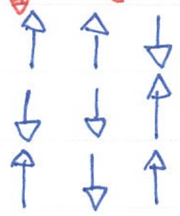
HH0055 Binary Model

The multiplicity function $g(E)$ for realistic atom may not be easy to compute. Thus, we start with simple models with analytic expression for $g(E)$

⟨1⟩ Binary statistical systems

Ising spins $m_i = \pm m$.



Ising spins take on two possible values and the energy in constant B field is

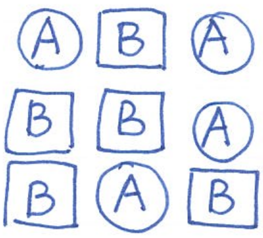
$$U = \sum_{i=1}^{N} U_i = -B \underbrace{\sum_{i=1}^{N} m_i}_{} \rightarrow \text{total } M$$

$$= -mBN_\uparrow + mBN_\downarrow \Longrightarrow \boxed{U = -mB(N_\uparrow - N_\downarrow)}$$

Introduce the notion of spin excess s.

$$N_\uparrow = \tfrac{1}{2}N + s \qquad N_\downarrow = \tfrac{1}{2}N - s \longrightarrow \boxed{N_\uparrow - N_\downarrow = 2s}$$

Note that $U = -2mBs \propto s$.



An binary alloy shares a similar energy. Ignore interactions between neighboring atoms, the energy of the alloy is

$$\boxed{U = \sum_{i=1}^{N} U_i = N_A u_A + N_B u_B}$$

Use the notion of "spin excess": $N_A = \frac{1}{2}N + s$, $N_B = \frac{1}{2}N - s$, the energy can be expressed as

$$U = \left(\tfrac{1}{2}N + s\right)u_A + \left(\tfrac{1}{2}N - s\right)u_B = N \cdot \left(\frac{u_A + u_B}{2}\right) + s\,(u_A - u_B)$$

The first part only depends on the total number $N = N_A + N_B$ while the second part is proportional to s!

Let us start with small N and compute the multiplicity function $g(E)$.

$N = 2$

$(\uparrow + \downarrow)(\uparrow + \downarrow) = \uparrow\uparrow + 2\uparrow\downarrow + \downarrow\downarrow$

It can be generalized to arbitrary N:

$$(\uparrow + \downarrow)(\uparrow + \downarrow)\cdots(\uparrow + \downarrow) = (\uparrow + \downarrow)^N$$

$$= \sum_S \frac{N!}{(\frac{1}{2}N+S)!\,(\frac{1}{2}N-S)!} \uparrow^{\frac{1}{2}N+S} \downarrow^{\frac{1}{2}N-S}$$

Note that $E = -2mBS$

$g(N,E) \longrightarrow g(N,S)$

The multiplicity function is $\boxed{g(N,S) = \frac{N!}{(\frac{1}{2}N+S)!\,(\frac{1}{2}N-S)!}}$

A more professional approach is by generating function.

According to the definition, $G(N,z) = \sum_{n=0}^{\infty} g_n(N)\, z^n$

Choose $n = N_\downarrow = 0, 1, 2, \cdots$ as variable

$g(N,E) \longrightarrow g_n(N)$ ← a family of special functions in N ☺

Use the power of z to denote the number of down spins.

$$G(N,z) = (1+z)(1+z)\cdots(1+z) \longrightarrow \boxed{G(N,z) = (1+z)^N}$$

The multiplicity function $g(N,E)$ can be extracted from the coefficients of $G(N,z)$

$$g(N,E) = g_n(N) = \frac{1}{n!}\frac{d^nG}{dz^n}\bigg|_{z=0} = \frac{1}{n!}\left[N(N-1)\cdots(N-n+1)\right]$$

$$= \frac{N!}{n!\,(N-n)!}$$ ← the same result!

