Department of Physics
Summer 2023
Thermodynamics
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# Sheet 05

Discussion: Thursday 22.06.23

## Exercise 1

Consider a simple fluid and show that the differential form of reversible heat would only be exact, if the unphysical condition $\frac{\partial P}{\partial T}\big|_V = 0$ were satisfied.

## Exercise 2

Represent the pressure of a simple fluid as a Legendre transform of the energy density $E/V$.

## Exercise 3 Gas with interaction

We consider a gas with an equation of state of the form (beginning of virial evolution):

$$P = RT\left[\frac{N}{V} + \left(\frac{N}{V}\right)^2 B(T)\right]. \tag{1}$$

The heat capacity has the form

$$C_V = \frac{3}{2}NR + NR\frac{N}{V}f(T)\,. \tag{2}$$

(a) Express $f(T)$ by $B(T)$. Show that $\frac{\partial E}{\partial V}\big|_T$ is not zero.

(b) Calculate $S(T,V)$ and $E(T,V)$.

(c) Calculate $H$, $F$ and $\mu$ as functions of $T$ and $V$.

## Exercise 4 Boyle temperature

Consider $1\,\mathrm{mol}$ of the van der Waals gas. Represent the pressure in the lowest powers of $n = 1/v$, where $v$ is the molar volume:

$$P = B_1(T)\cdot n + B_2(T)\cdot n^2 + \ldots \tag{3}$$

Determine $B_1(T)$ and $B_2(T)$. What can you say about the pressure of a v.d.W. gas compared to an ideal gas? Interpret $B_2(T)$ physically.

**Exercise 5** Hot water bottles

Read section 12.7 in the notes first to understand the problem.

(a) Consider the thermodynamic potentials $F$, $H$, and $G$ for an ideal gas and argue that these are not decomposable.

(b) Now consider a solid. Starting from $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V$, argue that we cannot decompose the energy into $E(S,V) \approx E_1(S) + E_2(V)$. Why is this different when we consider enthalpy $H$ or Gibbs energy $G$?

(c) What follows from (b) for the difference between $C_V$ and $C_P$ for solids? Under what conditions is the decomposition of $H$ and $G$ meaningful for liquids?

(d) Explain why the decomposability of one of the potentials leads to the intuitive feeling, that heat is a separate quantity within solids and fluids. This understanding had led science down the wrong path of „caloric theory“.