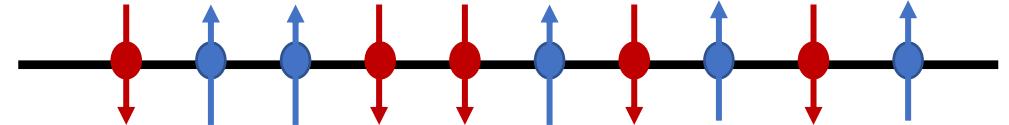


# Lecture 5

Large multiplicity limit

03.09.2018

# Two-state paramagnet model



- A system of  $N$  *independent, localised* particles with spin  $s = \pm 1$  at finite temperature
- At zero applied magnetic field, each spin can flip due to thermal vibrations with an equal probability
- Number of microstates with  $N_\uparrow$  up-spins out of  $N$  spins (multiplicity of that macrostate)

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

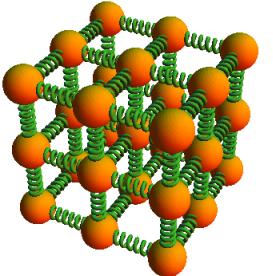
- Total number of microstates

$$\sum_{N_\uparrow=0}^N \Omega(N_\uparrow) = \sum_{n=0}^N \frac{N!}{N_\uparrow! (N - N_\uparrow)!} = 2^N$$

- Probability of a **macrostate** with  $N_\uparrow$  spins up

$$P(N_\uparrow) = 2^{-N} \Omega(N, N_\uparrow)$$

# Einstein crystal

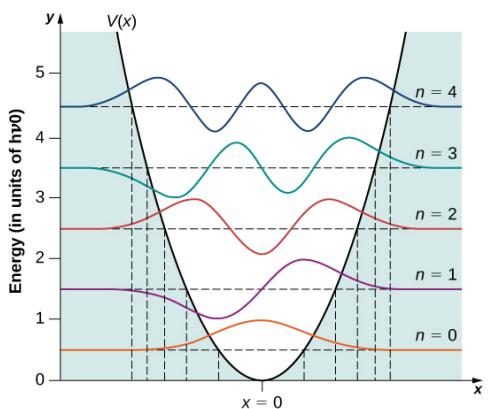


- Collection of independent and identical quantum harmonic oscillators
- Each quantum oscillator has a discrete spectrum of energy levels,  $n = 0, 1, 2 \dots$

$$\epsilon_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

- Energy of  $N$  independent oscillators

$$U_N = \sum_{i=1}^N \epsilon_{n_i} = \sum_{i=1}^N n_i \hbar\omega + \frac{N}{2} \hbar\omega$$



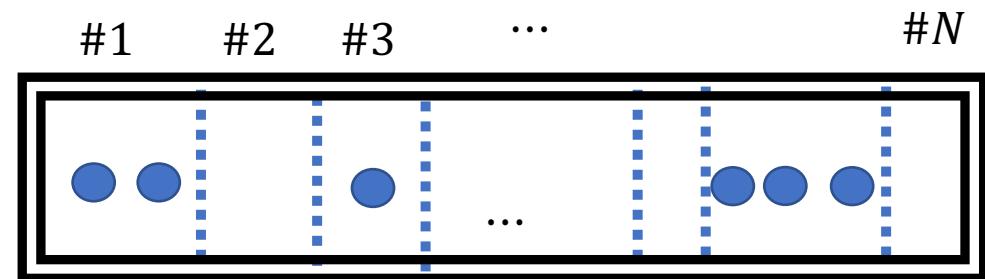
**Energy units for  $N$  quantum harmonic oscillators at frequency  $\omega$**

$$q = \frac{U_N - \frac{N}{2} \hbar\omega}{\hbar\omega} = \sum_{i=1}^N n_i$$

Multiplicity  $\Omega(q, N)$  of a macrostate with  $N$  oscillators and  $q$  units of energy distributed between them

$q$  energy units  $\sim q$  identical balls

$N$  oscillators  $\sim N$  identical boxes



Number of ways of distributing  $q$  balls between  $N$  boxes is the same as the number of combinations with  $q$  balls and  $(N-1)$ -walls between the lined up boxes

