

THERMODYNAMICS AND STATISTICAL MECHANICS

CHAPTER 4 –STATISTICAL MECHANICS: STATES OF A MODEL SYSTEM

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Statistical Mechanics

- Involves a detailed microscopy theory and the use of probability to relate microscopic *degree of freedom* to the macroscopic observables.
- It is primarily concerned with energy "storage" and the balance between *energy* and *entropy* at the microscopic level: how energy is distributed among the many internal degrees of freedom of an object.

Phase Transitions

- Phase transitions and critical phenomena are subtopics of equilibrium statistical mechanics and classical thermodynamics.
- Phase transition theory aims to qualitatively and quantitatively predict *changes of phase* and class phase transitions based on their universality class.

Background

It is an approach for dealing with systems that involve a number of particles.

- A stationary state is a state in which the physical quantities are independent of time. This means that stationary systems are ones for which the energy is well defined.
- An energy-level: if two (or more) different states of a system have the same value of the energy, they are in the same energy level.
- Degeneracy or multiplicity of an energy level: it is the number of different states of a system that correspond to a given energy level.

H atom

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

Where n is a positive integer; n is called the “principal quantum number”

Background

- The state of a H atom is determined by a set of four quantum numbers: n , ℓ , m_ℓ , and m_s
- Here n is the principal quantum number,
- ℓ is the angular momentum number (that goes from 0 to $n - 1$),
- m_ℓ is the z component of the angular momentum number (that goes from $-\ell$ to ℓ),
- m_s is the spin that is either $+1/2$ or $-1/2$.
- n , the principal quantum number, alone determines the energy of a given state, the corresponding energy levels are degenerate

Particle in a box

$$\Psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

And energy is

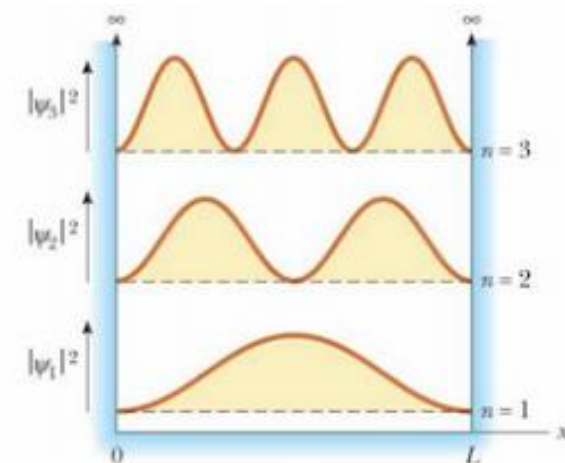
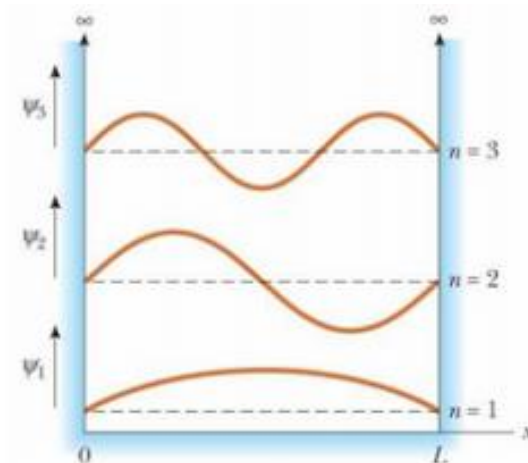
$$E_n = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2} = \frac{h^2}{8mL^2} n^2$$

where $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} = 4.136 \times 10^{-15} \text{ eV}\cdot\text{s}$ is Planck's constant and n_j are positive integers.

n_1	n_2	n_3	n^2	Degeneracy
1	1	1	3	None
1	1	2	6	} Threefold
1	2	1	6	
2	1	1	6	
1	2	2	9	} Threefold
2	1	2	9	
2	2	1	9	
1	1	3	11	} Threefold
1	3	1	11	
3	1	1	11	
2	2	2	12	None

*Note: $n^2 = n_1^2 + n_2^2 + n_3^2$.

