
Übungen zu Theoretische Physik IV

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<http://www.th.physik.uni-bonn.de/people/forste/exercises/ws1213/tp4>

–CLASS EXERCISES–

A 7.1 Positive Homogeneous Functions

Let

$$\Phi : \begin{array}{l} \mathbb{R}^n \rightarrow \mathbb{R} \\ (x_1, \dots, x_n) \mapsto \Phi(x_1, \dots, x_n) \end{array}$$

be a positive homogeneous function of degree k , that means

$$\Phi(\lambda x_1, \dots, \lambda x_n) = \lambda^k \Phi(x_1, \dots, x_n), \quad \forall \lambda \in \mathbb{R}_+.$$

- (a) Show *Euler's homogeneous function theorem*, that means that the above definition is equivalent to the condition

$$k\Phi(x_1, \dots, x_n) = \sum_{i=1}^n \frac{\partial \Phi}{\partial x_i} x_i.$$

Hint: Define $g(\lambda) = \Phi(\lambda x_1, \dots, \lambda x_n) - \lambda^k \Phi(x_1, \dots, x_n)$ and show that $g(\lambda)$ solves the differential equation $\lambda g'(\lambda) = kg(\lambda)$ with boundary condition $g(1) = 0$.

- (b) Show that the partial derivatives $\frac{\partial \Phi}{\partial x_i}$ are homogeneous functions of degree $k - 1$.

In thermodynamics a system is called *homogeneous* if it has the same specific properties in every partition of its volume. For such systems the functions of state E, S, F, H, G and Φ are positive homogeneous functions of degree 1 - one calls them *extensive*. The application of Euler's homogeneous function theorem on the entropy yields the Gibbs-Duhem relation

$$E = TS - PV + \mu N.$$

From task (b) it then directly follows, that the thermodynamical derivatives p, T, μ are homogeneous functions of degree 0 - one calls them *intensive*.

A 7.2 Free Enthalpy

In Exerciese H 6.1 we found the free enthalpy as the function of state of the isothermal-isobaric ensemble. Especially in the context of chemistry it is of particular importance because in the case of reactions which procede at constant pressure the systems is basically always in thermal equilibrium - e.g. in batteries or fuel cells. Reactions for which the free

enthalpy decreases are called *exergonic*, those in which it increases are called *endergonic*. Here we want to calculate the free enthalpy of the ideal gas in two different ways. Consider the entropy of the ideal gas given by¹

$$S(U, V, N) = Nk \left(s_0(N_0, V_0, U_0) + \log \left\{ \left(\frac{N_0}{N} \right)^{\frac{5}{2}} \left(\frac{U}{U_0} \right)^{\frac{3}{2}} \left(\frac{V}{V_0} \right) \right\} \right)$$

where s_0 is a constant and where we write U for the internal energy.

(a) Show that

$$S(T, p, N) = Nk \left(s_0(T_0, p_0) + \log \left\{ \left(\frac{T}{T_0} \right)^{\frac{5}{2}} \left(\frac{p_0}{p} \right) \right\} \right)$$

holds, where $T_0 = \frac{2}{3} \frac{U_0}{N_0 k}$ and $p_0 = \frac{2U_0}{3V_0}$.

- (b) Calculate the chemical potential μ of the ideal gas as a function of P and T and use your result to determine the free enthalpy $G(T, p, N)$.
- (c) Use the fact that G is a Legendre transform of the free energy to deduce an expression for $G(T, p, N)$ and compare the result to the one you obtained in (a).
- (d) Show in general that the free enthalpy and its derivative with respect to the temperature are related to the enthalpy by the *Gibbs-Helmholtz equation*

$$H = -T^2 \left(\frac{\partial(G/T)}{\partial T} \right)_p.$$

–HOMEWORK–

H 7.1 Entropy of the Ideal Gas

(3+4+3=10) Points

In statistical physics one calculates the entropy of a system as a function of the intensive variables within a microscopic model and then deduces the equations of state using the fundamental equation. Here we want to look at the reverse. Consider the two equations of state of the ideal gas

$$U = \frac{f}{2} NkT \quad \text{and} \quad pV = NkT,$$

as given empirically. Here we use U for the internal energy and denote the number of degrees of freedom by f (e.g. we calculated $f = 5$ for diatomic gases in exercise A 6.1).

¹Compare this expression with the formula for the entropy that we arrive at in exercise H 7.1. Here $f = 3$.

- (a) Use the differential form of the fundamental equation

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN,$$

to show that

$$pV^{(f+2)/f} = \text{const.} \quad \text{und} \quad VT^{f/2} = \text{const.}$$

holds for an ideal gas undergoing an adiabatic process, i.e. $dS = 0$, with constant number of particles N .

- (b) Deduce the equation

$$ds = \frac{1}{T}du + \frac{p}{T}dv,$$

where $s = S/N$, $u = U/N$, $v = V/N$ from the differential form of the fundamental equation.

- (c) Integrate the equation you found in (b) to show that the entropy of the ideal gas is given by

$$S(U, V, N) = S_0 \frac{N}{N_0} + Nk \left[\frac{f}{2} \log \frac{U}{U_0} + \log \frac{V}{V_0} - \frac{f+2}{2} \log \frac{N}{N_0} \right],$$

where S_0 , U_0 , V_0 and N_0 are integration constants.

H 7.2 Temperature Reduction in a Gravitational Field (3+2+2+3=10) Points

Regard the earth's atmosphere as an ideal gas with molar mass $\mu = mN_A$, where m is the molecular mass and N_A the Avogadro constant, which feels the homogeneous gravitational field of the earth with standard gravity g .

- (a) Use the thermal equation of state to show that for the change of pressure p with the height z above sea level,

$$\frac{dp}{p} = -\frac{\mu g}{RT}dz$$

holds, where $R = N_A k$ is the *gas constant*.

Hint: Which forces does a volume element of cross-sectional area A and height dz experience?

- (b) Show, using the assumption that the decrease of pressure you found in (a) is due to an adiabatic expansion, that pressure and temperature are related by

$$\frac{dp}{p} = \frac{f+2}{2} \frac{dT}{T},$$

where f is the number of degrees of freedom of the gas.

Hint: Use your result for the adiabatic expansion of an ideal gas from H 7.1 (a).

- (c) Calculate $\frac{dT}{dz}$ under the assumption that the atmosphere is mainly made of nitrogen, that means $f = 5$, in degrees per kilometre.
- (d) Determine the pressure P in the height z for the case that temperature and pressure have the values T_0 and p_0 at sea level and that the atmosphere is considered adiabatic.