I PHASE TRANSITIONS

Phase transitions are phenomena related to *interacting* systems with many degrees of freedom, where the particles show a collective behaviour if the state variables are changed. Examples include the condensation of a van der Waals-gas, which liquefies at low temperatures, the ferromagnetic states of coupled spin systems or the condensation of quarks and gluons into nuclei. From this point of view, Bose-Einstein-condensation is very different: It takes place already in ideal systems, purely as a consequence of the symmetry requirement on the bosonic wave function, without any interaction between the particles.

I.1 *Van der Waals-gases*

The Hamilton-function of ideal non-relativistic kinetic systems is given by

$$H(p_i, q_i) = \sum_i^N \frac{\boldsymbol{p}_i^2}{2m} \tag{I.463}$$

as a straightforward sum over the individual kinetic energies. The canonical partition function is then computed as

$$Z(T, V, N) = \frac{1}{N!} \left[\frac{1}{h^3} \int d^3 p \exp\left(-\beta \frac{\boldsymbol{p}^2}{2m}\right) \right]^N \cdot V^N = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \tag{I.464}$$

where the integral has units of an inverse length cubed, so we set it to λ^{-3} to make Z dimensionless. From the logarithmic partition function one obtains the Helmholtz free energy F,

$$F(T, V, N) = -k_B T \ln Z(T, V, N) \tag{I.465}$$

and through logarithmic derivatives $p = -\partial F/\partial V = N k_B T/V$ the equation of state of the ideal gas. The spatial integration $\int d^3 q$ contributions one power of V for every particle, therefore $Z \propto V^N$. The spatial integration is non-trivial, if there are interactions in the system, for instance through a (pairwise) potential in the Hamilton-function,

$$H(\{p_i\}, \{q_i\}) = \sum_i^N \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j}^N V(|\boldsymbol{q}_i - \boldsymbol{q}_j|) \tag{I.466}$$

where the summation condition $i < j$ makes sure that every interaction is only counted once. The potential keeps the partition function from separating.

$$Z(T, V, N) \neq \frac{1}{N!} Z(T, V, 1)^N \tag{I.467}$$

unlike in the non-interacting case. In summary, the effect of the mutual interaction between the particles is to introduce as a more elaborate $d^3 q$-integration, leading to a new expression for the accessible spatial part of phase space, depending on the interaction potential.

I.1.1   Typical shapes of interaction potentials

Non-ideal gases are characterised by interactions between their particles, for instance through a Lennard-Jones-potential

$$V(r) = 4\epsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right] \tag{I.468}$$

where the physical idea would be that at small distances there is repulsion between the atoms, caused by Pauli-exclusions of the electron shells (called Born-repulsion), and at large distances one gets induced electrical dipoles, leading to a Coulomb-attraction. The equilibrium position is given by

$$\frac{dV}{dr} = 0 = \left[-12\left(\frac{r_0}{r}\right)^{11} + 6\left(\frac{r_0}{r}\right)^5\right]\cdot\frac{r_0}{r^2} \quad \rightarrow \quad \left(\frac{r_0}{r}\right)^6 = \frac{1}{2} \quad \text{and therefore} \quad r \simeq 1.12 r_0 \tag{I.469}$$

The canonical (We assume that the particle number N is fixed and that volume and temperature are controlled) partition sum is then given by

$$Z(T, V, N) = \frac{1}{N!}\left[\frac{1}{h^3}\int d^3 p \exp\left(-\frac{\beta \boldsymbol{p}_i^2}{2m}\right)\right]^N \cdot \int \prod_i d^3 q_i \cdot \exp\left(-\beta\sum_{i<j} V(q_{ij})\right)$$

$$= Z_{\text{id}}(T, V, N) \cdot \underbrace{\int \prod_i d^3 q_i \cdot \exp\left(-\beta\sum_{i<j} V(q_{ij})\right)}_{\sim Z_{\text{int}}(T, V, N),\text{ not factorisable!}}$$

with the abbreviation $q_{ij} = |\boldsymbol{q}_i - \boldsymbol{q}_j|$; and the most important observation would be that this partition does not separate due to the integral involving the relative distances between the particle pairs.

