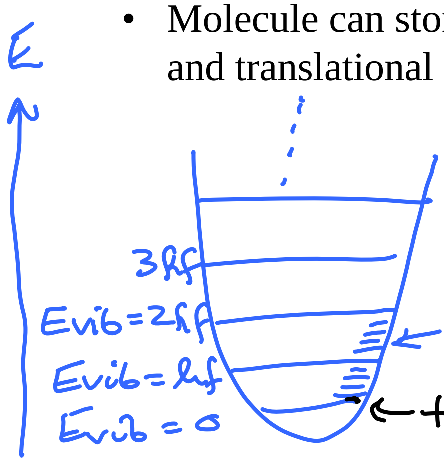
Review of Molecular Energies

Recall degrees of freedom discussion from previous lecture

- Molecule can store thermal energy in vibrational, rotational and translational degrees of freedom

note: relative scales!



← rotational energy states

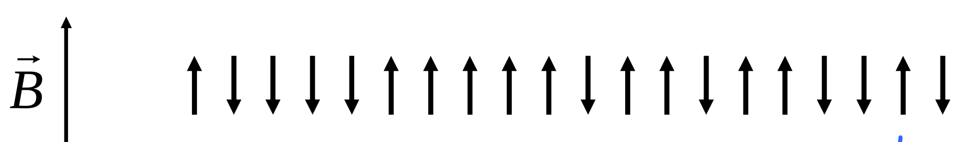
← translational energy states all smushed together

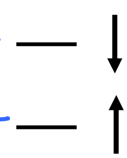
for each vibrational state, there are many possible rotational states

for each rotational state, there are many, many possible translational states

Review of Model Systems

Two-state paramagnet



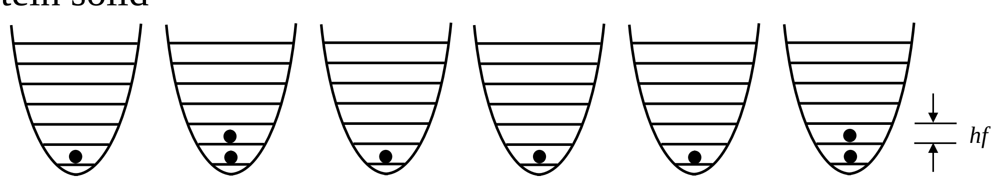


energy unit

$\Omega = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\, N_\downarrow!}$

only 2 states possible

Einstein solid



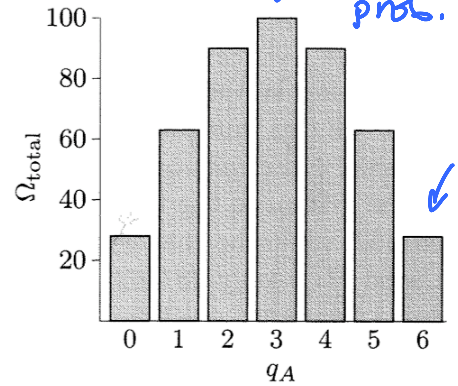
atoms = no. oscillators /3

$\Omega = \binom{q+N-1}{q}$

System of Two Einstein Solids

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

$$462 = \binom{6+6-1}{6}$$

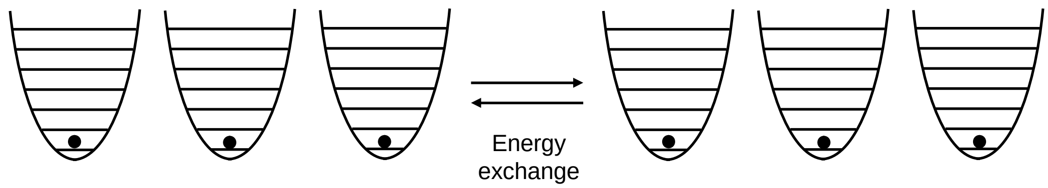


21.6% prob.

6% prob.

