Lecture 1, Jan 9, 2023

Lecture 2, Jan 12, 2023

Lecture 3, Jan 13, 2023

The Hydrogen Atom

- Recall:
    - Properties of the hydrogen atom indicated quantum behaviour – Rydberg's equation
    - Bohr introduced a quantization condition that explained the Hydrogen spectral lines
    - de Broglie proposed that matter has wavelike properties
    - Schrödinger then came up with the wave equation that explained Bohr's quantization condition
    - To solve the hydrogen atom, we take it to spherical coordinates and separate $\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$
- Summary of the Hydrogen solution:
    - $\Psi(r, \theta, \phi) + R_n(r)\Theta_{lm}(\theta)\Phi_m(\Phi)$
    - $n = 1, 2, 3, \cdots$
    - $E = -\frac{E_R}{n^2}$
    - $l = 0, 1, 2, \cdots, n-1$
    - $m = 0, \pm 1, \pm 2, \cdots, \pm l$
    - The ground state is $n = 1, l = 0, m = 0$
    - Total angular momentum is $L = \sqrt{l(l+1)}\hbar$; $L_z = m\hbar$ is quantized just like Bohr assumed
        - Think about a vector of length $L = \sqrt{l(l+1)}$ being projected onto the z axis
        - l controls the total angular momentum; m controls how much of it is in the z axis

Lecture 4, Jan 16, 2023

Electron Spin

- The Zeeman effect: in the presence of a strong magnetic field, the spectral lines spread out
    - This is because of the angular momentum from $L_z = m\hbar$ generating a magnetic dipole; the applied magnetic field makes it so that the states with different spin are no longer degenerate
    - With an even stronger field the lines split again due to spin
    - Spin can be detected with electron spin resonance
- Spin quantum number is m_s, with possible values $\pm\frac{1}{2}$
- This allows 2 electrons to occupy the same atomic orbital

Lecture 5, Jan 19, 2023

Multi-Electron Systems

- For helium, we have the famed 2-body problem that cannot be solved due to the repulsion between the two electrons
- We can use an approximate solution: independent particle approximation: treat each electron as moving in a time-average potential defined by the other electron to define an effective potential
    - The electron will screen some of the positive charge but there will always be an effective charge of +1 or more
    - Assume a hydrogenic (central force) wavefunction ψ' for the two electrons, which gives us an average electron distribution, from which we can get an effective potential U'
        - i.e. assume a potential $U(r) = -Z_{eff}(r)\frac{ke^2}{r}$

        - The effects of other electrons are smeared out to be radially symmetric and expressed through the effective charge Z_{eff}
    - Solve for the first electron to define a new ψ', and repeat with the second electron
    - Repeat this until the calculated energy converges
- Variational theorem: the true wavefunction always gives the absolute minimum energy
    - This can be used to determine the effective charge Z_{eff} due to the screening
    - Make Z a parameter, use solution $\psi(\vec{r}_1, \vec{r}_2) = e^{-Z_{eff}(r_1+r_2)}$
    - Determine E in terms of Z_{eff}, and set $\dfrac{\mathrm{d}E}{\mathrm{d}Z_{eff}} = 0$ to find the effective charge that results in the minimum energy
- In a multi-electron atom, the energy levels are no longer degenerate and now it depends on the details of the solutions
- e.g. in the 2s orbital we have a little peak below the p orbitals (and the Bohr radius)
    - This makes it so that 2s and 2p are no longer degenerate
    - The 2s is more tightly held and so has a bigger effective charge
    - Energy depends on both n and l (but not m or m_s)

Pauli Exclusion Principle

- No two electrons in a quantum system can occupy the same state
- No two electrons can have the same quantum numbers, so n, l, m, m_s is a unique "quantum address"
- Hund's Rule: the mos stable electronic state within a degenerate set of orbitals is the state with maximum spin multiplicity (i.e. the one with the largest number of unpaired electron spins)

Lecture 6, Jan 20, 2023

Fermions and Bosons

- All electrons are identical, so you can't distinguish between them
    - Therefore a mathematically suitable wavefunction must reflect this
    - This is the reason for the Pauli exclusion principle
- Since probabilities are described by $|\Psi|^2$, physically we cannot distinguish between Ψ and $-\Psi$; i.e. if two wavefunctions represent the same quantum state, they must be related through a constant or phase only
    - Since we can't distinguish between two particles, this means that their combined wavefunction must be symmetric or antisymmetric under particle exchange
    - i.e. $\Psi(A, B) = \Psi(B, A)$ or $\Psi(B, A) = -\Psi(A, B)$
    - Particles for which $\Psi(A, B) = \Psi(B, A)$ are called *bosons* (e.g. photons); particles for which $\Psi(B, A) = -\Psi(A, B)$ are called *fermions* (e.g. electrons)
- Electrons are fermions which is why they obey the Pauli exclusion principle: no two electrons can occupy the same quantum state
    - Suppose that electrons A and B do occupy the same quantum state, then $\Psi(A, B) = \Psi(B, A)$
    - However since electrons are fermions we also have $\Psi(B, A) = -\Psi(A, B)$
    - Combining the two we get that $\Psi(A, B) = \Psi(B, A) = 0$, i.e. the probability of two electrons in the same quantum state is zero
- Suitable functions for the PEP must satisfy:
    - Be indistinguishable to electron exchange
    - Normalizable wavefunction
    - Have to include spin
    - Wavefunction must be antisymmetric to electron exchange

Lecture 7, Jan 23, 2023

Stability and Bonding

- Elements with a high Z_{eff} have higher electron affinity, and tend to form nonmetals (e.g. the halogens)
- When two atoms are brought near each other, the electron density builds up between them and screens the proton charge
    - When the two electrons are moving towards each other, the state has higher energy; this is an *antibonding* state
    - When they are moving away from each other, the state has lower energy; this is a *bonding* state
- We can solve the problem of one electron and two protons, which corresponds to the case of ${H_2}^+$
    - In the antibonding state electron density depletes in the centre due to the destructive interference, so the electrons are concentrated near the outside
        - The higher energy of the antibonding state tends to pull the molecule apart
    - In the bonding state electron density builds up in the centre; the electrons are concentrated near the centre
        - The bonding state has lower energy since the high electron density in the centre is closer to the protons
    - In the bonding state, there is a minimum in the energy as a function of the inter-proton distance, which facilitates bonding
- Both bonding and antibonding states are reflected by a superposition of atomic orbitals to form molecular orbitals (LCAO-MO)
    - The two ways we can superimpose the two hydrogenic wavefunctions are $\Psi^+ = \Psi_1 + \Psi_2$ and $\Psi^- = \Psi_1 - \Psi_2$
    - In the case of Ψ^+, the two wavefunctions are in phase, so in the middle between the two atoms they add constructively; this reflects the buildup in electron density that lowers the energy
    - In the case of Ψ^-, the two wavefunctions are out of phase so interfere destructively between the two atoms; this reflects the depletion in electron density that raises the energy
- When the overlap is spherically symmetric you get a σ bond (s orbitals)

Lecture 8, Jan 26, 2023

Lecture 9, Jan 30, 2023

Formation of Molecular Bonds

- When two atoms come together, the sign of the electron wavefunctions determine the phase of the electron movements
- When the wavefunctions have the same sign, the wavefunctions interfere constructively and electron density builds up between the two nuclei; this gives the bonding orbital
    - This represent the two electrons being in phase and so they are always staying far away from each other
- When the wavefunctions have different signs, the wavefunctions interfere destructively so electron density in the middle of the nuclei cancels; this gives the antibonding orbital
    - The electrons are out of phase so they feel stronger repulsion
- For every bonding orbital there is an equivalent antibonding orbital
- A *nonbonding* orbital has the constructive and destructive interference parts perfectly cancel out
- The *orbital overlap* $\langle\psi_1|\psi_2\rangle = S_{ab} = S_{ba}$ is the extent to which the two orbitals overlap in space
    - If the two orbitals are orthogonal, they have zero overlap
- When two atoms are brought together, these bonding/antibonding/nonbonding orbitals are created
    - These are shown as states that are lower/higher energy than the original orbitals
    - A nonbonding orbital would be a lone pair
    - Antibonding orbitals are denoted by a star
    - Molecular orbitals are often symmetric; they are denoted g (gerade, even) if they are identical

under inversion, or u (odd) if they change sign
- The bond order is defined as the number of electrons in bonding orbitals minus the electrons in antibonding orbitals, divided by 2
  - A bond order of 0 or less cannot exist, e.g. He_2 does not exist because it would have a bond order of $\frac{2-2}{2} = 0$
- In the period 2 elements, the additional states create more molecular orbitals
  - In period 2 there are 8 orbitals (4 pairings of atomic orbitals, times 2 for bonding/antibonding)

Lecture 10, Feb 2, 2022

Heteronuclear Diatomic Orbitals

- When two atoms come together with different energies in the orbitals, the electrons in the molecular orbitals will be closer to the one with the lower energy
  - Electron density is greater in the negative ion (lower energy) side
- When the difference in energy is very large, the filled orbital on the negative ion has the same energy as the atomic orbital
- Atomic orbitals most effectively overlap to form molecular orbitals when:
  1. Shapes are conductive to good overlap – symmetry
  2. Their energies are similar in the separated atoms
- Electronegativity difference χ between a pair of atoms in a bond defines the unbalanced electron sharing or formation of a polar bond
  - $|\chi_A - \chi_B| = \sqrt{D_{AB} - (D_{A_2} D_{B_2})^{\frac{1}{2}}}$
  - Normalized so that fluorine is 4
- $\Delta\chi > 1.8$ is ionic; $\Delta\chi < 0.6$ is covalent; in between is polar covalent
- With polar covalent bonds, the bonds have a dipole; the vector sum of the all the bond dipoles is the overall molecular dipole
  - The dipole moment $\mu = qr$ where r is the distance between charges and q is the magnitude of charge separation

Hybridization

- Add together the s orbitals and p orbital wavefunctions to create hybridized orbitals in order to follow VSEPR shapes
- Examples:
  - Tetrahedral: NH_4
    - Nitrogen has valence shell electron configuration $2s^2 2p^3$
    - 1 electron from the s shell gets promoted into the same energy as a p shell, and then the s shell and 3 p shells hybridize to form sp^3 orbitals
    - The sp^3 orbitals have 4 symmetric lobes arranged in a tetrahedral pattern; each lobe will have 1 electron in it, which can σ bond with the s shell in the hydrogen
  - Linear: CO_2
    - The middle carbon forms sp hybrid orbitals, with 2 symmetric lobes arrange linearly
    - The 2 lobes from the sp orbitals σ bond with the p orbitals in the oxygen atoms
    - The remaining 2 p unhybridized orbitals form π bonds with the p orbitals in the hydrogen atoms

Lecture 11, Feb 3, 2022

Correspondence Principle

- Quantum effects are important when de Broglie wavelength is comparable to the spacial scale of the phenomenon

