	Lectures	Exercises/Home work problems	
C introduction		C1	C3
		C2	C4
Ordinary differential equations	Linear dynamics	E1	
	Non-linear dynamics	E2	
	Molecular dynamics		H1a/H1b
Stochastic methods	Monte Carlo integration	E3	
	Metropolis algorithm		H2a/H2b
Partial differential equations	Quantum structure		H3a

Ising model

Content:

- Ising model – a discrete model system
- Ising model: Mean field solution
- Ising model: Metropolis algorithm
- Ising model: Numerical results
- H2a: Binary alloy: CuZn
- H2a: Binary alloy: Mean field solution

Ising model

The Hamiltonian

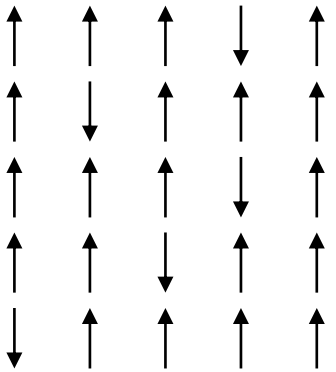
$$\mathcal{H} = -J \sum_{<ij>} s_i s_j - h \sum_i s_i$$

$s_i = \pm 1, \ i = 1, \ldots, N$

$< ij >$ - sum of all nearest neighboring pair of spins

J - coupling constant

h - external field

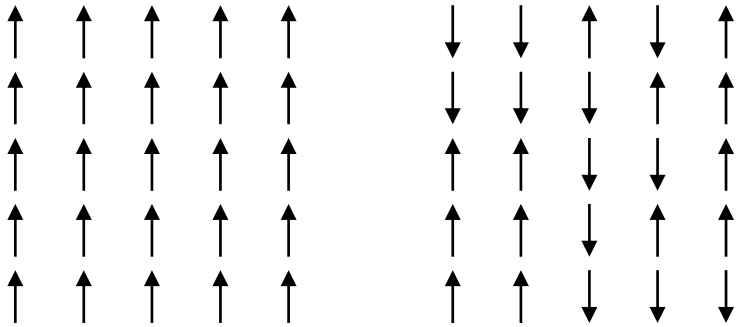


- a lattice model
- one of the simpliest and non-trivial model systems of interacting degrees of freedom
- introduced by Lenz and Ising to model phase transitions in magnetic materials in the 1920s
- solved exactly in 2D by Onsager 1944
- has not been solved exactly in 3D (yet)
- useful in condensed matter physics and field theory
- a (rather crude) model for magnetism
- can be used to model binary alloys in materials science
- can be used to model adsorbed particles in surface science
- can be extended in many directions

Ferromagnetic substance

low T

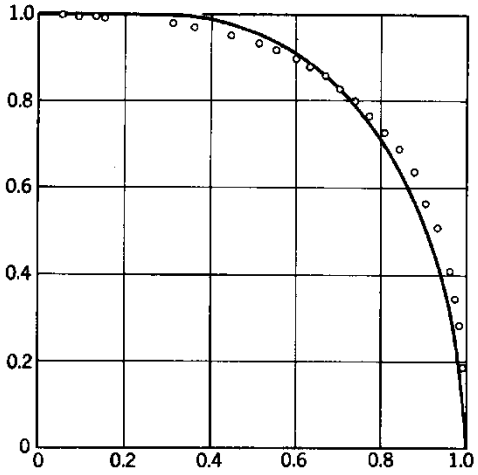
high T



ferromagnetic

paramagnetic

Magnetization

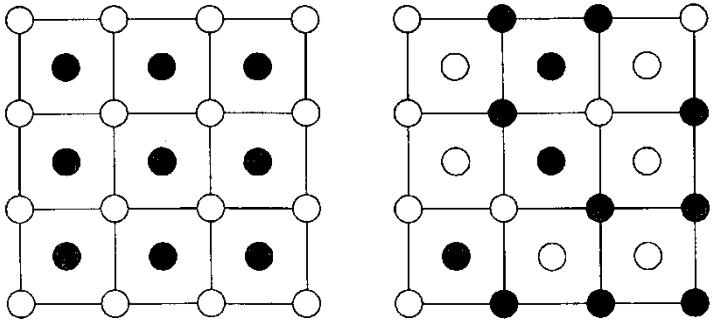


temperature

Binary alloy

low T

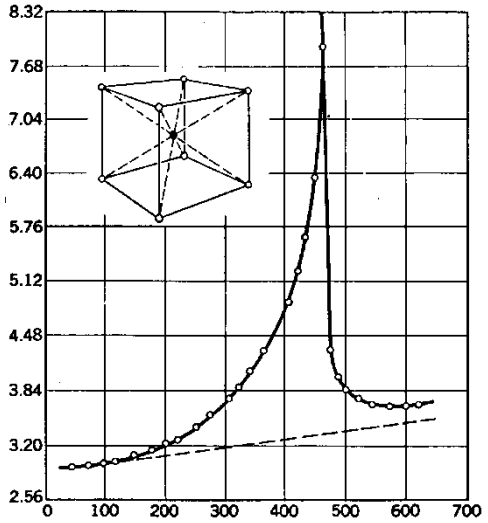
high T



ordered state

disordered state

Heat capacity



temperature

Ising model – statistical thermodynamics

Canonical ensemble:

The probability for the system to be in microstate ν:

$$P_\nu = \frac{1}{Z}\exp(-\beta E_\nu)$$

where $\beta = 1/k_B T$.

The partition function:

$$Z(\beta, h) = \sum_\nu \exp(-\beta E_\nu)$$

The magnetization

$$M_\nu = \sum_{i=1}^{N} s_i$$

The energy

$$E_\nu = -J \sum_{<ij>} s_i s_j - h \sum_i s_i$$

The mean magnetization

$$M \equiv \langle M_\nu \rangle = \frac{1}{Z}\sum_\nu M_\nu \exp(-\beta E_\nu)$$

The mean energy

$$U \equiv \langle E_\nu \rangle = \frac{1}{Z}\sum_\nu E_\nu \exp(-\beta E_\nu)$$

The isothermal susceptibility

$$\chi_T \equiv \left(\frac{\partial M}{\partial h}\right)_T = \frac{1}{k_B T}\left[\left\langle M_\nu^2 \right\rangle - \langle M_\nu \rangle^2\right]$$

The heat capacity at constant field

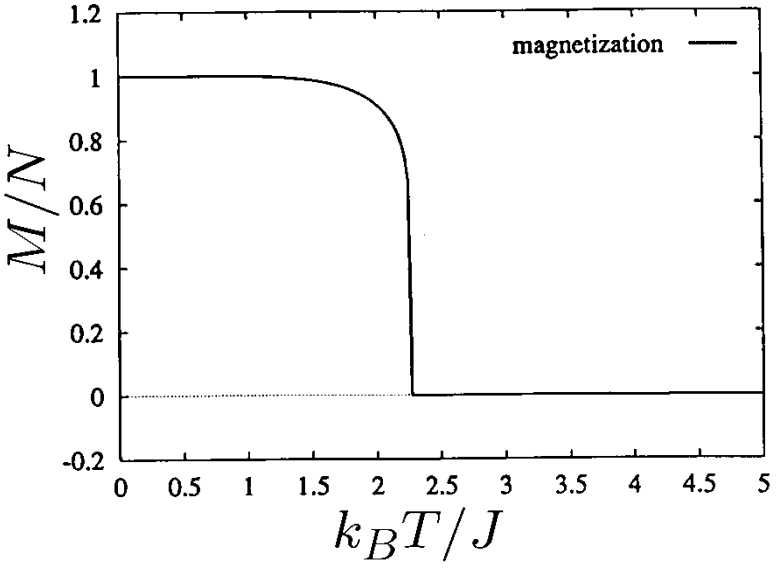
$$C_h \equiv \left(\frac{\partial U}{\partial T}\right)_h = \frac{1}{k_B T^2}\left[\left\langle E_\nu^2 \right\rangle - \langle E_\nu \rangle^2\right]$$

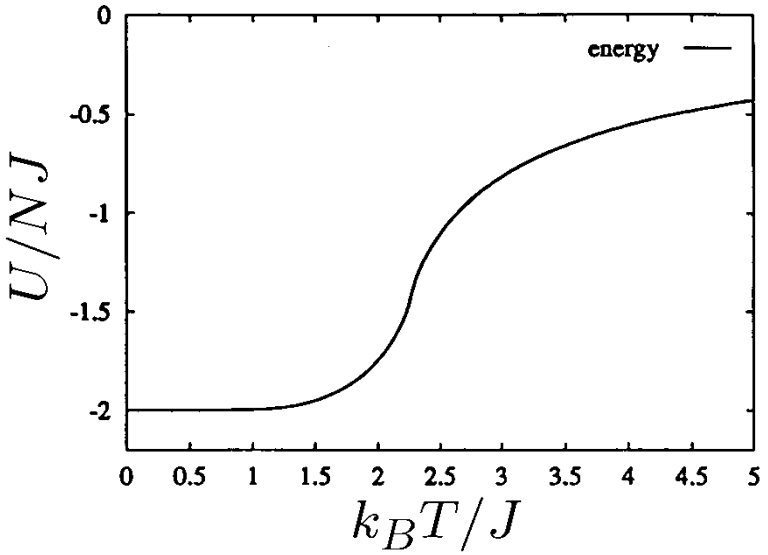
Ising model – the exact solution (2D)