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Binary Model

- Consider N distinct and separate sites: At each one of the sites there is a property that can have only one of two values.
- **A Microstates for this system:** a microstate of the system is given when we know how each individual spin is pointing.
- **A macrostate for this look like:** a macrostate the only thing that matters is the net difference between spins pointing up and spins pointing down

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Binary Model System

- Consider N distinct and separate sites: At each one of the sites there is a property that can have only one of two values. We consider a one-dimensional set of N non-interacting spins, each one of which can point up or down.
- The quantity is directly related to the magnetization of the system, a macroscopic property.
- The magnetization is defining as the net magnetic dipole moment per unit volume. In this case, the magnetization is equal to the product of the **spin excess, $2s$** , **times the magnetic dipole moment, μ** , associated with an individual spin, divided by the volume of the system, or

$$M = 2s\mu/V$$

Where the unit of μ is Am^2 , or $N.m T^{-1} (JT^{-1})$ and unit magnetization, M is Am .

Summary of Previous Class

1st and 2nd TdS equations:

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$TdS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

From 1st & 2nd TdS equations:

$$(C_P - C_V) = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T$$

$\left(\frac{\partial P}{\partial V} \right)_T$ is negative for all material, C_P can never be less than C_V . Also both heat capacities are equal when $\left(\frac{\partial V}{\partial T} \right)_P = 0$ and/or $T = 0$

Summary of Last Class

Energy level of H atom

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

The state of a H atom is determined by a set of four quantum numbers: n , ℓ , m_ℓ , and m_s

Develop an approach to allow us to determine, from the knowledge of microstates of a system and their corresponding multiplicity of degeneracy, what macroscopic properties of the system are.

- **A Microstates of this system:** given when we know how each individual spin is pointing.
- **A macrostate of this system:** thing that matters is the net difference between spins pointing up and spins pointing down

Begin with binary system, for example: Magnetization (net magnetic dipole moment per unit volume):

$$M = 2s\mu/V$$

Binary Model System

Magnetic moments are expressed in terms of a unit called **Bohr Magneton** which arises naturally in the treatment of quantized angular momentum.

$$\mu_B = \frac{e\hbar}{2m_e} = 9.2740154 \times 10^{-24} \frac{J}{T} = 5.7883826 \times 10^{-5} eV/T$$

Orbital: $\mu_L = -\frac{e}{2m_e} g_L L$

using angular momentum of quantum state is found to be $L = \sqrt{\ell(\ell + 1)} \hbar$

Where ℓ is angular momentum quantum number $\ell = 0, 1, 2, \dots, n - 1$ and the z-components of the angular momentum”

$$L_z = m_\ell \hbar$$

And z-direction $\mu_{Lz} = -g_L \frac{e\hbar}{2m_e} m_\ell = -m_\ell \mu_B$

since g-factor of orbital angular momentum is $g_L = 1$

Binary Model System

Spin: $\mu_S = -\frac{e}{2m_e} g_S S$

using spin momentum of quantum state is found to be $S = \sqrt{s(s+1)} \hbar$

Where S is total spin angular momentum quantum number. Above is the resulting the fine structure. The z-components of the angular momentum in terms of the magnetic quantum number

$$S_z = m_S \hbar$$

Where $m_S = \pm \frac{1}{2} \hbar$

And z-direction $\mu_{S_z} = -g_S \frac{e\hbar}{2m_e} m_S = -2m_S \mu_B = \pm \mu_B$

since electron spin g-factor is $g_S = 2.0023 \approx 2$

Binary Model System

Let us do a quick calculation for an $N = 3$ spin system: there two possible state for spin 1 (namely, up or down);

Description	Spins	Possibilities	Spin Excess
All three up	$\uparrow\uparrow\uparrow$	1	Up-down = $3 - 0 = 3$
Two up and one down	$\uparrow\uparrow\downarrow, \uparrow\downarrow\uparrow, \downarrow\uparrow\uparrow$	3	Up-down = $2 - 1 = 1$
One down and two up	$\uparrow\downarrow\downarrow, \downarrow\uparrow\downarrow, \downarrow\downarrow\uparrow$	3	Up-down = $1 - 2 = -1$
All three down	$\downarrow\downarrow\downarrow$	1	Up-down = $0 - 3 = -3$

For $N = 3$ spin there are 8 microstates ($8 = 2^3 = 2^N$). And there are $N+1$ different values for the **spin excess or the magnetization** ($4 = 3 + 1$)

Example 4-1

Let us consider $N = 4$ spin system. Determine the total number of microstates and Spin excess.

