

Simulations in Statistical Physics

Course for MSc physics students

János Kertész

Lecture 1

Requirements

- This course builds mostly on statistical physics and programming. The introduction contains a brief memory fresh up about statistical physics, but this is NOT enough to complete successfully the course, even less to pass the rigorosum in theoretical physics (research physics specialization). Minimum requirement for this course is the knowledge of statistical physics as it is taught in the course Theoretical Physics II (BSc applied physics specialization).
- Knowledge of one of the following programming languages is necessary: C, C++ or FORTRAN
- The knowledge of English is assumed.

Conditions for the exam

- Mid November all students get a home work task, which has to be solved individually. Using one of the above mentioned languages the student has to write a transparent, well commented running program. In addition, she/he has to prepare a pdf file where the results obtained by the program are shown and explained. The successful solution of the home work is the condition for completing the course (signature) and it is also taken into account for the mark. The complete solution (program + pdf file) should be sent to the email address kertesz@phy.bme.hu not later than 6 working days before the oral exam.
- The oral exam is based on questions about the material of the lectures.

Suggested literature

- D.W. Heermann: Computer simulation methods in theoretical physics, Springer, 1995
- D. Landau and K. Binder: A guide to Monte Carlo simulations in statistical physics (Cambridge UP, 2000)
- D. Rapaport: The art of molecular dynamics programming (Cambridge UP, 2004)
- J. Kertész and I. Kondor (eds): Advances in computer simulation (Springer, 1998)

Statistical Physics (brief summary)

We will assume knowledge of the elements of TD.

The goal of statistical physics is to

- Give microscopic explanation of equilibrium and non-equilibrium TD
- Calculate material properties from microscopic principles (specific heat C_p , resistivity etc.)
- Explain phenomena related to the large number of particles involved (fluctuation phenomena, superconductivity, phase transitions, pattern formation etc.)

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Closed system: All interactions with the world outside the system are excluded

TD equilibrium is reached after long time in a closed system.

A **subsystem** is a part of a closed system, which may have different types of interactions with it. If the subsystem is MUCH smaller than the rest, the latter is a **reservoir**, as its intensive TD quantities are not affected by the subsystem. Nevertheless, the subsystem can be macroscopically large ($N \sim 10^{23}$)

Micro-state: Classically it is a cell of volume h^{3N} in the $6N$ dimensional **phase space**, built from the coordinates and momenta of the particles. (Planck's constant h comes from the correspondence principle.) In QM it is a quantum state of the macroscopic system but we deal here mostly with classical systems.

Macro-state is the state of the macroscopic system as characterized by the TD and HD quantities.

In TD equilibrium **detailed balance**:

$P_i^{eq} w(i \rightarrow j) = P_j^{eq} w(j \rightarrow i)$ is fulfilled as a consequence of **microscopic reversibility**. Here P_i^{eq} is the probability that the equilibrium system is in the micro state i and $w(i \rightarrow j)$ is the probability of transition from state i to j per unit time. Detailed balance expresses that in equilibrium the direct and inverse reactions balance each other. If a system obeys detailed balance and there is no external drive, it converges to equilibrium.

Many of the quantities characterizing equilibrium are measured as **time averages** of a dynamical variable (here A):

$$\bar{A} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(q(t), p(t)) dt$$

where the $3N$ coordinates and momenta are not shown explicitly. This is what we observe in a measurement (not with $T \rightarrow \infty$ but with a macroscopic T).

In statistical physics we calculate the above quantity by **ensemble averages**:

$$\bar{A} = \frac{1}{h^{3N} N!} \int A(q, p) P^{eq}(q, p) dq dp$$

where both terms in the prefactor have QM origin. The $3N$ integrals in q go as allowed by the volume.

The equivalence between the time and ensemble averages can be established if the system is assumed to be **ergodic**, i.e., the trajectory in the phase space visits all the cells allowed by the conditions (e.g., energy).

