Statistical Thermodynamics

(Lecture 11)

1st semester, 2021
Advanced Thermodynamics (M2794.007900)
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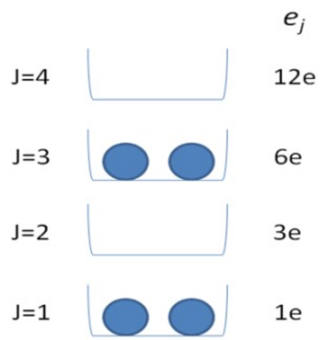
(*) Some materials in this lecture note are borrowed from the textbook of Ashley H. Carter.

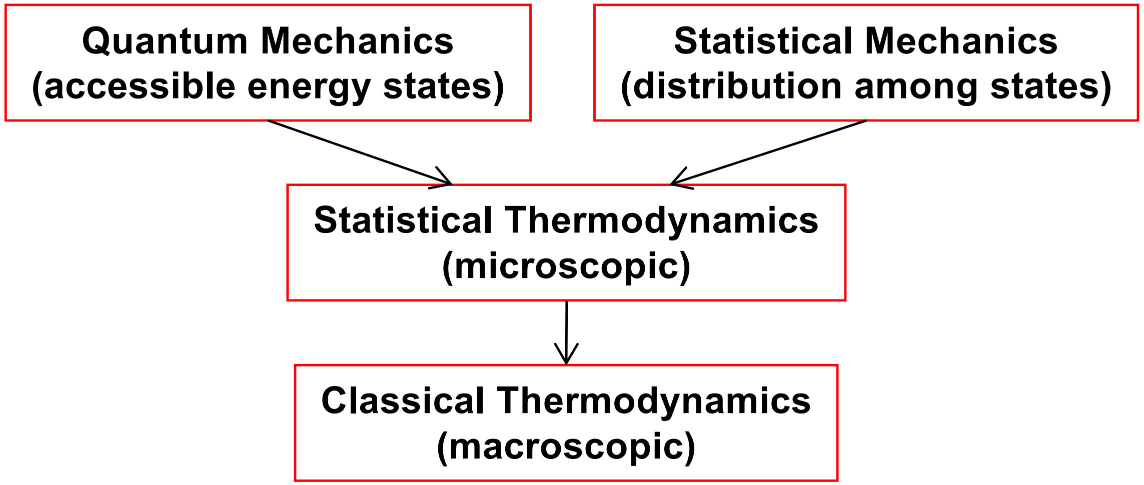
Introduction

- ➔ Establish the tie between macroscopic and molecular properties
- ➔ Stochastic (probabilistic) approach → Focus on equilibrium states
- ➔ Fundamental questions
  - What are the energy states available to the particles (atoms/molecules) comprising a macroscopic system?
  - How are these particles distributed among these states at equilibrium to satisfy the macroscopic constraints?



$$\sum_j N_j = N$$

$$\sum_j N_j \varepsilon_j = E$$


Quantum Mechanics (accessible energy states)

Statistical Mechanics (distribution among states)

