Lecture Tuesday, Feb 25
RECAP

micro-canonical ensemble:

$$\boxed{\begin{array}{c} d.o.f.s \\ E, N \end{array}}$$

canonical ensemble

$$E \boxed{T, N} \quad T$$
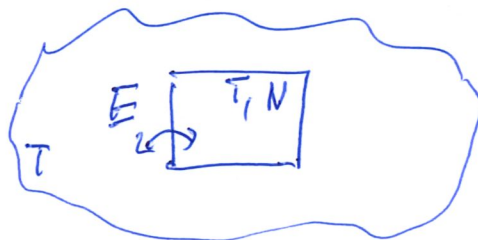
what are we interested in?

$\langle E \rangle$: internal energy of the box

S : entropy

key: partition function: $Z = \sum_{i=1}^{M} e^{-E_i/T}$

where M = dimension of state space

$$\rightarrow F = -T \ln Z \qquad \Rightarrow S = -\frac{dF}{dT}$$

$$\langle E \rangle = -T^2 \frac{d}{dT}\left(\frac{F}{T}\right)$$

examples:

2 d.o.f.s: $N = 2$

$\uparrow \downarrow$

| state space

$\uparrow\uparrow \quad \downarrow\uparrow \quad \uparrow\downarrow \quad \downarrow\downarrow$

$M = 4$

continuous d.o.f.: particle in box; model

$$\sum_{i=1}^{M} \quad\longrightarrow\quad \int \frac{L \cdot dp}{2\pi \hbar} \quad \cdots$$

5.3 Pressure and the equation of state

It is remarkable that we needed quantum physics to properly define the partition function: the classical description of a gas with N particles specified by position and velocity, all real numbers, leads to a state space that is not *countable*. Quantum physics have provided a countable state space and, as a side-effect, introduced the volume V as a parameter in the partition function.

Definition: A parameter (other than temperature) in the canonical partition function, which might enter via the definition of the energy or the state space, is called *control parameter*.

5.3.1 Definition of pressure

As the name suggests, we can usually change the control parameter in an experimental setup. For example, we might change the volume V of a gas container is several ways:
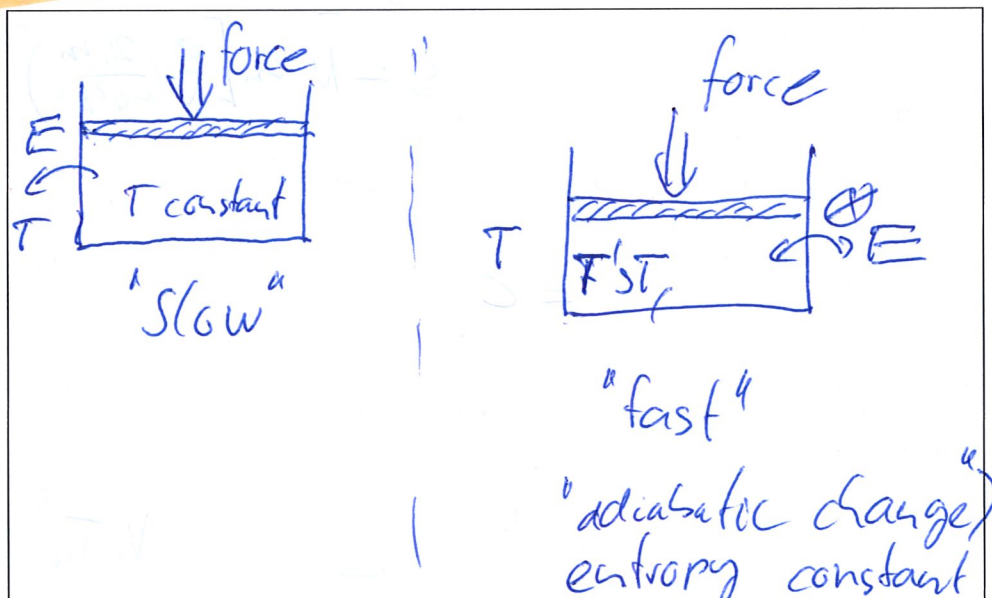
The response of the thermodynamical system to a change in the control parameter then defines new thermodynamical quantities.

