

Modern Statistical Mechanics

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EP1108-Modern Physics

Logistics

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- Introduction to Modern Statistical Mechanics by David Chandler,
ISBN 978-0-19-504277-1
- Lecture notes by Prof. Matthew Schwartz, Harvard University
<https://scholar.harvard.edu/schwartz/teaching>
- Statistical Mechanics by Kerson Huang, ISBN-10 : 8126518499
- These materials are simply for reference and self-interest. Technically,
the lecture notes and videos are sufficient for this course and the
exams and assignments

Tentative schedule

...can change

Week	Monday	Tues	Wed	Thurs
31.01-04.02	EP1b - Prem		EP1b - Prem	EP1b - Prem
	EP1a - Kirit			EP1a - Kirit
07.02-11.02	EP1b - Q&A			
	EP1a - Q&A			
14.02-18.02	EP1b - Prem		EP1b - Prem	EP1b - Kirit
	EP1a - Kirit			EP1a - Prem
21.02-25.02	EP1b - Kirit		EP1b - Kirit	EP1b - Kirit
	EP1a - Prem			EP1a - Prem
28.04-04.03	EP1b - Kirit(?)		EP1b - Kirit(?)	EP1B - Kirit(?)
	EP1a - Kirit(?)			EP1a - Kirit(?)

Ensembles

Motivation

- Statistical Mechanics is the way to deal with systems with a large number of particles
- If we look at any ordinary system microscopically, it consists of a huge number of particles (nuclei, electrons, atoms, or molecules) - in reality you rarely deal with 1 or 2 particles
- The dynamics of these particles is chaotic, which means that it is impossible to track their motion precisely because any little error in measurement will lead to an entirely different trajectory of the particle
- In order to meaningfully study such systems, we need to come up with some meaningful way to average out their properties
- This is the goal of statistical mechanics
- This way, modern statistical mechanics also provides a microscopic basis for thermodynamics

Context and applications

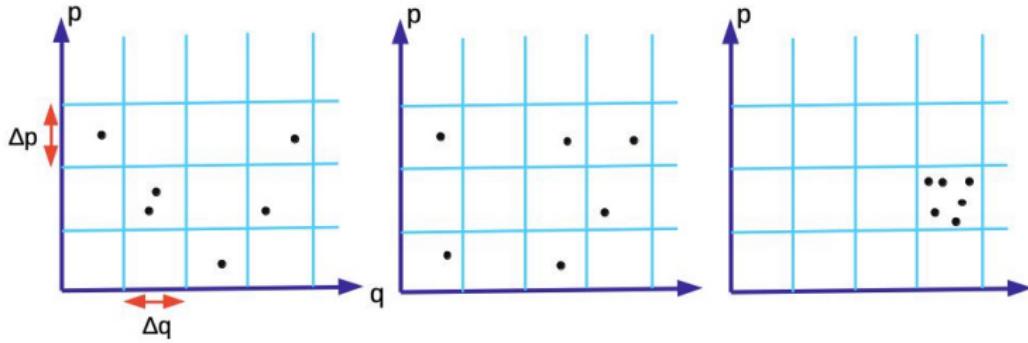
- Modern statistical mechanics is a very broad subject that has very many applications
- Being the foundation of thermodynamics, it forms the fundamental of all thermodynamic applications - for ex., engines
- It forms the basis of all materials that involve many-electrons (super-conductors, semi-conductors, insulators, magnets, etc...)
- Statistical mechanics is also required in neural networks, astrophysics, weather-forecasting, economics,... - the list is extremely diverse and long
- In this part I will try to give just a few small glimpses of this vast subject

