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WS 2021/22   **TPIV: Quantum physics and statistical physics**   **Sheet 01**

1. Deductions from the equation of state

The existence of the equation of state $f(p, V, T) = 0$ implies, on the one hand, that only two of the state variables p, V and T can be viewed as independent variables in the case of thermodynamic changes in state. On the other hand, the equation of state implies, among other things, the validity of the following relation

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} . \tag{1}$$

The index in brackets indicates which of the state variables must be viewed as constant in the case of the corresponding change in state. To see how such relations follow from the equation of state, we denote one of the variables p, V and T with x, y and z, and write $f(x, y, z) = 0$ for the equation of state . For constant z, assuming the solvability of the implicitly definite function $f(x, y, z) = 0$ for the variable x, then there exists a functional relationship such that $x = x(y)$.

(a) Show that $f(x, y, z) = 0$ leads to the relation

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} .$$

for a constant z.

(1 Point)

(b) For a constant z derive the following equation from the equation of state:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial f}{\partial y}\right)_x}{\left(\frac{\partial f}{\partial x}\right)_y} .$$

(1 Point)

(c) Prove the identity

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

and deduce from this the validity of Eq. (1).

(1 Point)

2. Equation of state of the Van der Waals gas

The equation of state of the Van der Waals gas reads

$$\left(p + \frac{a}{V^2}\right)(V - b) = NkT$$

where $a > 0$ and $b > 0$ represent substance-specific material constants. In contrast to the equation of state of an ideal gas, interactions between the particles are (approximately) taken into account here. However, since a and b depend on the number of particles, it is advantageous to to replace these quantities according to $a = N^2\alpha$ and $b = 4Nv_0$, where v_0 and α are independent of the number of particles. This gives us the equation of state

$$\left(p + \frac{\alpha}{(V/N)^2}\right)\left(\frac{V}{N} - 4v_0\right) = kT.$$

Due to the inherent volume of the gas particles, the following applies to the gas volume $V > 4Nv_0$.

(a) Determine the critical temperature T_k, above which the isotherms $p = p(V)$ of the van der Waals gas are strictly monotonic, see Fig. 1(a).
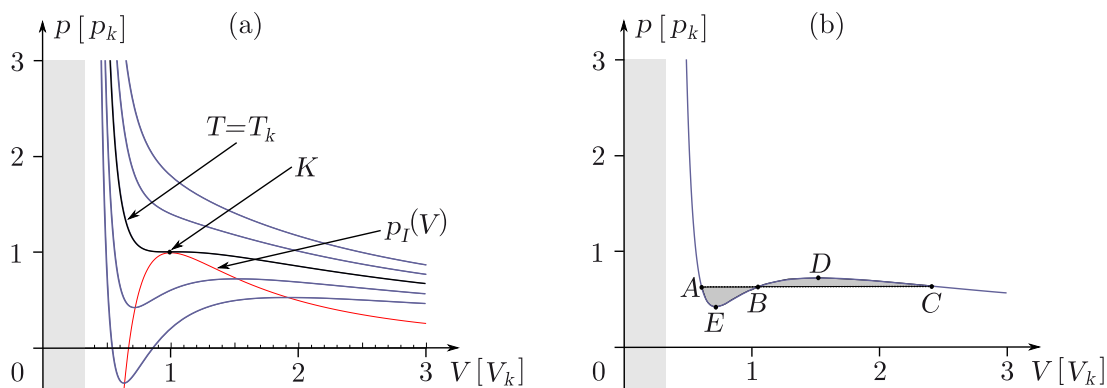
(2 Points)

Abbildung 1: (a) Isotherms of the Van der Waals gas and (b) Maxwell construction.

(b) For $T < T_k$ the isotherms have extrema, see Fig 1(b). Determine the curve $p_I(V)$, on which the extreme values lie. This curve has the so-called "critical

point" K in common with the isotherm $T = T_k$. Determine its "coordinates" (V_k, p_k). What can be said about the stability of the states lying on an isotherm $T < T_k$ between their two points of intersection with $p_I(V)$?

(3 Points)

(c) What does the Van der Waals equation of state look like if instead of p, V and T the introduces the critical variables related variables $\tilde{p} = p/p_k$, $\tilde{V} = V/V_k$ and $\tilde{T} = T/T_k$?

(1 Point)

(d) For every isotherm $T < T_k$ there is a certain pressure range in which there are three volumes for a fixed pressure. Since the volume (with a fixed number of particles) is also clearly defined in a homogeneous system with pressure and temperature, the Van der Waals equation can no longer describe a homogeneous system in this area. It is therefore obvious to identify the smallest volume with the liquid and the largest volume with the gas phase of a two-phase system. Then it is clear, however, that the isotherm in its analytical form cannot correspond to reality, since one knows from experiment that the liquid and gas phases can only coexist at a given temperature if the vapor pressure is uniform. If the isotherm is to be modified so that it can describe a two-phase system, part of the isotherm must also be isobars, as sketched in Fig. 1 (b). How can one find the vapor pressure isobars A B C for a given Van der Waals isotherm A E B D C? Give a qualitative answer without a detailed calculation.

Note:
The internal energy of a system depends only on the present state and not on how this state is reached. Since the temperature is constant by definition along an isotherm, the following applies

$$U_C - U_A = -\int_{V_A}^{V_C} p\, dV$$

both along A B C and along A E B D C.

(1 Point)

(e) In the following we restrict ourselves to the isotherms $T > T_k$. Give the work done by the system along an isotherm $T > T_k$ $\mathcal{L} = \int_{V_1}^{V_2} p\, dV$ if the volume is from V_1 to $V_2 > V_1$ expands. Is this work greater or less than with a correspon-

ding change in the state of the ideal gas?

(2 Points)

(f) Finally we want to investigate the adiabatic expansion of the van der Waals gas. To do this, we isolate the gas so that heat exchange with the environment is no longer possible ($\delta Q = 0$). In analogy to the derivation of the diabatic expansion formula of the ideal gas $pV^K = \text{const.}$, With K as the adiabatic exponent, derive the corresponding relation for the Van der Waals gas.

(2 Points)

3. Barometric height formula of the ideal gas in a homogeneous gravitational field

Derive the barometric height formula in the form

$$\frac{dT}{dh} = -\frac{K-1}{K}\frac{gM}{R},\qquad(2)$$

where g denotes the local gravitational acceleration, $K = 1 + R/C_V$ the adiabatic exponent and M the molar mass of the ideal gas.

Make the assumption that the change in volume of the ascending and descending convection vents can be described to a good approximation by the adiabatic expansion ($\delta Q = 0$), since the air is not a good conductor of heat. Show that the infinitesimal change in pressure dp between the heights h and $h + \delta h$, see Fig. 2, over $dp = -\rho g\, dh$ results, where ρ denotes the density of the gas. Using the ideal gas equation and the equation for the adiabatic volume change of an ideal gas $pV^K = \mathrm{const.}$, Eq. (2) can be derived.
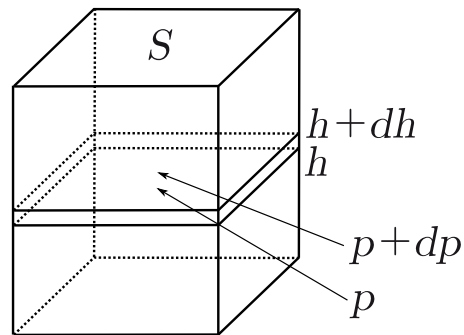

Abbildung 2: To derive the barometric altitude formula.

(2 Points)