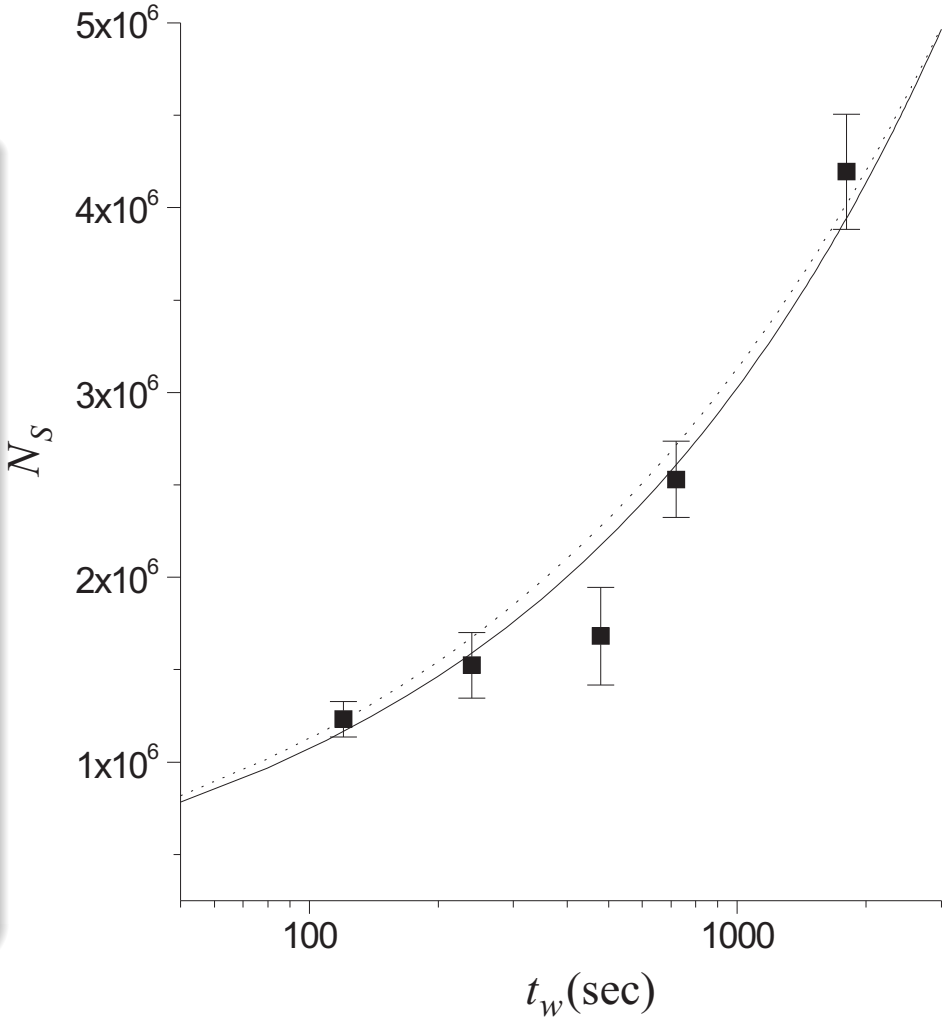
Spin Glasses: Low Temperature Free Energy Landscape



On the dynamical critical exponent z below and at the critical Temperature.

Experimental Approach based in Zeeman Energies

- They extract the dynamical correlation length as: $N_s(t_w^{\text{eff}}) = \xi(t_w^{\text{eff}})^3$.
- $\xi(t_w, T) = 0.653\,(t_w/\tau_0)^{0.169T/T_g}$. $\tau_0^{-1} = 4.1 \times 10^{12}\ \text{s}^{-1}$.
- $1/z(T) = 0.169T/T_g$. For example: $z(T = 0.7) \simeq 9$!!.



Proteins: Some facts.