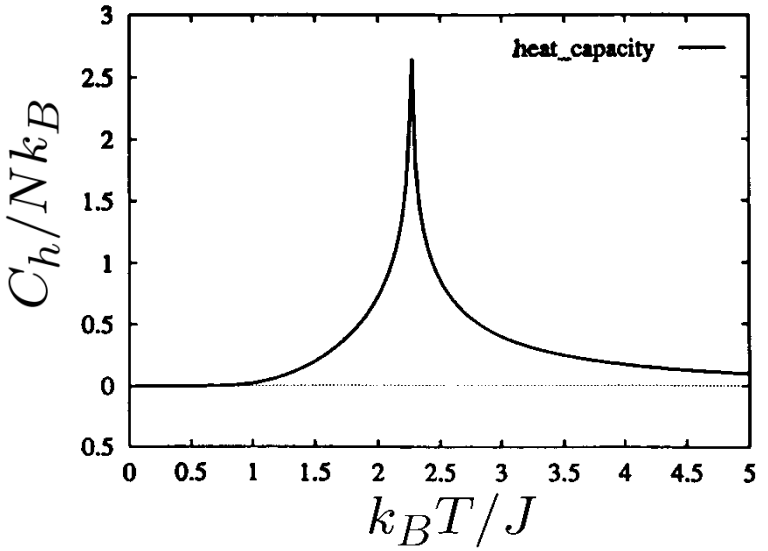
Due to Onsager, 1944

The transition temperature T_c

$$\frac{k_B T_c}{J} = \frac{2}{\ln(\sqrt{2}+1)} \approx 2.269$$







Ising model – mean field solution (h=0)

The exact solution

The energy

$$U = -J \sum_{<ij>} \left\langle s_i s_j \right\rangle$$

The mean field solution

The energy

$$U_{MF} = -J \sum_{<ij>} \langle s_i \rangle \langle s_j \rangle = -J 2 N m^2$$

The number of microstates

$$W = \frac{N!}{N_\uparrow! N_\downarrow!}$$

The entropy

$$S = k_B \ln W = \frac{N!}{N_\uparrow! N_\downarrow!}$$

The free energy

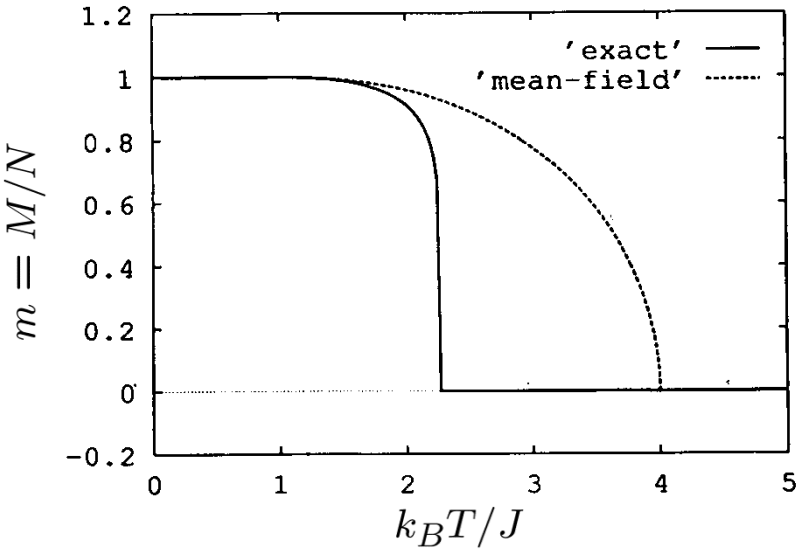
$$F = U - TS$$

Minimum if

$$m = \frac{k_B T}{8J} \ln \frac{1+m}{1-m}$$

which implies that

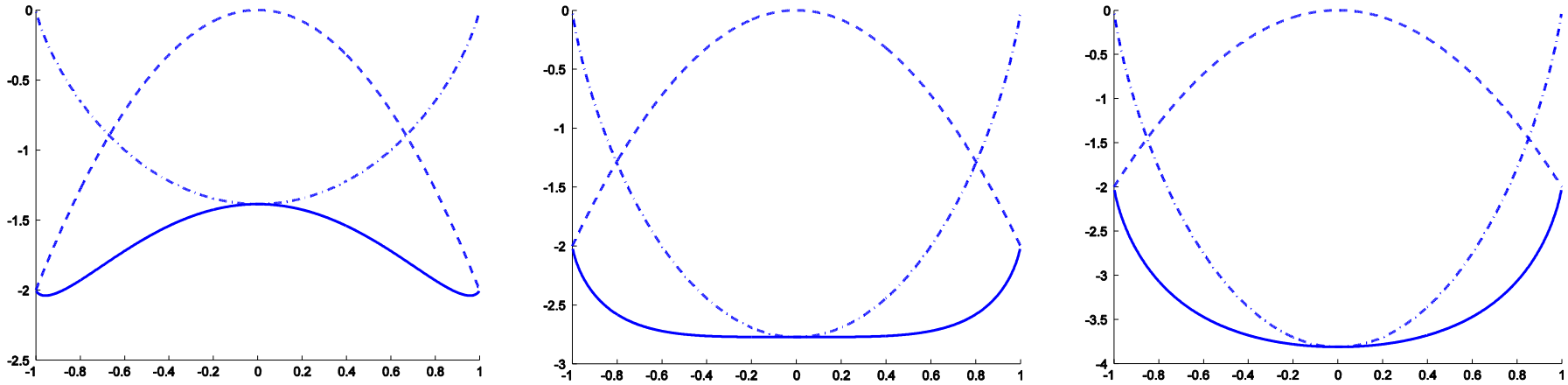
$$k_B T_c / J = 4.0$$



Ising model – mean field solution (h=0)

$$\frac{F_{MF}}{NJ} = -2m^2 + \frac{k_B T}{J}\left[\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2}\right]$$

$k_B T/J = 2.5$ $\quad$ $k_B T/J = k_B T_c/J = 4.0$ $\quad$ $k_B T/J = 5.5$



Dashed line: U

Dash-dotted line: $-TS$

Full line: $F = U - TS$

Ising model – Metropolis algorithm

1. Set the desired temperature T and external field h.

2. Initialize the system, *e.g.* use a random configuration or a configuration from a previous simulation.

3. Perform the desired number of Monte Carlo sweeps through the lattice.

4. Exclude the first configurations (let the system equilibrate).

5. Compute average quantities from subsequent configurations and estimate the error from statistically independent configurations.

3a. Make a trial change, e.g. by flipping a randomly chosen spin.

3b. Determine the change in energy ΔE

3c. If $\Delta E \leq 0$ accept the new configuration

3d. If $\Delta E > 0$ generate a random number r between 0 and 1, and if

$$\exp(-\Delta E/k_B T) \geq r$$

accept the new configuration, otherwise count the old configuration once more.

The Metropolis algorithm

The Metropolis algorithm is a particular way of ensuring that the transition rule satisfies detailed balance.

The transition matrix $w_{nm} = w_{n \leftarrow m}$ is split into two parts

$$w_{nm} = \tau_{nm} \alpha_{nm}$$

where τ_{nm} is the probability of making a trial change from state Ω_m to state Ω_n and α_{nm} is the probability of accepting the trial state.

