Theoretical Statistical Physics

Final Exam

Write your solutions comprehensibly so that the reasoning on which your calculations are based can be understood. Note down intermediate steps in your calculations. Please start the solution to every problem on a separate page.

1 Reversible heat pump (4 points)

An electric heater (i.e. a device that transforms work completely into heat) keeps a room at a temperature of $20\,°\mathrm{C}$. The ambient temperature is $10\,°\mathrm{C}$. By how much can one reduce the heating costs, if one uses a reversible heat pump instead?

A heat engine is a device that transfers heat from a hot reservoir at temperature T_h to a cold one at $T_c < T_h$ with the aim of converting as much of the transferred heat into mechanical work as possible. The efficiency η of any reversible heat engine is equal to that of the idealized Carnot cycle $\eta_\mathrm{C} = 1 - \frac{T_c}{T_h}$.

A heat pump, on the other hand, moves heat in the other direction from a cold reservoir to a hot one, the goal now being to use as little mechanical work as possible to do so. Since this is precisely a heat engine operating in reverse, its idealized efficiency is given by the reciprocal of η_C. A reversible heat pump would thus reduce the heating costs relative to those of the electric heater with efficiency $\eta_\mathrm{eh} = 1$ by a factor of

$$\frac{\eta_\mathrm{hp}}{\eta_\mathrm{eh}} = \frac{T_h}{T_h - T_c} \approx \frac{293\,\mathrm{K}}{10\,\mathrm{K}} = 29.3. \tag{1}$$

2 Black-body radiation (6 points)

Black-body radiation has the caloric equation of state $U = u(T)V$ and thermal equation of state $p = \frac{1}{3}u(T)$.

a) Derive from this information the Stefan-Boltzmann law

$$u(T) = \sigma T^4, \tag{2}$$

with σ a constant. Hint: You may use the Maxwell relation $\frac{\partial U}{\partial V}\big|_T = T\frac{\partial p}{\partial T}\big|_V - p$.

b) Use the Gibbs fundamental relation to calculate the entropy. Fix the integration constant by demanding that $S(T) \to 0$ as $T \to 0$.

c) Derive the equation for adiabatic changes of state.

a) Inserting $U = u(T)V$ and $p = \frac{1}{3}u(T)$ into the suggested Maxwell relation yields

$$u = \frac{T}{3}\frac{\mathrm{d}u}{\mathrm{d}T} - \frac{1}{3}u. \tag{3}$$

Separation of variables gives

$$\frac{\mathrm{d}u}{u} = 4\,\frac{\mathrm{d}T}{T}, \tag{4}$$

which integrates to

$$\ln u = \ln T^4 + a, \tag{5}$$

with $a \in \mathbb{R}$ constant. Exponentiation results in the Stefan-Boltzmann law for the temperature dependence of black-body radiation,

$$u = e^a T^4 \equiv \sigma T^4. \tag{6}$$

b) The Gibbs fundamental relation, the most important state function in all of thermodynamics, describes the set of equilibrium points of a system via its internal energy U as a function of *all* extensive parameters. For a non-magnetic single-component system, it reads $U = U(S, V, N)$, or in differential form at constant particle number ($\mathrm{d}N = 0$),

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V. \tag{7}$$

By the caloric equation of state,

$$\mathrm{d}U = V\frac{\partial u}{\partial T}\Big|_V \mathrm{d}T + u\mathrm{d}V = 4\sigma V T^3 \mathrm{d}T + \sigma T^4 \mathrm{d}V. \tag{8}$$

Solving (7) for $\mathrm{d}S$ and inserting (8) yields

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V = 4\sigma V T^2 \mathrm{d}T + \frac{4}{3}\sigma T^3 \mathrm{d}V. \tag{9}$$

Integrating (9) w.r.t. T at constant V (or vice versa), we find the entropy of black-body radiation

$$S(T, V) = S_0 + \frac{4}{3}\sigma V T^3. \tag{10}$$

Demanding $S(T) \to 0$ as $T \to 0$ requires $S_0 = 0$. Thus $S = \frac{4}{3}\frac{U}{T} = \frac{4pV}{T}$.

c) During an adiabatic process $\delta Q = T\mathrm{d}S = 0$, i.e. the entropy remains constant. Thus

$$VT^3 = \text{const.} \tag{11}$$

3 Maxwell distribution (6 points)

Consider a classical gas of particles in three dimensions. The energy of a particle with momentum $\boldsymbol{p}$ is given by $\epsilon(\boldsymbol{p}) = c|\boldsymbol{p}|$, where $c > 0$ is a fixed velocity.

a) Write down the (correctly normalized) Maxwell distribution for this situation.

b) Calculate the expectation value of the energy $\langle E \rangle$, and the variance $\big\langle (E - \langle E \rangle)^2 \big\rangle$.

