1. Microstates and Macrostates

1.1 Macroscopic and microscopic descriptions

Microstate

- Defined by the microscopic variables e.g. p_i, x_i for each particle
- Each microstate corresponds to an (orthogonal) quantum state of the whole system, e.g. energy eigenstates.
- A microstate provides a full, detailed description of the state of the system.

Macrostate

- Defined by macroscopic (e.g. thermodynamic) variables: e.g. (U, V, N)
- A macrostate is an incomplete description of the state of the system.
- Each macrostate may have a (very) large number of corresponding microstates

The statistical weight Ω

- The statistical weight of a macrostate is the number of microstates in the macrostate.
- We denote it by Ω
- The statistical weight is sometimes called the multiplicity — same thing.

1.2 Single particle states

Consider a system of N identical particles. The complete wavefunction for a system of N particles is a function of every coordinate of every particle: $\psi(r_1, r_2, \dots r_N)$. For N particles the number of interaction terms $\propto N$

We define a key simplification and describe the system in terms of single-particle states.

- We assume particles only weakly interact so they can be treated independently
- We then consider a single particle and calculate the possible states for that particle.
- For a system of identical independent particles, each particle can be described using the same set of single particle states.
- We can then define a microstate as $\psi = (j_1, j_2, \dots j_N)$ which would specify a microstate where particle 1 is ψ_{j_1} etc.

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1.3 Isolated system

For an isolated system U, V, and N are fixed. Rather than trying to work out which microstate the system is in, we consider the probabilities of the available microstates.

We consider systems in internal thermodynamic equilibrium, where the probabilities of microstates are constant. The microscopic state of the system may change continuously, however the probability of finding the system in any particular microstate does not vary once it has reached equilibrium.

1.4 The fundamental postulate

Since we have no further information about the microstates, we use the fundamental postulate of statistical mechanics

· In an isolated system, every accessible microstate is equally likely.

Justification: We have no other information to expect one particular microstate more than any other. This is what we mean by "equally likely".

Not all microstate are accessible. Microstates have to be consistent with the external constraints on U, N, V, i.e. they have to be in the macrostate. The prop probability of a microstate is then

$$P = 1/\Omega$$

for microstates that are in the macrostate, and zero for all other microstates. The larger Ω the more microstates, the less ordered the system statistically.

1.5 Configurations and distributions

Consider a system of N identical distinguishable particles each of which is described by the same set of single-particle states ψ_j for $j = 0, 1, 2...$

· We write a microstate of the system by specifying the single particle state for each particle i.e. $(j_1, j_2, ..., j_N)$
· The number of particles that are in the jth single-particle state are referred as the occupancy of that state, denoted by n_j
· The list of all the occupancies of the single-particle states $[n_0, n_1, ...]$ specifies a configuration, we denote this by the list $\underline{n}$.
· Not all configurations have the same number of microstates.
· The statistical weight of a configuration $\underline{n}$ is the number of microstates that belong to the configuration.

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- Since all microstates are equally likely, the probability of a particular configuration $\underline{n}$ is directly proportional to the number of microstates that belong to it. i.e. to the statistical weight of the configuration.

1.6 The equilibrium configuration

We refer to the most likely configuration as the equilibrium configuration. Note that the system is not always in the equilibrium configuration. According to the fundamental postulate all microstates are equally likely, and this includes those states that may correspond to situations far from equ. Nevertheless the equilibrium configuration is the most likely.

1.7 The Boltzmann entropy

Define the Boltzmann entropy of the system as

$$S = k_B \ln \Omega$$

where k_B is Boltzmann's constant. We treat it as a postulate now.

1.7.1 Einstein's argument

Consider a system AB comprising two independent systems A and B with numbers of microstates given by Ω_A and Ω_B. The total number of microstates of the combined system AB is

$$\Omega_{AB} = \Omega_A \times \Omega_B$$

For each microstate in A we can have any microstate in B. However, entropy is an extensive quantity, so the entropy of the combined system is the sum of the entropies of the two systems

$$S_{AB} = S_A + S_B$$

Therefore if S is a function of Ω, then it must satisfy

$$S(\Omega_A \times \Omega_B) = S(\Omega_A) + S(\Omega_B)$$

which requires that it be of the form

$$S = k \ln \Omega$$

2. Equilibrium and maximum entropy

2.1 Example: a system of spin-half particles

Consider an isolated system with N identical distinguishable spin-half particles.

Two single particles states ψ_j, $j = 1,2$ for spin up and down

System microstate: spin state for each particle: $(j_1, j_2, \ldots, j_N)$

Total number of possible microstates: 2^N

Boltzmann entropy $S = k_B \log \Omega = k_B N \log 2$

The configurations are specified by the occupancy numbers of the single-particle states $[n_1, n_2]$ where n_1 is the number with spin-up and n_2 spin-down. For N particles, the possible configurations are $\underline{n} = [m, N-m]$ for $m = 0, \ldots, N$. The likelyhood of each configuration depends on its statistical weight. The statistical weight of the configuration $[m, N-m]$ is

$$\Omega = \frac{N!}{m!(N-m)!}$$

The corresponding Boltzmann entropy for the configuration is

$$k_B \ln \Omega = k_B [\ln N! - \ln m! - \ln(N-m)!]$$

Using Stirling's approximation for large numbers, this gives

$$k_B \ln \Omega = k_B [N \ln N - m \ln m - (N-m) \ln(N-m)]$$

To find the equilibrium configuration, we need to find the configuration of the largest statistical weight.

$$\frac{\partial \Omega}{\partial m} = 0 \quad \Rightarrow \quad -\ln m + \ln(N+m) = 0 \quad \Rightarrow \quad m = \frac{N}{2}$$

The entropy of the equilibrium configuration is then

$$S = k_B (N \ln N - N \ln N/2) = k_B N \ln 2$$

This is the same as the entropy for the whole system.

Generally for large numbers we find that the entropy for the equilibrium configuration tends to the total entropy.

2.2 Systems with energy

Consider an isolated system with identical distinguishable particles, e.g. a solid comprising N identical atoms at fixed lattice sites

Since system is isolated, U and V are fixed

Each atom is described by the set of single-particle states ψ_j with energy levels ϵ_j. We wish to find the equilibrium configuration.

From the fundamental postulate, all accessible microstates are equally probable. However only microstates that have total energy U are accessible. We need to find the configuration with the largest statistical weight subject to the constraint of the total energy.

2.2.1 Maximizing the entropy

Each configuration is specified by a list of occupancy numbers of the single-particle states $[n_0, n_1, \ldots]$, where n_0 is the number of particles in the ground state. There are many distinct ways of distributing the particles among the single-particle states that result in the same configuration. Counting all the different arrangements for a configuration gives the statistical weight of that configuration, Ω

For configuration $[n_0, n_1, \ldots]$

The statistical density is $\Omega = \dfrac{N!}{\prod_j n_j!}$

The corresponding Boltzmann entropy is

$$k_B \ln \Omega = k_B \left[\ln N! - \sum_j \ln n_j! \right]$$

Constraints:

$$\sum_j n_j = N \qquad \sum_j \epsilon_j n_j = U$$

Using Lagrange's method of undetermined multipliers to maximize $\ln \Omega$ subject to the two constraints:

$$\frac{\partial}{\partial n_j} \left[\ln \Omega - \alpha \sum_{j'} n_{j'} - \beta \sum_{j''} \epsilon_{j''} n_{j''} \right] = 0 \qquad \text{for all } j$$

This requires that

$$\frac{\partial}{\partial n_j} \ln \Omega = \alpha + \beta \epsilon_j \qquad \text{for all } j$$

Substituting for $\ln\Omega$, gives

$$\frac{\partial}{\partial n_j}\ln\Omega = \frac{\partial}{\partial n_j}\left[\ln N! - \sum_{j'}\ln n_{j'}!\right] = -\frac{\partial}{\partial n_j}\ln n_j! = -\ln n_j$$

where we have used Stirling's formula for large n_j

$$-\ln n_j = \alpha + \beta \epsilon_j \quad \text{for all } j$$

$$n_j = \exp(-\alpha - \beta \epsilon_j)$$

This is the Boltzmann distribution

The two Lavange multipliers are associated with N and U.