The acceptance probability is assumed to satisfy

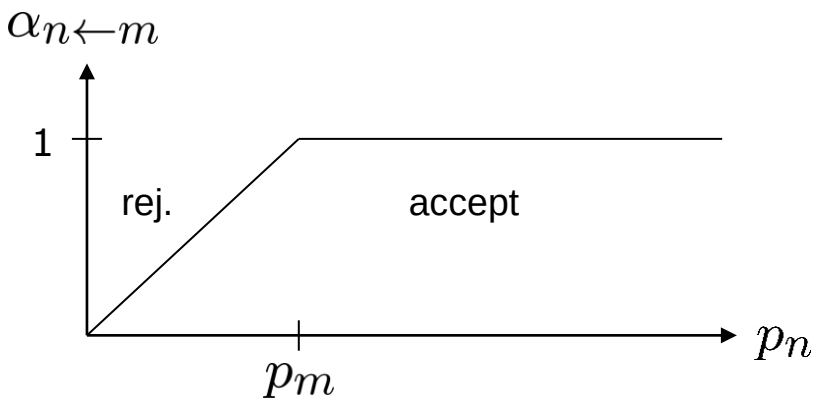
$$\alpha_{nm} = \begin{cases} 1 & \text{if } p_n \geq p_m \\ p_n / p_m & \text{if } p_n < p_m \end{cases}$$

and to ensure detailed balance the trail change then has to be symmetric

$$\tau_{nm} = \tau_{mn}$$

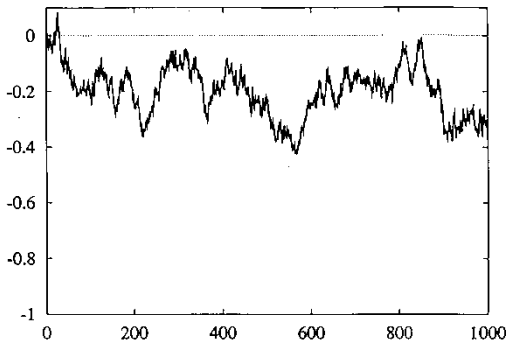
Moves that are not accepted are rejected and remain at the same location for at least one more step

$$w_{mm} = 1 - \sum_{n(\neq m)} w_{nm}$$



Equilibration

It is important to wait until
the system has **equilibrated.**



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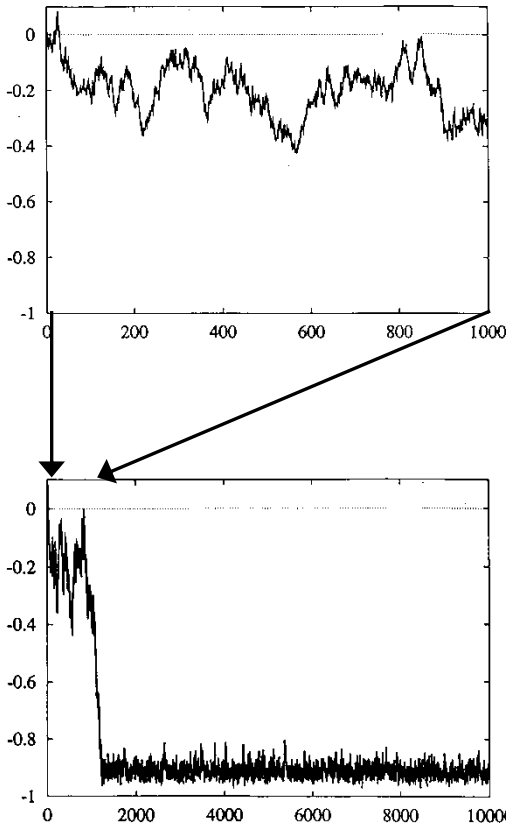

Equilibration

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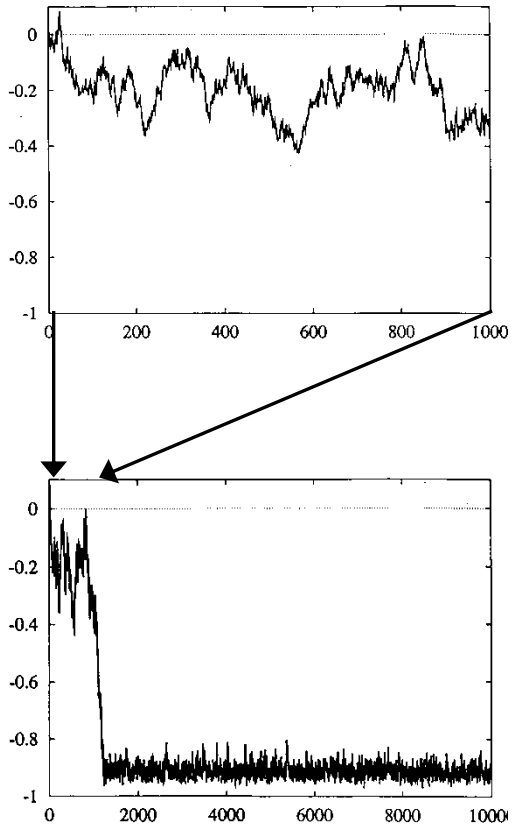
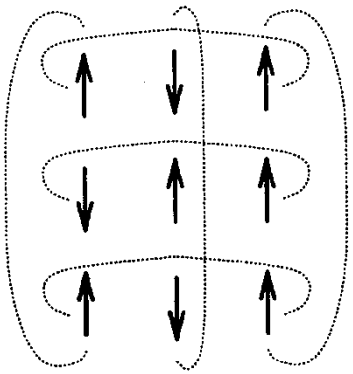
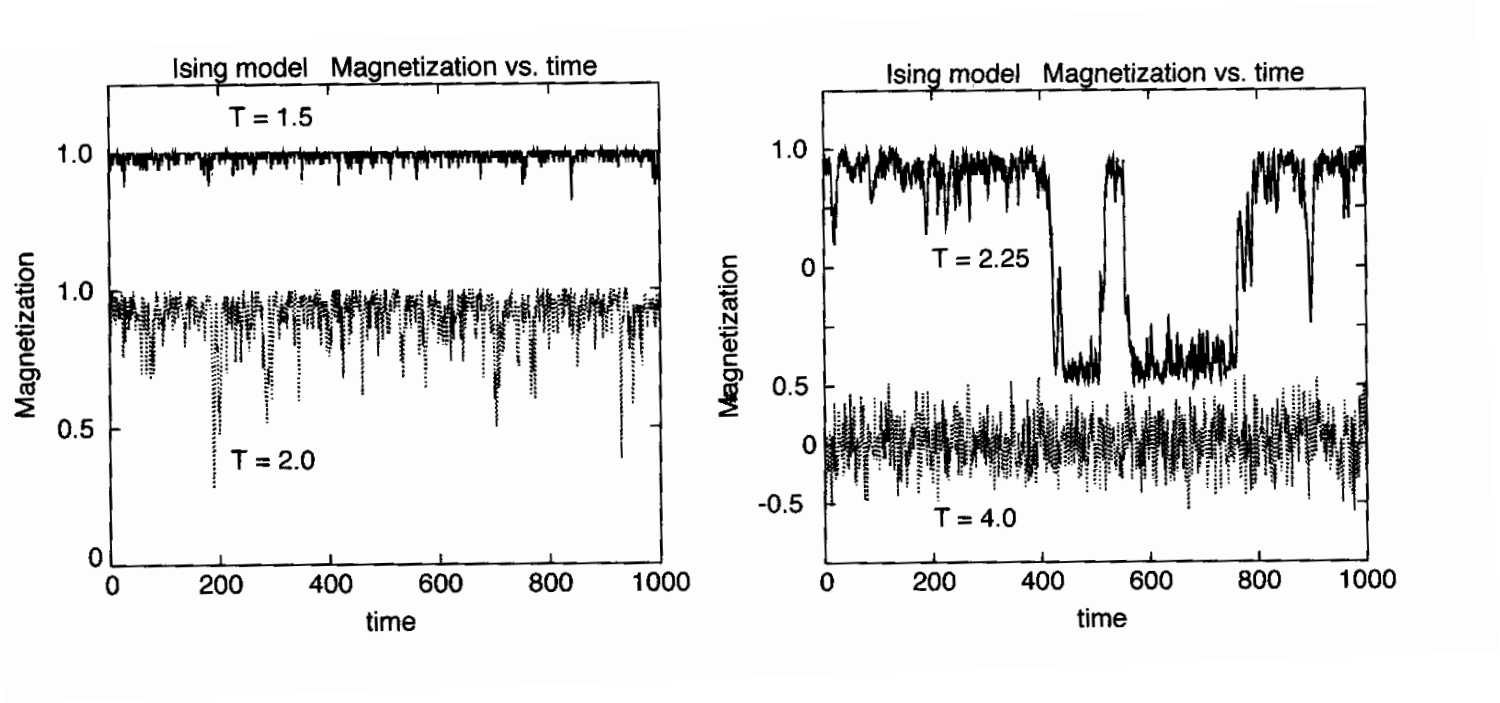


Boundary conditions

To mimic a large system **periodic boundary conditions** are commonly used.