**Number of ways of combining  $(N-1)$ -walls and  $q$  balls**

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

# Stirling's approximation for $N!$ when $N \gg 1$

Let's look at

$$\ln N! = \ln[N \cdot (N - 1) \cdot (N - 2) \cdots 2 \cdot 1]$$

$$\ln N! = \sum_{n=1}^N \ln n$$

When  $N \rightarrow \infty$ , we can replace the sum by an integral

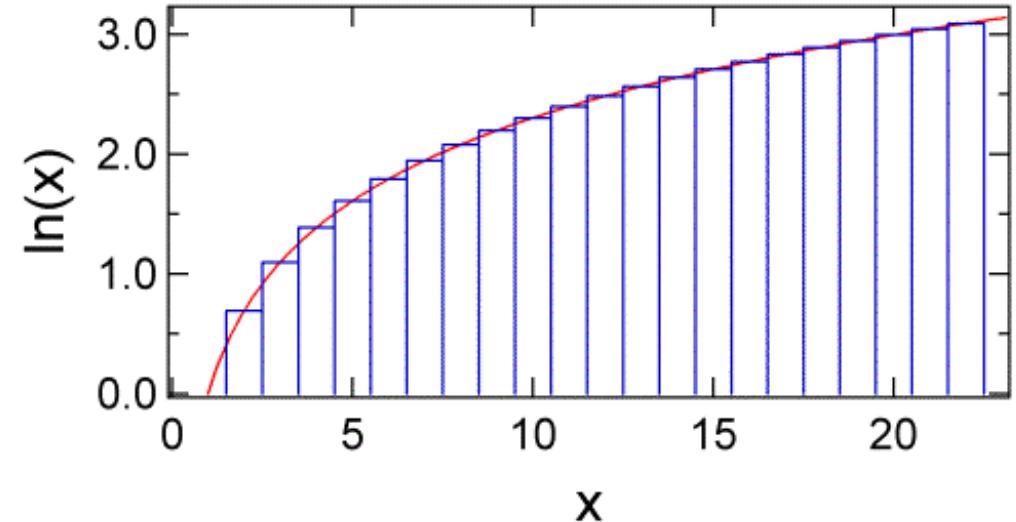
$$\ln N! = \sum_{n=1}^N \ln n \approx \int_0^N dn \ln n$$

$$\int_0^N dn \frac{dn}{dn} \ln n = n \ln n \Big|_0^N - \int_0^N dn \ n \frac{d \ln n}{dn}$$

$$= N \ln N - N$$

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

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



# Stirling's approximation for $N!$ when $N \gg 1$

Improved approximation from the Gamma function

$$n! = \Gamma(n+1) = \int_0^\infty dx \ x^n e^{-x}$$

$$x^n e^{-x} = e^{n \ln x - x}$$

- $n \ln x - x =_{(y=x-n)} n \ln(y+n) - y - n$   
 $= n \ln n - n + n \ln\left(1 + \frac{y}{n}\right) - y$
- $\ln\left(1 + \frac{y}{n}\right) \approx \frac{y}{n} - \frac{1}{2}\left(\frac{y}{n}\right)^2$

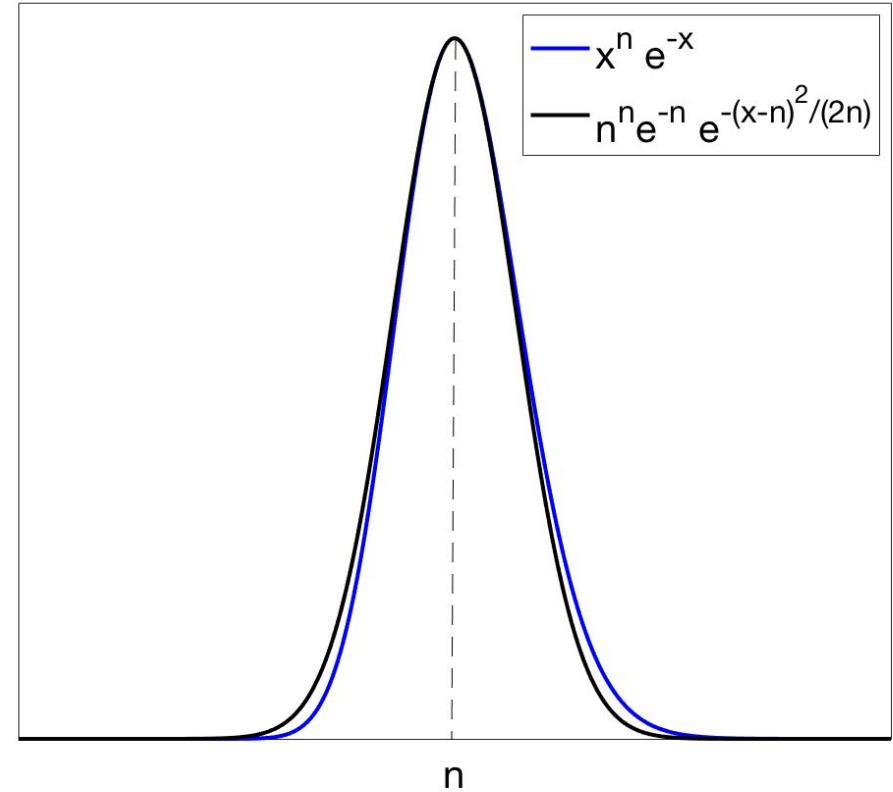
$$n \ln x - x \approx n \ln n - n + y - \frac{y^2}{2n} - y = n \ln n - n - \frac{y^2}{2n}$$

