

Simulations in Statistical Physics

Course for MSc physics students

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Lecture 7

Other ensembles

Microrcanonical: Energy is conserved. We allow for the variation of the energy within a narrow band. This is maintained by a „bag” of a „daemon” (Santa Claus).

Creutz:

- 1 Pick a site
- If the flip causes energy change too much for the tolerance bag, reject the flip and go to 1. Otherwise
- If energy is gained put the gain into the bag, if it is lost, extend it from the bag.
- Go to 1

Essentially deterministic, easy to parallelize.

General observation: In case of conservation the dynamic exponent z is larger. Dynamic universality classes within static ones

Conserved order parameter: Kawasaki dynamics

In fact, the ensemble we have dealt so far for the Ising model is the grand canonical one, as we have governed the system by the external field, the intensive variable conjugate to the extensive magnetization (order parameter).

Canonical ensemble: The variables are T and M , fixed, i.e., the order parameter is conserved.

The elementary step is: Exchange up-down spin pairs
Otherwise usual Metropolis can be applied.

Diffusive dynamics is more physical (pick neighboring spins)
For proper averages (detailed balance!) a time step elapses even if parallel spins are picked.

<http://www.inference.phy.cam.ac.uk/mackay/itprnn/ising/>

This method is able to simulate, e.g., an AB alloy.

Calculation of the entropy, free energy etc. (TD integrals)

Equilibrium statistical physics is not only about calculating averages of dynamic variables over ensembles. Quantities like S or F cannot be computed this way. As $F = E - TS$, it is enough to learn the (tedious) method on one of them.

The specific heat C can be computed from the fluctuations of the energy E , i.e. from the moments. $C = k_B T^2 < (\Delta E)^2 >$

Thus C is computable as an average at any T . By definition:

$$C = T \frac{\partial S}{\partial T} \quad \text{From which we have: } S(T) = S(T_0) + \int_{T_0}^T \frac{C(T)}{T} dT$$

Usually we are interested in entropy differences, thus the integration constant drops out. The third law assures $S(T = 0) = 0$ for well behaving systems, which can be used for low temperature behavior.

$$\frac{F(T)}{T} = S(\infty) + \int_0^{1/T} E(T') d\left(\frac{1}{T'}\right)$$

, which is a high temperature expression. If the two curves cross each other, there is a phase transition.

Monte Carlo kinetics

Often MC dynamics reflects physics. If there is randomness in the moves, which can be considered as elementary in a process, MC is an adequate way to describe it. The simplest example is diffusion. We have a field $u(\mathbf{r}, t)$, like the density of particles or charge or any density of a conserved scalar. Then from the continuity equation and the linear approximation (valid for small amplitude deviations from the homogeneous state) we have:

$$\frac{\partial u}{\partial t} = D \nabla^2 u \quad \text{Let us discretize this:}$$

$$u_i(t + \delta t) = u_i(t) + D \frac{\delta t}{(\delta x)^2} [u_{i-1}(t) - 2u_i(t) + u_{i+1}(t)] \quad (1d \text{ case})$$

In higher dimensions the Laplacian at site i is the sum of the field at the neighbors minus coordination number \times field at site i .