The P_i^{eq} -s can be calculated assuming the **principle of equal probabilities** for closed systems with energy E between $E+\delta E$, which states for this case (**microcanonical ensemble**):

$$P_i^{eq} = \begin{cases} \frac{1}{\Omega(E, \delta E)} & \text{if } E < H(q, p) < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

$\Omega(E, \delta E)$ is the number of micro-states having energy in this regime:

$$\Omega(E, \delta E) = \frac{1}{h^{3N} N!} \int_{E \leq H(q, p) \leq E + \delta E} dq dp$$

For quantities, which are not averages of dynamic variables extra definitions are needed. The **entropy** S is defined as:

$$S = -k_B \sum_i P_i^{eq} \ln P_i^{eq} \quad \text{where } k_B = 1.38 \times 10^{-23} \text{ J/K}$$

is Boltzmann's constant. If this is applied to the case of the microcanonical ensemble:

$S = k_B \ln \Omega(E, \delta E)$, which is **Boltzmann's relationship**. Having the entropy as a function of the energy, we can calculate the **temperature** T :

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

If we investigate a subsystem P_i^{eq} depends on the interactions the subsystem has with the reservoir. In physics, the most important case is, when there is thermal interaction (energy exchange, **canonical ensemble**). Then

$P_i^{eq} = \frac{e^{-\beta E_i}}{Z}$ where $\beta = 1/k_B T$ and $Z = \sum_j e^{-\beta E_j}$ is the **partition function**. It can be used to calculate the **free energy** (F):

$$F(T, V, N) = E - TS = -k_B T \ln Z$$

From the formulas it follows that for the specific heat C_V

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V, N} = k_B T^2 \overline{(\Delta E)^2}$$

where $\overline{(\Delta E)^2}$ is the mean square fluctuation of the energy

Formulas for this and other ensembles are summarized in the next table.

	Mikrokanonikus (E,V,N)	Kanonikus (T,V,N)	Nagykanonikus (T,V, μ)	(T,P,N)
megengedett változás	-	energia	energia és anyagmenny.	energia és térfogat
tartály	-	hő (β)	hő (β) és részecske ($\mu = -\alpha/\beta$)	hő (β) és térfogat ($P = \gamma/\beta$)
$\rho(i)$	$\frac{1}{\Omega(E,\delta E)} \quad E_i \in (E, E + \delta E)$	$e^{-\beta E_i} / Z$	$e^{-\beta(E_{i(N)} - \mu N)} / \mathcal{Z}$	$e^{-\beta(E_{i(V)} + PV)} / Y$
állapotösszeg	$\Omega(E, \delta E) = \omega(E)\delta E$	$Z = \sum_i e^{-\beta E_i} = \int_0^\infty \omega(E) e^{-\beta E} dE$	$\mathcal{Z} = \sum_N \sum_{i(N)} e^{-\beta(E_{i(N)} - \mu N)} = \sum_N e^{\beta \mu N} \int_0^\infty \omega_N(E) e^{-\beta E} dE$	$Y = \int_0^\infty e^{-\beta PV} \sum_{i(V)} e^{-\beta E_{i(V)}} = \int_0^\infty e^{-\beta PV} \int_0^\infty \omega_V(E) e^{-\beta E} dE dV$
potenciál	$S = k_B \ln \Omega$	$F = -k_B T \ln Z = E - TS$	$\Phi = -k_B T \ln \mathcal{Z} = E - TS - \mu N = -PV$	$G = -k_B T \ln Y = E - TS + PV = \mu N$
fund. egy.	$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$	$dF = -SdT - PdV + \mu dN$	$d\Phi = -SdT - PdV - N d\mu$	$dG = -SdT + VdP + \mu dN$
egyens. felt.	S max	F min	Φ min	G min
várható értékek		$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$	$\langle N \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$	$\langle V \rangle = -\frac{\partial \ln Y}{\partial \gamma}$
fluktuációk		$\langle (\Delta E)^2 \rangle = k_B T^2 C_V$	$\langle (\Delta N)^2 \rangle = k_B T N n \kappa_T$	$\langle (\Delta V)^2 \rangle = k_B T V \kappa_T$

The introduced statistical physics quantities and the laws of physics and probability theory enable to construct a profound microscopic basis of the laws of thermodynamics.