$$x^n e^{-x} \approx e^{n \ln n - n - \frac{y^2}{2n}} = n^n e^{-n} e^{-\frac{y^2}{2n}} = n^n e^{-n} e^{-\frac{(x-n)^2}{2n}}$$

$$n! \approx n^n e^{-n} \int_0^\infty dx e^{-\frac{(x-n)^2}{2n}} \approx n^n e^{-n} \int_{-\infty}^\infty dx e^{-\frac{(x-n)^2}{2n}} = n^n e^{-n} \sqrt{2\pi n}$$

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

$$\ln N! \approx N \ln N - N + \ln(2\pi N) \approx N \ln N - N, \text{ since } N \gg \ln N \text{ for } N \rightarrow \infty$$



# Large N Paramagnet

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

With

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

$$Find \Omega_{\max}: \quad N_\uparrow = \frac{N}{2}, \quad N_\downarrow = \frac{N}{2}$$

$$\Omega_{\max} \approx \frac{N^N e^{-N} \sqrt{2\pi N}}{\left( \left(\frac{N}{2}\right)^{\frac{N}{2}} e^{-\frac{N}{2}} \sqrt{2\pi \frac{N}{2}} \right)^2}$$

$$\Omega_{\max} \approx \frac{N^N e^{-N} \sqrt{2\pi N}}{\left(\frac{N}{2}\right)^{\frac{N}{2}} e^{-\frac{N}{2}} \left(2\pi \frac{N}{2}\right)} \rightarrow \Omega_{\max} \approx 2^N \sqrt{\frac{2}{\pi N}}$$

# Large N Paramagnet

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

Find the multiplicity of a macrostate for large N using  $N! \approx N^N e^{-N}$

$$\ln \Omega = N \ln N - N - N_{\uparrow} \ln N_{\uparrow} + N_{\uparrow} - (N - N_{\uparrow}) \ln(N - N_{\uparrow}) + (N - N_{\uparrow})$$

$$\ln \Omega = N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln(N - N_{\uparrow})$$

*Boltzmann entropy*

$$S = k \ln \Omega$$

*For a paramagnet*

$$S = k [N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln(N - N_{\uparrow})]$$

# Large N Paramagnet

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

With

$$N! \approx N^N e^{-N}$$

Find the multiplicity of a macrostate around the one with maximum multiplicity

Small deviation away from the state with  $\Omega_{\max}$ :  $N_{\uparrow} = \frac{N}{2} + x, N_{\downarrow} = \frac{N}{2} - x$ , for  $x \ll N$

$$\ln \Omega = N \ln N - \left( \frac{N}{2} + x \right) \ln \left( \frac{N}{2} + x \right) - \left( \frac{N}{2} - x \right) \ln \left( \frac{N}{2} - x \right)$$

$$\ln \Omega = N \ln N - \left( \frac{N}{2} + x \right) \ln \left( \frac{N}{2} \right) - \left( \frac{N}{2} + x \right) \ln \left( 1 + \frac{2x}{N} \right) - \left( \frac{N}{2} - x \right) \ln \left( \frac{N}{2} \right) - \left( \frac{N}{2} - x \right) \ln \left( 1 - \frac{2x}{N} \right)$$

use  $\ln(1 + y) \approx y - \frac{1}{2}y^2$

$$\ln \Omega \approx N \ln N - N \ln \left( \frac{N}{2} \right) - \left( \frac{N}{2} + x \right) \left( \frac{2x}{N} - \frac{1}{2} \left( \frac{2x}{N} \right)^2 \right) - \left( \frac{N}{2} - x \right) \left( -\frac{2x}{N} - \frac{1}{2} \left( \frac{2x}{N} \right)^2 \right)$$

Keep the lowest order terms on  $x$

$$\begin{aligned} \ln \Omega &\approx N \ln 2 + \frac{N}{2} \left( \frac{2x}{N} \right)^2 - \frac{2x^2}{N} - \frac{2x^2}{N} = N \ln 2 - \frac{2x^2}{N} \rightarrow \Omega \approx 2^N e^{-\frac{2x^2}{N}} \\ &\quad - \frac{\left( N_{\uparrow} - \frac{N}{2} \right)^2}{\frac{N}{2}} \\ \Omega(N, N_{\uparrow}) &\approx 2^N e^{-\frac{\left( N_{\uparrow} - \frac{N}{2} \right)^2}{\frac{N}{2}}} \end{aligned}$$

