STATISTICAL MECHANICS

* **Classical thermodynamics**
  - deals with relationships of macroscopic characteristics of a system in equilibrium
* **Statistical Mechanics**: For a system obtain general conclusions about macroscopic properties from its microscopic properties and laws of mechanics. Yields all and more than classical thermodynamics.

CHALLENGES

* Obtaining macroscopic characteristics from microscopic entities seems daunting; a system typically involves a large number of interacting entities typically in the order of Avagadros (10^{23}) elements.
* The main key lies in making use of the large number of entities to make definitive statistical inferences of macroscopic parameters.

ESSENTIAL INGREDIENTS

(a) Specification of the state of the system
- Detailed method for describing outcomes

(b) Statistical Ensemble
- Use of probability of occurences of a particular outcome using an ensemble of many experiments.

(c) Basic postulate about apriori probabilities

(d) Probability Calculations.

TERMINOLOGY

* **CLOSED SYSTEM:**
  A closed system is essentially isolated and has constant energy, number of particles constant volume and constant value of all external parameters

* **Accessible states:** All state that are compatible with the physical specification of the system.

EXAMPLE: SPIN 1/2 PARTICLES

- Spin $\frac{1}{2}$ particles have quantized magnetic spin: they assume a spin $+1/2$ or a spin $-1/2$.
- Consider N spin half particles
  The state of the system is specified by N numbers $m_1, m_2, \ldots m_N$
  where $m_i \in \{1/2, -1/2\}$
- Total number of possible states is 2^N

SPIN $\frac{1}{2}$ PARTICLE

- Energy associated with a spin $+1/2$ half particle $= -mB$ where m is a constant and B is the magnetic field
- It is $+mB$ for a spin $-1/2$ particle.

MULTIPLICITY FUNCTION

* Suppose of N spin $\frac{1}{2}$ particles $N_\uparrow$ have positive spin and $N_\downarrow$ have negative spin. with

$$N_\uparrow - N_\downarrow = 2s$$

where

s is the spin excess

* Multiplicity function:

$g(N,s)$ is the number of ways of having a spin excess of $2s$ with N particles

MULTIPLICITY FUNCTION

* Note that

$$N_\uparrow + N_\downarrow = N$$

and $$N_\uparrow - N_\downarrow = 2s$$

$$\Rightarrow \quad N_\uparrow = \frac{N+2s}{2}$$

and $$N_\downarrow = \frac{N-2s}{2}$$

* $g(N, 2s)$ is equal to the number of ways of choosing $N_\uparrow$ positions out of a total of N positions $= {}^{N}C_{N_\uparrow}$

Multiplicity function

$\circledast$ $g(N,s) = {}^{N}C_{N_\uparrow}$

$$= \frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}$$

Asymptotics

* **Stirlings Approximation:**

$$N! \cong \sqrt{2\pi N}\; N^N e^{-N}$$

$$\Rightarrow \lg N! = \frac{1}{2}\lg 2\pi N + N\lg N - N$$

$$= \frac{1}{2}\lg 2\pi + \left(N+\frac{1}{2}\right)\lg N - N$$

* $\lg g(N,s) = \lg\left(\frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}\right) = \lg N! - \lg N_\uparrow!$
$- \lg N_\downarrow!$

Approximation

$$\lg N! = \frac{1}{2}\lg 2\pi + \left(N+\frac{1}{2}\right)\lg N - N$$

$$= \frac{1}{2}\lg 2\pi + \left(N\uparrow + N\downarrow + \frac{1}{2} + \frac{1}{2}\right)\lg N - N$$

$$- \frac{1}{2}\lg N$$

$$= \frac{1}{2}\lg\frac{2\pi}{N} + \left(N\uparrow + \frac{1}{2}\right)\lg N + \left(N\downarrow + \frac{1}{2}\right)\lg N$$

$$- (N\uparrow + N\downarrow).$$

$$\therefore \lg N! - \lg N_\uparrow! - \lg N_\downarrow! = \left(\frac{1}{2}\lg\frac{2\pi}{N} - \lg 2\pi\right)$$

