Übungen zu Theoretische Physik IV
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http://www.th.physik.uni-bonn.de/people/forste/exercises/ws1213/tp4

−In-class exercises−

A 4.1 Exact differentials and integrability

In exercise A 3.1 we discussed the notion of derivatives in multidimensional analysis and total differentials. We saw, that every total differential is a linear form and can hence be written as a linear combination of the basis $\{\mathrm{d}x^i\}$ of the dual space. An element of the dual space, which is a total differential of a function, is called exact. Let $A = \sum_{i=1}^n a_i(x_1, \ldots, x_n)\,\mathrm{d}x^i$ be an arbitrary linear form. Then, A is exact iff the following, equivalent *integrability criteria* are fulfilled[1]:

- $\exists F$ with $A = dF$.

- $\frac{\partial a^i}{\partial x_j} = \frac{\partial a^j}{\partial x_i} \quad \forall i,j \in \{1, \ldots, n\}$.

- $\oint A = \oint \left(\sum_{i=1}^n a_i(x_1, \ldots, x_n)\,\mathrm{d}x^i \right) = 0$.

- $\int_{P_0}^{P_1} A = \int_{P_0}^{P_1} \left(\sum_{i=1}^n a_i(x_1, \ldots, x_n)\,\mathrm{d}x^i \right)$ is independent of the integration contour.

(a) Let $n = 2$. Consider the linear form $A = x_1 x_2 \mathrm{d}x^1 + x_1^2 \mathrm{d}x^2$. Show, that A is not exact, whereas $\frac{1}{x_1} A$ is. Calculate the *integral F*, which satisfies $\mathrm{d}F = \frac{1}{x_1} A = x_2 \mathrm{d}x^1 + x_1 \mathrm{d}x^2$.

The factor $\frac{1}{x_1}$, which in the above example converts a non-exact linear form A into an exact one, is an example for an *integrating factor*. Now, let A be an arbitrary, non-exact linear form. Then, g is an integrating factor, iff

$$\frac{\partial(ga^j)}{\partial x_i} = \frac{\partial(ga^i)}{\partial x_j}, \qquad \forall i,j \in \{1, \ldots, n\}$$

is satisfied.

(b) Again, let $n = 2$ and $A = x_1 x_2 \mathrm{d}x^1 + x_1^2 \mathrm{d}x^2$. Determine the integrating factor.

In the lecture we deduced the first law of thermodynamics (for a constant number of particles)

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$$

from the total differential of the entropy in the microcanonical ensemble. Here, the first term can be interpreted as the change of heat δQ of, and the second one as the work δA done upon the system.

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[1] This only holds necessarily for star domains.

(c) Show that, both δQ and δA are non-exact. It is hence impossible to define correspon-
ding thermodynamical functions of state. Determine an integrating factor for δQ.
Hint: Use, that $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$ *is an exact differential.*

The connection between work done upon the system or the change of heat of the system
and the thermodynamical functions of state is therefore only apparent in a differential way.
One can look at the integral $\int_C \delta Q = \int_C T\mathrm{d}S$ along a curve C (and analogously for δA),
but the value of such an integral will not only depend on the starting and endpoint of
the integral but also on the precise form of the curve. Especially will $\oint_C \delta Q$ along a closed
contour C be different from zero, a fact which is essential for thermodynamical cycles which
we will look at later.

A 4.2 Legendre Transformation

Let $f(x_1, \ldots, x_n)$ be a function. The aim of a Legendre transformation is, to change the de-
pendence of the function f from the variables $(x_1, \ldots, x_n)$ to the variables $(x_1, \ldots, x_{i-1}, u_i, x_{i+1}, \ldots, x_n)$,
where $u_i = \frac{\partial f}{\partial x_i}$. First, consider the case $n = 1$ and write shorthand $x = x_1$.
Let $T_{x_0}(x)$ be the family of tangents to the function $f(x)$ at the points x_0. It is given by

$$T_{x_0}(x) = f(x_0) + \frac{\partial f}{\partial x}\bigg|_{x=x_0} (x - x_0) \equiv f(x_0) + f'(x_0)(x - x_0)\,.$$

The intercepts $g(x_0)$ of these tangents are given by

$$g(x_0) = f(x_0) - x_0 f'(x_0)\,.$$

If the map $x \mapsto f'(x)$ is bijectiv, the funktion $g(x)$ contains the same information as $f(x)$
(this is the case when $f'(x)$ is strictly monotonic). One then calls g the *Legendre transform*
of f and

$$g = f - xu\,, \qquad u \equiv \frac{\partial f}{\partial x}\,.$$

Graphically $g(x)$ is the y-axis intercept of the tangent to $f(x)$ at the point $(x, f(x))$.

(a) Show, that g only depens on u.

(b) Calculate the Legendre transform g of the function $f(x) = x^2$ as well as its total
differential.

(c) What is the Legendre transform of the function $f(x) = x$?

(d) Show that the Legendre transformation is an involution, that means that its twofold
action on a function gives back the function itself.

The generalization for arbitrary n is now straightforward. If we want to replace the variable
x_i by $u_i = \frac{\partial f}{\partial x_i}$, we take

$$g(x_1, \ldots, x_{i-1}, u_i, x_{i+1}, \ldots, x_n) = f(x_1, \ldots, x_n) - x_i u_i\,.$$

(e) Show, that g does not depend on x_i.