# Large N Paramagnet

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

With

$$N! \approx N^N e^{-N}$$

Multiplicity of a macrostate around the one with maximum multiplicity

Small deviation away from the state with  $\Omega_{\max}$ :  $N_{\uparrow} = \frac{N}{2} + x, N_{\downarrow} = \frac{N}{2} - x$ , for  $x \ll N$

$$\Omega(N, x) \approx 2^N e^{-\frac{2x^2}{N}} \rightarrow \text{the probability is } P(x) \sim e^{-\frac{2x^2}{N}}$$

Using the normalization condition

$$\int_{-\infty}^{+\infty} dx P(x) = \int_{-\infty}^{+\infty} dx e^{-\frac{2x^2}{N}} = \sqrt{\frac{N\pi}{2}}$$

$$\Omega(N, N_{\uparrow}) \approx 2^N e^{-\frac{(N_{\uparrow}-\frac{N}{2})^2}{\frac{N}{2}}} \sqrt{\frac{2}{N\pi}} \rightarrow P(N, N_{\uparrow}) \approx e^{-\frac{(N_{\uparrow}-\frac{N}{2})^2}{\frac{N}{2}}} \sqrt{\frac{2}{N\pi}}$$

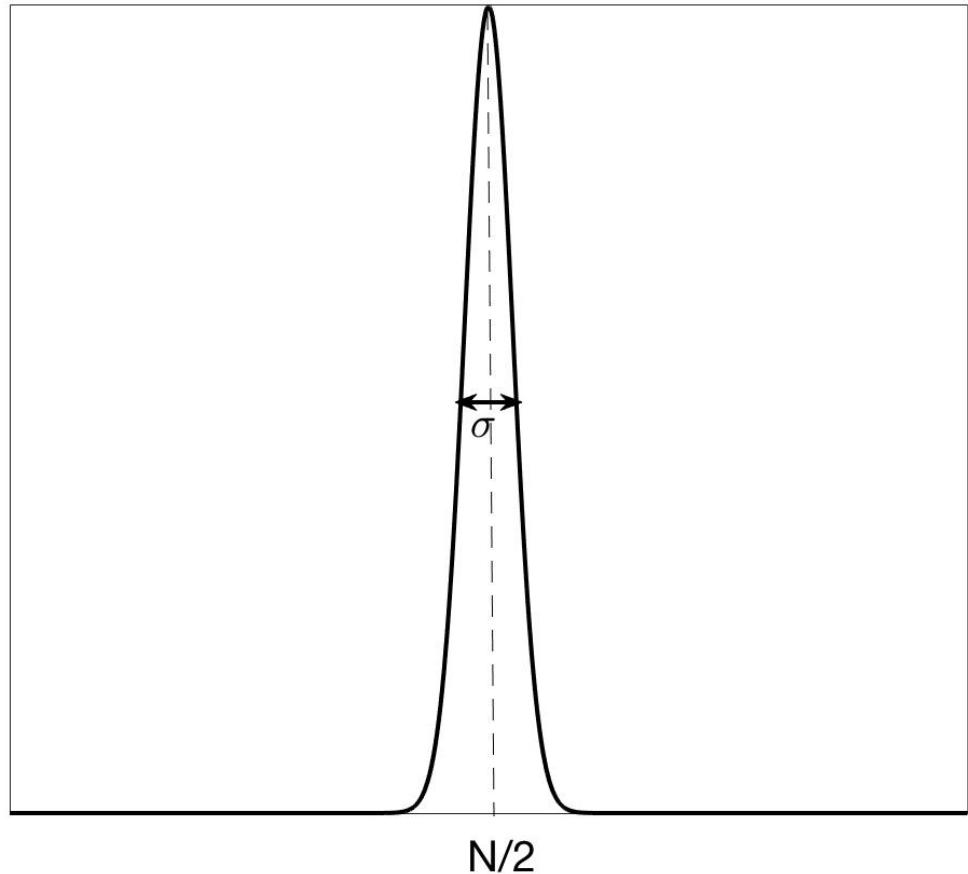
# Large N Paramagnet

The probability around the peak  $x = N_{\uparrow} - \frac{N}{2}$

$$P(x) \approx \sqrt{\frac{2}{N\pi}} e^{-\frac{2x^2}{N}}$$

$P(x)$  falls off to  $1/e$  of its peak when  $2x^2 = N \rightarrow x = \sqrt{\frac{N}{2}}$