1st law of TD: $dE = \delta Q + \delta W$ (conservation of energy)

2nd law of TD: In a closed system entropy increases in spontaneous processes. (Ω becomes larger – however this law holds only statistically, though for macroscopic systems the probability of violating the 2nd law is VERY small.)

3rd law of TD: The entropy of pure, homogeneous materials goes to zero as $T \rightarrow 0$. (Quantum effect: The ground state is not macroscopically degenerate.)

Ideal gases

In an **ideal gas** the interactions between the particles can be

ignored. Classically: $H(q, p) = \sum_{i=1}^{3N} p_i^2 / 2m$, in QM: $\hat{H} = \sum_{i=1}^{3N} \hat{p}_i^2 / 2m$

where we should in addition keep in mind that the identical particles are indistinguishable.

The partition function of the classical ideal gas is:

$$Z_N = \frac{Z_1^N}{N!}, \text{ where } Z_1 = \frac{V}{h^3} \left(\sqrt{2m\pi k_B T} \right)^{3/2}$$

The Maxwell distribution for the absolute value of the velocity is

$$P(v)dv = \left(\frac{m}{2\pi k_B T} \right)^{3/2} 4\pi e^{-mv^2 / 2k_B T} v^2 dv \quad \text{valid also for interacting systems. The average}$$

squared velocity is $\langle v^2 \rangle = \frac{3k_B T}{m}$, which is a manifestation of the equipartition theorem valid for classical systems.

If the de Broglie wavelength $\lambda_T = \frac{h}{\sqrt{2m\pi k_B T}}$ is not anymore

small, quantum corrections have to be taken into account, being different for bosons (effective attraction) and fermions (effective repulsion).

At low temperatures we have the „degenerate quantum gases” characterized by the Fermi-Dirac (upper sign) or Bose-Einstein (lower sign) distributions, i.e. for the average occupation number of particles in the one particle quantum state m :

$$\bar{n}_m = \frac{1}{e^{\beta(\varepsilon_m - \mu)} \pm 1}$$

For fermions at temperature $T \ll T_F$ Fermi temperature only the particles in the $k_B T$ neighborhood of the Fermi energy can be excited.

For Bosons with constant number of particles there is a phase transition at low temperatures: Bose-Einstein condensation.

Applications 1: Ideal gases

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Applications 2: Phase transitions

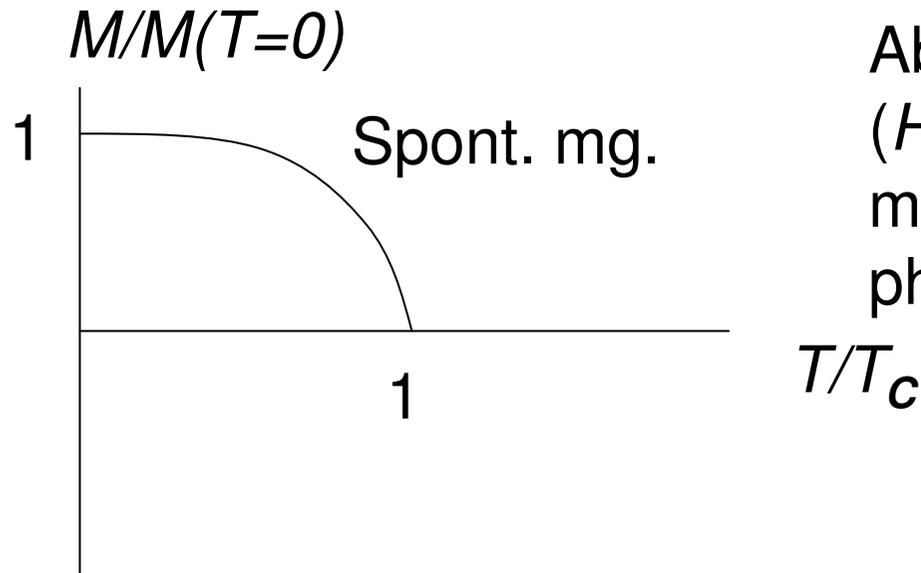
Phase: State of matter characteristic for a region of TD space, in which the equation of state is an analytical function of its variables.