Key definition: Consider a thermodynamical system enclosed in a volume V and exposed to a heat-bath with temperature T.

(a) A change of the volume V without changing the entropy of the system is called *adiabatic.*

(b) The change of the internal energy under an adiabatic change of the volume is called **pressure:**

$$p = -\left.\frac{\partial \langle E \rangle}{\partial V}\right|_{S}. \qquad S = \text{constant} \qquad (52)$$

derivative with resp. to V

COMMENT:

If the entropy of the container stays constant, it means that an energy exchange with the heat bath has *not* taken place. One way to realise is that the compression is very fast, so that there is no time for a heat exchange with the surrounding.

5.3.2 The equation of states

$$\langle E \rangle = \frac{3}{2} N T$$

$$S = N \cdot \ln\left[\frac{e}{N}\left(\frac{2\pi m}{4\pi^2 \hbar^2}\right)^{3/2} V T^{3/2}\right] + \frac{3}{2}N$$

WORKED EXAMPLE - the Ideal Gas

We already worked out $\langle E \rangle$ and the entropy S for the ideal gas (see (48) and (51)). Since all N particles are enclosed in the volume V at all times, N does not change during an adiabatic change of volume. Constant entropy then implies

$$V\,T^{3/2} = \text{constant}, \qquad \text{(adiabatic)}. \qquad (53)$$

$= C$

This equation already has some interesting experimental consequences: if we rapidly decrease the volume from V_H to $V_L < V_H$, the temperature in the container increases from T_0 to:

$$T_H = \left(\frac{V_H}{V_L}\right)^{2/3} T_0 > T_0. \qquad V_H T_H^{3/2} = V_0 T_0^{3/2}$$

Using (53), i.e.,

$$T = c\,V^{-2/3},$$

for the internal energy (48), we find:

$$\langle E \rangle = \frac{3}{2} N T \qquad \text{but...} \quad T = c \cdot V^{-2/3}$$

$$\Rightarrow S = \text{constant}$$

$$\langle E \rangle = \frac{3}{2} N \cdot c \, V^{-\frac{2}{3}}$$

$$p = -\frac{\partial \langle E \rangle}{\partial V}\bigg|_{S=N} = \frac{3}{2} N \cdot c \left(-\frac{2}{3}\right) V^{-5/3}$$

$$= N \cdot c \, V^{-5/3} = N \cdot c \, V^{-\frac{2}{3}} \frac{1}{V} = \frac{N \cdot T}{V}$$

We finally arrive at a relation between thermodynamical quantities:

Key observation:

$$p V = N T \qquad \text{(ideal gas law)}. \tag{54}$$

Definition: An thermodynamic equation, which relates state variables describing the state of matter under a given set of physical conditions, such as pressure, volume, temperature or internal energy, is called *equation-of-state*.

HISTORICAL REMARK: Elements of the Ideal Gas Law were discovered long before a stochastic description of gases were available. Accordingly, these laws were named after their discoverer:

