

Einstein Solids

Interacting Solids

Multiplicity of Solids

PHYS 4311: Thermodynamics & Statistical Mechanics

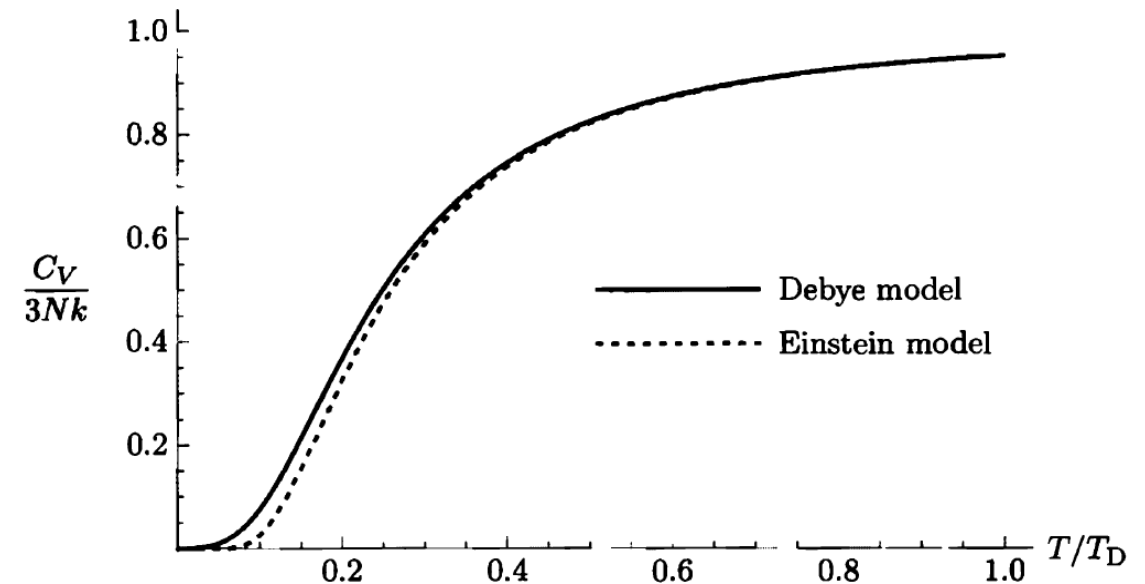
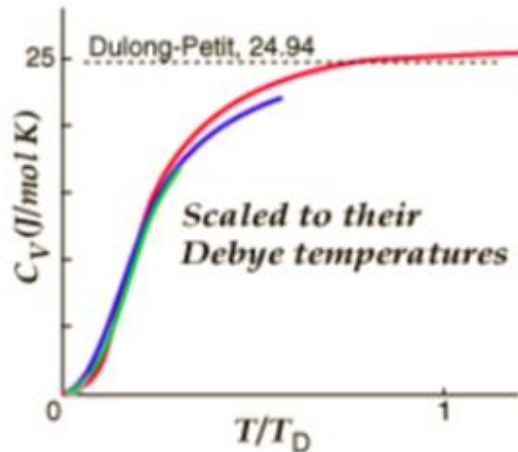
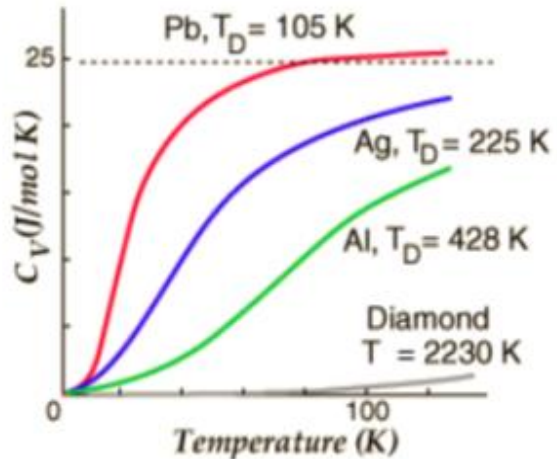
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Introduction

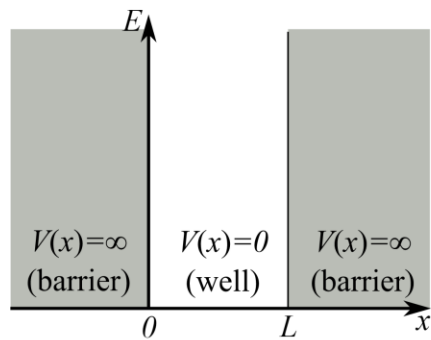
- Debye model (collective frequency motion)
- Dulong–Petit law (behavior at high temperatures) predicted by Debye model
 - Polyatomic molecules $3R$
- T^3 dependence predicted by Debye model, too.
- Einstein model not accurate at low temperatures

$$C_v = \frac{Nfk}{2} = \frac{3}{2}Nk = \frac{3}{2}nR$$



Debye Model: Particle in a Box

$$V(x) = \begin{cases} 0, & x_c - \frac{L}{2} < x < x_c + \frac{L}{2} \\ \infty, & \text{otherwise} \end{cases}$$



