PHY294 - QUANTUM AND THERMAL PHYSICS

GRADE 12 QUANTUM CHEM ON STEROIDS

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[1] *TeX file on GitHub*

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I

Quantum Physics

SECTION 1

The 3D Schrodinger Equation

SUBSECTION 1.1

The 3D Schrodinger Equation

In 3D, the wave function ψ depends on all three spatial coordinates, i.e. $\psi = \psi(x, y, z) = \psi(\mathbf{r})$, where $\mathbf{r}$ is the position vector. Similarly the potential energy will also depend on x, y, and z, i.e. $U = U(x, y, z) = U(\mathbf{r})$. Then the Schrodinger equation looks like:

Definition 1 **The 3D Schrodinger Equation**:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{2M}{\hbar^2}[U - E]\psi \tag{1.1}$$

SUBSECTION 1.2

2D Square Box

Before considering 3D systems, we look at an example of calculating ψ and allowed energies in 2D. In particular, we look at solving the Schrodinger equation for a particle in a 2D square box, analagous to a puck sliding on a frictionless surface surrounded by walls.

The Schrodinger equation in 2D:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = \frac{2M}{\hbar^2}[U - E]\psi \tag{1.2}$$

The method for solving the Schrodinger equation depends what the potential energy function $U(\mathbf{r})$ is. In the case of a particle in a 2D square box, the particle can never travel outside, so the potential energy outside of the box is infinity, and the potential energy inside is 0, so all of its energy is kinetic:

$$U(x, y) = \begin{cases} 0 & \text{when } 0 \le x \le a \text{ and } 0 \le y \le a \\ \infty & \text{otherwise} \end{cases} \tag{1.3}$$

To find the possible energies for this quantum system, we solve the Schrodinger equation with the above potential energy function. Since $U = 0$ inside the box, the Schrodinger equation becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = \frac{2ME}{\hbar^2}\psi \tag{1.4}$$

for all x and y inside the box. Regarding the boundary conditions, since the particle can't escape from the box, $\psi(x, y)$ must be zero outside the box, and since $\psi(x, y)$ must be continuous, it must be zero on the boundary as well.

1.2.1 Finding ψ using Separation of Variables

We solve the Schrodinger equation (which is a differential equation) by separation of variables, i.e. we try to find a solution with the form:

$$\psi(x,y) = X(x)Y(y) \tag{1.5}$$

To see if the Schrodinger equation has solutions of the above form, we substitute this "test" solution into Schrodinger's equation. First we simplify the partial derivatives:

$$\frac{\partial^2\psi}{\partial x^2} = Y(y)X''(x) \tag{1.6}$$

$$\frac{\partial^2\psi}{\partial y^2} = X(x)Y''(y) \tag{1.7}$$

Substituting these into the Schrodinger equation:

$$Y(y)X''(x) + X(x)Y''(y) = -\frac{2ME}{\hbar^2}X(x)Y(y) \tag{1.8}$$

Dividing both sides by $X(x)Y(y)$:

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} = -\frac{2ME}{\hbar^2} \tag{1.9}$$

Rearranging this equation, we get

$$\frac{X''(x)}{X(x)} = -\frac{2ME}{\hbar^2} - \frac{Y''(y)}{Y(y)} \tag{1.10}$$

This equation implies that a function of x doesn't depend on x, which implies that the function is a constant, i.e.

$$\frac{X''(x)}{X(x)} = \text{constant} \tag{1.11}$$

Referring to this constant as $-k_x^2$, we can rearrange the above equation:

$$X''(x) = -k_x^2 X(x) \tag{1.12}$$

This equation itself is a differential equation that we already know the solution to:

$$X(x) = B\sin k_x x \tag{1.13}$$

where B is a constant. To satisfy the boundary conditions (that $X(0) = X(a) = 0$), we find that k_x must be an positive integer multiple of π/a, i.e.

$$k_x = \frac{n_x\pi}{a} \tag{1.14}$$

Therefore,

$$X(x) = B\sin\frac{n_x\pi x}{a} \tag{1.15}$$

Following the same logic, we find that

$$Y(y) = C\sin\frac{n_y\pi y}{a} \tag{1.16}$$

Combining these two solutions, the complete wave function is given by

$$\psi(x,y) = X(x)Y(y) = BC\sin k_x x \sin k_y y \tag{1.17}$$

$$\psi(x,y) = A\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{a} \tag{1.18}$$

1.2.2 Finding Allowed Energies

Recall that

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} = -\frac{2ME}{\hbar^2} \tag{1.19}$$

We now know that X''/X is equal to $-k_x^2$ which is equal to $n_x\pi/a$. Similar logic follows for Y''/Y. Substituting this into the above equation, we get

$$-\frac{n_x^2\pi^2}{a^2} - \frac{n_y^2\pi^2}{a^2} = -\frac{2ME}{\hbar^2} \tag{1.20}$$

Solving for E, we find the allowed energy values:

$$E = E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2Ma^2}(n_x^2 + n_y^2) \tag{1.21}$$

SUBSECTION 1.3

Energy Levels of the Hydrogen Atom

The energy of a state is given by:

$$E = -\frac{E_R}{n^2} \tag{1.22}$$

SECTION 2

Electron Spin

SUBSECTION 2.1

Spin Angular Momentum

The angular momentum of an electron is the sum of two terms:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{2.1}$$

where **L** is the orbital angular momentum and **S** is the electron's **spin**. The magnitude of **L** is given by:

$$L = \sqrt{l(l+1)}\hbar \tag{2.2}$$

The magnitude of **S** is given by a similar formula:

$$S = \sqrt{s(s+1)}\hbar \tag{2.3}$$

The difference is that while l can take on integer values, s always has a fixed value for an electron: [1]

$$s = \frac{1}{2} \tag{2.4}$$

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[1] *Some other elementary particles have different values for s*

Therefore electron spin always has the same magnitude, and is sometimes called the *intrinsic angular momentum*:

$$S = \frac{\sqrt{3}}{2}\hbar \tag{2.5}$$

Recall that the z-component of **L** is given by

$$L_z = m\hbar \tag{2.6}$$

where m can take on integer values from $-l$ to l. Similarly, for the z-component of spin:

$$S_z = m_s\hbar \tag{2.7}$$

where m_s is the fourth quantum number that takes on integer values from $-s$ to s. But since $s = \frac{1}{2}$, m_s only has two possible values:

$$m_s = \pm\frac{1}{2} \tag{2.8}$$

and therefore

$$S_z = \pm\frac{1}{2}\hbar \tag{2.9}$$

These two possibilities are referred to as "spin up" or "spin down", also represented by arrows pointing up or down. [2].

Complete specification of an electron's state of motion requires specification of both its orbital motion (defined by quantum numbers n, l, m) *and* spin orientation (defined by m_s) – requires all 4 quantum numbers to specify its **quantum state**.

For Hydrogen, its energy is almost completely independent of spin orientation. For the n^{th} energy level, there are n^2 possible values of l and m. For each of these values, there are also two possible spin orientations. Therefore:

$$\text{degeneracy of } n^{th} \text{ level in } \textbf{hydrogen} = 2n^2 \tag{2.10}$$

The electron is entirely elementary – not made of any other particles. Therefore, its spin is not dependent of anything else – it is an intrinsic property of the electron.

Subsection 2.2

Magnetic Moments

Most evidence for electron's spin angular momentum relates to the magnetic moment associated with rotating electric charge.

Consider an electron orbiting a nucleus. This small orbiting charge is essentially a small current loop. Current loops produce magnetic fields which respond to externally applied magnetic fields.

We use **A** to represent a vector perpendicular to the plane of the loop.

$$\mathbf{\Gamma} = i\mathbf{A} \times \mathbf{B} \tag{2.11}$$

$$\mathbf{\Gamma} = \boldsymbol{\mu} \times \mathbf{B} \tag{2.12}$$

where $\boldsymbol{\mu} = i\mathbf{A}$ is the **magnetic moment** of the loop. An applied magnetic field **B** exerts a torque $\mathbf{\Gamma}$ on the current loop that tries to align the magnetic moment $\boldsymbol{\mu}$ with **B**. Due to this torque, if the magnetic moment of a current loop in a magnetic field

[2] **S** *is never actually parallel to the z-axis though (since S_z is smaller than S)*

isn't aligned with the field, it stores potential energy U, given by

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{2.13}$$

We can relate magnetic moment μ to angular momentum L in a ratio: [3] [4]

$$\frac{\mu}{L} = \frac{e}{2m_e} \tag{2.14}$$

Since electron charge is negative, the current flows in the opposite direction of the electron's velocity, and therefore μ and L point in opposite directions. So we can rewrite the above ratio:

$$\boldsymbol{\mu} = -\frac{e}{2m_e}\mathbf{L} \tag{2.15}$$

Since in quantum mechanics, angular momentum $\mathbf{L}$ is quantized (just $2l + 1$ possible orientations), then the magnetic moment $\boldsymbol{\mu}$ is also quantized with $2l + 1$ possible orientations.

Note that the above equation only gives the magnetic moment due to the *orbital* motion of an electron. Magnetic moment arises from an electron's spinning motion as well, but first we'll look at cases where the magnetic moments due to spin cancels out.

SUBSECTION 2.3

The Zeeman Effect

Due to electron motion, most atoms have a magnetic moment. When you apply a magnetic field, you apply torque and change the atom's potential energy – you change the atom's energy levels by $U = -\boldsymbol{\mu} \cdot \mathbf{B}$. This changes the energy of photons emitted/absorbed, therefore changing the spectrum. This is the **Zeeman Effect**.

We first look at cases where magnetic moments due to electron spin cancel out. There are many states of helium where the spins of its two electrons point in opposite directions and therefore their magnetic moments cancel out; they produce only one spectral line and are therefore called **singlet states**. Also, in all states of helium, one of the electrons has zero orbital angular momentum. Therefore, in singlet states, the total magnetic moment of the state is just the the magnetic moment due to the orbital motion of one of the electrons.

Without an applied magnetic field, for a given energy level, the angular momentum has $2l + 1$ different orientations that all have the same energy. Therefore the energy level is $(2l + 1)$-fold degenerate.

After applying a magnetic field, the energy level of each of the $2l + 1$ orientations changes by $U = -\boldsymbol{\mu} \cdot \mathbf{B}$, therefore removing the $(2l + 1)$-fold degeneracy.

The size of the energy shift due to the magnetic field is given by: [5]

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{2.16}$$

$$\text{some math...} \tag{2.17}$$

$$\Delta E = \left(\frac{e\hbar}{2m_e}\right) mB \tag{2.18}$$

$$\Delta E = m\mu_B B \tag{2.19}$$

where we define

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \cdot 10^{-24} A \cdot m^2 \tag{2.20}$$

as the **Bohr magneton** (has the units of a magnetic moment).