Boyle's law (1662): constant temperature, change pressure

$$T \text{ constant!}$$

$$\boxed{P = \frac{V_0}{V} P}$$

$$P V = N F = P_0 V_0$$
$$\text{const.}$$

Law of Charles and Gay-Lussac (1787): constant pressure, change temperature

$$P_0 \text{ constant}$$

$$P_0 \cdot V = N T \Rightarrow \boxed{\frac{V}{V_0} = \frac{T}{T_0}}$$

$$P_0 V_0 = N T$$

Dalton's law of partial pressures (1801): The pressure of a mixture of gases is equal to the sum of the pressures of all of the constituent gases alone (see exercises).
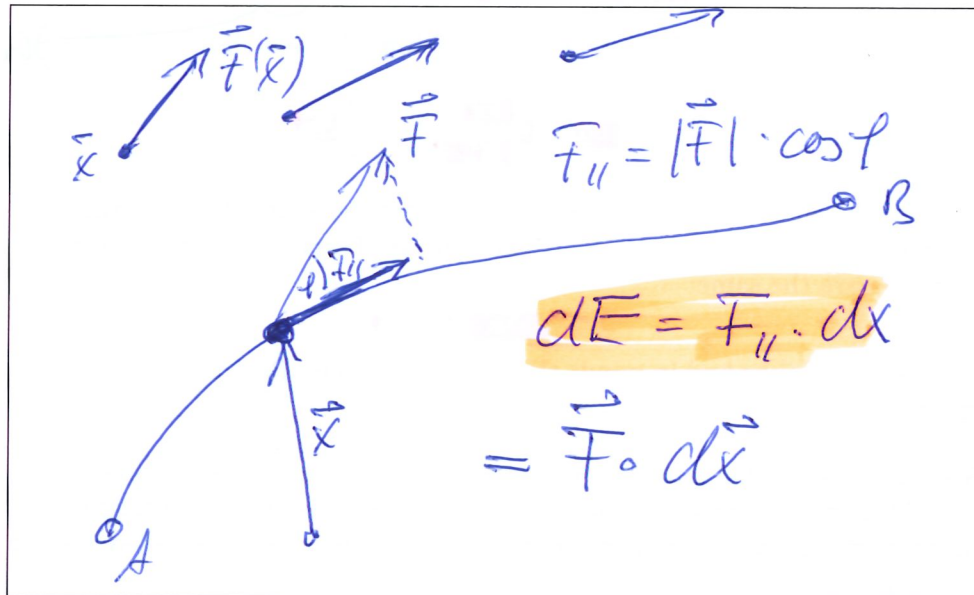

$$P = P_{AR} + P_{He}$$

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5.5 Thermodynamical cycles and engines

5.5.1 Pressure and force

We already used the everyday life intuition and increased the pressure in a container by exerting a force on its movable piston (see subsection 5.3.1). We here formalise this connection.

ILLUSTRATION:

$$F_{\parallel} = |\vec{F}| \cdot \cos\varphi$$
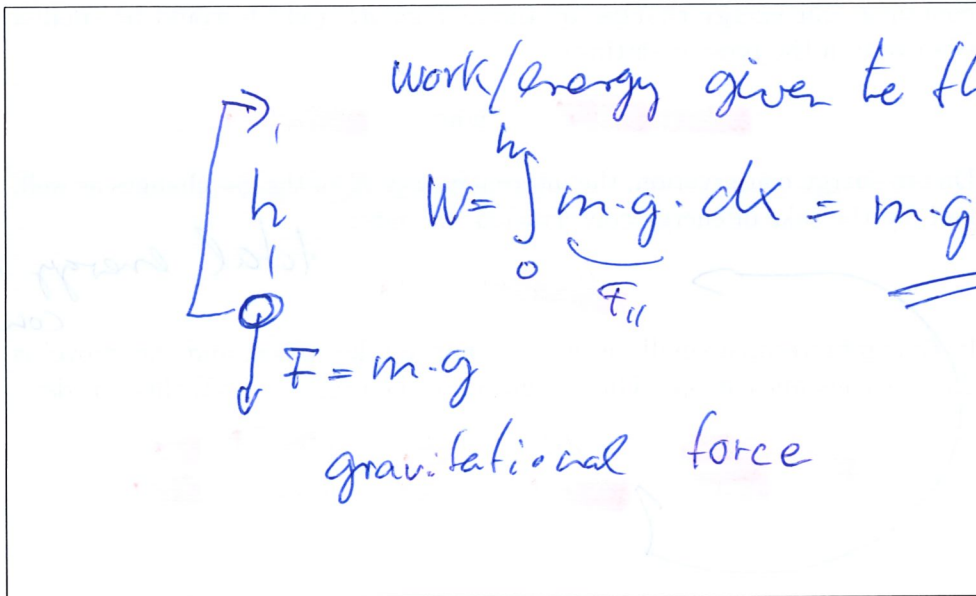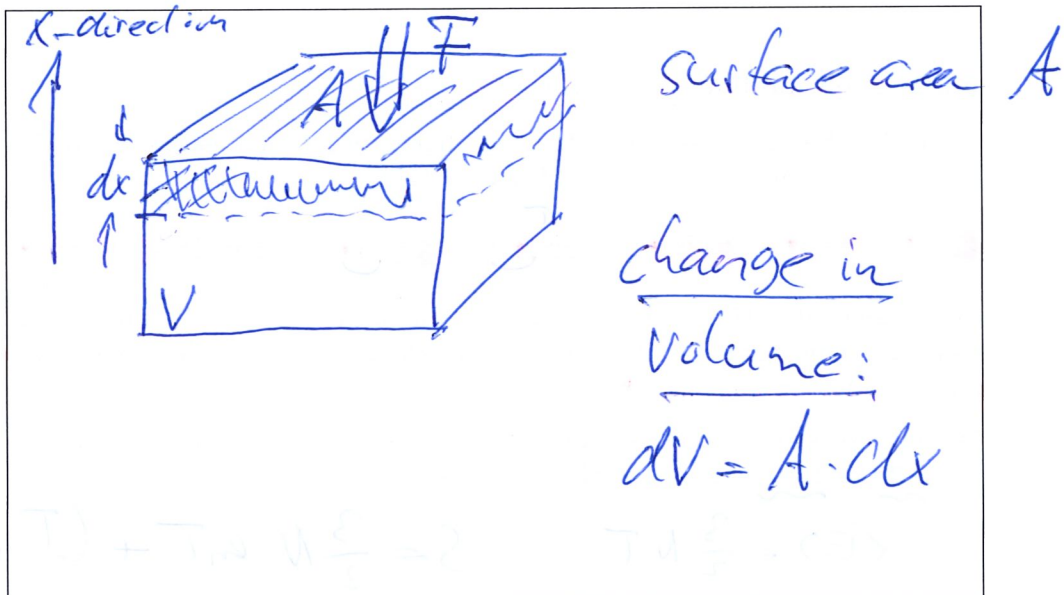
$$dE = F_{\parallel} \cdot dx$$

$$= \vec{F} \cdot d\vec{x}$$

law of Physics

$$\vec{a} \cdot \vec{b} = |\vec{a}| \cdot |\vec{b}| \cos\varphi$$

EXAMPLE - PARTICLE IN THE GRAVITATIONAL FIELD

work/energy given to the particle.

$$W = \int_0^h m \cdot g \cdot dx = m \cdot g \cdot h$$

$$\underbrace{}_{F_{\parallel}}$$

$$F = m \cdot g$$

gravitational force

Let us apply this to a gas container with a force F applied to the piston. The force changes the postion of the piston by dx. The piston as a cross-section A. Thus, the volume changes by $dV = A\,dx$.

x-direction

surface area A

change in volume:

$$dV = A \cdot dx$$

Since we move the piston against the force $F > 0$ from the pressure in the container, our energy changes by the amount dE (which would be smaller than zero in the present setting):

$$dE = F\,dx, \qquad \text{note:} \qquad dx < 0.$$

Due to energy conservation, the internal energy E_i of the gas changes as well, and, by the sake of energy conservation, we have:

$$dE_i + dE = 0. \qquad \text{total energy is conserved}$$

If dx is infinitesimal small, no heat exchange takes place, and the 'move' is done at constant entropy. Our definition of the presssure (52) then yields:

$$p = -\frac{dE_i}{dV} = -\frac{1}{A}\frac{dE_i}{dx} = \frac{1}{A}\frac{dE}{dx} = \frac{1}{A}\frac{F\,dx}{dx} = \frac{F}{A}.$$

Interpretation: The pressure in a container of gas is also given by the force per unit area of container wall.

