Theoretical Statistical Physics

Solution to Exercise Sheet 2

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1 Paramagnet (3 points)

We describe magnetic substances by the following thermodynamic variables: the temperature T, the magnetic field H, and the magnetization M. Show that for paramagnetic substances, for which[1]

$$M = \frac{C}{T} H, \tag{1}$$

the internal energy U depends only on T.

The change in internal energy for a paramagnet is

$$\mathrm{d}U = T\,\mathrm{d}S + H\,\mathrm{d}M. \tag{2}$$

As a function $U(T, M)$, the internal energy's total differential is

$$\mathrm{d}U = \underbrace{\left.\frac{\partial U}{\partial T}\right|_M}_{C_M} \mathrm{d}T + \left.\frac{\partial U}{\partial M}\right|_T \mathrm{d}M. \tag{3}$$

Equating (2) and (3) and solving for $\mathrm{d}S$ yields

$$\mathrm{d}S = \frac{C_M}{T}\,\mathrm{d}T + \frac{1}{T}\left(\left.\frac{\partial U}{\partial M}\right|_T - H\right)\mathrm{d}M. \tag{4}$$

Since $\mathrm{d}S$ is exact,

$$\left.\frac{\partial}{\partial M}\frac{C_M}{T}\right|_T = \left.\frac{\partial}{\partial T}\frac{1}{T}\left(\left.\frac{\partial U}{\partial M}\right|_T - H\right)\right|_M. \tag{5}$$

Performing the T-derivative on the r.h.s.,

$$\cancel{\left.\frac{\partial}{\partial M}\frac{C_M}{T}\right|_T} = -\frac{1}{T^2}\left(\left.\frac{\partial U}{\partial M}\right|_T - H\right) + \cancel{\frac{1}{T}\frac{\partial^2 U}{\partial T \partial M}} - \frac{1}{T}\left.\frac{\partial H}{\partial T}\right|_M, \tag{6}$$

and canceling terms leaves us with

$$\left.\frac{\partial U}{\partial M}\right|_T = H - T\left.\frac{\partial H}{\partial T}\right|_M. \tag{7}$$

Inserting (1) in the form $H = \frac{T}{C} M$ results in

$$\left.\frac{\partial U}{\partial M}\right|_T = 0, \tag{8}$$

from which we infer $U(T, M) = U(T)$.

[1] (1) is known as Curie's law, where C is a material-specific constant (not to be confused with the heat capacity).

2 Heating water (3 points)

One kilogram of water at 0 °C is put into thermal contact with a heat bath at 100 °C. What is the change in entropy of water, heat bath, and total system by the time the temperature of the water has reached 100 °C? How can one heat up the water to that temperature without changing the entropy of the total system? Use $c_p = 4180\,\frac{\mathrm{J}}{\mathrm{kg\,K}}$.

We start with a short discussion of heat capacities. C determines the amount of energy needed to bring about a certain change in temperature.

For a gas, C_V is determined by the change in internal energy U concurrent with a change in temperature at fixed volume, i.e. $C_V = \frac{\partial U}{\partial T}\big|_V$, whereas C_p is the change in enthalpy H at fixed pressure, i.e $C_p = \frac{\partial H}{\partial T}\big|_p$. Since $\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V$ ($+V\,\mathrm{d}p$, but $\mathrm{d}p = 0$ at constant pressure) C_p is greater than C_V since the volume must increase, i.e. $\mathrm{d}V > 0$ during a heating process if the pressure is to be kept constant. Thus heating at constant pressure requires more energy than at constant volume as some of the energy is expended towards driving the expansion.

For liquids and solids which can, to a good approximation, be assumed incompressible, C_V and C_p are practically identical.

Coming back to the exercise, the entropy is the integral over heat transfer divided by temperature. As long as it does not start to boil, heating a liquid involves no work. Thus, $\mathrm{d}U = \delta Q + \underbrace{\delta W}_{0} = \delta Q$, and

$$\begin{aligned}\Delta S_{\mathrm{H_2O}} &= \int \frac{\delta Q}{T} = \int \frac{\mathrm{d}U}{T} = C_V \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T} = C_V \ln\left(\frac{T_2}{T_1}\right) \\ &\approx C_p \ln\left(\frac{T_2}{T_1}\right) = c_p m_{\mathrm{H_2O}} \ln\left(\frac{T_2}{T_1}\right) \approx 1305\,\frac{\mathrm{J}}{\mathrm{K}},\end{aligned} \tag{9}$$

where $c_p = 4180\,\frac{\mathrm{J}}{\mathrm{kg\,K}}$ is the specific heat, i.e. heat capacity per unit mass, $m_{\mathrm{H_2O}} = 1\,\mathrm{kg}$ is the total mass of water, $T_1 = 273\,\mathrm{K}$, and $T_2 = 373\,\mathrm{K}$. In the case of the heat bath with constant temperature, the integral simplifies to

$$\Delta S_{\mathrm{HB}} = \int \frac{\delta Q}{T} = \frac{\Delta Q_{\mathrm{HB}}}{T_{\mathrm{HB}}} = -\frac{\Delta Q_{\mathrm{H_2O}}}{T_{\mathrm{HB}}} = -\frac{c_p m_{\mathrm{H_2O}} \Delta T_{\mathrm{H_2O}}}{T_{\mathrm{HB}}} \approx -1121\,\frac{\mathrm{J}}{\mathrm{K}}. \tag{10}$$

By the time the heat bath and water reach thermal equilibrium, the combined system's entropy will have increased by $\Delta S_{\mathrm{tot}} \approx 184\,\frac{\mathrm{J}}{\mathrm{K}}$.