- Characterization of the phases:
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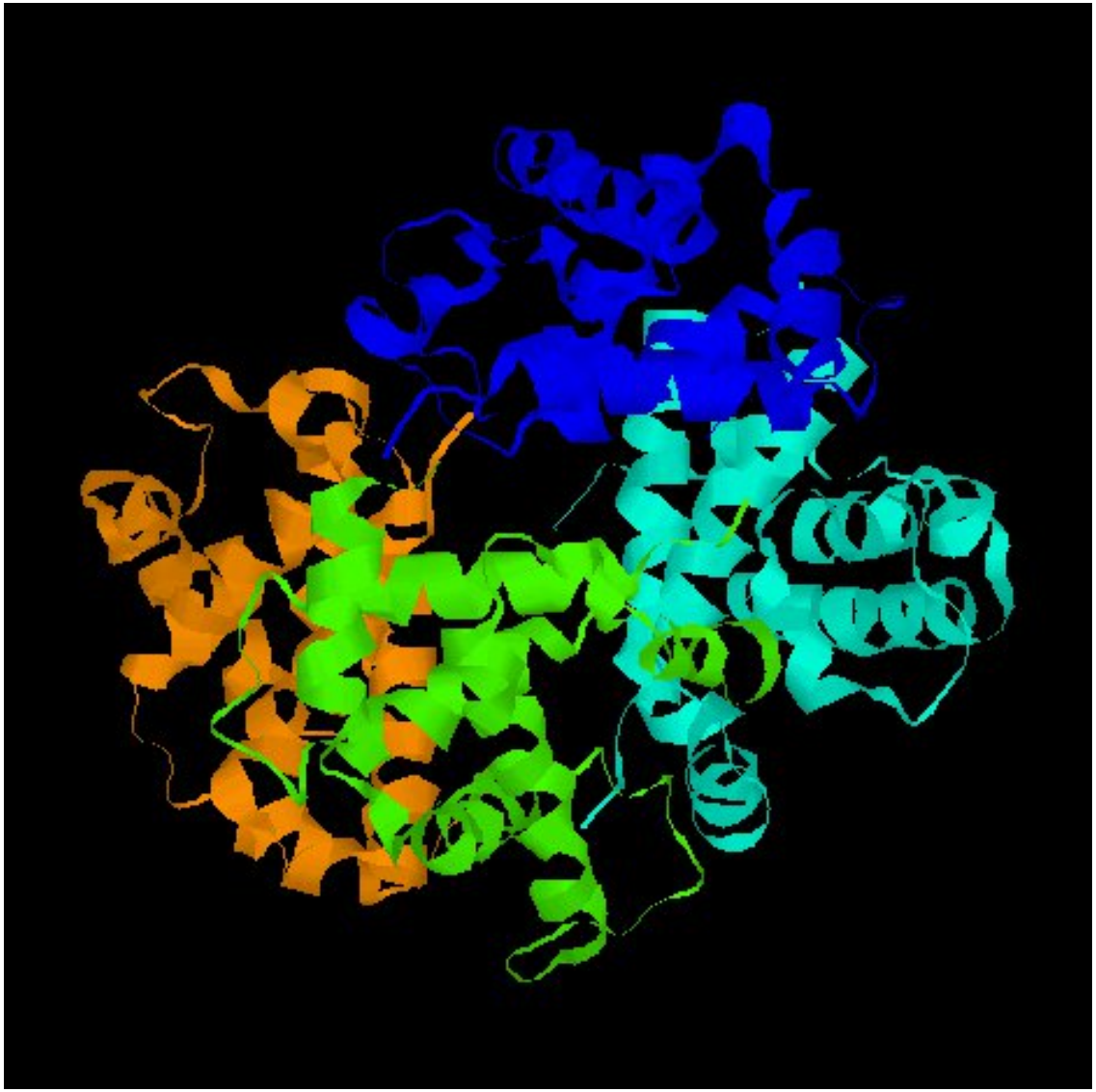
- Energy Scales:
  - Bonded Interactions. From 200 kJ/mole to 600 kJ/mole (2 eV/molecule-6 eV/molecule).
  - Unbonded. From 4 kJ/mole to 5 kJ/mole (0.04-0.05 eV/molecule).

Proteins: Hemoglobin



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- Levinthal Paradox.
  The protein during the folding does not explore all the configuration space only a small part of it $\rightsquigarrow$ Energy funnel.
  Each peptide bond has z different conformations. Hence, the dimension of the conformations space is z^N. Taking for simplicity $z = 2$ and $N = 100$: $2^{10} \simeq 10^{30}$. The minimum time to change the conformation of the peptidic bond is 10^{-11} s, hence as estimate is $10^{30} \times 10^{-11}\ \mathrm{s} = 10^{19}$ s (which is 20 times the age of the Universe!!!!) to sweep all the states of the conformations space of the protein.

Proteins: Some facts.

