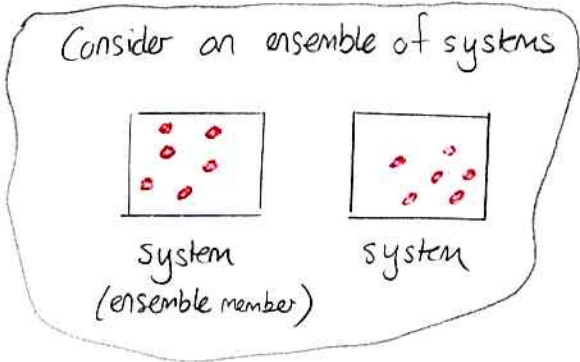Thurs: Read

   Exam II ppd to 23 April

Fr Mon. Hw by 6pm

States and Ensembles: General Framework

The general framework for statistical analysis of physical systems is:
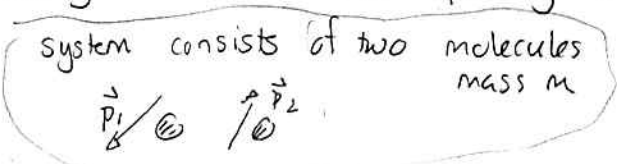
Consider an ensemble of systems

System (ensemble member)

system

For each ensemble member:
* list the possible states for a single ensemble member – label "s"
* Determine probability with which state "s" occurs – denote this p_s

Entropy of system

$$S = -k \sum_{\text{all states "s"}} p_s \ln[p_s]$$

This framework is just as applicable when each system contains a single constituent as when it contains many constituents.
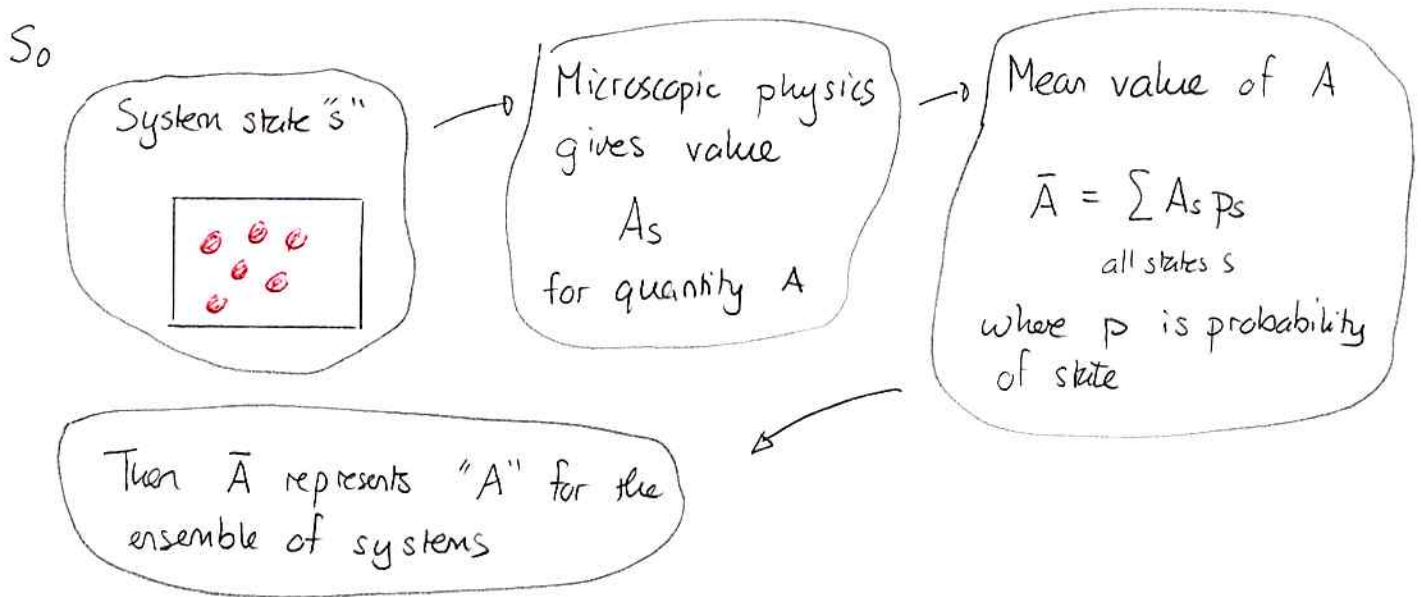
We can use the framework to describe/assign measurable quantities. Suppose that "A" is a quantity that depends on the state of the system (e.g. energy E, z-component of angular momentum, L_z, ...). We can use microscopic physics to assign values to the quantity for each state s. For example