3. Boltzmann Distribution

3.1 Temperature – the significance of β

The fundamental equation of thermodynamics is

$$T dS = dU + dW$$

For a system with constant V, $dW = 0$, so we have $dU = T dS$. This leads to the thermodynamic relationship for the ~~temperature~~.

$$\frac{1}{T} = \cancel{dU}\left(\frac{dS}{dU}\right)_{V,N}$$

In the statistical description we began with the Boltzmann definition of entropy.

$$S = k_B \ln\Omega$$

We found the equilibrium configuration by maximizing the entropy of the configuration, $k_B \ln\Omega$ with respect to the occupancies n_j. Now consider changing the internal energy of the system by a small amount δU, keeping V and N fixed and allowing the system to come to equilibrium will result in a new equilibrium configuration, with a new set of occupancies. We assume that the energy levels ϵ_j do not change since we are keeping V fixed. The change in internal energy is given by

$$\delta U = \sum_j \epsilon_j \delta n_j$$

The corresponding change in the Boltzmann entropy is given by

$$\delta S = k_B \sum_j \frac{\partial \ln\Omega}{\partial n_j}\delta n_j$$

Lecture 3: The Boltzmann Distribution

However, we have already shown that for equilibrium,

$$\frac{\partial \ln \Omega}{\partial n_j} = \alpha + \beta \varepsilon_j$$

Therefore

$$\delta S = k_B \alpha \sum_j \delta n_j + k_B \beta \sum_j \varepsilon_j \delta n_j = k_B \beta \delta U$$

where we have used $\sum \delta n_j = 0$ since N is fixed. Hence for the Boltzmann entropy we have

$$\beta = \frac{1}{k_B}\left(\frac{\partial S}{\partial U}\right)_{V,N}$$

This is exactly the same form as the thermodynamic relationship between entropy and temperature if $T = k_B \beta$ and so we see that β is related to the thermodynamic temperature,

$$\beta = 1/k_B T$$

β is referred to as "thermodynamic beta" or "coldness"
The distribution of particles among states in the Boltzmann distribution varies exponentially with the energy of the state. Rewriting the Boltzmann distribution in terms of the temperature T we have

$$n_j = e^{-\alpha} e^{-\varepsilon_j/k_B T} \propto e^{-\varepsilon_j/k_B T}$$

3.2 The number of particles - the significance of α

The Lagrange multiplier constant α was introduced as a constraint on the total number of particles. Fixing the number of particles then determines the value of α, thus

$$N = \sum_j n_j \rightarrow N = e^{-\alpha} \sum_j e^{-\beta \varepsilon_j} \rightarrow e^{-\alpha} = \frac{N}{\sum_j e^{-\beta \varepsilon_j}}$$

The value of α normalises the distribution to the total number of particles. The summation is called the partition function, denoted by Z.

$$Z = \sum_j e^{-\beta \varepsilon_j}$$

In terms of the partition function,

$$e^{-\alpha} = \frac{N}{Z}$$

Finally substituting for α, we have for Boltzmann distribution,

$$n_j = \frac{N}{Z} e^{-\beta \varepsilon_j} = \frac{N}{Z} e^{-\varepsilon_j/k_B T}$$

where $\beta = 1/k_B T$ and z is the single-particle partition function.
The probability that a given particle is in the jth state is given by

$$P_j = \frac{e^{-\beta \epsilon_j}}{z}$$

3.3 Zeroth Law

Consider two isolated systems, which need not be the same as each
other, having internal energies U_1 and U_2. For each system, at equilibrium
their Boltzmann entropies are maximal, and we have

$$\beta_1 = \frac{1}{k_B}\left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} \qquad \beta_2 = \frac{1}{k_B}\left(\frac{\partial S_2}{\partial U_2}\right)_{V,N}$$

The entropy of the combined system is

$$S = S_1 + S_2$$

Now consider placing the systems in weak thermal contact so that
energy can transfer between them. If energy δU transfers from
system 1 to 2, then the change in the total entropy of the
combined system is given by

$$\delta S = \left(\frac{\partial S_2}{\partial U_2}\right)_{V,N} \delta U - \left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} \delta U = (\beta_2 k_B - \beta_1 k_B)\delta U$$

when the combined system is in equilibrium it will have maximum
entropy and so at equilibrium, $\delta S = 0$

This requires that $\beta_1 = \beta_2$

Therefore systems in thermal equilibrium with each other must
have the same value of β.
Thus the zeroth law of thermodynamics follows from the maximum
entropy definition of equilibrium.

4. Systems in heat baths

4.1 Ensembles

Definition: An ensemble is a probability distribution for the microstates of a system.

An example of an ensemble is the uniform probability distribution we have been using for an isolated system. (fundamental postulate) So

$$P_j = \frac{1}{\Omega}$$

where Ω is the statistical weight. We refer to this particular ensemble as the microcanonical ensemble. It's applicable to a system with fixed internal energy.

The ensemble does not change with time for a system that is in equilibrium. If we know the appropriate ensemble for the system, we can use it to calculate macroscopic properties and behavior of the system.

4.2 The canonical ensemble

The only requirement for Boltzmann distribution is that the particles need to be in weak thermal contact with each other. Consider an isolated system AB consisting of two components, a system A and a heat bath B in weak thermal contact. A heat bath has large heat capacity compared to the system so its temperature stays unaffected after the exchange. For a given U, the number of microstates of the heat bath will be very large. From the definition of Boltzmann entropy we have for the statistical weight

$$\Omega(U) = e^{S/k_B}$$

For a small change in the internal energy of the heat bath δU, the entropy change is

$$\delta S = \left(\frac{\partial S}{\partial U}\right)_V \delta U = \frac{1}{T}\delta U$$

which gives a statistical weight

$$\Omega(U+\delta U) = e^{(S+\delta S)/k_B} = \Omega(U)e^{\delta S/k_B} = \Omega(U)e^{\delta U/k_B T}$$

Thus, the statistical weight of a heat bath increases exponentially with its internal energy.

Returning to the combined system AB, its microstates are formed from all the possible combinations of A and B that results in total energy U. For a particular microstate ~~with~~ of A with energy ϵ_j, the microstates of the heat bath are those with internal energy $U-\epsilon_j$, and there are $\Omega(U-\epsilon_j)$ microstates.

Total statistical weight of the combined system

$$\Omega_{AB} = \sum_j \Omega(U - \epsilon_j) = \Omega(U) \sum_j e^{-\epsilon_j / k_B T}$$

The probability of a particular microstate of A is proportional to the number of microstates of AB that use it. Which is the statistical weight associated with microstate divided by the total statistical weight of the combined system.

$$P_j = \frac{\Omega(U - \epsilon_j)}{\Omega_{AB}} = \frac{e^{-\epsilon_j / k_B T}}{\sum_j e^{\epsilon_j / k_B T}} = \frac{1}{Z} e^{-\epsilon_j / k_B T}$$

where Z is the partition function for system A. This probability distribution is again the Boltzmann distribution, it defines the canonical ensemble.

4.3 General expression for entropy (Gibbs entropy)

Consider a large assembly of N identical, independent systems distributed among the system microstates according to a probability distribution P_j. The systems are distinguishable. The total number of systems in the jth state is given by Np_j. Then the number of microstates for this distribution is

$$\Omega = \frac{N!}{\prod_j (Np_j)!}$$

Using Stirling's formula

$$\ln \Omega = N \ln N - N - \sum_j [Np_j \ln(Np_j) - Np_j]$$

Noting that $\sum p_j = 1$, this becomes $\ln \Omega = -N \sum_j p_j \ln p_j$

The total Boltzmann of the assembly is then

$$S_B = k_B \ln \Omega = -N k_B \sum_j p_j \ln p_j$$

Assuming the entropy to be extensive, the entropy of a single system is

$$S = -k_B \sum_j p_j \ln p_j$$

This is the Gibbs entropy and is a generalization of the Boltzmann entropy. For the case of an isolated system described by the microcanonical ensemble, the probability of all microstates are equal and this reduces to the Boltzmann definition of entropy.