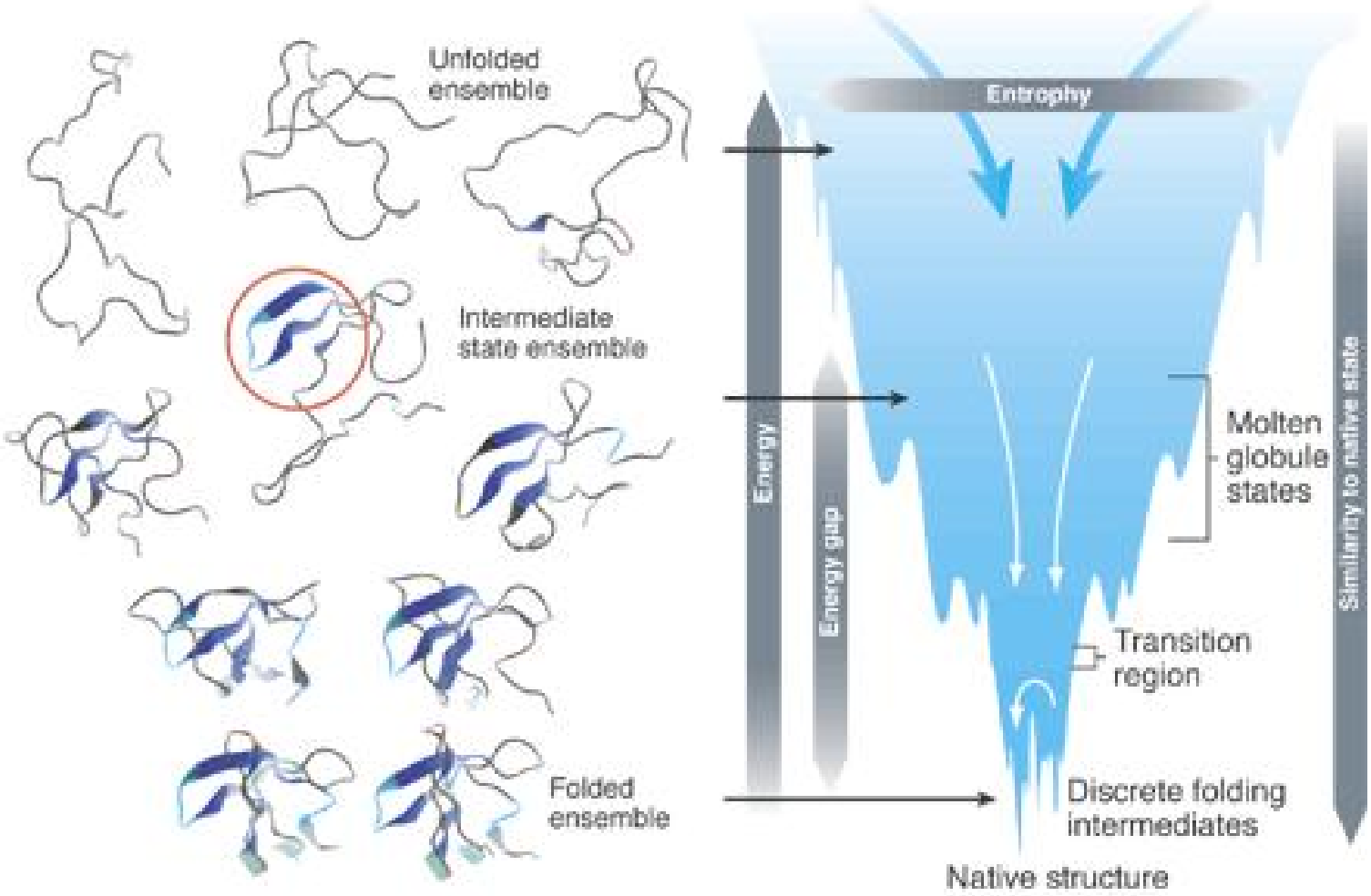
Hence, it is possible to identify:

- Hard degrees of freedom. Linked to covalent bonds and the peptide bond. They are very rigid at room temperature (Energy $\gg k_{\mathrm{B}} T_{\mathrm{room}} \simeq 0.025$ eV).
- Soft degrees of freedom. Torsion angles along the backbone chain and of the side chains. (Energy $\simeq k_{\mathrm{B}} T_{\mathrm{room}}$).