system consists of two molecules
mass m

$\vec{p}_1$ $\vec{p}_2$

$S = (p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, p_{2z})$

Energy
$$E_s = \frac{1}{2m}(\vec{p}_1^{\,2} + \vec{p}_2^{\,2})$$

So

System state "s"

Microscopic physics gives value
A_s
for quantity A

Mean value of A
$$\bar{A} = \sum A_s P_s$$
all states s
where p is probability of state

Then $\bar{A}$ represents "A" for the ensemble of systems

We often use this framework to describe quantities associate with energy. These include: $E, F, G, H, \ldots$

The remaining issue is to provide rules for determining the probabilities with which various states occur. This will depend on:

1) is the system isolated?

2) does the system exchange energy with a surrounding reservoir?

3) does the system exchange particles with a surrounding reservoir

Microcanonical ensemble.

Consider an ensemble of systems where:

1) every system has the same fixed number of particles.

2) if the energy is discrete then every system has the same fixed energy, E.

3) if " " " continuous " " " " energy in the range $E \to E + dE$

This is called the microcanonical ensemble. Consider the discrete energy case. Then the number of states available is $\Omega(E)$. An assumption for this ensemble is that all such states are equally likely. Thus

$$P_s = 1/\text{number states} \implies \boxed{P_s = \frac{1}{\Omega(E)}} \quad \text{microcanonical}$$

← any states

In this case the entropy satisfies:

$$S = -k \sum_s p_s \ln p_s$$

$$= -k \sum_{\text{all } s} \frac{1}{\Omega} \ln\left[\frac{1}{\Omega}\right] = -k \Omega(E) \ln\left[\frac{1}{\Omega(E)}\right] \underbrace{\sum_{\text{all } s} 1}_{= \Omega(E)}$$

$\underbrace{}_{\text{same all states}}$

$$\Rightarrow S = -k \ln\left[\frac{1}{\Omega(E)}\right] \Rightarrow \quad S = k \ln\left[\Omega(E)\right]$$

and we see that this yields the previous result for entropy. So

For an ensemble of systems, each of which has energy E
(or range $E \to E+dE$), the entropy satisfies

$$S = k \ln\left[\Omega(E)\right]$$

where $\Omega(E)$ is the multiplicity. (MICROCANONICAL ENSEMBLE)

1 Microcanonical ensemble: spin-1/2 system

Consider a system consisting of N non-interacting spin-1/2 particles, each with dipole moment μ and in a field with magnitude B. For spin up the energy is $-\mu B$ and for spin down it is μB.

a) Let n_+ be the number of particles with spin up. Find an expression for the system energy E in terms of n_+. Find an expression for n_+ in terms of E.

b) Determine an expression for the multiplicity of the system in terms of n_+ and use this to determine an expression for the entropy in terms of n_+, assuming $N \gg 1$. Describe how this can be used to express the entropy in terms of E. $\hookrightarrow n_+$

c) Determine an expression for the temperature of the system in terms of n_+ and also in terms of E.

d) Describe conditions for which $T > 0$ and $T < 0$.

e) Determine an expression for the probability with which a particle has spin up in terms of temperature.