Full width of  $P(x)$  around the peak  $\sigma = 2\sqrt{N/2} = \sqrt{2N}$



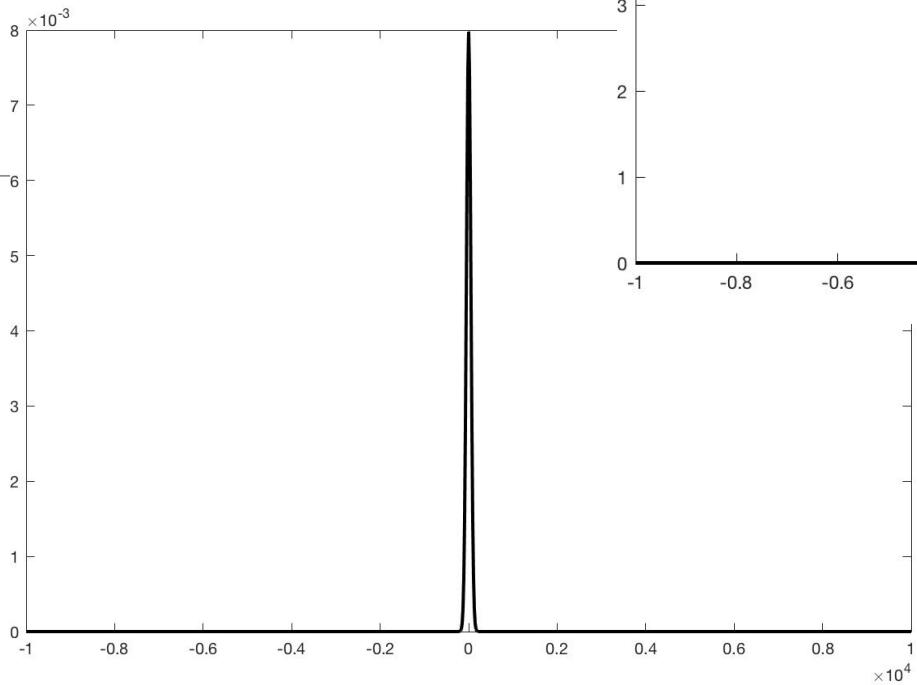
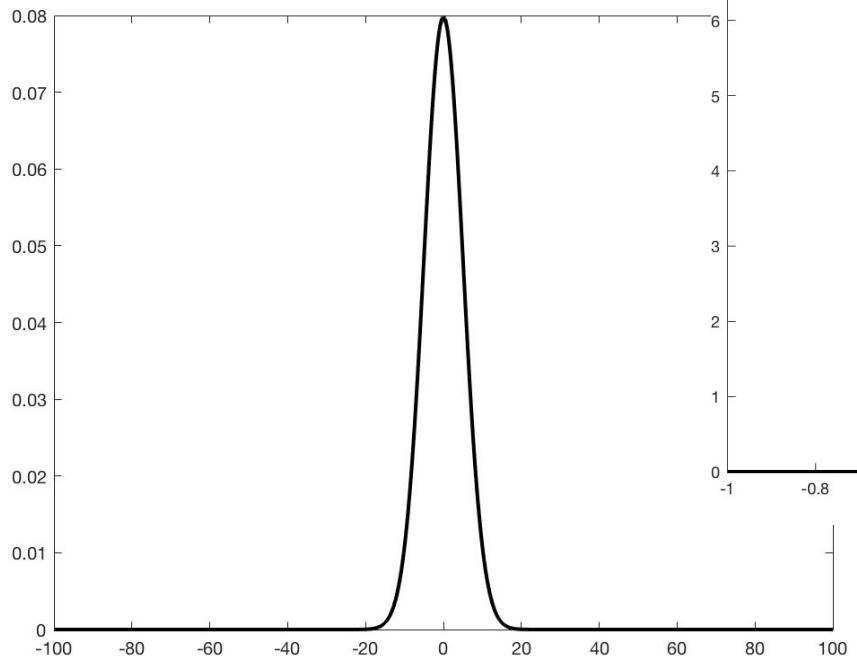
# Large N Paramagnet

The probability around the peak  $x = N_{\uparrow} - \frac{N}{2}$

$$P(x) \approx \sqrt{\frac{2}{N\pi}} e^{-\frac{2x^2}{N}}$$

Full width of  $P(x)$ :  $\sigma = 2\sqrt{N/2} = \sqrt{2N}$

Fluctuations  $\frac{\sigma}{\langle N_{\uparrow} \rangle} = \frac{\sqrt{2N}}{N/2} \approx \frac{1}{\sqrt{N}} \rightarrow 0$