Macro and micro states

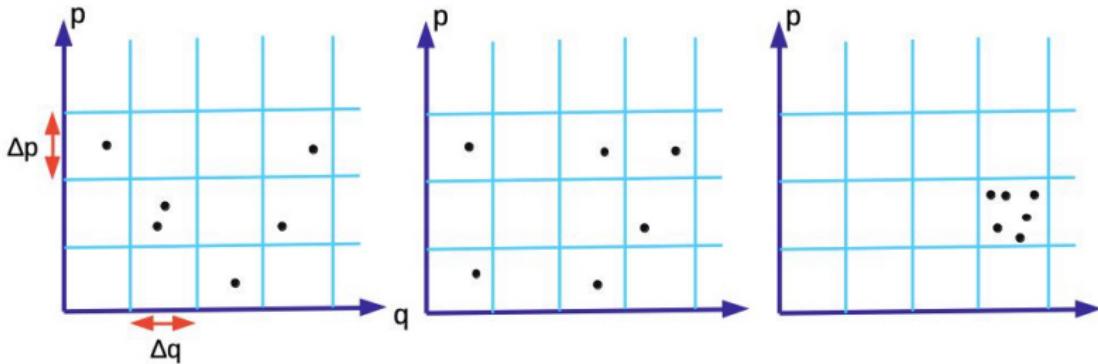
- A system is typically specified by its volume V
- We can further specify the number of particles in this system N and its total energy E
- Thus, a macrostate of this system can be specified by specifying its (E, V, N)
- However, given a macro-state there are a lot of different ways to arrange the particles inside the system giving the same macro-state. Each such arrangement is called a micro-state
- A collection of such microstates is called an ensemble

Microstates in an ideal gas

- Consider a gas of N atoms which can have position \mathbf{q}_i and momentum \mathbf{p}_i . It is in a volume V with energy E
- To get an exact picture of the state a system is in, we have to define all the positions \mathbf{q}_i and momenta \mathbf{p}_i for all the particles in the system $i = 1, 2, 3, \dots, N$
- This is an infinite dimensional space because the variables \mathbf{q}_i and \mathbf{p}_i can vary continuously
- To simplify, let's discretize the real space in cubes with edges of size Δq and the momenta in steps of length Δp



Microstates



- This combined space of position (q) and momentum (p) is called **phase-space**
- Each particle can be placed in any of these blocks
- A microstate is a specification of which particle is located in which block of this phase space. The number of microstates is denoted by $\Omega(N, V, E)$, which also specifies that this number is a function of N , V , and E

Microcanonical ensemble

- When we consider an ensemble of all the microstates of a system with a specific N, V, E , then it is called a micro-canonical ensemble
- The entropy of this system is defined as

$$\checkmark S = k_B \ln(\Omega) \quad (1)$$

- The temperature is defined as

$$\checkmark \beta = \frac{1}{k_B T} = \frac{1}{k_B} \frac{\partial S}{\partial E} \Big|_{N,V} = \frac{1}{\Omega} \frac{\partial \Omega}{\partial E} \Big|_{N,V} \quad (2)$$

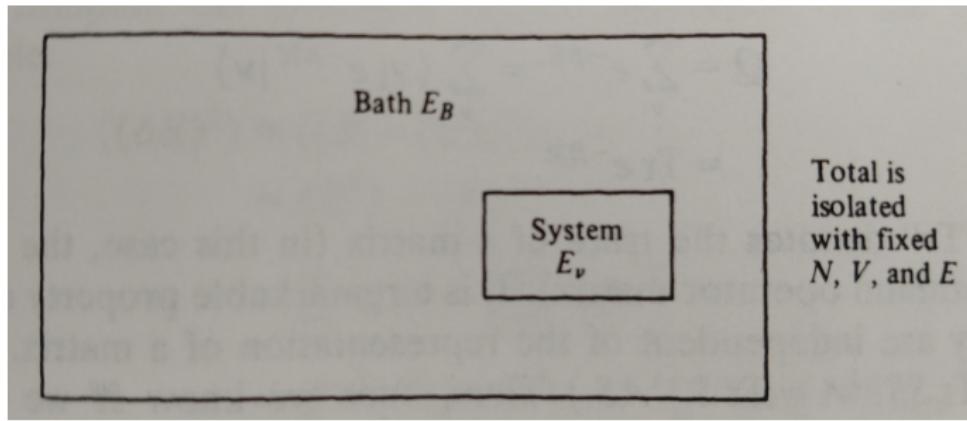
- It can be shown that this is actually equivalent to the classical thermodynamic definition of entropy

$$dS = \frac{\delta Q_{\text{rev}}}{T} \quad (3)$$

- Statistical postulate** - All microstates in a micro-canonical ensemble are equally probable

