

III. P.S. Microcanonical Ensemble

As a postscript, I want to review briefly the main alternative ~~microcanonical~~ scheme for the construction of Statistical Mechanics - what we might call the Boltzmannite route (as opposed to the Gibbsian one that I mostly followed).

- As a starting point, let us consider a closed isolated system and let us continue adherence to the postulate that in equilibrium, all microstates in such a system are equiprobable.

However, if we are serious about the system being isolated, we are in fact not choosing out of all possible quantum states: the system must conserve energy and so we must impose the restriction that its energy is exactly equal to some value E , i.e., we must restrict consideration to the subset of microstates such that

$$E_\alpha = E$$

and so

{	$P_\alpha = \frac{1}{\Omega(E)}$	if $E_\alpha = E$	}	<u>Microcanonical Distribution</u>
	$P_\alpha = 0$	otherwise		

↑
of microstates with $E_\alpha = E$

(microcan. ensemble is a set of systems with fixed E , satisfy this)

Note. It is possible to show (from Liouville's theorem) that the distribution p_2 in steady state can only be a function of conserved quantities (integrals of motion: E , momentum, angular momentum - but we can usually find a frame in which the system is at rest so E is all that remains)

11.1 Construction of Thermodynamics

• It is then argued that because of the equiprobability of microstates, a system given a fixed energy E will settle to a distribution of energy between its constituent parts such that the # of microstates associated with that distribution is maximal.

→ This is effectively the principle of maximum entropy

This is best understood if we consider two ^{sub}systems each of which is initially in a microcanonical equilibrium with

$$\Omega_1(E_1^{(0)}) \text{ and } \Omega_2(E_2^{(0)})$$

If we join them together, they have total combined energy $E = E_1^{(0)} + E_2^{(0)}$ but can now distribute it differently between themselves, so the # of microstates corresponding to all such possibilities is

$$\Omega(E) = \sum_{E_1} \Omega_1(E_1) \Omega_2(E - E_1)$$

sum over all (in general discrete) possible values $0 \leq E_1 \leq E$

as before, assume the two systems have indep. energy levels, so $\Omega = \Omega_1 \Omega_2$
↓ see p.64

At this point it is convenient to introduce Boltzmann entropy

$$S = k_B \ln \Omega(E)$$

(which is indeed what entropy is for the microcanonical distribution) and so

$$\Omega(E) = \sum_{E_1} e^{[S_1(E_1) + S_2(E-E_1)]/k_B}$$

Since S is an extensive quantity (for indep. systems, ~~$S = S_1 + S_2$~~ because $\Omega = \Omega_1 \Omega_2$), it must be $\propto N$ (# of particles) and so the exponent in the above is very large. This means we can approximate the sum \sum_{E_1} by just ~~one~~ one of its members for which

$$S_1(E_1) + S_2(E-E_1) \rightarrow \max \text{ (over all values of } E_1 \text{)}$$

and in general all other members of the sum will be exponentially small.

As we saw on pp. 71-72, the ^{above} max ~~is obtained~~ is obtained for E_1 such that

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

which provides us with the definition of temperature

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

(0th law)

Consider a large isolated system with fixed energy E ("the Universe") and separate from it a small subsystem.

Probability for the subsystem to have energy ϵ (expected mostly to be $\ll E$) is

$$P(\epsilon) = \frac{\Omega_R(E-\epsilon) \Omega_s(\epsilon)}{\Omega_{tot}(E)} = \frac{\Omega_s(\epsilon)}{\Omega_{tot}(E)} e^{\frac{1}{k_B} S_R(E-\epsilon)}$$

$\Omega_R(E-\epsilon)$: # of microstates of the rest of the big system ("reservoir" or "heat bath") with energy $E-\epsilon$
 $\Omega_{tot}(E)$: total # of microstates
 $\Omega_s(\epsilon)$: # of microstates of the subsystem that have energy ϵ
 $\frac{1}{k_B} S_R(E-\epsilon)$: entropy of reservoir

