

Statistical Physics: Outline Notes

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1 Microstates and Macrostates

- **Microstate:**

Described by microscopic variables (x_i and p_i for individual particles), each microstate corresponds to an (orthogonal) quantum state of the whole system.

- **Macrostate:**

Described by macroscopic variables (e.g. thermodynamic variables), each macrostate corresponds to a varying number of microstates.

- **Statistical weight / Multiplicity / Thermodynamic probability:** Ω

The statistical weight is just the number of microstates that each macrostate corresponds to.

- **Single-particle state:**

By assuming weakly interacting conditions (independent), we solve Schrödinger equation for one particle of the gas. These states are the single-particle states ψ_j , $j \in \mathbb{N}$.

For a system of identical independent particles, we write a microstate as

$$\Psi = (j_1, \dots, j_N), \quad (1)$$

where particle i is in state ψ_{j_i} .

Single-particle State and Microstate

The set of single-particle states describes the possible states for just one particle.

A microstate specifies the single-particle state for every particle in the system.

- **Isolated system:** fixed U, V, N

- **The fundamental postulate:** a statement of ignorance

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

- **Occupancy:** n_j

Occupancy is the number of particles (in the system) that are in the j^{th} single-particle state.

- **Configuration:** \mathbf{n} , list of occupancies

The list of all the occupancies of the single-particle states specifies a configuration:

$$\mathbf{n} = [n_0, n_1, \dots, n_N]. \quad (2)$$

The statistical weight of a configuration \mathbf{n} is the number of microstates that belong to the configuration.

The Hierarchy

The hierarchy of these three concepts come in the following way:

$$\text{Macrostate} > \text{Configuration} > \text{Microstate.} \quad (3)$$

A macrostate may correspond to multiple configurations, which also corresponds to several microstates.

Example

Now consider energies, where state ψ_j has energy $\epsilon_j = j\epsilon$. Microstates $(1, 4, 3, 4, 0, 1, 1, 1)$ and $(0, 4, 1, 4, 1, 3, 1, 1)$ are just two of the many microstates that belong to the configuration $[1, 4, 0, 1, 2, 0, 0, 0]$, whereas the configuration $[0, 0, 8, 0, 0, 0, 0, 0]$ has only one microstate $(2, 2, 2, 2, 2, 2, 2, 2)$.

Nevertheless, the configuration $[0, 0, 8, 0, 0, 0, 0, 0]$ is just one of the configurations corresponding to the macrostate that measures a total energy of 16ϵ .

- **Equilibrium configuration** / Equilibrium state / Equilibrium distribution:

By fundamental postulate, the equilibrium configuration is the one that has the largest number of microstates (most probable).

Note that there would be fluctuations. Even when the system is in internal thermodynamic equilibrium, the system is not always in this exact equilibrium state configuration.

- **Boltzmann Entropy** & Einstein's argument:

$$S = k_B \ln \Omega. \quad (4)$$

2 Equilibrium and Maximum Entropy

Finding equilibrium configuration \equiv Maximizing S with respect to parameters (5)

Example: a system of spin-half particles (fermions)

Consider an isolated system consisting of N identical distinguishable spin-half particles. There are two single particle states ψ_j , $j = 1, 2$ corresponding to spin-up and spin-down states respectively. Therefore, a microstate can be represented as

$$(j_1, \dots, j_N).$$

Therefore, the total number of possible microstates is 2^N , and the Boltzmann entropy is

$$S = k_B \ln \Omega = k_B N \ln 2.$$

Now consider the equilibrium configuration. For N particles, the possible configurations are

$$\mathbf{n} = [m, N - m]$$

for some positive integer m . The corresponding statistical weight is

$$\Omega = \frac{N!}{m!(N-m)!}, \tag{6}$$

which follows directly from the combination formula. By Stirling's approximation,

$$\ln N! \approx N \ln N - N, \tag{7}$$

$$S \approx k_B [N \ln N - m \ln m - (N - m) \ln(N - m)].$$

To find the equilibrium configuration, we need to maximize the entropy with the system parameters (only m in this case):

$$\frac{\partial \Omega}{\partial m} = 0 \Rightarrow m = \frac{N}{2}.$$

Then, the entropy of the equilibrium configuration is

$$S = k_B N \ln 2.$$

Note that the entropy of the equilibrium configuration is the same as the entropy of the system.

Generally, for sufficiently large systems, we can safely use the equilibrium configuration to calculate the entropy of the system.

Systems with Energy

We shall see how this leads to the Boltzmann distribution.

Consider an isolated system with fixed U, V, N . Each atom is described by the set of single-particle states ψ_j with energy levels ϵ_j .

To find the equilibrium configuration, we need to maximize entropy. The configuration in this situation should be represented as

$$[n_0, n_1, \dots],$$

where n_j is the number of particles in state ψ_j . The number of microstates corresponding to this configuration is

$$\Omega = \frac{N!}{\prod n_j!}. \quad (8)$$

There are also constraints of total number of particles N and total energy U :

$$\sum n_j = N, \quad \sum \epsilon_j n_j = U. \quad (9)$$

Using Lagrange's method, we construct a equation with constraints:

$$\frac{\partial}{\partial n_j} \left[\ln \Omega - \alpha \left(\sum n_i - N \right) - \beta \left(\sum \epsilon_k n_k - U \right) \right] = 0, \quad \forall j. \quad (10)$$

This means that

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

and

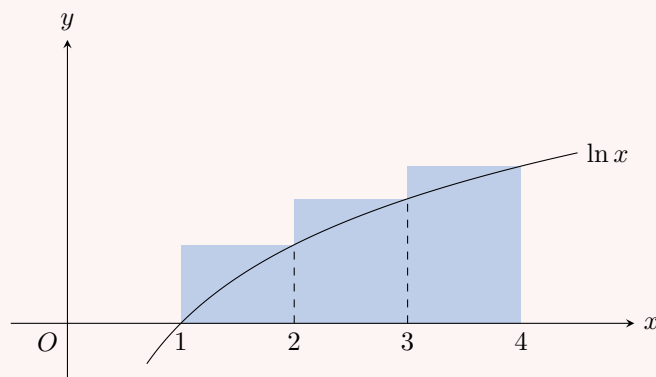
$$\frac{\partial}{\partial n_j} \ln \Omega = \frac{\partial}{\partial n_j} \left[\ln N! - \sum \ln n_i! \right] = -\frac{\partial}{\partial n_j} \ln n_i! \approx -\ln n_j.$$

Therefore, we know that

$$n_j = \exp(-\alpha - \beta \epsilon_j). \quad (11)$$

Stirling's Approximation

Consider the function of $\ln x$.



We see that the area under curve is definitely less than the shaded area. Therefore, up to a large integer N ,

$$\int_1^N dx \ln x < \sum_{n=1}^N \ln n \quad (12)$$

By $\int dx \ln x = x \ln x - x$ up to a constant, we see

$$N \ln N - N < \ln N!. \quad (13)$$

For a very large N , the differences are negligible, but we should remember that this is an underestimation:

$$\ln N! \approx N \ln N - N \quad (\text{underestimation}) \quad (14)$$

3 The Boltzmann Distribution

We have shown that a system of distinguishable particles with energy in equilibrium is the Boltzmann distribution. The Lagrange multipliers α and β are claimed to be arbitrary constants, but they actually have significant physical meanings.

