Cycles

☑ eq. of state: non-relat. ideal (non-interac) gas

$$p \cdot V = N \ast T$$

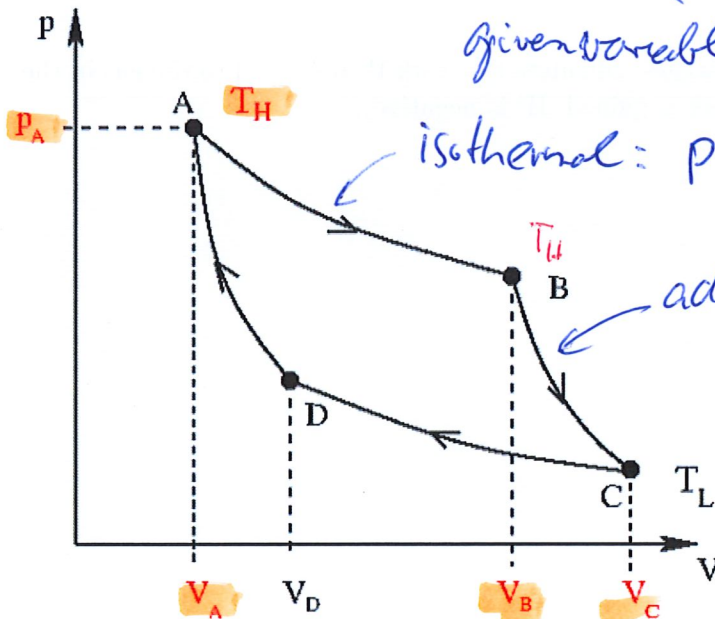☑ Entropy (const?): $V T^{3/2} = const.$

☑ change of internal energy | change of heat | work delivered to the gas

$$dE_i = dQ - p \, dV_i \quad \boxed{dQ = T \, dS}$$

RECAP

The figure below shows the Carnot Cycle in the p-V-diagramme.

given variables are in "red"

isothermal: $p = \dfrac{(N \cdot T)}{V}$

adiabatic: entropy = const.

$\rightarrow V T^{3/2} = const$

$\rightarrow p = \dfrac{N \, T(v)}{V} = \dfrac{const}{V^{5/2}}$

WORKED DETAILS:

expand to V_B expand to V_C

Consider p_A, T_H and the volumes V_A, V_B and V_c as given. Assigning input to variables is quite tedious, since picking the wrong combination of variables could easily lead to inconsistencies. The above choice is inspired by a real experiment: we start at state A at normal condition with p_A the atmospheric pressure, T_H the temperature of the surrounding and V_A our volumen initially. We then slowly expand (isothermal) until we reach V_B. We then rapidly expand (adiabatic) until we reach V_C. The temperature and pressure at B and C is what we could measure, and, hence, we should be able to calculate those. We then slowly compress (isothermal) until we reach V_D and then rapidly back to V_A. We cannot just give a value for V_D, since if we pick this value wrong, we would not getting back to V_A with the final compression. This is telling us that we need to calculate V_D in order to complete the cycle.

- Calculate at each of the points A,B,C,D whatever is missing from: volume, pressure, temperature.

Let us now calculate the ==work delivered== to the internal energy of the gas:

Stage 1: from $A \to B$

T const: $p = \frac{(NT)}{V}$ $\qquad dW = -P_{(V)} dV$

$$W_{A \to B} = -\int_A^B P(V) \cdot dV = -\int_{V_A}^{V_B} \frac{dV}{V} \cdot (N T_H)$$

$$= -N T_H \left[\ln V \right]_{V_A}^{V_B} = -N T_H \cdot \left(\ln V_B - \ln V_A \right)$$

$$= -N T_H \ln\left(\frac{V_B}{V_A}\right) = -P_A V_A \ln\left(\frac{V_B}{V_A}\right) < 0 ?$$

gas delivers: $|W_{A \to B}|$

Stage 2: from $B \to C$

adiabatic: $dE_i = \cancel{dQ}_{=0} - p\,dV$ $\quad \boxed{E_i = \frac{3}{2} NT}$

$$W_{BC} = -\int_B^C p\,dV = \int_B^C dE_i = E_i(C) - E_i(B)$$

$$= \frac{3}{2} N T_L - \frac{3}{2} N \cdot T_H = -\frac{3}{2} N T_H \left(1 - \frac{T_L}{T_H}\right)$$

$$= -\frac{3}{2} \cancel{N} P_A V_A \left(1 - \frac{T_L}{T_H}\right) < 0 ?$$

gas delivers work!