5. The partition function and thermodynamics

5.1 Link to thermodynamics

The mean energy (E) can be expressed straightforwardly in terms of the partition function:

$$\langle E \rangle = \sum_j P_j \epsilon_j = \frac{1}{Z} \sum_j \epsilon_j e^{-\beta \epsilon_j}$$

Note that

$$\frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta} \sum_j e^{-\beta \epsilon_j} = - \sum_j \epsilon_j e^{-\beta \epsilon_j}, \quad \text{so} \quad \langle E \rangle = \frac{-1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta}$$

We identify the mean energy of the system as internal energy U.

In terms of T ($= 1/k_B \beta$), we have

$$U = - \frac{\partial \ln Z}{\partial T} \frac{dT}{d\beta} = k_B T^2 \frac{\partial \ln Z}{\partial T}$$

5.2 Fluctuations

Since the system can exchange heat with its surroundings, the energy is no longer fixed, we can calculate the energy fluctuations.

$$(\Delta E)^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$\langle E^2 \rangle = \sum_j \epsilon_j^2 P_j = \frac{1}{Z} \sum_j \epsilon_j^2 e^{-\beta \epsilon_j} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad \text{and} \quad \langle E \rangle = - \frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

However differentiating $\ln Z$ twice we have

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \underbrace{\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}}_{\langle E^2 \rangle} - \underbrace{\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2}_{\langle E \rangle^2}$$

Therefore the variance of the energy is

$$(\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = - \frac{\partial U}{\partial \beta} = - \frac{\partial U}{\partial T} \frac{dT}{d\beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_v$$

$\frac{\partial U}{\partial T}$ is the heat capacity of the system at constant volume

The standard deviation of energy fluctuation is

$$\Delta E = \sqrt{\frac{C_v}{k_B}} \, k_B T$$

Heat capacity is an extensive quantity. For a system of n degrees of freedom, it gives $C_v = n k_B / 2$ and

$$\Delta E = \sqrt{\frac{n}{2}} k_B T \implies \Delta E = \frac{C_v T}{\sqrt{n/2}} \sim \frac{\langle E \rangle}{\sqrt{n}}$$

5.3 The bridge equation

For a fixed volume system in contact with a heat bath, the free energy is the Helmholtz function

$$F = U - TS$$

At equilibrium the free energy is a minimum. In terms of the statistical description, using the Gibbs entropy we have for TS,

$$TS = -k_B T \sum_j p_j \ln p_j$$

$$p_j = \frac{e^{-\epsilon_j / k_B T}}{Z} \rightarrow \ln p_j = -\frac{\epsilon_j}{k_B T} - \ln Z$$

$$TS = \sum_j p_j \epsilon_j + k_B T \sum_j p_j \ln Z = U + k_B T \ln Z$$

Rearranging we get

$$F = U - TS = -k_B T \ln Z$$

Once we know the partition function for our system, we can in principle calculate any thermodynamic quantity via our expression for the Helmholtz func.

5.4 Factorization of the partition function

The partition function for a system described by the canonical ensemble is given by:

$$Z = \sum_j e^{-\beta \epsilon_j}$$

where the summation is over all microstates of the system.

Consider a single particle system with microstates ψ_j and corresponding energy levels ϵ_j. The partition function is

$$Z_{(1)} = \sum_j e^{-\beta \epsilon_j}$$

Consider two weakly interacting particles with microstates $\psi = \psi_{j_1} \psi_{j_2}$ and energies $\epsilon_{j_1} + \epsilon_{j_2}$. The partition function now is

$$Z_{(2)} = \sum_{j_1} \sum_{j_2} e^{-\beta (\epsilon_{j_1} + \epsilon_{j_2})} = \left(\sum_{j_1} e^{-\beta \epsilon_{j_1}} \right) \left(\sum_{j_2} e^{-\beta \epsilon_{j_2}} \right) = Z_{(1)}^2$$

Similarly for N weakly interacting particles, the partition function is

$$Z = Z_{(1)}^N, \quad \ln Z = \ln Z_{(1)}^N = N \ln Z_{(1)}$$

$$F = -k_B T \ln Z = -N k_B T \ln (Z_{(1)}), \quad U = k_B T^2 \frac{\partial \ln Z}{\partial T} = N k_B T^2 \frac{\partial \ln Z_{(1)}}{\partial T}$$

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Factorization of the partition function can also apply for composite systems comprised of weakly interacting components. Consider a single diatomic molecule in a gas:

$$\epsilon = \epsilon_{trans} + \epsilon_{vib} + \epsilon_{rot}$$

The partition function then factorises

$$Z = \sum_{j_t} \sum_{j_v} \sum_{j_r} \exp[-\beta(\epsilon_{j_t} + \epsilon_{j_v} + \epsilon_{j_r})] = Z_{trans} \cdot Z_{vib} \, Z_{rot}$$

$$\rightarrow \ln Z = \ln Z_{trans} + \ln Z_{vib} + \ln Z_{rot}$$

5.5 Application to quantum harmonic oscillators

Think of a single atom in a solid. The energy levels for 1D harmonic oscillator:

$$\epsilon_j = (j + \tfrac{1}{2})\hbar\omega \qquad j = 0, 1, 2, \dots$$

The partition function is then

$$Z = e^{-\frac{1}{2}\hbar\omega\beta} \sum_{j=0}^{\infty} e^{-j\hbar\omega\beta} = e^{-\frac{1}{2}\hbar\omega\beta} / 1 - e^{-\hbar\omega\beta} \qquad \left(\sum_0^\infty x^j = 1/1-x\right)$$

The internal energy is given by

$$U = -\frac{\partial \ln Z}{\partial \beta} \;,\quad \ln Z = -\tfrac{1}{2}\hbar\omega\beta - \ln(1 - e^{-\hbar\omega\beta})$$

$$U = \tfrac{1}{2}\hbar\omega + \frac{1}{1-e^{-\hbar\omega\beta}}(-e^{-\hbar\omega\beta})(-\hbar\omega) = \left(\tfrac{1}{2} + \frac{1}{e^{\hbar\omega\beta}-1}\right)\hbar\omega$$

For a solid of N identical distinguishable oscillators, the internal energy is N times this.
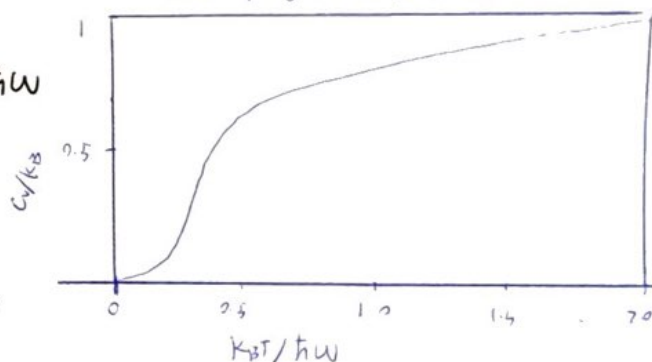
- Behavior at low temperature

$$\hbar\omega\beta \gg 1 \rightarrow \frac{1}{e^{\hbar\omega\beta}-1} \ll 1 \rightarrow U \approx \tfrac{1}{2}\hbar\omega$$

- Behavior at high temperature

$$\hbar\omega\beta \gg 1 \rightarrow e^{\hbar\omega\beta} \approx 1 + \hbar\omega\beta + \dots$$

$$\rightarrow U \approx \left(\tfrac{1}{2} + \frac{1}{\hbar\omega\beta}\right)\hbar\omega = \frac{\hbar\omega}{2} + k_B T \approx k_B T$$

Heat capacity for 1D quantum HO

5.5.1 Einstein Solid

The heat capacity for 1D harmonic oscillator is

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

Substitute $\beta = 1/k_B T$ for U and differentiate wrt T

$$C_v = \frac{1}{(e^{\hbar\omega/k_B T}-1)^2} e^{\hbar\omega/k_B T} \left(\frac{\hbar\omega}{k_B T^2}\right)\hbar\omega = \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}\left(\frac{\theta_E}{T}\right)^2 k_B \;,\quad \theta_E = \frac{\hbar\omega}{k_B}$$

The Einstein solid model treats each atom in the solid as a 3D quantum harmonic oscillator. All oscillators have the same frequency ω. For N atoms, this results in a heat capacity of $3N C_v$. The parameter θ_E is referred to as the Einstein temperature and is a characteristic of the solid.

