Thermodynamics and Statistical Mechanics

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The entropy of a binary system

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Sep 8, 2011

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The entropy of a binary system

N particles

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- N particles
- indistinguishable

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- Two states: up or down; they are all either up or down.

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- N particles
- indistinguishable
- Two states: up or down; they are all either up or down.
- So

$$N = N^{\uparrow} + N^{\downarrow} \tag{1}$$

Enumerating states

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The entropy of a binary system

Description	5	g	States
4 "heads" (4 ↑)	2	1	1111
3 "heads" $(3 \uparrow, 1 \downarrow)$	1	4	$\downarrow\uparrow\uparrow\uparrow\uparrow$, $\uparrow\downarrow\uparrow\uparrow$, $\uparrow\uparrow\downarrow\uparrow$, $\uparrow\uparrow\uparrow\downarrow$
2 "heads" $(2 \uparrow, 2 \downarrow)$	0	6	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
1 "head" $(1 \uparrow, 3 \downarrow)$	-1	4	↓↓↓↑, ↓↓↑↓, ↓↑↓↓
all tails (4 ↓)	-2	1	++++

■ State table for binary system: four coins or four spins (N = 4).

Enumerating states

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- Define spin excess s

$$2s \equiv N^{\uparrow} - N^{\downarrow}$$
 $N^{\uparrow} = \frac{N}{2} + s$ $N^{\downarrow} = \frac{N}{2} - s$ (2)

Enumerating states

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■ many more possibilities to create zero net alignment.

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The entropy of a binary system

Can list the possible states

$$\uparrow\uparrow\uparrow\uparrow\uparrow +4 \uparrow\uparrow\uparrow\downarrow\downarrow +6 \uparrow\uparrow\downarrow\downarrow\downarrow +4 \uparrow\downarrow\downarrow\downarrow\downarrow + \downarrow\downarrow\downarrow\downarrow\downarrow$$
 (3)

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 (3)

represent

$$\uparrow \uparrow \uparrow = \uparrow^3 \tag{4}$$

recognize the coefficients as arising from a binomial expansion:

$$(\uparrow + \downarrow)^4 \tag{5}$$

Binomial expansion

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The entropy of a binary system

■ For arbitrary *N*,

$$(\uparrow + \downarrow)^{N} = \uparrow^{N} + N \uparrow^{N-1} \downarrow + \frac{1}{2} N(N-1) \uparrow^{N-2} \downarrow^{2} + .(6)$$

$$= \sum_{t=0}^{N} \frac{N!}{(N-t)! \ t!} \uparrow^{N-t} \downarrow^{t}$$
(7)

Binomial expansion

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- t runs from 0 to N; s runs from -N/2 to N/2
- \blacksquare multiplicity g(N, s) is

$$g(N,s) = \frac{N!}{\left(\frac{N}{2} + s\right)! \left(\frac{N}{2} - s\right)!} = \frac{N!}{\left(N^{\uparrow}\right)! \left(N^{\downarrow}\right)!} \tag{8}$$



Large multiplicities

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The entropy of a binary system

■ Take the logarithm for large number multiplicity

$$\ln g(N,s) = \ln N! - \ln N^{\uparrow} - \ln N^{\downarrow}$$
 (9)

Large multiplicities

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The entropy of a binary system

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That's the entropy!

$$\sigma = \ln g \tag{10}$$

Large multiplicities

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The entropy of a binary system

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■ Need a way to handle N!. Stirling approximation:

$$\ln N! \simeq \frac{1}{2} \ln 2\pi + (N + \frac{1}{2}) \ln N - N$$
 (11)

valid for large N.

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The entropy of a binary system

■ Substitute the Sterling approx in:

$$\ln g(N,s) = \frac{1}{2} \ln 2\pi + (N + \frac{1}{2}) \ln N - N \qquad (12)$$

$$- (\frac{1}{2} \ln 2\pi + (N^{\uparrow} + \frac{1}{2}) \ln N^{\uparrow} - N^{\uparrow}) (13)$$

$$- (\frac{1}{2} \ln 2\pi + (N^{\downarrow} + \frac{1}{2}) \ln N^{\downarrow} - N^{\downarrow}) (14)$$

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$$- (\frac{1}{2} \ln 2\pi + (N^{\downarrow} + \frac{1}{2}) \ln N^{\downarrow} - N^{\downarrow}) (14)$$

■ Expand: $N = N^{\uparrow} + N^{\downarrow}$; add $\pm (1/2) \ln N$ to the first equation (highlighted),

$$\ln g(N,s) = \frac{1}{2} \ln 2\pi + \left[(N^{\uparrow} + \frac{1}{2}) + (N^{\downarrow} + \frac{1}{2}) \right] \ln N - N^{\uparrow} - N^{\downarrow}$$

$$-\frac{1}{2} \ln 2\pi + \left[-(N^{\uparrow} + \frac{1}{2}) \right] \ln N^{\uparrow} + N^{\uparrow}$$

$$-\frac{1}{2} \ln 2\pi + \left[-(N^{\downarrow} + \frac{1}{2}) \right] \ln N^{\downarrow} + N^{\downarrow}$$

$$= \ln \frac{1}{\sqrt{2\pi N}} + (N^{\uparrow} + \frac{1}{2}) \ln \frac{N}{N^{\uparrow}} + (N^{\downarrow} + \frac{1}{2}) \ln \frac{N}{N^{\downarrow}}$$

Next, simplify $\ln \frac{N}{N^{\perp}}$, $\ln \frac{N}{N^{\perp}}$ using s/N:

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The entropy of a binary system