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$$= -\frac{3}{2} P_A V_A \left(1 - \left(\frac{V_B}{V_C}\right)^{2/3}\right)$$

Stage 3: from $C \to D$

isothermal: $T = $ const

$$W_{C \to D} = -\int_C^D p\,dV = -\int_C^D \left(N T_L \frac{dV}{V} \right)$$

$$= -N T_L \ln\left(\frac{V_D}{V_C}\right) = N T_L \ln\left(\frac{V_B}{V_A}\right) > 0 \, !$$

work is delivered to the gas!

Stage 4: from $D \to A$

adiabatic: $dE_i = \cancel{dQ} - p\,dV$ $\boxed{E_c = \frac{3}{2} N T}$

$$W_{DA} = -\int_D^A p\,dV = -E_i(A) + E_i(D)$$

$$= \frac{3}{2} N \left(T_H - T_L \right) = -W_{BC} > 0$$

work is delivered to the gas!

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Stage 1: isothermal

$$dW_1 = -p\,dV\,, \qquad p = \frac{N\,T_H}{V}\,, \qquad dW_1 = -N\,T_H\,\frac{dV}{V}\,,$$

$$W_1 = -N\,T_H\,\ln\left(\frac{V_B}{V_A}\right) = -p_A\,V_A\,\ln\left(\frac{V_B}{V_A}\right).$$

This is negative meaning that the gas is doing the work $|W_1|$ (engine!).

Stage 2: Adiabatic
Since there is no heat flow, the work done to the gas is directly given by the change in the internal energy:

$$W_2 = E_i(C) - E_i(B) = -\frac{3}{2}\,NT_H\left(1 - \frac{T_L}{T_H}\right) = -\frac{3}{2}\,NT_H\left(1 - \left(\frac{V_B}{V_C}\right)^{2/3}\right)$$

$$= -\frac{3}{2}\,p_A\,V_A\left(1 - \left(\frac{V_B}{V_C}\right)^{2/3}\right).$$

Again this part of the cycle delivers work.

Stage 3: Isothermal again (see stage 1)

$$W_3 = -N\,T_L\int_{V_C}^{V_D}\frac{dV}{V} = -N\,T_L\,\ln\left(\frac{V_D}{V_C}\right) = N\,T_L\,\ln\left(\frac{V_B}{V_A}\right).$$

This is positive and energy (work) is delivered to the gas.

Stage 4: Adiabatic again (see stage 2)

$$W_4 = E_i(A) - E_i(D) = \frac{3}{2}\,N\,(T_H - T_L) = -W_2\,.$$

The energy that the gas looses at stage 2 is exactly regained through the process at stage 4.

The total amount of work delivered to the gas throughout one Carnot cycle is hence given by:

$W_{A \to B} \quad W_{B \to C} \quad W_{C \to D} \quad W_{D \to A}$

$$W = W_1 + W_2 + W_3 + W_4 .$$

Using $W_2 + W_4 = 0$ and the explicit expressions for W_1 and W_3, we find:

$$W = - N (T_H - T_L) \ln \left(\frac{V_B}{V_A} \right) = - p_A V_A \left(1 - \frac{T_L}{T_H} \right) \ln \left(\frac{V_B}{V_A} \right) \quad (59)$$

$$= - p_A V_A \left(1 - \left(\frac{V_B}{V_C} \right)^{2/3} \right) \ln \left(\frac{V_B}{V_A} \right) . \quad < 0 \Rightarrow \text{gas delivers work!}$$

$$(\text{engine } !)$$

Let us now study the heat flow in each stage. The key equation is C4:

$$dE_i = dQ + dW , \qquad dW = -p \, dV .$$

isothermal

Stage 1: The internal energy is a function of the temperature only, i.e., $E_i = 3/2 \, N \, T$. This means that during an isothermal process - expansion or compression - the internal energy does *not change*: $dE_i = 0$. We therefore find: iso thermal !

$$0 = dQ + dW , \qquad \Rightarrow \qquad Q_1 = - W_1 .$$

Remember, $W_1 < 0$, i.e., the gas is doing work, and therefore $Q_1 > 0$, i.e., heat is flowing into the gas.

Stage 2/4: Those are adiabatic processes: the entropy is constant:

$$dS = 0 \qquad \Rightarrow \qquad dQ = T \, dS = 0.$$

No heat exchange takes place: $Q_2 = Q_4 = 0$.