Answer a) $E = -\mu B n_+ + \mu B\, n_-$ $\qquad\qquad n_+ + n_- = N$

$\qquad\qquad = -\mu B (n_+ - n_-)$ $\qquad\qquad \Rightarrow\ n_- = N - n_+$

$\qquad\qquad = -\mu B (n_+ - N + n_+)$ $\qquad\qquad \Rightarrow$ $\boxed{E = \mu B (N - 2n_+)}$

Inverting gives $\boxed{n_+ = \tfrac{1}{2}\left(N - \dfrac{E}{\mu B}\right)}$

b) $\Omega(n_+) = \dbinom{N}{n_+} = \dfrac{N!}{n_+!\,(N-n_+)!}$

Then

$$S = k \ln[\Omega] = k \ln\left[\dfrac{N!}{n_+!\,(N-n_+)!}\right]$$

$$= k\left\{\ln(N!) - \ln(n_+!) - \ln[(N-n_+)!]\right\}$$

$$\approx k\left\{N\ln N - N - (n_+\ln n_+ - n_+) - [(N-n_+)\ln(N-n_+) - (N-n_+)]\right\}$$

$$= k\left\{N\ln(N) - n_+\ln(n_+) - (N-n_+)\ln(N-n_+) - \cancel{N} + \cancel{n_+} + \cancel{N - n_+}\right\}$$

Thus
$$S = k\left\{N\ln(N) - n_+\ln(n_+) - (N-n_+)\ln(N-n_+)\right\}$$

$$S(E,N) = k\left\{N\ln(N) - \tfrac{1}{2}\left(N-\tfrac{E}{\mu B}\right)\ln\left[\tfrac{1}{2}\left(N-\tfrac{E}{\mu B}\right)\right] - \tfrac{1}{2}\left(N+\tfrac{E}{\mu B}\right)\ln\left[\tfrac{1}{2}\left(N+\tfrac{E}{\mu B}\right)\right]\right\}$$

This entropy can generate all the subsequent thermodynamics.

c) In general
$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S}{\partial n_+}\right)_N \frac{\partial n_+}{\partial E}$$

$\hookrightarrow$ expressing S in terms of n_+, N

First $\qquad \dfrac{\partial n_+}{\partial E} = -\dfrac{1}{2\mu B}$

Second $\qquad \left(\dfrac{\partial S}{\partial n_+}\right)_N = -k\ln(n_+) - k n_+ \cancel{\tfrac{1}{n_+}} - k(-1)\ln(N-n_+) - k(N-n_+)\dfrac{(-1)}{(N-n_+)}$

$$= -k\ln(n_+) + k\ln(N-n_+) \cancel{-k + k}$$

$$= k\ln\left(\frac{N-n_+}{n_+}\right)$$

$$=\!\!\Rightarrow \quad \frac{1}{T} = -\frac{1}{2\mu B}k\ln\left[\frac{N-n_+}{n_+}\right] \qquad =\!\!\Rightarrow \quad \boxed{T = \frac{-2\mu B}{k\ln\left[\frac{N-n_+}{n_+}\right]}}$$

Then to express this in terms of energy
$$N-n_+ = \tfrac{1}{2}\left[N+\frac{E}{\mu B}\right] \qquad =\!\!\Rightarrow \qquad \frac{N-n_+}{n_+} = \frac{\left[N+E/\mu B\right]^{1/2}}{\left[N-E/\mu B\right]^{1/2}}$$

$$=\!\!\Rightarrow \quad \frac{N-n_+}{n_+} = \left[\frac{N+E/\mu B}{N-E/\mu B}\right]$$

$$=\!\!\Rightarrow \quad \boxed{T = -2\mu B \Big/ k\ln\left[\frac{N+E/\mu B}{N-E/\mu B}\right]}$$

d)

$$T > 0$$

$$\Updownarrow$$

$$\ln\left[\frac{N + E/\mu B}{N - E/\mu B}\right] < 0$$

$$\Updownarrow$$

$$\frac{N + E/\mu B}{N - E/\mu B} < 1$$

$$\Updownarrow$$

$$N + E/\mu B < N - E/\mu B$$

$$\Updownarrow$$

$$E < 0$$

$$\Updownarrow$$

$$\mu B (N - 2n_+) < 0$$

$$\Updownarrow$$

$$n_+ > \frac{N}{2}$$

more than ½ particles in lower energy state

$$T < 0$$

$$\Updownarrow$$

$$\ln[\ldots] > 0$$

$$\frac{N + E/\mu B}{N - E/\mu B} > 1$$

$$\vdots$$

$$E > 0$$

$$\vdots$$

$$n_+ < \frac{N}{2}$$

more than half particles in higher energy state.