Dual Requirement for the folding:

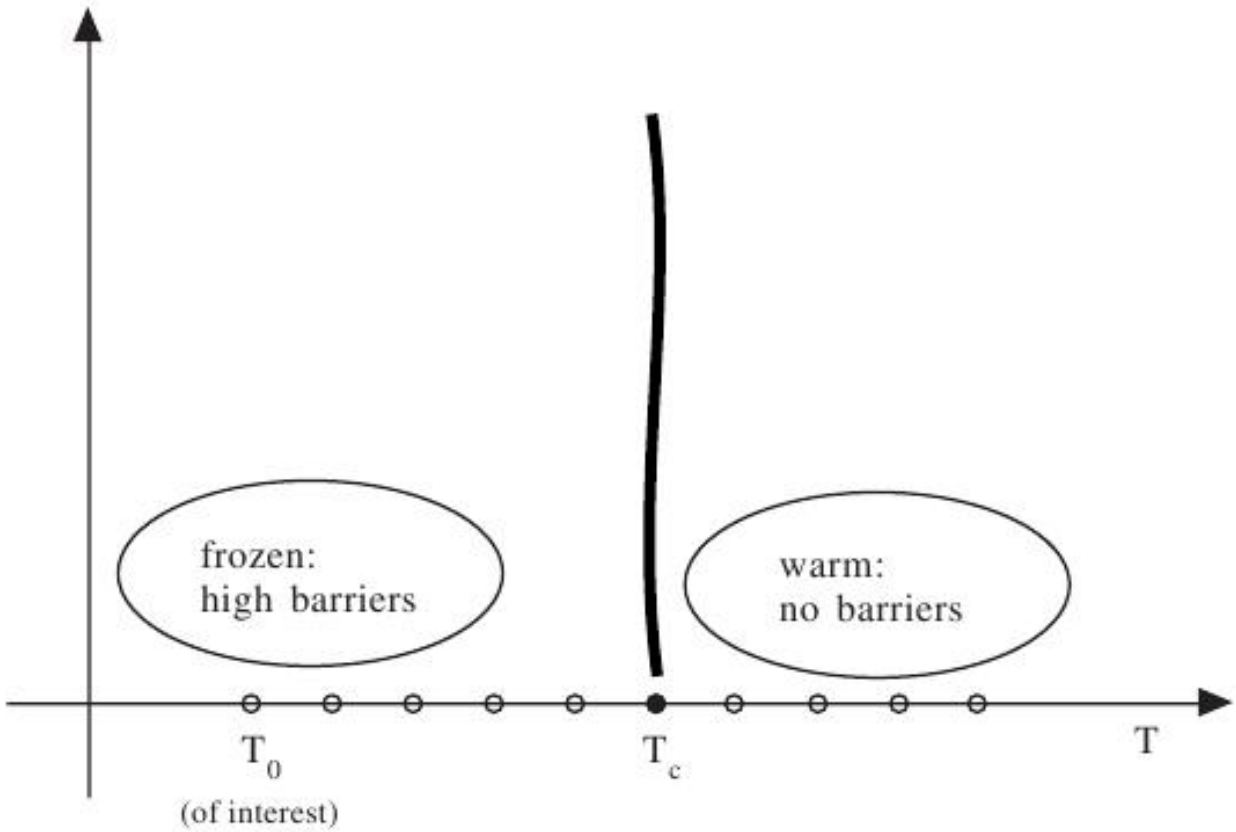
- Kinetic accessibility.
- Stability.

Proteins: Low Temperature Free Energy Landscape



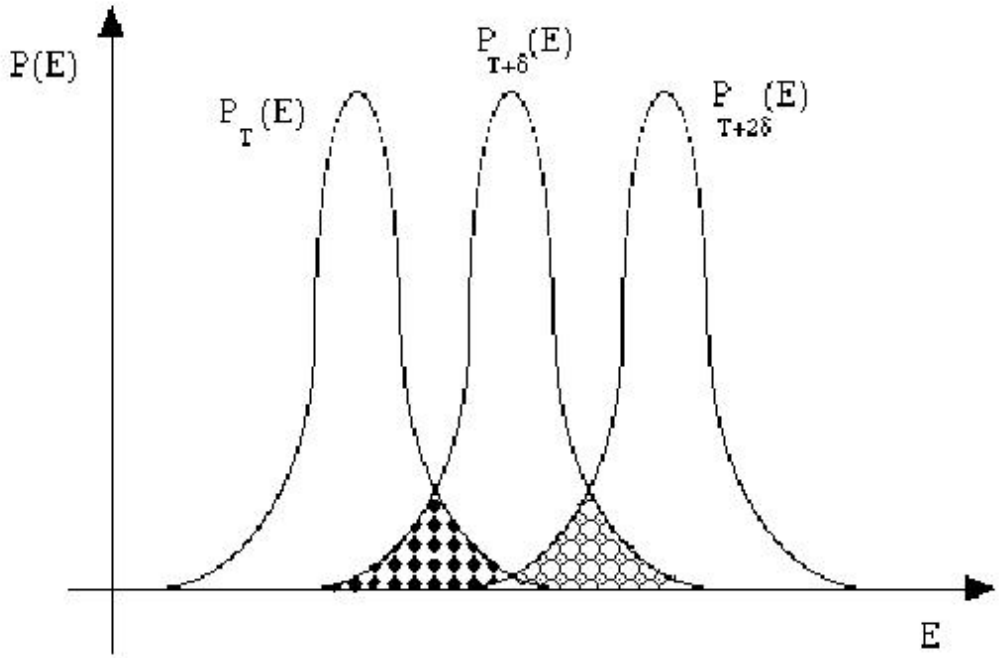
Parallel Tempering.