a) The unnormalized Maxwell distribution is

$$f(\boldsymbol{p}) = e^{-\beta\epsilon(\boldsymbol{p})}. \tag{12}$$

Integrating $f(\boldsymbol{p})$ over $\boldsymbol{p} \in \mathbb{R}^3$, we get

$$\int_{\mathbb{R}^3} f(\boldsymbol{p})\,\mathrm{d}^3p = 4\pi \int_0^\infty p^2 e^{-\beta c p}\mathrm{d}p = 4\pi\partial_{\beta c}^2 \int_0^\infty e^{-\beta c p}\mathrm{d}p = 4\pi\partial_{\beta c}^2 \frac{1}{\beta c} = \frac{8\pi}{(\beta c)^3}. \tag{13}$$

Thus $f(\boldsymbol{p}) = \mathcal{N} e^{-\beta\epsilon(\boldsymbol{p})}$ with $\mathcal{N} = \frac{(\beta c)^3}{8\pi}$ is normalized.

b) The expected energy is

$$\begin{aligned}\langle E\rangle &= \int_{\mathbb{R}^3} \epsilon(\boldsymbol{p}) f(\boldsymbol{p})\,\mathrm{d}^3p = -4\pi c\mathcal{N}\partial_{\beta c}^3 \int_0^\infty e^{-\beta c p}\mathrm{d}p \\ &= -4\pi c\mathcal{N}\partial_{\beta c}^3 \frac{1}{\beta c} = 24\pi c\mathcal{N}\frac{1}{(\beta c)^4} = \frac{3}{\beta} = 3k_\mathrm{B}T.\end{aligned} \tag{14}$$

The expected squared energy is

$$\begin{aligned}\langle E^2\rangle &= \int_{\mathbb{R}^3} \epsilon(\boldsymbol{p})^2 f(\boldsymbol{p})\,\mathrm{d}^3p = 4\pi c^2\mathcal{N}\partial_{\beta c}^4 \int_0^\infty e^{-\beta c p}\mathrm{d}p \\ &= 96\pi c^2\mathcal{N}\frac{1}{(\beta c)^5} = \frac{12}{\beta^2} = 12k_\mathrm{B}^2T^2,\end{aligned} \tag{15}$$

which results in the variance

$$\sigma_E^2 = \left\langle (E - \langle E\rangle)^2\right\rangle = \langle E^2\rangle - \langle E\rangle^2 = 3k_\mathrm{B}^2T^2. \tag{16}$$

4 Ideal paramagnet (8 points)

Consider an ideal paramagnet defined as a system of N independent Ising spins with magnetic moment m in an external field h.

a) Write down the Hamiltonian H of the system.

b) Give the definition of the canonical partition function and compute it for this H.

c) Compute the free energy, the magnetization, and the energy.

d) Calculate the specific heat and the magnetic susceptibility.

a) The Hamiltonian of N uncoupled Ising spins of magnetic moment m in a field h is

$$H(s) = -hm\sum_{j=1}^{N} s_j, \tag{17}$$

where $s = (s_1, \ldots, s_N) \in \mathcal{S}_N = \{\pm 1\}^N$ denotes one of the 2^N possible spin configurations.

b) The canonical partition function is sum of all spin configurations weighted by their energy according to Boltzmann's factor,

$$\begin{aligned}Z_c &= \sum_{s\in\mathcal{S}_N} e^{-\beta H(s)} = \sum_{s_1\in\{\pm1\}} \cdots \sum_{s_N\in\{\pm1\}} e^{\beta hm\sum_{j=1}^N s_j} = \prod_{j=1}^{N}\sum_{s_j\in\{\pm1\}} e^{\beta hms_j} \\ &= \prod_{j=1}^{N}\left(e^{\beta hm} + e^{-\beta hm}\right) = [2\cosh(\beta hm)]^N.\end{aligned} \tag{18}$$

c) The free energy is

$$F = -\frac{1}{\beta}\ln Z_c = -\frac{N}{\beta}\ln[2\cosh(\beta hm)]. \tag{19}$$

The magnetization is the free energy's first derivative w.r.t. the field h,

$$M = -\frac{\partial F}{\partial h} = \frac{N}{\beta}\frac{\sinh(\beta hm)}{\cosh(\beta hm)}\beta m = Nm\tanh(\beta hm). \tag{20}$$

The internal energy is

$$U = -\frac{\partial \ln Z_c}{\partial \beta} = -Nhm\tanh(\beta hm). \tag{21}$$

d) The specific heat capacity is

$$c_h = \frac{C_h}{N} = \frac{1}{N}\frac{\partial U}{\partial T}\Big|_h = \frac{1}{N}\frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} = -hm\left(hm - hm\frac{\sinh^2(\beta hm)}{\cosh^2(\beta hm)}\right)\left(-\frac{1}{k_\mathrm{B}T^2}\right)$$
$$= k_\mathrm{B}\frac{\beta^2h^2m^2}{\cosh^2(\beta hm)}, \tag{22}$$

where we used $\sinh^2(x) = \cosh^2(x) - 1$. The magnetic susceptibility is the change in magnetization w.r.t. a change in the field h,

$$\chi = \frac{\partial M}{\partial h} = \frac{\beta N m^2}{\cosh^2(\beta hm)}. \tag{23}$$

5 3-level system (8 points)

The Hamiltonian for a three-level quantum system is given by

$$H = \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \eta \\ 0 & \eta & 0 \end{pmatrix}, \tag{24}$$

with energies $\epsilon > 0$ and $\eta > 0$. Calculate the canonical density operator, the canonical partition function, and the free energy. Calculate the expectation value of the energy, and the expectation value of the observable

$$A = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \tag{25}$$

If $\eta > \epsilon$, what is the low-temperature behavior of these expectation values?