6. Systems with variable particle number

6.1 The grand canonical ensemble

We are now going to allow the system to exchange both heat and particles with its surroundings. Consider a system that can have variable number of particles in it.

The system has a set of microstates Ψ_j, each with energy ϵ_j and number of particles N_j. We try to find the probability distribution for its microstates when it is in thermal and particle equilibrium with its surroundings.

We will start with a large number of of identical systems and maximize the entropy of a configuration. The systems are allowed to exchange energy and particle with each other. The total energy and number of particles in the assembly are fixed, also the total number of systems.

A microstate of the assembly is given by specifying the microstate of each individual system in the assembly. We write $[n_0, n_1, \ldots]$ where n_0 is the number of systems that are in microstate Ψ_0, n_1 the number of ...

The statistical weight associated with a configuration of the assembly is

$$\Omega = \frac{N_A!}{\prod_j n_j!}$$

Where N_A is the total number of systems in the assembly. We will find the equilibrium distribution by maximizing the entropy of the whole assembly subject to the constraints on total energy, total number of particles and total number of systems.

$$\sum_j n_j = N_A \qquad \sum_j n_j \epsilon_j = N_A U \qquad \sum_j n_j N_j$$

where N is the mean number of particles per system. Again we use Lagrange's method of undetermined multipliers to maximize $\ln \Omega$ subject to the constraints.

$$\frac{\partial}{\partial n_j} \left[\ln \Omega - \alpha \sum_{j'} n_{j'} - \beta \sum_{j'} n_{j'} \epsilon_{j'} - \lambda \sum_{j'} n_{j'} N_{j'} \right] = 0 \qquad \text{for all } j$$

$$\frac{\partial \ln \Omega}{\partial n_j} - \alpha - \beta \epsilon_j - \lambda N_j = 0 \qquad \text{for all } j$$

$$n_j = e^{-\alpha - \beta \epsilon_j - \lambda N_j}$$

The probability that a system is in the jth microstate with ϵ_j and N_j is

$$P_j = \frac{n_j}{N_A} = \frac{e^{-\alpha}}{N_A} e^{-\beta \epsilon_j - \lambda N_j}$$

This is the probability distribution for a system that is in a heat and particle bath.

6.2 The grand partition function

Recognize $e^{-\alpha}/N_A$ as a normalization factor

$$\sum_j p_j = 1$$

$$\Rightarrow \quad p_j = \frac{1}{Z} e^{-\beta \epsilon_j - \lambda N_j} \qquad \text{where} \qquad Z = \sum_j e^{-\beta \epsilon_j - \lambda N_j}$$

Z is the grand partition function (of ~~the~~ a system, not the whole assembly)
The summation is over all microstates of the system.

6.3 The temperature and the chemical potential

Use the probability distribution for the microstates of the system to calculate
the Gibbs theory.

$$S = -k_B \sum_j p_j \ln p_j = -k_B \sum_j p_j (-\beta \epsilon_j - \lambda N_j - \ln Z)$$

$$= k_B \beta \sum_j p_j \epsilon_j + k_B \lambda \sum_j p_j N_j + k_B \ln Z \sum_j p_j$$

$$= k_B \beta U + k_B \lambda N + k_B \ln Z$$

where U is the internal energy of the system and N the mean particle number.
For fixed V and fixed N

$$dS = k_B \beta \, dU \rightarrow \left(\frac{\partial S}{\partial U} \right)_{N,V} = k_B \beta \qquad , \quad \beta = 1/k_B T$$

Now keep V and U fixed

$$dS = k_B \lambda \, dN \rightarrow \left(\frac{\partial S}{\partial N} \right)_{U,V} = k_B \lambda$$

The fundamental equation of thermodynamics becomes

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

where μ is the chemical potential. We can see that

$$\left(\frac{\partial S}{\partial N} \right)_{U,V} = -\frac{\mu}{T} \quad , \qquad \lambda = -\mu/k_B T$$

Particles will tend to flow from the higher chemical potential to the lower.
The probability that the system is in the jth microstate in chemical potential is

$$p_j = \frac{1}{Z} e^{-(\epsilon_j - \mu N_j)/k_B T} \quad , \quad Z = \sum_j e^{-(\epsilon_j - \mu N_j)/k_B T}$$

This is the grand canonical ensemble.
It is the probability distribution for a system in equilibrium with a particle
bath and a heat bath.

6.4 Grand potential

Returning to the expression for the entropy of the system and substituting $\lambda = -M/k_B T$ and $\beta = 1/k_B T$ we have

$$S = \frac{1}{T} U - \frac{M}{T} N + k_B \ln Z$$

from which we can see that

$$-k_B T \ln Z = U - TS - MN$$

We have an expression relating the grand partition function to a thermodynamic potential, the grand potential,

$$\Phi = U - TS - MN$$

The grand partition function is the key link to the thermodynamics for systems that are in heat and particle baths.

$$\Phi = -k_B T \ln Z$$

If we know Z, we can use it to calculate any thermodynamic variables via the grand potential.

$$dU = T dS - P dV + M dN. \rightarrow d\Phi = -S dT - P dV - N dM$$

Taking derivatives we obtain

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,M} , \quad P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,M} , \quad N = -\left(\frac{\partial \Phi}{\partial M}\right)_{V,T}$$

7. Gases and density of states

7.1 Distinguishable and indistinguishable particles

Distinguishable: atoms in a solid

Indistinguishable: gases, liquids, electrons in metals, photons

The real difference between distinguishable and indistinguishable is in the nature of the single-particle states that we use to describe the system

In gas we use one set of single particle states, occupying the whole volume of the gas. This set of states is essentially shared between all the particles of the gas.

In a solid, each lattice site has its own, local copy. We can therefore distinguish between these two descriptions:

- the atom at site A in state 1 and the atom at site B in state 2
- the atom at site A in state 2 and the atom at site B in state 1

Now as we look at gas we will need a different approach to count microstates.

7.2 Density of states

Consider a gas of identical particles. The particles are indistinguishable. Rather than being localized, they share a common volume and occupy a shared set of single-particle states. For a gas, the number of available states is given by the density of states calculation. We begin by calculating the single particle states for a gas particle.

The Schrödinger equation for a non-relativistic particle in free space is

$$\frac{-\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi$$

This has the travelling wave solution

$$\psi = A e^{i\vec{k}\cdot\vec{r}}$$

with energy given by the dispersion relation

$$\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad , \quad k^2 = |\vec{k}|^2$$

We need to be able to count the number of states available to the particles as a function of energy. Since in free space energy is directly related to the momentum, we consider the momentum states.

Consider a cubic region of $V = L^3$. Suppose we start with a travelling wave state $A e^{i\vec{k}\cdot\vec{r}}$ then we generate a complete set of wavefunctions that are orthogonal over V by adding to $\vec{k}_0$ a wavevector

$$k = (k_x, k_y, k_z) = \left(\frac{2\pi l}{L}, \frac{2\pi m}{L}, \frac{2\pi n}{L}\right) \quad \text{for any int } l, m, n$$

These orthogonal states are uniformly spaced in k-space with a k-space volume of $(2\pi/L)^3$ per state. The density of states in k-space is then

$$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{(2\pi)^3}$$

This does not depend on any boundary conditions our region might have.

The number of states in an elemental volume of k-space, $d^3k = dk_x\, dk_y\, dk_z$ is

$$dg = V \frac{d^3k}{(2\pi)^3} = V \frac{d^3p}{h^3}$$

where $d^3p = dp_x\, dp_y\, dp_z$ is the corresponding element of momentum space ($p = \hbar k$)

We can integrate to get number of states with wavenumber k to $k+dk$

$$dg = g(k)\, dk = V \frac{1}{(2\pi)^3} 4\pi k^2 dk = \frac{1}{2\pi^2} V k^2\, dk$$

$$\rightarrow g(k) = \frac{1}{2\pi^2} V k^2$$

$g(k)$ is the density of states in wavenumber.