  - The phase of wavefunctions also need to be conserved – if the time scale of action is comparable to quantum decoherence then quantum effects are important
  - Important for quantum computers
- The core of quantum mechanics is the quantization of energy given as ΔE
  - The classical limit is defined as $\Delta E \ll kT$
  - In this limit thermal collisions blur out any resemblance of a wave and the system behaves classically
- The correspondence principle states that there is a continuous bridge from discrete quantized resonance conditions of the quantum world to the continuum variables of classical mechanics
  - e.g. for the infinite potential well $E = \dfrac{h^2 n^2}{8mL^2}$, if L or m are on the classical scale, then E is extremely small and energy approaches a continuum
- Example: Protein motion
  - Functionally relevant motions of proteins are on the scale of 1 to 10 angstroms
  - de Broglie wavelength calc be calculated using the mass and thermal velocity, and turns out to be $1.8 \times 10^{-13}\,\mathrm{m}$
  - This is much smaller than an atom so the system is not quantum

Long Range Intermolecular Forces

- Ionic bonds, covalent bonds, metallic bonds
- Metallic bonds are covalent bonding with different degrees of ionic character
  - Metals typically involve 3d or higher valence orbitals
  - This creates an electronic continuum and facilitates conduction

Short Range Intermolecular Forces

- Ion Coulombic dipole coupling: polar molecule with a permanent dipole moment interact with ions
  - Dipole moments result from large differences in electronegativities between bonded atoms
  - Potential function on the order of $\dfrac{1}{r^6}$
  - Bonding from 40-600 kJ/mol
  - e.g. dissolving a sodium ion in water perturbs 80 water molecules
- The hydrogen bond
  - Hydrogen bonds to oxygen, nitrogen or fluorine
  - The high specificity of this force imposes directions on biological molecules
  - Hydrogen bonds encode information in DNA, provide protein building sites, nucleation sites, etc
  - Also on the order of $\dfrac{1}{r^6}$
  - Bond energies of 10-40 kJ/mol
- Dipole-dipole interactions
  - Same physics as hydrogen bonds but 2 to 8 times weaker
  - Bond orders of 5-25 kJ/mol
  - Also on the order of $\dfrac{1}{r^6}$ for potentials
- Ion induced dipole interactions
  - Ions polarize an otherwise neutral atom, creating a dipole
  - Only occurs when the ion is in close proximity
  - Oxygen transport uses this to bind oxygen to ion in heme proteins
  - 3-15 kJ/mol
  - Potential on the order of $\dfrac{1}{r^4}$
- Dipole-induced dipole interaction
  - Even weaker, works the same
- Induced dipole-induced dipole: van der Waals force (aka dispersion or London forces)
  - Spontaneous movement of charges create temporary dipoles that induce more dipoles
  - Occurs when all molecules are strictly nonpolar

    - Weakest force, but powerful in numbers

Lecture 12, Feb 6, 2023

Hydrogen Bonds

- Hydrogen atoms are bonded to oxygen, nitrogen or fluorine
    - The hydrogen is partially positive; the other atom is partially negative due to electronegativity differences
    - Chlorine does not form hydrogen bonds because it's screened due to ionic bonding
- This force imposes directions on biological molecules
- Typically denoted with a hashed line
- Only a hydrogen bonded to oxygen, nitrogen or fluorine can hydrogen bond
- Carbon doesn't form hydrogen bonds because its typical high valence of 4 contributes to more screening
- Hydrogen bonds give water special properties:
    - higher boiling point and melting point relative to its degree of hydrogen bonding
    - Higher density in liquid phase and anomalous negative thermal expansion
    - High heat of fusion and heat of vaporization
    - High specific heat – drives the Gaia effect
    - High dielectric constant (critical to hydrogen transfer)
    - Anomalous long-range correlations in its liquid structure
    - Anomalous high surface tension, yet low bulk viscosity
        - This is due to the fluctuation of hydrogen bonds
- Water has the most hydrogen bonding per unit mass than anything else – why is it a liquid at room temperature with such low viscosity?

Lecture 13, Feb 9, 2023

Unique Properties of Water and Hydrogen Bonds

- Water's hydrogen bond network imposes a minimum volume constraint to drive hydrophobic collapse
    - This forces minimum volume constraints on structures like proteins and drives folding
    - Like how oil forms a sphere in water, but not in hexane
- Hydrogen bonds connect long range forces and makes it flexible so it can flow
- Levinthal's Paradox: Given the astronomical number of permutations, how can proteins find their biological structures?
    - For every amino acid linkage there's 3 degenerate orientations, so even just with that there's 3^{100} permutations or 10^{47}
    - Even sampling one orientation every 10^{-13} seconds (fastest possible) this would take longer than the age of the universe
    - Yet proteins fold on the order of micro to milliseconds
    - Solution: inherent correlations involved in the fluctuations; the assumption that all degrees of freedom are independent is wrong
    - Analogy: What is the optimal strategy to find a parking lot?
        - You instructively try to look further out to see more of the lot at once
        - In this analogy correlated actions are analogous to seeing more of the lot

Lecture 14, Feb 10, 2023

Molecular Spectroscopy

- Why does a molecule or atom absorb light?
    - The incoming photon is an electromagnetic wave, which moves the electron

  - This physically distorts the electron density and changes it into the shape of another stable configuration, e.g. 2s to 2p
- Spectroscopy measures emission wavelengths
  - The spectrum has a finite width which comes from the uncertainty principle, $\Delta E \Delta t \geq \frac{\hbar}{2}$ where Δt is the lifetime of the excitation
  - There is also a fundamental line resolution (distance between lines)
- Selection rules exist to determine whether transitions can take place – not all transitions happen
  - Transitions are either allowed (high probability) or forbidden (low probability)
  - Not a hard yes or no but probabilistic
- The dipole moment μ in an atom creates a potential difference when an electric field (photon) comes along $U = \mu E$
- The expectation value for the electric field to create a dipole moment via the mixing of electron distributions from the ground and excited states is only nonzero when we have a symmetry
  - Example: from an s orbital to p orbital involves a change in symmetry, so the transition is allowed (symmetry allowed); from 1s to 2s has no change in symmetry so it's not allowed (symmetry forbidden)
  - The change in l is always ± 1
  - There must be no spin multiplicity: $\Delta S = 0$

Lecture 15, Feb 13, 2023

Absorption of Photons

- The probability of absorption of a photon by a molecule depends on the dipole strength $D_{0A} = \|\vec{\mu}_{0A}\|^2$ where 0 is the ground state and A is the excited singlet state
- Beer's law: $\frac{I(\lambda)}{I_0(\lambda)} = e^{-\varepsilon(\lambda)Cb}$
  - Exponential decay of transmitted light intensity
  - C is the amount of material (concentration)
  - b is the path length
  - ε is the molar absorptivity (absorption strength)

Vibrational Energies

- Harmonic oscillator is a very good approximation for the potential
- The true potential is the Morse potential
- Molecules have dipole moments, which allows absorption of electromagnetic radiation
  - $\frac{\mathrm{d}\mu}{\mathrm{d}r} > 0$, i.e. the electric dipole must change with bond length during a vibration
  - This is why oxygen and nitrogen gas don't cause climate change but water vapour does
    - Carbon dioxide is normally linear, but when it vibrates there is a dipole
  - Vibrational energies are close together so the transitions are infrared
- Due to the deviation between the real potential and the harmonic oscillator, this gives it antiharmonic character which allows energy redistribution
- Example: water
  - 3 normal modes of vibrations (9 DoF from each atom - 3 translation - 3 rotation, to put it in molecular frame)
  - all 3 have dipole moments, so they are all IR active, making it a very good infrared absorber
- Quantum harmonic oscillator: $U = \frac{1}{2}kx^2$
  - Boundary conditions: symmetry, and approaches zero for $x \to \infty$
  - Solution has energies given by $E = \frac{1}{2}(n+1)h\nu$
  - This has a zero point energy of $\frac{1}{2}h\nu$ – even at 0 kelvin, atoms are still moving

    - This is due to the uncertainty relation
  - Energies are equally spaced, unlike the particle in a box
  - The actual wavefunctions are given by $\psi_n(x) = N_n e^{-\beta^2 x^2/2} H_n(\beta x)$, where n is an integer quantum number, $\beta = \sqrt{\frac{mv}{h}}$, and H_n are the *Hermite polynomials*

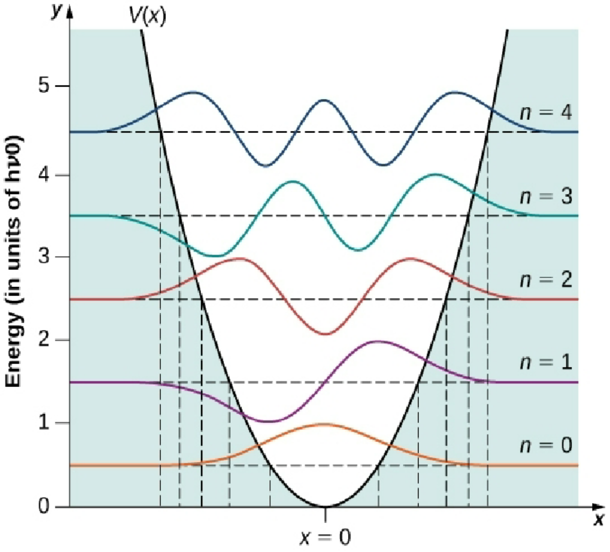

Figure 1: Shapes and energies of the quantum harmonic oscillator solutions

Lecture 16, Feb 16, 2023

IR Spectroscopy

- With infrared light we can see the vibrational motion of atoms in a bond
- A vibrating molecule behaves like two masses joined by a spring
- The potential is $U = \frac{1}{2}kx^2$
  - k is the force constant related to the bond strength – double and triple bonds are stronger and have larger k
  - The same resonant frequency works also in the quantum case
- In a real molecular bond the potential differs, giving it an *anharmonic character*: $E = \left(v + \frac{1}{2}\right)h\nu - x\left(v + \frac{1}{2}\right)^2 h\nu$
  - This allows the states which are otherwise stationary to move
  - The deviation from the harmonic oscillator potential makes different modes coupled which allows for energy transfer
  - $\Delta v = \pm 1$
- Using the absorbance spectrum we can figure out what bonds and structures exist in an atom
  - The width of the lines tell you the lifetime, which comes from the Heisenberg uncertainty principle
- To calculate the number of vibrational modes:
  - Each atom has 3 degrees of freedom
  - For a nonlinear molecule subtract 6 degrees (3 translational + 3 rotational of the base atom)
  - For a linear molecule subtract 5 degrees (3 translational + 2 rotational of the base atom)
- Spin multiplicity selection rule: $\Delta S = 0$

Transitions of an Excited Molecule

- When a vibration is excited, it first undergoes internal conversions (between vibrations), and then falls down back to the ground state via fluorescence from the bottom level
  - With high energy the vibrational energy levels are a lot closer together so energy transition happens very quickly
- The triplet is lower in energy than the singlet (Hund's rule)
  - A singlet state is when an electron undergoes a transition and ends up with opposite spin with another lone electron
  - A triplet state is where both are spin up or down
  - The triplet is always lower energy than the singlet state by Hund's rule
  - Singlet states can flip to the triplet through intersystem crossing, due to the orbital angular motion generating a magnetic field
- Radiative transitions are when photons are absorbed or emitted; non-radiative transitions are when energy is transferred between states in a molecule or to the surroundings (internal conversion)