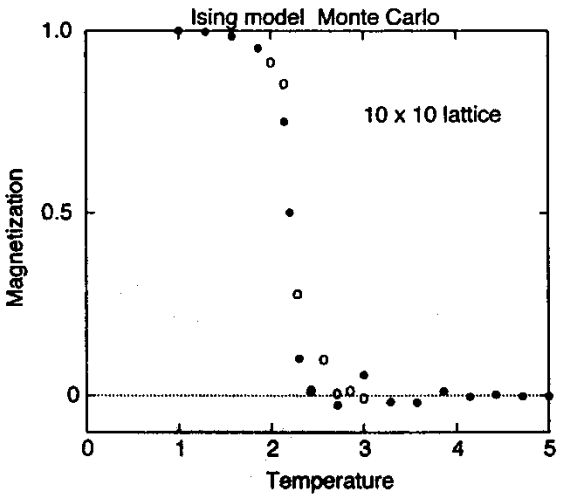


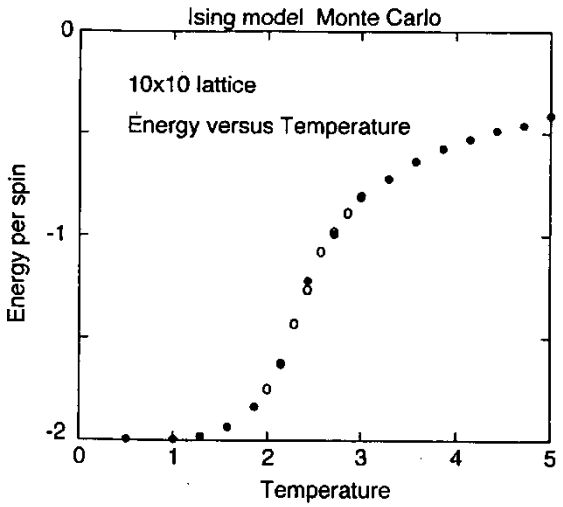
Ising model – Numerical results

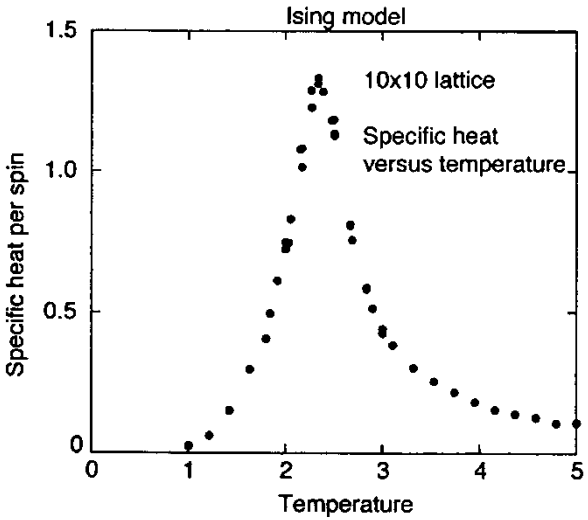


The temperature T in units of J/k_B.

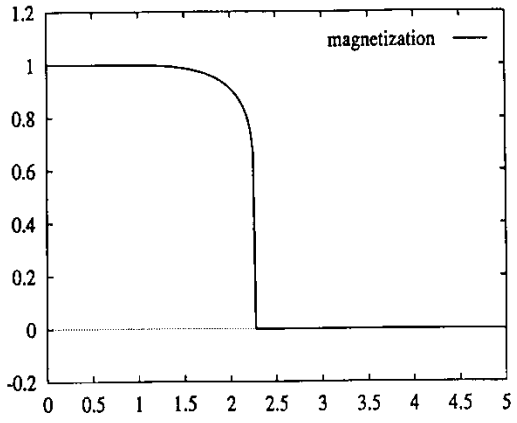
Ising model – Numerical results

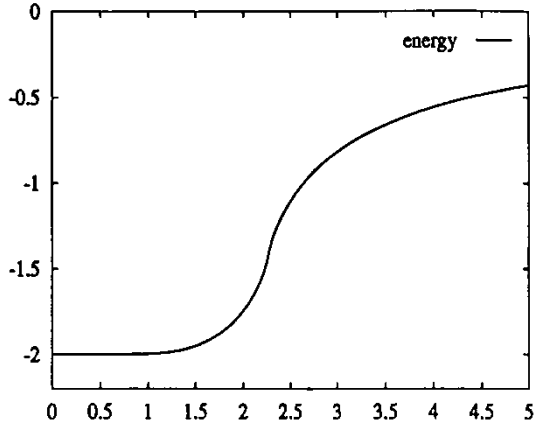


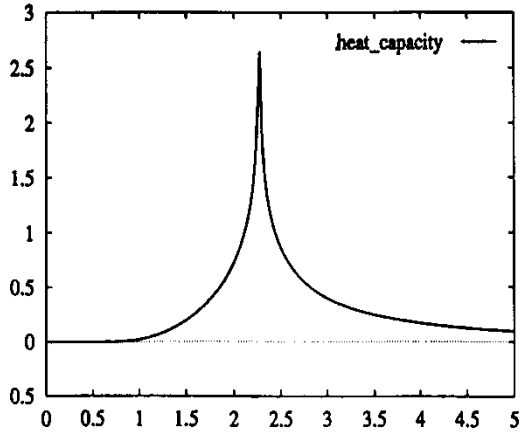




Ising model – Exact results







Binary alloy

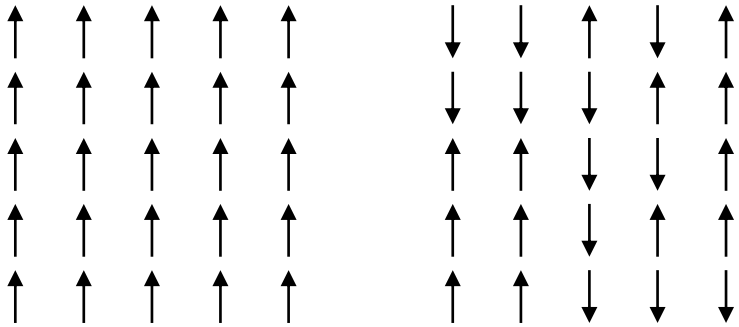
Content:

- H2a: Binary alloy, the CuZn system

Ferromagnetic substance

low T

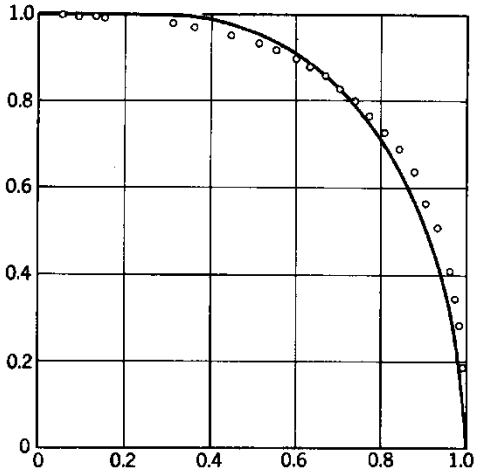
high T



ferromagnetic

paramagnetic

Magnetization

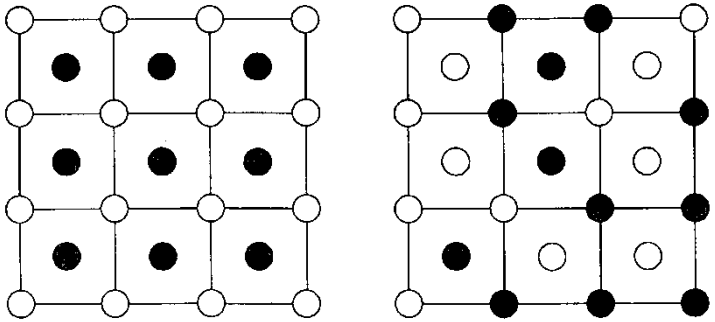


temperature

Binary alloy

low T

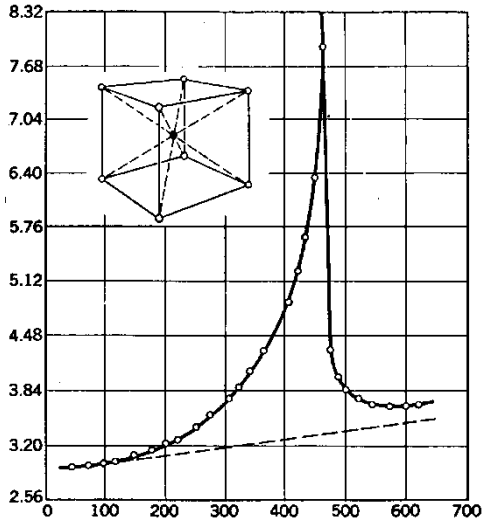
high T



ordered state

disordered state

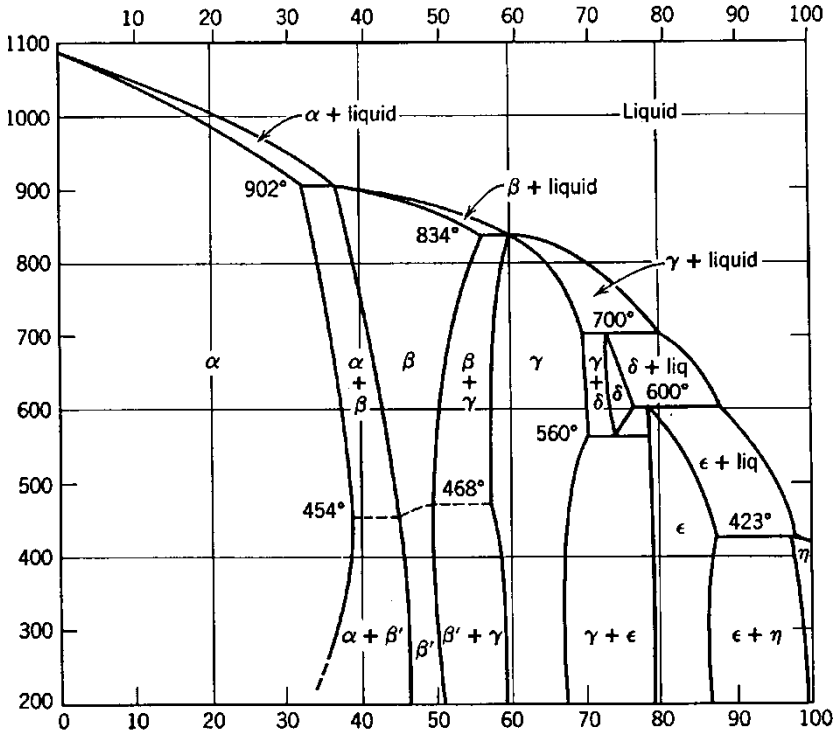
Heat capacity



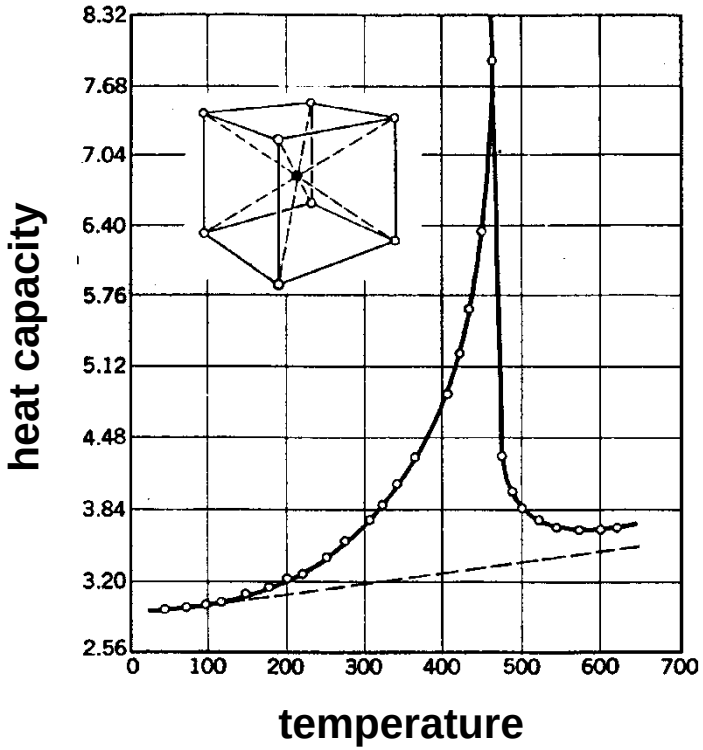
temperature

The Cu-Zn system – a binary alloy

Equilibrium phase diagram

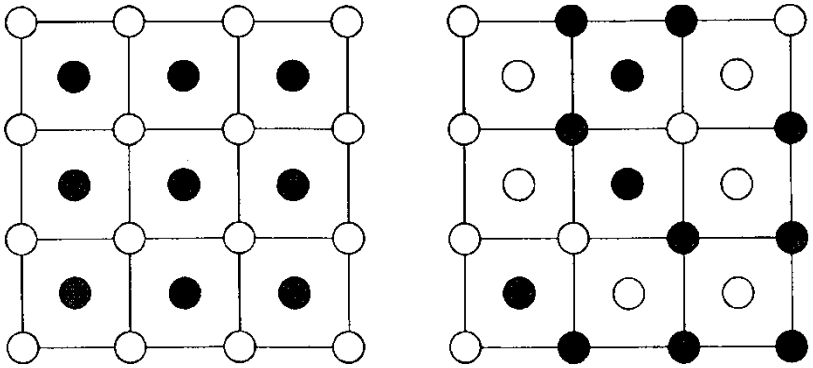


CuZn (β-brass)



Binary alloy – simple model

AB alloy with bcc structure
ex. Cu-Zn (β-brass)



- N atoms A, N atoms B

- bcc-lattice = two interpenetrating sc-lattices (a and b)

Long-range order parameter P

Number of A atoms on the a sublattice
$= \frac{1}{2}(1+P)N$

$P = \pm 1$ perfect order
$P = 0$ no order

Short-range order parameter r

q = number of nearest-neighbor bonds that are AB bonds

$$r = \frac{1}{4}(q-4)$$

$r = 1$ complete order
$r = 0$ complete disorder

Binary alloy – mean field solution

The energy

$$E = N_{AA}E_{AA} + N_{BB}E_{BB} + N_{AB}E_{AB}$$

where N_{ij} is the number of nearest-neighbor ij bonds, and E_{ij} is the energy of an ij bond.

Mean field approximation

Assume no correlations, i.e.

$$\begin{aligned} N_{AA} &= 8\,[\tfrac{1}{2}(1+P)N]\,[\tfrac{1}{2}(1-P)] = 2(1-P^2)N \\ N_{BB} &= 8\,[\tfrac{1}{2}(1+P)N]\,[\tfrac{1}{2}(1-P)] = 2(1-P^2)N \\ N_{AB} &= 8N\,[\tfrac{1}{2}(1+P)]^2 + 8N\,[\tfrac{1}{2}(1-P)]^2 = 4(1+P^2)N \end{aligned}$$

This implies that

$$E_{MF} = E_0 - 2NP^2\Delta E$$

where

$$\begin{aligned} E_0 &= 2N(E_{AA} + E_{BB} + 2E_{AB}) \\ \Delta E &= E_{AA} + E_{BB} - 2E_{AB} \end{aligned}$$

Binary alloy – mean field solution

The number of configurations

$$W = \left[\frac{N!}{[\frac{1}{2}(1+P)N]!\ [\frac{1}{2}(1-P)N]!} \right]^2$$

The entropy

$$\begin{aligned} S &= k_B \ln W \\ &= 2Nk_B \ln 2 - Nk_B[(1+P)\ln(1+P) + (1-P)\ln(1-P)] \end{aligned}$$

The free energy

$$\begin{aligned} F &= U - TS \\ &= E_0 - 2NP^2\Delta E \\ &- 2Nk_BT \ln 2 + Nk_BT[(1+P)\ln(1+P) + (1-P)\ln(1-P)] \end{aligned}$$

The equilibrium structure is obtained by finding the minimum of F with respect to the order parameter P. It leads to a phase transition at

$$T_c = 2\Delta E/k_B$$

	Lectures	Exercises/Home work problems	
C introduction		C1	C3
		C2	C4
Ordinary differential equations	Linear dynamics	E1	
	Non-linear dynamics	E2	
	Molecular dynamics		H1a/H1b
Stochastic methods	Monte Carlo integration	E3	
	Metropolis algorithm		H2a/H2b
Partial differential equations	Quantum structure		H3a

Variational Monte Carlo

Content:

- Variational Quantum Monte Carlo
- Multi-dimensional case
- H2b: Variational Monte Carlo for He

Variational Quantum Monte Carlo

Aim: To obtain a good estimate of the ground state energy E_0 for a quantum system.

Based on the variational theorem

$$E[\psi_T] = \frac{\langle \psi_T \mid \mathcal{H} \mid \psi_T \rangle}{\langle \psi_T \mid \psi_T \rangle} \geq E_0$$

where

ψ_T is a trial wave function

Choose a physically reasonable form for the trial wave wave function that depends on one or more parameters α_i. Determine $E[\psi_T]$ and vary α_i until a minimum is obtained.

Multi-dimensional case

Write in terms of a normalized weight function $\rho(\boldsymbol{X})$, or probability distribution

$$E[\psi_T] = \frac{\int d\boldsymbol{X}\psi_T^*(\boldsymbol{X})\mathcal{H}\psi_T(\boldsymbol{X})}{\int d\boldsymbol{X}\psi_T^*(\boldsymbol{X})\psi_T(\boldsymbol{X})} = \int d\boldsymbol{X}E_L(\boldsymbol{X})\rho(\boldsymbol{X})$$

where

$$E_L(\boldsymbol{X}) = \frac{\mathcal{H}\psi_T(\boldsymbol{X})}{\psi_T(\boldsymbol{X})}$$

is the called the local energy and

$$\rho(\boldsymbol{X}) = \frac{\mid \psi_T(\boldsymbol{X}) \mid^2}{\int d\boldsymbol{X} \mid \psi_T(\boldsymbol{X}) \mid^2}$$

is the weight function. Use the Metropolis algorithm to evaluate the multi-dimensional integral.