We can now calculate the corresponding density of states in energy. If we define $g(\epsilon)$ to be the density of states in energy, then the number of states with energies between ϵ and $\epsilon + d\epsilon$ corresponding to wavenumbers k to $k+dk$ is

$$dg = g(\epsilon)\, d\epsilon = g(k)\, dk \rightarrow g(\epsilon) = g(k) \frac{dk}{d\epsilon}$$

Using the dispersion relationship

$$k = \frac{\sqrt{2m\epsilon}}{\hbar}, \quad \frac{d\epsilon}{dk} = \frac{\hbar^2 k}{m} = \hbar\sqrt{\frac{2\epsilon}{m}}$$

$$g(\epsilon) = \frac{1}{2\pi^2} V \frac{2m\epsilon}{\hbar^2} \times \frac{1}{\hbar}\sqrt{\frac{m}{2\epsilon}} = \frac{2\pi V}{\hbar^3} (2m)^{3/2} \epsilon^{1/2}$$

Using the density of states, a summation can be replaced with an integration.

Note:
- The number of states between ϵ and $\epsilon + d\epsilon$ is proportional to the volume

- The density of states does not depend on the b.c.s or the choice of wavefunction basis.

- This is only for translational motion. Particles may have internal states e.g. spin. If there is no energy associated with the internal states, that will give a degeneracy i.e. for each translational state there will be several distinct single particle states corresponding to the different internal states. We will represent this as a degeneracy factor D, the number of single particle states per translation state.

8. Classical ideal gas

8.1 The Boltzmann distribution for a classical ideal gas

Consider a dilute ideal gas i.e. no interaction between the particles of the gas. We assume single particle states are valid. We start from the canonical ensemble of a single particle.

Consider a single molecule of gas in a container at temperature T. The molecule can be treated as a system in a heat bath. The microstates are the single-particle states and the probability that the molecule is in the jth particle state, which has energy ϵ_j is given by the canonical ensemble

$$P_j = \frac{1}{Z} e^{-\epsilon_j/k_BT} \quad \text{where} \quad Z = \sum_j e^{-\epsilon_j/k_BT}$$

For N particles, provided $P_j N \ll 1$, we can neglect multiple occupancies of states. Then each molecule can be treated as a system in a heat bath provided by the rest of the molecules. The average number of particles in the jth single-particle state is the mean occupancy of the state,

$$f_j = NP_j = \frac{N}{Z} e^{-\epsilon_j/k_BT}$$

where Z is the single particle partition function. This is the Boltzmann distribution for a classical gas. It only works for $f_j \ll 1$

8.2 Partition function for an ideal gas

The partition function for a single particle is the sum over all states. However the energy levels for the single-particle translation states are very closely spaced so we can replace the summation with an integral over the density of states.

$$Z = \int_0^\infty D g(\epsilon) e^{-\epsilon/k_BT} d\epsilon$$

where D is the degeneracy and $g(\epsilon)$ is the density of states. Substituting the previously calculated density of states $g(\epsilon)$ for a free particle, and use standard integral

$$Z = \int_0^\infty D \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{\frac{1}{2}} e^{-\epsilon/k_BT} d\epsilon \quad , \quad \int_0^\infty x^{\frac{1}{2}} e^{-ax} dx = \frac{\pi^{\frac{1}{2}}}{2a^{3/2}}$$

this gives the partition function for a single particle

$$Z = DV \left(\frac{2\pi m k_BT}{h^2} \right)^{3/2}$$

8.3 Thermodynamics of an ideal classical gas

For N independent identical particles, we can not distinguish between different permutations of the particles, so we divide by $N!$. The N particle partition function is then

$$Z = \frac{Z_{(1)}^N}{N!}$$

where $Z_{(1)}$ is the partition function for a single molecule. The factor $N!$ is only correct for very dilute gases so cases of over 1 particle in a state can be ignored.

The log of the partition function is (stirling's approximation)

$$\ln Z = N \ln Z_{(1)} - (N \ln N - N)$$

$$= N(\ln Z_{(1)} - \ln N + 1)$$

$$= N\left[\ln D + \ln V + \frac{3}{2}\ln T - \ln N + \frac{3}{2}\ln\left(\frac{2\pi m k_B}{h^2}\right) + 1\right]$$

The internal energy is then

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} = \frac{3 N k_B T}{2}$$

Agrees with the thermodynamics result for a monoatomic ideal gas

The Helmhotz function is:

$$F = -k_B T \ln Z$$

$$= -k_B T N\left[\ln D + \ln V + \frac{3}{2}\ln T - \ln N + \frac{3}{2}\ln\left(\frac{2\pi m k_B}{h^2}\right) + 1\right]$$

We can calculate the pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{N k_B T}{V} \qquad \text{(ideal gas law)}$$

Calculating the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B T\left(\frac{\partial \ln Z}{\partial T}\right)_V + k_B \ln Z$$

$$= N k_B\left[\ln D + \ln V + \frac{3}{2}\ln T - \ln N + \frac{3}{2}\ln\left(\frac{2\pi m k_B}{h^2}\right) + \frac{5}{2}\right]$$

This is the Sackur-Tetrode equation for the entropy of a monoatomic ideal gas.

8.4 Maxwell-Boltzmann speed distribution

The number of particles with speeds v to $v + dv$ is given by

$$n(v)dv = D\, g(v)\, f(v)\, dv$$

where $g(v)$ is the density of the states in speed and $f(v)$ is the mean occupancy of states with speed v. The number of states with speeds v to $v + dv$, corresponding to wavenumbers k to $k + dk$ is

$$dg = g(v)\,dv = g(k)\,dk \quad \rightarrow \quad g(v) = g(k)\frac{dk}{dv}$$

But, $v = p/m = \hbar k/m$ and using the previously derived density of states in wavenumber gives

$$g(v) = g(k)\frac{dk}{dv} = V\frac{k^2}{2\pi^2}\frac{m}{\hbar} = V\frac{m^3 v^2}{2\pi^2\hbar^3} = 4\pi V\frac{m^3}{\hbar^3}v^2$$

The mean occupancy is

$$f(\epsilon) = \frac{N}{Z_1}e^{-\epsilon/k_BT}$$

$$f(v) = \frac{N}{Z_1}e^{-mv^2/2k_BT}$$

$$= \frac{N}{\cancel{V}N}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}e^{-mv^2/2k_BT}$$

Therefore

$$n(v)\,dv = \cancel{D}4\pi V\frac{m^3}{\hbar^3}v^2\frac{N}{\cancel{V}N}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}e^{-mv^2/2k_BT}\,dv$$

$$= N\sqrt{\frac{2}{\pi}}\left(\frac{m}{k_BT}\right)^{3/2}v^2 e^{-mv^2/2k_BT}\,dv$$

This is the Maxwell-Boltzmann speed distribution. Purely classical result. It is used to define ~~terminal~~ a thermal speed

$$V_T = \sqrt{\frac{k_BT}{m}}$$

The three characteristic speeds are
 · The most probable speed, $V_{max} = \sqrt{2}\,V_T$
 · The mean speed, $\langle V \rangle = \sqrt{8/\pi}\,V_T$
 · The RMS speed, $V_{RMS} = \cancel{\sqrt{\langle V^2\rangle}}\,\sqrt{\langle V^2\rangle} = \sqrt{3}\,V_T$

The RMS speed is related to the kinetic energy

$$\text{mean KE} = \frac{1}{2}m V_{RMS}^2 = \frac{3}{2}k_BT$$

again in agreement with equipartition

In terms of the thermal speed, with $v' = v/V_T$, the Maxwell-Boltzmann speed distribution is

$$n(v')\,dv' = N\sqrt{\frac{2}{\pi}}v'^2 e^{-v'^2/2}\,dv'$$

9. Quantum statistics: fermions and bosons

Fermions: Particles with half-integer spin
   Wavefunctions are antisymmetric with respect to exchange of the particle labels
   giving a maximum occupancy of one for a single-particle state.
   Examples: electron, proton, neutron, ^{3}He, quark, neutrino

