Theoretical Statistical Physics

Solution to Exercise Sheet 9

1 Oscillators (3 points)

Calculate the canonical partition function for a system of N classical harmonic oscillators, and determine the thermodynamics of this system.

The Hamiltonian for a single classical harmonic oscillator in n dimensions with isotropic potential and continuous degrees of freedom $\boldsymbol{q}$ and $\boldsymbol{p}$ reads $H_1(\boldsymbol{p}, \boldsymbol{q}) = \frac{\boldsymbol{p}_i^2}{2m} + \frac{k}{2}\boldsymbol{x}^2$. Its canonical partition function can be computed using Gaussian integrals,

$$Z_1(T) = \frac{1}{h^n} \int_{\mathbb{R}^n} \int_{\mathbb{R}^n} e^{-\beta H_1(\boldsymbol{p},\boldsymbol{q})} \, \mathrm{d}^n q \, \mathrm{d}^n p = \frac{1}{h^n} (2\pi m/\beta)^{\frac{n}{2}} (2\pi/\beta k)^{\frac{n}{2}} = \frac{1}{(\beta \hbar \omega)^n}. \tag{1}$$

Assuming the oscillators to be both distinguishable and non-interacting, the partition function for a system of N such oscillators is just a product of single-oscillator partition functions,

$$Z(T, N) = Z_1(T)^N = \frac{1}{(\beta \hbar \omega)^{nN}}. \tag{2}$$

This results in the Helmholtz free energy

$$F(T, N) = -\frac{1}{\beta} \ln(Z) = nNk_\mathrm{B}T \ln(\beta \hbar \omega), \tag{3}$$

which unsurprisingly diverges in the thermodynamic limit $N \to \infty$. Since F does not depend on the volume, we get a vanishing pressure,

$$p = -\frac{\partial F}{\partial V}\Big|_{N,T} = 0. \tag{4}$$

This is due to the lack of interactions between oscillators and because the angular frequency is independent of volume and density.

The internal energy is

$$U(N, T) = -\frac{\partial \ln(Z)}{\partial \beta} = nNk_\mathrm{B}T, \tag{5}$$

which gives a heat capacity of $C = \partial U/\partial T = nNk_\mathrm{B}$.

Unlike the pressure, the entropy for a system of N oscillators - interacting or not - should not vanish, and indeed using $F = U - T\,S$, we find

$$S = \frac{1}{T}(U - F) = nNk_\mathrm{B}\Big[1 - \ln(\beta\hbar\omega)\Big]. \tag{6}$$

Just like in exercise 1 on sheet 8, where we derived the Sackur-Tetrode equation for the entropy of an ideal gas, the low temperature limit remains problematic. Equation (6) suggests that the entropy of a system of harmonic oscillators becomes negative for $\frac{\hbar\omega}{k_\mathrm{B}T} > e$. This is the regime where the thermal energy $k_\mathrm{B}T$ becomes comparable to the harmonic oscillator spacing of energy levels $\hbar\omega$, suggesting that we need to employ quantum mechanics to model the low temperature behavior of the entropy correctly.

2 Mean-field critical exponents (3 points)

The mean-field magnetization per spin $m = m(T,h)$ of an Ising ferromagnet is

$$m = \tanh(2d\,\beta\,J\,m + \beta\,h), \tag{7}$$

with $\beta = \frac{1}{k_\mathrm{B}T}$ (and $J > 0$). We have seen that in the zero-field limit $h \to 0^+$, a non-zero solution exists for $T < T_c$ where $2d\,\beta_c\,J = 1$. Determine how this solution $m = m(T, 0^+)$ behaves as a function of $T_c - T$ as $T \nearrow T_c$, and how $m(T_c, h)$ depends on h for $h \to 0^+$.
Hint: Use the Taylor expansion of tanh around zero. Determine only the leading behaviour.

From $2d\,\beta_c\,J = 1$ follows the critical temperature $T_c = 2d\,J/k_\mathrm{B}$ i.t.o. which (7) reads

$$m(T,h) = \tanh\left(\frac{T_c}{T}\,m + \beta h\right). \tag{8}$$

In the zero-field limit, (8) reduces to $m(T,0^+) = \tanh\left(\frac{T_c}{T}\,m\right)$. At $T = T_c$, we know that $m = 0$ is the only solution of this transcendental equation. Since m is continuous[1], we infer $m \ll 1$ near $T \lesssim T_c$. We may therefore use the Taylor expansion of tanh around zero,

