



General Physics I

Lect.24 The third law of thermodynamics

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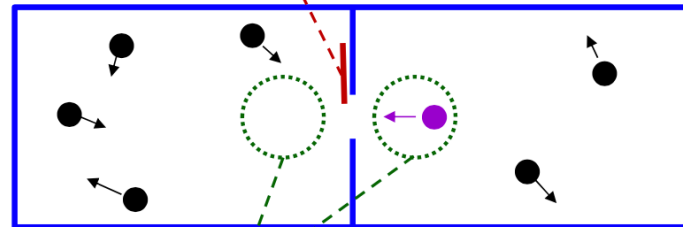
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Entropy and Maxwell's Demon

- In 1867 Maxwell proposed the following thought experiment that seemed to violate the second law of thermodynamics.
- Suppose we have two boxes connected by a trap door and a 'demon' named Elena, that opens the door if a fast molecule moving right to left is detected or a slow one moving left to right. With time the fast molecules end up on the left and the slow on the right – heat has flowed from right to left, but no work has to be done in opening and shutting the door.
- A simpler version is that the door is opened if a molecule moving right to left is detected – so all the molecules end up on the left – again with a reduction in entropy.

Q: Whether the 2nd law still holds when individual coordinates/states of the system are measured and manipulated

Trap door opened when particle is detected moving right to left



Particle detectors

Explanations of Maxwell's Demon

Feynman's explanation: The demon = a trap door with a spring. A fast molecule comes through, because it is able to lift the **trap door**. The slow molecule cannot get through, and bounces back. But the mechanism will heat up given a finite specific heat. Eventually the Brownian motion will kill its effectiveness.

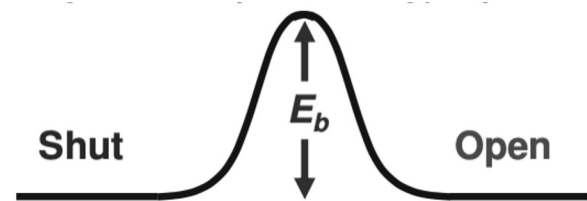
The trap door, subject to Brownian motion, requires an energy barrier to distinguish between 'open' and 'shut' states. Without this barrier, the door would randomly move between these states. Moving the door over this barrier requires work, which, once expended, is irrecoverable and dissipates as heat, increasing the surrounding entropy.

Moving from the barrier to the other side is irreversible process. The energy used to overcome the barrier is irretrievably lost as heat, ensuring it cannot spontaneously flow back to push the door back over the barrier.

Trap door demon: calculation

Equal energy open and shut states separated by barrier. If there are initially n_0 molecules on each side of the box ($2n_0$ in total). If all move to one side, the entropy drop is $2n_0 k_B \ln 2$. To open and shut the door requires 2 barrier crossings, so work $2n_0 E_b$ is dissipated as heat giving an entropy rise of the surroundings of $2n_0 E_b / T$. To **obey** the second law:

$$2n_0 k_B \ln 2 < \frac{2n_0 E_b}{T} \longrightarrow e^{-\frac{E_b}{k_B T}} < \frac{1}{2} \quad \text{Boltzmann factor}$$



For a **violation** of the second law of thermodynamics, the door would need to spend more than 50% of its time in a state of crossing the barrier, rather than being stably positioned on either side. This scenario is not characteristic of a properly functioning door.

Measurement is an irreversible process

The Maxwell demon problem provide us a new way of thinking:

measurement = determining/recording the state of a system

The moving of the trap door in the MD problem achieves a well defined result, so it has to be an irreversible process. If result is rather produced by a reversible process, the system can just diffuse back and undo the result—the measurement does not exist!

At this point we have cannot circumvent what is arguably one of the major unsolved problems of science: measurement in Quantum Mechanics. When you set up a device that records which of the component eigenstates a wavefunction is in, you get a random, but definitive answer weighted according to the squares of the magnitudes of the coefficients of the component states. A key feature of all this is that a measurement occurs when the propagating wavefunction ‘hits’ or ‘becomes linked to’ an irreversible process, and this is recognized as a key mystery in the QM. Collapse of the wavefunction is a QM **irreversible** process, and maybe this realization will assist in working out what ‘collapse’ is.

Irreversibility

- We know not all laws of physics are reversible. But where does irreversibility come from? If we put $t=-t$ in the physics governed by Newton's laws, we have another solution, and every phenomenon is reversible.
- We've shown in isothermal expansion

$$\begin{aligned}\Delta S &= \int_{V_1}^{V_2} P \frac{dV}{T} = \int_{V_1}^{V_2} \frac{NkT}{V} \frac{dV}{T} \\ &= Nk \ln \frac{V_2}{V_1},\end{aligned}$$

- For instance, if we expand the volume by a factor of 2, the entropy change is $Nk \ln 2$. The entropy increase just as the molecules are distributed differently.
- Consider mix of two gases, we started with an arrangement which is, in some sense, ordered. Due to the chaos of the collisions, it becomes disordered. It is the change from an ordered arrangement to a disordered arrangement which is the source of the irreversibility.