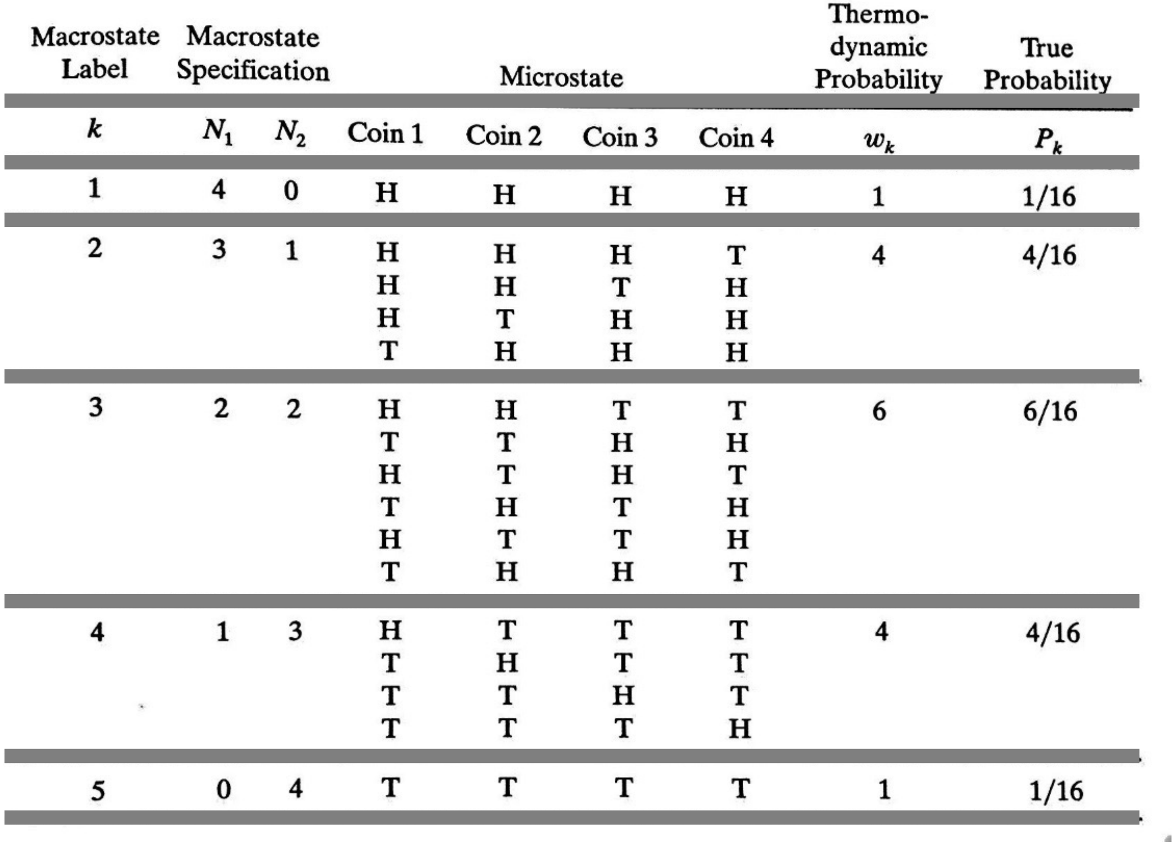
Statistical Thermodynamics (microscopic)

Classical Thermodynamics (macroscopic)

Coin-Tossing Experiment

- Let’s apply some elementary concepts of statistical thermodynamics to a coin-tossing experiment.

  (Assumption) Coins are distinguishable.



Macrostate Label	Macrostate Specification		Microstate				Thermodynamic Probability	True Probability
k	N_1	N_2	Coin 1	Coin 2	Coin 3	Coin 4	w_k	P_k
1	4	0	H	H	H	H	1	1/16
2	3	1	H H H T	H H T H	H T H H	T H H H	4	4/16
3	2	2	H T H T H T	H T T H T H	T H H T T H	T H T H H T	6	6/16
4	1	3	H T T T	T H T T	T T H T	T T T H	4	4/16
5	0	4	T	T	T	T	1	1/16

N_1: number of heads

N_2: number of tails ($N_2 = N - N_1$)

w_k: thermodynamic probability
=number of microstates in
macrostate k

$$P_k = \frac{w_k}{\Omega} \quad \text{where} \quad \Omega = \sum_{k=1}^{N_{\text{macro}}} w_k$$

or Ω : total number of microstates

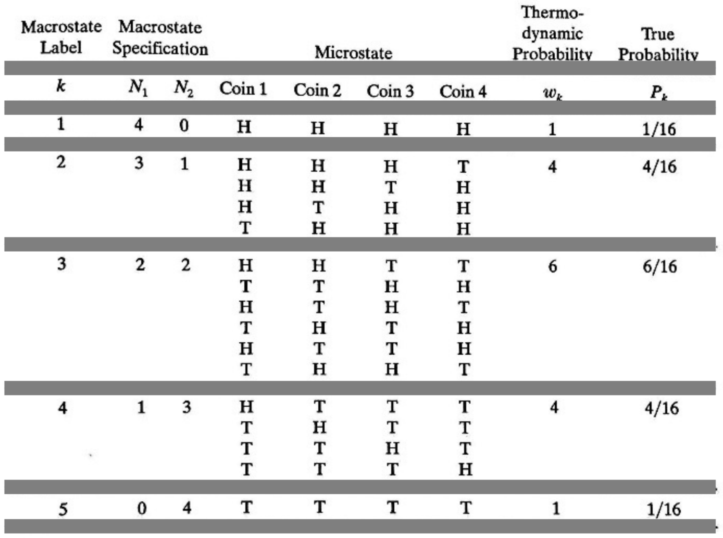
Coin-Tossing Experiment

- Continue on.