Example: Helium

Hamiltonian in atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$)

$$\mathcal{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Trial wavefunction

$$\psi_T(\boldsymbol{r}_1, \boldsymbol{r}_2) = \phi(r_1)\phi(r_2)f(r_{12})$$

with

$$\begin{aligned} \phi(r) &= \exp\left[-\alpha_1 r\right] \\ f(r) &= \exp\left[\frac{\alpha_2 r}{1+\alpha_3 r}\right] \end{aligned}$$

Example: Helium

The cusp conditions (boundary conditions)

$$\lim_{r\to 0}\frac{1}{\phi}\frac{\partial\phi(r)}{\partial r} = -2$$

$$\lim_{r\to 0}\frac{1}{f}\frac{\partial f(r)}{\partial r} = \frac{1}{2}$$

imply that

$$\psi_T(\boldsymbol{r}_1,\boldsymbol{r}_2) = \exp\left[-2r_1\right]\ \exp\left[-2r_2\right]\ \exp\left[\frac{r_{12}}{2(1+\alpha r_{12})}\right]$$

and that the local energy can be written as

$$E_L(\boldsymbol{r}_1,\boldsymbol{r}_2) = -4 + \frac{(\widehat{\boldsymbol{r}}_1-\widehat{\boldsymbol{r}}_2)\cdot\widehat{\boldsymbol{r}}_{12}}{(1+\alpha r_{12})^2}$$
$$+\frac{\alpha}{(1+\alpha r_{12})} + \frac{\alpha}{(1+\alpha r_{12})^2} + \frac{\alpha}{(1+\alpha r_{12})^3} - \frac{1}{4(1+\alpha r_{12})^4}$$

The Metropolis algorithm

The Metropolis algorithm is a particular way of ensuring that the transition rule satisfies detailed balance.

The transition matrix $w_{nm} = w_{n \leftarrow m}$ is split into two parts

$$w_{nm} = \tau_{nm} \alpha_{nm}$$

where τ_{nm} is the probability of making a trial change from state Ω_m to state Ω_n and α_{nm} is the probability of accepting the trial state.

The acceptance probability is assumed to satisfy

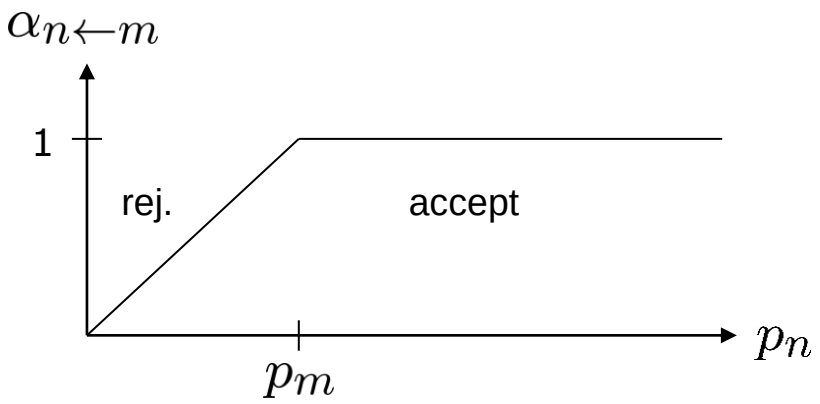
$$\alpha_{nm} = \begin{cases} 1 & \text{if } p_n \geq p_m \\ p_n / p_m & \text{if } p_n < p_m \end{cases}$$

and to ensure detailed balance the trail change then has to be symmetric

$$\tau_{nm} = \tau_{mn}$$

Moves that are not accepted are rejected and remain at the same location for at least one more step

$$w_{mm} = 1 - \sum_{n(\neq m)} w_{nm}$$



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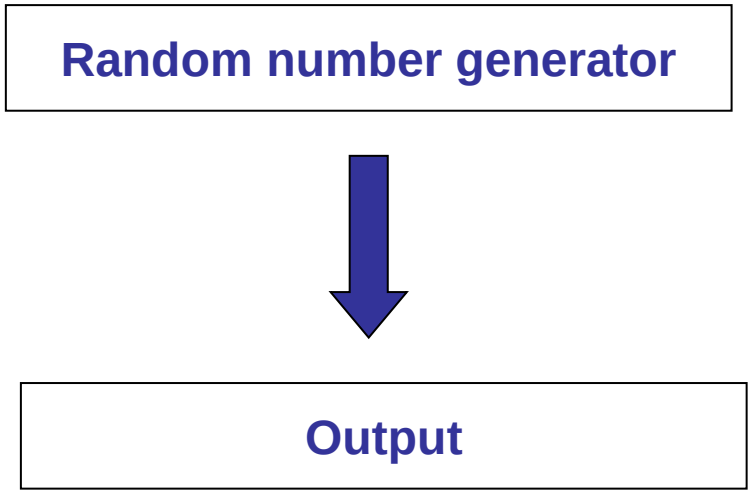
Random numbers

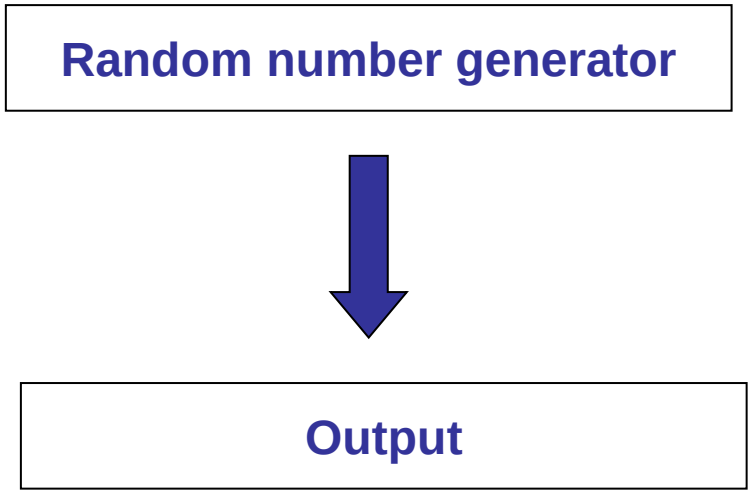
Content:

- Random number generators
- Uniform random numbers
- Non-uniform random numbers:
  1. Transformation method
  2. Rejection method

Random numbers



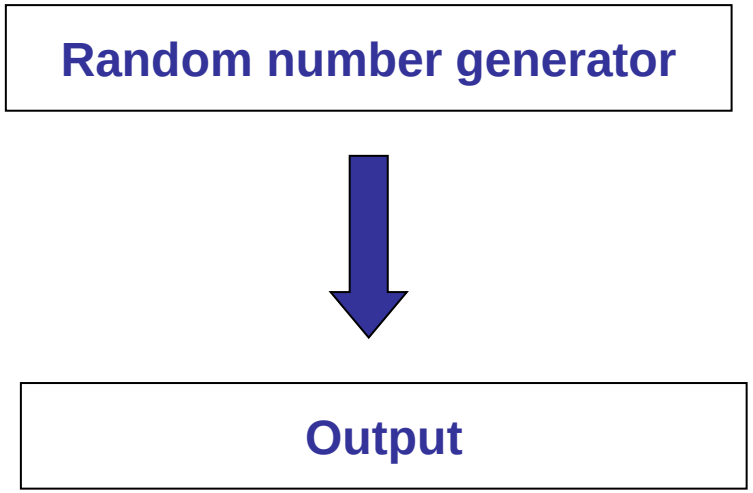
Random numbers



It may seem perverse to use a computer, that most precise and deterministic of all machines conceived by the human mind, to produce ”random” numbers. More than perverse, it may seem to be a conceptual impossibility. Any program, after all, will produce output that is entirely predictable, hence not truly ”random”.

Press *et al*. Numerical Recipes

Random numbers



A perfect random number generator should produce numbers (”pseudorandom numbers”) that appear to be perfectly random, unless you happen to know both the algorithm and its internal state.

Is this a sequence of random numbers ?

0.242797434
0.696527659
0.540087878
0.256856381
0.985251605
0.123984143
0.801557302
0.773549854
0.052133180
0.202336564
0.670698583
0.431537956
0.858359396
0.446797788
0.330280125
0.017940610
0.527835488
0.330602377
0.434296846
0.227186769
0.327907294
0.137846455
0.785346388
0.317193448
0.070166930
0.295625895
0.584298729
0.309196233
0.660883903
0.475833952
0.341453462
0.808556079
0.402291059
0.305753976
0.807047486
0.047531273
0.858093679
0.980155766
0.478444427
0.215273425
0.100494504
0.011168224
0.704353213
0.064954675

Linear congruential random number generator

Linear congruential generator, the most commonly used

$$I_{j+1} = (aI_j + c) \pmod{m}$$

1. choose an initial "seed" value I_0
2. generate a sequence of integers I_j
3. a random number in the interval]0,1[is obtained from $\xi_j = I_j/m$

The sequence is generated according to:

2a. input I_j

2b. construct $aI_j + c$

2c. divide by m and determine the remainder

2d. use that as the new integer I_{j+1}

Careful choice of a, c and m leads to a full period sequence, a sequence where all integers between 0 and m appear once and only once.