Experimental determination of entropy

Experimentally, the heat capacity (at constant pressure) can be used to measure the entropy change

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

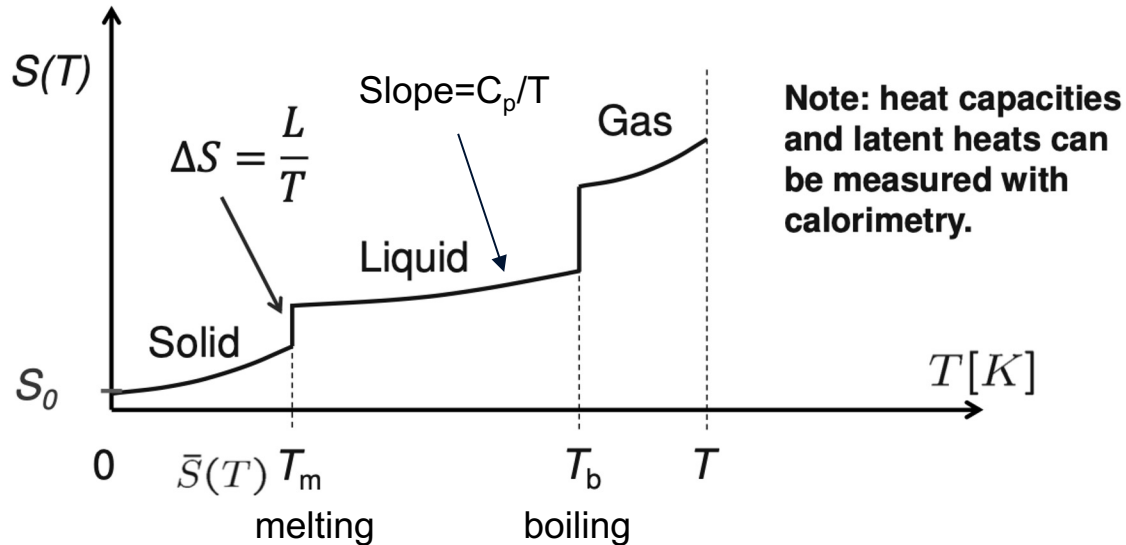
C_p is because it is easy to do in research, and we can integrate numerically to get the entropy at that pressure as a function of temperature:

$$S(T) = S(T = 0) + \int_0^T \left(\frac{\partial S}{\partial T}\right)_p dT = S(0) + \int_0^T \frac{C_p}{T} dT$$

As a substance is heated from zero temperature, we expect it will also go through one or more phase transitions. Recall the latent heat in L21, the entropy increase is:

$$\Delta S = \frac{L}{T}$$

Entropy-Temperature diagram



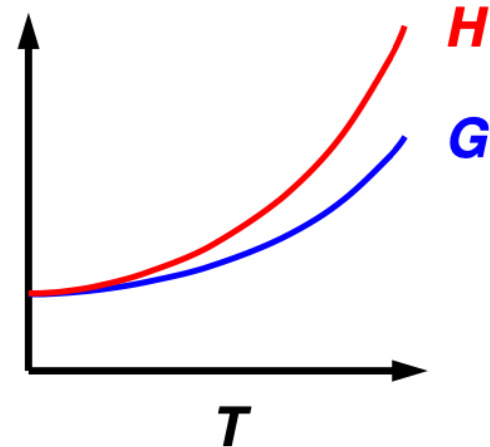
- A typical substance with phase transitions
- We can the entropy in every temperature, given the the S_0
- S_0 is given by the 3rd law of thermodynamics

Nernst's Experiment

- Recall in L22 we show that dG gives the maximum amount of non-‘ pV ’ work that can be done for changes occurring at constant T and P .
- In this particular case, it is the electrical work in the external circuit as measured by the cell voltage. Nernst examined the data on chemical thermodynamics and his own measurements of electrochemical cells
- Nernst looked at the relation between ΔH and ΔG for chemical reactions as the temperature was reduced: $\Delta G = \Delta H - T \Delta S$ at constant T, P
- After analyzing the data, Nernst found that not only ΔG to tend to be equal to ΔH as T goes to zero, but also they approached each other asymptotically.
- This suggested that ΔS approaches zero as T approaches absolute zero.