Computing the equation of state by isolating the pressure as a function of temperature and volume from the derivative of the Helmholtz free energy $F(T, V, N) = -k_B T \ln Z(T, V, N)$, which in turn depends logarithmically on the canonical partition function yields

$$p = -\frac{\partial F}{\partial V} = p_{\text{id}} + p_{\text{int}} = \rho k_B T(1 + B\rho + \dots) \tag{I.470}$$

such that one immediately notices a correction to the ideal equation of state parameterised by B. The correction is proportional to the number of particle pairs, $\rho^2 \sim N^2 \sim N(N-1)$.

The parameter B can be determined approximatively from a so-called virial expansion, weirdly enough, one can achieve this and make the problem simpler by making it more complicated: Using the macrocanonical partition $\mathcal{Z}(T, V, \mu)$ one can derive B. The first step is to write out a power-series in the fugacity $z = \exp(\beta\mu)$, where higher-order terms will be neglected. The chemical potential μ is re-introduced as being small but nonzero, and the same applies to the fugacity:

$$\mathcal{Z}(T, V, \mu) = \sum_N \underbrace{Z(T, V, N)}_{=Z_N}\cdot z^N = Z_0 + z Z_1 + z^2 Z_2 + \dots \tag{I.471}$$

where $Z_0 = 1$, as can be easily checked. The interesting term is Z_2, because it will contain the d^3q-integration over particle pairs, whose mutual interactions make the gas non-ideal:

$$Z_2 = \frac{1}{2!\lambda^6} \int d^3q_1 \int d^3q_2 \exp(-\beta V(q_{12})) \tag{I.472}$$

For evaluating the integration one can introduce relative coordinates, $\boldsymbol{q}_2 = \boldsymbol{q}_1 + \boldsymbol{r}$ with corresponding volume elements, $d^3q_2 = d^3r$ for fixed $\boldsymbol{q}_1$. Then, Z_2 becomes

$$Z_2 = \frac{1}{2!\lambda^6} \int d^3q_1 \int d^3r \exp(-\beta V(r)) = \frac{4\pi V}{2\lambda^6} \int r^2 dr \exp(-\beta V(r)) \tag{I.473}$$

where the first integral becomes simply the volume and the second integral can be simplified using spherical symmetry of the interaction potential. The macrocanonical potential

$$J = -k_B T \ln \mathcal{Z} = -pV \quad \rightarrow \quad \frac{pV}{k_B T} = \ln \mathcal{Z} \simeq \ln(1 + zZ_1 + z^2 Z_2 + \ldots) \tag{I.474}$$

The logarithm can now be expanded using the smallness of the fugacities with the Taylor-expansion $\ln(1 + x) \simeq x - \frac{x^2}{2}$, such that the ideal gas law starts acquiring corrections from terms that reflect the number of particle pairs!

$$\frac{pV}{k_B T} \simeq zZ_1 + z^2 Z_2 - \frac{z^2}{z} Z_1^2 + \ldots \tag{I.475}$$

at order z^2, with the new quadratic term $\propto Z_1^2$ appearing due to the Taylor-expansion. Therefore, this can be compared with our previous result

$$\frac{pV}{k_B T} \simeq V(\rho + B\rho^2 + \ldots) \tag{I.476}$$

and B is then obtained through a comparison of coefficients. From the fugacity one can derive derivative expressions according to

$$z = \exp(\beta\mu) \quad \rightarrow \quad \mu = \frac{1}{\beta} \ln z \quad \text{and therefore} \quad \frac{\partial}{\partial\mu} = \beta z \frac{\partial}{\partial z} \tag{I.477}$$

such that the particle number N follows from the macrocanonical partition through differentiation by z instead of μ:

$$N = \frac{1}{\beta} \frac{\partial}{\partial\mu} \ln \mathcal{Z} = z \frac{\partial}{\partial z} \ln \mathcal{Z} = \frac{\partial \ln \mathcal{Z}}{\partial \ln z} \simeq zZ_1 + z^2(2Z_2 + Z_1^2) \tag{I.478}$$

where we see a term $z = \frac{N}{Z_1} = \rho\lambda^3$ proportional to particle number, which reproduces the ideal gas, clearly from the 1-particle partition sum, as in the ideal, separating case. At quadratic order in z one first obtains an implicit relation

$$\frac{N}{Z_1} = z + \left(\frac{2Z_2 - Z_1^2}{Z_1}\right) z^2 \tag{I.479}$$

which is in fact a quadratic equation

$$Z = \frac{N}{Z_1}\left(1 - \frac{N}{Z_1}\frac{2Z_2 - Z_1^2}{Z_1}\right) \tag{I.480}$$

With the approximation $\sqrt{1+x} \sim 1 + \frac{x}{2} - \frac{x^2}{8}$ on the arrives, collecting all results, at

$$\frac{pV}{k_BT} = \ln \mathcal{Z} = Z_1\frac{N}{Z_1}\left(1 - \frac{N}{N_1}\left(\frac{2Z_2 - Z_1^2}{Z_1}\right)\right) + \frac{N^2}{Z_1}\left(Z_2 - \frac{Z_1^2}{2}\right) = N\cdot\left[1 - \left(Z_2 - \frac{Z_1^2}{2}\right)\frac{N}{Z_1^2}\right] \tag{I.481}$$

Since N and V both extensive one can make a replacement in the last term which makes an identification of the term involving Z_1 and Z_2 with B(T) possible, keeping in mind that $\rho V = N$,

$$B(T) = -\frac{V}{Z_1^2}\cdot\frac{Z_2 - Z_1^2}{2} = -\frac{1}{2}\int d^3r[\exp(-\beta V(r)) - 1] = -2\pi\int r^2 dr[\exp(-\beta V(r)) - 1] \tag{I.482}$$

As an approximation to the potential we use a piecewise constant function,

$$B(T) = \underbrace{-2\pi\int_0^d dr\, r^2}_{\text{small } r} - \underbrace{\int_d^{d+\delta} dr\, r^2[\exp(\beta\epsilon) - 1]}_{\text{intermediate } r} \simeq \frac{2\pi}{3}d^3 \quad - \quad 2\pi d^2\delta\beta\epsilon \tag{I.483}$$

which in the limit $\delta \ll d$ and $\beta\epsilon \ll 1$ gives as a final result a correction to the ideal gas law

$$\frac{pV}{k_BT} = N\left(1 + B(T)\frac{N}{V}\right) \tag{I.484}$$

in the form of a van der Waals-term, reflecting the interaction between the particles. The interaction strength, the shape of the interaction potential and the physical extension of the attractive and repulsive part determine together the numerical value of B.

I.2 *Ising-model for ferromagnetism*

The Ising-model is a discrete set of spin states, mostly arranged on a regular lattice, which can interact with an external magnetic field as well as mutually with the direct neighbours in the lattice. In contrast to paramagnetism where only the interaction with an external magnetic field and the corresponding term $\mathbf{B}\cdot d\mathbf{M}$ with a changing magnetisation $d\mathbf{M}$ exist, the collective interactions give rise to ferromagnetic effects such as spontaneous magnetisation. The Hamilton-function of interacting spins is given by

$$H = -J\sum_{(i,j)} S_iS_j - B\mu\sum_i S_i \quad \text{with} \quad \sum_{(i,j)} = \sum_i \sum_{i-n\le j\le i+n} \tag{I.485}$$

with a fixed summation over the neighbours of each spin at finite range while $i \ne j$ in the first term. Multiplying with β and defining $K = \beta J$ as well as $Q = \beta\mu B$ yields