The most well-known application of the Legendre transform is the transition from the Lagrange- to the Hamilton function in classical mechanics. But also in the context of thermodynamics it has broad applications. Thermodynamical systems are completely determined by three functions of state. Using Legendre transformations one can go to a different choice for those functions of state. In the microcanonical ensemble, the functions of state are, for example, given by its inner energy E, the volume V and number of particles N, while they are given by temperature T, V and N in the canonical ensemble. The thermodynamic potential of the microcanonical ensemble is the entropy $S(E, V, N)$ and its Legendre transform, the free energy $F(T, V, N)$, is the thermodynamic potential of the canonical ensemble.

<div align="center">−HOMEWORK−</div>

H 4.1 Real gas   *(3+4+3=10) Points*
We want to consider a real gas in the canonical ensemble. Let N ($N \gg 1$) the number of molecules in a box with volume V. The system has temperature T and its Hamilton function is given by

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<k} U(|x_i - x_k|),$$

where x_i and p_i describe position and momentum of the i-th molecule and the potential U only depends on the relative distance of the molecules. As a good approximation to the two-particle potential, we will use the *Sutherland potential*

$$U(r) = \begin{cases} \infty & r < r_0 \\ -U_0 \left(\frac{r_0}{r}\right)^6 & r \geq r_0 \end{cases},$$

which treats the molecules as solid balls with radius $r_0/2$.

(a) Consider the canonical partition function

$$Z = \frac{1}{N! h^{3N}} \int d^{3N}x \, d^{3N}p \, \exp\{-\beta H(x_i, p_i)\} .$$

Show, that

$$Z = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \left\{ V^N + V^{N-2} \sum_{i<k} \int d^3x_i \int d^3x_k \left(\exp\{-\beta U(|x_i - x_k|)\} - 1\right) + \ldots \right\},$$

by expanding Z around the parameter $1 \gg f_{ik} = \exp\{-\beta U(|x_i - x_k|)\} - 1$.
Hint: $\prod_{i<k}(1 + f_{ik}) = 1 + \sum_{i<k} f_{ik} + \ldots$.

(b) Show, that

$$Z = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} V^N \left\{ 1 + \frac{N^2 u}{2V} + \ldots \right\}$$

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and that

$$p = \frac{\partial}{\partial V} (kT \log Z) \approx \frac{NkT}{V} \left(1 - \frac{u}{2}\frac{N}{V}\right),$$

is fulfilled, where we write shorthand

$$u = 4\pi \int_0^\infty r^2 \mathrm{d}r \left(\exp\{-\beta U(r)\} - 1\right).$$

Hence, the equation of state of the real gas only differs to the one of the ideal gas by a correcting factor $\left(1 - \frac{u}{2}\frac{N}{V}\right)$.

(c) Now we want to use the Sutherland potential to calculate the integral in u. Show, that the equation of state is given by

$$p = \frac{NkT}{V} \left\{1 + \frac{2\pi N r_0^3}{3V} \left(1 - \frac{U_0}{kT}\right)\right\}.$$

Hint: Use $\beta U_0 \ll 1$ to expand the exponential up to linear order.

One can rewrite the equation of state as

$$\left(p + \frac{aN^2}{V^2}\right)\left(\frac{V}{N} - b\right) = kT,$$

which is the equation of state of a Van-der-Waals gas, by using that the volume $4\pi r_0^3/3$ of the molecules is, in the case of not too high pressures, small compared to the volume per particle V/N. In this way, one can calculate the Van-der-Waals parameters

$$a = \frac{2\pi}{3} r_0^3 U_0, \qquad b = \frac{2\pi}{3} r_0^3$$

from statistical physics.

H 4.2 Gibbs' paradoxon *(2+3=5) Points*
A thermodynamically isolated container is divided into two chambers by an isolated wall. Both chambers contain ideal gases with constant heat capacity $c_V = T \left(\frac{\partial S}{\partial T}\right)_{V,N}$. The first chamber contains N_1 particles at the temperature T_1 and pressure p_1, the second chamber contains N_2 particles at the temperature T_2 and pressure p_2.

(a) Now the wall is made movable and its thermal isolation is removed. After the system going to its equilibrium both gases have the same pressure p and the same temperature T. Calculate these using the equations of state of the ideal gas.

(b) The wall is now removed. Calculate the change in total entropy S induced by the mixing in cases the gases are (1) different and (2) identical. Here, the entropy of an ideal gas is approximated by

$$S = Nk\left[\log V + \frac{3}{2}\left(1 + \log(2pmkT/h^2)\right)\right].$$

Why does the second case lead to an objection?

H 4.3 Energy fluctuations in the canonical ensemble *5 Punkte*

In the case of a canonical ensemble, the probability of the energy to take the value E_i is given by

$$P(E_i) = \frac{1}{Z} \exp\left(-\beta E\right) ,$$

where $Z = \sum_k \exp\left(-\beta E_k\right)$. Show, that the variance of the energy is given by

$$(\Delta E)^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = kT^2 \frac{\partial \langle E \rangle}{\partial T} .$$

The relative standard deviation $\frac{\sqrt{(\Delta E)^2}}{\langle E \rangle}$ is hence proportional to $N^{-\frac{1}{2}}$. In the limit $N \to \infty$ the energy distribution of the canonical ensemble approaches the one of the microcanonical ensemble, which, for a given energy value E_0 of the system is given by $\delta(E - E_0)$.