  Macrostate (or configuration) is specified by the number of particles in each of the energy levels of the system. (= thermodynamic state in the classical theory)

  Microstate is specified by the number of particles in each energy state. In general, there are more than one energy state (i.e. quantum state) for each energy level (or the energy level has degeneracy.)

  First Postulate of Statistical Mechanics
  "In equilibrium, each *microstate* can occur with an equal probability."



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5	0	4	T	T	T	T	1	1/16

Coin-Tossing Experiment

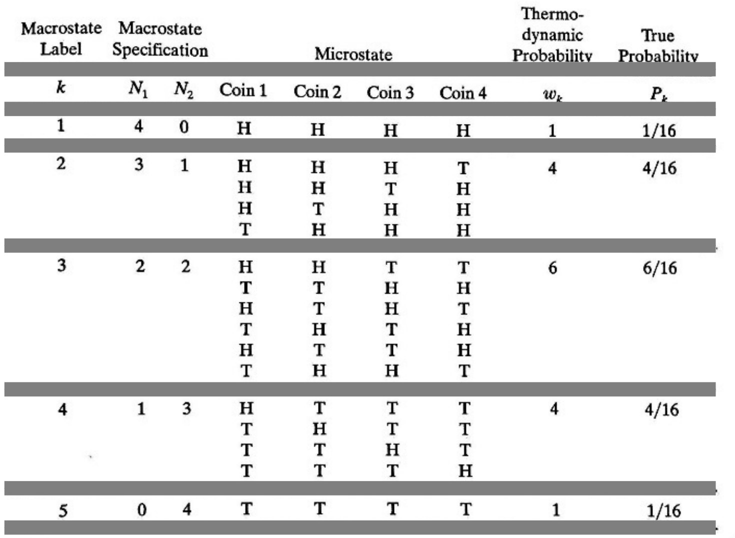
- Continue on.

The average occupation number is

$$\overline{N}_j = \frac{\sum_k N_{jk} w_k}{\sum_k w_k} = \frac{\sum_k N_{jk} w_k}{\Omega} = \sum_k N_{jk} P_k$$

$$e.g.\ \overline{N}_1 = \frac{1}{16}\left[(4\times 1)+(3\times 4)+(2\times 6)+(1\times 4)+(0\times 1)\right] = 2$$

$$(\rightarrow \text{average number of heads})$$



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5	0	4	T	T	T	T	1	1/16

Let's generalize the coin-tossing experiment with a larger number of coins.

How many ways are there to select from the N candidates N_1 heads and N-N_1 tails with distinguishable coins?

$$w_k = \frac{N!}{N_{1k}!(N-N_{1k})!}$$

Coin-Tossing Experiment

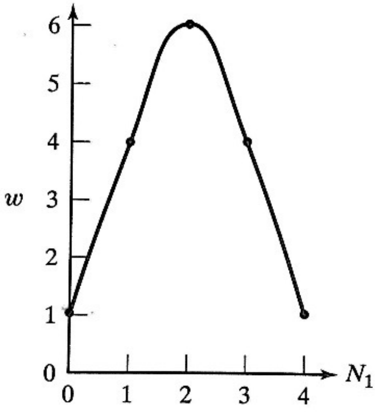
- Continue on.

Calculate the maximum thermodynamic probability for different number of coins.