$N_A = N_B = 3$

$q = q_A + q_B$



7 macrostates

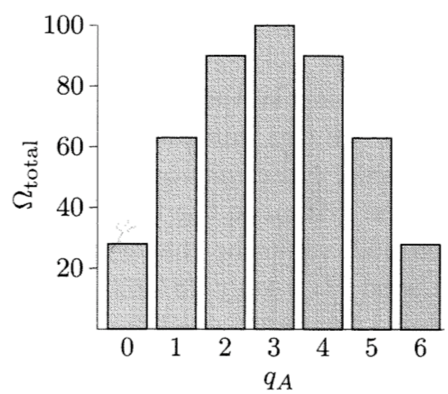
Probabilities of Macrostates

- Fundamental assumption of Statistical Mechanics
  - In an isolated system in thermal equilibrium, all accessible microstates are equally probably

- If all *microstates* are equally probable, some *macrostates* will be more probable than others

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

$$462 = \binom{6+6-1}{6}$$



Larger System

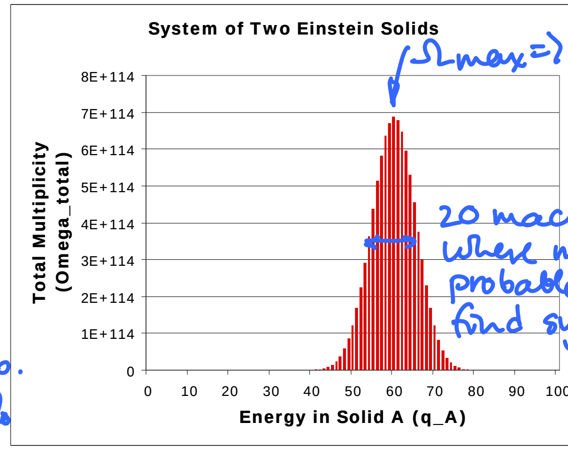
Increasing size of two weakly-coupled Einstein solids…

N_A	300 oscillators
N_B	200 oscillators
q_total	100 units of energy

q_A	Omega_A	q_B	Omega_B	Omega_total
0	1.00E+00	100	2.77E+81	2.77E+81
1	3.00E+02	99	9.27E+80	2.78E+83
2	4.52E+04	98	3.08E+80	1.39E+85
3	4.55E+06	97	1.02E+80	4.62E+86
4	3.44E+08	96	3.33E+79	1.15E+88
5	2.09E+10	95	1.08E+79	2.27E+89
46	4.31E+57	54	5.68E+55	2.45E+113
47	3.18E+58	53	1.21E+55	3.85E+113
48	2.30E+59	52	2.55E+54	5.86E+113
49	1.63E+60	51	5.29E+53	8.62E+113
50	1.14E+61	50	1.08E+53	1.23E+114
51	7.81E+61	49	2.17E+52	1.69E+114
52	5.27E+62	48	4.28E+51	2.26E+114
53	3.50E+63	47	8.31E+50	2.91E+114
54	2.29E+64	46	1.59E+50	3.64E+114
55	1.47E+65	45	2.98E+49	4.39E+114
56	9.34E+65	44	5.50E+48	5.14E+114
57	5.83E+66	43	9.96E+47	5.81E+114
58	3.59E+67	42	1.77E+47	6.35E+114
59	2.18E+68	41	3.08E+46	6.72E+114
60	1.30E+69	40	5.27E+45	6.87E+114
61	7.69E+69	39	8.82E+44	6.78E+114
62	4.48E+70	38	1.44E+44	6.47E+114
63	2.57E+71	37	2.32E+43	5.96E+114
93	8.88E+91	7	2.82E+12	2.50E+104
94	3.71E+92	6	9.57E+10	3.56E+103
95	1.54E+93	5	2.80E+09	4.32E+102
96	6.34E+93	4	6.87E+07	4.35E+101
97	2.59E+94	3	1.35E+06	3.50E+100
98	1.05E+95	2	2.01E+04	2.11E+99
99	4.21E+95	1	2.00E+02	8.43E+97
100	1.68E+96	0	1.00E+00	1.68E+96

↳ 101 macrostates

prob. ← ~7%



$\Omega_{max} \Rightarrow q_A = 60$

20 macrostates where most probable to find system

$N_A = 300$; $N_B = 200$; $q = 100$

$q_A = 10$ prob $\sim 10^{-26}$

Large Numbers

As size of systems increases, need to discuss differences between

- Small numbers: 10
- Large numbers: 10^{23} ← $10^{23} + 23 = 10^{23}$
- Very large numbers: $10^{10^{23}}$ ← $10^{10^{23}} \times 10^{23} = 10^{10^{23}}$

When making approximations need to keep track for future operations:

→ take differences later of large numbers

→ or divide by very large numbers.

