Theo. 4. Statistical Physics

Lecture 6.

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Last time: Finish Carnot engine, Clausius's theorem

Introduction of entropy, variable conjugate to temp.

Today: Microstates & macrostates. Statistical definition of temperature.

Boltzmann distribution

From last time, we established a defining relationship for entropy, as a function of state,

$$S(B) - S(A) \equiv \int_A^B \frac{đQ_{rev}}{T}.$$

Note: this defines entropy up to an overall integration const.

This led to the differential relation

$đQ_{rev} = T\,dS$ for reversible heat exchange.

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

We also have from $dE = đQ + đW$

$$dE = TdS + \sum_i F_i\,dx_i$$

We did some behind-the-scenes gymnastics to write this relationship; $dE = đQ_{rev} + đW$

$= T\,dS + \sum_i J_i\,dx_i$ for reversible (quasi-static) transformations. But we remark that this equation only involves functions of state and is hence valid for any thermodynamic system.

Deriving entropy and temperature from statistics.

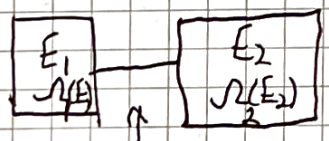
In the previous lecture, we saw that the second law & the consideration of Carnot engines led to the notion of a universal efficiency, $\eta(T_H, T_C)$, which we took to be $\eta(T_H, T_C) = \frac{T_H - T_C}{T_H}$, and this $\eta \leq 1$ is equivalent to saying heat naturally flows from hot to cold. (It forbids T being less than 0 too)

We can also see the emergence of the notion of temperature from a completely statistical description of a system.

Blundell

Blundell, Sec. 4.4.

Consider two subsystems with E_1 & E_2 total internal energy that are in thermal contact but can exchange energy. The E_1 energy of the first subsystem corresponds to a large (but calculable) number of possible <u>microstates</u> that partitions the energy E_1 into the internal degrees of freedom. Denote the number of microstates as $\Omega_1(E_1)$ for the first subsystem and $\Omega_2(E_2)$ for the second subsystem.



can exchange energy, otherwise isolated.

We have three statements / assumptions about how the microscopic physics express the macroscopic total energy in practice and as an equilibrium contribution.

1.) Each of the possible microstates is equally likely to occur (for any macroscopic time interval).

2.) The system's internal dynamics ensure that the microstates are continually changing.

3.) Given enough time, the system will explore all possible microstates + spend an equal time in each. This is known as the ergodic hypothesis.

As a consequence of these assumptions, the equilibrium condition of the system will cause the system to adopt the macrostate that has the largest number of microstates: since we are typically discussing systems with 10^{23} dofs, the combinatorial penalty for deviating from the most number of microstates is a very steep penalty = exceedingly unlikely. (See HW 3.)

Given the two subsystems can trade energy, but are otherwise isolated, we see that the end equilibrium condition requires $E_{tot} = E_1 + E_2 = \text{const.}$

Moreover, we can express the condition that $\Omega_1(E_1)\,\Omega_2(E_2)$ is maximized as the requirement that $\frac{d}{dE_1}\left(\Omega_1(E_1)\,\Omega_2(E_2)\right) = 0$

(Extremization condition.)

Applying chain rule,

$$\left(\frac{d\Omega_1(E_1)}{dE_1}\right)\Omega_2(E_2) + \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2}\frac{dE_2}{dE_1} = 0$$

We have $\frac{dE_2}{dE_1} = -1$ since $E_{tot} = \text{const.}$

$$\Rightarrow \quad \Omega_2(E_2)\frac{d\Omega_1(E_1)}{dE_1} = \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2}$$

$$\Rightarrow \quad \frac{1}{\Omega_1}\frac{d\Omega_1(E_1)}{dE_1} = \frac{1}{\Omega_2(E_2)}\frac{d\Omega_2(E_2)}{dE_2}$$

Recognize $d\ln\Omega_1(E_1) = \frac{1}{\Omega_1}d\Omega_1(E_1)$

$$\Rightarrow \quad \frac{d\ln\Omega_1(E_1)}{dE_1} = \frac{d\ln\Omega_2(E_2)}{dE_2}$$

This expression is the mathematical condition that the product of the number of microstates is maximized. Intuitively, we expect this condition to correspond to the thermal equilibrium condition, and so we can use this as a <u>definition for temperature</u>:

$$\frac{1}{k_B T} = \frac{d\ln\Omega}{dE}$$

with $k_B = 1.3807 \cdot 10^{-23}\ J/K$.