Lecture 17, Feb 17, 2023

Combining Electronic and Vibrational Spectra

- The electronic transition happens much faster than nuclear motion; so this limits where we can land on the upper state
  - This is a vertical transition
  - The favoured transitions are to vibrational states that have the same probabilities before and after the transition (there is more overlap)
  - In the excited state there is a slight distortion; the atoms move further apart because they are higher energy, and electron density between atoms is depleted

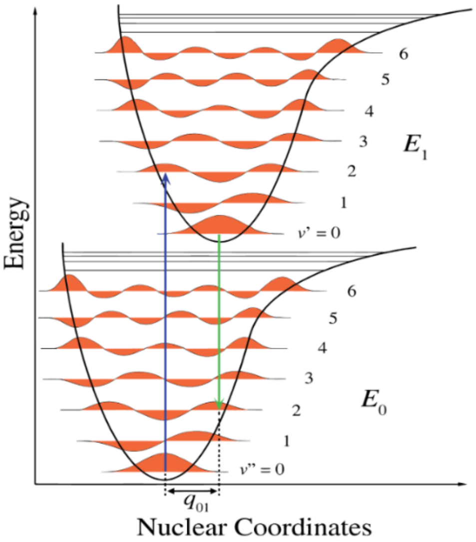

Figure 2: Overlap between vibrational wavefunctions decides transition probability

- After the electronic transition, internal transitions happen between vibrational states
  - This happens very fast because there are a lot of vibrational motions
- After falling to the vibrational ground state, it then falls back down the electronic transition and emits a photon (fluorescence)
  - This transition probabilities is determined in the same way as going up
- Phosphorescence happens after inter system crossing

    - This is much weaker because it's less likely, but it's longer lived
    - e.g. old CRT monitors
- The spectrum of an atom is a sharp line, for a diatomic atom there are multiple lines that begin to merge together, and for a polyatomic atom the lines completely merge together
- As proteins unfold, their spectrum shape changes – we can watch DNA unfold in transcription in real time using this

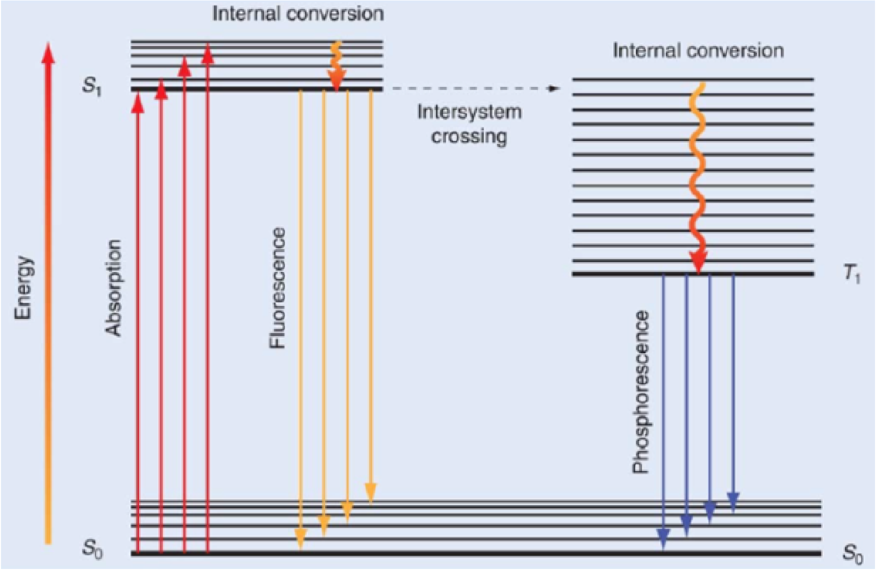

Figure 3: Summary of possible transitions for excited molecules

Lecture 18 (2-1), Feb 27, 2023

Overview of Thermal Physics

- Systems of particles typically exhibit *universal* behaviour: behaviour that applies to all systems, regardless of composition
- e.g. speed of particles in any gas that isn't too cold or too dense follows a Maxwell-Boltzmann speed distribution $n(v) \propto ve^{-kv^2}$ in 2D, $n(v) \propto v^2 e^{-kv^2}$ in 3D
- Statistical mechanics forms an "explanation" of thermodynamics, providing a bridge between the microscopic and the macroscopic, through the main postulate of SM
- What do we need to describe a system of N particles microscopically?
    - This gives the most detailed description
    - In classical mechanics we would have $\vec{r}_i(t), \dot{\vec{r}}_i(t)$ for $i = 1, \cdots, N$
    - For large N (on the order of 10^{23}) this would be hopeless to compute and useless to interpret
- To describe them macroscopically instead we use:
    1. The number of particles N
    2. The volume V
    3. The pressure p
    4. The temperature T
- Statistical mechanics connects these two
- Note both thermodynamics and statistically mechanics deal with systems in thermodynamic equilibrium:
    1. The system is uniform throughout its volume (density, pressure, temperature)
    2. These properties do not change in time
    3. No macroscopic fluxes – on average the net flow through any surface is zero
- Ideal classical gases have many particles, can be treated as point like objects classically and obeys the ideal gas law $pV = NkT$ where k is the Boltzmann constant $k = 1.38 \times 10^{-23}$ J/K

Lecture 19 (2-2), Mar 2, 2023

Temperature as a Measure of Average Kinetic Energy

- Several assumptions:
    - Molecules are uniformly distributed in space (at TD equilibrium)
    - Velocities are isotropically distributed (i.e. the number of particles with velocity in any given direction is the same)
        - This means $\frac{1}{N}\sum_{i=1}^{N} v_{xi} = 0$ since there are always the same number of particles going in the positive vs. negative directions
    - The major assumption of the molecular model: all molecules have the same average speed in time
        - Let $\frac{1}{N}\sum_{i=1}^{N} v_{xi}^2 = \bar{v}^2$
        - For now we assume all molecules move with the same speed that is the average
- Consider one wall with area A; what is the average force exerted on the wall due to the molecules?
    - How many molecules collide with the wall in time Δt?
        - Consider a volume formed by extending the area A a distance L into the gas, where $L = \bar{v}\Delta t$
        - Assume all molecules in the volume are moving either in the $+x$ or $-x$ directions (by isotropy this means each would have half the molecules)
            - We can integrate over solid angles if we don't make this assumption, but the conclusion is the same
            - Combined with the speed, this means all molecules in the box that are moving in the $+x$ direction would hit the wall, and no molecules outside the box will hit the wall (i.e. half of the molecules hit the wall)
        - Therefore the number of molecules that hit is $\frac{1}{2}\frac{N}{V}V = \frac{1}{2}\frac{N}{V}LA = \frac{1}{2}\frac{N}{V}\bar{v}\Delta t A$
    - What is the force caused by the collisions?
        - Each molecule has momentum $m\bar{v}$, which becomes $-m\bar{v}$ after colliding with the wall; therefore the total momentum transferred is $2m\bar{v}$
        - Total momentum transferred is then $\frac{N}{V}m\bar{v}^2\Delta t A$
        - Since $F = \frac{\mathrm{d}p}{\mathrm{d}t}$ the force is $\frac{N}{V}m\bar{v}^2 A$
    - Therefore the pressure produced by this is $m\bar{v}^2\frac{N}{V}$
- Bring in the ideal gas law: $p = kT\frac{N}{V} = m\bar{v}^2\frac{N}{V}$, we get the conclusion that $kT = m\bar{v}^2$
    - Therefore temperature is a measure of the kinetic energy
    - But note $\bar{v}$ is only in the x direction - what if we bring in the other directions?
    - With our isotropic assumption, we know that $\bar{v}$ is the same in any direction
    - Now consider $\overline{\vec{v}^2} = \frac{1}{N}\sum_i \|\vec{v}\|^2 = \frac{1}{N}\sum_i v_{xi}^2 + v_{yi}^2 + v_{zi}^2 = 3\bar{v}^2$
    - Therefore $kT = m\bar{v}^2 = \frac{1}{3}m\overline{\vec{v}^2} \implies \frac{1}{2}m\overline{\vec{v}^2} = \frac{3}{2}kT$
- $\overline{\vec{v}^2} = \frac{3kT}{m}$ let $v_{rms} = \sqrt{\overline{\vec{v}^2}} = \sqrt{\frac{3kT}{m}}$
    - If we plugin numbers for e.g. nitrogen, we get hundreds of meters per second
    - This is also roughly the speed of sound

Important

For an ideal gas, $\frac{3}{2}kT$ is the average kinetic energy of the molecules in the gas

Classical Equipartition Theorem

- T being a measure of average kinetic energy is an example of the classical equipartition theorem, which is proven using SM

Theorem

Classical equipartition theorem: In thermodynamic equilibrium of a classical ideal gas, the average energy per degree of freedom of a molecule is:

1. Translational: $\frac{1}{2}kT$
2. Rotational: $\frac{1}{2}kT$
3. Vibrational: kT

- Depending on the kind of molecule, we can calculate what degrees of freedom it has and how many, from which we can calculate the average energy from the temperature
- This allows us to predict the heat capacity of gases
  - Actual heat capacities deviated from the prediction of the classical equipartition theorem because of quantum mechanics
- e.g. For a diatomic molecule, each atom has 3 DoF; overall in the molecule there are 3 translational degrees of freedom of the CoM, and 2 rotational degrees of freedom, and 1 vibrational degree of freedom
  - Therefore the average energy is $\frac{3}{2}kT + \frac{2}{2}kT + kT = \frac{7}{2}kT$
  - $U = N\frac{7}{2}kT$
- The idea of the equipartition theorem is that through collisions energy is distributed into all degrees of freedom (translational, rotational and vibrational)
- The reason reality deviates from this is due to the quantized vibrational energies in $\hbar\omega$ (since vibrations are harmonic oscillators), so if a molecule doesn't have enough energy it can't transfer energy into the vibrational degrees of freedom
  - If $kT \gg \hbar\omega$ then this won't have much effect, but at much lower temperatures this becomes important

Lecture 20 (2-3), Mar 3, 2023

Equipartition Theorem Continued

- For an n-atom molecule, there is always $3n$ total degrees of freedom since there are 3 DoF for each atom
  - For linear and nonlinear molecules, CoM translation takes up 3 DoF
  - For nonlinear molecules, rotation takes up 3 DoF; for linear molecules rotation only take up 2 DoF because rotation around the axis of symmetry is not a degree of freedom
  - This leaves $3n - 6$ vibrational degrees of freedom for nonlinear molecules and $3n - 5$ for linear molecules
- This gives energy per molecule of $3\frac{kT}{2} + 2\frac{kT}{2} + 2(3n-5)\frac{kT}{2} = \frac{kT}{2}(6n-5)$ for a linear molecule and $\frac{kT}{2}(6n-6) = (3n-3)kT$ for a nonlinear molecule