Large Numbers

Dealing with factorials of large and very large numbers

- Requires approximation: Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$ → more exact approx. form

$$\ln N! \approx N \ln N - N$$

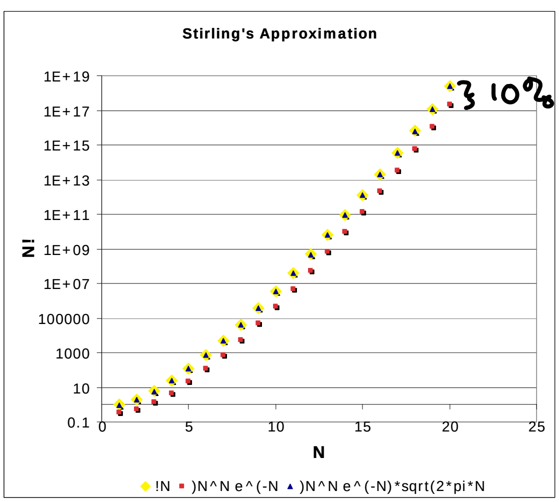
$N! \Rightarrow N^N$

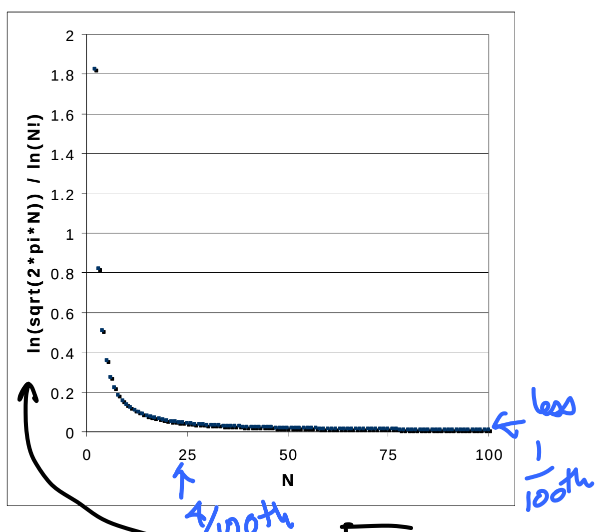
$N! \approx \left(\frac{N}{e}\right)^N$

$= N^N e^{-N} \rightarrow \ln N! \approx N \ln N - N$

Sterling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \qquad \ln N! \approx N \ln N - N$$





$$\frac{\ln \sqrt{2\pi N}}{\ln N!}$$

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

For a Large Einstein Solid

- Large N and q, where $q >> N$

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \approx \frac{(q+N)!}{q!\,N!}$$

because q & N large

$$\ln\Omega = (q+N)\ln(q+N) - \cancel{(q+N)} - q\ln q + \cancel{q} - N\ln N \cancel{+N}$$
$$= (q+N)\underbrace{\ln(q+N)} - q\ln q - N\ln N$$

$$\ln(q+N) = \ln\left[q\left(1+\frac{N}{q}\right)\right]$$
$$= \ln q + \underbrace{\ln\left(1+\frac{N}{q}\right)}$$

using Taylor expansion for $\ln(1+x)$ where $x \ll 1$

$$\ln\left(1+\frac{N}{q}\right) \approx \frac{N}{q} \qquad q >> N$$

$$\ln(q+N) \approx \ln q + \frac{N}{q}$$

$$\therefore \ln\Omega = (q+N)\left[\ln q + \frac{N}{q}\right] - q\ln q - N\ln N$$
$$= N\ln\left(\frac{q}{N}\right) + N\left(1+\underbrace{\frac{N}{q}}\right)$$

small compared to 1

$$= N\ln\left(\frac{q}{N}\right) + N$$

exponentiate

$$\Omega = \left(\frac{q}{N}\right)^N (e)^N = \left(\frac{eq}{N}\right)^N$$

where $q >> N$

N & q are large

Ω very large

Sharpness of the Multiplicity Function

- As we increased the number of oscillators, the width of the multiplicity function narrowed significantly
  - Started with 3 oscillators then few hundred
  - Now, moving from small to "large" numbers
  - Determining width of multiplicity function