Canonical Ensemble

- Canonical ensemble is the collection of all the micro-states of a system with a given N , V , and temperature T , while the energy can vary.
- Such a system can be viewed as a part of a large thermal bath, with which it can exchange energy while maintaining the same temperature
- The system is in micro-state ν with energy E_ν and the total energy of system+bath is fixed, i.e., $E_\nu + E_B = E$



Canonical ensemble

- Given the system is in state ν , the number of microstates available to the whole system is $\Omega(E_B)$ (dropping N and V since they are fixed for both system and bath)
- By the statistical postulate that all microstates are equally likely, we can say that the probability of finding the system in state ν is proportional to

$$P_\nu \propto \Omega(E_B) = \Omega(E - E_\nu) \quad (4)$$

- Now assume $E_\nu \ll E$, then it can be showed that (H.W. - by using Taylor series expansion)

$$\underline{P_\nu \propto \exp(-\beta E_\nu)} \quad (5)$$

- This is the Boltzmann distribution function

Partition function

- The constant of proportionality can be obtained by applying the normalization condition

$$\sum_{\nu} P_{\nu} = 1 \quad (6)$$

$$\implies P_{\nu} = Q^{-1} \exp(-\beta E_{\nu}) \quad (7)$$

- where

$$Q = \sum_{\nu} e^{-\beta E_{\nu}} \quad (8)$$

- $Q(\beta, N, V)$ is called as the partition function. This is a very useful function because many thermodynamic quantities can be derived from this function

Average energy

- Suppose we want to find what is the average energy of a system in a canonical ensemble. This will be given by

$$\langle E \rangle = \sum_{\nu} P_{\nu} E_{\nu} \quad (9)$$

$$= \sum_{\nu} e^{-\beta E_{\nu}} E_{\nu} / Q \quad (10)$$

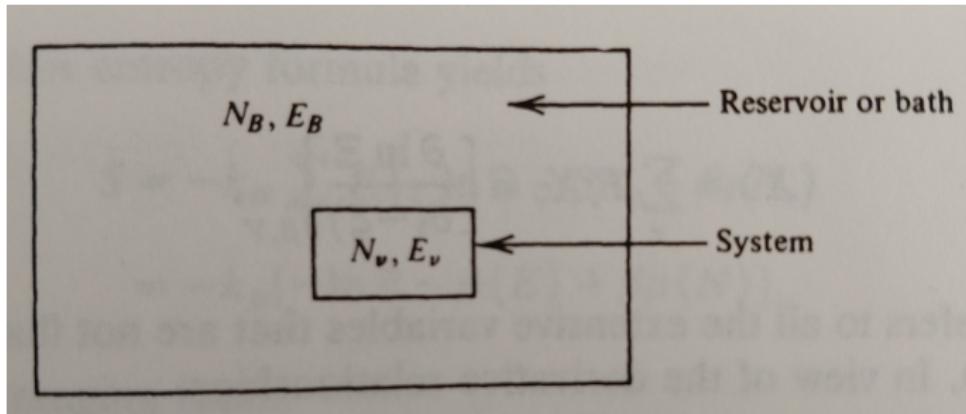
$$= -\frac{1}{Q} \frac{\partial Q}{\partial \beta} \Big|_{N,V} \quad (11)$$

$$= -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \quad (12)$$



Grand canonical ensemble

- Now consider a system with fixed volume which is in equilibrium with a thermal bath, but N also varies along with E



- The total energy $E = E_v + E_B$ and the total number of particles $N = N_v + N_B$ is fixed
- The possible micro-states of such a system form the grand-canonical ensemble

Chemical Potential

- Now, the probability of finding a given microstate of the system with (E_ν, N_ν) is proportional to the number of microstates of the bath with the corresponding $(E - E_\nu, N - N_\nu)$
- As before, we can write

$$\checkmark P_\nu \propto \Omega(E - E_\nu, N - N_\nu) \quad (13)$$

- Now define the chemical potential μ as

$$\checkmark -\beta\mu = \frac{1}{\Omega} \frac{\partial \Omega}{\partial N} \Big|_{V,E} = \frac{1}{k_B} \frac{\partial S}{\partial N} \Big|_{E,V} \quad (14)$$