$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x) \Psi(x, t)$$



$$\Psi(x, t) = (A \sin kx + B \cos kx) e^{-i\omega t}$$

$$E = \frac{\hbar^2 k^2}{2m}$$



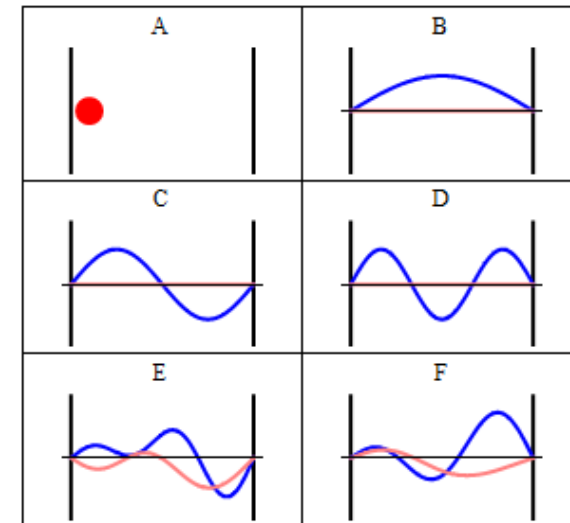
$$T \sim 0$$



$$T \gg 0$$



$$0 \ll T \ll \infty$$

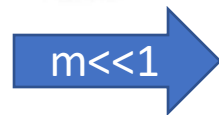


Quantum Harmonic Oscillator

Classical:

$$V = \frac{m\omega^2 x^2}{2}$$

$$T = \frac{1}{2}mv^2$$

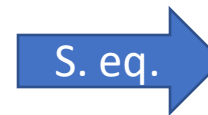


Quantum:

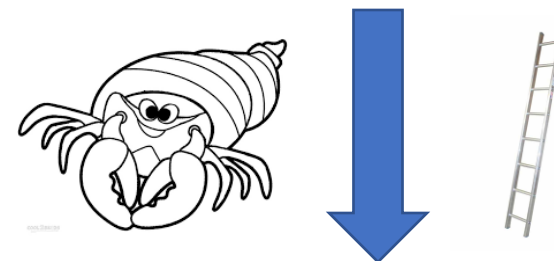
$$\mathcal{H} = \frac{m\omega^2 \hat{x}^2}{2} + \frac{\hat{p}^2}{2m}$$

where

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$



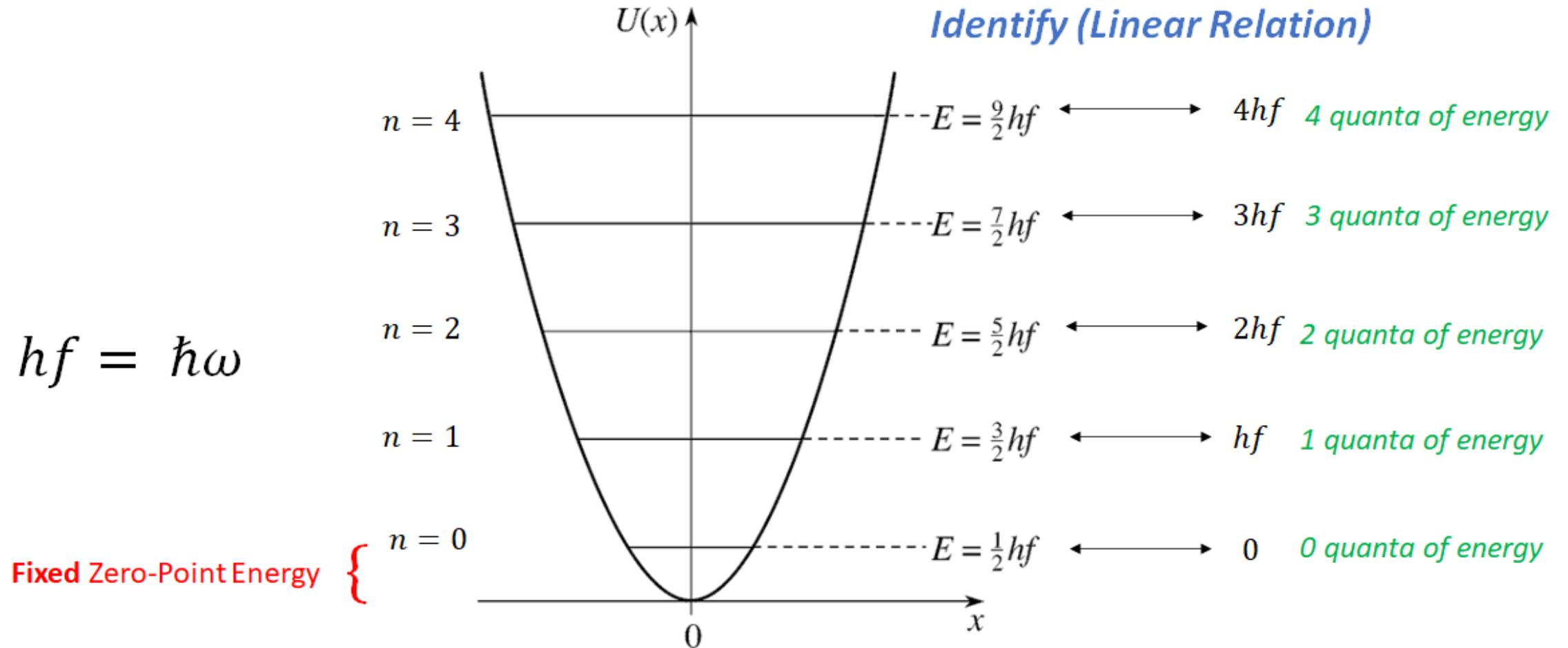
$$\mathcal{H} |\psi\rangle = E |\psi\rangle$$