$$+ \left(N_\uparrow + \frac{1}{2}\right)\lg\frac{N}{N_\uparrow} +$$

$$\left(N_\downarrow + \frac{1}{2}\right)\lg\frac{N_\downarrow}{N}.$$

Approximation

$$\Rightarrow g(N,s) \approx \frac{1}{2}\lg\frac{1}{2\pi N} - \left(N_{\uparrow}+\frac{1}{2}\right)\lg\frac{N_{\uparrow}}{N}$$
$$-\left(N_{\downarrow}+\frac{1}{2}\right)\lg\frac{N_{\downarrow}}{N}.$$

$$\lg\left(\frac{N_{\uparrow}}{N}\right) = \lg\left(\frac{N+2s}{2N}\right) = \lg\frac{1}{2}\left(1+\frac{2s}{N}\right)$$
$$= -\lg 2 + \lg\left(1+\frac{2s}{N}\right)$$
$$\approx -\lg 2 + \frac{2s}{N} - \frac{2s^2}{N^2}$$

$$\left(\lg(1+x) = x - \frac{1}{2}x^2\right. \; ; \quad x \ll 1.$$

$$\therefore \lg\frac{N_{\downarrow}}{N} = \lg\frac{1}{2}\left(1-\frac{2s}{N}\right) = -\lg 2 - \frac{2s}{N} \quad \frac{2s^2}{N^2}$$

Approximation of the multiplicity function

$$\Rightarrow g(N,s) = \frac{1}{2}\lg\left(\frac{1}{2\pi N}\right) - \left(N_\uparrow + \frac{1}{2}\right)\lg\left(\frac{N_\uparrow}{N}\right) - \left(N_\downarrow + \frac{1}{2}\right)\lg\left(\frac{N_\downarrow}{N}\right)$$

$$= \frac{1}{2}\lg\left(\frac{1}{2\pi N}\right) - \left(N_\uparrow + \frac{1}{2}\right)\left(-\lg 2 + \frac{2s}{N}\right.$$

$$- \left(N_\downarrow + \frac{1}{2}\right)\left(-\lg 2 - \frac{2s}{N} - \frac{2s^2}{N^2}\right)$$

$-$?

$$= \frac{1}{2}\lg\frac{1}{2\pi N} + N\lg 2 - \left(\frac{2s}{N}\right)\left[N_\uparrow - N_\downarrow\right) + 2s^2/N^2\left(N_\uparrow + N_\downarrow\right) + \lg 2 + 2s^2/N^2 + 2s^2/N^2$$

Approximation

$$\lg g(N,s) = \frac{1}{2}\lg\frac{1}{2\pi N} + N\lg 2 - \left(\frac{2s}{N}\right)(N_\uparrow - N_\downarrow) + 2s^2/N^2 (N_\uparrow + N_\downarrow) + \lg 2 + 2s^2/N^2 + 2s^2/N^2$$

$$= \frac{1}{2}\lg\left(\frac{1}{2\pi N}\right) + N\lg 2 - \frac{4s^2}{N} + \frac{2s^2}{N} + \lg 2 + \frac{4s^2}{N^2}.$$

$$= \lg\left(2^N\sqrt{\frac{1}{2\pi N}}\cdot 2\right) - \frac{2s^2}{N} + \frac{4s^2}{N^2}$$

$$\simeq \lg\left(2^N\sqrt{\frac{2}{\pi N}}\right) - \frac{2s^2}{N} \quad ; \quad \frac{4s^2}{N^2} \ll \frac{2s^2}{N} \text{ for } N \gg 1$$

$$\Rightarrow \boxed{g(N,s) \simeq 2^N\sqrt{\frac{2}{\pi N}}\, e^{-\frac{2s^2}{N}}}$$

THE Mutiplicity function

Thus

$$g(N,\delta) \simeq 2^N \sqrt{\frac{2}{\pi N}}\ e^{-\frac{2\delta^2}{N}}$$

$$= g(N,0)\ e^{-2\delta^2/N}$$

Spin Excess

* Assume that there are no constraints on the system of N particles with an external magnetic field B a constant

* Thus all 2^N states are accessible

* Postulate: All accessible states are equally likely

Spin Excess

- Thus, probability of any one state $= \frac{1}{2^N}$.