$$\tanh(x) = x - \frac{x^3}{3} + \mathcal{O}(x^5), \tag{9}$$

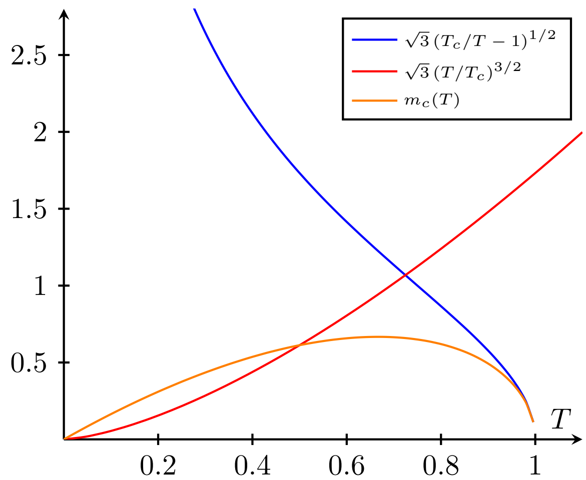
to expand $m(T,0^+)$ near but below T_c as

$$m_c \approx \frac{T_c}{T}\,m_c - \frac{1}{3}\frac{T_c^3}{T^3}\,m_c^3. \tag{10}$$

Solving for m_c yields

$$m_c(T) \approx \sqrt{3}\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\left(\frac{T_c}{T} - 1\right)^{\frac{1}{2}}. \tag{11}$$

The first factor depends only weakly on T around T_c. The dominant contribution comes from the second factor whose derivative is singular at $T = T_c$, as can be seen from the following plot.



[1] m continuous holds generally, even at the Curie point, i.e. during the second-order phase transition between the ferro- and paramagnetic state. According to Ehrenfest's classification, the order of a phase transition is determined by the order of the first discontinuous derivative of the free energy. $m = \frac{\partial F}{\partial h}$ is the free energy's first derivative w.r.t. the applied field and increases continuously from zero as the temperature is lowered below the Curie temperature. The magnetic susceptibility $\xi = \frac{\partial^2 F}{\partial^2 h}$ is the second derivative. It changes discontinuously.

Expanding the critical magnetization (11) to first order in $(T_c - T)$ gives

$$m_c(T) \approx \sqrt{3/T_c}\,(T_c - T)^{\frac{1}{2}} + \mathcal{O}[(T_c - T)^{\frac{3}{2}}]. \tag{12}$$

Thus, near the critical point, the magnetization follows a simple power law with critical exponent $\gamma_1 = \frac{1}{2}$.
Expanding $m_c(T_c, h) = \tanh(m_c + \beta_c h)$ to first order in h around $h = 0$ gives

$$m_c(T_c, h) = \tanh(m_c) + \frac{\beta_c}{\cosh^2(m_c)}\, h + \mathcal{O}(h^2). \tag{13}$$

Again using $m_c \ll 1$ near T_c, we can expand $\tanh(m_c) \approx m_c - \frac{m_c^3}{3}$ and approximate $\cosh(m_c) \approx 1$ to get

$$m_c \approx m_c - \frac{m_c^3}{3} + \beta_c\, h. \tag{14}$$

Solving for m_c, we find

$$m_c \approx \sqrt[3]{3\beta_c\, h} \propto h^{\frac{1}{3}}, \tag{15}$$

which is again a power law with critical exponent $\gamma_2 = \frac{1}{3}$.

3 When Ising stole Christmas (4 points)

Calculate the free energy of the d-dimensional Ising model with ferromagnetic nearest-neighbour interaction for zero magnetic field.
Hints:

1. Start with $d = 1$, then $d = \infty$, then $d = 2$, then $d = \infty - 1$, etc.
2. This is a bonus question: You get 4 extra points for $d = 1$, $4^{(4^4)}$ for $d = 2$, and $\aleph_4$ for $3 \leq d < \infty$.

$d = 1$ The energy of a chain of N Ising spins occupying the spin configuration s is given by the Hamiltonian

$$H(s) = J\sum_{i=1}^{N}(1 - s_i s_{i+1}) - h\sum_{i=1}^{N} s_i. \tag{16}$$

The sum over 1 just gives rise to an overall constant NJ, which we drop to simplify our calculation. Further, we assume periodic boundary conditions such that $s_1 = s_{N+1}$, making the chain a ring of spins. We will study the Ising model in the canonical ensemble for which the partition function is

$$Z_c = \sum_{s \in \mathcal{S}_N} e^{-\beta\, H(s)}, \tag{17}$$

where $\mathcal{S}_N$ is the set of all possible spin configurations of cardinality $|\mathcal{S}_N| = 2^N$. From (17), the free energy may be computed as

$$F = -\frac{1}{\beta}\ln(Z_c). \tag{18}$$

We will leave $h \neq 0$ for now and take $h = 0$ only in the end. Inserting (16) into (17), we get

$$\begin{aligned} Z_c &= \sum_{s_1,\ldots,s_N \in \{\pm 1\}} e^{\beta\left(J\sum_{i=1}^{N} s_i s_{i+1} + h\sum_{i=1}^{N} s_i\right)} \\ &= \sum_{s_1,\ldots,s_N \in \{\pm 1\}} e^{\beta(J s_1 s_2 + h s_1)} \ldots e^{\beta(J s_N s_1 + h s_N)} \\ &= \sum_{s_1,\ldots,s_N \in \{\pm 1\}} M_{s_1 s_2} M_{s_2 s_3} \ldots M_{s_N s_1}, \end{aligned} \tag{19}$$