Evenly-spaced energies

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

Discrete Evenly-Spaced Quanta of Energy

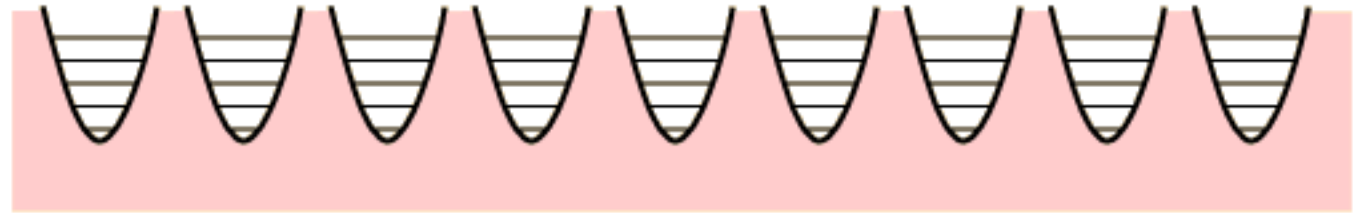
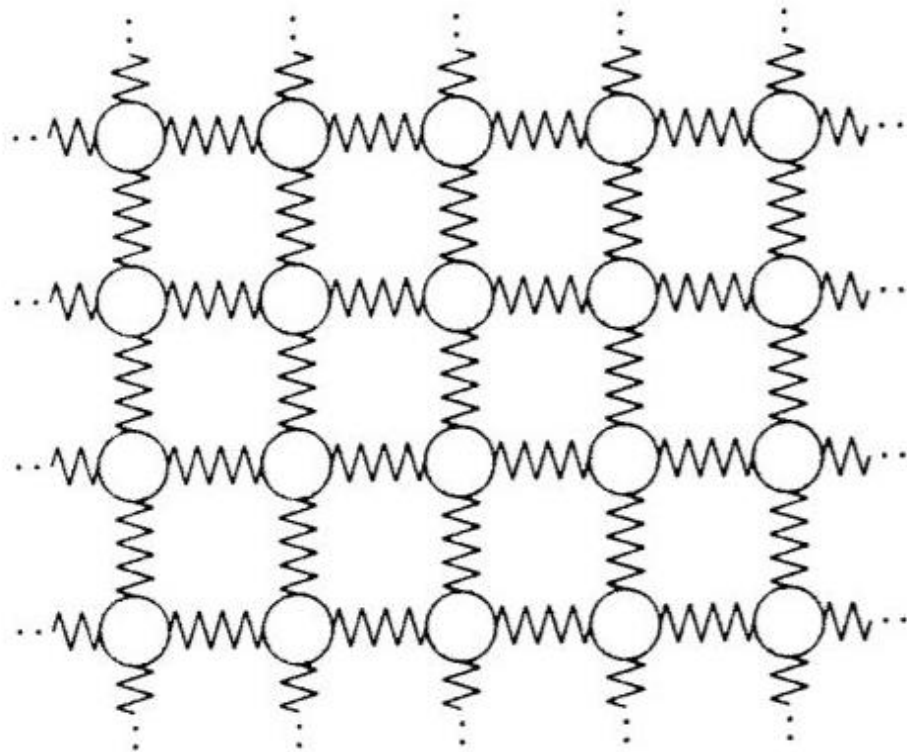


What about in 3D?

A single particle can "oscillate" each of the 3 cartesian directions: x , y , z .

If we were just to look at a single atom subject to the harmonic oscillator potential in each cartesian direction, its total energy is the **sum of energies** corresponding to oscillations in the x direction, y direction, and z direction.

Einstein Solid Model: Collection of Many Isotropic/Identical Harmonic Oscillators



If our solid consists of **N "oscillators"** then there are **$N/3$ atoms** (each atom is subject to the harmonic oscillator potential in the 3 independent cartesian directions).

What is the Multiplicity of an Einstein Solid with N oscillators?

Our system has exactly **N oscillators** and **q quanta of energy**. This is the macrostate.

There would be a **certain number of microstates** resulting from individual oscillators having different amounts of energy, but the whole solid having total q quanta of energy. Note that each microstate is *equally probable*!

What is the Multiplicity of an Einstein Solid with N oscillators?

Recall that energy comes in **discrete** quanta (units of hf) or "packets"! **Each** of the N oscillators will have an energy measure in **integer** units of hf !

Question: Let an Einstein Solid of **N oscillators** have a **fixed** value of exactly **q quanta** of energy. What is the ***multiplicity*** (*number of microstates*) of the solid?

What is the Multiplicity of an Einstein Solid with N oscillators?

Different distributions of energy among the oscillators correspond to different microstates. Therefore, the multiplicity is equal to the number of different combinations of quanta of energy in each oscillator.

With the total number of quanta q being known, the energy of the N th oscillator is already determined when we know the energies of the 1st through $(N - 1)$ th oscillators, so we only need to calculate the number of combinations of quanta up to the $(N - 1)$ th oscillator.

What is the Multiplicity of an Einstein Solid with N oscillators?

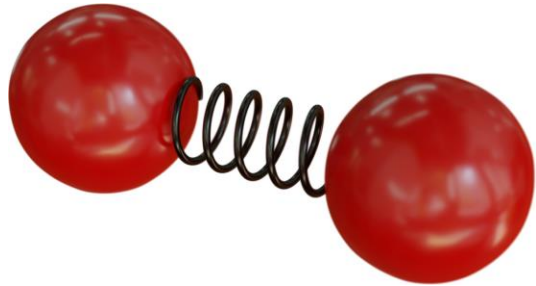
Now let us imagine that all the quanta are grouped together while some are "separated" from the rest to supply each oscillator, and that each separation takes place in a distinct location between quanta.

Now, calculate the number of possible sets of locations out of $q + N - 1$ positions where the $N - 1$ separations can occur to find the multiplicity, which comes out to be:

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

Example

Einstein solid with 6 oscillators (2 atoms) and 10 quanta of energy.



