Theo 4. Statistical Physics.

Lecture 5.

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Last time: 2nd law, cycles, Carnot engine

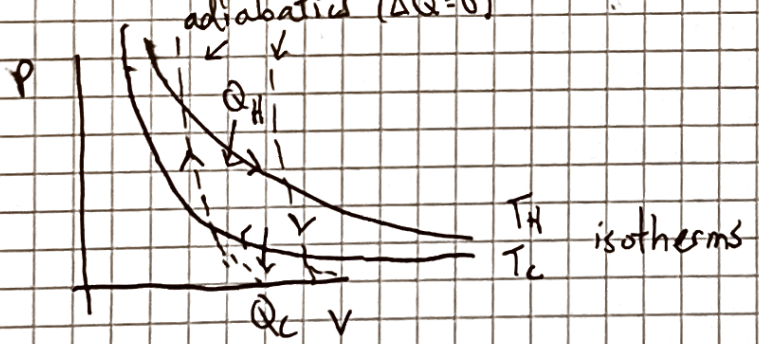
Today: More on Carnot engine

What is the variable conjugate to temperature?

$\Rightarrow$ introduction of <u>entropy</u>.

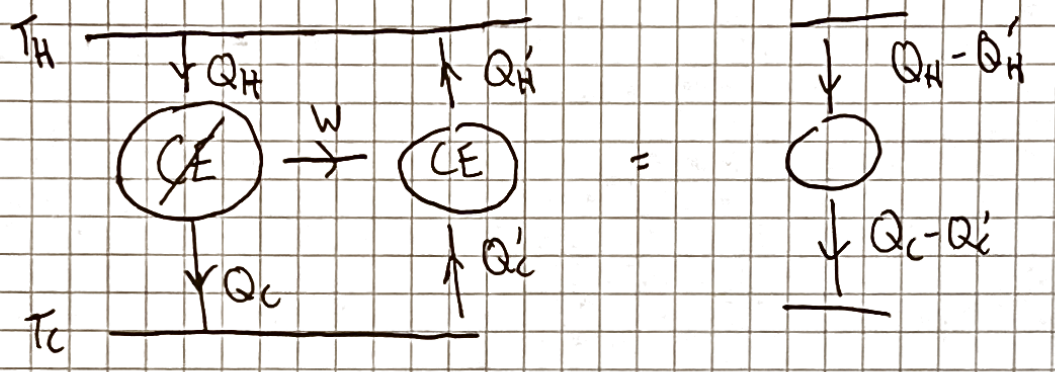
Microstates, ensembles.

From last time, we introduced the Carnot engine: a reversible cycle that operates between two temperatures T_H and T_C. As applied to an ideal gas, we constructed a Carnot cycle by using adiabatic transformations to perform work ($\uparrow$ net) / isotherms to extract / dump heat energy.



Remark: reversible means that input & output actions are reversed, but because efficiency is always less than 1, there is no violation of the second law of thermodynamics.

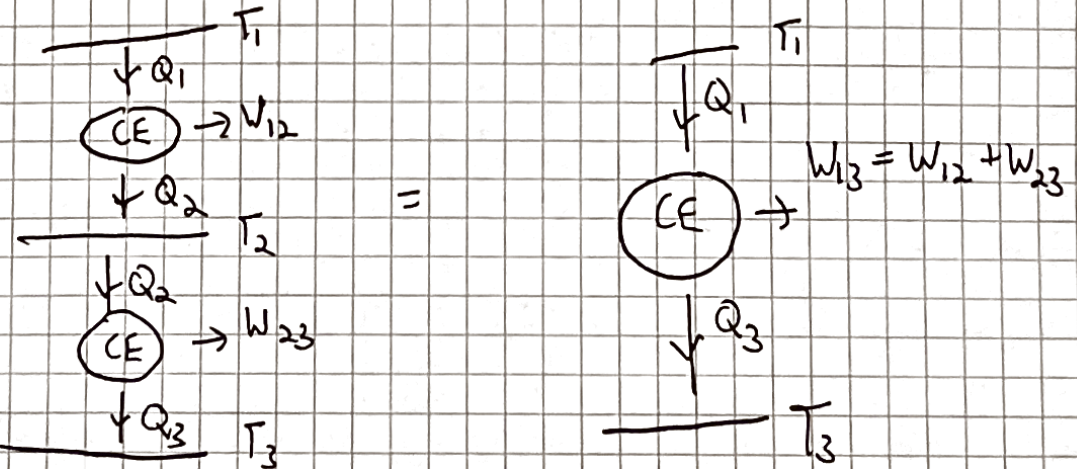
Compared to any random engine, the Carnot engine is the most efficient possible. To prove this, we can run the Carnot engine in reverse, coupled to a given (test) engine, that provides the input work. The heat exchange of the test engine is Q_H input, Q_C exhaust, W work output, and the Carnot refrigerator uses W work input, draws Q_C' heat in & pumps out Q_H' heat.