3.1 Thermodynamic Beta (Coldness) and Temperature

For reversible changes,

$$\delta Q = T dS = dU + \delta W. \quad (15)$$

With fixed V , $\delta W = 0$, so we know

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N}. \quad (16)$$

Now we consider a small change in internal energy δU . By assuming that the energy levels ϵ_j do not change (due to fixed V), we get

$$\delta U = \delta \left(\sum \epsilon_j n_j \right) = \sum \epsilon_j \delta n_j. \quad (17)$$

The corresponding change in Boltzmann entropy is given by

$$\begin{aligned} \delta S &= k_B \sum \frac{\partial \ln \Omega}{\partial n_j} \delta n_j \\ &= k_B \sum (\alpha + \beta \epsilon_j) \delta n_j \\ &= k_B \alpha \sum \delta n_j + k_B \beta \sum \epsilon_j \delta n_j \\ &= k_B \beta \delta U. \end{aligned}$$

Therefore,

$$\beta = \frac{1}{k_B} \left(\frac{\partial S}{\partial U} \right)_{V,N} \Rightarrow \beta = \frac{1}{k_B T}. \quad (18)$$

3.2 The Number of Particles and Partition Function

We can see the meaning of α by simply playing with the formula of number of particles:

$$N = \sum n_j \Rightarrow N = e^{-\alpha} \sum e^{-\beta \epsilon_j} \Rightarrow e^{-\alpha} = \frac{N}{\sum e^{-\beta \epsilon_j}}. \quad (19)$$

The value of α normalizes the distribution to the total number of particles.

We define the summation in the denominator as the **partition function** (or more precisely in this case

the partition function for a single particle), denoted by Z (German Zustandssumme):

$$Z = \sum e^{-\beta\epsilon_j}. \quad (20)$$

The probability that a given particle is in the j^{th} state is then given by

$$p_j = \frac{e^{-\beta\epsilon_j}}{Z}. \quad (21)$$

3.3 Reclaiming the Zeroth Law

The Zeroth Law of Thermodynamics

If two systems A and B are both in thermal equilibrium with a third system C , then they must be in thermal equilibrium with each other.

For two isolated systems with internal energies U_1 and U_2 , at equilibrium we have

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

The total entropy is

$$S = S_1 + S_2.$$

Now combine the two systems. At equilibrium, the entropy is maximal and so $\delta S = 0$. If energy flows from system 1 to 2,

$$\delta S = \left(\frac{\partial S_2}{\partial U_2} \right)_{V,N} \delta U - \left(\frac{\partial S_1}{\partial U_1} \right)_{V,N} \delta U = (\beta_2 k_B - \beta_1 k_B) \delta U = 0.$$

Therefore, equilibrium means $\beta_1 = \beta_2$. Systems in thermal equilibrium with each other must have the same value of β .

4 Systems in Heat Baths (Canonical Ensemble)

4.1 Ensembles and Thermodynamic Systems

Ensembles

An ensemble is...

- a probability distribution for the microstates of a system.
- a large number of identical copies of the system such that all possible states of the system are represented in a proportion that allows the observer of all copies to correctly deduce the probability of each state of the system.

If you know the statistical ensemble of a system, then you know the probability of finding the system in a certain state. Obviously, the ensemble is not dependent on time.

An example of an ensemble is the uniform probability distribution for an **isolated system** (by the fundamental postulate). This is referred to as a **microcanonical ensemble**, which is applicable to a system with fixed internal energy.

Type of Systems	Exchange of...		Constant Parameters	Ensemble
	Mass	Energy		
Isolated system	No	No	N, V, U	Microcanonical ensemble
Closed system	No	Yes	N, V, T	Canonical ensemble
Open system	Yes	Yes	μ, V, T	Grand canonical ensemble

4.2 Canonical Ensemble

In fact, the Boltzmann distribution is quite general and describes any system in contact with a heat bath. Consider an isolated system AB consisting of a system A and a heat bath B, which are in weak thermal contact with each other.

Heat Bath

A heat bath can be any body with a heat capacity very large (infinity in theory) compared to the system that it serves so that its temperature is unaffected by thermal exchange with the system.

From Boltzmann entropy, for the heat bath with internal energy U ,

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

With a small change in internal energy δU , the entropy change is

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

and this leads to a statistical weight

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

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

Combination of Statistical Weight

For a particular microstate of A with discrete energy levels ϵ_j , the microstates of the heat bath are those with internal energy $U - \epsilon_j$. So, the total statistical weight of the combined system AB is:

$$\Omega_{AB} = \sum \Omega_A(\epsilon_j) \Omega_B(U - \epsilon_j) \quad (22)$$

In this situation, the system A is so small such that we can safely assume there's only one microstate for each energy ϵ_j . Therefore,

$$\Omega_{AB} = \sum \Omega(U - \epsilon_j) = \Omega(U) \sum e^{-\epsilon_j/k_B T}. \quad (23)$$

Therefore, we get the probability distribution for the microstates of a system in contact with a heat bath (Canonical ensemble):

$$p_j = \frac{\Omega(U - \epsilon_j)}{\Omega_{AB}} = \frac{e^{-\epsilon_j/k_B T}}{\sum e^{-\epsilon_i/k_B T}} = \frac{e^{-\epsilon_j/k_B T}}{Z}. \quad (24)$$

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 p_j defines the ensemble.

The systems are distinguishable. The total number of systems in the j^{th} state is given by Np_j (**mean occupancy** or **mean occupation number**). Then, the statistical weight of the whole system is

$$\Omega = \frac{N!}{\prod (Np_j)!}. \quad (25)$$

By Stirling's formula and noting that $\sum p_j = 1$,

$$\begin{aligned} \ln \Omega &= N \ln N - N - \sum [Np_j \ln(Np_j) - Np_j] \\ &= -N \sum p_j \ln p_j. \end{aligned}$$

Gibbs Entropy

This ends up with a new expression for entropy (**Gibbs entropy**):

$$S = -k_B \sum p_j \ln p_j. \quad (26)$$

For isolated systems, the probabilities are equal (microcanonical ensemble) and this reduces to the Boltzmann definition of entropy. This expression can also be used to calculate the entropy of a system in contact with a heat bath (canonical ensemble).

Graphical examples: two-state systems

By Boltzmann distribution with the two energy levels having a difference in energy $\Delta\epsilon$,

$$p_1 = \frac{1}{1 + \exp(-\beta\Delta\epsilon)}, \quad p_2 = \frac{\exp(-\beta\Delta\epsilon)}{1 + \exp(-\beta\Delta\epsilon)}.$$

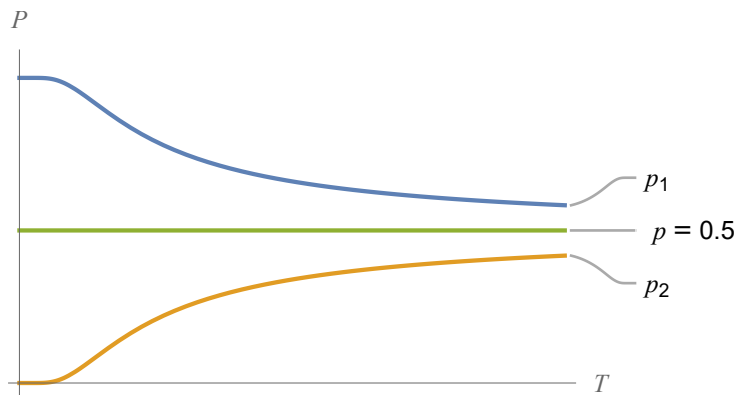


Figure 1: Probability of two states vs. temperature. They both tend to $1/2$ as $T \rightarrow \infty$.