# Einstein crystal: «low T» limit

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

Assume  $q \ll N$  and  $\ln n! = n \ln n - n$ :

$$\ln \Omega = (N + q) \ln(N + q) - (N + q) - q \ln q + q - N \ln N + N$$

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

$$\ln \Omega = q \ln \frac{N}{q} + (N + q) \ln \left(1 + \frac{q}{N}\right)$$

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

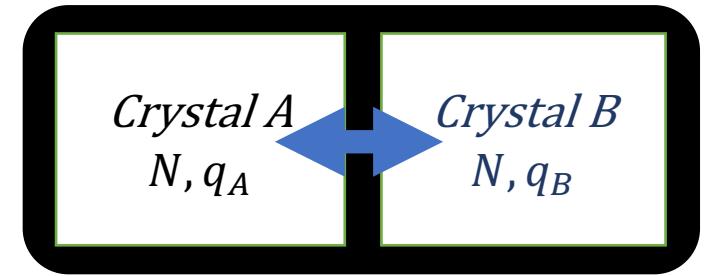
$$\ln \Omega \approx q \ln \frac{N}{q} + q + \frac{q^2}{N} \approx \ln \left(\frac{Ne}{q}\right)^q$$

$$\Omega_{low\,T}(q, N) \approx \left(\frac{Ne}{q}\right)^q, \quad \text{for } q \ll N$$

Similarly,

$$\Omega_{high\,T}(q, N) \approx \left(\frac{qe}{N}\right)^N, \quad \text{for } N \ll q$$

# Two large Einstein crystals: «high T» limit



$$\Omega_t = \Omega_A \cdot \Omega_B \approx \frac{(N_A + q_A)!}{q_A! N_A!} \cdot \frac{(N_B + q_B)!}{q_B! N_B!}, \quad \text{for } N_A, q_A, N_B, q_B \gg 1$$

Assume  $q \gg N$  and  $N_A = N_B = N, q_A + q_B = q$ :

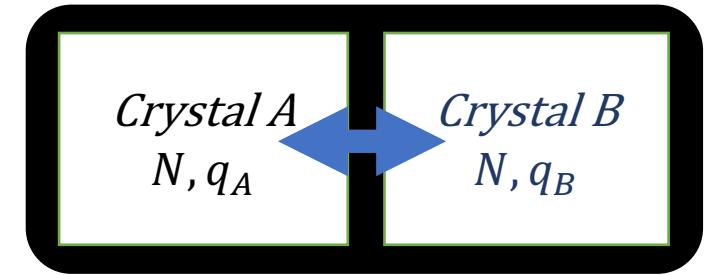
$$\Omega_t \approx \left(\frac{q_A e}{N}\right)^N \left(\frac{q_B e}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N$$

$\Omega_t$  is maximum when  $q_A = q_B = \frac{q}{2}$

$$\Omega_t^{max} = \left(\frac{eq}{2N}\right)^{2N}$$

# Two large Einstein crystals: «high T» limit

$$\Omega_t = \Omega_A \cdot \Omega_B \approx \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N, \quad \text{for } q \gg N \quad N_A = N_B = N, q_A + q_B = q$$



Expand around the peak:  $q_A = \frac{q}{2} + x, \quad q_B = \frac{q}{2} - x$

$$\Omega_t \approx \left(\frac{e}{N}\right)^{2N} \left[ \left(\frac{q}{2}\right)^2 - x^2 \right]^N$$

$$\ln \Omega_t \approx 2N \ln \frac{e}{N} + N \ln \left[ \left(\frac{q}{2}\right)^2 - x^2 \right] = 2N \ln \frac{e}{N} + 2N \ln \frac{q}{2} + N \ln \left[ 1 - \left(\frac{2x}{q}\right)^2 \right]$$

$$\ln \Omega_t \approx \ln \left(\frac{eq}{2N}\right)^{2N} - N \left(\frac{2x}{q}\right)^2 = \ln \Omega_t^{max} - N \left(\frac{2x}{q}\right)^2$$

$$\Omega_t = \Omega_t^{max} \cdot e^{-N(2x/q)^2}$$

$$\Omega_t(q_A) = \Omega_t^{max} \cdot e^{-\frac{4N}{q^2} \left(q_A - \frac{q}{2}\right)^2}, \quad \Omega_t^{max} = \left(\frac{eq}{2N}\right)^{2N}$$

# Two large Einstein crystals: «high T» limit

$$\Omega_t = \Omega_A \cdot \Omega_B \approx \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N,$$