Oscillator Label	1	2	3	4	5	6	
	5	1	0	2	0	2	10 total
	2	3	4	1	0	0	10 total
	0	10	0	0	0	0	10 total
	⋮	⋮	⋮	⋮	⋮	⋮	
Quanta of Energy (measured in hf)	x_1	x_2	x_3	x_4	x_5	x_6	

Multiplicity Calculation

First **label** each oscillator with a unique number from 1, 2,... N .

The problem of finding the multiplicity of an Einstein Solid of N **oscillators** and q **quanta** of energy is **equivalent** to finding the number of **non-negative integer sequences** (x_1, x_2, \dots, x_N) such that $x_1 + x_2 + \dots + x_N = q$ each x_j represents the **number of quanta of energy that oscillator j has**.

Multiplicity Calculation

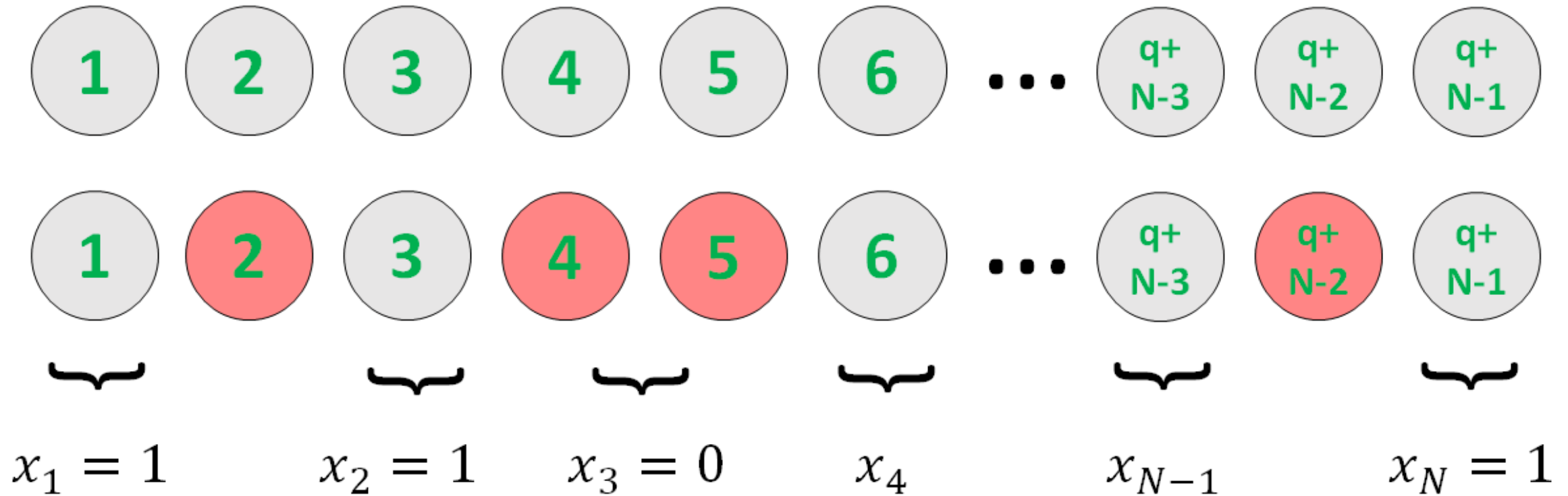
Consider a seemingly unrelated problem.

Consider $q + N - 1$ white balls. How many ways can we paint $N - 1$ of them red?

Just select $N-1$ of them in $\binom{q + N - 1}{N - 1}$ ways. Then paint them red.

Define x_j as the number of **unpainted balls** in between the $(j - 1)^{th}$ **red ball** and j^{th} **red ball**.

Paint $N - 1$ balls **red** in $\binom{q + N - 1}{N - 1}$ ways



$$x_1 + x_2 + \dots + x_N = (q + N - 1) - (N - 1) = q$$

Total

Painted

Unpainted

Multiplicity Calculation

Notice that each way of selecting $N - 1$ balls of $q + N - 1$ balls and painting them gives a unique sequence (x_1, x_2, \dots, x_N) where we have $x_1 + x_2 + \dots + x_N = q$.

The number of selecting $N - 1$ balls from $q + N - 1$ balls is equal to $\binom{q + N - 1}{N - 1}$. Therefore, the ***multiplicity of an Einstein Solid of N oscillators and q quanta of energy is exactly:***

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

Large vs Very Large Numbers

- "Small numbers": manipulated traditionally
 - Examples: 5, 25, 75
- "Large numbers": effectively unchanged by addition of small numbers
 - On the order of 10^{23}
 - Usually involve small numbers as exponents
- "Very large numbers": effectively unchanged by addition of or multiplication by small or large numbers
 - On the order of $10^{10^{23}}$
 - Involve large numbers as exponents

Stirling's Approximation

- Used to approximate $n!$ in cases where a given number n is too large to calculate it normally
- Derivation of a simple form of Stirling's approximation for large n :

$$\ln n! = \ln \prod_{k=1}^n k = \sum_{k=1}^n \ln k \approx \int_0^n \ln x \, dx = n \ln n - n \quad \xrightarrow{\text{exp}} \quad n! \approx n^n e^{-n}$$

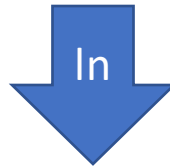
- More accurate form obtained by manipulating the gamma function:

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

Multiplicity of a Large Einstein Solid

- Stirling's approximation allows for the calculation of multiplicity for large values of N and q

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



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

Interacting Systems of Einstein Solids

Assume we place two Einstein Solids in thermal contact (allowed to exchange energy units). Both Einstein Solids have energy, U_a and U_b , and some number of oscillators, N_a and N_b . Assuming the Total Energy of the composite system remains constant then we can say:

$$N = N_a + N_b \text{ and } U = U_a + U_b \text{ } (q_{tot} = q_a + q_b)$$

Each oscillator can have a number 0 to q_{tot} energy units. And, as time passes, we can assume the two solids exchange energy into random microstates given the restriction that q_{tot} remains constant within the composite system.