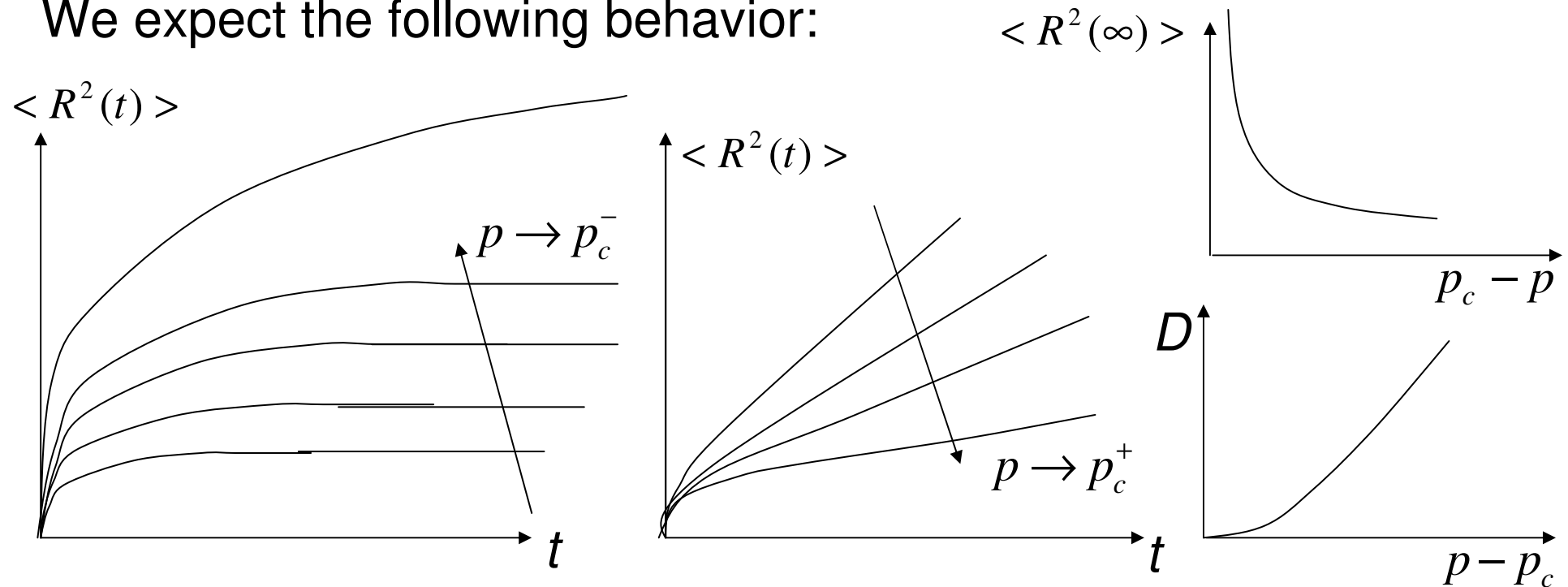
If $D \frac{\delta t}{(\delta x)^2} = 1$ is taken by appropriate choice of the units $u(\mathbf{r}, t)$ can be interpreted as the probability of finding a randomly walking particle at site \mathbf{r} at time t . This can be simulated by MC.

The most important quantity for RWs is the mean square displacement $\langle R^2(t) \rangle = \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle$ for which asymptotically we have:

$$\lim_{t \rightarrow \infty} \langle R^2(t) \rangle = 2dDt$$

There is no need to study the RW on a lattice by MC – it can be treated analytically. The situation is different if the RW takes place on a percolation lattice with occupation probability p .

We expect the following behavior:



The algorithm on a lattice with coordination number z :
Occupy the lattice sites with probability p

- 1 The walker at site i chooses one neighbor site with probability $1/z$
- 2 If that site is occupied move the walker there
- 3 time = time + 1
- 4 go to 1

Averages have to be taken over a) starting positions, b) disorder

Record the number of steps in the different directions and not the position to avoid spurious jumps at the periodic BC-s

$$R^2 = (n_x^+ - n_x^-)^2 + (n_y^+ - n_y^-)^2 + (n_z^+ - n_z^-)^2$$

The time of simulation should not exceed L^2/D .

Due to the Einstein relation between diffusion and mobility, this is an efficient way to measure conductivity in a random medium.

The Ising model is another example where physical meaning can be given to the MC time. In a classical magnetic model the Hamiltonian does not tell anything about the dynamics, it only determines the weights of the equilibrium configurations. How is this equilibrium reached? Imagine that the system is in a heat bath, and the spins take place on the sites of a lattice, which undergoes thermal vibrations, i.e., the system is in an equilibrium of a phonon gas. The thermalization is just due to the interaction between the phonons and the spins. The lattice vibrations kick the spins resulting in random flips according to the statistical weights. This is well modeled by the Metropolis algorithm.