Walther Hermann
Nernst (1864 –1941)



Nernst's postulate--the third law

“Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy”

-- Nernst

- Based on the observation, Nernst proposed the **third law of thermodynamics** based on his experimental observation, provides an absolute scale for the entropy.

$$\lim_{T \rightarrow 0} S(T) = 0$$

- The third law is in some way not as “inspiring”, as the other laws derive a new function of state of the system: the zeroth law gave us temperature; the first law energy; and the second law entropy. There is no such reward from the third law.

Generalization by Planck

“The entropy of all systems in internal equilibrium is the same at absolute zero and may be taken as zero.”

-- Planck (1911)

- Consider the Boltzmann factor, $\exp(-E/k_B T)$. With T approaching zero, the probability of the particle to stay in any non-zero energy state approach zero. The non-zero comes from the fact that every configuration of a system need to have a different energy (e.g., some potential energy differences).
- So if the system is in equilibrium, i.e. still capable of moving from microstate to microstate, it will drop into the ground energy state with $\Omega=1$.
- From Boltzmann, $S = k \log \Omega$. Entropy is a measure of the number of microstates of the system. If all the components are in their respective ground states, there is only one microstate for the whole collection, so the entropy S has to be 0.

Note this is not 100% correct if we add degeneracy of quantum state, but ground state entropy still shouldn't grow extensively with N

Consequences of the Third Law

- Heat capacities $C_{x=p,V}$ go to 0 as $T \rightarrow 0$. $C_x = T \left(\frac{\partial S}{\partial T} \right)_x$
- Experimentally S is observed to go smoothly to zero (no infinite gradient) and given T is also going to zero, C_x also goes to zero.

- From canonical ensemble point of view, we consider at low enough temperatures only the first excited state with energy ε , has any significant probability of occupation other than the ground state giving a system energy as $T \rightarrow 0$. The total energy and heat capacity C_x are:

$$U = \frac{\varepsilon}{1 + e^{\varepsilon/kT}}$$

$$\left(\frac{\partial U}{\partial T} \right)_x = \frac{\varepsilon e^{\varepsilon/kT}}{kT^2 (1 + e^{\varepsilon/kT})^2} \rightarrow \frac{\varepsilon e^{-\varepsilon/kT}}{kT^2} \rightarrow 0$$

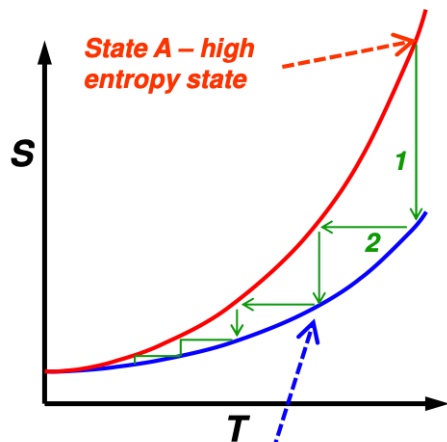
- In contrast, from classical theory $U = kT/2$ per d.o.f., hence C_x is finite but non-zero.
- In this sense, **the third law** is an admission that the low temperature world is not classical. It is *quantum*.

How cooling works

- All reversible processes can be broken down into a series of Carnot cycles, recall the four step cycle when we first introduce the ideal engine/refrigerator.
- To cool a substance at pressure P_A from temperature T_1 :
 1. Keep it in contact with a thermal reservoir at T_1 and compress it (i.e. do work on it so that heat flows out and its entropy drops) isothermally to a higher pressure P_B
 2. Disconnect it from the reservoir and allow it to expand adiabatically (i.e. at constant entropy) which will cause it to cool.
 3. Split into two parts – one large (gives you a reservoir at this lower temperature) and one small.
 4. Repeat with the smaller part as the “system”, larger part as a “reservoir” to sink the heat, so the temperature change is more efficient.

The entropy need to be positive for positive temperatures, as it integrates the positive heat capacity (more precisely, C/T) from zero to a positive number. So we have to start with finite entropy, reducing it via isothermal compression.

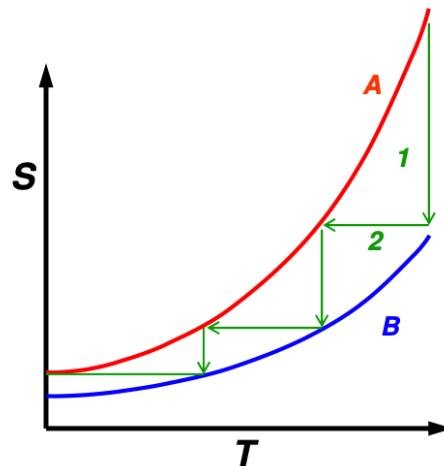
Zero temperature is unreachable



State 'B' low entropy case – e.g. compressed gas or magnetised paramagnetic material