(use Stirling's formula, $\ln n! \approx n \ln n - n$ for large n)

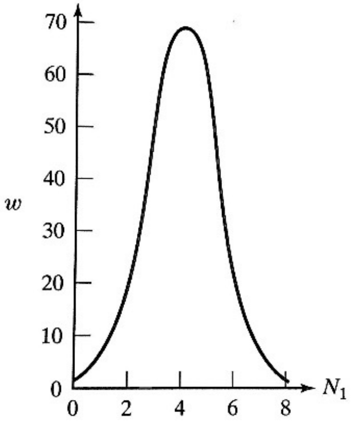
$N = 4$

$$w_{\max} = \frac{4!}{2!2!} = 6$$



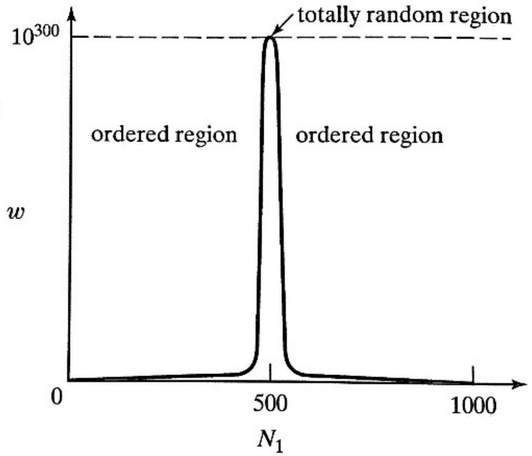
$N = 8$

$$w_{\max} = \frac{8!}{4!4!} = 70$$



$N = 1000$

$$w_{\max} = \frac{1000!}{500!500!} \approx 10^{300}$$



The peak always occurs at $N/2$, but grow rapidly and becomes much sharper as N increases.
In other words, the most probable configuration is that of total randomness.

Coin-Tossing Experiment

- Continue on.

The “ordered regions” almost never occur. (w is extremely small compared to w_{max})

This leads to the very important conclusion!

$$\boxed{\Omega = \sum w_k \approx w_{\max}}$$

i.e. The total number of microstates is very nearly equal to the maximum number.

For thermodynamic problem, the “outcomes” are the occupation numbers of each of n energy levels for the most probable macrostate, i.e. $w_{max}(N_1, N_2, \ldots, N_n)$. This most probable macrostate is the equilibrium state of the thermodynamic system.

In extending our formula of tossing coins from two levels to n levels,

$$w = \frac{N!}{N_1!N_2!\ldots N_n!} = \frac{N!}{\prod_{j=1}^{n} N_j!}$$

Assembly of Distinguishable Particles

- The fundamental problem of statistical thermodynamics is to determined the most probable state or the equilibrium state, in given constraints.

$$\text{Find } w_{\max}(N_1, N_2, \ldots, N_n) \text{ under the constraints:}$$

$$\sum_{j=1}^{n} N_j = N \text{ (conservation of particles)}$$

$$\sum_{j=1}^{n} N_j \varepsilon_j = U \text{ (conservation of energy)}$$

→ Method of Langrange multiplier

As a system proceeds toward a state of equilibrium, the entropy increases, and at equilibrium attains its maximum value. (Classical point of view)

The system tends to change spontaneously from states with low thermodynamic probability to states with high probability. (Statistical point of view)

Thermodynamic Probability and Entropy

- Boltzmann made the connection between the classical concept of entropy and the thermodynamic probability.

$$\boxed{S = f(w)}$$

The entropy is an extensive property. Therefore, the combined entropy of the two subsystems is simply the sum of the entropies of each subsystem.

$$S_{total} = S_A + S_B \quad \text{or} \quad f(w_{total}) = f(w_A) + f(w_B)$$

From the characteristic of the thermodynamic probability,

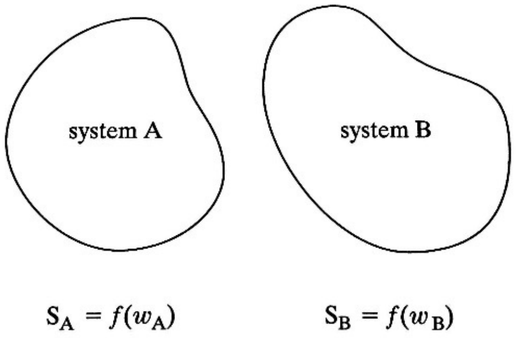
$$w_{total} = w_A w_B$$

Then,

$$f(w_{total}) = f(w_A w_B)$$

Finally,

$$f(w_A) + f(w_B) = f(w_A w_B)$$



Thermodynamic Probability and Entropy

- Continue on.