We know that the 2nd law requires $Q_H - Q_H' \geq 0$, thus the efficiencies of CE and CE are

$$\eta_{CE} = \frac{W}{Q_H} \leq \eta_{CE} = \frac{W}{Q_H'}$$, since the work output is the same.

Moreover, a series of Carnot engines operate as a single Carnot engine. Consider $T_1 > T_2 > T_3$, then



Hence, a powerful consequence of reversibility is "superposition" and "subtraction" of Carnot engines. This is the thermodynamic equivalent of frictionless ~~motion~~ motion in mechanics.

We can also postulate a universal efficiency property of reversible (Carnot) engines that results from the fact that reversible engines can be coupled in sequence to run each other backwards. This then amounts to some heat flow from the heat source to sink with no work performed, and can only depend on the temperatures T_H & T_C. We denote this universal efficiency as $\eta(T_H, T_C)$.

For the Carnot engine series before, we have

$Q_2 = Q_1 - W_{12} = Q_1(1-\eta(T_1,T_2))$ since $\eta(T_1,T_2) = \frac{W_{12}}{Q_1}$

$Q_3 = Q_2 - W_{23} = Q_2(1-\eta(T_2,T_3))$

$\Rightarrow Q_3 = Q_1(1-\eta(T_1,T_2))(1-\eta(T_2,T_3))$

$Q_3 = Q_1 - W_{13} = Q_1(1-\eta(T_1,T_3))$

Although we have not yet defined the functional form of $f(T_H, T_C)$, we must require

(*) $1-\eta(T_1,T_3) = (1-\eta(T_1,T_2))(1-\eta(T_2,T_3))$

Given $1-\eta(T_1,T_2) = \frac{Q_2}{Q_1}$, we adopt the convention that $1-\eta(T_1,T_2) \equiv \frac{T_{\text{@}2}}{T_1}$, such that

$$\eta(T_1,T_2) = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

$$\text{or } \eta(T_H,T_C) = \frac{T_H - T_C}{T_H}$$

This is the simplest ansatz that obeys the property required by (★)!

$$1-\eta(T_1,T_3) = (1-\eta(T_1,T_2))\,(1-\eta(T_2,T_3))$$

$$\frac{T_3}{T_1} = \frac{T_2}{T_1}\times\frac{T_3}{T_2} \quad \checkmark$$

This also forces to require temperature is never negative nor zero. Reaching absolute zero would correspond to a perfect efficiency. Convention ~~fixed~~ fixes that the triple point of water is then $T = 273.16\,K$.

We have now established a direct link between heat energy and temperature:

$$1-\eta(T_1,T_2) = \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$\Rightarrow \quad Q_2 = \frac{T_2}{T_1}\,Q_1$$

and this is also true as a inexact differential relation:

$$đQ_2 = \frac{T_2}{T_1}\,đQ_1$$

In words, a differential amount of heat taken from a given reservoir scales as the temperature of the reservoir.

Summary thus far:

We have a state function of the total internal energy of a system,

$$dE = đW + đQ.$$

We can understand $\delta W = \sum_i F_i \, dx_i$ as the differential work added/subtracted to the system by generalized forces and their generalized displacements.

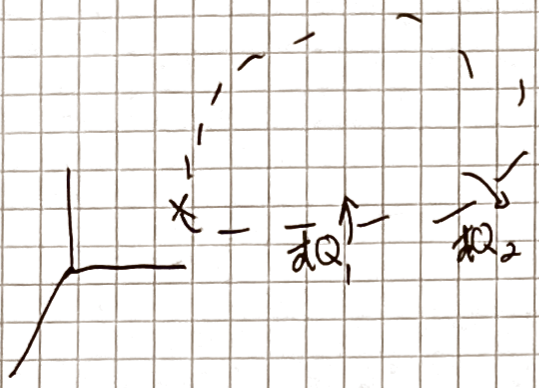
But what about δQ? The heat energy being proportional to the system variable "temperature" should also be quantified with some extensive displacement. It is motivated then to consider differentials of heat or closed integrals or cycles to identify the conjugate variable to temperature, which we will see as entropy. Entropy, denoted S, is the state fn. conjugate to temperature.