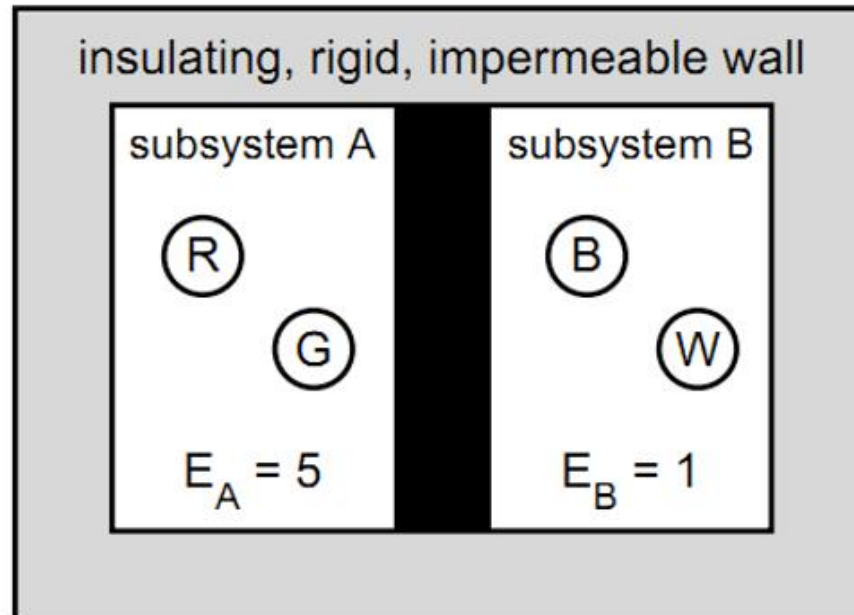
The total multiplicity of a composite system is just the product of the individual multiplicities of each member of the system:

$$\Omega_{\text{total}} = \Omega_A \Omega_B$$

Example 2: two interacting Einstein solid

Einstein solid with $N_A=2$, $q_A=5$, $\Omega_A=6$

Einstein solid with $N_B=2$, $q_B=1$, $\Omega_B=2$



Note: E_A and E_B used in the table is equivalent to our q_A and q_B from textbook.

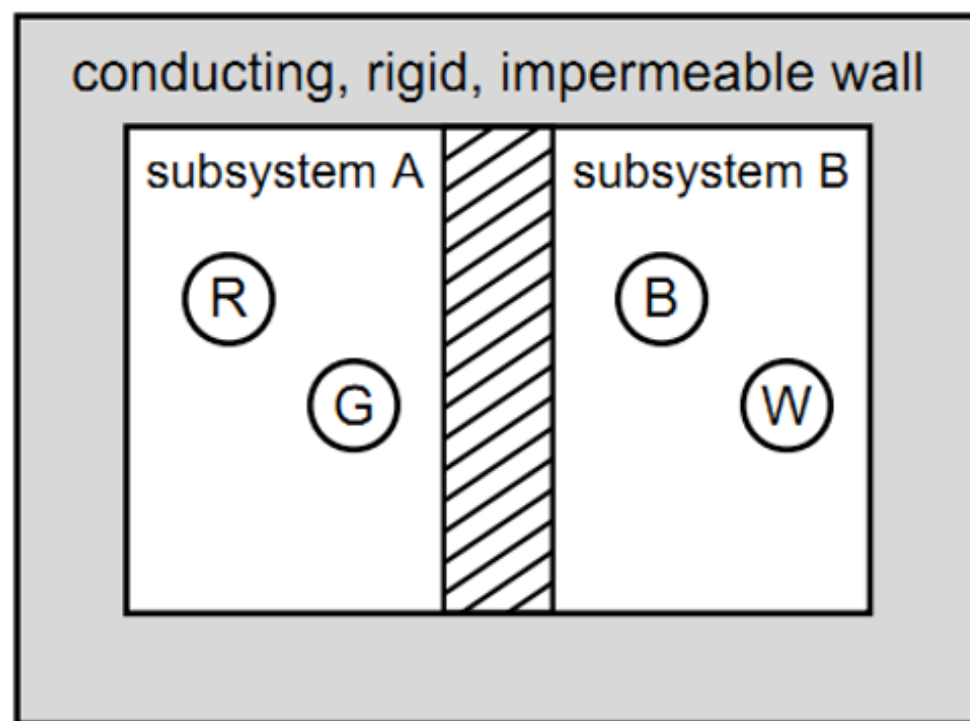
E_A	accessible microstates of A		E_B	accessible microstates of subsystem B	
5	5,0	0,5	1	1,0	0, 1
	4,1	1,4			
	3,2	2,3			

Table 4.2: The 12 equally probable microstates of the isolated composite system composed of subsystems A and B with $N_A = 2$, $E_A = 5$, $N_B = 2$, and $E_B = 1$. The 12 microstates consist of all combinations of the microstates of A and B.