$$\boxed{f(w_A)+f(w_B)=f(w_A w_B)}$$

The only function to satisfy the above condition is the logarithm.

$$\boxed{S = k\ln w}$$

$$\text{where } k : \text{Boltzmann constant } (1.38\times10^{-23}\, JK^{-1})$$

Quantum States and Energy Levels

- Schrödinger's equation: the governing equation for the dynamical behavior of matter on the atomic scale (just as Newton's law for macroscopic particles)
- Time independent Schrödinger's equation

$$\nabla^2\psi + \left(\frac{8\pi^2 m}{h^2}\right)(\varepsilon-\phi)\psi = 0$$

Time independent Schrödinger's Equation

$$\varepsilon = \text{kinetic energy} + \text{potential energy} = 1/2\left(p^2/m\right) + \phi$$

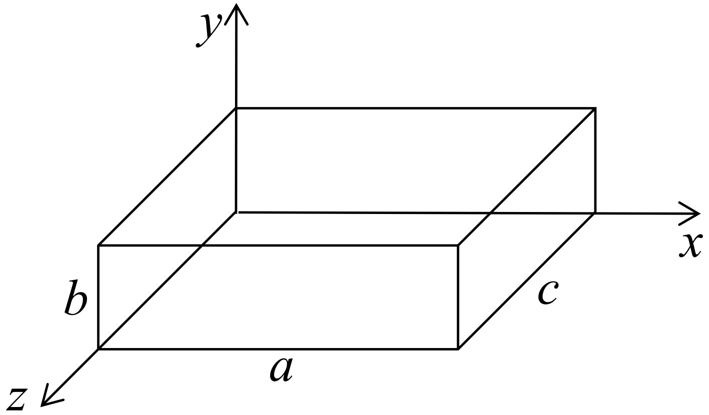
$$\psi = \text{wave function } (|\psi|^2\text{: probability density of finding a particle})$$

$$\varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z$$
$$\phi = \phi_x + \phi_y + \phi_z$$
$$\psi = \psi_x\psi_y\psi_z$$

- The equation has solutions only for specific values of $(\varepsilon-\phi)$, termed the eigenvalues of the energy.

Quantum States and Energy Levels

- Apply Schrödinger’s equation to the translational kinetic energy states of a dilute monatomic ($\phi = 0,\ \varepsilon = \varepsilon_{tr}$ only) particle in the absence of external force fields (“particle in a box” → $\psi = 0$ on the boundary)



$$\psi = \psi_{tr}(x)\psi_{tr}(y)\psi_{tr}(z)$$

$$\varepsilon = \varepsilon_{tr} = \varepsilon_{tr}(x) + \varepsilon_{tr}(y) + \varepsilon_{tr}(z)$$

- Substituting into Schrödinger’s equation and separating variables,

$$\frac{1}{\psi_{tr}(x)}\frac{d^2\psi_{tr}(x)}{dx^2} = -\left(\frac{8\pi^2 m}{h^2}\right)\varepsilon_{tr}(x)$$

with the boundary conditions: $\psi_{tr}(0) = \psi_{tr}(a) = 0$

Quantum States and Energy Levels

- The solution to the equation, $\frac{1}{\psi_{tr}(x)}\frac{d^2\psi_{tr}(x)}{dx^2} = -\left(\frac{8\pi^2 m}{h^2}\right)\varepsilon_{tr}(x)$

$$\psi_{tr}(x) = A\sin\left(x\sqrt{\frac{8\pi^2 m\varepsilon_{tr}(x)}{h^2}} + B\right)$$