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[3] *Both μ and L are a result of the electron's orbital motion. Some math is skipped here lol.*

[4] *This ratio is called the **gyromagnetic ratio**. It is constant – only depends on the charge and mass of the electron.*

[5] *note that the energy shift is dependent on quantum number m; therefore it's often called the **magnetic quantum number***

Since m can only take on consecutive integer values, we see that the energy separation of adjacent energy levels is equal to:

$$\text{separation of adjacent levels} = \mu_B B \tag{2.21}$$

We can also express μ_B in units of joules/tesla:

$$\mu_B = 5.79 \cdot 10^{-5} eV/T \tag{2.22}$$

We interpret this to mean: if you apply a 1 tesla magnetic field, it causes a separation of adjacent levels by $5.79 \cdot 10^{-5} eV$.

Note that we've only considered

SUBSECTION 2.4

Spin Magnetic Moments

The magnetic moment of an electron due to its spinning motion is equal to

$$\boldsymbol{\mu_{spin}} = -\frac{e}{m_e}\mathbf{S} \tag{2.23}$$

The total magnetic moment of any electron is equal to the sum of its orbital and spin magnetic moments:

$$\boldsymbol{\mu_{tot}} = \boldsymbol{\mu_{orb}} + \boldsymbol{\mu_{spin}} = -\frac{e}{2m_e}(\mathbf{L} + 2\mathbf{S}) \tag{2.24}$$

SUBSECTION 2.5

Anomalous Zeeman Effect

Anomalous Zeeman Effect occurs when the spin magnetic moment don't cancel out as they did for the normal Zeeman Effect.

We look at a hydrogen atom in a state with zero orbital angular momentum (in the s state, with $l = 0$). Therefore only the spin angular momentum contributes to the magnetic moment.

When we apply a magnetic field $\mathbf{B}$, the energy shift is

$$\Delta E = \pm\mu_B B \tag{2.25}$$

If the electron is spin up, its energy is raised; if it's spin down, its energy is lowered. Therefore the separation between the two levels is

$$\text{separation of adjacent levels} = 2\mu_B B \tag{2.26}$$

SECTION 3

Multielectron Atoms

Unlike the Bohr model, the Schrodinger equation is able to predict the properties of multielectron atoms and moleculues.

SUBSECTION 3.1

The Independent-Particle Approximation

For two or more electrons, there is no exact solution to the Schrodinger equation – only approximations. The **independent particle approximation** (IPA) is the basis for most calculations of multielectron atoms.

Essential feature of IPA: each electron is considered to move independently in a field of the other $Z-1$ electrons and the nucleus. Furthermore we can assume the distribution of the other $Z-1$ electrons is spherically symmetric around the nucleus. [6] Therefore the charge distribution seen by any one electron is spherically symmetric, meaning that the IPA potential energy is only a function of r, i.e. $U(r)$.

First, if an electron is *outside* a spherical distribution of total charge Q, the force experienced by the electron is the same force as if Q was a point charge at $r = 0$:

$$F = k\frac{Qe}{r^2} \tag{3.1}$$

Second, if the electron is *inside* a spherical shell of charge, it experiences no force from the shell at all.

So, if the electron is close enough to the nucleus, it will be inside all the other electrons – the only force it experiences is the force from the nuclear charge Ze:

$$F = \frac{Zke^2}{r^2} \tag{3.2}$$

If the electron is outside all other electrons, the force it experiences is:

$$F = \frac{ke^2}{r^2} \tag{3.3}$$

The potential energy $U(r)$ of the electron is the integral of the force. It is given by

$$U(r) = -Z_{eff}(r)\frac{ke^2}{r} \tag{3.4}$$

where $Z_{eff}(r)$ is the **effective charge** felt by the electron. When r is inside the other electrons:

$$Z_{eff} \approx Z \tag{3.5}$$

When r is outside the other electrons:

$$Z_{eff} \approx 1 \tag{3.6}$$

Subsection 3.2

IPA Energy Levels

The ground state energy of the innermost electron ($1s$) is approximately

$$E_{1s} \approx -Z^2 E_R \tag{3.7}$$

In hydrogen, all orbitals with the same principle quantum number n have the same energy and therefore all states with the same n are degenerate (degeneracy of n^2). In multielectron atoms, states with smaller l values penetrate closer to the nucleus and are lower in energy and therefore remove the degeneracy between the different orbital types. In multielectron atoms, only states of the same orbital types are degenerate, with a degeneracy of $2(2l + 1)$.

[6] *For this reason, the IPA is sometimes called the central-field approximation*

The clustering of electrons into spatial shells occurs in multielectron atoms. The most probable radius of these shells is roughly

$$r_{mp} \approx \frac{n^2 a_B}{Z_{eff}} \tag{3.8}$$

SUBSECTION 3.3

The Pauli Exclusion Principle

Theorem 1 **Pauli Exclusion Principle**: No two electrons in a quantum system can occupy the same quantum state.

Note that the Pauli exclusion principle applies to other particles as well, not just electrons.

PART

II

Thermal Physics

Thermal physics is a combination of Thermodynamics and Statistical Mechanics. We will focus on statiscal mechanics.

Section 4

Lecture 1 – Ideal Gas Law

- what is temperature? The thing that's measured by thermometers
- Types of thermometers:
  - Mercury bulb: Expansion of mercury
  - Bi-metallic Strip: Different metals expand differently
  - IR Thermometer: Infrared spectrum depends on temperature
  - Thermistor: resistance depends on temperature
  - Gas bulb Thermomemter: Pressure depends on temperature

How the gas bulb thermometer works:

- Ideal gas law:

$$P = kT\frac{N}{V} \tag{4.1}$$

$$P = RT\frac{n}{V} \tag{4.2}$$

$$kN = Rn. \tag{4.3}$$

- assume that gas molecules bounce elastically off of the walls of the gas container
- for simplicity: igonore collisions between molecules
- therefore we can treat one particle at a time
- consider a particle in a box at speed v – x component is v_x
- in an elastic collision, the x component simply changes sign
- the pulse force the particle exerts on the wall during a bounce is:

$$F_x = m\frac{\Delta v_x}{\Delta t_c} = m\frac{2v_x}{\Delta t_c}. \tag{4.4}$$

- let's take the average force:

$$\overline{F_x} = m\frac{2v_x}{\Delta t} \tag{4.5}$$

$$\Delta t = \frac{2L}{v_x} \tag{4.6}$$

$$\overline{F_x} = \frac{mv_x^2}{L}. \tag{4.7}$$

- Pressure for one particle can be given by:

$$P = \frac{\overline{F_x}}{A}$$
$$P = \frac{mv_x^2}{V}.$$

- Pressure for N particles:

$$P = \sum_{i=1}^{N} \frac{mv_{x,i}^2}{V} = \frac{m}{V}\sum_{i=1}^{N} v_{x,i}^2.$$

Theorem 2 **Kinetic Theory**

$$P = \frac{m\overline{v^2}}{3}\frac{N}{V}.$$

- comparing this result to the ideal gas law:

$$\frac{m\overline{v^2}}{3} = kT.$$

- note that average kinetic energy per particle is

$$\overline{E} = \frac{m\overline{v^2}}{2}.$$

- then we obtain:

$$T = \frac{m\overline{v^2}}{3k} = \frac{2\overline{E}}{3k}.$$

Definition 2 **Temperature (for an ideal gas)**: For an ideal gas, temperature is a measure of the average kinetic energy per particle

$$T \equiv \frac{m\overline{v^2}}{3k} = \frac{2\overline{E}}{3k}$$
.

- using this definition of temperature, we derived the **ideal gas law** as well

$$P = kT\frac{N}{V}.$$

- experimentally this is what a thermometer measures

$$\overline{E} = \frac{3}{2}kT.$$

SECTION 5

Lecture 2 – Equipartition

- how does this apply to things that aren't gases?
- can we say something about speed distribution?
- why do things come into thermal equilibrium?
- what does this have to do with the second law of thermodynamics?
- What is the total energy U, in an ideal gas at temperature T?

$$U = N\overline{E} = 3\frac{NkT}{2}.$$

- so increasing U increases T

Definition 3 **Heat Capacity**: the energy required for a unit change in temperature

$$C_V \equiv \frac{\partial U}{\partial T}|_{V,N,\ldots} = \frac{3Nk}{2} = \frac{3nR}{2}$$
$$C_V = \frac{3R}{2}\text{for 1 mole of an ideal gas.}$$

- recall that $Nk = nR$
- for an Ideal Gas (theory): $C_v = 12.47\frac{J}{K\cdot mol}$

Theorem 3 **Equipartition Theorem**: At temperature T, the average energy of any quadratic degree of freedom is $\frac{1}{2}kT$, i.e.

$$U = D\frac{kT}{2}$$
$$U = \frac{dNkT}{2}$$
$$U = d\frac{nRT}{2}.$$

- then the heat capacity:

$$C_V = \frac{dnR}{2}.$$

- then for an ideal gas (which has 3 DOF per particle):

$$U = N\overline{E} = \frac{3}{2}Nmv^2 = 3N\frac{kT}{2}. \tag{5.1}$$

SUBSECTION 5.1

Rigid body quadratic degrees of freedom

- there are three translational degrees of freedom:
- and there are three rotational degrees of freedom:

$$E = \frac{1}{2}I\omega^2.$$

- shouldn't there be 6 degrees of freedom?
- Rotational Quantum Modes: monoatmoic molecules:
- From quantum mechanics, the rotational energy levels for a rigid object are:

$$E_J = \frac{\hbar}{2I} J(J+1).$$

- for a solid sphere:

$$I = \frac{2}{5} mr^2.$$

- in the case of an atom, r is the radius of the nucleus – where all the mass is
- for Argon, treating the nucleus as a solid sphere, we get:

$$E_1 = .$$

- for monoatmoic molecules:
  - the mass is all in the nucleus
  - the moment of inertia is very very small
  - the first excited rotational mode is at a high energy
  - the first excited quantum mode is not excited at any sensible temperature (the modes are "frozen out")
  - **monoatomic molecules only have 3 DOF**
- For diatomic molecules:
  - the mass is all in the nuclei, which are separated by 10^{-10} m
  - Along the long (green) axis, it behaves the same as a monoatomic molecule (frozen rotational mode)
  - the other two axes have much higher moments with very low energy rotational modes
  - at low enough temperatures, these rotational modes will also be frozen out, but...
  - at room temperature, many modes are accessible, so the equipartition theorem applies to them
  - **Diatomics have 5 degrees of freedom** – 3 translational and 2 rotational