How to thermalize these systems?



Parallel Tempering.

In a canonical simulation (fixed T) the energy fluctuates:



The width of the Energy Histogram is proportional to the Specific Heat:

$$\text{width} = \langle E^2 \rangle - \langle E \rangle^2 \simeq VC_V$$

Parallel Tempering: The algorithm

- We simulate N inverse temperatures $(\beta_1, \ldots, \beta_N)$ and N non-interacting real replicas (copies).
- The partition function of the system reads

$$\mathcal{Z}_{\mathrm{EXT}} = \prod_{i=1}^{N} \mathcal{Z}(\beta_i) \ ,$$

and, as usual,

$$\mathcal{Z}(\beta_i) = \sum_{\{X_i\}} \exp\left[-\beta_i \mathcal{H}(X_i)\right] \ .$$

Parallel Tempering: The algorithm

For a given set of β's, $(\beta_1, ..., \beta_N)$, the probability of picking a configuration $X = (X_1, ..., X_N)$ is

$$P(X; \beta_1, ..., \beta_N) = \frac{1}{\mathcal{Z}_{\mathrm{EXT}}} \exp\left[-\sum_{i=1}^{N} \beta_i \mathcal{H}(X_i) \right] .$$

We will define a Markov process for this extended system. To do this we need to define a transition probability matrix $W(X, \beta; X', \beta')$.

Parallel Tempering: The algorithm

The detailed balance condition for this system reads

$$\begin{aligned} P(\cdots, & X & , \cdots, X', \cdots; \cdots, \beta, \cdots, \beta', \cdots) W(X, \beta; X', \beta') \\ & = & P(\cdots, X', \cdots, X, \cdots; \cdots, \beta, \cdots, \beta', \cdots) W(X', \beta; X, \beta') \end{aligned}$$

We finally obtain

$$\frac{W(X, \beta; X', \beta')}{W(X', \beta; X, \beta')} = \exp(-\Delta)$$

where

$$\Delta = (\beta' - \beta)(\mathcal{H}(X) - \mathcal{H}(X'))$$

Parallel Tempering: The algorithm

The solution is:

$$W(X,\beta;X',\beta') = \begin{cases} 1 & \Delta < 0\,, \\ \exp(-\Delta) & \Delta > 0 \end{cases}$$

If $\Delta < 0$ we accept the change, otherwise we update with probability $\exp(-\Delta)$.
The full procedure for the PT method is then:

1. Update independently the N replicas using a standard MC method simulating the usual canonical ensemble.
2. Try to exchange (X,β) and (X',β'). Accept the change if $\Delta < 0$ and, if $\Delta > 0$, change with probability $\exp(-\Delta)$. Reject otherwise.

Parallel Tempering: The algorithm

The logarithm of the probability of exchanging is:

$$-\Delta = \delta(\mathcal{H}(X_{n+1}) - \mathcal{H}(X_n)) \simeq -\delta\left(\delta\frac{d}{d\beta}E\right) = -\delta^2 V C_V$$