- At constant volume we can write

$$\checkmark dS = \frac{\partial S}{\partial N} \Big|_{V,E} dN + \frac{\partial S}{\partial E} \Big|_{V,N} dE = -k_B\beta\mu dN + k_B\beta dE \quad (15)$$

Grand canonical partition function

- This gives the chemical potential as

$$\mu = \left. \frac{\partial E}{\partial N} \right|_{S,V} \quad (16)$$

- This is the energy required to put one more particle in the system
- Returning back to the grand-canonical ensemble, using $P_\nu \propto \Omega(E - E_\nu, N - N_\nu)$, doing Taylor expansion, and using the identities $-\beta\mu = \partial(\ln \Omega)/\partial N$ and $\beta = \partial(\ln \Omega)/\partial E$, it can be shown that

↗ $P_\nu \propto \exp(-\beta E_\nu + \beta \mu N_\nu)$ (17)

✓ The normalization factor is called as the grand canonical partition function

↗ $\mathcal{Z} = \sum_\nu \exp(-\beta E_\nu + \beta \mu N_\nu)$ (18)

Average N

- Average N

$$\langle N \rangle = \sum_{\nu} P_{\nu} N_{\nu} = \sum_{\nu} N_{\nu} e^{-\beta E_{\nu}} e^{\beta \mu N_{\nu}} / \mathcal{Z} \quad (19)$$

 $= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$ (20)

- H.W. show that

$$\langle E \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \mu \langle N \rangle \quad (21)$$



Examples

Ideal monoatomic gas

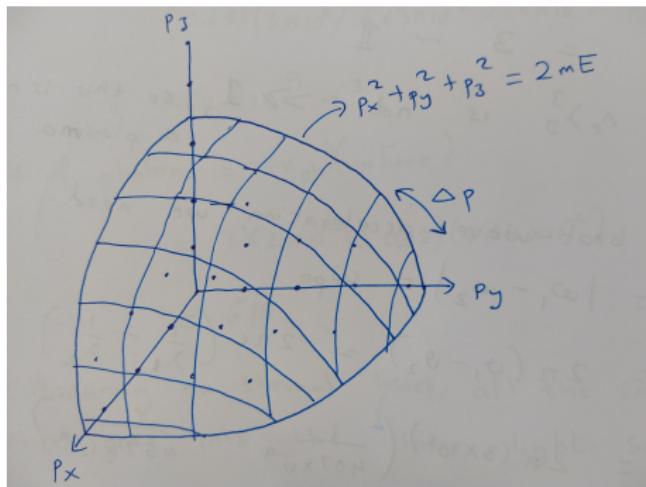
- Consider a microcanonical ensemble consisting of ideal gas particles
- To count the number of microstates, we divide 6D phase space into small cubes of width Δq and Δp , where q represents space co-ordinates x, y, z and p is the momentum coordinates p_x, p_y, p_z .
- A micro-state is defined by specifying in which block each particle resides.
- The number of microstates is the way N particles can be distributed in the available number of blocks. There are $(V/\Delta q^3)$ blocks in position space
- Each particle can be put in any one of these blocks. So the number of ways to do this is $(V/\Delta q^3)^N$

Momentum space

- The energies of all the N particles should add up to E , thus

$$\cancel{2mE = p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + \dots + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2} \quad (22)$$

- First consider the simple case of a single particle system and count the number of ways this particle can be arranged in a 3D momentum space such that $2mE = p_x^2 + p_y^2 + p_z^2$



- The number of ways to arrange this particle on a sphere of radius $\sqrt{2mE}$ which is divided up into small cubes of area Δp^2 is

$$\checkmark \frac{\text{Area of sphere}}{(\Delta p)^2} \quad (23)$$

considering that Δp is so small that the blocks on the sphere are almost a square