5.1.1 Idealized Solids

- model a solid as atoms connected by springs
- 3 kinetic DOF per atom:

$$E = \frac{1}{2} mv^2.$$

- AND 3 potential DOF in the spring:

$$E = \frac{1}{2} k \Delta x^2.$$

- Total: $d = 6$

5.1.2 C_V vs C_P

Heat capacity at constant volume:

$$C_V \equiv \frac{\partial U}{\partial T}.$$

- hard to measure for solids since they tend to expand thermally

Heat capacity at constant pressure:

$$C_P \equiv \left.\frac{\partial U}{\partial T}\right|_P + P \left.\frac{\partial V}{\partial T}\right|_P.$$

- first term is energy absorbed by the material
- second term is work done on the surrounding gas

5.1.3 Summary

- equipartition theorem seems pretty powerful:
  - predicts energy per mode as a function of temperature
  - can be used to calculated a bunch of things
- But:
  - we didn't really prove it
  - it doesn't really work when quantum levels matter
  - it isn't always really clear that "degrees of freedom" are well defined
  - works in average energy, so only gives mean-squared values for speeds, etc.
  - still don't know what entropy is
  - presumes but doesn't explain equilibrium

SECTION 6

Lecture 3 – Two State Systems

SUBSECTION 6.1

Statistics

6.1.1 Microstates and Macrostates

- **Microstate**: a specific configuration (e.g. HTH)
  - all microstates are equally likely
- **Macrostate**: defined by some combined quantities (e.g. 2H)
  - may include many different microstates
  - not all macrostates are equally likely
- **Multiplicity** Ω: the number of microstates in a macrostate
  - multiplicity is given by:

$$\Omega(n) = \binom{100}{n}.$$

  - multiplicity of a two state system:

$$\Omega(N,n) = \binom{N}{n}.$$

- Probability of n heads after N coin flips:

$$P(N,n) = \frac{\Omega(N,n)}{\Omega_{tot}} = \frac{\Omega(N,n)}{2^N}.$$

- for 50 coins:

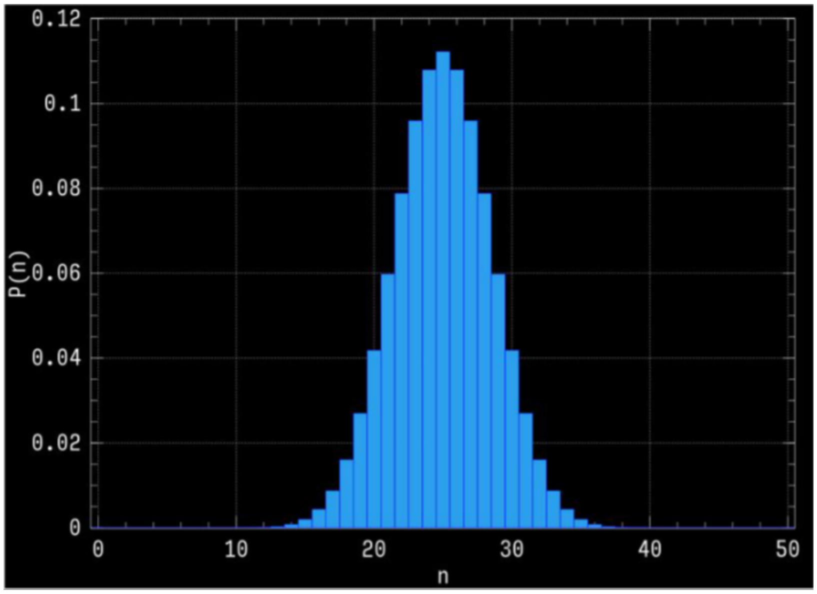


Figure 1. Probability of n coins flipped heads.

SUBSECTION 6.2

Paramagnets: an example of a two state system

- consider a system of N little magnetic dipoles that can either point up or down relative to an externally applied magnetic field
- they don't influence each other
- external magnetic field applies a torque trying to align the dipoles with the field
- aligned has lower energy than unaligned
- ignoring the cost of energy: equal numbers of dipoles pointed up as down has a far higher probability

SECTION 7

Lecture 4 – Einstein Solid

- model a solid as N independent harmonic oscillators

- the quantum energy levels for a harmonic oscillator are:

$$E = \left(q + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{m}}.$$

- so each oscillator has evenly spaced energy levels

$$E - E_o = q\hbar\sqrt{\frac{k}{m}}$$
$$\implies E = q\hbar\sqrt{\frac{k}{m}}.$$

- we don't really care about the ground state E_o since it is constant, so we can ignore it
- each identical, independent oscillator can have exactly an integer quanta of energy
- imagine a system of 3 oscillators with a total of 2 quanta of energy
- this energy can be distributed several different ways between the three oscillators

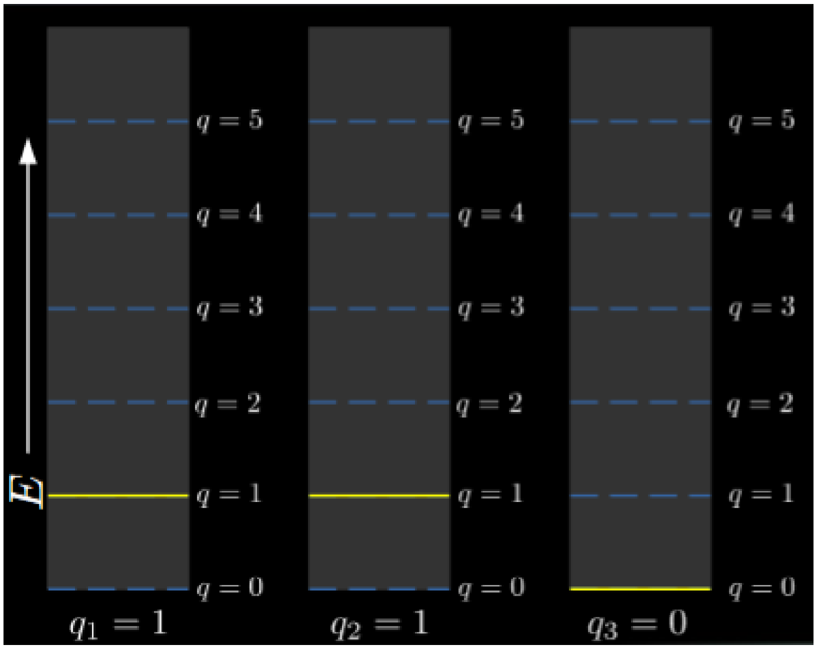


Figure 2. One possible arrangement of the three oscillators

- the **microstate** is the exact configuration, e.g (0, 0, 2)
- the **macrostate** is the number of quanta of energy
- the **multiplicity** is the number of microstates that have this macrostate
- the multiplicity of the macrostate $q_{tot} = 2$ is:

$$\Omega(2) = 6.$$

- generally, **the multiplicity for q quanta of energy distributed between N oscillators** is:

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

- proof: we can draw configurations like this, where * is a quanta of energy and | separates the oscillators:

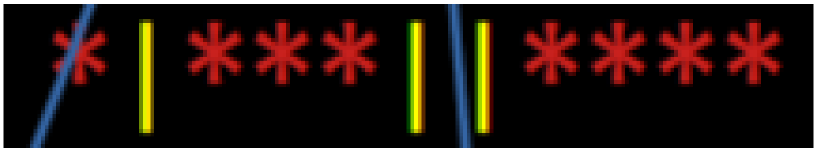


Figure 3. Representation of configuration of quanta of energy.

- so there are $q+N-1$ symbols, q of which are a *
- Ω grows rapidly with q and N, but grows more rapidly with N (number of oscillators)

7.0.1 Interaction of Einstein Solids

- imagine two Einstein solids:
  - each with $N = 32$ oscillators
  - $q_1 + q_2 = q_{tot} = 120$ quanta of energy distributed between them
- how does Ω change with the distribution of q_1 and q_2?
- the multiplicity (number of different possible ways of arranging the quantas of energy) increases as you more evenly distribute the energy
- multiplicity of two solids:

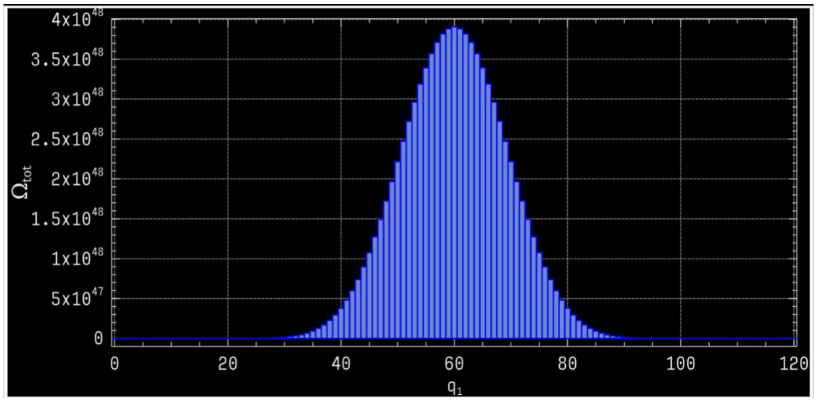


Figure 4. Multiplicity of two interacting solids.

- as you increase N and q, the probability distribution becomes narrower – the possibility of finding the microstates in an arrangement outside of the most probable one becomes lower and lower

- in real life, where there are huge numbers of atoms in solids, the probability distribution is extremely narrow – much more likely to find system with evenly distributed energy

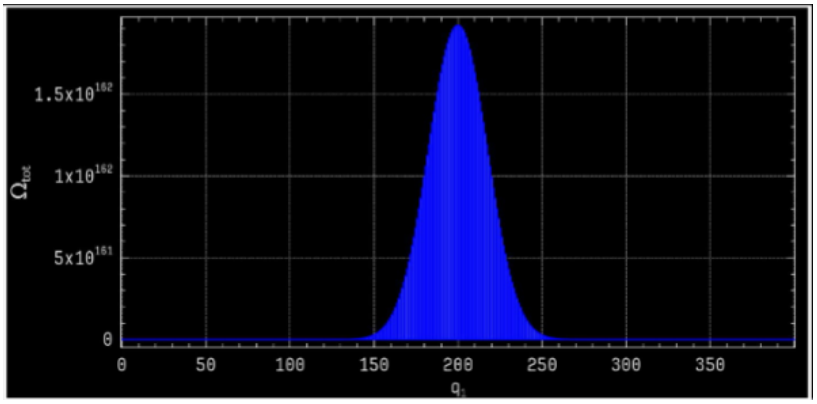


Figure 5. Mulitiplicity as you increase N and q

- so if you imagine two Einstein solids:
  - allow energy to flow between them freely
  - assume that every accessible microstate is equally likely
- therefore the probability that we will find the combined system in this macrostate is proportional to the multiplicity of the macrostate
- seems like this might be an explanation for thermal equilibrium…