for  $q \gg N$   $N_A = N_B = N, q_A + q_B = q$

Expand around the peak:  $q_A = \frac{q}{2} + x, q_B = \frac{q}{2} - x$

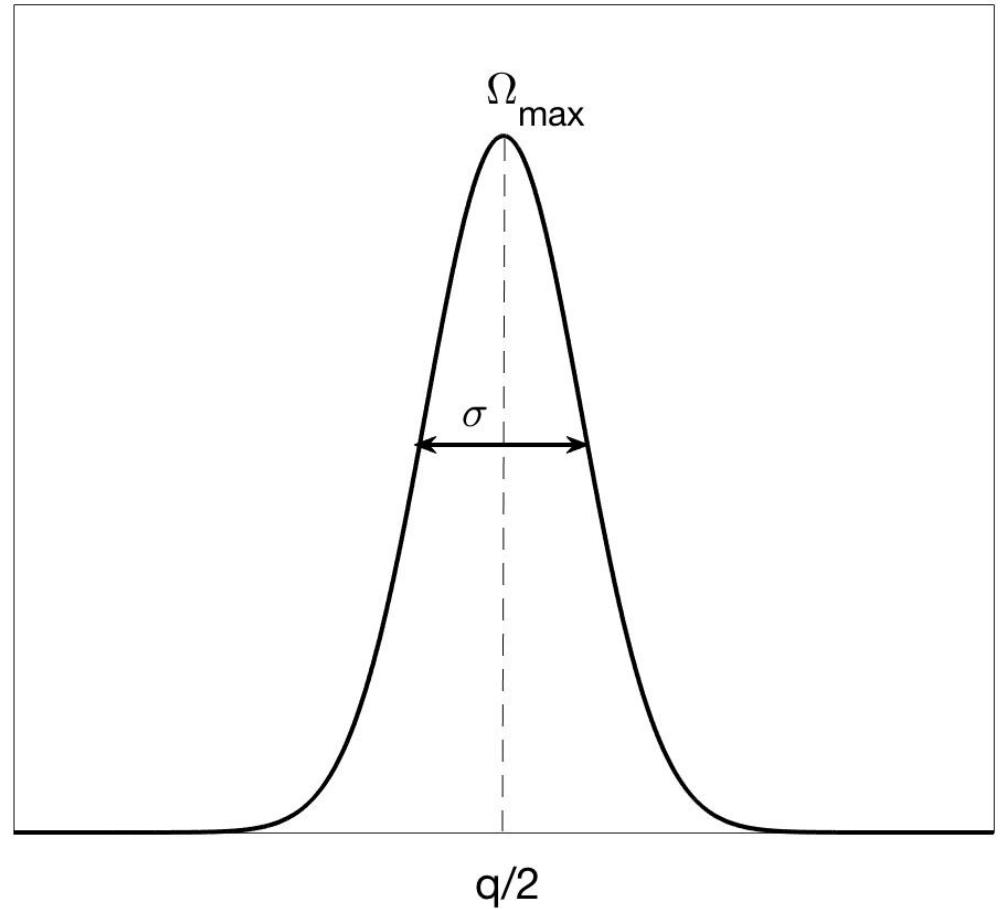
$$\Omega_t = \Omega_t^{\max} \cdot e^{-N\left(\frac{2x}{q}\right)^2}, \Omega_t^{\max} = \left(\frac{eq}{2N}\right)^{2N}$$

$\Omega_t$  falls off to  $1/e$  of its maximum when

$$N \left(\frac{2x}{q}\right)^2 = 1 \rightarrow x = \frac{q}{2\sqrt{N}} \rightarrow \sigma = \frac{q}{\sqrt{N}}$$

Fluctuations around the mean

$$\frac{\sigma}{\langle q \rangle} = \frac{q/\sqrt{N}}{q/2} \approx \frac{1}{\sqrt{N}} \rightarrow 0$$



# Two large Einstein crystals: «high T» limit

$$\Omega_t = \Omega_A \cdot \Omega_B \approx \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N,$$