We will make the claim of Clausius's theorem:

Clausius's thm. For any cyclic transformation (reversible or not),

$$\oint \frac{\delta Q}{T} \leq 0$$, where δQ is the heat increment supplied to the system at temperature T.

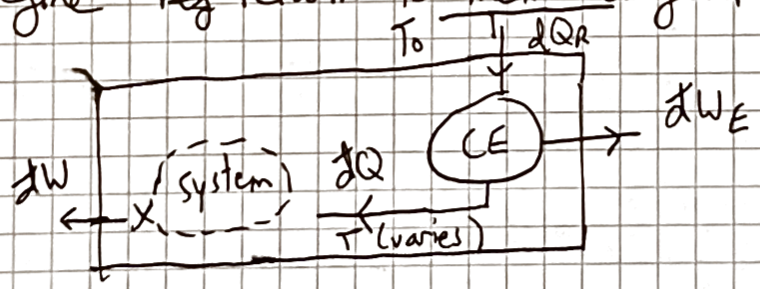
Note δQ can change sign, and the T is changing (or even not well-defined) around the cycle. To prove the theorem, first draw an arbitrary cycle in the appropriate multidimensional thermodynamic coordinate space.



At each instant, the system receives dQ and dW of heat and work. Consider coupling all dQ to a Carnot engine that operates with a fixed coupling to a reservoir T_0. This allows the Carnot engine to match the dQ by a corresponding dQ_R, taken from the reservoir, where we use the differential relation of heat energy & temperature from before:

$$dQ_R = T_0 \frac{dQ}{T}.$$

After the loop closes, the system & Carnot engine return to their original states.



So the box is a net system that takes $\oint dQ_R = Q_R$ from a reservoir and produces $\oint dW + \int dW_E = W = Q_R$ of work. But the net work for a closed cycle is ≤ 0, so $Q_R = W \leq 0$, and we have

$$\oint dQ_R \leq 0 \Rightarrow \oint T_0 \frac{dQ}{T} \leq 0 \Rightarrow \oint \frac{dQ}{T} \leq 0, \text{ since } T_0 > 0.$$

There are several consequences of Clausius's theorem:

1. Reversible cycles have $\oint \frac{dQ_{rev}}{T} = 0$, since traversing the contour in the opposite direction changes $dQ_{rev} \to -dQ_{rev}$, giving $\oint \frac{dQ_{rev}}{T}$ both ≤ 0 and ≥ 0. Moreover, $\int_A^B \frac{dQ_{rev}}{T}$ is <u>independent of path</u>, since I can always close the path from B back to A with some fixed T. The sum is a closed path with $\oint \frac{dQ_{rev}}{T} = 0$ and so moving to another point B cannot depend on the path I took. (arbitrary)

This <u>path independence</u> <u>defines</u> the function of state <u>entropy</u> S,

$$S(B) - S(A) \equiv \int_A^B \frac{dQ_{rev}}{T}, \text{ which gives}$$

also a differential relationship. for $dQ = T\,dS$.
(This integral definition only defines entropy up to a constant.) Reversible processes have a fixed relationship of heat exchange + temperature, corresponding to raising or lowering entropy:

$$dQ_{rev} = T\,dS.$$

We can conclude $dE = dQ + dW$

$$= T\,dS + \sum_i F_i\,dx_i$$

This is a central result of thermodynamics.

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Recall functions of state are characterizations of a macroscopic system that are well-defined quantities in equilibrium.

As you have likely heard, entropy only increases. Consider combining an irreversible change from A to B and a reversible path from B to A:

$$\int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ_{rev}}{T} \leq 0 \quad \leftarrow \text{Clausius's thm.}$$

$$\int_A^B \frac{đQ}{T} + S(A) - S(B) \leq 0$$

$$\int_A^B \frac{đQ}{T} \leq S(B) - S(A).$$

Again, making a differential relation gives

$$dS \geq \frac{đQ}{T} \quad \text{for any transformation.}$$

Joining several subsystems in equilibrium ~~via adiabatics~~ gives a joint equilibrium with net $đQ = 0$ and $\Delta S \geq 0$ since every spontaneous internal change can only increase S. We see that increasing entropy defines an ~~action~~ arrow of time & the path to equilibrium.

Next time: microstates & macrostates.