Comparing to our heat relation, $dQ_{rev} = TdS$, we see that dS is ~~denied~~ identified with $k_B\, d\ln\Omega$, and hence entropy is the measure of the number of microstates available of the ~~sta~~ system. The growth of entropy is that a closed system tends to a macrostate with more microstates.

We can now also emphasize the role of statistics in constructing these physical / empirical laws. In order to calculate efficiently with microstates, we will have to consider averaging with some fixed constraint that will relate the microstates to each other. These are formulated as ensembles. We have three types of ensembles & they are distinguished by the constraint of total energy & particle number or lack thereof.

(1) Microcanonical ensemble: All systems have same fixed energy.

(2) Canonical ensemble. All systems can exchange energy with a large reservoir of heat, so that the system temperature is fixed.

(3) Grand canonical ensemble: All systems can exchange energy and particles with a large reservoir. Results in fixed system temperature and chemical potential.

We will elaborate more on these ensembles and ways to calculate ensemble averages when we have done more statistics, but for the moment, we will use the canonical ensemble to motivate the Boltzmann distribution.

Consider again the equation $\frac{1}{k_B T} = \frac{d \ln \Omega}{dE}$ (★)

How does this dictate the functional form of Ω?

Consider the microstates when E is lowered by an infinitesimal amount, $\ln \Omega(E-\epsilon)$.

Performing a Taylor expansion + discarding terms at $O(\epsilon^2)$, we have

$$\ln \Omega(E-\epsilon) = \ln \Omega(E) - \left(\frac{d \ln \Omega(E)}{dE}\right)\epsilon + \dots$$

$$= \ln \Omega(E) - \frac{\epsilon}{k_B T} + \dots$$

We can exponentiate this for

(★★) $\Omega(E-\epsilon) = \Omega(E)\, e^{-\epsilon/k_B T}$

(★) or (★★) Interpretation: the "natural" step in energy is counted in units of $k_B T$. The growth or decrease in the number of microstates as you raise or lower the system energy by one unit of $k_B T$ is a factor of e^{+1} or e^{-1}. The factor $e^{-\epsilon/k_B T}$ is called a Boltzmann factor.

We can also determine a probability distribution associated with the Boltzmann factor for canonical ensembles: recall canonical ensembles share energy with a reservoir, and equilibrium is reached when the system + reservoir have the same temperature.

(You can also think of the system + reservoir together as a microcanonical ensemble. Subsystems express a dynamical equilibrium condition of temp. equality.)

We assume that the system energy is ϵ and the reservoir energy is $E-\epsilon$. We also assume that the system has a unique microstate for each ϵ, so

$$P(\epsilon) \propto \Omega(E-\epsilon) \cdot 1$$

$\Omega(E-\epsilon)$: # of microstates for reservoir

1: # of microstates for system.

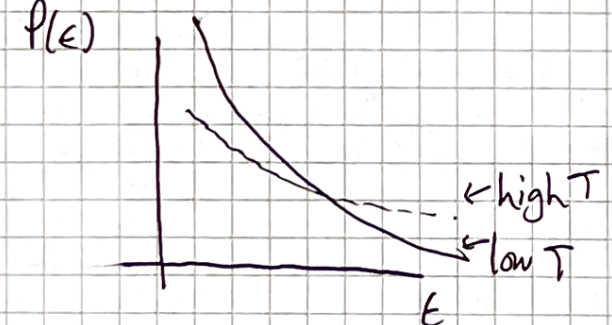
We see that $P(\epsilon) \propto e^{-\epsilon/k_B T}$

In order to properly normalize the discrete probability, we simply sum over all possible probabilities.

Thus, a small system coupled to a large reservoir at temperature T will be observed at an energy E_r according to the Boltzmann distribution (also the canonical distribution):

$$P(\text{microstate } r) = \frac{e^{-E_r/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

The denominator is known as the partition function + is labeled $Z = \sum_i e^{-E_i/k_B T}$



Analogous to decay lifetimes!

So, again, $k_B T$ sets the "natural" energy scale of the system & deviating from $k_B T$ is a price of e^{+1} or e^{-1}.