By Imposing that $\Delta = O(1)$, one obtains

$$\delta \simeq \left(\frac{1}{VC_V}\right)^{\frac{1}{2}}$$

Parallel Tempering: The algorithm

At the critical point the specific heat ($C(\beta)$) diverges as

$$VC(L, \beta_c) \propto L^{\alpha/\nu+d}$$

such that the condition on δ reads

$$\delta \propto L^{-(d+\alpha/\nu)/2}$$

while in the non critical region $VC(L, \beta)$ diverges with the volume, L^d, and

$$\delta \propto L^{-d}$$

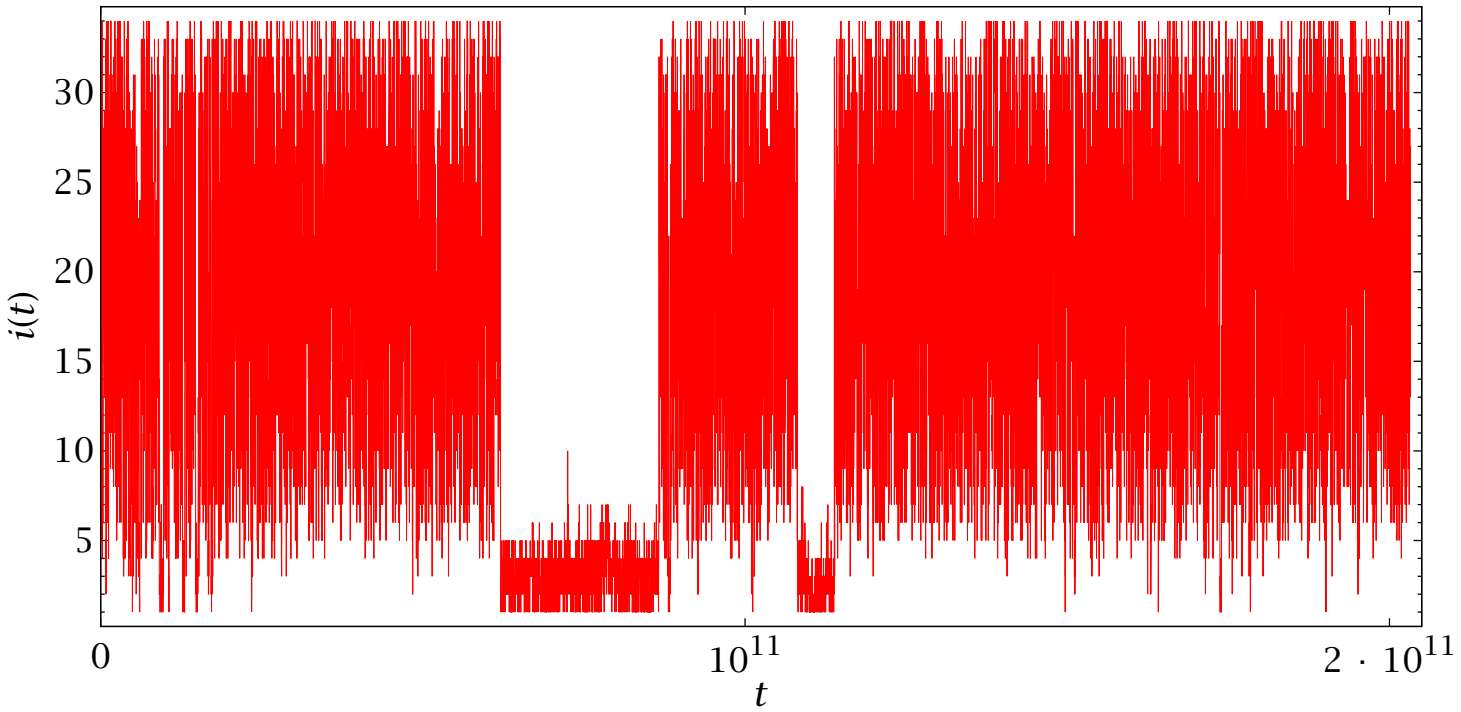
Parallel Tempering: Examples

Parameters for the three dimensional Ising Spin Glass with Binary Couplings (largest lattice).

L	$T_{\min}$	$T_{\max}$	N_T	N_s	System
8	0.150	1.575	10	4000	PC
8	0.245	1.575	8	4000	PC
12	0.414	1.575	12	4000	PC
16	0.479	1.575	16	4000	Janus
24	0.625	1.600	28	4000	Janus
32	0.703	1.549	34	1000	Janus
32	0.985	1.574	24	1000	Janus

Parallel Tempering: Examples

Random Walk in Temperature of a single configuration. Critical Temperature corresponds to $i_c = 17$.