$$q_{tot} = q_A + q_B = 6$$

$$\Omega_{tot} = \Omega_A \Omega_B = 12$$

Now, allow the barrier to accommodate energy transfer
(the two Einstein solids interacting with each other)



$$E_{tot}(q_{tot}) = q_A + q_B = 6$$

$$\Omega_{tot} = \sum_{E_{tot}=6} \Omega_A(q_A) \Omega_B(q_B) = 84$$

E_A	microstates	$\Omega_A(E_A)$	E_B	microstates	$\Omega_B(E_B)$	$\Omega_A\Omega_B$	$P_A(E_A)$
6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	0	0,0	1	7	7/84
5	5,0 0,5 4,1 1,4 3,2 2,3	6	1	1,0 0,1	2	12	12/84
4	4,0 0,4 3,1 1,3 2,2	5	2	2,0 0,2 1,1	3	15	15/84
3	3,0 0,3 2,1 1,2	4	3	3,0 0,3 2,1 1,2	4	16	16/84
2	2,0 0,2 1,1	3	4	4,0 0,4 3,1 1,3 2,2	5	15	15/84
1	1,0 0,1	2	5	5,0 0,5 4,1 1,4 3,2 2,3	6	12	12/84
0	0,0	1	6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	7	7/84

Table 4.3: The 84 equally probable microstates accessible to the isolated composite system composed of subsystems A and B after the removal of the internal constraint. The total energy is $E_{\text{tot}} = E_A + E_B = 6$ with $N_A = 2$ and $N_B = 2$. Also shown are the number of accessible microstates in each subsystem and the probability $P_A(E_A)$ that subsystem A has energy E_A .

Note: E_A and E_B used in the table is equivalent to our q_A and q_B from textbook.

Fundamental Assumption of Statistical Mechanics

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
				<hr/>
				462 = $\binom{6+6-1}{6}$

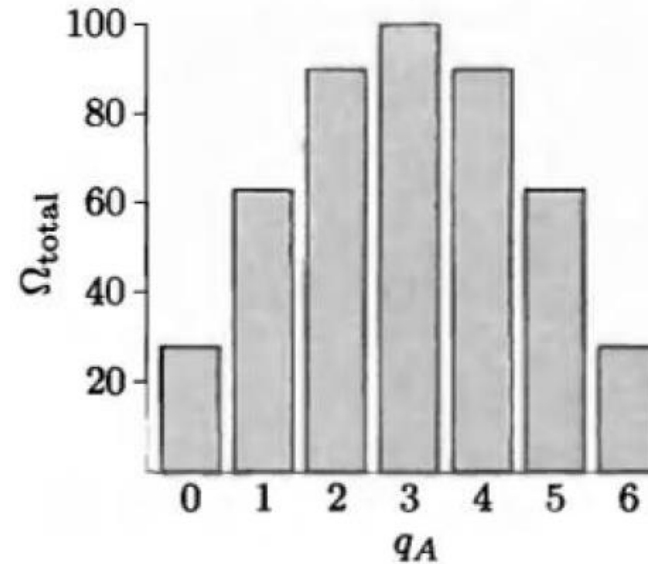


Figure 2.4. Macrostates and multiplicities of a system of two Einstein solids, each containing three oscillators, sharing a total of six units of energy.

In an isolated system in thermal equilibrium, all accessible microstates are equally probable

However, some macrostates are more probable than others

Example: Probability of finding system in 4th macrostate = $100/462$

Probability of finding system in 1st macrostate = $28/462$

Second Law of Thermodynamics

If you were to look at the system when most or all the energy is in solid B and waited, you will be very likely to find the energy flow from B to A

This tells us that heat is a probabilistic phenomenon that is not absolutely certain but nevertheless extremely likely to occur

This allows us to consider a new law of physics: **the second law of thermodynamics**

This law tells us that the spontaneous flow of energy stops when a system is at or near its most likely macrostate so in other words the total multiplicity of a system increases

q_A	Ω_A	q_B	Ω_B	Ω_{total}
0	1	100	2.8×10^{81}	2.8×10^{81}
1	300	99	9.3×10^{80}	2.8×10^{83}
2	45150	98	3.1×10^{80}	1.4×10^{85}
3	4545100	97	1.0×10^{80}	4.6×10^{86}
4	3.4×10^8	96	3.3×10^{79}	1.1×10^{88}
\vdots	\vdots	\vdots	\vdots	\vdots
59	2.2×10^{68}	41	3.1×10^{46}	6.8×10^{114}
60	1.3×10^{69}	40	5.3×10^{45}	6.9×10^{114}
61	7.7×10^{69}	39	8.8×10^{44}	6.8×10^{114}
\vdots	\vdots	\vdots	\vdots	\vdots
100	1.7×10^{96}	0	1	1.7×10^{96}
				9.3×10^{115}

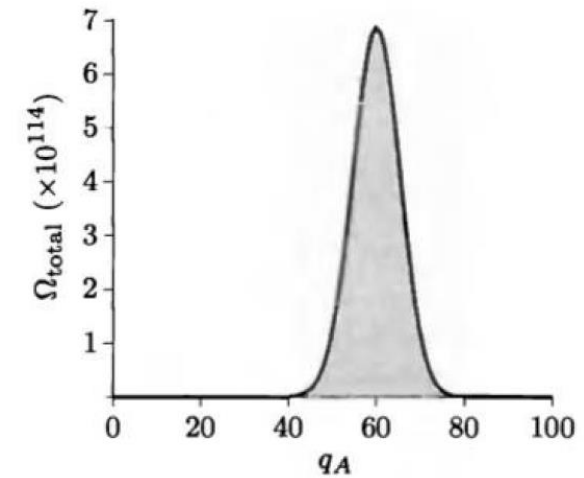


Figure 2.5. Macrostates and multiplicities of a system of two Einstein solids, with 300 and 200 oscillators respectively, sharing a total of 100 units of energy.