Note that

$n = N_\downarrow = \frac{1}{2}N - S$

$N - n = N_\uparrow = \frac{1}{2}N + S$

$$\Longrightarrow \boxed{g(N,s) = \frac{N!}{(\frac{N}{2}-s)!\,(\frac{N}{2}+s)!}}$$

② Harmonic oscillators:

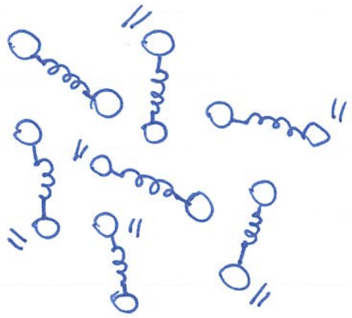
In the effective Hamiltonian $H = \frac{p^2}{2M} + \frac{1}{2}kx^2$

simplified molecule.

M is the reduced mass, x & p are relative coordinate and momentum. Because of the non-vanishing commutator $[x, p] = i\hbar$, one can obtain the energy levels for a harmonic oscillator

$$\boxed{\varepsilon_s = \left(s + \frac{1}{2}\right)\hbar\omega, \quad s = 0, 1, 2, \cdots}$$

The zero-point energy is often dropped for calculation simplicity.



N oscillators

The total energy is $\boxed{E = \sum_{i=1}^{N} s_i \hbar\omega \equiv n\hbar\omega}$

We are now interested in computing $g(N, E)$ for these N oscillators.

The generating function $G(N, z)$ consists of all possible configurations:

$$G(N, z) = (1 + z + z^2 + \cdots)(1 + z + z^2 + \cdots) \cdots\cdots (1 + z + z^2 + \cdots)$$

$$\Rightarrow \quad \boxed{G(N, z) = \left(\frac{1}{1 - z}\right)^N}$$

Taking derivative to get $g_n(N)$

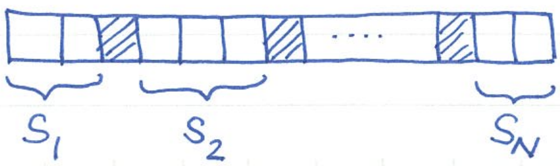
$$g_n(N) = \frac{1}{n!} \frac{d^n}{dz^n} G(N, z)\bigg|_{z=0} = \frac{1}{n!} \frac{d^n}{dz^n} (1 - z)^{-N}\bigg|_{z=0}$$

$$= \frac{1}{n!} N \cdot (N+1) \cdots\cdots (N+n-1)$$

Note that $E = n\hbar\omega$, $\boxed{g(N, E) = g_n(N) = \frac{(N+n-1)!}{n!\,(N-1)!}}$

Another trick to obtain $g(N, E)$.

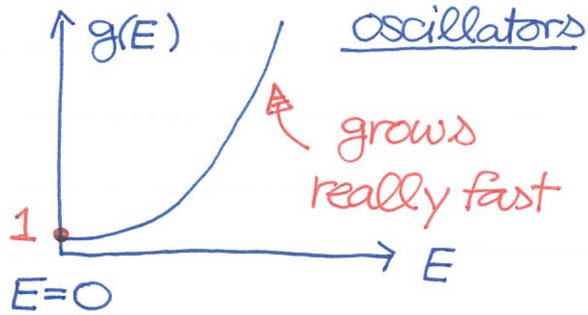
$s_1 + s_2 + \cdots + s_N = n$



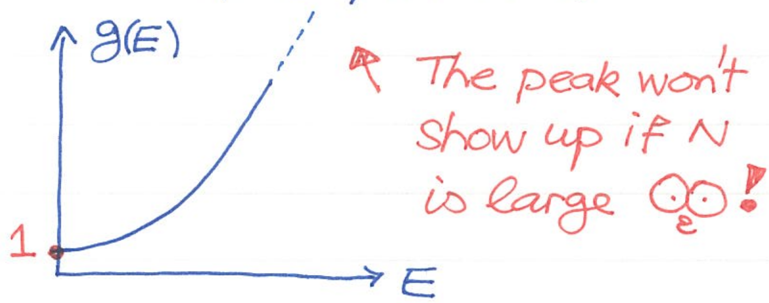
number of blocks $= n + (N-1)$

$$\Rightarrow \quad g_n(N) = \frac{(N+n-1)!}{n!\,(N-1)!}$$

(3) **Profile of the multiplicity function:** We now obtain $g(E)$ for binary model and oscillators. Do they share anything in common. It is inspiring to plot them out explicitly.