Parallel Tempering: Checks

To test:

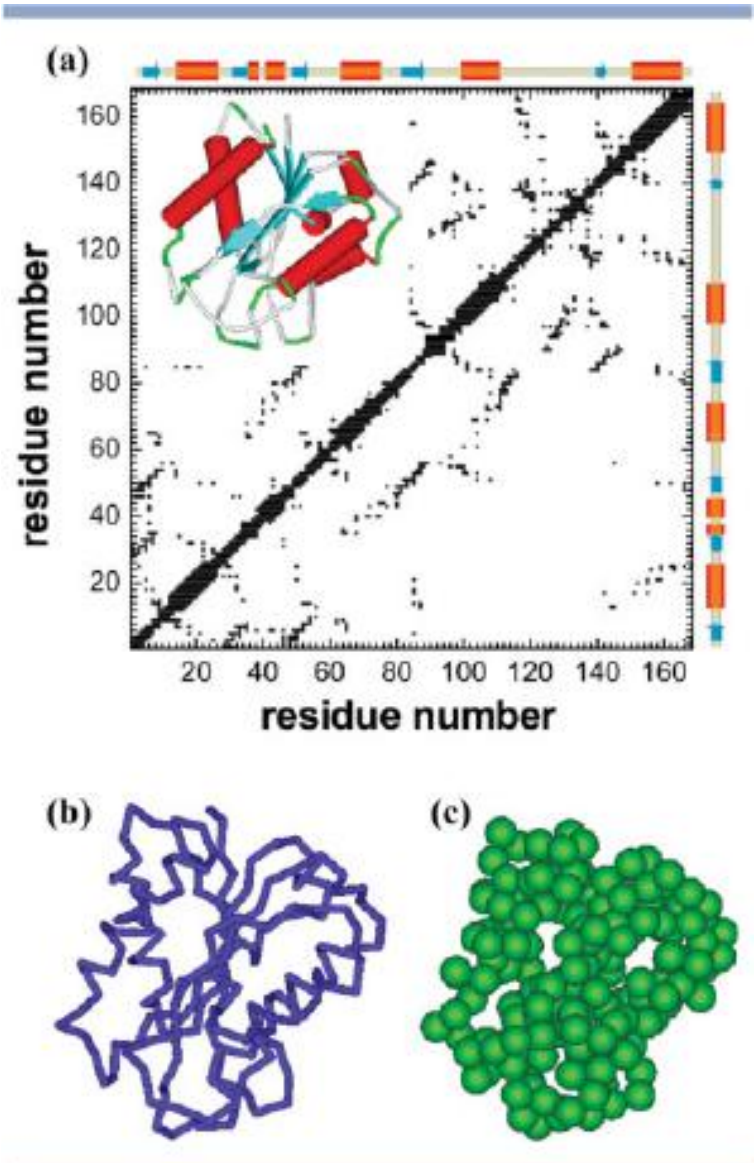
1. Check the energy histograms.
2. We should obtain an uniform probability distribution in the β's space: A given configuration must lie the same time on each temperature.
3. The acceptance factor for each proposed exchange must be monitorized, it should be in the range, for example, 0.2–0.5.

In case of problems (for a given $T_{\min}$):