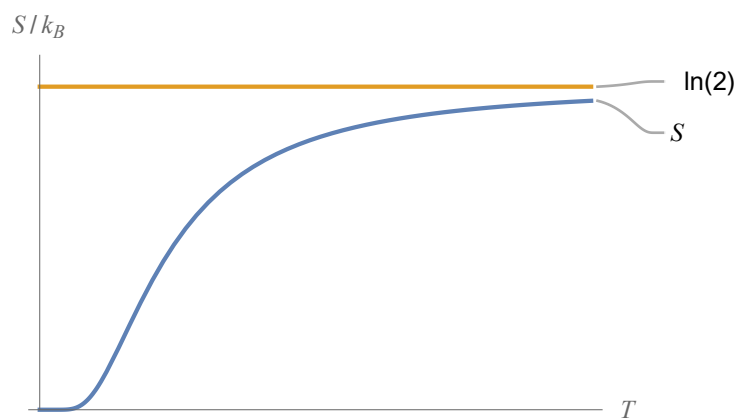


Figure 2: Entropy of the two state system. It tends to $k_B \ln(2)$ as $T \rightarrow \infty$.

5 The Partition Function and Thermodynamics

5.1 Link to Thermodynamics

- The mean energy: internal energy

$$\langle E \rangle = \sum \epsilon_j p_j = U \quad (27)$$

Noting that $Z = \sum e^{-\beta \epsilon_j}$, we get

$$\langle E \rangle = U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}. \quad (28)$$

In terms of T , we have

$$\langle E \rangle = U = -\frac{1}{Z} \frac{\partial Z}{\partial T} \frac{\partial T}{\partial \beta} = k_B T^2 \frac{\partial \ln Z}{\partial T}. \quad (29)$$

- Energy fluctuations: By variance,

$$(\Delta E)^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2. \quad (30)$$

Noting that

$$\langle E^2 \rangle = \sum \epsilon_j^2 p_j = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \neq \frac{\partial^2 \ln Z}{\partial \beta^2}$$

and

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta},$$

by differentiating $\ln Z$ twice, we get

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)^2 = \langle E^2 \rangle - \langle E \rangle^2. \quad (31)$$

Therefore, we get

$$(\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial U}{\partial \beta}. \quad (32)$$

In terms of temperature,

$$(\Delta E)^2 = -\frac{\partial U}{\partial T} \frac{\partial T}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_V, \quad (33)$$

since the system is at constant volume.

Therefore, the standard deviation of the energy fluctuations is

$$\Delta E = \sqrt{\frac{C_V}{k_B}} k_B T. \quad (34)$$

For a system with n degrees of freedom, $C_V = nk_B/2$, and

$$\Delta E = \sqrt{\frac{n}{2}} k_B T \quad \Rightarrow \quad \Delta E = \frac{C_V T}{\sqrt{n/2}} \sim \frac{\langle E \rangle}{\sqrt{n}}. \quad (35)$$

5.2 The Bridge Equation

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

$$F = U - TS. \quad (36)$$

At equilibrium, the free energy is a minimum, as any reaction with $\Delta F < 0$ (negative free energy change) is thermodynamically favorable.

By the Gibbs entropy,

$$\begin{aligned} TS &= -k_B T \sum p_j \ln p_j \\ &= -k_B T \sum p_j \left(-\frac{\epsilon_j}{k_B T} - \ln Z \right) \quad \left(p_j = \frac{e^{-\beta \epsilon_j}}{Z} \right) \\ &= \sum \epsilon_j p_j + k_B T \sum p_j \ln Z \\ &= U + k_B T \ln Z. \end{aligned}$$

After rearranging, we get

$$F = U - TS = -k_B T \ln Z. \quad (37)$$

This equation expresses the Helmholtz free energy in terms of the statistical description. we can even reclaim the expression of U by noting that $S = - \left(\frac{\partial F}{\partial T} \right)_V$,

$$\begin{aligned} U &= F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V \\ &= -k_B T \ln Z + k_B T^2 \frac{\partial \ln Z}{\partial T} + k_B T \ln Z \\ &= k_B T^2 \frac{\partial \ln Z}{\partial T}. \end{aligned}$$

5.3 Factorization of the Partition Function

We should emphasize that the partition function of a system of canonical ensemble is

$$Z = \sum e^{-\beta \epsilon_j}, \quad (38)$$

where the summation is over all the **microstates** (instead of energy levels, especially when there are degenerate states) of the system.

- Partition function for a single particle system, $Z_{(1)}$;
- Partition function for two identical weakly interacting distinguishable particles, $Z_{(2)}$;
- Partition function for N identical weakly interacting **distinguishable** particles:

$$Z = Z_{(1)}^N \quad (39)$$

Note that for **indistinguishable** particles, the partition function is given by

$$Z = \frac{Z_{(1)}^N}{N!}, \quad (40)$$

where the factorial arises to compensate for over-counting. (We can no longer distinguish between different permutations of the particles, so we have to divide by the number of permutations $N!$.)

So, we see that $\ln Z$ is an extensive quantity for such a system (canonical ensemble). This is important, as $\ln Z$ is a key link to thermodynamic quantities.

Factorization of the partition function can also apply for composite systems comprised of **weakly interacting components** (so that the wavefunction factorizes). As an example,

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

and

$$\ln Z = \ln Z_{\text{trans}} + \ln Z_{\text{vib}} + \ln Z_{\text{rot}}. \quad (41)$$

5.4 Application to Quantum Harmonic Oscillators

Consider a 1D quantum harmonic oscillator in thermal equilibrium at temperature T . This suggests a canonical ensemble. The non-degenerate energy levels,

$$\epsilon_j = \left(j + \frac{1}{2}\right) \hbar\omega, \quad (42)$$

gives the partition function

$$Z = e^{-\hbar\omega\beta/2} \sum e^{-j\hbar\omega\beta} = \frac{e^{-\hbar\omega\beta/2}}{1 - e^{-\hbar\omega\beta}}. \quad (43)$$

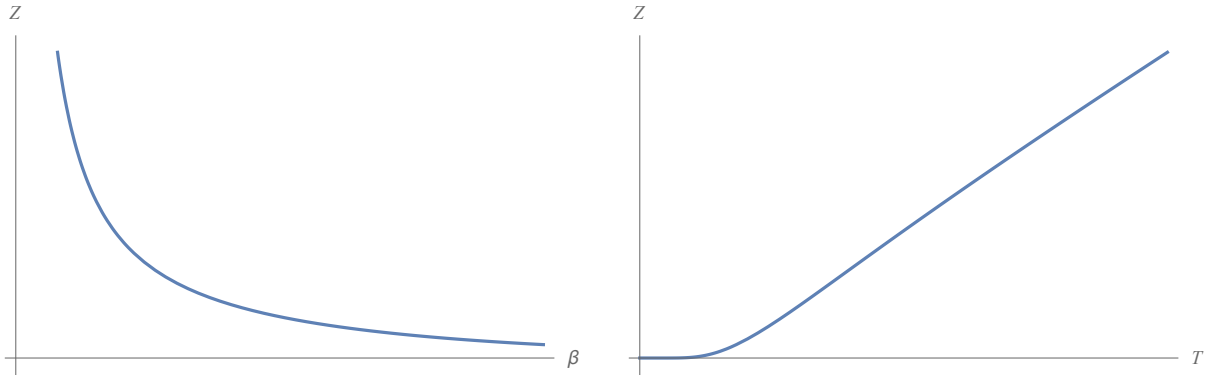


Figure 3: The partition function of quantum harmonic oscillators.