- Probability that the systems has a spin excess $2s$ = $\frac{(\#\text{ of states with spin excess } 2s)}{2^N}$

$$= \frac{g(N,s)}{2^N}$$

Mean of Spin Excess

$$- \quad \langle 2s \rangle = \sum_{s=-\frac{N}{2}}^{N/2} s\, p(s)$$

$p(s)$ is the probability that spin excess $= 2s$

$$\therefore \quad \langle 2s \rangle \simeq \sum_{s=-\frac{N}{2}}^{N/2} 2s \frac{g(N,0)\, e^{-2s^2/N}}{2^N}$$

$$= \frac{g(N,0)\cdot 2}{2^N}\Big[-\cancel{\tfrac{N}{2}}\, e^{-2\left(\frac{N}{2}\right)^2/N} - \cancel{\left(\tfrac{N-1}{2}\right)} e^{-2\frac{(N-1)^2}{2N}} \cdots - \tfrac{1}{2}\,\cancel{e}^{-2\left(\frac{1}{2}\right)^2/N} - 0$$

$$+ \cancel{N/_2}\, e^{-2\left(\frac{N}{2}\right)^2/N} + \cancel{\left(\tfrac{N-1}{2}\right)} e^{-2\frac{(N-1)^2}{2N}} + \cancel{\tfrac{1}{2}}\, e^{-2(1/2)^2/N} \Big]$$

$$= 0$$

Variance of Spin Excess

$$-\langle s^2\rangle = \sum_s s^2 p(s) = \sum_s s^2 \frac{g(N,0)}{2^N} e^{-2s^2/N}$$

$$-\langle s^2\rangle = \frac{g(N,0)}{2^N} \sum_s s^2 e^{-2s^2/N}$$

$$\simeq \frac{g(N,0)}{2^N} \int_{-\infty}^{\infty} s^2 e^{-2s^2/N} ds$$

Let $\frac{2s^2}{N} = x^2$

$\Rightarrow s = \sqrt{\frac{N}{2}}\, x$

$$= \frac{g(N,0)}{2^N} \int_{-\infty}^{\infty} \frac{N}{2} x^2 e^{-x^2} \sqrt{\frac{N}{2}}\, dx$$

$$= \frac{g(N,0)}{2^N} \left(\frac{N}{2}\right)^{3/2} \int_{-\infty}^{\infty} x^2 e^{-x^2} dx$$

$$= \frac{1}{4} N$$

Variance of Spin Excess

$$\Rightarrow \quad \langle s^2 \rangle = \frac{1}{4} N$$

$$\Rightarrow \quad \langle (2s)^2 \rangle = 4 \langle s^2 \rangle = N.$$

$$\therefore \quad \sqrt{\langle (2s)^2 \rangle} = \sqrt{N}.$$

Fractional Spin Excess $= \dfrac{\sqrt{\langle (2s)^2 \rangle}}{N}$

$$= \frac{1}{\sqrt{N}}$$

Which is very small.

Postulate

1. For a closed-system all accessible states are equally likely.

Most Probable configuration

* S_1 and S_2 are two systems with N_1 and N_2 spin ½ particles respectively.

* S_1 has energy U_{10} and S_2 has energy U_{20}; initially

* $S = S_1 \cup S_2$ is a closed-system.
[Note that S has a constant

- energy $U_{10} + U_{30}$]

Most Probable Configuration

→ Given the above conditions what is the most probable energy U_1 of system S_1 (and $(U-U_1)$ of system S_2), with the added constraint that N_1 and N_2 do not change.

→ Note that $U_{10} = -2\delta_{10} m B$

$U_{20} = -2\delta_{20} m B$

for some δ_{10} and δ_{20}.

Most Probable Configuration

→ $U_{10} = -2s_{10} m B$

$U_{20} = -2s_{20} m B$

.

→ Suppose $s_{10} + s_{20} = s$. Then s is a constant.

→ Let $2s_1$ and $2s_2$ represent the spin excess of S_1 and S_2 respectively. Then

$$2s_1 + 2s_2 = 2s$$ for any configuration.

Most Probable Configuration

- As S is a closed-system all of its accessible states are equally likely.