Now $S_R(E-\epsilon) = S_R(E) - \epsilon \left(\frac{\partial S_R}{\partial E} \right) + \dots$

Then

$$P(\epsilon) \approx \frac{e^{S_R(E)/k_B}}{\Omega_{tot}(E)} \underbrace{\Omega_s(\epsilon)}_{\text{density of states}} e^{-\frac{\epsilon}{k_B T}}$$

$\frac{e^{S_R(E)/k_B}}{\Omega_{tot}(E)}$: constant
 $\frac{\partial S_R}{\partial E} = \frac{1}{T}$: temperature of the system (same for reservoir and for subsystem, see p 94.)
 find it by normalising!

Clearly all microstates of the small system that have the same energy are equiprobable, so

$$P_\alpha = \frac{e^{-E_\alpha/k_B T}}{Z} \quad \text{and} \quad Z = \sum_\alpha e^{-E_\alpha/k_B T} = \sum_\epsilon \Omega(\epsilon) e^{-\epsilon/k_B T}$$

Gibbs distribution partition function

So we have recovered the canonical ensemble!

NB: Energy of the subsystem is no longer fixed, but we can introduce mean energy

$$U = \sum_\alpha E_\alpha P_\alpha \Leftrightarrow \text{temperature } T.$$

Note. How good was the ~~approx~~ Taylor expansion?

$$S_R(E-E) = S_R(E) - E \frac{\partial S_R}{\partial E} + \frac{1}{2} E^2 \frac{\partial^2 S_R}{\partial E^2} + \dots$$

$$= S_R(E) - \frac{E}{T} + \frac{E^2}{2} \frac{\partial}{\partial E} \frac{1}{T} + \dots$$

$$= S_R(E) - \frac{E}{T} - \frac{E^2}{2T^2} \left(\frac{\partial T}{\partial E} \right) + \dots$$

$$\frac{\textcircled{2}}{\textcircled{1}} = \frac{E}{2T} \frac{1}{C_V} \ll 1 \quad \text{if } E \ll C_V T \sim \text{energy of the reservoir}$$

Note. It is popular to argue that Maxwell's Distribution for ideal gas can be recovered in this way.

Consider each particle as a little subsystem in thermal contact (via collisions) with a reservoir

— all other particles. Then

$$p(\vec{v}) = e^{-\frac{mv^2}{2k_B T}} \cdot \text{const}$$

↑
normalisation $\frac{1}{(2\pi k_B T/m)^{3/2}}$

~~In fact, Maxwell's Distribution is not the average occupation number corresponding to a given state~~
 In fact, Maxwell's Distribution is ~~not~~ the average occupation number corresponding to a given state — and we will derive it in this form as the hot dilute limit of quantum statistics (in HT!)

How do we calculate the entropy of this subsystem (given that we only so far have the Boltzmann entropy p.94). We can do this via the requirement of additivity (this construction is analogous to §6, p.54):

$$S_{\text{tot}} = S + \langle S_R(E-E) \rangle$$

\uparrow world \uparrow subsystem \uparrow avg. entropy of the reservoir

Then $S = S_{\text{tot}} - \langle S_R(E-E) \rangle =$

$$= k_B \ln \Omega_{\text{tot}}(E) - \sum_{\epsilon} p(\epsilon) k_B \ln \Omega_R(E-\epsilon) =$$

$$= -k_B \sum_{\epsilon} p(\epsilon) \ln \frac{\Omega_R(E-\epsilon)}{\Omega_{\text{tot}}(E)} = -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha}$$

So, we have

NB $\sum_{\epsilon} p(\epsilon) = 1$

$\Omega(\epsilon) p_{\alpha}$

$p(\epsilon)/\Omega(\epsilon) = p_{\alpha}$

α here are microstates with $E_{\alpha} = E$

recovered Gibbs entropy.

We can now construct, for our subsystem, the entire thermodynamics of the canonical ensemble as before (§§7-9).