5.5.2 Thermodynamical cycles

From the above, we also can relate the change in internal energy E_i to the change of volume *without any exchange of heat*:

$$dE_i = -dE = -F\,dx = -p\,A\,dx = -p\,dV \qquad \text{(constant entropy).} \tag{57}$$

Let us generalise this a bit: Let us keep volume V and particle number N constant, while changing the temperature. How does the internal energy E_i and the entropy S change?

We have worked out explicit expression for both for the case of the ideal case (see (48) and (51)). T is now the only variable:

$$\langle E \rangle = \frac{3}{2} N T \qquad\qquad S = \frac{3}{2} N \ln T + (T \text{ independent})$$

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Handwritten (boxed):

change T $\qquad$ (N-constant) $\qquad$ d⟨E⟩

$$d\langle E\rangle = \frac{3}{2} N \cdot dT \qquad dS = \frac{3}{2} N \frac{1}{T} \rightsquigarrow dS = \frac{3}{2} N \frac{dT}{T}$$

$$d\langle E\rangle = dE_i = T \cdot dS$$
$$= E_i$$

Volume constant

Combining both equations, we find:

$$dE_i \;=\; T\,dS \;=:\; dQ\,. \qquad \text{"heat"}$$

If we change the temperature (while volume and particle number are constant), we adding or removing 'heat' from the internal system. The 'heat' dQ is defined as positive if it increases the internal energy.

Assuming that the particle number N does not change in the container, the entropy is a function of the temperature T of the heat bath and the volume V. We can make T the subject of this equation: $T = T(S, V)$. Inserting this into the expression of the internal energy, it also becomes a function of S and V: $E_I[V, T] \to E_I(S, V)$. Using the multi-variate Taylor expansion to first order, we find:

$$E_i(S, V) \;=\; E_i(S_0, V_0) \;+\; \frac{\partial E_i}{\partial T}\bigg|_V (S - S_0) \;+\; \frac{\partial E_i}{\partial V}\bigg|_V (V - V_0) \;+\; \dots$$

We write the last equation in terms of the the differentials $dE_i = E_i(T, V) - E_i(T_0, V_0)$, $dS = S - S_0$, $dV = V - V_0$:

$$dE_i \;=\; T\,dS \;-\; p\,dV\,, \tag{58}$$

where we have used (57). Note that this equation is exact as long as the differentials are infinitesimal small.

Handwritten (bottom):

$$E_i(S\,V) = E_i(S_0\,V_0) + \frac{\partial E_i}{\partial S}\bigg|_V \cdot (S - S_0) + \frac{\partial E_i}{\partial V}\bigg|_S \cdot (V - V_0)$$

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T $\qquad$ Taylor $\qquad$ $-p$

Key equations for thermodynamical cycles:

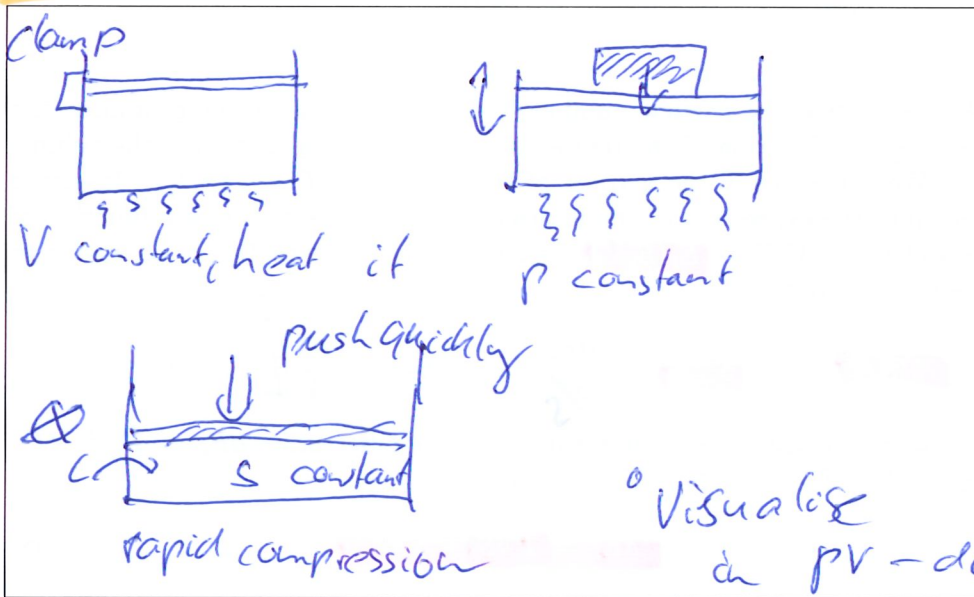C1 The equation of state: $pV = NT$

C2 The internal energy: $E_i = 3/2\,NT$

C3 The equation of constant entropy: $V\,T^{3/2} = \text{constant}$

C4 The change of internal energy: $dE_i = dQ + p\,dV$ $dQ = T\,dS$.

Work done to the gas   *heat*

We can now expose the gas container to a variety of external changes: we can heat it at constant volume, we can heat it at constant pressure, we can compress is rapidly or slowly or a combination of all that.


Clamp

V constant, heat it

p constant

push quickly

S constant

rapid compression

Visualise
on pV - diagramme

To keep track of such changes, it is convenient to visualise these changes in a p-V-diagramme. Each point in this diagramme has a unique pair (p,V). With the help of the equation of state C1, $pV = NT$, we can also associate a temperature ot each point, and, because C2, also an internal energy. Each point thus describes uniquely the state of the gas in the container.

A change of the state of the gas by a change in external parameters hence can be describes as a line in the p-V-diagramme.

WORKED EXAMPLES

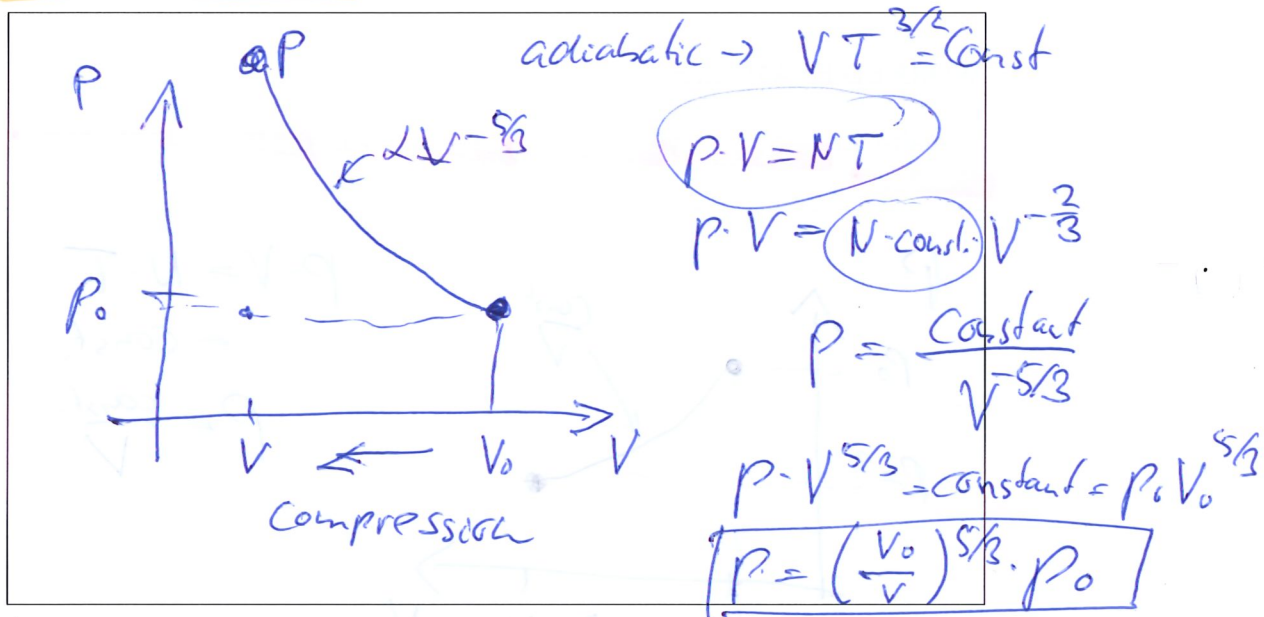Visualise an isothermal (constant T) expansion and calculate the change in pressure.