Number of microstates

- Going to N particles, we will have a $3N$ dimensional phase-space
- ✓ The number of ways in which N particles can be given the momenta \mathbf{p}_i such that their total energy is E is given by the area of a $3N$ dimensional sphere of radius $\sqrt{2mE}$, divided by Δp^{3N-1} , which is the area of one block
- ✓ It can be derived that the area of a d dimensional unit sphere is $\sigma_d = 2\pi^{d/2}/(d/2 - 1)!$
- (Hint: Consider $I = \int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$;
 $I^N = \int_0^{\infty} e^{-r^2} \sigma_N r^{N-1} dr = \pi^{N/2}$)
- Using this result, the number of ways we can arrange $3N$ particles on the surface of this sphere is

$$\checkmark \Omega_p = \frac{2\pi^{3N/2}}{(3N/2 - 1)!} \left(\frac{\sqrt{2mE}}{\Delta p} \right)^{3N-1} \quad (24)$$

Average energy

- The total number of microstates is just the product of the two

$$\Omega = \left(\frac{V}{\Delta q^3} \right)^N \frac{2\pi^{3N/2}}{(3N/2 - 1)!} \left(\frac{\sqrt{2mE}}{\Delta p} \right)^{3N-1} \quad (25)$$

- Lets calculate the temperature of this gas

$$\beta = \frac{1}{\Omega} \left(\frac{\partial \Omega}{\partial E} \right) \Big|_{N,V} \quad (26)$$

$$= \frac{1}{E^{(3N-1)/2}} \frac{\partial E^{(3N-1)/2}}{\partial E} = \frac{3N-1}{2} E^{-1} \quad (27)$$

- Approximately $3N - 1 \approx 3N$, this gives

✓

$$\frac{3}{2} k_B T = \frac{E}{N} = \langle E \rangle \quad (28)$$

- This matches with the average energy of ideal gas atom derived from kinetic theory.

Quantum states

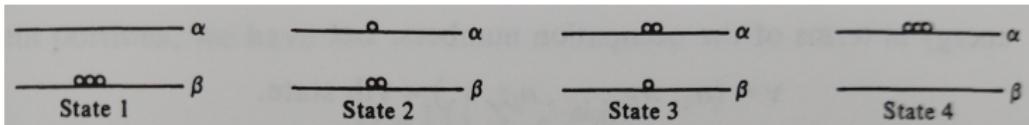


Fig. 4.1. The four states of a three-particle system with two single particle states.

- Consider a system of quantum states with energy $\epsilon_1, \epsilon_2, \dots, \epsilon_j, \dots$; where ϵ_j is the energy of the j^{th} quantum state
- Lets say we have N particles. A micro-state corresponds to a specific way of distributing these N particles in these quantum states
- This microstate can be specified by giving the number of particles n_j in the j^{th} state - this is called “occupation number”
- Microscopic particles are indistinguishable, therefore states which involve the same set of occupation numbers, but just a change in the arrangement of individual particles are counted as the same state - in other words we cannot distinguish microstates in which particle A and particle B interchange their levels because we cannot distinguish between particles A and B

Partition function

- Therefore, a microstate is completely specified by the set of occupation numbers: $\{n_1, n_2, n_3, \dots, n_j, \dots\}$
- The total energy of a microstate will be $E = \sum_j n_j \epsilon_j$. The canonical partition function will be

$$\checkmark Q = \sum_{\nu} e^{-\beta \sum_j n_j \epsilon_j} \quad (29)$$

- The sum over all states \sum_{ν} involves summing over all combinations of n_j 's such that $\sum_j n_j = N$, because N is fixed in canonical ensemble
- It is very complicated to take such a restricted sum. Instead we make use of the grand canonical partition function
- In the grand canonical function, N can vary, so we can freely vary n_j
- Bosons are particles which have integer spin (spin is an intrinsic property of quantum wave functions), (named after Satyendra Nath Bose)
- Examples are photons, gluons, He

Bosonic partition function

- Lets calculate grand canonical partition function of Bosons

✓

$$\mathcal{Z} = \sum_{n_1, n_2, \dots, n_j, \dots} \exp[-\beta(\sum_j n_j \epsilon_j - \mu \sum_j n_j)] \quad (30)$$

- The $\sum_{n_1, n_2, \dots, n_j, \dots}$ means each n_j is summed from 0 to ∞
- ✓ Expressing the exponential of a sum as the product of exponentials, we can write

$$\mathcal{Z} = \sum_{n_1, n_2, \dots, n_j, \dots} \prod_j \exp[-\beta(\epsilon_j - \mu)n_j] \quad (31)$$

$$= \prod_j \sum_{n_j=0}^{\infty} \exp[-\beta(\epsilon_j - \mu)n_j] \quad (32)$$

$$= \prod_j \frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} \quad (33)$$