At first glance, they look quite different. BUT! If we are interested in fluctuations near the ground state $(\uparrow\uparrow\uparrow\cdots\uparrow)$, it's more convenient to set its energy to zero. Re-plot the multiplicity function,



After shifting the energy, both multiplicity functions look similar $\rightarrow$ $g(E)$ grows extremely fast as E increases.

Making use of Stirling approximation, the multiplicity fn can be brought into more friendly form.

$$\boxed{\log(N!) \approx N\log N - N}$$

For Binary Model, $g = \dfrac{N!}{(\frac{N}{2}+s)!\,(\frac{N}{2}-s)!}$

$$\log g \cong N\log N - \cancel{N} - \left(\tfrac{N}{2}+s\right)\log\left(\tfrac{N}{2}+s\right) + \cancel{\left(\tfrac{N}{2}+s\right)}$$
$$- \left(\tfrac{N}{2}-s\right)\log\left(\tfrac{N}{2}-s\right) + \cancel{\left(\tfrac{N}{2}-s\right)}$$

$$\rightarrow \log g \cong -\left(\tfrac{N}{2}+s\right)\log\left(\tfrac{1}{2}+\tfrac{s}{N}\right) - \left(\tfrac{N}{2}-s\right)\log\left(\tfrac{1}{2}-\tfrac{s}{N}\right)$$
$$= -\tfrac{N}{2}\left(1+\tfrac{2s}{N}\right)\left[\log\left(1+\tfrac{2s}{N}\right) - \log 2\right]$$
$$- \tfrac{N}{2}\left(1-\tfrac{2s}{N}\right)\left[\log\left(1-\tfrac{2s}{N}\right) - \log 2\right]$$

Set $x = 2S/N$, $\log g \approx N \log 2 - \frac{N}{2}\left[(1+x)\log(1+x) + (1-x)\log(1-x)\right]$

$\hookrightarrow x^2 + \frac{1}{6}x^4 + O(x^6)$

Thus, the multiplicity fn is

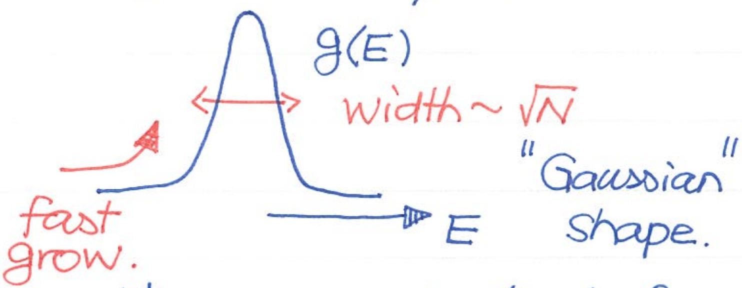
$$\log g \approx N \log 2 - \frac{N}{2} x^2 \approx N \log 2 - \frac{2S^2}{N}$$

In the large N limit, the energy can be approximated as a continuous variable between $(-\infty, \infty)$.

$$\boxed{g(N,S) = g(N,0)\, e^{-2S^2/N}} \quad \text{with} \quad g(N,0) = \sqrt{\frac{2}{\pi N}}\, 2^N$$