Then, the formula of internal energy gives

$$U = -\frac{\partial \ln Z}{\partial \beta} = \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega\beta} - 1}\right) \hbar\omega. \quad (44)$$

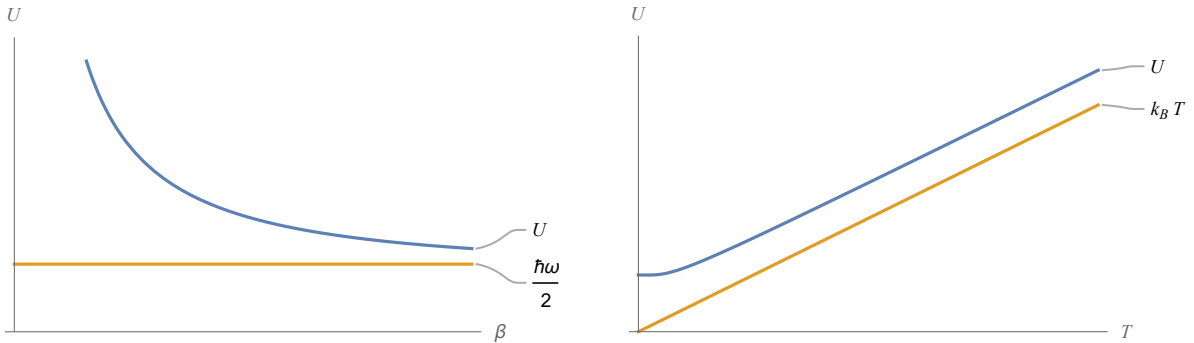


Figure 4: The internal energy of quantum harmonic oscillators.

At low temperature, we see that

$$U \approx \frac{1}{2} \hbar\omega. \quad (45)$$

At high temperature, we see that

$$U \approx k_B T, \quad (46)$$

which agrees with the classical result.

5.5 The Einstein Solid

Heat capacity for 1D harmonic oscillator:

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V. \quad (47)$$

By defining the Einstein temperature,

$$\theta_E = \frac{\hbar \omega}{k_B}, \quad (48)$$

$$C_V = \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \left(\frac{\theta_E}{T} \right)^2 k_B. \quad (49)$$

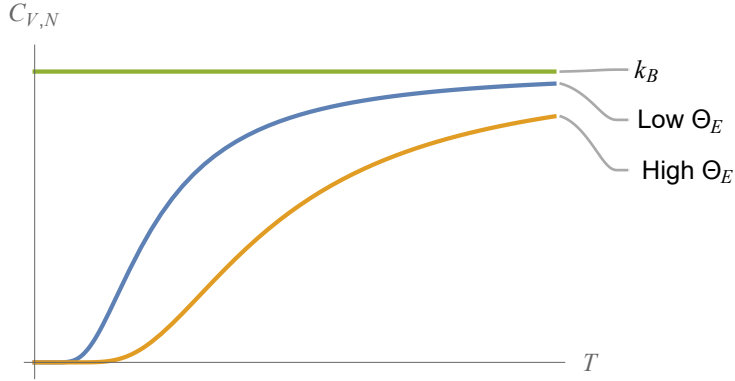


Figure 5: The plot of heat capacity vs. temperature. As $T \rightarrow 0$, $C \rightarrow 0$, which agrees with the third law of thermodynamics. The curve is approximately cubic ($\sim \alpha T^3$) for low C .

The Einstein solid model treats each atom in the solid as a 3D quantum harmonic oscillator (equivalent to three 1D oscillators).

From previous workings of Z , we know

$$\ln Z = -\frac{1}{2} \frac{\Theta_E}{T} - \ln \left[1 - \exp \left(-\frac{\Theta_E}{T} \right) \right], \quad (50)$$

and so we can work out the Helmholtz potential.

- By taking the result for 1D harmonic oscillator, Einstein made a simple generalization to say the corresponding internal energy and heat capacity for the corresponding 3D solid would be the value per particle multiplied by $3N$ to scale up to the number of particles, and incorporate the three degrees of freedom.

Therefore, for the whole 3 solid,

$$F = 3N(-k_B T \ln Z) = \frac{3}{2}N\Theta_E k_B + 3Nk_B T \ln \left[1 - \exp\left(-\frac{\Theta_E}{T}\right) \right]. \quad (51)$$

By $S = -\left(\frac{\partial F}{\partial T}\right)_V$,

$$S = 3Nk_B \left[\frac{\Theta_E}{T} \left(\frac{1}{\exp(\Theta_E/T) - 1} - \ln \left[1 - \exp\left(-\frac{\Theta_E}{T}\right) \right] \right) \right]. \quad (52)$$

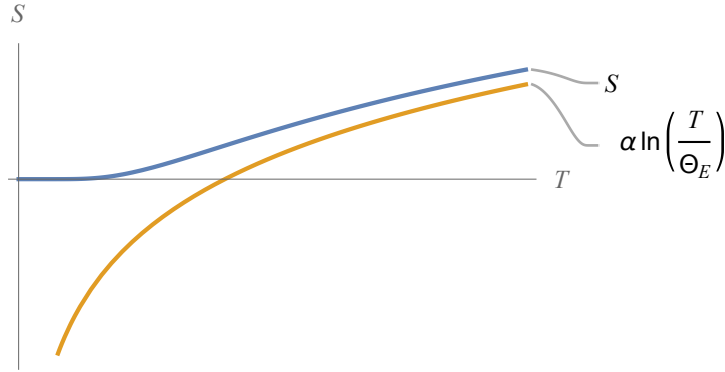


Figure 6: The entropy of an Einstein solid. At large T , it shows a $\propto \ln\left(\frac{T}{\Theta_E}\right)$ dependence.

6 Systems in Heat and Particle Bath (Grand Canonical Ensemble)

6.1 Grand Canonical Ensemble

Now consider a system with both variable energy and variable number of particles.

The system is described by a set of microstates ψ_j . Each microstate will have an energy ϵ_j and a number of particles N_j .

When we first derived the Boltzmann distribution, we had a large number of identical “particles”, rather than “systems”, but we could equally have used “systems” and the derivation would have been the same.

Consider an assembly comprising a large number of identical systems. The systems are allowed to exchange energy and particles with each other. However, the **total energy** and the **total number of particles** in the assembly are fixed. The **total number of systems** is also fixed.