Example

(Schroeder Problem 2.6) Calculate the multiplicity of an Einstein solid with 30 oscillators and 30 units of energy ($q=30$). (Do not attempt to list all the microstates, just calculate the total number).

Solution:

$$\begin{aligned}\Omega(N,q) &= (N+q-1)!/q!(N-1)! = (30 + 30 - 1)!/30!(29!) \\ &= 5.9 \times 10^{16}\end{aligned}$$

Example

(Adapted from Schroeder 2.8e) Suppose we have a system of two interacting Einstein solids, A and B, with an equal number of oscillators. When will this system exhibit "irreversible", or directional, behavior?

Remember: The second law states that spontaneous flow will occur while the most likely macrostate has not been reached.

Solution:

If q_A is not equal to q_B , there will be directional flow of energy until the most likely state is achieved, at which point there will be random fluctuations about this equilibrium

Example

(Rutgers University Slides) Consider the system consisting of two Einstein solids ***P*** and ***Q*** in thermal equilibrium. Assume that we know the number of atoms in each solid and q . What do we know if we also know

- a) the quantum state of each atom in each solid?
- b) the total energy of each of the two solids?
- c) the total energy of the combined system?

Note: "Macrostate" here means the macrostate of the whole system. "Macropartition" means the component macrostates of each of the two Einstein solids.

	Macrostate	Microstate	Macropartition
a)			
b)			
c)			

Solution

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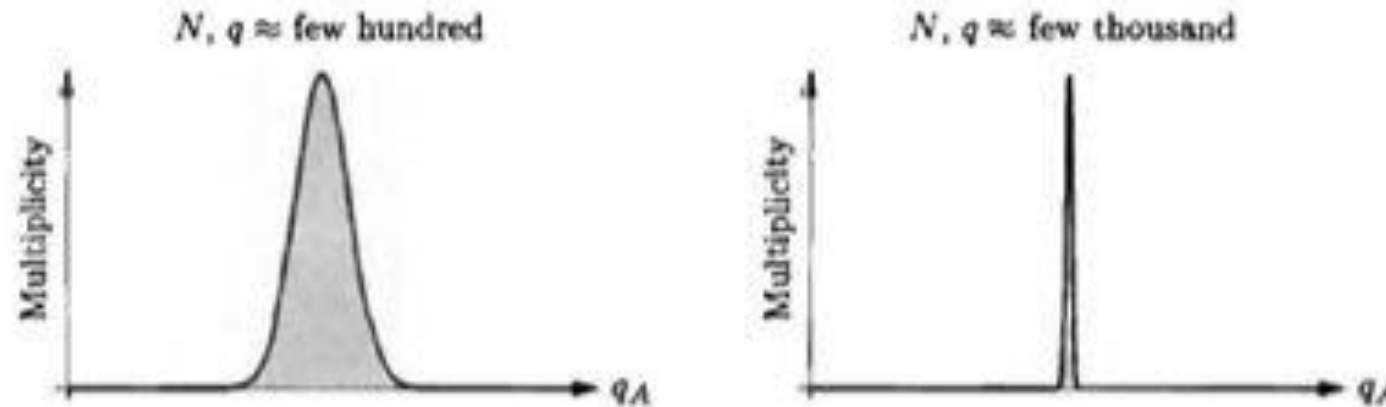
- a) the quantum state of each atom in each solid?
- b) the total energy of each of the two solids?
- c) the total energy of the combined system?

Note: "Macrostate" here means the macrostate of the whole system. "Macropartition" means the component macrostates of each of the two Einstein solids.

	Macrostate	Microstate	Macropartition
a)	X	X	X
b)	X		X
c)	X		X (fluctuations)

Sharpness of Multiplicity Functions

For Einstein solids with the number of oscillators/energy units in the hundreds, there is still reasonable range of fluctuation between different macrostates, compared to the total scale.



When the number of oscillators/energy units is in the thousands, this range is a considerably smaller portion of the full scale. In other words, a smaller fraction of the possible energy distributions are reasonably probable, with this fraction centered around an equal distribution of energy.

For a large Einstein solid, with N in the order of 10^{23} , how sharp will this peak become?

Multiplicity of a Large Einstein Solid (High Temperature)

First, we can further simplify the equation for multiplicity by assuming a high temperature ($q \gg N$):

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

Simplify the $\ln(q+N)$ term:

$$\begin{aligned} \ln(q + N) &= \ln \left[q \left(1 + \frac{N}{q} \right) \right] \\ &= \ln q + \ln \left(1 + \frac{N}{q} \right) \quad \text{(Use approximation from Taylor series of } \ln: \\ &\approx \ln q + \frac{N}{q}. \quad \ln(1+x) \approx x, \text{ for } |x| \ll 1) \end{aligned}$$

Plug back in and simplify:

$$\ln \Omega \approx N \ln \frac{q}{N} + N + \frac{N^2}{q}.$$

Ignore the last term, because $q \gg N$. Exponentiate to get the simplified multiplicity:

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

For two interacting Einstein solids, with a large N and q , and where $q \gg N$:

$$\Omega_{total} = \left(\frac{eq_A}{N} \right)^N \left(\frac{eq_B}{N} \right)^N = \left(\frac{e}{N} \right)^{2N} (q_A q_B)^N$$

The maximum multiplicity will be when the heat is equally distributed ($q_A = q_B = q/2$)

$$\Omega_{max} = \left(\frac{e}{N} \right)^{2N} \left(\frac{q}{2} \right)^{2N}$$

Sharpness of Multiplicity Functions

To see what the graph looks like near the peak, we can add a value x ($x \ll q$) and substitute into the multiplicity equation:

$$q_A = \frac{q}{2} + x, \quad q_B = \frac{q}{2} - x, \quad \longrightarrow \quad \Omega = \left(\frac{e}{N}\right)^{2N} \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N.$$