Section 8

Lecture 5 – Large Numbers

- putting 2 einstein solids in thermal contact so that every microstate of the combined system is equally likely
- while each of the microstates of $q_1 = 0$ are as likely as any other microstate, there are so few of them that we will never see it
- there are way more possible arrangements where the energy quanta are evenly split between the two materials
- dealing with real numbers (e.g. considering 1 mole of an Eintstein solid), numbers become extremely large and Ω becomes unreasonably large

8.0.1 Dealing with (very) Large Numbers

- for *large* numbers, you can ignore adding a small number to a large number (unless you later subtract)
- for *very large* numbers, you can ignore multiplying by a large number (unless you later divide)

Theorem 4 **Stirling's Approximation:**

$$N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \quad \text{when } N \gg 1.$$

- this approximation is good to 0.8% for $N = 10$ and around 0.03% for $N = 300$

$$\ln(N!) \approx N\ln(N) - N \quad \text{when } N \gg 1.$$

Subsection 8.1

Large N Multiplicity of Einstein Solids

$$\Omega \approx \left(\frac{eq}{N}\right)^N \text{ when } q \gg N \text{ and } N \gg 1 \tag{8.1}$$

- for two Einstein solids:

$$\Omega_1 \approx \left(\frac{eq_1}{N}\right)^N \text{ and } \Omega_2 \approx \left(\frac{eq_2}{N}\right)^N$$
$$\Omega_{tot} = \Omega_1\Omega_2 = \left(\frac{e}{N}\right)^{2N}(q_1q_2)^N.$$

- the peak will be at $q_1 = q_2 = \frac{q}{2}$
- define $x = q_1 - \frac{q}{2} = \frac{q}{2} - q_2$ (x is how far we are from the centre)
- then:

$$\Omega_{tot} = \left(\frac{e}{N}\right)^{2N}\left[\left(\frac{q}{2}\right)^2 - x^2\right]^N$$
$$\Omega_{tot} \approx \Omega_{max}\cdot e^{N(\frac{2x}{q})^2}$$
$$\Omega_{max} = \left(\frac{e}{N}\right)^{2N}\left(\frac{q}{2}\right)^{2N}.$$

- width of distribution is very very thin, but not zero:

$$\sigma = \frac{q}{2\sqrt{N}}.$$

- if $N = 10^{24}$ then $\sigma = \frac{q}{2\cdot 10^{12}}$

Subsection 8.2

Introducing Entropy

- systems in thermal contact will tend to be found in states with the highest multiplicity Ω
- **multiplicity increases**
- but dealing with numbers this big is a pain, so we introduce **entropy**:

$$S \equiv k\ln(\Omega).$$

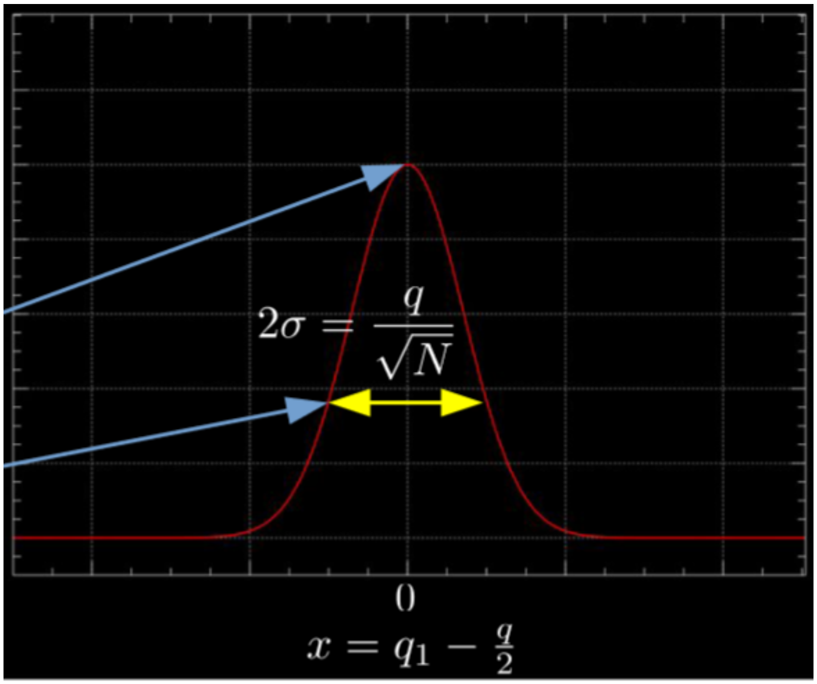


Figure 6.

- systems in thermal contact will tend to be found in states with the highest entropy S
- **entropy increases**
- this is the **second law of thermodynamics**

Section 9

Lecture 6 – Multiplicity of an Ideal Gas

- an ideal gas is just particles in a box
- recall that particles in a cubic box have energy quantized by:

$$E = \frac{h_2}{8m}\left(\frac{n_1^2 + n_2^2 + n_3^2}{V^{\frac{2}{3}}}\right).$$

  where n is quantized (integers)

- multiplicity is given by

$$\Omega_N = f(m, N)V^N U^{\frac{3N}{2}}.$$

- putting two ideal gases in contact with each other:

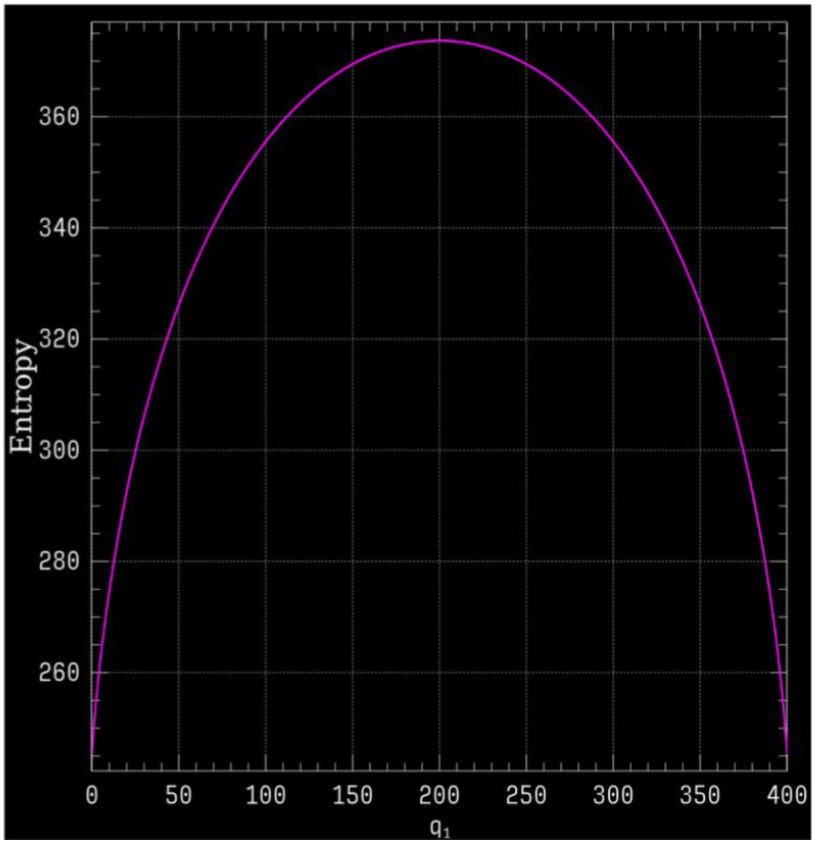


Figure 7. Entropy

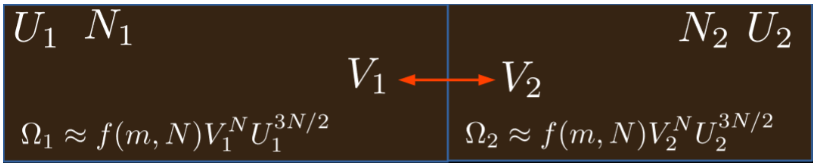


Figure 8. Set up for multiplicity of ideal gas.

- where $N_1 = N_2 \gg 1$
- $\Omega_{tot} = \Omega_1 \cdot \Omega_2$
- if we let energy U flow between the two samples, then Ω_{tot} is a function of U_1 and U_2, and reaches a maximum when $U_1 = U_2 = U/2$, i.e. when energy is evenly distributed
- same thing happens when you let volume V vary or number of particles N flow between the samples – multiplicity peaks when $V_1 = V_2$, when $N_1 = N_2$
- in terms of entropy:
- entropy of a large N Einstein solid: $S_1 = Nk[\ln\left(\frac{q_1}{N}\right) + 1]$
- due to how logarithms work: $S_{tot} = S_1 + S_2$

- we see that the entropy is higher when the energy is equally distributed between equally sized solids
- the entropy of an ideal gas: Sackur-Tetrode Equation

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right].$$

  - increases with N, V, m, and U

SUBSECTION 9.1

Entropy of Mixing

- removing the barrier between two gases
  - assume that initially $N_1 = N_2, V_1 = V_2, U_1 = U_2$
- treat the two types of gas separately
- for both gases: N_1, U_1, m_1 all remain constant, but V_1 doubles:

$$\Delta S_1 = \Delta S_2 = N_1 k \ln\left(\frac{V_i}{V_f}\right) = N_1 k \ln(2)$$
$$\Delta S_{tot} = 2kN\ln(2).$$

- what about mixing identical gases?
- originally, each container has an entropy of

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right].$$

- total entropy is just double that
- after removing the barrier, we have one system, with $N = 2N_1, V = 2V_1, U = 2U_1$
- plugging this into the Sackur-Tetrode equation, we get

$$S = 2Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right].$$

  which is the same as what we had originally

- therefore $\Delta S = 0$ for identical gases

SECTION 10

Lecture 7 – What is Temperature?