Bosons: Particles with integer spin
   Wavefunctions are symmetric with respect to exchange of particle labels
   so there is no limit on the occupancy of a single-particle state.
   Examples: photon, W, Z, Higgs, ^{4}He

9.1 Equilibrium distributions

Consider a system of indistinguishable identical particles. There are a large
number of these single-particle states in the system. Each single-particle state
j will have an occupancy n_j and energy $n_j \epsilon_j$. We can treat each single-particle
state as a distinct system in its own right. We can also treat them
as weakly interacting: although particles and energy can move between the
different single particle states, the energy levels are not affected.
Consider the jth single particle state with energy level ϵ_j. It will have a
set of microstates corresponding to each of the possible values of its
occupancy n with corresponding energy $n\epsilon_j$. The grand partition function is

$$Z = \sum_n \exp(-(n\epsilon_j - n\mu)\beta) = \sum_n e^{n(\mu - \epsilon_j)\beta}$$

where the summation is over the possible values of the occupancy n.
The probability that there are n particles in this single particle state is

$$p(n) = \frac{1}{Z} e^{n(\mu - \epsilon_j)\beta}$$

The expectation (mean occupancy) of the state in equilibrium is given
by
$$\langle n \rangle = \sum_n n\, p(n) = \frac{1}{\beta Z} \frac{\partial Z}{\partial \mu}$$

9.2 Fermions

Possible occupancy values are 0 or 1. The grand partition function is
$$Z = \sum_{n=0}^{1} e^{n(\mu - \epsilon_j)\beta} = 1 + e^{(\mu - \epsilon_j)\beta}$$

Then the mean occupancy of the jth single-particle state is
$$\langle n \rangle = \frac{1}{1 + e^{(\mu - \epsilon_j)\beta}} e^{(\mu - \epsilon_j)\beta} = \frac{1}{e^{(\epsilon_j - \mu)\beta} + 1}$$

Using $\beta = 1/k_B T$, we write the mean occupancy for fermions for a state as

$$f_{FD} = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1} \qquad \text{Fermi-Dirac distribution}$$

9.3 Bosons

The Pauli exclusion principle does not apply so the grand partition function is

$$Z = \sum_{n=0}^{\infty} e^{n(\mu - \epsilon_j)\beta} = \frac{1}{1 - e^{(\mu - \epsilon_j)\beta}}$$

Standard result $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$

The mean occupancy is then

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

which gives for the Bose-Einstein distribution

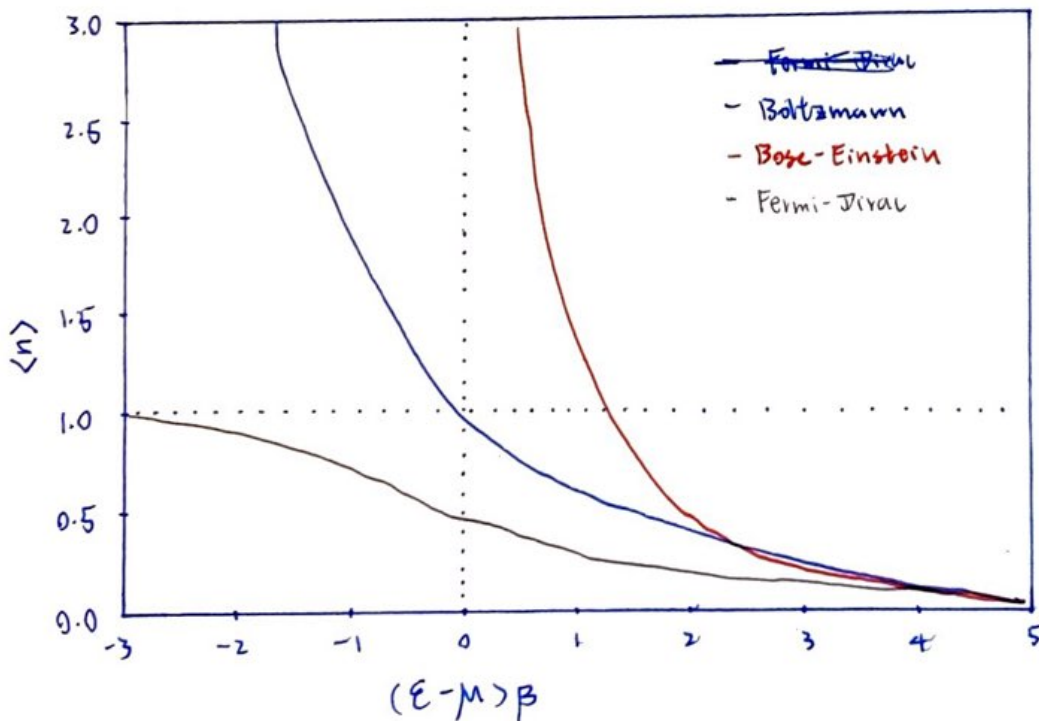$$f_{BE} = \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1}$$

9.4 Summary

Writing the classical Boltzmann distribution in the same form for comparison

$$f = \frac{1}{e^{(\epsilon - \mu)/k_B T} \pm 1} \quad \begin{cases} +1 & \text{Fermi-Dirac} \\ -1 & \text{~~Ferm~~ Bose-Einstein} \end{cases}$$

$$f = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 0} \qquad \text{Boltzmann (classical)}$$

- Both Fermi-Dirac and Bose-Einstein approximate to the Boltzmann in the dilute limit, $(\epsilon - \mu)/k_B T \gg 1$
- For the Bose-Einstein distribution, $\mu < \epsilon$
- For the Fermi-Dirac distribution, $\langle n \rangle \approx 1$ for $(\epsilon - \mu) \ll k_B T$

10. Photon gas

10.1 Cavity (black-body) radiation

Consider a cavity of volume V with internal walls at fixed temperature T. The radiation inside the cavity is in thermal contact with the walls of the cavity — radiation can be absorbed, reflected, and emitted at the walls. The radiation will therefore be in thermal equilibrium at temperature T so we can use the Bose-Einstein distribution to describe it. For a photon gas, the number of particles is not conserved. Therefore the chemical potential, $\mu = 0$. Then for photons

$$f_{BE} = \frac{1}{e^{\mathcal{E}/k_B T} - 1} = \frac{1}{e^{\hbar \omega / k_B T} - 1}$$

The number of photons with angular frequency ω to $\omega + d\omega$ is given by

$$n(\omega) d\omega = D g(\omega) f_{BE}(\omega) d\omega$$

where $g(\omega)$ is the density of states in ω, and D is the degeneracy factor

10.1.1 Density of states for photons

The wave equation for E-M waves in free space is

$$\nabla^2 \underline{E} = \frac{1}{c^2} \frac{\partial^2 \underline{E}}{\partial t^2} \quad \text{with solutions} \quad \underline{E} = \underline{E}_0 e^{i(\underline{k} \cdot \underline{r} - \omega t)}$$

which gives the energy dispersion relationship

$$\omega = kc$$

The number of states with wavenumber k to $k + dk$ is given by the density of states in wavenumber.

$$dg = g(k) dk = \frac{V}{2\pi^2} k^2 dk$$

Using the dispersion relationship allows us to derive the density of states in ω thus

$$g(\omega) = g(k) \frac{dk}{d\omega} = \frac{V}{2\pi^2} k^2 \times \frac{1}{c}$$

$$\rightarrow dg = g(\omega) d\omega = \frac{V}{2\pi^2 c^3} \omega^2 d\omega$$

10.1.2 Planck radiation law

For each travelling wave mode there are two independent polarizations, and so the degeneracy factor is $D = 2$. This then gives for the number of photons.