A microstate of the assembly is given by specifying the microstate of each individual system in the assembly. The configuration of the assembly is then a list of occupancies

$$\mathbf{n} = [n_0, n_1, \dots],$$

where n_i is the number of systems that are in microstate ψ_i . The corresponding statistical weight is

$$\Omega = \frac{N_A!}{\prod n_j!}, \quad (53)$$

where N_A is the total number of systems in the assembly.

The three constraints come from the fixed number of particles and systems, and fixed total energy. Let U be the mean energy per system and N be the mean number of particles per system, we have

$$\sum n_j = N_A, \quad \sum n_j \epsilon_j = N_A U, \quad \sum n_j N_j = N_A N. \quad (54)$$

Applying Lagrange’s method, at equilibrium where $\ln \Omega$ is maximized, we have

$$\frac{\partial}{\partial n_j} \left[\ln \Omega - \alpha \left(\sum n_i - N_A \right) - \beta \left(\sum n_k \epsilon_k - N_A U \right) - \lambda (N - N_A N) \right] = 0, \quad \forall j. \quad (55)$$

Therefore, we have

$$\frac{\partial \ln \Omega}{\partial n_j} = \alpha + \beta \epsilon_j + \lambda N_j, \quad \forall j. \quad (56)$$

By Stirling's approximation, we get

$$n_j = e^{-\alpha - \beta \epsilon_j - \lambda N_j}. \quad (57)$$

The probability that a system is in j^{th} microstate is then

$$p_j = \frac{n_j}{N_A} = \frac{e^{-\alpha}}{N_A} e^{-\beta \epsilon_j - \lambda N_j}. \quad (58)$$

This is the probability distribution for a system that is in a heat and particle bath. **The other systems in the assembly act as the bath.**

6.2 Grand Partition Function

We shall recognize $e^{-\alpha}/N_A$ as a normalization factor again. By the conservation of probability, we see that

$$p_j = \frac{1}{\mathcal{Z}} e^{-\beta \epsilon_j - \lambda N_j}, \quad (59)$$

where

$$\mathcal{Z} = \sum e^{-\beta \epsilon_j - \lambda N_j} \quad (60)$$

is the grand partition function.

Note that this is the grand partition function of a system, not of the whole assembly.

As always, the summation is over all the microstates of the system.

6.3 The Temperature and the Chemical Potential

By the Gibbs entropy,

$$\begin{aligned} S &= -k_B \sum p_j \ln p_j \\ &= -k_B \sum p_j (-\beta \epsilon_j - \lambda N_j - \ln \mathcal{Z}) \\ &= k_B \beta \sum p_j \epsilon_j + k_B \lambda \sum p_j N_j + k_B \ln \mathcal{Z} \sum p_j \\ &= k_B \beta U + k_B \lambda N + k_B \ln \mathcal{Z}. \end{aligned}$$

By thermodynamics,

$$dU = T dS + \mu dN, \quad (61)$$

where V is kept constant. Rearranging gives

$$dS = \frac{1}{T} dU - \frac{\mu}{T} dN. \quad (62)$$

Taking the differential of the Gibbs entropy, we immediately find that

$$\beta = \frac{1}{k_B T}, \quad \lambda = -\frac{\mu}{k_B T}. \quad (63)$$

Grand canonical Ensemble

Therefore, we have found the **grand canonical ensemble**:

$$p_j = \frac{1}{\mathcal{Z}} e^{-(\epsilon_j - \mu N_j)/k_B T}, \quad (64)$$

where \mathcal{Z} is the grand partition function,

$$\mathcal{Z} = \sum e^{-(\epsilon_j - \mu N_j)/k_B T}. \quad (65)$$

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

6.4 The Grand Potential

Like what we have done with the Helmholtz potential, we can define a **grand potential**. By plugging the expressions for β and λ , we see

$$\Phi = -k_B T \ln \mathcal{Z} = U - TS - \mu N. \quad (66)$$

The grand partition function is the key link to thermodynamics for systems that are in heat and particle baths. Therefore, if we know \mathcal{Z} , we can use it to calculate any thermodynamic variables via the grand potential. From the expression of internal energy,

$$dU = T dS - p dV + \mu dN \quad \Rightarrow \quad d\Phi = -S dT - p dV - N d\mu. \quad (67)$$

Partial derivatives gives

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V, \mu}, \quad p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T, \mu}, \quad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{V, T}. \quad (68)$$

7 Gases and Density of States: Quietus of Distinguishability

7.1 Distinguishable and Indistinguishable Particles

The number of distinct microstates we can count depends on whether particles are distinguishable or not.

$$\begin{cases} \text{Distinguishable:} & \text{atoms in a solid} \\ \text{Indistinguishable:} & \text{gases, liquids, electrons in metals, photons} \end{cases} \quad (69)$$

In a gas, there is no way we can differentiate the following two descriptions:

- particle A in state 1 and particle B in state 2;
- particle A in state 2 and particle B in state 1.

These two descriptions are actually the same microstate, provided that the particles A and B are indistinguishable. What we can observe is actually “State 1 is occupied by a particle and state 2 is occupied by a particle”.

In a solid, we can distinguish the particles through the lattice sites in the following way:

- 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.

We would say the particles are distinguishable, but what we really mean is the lattice sites of the particles are distinguishable.

Upon now, our formula for the statistical weight of a configuration of particles is **only true for distinguishable particles**. Now we will look at gases and so we will need a different approach to count the microstates.

7.2 Density of States

Consider a gas of identical indistinguishable particles.

For a gas, the number of available states is given by the density of states calculation. Now we first focus on a non-relativistic particle in free space.

The related Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \epsilon\psi, \quad (70)$$

and this has the travelling wave solutions

$$\psi = Ae^{i\mathbf{k}\cdot\mathbf{r}} \quad (71)$$

with energy given by the dispersion relationship

$$\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}. \quad (72)$$

As we can see, the energy in free space is directly related to the momentum, so we may consider the momentum states.

Consider first a cubic region of space $V = L^3$. Suppose we start with a travelling wave state with a wavefunction $Ae^{i\mathbf{k}_0\cdot\mathbf{r}}$, then we can **generate a complete set of wavefunctions that are orthogonal over the volume V** by adding to \mathbf{k}_0 a wavevector \mathbf{k} :

$$\mathbf{k} = (k_x, k_y, k_z) = \left(\frac{2\pi l}{L}, \frac{2\pi m}{L}, \frac{2\pi n}{L} \right), \quad \forall l, m, n \in \mathbb{N}. \quad (73)$$

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

$$\left(\frac{L}{2\pi} \right)^3 = \frac{V}{(2\pi)^3}. \quad (74)$$

Remember, each microstate corresponds to an (orthogonal) quantum state of the whole system, which, in this case, is the gas particle.

This does not depend on any boundary conditions our region might have. Boundary conditions may constrain the phase of the wavefunction, but **they will not change the spacing of the orthogonal states**.

The number of states with wavenumber k to $k + dk$ is:

$$d\Omega = g(k) d^3k = \frac{1}{2\pi^2} V k^2 dk \Rightarrow g(k) = \frac{1}{2\pi^2} V k^2, \quad (75)$$

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

By

$$d\Omega = g(k) dk = g(\epsilon) d\epsilon, \quad (76)$$

we know

$$g(\epsilon) = g(k) \frac{dk}{d\epsilon} = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}, \quad (77)$$

which is the density of states in energy for a non-relativistic particle.