- when placed in thermal contact, the system will tend to the state with the highest entropy (i.e. $S_1 + S_2$ is maximal)
- but also: the system will tend to the state where the temperatures are the same

- peak in entropy occurs when

$$\frac{\partial S_{tot}}{\partial q_1} = 0.$$

  i.e. when

$$\frac{\partial S_1}{\partial q_1} = \frac{\partial S_2}{q_2}.$$

- but since $U = qE_0$, peak in entropy occurs when

$$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{U_2}.$$

- i.e. peak occurs where you take some energy from one body and put it in the other, causing opposing changes in entropy in each body, but these changes in entropy are equal to each other and cancel out to zero (total entropy doesn't change)

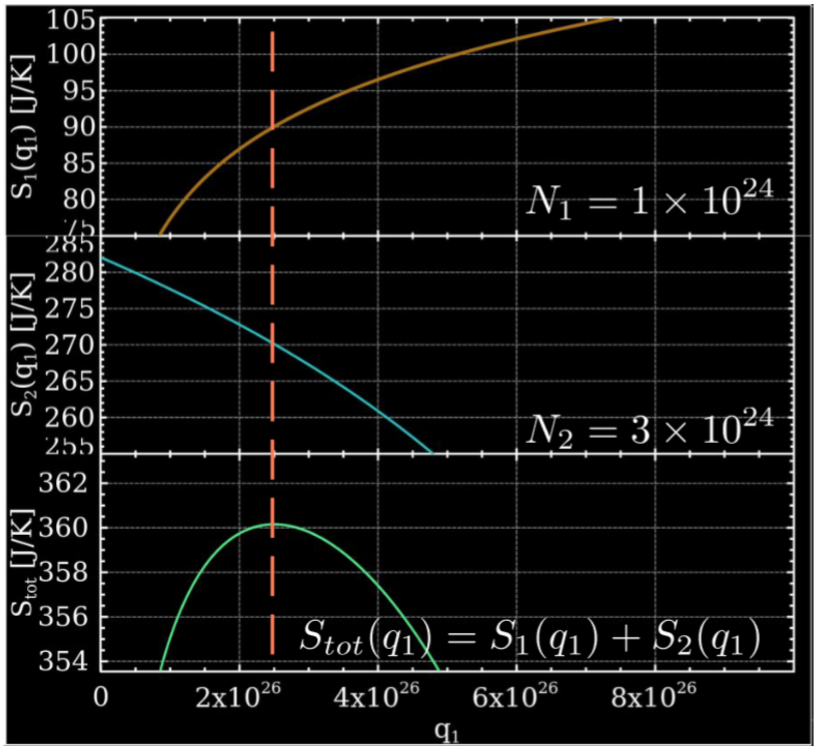


Figure 9. Where entropy peaks.

- thermal equilibrium is when:
  1. temperatures are equal
  2. entropy is maximized

Definition 4 **Temperature (for any system)**:

$$T = \frac{\partial U}{\partial S} \quad \text{or} \quad \frac{1}{T} = \frac{\partial S}{\partial U}.$$

- $(T)^{-1}$ is how much entropy increases when energy is added to a system, with "everything else" held constant
- low temperature means S increases a lot, high temperature means S does not increases as much

SECTION 11

Lecture 8 – Thermodynamic Identity

- using this model to predict heat capacity:
  1. from quantum mechanics, find the multiplicity $\Omega(U, N, V, \ldots)$
  2. find the entropy $S = k\ln(\Omega)$
  3. find $T(U, N, V, \ldots) = \left(\frac{\partial S}{\partial U}\right)^{-1}$
  4. solve for $U(T, N, V, \ldots)$
  5. find $C_V = \frac{\partial U}{\partial T}$

SUBSECTION 11.1

Pressure

- consider again two systems in contact with each other, but this time we allow both volume V and energy U to change
- equilibrium occurs when S_{max}
- at S_{max}, $\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}$ and $\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}$
- also $T_1 = T_2$ and $P_1 = P_2$

Definition 5 **Pressure (for any system)**:

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}.$$

- successfully reproduces the ideal gas law if we plug in the Sacker-Tetrode equation

SUBSECTION 11.2

Chemical Potential

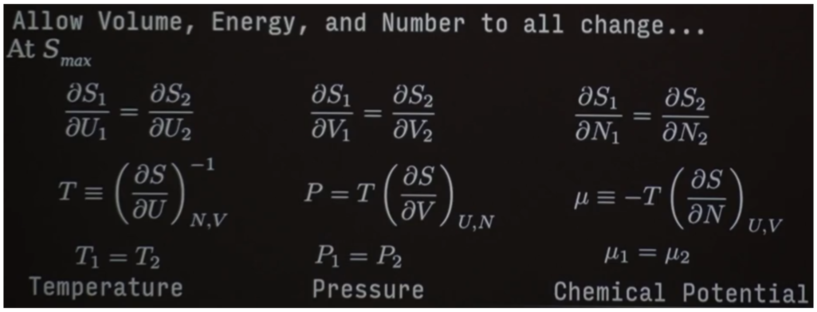
- now we allow volume, energy *and* number N to all change
- at equilibrium, i.e. at S_{max}, we have that $\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2}$
- we make another definition, for chemical potential:

Definition 6 **Chemical Potential (for any system)**:

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}.$$

  - at equilibrium, $\mu_1 = \mu_2$

- summary of conditions of thermal equilibrium below:



Allow Volume, Energy, and Number to all change...
At S_{max}

$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}$	$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}$	$\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2}$
$T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1}_{N,V}$	$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}$	$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$
$T_1 = T_2$	$P_1 = P_2$	$\mu_1 = \mu_2$
Temperature	Pressure	Chemical Potential

Figure 10. Summary of conditions of thermal equilibrium.

Subsection 11.3

Thermodynamic Identity

- from above, we have that

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN.$$

- but we defined:

$$T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1}_{N,V} \quad P = T\left(\frac{\partial S}{\partial V}\right)_{U,N} \quad \mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}.$$

- so we have

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN.$$

- solving for U :

Theorem 5 **Thermodynamic Identity for any system**: describes behaviour of systems in thermal equilibrium

$$dU = TdS - PdV + \mu dN.$$

  - this is the foundation for classical thermodynamics

- Chemcial Potential:
  - keep entropy and volume constant:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

    - chemical potential is the amount of energy you need to add when you add a particle, in order to keep the entropy constant
    - since chemical potential is usually negative, you need to take away energy when you add a particle

  - keep energy and volume constant:

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}.$$

    - chemical potential (divided by temperature) is the amount the entropy changes when you add a particle while keeping energy and volume constant
    - since chemical potential is usually negative, entropy increases when adding particles
  - keep energy and entropy constant:

$$\frac{\mu}{P} = \left(\frac{\partial V}{\partial N}\right)_{U,S}.$$

    - chemical potential (divided by pressure) is the amount you must change the volume when you add a particle in order to keep the energy constant
    - since μ is generally negative, you have to decrease the volume when adding a particle

- can apply above methods for pressure and temperature as well

Section 12

Lecture 9 – Boltzmann Factors

- can we apply the thermodynamic identity to calculate cool things?

Subsection 12.1

Stellar Spectral Types

- atoms in star's atmosphere absorbs certain wavelengths of light
- why do hydrogen absorption lines disappear for cool stars?

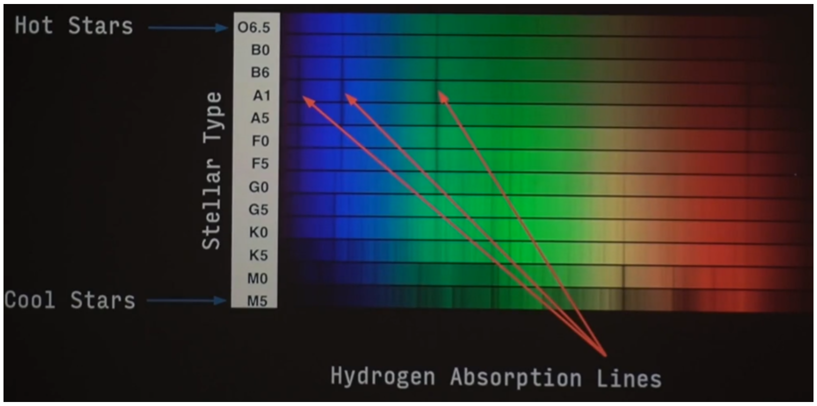


Figure 11. Absorption spectra for different star temperatures.

- these 3 absorption lines are from hydrogen transitions from $n = 2$ to $n > 2$
- transitions from $n = 1$ are in the UV

- the line strength depends on the number of hydrogen atoms starting in the $n = 2$ level
- since cooler stars are not as hot, there are less H atoms starting in the $n = 2$ level, therefore absorption lines are dimmer
- what is the probability that an atom will be in a particular $n = 2$ mode compared to a particular $n = 1$ mode? (call these s_1 and s_2)

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}.$$

- Ω_R is the multiplicity of the Sun's atmosphere (the reservoir) when the atom (the subsystem) is in state 2
- after some math, subbing in $S = k\ln(\Omega)$, and we only allow energy to flow ($dN = 0, dV = 0$), and using the thermodynamic identity, we obtain:

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}.$$

  - where $E(s)$ is the energy level of the subsystem in microstate s_2
  - T is temperature of reservoir
  - **Boltzmann Factor**: $e^{-E(s)/kT}$
- the probability of a given microstate s_i of a subsystem in equilibrium with a reservoir at temperature T :

$$P(s_i) = \frac{1}{Z}e^{-E(s_i)/kT}.$$

- Z is the **Partition Function** – the sum of the Boltzmann Factors of all possible microstates that the subsystem could ever be in:

$$Z = \sum_s e^{-E(s)/kT}.$$

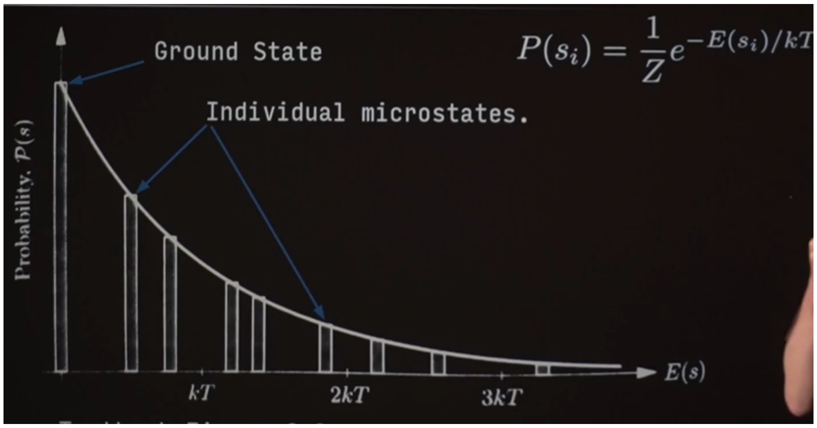


Figure 12. Plotting probability of being in a certain state. Increasing energy of subsystem means taking energy away from reservoir, which decreases the multiplicity of the reservoir, which decreases the entropy, therefore making it less likely (lower probability).

- there may be multiple microstates with the same energy, but each has the same probability
- multiplicity of $n = 1$ is 1, of $n = 2$ is 4, then

$$\frac{P(n=2)}{P(n=1)} = 4e^{-\Delta E/kT}.$$

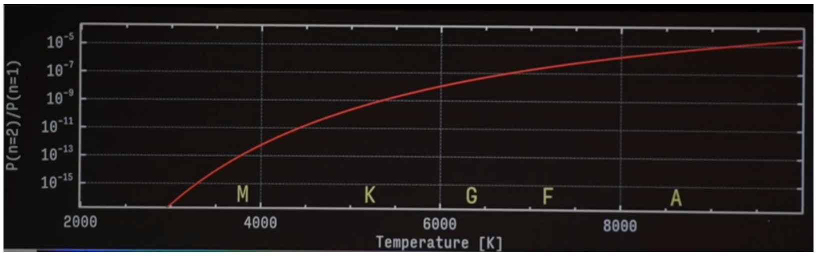


Figure 13. Plot of probability of $n = 2$ state vs $n = 1$ state (probability ratio).