Heat and Work

- For ideal gases energy is given by the equipartition theorem, equal to the number of particles times the energy of each particle
  - The ideal gas assumes the total energy is just the kinetic energy; this implies that the particles don't interact, because interactions would require potential energy
  - However interactions between particles is required for the gas to reach equilibrium

  - An ideal gas is a gas where there is just enough interaction to enable the gas to go to TD equilibrium, but interactions are rare enough that the ideal gas law holds
- How do we change the energy of a system?
  - We will use a diatomic molecule, $U = \frac{7}{2}kTN$
  - Consider putting a thermostat (a very large thermal body) with temperature T' in contact with a small body of temperature T; heat transfer will occur
  - After a while, the thermostat is removed, and now we have a system with temperature T'
  - The initial energy is $U_i = \frac{7}{2}NkT$, the final energy is $U_f = \frac{7}{2}NkT'$, which give a difference in energy of $\frac{7}{2}Nk(T' - T)$ which is the total heat absorbed
  - This is the first law of thermodynamics, $\Delta U = Q + W$ or energy conservation
- When we do work on the system, the particles that hit the wall will bounce back with greater velocity; this is why doing work on the system heats it up

Heat Capacity

Definition

The heat capacity is the amount of energy needed to change T by 1 degree

- However we have to specify which quantity we would like to keep fixed, whether that's V or p or something else
- We know $U = \frac{7}{2}NkT$ which gives a heat capacity of $\frac{7}{2}Nk$
- Heat capacity should stay constant with increasing T, but it does not – the constant only occurs around temperatures of 10000K
  - Below this temperature the heat capacity increases to discrete levels with increasing T
  - This is because of quantum mechanics
- At low temperatures there are only translational movements, then vibrational and transitional, and finally rotational, vibrational and translational at higher temperatures
  - At lower temperatures the collisions do not have enough energy to excite vibrational/rotational modes
  - Because of quantum mechanics, the molecules can either not rotate but rotate with some minimum energy

Lecture 21 (2-4), Mar 6, 2023

Discrepancy in Heat Capacity – Effect of Quantum Mechanics

- Based on quantum mechanics, can we estimate the energy where molecules have enough energy to excite rotations?
- Consider a hydrogen molecule: interatomic distance of $0.7 \times 10^{-10}\,\mathrm{m}$ and mass of $1 \times 10^{-27}\,\mathrm{kg}$
  - The momentum is $L = I\dot{\phi}$ classically, rotational energy is $\frac{1}{2}I\dot{\phi}^2 = \frac{L^2}{2I}$
  - Moment of inertial is given by $I \sim mr^2$
  - Angular momentum is quantized, we can consider it as either $L = 0$ for no rotation or $L \geq \hbar^2$ for some rotation
  - Therefore the minimum energy of rotation is $E \sim \frac{\hbar^2}{I}$
  - $I \sim 1 \times 10^{-27}\,\mathrm{kg}(0.7 \times 10^{-10}\,\mathrm{m})^2 = 1 \times 10^{-48}\,\mathrm{kg\,m^2}$
  - This gives the minimum energy on the order of $1 \times 10^{-20}\,\mathrm{J}$
  - If we compare this to kT, we get that a temperature on the order of 1000K is needed to have enough energy to excite rotations

First Law of Thermodynamics

- $\Delta U = Q + W$, where Q is the heat absorbed and W is the work done on the system
- Consider a piston of area A being pushed against a gas with pressure p, volume V for length $\mathrm{d}x$
  - $\mathrm{d}x$ is positive of the gas expands, negative if it contracts
  - The force is pA, therefore the work done by the gas is $pA\,\mathrm{d}x = p\,\mathrm{d}V$
  - Let $\mathrm{d}U = \delta Q - p\,\mathrm{d}V$, where δQ is some small amount of heat resulting from this
    - Note the sign on $p\,\mathrm{d}V$ since here it's the work done on the gas, not by the gas
  - This is the first law expressed in terms of infinitesimal changes

Isothermal Processes

Definition

A *quasistatic* process is one where the process is slow enough such that the system is in thermodynamic equilibrium for every moment of the process

- How do finite changes of V affect the state of the system?
  - We need to make assumptions about the nature of the change
  - This question is easy to answer if the process is *quasistatic*
    - In a non-quasistatic expansion we'll get a depletion of gas density near the piston as it moves, so the force it experiences will be less
    - Therefore the work done in a quasistatic expansion is strictly larger than the work in a non-quasistatic expansion
  - For such processes we can find the work done by $W = \int_{V_i}^{V_f} p(V, T)\,\mathrm{d}V$
    - If the temperature is constant (*isothermal* process), then $W = \int_{V_i}^{V_f} \frac{NkT}{V}\,\mathrm{d}V = NkT \ln\left(\frac{V_f}{V_i}\right)$
    - To keep the process as isothermal we need to keep it in contact with a thermal reservoir, and now the process must be slow enough that we get both pressure and temperature equilibrium
  - For an isothermal process $\Delta U = Q - NkT\ln\left(\frac{V_f}{V_i}\right)$, but since U is dependent only on T for an ideal gas, we must have $Q = NkT\ln\left(\frac{V_f}{V_i}\right)$
- For an isothermal process $pV = \mathit{const}$ so on a P-V diagram this shows up as a curve $P = \frac{C}{V}$
  - The area under this curve is the work done by the process

Lecture 22 (2-5), Mar 9, 2023

Adiabatic Processes

- In an adiabatic process there is no heat exchange between a system and its surroundings ($Q = 0$)
- Since there is no heat $\Delta U = -p\Delta V$ at every step
- From $U = \frac{f}{2}NkT$ (where $f = 3$ for monoatomic gases and $f = 7$ for diatomic gases) we have $\Delta U = \frac{f}{2}Nk\Delta T$ so $-p\Delta V = \frac{f}{2}Nk\Delta T$
- Bring in the ideal gas law $Nk\Delta T = \Delta(pV) = V\Delta p + p\Delta V$, combine with above $-p\Delta V = \frac{f}{2}(V\Delta p + p\Delta V)$
- $-\left(1 + \frac{f}{2}\right)p\Delta V = \frac{f}{2}V\Delta p \implies -\frac{1 + \frac{f}{2}}{\frac{f}{2}}\frac{\Delta V}{V} = \frac{\Delta p}{p} \implies \frac{2 + f}{f}\frac{\mathrm{d}V}{V} = \frac{\mathrm{d}p}{p}$
- $-\frac{2 + f}{f}\,\mathrm{d}\ln V = \mathrm{d}\ln p$, integrate to get $-\frac{2 + f}{f}\ln\frac{V_2}{V_1} = \ln\frac{p_2}{p_1}$

- Therefore $\left(\frac{V_1}{V_2}\right)^{\frac{2+f}{f}} = \frac{p_2}{p_1}$, or $V_1^{\frac{2+f}{f}} p_1 = V_2^{\frac{2+f}{f}} p_2$
  - This means $V_2^{\frac{2+f}{f}} p_2$ is a constant
  - $\frac{2+f}{f} = 1 + \frac{2}{f} = \gamma > 1$, which means that for the same pressure, the volume will be smaller; or for the same volume, the pressure will be smaller
  - The adiabatic curve on the P-V diagram falls steeper than the isotherm

Heat Capacities

- In general $C = \frac{Q}{\Delta T}$ is ill-defined because Q depends on the environment, i.e. how the gas is being heated
- If V is constant then $\Delta U = Q$ since there is no work; therefore we can define a constant volume heat capacity $C_v = \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$
  - For an ideal gas $U = \frac{f}{2}NkT$ so $C_V = \frac{f}{2}kN$
- If P is constant, Q and U have no straightforward relationship
  - $Q = \Delta U + p\Delta V$
  - $C_p = \left(\frac{\Delta U + p\Delta V}{\Delta V}\right)_p = \left(\frac{\Delta U}{\Delta T}\right)_p + p\left(\frac{\Delta V}{\Delta T}\right)_p$
  - $C_p = \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial V}{\partial T}\right)_p$ for any gas in general
  - For the ideal gas $\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V = \frac{f}{2}NkT$ are the same since energy only depends on the temperature
  - $\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial}{\partial T}\frac{NkT}{p}\right)_p = \frac{Nk}{p}$
  - Combing these we get $C_p = \frac{f}{2}Nk + Nk = \frac{f+2}{2}Nk = \frac{f+2}{2}C_v = \gamma C_v$
  - $C_p > C_v$ always holds true for any gas
    - For an ideal gas it is because some of the energy goes towards the expansion of the gas
    - This also works for everything else even if it contracts when being heated

Directional Asymmetry of Time

- e.g. heat only flows from hot to cold, diffusion only happens from dense to diffuse
- This is due to the randomness inherent to a system of many bodies
- There is one unifying principle, the fundamental postulate of statistical mechanics: Consider a closed (constant energy, isolated) system of many particles, in the system every accessible microstate is equally likely

Lecture 23 (2-6), Mar 10, 2023

Fundamental Postulate of Statistical Mechanics

- In an isolated gas of many particles ($N \sim 10^{23}$) there are many ways we can distribute a fixed amount of energy E amount the particles
  - Each of these ways the energy is distributed is a *microstate*; there are many such microstates
  - The total energy is a *macrostate*
- Collisions lead to a change in the way energy is distributed, leading to randomness
- The fundamental postulate of statistical mechanic says that all accessible microstate is equally likely

    - Accessible microstates are ones that have the right amount of total energy that matches a given macrostate
    - We give up the mechanistic description – it's impractical to know the trajectory of each particle
    - Instead we replace it with the probabilistic distribution
        - As N gets large, probabilities become certainties as probability distribution peaks become sharper
- The *multiplicity function* is the number of microstates accessible to a given macrostate
    - Once you have the multiplicity function of a system, you can deduce everything about the system

Electronic Paramagnet

- A material that has a macroscopic magnetic moment
- We'll model the microscopic magnetic moments as spins
    - The 2 degrees of freedom are the spins
    - $s_i = \{ +1, -1 \}$ for $i = 1, \cdots, N$
- We ignore spin-spin interaction, spin-atom interaction
    - Without these simplifications this would be extremely hard to solve
    - However without spin-spin interaction this system does not reach equilibrium
- In this N-spin system we have 2^N possible microstates
    - Microstates are discrete and finite – this is not always the case
- Motivation: If we put a magnet in a magnetic field, it has energy $U = -\mu \cdot \vec{B}$, which is minimized when the 2 vectors are aligned
    - Therefore $U_i = -\mu_0 B s_i$ so $U = -\mu_0 B \sum_{i=1}^{N} s_i = -\mu_0 BS$ where S is the total spin, the sum of the individual spins
- S is the macrostate, which can be observed macroscopically
    - S is an integer in the range $[-N, N]$, in increments of 2 (since flipping a spin changes the total spin by 2)
    - This gives us a total of $N + 1$ possible macrostates
        - Instead of talking about S, we just need to specify $N_\uparrow$ since $N_\downarrow = N - N_\uparrow$
        - $S = 2N_\uparrow - N$
        - There are $N + 1$ possible values of $N_\uparrow$ so there are $N + 1$ macrostates
    - U, S, $N_\uparrow$ can all be used equivalently to specify a macrostate
- For this system, the multiplicity function is easy to calculate
    - $\Omega(N_\uparrow, N) = \binom{N}{N_\uparrow} = \dfrac{N!}{(N - N_\uparrow)!N_\uparrow!}$