This way time dependent phenomena like nucleation, spinodal decomposition, relaxation become accessible by MC

<http://www.inference.phy.cam.ac.uk/mackay/itprnn/ising/>

Relaxation problems (slowing down)

We have already seen how **critical slowing down** hampers the approach to equilibrium near to a critical point.

There are other sources causing problems with the relaxation:
Slowing down due to conservation

Back to the diffusion eq: $\frac{\partial u}{\partial t} = D\nabla^2 u$ without sources and sinks and special BC-s the (equilibrium) solution is constant u_0 . Let us define the deviation from this solution as $\delta u(\mathbf{r}, t)$, for which the same diffusion equation holds. We can solve it by the Fourier method $u_{\mathbf{k}}(t) = \int_V \delta u(\mathbf{r}, t) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}$ for which $\dot{u}_{\mathbf{k}}(t) = -Dk^2 u_{\mathbf{k}}(t)$

with the solution $u_{\mathbf{k}}(t) = u_{\mathbf{k}}(0) e^{-Dk^2 t}$ This is a plain exponential

relaxation with the hydrodynamic relaxation time $\tau_{HD} = 1/Dk^2$ meaning that the longest wavelength inhomogeneities relax very slowly, typically as $\sim L^2 / D$

Critical slowing down

As already discussed, close to the critical point the correlation length ξ diverges and so does the related relaxation time:

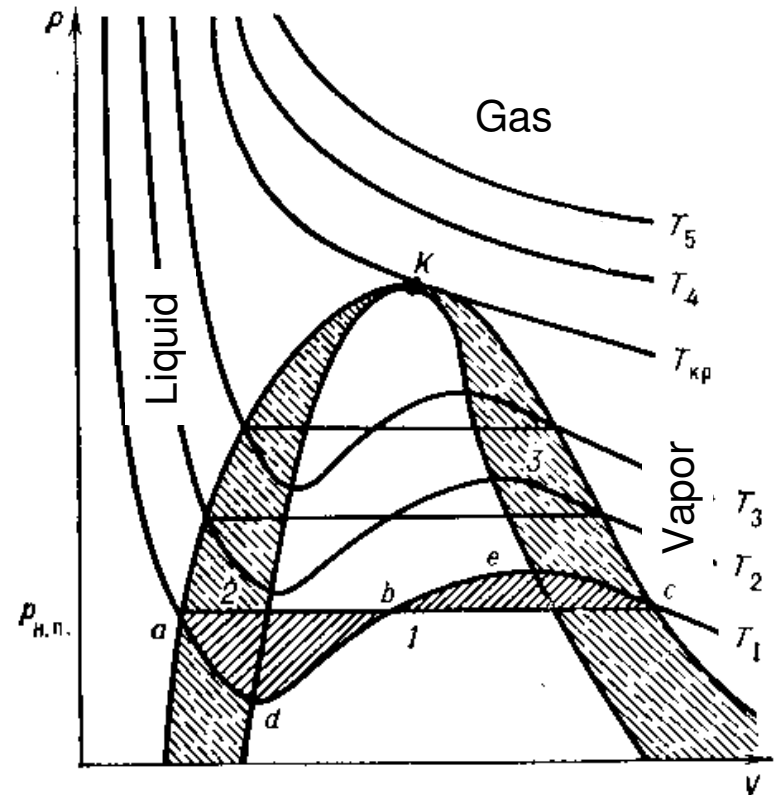
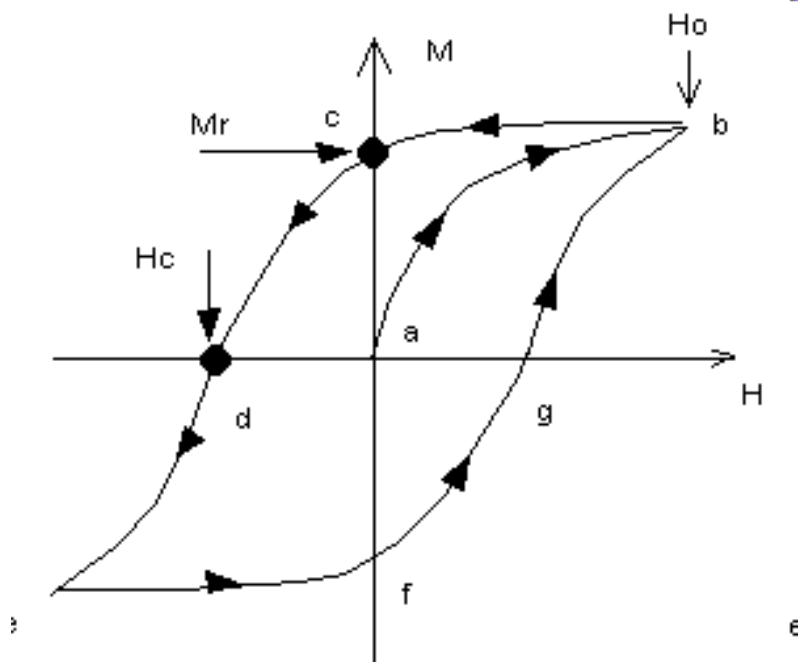
$\tau_1 \sim \xi^z$ This can be transformed into: $\tau_1 \sim \varepsilon^{-\Delta_1}$, where ε is the reduced temperature and $\Delta_1 = z/\nu$. The index is for linear, because there is also a so called non-linear relaxation time, which describes the relaxation of the order parameter from initial values far from the equilibrium one. The corresponding exponent is $\Delta_{nl} = z/\nu - \beta$ (Rácz, 1976).