All natural environments that such collections of spin-½ particles encounter have $T > 0$ and in such cases if the system is in equilibrium with its environment then the majority of particles are in the lower energy state.

But if we manipulate the system rapidly enough it can reach an unstable equilibrium state in which the majority of particles are in the higher energy state. Then heat will flow from the environment to the system so that the system temperature increases
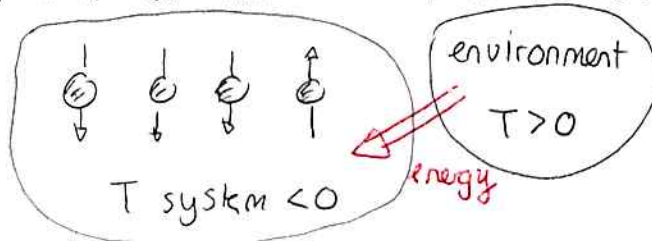
T system < 0   environment T > 0   energy

e) Probability of spin up is

$$P_+ = \frac{n_+}{N}$$

We need n_+ from $\qquad T = \dfrac{-2\mu B}{k \ln\left(\frac{N-n_+}{n_+}\right)}$

$$\Rightarrow \quad \ln\left(\frac{N-n_+}{n_+}\right) = -\frac{2\mu B}{kT}$$

$$\Rightarrow \quad \frac{N-n_+}{n_+} = e^{-2\mu B/kT}$$

$$\Rightarrow \quad \frac{N}{n_+} - 1 = e^{-2\mu B/kT}$$

$$\Rightarrow \quad \frac{N}{n_+} = 1 + e^{-2\mu B/kT}$$

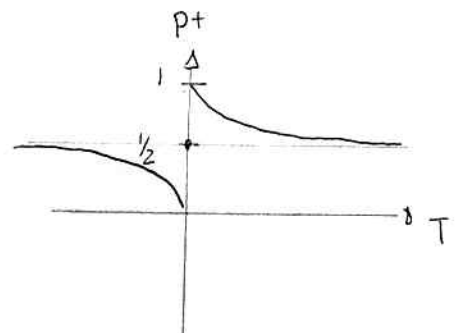$$\Rightarrow \quad \frac{n_+}{N} = \frac{1}{1+e^{-2\mu B/kT}} \qquad \Rightarrow \quad \boxed{P_+ = \frac{1}{1+e^{-2\mu B/kT}}}$$

Similarly

$$\boxed{P_- = \frac{e^{-2\mu B/kT}}{1+e^{-2\mu B/kT}}}$$

Note that

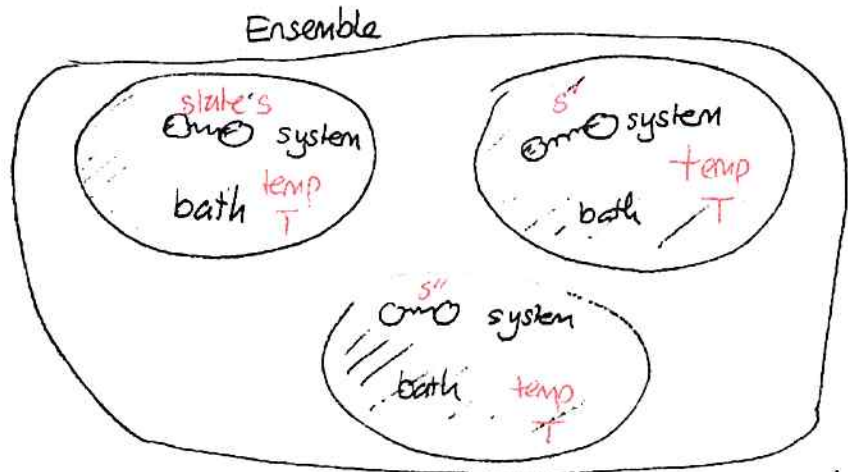| temp	P_+	P_-
$T=0$	1	0
$T>0$	$P_+ > \frac{1}{2}$	$P_- < \frac{1}{2}$
$T<0$	$P_+ < \frac{1}{2}$	$P_- > \frac{1}{2}$

Canonical ensemble

How can we assess an ensemble "at a particular temperature, T?"
We can use the preceeding formalism by considering a ensemble in
which each member consists of a system plus a bath at temperature T

Using the same
basic assumptions
of statistical
physics we
can show.