Use logarithms to simplify the 2nd factor 

$$\begin{aligned} \ln \left[\left(\frac{q}{2}\right)^2 - x^2 \right]^N &= N \ln \left[\left(\frac{q}{2}\right)^2 - x^2 \right] \\ &= N \ln \left[\left(\frac{q}{2}\right)^2 \left(1 - \left(\frac{2x}{q}\right)^2 \right) \right] \\ &= N \left[\ln \left(\frac{q}{2}\right)^2 + \ln \left(1 - \left(\frac{2x}{q}\right)^2 \right) \right] \\ &\approx N \left[\ln \left(\frac{q}{2}\right)^2 - \left(\frac{2x}{q}\right)^2 \right]. \end{aligned}$$

(Use approximation from Taylor series of \ln :
 $\ln(1+x) \approx x$, for $|x| \ll 1$)

(Exponentiate the result and substitute back
 into the multiplicity equation)

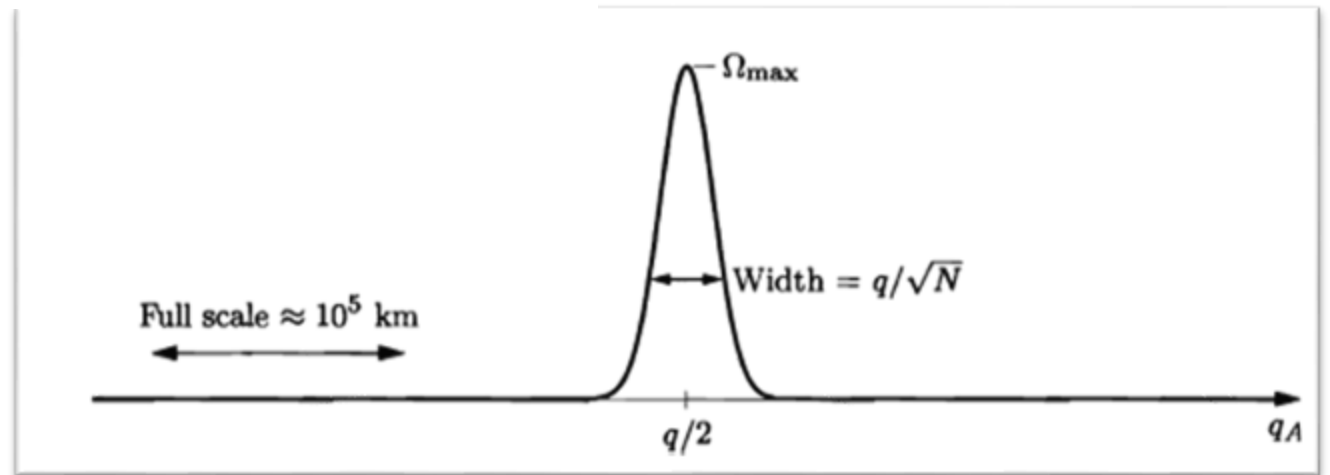
Sharpness of Multiplicity Functions

$$\Omega = \left(\frac{e}{N}\right)^{2N} e^{N \ln(q/2)^2} e^{-N(2x/q)^2} = \Omega_{\max} \cdot e^{-N(2x/q)^2}$$

This is a Gaussian function (bell curve), where the peak of Ω_{\max} occurs at $x=0$. To see how sharp this bell is, we can find where the multiplicity is $1/e$ of its max.

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

If $N = 10^{20}$, this occurs when x is roughly a ten-billionth of scale of the graph (which is from 0 to q). This means that any random fluctuations away from the most likely macrostate are essentially unmeasurable.



Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Let's use what we've learned about Einstein solids to calculate their heat capacity at constant volume.

From quantum mechanics...

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

a quantum of energy

$$\varepsilon \equiv \hbar\omega$$

Total energy

$$U \equiv \frac{N'\varepsilon}{2} + q\varepsilon$$

From geometric considerations...

$$N' = 3N$$

From statistical mechanics...

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

From Stirling's approximation...

$$\ln n! = n \ln n - n$$

Introducing the statistical mechanics definitions of entropy S and temperature T , we put everything together...

$$S/k = \ln \Omega = \ln \frac{(q + N' - 1)!}{q!(N' - 1)!} \longrightarrow S/k \approx (q + N') \ln(q + N') - N' \ln N' - q \ln q$$

$\Omega = \frac{(q + N' - 1)!}{q!(N' - 1)!}$
 $\ln n! = n \ln n - n$

$$\frac{1}{T} \stackrel{\text{Introducing temperature}}{=} \frac{\partial S}{\partial U} = \frac{\partial S}{\partial q} \frac{dq}{dU} = \frac{1}{\varepsilon} \frac{\partial S}{\partial q} = \frac{k}{\varepsilon} \ln(1 + N'/q)$$

$$U \stackrel{U = \frac{N'\varepsilon}{2} + q\varepsilon}{=} \frac{N'\varepsilon}{2} + \frac{N'\varepsilon}{e^{\varepsilon/kT} - 1}$$

$$C_V = \frac{\partial U}{\partial T} = \frac{N'\varepsilon^2}{kT^2} \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} - 1)^2} = 3Nk \left(\frac{\varepsilon}{kT} \right)^2 \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} - 1)^2} \longrightarrow \lim_{T \rightarrow \infty} C_V = 3Nk$$

Works Cited

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