$$n(\omega) d\omega = 2 \times \frac{V}{2\pi^2 c^3} \omega^2 \times \frac{1}{e^{\hbar \omega / k_B T} - 1} d\omega$$

$$= \frac{V}{\pi^2 c^3} \frac{\omega^2}{e^{\hbar \omega / k_B T} - 1} d\omega$$

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The spectral energy density, $u(\omega)$ is then given by

$$u(\omega)\,d\omega = \hbar\omega\,\frac{n(\omega)}{V}\,d\omega$$

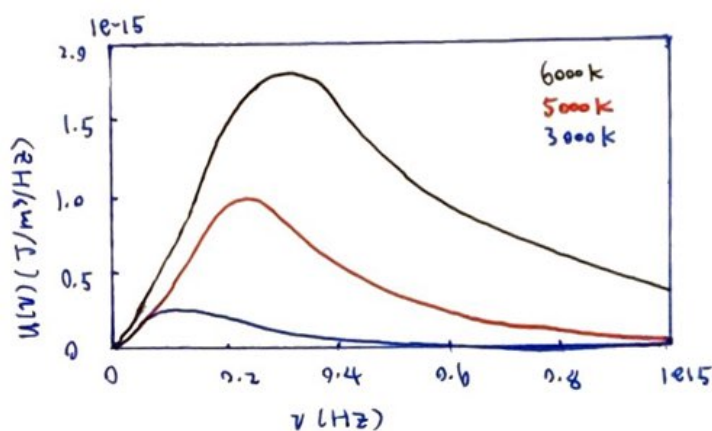$$= \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3}{e^{\hbar\omega/k_BT}-1}\,d\omega$$

This is the Planck radiation law. In terms of frequency $\nu = \frac{\omega}{2\pi}$, the spectral energy density is given by

$$u(\nu)\,d\nu = \frac{8\pi h}{c^3}\,\frac{\nu^3}{e^{h\nu/k_BT}-1}\,d\nu$$

Note that energy density increases with temperature.
The peak of the spectrum depends on temperature

$$\nu_{max} \approx 2.82\,\frac{k_BT}{h} \qquad \text{Wien's displacement law}$$

$1e\text{-}15$

$u(\nu)\,(\,J/m^3/Hz\,)$ vs $\nu\,(Hz)$

6000 k
5000 k
3000 k

10.2 Stefan-Boltzmann Law

If we integrate spectral energy density, we obtain total energy density

$$U = \int_0^\infty u(\nu)\,d\nu$$

$$= \frac{8\pi h}{c^3}\left(\frac{k_BT}{h}\right)^4 \int_0^\infty \frac{x^3}{e^x-1}\,dx$$

$$= \frac{8\pi^5 h}{15\,c^3}\left(\frac{k_BT}{h}\right)^4$$

Using $x = h\nu/k_BT$ to transform into a standard form integral, which gives $\frac{\pi^4}{15}$

U is the total energy density. From this we can calculate the radiation flux. For isotropic radiation, the radiance is given by

$$L = \frac{1}{4\pi}\,Uc$$

Then if the cavity has a small entrance (does not alter thermal equilibrium) the radiation flux leaving the cavity entrance is

$$j^* = 2\pi\frac{L}{2} = \frac{Uc}{4}$$

Substituting for energy density this gives

$$j^* = \sigma T^4, \text{ where } \sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2} \approx 5.67 \times 10^{-8} \text{ J s}^{-1} \text{ m}^{-2} \text{ K}^{-4}$$

This is the Stefan-Boltzmann law for emissivity of a black body i.e. the energy flux leaving a black body.

11 Bose-Einstein condensation

Consider a system comprising a fixed number of non-relativistic bosons with mass m in thermal equilibrium at temperature T. The occupancy of the jth state with energy ϵ_j is given by the Bose-Einstein distribution.

$$f_{BE}(\epsilon_j) = \frac{1}{e^{(\epsilon_j - \mu)/k_B T} - 1}$$

The occupancies of the states must sum to the total number of particles,

$$N = \sum_j f_{BE}(\epsilon_j)$$

Assuming that the states are closely spaced, we replace the summation with an integral over the density of states

$$N = \int_0^\infty f_{BE}(\epsilon) g(\epsilon) d\epsilon$$

For simplicity we assumed a degeneracy factor of 1. Recall that the density of states for a non-relativistic particle is

$$g(\epsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}$$

giving

$$N = \int_0^\infty \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1} \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$$

$$= \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{e^{(\epsilon - \mu)/k_B T} - 1} d\epsilon$$

The total number of particles in the system is a function of both the chemical potential and the temperature. Therefore when the number of particles is fixed, changing the temperature will cause the chemical potential to adjust such that the sum over the occupancies of the states remains constant. However to ensure finite occupancy in every state, the chemical potential must also satisfy $\mu < \epsilon_0$, where ϵ_0 is the ground state energy. which we take to be zero. Setting $\mu = 0$ in the above integral over the density of states gives

$$N_{\mu=0} = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{e^{\epsilon/k_B T} - 1} d\epsilon = 2\pi V \left(\frac{2m k_B T}{h^2}\right)^{3/2} \int_0^\infty \frac{x^{1/2}}{e^x - 1} dx$$

$$= \zeta\left(\frac{3}{2}\right) V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

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where we have used the result of a standard integral

$$\int_0^\infty \frac{x^{1/2}}{e^x - 1} dx = \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right)$$

and the Riemann zeta function has value $\zeta\left(\frac{3}{2}\right) \approx 2.61$. Since setting $\mu = 0$ corresponds to the maximum value of this integral, it indicates that $N_{\mu=0}$ is the maximum number of particles that the system can contain for a given temperature T. Equivalently, for a given number of particles N, there is a minimum temperature below which the system cannot be cooled

$$T > T_B = \frac{h^2}{2\pi m k_B} \left(\frac{N}{V \zeta(3/2)}\right)^{2/3}$$

There is a problem in our calculation. The approximation of the summation over the discrete energy states with the density of states integral is only valid if the integrand varies slowly compared with the spacing of the energy levels (i.e. $k_B T \gg \delta E$). For low temperatures this condition is not satisfied at the lower end of the integration near $\epsilon = 0$. Up to now, as we go lower in temperature the expected occupancy of those states become bigger and the error in neglecting them becomes more significant.

We refine our approximation by including an extra term:

$$N = n_0 + \int_0^\infty f_{BE}(\epsilon) g(\epsilon) d\epsilon$$

where the occupancy of the ground state is

$$n_0 = \frac{1}{e^{-\mu/k_B T} - 1}$$

and the integral accounts for other states, the excited states. For temp $T < T_B$ we expect the number of particles in the ground state to be large

$$n_0 = \frac{1}{e^{-\mu/k_B T} - 1} \approx -\frac{k_B T}{\mu} \rightarrow -\mu \approx \frac{k_B T}{n_0}$$

Thus μ is close to zero and for $T < T_B$ we use $N_{\mu=0}$ for the density of states integral. The fraction of particles in these excited states is then

$$\frac{N - n_0}{N} \approx \frac{N_{\mu=0}(T)}{N} = \left(\frac{T}{T_B}\right)^{3/2}$$

T_B is the critical temperature.

Below this temperature, the number of particles in the ground state becomes macroscopically large. This is Bose-Einstein condensation.

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12 Fermi gases

12.1 The Fermi level

$$f_{FD} = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$

At low temperatures, there is a rapid transition between filled and unfilled states, the distribution becoming a step function as the temperature tends to zero,

$$\lim_{T \to 0} f_{FD} = \begin{cases} 1 & \text{if } \epsilon < \mu \\ 0 & \text{if } \epsilon > \mu \end{cases}$$

At $T = 0$, all states below $\epsilon = \mu$ are filled, and all states above are empty. In this case we refer to the gas as being degenerate (not the same as energy degeneracy). The chemical potential at $T=0$ defines the Fermi energy

$$\epsilon_F = \mu |_{T=0}$$

Note that the chemical potential itself depends on the temperature. Since the Fermi level is the boundary between the filled $(\epsilon < \epsilon_F)$ and the empty $(\epsilon > \epsilon_F)$ states at $T=0$, the total number of states up to the Fermi level must equal to the number of particles in the system

$$N = \int_0^{\epsilon_F} D g(\epsilon) d\epsilon$$

So for free, non-relativistic electrons with a degeneracy factor of z due to their spin the total number of electrons in a volume V satisfies

$$N = \int_0^{\epsilon_F} 2 \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$$

$$= \left(\frac{2m\epsilon_F}{h^2} \right)^{3/2} \frac{8\pi V}{3}$$

From which we obtain the Fermi energy

$$\epsilon_F = \frac{h^2}{2m} \left(\frac{3}{8\pi} \right)^{2/3} \left(\frac{N}{V} \right)^{2/3}$$

Define the Fermi temperature as $T_F = \epsilon_F / k_B$. For $T \gg T_F$, the occupancy f_{FD} is very small for all energies and the gas approximates the classical Maxwell-Boltzmann. For $T \sim T_F$ quantum statistics are needed, for $T \ll T_F$ the degenerate situation is a very good approximation.