Lecture 24 (2-7), Mar 13, 2023

Einstein Solid

- Consider a collection of N particles, with each particle being in a fixed harmonic oscillator potential; each particle's potential is independent of other particles
- Recall the allowed energy levels are $\hbar\omega\left(n + \frac{1}{2}\right)$, so each particle is described by its energy level $n = 0, 1, 2, \cdots$
    - n is also called the number of *quanta* in the given state
- The overall energy of the system is $U = \hbar\omega \sum_{i=1}^{N} n_i + \frac{\hbar\omega}{2} N$
    - Note we will ignore the $\frac{1}{2}$ since it's only a constant offset that makes no difference
- This makes our microstate $\{ n_1, \cdots, n_N \}$ and our macrostate $q = \sum_{i=1}^{N} n_i$

    - Unlike in the electronic paramagnet, now we have a (countably) infinite number of microstates since n_i has no upper limit
    - This is much more realistic because in real systems there will be a small number of particles with a lot of energy (but the energy also can't be infinite)
- What is the multiplicity $\Omega(q, N)$?
    - If we think of each of the particles as a box, and q as the total number of balls (each ball is an energy unit), this becomes a partitioning problem of how many ways we can put q identical balls into N boxes
    - We can consider each "divider" between two partitions as an item, then each permutation of the dividers and the "balls" is one microstate; there are $N - 1$ dividers
    - However we can swap around the dividers and the balls and the microstate is the same, so we need to divide through by the number of ways to permute the dividers, and the ways to permute the balls
    - $\Omega(q, N) = \dfrac{(N - 1 + q)!}{(N - 1)!q!}$

Two Einstein Solids Together

- For a single system, by the postulate of SM, the probability of any accessible microstate given a macrostate q is $\dfrac{1}{\Omega(q, N)}$
- Consider bring together two Einstein solids with N_A, q_A and N_B, q_B, initially isolated from the world and each other, then brought into contact
    - We will allow for an unspecified processes to bring this system to TD equilibrium (however in our simple model this can never happen)
- The combined system will be a single system with $N = N_A + N_B, q = q_A + q_B$
    - In equilibrium the two systems still have number of particles N_A, N_B but the energy can flow; we don't know what the individual energies are, we just know $q'_A + q'_B = q = q_A + q_B$
    - In thermal equilibrium, what are the probabilities of different values of q'_A, q'_B occurring?
- In the combined system, all microstates are equally likely; for a given value of q'_A, what is the multiplicity?
    - The total multiplicity is $\Omega(q'_A, N_A)\Omega(q - q'_A, N_B)$, which is directly proportional to the probability of the macroscopic distribution q'_A since each microstate is equally likely
    - The key takeaway is that the more microstates correspond to a given distribution, the more likely that distribution is
    - It turns out that the distribution giving the largest value of $\Omega(q'_A, N_A)\Omega(q - q'_A, N_B)$ is when the energy is evenly divided so that the average energy per particle is the same in both solids
    - In the limit as $N \to \infty$, the probability distribution becomes delta functions

Lecture 25 (2-8), Mar 16, 2023

General Thermal Equilibrium – Statistical Definition of Temperature and Entropy

- We don't need to be restricted to the Einstein solid
- Consider a system 1 with energy E_1, system 2 with energy E_2, being brought together an allowed to reach thermal equilibrium (N, V are not exchanged)
- In TD the overall system has energy $E = E_1 + E_2$ with $E'_1 = \dfrac{E}{2} - \Delta$ distributed to the first system, $E'_2 = \dfrac{E}{2} + \Delta$ distributed to the second system
- The probability of having a particular Δ is $P(\Delta) = \dfrac{\Omega_1(\frac{E}{2} - \Delta)\Omega_2(\frac{E}{2} + \Delta)}{\sum_{\tilde{\Delta}=-E/2}^{E/2} \Omega_1(\frac{E}{2} - \tilde{\Delta})\Omega_2(\frac{E}{2} + \tilde{\Delta})}$
- We wish to find $\max\limits_{\Delta} P(\Delta)$
    - $\dfrac{\partial}{\partial \Delta}\Omega_1\left(\dfrac{E}{2} - \Delta\right)\Omega_2\left(\dfrac{E}{2} + \Delta\right) = 0$

  - $$\frac{\partial\Omega_1\left(\frac{E}{2}-\Delta\right)}{\partial\left(\frac{E}{2}-\Delta\right)}(-1)\Omega_2\left(\frac{E}{2}+\Delta\right)+\frac{\partial\Omega_2\left(\frac{E}{2}+\Delta\right)}{\partial\left(\frac{E}{2}+\Delta\right)}(1)\Omega_1\left(\frac{E}{2}-\Delta\right)=0$$
  - $$\frac{1}{\Omega_1\left(\frac{E}{2}-\Delta\right)}\frac{\partial\Omega_1\left(\frac{E}{2}-\Delta\right)}{\partial\left(\frac{E}{2}-\Delta\right)}=\frac{1}{\Omega_2\left(\frac{E}{2}+\Delta\right)}\frac{\partial\Omega_2\left(\frac{E}{2}+\Delta\right)}{\partial\left(\frac{E}{2}+\Delta\right)}$$
  - $$\frac{\partial}{\partial\left(\frac{E}{2}-\Delta\right)}\ln\Omega_1\left(\frac{E}{2}-\Delta\right)=\frac{\partial}{\partial\left(\frac{E}{2}+\Delta\right)}\ln\Omega_2\left(\frac{E}{2}+\Delta\right)$$
  - $$\frac{\partial}{\partial E_1'}k\ln\Omega_1(E_1')=\frac{\partial}{\partial E_2'}k\ln\Omega_2(E_2')$$
    - The left hand side is a property of system 1, the right hand side is a property of system 2
    - This means as two bodies are brought into contact, it will change until this quantity $\frac{\partial}{\partial E}k\ln\Omega(E)$ becomes the same for the two bodies
  - This leads us to define $\frac{\partial}{\partial E_1'}k\ln\Omega_1(E_1')=\frac{1}{T_1(E_2',N,V)}, \frac{\partial}{\partial E_2'}k\ln\Omega_2(E_2')=\frac{1}{T_2(E_2',N,V)}$
    - Temperature is a function of E, N, V
  - We can also define entropy as $k\ln\Omega(E)$; since the macrostate that has the largest multiplicity is the most likely, this means entropy will be maximized

Definition

The *entropy* of a system is defined as

$$S(E,N,V)=k\ln\Omega(E,N,V)$$

The *temperature* of a system is defined as

$$\frac{1}{T(E,N,V)}=\left(\frac{\partial S}{\partial E}\right)_{N,V}$$

- Since each macrostate must have $\Omega \geq 1$, we have $S \geq 0$
  - Consider the case of the electronic paramagnet, the state $N_\uparrow = N$ or $N_\uparrow = 0$ only have one microstate, so $\Omega = 1, S = 0$
    - This a very ordered system
  - If $N_\uparrow \sim \frac{N}{2}$ we have a lot of microstates, so we have $S \gg 1$; this is a disordered system
  - This is why entropy is sometimes referred to as the "degree of disorder"
    - In this case, "disorder" is how many microstates a macrostate can exist in
  - We can also consider entropy as the inverse of how much information you have: in the $N_\uparrow = N$ state we know exactly which microstate the system is in, but in the $N_\uparrow \sim \frac{N}{2}$ state there are many microstates that the system could be in, so we have very little information about the exact microstate
- Also notice $T \geq 0$ because $\frac{\partial S}{\partial E} \geq 0$ for most "normal" systems (note this is not true for the electronic paramagnet)
  - If you heat the system, energy is introduced so there are more ways to distribute the energy, therefore entropy should also increase

Lecture 26 (2-9), Mar 17, 2023

2 Einstein Solids

- The thermodynamic limit: in the limit as $N \to \infty, V \to \infty, E \to \infty$ (all extensive properties), but keeping the density and energy density $\frac{E}{N}, \frac{N}{V}$ fixed, the results of statistical mechanics become certainties instead of probabilistic

- Recall for the Einstein solid $E = \hbar\omega q, \Omega = \dfrac{(N-1+q)!}{(N-1)!q!}$
  - We keep $\dfrac{q}{N}$ fixed, but we could either have $\dfrac{q}{n} \ll 1$ or $\dfrac{q}{n} \gg 1$
- First consider the classical limit, where $\dfrac{q}{n} \gg 1$
  - For large N the multiplicity function just becomes $\dfrac{(N+q)!}{N!q!}$
  - $\ln\Omega = \ln(N+q)! - \ln N! - \ln q!$
  - Stirling approximation: $\ln n! \approx n\ln n$ for large n
  - $\ln\Omega \approx (N+q)\ln(N+q) - N\ln N - q\ln q = N\ln\left(q\left(1+\dfrac{N}{q}\right)\right) + q\ln\left(q\left(1+\dfrac{N}{q}\right)\right) - N\ln N - q\ln q$
  - $\ln\Omega = N\ln q + N\ln\left(1+\dfrac{N}{q}\right) + q\ln q + q\ln\left(1+\dfrac{N}{q}\right) - N\ln N - q\ln q$
  - $\ln\Omega \approx N\ln q + N\dfrac{N}{q} + N - N\ln N = N\ln q + N\ln e - N\ln N = \ln q^N + \ln e^N - \ln N^N$
  - $\ln\Omega = N\ln\dfrac{qe}{N}$ or equivalently $\Omega(q,N) = \left(\dfrac{qe}{N}\right)^N$
  - Entropy is $S = kN\ln\dfrac{qe}{N} = kN\ln\dfrac{Ee}{\hbar\omega N}$
  - $\dfrac{1}{T} = \dfrac{\partial S}{\partial E} = \dfrac{kN}{E}$ or $\dfrac{E}{N} = kT$
    - * This is equipartition!
  - Note the assumption that $\dfrac{q}{N} \gg 1 \implies kT \gg \hbar\omega$
- What about $\dfrac{q}{N} \ll 1$?
  - $\Omega(q,N) = \dfrac{(N+q)!}{N!q!}$ is symmetric with respect to switching q and N
  - This means we can do this case in exactly the same way just by swapping N and q
  - $\Omega = \left(\dfrac{Ne}{q}\right)^q$
  - $S = k\ln\left(\dfrac{Ne}{q}\right)^q = k\dfrac{E}{\hbar\omega}\ln\dfrac{Ne\hbar\omega}{E}$
  - $\dfrac{1}{T} = \dfrac{k}{\hbar\omega}\ln\left(\dfrac{N\hbar\omega}{E}\right)$
  - $\dfrac{E}{N} = \hbar\omega e^{-\frac{\hbar\omega}{kT}}$
    - * Equipartition does not hold
    - * If temperature is not enough to excite vibrational normal modes the energy per particle drops off exponentially