To make things more complicated HD relaxation, i.e., slowing down is also influenced by criticality.

We saw that the characteristic time is L^2 / D but, according to the dynamic theory of critical phenomena, D is influenced by criticality. E.g., we can expect that $D \sim \chi^{-1} \sim |\varepsilon|^\gamma$ i.e., D goes to 0 at the critical point leading to an additional divergence in the relaxation time.

Metastability

At first order transitions the correlation length remains finite. The mechanism of the first order transition is usually nucleation, which is related to metastability. Examples can be observed at hysteresis or undercooling, overheating, over-compressing etc.



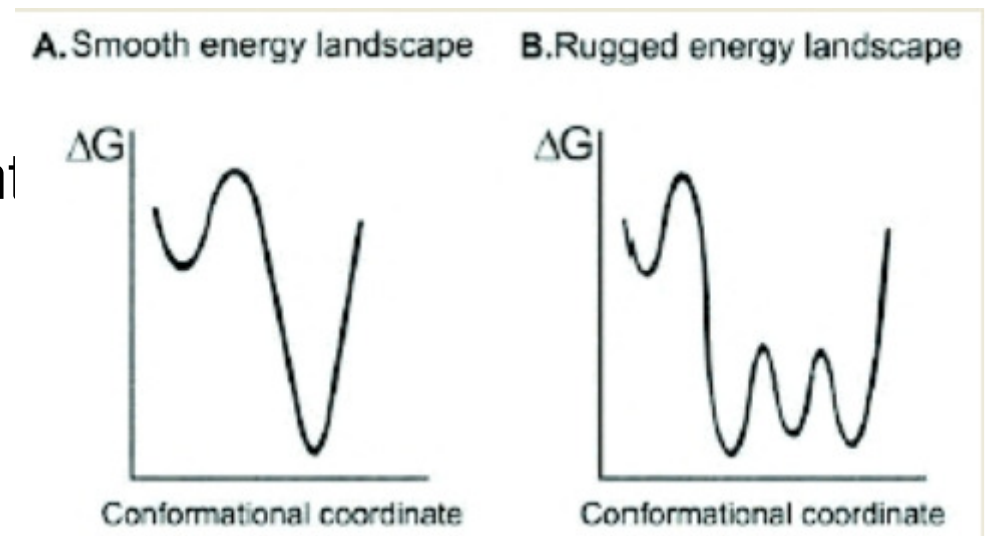
<http://www.honeylocust.com/hysteresis/hys1.html>

The reason for the first order phase transition is that at that point the free energy of the old phase becomes larger than that of the new one.