Average occupation number

- Lets calculate on an average how many particles will be present in state j , $\langle n_j \rangle$

$$\langle n_j \rangle = \sum_{\nu} n_j \exp[-\beta(E_{\nu} - \mu N_{\nu})]/\mathcal{Z} \quad (34)$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial(-\beta \epsilon_j)} \quad (35)$$

$$= \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1} \quad (36)$$

- This is the Bose-Einstein distribution function, developed by S. N. Bose
- It is singular when $\epsilon_j = \mu$. This gives rise to phenomenon of Bose-Einstein condensation predicted by Einstein (7 Nobel prizes have been awarded for work related to Bose Einstein statistics)

Fermionic statistics

- Fermions are particles with half integer spins (named after Enrico Fermi)
- According to Pauli's exclusion principle, a single quantum state can accommodate only one fermion (unlike bosons which can be accommodated as many as needed)
- Just like for bosons, we again write down the grand canonical partition function

$$\checkmark \quad \mathcal{Z} = \sum_{n_1, n_2, \dots, n_j, \dots} \prod_j \exp[-\beta(\epsilon_j - \mu)n_j] \quad (37)$$

- The difference is that n_j can only be 0 or 1 due to Pauli's exclusion principle
- Again, it can be shown that the sum and product can be interchanged

$$\checkmark \quad \mathcal{Z} = \prod_j \sum_{n_j=0}^1 \exp[-\beta(\epsilon_j - \mu)n_j] = \prod_j [1 + e^{-\beta(\epsilon_j - \mu)}] \quad (38)$$

Average occupation number

- Lets calculate the average occupation number as before

$$\checkmark \langle n_j \rangle = \frac{1}{Z} \frac{\partial Z}{\partial(-\beta\epsilon_j)} \quad (39)$$

$$= \frac{\prod_{m \neq j} [1 + e^{-\beta(\epsilon_m - \mu)}]}{\prod_m [1 + e^{-\beta(\epsilon_m - \mu)}]} (e^{-\beta(\epsilon_j - \mu)}) \quad (40)$$

$$= \frac{e^{-\beta(\epsilon_j - \mu)}}{1 + e^{-\beta(\epsilon_j - \mu)}} \quad (41)$$

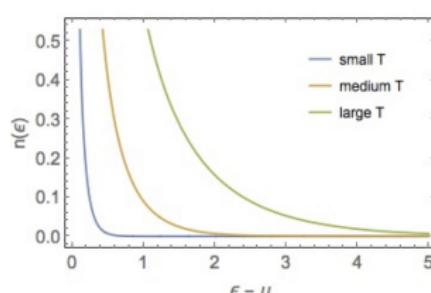
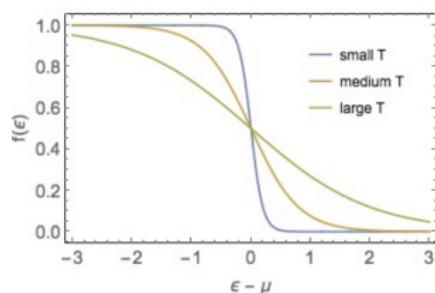
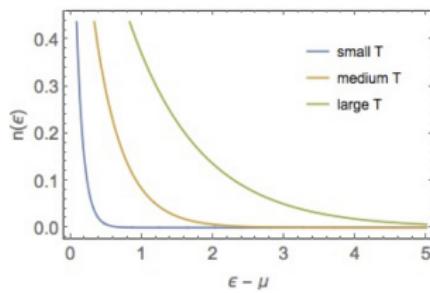
$$= \frac{1}{1 + e^{\beta(\epsilon_j - \mu)}} \quad (42)$$

- This is called as Fermi-Dirac distribution function

The distributions

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} + K} \quad (43)$$

- where $K = 1$ for Fermi-Dirac, $K = 0$ for Maxwell-Boltzmann, and $K = -1$ for Bose-Einstein