Description	Spins	Possibilities	Spin Excess
All three up	$\uparrow\uparrow\uparrow$	1	Up-down = $4 - 0 = 4$
Three up and one down	$\uparrow\uparrow\uparrow\downarrow, \uparrow\uparrow\downarrow\uparrow, \uparrow\downarrow\uparrow\uparrow, \downarrow\uparrow\uparrow\uparrow$	4	Up-down = $3 - 1 = 2$
Two up and two down	$\uparrow\uparrow\downarrow\downarrow, \uparrow\downarrow\uparrow\downarrow, \downarrow\uparrow\uparrow\downarrow, \uparrow\downarrow\downarrow\uparrow, \downarrow\uparrow\downarrow\uparrow, \downarrow\downarrow\uparrow\uparrow$	6	Up-down = $2 - 2 = 0$
One up and three down	$\uparrow\downarrow\downarrow\downarrow, \downarrow\uparrow\downarrow\downarrow, \downarrow\downarrow\uparrow\downarrow, \downarrow\downarrow\downarrow\uparrow$	4	Up-down = $1 - 3 = -2$
All four down	$\downarrow\downarrow\downarrow\downarrow$	1	Up-down = $0 - 4 = -4$

there are a total of sixteen different microstates and five different values for spin excess (or magnetization) and **spin excess or the magnetization** ($5 = 4 + 1 = N + 1$). .

Binary Model System

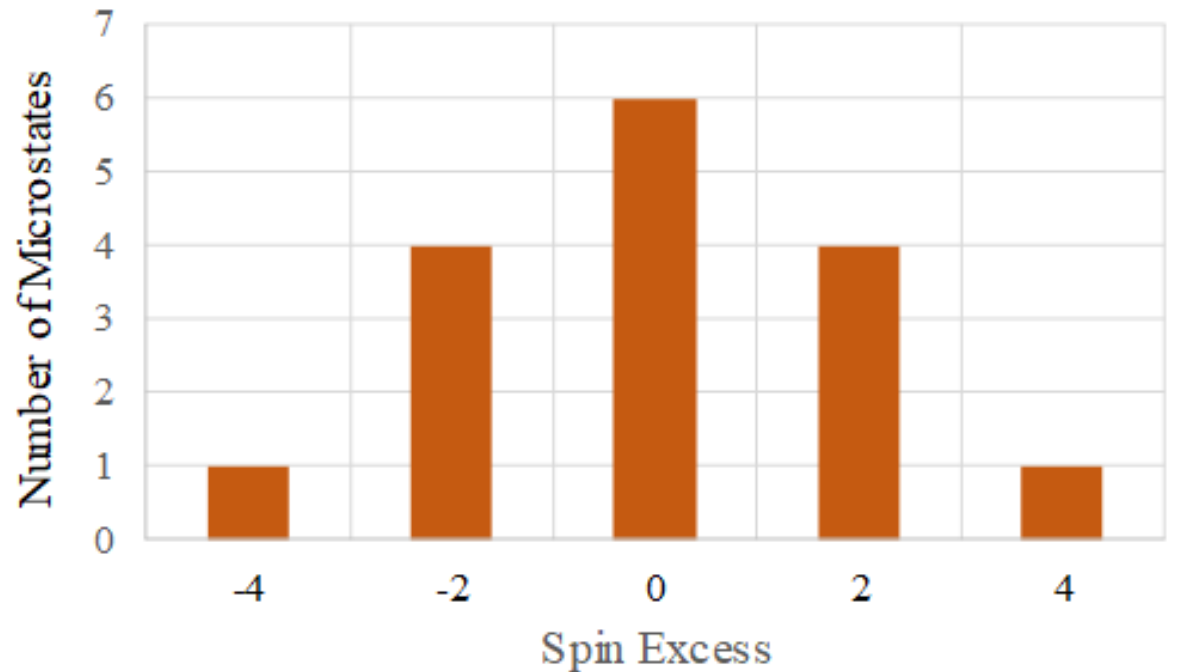
For $N = 4$, there are $2^4 = 16 = 2^N$ microstates and $4 + 1 = 5 = N + 1$ values of the magnetization.