Simplifies as:

$$\ln \frac{N}{N^{\uparrow}} = \ln \left(\frac{N}{\frac{N}{2} + s} \right) \tag{19}$$

$$= \ln 2 \left(\frac{N+2s}{N} \right)^{-1} \tag{20}$$

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Defining

$$x \equiv \frac{2s}{N} \tag{21}$$

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Defining

$$\ln \frac{N}{N^{\uparrow}} = \ln 2 - \ln (1+x)$$

$$(+x)$$

(21)

$$\ln \frac{N}{N^{\downarrow}} = \ln 2 - \ln (1 - x)$$

 $x \equiv \frac{2s}{M}$

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The entropy of a binary system

• under the small x expansion of $\ln 1 + x \simeq x - x^2/2$:

$$\ln \frac{N}{N^{\uparrow}} = \ln 2 - x + \frac{x^2}{2} \tag{24}$$

$$\ln \frac{N}{N^{\downarrow}} = \ln 2 + x + \frac{x^2}{2} \tag{25}$$

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The entropy of a binary system

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$$\ln \frac{N}{N^{\uparrow}} = \ln 2 - x + \frac{x^2}{2} \tag{24}$$

$$\ln \frac{N}{N^{\downarrow}} = \ln 2 + x + \frac{x^2}{2} \tag{25}$$

simplify the second two terms in eq. 18 as follows:

$$(N^{\uparrow} + \frac{1}{2}) \ln \frac{N}{N^{\uparrow}} = (N^{\uparrow} + \frac{1}{2}) \left[\ln 2 + \frac{1}{2} x^{2} - x \right] (26)$$

$$+ (N^{\downarrow} + \frac{1}{2}) \ln \frac{N}{N^{\downarrow}} = (N^{\downarrow} + \frac{1}{2}) \left[\ln 2 + \frac{1}{2} x^{2} + x \right] (27)$$

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$$= (N+1)\left[\ln 2 + \frac{x^2}{2}\right] - (N^{\uparrow} - N^{\downarrow})x \tag{28}$$

$$\simeq N \left[\ln 2 + \frac{1}{2} \left(\frac{2s}{N} \right)^2 \right] - (2s) \left(\frac{2s}{N} \right) + \ln 2 \qquad (29)$$

$$= N \ln 2 - 2 \left(\frac{s^2}{N} \right) + \ln 2 = \ln 2^{N+1} - 2 \left(\frac{s^2}{N} \right)$$
 (30)

finally:

$$\ln g(s, N) = \ln \frac{1}{\sqrt{2\pi N}} + \ln 2^{N+1} - 2\left(\frac{s^2}{N}\right)$$
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$$g(s, N) = g(0, N) \exp{-\frac{2s^2}{N}}$$
 $g(0, N) = \sqrt{\frac{2}{\pi N}} 2^N$ (32)

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The entropy of a binary system

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■ That's the result! It's a Gaussian distribution. Recognize through the formula

$$g(s, N) = g(0, N)e^{-(s/\beta)^2}$$
 (33)

if
$$\beta = \sqrt{N/2}$$
.

■ Which state of spin excess *s* is most probable, then? Applying the "fundamental assumption," we have

$$P(s,N) = \frac{g(s,N)}{\int_{-\infty}^{\infty} g(s,N) ds}$$
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$$\int_{-\infty}^{\infty} dx \ e^{-(x/\beta)^2} = |\beta| \sqrt{\pi}$$
 (36)

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$$P(s,N) = \frac{e^{-(s/\beta)^2}}{\beta\sqrt{\pi}}$$
 (37)

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$$P(s,N) = \frac{e^{-(s/\beta)^2}}{\beta\sqrt{\pi}}$$
 (37)

$$P(s,N) = \sqrt{\frac{2}{\pi N}} \exp{-\frac{2s^2}{N}}$$
 (38)

■ Plotted in Figure 1 for N = 100.

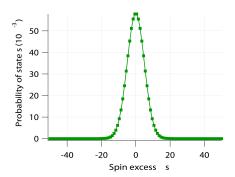


Figure: Multiplicity function for N = 100.

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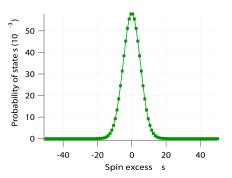


Figure: Multiplicity function for N = 100.

■ The excess s which is most probable—that which has the maximum number of possible configurations—is s = 0.

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■ Sharp peak: drops off quickly with |s| > 0.

- Sharp peak: drops off quickly with |s| > 0.
- Full width at half maximum: g is $\frac{1}{2}$ its maximum at $s=\pm\frac{1}{2}\sqrt{N\ln 2}$, so defining a half-width of the peak Δs ,

$$\Delta s = \sqrt{N \ln 2} \tag{39}$$

■ In a relative sense for the size of the system, the probability of a spin excess s can be defined as $\Delta s/N$, the mean fractional fluctuation that one would observe on measurement:

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■ N=100 electron spins about half as likely to have a net excess of ~ 8 spin moments $(8\mu_B)$ as it is to be equally balanced. (At any instant.)

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■ Tend to observe a fractional deviation of about 9% from measurement to measurement (noise!)

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- Tend to observe a fractional deviation of about 9% from measurement to measurement (noise!)
- Consider a macroscopic volume of a paramagnet, say one cc of Pd with roughly $N=10^{22}$ electron spins. Fractional deviation $\frac{\Delta s}{N}$ about s=0 becomes $\sim 10^{-11}!$

- Tend to observe a fractional deviation of about 9% from measurement to measurement (noise!)
- Consider a macroscopic volume of a paramagnet, say one cc of Pd with roughly $N=10^{22}$ electron spins. Fractional deviation $\frac{\Delta s}{N}$ about s=0 becomes $\sim 10^{-11}!$
- For all intents and purposes, this system has a single value of magnetization, M=0.