

Exercises 3

Exercises on May 2 – May 6

3.1 Heat Capacities

The heat capacity of a thermodynamic system is defined to be $C_X = T (\partial S / \partial T)_X$, where X may be P or V , resp. By using the MAXWELL relations show that

$$C_V = C_P + T \left(\frac{\partial P}{\partial V} \right)_T \left(\left(\frac{\partial V}{\partial T} \right)_P \right)^2.$$

Hint: You may make use of the known rules for functional determinants, e. g. functional determinants, esp. $\partial(u, v) / \partial(x, v) = (\partial u / \partial x)_v$ or the chain rule.

3.2 Thermodynamic Relations in a Magnetic System

Consider a magnetic system characterised by the entropy S , the temperature T , the magnetisation M , and an external magnetic field B . Its properties are described by the thermodynamic response functions: the specific heat at constant magnetisation or constant magnetic field, resp., $c_M = T(\partial S / \partial T)_M$, $c_B = T(\partial S / \partial T)_B$, the isothermal ($dT = 0$) as well as the adiabatic ($\delta S = 0$) susceptibility, $\chi_T = (\partial M / \partial B)_T$, $\chi_S = (\partial M / \partial B)_S$, and the magnetisation temperature coefficient, $\alpha_B = (\partial M / \partial T)_B$.

Show that the following equations hold:

- a) $\frac{c_B}{c_M} = \frac{\chi_T}{\chi_S}$
(Hint: Write c_B and c_M in terms of thermodynamic derivatives of B and M alone by using $dB = 0$ at c_B and $dM = 0$ at c_M ; then re-sort the terms in c_B/c_M in a suitable way.)
- b) $c_B - c_M = T \frac{\alpha_B^2}{\chi_T}$
(Hint: Using the chain rule, reduce c_B to c_M ; then use the MAXWELL relations for S , T , B , and M).

3.3 Adiabatic equation of state of an ideal gas (second time)

For an ideal gas, $pV = nRT$ und $c_V = T(\partial S / \partial T)_V = \frac{f}{2}nR = \text{const.}$

- a) Show that $dU = c_V dT$, and calculate the internal energy $U(T, V)$ and the entropy $S(T, V)$.
- b) Show that the adiabatic ($S = \text{const.}$) equation of state at constant particle number is given by $pV^\gamma = \text{const.}$

- c) Consider a mixture of two ideal gases (1 and 2) in the molar ratio of $x_1 : x_2$. Show that, for the mixture, the exponent γ is given by

$$\frac{1}{\gamma - 1} = \frac{x_1}{\gamma_1 - 1} + \frac{x_2}{\gamma_2 - 1}.$$

3.4 Probabilities: Central Limit Theorem

A random variable X may assume the values $x \in M$ with probability $p(x)$ (M is called the event space of the random experiment). The quantity X is drawn N times independently; the average of the values drawn defines a new random variable Y :

$$Y : y = \frac{1}{N} \sum_{i=1}^N x_i.$$

We now aim to find the probability distribution of Y , $P_N(y)$, in the limit of $N \rightarrow \infty$:

- a) For the time being, assume N to have a fixed value. What is the probability for the event (x_1, x_2, \dots, x_N) ? Formally find the probability distribution $P_N(y)$ in terms of the $p(x_i)$.

The characteristic function of a probability distribution is a very useful function. $p(x)$,

$$\phi(k) = \int e^{ik(x - \langle x \rangle)} p(x) dx,$$

which is related to the FOURIER transform of $p(x)$.

- b) Show that the characteristic function of $P_N(y)$ is

$$\Phi_N(k) = \int e^{i \frac{k}{N} \sum_{i=1}^N (x_i - \langle x \rangle)} p(x_1) p(x_2) \dots p(x_N) dx_1 dx_2 \dots dx_N = \left[\phi \left(\frac{k}{N} \right) \right]^N.$$

- c) Using the assumption that all moments (see below) of the distribution $p(x)$ exist, show that, in the limit of $N \rightarrow \infty$,

$$\Phi_N(k) \rightarrow e^{-\frac{\sigma^2}{2N} k^2}.$$

To that end, expand w. r. t. k/N . Finally, find the probability distribution

$$\overline{P}(y) = \lim_{N \rightarrow \infty} P_N(y).$$

Definition: The n -th moment of a distribution $p(x)$ is $\langle x^n \rangle := \int x^n p(x) dx$.

Enjoy!