The maximum in the value of the number of microscopic states as a function of the spin excess, $2s$ (in this for spin excess 0).

For any other number N of spins:

- Total number of microstates: 2^N ; and,
- Number of different values of the spin excess:
 $N + 1$

Even if N is not too large, 2^N is much larger than $N + 1$. For example, consider $N = 10$. The number of microstates is $2^{10} = 1024$; and the number of different values of the spin excess $10 + 1 = 11$.



Binary Model System

We use again our results for $N=4$ as a guide. We can symbolically write all sixteen microstates as a result of the following formal products:

$$(\uparrow+\downarrow)_1(\uparrow+\downarrow)_2(\uparrow+\downarrow)_3(\uparrow+\downarrow)_4 = (\uparrow+\downarrow)^4$$

The sub-indices stand for each of the four different spins, and the parenthesis to the power 4 is just a compact way of writing the expression.

If we group the results in terms of just excel (i.e., not worrying about which individual spin is up or down) we get the following:

$$(\uparrow+\downarrow)^4 = 1.\uparrow\uparrow\uparrow\uparrow + 4.\uparrow\uparrow\uparrow\downarrow + 6.\uparrow\uparrow\downarrow\downarrow + 4.\uparrow\downarrow\downarrow\downarrow + 1.\downarrow\downarrow\downarrow\downarrow$$

Binary Model System

These coefficients are the same as those that appear in the binomial expansion.

$$(x + y)^4 = 1 \cdot x^4 + 4 \cdot x^3 y + 6 \cdot x^2 y^2 + 4 \cdot x y^3 + 1 \cdot y^4$$

The binomial expression is:

$$(x + y)^N = \sum_{t=0}^N \frac{N!}{(N-t)! t!} x^{N-t} y^t$$

For spins, $t = 0$ corresponds to $N_{\uparrow} = N$ (and $N_{\downarrow} = 0$) and $t = N$ corresponds to $N_{\uparrow} = 0$ (and $N_{\downarrow} = N$). with this then:

$$(\uparrow + \downarrow)^N = \sum_{t=0}^N \frac{N!}{N_{\uparrow}! N_{\downarrow}!} \uparrow^{N_{\uparrow}} \downarrow^{N_{\downarrow}}$$

Binary Model System

We can write this more conveniently by noting that:

$$2s = N_{\uparrow} - N_{\downarrow} \quad \text{and} \quad N = N_{\uparrow} + N_{\downarrow}$$

Solving these two equations for N_{\downarrow} and N_{\uparrow} in terms of N and s (assuming for simplicity that N is even) yields:

$$N_{\uparrow} = \frac{N}{2} + s \quad \text{and} \quad N_{\downarrow} = \frac{N}{2} - s$$

$$t = 0 \Leftrightarrow N_{\uparrow} = N \rightarrow N = \frac{N}{2} + s \Leftrightarrow s = \frac{N}{2}$$

And

$$t = N \Leftrightarrow N_{\uparrow} = 0 \rightarrow 0 = \frac{N}{2} + s \Leftrightarrow s = -\frac{N}{2}$$

Binary Model System

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

$$(\uparrow + \downarrow)^N = \sum_{t=0}^N \frac{N!}{N_{\uparrow}! N_{\downarrow}!} \uparrow^{N_{\uparrow}} \downarrow^{N_{\downarrow}} = \sum_{s=-N/2}^{s=+N/2} \frac{N!}{\left(\frac{N}{2} + s\right)! \left(\frac{N}{2} - s\right)!} \uparrow^{\left(\frac{N}{2} + s\right)} \downarrow^{\left(\frac{N}{2} - s\right)}$$

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

Here $g(n, s)$ is the number of microstates for a system of N spins with spin excess $2s$.

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

Binary Model System

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

$$(\uparrow + \downarrow)^N = \sum_{t=0}^N \frac{N!}{N_{\uparrow}! N_{\downarrow}!} \uparrow^{N_{\uparrow}} \downarrow^{N_{\downarrow}} = \sum_{s=-N/2}^{s=+N/2} \frac{N!}{\left(\frac{N}{2} + s\right)! \left(\frac{N}{2} - s\right)!} \uparrow^{\left(\frac{N}{2} + s\right)} \downarrow^{\left(\frac{N}{2} - s\right)}$$

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

Here $g(n, s)$ is the number of microstates for a system of N spins with spin excess $2s$.

