

Problem Sheet 2

I. THE IDEAL GAS

The ideal gas is a theoretical idealization. It assumes point-like particles (no spatial extension) with essentially no interactions (apart from some infinitesimal interaction which is necessary to ensure equilibration).

A. Equation of state

Derive the equation of state

$$P = \frac{N}{V}T = nT \quad (1.1)$$

($k_B = 1$) from kinetic considerations. (Here N is the number of point-like gas particles.) Namely: Calculate what is the average momentum change (= force impulse $\Delta p = F\Delta t$) which particles receive when reflecting from the wall? Determine how many particles reflect under certain angles from a wall, per unit time and unit area. Average over the angles. In the end you will get an answer which contains the average of the square of the velocity component in one direction, $\overline{v_x^2}$, which we will compute below.

Using that the total energy $E(p_i, q_i)$ is only made of kinetic energy, $E = \sum_i p_i^2/2m$, and using the distribution function $\rho(p, q) = \rho(E_{p,q}) \sim \exp[-\beta E(p, q)]$ (with $\beta = 1/T$) derive the equipartition theorem for the kinetic energy in the form

$$\frac{\overline{mv_x^2}}{2} = \frac{T}{2} \quad (1.2)$$

Show that

$$E = \frac{3}{2}TN \quad (1.3)$$

independent of volume! How do you understand the independence of the volume? Will that still be true in non-ideal gases, and if no, why not? Do you expect that the energy increases or decreases with the volume? What does it depend on?

The specific heat is defined as $C_V = dQ/dT|_V$ and $C_P = dQ/dT|_P$ depending on whether V or P is held constant. Show that the specific heat per particle is $C_V/N = 3/2$ at constant volume and $C_P/N = 5/2$. Is C_P always bigger than C_V ? If yes, explain why!

[Remark: if the gas particles are not exactly point-like this is not true. The rotational degrees of freedom more complicated molecules will then also contribute to the kinetic energy, by $T/2$ per degree of freedom: 2 per molecule in linear molecules, and 3 in non-collinear molecules. - For those who like a challenge: How would you prove this?]

II. THERMODYNAMIC DERIVATIVES

For any three variables which satisfy a constraint $f(X, Y, Z) = 0$ (e.g., the equation of state $P - f_P(V, T) = 0$) one has the relation

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1. \quad (2.1)$$

Prove this! Check it explicitly in the case of the ideal gas $X, Y, Z = P, V, T$.

III. REVERSIBLE PROCESSES OF AN IDEAL GAS

Below we always consider an ideal gas in a closed container whose volume can be changed by a piston. The container is either considered as thermally isolated ($\delta Q = 0$) or we consider that it can exchange heat (reversibly) with another heat reservoir (much bigger container at the same temperature).

A. Isothermal expansion

Let the gas start with a volume V_1 and at temperature T_1 . Let it expand to volume $V_2 > V_1$, maintaining the temperature.

How much work does the expanding gas do? How much heat does it absorb? What is the change in internal energy? Has the entropy of the gas in the container changed? By how much?

B. Isobaric compression

Take the gas at $T = T_1$, $V = V_2$ and compress it at constant pressure back to V_1 (and let it exchange heat with the reservoir). What is the final temperature T_2 ? How much work was done? What is the final internal energy? How much heat was exchanged, and how much entropy has the gas lost?

C. Isochoric heating ($V = \text{const}$)

Imagine to finally heat reversibly the container of gas at fixed volume V_1 back to T_1 . This completes a cyclic process. What is the [rather unpractical] condition for reversibility in this last step?

By how much do pressure and entropy increase? How much work is done? How much heat is absorbed?

D. Reversible cycle

Take the above three steps together. Verify that the changes in state functions such as entropy, internal energy, pressure, volume and temperature all add up to zero, as it must be.

Determine how much work (W) was extracted over the whole cycle! How much heat (Q) went into the system during step 1 and 3 together? Note that the result that $W \neq 0$, $Q \neq 0$ shows that work and heat are not functions of the thermodynamic state only, but of the way the system is prepared and processes!

Carnot tells us that the maximal efficiency of a heat engine working between reservoirs T_1 and $T_2 < T_1$ is

$$\frac{W}{Q} \leq \frac{T_1 - T_2}{T_1}. \quad (3.1)$$

Verify that you get a result that is strictly lower than Carnot's bound! Why must that be so?

(The ratio for the above cycle should come out to be:

$$\frac{W}{Q} = \frac{\ln x - 1 + 1/x}{\ln x + 3/2(1 - 1/x)} \quad (3.2)$$

where $x = V_2/V_1 > 1$.)