- How different is this thermodynamics, based on average energy and average entropy from the microcanonical version, based on "exact" energy and entropy?

It turns out they are nearly the same provided $N \rightarrow \infty$ ("thermo-limit") because the canonical distribution can be approximate by microcanonical one with $E=U$ quite well in this limit.

11.3 Microcanonical from Canonical (Boltzmann from Gibbs)

What if we started from Gibbs distribution and approximated it with a microcanonical distribution with exact fixed energy $E=U$ (= mean energy)?

~~What if we started from Gibbs distribution and approximated it with a microcanonical distribution with exact fixed energy $E=U$ (= mean energy)?~~

This is equivalent to saying that

$$p_\alpha \approx \begin{cases} \frac{e^{-U/k_B T}}{Z} = \frac{1}{\Omega(U)} & \text{for } E_\alpha = U \\ 0 & \text{for } E_\alpha \neq U \end{cases}$$

because $Z = \Omega(U) e^{-U/k_B T}$
 \uparrow # of states with $E_\alpha = U$.

and so Gibbs entropy is

$$S = -k_B \sum_\alpha p_\alpha \ln p_\alpha = k_B \ln \Omega(U) \quad \text{Boltzmann entropy}$$

and free energy is

$$F = -k_B T \ln Z = -k_B T \ln \Omega + U = U - TS \text{ etc.}$$

This approximation is dependent on the actual energy distribution being quite tight and sharply peaked around the mean energy. It is indeed because from Gibbs can prove (Ex.) that

$$\frac{\langle \Delta E^2 \rangle}{U^2} = \frac{C_V k_B T^2}{U^2} \propto \frac{1}{N} \rightarrow 0 \text{ as } N \rightarrow \infty$$

11.4 Summary

"Gibbsian Heresy"

Fundamental postulate:

maximise Gibbs (Shannon) entropy

$$S = -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha} \rightarrow \max$$

subject to constraints ["2nd law"]



Imposing $\langle E_{\alpha} \rangle = U$ (fixed avg energy) gives Gibbs (canonical) distr.

$$p_{\alpha} = \frac{e^{-\beta E_{\alpha}}}{Z(\beta)}, \quad Z(\beta) = \sum_{\alpha} e^{-\beta E_{\alpha}}$$

$\beta = \frac{1}{k_B T}$ temperature defined as L. multiplier



$$U = - \frac{\partial \ln Z}{\partial \beta}$$

$$S = \frac{U}{T} + k_B \ln Z$$

(extensive!)

Pressure

$$p = - \left(\frac{\partial U}{\partial v} \right)_{p_1 \dots p_L} \text{ (def)}$$



$$dU = TdS - pdV$$



$$T = \left(\frac{\partial U}{\partial S} \right)_V, \quad p = - \left(\frac{\partial U}{\partial v} \right)_S$$



T and p equalise between systems in eq. ("0th law")



The rest of thermodynamics and S.M.

"Boltzmannite Orthodoxy"

Fundamental postulate:

equal a priori probabilities



$$p_{\alpha} = \frac{1}{\Omega(E)} \text{ if } E_{\alpha} = E$$

$$0 \text{ otherwise}$$

fixed energy E
isolated system

microcanonical distr.



Equilibrium = distr. of energy with max # of microstates



Boltzmann entropy

$$S = k_B \ln \Omega(E) \rightarrow \max \text{ ["2nd law"]}$$



definition of temperature

$$\left(\frac{\partial S}{\partial E} \right)_V = \frac{1}{T} \text{ equalises between systems in eq. ("0th law")}$$

$$T \left(\frac{\partial S}{\partial v} \right)_E = p \text{ ditto}$$



$$dE = TdS - pdV$$



Equivalent because $E \approx U$
fluctuations $\rightarrow 0$ as $N \rightarrow \infty$

"First law"

$$dU = \delta Q + \delta W$$

(def. of heat)



For a system in contact with heat bath recover Gibbs distr. and entropy