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

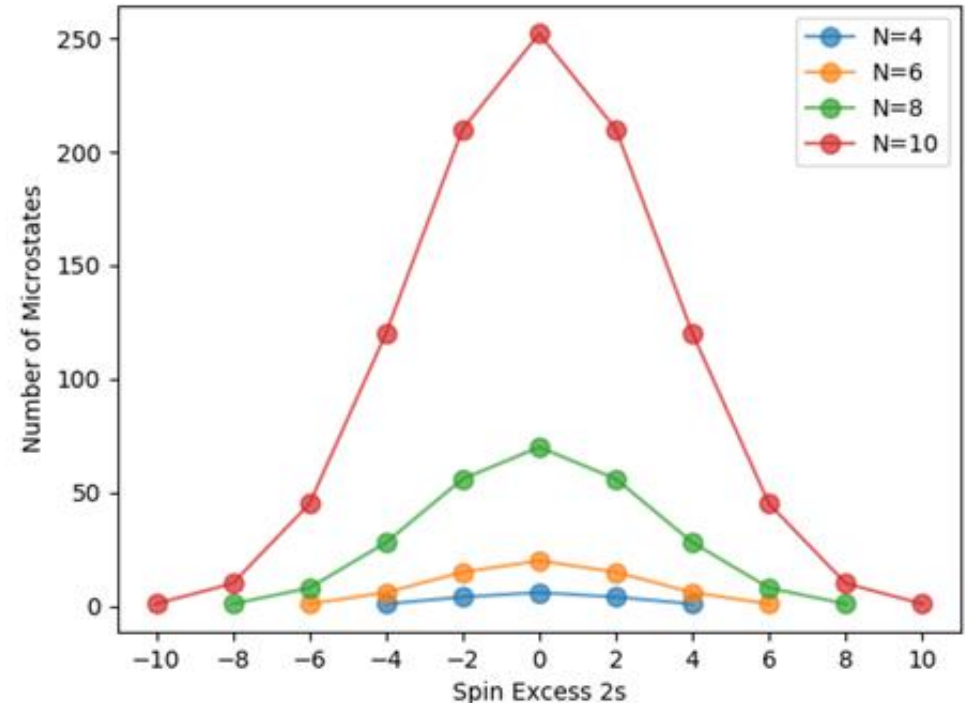
Binary Model System

We know that for N spins there are 2^N different microstates. This same number is what we should get if we do the sum:

$$\# \text{ microstates} = \sum_{s=-\frac{N}{2}}^{s=+\frac{N}{2}} g(N, s)$$

$$= \sum_{s=-\frac{N}{2}}^{s=+\frac{N}{2}} \frac{N!}{\left(\frac{N}{2} + s\right)! \left(\frac{N}{2} - s\right)!}$$

$$= \sum_{t=0}^N \frac{N!}{(N-t)! t!}$$



Number of distinct arrangements of a binary system.

