

# Problem Sheet 3

## I. HEAT IN THE IDEAL GAS

Find the error in the following wrong argument:

We know that the internal energy of a body satisfies

$$dE = \delta Q + \delta W. \quad (1.1)$$

Thereby we have for the heat

$$\delta Q = C_V dT \quad (1.2)$$

and the work

$$\delta W = -pdV. \quad (1.3)$$

From this we conclude that

$$\left. \frac{\partial E}{\partial V} \right|_T = -p. \quad (1.4)$$

On the other hand we know that  $E = E(T)$  is independent of  $V$ , and thus (1.4) is obviously wrong. Where is the flaw in the argument?

### A. Free energy of the ideal gas

Use

$$E = \frac{3}{2}TN, \quad (1.5)$$

derived in the last problem, and the relation

$$F - T\partial F/\partial T|_V = E = \frac{3}{2}TN \quad (1.6)$$

to find an expression for the free energy of the ideal gas by integrating (1.6). Pay attention to a free constant which depends on  $V$  when you integrate!

Then use

$$\partial F/\partial V|_T = -P = -NT/V \quad (1.7)$$

to fix the remaining freedom in the expression you found (up to one free constant factor). Use the fact that the free energy per particle,  $f \equiv F/N$ , should only depend on intensive quantities like temperature  $T$  and density  $n = N/V$ ! What dimension must the free factor have? From this dimensional analysis, can you infer what combination of  $\hbar$  and  $m$  (particle mass) this factor must be? Note that only a purely numerical factor remains undetermined by this reasoning!

## B. Entropy and equation of state - once more

Calculate the microcanonical entropy for an ideal gas of  $N$  particles of mass  $m$  (monoatomic) in a volume  $V$ . It is defined as the logarithm of the phase space volume in a small energy interval of size  $\Delta E$  around  $E$ . For small  $\Delta E$  this can be written as :

$$S_{\text{micro};\Delta E}(E) = \log \left[ \Delta E \int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N}} \delta(E - E(p, q)) \right] \quad (1.8)$$

using that the energy  $E(p, q) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$  is of purely kinetic origin.

To leading order (terms proportional to  $N$ ) this yields the same as the canonical definition of entropy (this is the equivalence of ensembles!). If you want to make contact between microcanonical and canonical expressions for the entropy beyond this leading order, what value for  $\Delta E$  would you choose to come as close as possible to the canonical expression? In particular, how should  $\Delta E$  scale with  $N$ ?

Calculate the temperature associated to  $E$  as  $T = [\partial S / \partial E]_V^{-1}$  and recover the equipartition theorem.

Derive (once again) the equation of state by calculating the pressure:

$$P = \partial E / \partial V|_S = \dots = \frac{NT}{V}. \quad (1.9)$$

(Make use, e.g., of the identity for partial derivatives which you proved in the last problem!

Knowing  $S(E, V)$ , obtain the thermodynamic potential  $E(S, V)$ . Also obtain the Legendre transform of the latter with respect to  $S$ , the free energy  $F(T, V)$ , and compare with the result from the last exercise!

## C. Pathology of the entropy of classical systems at low $T$

Show from the above that the entropy of the ideal gas has a behavior (at a fixed volume)

$$S(T) = S_0(T_0) + C_V \ln(T/T_0) \quad (1.10)$$

where  $T_0$  is an arbitrary reference temperature. This implies that  $S(T \rightarrow 0) \rightarrow \infty$ , in clear contradiction to Nernst's theorem  $S(T \rightarrow 0) \rightarrow 0$  and the general law that  $S(T) > 0$ . Remember that the positivity of the entropy follows from the definition of entropy as the logarithm of the number of relevant quantum states, which is always  $> 1$ .

Another important example exhibiting the same pathology is the 1d harmonic oscillator with

$$E(p, q) = \frac{k}{2}q^2 + \frac{m}{2}p^2. \quad (1.11)$$

Calculate the (classical) entropy, both canonically and microcanonically for  $N$  independent harmonic oscillators, and convince yourself of the equivalence of the ensembles! Show in particular that the entropy has the same logarithmic behavior at low  $T$ .

Argue that this pathology,  $S(T) \sim \ln(T)$ , occurs generically in *classical* systems with kinetic degrees of freedom. (The ideal gas is the cleanest example of this kind.)

How can one cure this pathology? An essential element of the cure comes from quantum mechanics, the uncertainty principle and the discreteness of levels. Try to figure out what the essential mechanism is!

Take the above two examples and find the scale of temperature  $T_Q$  below which quantum mechanics must be taken into account there! *Hint:* Start with the harmonic oscillator and identify the temperature scale  $T_Q$  (up to a numerical factor). *Suggestion:* Those who know already how to do it: compute the entropy for a collection of independent quantum harmonic oscillator and convince yourself that while at high  $T$  you find essentially the classical result,  $S$  remains positive and tends to zero when  $T \rightarrow 0$ .

For the ideal gas, you can think first about the case of a very low density, i.e., a volume  $V$  with only a few particles (very low, fixed density  $n = N/V$ ). In the limit of a single particle in the volume what is your expectation for the temperature scale  $T_Q$ ? (Note that this scale will depend on the volume!)

Later we will see that in the case of finite density quantum statistics becomes important once the temperature falls below the energy scale  $T_Q$  which corresponds to a volume equal to the volume per particle. Express this value of  $T_Q$  as a function of  $\hbar$ ,  $m$  and density  $n$ !