Equilibrating water and heat bath without producing entropy would require an idealized Carnot engine capable of reversibly transferring heat from the bath to the water. Since such a Carnot engine cannot exist under real circumstances, this is just another way of saying that reaching equilibrium without producing entropy is impossible.

3 Power station (2 points)

A 1000 MW power plant is run at a river, the water of which is used as a coolant. The heat source in the power plant is at a temperature of 600 K, the water taken from the river is at 290 K. By how many degrees is the river heated up by the power plant if the efficiency of the plant is 50 % of the maximally possible efficiency? (Data: cross-sectional area of the river $A = 75\,\mathrm{m}^2$, flow velocity $v = 1\,\frac{\mathrm{m}}{\mathrm{s}}$, specific heat of the water $c_p = 4180\,\frac{\mathrm{J}}{\mathrm{kg\,K}}$, density of water $\rho = 1000\,\frac{\mathrm{kg}}{\mathrm{m}^3}$.)

The change in temperature resulting from adding the heat Q to a body of mass m and heat capacity c_p is

$$\Delta T = \frac{Q}{c_p m} = \frac{P}{c_p \dot{m}}. \tag{11}$$

The rate at which water flows past the power station is $\dot{m} = \rho A v = 75\,000\,\frac{\mathrm{kg}}{\mathrm{s}}$. To derive the power P, i.e. the amount of heat dumped into the water by the power station per second, we need to know its efficiency. The maximal possible efficiency is that of the idealized Carnot cycle, $\eta_c = 1 - \frac{T_1}{T_2}$, which reversibly transfers energy from a warm region T_2 to a cool region $T_1 < T_2$ and, in the process, converts some of that energy to mechanical work. Thus

$$\eta_{\mathrm{ps}} = \frac{1}{2}\eta_c = \frac{1}{2}\left(1 - \frac{290\,\mathrm{K}}{600\,\mathrm{K}}\right) \approx 25.83\,\%. \tag{12}$$

Solving $P_{\mathrm{out}} = \eta_{\mathrm{ps}} P_{\mathrm{tot}}$ and $P_{\mathrm{tot}} = P_{\mathrm{out}} + P$ for P, we find the energy released into the water per second to be

$$P = \frac{1 - \eta_{\mathrm{ps}}}{\eta_{\mathrm{ps}}} P_{\mathrm{out}} \approx 2870\,\frac{\mathrm{MJ}}{\mathrm{s}}. \tag{13}$$

Inserting $\dot{m}$ and P into (11), we find a temperature increase for water flowing past the power station of

$$\Delta T \approx 9.16\,\mathrm{K}. \tag{14}$$

4 Carnot engine

(2 points)

The internal energy of two bodies consisting of the same substance is given by

$$U = CT, \tag{15}$$

where C is a constant. Their initial temperatures are T_1 and T_2, respectively. We let a Carnot engine work between the two bodies until both reach the final temperature T_f. What is T_f, and how much work has been produced when it is reached?

Since a Carnot engine works reversibly, it produces no change in entropy, $\Delta S = 0$. Moreover, due to reversibility, the second law of thermodynamics (for closed systems) $\delta Q \leq T\,\mathrm{d}S$ holds as an equality. Together with $\delta Q = C\,\mathrm{d}T$, this gives

$$0 = \int \mathrm{d}S = \int \mathrm{d}S_1 + \int \mathrm{d}S_2 = C\int_{T_1}^{T_f} \frac{\mathrm{d}T}{T} + C\int_{T_2}^{T_f} \frac{\mathrm{d}T}{T} = C\ln\left(\frac{T_f^2}{T_1 T_2}\right), \tag{16}$$

from which we infer $T_f = \sqrt{T_1 T_2}$. To calculate the work performed during equilibration, note that the two bodies form a closed system and thus $\Delta U = \Delta Q + \Delta W = 0$. Using $\Delta Q = C\int \mathrm{d}T = C\Delta T$, we find the individual heats to be

$$\Delta Q_1 = C\big(T_f - T_1\big), \qquad \Delta Q_2 = C\big(T_f - T_2\big). \tag{17}$$

Thus the total work performed is

$$\begin{aligned} \Delta W &= -(\Delta Q_1 + \Delta Q_2) = -C\big(2T_f - T_1 - T_2\big) = C\Big(T_1 + T_2 - 2\sqrt{T_1 T_2}\Big) \\ &= C\Big(\sqrt{T_1} - \sqrt{T_2}\Big)^2. \end{aligned} \tag{18}$$