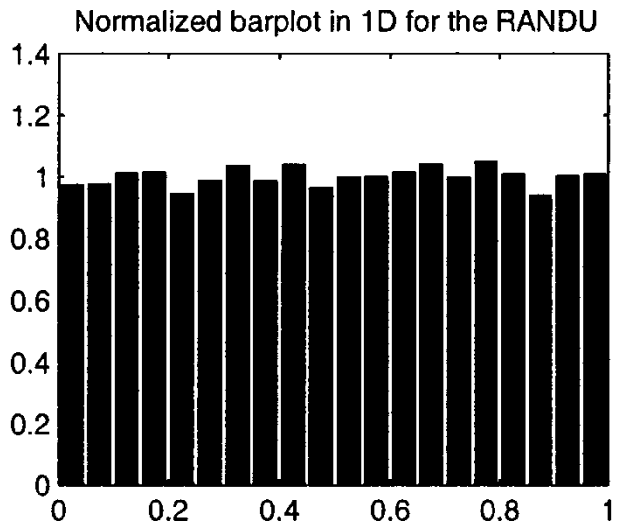
Minimal standard generator

$$\begin{aligned} a &= 16807 \\ c &= 0 \\ m &= 2^{31} - 1 = 2\ 147\ 483\ 647 \end{aligned}$$

proposed by Lewis, Goodman, and Miller.

Tests of random numbers

Do the random numbers have the correct distribution?



The infamous generator **RANDU** by IBM

”We can guarantee that each number is random individually, but we don’t guarantee that more than one of them is random.”

Linear congruential generator

$$I_{j+1} = (aI_j + c) \pmod{m}$$

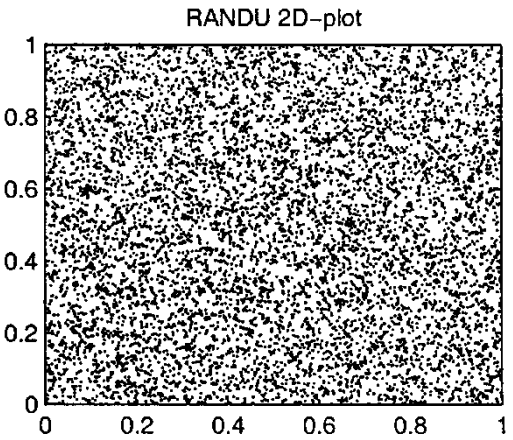
RANDU

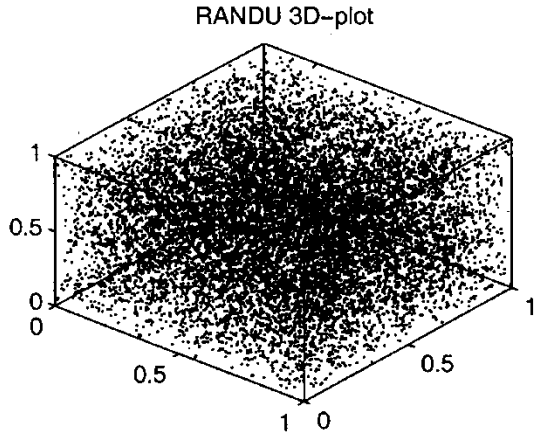
$$\begin{aligned} a &= 65539 \\ c &= 0 \\ m &= 2^{31} = 2\ 147\ 483\ 648 \end{aligned}$$

used by IBM mainframe computers (and others) during the 1960s

Tests of random numbers

Are subsequent random numbers uncorrelated?





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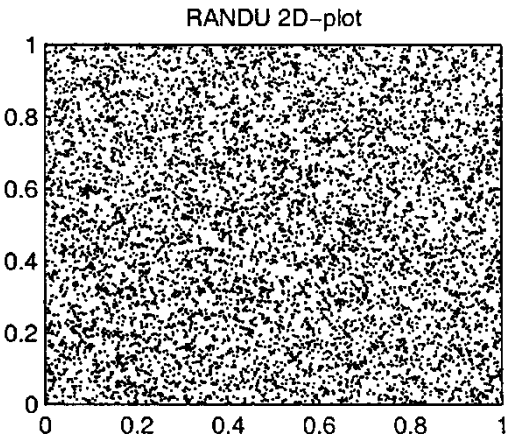
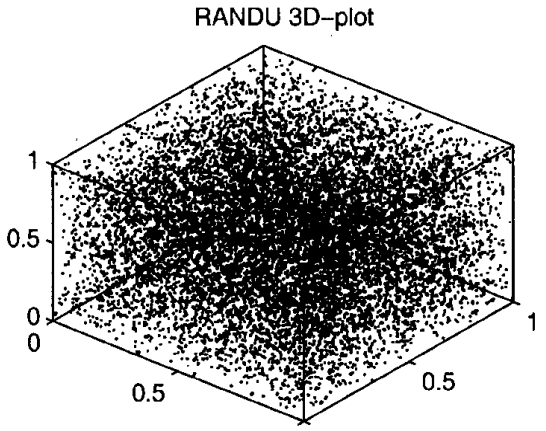
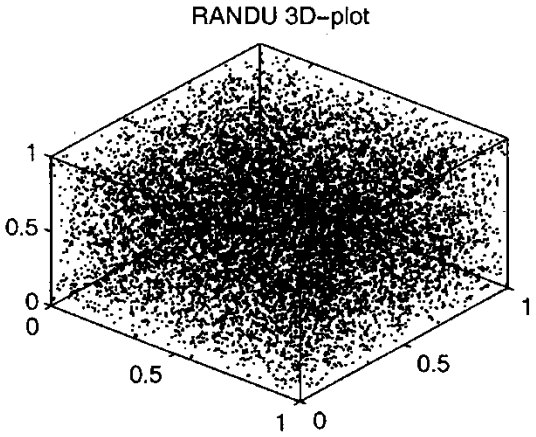
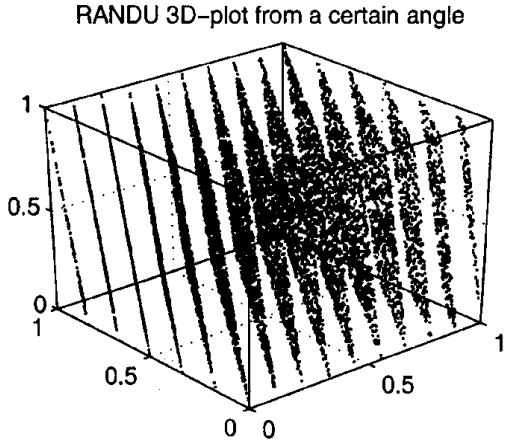








Random numbers

Content:

- Random number generators
- Uniform random numbers
- Non-uniform random numbers:
  1. Transformation method
  2. Rejection method