- For each state of S_1 which has spin excess of $2s_1$; S_2 can be in any of the $g_2(N_2, s-s_1)$ states

→ There are $g_1(N_1, s_1)$ number of possible ways in which S_1 can have spin excess s_1

Most probable Configuration

→ Thus, total number of states of S, where S_1 has a spin excess s_1 is given by

$$f(s_1) \hat{=} g_1(N_1, s_1)\, g_2(N_2, s-s_1).$$

$$= g_1(0)\, g_2(0)\, e^{-\frac{2s_1^2}{N_1}}\, e^{-\frac{2(s-s_1)^2}{N_2}}$$

Most probable configuration

→ As all accessible states are equally likely, the most probable s_1 is provided by the s_1 that has the most number of states which is obtained by

$$\max_{s_1} f(s_1)$$

$$= \max_{s_1} g_1(0)\, g_2(0)\, e^{-\frac{2s_1^2}{N_1}}\, e^{-\frac{2(s-s_1)^2}{N_2}}$$

Most probable energy configuration

→ Thus we are interested in

$$\hat{s}_1 = \arg\max_{s_1} e^{-2s_1^2/N_1} e^{-\frac{2(s-s_1)^2}{N_2}}$$

$$= \arg\max_{s_1} \ln e^{-2s_1^2/N_1 - \frac{2(s-s_1)^2}{N_2}}$$

$$= \arg\max_{s_1} \left[-\frac{2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2} \right]$$

which is obtained by solving

$$\frac{d}{ds_1} \left[\frac{s_1^2}{N_1} + \frac{(s-s_1)^2}{N_2} \right] = 0$$

Most probable Energy Configuration

Most probable ε_1 satisfies

$$-\frac{d}{d\varepsilon_1}\left[+\frac{2\varepsilon_1^2}{N_1} + \frac{2(\varepsilon-\varepsilon_1)^2}{N_2} \right]\Bigg|_{\varepsilon_1=\hat{\varepsilon}_1} = 0$$

$$\Rightarrow \left[\frac{4\varepsilon_1}{N_1} + \frac{4(\varepsilon-\varepsilon_1)}{N_2}\frac{d}{d\varepsilon_1}(\varepsilon-\varepsilon_1)\right]\Bigg|_{\varepsilon_1=\hat{\varepsilon}_1} = 0$$

$$\Rightarrow \left[\frac{4\varepsilon_1}{N_1} - \frac{4(\varepsilon-\varepsilon_1)}{N_2}\right]\Bigg|_{\varepsilon_1=\hat{\varepsilon}_1} = 0$$

$$\Rightarrow \frac{\hat{\varepsilon}_1}{N_1} = \frac{\varepsilon-\hat{\varepsilon}_1}{N_2}$$

$$\Rightarrow \boxed{\hat{\varepsilon}_1 = \frac{N_1\varepsilon}{N_1+N_2}}$$

Most probable Energy Configuration

→ Thus, the most probable energy configuration is given by

S_1 having energy $-2\hat{\varepsilon}_1 mB$

and S_2 having energy $-2\hat{\varepsilon}_2 mB$

$$\hat{\varepsilon}_2 = \varepsilon - \hat{\varepsilon}_1 = \varepsilon - \frac{N_1}{N_1+N_2}\varepsilon$$

$$= \frac{N_2 \varepsilon}{N_1+N_2}.$$

Measure of deviation from most probable

- Let $s_1 = \hat{s}_1 + \delta$; then $s_2 = \hat{s}_2 - \delta$

The number of states of S with S_1 having spin excess $2s_1$ is

$$g_1(N_1, s_1)\, g_2(N_2, s_2) = g_1(N_1, 0)\, g_2(N_2, 0)\, e^{-2s_1^2/N_1}\, e^{-2s_2^2/N_1}$$

$$= g_1(N_1,0)\, g_2(N_2,0)\, e^{-\frac{2(\hat{s}_1^2 + \delta^2 + 2\hat{s}_1\delta)}{N_1} - \frac{2(\hat{s}_2^2 + \delta^2 - 2\hat{s}_2\delta)}{N_2}}$$

$$= \underbrace{g_1(N_1,0)\, g_2(N_2,0)\, e^{-2\hat{s}_1^2/N_1}\, e^{-2\hat{s}_2^2/N_2}}_{(g_1 g_2)_{max}}\, e^{-4\delta(\hat{s}_1/N_1 - \hat{s}_2/N_2)}\cancel{)}\; e^{-2\delta^2/N_1 - 2\delta^2/N_2}$$

$$= (g_1 g_2)_{max} \exp\left[-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right]$$