- The density of states **does not depend on the boundary conditions** or the choice of wavefunction basis.
- This is just the density of states for translational motion. Particles may have internal states, which, if not related to energy, would give a **degeneracy factor** D (the number of single-particle states per translation state).

8 Classical Ideal Gas

8.1 Boltzmann Distribution for Classical Dilute Ideal Gas

Consider a dilute ideal gas. By ideal we mean no interaction between the particles of the gas, so the single-particle states are valid.

Consider a single particle of the gas at temperature T . Therefore, we can use the canonical ensemble as the probability distribution,

$$p_j = \frac{1}{Z} e^{-\epsilon_j/k_B T}, \quad \text{where} \quad Z = \sum e^{-\epsilon_j/k_B T}. \quad (78)$$

Z is the partition function for a single particle: the sum is over the single-particle states.

- (Important) For N particles, provided $p_j N \ll 1$, we can neglect multiple occupancies of states.
- The average number of particles in the j^{th} single-particle state is the mean occupancy of the state,

$$f_j = N p_j = \frac{N}{Z} e^{-\epsilon_j/k_B T}, \quad (79)$$

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

8.2 Partition Function for an Ideal Gas

The energy levels for the single-particles translation states are very closely spaced so we can replace the summation with an integral over the density of states:

$$Z = \int_0^\infty D g(\epsilon) e^{-\epsilon/k_B T} d\epsilon, \quad (80)$$

where D is the degeneracy factor and $g(\epsilon)$ is the density of states.

Substituting $g(\epsilon)$ and we get the partition function for a single particle:

$$Z = DV \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}. \quad (81)$$

8.3 Thermodynamics for an Ideal Classical Gas

For indistinguishable gas particles, the N particle partition function is

$$Z = \frac{Z_{(1)}^N}{N!}. \quad (82)$$

The factor $N!$ is only correct for very dilute gases where the probability of more than one particle in a state can be safely ignored. It makes no difference for some thermodynamic quantities, but is important for entropy.

By Stirling's approximation,

$$\begin{aligned} \ln Z &= N \ln Z_{(1)} - N \ln N + N \\ &= N \left[\ln D + \ln V + \frac{3}{2} \ln T - \ln N + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) + 1 \right]. \end{aligned}$$

- Internal energy:

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} = \frac{3}{2} N k_B T, \quad (83)$$

which agrees with the thermodynamics result for a monatomic ideal gas.

- Ideal gas law: By Helmholtz function, $F = -k_B T \ln Z$, we know the **ideal gas law**,

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_T = \frac{N k_B T}{V}. \quad (84)$$

- Sackur-Tetrode equation for the entropy of a monatomic ideal gas:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = N k_B \left[\ln D + \ln V + \frac{3}{2} \ln T - \ln N + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) + \frac{5}{2} \right]. \quad (85)$$

8.4 Maxwell-Boltzmann Speed Distribution

Given $g(v)$ the density of states in speed, $f(v)$ the mean occupancy of states with speed v , and degeneracy D , the number of particles with speed v to $v + dv$ is

$$n(v) dv = D g(v) f(v) dv. \quad (86)$$

By $v = \hbar k / m$,

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

$$f(v) = \frac{N}{Z_{(1)}} e^{-mv^2/2k_B T} = \frac{N}{DV} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} e^{-mv^2/2k_B T},$$

and therefore we get the Maxwell-Boltzmann speed distribution,

$$n(v) dv = N \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} dv \quad (87)$$

By defining a thermal speed,

$$v_T = \sqrt{\frac{k_B T}{m}}, \quad (88)$$

- The most probable speed, $v_{\max} = \sqrt{2}v_T$;
- The mean speed, $\langle v \rangle = \sqrt{\frac{8}{\pi}}v_T$;
- The RMS speed, $v_{\text{RMS}} = \sqrt{\langle v^2 \rangle} = \sqrt{3}v_T$.

9 Fermions & Bosons: Exordium of Quantum Statistics

- Fermions: particles with **half integer spin**

Fermions have antisymmetric wavefunctions with respect to exchange of the particle labels, giving a maximum occupancy of one for a single-particle state (**Pauli exclusion principle**).

Examples: electron, proton, neutron, ${}^3\text{He}$, quark, neutrino.

- Bosons: particles with **integer spin**

Bosons have symmetric wavefunctions with respect to exchange of the particle labels, so there is no limit on the occupancy of a single-particle state.

Examples: photon, W, Z, Higgs, photon, ${}^4\text{He}$.

9.1 Equilibrium Distributions

Consider a system of indistinguishable identical particles. The fundamental indistinguishability of quantum particles means that specifying the occupancy for each of the single-particle states completely specifies a microstate of the system.

We can treat each single-particle state as a distinct system (assuming weakly interacting conditions) that has its own set of microstates corresponding to the possible values of its occupancy. The energy of the j^{th} energy level is given by $\epsilon = n\epsilon_j$, where $n = 0, 1, \dots$ is the number of particles that are in this state.

Therefore, the system corresponding to the j^{th} single-particle state will have a set of microstates corresponding to the possible values of its occupancy n_j .

By the grand partition function,

$$\mathcal{Z} = \sum e^{-(\epsilon_k - \mu N_k)/k_B T} = \sum e^{n\beta(\mu - \epsilon_j)}, \quad (89)$$

and the probabilities of the single-particle states are

$$p(n) = \frac{1}{\mathcal{Z}} e^{n\beta(\mu - \epsilon_j)}. \quad (90)$$

So, the mean occupation number is

$$\langle n \rangle = f = \sum n p(n) = \frac{1}{\mathcal{Z}} \sum n e^{n\beta(\mu - \epsilon_j)}. \quad (91)$$

By some tricks we get

$$\langle n \rangle = f = \frac{k_B T}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mu}. \quad (92)$$

9.2 Fermions and the Fermi-Dirac Distribution

For fermions, by Pauli exclusion principle, the only possible values of n are 0 and 1. Therefore,

$$\mathcal{Z} = 1 + e^{\beta(\mu - \epsilon)},$$

and this gives the **Fermi-Dirac distribution**:

$$f_{\text{FD}} = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1}, \quad (93)$$

where ϵ is the energy corresponding to the j^{th} state.

$$T \text{ is constant, } \begin{cases} \epsilon \rightarrow 0 & f_{\text{FD}} \rightarrow \frac{1}{\exp\left(\frac{-\mu}{k_B T}\right) + 1} \\ \epsilon \rightarrow \mu & f_{\text{FD}} \rightarrow 1/2 \\ \epsilon \rightarrow \infty & f_{\text{FD}} \rightarrow \exp\left(\frac{-\epsilon}{k_B T}\right) \end{cases} \quad \epsilon \text{ is constant, } \begin{cases} T \rightarrow 0 & f_{\text{FD}} \rightarrow 0 \\ T \rightarrow \infty & f_{\text{FD}} \rightarrow 1/2 \end{cases} \quad (94)$$

9.3 Bosons and the Bose-Einstein Distribution

For bosons, n can take any values. Therefore,

$$\mathcal{Z} = \sum_{n_j=0}^{\infty} e^{n_j \beta(\mu - \epsilon_j)} = \frac{1}{1 - \exp[\beta(\mu - \epsilon_j)]} \quad \left(\sum_{n_j} \neq \sum_j \right),$$

and this gives the **Bose-Einstein distribution**:

$$f_{\text{BE}} = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) - 1}, \quad (95)$$

where ϵ is the energy corresponding to the j^{th} state.