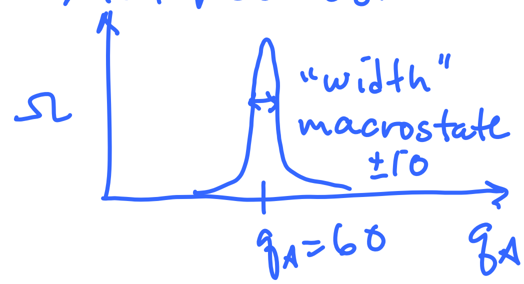
$N_A = N_B = 3$; $q = 6$ → 7 macrostates

most probable state ~22%

$N_A = 300$; $N_B = 200$; $q = 100$ → 101 macrostates

most probable state ~7%

least 10^{-20}



Sharpness of the Multiplicity Function

- Consider two Einstein solids, where $N_A = N_B = N$

$$\Omega_{total} = \Omega_A \Omega_B = \left(\frac{e\, q_A}{N}\right)^N \left(\frac{e\, q_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} \left(q_A\, q_B\right)^N$$

q_A in solid A

$q = q_A + q_B$

at maximum multiplicity $q_A = \frac{q}{2}$

→ small distance from $\frac{q}{2}$ → x

$$q_A = \frac{q}{2} + x \;;\; q_B = \frac{q}{2} - x$$

$$\Omega_{total} = \left(\frac{e}{N}\right)^{2N} \underbrace{\left(\left(\frac{q}{2}\right)^2 - x^2\right)^N}$$

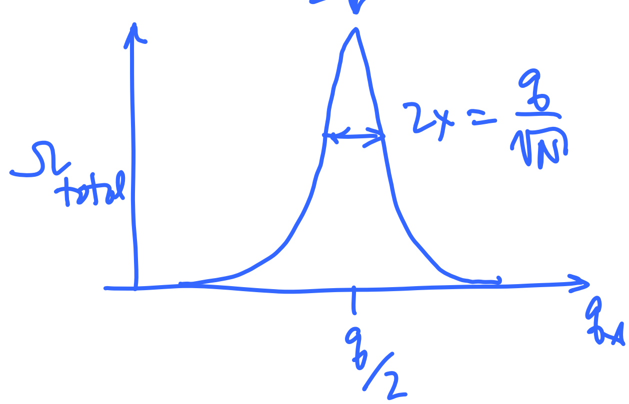
$$\ln\left[\left(\tfrac{q}{2}\right)^2 - x^2\right]^N = N\ln\left[\left(\tfrac{q}{2}\right)^2 - x^2\right]$$
$$= N\ln\left[\left(\tfrac{q}{2}\right)^2\left(1-\left(\tfrac{2x}{q}\right)^2\right)\right]$$
$$= N\ln\left(\tfrac{q}{2}\right)^2 + N\underbrace{\ln\left(1-\left(\tfrac{2x}{q}\right)^2\right)}_{\approx -\left(\frac{2x}{q}\right)^2}$$
$$\approx N\left[\ln\left(\tfrac{q}{2}\right)^2 - \left(\tfrac{2x}{q}\right)^2\right]$$
$$\left[\left(\tfrac{q}{2}\right)^2 - x^2\right] \approx \left(\tfrac{q}{2}\right)^{2N} e^{-(2x/q)^2 N}$$
$$\Omega = \left(\frac{e}{N}\right)^{2N}\left(\frac{q}{2}\right)^{2N} e^{-(2x/q)^2 N}$$

Gaussian Distribution

from derivation on last page:

$$\Omega = \Omega_{max}\, e^{-N(2x/q)^2}$$

$x = 0 \rightarrow$ peak function at $q/2$, Ω_{max}



width when Ω is $\frac{1}{e}$ of Ω_{max}

$$1 = N(2x/q)^2$$
$$x = \frac{q}{2\sqrt{N}}$$