1. Increase the number of temperatures.
2. Increase the higest temperature.

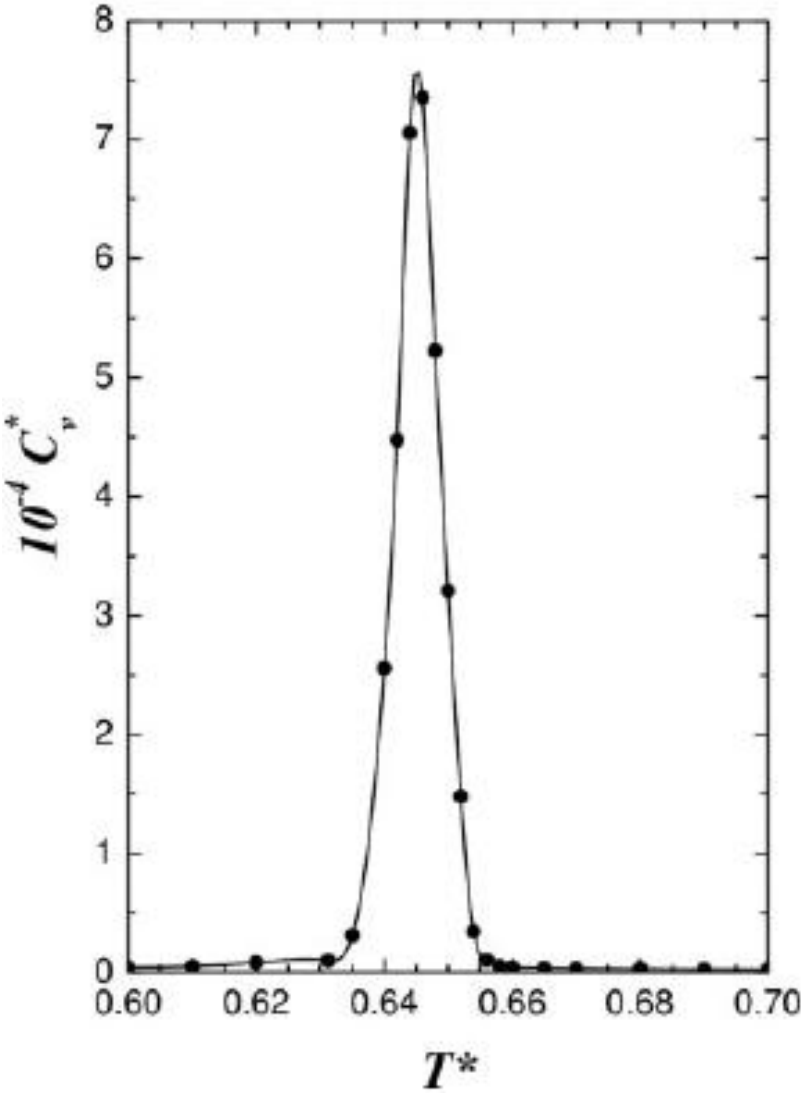
Parallel Tempering: Proteins

Contact map of Apoflavodoxin.



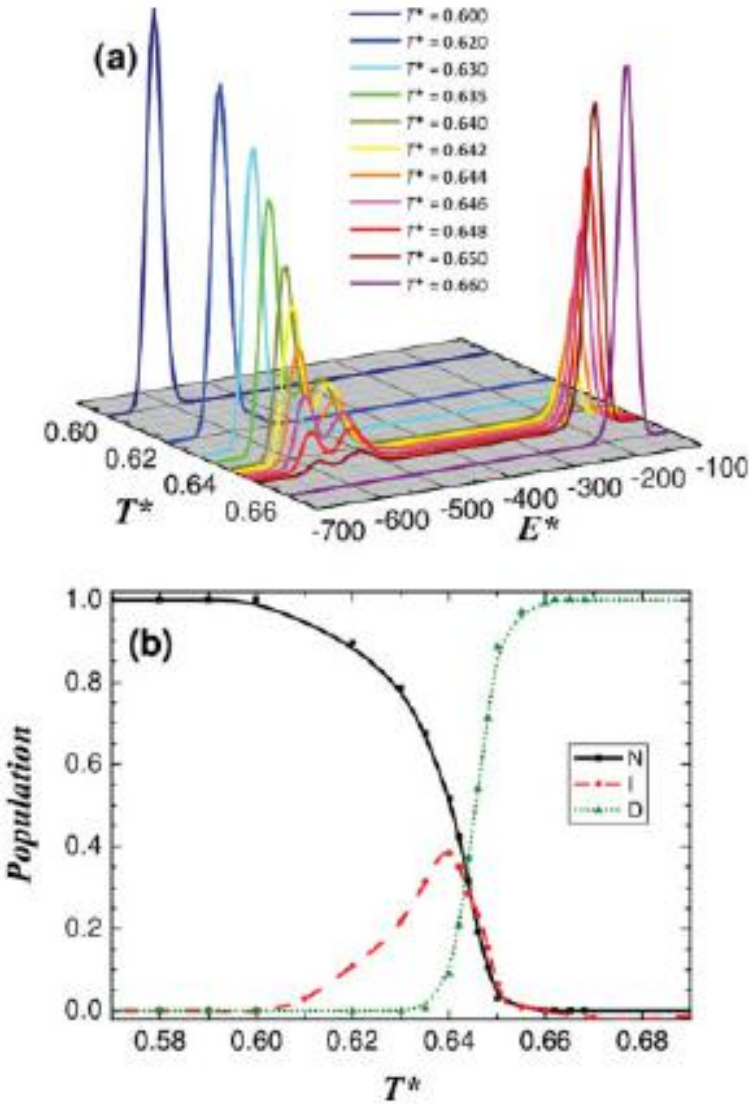
Parallel Tempering: Proteins

Specific Heat of Apoflavodoxin.



Parallel Tempering: Proteins

Energy Histograms and Populations.



Othe PT issue.

- Parallelization.
- MultiSpin Coding.
- Strong First Order Phase Transitions.
- Phase transitions in proteins (folding).

Some References.

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