$$\beta H = -K \sum_{(i,j)} S_i S_j - Q \sum_i S_i \qquad (I.486)$$

The modelling of interactions between spins follows the idea that parallel orientation is energetically favoured and antiparallel orientation disfavoured. The construction of a (canonical) partition sum now involves a Boltzmann-weighted summation over all lattice sites,

$$Z(K, Q, N) = \underbrace{\sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1}}_{2^N \text{ possible states}} \exp(-\beta H) \qquad (I.487)$$

with possibly periodic boundary condition to avoid edge effects. If $J > 0$ (or $K > 0$), parallel alignment is preferred leading ultimately to a spontaneous magnetisation if the temperature is not too high (below the Curie-temperature), which is referred to as ferromagnetism. The magnetisation is given by

$$M(K, Q) = \mu \left\langle \sum_i S_i \right\rangle \qquad (I.488)$$

The canonical partition sum for a 1-dimensional chain if $Q = 0$ is given by

$$Z = \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \exp(K(S_1 S_2 + S_2 S_3 + ... + S_{N-1} S_N))$$

$$= \sum_{S_1=\pm 1} \cdots \sum_{S_{N-1}=\pm 1} \exp(K(S_1 S_2 + S_2 S_3 + ... + S_{N-2} S_{N-1})) \cdot \underbrace{\sum_{S_N=\pm 1} \exp(K(S_{N-1} S_N))}_{=\exp(+K)+\exp(-K)=2\cosh K}$$

$$= (2 \cdot \cosh K)^N$$

so iteratively one obtains $Z = (2 \cosh K)^N$, and therefore for the Helmholtz energy F

$$F = -k_B T N \cdot \ln\left(2 \cosh \frac{J}{k_B T}\right) \qquad (I.489)$$

which reminds us of the result for paramagnetism, and would not show any spin correlation over large distances; in 1-dimensional lattices one does not observe ferromagnetic phase transitions.

I.2.1   Transfer matrix method for the Ising-model

There is an alternative elegant way of computing the canonical partition including effects of Q, starting again with the Hamilton-function and an additional cyclic boundary condition on the spin chain, $S_{N+1} = S_1$:

$$\beta H = -K \sum_{(i,j)} S_i S_j - Q \sum_i S_i \qquad (I.490)$$

Defining the transfer function

$$T(i, i+1) = \exp\left(KS_i S_{i+1} + \frac{1}{2}Q(S_i + S_{i+1})\right) \tag{I.491}$$

one can write the Boltzmann-factor as

$$\exp(-\beta H) = T(1,2) \cdot T(2,3) \cdots T(N,1) \tag{I.492}$$

including the periodic boundary, as mentioned before. There are only 3 possible values appearing in in the transfer function T for the possible choices ± 1 for S_i and S_j:

$$T = \begin{pmatrix} \exp(K+Q) & \exp(-K) \\ \exp(-K) & \exp(K-Q) \end{pmatrix} \tag{I.493}$$

So let's introduce a quantum mechanical notation with state vectors,

$$|S_i = +1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |S_i = -1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{I.494}$$

such that the entries in the transfer function T follow from forming the expectation values

$$T(i, i+1) = \langle S_i | T | S_{i+1} \rangle \tag{I.495}$$

This helps us to write the canonical partition as

$$Z = \sum_{\{S_i\}} \exp(-\beta H) = \sum_{\{S_i\}} \langle S_1 | T \underbrace{|S_2\rangle\langle S_2|}_{=\mathrm{id}} T |S_3\rangle \cdots \langle S_N | T | S_1 \rangle$$

$$= \sum_{S_1 = \pm 1} \langle S_1 | T^N | S_1 \rangle = (T^N)_{11} + (T^N)_{22} = \mathrm{tr}(T^N) = \lambda_1^N + \lambda_2^N$$

as the sum of the two possible eigenvalues of the transfer matrix, which is diagonal, ensuring that the eigenvalues exist and are real. The fastest way for getting the eigenvalues is the computation of the characteristic polynomial:

$$\det \begin{pmatrix} \exp(K+Q) & \exp(-K) \\ \exp(-K) & \exp(K-Q) \end{pmatrix} = 0 \tag{I.496}$$

which is a polynomial of order 2,

$$[\exp(K+Q) - \lambda] \cdot [\exp(K-Q) - \lambda] - \exp(-2K) =$$

$$\lambda^2 - 2\exp(K)\cosh Q \cdot \lambda + \exp(2K) - \exp(-2K) = 0 \tag{I.497}$$