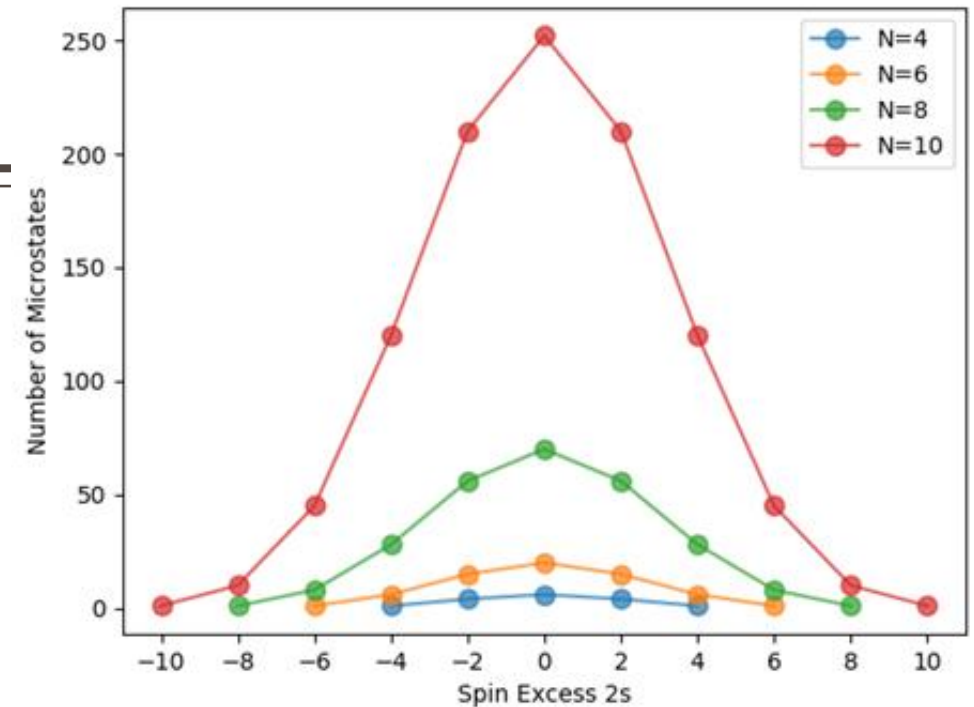
Binary Model System

$$\sum_{t=0}^N \frac{N!}{(N-t)! t!} 1^{N-t} 1^t = (1+1)^N = 2^N$$

So, in fact:

$$\# \text{ microstates} = \sum_{s=-\frac{N}{2}}^{s=+\frac{N}{2}} g(N, s) = 2^N$$

The multiplicity function $g(N, s)$ is very sharply peaked.



Number of distinct arrangements of a binary system.

N	(FWHM/M)
4	0.66
6	0.3
8	0.1
10	0.06

Multiplicity Function

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

For Large number,

$$\text{Log } g(N, s) = \text{Log } N! - \text{Log} \left(\frac{1}{2}N + s\right)! - \text{Log} \left(\frac{1}{2}N - s\right)!$$

Here: $N_{\uparrow} = \frac{1}{2}N + s$ and $N_{\downarrow} = \frac{1}{2}N - s$

$$\text{Log } g(N, s) = \text{Log } N! - \text{Log } N_{\uparrow}! - \text{Log } N_{\downarrow}!$$

Multiplicity Function

Let's apply the Stirling's approximation when $N \gg 1$, which is an approximation for factorials

$$N! \approx (2\pi)^{\frac{1}{2}} N^{N+1/2} \exp\left[-N + \frac{1}{12N} + \dots\right]$$

With this approximation, the $\text{Log } N!$ becomes

$$\text{Ln } N! \approx \frac{1}{2} \text{Ln } 2\pi + \left(N + \frac{1}{2}\right) \text{Ln } N - N + \frac{1}{12N} + \dots$$

We can drop the last terms for large N :

$$\text{Ln } N! \approx \frac{1}{2} \text{Ln } 2\pi + \left(N + \frac{1}{2}\right) \text{Ln } N - N$$

With $N = N_{\uparrow} + N_{\downarrow}$ rearranged as:

$$\text{Ln } N! \approx \frac{1}{2} \text{Ln } 2\pi - \frac{1}{2} \text{Ln } N + \left(N_{\uparrow} + \frac{1}{2} + N_{\downarrow} + \frac{1}{2}\right) \text{Ln } N - (N_{\uparrow} + N_{\downarrow})$$

Multiplicity Function

rearranged as:

$$\ln N! \approx \frac{1}{2} \ln \frac{2\pi}{N} + \left(N_{\uparrow} + \frac{1}{2}\right) \ln N + \left(N_{\downarrow} + \frac{1}{2}\right) \ln N - (N_{\uparrow} + N_{\downarrow})$$

Similarly, for large $N_{\uparrow}!$ and $N_{\downarrow}!$

$$\ln N_{\uparrow}! \approx \frac{1}{2} \ln 2\pi + \left(N_{\uparrow} + \frac{1}{2}\right) \ln N_{\uparrow} - N_{\uparrow}$$

$$\ln N_{\downarrow}! \approx \frac{1}{2} \ln 2\pi + \left(N_{\downarrow} + \frac{1}{2}\right) \ln N_{\downarrow} - N_{\downarrow}$$

