

Review of previous lecture (April 25)

partition function and density matrix of canonical ensemble

$$Z_c(T) = \text{Tr} \exp\left(-\frac{H_c}{k_B T}\right)$$

$$\rho_c = Z_c^{-1} \exp\left(-\frac{H_c}{k_B T}\right)$$

$$\text{Tr} \rho_c = 1$$

state function of the canonical ensemble: free energy

$$F(T, V, N) = -k_B T \cdot \log Z_c(T) = E - TS_c$$

$$dF = -S_c dT - p dV + \mu dN$$

ergodicity

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(\{x_i(t), p_i(t)\}) = \int \frac{d^3x}{h^{3N}} \frac{d^3p}{N!} \underbrace{P_{eq}(\{x_i, p_i\})}_{\text{equilibrium probability distribution}} A(\{x_i, p_i\})$$

equilibrium probability
distribution

\Rightarrow time average = ensemble average

II Phase transitions

phases and phase boundaries

consider a system in a volume V

the free energy $F(T, V, N)$ is an extensive quantity:

$$F(V) = V \cdot f_b(V) + S f_s(s) + O(L^{d-2}) + \dots$$

↓
bulk free energy
per unit volume

↘
surface free
energy per unit area

consider $V \rightarrow \infty$ (if limit exists):

$$f_b = \lim_{V \rightarrow \infty} \frac{F(V)}{V} \quad \text{resp.}$$

$$f_b = \lim_{N_L \rightarrow \infty} \frac{F(N_L)}{N_L}$$

(for lattice systems
with N_L lattice sites)

$$f_s = \lim_{S \rightarrow \infty} \frac{F(V) - f_b \cdot V}{S}$$

To make this limit $V \rightarrow \infty$ meaningful, it is typically taken in such a way that the particle density remains constant, i.e.

$$\lim_{V \rightarrow \infty, n = \frac{N}{V} = \text{const}}$$

This limit is called the thermodynamic limit.

Consider the product $\beta \cdot H$ (as it appears in the exponential weight in the canonical ensemble)

Let $\beta \cdot H$ depend on D couplings/parameters K_i and the corresponding degrees of freedom Θ_i :

$$-\beta H[K] = \sum_{i=1}^D K_i \Theta_i$$

↳ note that this sum also depends on T due to the factor β

example: Ising model (spins on a lattice)

$$H = - \sum_i B_i \sigma_i - \sum_{i,j} J_{ij} \sigma_i \sigma_j - \sum_{i,j,k} K_{ijk} \sigma_i \sigma_j \sigma_k + \dots$$

external magnetic field

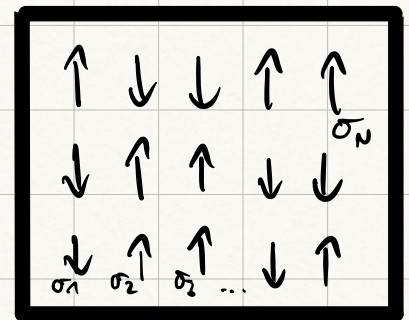
two-spin interactions

three spin int.

$$\Rightarrow \{k\} = \{T, B_i, J_{ij}, K_{ijk}, \dots\}$$

$$\{\theta\} = \{\sigma_i, \sigma_i \sigma_j, \sigma_i \sigma_j \sigma_k, \dots\}$$

$$S_i = \pm 1$$



Then the bulk free energy per unit volume is a function of all couplings: $f_b = f_b(\{k\})$

Phases are defined based on the analytic properties of $f_0(\{k\})$.

phases are regions in which f_0 is analytic

the axes of the phase diagram are the couplings k_i , hence the dimension of the phase diagram is D .

phase boundaries are points, lines, planes of non-analyticities of $f_0(\{k\})$ as a function of k_i

classification of phase transitions (Ehrenfest):

- a) at least one $\frac{\partial f_0[k]}{\partial k_i}$ is discontinuous across a phase boundary (first order phase transition)
- b) all $\frac{\partial f_0[k]}{\partial k_i}$ are continuous across the phase boundary (continuous or 2nd order phase transition)

it can be shown that $f_0[k]$ is always continuous.

↳ later more

note that the phase definition is ambiguous as there are cases in which a path exists along which $f_0[k]$ is always analytic and allows to go from one side of a phase boundary to another.

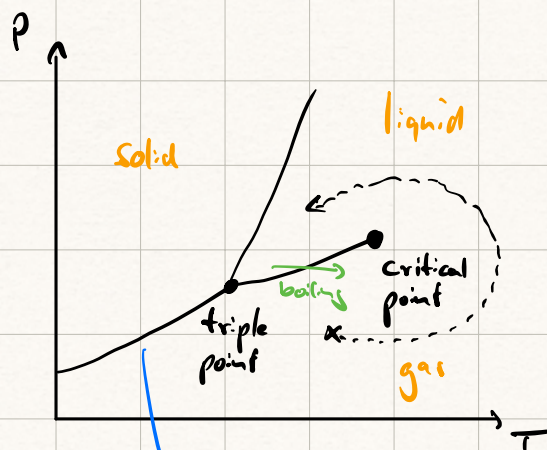
example: liquid gas transition

When boiling a liquid there is latent heat involved, i.e. the difference in entropy

$$\Delta S = S_{\text{gas}} - S_{\text{liquid}} > 0$$

at the two sides of the phase boundary.

Since $S = - \left. \frac{\partial F}{\partial T} \right|_V$, such a transition is of first order.



phase boundaries can be visualized as walls in the D -dim phase space, walls need to have dimension $D-1$ to act as phase boundary, walls can have a finite "height" that allows to pass from one side to the other

How can phase transitions occur in the first place?

$$F = -k_B \cdot T \cdot \log Z_c \quad \beta = \frac{1}{k_B \cdot T}$$

$$\Rightarrow e^{-\beta F} = \text{Tr} \left[e^{-\beta H} \right]$$

↑
Sum of terms

↖ analytic function (if H is analytic)

How can f_b develop non-analyticities?

For the definition of phases the thermodynamic limit $V, N \rightarrow \infty$ plays a central role.

Phases are generally only defined in this limit!

Central question in statistical physics:

How can the phase diagram of a system be computed as a function of the parameters k : including the nature of the phase transitions.

Phase transitions at $T=0$ and the Ising model

consider Ising model with a constant external magnetic field B and a constant two-spin interaction J that couples nearest neighbors

$$H = -B \sum_{i=1}^N \sigma_i - J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$$

free energy: $F(T, B, J) = -k_B T \log \text{Tr} e^{-\beta H}$

$$\hookrightarrow \sum_{\sigma_1 = \pm 1} \sum_{\sigma_2 = \pm 1} \dots \sum_{\sigma_N = \pm 1}$$

magnetization (per site): $m = \frac{1}{N} \sum_{i=1}^N \langle \sigma_i \rangle$

$$= \frac{1}{N} \sum_{i=1}^N \text{Tr} (\sigma_i)$$

$$= \frac{1}{N} \sum_{i=1}^N \frac{\text{Tr} (\sigma_i e^{-\beta H})}{\text{Tr} e^{-\beta H}}$$

$$= -\frac{1}{N} \frac{\text{Tr} \left(\frac{\partial H}{\partial B} e^{-\beta H} \right)}{\text{Tr} e^{-\beta H}}$$

$$= -\frac{1}{N} \frac{\partial F}{\partial B} = -\frac{\partial f}{\partial B}$$