Step 1: isothermal compression/magnetisation

Step 2: Adiabatic expansion/demagnetisation

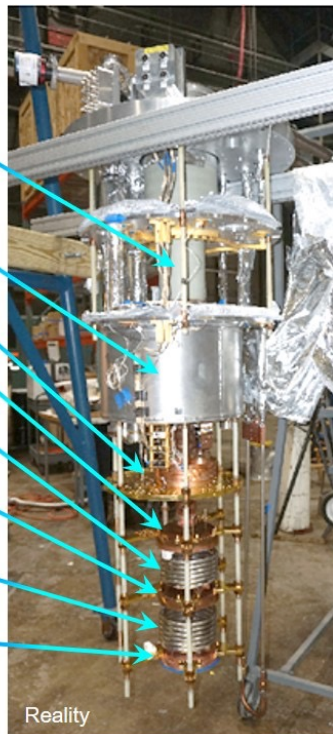


(left) Two curves pass the origin, then zero temperature is unreachable.
 (right) If two curves would exhibit different interceptions on the vertical axis, then the zero temperature would be reached by finite steps of cooling processes.

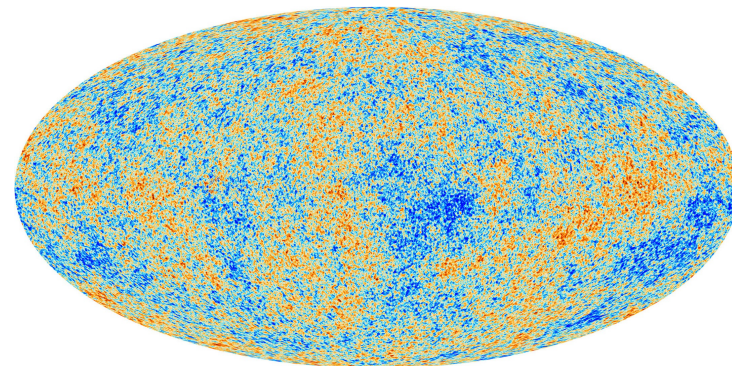
Consider two $S(V, T)$ curves at two different volumes $V_1 > V_2$. The cooling process can be designed as repeated adiabatic compression followed by isothermal expansion. Third law of thermodynamics stated that the ground state entropy should be zero. This is consistent with that **“zero temperature is unreachable by finite steps”**.

How close can we get now?

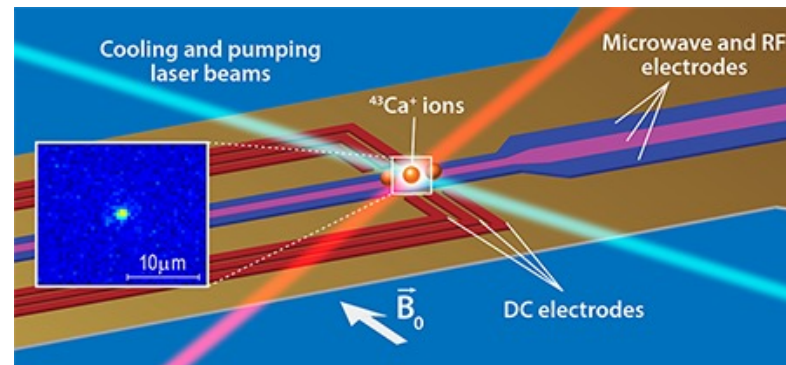
- 3He Pumping Line
- 4K Bath
- 1K Pot and Plate
- Still, 0.8-0.9 K
- Heat Exchanger Assemble No.1
- Intermediate heat exchanger (0.5K)
- Heat Exchanger Assemble No.2
- Mixing Chamber 80 mW at 0.25 K



Dilution Fridge ($\sim 0.1\text{K}$)



Cosmic Microwave Background (2.7K)



Trapping Ion/Doppler Cooling ($\sim 10^{-6}\text{K}$)

Summary of thermodynamic laws

The 0th Law of Thermodynamics: This law defines thermal equilibrium. It states that if two objects, A and B, are each in thermal equilibrium with a third object, C, then A and B are also in thermal equilibrium with each other. Essentially, they all share the same temperature.

The 1st Law of Thermodynamics: This law concerns energy conservation and transfer, expressed as $\Delta U = W + Q$, where ΔU is the change in internal energy, W is work done, and Q is heat transferred. This principle also underlines the impossibility of creating a perpetual motion machine of the first kind, affirming that there is no such thing as a free lunch in terms of energy.

The 2nd Law of Thermodynamics: This law states that the entropy of an isolated system does not decrease over time. It asserts that it is impossible to completely convert heat from a single source into work without causing any other change. This law rules out the possibility of a perpetual motion machine of the second kind.

The 3rd Law of Thermodynamics: This law posits that absolute zero temperature is unattainable through any finite series of thermodynamic processes. In other words, no matter how many steps are taken, a system cannot be brought exactly to the temperature of zero Kelvin.