- at low temperatures, the $n = 2$ level is insufficiently populated for hydrogen absorption lines to appear
- point is, this equation is crazy:

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}.$$

- basically, if you measure the temperature of something, you can predict the probability that a subsystem will be at a particular energy level, which is cool and a lot can be done with this
- **note: this is only applicable for fixed N and V**

SECTION 13

Lecture 10 – Average Values

- consider some parameter $X(s)$ that is a function only of the quantum-mechanical mode the subsystem is in (e.g. energy, angular momentum, quantum number, velocity, etc.), then its **average value** is

$$\overline{X} = \sum_s P(s)X(s) = \frac{1}{Z}\sum_s X(s)e^{-E(s)\beta}.$$

  where $\beta \equiv 1/kT$
- in particular, **average energy** $\overline{E}$ is

$$\overline{E} = \frac{1}{Z}\sum_s E(s)e^{-E(s)\beta}$$

some math…

$$= -\frac{1}{Z}\frac{\partial Z}{\partial \beta}.$$

- this can be used to predict a lot of complex behaviours (e.g. heat capacity) very accurately

SUBSECTION 13.1

Generalized Equipartition Theorem

- consider a quantum system where the energy levels are given by $E_n = Cn^m$ where $n = 0, 1, 2, \ldots, \infty$, and no degeneracy
- in this subsystem, keep the number of particles and volume fixed, then

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \text{ a lot of math\ldots } = \frac{kT}{m}.$$

Theorem 6 **Equipartition Theorem (no degeneracy)**: when $E_n = Cn^m$ with $n = 0, 1, 2, \ldots, \infty$, no degeneracy, and $C/kT \ll 1$, then average energy $\overline{E}$ is given by

$$\overline{E} = \frac{kT}{m}.$$

- now consider the same system, except there is degeneracy, and the number of modes is given by $N_s = Dn^a$

Theorem 7 **Equipartition Theorem (with degeneracy)**: when $E_n = Cn^b$ with $n = 0, 1, 2, \ldots, \infty$, $N_s = Dn^a$, and $C/kT \ll 1$, then average energy $\overline{E}$ is given by

$$\overline{E} = \frac{(a+1)kT}{b}.$$

SECTION 14

Lecture 11 – Maxwell Speed Distribution

- can we use Boltzmann factors to calculate the speed distribution of particles in an ideal gas?
- should be able to – Boltzmann factors can be used to calculate probability of finding a particle in a certain quantum mode
- we want to calculate $D(v)$, the probability density for the speed
- the molecule has *some* speed, so:

$$\int_0^\infty D(v)dv = 1.$$

- we also know that

$$D(v) \propto (\text{probability of being in a state with speed } v) \times (\text{density of states with speed } v)$$
$$D(v) \propto e^{-E(v)/kT} \times N(v)$$

- and since $N(v) \propto v^2$

$$D(v) \propto e^{-mv^2/2kT} \times v^2$$
$$D(v) = Cv^2 e^{-mv^2/2kT}.$$

where C is some constant

- subbing this into the integral and solving for C, we obtain this result for $D(v)$:

$$D(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}.$$

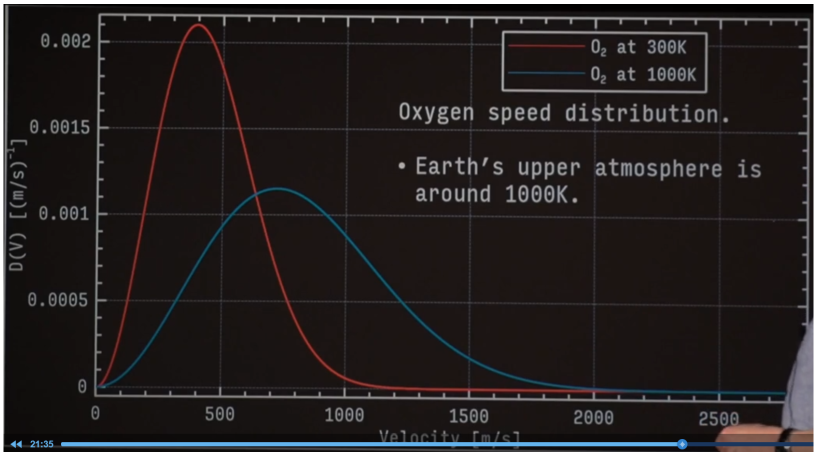


Figure 14. Maxwell speed distribution for oxygen at different temperatures.

- every planet has an escape velocity
- upper atmosphere of Earth is around 1000K – extremely tiny fraction of oxygen at this temperature is actually fast enough to escape compared to how much oxygen is on Earth
- helium at 1000K is faster and therefore our atmosphere has less helium
- cool thing: we can calculate atmospheric composition from Boltzmann statistics

SECTION 15

Lecture 12 – Free Energy

Recap:

- **Boltzmann Factor:** the probability that a subsystem is in a particular quantum mode s with energy E is proportional to

$$e^{-E(s)/kT}.$$

  - a subsystem where every possible quantum mode can be enumerated (e.g. molecules in a box) and we can list their degeneracies
  - subsystem is in equilibrium with some bath at temperature T

- the proportionality constant is $1/Z$ where Z is the **Partition Function** (sum of all Boltzmann factors):

$$Z = \sum_s e^{-E(s)/kT}.$$

- partition function can be used to calculate the average value of some quantity, notably the energy:

$$\overline{E} = \frac{1}{Z}\sum_s E(s)e^{-E(s)\beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$\beta \equiv \frac{1}{kT}.$$

- the partition function can do a lot more. . .

SUBSECTION 15.1

Partition Function for Combined Systems

- Distinguishable subsystems: imagine s_1 and s_2 represent the quantum states of two distinguishable non-interacting subsystems
  - for example: s_1 is the rotational mode and s_2 is the translational mode of a particle
  - another example: s_1 is translational mode for an O_2 molecule in a box and s_2 is the translational mode for an N_2 molecule the same box
- then

$$Z = Z_1 Z_2.$$

- more generally:

$$Z_{tot} = \prod_i Z_i.$$

- but what if they are indistinguishable?
- conisder two indistinguishable subsystems (eg. two He atoms in the same box):
- if we say that $Z = Z^2$ then we will have overcounted by a factor of $N!$ since for example $s_1 = 4, s_2 = 1$ represents the exact same state as $s_1 = 1, s_2 = 4$
- i.e. for indistinguishable subsystems:

$$Z_{tot} = \frac{Z_1^N}{N!}.$$

SUBSECTION 15.2

Helmholtz Free Energy

Definition 7 **Helmholtz Free Energy**:

$$F \equiv U - TS.$$

But also:

$$F = -kT \ln Z.$$

- F is a function of the partition function Z which can be calculated for quantum systems, which means that we can also determine F for quantum systems

- also, since $F \equiv U - TS$, we can use it to calculate S, P, and μ, which is huge:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

- **Steps to knowing stuff**:
  1. calculate Z
  2. from Z, calculate U, C_V, F, S, P, μ

SUBSECTION 15.3

Ideal Gases (again)

- first we calculate Z for 1 particle in a cubic box of length L
- can be separated into 3 distinguishable subsystems: translational, diatomic rotational, and diatomic vibrational modes $(Z_{tr}, Z_{rot}, Z_{vib})$
- since they are distinguishable:

$$Z_1 = Z_{tr} Z_{rot} Z_{vib} = Z_{tr} Z_{int}.$$

- now for N molecules, since they are indistinguishable:

$$Z_N = \frac{Z_{tr}^N Z_{int}^N}{N!}.$$

- we know that

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}.$$

- we can use this to calculate a bunch of things: from this we get

$$C_V = \frac{3}{2}Nk + \frac{\partial U_{int}}{\partial T}$$
$$P = \frac{kTN}{V} \quad \text{(ideal gas law)}.$$

- this is incredibly powerful – if we can enumerate the quantum modes for a subsystem, then we can calculate the partition function for it, and from this we can calculate a huge number of things
- note: this is assuming that the number of particles and volume stays constant
- so far, we've only looked at the partition function where energy can change but number of particles N is constant
- next: we look at the grand partition function where both energy and N can change

SECTION 16

Lecture 13 – Gibbs Factors

- when we let the number of particles N vary, we call it **Gibbs Factors** instead of Boltzmann factors

- but volume is still kept constant
- then we get

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-[E(s_2)-\mu N(s_2)]/kT}}{e^{-[E(s_1)-\mu N(s_1)]/kT}}.$$

- where the **Gibbs Factor** is

$$e^{-[E(s)-\mu N(s)]/kT}.$$

  - $E(s)$ is the energy level of the subsystem in microstate state s
  - N is the number of particles in the subsystem in microstate state s
- then the probability of a given microstate of a subsystem in equilibrium with a reservoir at temperature T is:

$$P(s) = \frac{1}{\mathcal{Z}} e^{-[E(s)-\mu N(s)]/kT}.$$

  where $\mathcal{Z}$ is the **Grand Partition Function**:

$$\mathcal{Z} = \sum_s e^{-[E(s)-\mu N(s)]/kT}.$$

- pretty much same as Boltzmann stuff except now we keep track of entropy change when number of particles change – therefore we have a μN term

Section 17

Lecture 14 – Degenerate Fermi Gas

- **Bosons vs Fermions**:
  - Fermions: only one particle allowed in a given quantum state (electrons, protons, neutrons, anything with spin half)
  - Bosons: no limit to number of particles allowed in a given quantum state (photons, pions, etc.)
- previously we said that for indistinguishable subsystems

$$Z_{tot} = \frac{Z_1^N}{N!}.$$

  but this is only true when $Z \gg N$
- since bosons can occupy the same quantum state, the number of allowed states will be greater than fermions, but this difference in number of allowed states becomes negligible when the total number of states is much larger than the number of particles
- how to deal with fermions when $Z \gg N$ is not true and whether or not the particles are bosons or fermions matters?
- instead of thinking about what quantum mode a particle is in, think about how many particles are in a certain quantum mode with $E = \epsilon$
- for fermions: $N = 0$ or $N = 1$