With these all approximation,

$$\ln g(N, s) = \ln N! - \ln N_{\uparrow}! - \ln N_{\downarrow}!$$

Multiplicity Function

$$\begin{aligned}
 \text{Ln } g(N, s) &= \frac{1}{2} \text{Ln } \frac{2\pi}{N} + \left(N_{\uparrow} + \frac{1}{2}\right) \text{Ln } N + \left(N_{\downarrow} + \frac{1}{2}\right) \text{Ln } N - (N_{\uparrow} + N_{\downarrow}) \\
 &- \left[\frac{1}{2} \text{Ln } 2\pi + \left(N_{\uparrow} + \frac{1}{2}\right) \text{Ln } N_{\uparrow} - N_{\uparrow} \right] - \left[\frac{1}{2} \text{Ln } 2\pi + \left(N_{\downarrow} + \frac{1}{2}\right) \text{Ln } N_{\downarrow} - N_{\downarrow} \right] \\
 \text{Ln } g(N, s) &= \frac{1}{2} \text{Ln } \left(\frac{1}{2\pi N} \right) - \left(N_{\uparrow} + \frac{1}{2}\right) \text{Ln } \left(\frac{N_{\uparrow}}{N} \right) - \left(N_{\downarrow} + \frac{1}{2}\right) \text{Ln } \left(\frac{N_{\downarrow}}{N} \right)
 \end{aligned}$$

Now it is again convenient to return to expression $\text{Ln } \left(\frac{N_{\uparrow}}{N} \right)$ and $\text{Ln } \left(\frac{N_{\downarrow}}{N} \right)$ in terms of the spin excess, $2s = N_{\uparrow} - N_{\downarrow}$ and $N = N_{\uparrow} + N_{\downarrow}$

$$\text{Ln } \left(\frac{N_{\uparrow}}{N} \right) = \text{Ln } \left(\frac{\frac{1}{2}N + s}{N} \right) = \text{Ln } \left(\frac{1}{2} \right) \left(\frac{N + 2s}{N} \right) = \text{Ln } \left(\frac{1}{2} \right) + \text{Ln } \left(1 + \left(\frac{2s}{N} \right) \right)$$

With $2s \ll N$, so we can approximate the logarithm by noting that:

Multiplicity Function

$$\text{Ln}(1 + x) \approx x - \frac{1}{2}x^2 + \dots$$

Where x is small

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

$$\begin{aligned} \left(N_{\uparrow} + \frac{1}{2} \right) \text{Ln} \left(\frac{N_{\uparrow}}{N} \right) &\approx \left(\frac{N}{2} + s + \frac{1}{2} \right) \left(-\text{Ln} 2 + \frac{2s}{N} - \frac{1}{2} \left(\frac{2s}{N} \right)^2 \right) \\ &\approx \left[-\frac{N}{2} \text{Ln} 2 + s - \frac{s^2}{N} - s \text{Ln} 2 + \frac{2s^2}{N} - \frac{2s^3}{N^2} - \frac{1}{2} \text{Ln} 2 + \frac{s}{N} - \left(\frac{s}{N} \right)^2 \right] \\ &\approx \left[-\left(\frac{N+1}{2} \right) \text{Ln} 2 + s \left(\frac{N+1}{N} \right) - s \text{Ln} 2 + \frac{s^2}{N} - \left(\frac{s}{N} \right)^2 - \frac{2s^3}{N^2} \right] \end{aligned}$$

Multiplicity Function

$$\text{Similarly: } \text{Ln} \left(\frac{N_{\downarrow}}{N} \right) = \text{Ln} \left(\frac{\frac{1}{2}N-s}{N} \right) = \text{Ln} \left(\frac{1}{2} \right) \left(\frac{N-2s}{N} \right) = \text{Ln} \left(\frac{1}{2} \right) + \text{Ln} \left(1 - \left(\frac{2s}{N} \right) \right)$$

$$\text{By applying the expansion of logarithm: } \text{Ln} \left(\frac{N_{\downarrow}}{N} \right) \approx -\text{Ln} 2 - \frac{2s}{N} - \frac{1}{2} \left(\frac{2s}{N} \right)^2$$