Phase transition: The transition between phases. In the coordinate system of intensive parameters the phases are separated by lines (phase diagram). Phase transitions are characterized by lines and points of non-analyticity. (Only possible in the Thermodynamic Limit ($N, V, E \dots \rightarrow \infty$, densities finite.)

Order of the transition: Which derivative of the Gibbs free energy (free enthalpy) becomes discontinuous.

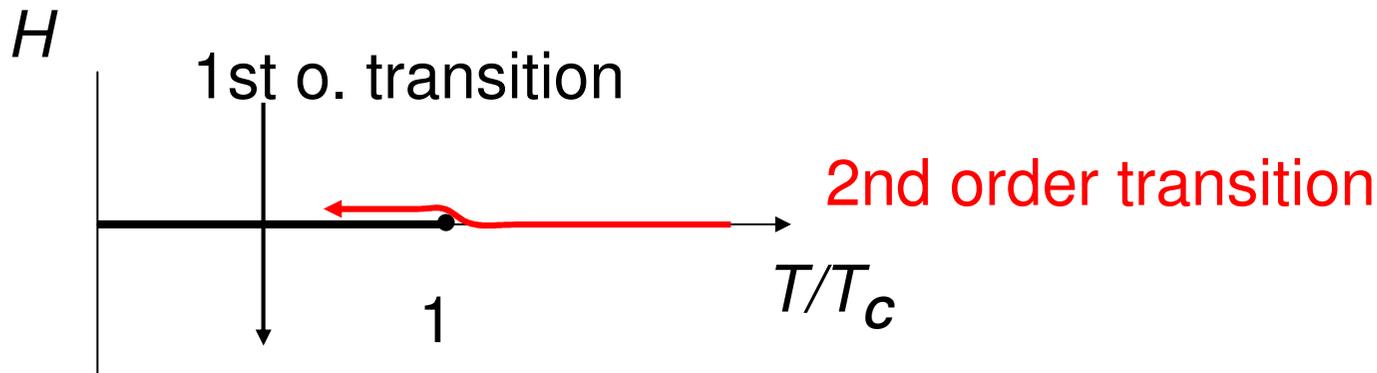
Order parameter: Indicator of the order, it also reflects the symmetry properties of the transition.

Para-ferromagnetic phase transition:

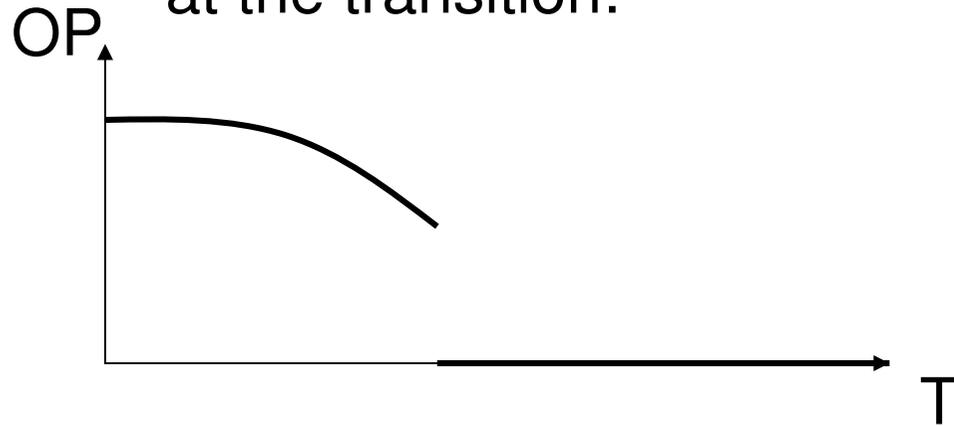


Above the Curie temperature T_c ($H = 0$) there is no spontaneous magnetization (paramagnetic phase).