- Maxwell-Boltzmann, Fermi-Dirac, and Bose-Einstein distributions

Applications

- Semiconductors
- Superconductors
- Magnetic materials
- Solid state devices
- Lasers
- Nano particles
- many more

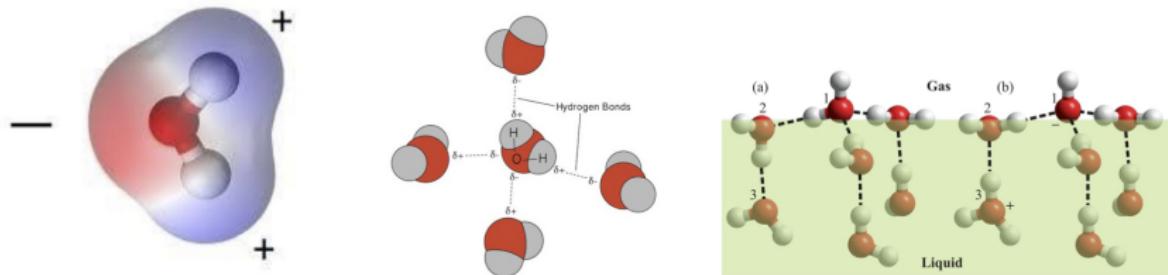
Phase Transitions

Phases

- We are familiar with the three phases of matter - solid, liquid, and gas
- Solids and liquids have very low compressibility, i.e., their density changes very little with large changes in pressure. Comparatively gases change their density very easily with small changes in pressure
- Solids and liquids are therefore called as **condensed matter**
- Consider an unopened bottle of water, at constant T and V . There are both liquid water and water vapour present inside
- If the bottle is opened, at constant T and P , then the water evaporates and only gas is left
- Generally at constant T and P only a single phase can exist in equilibrium .

Free energy

- Consider liquid water. H_2O molecules contain tiny bits of charge concentrations that lead to molecular attraction.
- At the surface however, this attractive potential is unsaturated, leading to surface tension



- The molecules inside the liquid are at a comparatively lower energy compared to molecules at the surface
- There is a free energy associated with this surface, it is called Gibbs free energy and it is equal to $G = \gamma A$, where γ is the surface tension coefficient and A is the surface area

Chemical potential

- Recall that the chemical potential is the energy required to add a particle to system keeping volume and entropy constant

$$\mu = \left. \frac{\partial E}{\partial N} \right|_{S,V} \quad (44)$$

- It can be shown from thermodynamics that the change in free energy of a substance at constant pressure and temperature is given by

 $dG = \mu(P, T)dN \quad (45)$

- Now if the same substance is present in two different states (for ex., solid and liquid), then the change in free energy is

 $dG = \mu_1 dN_1 + \mu_2 dN_2 \quad (46)$

- If total number of particles is fixed $N = N_1 + N_2$, then $dN_1 = -dN_2$

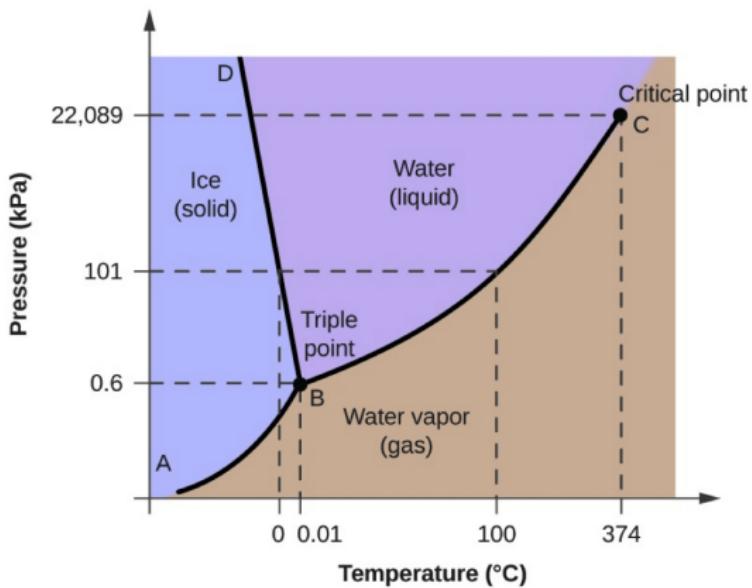
Free energy and chemical potential

- This gives

$$\checkmark dG = (\mu_1 - \mu_2)dN_1 \quad (47)$$

- If $\mu_1 > \mu_2$, then the system can minimize free energy by transferring all molecules N_1 to state 2
- Likewise, if $\mu_1 < \mu_2$ by putting all particles N_2 to state 1
- So, the substance will exist in that phase whose chemical potential is minimum at that given T and P
- This can be represented on a 2D phase diagram showing T and P