12.2 Thermodynamic properties of degenerate Fermi gases

The internal energy of the gas is given by

$$U = \int_0^\infty n(\epsilon) \epsilon d\epsilon$$

$$= \int_0^\infty D g(\epsilon) f_{FD}(\epsilon) \epsilon d\epsilon$$

In the limit $T \to 0$, this becomes
$$U = \int_0^{\epsilon_F} D g(\epsilon) \epsilon \, d\epsilon$$

Since the density of states varies as $g(\epsilon) \propto \epsilon^{1/2}$ for a non-relativistic free particle this gives
$$U = A \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = \frac{2A}{5} \epsilon_F^{5/2}$$

Similarly the total number of particles satisfies
$$N = A \int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon = \frac{2A}{3} \epsilon_F^{3/2}$$

from which we can calculate the total internal energy as
$$U = \frac{3}{5} N \epsilon_F$$

Therefore, even at zero temperature, the degenerate Fermi gas can have significant internal energy. However at $T=0$, the entropy is zero.
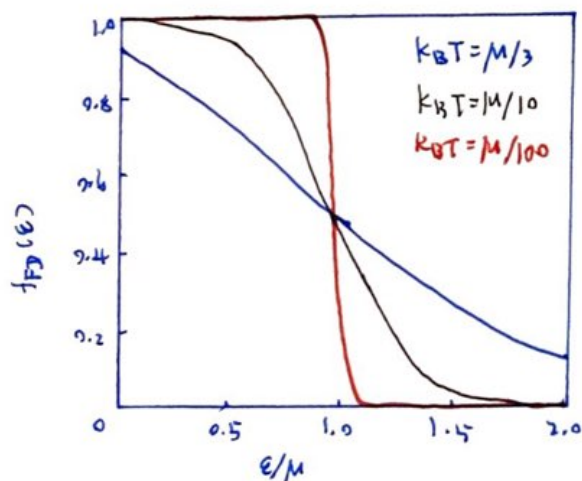
We can also calculate pressure. From the fundamental thermodynamic equation for a gas.
$$P = -\left(\frac{\partial U}{\partial V}\right)_S = -\frac{3}{5} N \left(\frac{\partial \epsilon_F}{\partial V}\right)_S = \frac{2}{5} \frac{N}{V} \epsilon_F$$
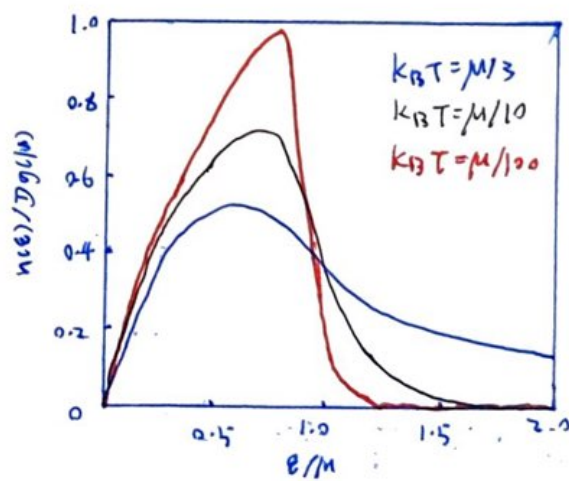
Substituting the Fermi energy for free electron gives
$$P = \frac{h^2}{5m} \left(\frac{3}{8\pi}\right)^{2/3} \left(\frac{N}{V}\right)^{5/3}$$

Pressure increases non-linearly with density. The Fermi gas has significant pressure at zero temperature. This is the degeneracy pressure.

Fermi-Dirac distribution for different values of temperature

Energy distribution of particles for a free, non-relativistic Fermi gas for different values of temperature

12.3 Electrons in metal

To first approximation, we can consider the electrons as free particles in a smooth potential due to the positive ions and the other electrons. These electrons will therefore behave as a Fermi gas.

e.g. Copper

density $= 8.96 \times 10^3$ kg m^{-3}, atomic mass $= 63.5$ u

Each ions contributes one electron to the conduction band, so the number of electrons per unit volume is

$$\frac{N}{V} = 8.5 \times 10^{28} \text{ m}^{-3}$$

Using the density of states for free electrons, this gives a Fermi energy and Fermi temperature

$$\epsilon_F = 7.05 \text{ eV} , \quad T_F = 8.18 \times 10^4 \text{ K}$$

At room temperature, $T \ll T_F$ and the valence electrons approximate well to a degenerate Fermi gas. The gas is not fully degenerate.

For an isotropic system, the Fermi energy corresponds to a sphere in $\underline{k}$-space. The surface corresponding to the Fermi energy in k-space is called the Fermi surface. We can define the Fermi momentum and the Fermi speed as the momentum and speed of particles at the Fermi level

$$p_F = \hbar \underline{k}_F = \sqrt{2m\epsilon_F} , \quad V_F = \sqrt{2\epsilon_F/m}$$

For copper, this gives the velocity of the electrons near the Fermi level as $V_F \approx 1.6 \times 10^6$ m s^{-1}. In practice, the ion lattice affects the shape of the Fermi surface.

12.4 White dwarf stars

The primary source of energy for main sequence stars is the fusion of hydrogen to helium. The gravitational force is balanced by radiation pressure with energy supplied by the fusion process. The more massive the star, the higher the rate of fusion and the hotter and larger it is. Once the supply of hydrogen is exhausted, the star will begin to collapse under its own gravity. Eventually the degeneracy pressure from the electrons in the star may be sufficient to balance the gravity. A white dwarf is such a star.

Consider a star of mass M and radius R. Assuming that the star is of uniform density, the gravitational potential energy is

$$U_G = -\frac{3}{5}\frac{GM^2}{R} = -C_1\frac{M^2}{R}$$

The internal energy of a uniform degenerate electron gas is

$$U_D = \frac{3}{5}N\epsilon_F$$

$$= \frac{3}{5}\left(\frac{h^2}{2m}\right)\left(\frac{3}{8\pi}\right)^{2/3}\frac{N^{5/3}}{V^{2/3}}$$

Substituting $V = \frac{4}{3}\pi R^3$ for the volume and $N = M/\mu_e$ for the number of electrons where μ_e is the mass per electron, gives

$$U_D = C_2\frac{M^{5/3}}{R^2} \quad \text{where} \quad C_2 = \frac{9^3\sqrt{12}\,h^2}{160\pi^{4/3}m_e\mu_e^{5/3}}$$

The total potential energy is then

$$U = U_G + U_D = -C_1\frac{M^2}{R} + C_2\frac{M^{5/3}}{R^2}$$

For the star to be stable U must be a minimum

$$\frac{dU}{dR} = 0 \quad \rightarrow \quad R = \frac{2C_2}{C_1}M^{-\frac{1}{3}}$$

For a star comprised of low mass nuclei (He, C, etc.) there are approximately equal numbers of neutrons and protons, giving approximately two nucleons per electron and $\mu_e \approx 2m_p$. Substituting in values and expressing in terms of the standard solar mass $M_\odot$ and Radius $R_\odot$, this gives

$$R/R_\odot \approx 0.01\,(M/M_\odot)^{-\frac{1}{3}}$$

The stable radius varies inversely with the mass. The corresponding density is

$$\rho \approx 1.3 \times 10^9\,(M/M_\odot)^2\,\text{kg/m}^3$$

The fermi energy is

$$\epsilon_F \approx 0.19\,(M/M_\odot)^{4/3}\,\text{MeV}$$

Note that a full treatment involves solving the hydrostatic equilibrium equation and accounting for relativistic effects in the dispersion.

This leads to an upper limit on the mass for which the star is stable, the Chandrasekhar limit $M \approx 1.4\,M_\odot$