Note that $\mu < \epsilon$ to ensure the distribution is finite.

$$T \text{ is constant, } \begin{cases} \epsilon \rightarrow \mu & f_{\text{BE}} \rightarrow \infty \\ \epsilon \rightarrow \infty & f_{\text{BE}} \rightarrow \exp\left(\frac{-\epsilon}{k_B T}\right) \end{cases} \quad \epsilon \text{ is constant, } \begin{cases} T \rightarrow 0 & f_{\text{BE}} \rightarrow 0 \\ T \rightarrow \infty & f_{\text{BE}} \rightarrow \frac{k_B T}{\epsilon - \mu} \end{cases} \quad (96)$$

9.4 Summary

$$f = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + a} = \begin{cases} a = 1 & \text{Fermi-Dirac distribution} \\ a = -1 & \text{Bose-Einstein distribution} \\ a = 0 & \text{Boltzmann distribution (classical, only true for dilute gases)} \end{cases} \quad (97)$$

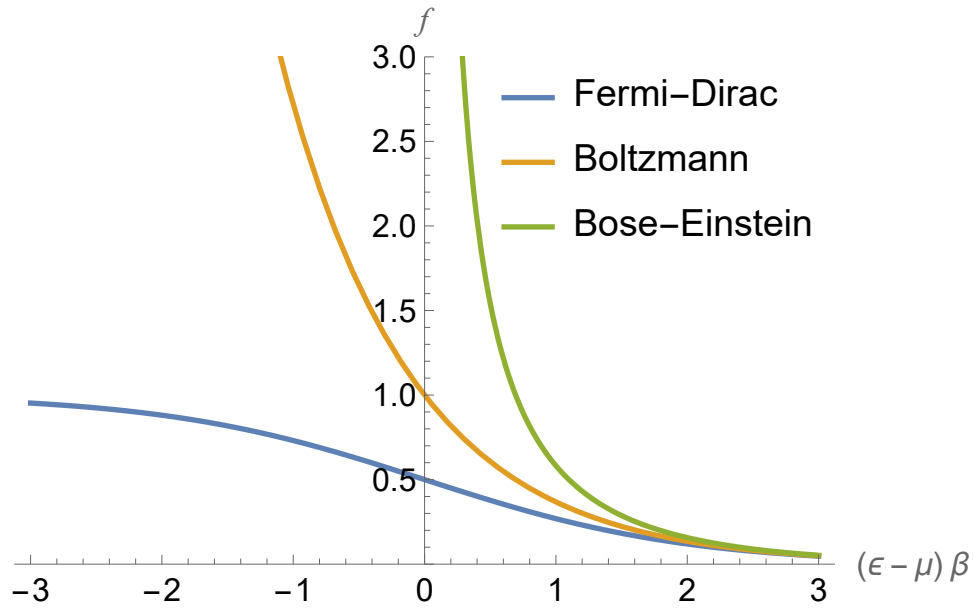


Figure 7: The three distributions plotted together. They tend to the same value as $\frac{\epsilon - \mu}{k_B T} \gg 1$.

Both the Fermi-Dirac and Bose-Einstein distributions approximate to the Boltzmann distribution in the dilute limit:

$$\frac{\epsilon - \mu}{k_B T} \gg 1. \quad (98)$$

10 Photon Gases

For a photon (boson), we can use the Bose-Einstein distribution:

$$f_{\text{BE}} = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) - 1}, \quad (99)$$

where $\mu < \epsilon$.

10.1 Cavity (black-body) Radiation

Consider a cavity of volume V with internal walls at fixed temperature T .

- Thermal equilibrium \rightarrow Bose-Einstein distribution;
- Radiation can be absorbed, reflected, and emitted at the walls, so there is no conservation of particles, and the chemical potential $\mu = 0$.

Therefore,

$$f_{\text{BE}} = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}. \quad (100)$$

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

$$n(\omega) d\omega = Dg(\omega)f_{\text{BE}}(\omega) d\omega, \quad (101)$$

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

By dispersion relation $\omega = ck$,

$$d\Omega = d\omega g(k) \frac{dk}{d\omega} = \frac{V}{2\pi^2 c^3} \omega^2 d\omega. \quad (102)$$

- Planck radiation law:

For each travelling wave mode there are two orthogonal polarizations, so $D = 2$. Then,

$$n(\omega) d\omega = Dg(\omega)f_{\text{BE}}(\omega) d\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega. \quad (103)$$

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

$$u(\omega) d\omega = \hbar\omega \frac{n(\omega)}{V} d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega, \quad (104)$$

and this is the **Planck radiation law**. In terms of frequency $\nu = \omega/2\pi$,

$$u(\nu) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} d\nu. \quad (105)$$

Note that energy density increases with temperature.

- Wien's displacement law:

The peak of the spectrum depends on the temperature:

$$\nu_{\max} \approx 2.82 \frac{k_B T}{h}. \quad (106)$$

10.2 Stefan-Boltzmann Law

By integrating with respect to frequency, we get the total energy density:

$$U = \int_0^\infty u(\nu) d\nu = \frac{8\pi^5 h}{15c^3} \left(\frac{k_B T}{h}\right)^4 \quad (107)$$

The radiation power per unit solid angle is

$$L = \frac{1}{4\pi} U c. \quad (108)$$

By some magic we get the radiation flux leaving the cavity entrance:

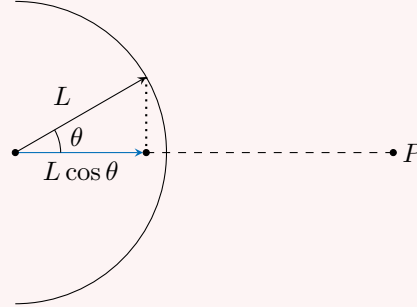
$$j^* = 2\pi \frac{L}{2} = \frac{U c}{4}. \quad (109)$$

Substituting $j^* = \sigma T^4$ gives

$$\sigma = \frac{2\pi^5 k_B^4}{15h^3 c^2} \approx 5.67 \times 10^{-8} \text{ Js}^{-1} \text{ m}^{-2} \text{ K}^{-4}. \quad (110)$$

Magic

To get j^* , consider how a sphere that radiates energy contributes to a distant point P .



Firstly, we know that only a half sphere would have radiation that contributes to P . Then, although L may not be a vector, but we still see that only a fraction of L at angle θ directs at P . This is Lambert's cosine law. Therefore,

$$j^* = \int d\Omega (L \cos \theta) = L \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin \theta \cos \theta = 2\pi \frac{L}{2}. \quad (111)$$

11 Bose-Einstein Condensates

For bosons, the occupancy of the j^{th} state with energy ϵ_j at temperature T is given by

$$f_{\text{BE}}(\epsilon_j) = \frac{1}{\exp\left(\frac{\epsilon_j - \mu}{k_B T}\right) - 1}. \quad (112)$$

Although this is a grand canonical ensemble, the total occupancies must sum to the total number of particles, so

$$N = \sum f_{\text{BE}}(\epsilon_j). \quad (113)$$

By assuming that the states are closely spaced, we can replace the summation by an integral. Assume the degeneracy factor $D = 1$, and we know

$$N = \int_0^\infty f_{\text{BE}}(\epsilon) g(\epsilon) d\epsilon. \quad (114)$$

Recall the formula of the density of states for a non-relativistic particle. After some tedious calculation, we get

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

- Boson gases typically have $\mu < 0$, and the chemical potential cannot rise above the value of the ground state energy, which we will assume to be zero.