Stage 3: It is an isothermal again:

$$Q_3 = - W_3.$$

This time, $W_3 > 0$ and the gas was receiving work. As a consequence, $Q_3 < 0$ and heat is flowing out of the gas container.

For the Carnot process, the container was receiving heat only during stage 1:

$$Q_{in} = Q_1 = - W_1 \, .$$

Remember that W was the work *delivered* to the gas. Hence, we have:

$$W_{done} = -W \, .$$

We therefore find:

$$\eta = \frac{-W}{Q_{in}} = \frac{-W}{-W_1} = \frac{N(T_H - T_L)\ln\frac{V_B}{V_A}}{N\, T_H \cdot \ln\left(\frac{V_B}{V_A}\right)}$$

$$= 1 - \frac{T_L}{T_H} \, ;$$

Altogether, we find the important result

$$\eta = 1 - \frac{T_L}{T_H} \qquad \text{(Carnot cycle)}.$$

COMMENTS

- The higher the temperature difference, the more efficient is the thermodynamical engine.

- If we reverse the order of the stages of the Carnot process (all calculations remain the same), the gas is receiving work and transports heat from the cold to the hot reservoir. This is what a `refrigerator` does!

- In winter, a refrigerator works better in the kitchen than in the garage since the temperature difference between inside and the surrounding is bigger.

- From all thermodynamical cycles, the Carnot process has the best efficiency[10] If for some reason, T_H and T_L approach each other, *all* thermodynamical engines stop working.

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[10]We have not discussed this here. A derivation can be found e.g. in the textbook [1].

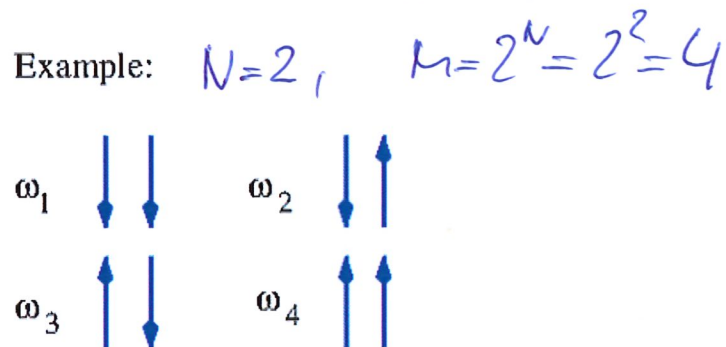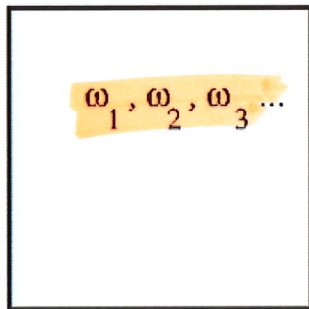# 6 The grand-canonical ensemble

6.1 The particle reservoir

micro

canonical

Starting point is always a statistical ensemble characterised by a number of states $\omega_1, \omega_2, \omega_3 \ldots, \omega_M$. We then add physics information: e.g. that the total energy E or the particle number N of the system is conserved.

We then introduced the *thermodynamical equilibrium*: each of the M micro states ω_i has the same probability $q_i = 1/M$ to occur. We then introduced an extremely useful quantity, which helps to understand the statistical systems - the entropy:
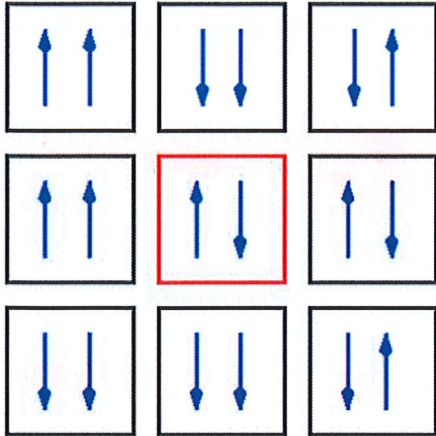
$$S(E, N) = -\sum_{i=1}^{M} q_i \ln q_i = \ln M .$$

In general, the entropy is a function of the conserved quantities.

Example: $N = 2, \quad M = 2^N = 2^2 = 4$

$\omega_1, \omega_2, \omega_3 \ldots$

ω_1 ↓↓

ω_2 ↓↑

ω_3 ↑↓

ω_4 ↑↑

We have used the above graph for an illustration in subsection 4.1.

We the took a different angle of perspective and have consider the above prototype of a system surrounded by many identical system.