Ensemble

Let s be any state of the system and let E_s be
the energy of this state. Then the probability that the system
will be in state s is

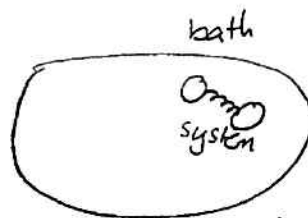$$P_s = \frac{e^{-E_s/kT}}{Z}$$

where

$$Z = \sum_{\text{all states } s} e^{-E_s/kT}$$

is the partition function.

Proof: We can prove this result by considering the ensemble of systems plus baths. Let

E_b = energy of bath

E_s = energy of system

bath
system

Then $E_{tot} = E_b + E_s$ is the energy of the bath + system. If the bath is large enough then the total energy will essentially the same regardless of the system slate and energy.

Then the probability with which the system is in state s is

$$P_s = \alpha \, \Omega_b(E_b) = \alpha \, \Omega_b(E_{tot} - E_s)$$

where Ω_b is the multiplicity of the bath states Here α is a constant independent of s. Then

$$\sum P_s = 1 \implies \alpha \sum_s \Omega_b(E_{tot} - E_s) = 1$$

$$\implies \alpha = \frac{1}{\sum_s \Omega_b(E_{tot} - E_s)}$$

So

$$P_s = \frac{\Omega_b(E_{tot} - E_s)}{\sum_s \Omega_b(E_{tot} - E_s)}$$

Then if the bath is large compared to the system we have that the bath entropy is

$$S_b(E_b) = k \ln\left[\Omega_b(E_b)\right]$$

$$\implies \Omega_b(E_b) = e^{S_b(E_b)/k}$$

So

$$\Omega_b (E_{tot} - E_s) = e^{S_b(E_{tot} - E_s)/k}$$

and we now approximate when $E_s \ll E_{tot}$ using a Taylor series

$$f(x) = f(x_0) + \frac{x-x_0}{1!} \frac{df}{dx}\bigg|_{x_0} + \frac{(x-x_0)^2}{2!} \frac{d^2 f}{dx^2}\bigg|_{x_0} + \cdots$$

The useful identifications here are:

$$f \equiv S_b(E_b)$$

$$x \equiv E_{tot} - E_s \equiv E_b$$

$$x_0 = E_{tot}$$

Thus

$$S_b(E_{tot} - E_s) = S_b(E_{tot}) + \frac{-E_s}{1!} \frac{\partial S_b}{\partial E_b}\bigg|_{E_{tot}} + \frac{E_s^2}{2!} \frac{\partial^2 S_b}{\partial E_b^2}\bigg|_{E_{tot}}$$

Then $\frac{\partial S_b}{\partial E_b} = \frac{1}{T}$ where T is the bath temperature. So

$$S_b(E_{tot} - E_s) = S_b(E_{tot}) - \frac{E_s}{T} + \frac{1}{2} E_s^2 \frac{\partial^2 S_b}{\partial E_b^2} + \cdots$$

We will ignore the $\frac{\partial^2 S_b}{\partial E_b^2}$ term. Then

$$S_b(E_{tot} - E_s) \approx S_b(E_{tot}) - E_s/T$$

So

$$\Omega_b(E_{tot} - E_s) \approx e^{S_b(E_{tot})} e^{-E_s/kT}$$

Now

$$\sum_s \Omega_b(E_{tot} - E_s) = e^{S_b(E_{tot})} \sum_s e^{-E_s/kT}$$

This leaves.

$$P_s \cong \frac{e^{S_b(E_{tot})} e^{-E_s/kT}}{e^{S_b(E_{tot})} \sum_s e^{-E_s/kT}} = \frac{e^{-E_s/kT}}{\sum_s e^{-E_s/kT}}$$

This establishes the key result.