Therefore, assuming that $\mu = 0$, we get

$$N_{\mu=0} = \zeta\left(\frac{3}{2}\right) V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}, \quad (115)$$

where the zeta function approximates to $\zeta(3/2) \approx 2.61$.

Since setting $\mu = 0$ corresponds to the maximum value of this integral, this would indicate that $N_{\mu=0}$ is the maximum number of particles that the system can contain at a given temperature T .

Equivalently, this indicates that for a given number of particles N , there is a **minimum temperature** T_B below which the system cannot be cooled:

$$T > T_B = \frac{h^2}{2\pi m k_B} \left(\frac{N}{V \zeta(3/2)}\right)^{2/3}. \quad (116)$$

The above deduction is impeccable, so the problem comes from our initial assumptions.

The approximation of the summation over 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. $k_B T \gg \delta_\epsilon$). For low temperatures, this condition is not satisfied at the lower end of the integration near $\epsilon = 0$.

To resolve this problem, we introduce an extra term to account for the ground state contribution separately. Therefore,

$$N = n_0 + \int_0^\infty f_{\text{BE}}(\epsilon) g(\epsilon) d\epsilon, \quad (117)$$

where n_0 is the occupancy of the ground state: (the ground state has $\epsilon = 0$ and $\mathbf{p} = 0$)

$$n_0 = \frac{1}{\exp\left(-\frac{\mu}{k_B T}\right) - 1}. \quad (118)$$

The integral actually neglected the ground state (as $\epsilon = 0$), so, though unchanged, it accounts for the excited states only. For temperatures $T < T_B$ we can expect the number of particles in the ground state n_0 to be large, and so

$$n_0 = \frac{1}{\exp\left(-\frac{\mu}{k_B T}\right) - 1} \approx -\frac{k_B T}{\mu} \quad \Rightarrow \quad -\mu \approx \frac{k_B T}{n_0}. \quad (119)$$

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

$$\frac{N - n_0}{N} \approx \frac{N_{\mu=0}(T)}{N} = \left(\frac{T}{T_B}\right)^{3/2}. \quad (120)$$

T_B is the critical temperature, or the Bose temperature. Below this temperature, the number of particles in the ground state becomes macroscopically large. This is Bose-Einstein condensation. After rearranging we can also see

$$\frac{n_0}{N} = 1 - \left(\frac{T}{T_B}\right)^{3/2}. \quad (121)$$

As a boson gas is cooled below the critical temperature, more and more particles join the ground state, with zero energy and zero momentum. They form **a single collective quantum wave**. As the particles possess no momentum, the collective particles have **zero viscosity**.

12 Fermi Gases

As a reminder, the mean occupancy of fermions is given by the following equation:

$$f_{\text{FD}} = \frac{1}{\exp\left(\frac{\epsilon_j - \mu}{k_B T}\right) + 1}. \quad (122)$$

12.1 The Fermi Level

At low temperatures, we see the mean occupancy becoming a step function:

$$\lim_{T \rightarrow 0} f_{\text{FD}} = \begin{cases} 1 & \epsilon < \mu \\ 0 & \epsilon > \mu. \end{cases} \quad (123)$$

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 **degenerate**.

The chemical potential at $T = 0$ defines the **Fermi energy**:

$$\epsilon_F = \mu|_{T=0}. \quad (124)$$

Note that the chemical potential itself also depends on the temperature.

The Fermi level is the boundary between the filled ($\epsilon < \epsilon_F$) and the empty ($\epsilon > \epsilon_F$) states at $T = 0$.

By the step function (Pauli's exclusion) above, the total number of states up to the Fermi level equals the number of particles in the system,

$$N = \int_0^{\epsilon_F} Dg(\epsilon) d\epsilon. \quad (125)$$

For free, non-relativistic electrons, $D = 2$ for their spin, and we get

$$N = \left(\frac{2m\epsilon_F}{h^2}\right)^{3/2} \frac{8\pi V}{3}. \quad (126)$$

We shall also obtain an energy for a fixed number of particles:

$$\epsilon_F = \frac{h^2}{2m} \left(\frac{3}{8\pi}\right)^{2/3} \left(\frac{N}{V}\right)^{2/3}. \quad (127)$$

It is also useful to define a corresponding temperature called the Fermi temperature:

$$T_F = \frac{\epsilon_F}{k_B}. \quad (128)$$

- For $T \gg T_F$, the occupancy f_{FD} is very small for all energies and the gas approximates the classical Maxwell-Boltzmann.
- For $T \sim T_F$, this is no longer the case, and quantum statistics is needed.
- For $T \ll T_F$, the degenerate situation is a very good approximation.

12.2 Thermodynamic Properties of Degenerate Fermi Gases

12.2.1 Internal Energy

In the limit $T \rightarrow 0$,

$$U = \int_0^\infty n(\epsilon) \epsilon \, d\epsilon = \int_0^{\epsilon_F} Dg(\epsilon) \epsilon \, d\epsilon. \quad (129)$$

As the density of states varies as $g(\epsilon) \propto \epsilon^{1/2}$ for a non-relativistic particle, this gives

$$U = A \int_0^{\epsilon_F} \epsilon^{3/2} \, d\epsilon = \frac{2A}{5} \epsilon_F^{5/2}. \quad (130)$$

As the number of particles satisfies

$$N = A \int_0^{\epsilon_F} \epsilon^{1/2} \, d\epsilon = \frac{2A}{3} \epsilon_F^{3/2}, \quad (131)$$

we can get

$$U = \frac{3}{5} N \epsilon_F. \quad (132)$$

Therefore, even at zero temperature, the degenerate Fermi gas can have significant internal energy. However, at $T = 0$, entropy is zero.

12.2.2 Degenerate Pressure

By partial differentiation,

$$p = - \left(\frac{\partial U}{\partial V} \right)_S = \frac{2}{5} \frac{N}{V} \epsilon_F. \quad (133)$$

Substitution gives

$$p = \frac{h^2}{5m} \left(\frac{3}{8\pi} \right)^{2/3} \left(\frac{N}{V} \right)^{5/3}. \quad (134)$$

The Fermi gas also has significant pressure at zero temperature; this is the degenerate pressure.

12.3 Applications

In a metal, the valence electrons are weakly bound and non-localized. Therefore, we can consider the electrons as free particles in a smooth potential due to the positive ions and other electrons. These electrons will therefore behave as a Fermi gas.

In main sequence stars, the gravitational force is balanced by radiation pressure with energy supplied by the fusion process of hydrogen or helium. However, once the supply of hydrogen is exhausted, the star will begin to collapse under its own gravity. Eventually, the degenerate pressure from the electrons in the star may be sufficient to balance the gravity. A white dwarf is such a star.

For the star to be stable, the total potential energy (gravitational and internal) should be minimized.