Solving the characterisitc polynomial,

$$\det\begin{pmatrix} -\epsilon-\lambda & 0 & 0 \\ 0 & -\lambda & \eta \\ 0 & \eta & -\lambda \end{pmatrix} = -\lambda^2(\lambda+\epsilon) + \eta^2(\lambda+\epsilon) = -(\lambda^2-\eta^2)(\lambda+\epsilon) \stackrel{!}{=} 0, \tag{26}$$

we find that H has eigenvalues $\lambda_1 = -\epsilon$, $\lambda_2 = -\eta$, $\lambda_3 = \eta$. To simplify calculations, we will work with the diagonal form

$$H_d = \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & -\eta & 0 \\ 0 & 0 & \eta \end{pmatrix}. \tag{27}$$

The canonical density operator is defined

$$\rho_c = e^{\beta(F-H)} = e^{\ln Z_c^{-1}}e^{-\beta H} = \frac{1}{Z_c}e^{-\beta H}, \tag{28}$$

where we used $F = -\frac{1}{\beta}\ln Z_c$ and the operator exponential $e^{-\beta H}$ is defined by its power series. However, for the special case of a diagonal matrix we can simply exponentiate individual entries, yielding

$$\rho_c = \frac{1}{Z_c}e^{-\beta H_d} = \frac{1}{Z_c}\begin{pmatrix} e^{\beta\epsilon} & 0 & 0 \\ 0 & e^{\beta\eta} & 0 \\ 0 & 0 & e^{-\beta\eta} \end{pmatrix} \tag{29}$$

where the partition function Z_c normalizes the density operator,

$$Z_c = \mathrm{tr}\big(e^{-\beta H_d}\big) = e^{\beta\epsilon} + e^{-\beta\eta} + e^{\beta\eta}. \tag{30}$$

The free energy reads

$$F = -\frac{1}{\beta}\ln Z_c = -\frac{1}{\beta}\ln\Big(e^{\beta\epsilon} + e^{-\beta\eta} + e^{\beta\eta}\Big). \tag{31}$$

The expected energy is

$$\begin{aligned}\langle H\rangle = \mathrm{tr}(\rho_c H_d) &= \frac{1}{Z_c}\begin{pmatrix}-\epsilon\, e^{\beta\epsilon} & 0 & 0\\ 0 & -\eta e^{-\beta\eta} & 0\\ 0 & 0 & \eta e^{\beta\eta}\end{pmatrix}\\ &= -\frac{1}{Z_c}\Big(\epsilon\, e^{\beta\epsilon} + \eta\big(e^{-\beta\eta} - e^{\beta\eta}\big)\Big) = -\frac{1}{Z_c}\Big(\epsilon\, e^{\beta\epsilon} + 2\eta\sinh(\beta\eta)\Big).\end{aligned} \tag{32}$$

To compute A's expectation value as $\langle A\rangle = \mathrm{tr}(\rho_c A)$, we need to transform it into the eigenbasis of H in which we expressed ρ_c. To that end, we calculate $A_d = P^{-1}AP$, where $P^{-1} = P^{\mathrm{T}} = P$ is the orthonormal matrix of normalized eigenvectors of H given by

$$P = \begin{pmatrix}1 & 0 & 0\\ 0 & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}\\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}},\end{pmatrix} \tag{33}$$

so that

$$A_d = \begin{pmatrix}0 & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}} & -1 & 0\\ \frac{1}{\sqrt{2}} & 0 & 1\end{pmatrix}. \tag{34}$$

The expected value of the observable A is thus

$$\langle A\rangle = \mathrm{tr}(\rho_c A) = -\frac{1}{Z_c}\big(e^{\beta\eta} - e^{-\beta\eta}\big) = -\frac{2}{Z_c}\sinh(\beta\eta). \tag{35}$$

The low-temperature behavior of $\langle H\rangle$ and $\langle A\rangle$ for $\eta > \epsilon$ is

$$\langle H\rangle = -\frac{\epsilon\, e^{\beta\epsilon} + \eta\big(e^{\beta\eta} - e^{-\beta\eta}\big)}{e^{\beta\epsilon} + e^{-\beta\eta} + e^{\beta\eta}} \xrightarrow{\beta\to\infty} -\eta, \tag{36}$$

$$\langle A\rangle = \frac{e^{-\beta\eta} - e^{\beta\eta}}{e^{\beta\epsilon} + e^{-\beta\eta} + e^{\beta\eta}} \xrightarrow{\beta\to\infty} -1. \tag{37}$$

As expected, the low-temperature energy is determined by the lowest energy state $-\eta$.