The mechanism is nucleation. In homogeneous nucleation there is a competition between the bulk free energy of the droplet and its surface energy. As the former overtakes with increasing size, there is a critical nucleus size above which the transition is very rapid. However, such a critical nucleus has to be created by spontaneous fluctuations – which takes (sometimes enormously long) time.

Clearly, hysteresis, „phase diagram” within the miscibility gap etc. are velocity dependent

Metastability reflects the (free) energy landscape



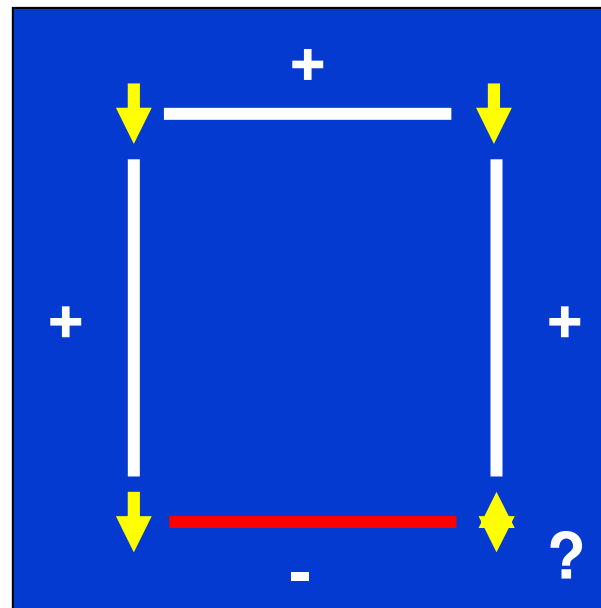
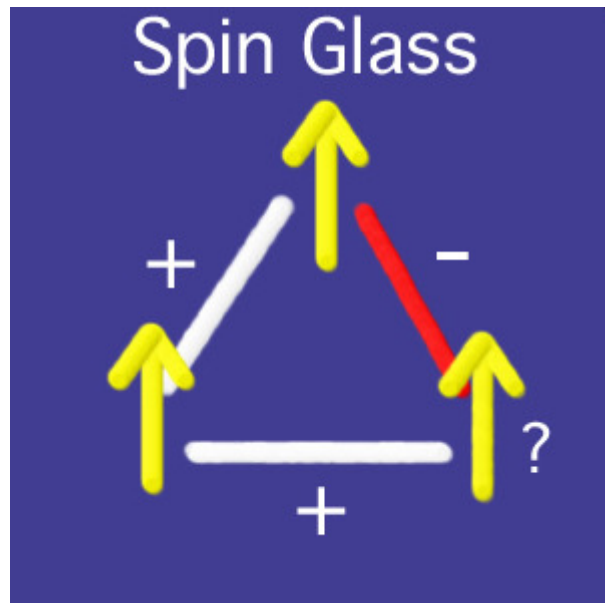
Glassy behavior

Model glass: spin-glass

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j$$

where J -s are random quenched variables with 0 mean, e.g., $\pm J$ with 1/2 probability.

Frustration:



Macroscopically
degenerate
ground state
third law violated

How to find the ground state in a rugged energy landscape?

No simple optimization scheme works. NP-complete optimization problem: The computational complexity (roughly the CPU time needed to solve the problem) grows faster than any power of the system size (practically exponentially).

Many important problems

- Traveling salesman
- Graph partitioning
- Graph coloring

...

If one NP complete can be reduced to polynomial computing time, then all can be.

This is math. In reality we need good approximations, which work fast.

Simulated annealing

In a simple landscape the ground state can be found quickly by putting $T=0$ in a MC simulation. This method leads to spurious result in a rugged landscape as the system gets stuck in an improper minimum.

Simulated annealing uses the trick that a) it lets the system cool down slowly and b) it allows warming up again.

Traveling salesman problem: The salesman has to visit N cities randomly positioned in the plane such that it returns and the length of the path is minimum. (Basic problem e.g., in circuit design.)

Hamiltonian = path length

Elementary move = exchange two cities in the path

Use Metropolis simulated annealing. ($T \sim$ alcohol 😊)

<http://www.math.uu.nl/people/beukers/anneal/anneal.html>