Non-uniform random numbers – Transformation method

ξ – uniform random number, η – non-uniform random number

Discrete case: $i = 1, \ldots, N$

Probability function

$$p_i \equiv p(i) \; ; \; \sum_{i=1}^{N} p_i = 1$$

Cumulative probability function

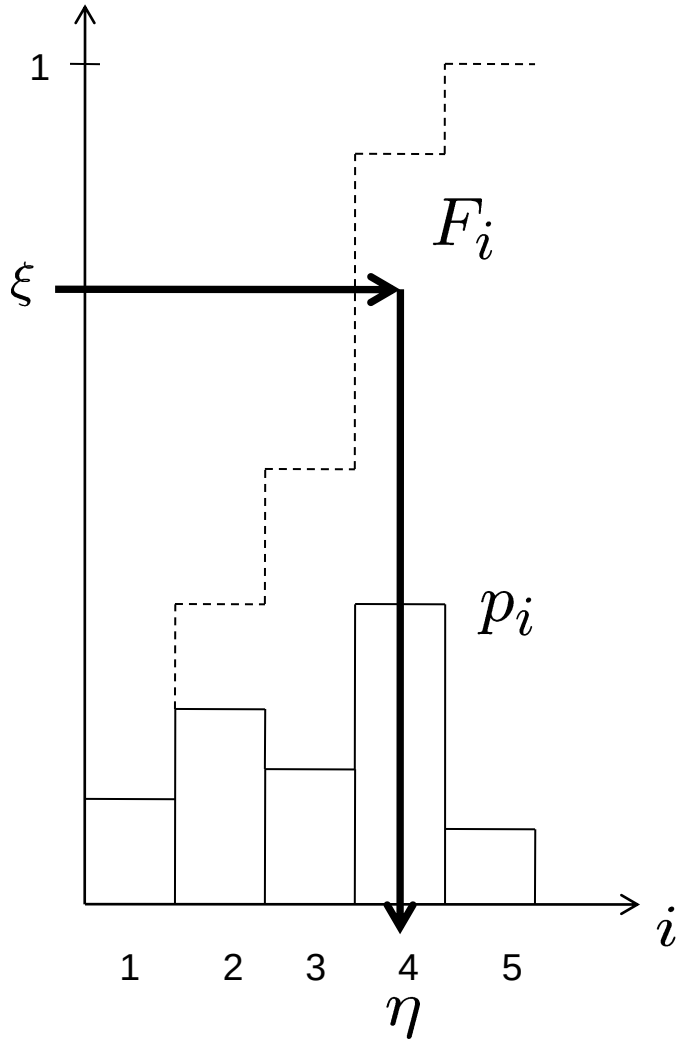
$$F_i \equiv \sum_{j=1}^{i} p_j$$

Transformation method

$$F_{i-1} \leq \xi \leq F_i$$

and

$$\eta = i$$



Non-uniform random numbers – Transformation method

ξ – uniform random number, η – non-uniform random number

Continuous case: x ; $a \leq x \leq b$

Probability function

$$p(x) \; ; \; \int_a^b p(x)\, dx = 1$$

Cumulative probability function

$$F(x) \equiv \int_a^x p(x')dx'$$

Transformation method

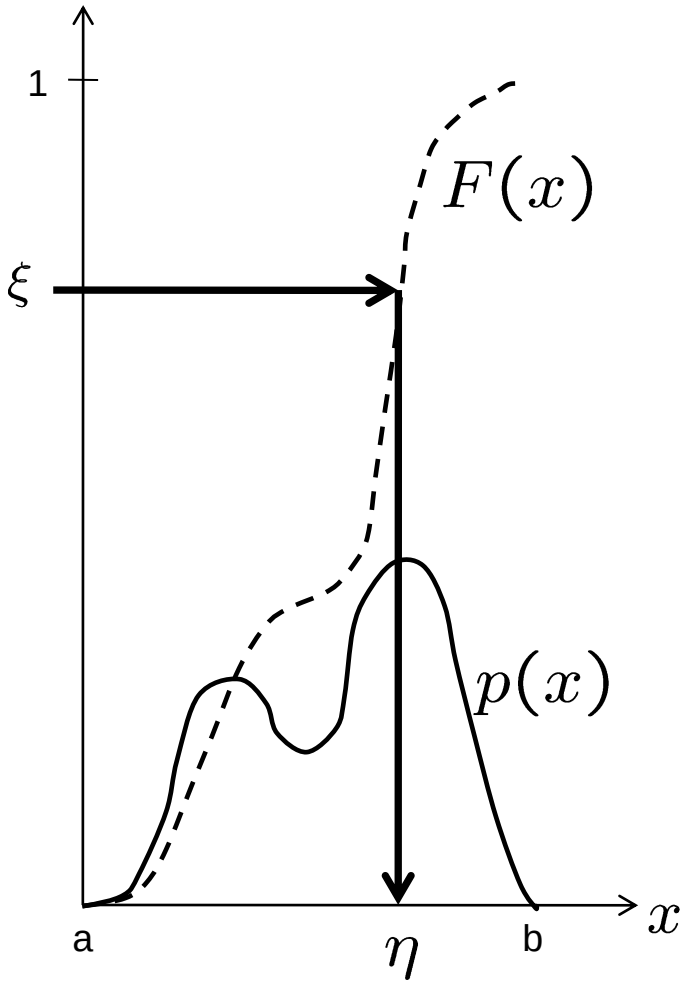
$$F(x - dx) \leq \xi < F(x)$$

i.e.

$$F(x) = \xi$$

and

$$\eta = F^{-1}(\xi)$$



Transformation method - examples

Uniform distribution

$$p(x) = \begin{cases} 1/(b-a) & \text{if } \; a \leq x \leq b \\ 0 & \text{otherwise} \end{cases}$$

which implies that

$$\eta = a + (b-a)\xi$$

Exponential distribution

$$p(x) = \begin{cases} \lambda^{-1} \exp(-x/\lambda) & \text{if } \; 0 \leq x < \infty \\ 0 & \text{otherwise} \end{cases}$$

which implies that

$$\eta = -\lambda \ln(1-\xi)$$

or

$$\eta = -\lambda \ln(\xi)$$

Gaussian distribution

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-(x-\mu)^2/2\sigma^2\right]$$

$$-\infty < x < \infty$$

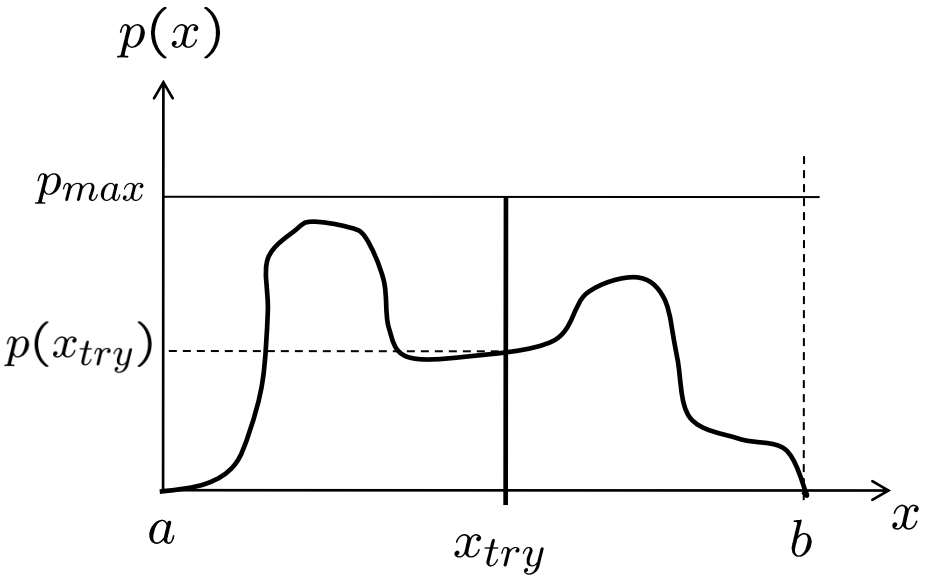
which implies that (Box-Müller method)

$$\begin{cases} \eta_1 = \mu + \sigma\sqrt{-2\ln\xi_1}\ \cos(2\pi\xi_2) \\ \eta_2 = \mu + \sigma\sqrt{-2\ln\xi_1}\ \sin(2\pi\xi_2) \end{cases}$$

Non-uniform random numbers – Rejection method

ξ – uniform random number, η – non-uniform random number

The *rejection method* is more general than the transformation method and can be used for both discrete and continuous random numbers.



Consider a probability distribution $p(x)$ on the interval [a,b]. Choose a value p_{max} such that

$$p_{max} \geq p(x), \quad a < x < b$$

1. Generate a uniform random number ξ_1 and determine a trial value

$$x_{try} = a + (b - a)\xi_1$$

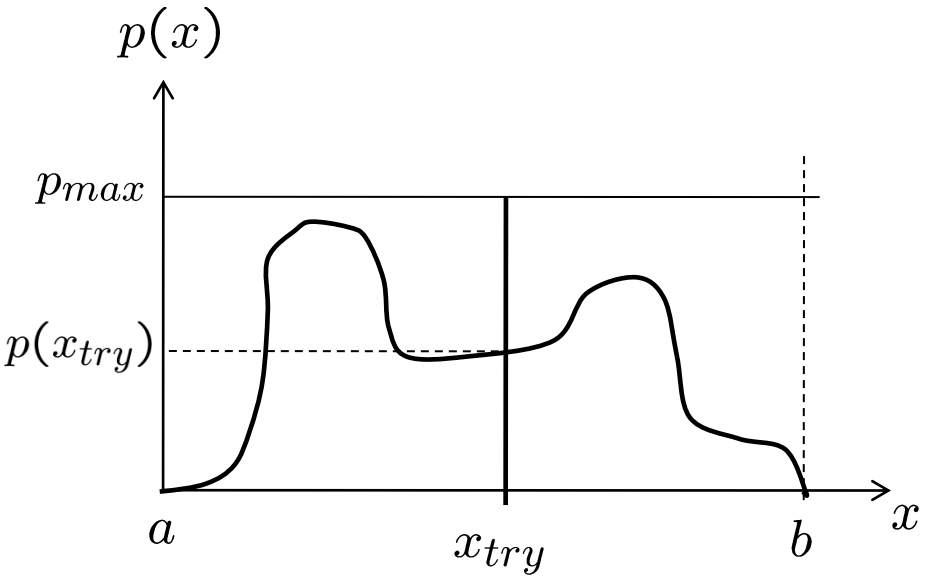
2. Generate another random number ξ_2 and accept the trial value

$$\eta = x_{try} \quad \text{only if} \quad \xi_2 \leq \frac{p(x_{try})}{p_{max}}$$

Non-uniform random numbers – Rejection method

ξ – uniform random number, η – non-uniform random number

The *rejection method* is more general than the transformation method and can be used for both discrete and continuous random numbers.



The method can be made more efficient and also applicable on infinite intervals by instead of p_{max} introducing a comparison function

$$f(x) \geq p(x) \quad \forall x$$

and with $\int f(x)dx$ finite.