- Applying B.C. $\psi_{tr}(0) = 0 \Rightarrow B = 0, \quad \psi_{tr}(a) = 0 \Rightarrow A\sin\left(a\sqrt{\frac{8\pi^2 m\varepsilon_{tr}(x)}{h^2}}\right) = 0$

$$a\sqrt{\frac{8\pi^2 m\varepsilon_{tr}(x)}{h^2}} = n_x\pi \Rightarrow \varepsilon_{tr}(x) = \left(\frac{h^2}{8m}\right)\left(\frac{n_x{}^2}{a^2}\right) \quad (n_x = 1, 2, 3, \dots)$$

- Similarly for y and z:

$$\varepsilon_{tr}(y) = \left(\frac{h^2}{8m}\right)\left(\frac{n_y{}^2}{b^2}\right) \qquad \varepsilon_{tr}(z) = \left(\frac{h^2}{8m}\right)\left(\frac{n_z{}^2}{c^2}\right)$$

- Total translational energy: $\varepsilon = \varepsilon_{tr}(x) + \varepsilon_{tr}(y) + \varepsilon_{tr}(z) = \left(\frac{h^2}{8m}\right)\left[\left(\frac{n_x{}^2}{a^2}\right) + \left(\frac{n_y{}^2}{b^2}\right) + \left(\frac{n_z{}^2}{c^2}\right)\right]$

Quantum States and Energy Levels

- The total solution:

$$\psi = \psi_{tr}(x)\psi_{tr}(y)\psi_{tr}(z) = \left[A_x \sin\left(\frac{n_x \pi x}{a}\right)\right]\left[A_y \sin\left(\frac{n_y \pi y}{b}\right)\right]\left[A_z \sin\left(\frac{n_z \pi z}{c}\right)\right]$$

If any of $n_x, n_y, n_z = 0 \Rightarrow \psi = 0$ for all x, y, z (no particle in a box)

$\Rightarrow$ there is a finite zero-point translational energy when $n_x, n_y, n_z = 1$

- Let $a = b = c = V^{1/3}$

$$\varepsilon_{tr} = \left(\frac{h^2}{8mV^{2/3}}\right)\left(n_x^{\ 2} + n_y^{\ 2} + n_z^{\ 2}\right)$$

- For $\varepsilon_{tr} = const$, there are numerous combinations of n_x, n_y, n_z

→ numerous quantum states with the same energy

→ the energy levels are degenerate

→ degeneracy = number of quantum states with the same energy = g_{tr}

Quantum States and Energy Levels

$$n_x, n_y, n_z = 1, 2 \text{ or } 3$$

$$n_x{}^2 + n_y{}^2 + n_z{}^2 = 14 \, (\text{or } \varepsilon_{\text{tr}} = fixed)$$

$$\varepsilon_{\text{tr}} = \frac{h^2}{8mV^{2/3}}(n_x{}^2 + n_y{}^2 + n_z{}^2) = \frac{14h^2}{8mV^{2/3}}$$

n_x	n_y	n_z
1	2	3
1	3	2
2	1	3
2	3	1
3	2	1
3	1	2

$$\Rightarrow \; g_{tr} = 6$$

For zero-point energy,

$$n_x, n_y, n_z = 1 \;\; \Rightarrow \; \varepsilon_{\text{tr}} = \frac{h^2}{8mV^{2/3}}(n_x{}^2 + n_y{}^2 + n_z{}^2) = \frac{3h^2}{8mV^{2/3}} \;\; \Rightarrow \; g_{tr} = 1$$

Density of Quantum States

- In quantum theory, the energy levels are discrete, but in classical physics, the energy levels are continuous. Why is the discrepancy?

Let's consider translational energy mode.

At room temperature, the mean kinetic energy of a helium gas atom is,

$$\varepsilon_{tr} = \frac{3}{2}kT = \frac{3}{2} \times (1.38\times10^{-23}) \times 293 = 6.2\times10^{-21} J$$

Then, the nominal quantum number n_j for one-liter volume of helium gas is,

$$\varepsilon_{tr} = \left(\frac{h^2}{8mV^{2/3}}\right)\left(n_j^{\,2}\right) \rightarrow n_j = \left(\frac{\varepsilon_{tr}\times 8mV^{2/3}}{h^2}\right)^{1/2} \approx 2.7\times10^{9}$$

This implies that there are so many energy levels below this small energy value (6.2x10^{-21}J), and thus the energy levels are very closely spaced and may be treated as an energy continuum.