Distribution of Energies

- What is the probability of the energies of the system being different?
- Take two Einstein solids with the same N and flow
- $P(x) \sim \Omega_A\left(\dfrac{q}{2} - x\right)\Omega_B\left(\dfrac{q}{2} + x\right) = \left(\dfrac{\left(\frac{q}{2} - x\right)e}{N}\right)^N \left(\dfrac{\left(\frac{q}{2} + x\right)e}{N}\right)^N = \left(\dfrac{e^2}{N^2}\right)^N \left(\dfrac{q^2}{4} - x^2\right)^N$
- Take the ratio $\dfrac{P(x)}{P(0)} = \dfrac{\left(\frac{q^2}{4} - x^2\right)^N}{\left(\frac{q^2}{4}\right)^N} = \left(1 - \dfrac{qx^2}{q^2}\right)^N$
- $\ln\dfrac{P(x)}{P_0} = N\ln\left(1 - \left(\dfrac{x}{\frac{q}{2}}\right)^2\right)$

- $\frac{|x|}{\frac{q}{2}}$ is the relative energy balance
- Consider small energy balances, we can approximate it as $-N\left(\frac{x}{\frac{q}{2}}\right)^2$
- $P(x) = P_0 e^{-N\left(\frac{x}{\frac{q}{2}}\right)^2}$
- As $N \to \infty$, $P(x)$ becomes nonzero only at $x = 0$, making it a delta function, so the distribution of temperatures is now a certainty

Lecture 27 (2-10), Mar 20, 2023

Thermodynamic Potential

- The postulate directly implies that for a closed system that reaches thermodynamic equilibrium, it is most likely to find itself in a state of maximum S
- This can be seen as an alternative way to state the second law, that S is always increasing
- For an isolated system (constant E), we say that the entropy is the "thermodynamic potential"
    - Just like how a classical system tries to minimize its potential (e.g. a falling object), the system will try to maximize its entropy
    - Just like $\vec{F} = -\vec{\nabla}U$ is the driving force for a classical system, $\frac{1}{T} = \frac{\partial S}{\partial E}$ is the driving force for reaching thermal equilibrium
        - In equilibrium forces are in balance, just like how in thermal equilibrium the temperature must be in balance
- Since $\frac{\partial S}{\partial V}$ is the pressure and $\frac{\partial S}{\partial N}$ is the chemical potential, the partial derivatives of S determine the "force towards equilibrium"

General Properties of Entropy

- For now, only consider E
- For the Einstein solid, under $\frac{q}{N} \gg 1 \implies \frac{kT}{\hbar\omega \gg 1}$ we had $S(E) = kN \ln \frac{Ee}{N\hbar\omega}$
    - For this system and all "normal" systems, the slope of $S(E)$ to E is always positive (and so $T > 0$)
    - Additionally, this graph flattens out with increasing E; therefore $\frac{\partial^2 S}{\partial E^2}$, and so with increasing E, $\frac{\partial S}{\partial E} = \frac{1}{T}$ goes down or T goes up
        - This means that the heat capacity is positive
    - Such systems are *thermodynamically stable*
        - For systems held together by gravity (e.g. stars), this pattern is broken and the system actually cools down with more energy
- Recall that for the paramagnet $\Omega(N_\uparrow, N) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}$
    - This is not a "normal" system since it has a maximum energy
    - The plot of Ω against $N_\uparrow$ has a maximum at about $N_\uparrow = \frac{N}{2}$
    - To convert this to energy, we have to flip the graph (since $N_\uparrow = N$ has minimum energy)
    - The entropy curve is concave down with a maximum
        - In the first half of the curve between U_{min} and 0 the temperature is positive and increasing with E
        - In the second half of the curve, the temperature is negative
            - This is a metastable region that can only exist for a short amount of time
        - At the maximum, the temperature becomes infinite
    - When the total spin is maximum, we have minimum energy; as we heat up the magnet, the total spin decreases with temperature

- The total spin at high temperature is $S \sim \dfrac{\mu_0 B}{kT}$ (Curie's law)

Lecture 28 (2-11), Mar 23, 2023

Ideal Gas (Sackur-Tetrode Formula)

- For a given U, how many microstates are there?
- $U = \displaystyle\sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} \implies \sum_{i=1}^{N} \vec{p}_i^2 = \sum_{i=1}^{N} p_{xi}^2 + p_{yi}^2 + p_{zi}^2 = 2mU$
  - How many ways can be distribute this momentum to get the same U?
  - We want the sum of the squares of $3N$ numbers to equal $2mU$
  - This is a sphere that lives in $3N$-dimensional space, or S^{3N-1} in $\mathbb{R}^{3N}$, with radius $r^2 = 2mU \implies r = \sqrt{2mU}$
- p_x, p_y, p_z are all quantized in units of $\dfrac{\pi\hbar}{L}$ (where $L^3 = V$), like in the case of the infinite square well; these points form a grid in space, the sphere will hit some of these grid points, and each hit is a microstate
  - We only need the sphere to be close to these grid points
  - We expect that the number of hits is proportional to the area of the sphere, proportional to r^{3N-1}, with r defined by the energy
- The area of a $3N-1$-dimensional sphere in $3N$ dimensions can be shown to be $\dfrac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} R^{3N-1}$
  - If $\dfrac{3N}{2}$ is an integer this is $\dfrac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}$
  - Therefore $\Omega(N,U) \sim \dfrac{2\pi^{\frac{3}{2}}N}{\left(\frac{3}{2}N-1\right)!}\left(\sqrt{2mU}\right)^{3N-1}$, but we have to fix it first:
    - The dimensions aren't consistent: to fix it, we divide $\sqrt{2mU}$ by a factor of $\dfrac{\pi\hbar}{L}$ first to make it unitless and make the units match
      - This basically converts the p_i to n_i
    - The n_i are always positive, so the p_i must all be positive; this means we have to reduce the surface area by a factor of 2 for every axis
      - e.g. for a circle, if we restrict it to $x, y > 0$, we have to divide by a factor of 4; for a sphere, restricting it to the first quadrant divides by a factor of 8
    - The particles should be indistinguishable according to quantum mechanics, which means that if we swap the momenta of two particles, it stays in the same microstate
      - There are $N!$ ways to permute the momenta, which all lead to identical microstates, so we have to reduce Ω by a factor of $N!$
      - This is called the Gibbs factor, which he derived before QM
  - $\Omega(N,U) = \dfrac{2\pi^{\frac{3}{2}}N}{N!\left(\frac{3}{2}N-1\right)!2^{3N}}\left(\dfrac{\sqrt{2mU}L}{\pi\hbar}\right)^{3N-1}$
- Now to find the entropy $S = k\ln\Omega$
  - First use Stirling's approximation, $N! = \left(\dfrac{N}{e}\right)^N$ and ignore the -1
  - Substitute $L = V^{\frac{1}{3}}$
  - $\Omega(N,U) = \dfrac{e^N}{N^N}\dfrac{2}{(2^3)^N}\dfrac{2(\pi^{\frac{3}{2}})^N(e^{\frac{3}{2}})^N}{(3^{\frac{3}{2}})^N(N^{\frac{3}{2}})^N}\dfrac{V^N}{(\pi\hbar)^{3N}}\left((2mU)^{\frac{3}{2}}\right)^N$

    $= \ldots$ I gave up ...

  - $S = k\ln\Omega$

    $= k\ln 2 + kN\ln\left(\left(\left(\frac{4\pi mU}{N}\right)^{\frac{3}{2}}\frac{1}{(2\pi\hbar)^3}\frac{V}{N}\right)+\frac{5}{2}\right)$

    $= kN\ln\left(\left(\left(\frac{4\pi mU}{N}\right)^{\frac{3}{2}}\frac{1}{(2\pi\hbar)^3}\frac{V}{N}\right)+\frac{5}{2}\right)$

    - This is known as the Sackur-Tetrode formula for the entropy of an ideal gas
  - Taking $\frac{1}{T} = \frac{\partial S}{\partial U} = Nk\frac{3}{2}\frac{1}{U} \implies U = \frac{3}{2}kNT$ which is the same as the one we got from equipartition
- What can we learn from this formula?
  - S is on the same order as kN
  - For all the extensive quantities, e.g. N, U, V, if we double them, the entropy also doubles
  - S increases with U, and levels off – this is a normal system, the temperature increases with energy and we have a positive heat capacity
  - If we lower U enough, then eventually the stuff inside the log will become less than 1, and we'll get a negative entropy, which is impossible – therefore this formula does not work for gases with very low energy

Lecture 29 (2-12), Mar 24, 2023

When is a Gas No Longer Ideal?

- $S(U,N,V) = kN\left(\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{2Nh^2}\right)^{\frac{3}{2}}\right)+\frac{5}{2}\right)$
- From this we can get $\frac{1}{T} = \frac{\partial S}{\partial U} = Nk\frac{3}{2}\frac{1}{U}$ so $U = \frac{3}{2}kNT$
- Written in terms of temperature, $S(T,N,V) = kN\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right)+\frac{5}{2}\right)$
- For sufficiently low T this will give us a negative entropy, so some assumption must have been violated for a very cold gas
- The thermal de Broglie wavelength is $\lambda = \frac{h}{\sqrt{mkT}}$ (the regular de Broglie wavelength but with $p = \sqrt{mkT}$)
  - Larger mass and temperature decreases the thermal de Broglie wavelength
- Using λ and $l^3 = \frac{V}{N}$, we get $S(T,N,V) \sim kN\ln\frac{l^3}{\lambda^3}$
  - l is the typical distance between particles
  - The ideal gas holds whenever $l \gg \lambda$ – that is, the typical distance between the particles is much larger than their de Broglie wavelength
  - When $l \gg \lambda$, the particles don't feel the quantum effects of the particles; when the two are comparable, quantum effects become important
- We can make a gas a "quantum gas" either by increasing the density (decreasing l) or lowering the temperature (increasing λ)
  - This is why we said that the ideal gas law only works when the gas is "not too cold" and "not too dense"

Statistical Definition of Volume

- Recall that to define temperature, we considered two systems being brought together where only energy can be exchanged; to define pressure, we consider the same case, but now volume can be exchanged (i.e. one system expands while the other contracts)

- Consider 2 systems, with $N_1, N_2, V_1, V_2, E_1, E_2$, and $V_1 + V_2 = V, E_1 + E_2 = E$ are both fixed; we wish to find the equilibrium state (that is, we want to maximize $S_{tot} = S_1 + S_2$, subject to E_1, V_1)
- $S = S_1(E_1, V_1, N_1) + S_2(E - E_1, V - V_1, N_2)$
  - First, we need $\dfrac{\partial S}{\partial E_1} = \dfrac{\partial S}{\partial V_1} = 0$
  - As we previously studied, $\dfrac{\partial S}{\partial E_1} = 0$ gives us $\dfrac{\partial S_1}{\partial E_1} = \dfrac{\partial S_2}{\partial E_2} \implies \dfrac{1}{T_1} = \dfrac{1}{T_2}$
  - $\dfrac{\partial S}{\partial V_1} = \dfrac{\partial S_1}{\partial V_1} + \dfrac{\partial S_2}{\partial (V - V_1)}(-1) = 0 \implies \dfrac{\partial S_1}{\partial V_1} - \dfrac{\partial S_2}{\partial V_2} = 0$
  - Therefore equilibrium occurs when $\dfrac{\partial S_1}{\partial V_1} = \dfrac{\partial S_2}{\partial V_2}$, subject to $V_1 + V_2 = V$
  - $\dfrac{\partial S}{\partial V}$ has units of pressure over temperature
- This allows us to define the pressure p such that $\dfrac{p}{T} = \dfrac{\partial S}{\partial V}$, so that two systems come to equilibrium in volume when the pressure of the two systems are equal
- Let's plug in our new definition of pressure into the Sackur-Tetrode formula
- $\dfrac{p}{T} = \dfrac{\partial S}{\partial V} = \dfrac{kN}{V}$
- Rearrange this and we get $pV = NkT$ which is the ideal gas law!
- Note that in order to have exchange of volume, there must be exchange of energy (because moving the wall would do work); the problem of exchanging volume without exchanging energy is ill-defined