Deviation from most probable configuration

Thus, with $s_1 = \hat{s}_1 + \delta$,

$$\frac{g_1(N_1, s_1)\, g_2(N_2, s - s_1)}{(g_1 g_2)_{max}} = e^{-2\delta^2\left[\frac{1}{N_1} + \frac{1}{N_2}\right]}$$

Suppose $N_1 \approx N_2$ then

$$f(\delta) := g_1(N_1, \hat{s}_1 + \delta)\, g_2(N_2, \hat{s}_2 - \delta) = e^{-4\delta^2/N_1} (g_1 g_2)_{max}.$$

Suppose we want to estimate

$$\sum_{|\delta| > \delta_1} f(\delta) = \sum_{|\delta| > \delta_1} (g_1 g_2)_{max}\, e^{-4\delta^2/N_1}$$

$$\approx (g_1 g_2)_{max} \int_{|\delta| > \delta_1} e^{-4\delta^2/N_1}\, d\delta$$

Estimate of deviation

Therefore the number of states that deviate more than $|\delta_1|$ is given by

$$\approx (g_1 g_2)_{max} \int_{|\delta| > \delta_1} e^{-4\delta^2/N_1} \, d\delta$$

$$= (g_1 g_2)_{max} 2 \int_{\delta_1}^{\infty} e^{-4\delta^2/N_1} \, d\delta$$

$$= 2(g_1 g_2)_{max} \int_{\sqrt{2/N_1}\,\delta_1}^{\infty} e^{-x^2} \sqrt{\frac{N_1}{2}} \, dx$$

$$= (2 g_1 g_2)_{max} \sqrt{\frac{N_1}{2}} \int_{\sqrt{2/N_1}\,\delta_1}^{\infty} e^{-x^2} \, dx .$$

$$x^2 = +\frac{4\delta^2}{N_1}$$

$$\Rightarrow x = \sqrt{\frac{2}{N_1}}\,\delta$$

$$dx = \sqrt{\frac{2}{N_1}}\, d\delta$$

Deviation probability

- Thus, the total # of states that deviate more than $|\delta_1|$ is

$$-\ (g_1 g_2)_{max} \sqrt{\frac{N_1}{2}} \int_{\sqrt{\frac{2}{N_1}}\delta_1}^{\infty} e^{-x^2}\,dx$$

- $\delta_1 = 0$ yields total # of states (which are equally likely).

- $\therefore$ $$p(|\delta| > \delta_1) = \frac{\displaystyle\int_{\sqrt{2/N_1}\,\delta_1}^{\infty} e^{-x^2}\,dx}{\displaystyle\int_0^{\infty} e^{-x^2}\,dx}.$$

Probability of deviation is small.

$$p(|\delta| > \delta_1) = \frac{\displaystyle\int_{\sqrt{2/N_1}\,\delta_1}^{\infty} e^{-x^2}\,dx}{\displaystyle\int_0^{\infty} e^{-x^2}\,dx}$$

$$= \left(\frac{2}{\pi}\right)^{1/2} \operatorname{erfc}\left(\frac{2}{N_1}\delta_1\right)$$

$$\approx \frac{1}{2\delta_1}\left(\frac{N_1}{\pi}\right)^{1/2} e^{-4\delta_1^2/N_1}$$

$$\approx \frac{1}{2\sqrt{\pi}\sqrt{N_1}}\left(\frac{N_1}{\delta_1}\right) e^{-4\frac{\delta_1}{N_1}\cdot\delta_1}$$

Suppose $\frac{\delta_1}{N_1} = 10^{-10}$ and $N_1 = 10^{22}$. Then $p(|\delta| > \delta_1) = 10^{-175.3}$