where the $M_{ss'}$ are matrix elements defined by

$$M_{ss'} = e^{\beta J s s' + \beta h s}. \tag{20}$$

This allows us to write the partition function as:

$$Z_c = \sum_{s_1 \in \{\pm 1\}} (M^N)_{s_1 s_1} = \mathrm{tr}(M^N) = \lambda_1^N + \lambda_2^N, \tag{21}$$

where λ_i are the two eigenvalues of M and we used that the trace is basis independent, so we may perform it in a basis in which M takes diagonal form.[2] Let λ_1 be the eigenvalue of larger magnitude. In the thermodynamic limit, we then get

$$\lim_{N\to\infty} Z_c = \lim_{N\to\infty} \lambda_1^N \big(1 + \lambda_2^N/\lambda_1^N\big) \sim \lambda_1^N. \tag{22}$$

Hence, all we need to do to find Z_c is to compute the larger of the two eigenvalues of

$$M = \begin{pmatrix} e^{\beta(J+h)} & e^{\beta(-J+h)} \\ e^{-\beta(J+h)} & e^{\beta(J-h)} \end{pmatrix}. \tag{23}$$

The eigenvalues of a general 2×2 matrix A are

$$\lambda_\pm = \frac{\mathrm{tr}(A)}{2} \pm \sqrt{\frac{\mathrm{tr}(A)^2}{4} - \det(A)}. \tag{24}$$

For M, we get

$$\begin{aligned} \mathrm{tr}(M) &= e^{\beta(J-h)} + e^{\beta(h+J)} & \det(M) &= e^{\beta(h+J)-\beta(h-J)} - e^{\beta(h-J)-\beta(h+J)} \\ &= 2\,e^{\beta J}\cosh(\beta h), & &= 2\sinh(2\beta J). \end{aligned} \tag{25}$$

Thus the larger eigenvalue reads

$$\lambda_1 = e^{\beta J}\cosh(\beta h) + \sqrt{e^{2\beta J}\sinh^2(\beta h) + e^{-2\beta J}}, \tag{26}$$

and the free energy per spin is

$$\begin{aligned} f(h,T) = \lim_{N\to\infty} \frac{F(h,T)}{N} &\overset{(18)}{=} -k_\mathrm{B} T \lim_{N\to\infty} \frac{1}{N} \ln\big[Z_c(h,T)\big] \\ &= -k_\mathrm{B} T \ln\left[e^{\beta J}\cosh(\beta h) + \sqrt{e^{-2\beta J} + \sinh^2(\beta h) e^{\beta J}}\right]. \end{aligned} \tag{27}$$

For vanishing field $h = 0$ this result simplifies to

$$f(0,T) = -k_\mathrm{B} T \ln\Big(e^{\beta J} + e^{-\beta J}\Big) = -k_\mathrm{B} T \ln\big(2\cosh(\beta J)\big). \tag{28}$$

$\boldsymbol{d = 2}$ In two dimensions, the Ising model is still solvable for vanishing external field. This is the Onsager solution, presented in Kerson Huang's "Statistical Mechanics" (pp. 268 - 293). Reproducing here the full derivation would be too lengthy. The final result, eq. (15.133), for the free energy per spin reads

$$\beta f(0,T) = -\ln\big[2\cosh(2\beta J)\big] - \frac{1}{2\pi}\int_0^\pi \mathrm{d}\phi \ln\left[\frac{1}{2}\Big(1 + \sqrt{1 - \kappa^2 \sin^2(\phi)}\Big)\right], \tag{29}$$

where $\kappa = 2\tanh(2\beta J)/\cosh(2\beta J)$. The interesting thing about this solution is that it displays a phase transition at a critical temperature. This can be seen simply from the fact that the

[2] Note that M is a matrix of rank 2, same as its dimension and is therefore diagonalizable.

elliptic integral has a singularity at $K = 1$. This divergence turns out to be a logarithmic one. The value of the critical temperature is found to be

$$2\tanh^2\left(\frac{2J}{k_\mathrm{B}T_c}\right) \overset{!}{=} 1 \quad \Rightarrow \quad T_c \approx 2.27\,\frac{J}{k_\mathrm{B}}. \tag{30}$$

The magnetization may also be computed (another tedious task). The deceivingly simple result

$$m(0,T) = \begin{cases} 0 & T > T_c \\ \{1 - [\sinh(2\beta J)]^{-4}\}^{\frac{1}{8}} & (T < T_c) \end{cases}, \tag{31}$$

is a spontaneous magnetization in the sense that it is non-zero only below the critical temperature and its derivative diverges in the limit $T \to T_c^-$. We plot it below.