Lecture 30 (2-13), Mar 27, 2023

Clausius' Definition of Entropy

- Consider keeping N and V fixed, then for infinitesimal changes ΔU, $\dfrac{\Delta S}{\Delta U} = \dfrac{1}{T} \implies \Delta S = \dfrac{\Delta U}{T}$
- Since we keep volume fixed, $\Delta U = \delta Q$ therefore $S = \dfrac{\delta Q}{T}$ – this is the Clausius definition of entropy (the original thermodynamic definition of entropy)
  - In the Clausius definition only changes in S are defined
- Clausius also postulated that $\Delta S \geq 0$ in a closed system, which is formulated as the second law
- $S = \dfrac{\delta Q}{T}$ and $\Delta S \geq 0$ implies a unidirectional flow of heat; heat always flows from a hotter object to a colder object, so that the loss in entropy of the hotter object is less than the gain in entropy of the colder object
- Since $c_v = \dfrac{\Delta U}{\Delta T}$ we have $\Delta S = \dfrac{\Delta U}{T} = c_v \dfrac{\Delta T}{T}$
  - Integrating, we have $S(T_2) - S(T_1) = \displaystyle\int_{T_1}^{T_2} \frac{c_v(T)}{T}\,\mathrm{d}T$
  - This allows us to measure changes in entropy

Other Properties of Entropy

- For an ideal gas, $c_v = \dfrac{3}{2}Nk$ which is independent of T
  - $S(T_2) - S(T_1) = \displaystyle\int_{T_1}^{T_2} \frac{\frac{3}{2}Nk}{T}\,\mathrm{d}T = \frac{3}{2}Nk \ln\frac{T_2}{T_1}$
  - As $T_2 \to 0$, we have $S(T_2) - S(T_1) \to -\infty$; but S is log of multiplicity, so it should be finite and positive
  - This is another way that we can show the classical ideal gas model fails
- In order to make sure S stays finite as $T_2 \to 0$, we must place constraints on c_v
  - A sufficient condition is to have $c_v \sim T^\alpha, \alpha > 0$ so that when we integrate we get $\dfrac{1}{\alpha}T^\alpha$, which is finite as $T \to 0$ if $\alpha > 0$

    - This is known as Nernst's theorem

Metals as Ideal Quantum Gases (Fermi Gases)

- In a metal electrons are delocalized and freely float around, but they are very dense and have large de Broglie wavelengths due to their tiny mass, so they exhibit quantum behaviour at room temperature
- For such a system $c_v \sim aT + bT^3$
    - The first term comes from the contribution of electrons; the second term comes from contribution of phonons (quantum waves)
- For "strange metals", $c_v \sim T^{\frac{p}{q}}$

Lecture 31 (2-14), Mar 30, 2023

Chemical (Diffusive) Equilibrium

- Consider once again 2 systems with U_1, N_1, V_1 and U_2, N_2, V_2 being brought together; what happens if we allow exchange of U and N?
- Initially if we keep the barrier, the energy will exchange such that thermal equilibrium is reached with systems having U_1' and U_2'
    - Note we have to allow exchange of energy because particles carry energy, so we can't exchange particles without exchanging energy
- We want to determine $U_1'', U_2'', N_1'', N_2''$ that maximizes entropy: $S = S_1(U_1'', N_1'') + S_2(U - U_1'', N - N_1'')$
    - We want $\dfrac{\partial S}{\partial U_1''} = 0 \implies \dfrac{\partial S_1}{\partial U_1''} = \dfrac{\partial S_2}{\partial (U - U_1'')}$
    - And also $\dfrac{\partial S}{\partial N_1''} = 0 \implies \dfrac{\partial S}{\partial N_1''} = \dfrac{\partial S}{\partial (N - N_1'')}$
    - Therefore we have that the system property $\dfrac{\partial S_i}{\partial N_i}$ for both systems must be equal
    - S has units of energy per temperature, so $\dfrac{\partial S}{\partial N}$ also has units of energy per temperature
- Define $-\dfrac{\mu}{T} = \dfrac{\partial S}{\partial N}$, where μ is the *chemical potential* (or *diffusive potential*)
    - μ has units of energy
    - Note we defined it with the minus sign, so that the particles end up flowing from regions with higher chemical potential to lower chemical potential
- Example: ideal gas
    - $\dfrac{\mu}{T} = -\dfrac{\partial}{\partial N} kN \left(\ln \left(\dfrac{V}{N} \left(\dfrac{U}{3N} \right)^{\frac{3}{L}} \left(\dfrac{4\pi m}{h^2} \right)^{\frac{3}{2}} \right) + \dfrac{5}{2} \right)$

      $= -k \ln \left(\dfrac{V}{N} \left(\dfrac{1}{2} kT \right)^{\frac{3}{2}} \left(\dfrac{4\pi m}{h^2} \right)^{\frac{3}{2}} \right)$
    - Where we have replaced $\dfrac{U}{3N} = \dfrac{1}{2} kT$
    - Therefore $\mu(T, V, N) = -kT \ln \left(\dfrac{\text{const}}{n \lambda_d^3} \right)$
    - As the number density n increases, the log goes down, so we need the minus sign to have μ higher in regions of higher number density
    - μ is a proxy for the density

Applications to Chemistry

- Suppose we have a gas of N_h hydrogen atoms occupying some space; as hydrogen atoms bump into each other, some of them may be ionized so we have some protons N_p and electrons N_e
- All 3 gases exist in thermal and chemical equilibrium

- The equilibrium condition is specified by two of the energies and a Δ (for every Δ in hydrogen gained, we lose Δ protons and Δ electrons)
- Note we need to consider each hydrogen has lower energy than a proton and an electron together; to do this we need to consider the rest energies of the particles to get the ionization energy
- Maximize entropy: $\frac{n_e n_p}{n_h} = \frac{1}{\left(\frac{4\pi}{h^2} m_e \frac{kT}{2}\right)^{\frac{3}{2}}} = e^{-\frac{I}{kT}}$ where $n_e = \frac{N_e}{V} = \frac{N_p}{V} = n_p, n_h = \frac{N_h}{V}$ and I is the ionization energy, 13.6 eV
    - This is known as the Saha equation
    - At low temperatures, $-\frac{I}{kT} \gg 1$ so $n_e n_p \approx 0$ – there is very little interaction because the particles move slowly
    - As the gas is heated, increased particle velocity leads to more interaction and more breakdown
- In general if we have stoichiometric coefficients, we can do the derivation to find each number density being taken to the power of their stoichiometric coefficient
- We can also express the law as $\frac{n_B^{\nu_B} n_C^{\nu_C}}{n_A^{\nu_A}} = K(T)$, which is known as the law of mass action
- $e^{-\frac{I}{kT}}$ is known as the *Boltzmann factor*

Lecture 32 (2-15), Mar 31, 2023

Thermodynamic Equilibrium and Maxwell's Relations

- To actually maximize the entropy $S(U, V, N)$ we need both $\frac{\partial S}{\partial U} = \frac{\partial S}{\partial V} = \frac{\partial S}{\partial N} = 0$ and for the Hessian matrix of second derivatives to have negative eigenvalues
- Suppose we have some system with $S = S(U, V, N)$ which is some function; we know $\mathrm{d}S = \frac{\partial S}{\partial U}\,\mathrm{d}U + \frac{\partial S}{\partial V}\,\mathrm{d}V + \frac{\partial S}{\partial N}\,\mathrm{d}N$
    - This means $\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N$
    - In this form, the equation is known as the *thermodynamic identity for the entropy*
    - This equation gives the change in entropy for some change in energy, volume, or number of particles
- We can invert $S(U, V, N)$ to get $U(S, V, N)$, the energy in terms of entropy, volume, and number of particles
- Solving for $\mathrm{d}U$, we have $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\mathrm{d}N$; this is the *thermodynamic identify for the energy*
    - We can match this to what we get from $U(S, V, N)$
    - This gives us 2 new definitions: $p = \frac{\partial U}{\partial V}, \mu = \frac{\partial U}{\partial N}$
- These definitions are collectively known as *Maxwell's relations*: $\frac{1}{T} = \frac{\partial S}{\partial U}, \frac{p}{T} = \frac{\partial S}{\partial V}, \frac{\mu}{T} = -\frac{\partial S}{\partial N}, T = \frac{1}{\frac{\partial S}{\partial U}} p = \frac{\partial U}{\partial V}, \mu = \frac{\partial U}{\partial N}$
- To be a maximum, the Hessian must have all negative eigenvalues
- We define thermodynamic equilibrium to be stable when all these conditions hold:
    - $c_V > 0$
    - $\frac{\partial P}{\partial V} < 0$
        - Suppose $\frac{\partial P}{\partial V} > 0$ in some system, then P increases with pressure or v
        - In this case pushing on the substance causes is pressure to be even lower, so this is unstable since the system will just keep on increasing or decreasing in volume
        - This arises when we model particles that interact with each other
    - $\frac{\partial \mu}{\partial N} > 0$