Solving for the two zeros $\lambda_\pm$ yields

$$\lambda_\pm = \exp(K) \cdot \cosh Q \pm \sqrt{\cosh^2 Q - 2\exp(-2K)\sinh 2K} \tag{I.498}$$

such that the canonical partition becomes

$$Z = \lambda_+^N + \lambda_-^N = \lambda_+^N \left[1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right] \to \lambda_+^N \text{ for large N} \qquad \text{(I.499)}$$

The previous result is recovered if $Q = 0$: Then, the first eigenvalue is $\lambda_+ = \exp(K) + \exp(-K) = 2 \cosh K$.

The magnetisation is determined either by direct summation or by differentiation of the canonical partition,

$$M(T, B) = \frac{1}{Z} \sum_{\{S_i\}} \mu \left(\sum_i S_i \exp(-\beta H) \right) = \mu \partial_Q \ln Z = \frac{\mu N}{\lambda_+} \partial_Q \lambda_+ \qquad \text{(I.500)}$$

and comes out as

$$M(T, B) = \frac{\mu N \sinh Q}{\sqrt{\cosh^2 Q - 2 \exp(-2K) \sinh 2K}} \qquad \text{(I.501)}$$

which shows an interesting behaviour: For $B = 0$ and $T \neq 0$ the magnetisation $M(T, B) = 0$ so that one does not observe a spontaneous transition to a magnetised state. If the fields are strong, on the contrary, the magnetisation is $M(T, B) = \mu N$ as all spins are aligned. The entropy follows from differentiation of the Helmholtz free energy with respect to temperature,

$$F = -N k_B T \ln(2 \cosh K) \to S = -\frac{\partial F}{\partial T} = N k_B (\ln(2 \cosh K) - K \tanh K) \qquad \text{(I.502)}$$

with the limit $S = N k_B \ln Z$ at high temperature and $S = 0$ at low temperature, in accordance with the third law of thermodynamics.

I.2.2   Isothermal susceptibility χ

The rate of change of the magnetisation with the external magnetic field is the magnetic susceptibility, which in this model is determined to be

$$\chi = \frac{1}{N} \frac{\partial M}{\partial B} = \frac{\beta \mu}{N} \partial_Q M = \frac{\beta \mu^2}{N} \partial_Q^2 \ln Z = \beta \mu^2 \partial_Q^2 \ln \lambda_+ = \frac{\beta \mu^2}{1 - \tanh K} \qquad \text{(I.503)}$$

which behaves as $1/T$ for large T: This is the statement of the Curie-law. Looking at its microscopic interpretation by substitution of the Hamilton-function yields

$$\chi = \frac{\beta \mu^2}{N} \partial_Q \left(\frac{1}{Z} \sum_{\{S_i\}} \left(\mu \sum_i S_i \right) \exp \left(K \sum_{(i,j)} S_i S_j + Q \sum_i S_i \right) \right) =$$

$$\frac{\beta \mu^2}{N} \sum_{\{S_i\}} \left(\mu \sum_i S_i \right) \exp(-\beta H) = \frac{\beta \mu^2}{N} \left(\sum_{i,j} \langle S_i S_j \rangle \right) \quad \text{(I.504)}$$

such that the susceptibility χ is actually the variance in the spin-configurations.

There is no known computation for the Ising partition function in 3 dimensions or more, and only a very complicated expression for 2-dimensional lattices. Actually,

it's a pity that the 1-dimensional chain does not go a lot beyond paramagnets and that phase transitions are reserved to the higher-dimensional cases. But it is one of the few examples where mutual interactions in non-ideal systems are exactly computable.