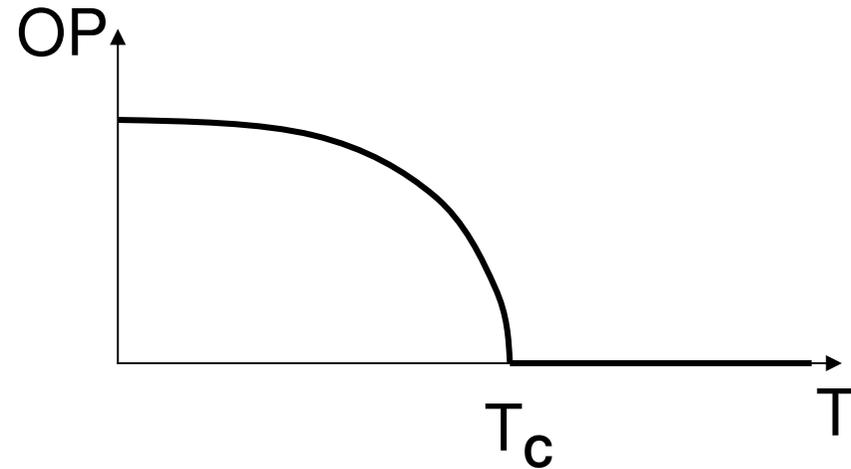
Low temperature phase: Broken symmetry.
Order parameter: Normalized magnetization
Phase diagram:



First order transitions are discontinuous: The order parameter changes discontinuously at the transition:



Second order transitions are continuous:



The continuous transition point is also called critical point (c.f. liquid-gas transitions) and the related phenomena are critical phenomena:

1. Many physical quantities show power law behavior
2. Critical behavior of different systems can be ordered into universality classes, which can be identified by the critical exponents

E.g., the correlation function in a magnetic system is:

$$G(r) = \langle \mathbf{s}(R) \cdot \mathbf{s}(R + r) \rangle - \langle \mathbf{s} \rangle^2$$

Where \mathbf{s} is the local magnetic moment („spin”), and the bracket means thermal average.

Close to the critical point it behaves like:

$$G(r) \approx \frac{1}{r^{d-2+\eta}} \exp\left(\frac{-r}{\xi}\right)$$

where $\xi \propto |T - T_c|^{-\nu}$ is the correlation length.

The correlation length, i.e., the characteristic size of the regions, where the fluctuations are correlated diverges at the critical point, $T = T_c$ and $h = 0$ (h is the external field.)

ν and η critical exponents.

Near to the critical point G is a generalized homogeneous function of its variables:

$$G(r, t, h) \propto b^{-2\beta/\nu} G(r/b, b^{y_t} t, b^{y_h} h) \quad \text{for } t \rightarrow 0^\pm, h \rightarrow 0.$$

Where $t = (T - T_c) / T_c$ is the reduced temperature. The notation of the exponents follows the conventions. We will use the following relationships:

$$\chi = \beta V \int G(\mathbf{r}) d^3 r = \beta \langle (\mathbf{s} - \langle \mathbf{s} \rangle)^2 \rangle$$

$$\chi = \frac{\partial M}{\partial h} \qquad M = \frac{\partial F}{\partial h} \qquad C = \frac{\partial F}{\partial T}$$

M : magnetization (OP), χ : susceptibility C : specific heat

Starting from the generalized homogeneity of G , we obtain:

$$C_{(h=0)} \sim |t|^{-\alpha}$$

$$M_{(h=0)} \sim (-t)^\beta, \quad t < 0$$

$$\chi_{(h=0)} \sim |t|^{-\gamma}$$

$$M_{(t=0)} \sim h^{1/\delta}$$

We have altogether 8 exponents $(\alpha, \beta, \gamma, \delta, \eta, \nu, y_t, y_h)$

$$y_t = 1/\nu, \quad y_h = d - \beta/\nu,$$

Scaling relations:

$$\alpha + 2\beta + \gamma = 2$$

$$\delta = 1 + \gamma/\beta$$

$$d\nu = 2 - \alpha$$

$$\nu = \gamma/(2 - \eta)$$

Two independent exponents to identify universality classes