Lecture 33 (2-16), Apr 3, 2023

Boltzmann Distribution

- A *microcanonical distribution* is $\dfrac{1}{\Omega(U, V, N)}$
- Consider a system with fixed V and N, with varying E in thermal contact with a thermal reservoir with energy U_R; the system and the reservoir form a closed system with U_{tot} fixed
- The probability of any microstate of the system and the reservoir is the same, $\dfrac{1}{\sum_{E'} \Omega(E)\Omega_R(U_{tot} - E')}$
- Specify a microstate in the system S by s; what is the probability of S being in a particular microstate s with energy E_s?
  - Note we're not trying to find the probability of the system having energy E_s, since there can be many microstates with the same energy; we're looking for the probability of each microstate with this energy
  - If the system is in s, the reservoir can be in any microstate with energy $U_{tot} = E_s$
  - Therefore we have $\dfrac{\Omega_R(U_{tot} - E_s)}{\sum_{E'} \Omega(E')\Omega_R(U_{tot} - E')}$
- $\dfrac{P(E_{\bar{s}_1})}{P(E_{\bar{s}_2})} = \dfrac{\Omega_R(U_{tot} - E_{\bar{s}_1})}{\Omega_R(U_{tot} - E_{\bar{s}_2})} = e^{\frac{1}{k} S_R(U_{tot} - E_{\bar{s}_1}) - S_R(U_{tot} - E_{\bar{s}_1})}$ where S_R is the entropy
- Assume the reservoir is big, so $S_R(U_{tot} - E) \approx S_R(U_{tot}) - E \left.\dfrac{\partial S_R}{\partial U}\right|_{U=U_{tot}}$ (i.e. the changes in entropy are small enough that we can use a linear approximation)
  - $\dfrac{P(E_{\bar{s}_1})}{P(E_{\bar{s}_2})} = e^{\frac{1}{k}\left(\left(E_{\bar{s}_2} - E_{\bar{s}_2}\right) \frac{\partial S_R}{\partial U}\big|_{U=U_{tot}}\right)} = e^{\frac{1}{k}\left(\left(E_{\bar{s}_2} - E_{\bar{s}_2}\right)\frac{1}{T}\right)}$
  - Therefore we find $\dfrac{P(E_{\bar{s}_1})}{P(E_{\bar{s}_2})} = e^{-\frac{E_{\bar{s}_1} - E_{\bar{s}_2}}{kT}}$ – the relative probability only depends on the difference in energy and temperature
  - $\dfrac{P(E_{\bar{s}_1})}{e^{-\frac{E_{\bar{s}_1}}{kT}}} = \dfrac{P(E_{\bar{s}_2})}{e^{-\frac{E_{\bar{s}_2}}{kT}}}$ is true for any $\bar{s}_1$ and $\bar{s}_2$, therefore this ratio must not depend on $\bar{s}$, so let it be a constant, $\dfrac{1}{Z}$
- Therefore $P(E_{\bar{s}}) = \dfrac{1}{Z} e^{-\frac{E_{\bar{s}}}{kT}}$, which is known as the *Boltzmann distribution* (or *canonical distribution*)
  - Z is independent of $\bar{s}$ and characterizes the system; it is a normalization, so that $\displaystyle\sum_{\bar{s}} P(E_{\bar{s}}) = 1$
  - $Z = \displaystyle\sum_{\bar{s}} e^{-\frac{E_{\bar{s}}}{kT}}$
  - Z is known as the Boltzmann partition function (function of state)
- We may also compute it by $Z = \displaystyle\sum_E e^{-\frac{E}{kT}} \Omega(E) = \sum_E e^{-\frac{E}{kT}} e^{\frac{1}{k} S(E)} = \sum_E e^{-\frac{E - TS(E)}{kT}}$
  - Instead of summing over all microstates, we instead sum over all possible energies (i.e. the spectrum of $\hat{H}$)
  - The quantity $F = E - TS(E)$ is known as the Helmholtz free energy
- The probability that the system has energy E is just $\dfrac{1}{Z} e^{-\frac{E - TS(E)}{kT}} = \dfrac{1}{Z} e^{-\frac{F}{kT}}$, which is maximized when F is minimized – therefore macroscopically, the system behaves as to minimize the Helmholtz free energy
  - The thermodynamic potential for the system is therefore the Helmholtz free energy

Lecture 34 (2-17), Apr 6, 2023

Properties of the T, V, N System

- Such systems are a lot easier to study, since keeping T constant is easier and Z is a lot easier to find than Ω
- Recall: for a T, V, N system in contact with a thermal reservoir, the probability of the system being in any microstate is given by $\frac{1}{Z}e^{-\beta E}$, where E is the energy of the microstate and $\beta = \frac{1}{kT}$
- $Z(T, V, N) = \sum e^{-\beta E}$ is called the *partition function* and plays a role analogous to the multiplicity function
- $\mathrm{d}F(T, V, N) = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N = \frac{\partial F}{\partial T}\,\mathrm{d}T + \frac{\partial F}{\partial V}\,\mathrm{d}V + \frac{\partial F}{\partial N}\,\mathrm{d}N$ is the thermodynamic identity for F
  - From this we get a new set of Maxwell's equations
  - Note: derivation not shown
- The probability that the system has some energy is then $P(E) = \frac{1}{Z}e^{-\beta E}\Omega(E) = \frac{1}{Z}e^{-\beta E}e^{\frac{S}{k}} = \frac{1}{Z}e^{-\beta(E-TS)}$
  - P is maximized when $E - TS = F$ is minimized, so we call F the free energy – the system wants to minimize F
  - F is the thermodynamic potential similar to energy except it's minimized
- At low T, $F \approx E$, so at low temperature the minimum of F is the minimum of E – the system goes to its ground state
- At high T, $F \approx -TS$, so the minimum of F is the maximum of S – the system goes to maximum entropy
- Such systems are ordered at low temperature (ground state) and unordered at high temperature (high entropy)
  - When the system heats up, the order and disorder fight
  - Phase transitions happen when one wins over the other

Partition Function of the Einstein Solid

- Recall the energy of a microstate is $-\hbar\omega(q_1 + \cdots + q_N)$
- $$\begin{aligned} Z &= \sum_{q_1=0}^{\infty} \cdots \sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega}{kT}(q_1+\cdots+q_N)} \\ &= \sum_{q_1=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_1} \cdots \sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q_N} \\ &= \prod_{i=1}^{N} Z_i \\ &= Z_1^N \end{aligned}$$
  - Z_1 is the partition function for a single harmonic oscillator
  - This is a general result – for systems where the energy is the sum of energies of smaller parts, the partition function factors into a product of the partition functions of the smaller parts
  - This is a useful property that the multiplicity function does not

- $Z_1 = \sum_{q=0}^{\infty} e^{-\frac{\hbar\omega q}{kT}}$

  $= \sum_{q=0}^{\infty} \left(e^{-\frac{\hbar\omega}{kT}}\right)^q$

  $= \dfrac{1}{1 - e^{-\hbar\omega}kT}$

  $= \dfrac{1}{1 - e^{-\beta\hbar\omega}}$
  - This gives $Z = \left(\dfrac{1}{1 - e^{-\beta\hbar\omega}}\right)^N$
- Let's calculate the average energy of the system as a function of temperature
- $\bar{E} = \sum P(\text{microstate})E(\text{microstate})$

  $= \dfrac{1}{Z}\sum E(\text{microstate})e^{-\beta E(\text{microstate})}$

  $= \dfrac{1}{Z}\sum -\dfrac{\partial}{\partial\beta}e^{-\beta E(\text{microstate})}$

  $= -\dfrac{1}{Z}\dfrac{\partial}{\partial\beta}\sum e^{-\beta E(\text{microstate})}$

  $= -\dfrac{1}{Z}\dfrac{\partial}{\partial\beta}Z$

  $= -\dfrac{\partial}{\partial\beta}\ln Z$
- Substitute: $\bar{E} = -\dfrac{\partial}{\partial\beta}\ln\left(\dfrac{1}{1 - e^{-\beta\hbar\omega}}\right)^N$

  $= N\dfrac{\partial}{\partial\beta}\ln\left(1 - e^{-\omega\hbar\omega}\right)$

  $= \dfrac{N\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$
- $\dfrac{\bar{E}}{N} = \dfrac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$
  - Unlike our previous approximations this works at all temperatures
  - At low temperature, $\dfrac{\hbar\omega}{kT} \gg 1$ so $\dfrac{\bar{E}}{N} \approx \hbar\omega e^{-\frac{\hbar\omega}{kT}}$ (midterm solution)
  - At high temperature $e^{\frac{\hbar\omega}{kT}} \approx 1 + \dfrac{\hbar\omega}{kT}$ so $\dfrac{\bar{E}}{N} \approx kT$ which is equipartition!
- Note we have: $Z_1 = \sum_{q=0}^{\infty} e^{-\frac{\hbar\omega}{kT}q} = 1 + e^{-\frac{\hbar\omega}{kT}} + e^{-2\frac{\hbar\omega}{kT}} + e^{-3\frac{\hbar\omega}{kT}} + \cdots$
  - Terms with $q\hbar\omega \gg kT$ will have pretty much no contribution to Z_1, so these states with higher energy do not contribute
  - Z is called the partition function because roughly it describes the partition between states with high energy and states with low energy

Lecture 35 (2-18), Apr 10, 2023

Maxwell-Boltzmann Speed Distribution

- We will consider as our "system" one of the particles and the rest of the particles as the "thermostat"; for our "system", what is $P(v)$, i.e. the probability density function of the speed?
- Applying the Boltzmann distribution gives us $P(v)\,\mathrm{d}v = ce^{-\frac{E}{kT}}v^2\,\mathrm{d}v = ce^{-\frac{mv^2}{2kT}}v^2\,\mathrm{d}v$

  - $v^2\,\mathrm{d}v$ is the number of microstates that have speed in $[v, v + \mathrm{d}v]$; this is proportional to the surface area of a sphere with radius v
  - The exponential term is the probability of each microstate with energy v
- After applying normalization, in 3D we get $P(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$
  - In 2D, the number of microstates with speed in $[v, v + \mathrm{d}v]$ would be proportional to $v\,\mathrm{d}v$, since it is now proportional to the circumference of a circle with radius v
    - In 2D the function is linear near $v = 0$ and the peak is closer to 0
  - Note this distribution is for a classical gas, which breaks down as $v \to 0$
- $P(v)$ is maximum at $v^* = \sqrt{\frac{2kT}{m}}$
  - $\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{m}{2}\int_0^\infty P(v)v^2\,\mathrm{d}v$ works out to be $\frac{3}{2}kT$, which once again verifies equipartition

Intuition for the Partition Function

- Let the ground state have energy $E_0 = 0$, then $Z = \sum e^{-\frac{E}{kT}} = 1 + e^{-\frac{E_1}{kT}} + e^{-\frac{E_2}{kT}} + \ldots$
- The partition function tells us roughly which states are important and which ones are not important at a given temperature; it "partitions" the microstates into significant ones and insignificant ones
- If $E \gg kT$, its contribution to Z will be very small, making them insignificant; they are *decoupled* from thermodynamics at the given temperature
  - Because Z determines F, the thermodynamic potential, which determines macroscopic properties, this means these states are unimportant to the macroscopic behaviour
- e.g. at room temperature $kT \approx 0.02\text{eV}$, which allows us to ignore excitations in the electronic and nuclear states, because they have energies that are significantly larger
  - This is why we only need to consider translational, rotational and vibrational energies and not electronic and nuclear structures

Equivalence of T, V, N and E, V, N Systems

- The Boltzmann distribution was derived with a different set-up, yet it still gives the same results in the case of the Einstein solid in the thermodynamic limit, if we use the average energy $\bar{E} = \langle E \rangle$
- We can show that in the TD limit, the two formulations will arrive at the same results
- The main difference is that for the Boltzmann distribution E varies, but E is constant for the multiplicity function approach
- We can find $\langle E \rangle$ as shown in the previous lecture and similarly $\langle E^2 \rangle$ and using this we can find $\frac{\sigma_E^2}{N}$; this turns out to scale as $\frac{1}{\sqrt{N}}$
- In the thermodynamic limit with very large N, the variance of E becomes negligible compared to N, so the spread of energies is minimal and the average energy becomes functionally the same as the energy itself