Canonical ensemble

We then allowed an *energy exchange* between those systems. We say that our "small" system is immersed in the big system, which is the so-called heat-bath.

We still are interested in the properties of our "small" system: now, the energy of our small system is not conserved anymore, but we can define the average of the energy as internal energy of our small system, i.e., $\langle E \rangle$, with is a function of temperature T and particle number N of boxes.

In subsection 4.1, we found a clever way to describe a clever mathematical way to describe the whole of the system - occupation numbers: n_i is the number of the state ω_i realised in any of the boxes. This also tells us something about our small system. n_i divided by N, the number of boxes, is an estimate for the p_i of finding state ω_i realised in our "small" box.

We then were able to work out the entropy of the whole system as as function of the total energy (which we repeat here for later use).

$$S(E) = -N \sum_{i=1}^{M} p_i \ln p_i, \quad \Longrightarrow \max \quad (60)$$

$\hookrightarrow$ thermod. equ.

$$\sum_{i=1}^{M} p_i = \frac{1}{N} \sum_{i=1}^{M} n_i = 1, \quad (61)$$

$$\sum_{i=1}^{M} p_i E_i = \frac{1}{N} \sum_{i=1}^{M} n_i E_i = E/N. \quad (62)$$

total energy = constant = E

Eq.(61) just tells us that the number of boxes is N, and (62) is saying that the energy of the whole system is E.

We the used the assumption that we are in a thermodynamical equilibrium. for which the entropy is maximal. This entirely fixes the probabilities p_i from (60, 61, 62):

$$p_i = \frac{1}{Z} \exp\{-\beta\, E_i\}\,, \qquad Z = \sum_{i=1}^{M} \exp\{-\beta\, E_i\} \qquad \beta = 1/T\,.$$

COMMENTS:

- It is remarkable that the only input left from the "big" system is the temperature T.

- There is no right or wrong using the *micro-canonical* or the *canonical* description. Both are different experimental settings: the micro-canonical description referes to an isolated system as a function of the conserved quantities e.g. energy; the canonical descriptions describes a "small" system embedded in a "large" system (heatbath) with energy exchange.

After these revisions, we are now ready to embark yet to another perspective. While the description of a fixed particle number in each of the boxes is quite natural for the spin system, but less so for the ideal gas:
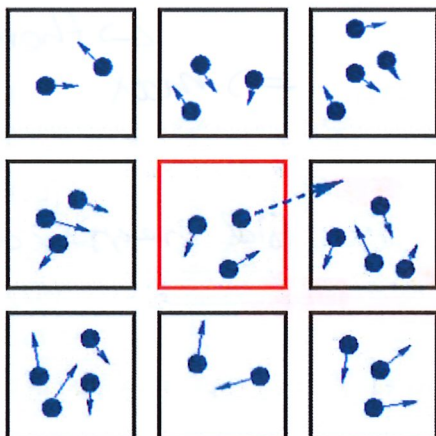
If we do not think of he boxes as bounded by real walls, we need to allow that our "small" system looses and gains particles from the surrounding. We say that our "small" system is embedded in a *particle reservoir*. In addition to the *energy exchange* between the boxes, we now also allow *particle exchange*.

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6.2   The grand-canonical partition function

Luckily, we have now all the mathematics in place to describe the new scenario. We still consider M micro-states in each box, $\omega_1 \ldots \omega_M$, but each definition of a microstate now includes the number N_i of particles in the box for state ω_i. We still work with occupation numbers n_i and corresponding probabilities p_i of finding a state ω_i in a box. We now have a new constraint: namely, that the total number of particles in all boxes is fixed, call it $N\,N_p$. Remember, N is the number of boxes and, hence, N_p could be interpreted as a reference for the particle number per box. We have now the constraint:

$$\sum_{i=1}^{N} n_i\,N_i = N\,N_p \qquad \Rightarrow \qquad \sum_{i=1}^{N} p_i\,N_i = N_p .$$

If we recall the calculation of the entropy in subsection 4.1, it does not refer to the defintion of the microstate ω_i at all. Hence, the equations (60, 61, 62) are unchanged. We just have a further constraining equation:

$$S(E) = -N \sum_{i=1}^{M} p_i \ln p_i , \qquad \Rightarrow \text{max} \tag{63}$$

$$\sum_{i=1}^{M} p_i = 1 , \qquad \sum_{i=1}^{M} p_i\,E_i = E/N , \tag{64}$$

$$\sum_{i=1}^{N} p_i\,N_i = N_p . \tag{65}$$

The next step is to recall that we are in a thermodynamical equilibrium, which maximises the entropy:

Lagrange method: Lagrange multiplier / Constraint

$$S = -N \cdot \sum_i p_i \ln p_i + N \cdot \beta \cdot \left(\sum_i p_i E_i - E \right)$$

$$- N \beta \mu \cdot \left(\sum_i p_i N_i - N_p \right)$$

$$+ \ln Z_g N \cdot \left(\sum_i p_i - 1 \right)$$

$$\frac{dS}{dp_i} = 0 = -N \cdot \ln p_i - N + N \beta E_i - N \beta \mu N_i + N \ln Z_g$$

We finally obtain:

$$p_i = \frac{1}{Z_g} \exp\left\{ -\beta E_i + \beta \mu N_i \right\}. \tag{66}$$

With the first equation in (64), we fix the first Lagrange multiplier:

$$\sum_i p_i = 1 \implies Z_g = \sum_{i=1}^{M} \exp\left\{ -\beta E_i + \beta \mu N_i \right\}. \tag{67}$$

grand-canonical partition function

The other constraint equations become:

$$\sum p_i E_i \implies \sum_{i=1}^{M} E_i \exp\left\{ -\beta E_i + \beta \mu N_i \right\} = \frac{E}{N} Z_g, \tag{68}$$

$$\sum p_i N_i \implies \sum_{i=1}^{M} N_i \exp\left\{ -\beta E_i + \beta \mu N_i \right\} = N_p Z_g. \tag{69}$$

These are two equations for the unknown Lagrange multipliers β and μ, which determines those in terms of the only parameter in the system: E and N_p.

$$\ln(a \cdot b) = \ln a + \ln b \qquad \frac{1}{z_g} e^{-\beta E_i + \beta \mu N_i}$$

The following calculation should be familiar from a analogous one in subsection 4.1. Inserting (66) into the entropy equation (63) yields:

$$S = -N \sum_i p_i \ln p_i = -N \cdot \sum_i \frac{1}{z_g} e^{-\beta E_i + \beta \mu N_i}$$
$$\left[\ln z_g - \beta E_i + \beta \mu N_i \right]$$
$$= N \cdot \ln z_g + \beta \cdot N \langle E \rangle - N \cdot \beta \mu \langle N \rangle = N \ln z_g + \beta E$$

$$-\beta \mu N N_p$$

$$S(E, N_p) \;=\; \beta(E, N_p)\, E \;-\; N\,[\beta\mu](E, N_p)\, N_p \;+\; N \ln Z_g \; .$$

We defined the temperature in (11), which we recall here:

$$\frac{1}{T(E, N_p)} = \left. \frac{\partial S(E, N_p)}{\partial E} \right|_{N_p} .$$

After a short calculation:
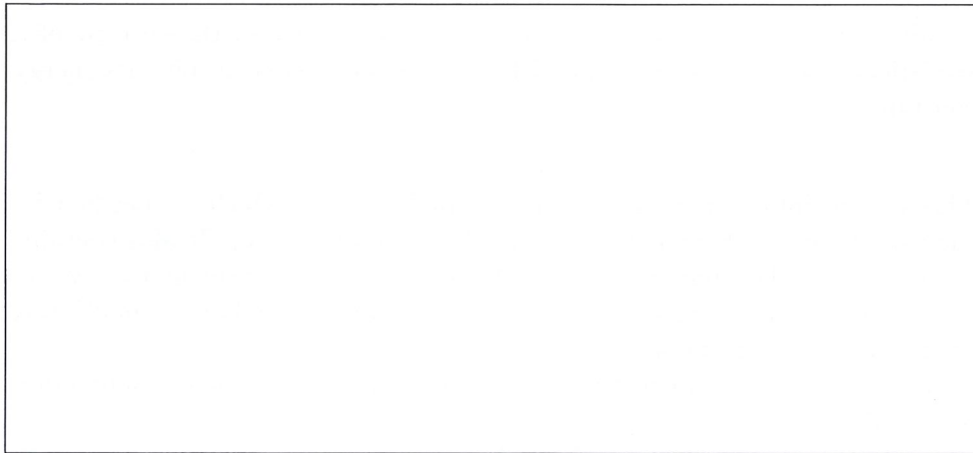
we find that for the Lagrange multiplier β the same expression as before (see (22)):

$$\frac{1}{T(E, N_p)} = \beta(E, N_p) . \qquad (70)$$

We still have to find a meaning for the last remaining Lagrange multiplier μ. We calculate:

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