for  $q \gg N$   $N_A = N_B = N, q_A + q_B = q$

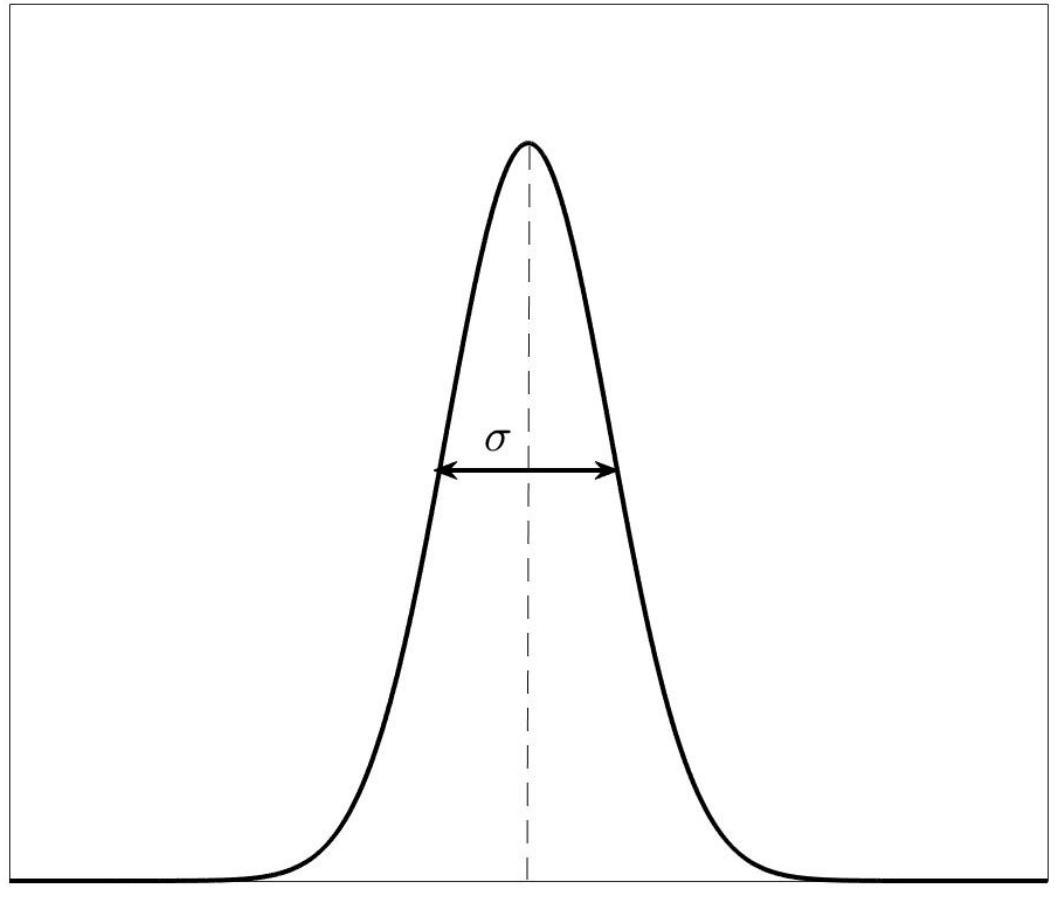
Expand around the peak:  $q_A = \frac{q}{2} + x, q_B = \frac{q}{2} - x$

$$\Omega_t = \Omega_t^{max} \cdot e^{-N\left(\frac{2x}{q}\right)^2}, \Omega_t^{max} = \left(\frac{eq}{2N}\right)^{2N}$$

$$\int_{+\infty}^{-\infty} dx e^{-\frac{4N}{q^2}x^2} = \frac{q}{2} \sqrt{\frac{\pi}{N}}$$

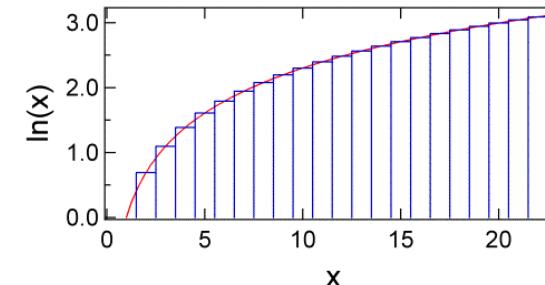
Probability of having  $q_A$  energy units

$$P(q_A) = \frac{2}{q} \sqrt{\frac{N}{\pi}} e^{-\frac{4N}{q^2}\left(q_A - \frac{q}{2}\right)^2}$$

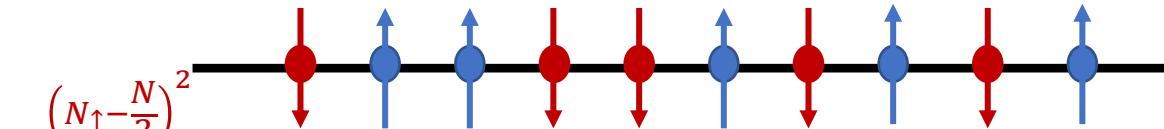


# Take home---

- Stirling approximation for large systems  $N! \approx N^N e^{-N} \sqrt{2\pi N}$ , for  $N \gg 1$



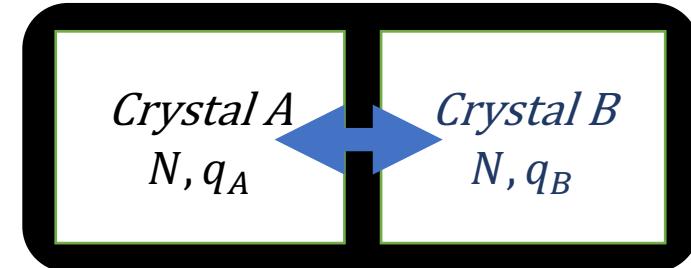
- Paramagnets: Multiplicity near its maximum



$$\Omega(N, N_\uparrow) \approx \Omega_{max} e^{-\frac{(N_\uparrow - \frac{N}{2})^2}{\frac{N}{2}}}$$

- Interacting Einstein crystals: Multiplicity near its maximum

$$\Omega_t(q_A) \approx \Omega_{t,max} e^{-\frac{4N}{q^2} \left( q_A - \frac{q}{2} \right)^2}$$



- In the thermodynamic limit  $N \rightarrow \infty$ , any random fluctuation away from the most likely states is extremely unlikely