To check the validity of the approximation we need to compare

$$\frac{1}{2} E_s^2 \frac{\partial^2 S_b}{\partial E_b^2}$$

to E_s/T. Here

$$\frac{1}{2} E_s^2 \frac{\partial^2 S_b}{\partial E_b^2} = \frac{1}{2} E_s^2 \frac{\partial}{\partial E_b}\left(\frac{1}{T}\right) = -\frac{E_s^2}{2T^2} \frac{\partial T}{\partial E_b}$$

Then the ratio

$$\left|\left(\frac{1}{2} E_s^2 \frac{\partial^2 S_b}{\partial E_b^2}\right) \Big/ \left(E_s/T\right)\right| = \frac{E_s}{T} \frac{\partial T}{\partial E_b}$$

Then typically the energy has form $E_s = N_s \epsilon_s$ where ϵ is the energy per system particle. Similarly for the bath. So the ratio is

$$|\cdots| = \frac{N_s \epsilon_s}{T} \frac{\partial T}{\partial E_b} \frac{\partial E_b}{\partial E_b} = \left|\frac{N_s}{N_b} \frac{\epsilon_s}{T} \frac{\partial T}{\partial E_b}\right|$$

$$= \frac{N_s}{N_b} \left|\frac{\epsilon_s}{T} \frac{\partial T}{\partial E_b}\right|$$

If $N_s \ll N_b$ and the other term is fixed by the system, then we get $|\cdots| \ll 1$. Thus the approximation is valid for $N_s \gg N_b$

2 Single particle system in contact with a reservoir

Consider a system that consists of a single particle. The system is such that there are four possible states for the particle, each with a distinct energy. The energies are: $0, \epsilon, 2\epsilon, 3\epsilon$.

a) List the possible states of the system and the associated energies.

b) Determine the probability with which the particle will be in each state for the case where $\epsilon = 0.5\,\text{eV}$ and $T = 10^4\,\text{K}$.

Answer: a)

state	energy
$S = 0$	$E_o = 0$
$S = 1$	$E_1 = 1$
$S = 2$	$E_2 = 2$
$S = 3$	$E_3 = 2$

b) $\qquad P_s = \dfrac{e^{-E_s/kT}}{Z} \qquad\qquad Z = \sum_s e^{-E_s/kT}$

Now $kT = 1.38 \times 10^{-23}\,\text{J/k} \times 10^4\,\text{K} = 1.38 \times 10^{-19}\,\text{J}$

$$= 1.38 \times 10^{-19}\,\text{J} / 1.6 \times 10^{-19}\,\text{J} = 0.8625\,\text{eV}$$

Then $\quad E_s = S\epsilon = 0 \qquad E_s/kT = S\dfrac{\epsilon}{0.8625\text{eV}} = S\dfrac{0.5\text{eV}}{0.8625\text{eV}} = 0.58\,S$

S	$e^{-E_s/kT}$	$P_s = e^{-E_s/kT}/Z$
0	1	0.49
1	0.56	0.27
2	0.31	0.15
3	0.18	0.09

$Z = \sum e^{-E_s/kT} = 2.05$

Note that we often encounter $1/kT$. Thus we define

$$\beta := 1/kT$$

and so

$$P_s = \frac{e^{-E_s\beta}}{Z}$$ and $$Z = \sum_s e^{-E_s\beta}$$

Mean value of energy

According to the general scheme, the energy of the system is represented by the mean value

$$\bar{E} = \sum E_s P_s$$

Then we can show:

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

and

$$\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta}$$

so that

$$\sigma_E^2 = -\frac{\partial \bar{E}}{\partial \beta}$$

Proof of energy mean value

$$\bar{E} = \sum E_s P_s$$

$$= \sum E_s \frac{e^{-E_s \beta}}{Z}$$

$$= \frac{1}{Z} \sum E_s e^{-E_s \beta}$$

$$= \frac{1}{Z} \sum_s \left(-\frac{\partial}{\partial \beta} e^{-E_s \beta} \right)$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \underbrace{\sum_s e^{-E_s \beta}}_{Z} \qquad = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta} \left(\ln Z \right)$$