$$p \cdot V = N \cdot T = \text{Const.}$$

$$p = \frac{\text{const.}}{V}$$
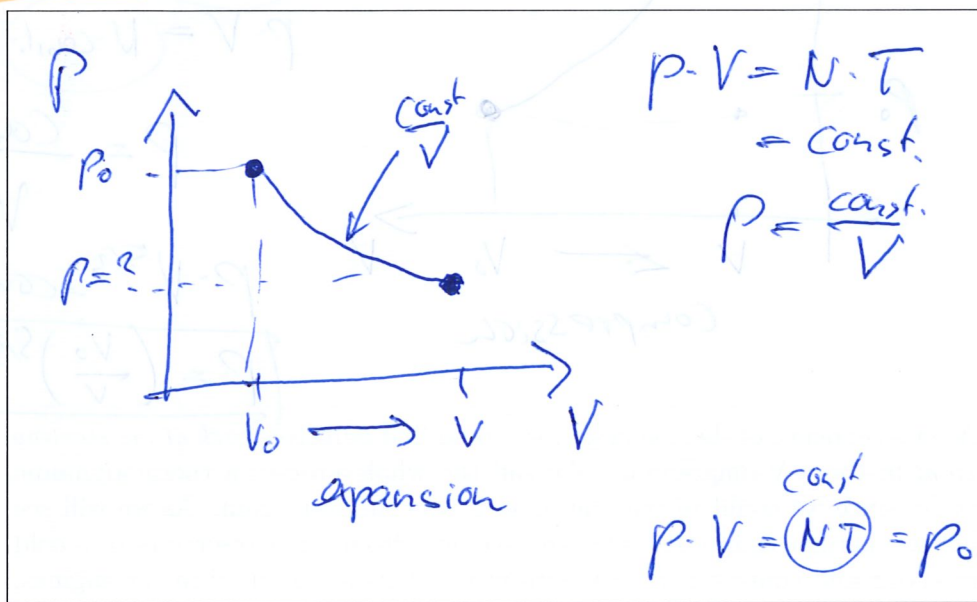
(true for any point on the pV-diag.)

$$p \cdot V = \boxed{N T}^{\text{const}} = p_0 V_0$$

$$\boxed{p = \frac{V_0}{V} \cdot p_0}$$

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After a sequence of these changes, we could find ourselves *back at the starting point* in the p-V-diagramme. We call the whole process a thermodynamic cycle, since we could repeat the process over an over again. As we will see below, thermodynamical cycle can take heat from a hot reservoirs to a cold reservoir and convert part of it into work. This is e.g. used in car engines, refrigerators or heat pumps.

5.5.3 The Carnot cycle

The proto-type of a thermodynamic cycle was proposed by the French physicist Sadi Carnot in 1824, and is nowadays know as the Carnot process. Our case container has access to two different heat reservoirs, one 'hot' reservoir with temperature T_H and one 'cold' with T_L.

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