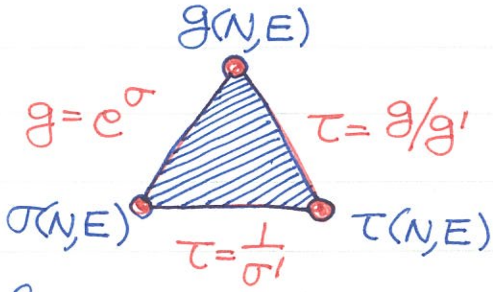
The peak value $g(N,0)$ is chosen to satisfy the sum rule,

$$\int_{-\infty}^{+\infty} dS \; g(N,S) = 2^N$$



From the above calculations, it seems easier to deal with $\log g$ (rather than g itself) when N is large, i.e in the thermodynamic limit. As will become clear later, we define the entropy $\sigma(E)$ and the temperature $\tau(E)$ as

$$\boxed{\begin{aligned} \sigma(E) &\equiv \log g(E) \\ \frac{1}{\tau} &\equiv \left(\frac{\partial \sigma}{\partial E}\right)_N = \frac{1}{g}\left(\frac{\partial g}{\partial E}\right)_N \end{aligned}}$$



The relations shown in the triangle may seem weird at this point. But, as we understand the microscopic origin of thermal equilibrium, σ and τ are in fact related this way.

Use photons in equilibrium as a demonstrating example.
Consider N oscillators of frequency $\omega \longrightarrow \boxed{\upsilon = n\hbar\omega}$

$$g(N,U) = \frac{(N+n-1)!}{n!(N-1)!}$$ and entropy $\sigma = \log g$

$$\sigma = \log(N+n-1)! - \log n! - \log(N-1)!$$

$$\cong (N+n-1)\log(N+n-1) - \cancel{(N+n-1)}$$
$$- n\log n \qquad + \cancel{n}$$
$$- (N-1)\log(N-1) \qquad + \cancel{(N-1)}$$

$$\rightarrow \boxed{\begin{aligned}\sigma \approx\ & (N+n-1)\log(N+n-1)\\ & -n\log n\\ & -(N-1)\log(N-1)\end{aligned}}$$

By definition, $\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_N = \frac{1}{\hbar\omega}\left(\frac{\partial\sigma}{\partial n}\right)_N$

$$\boxed{\left(\frac{\partial\sigma}{\partial n}\right)_N = \frac{\hbar\omega}{\tau}} \rightarrow \frac{\hbar\omega}{\tau} = \log(N+n-1) + \cancel{1} - \log n - \cancel{1}$$

$$= \log\left(\frac{N-1+n}{n}\right)$$

Taking exponential on both sides,

$$\frac{N-1}{n} + 1 = e^{\frac{\hbar\omega}{\tau}} \rightarrow n = \frac{N-1}{e^{\frac{\hbar\omega}{\tau}} - 1}$$

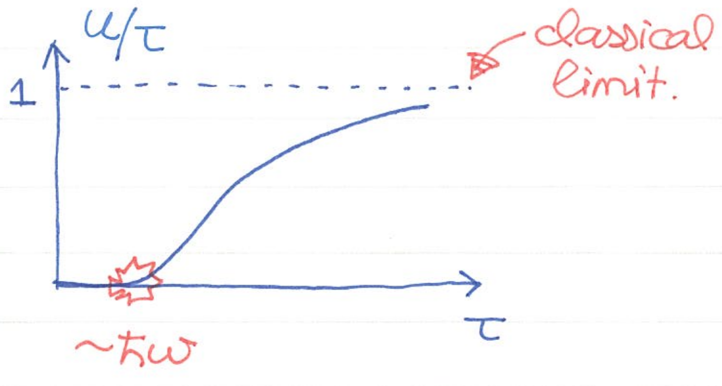
We're ready to compute the average energy for each oscillator,

$$u = \frac{U}{N} = \frac{n\hbar\omega}{N} = \left(\frac{N-1}{N}\right)\cdot\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1} \approx \frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}$$

In the large N limit, we recover Planck's famous result

$$\boxed{u = \frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}} \rightarrow \tau \text{ (high temp)}$$

It's quite remarkable that Planck distribution of photons is hidden in the multiplicity fn $g(N,U)$ for harmonic oscillators ☺



清大東院
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