- so then the Gibbs Factors are:
  - for empty state ($N = 0, E = 0$): 1
  - for full state ($N = 1, E = \epsilon$): $e^{-[\epsilon-\mu]/kT}$
- grand partition function is sum of these factors: $\mathcal{Z} = 1 + e^{-[\epsilon-\mu]/kT}$
- and the probability that there will be 1 particle in this mode is

$$P(1) = \frac{1}{\mathcal{Z}} e^{-[\epsilon-\mu]/kT}.$$

- then if we want to find the average number of particles in this quantum mode:

$$\overline{n} = \sum_n P(n) = (0 \cdot P(0)) + (1 \cdot P(1)).$$

- simplifying, this gives us the average number of particles in the quantum mode (some value between 0 and 1):

$$\overline{n}_{FD} = \frac{1}{e^{(\epsilon-\mu)/kT} + 1}.$$

- plot of this function: the **Fermi Dirac Distribution Function**

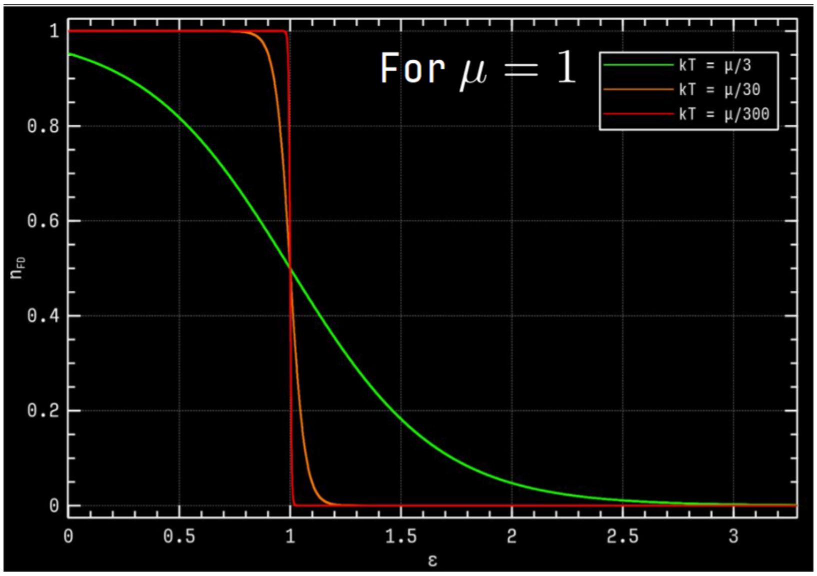


Figure 15. The Fermi Dirac Distribution.

- we see that at very low temperatures, there will pretty much always be a particle occupying a low energy state (below $\epsilon = \mu = \epsilon_F$) and the chance of a particle occupying an energy state higher than that is zero
- particles try to bunch up in low energy states
- but at higher temperatures, particles start to move to higher energy states and it begins to look more like a Boltzmann distribution

Subsection 17.1

Neutron Stars

- consider a gravitationally bound object made only of neutrons
  - gravity is holding it together
  - neutrons are uncharged so no electrostatic repulsion
  - neutrons are fermions
- how small does it get? Why doesn't it contract to zero size?
- after a bunch of math we find that:
  - pressure is given by

$$P = \frac{h^2}{20m}\left(\frac{3}{\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{5/3}.$$

  - notice that this is **not** the ideal gas law
    - it is a faster function of V and N and it is independent of T
    - the fermi energy ϵ_F of neutron stars are so high that even very hot neutron stars are essentially at zero temperature (hence independence of T) and the neutrons will try to bunch up in the lowest quantum mode
    - it is called the **Degeneracy Pressure** since it is only caused by the fact that neutrons are fermions (can't occupy same quantum mode) and it has nothing to do with electrostatic repulsion
  - we also find: radius decreases with neutron star mass
  - maximum velocity of the neutrons increases with the mass of the star, and as v_{max} approaches the speed of light, the neutron star becomes unstable since the degeneracy pressure can no longer hold it up and collapses into a black hole
  - neutron stars are typically have a radius of 11 km – they have more mass than the sun but are only around the size of a city
- point is: it's crazy how we can calculate so much about neutron stars only from statistics

Section 18

Lecture 15 – Blackbody Radiation

- previously we looked at how to deal with fermions when $Z \gg N$ is not true
- now: how to deal with bosons when $Z \gg N$ is not true?
- again we think about the number of particles in a particular quantum mode with $E = n\epsilon$ and $N = n$
- for bosons, n goes from 0 to ∞

- then, following the same logic that we did for fermions:

$$\text{Gibbs Factors:} \quad e^{-n(\epsilon-\mu)/kT}$$

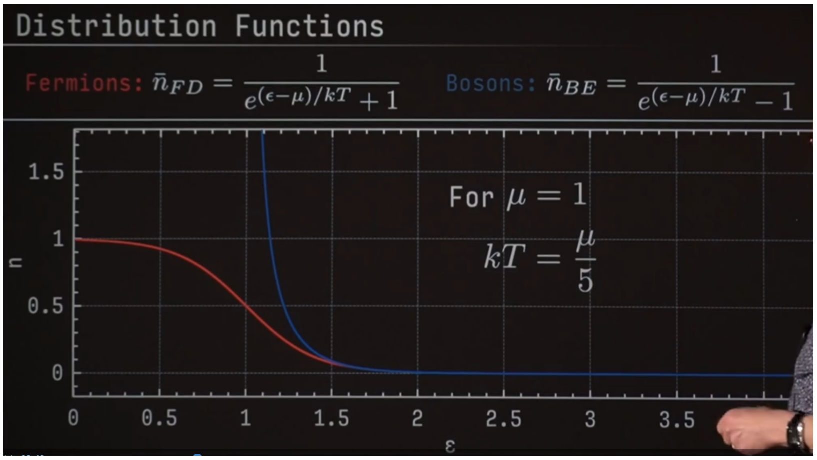
$$P(n) = \frac{1}{\mathcal{Z}} e^{-n(\epsilon-\mu)/kT}$$

$$\mathcal{Z} = \sum_{n=0}^{\infty} e^{-n(\epsilon-\mu)/kT} = \frac{1}{1-e^{-(\epsilon-\mu)/kT}}$$

$$\overline{n} = \sum_{n=0}^{\infty} nP(n) = \frac{1}{e^{(\epsilon-\mu)/kT}-1}.$$

  where the average number of particles occupying a particular quantum mode is given by the **Bose-Einstein Distribution Function**:

$$\overline{n}_{BE} = \frac{1}{e^{(\epsilon-\mu)/kT}-1}.$$



Distribution Functions

Fermions: $\bar{n}_{FD} = \dfrac{1}{e^{(\epsilon-\mu)/kT}+1}$ Bosons: $\bar{n}_{BE} = \dfrac{1}{e^{(\epsilon-\mu)/kT}-1}$

For $\mu = 1$

$kT = \dfrac{\mu}{5}$

Figure 16. Bose-Einstein Distribution Function.

- we can see that instead of reaching a maximum of 1, the number of particles in a quantum mode goes to infinity as the energy decreases since all particles want and are able to occupy the lowest state

Subsection 18.1

Blackbodies

- all incident light is absorbed (none reflected)
- we care because we observe that hot things glow – why? how?
- can model a blackbody as a box with a tiny hole (hole is black)
- we want to find the energy of photons in the box
- we can first ignore the hole and calculate energy density in the box, then later put the hole back and look at what leaks out
- our strategy:

1. Find the energy levels E_s of all photons that could be in the box (listing all quantum modes)
2. Find the occupancy $\overline{n}_s$ for these energy levels (find how many photons are in each quantum mode)
3. $U = \sum_s E_s \overline{n}_s$: add it all up

Step 1: Find the energy levels of photons in box

- there are standing waves in the box
- energy is given by

$$E = |\boldsymbol{p}|c = \frac{jhc}{2L}$$

where

$$j = \sqrt{j_x^2 + j_y^2 + j_z^2}.$$

Step 2: Find $\overline{n}$ per mode

- on average, how many photons are in each mode? i.e. what is the occupancy?
- photons are bosons so $\overline{n}$ is given by the formula for $\overline{n}_{BE}$
- we know ϵ, but what is μ for a photon?
- μ for a photon is given by

$$\mu_{\text{photon}} = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}.$$

  - T is the temperature of the reservoir (walls of the box)
  - ∂S is change in entropy of the reservoir
- recall: photons are not conserved, so if you keep the reservoir's energy constant, the reservoir's entropy doesn't change at all when you add a photon to the subsystem (reservoir = walls of the box), therefore:

$$\mu_{photon} = 0.$$

  - doesn't cost anything in terms of entropy to create another photon – they're "free"
- now we know μ_{photon}, so the occupancy for a certain wavelength is:

$$\overline{n}_\lambda = \frac{1}{e^{\epsilon/kT} - 1}.$$

where ϵ is the energy E of the wavelength we found in Step 1

Step 3: Find total energy, U

- we use $U = \sum_s E\overline{n}$
- we can assume that size of the box and temperature is large, so we can replace sums with integrals

$$U = \int_0^\infty \frac{8\pi L^3 \epsilon^3}{(hc)^3 (e^{\epsilon/kT} - 1)} d\epsilon.$$

- note that $V = L^3$, so the energy density of photons in an enclosed box of uniform wall temperature T is

$$\frac{U}{V} = \int_0^\infty \frac{8\pi\epsilon^3}{(hc)^3(e^{\epsilon/kT} - 1)} d\epsilon.$$

- then the energy density per energy band of photons is

$$u = \frac{d(U/V)}{d\epsilon} = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}.$$

- plotting this:

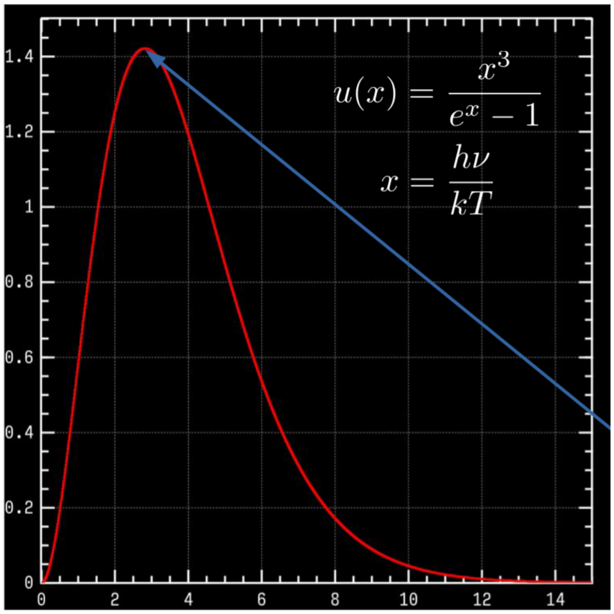


Figure 17. Plot of u.