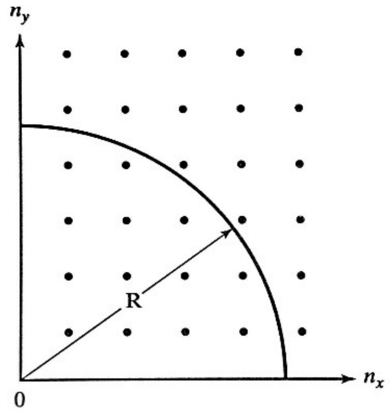
Density of Quantum States

- Under the conditions that the quantum numbers are large and the energy levels are very close together, we can regard the n's and the ε's as continuous functions.

Let's evaluate the density of states $g(\varepsilon)$, or degeneracy.

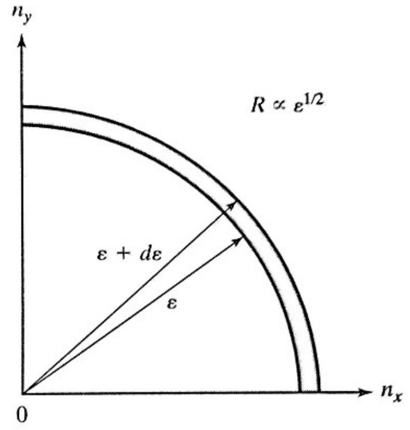
$$n^2 = n_x^{\ 2} + n_y^{\ 2} + n_z^{\ 2} = \frac{8mV^{2/3}}{h^2}\varepsilon_{\mathrm{tr}} \equiv R^2$$

The possible combination (n_x, n_y, n_z) in a given ε_{tr},corresponds to points on a sphere of radius R in (n_x, n_y, n_z) space.



Thus,

$$\begin{aligned} g(\varepsilon)d\varepsilon &= N(\varepsilon + d\varepsilon) - N(\varepsilon) \\ &= \left[N(\varepsilon) + \frac{dN(\varepsilon)}{d\varepsilon}d\varepsilon + H.O.T. \right] - N(\varepsilon) \\ &\approx \frac{dN(\varepsilon)}{d\varepsilon}d\varepsilon \end{aligned}$$



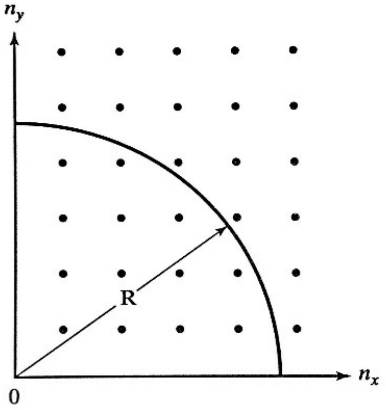
Density of Quantum States

➔ Continue on.

$$\boxed{g(\varepsilon)d\varepsilon \approx \frac{dN(\varepsilon)}{d\varepsilon}d\varepsilon}$$

Define $N(\varepsilon)$, as the number of states contained within the octant of the sphere of radius *R*.

$$N(\varepsilon) = \frac{1}{8}\cdot\frac{4}{3}\pi R^3 = \frac{\pi}{6}V\left(\frac{8m}{h^2}\right)^{3/2}\varepsilon_{\text{tr}}{}^{3/2}$$



Then,

$$g(\varepsilon)d\varepsilon = \frac{dN(\varepsilon)}{d\varepsilon}d\varepsilon = \frac{4\sqrt{2}\pi V}{h^3}m^{3/2}\varepsilon_{\text{tr}}{}^{1/2}d\varepsilon$$

To complete our discussion, we need to consider additional energy states regarding spin!

$$g(\varepsilon)d\varepsilon = \gamma_s\frac{4\sqrt{2}\pi V}{h^3}m^{3/2}\varepsilon_{\text{tr}}{}^{1/2}d\varepsilon$$

$$\gamma_s = 1 \text{ for spin zero bosons}$$

$$\gamma_s = 2 \text{ for spin one-half fermions}$$