Phase diagrams



- The boundary between 2 phases is set by where the chemical potential of the 2 phases become equal.
- Triple point is where all 3 phases co-exist, i.e., chemical potential of all 3 phases is same

Order of phase transition

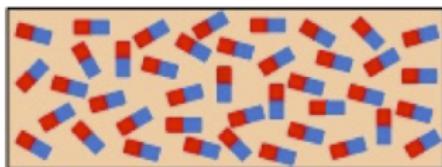
- A characteristic of phase transition is that the substance finds a way to drastically change its free energy
- Again from thermodynamics, it can be shown that $(\partial G / \partial T)|_P = -S$
- During a phase transition the substance finds a way to suddenly change its entropy
- This means that $(\partial G / \partial T)|_P$ changes discontinuously across a phase transition. This is called a first-order phase transition
- If the n^{th} order derivative $(\partial^n G / \partial T^n)|_P$ is discontinuous, while all lower order derivatives are continuous, then it is called a n^{th} -order phase transition

Paramagnetism

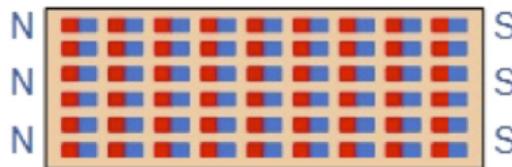
- Paramagnet is a material that is attracted to an applied magnetic field
- Ferromagnetic material is a material that has a natural magnetic field
- In a paramagnetic material , there is an unpaired electron in an orbital which produces a magnetic moment.
- When these magnetic moments are aligned, the substance becomes ferromagnetic, i.e., it develops a coherent magnetic field.
- When the temperature is raised, this ferromagnetism is destroyed and iron becomes paramagnetic

Free energy

Magnetic Materials



Loose and Random
Magnetic Domains



Effect of Magnetization
Domains Lined-up in Series

- We first need to identify the free energy for this problem
- The free energy for this problem is defined as $F = E - TS$
- Just for simplicity imagine that the atoms are lined up and consider pairs of them
- If a pair is aligned, their energy is $-\epsilon$ and if they are misaligned their energy is ϵ .

Free energy

- Consider the ferromagnetic state in which all pairs are aligned, the total energy is $-N\epsilon$ and the entropy is 0
- So in aligned states $F = -N\epsilon$
- In the opposite case of paramagnetic scenario, consider all pairs are totally uncorrelated and random
- In this case on an average half the pairs will be aligned while half will be misaligned, so the average energy will be 0
- The entropy is $S = k_B \ln \Omega = k_B \ln(2^N) = Nk_B \ln 2$
- Here the free energy is $F = -Nk_B T \ln 2$

Curie temperature

- When the temperature is very low, free energy can be minimized by being in the aligned state because $-N\epsilon < -Nk_B T \ln 2$
- When T is very high, then the free energy can be minimized by being in the misaligned state because $-Nk_B T \ln 2 < -N\epsilon$
- The phase transition will occur when $-Nk_B T \ln 2 \approx -N\epsilon$
- The transition temperature will be


$$T_c \approx \frac{\epsilon}{k_B \ln 2} \quad (48)$$

- This is called as the "Curie temperature" (after Marie Curie)
-  This is actually a second order transition because the alignment will smoothly change across this transition starting with very few pairs aligned and their number will slowly grow as the temperature reduces further

Further courses

- EP2200 - Thermodynamics
- EP3120 - Statistical Mechanics
- EP3317 - Thermal Physics
- EP4268 - Solid state Physics
- EP4500 - Advanced Statistical Mechanics