- frequency of light inside the box takes that shape and peaks at $\nu_{peak} \approx 2.82kT/h$

- so as T increases the curve shift right, as T decreases the curve shifts left

- evaluating the integral for the total energy density, we get

$$\frac{U}{V} = \frac{8\pi^5 k^4}{15(hc)^3} T^4.$$

Letting Light Out

- now we poke a hole in the box and see how much energy escapes

- after a lot of math, we find that the amount of energy that escapes in time dt is

$$E_{esc} = \frac{A}{4}\frac{U}{V} c dt.$$

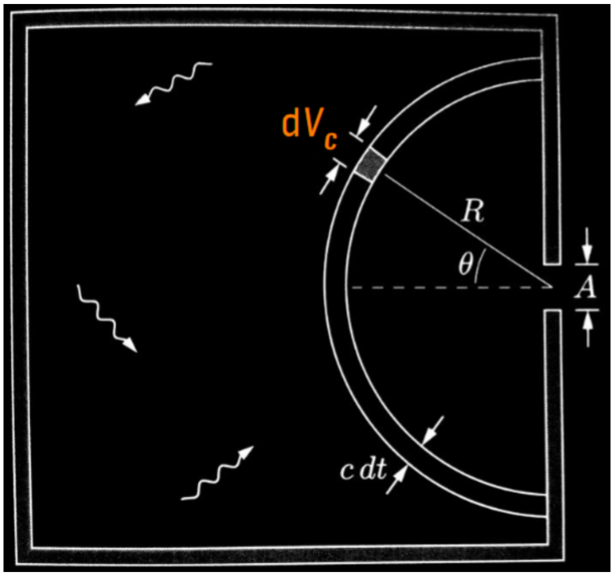


Figure 18. Setup for huge amounts of math that is skipped in these notes lol.

- then power is

$$P = \frac{E_{esc}}{dt} = c\frac{A}{4}\frac{U}{V}.$$

- and so the power that escapes per unit area of the hole is given by:

$$\frac{P}{A} = \frac{c}{4}\frac{U}{V} = \frac{2\pi^5 k^4}{15h^3c^2}T^4 = \sigma T^4.$$

- this is true for any black object (not just a hole in a box)
- this doesn't account for reflective things though – they behave differently

Subsection 18.2

Cool Applications in Astrophysics

- consider the universe
- the further away we look in the universe, the farther back in time we look
- the universe is expanding and cooling and is now transparent, but a long time ago, it was very hot and filled with plasma (blackbody) and was opaque
- if we look far enough, we should be able to see what the universe looked like when it was filled with opaque plasma
- the plasma is moving away from us at very close to the speed of light
- instead of seeing visible light, the light from the plasma has been doppler shifted down to the microwave region
- this is what we call the **Cosmic Microwave Background**
- we have measured the spectrum coming from the night sky, and we see that it has the exact same spectrum as a blackbody curve – nearly zero error

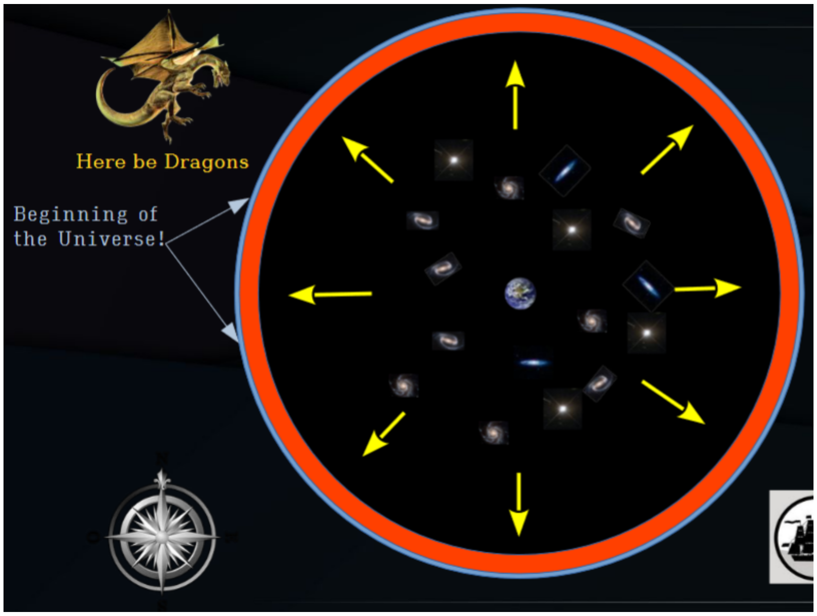


Figure 19. The universe (not to scale lol).

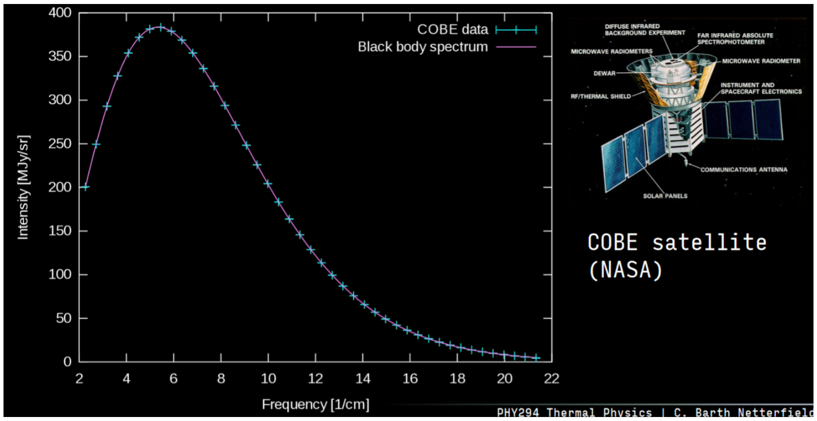


Figure 20. Spectrum of the Cosmic Microwave Background.

- point is: blackbody radiation is extremely important – it was one of the huge proofs of quantum mechanics early on – and it's crazy how it can be calculated using statistics

Section 19

Lecture 16 – The Debye Theory

Subsection 19.1

Heat Capacity of a Metal

- recall that we can calculate heat capacity through

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

  where $U = \sum_s \epsilon_s \overline{n}$

- there are two ways to store energy in a metal:
  1. the conduction electrons form a fermi gas
  2. there are vibrational modes in the solid

- we first look at the heat capacity of the electrons by looking at the heat capacity of a fermi gas for $T > 0$:
  - we find that at low T, C_V is proportional to T:

$$C_V = \gamma T.$$

- we now look at heat capacity of vibrational modes:
  - we can model the vibrations as acoustic waves (instead of using an Einstein solid since the vibrations aren't independent of each other)
  - we define **phonons** as the acoustic modes in a solid:

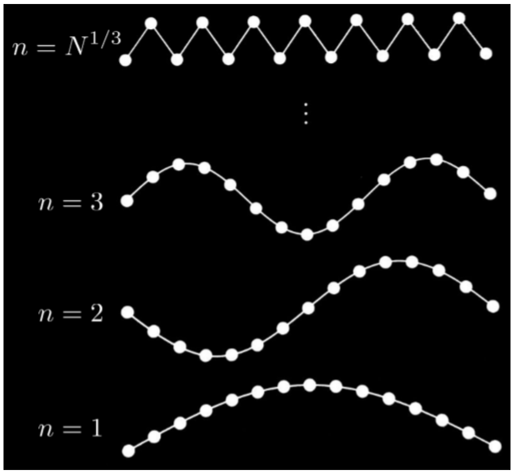


Figure 21. Phonons in a solid. Can think of them as the sound equivalent of photons.

  - phonons have 3 "polarizations" (directions of vibration)
  - after a lot of math and using the Debye approximation, we get that at low T, C_V is:

$$C_V = \frac{12\pi^4}{5}\left(\frac{T}{T_D}\right)^3 Nk.$$

- so at low temperatures:

$$C_V = \gamma T + \frac{12\pi^4 Nk}{5T_D^3}T^3.$$

where

$$T_D \equiv \frac{\epsilon_0}{k}\left(\frac{6N}{\pi}\right)^{\frac{1}{3}} = \frac{hc_s}{2Lk}\left(\frac{6N}{\pi}\right)^{\frac{1}{3}}.$$

is the Debye temperature – a function of the speed of sound and the size of the metal

- dividing through by T, we can rewrite the equation for heat capacity as

$$\frac{C_V}{T} = \gamma + \frac{12\pi^4 Nk}{5T_D^3}T^2.$$

- this tells us that plotting C_V/T for different materials with respect to T^2 should produce a straight line with an intercept of γ and a slope given by the coefficient of T^2, and it does:

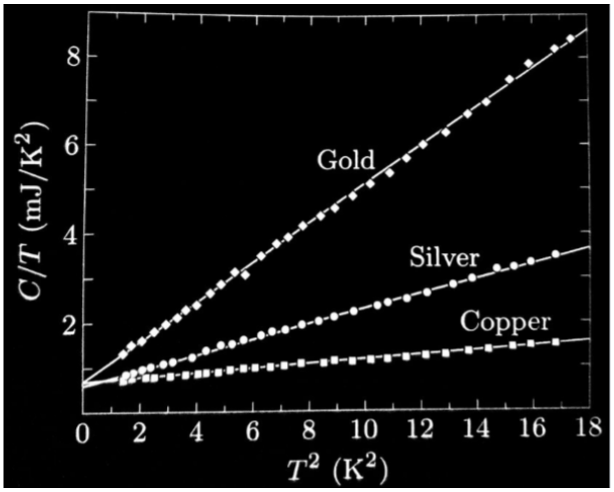


Figure 22. C_V/T vs T^2 for different metals.

SECTION 20

Lecture 17 – Bose Condensate

- previously we looked at fermions at low temperatures
- we now look at bosons at low temperatures
- as bosons, constrained to a small volume, are sufficiently cooled, they all end up in the ground state – called **Bose Condensate**
- consider a cold box of rubidium atoms (which are bosons)
- how many will be in the ground state?
- approach the problem by thinking about the occupancy of quantum modes (instead of the probability of a single particle being in a certain quantum mode)
- recall that the occupancy of a certain quantum mode is given by

$$\overline{n}_{BE} = \frac{1}{e^{(\epsilon-\mu)/kT} - 1}.$$

- so just find μ, plug it in, and find occupation
- example: for $N = 10000, T = 100$ nK, we get a numerical solution of $\mu = 2.56952 \times 10^{-32}$
- plugging μ into the formula for occupancy, we get that the occupancy of the ground state is 7206 – roughly 72% of the particles are in ground state
- this shows us that bose condensates should form – and they do!
- so for a quantum system:
  - don't think about particles moving around described by quantum mechanics
  - instead think about quantum modes that may or may not be occupied
  - N is conserved, but don't think of it as describing the number of 'objects', instead should be thought of as $N = \sum_s \overline{n}$
  - the existence of bose condensates (among other things) show that this way of thinking is correct