$$\begin{aligned} \left(N_{\downarrow} + \frac{1}{2} \right) \text{Ln} \left(\frac{N_{\downarrow}}{N} \right) &\approx \left(\frac{N}{2} - s + \frac{1}{2} \right) \left(-\text{Ln} 2 - \frac{2s}{N} - \frac{1}{2} \left(\frac{2s}{N} \right)^2 \right) \\ &\approx \left[-\frac{N}{2} \text{Ln} 2 - s - \frac{s^2}{N} + s \text{Ln} 2 + \frac{2s^2}{N} + \frac{2s^3}{N^2} - \frac{1}{2} \text{Ln} 2 - \frac{s}{N} - \left(\frac{s}{N} \right)^2 \right] \\ &\left[-\left(\frac{N+1}{2} \right) \text{Ln} 2 - s \left(\frac{N+1}{N} \right) + s \text{Ln} 2 + \frac{s^2}{N} - \left(\frac{s}{N} \right)^2 + \frac{2s^3}{N^2} \right] \end{aligned}$$

Multiplicity Function

$$\begin{aligned} & \left(N_{\uparrow} + \frac{1}{2}\right) \text{Ln} \left(\frac{N_{\uparrow}}{N}\right) + \left(N_{\downarrow} + \frac{1}{2}\right) \text{Ln} \left(\frac{N_{\downarrow}}{N}\right) \\ & \approx \left[-\left(\frac{N+1}{2}\right) \text{Ln} 2 + s \left(\frac{N+1}{N}\right) - s \text{Ln} 2 + \frac{s^2}{N} - \left(\frac{s}{N}\right)^2 - \frac{2s^3}{N^2} \right] \\ & + \left[-\left(\frac{N+1}{2}\right) \text{Ln} 2 - s \left(\frac{N+1}{N}\right) + s \text{Ln} 2 + \frac{s^2}{N} - \left(\frac{s}{N}\right)^2 + \frac{2s^3}{N^2} \right] \end{aligned}$$

By neglecting higher order term of s^2/N^2

$$\begin{aligned} & \left(N_{\uparrow} + \frac{1}{2}\right) \text{Ln} \left(\frac{N_{\uparrow}}{N}\right) + \left(N_{\downarrow} + \frac{1}{2}\right) \text{Ln} \left(\frac{N_{\downarrow}}{N}\right) \approx -(N+1) \text{Ln} 2 + \frac{2s^2}{N} \\ & \left(N_{\uparrow} + \frac{1}{2}\right) \text{Ln} \left(\frac{N_{\uparrow}}{N}\right) + \left(N_{\downarrow} + \frac{1}{2}\right) \text{Ln} \left(\frac{N_{\downarrow}}{N}\right) \approx (N+1) \text{Ln} \left(\frac{1}{2}\right) + \frac{2s^2}{N} \end{aligned}$$

Multiplicity Function

$$\begin{aligned} \ln g(N, s) &\approx \frac{1}{2} \ln \left(\frac{1}{2\pi N} \right) - \left(N_{\uparrow} + \frac{1}{2} \right) \ln \left(\frac{N_{\uparrow}}{N} \right) - \left(N_{\downarrow} + \frac{1}{2} \right) \ln \left(\frac{N_{\downarrow}}{N} \right) \\ &\approx \frac{1}{2} \ln \left(\frac{1}{2\pi N} \right) - \left[(N+1) \ln \left(\frac{1}{2} \right) + \frac{2s^2}{N} \right] \\ &\approx \ln \left(\frac{1}{2\pi N} \right)^{\frac{1}{2}} + \ln 2^{N+1} - \frac{2s^2}{N} \\ &\approx \ln \left[\left(\frac{2}{\pi N} \right)^{\frac{1}{2}} 2^N \right] - \frac{2s^2}{N} \end{aligned}$$

Multiplicity Function

$$g(N, s) = \left[\left(\frac{2}{\pi N} \right)^{\frac{1}{2}} 2^N \right] \exp \left(-\frac{2s^2}{N} \right) = g(N, 0) \exp \left(-\frac{2s^2}{N} \right)$$

Where

$$g(N, 0) = \left[\left(\frac{2}{\pi N} \right)^{\frac{1}{2}} 2^N \right]$$

The form of the approximate multiplicity function

$$g(N, s) = g(N, 0) \exp \left(-\frac{2s^2}{N} \right)$$

Such a **distribution of s** is called a **Gaussian distribution**. The integral of above over range of $-\infty$ to $+\infty$ for s gives the correct value 2^N for the total number of states.

Thank you very much for your attention