

Lecture by Professor Tigran Tchrakian

Statistical Mechanics

Tobias Hofbaur

March 26, 2007

Contents

1	Introduction and Boltzmann's hypothesis	3
1.1	Thermodynamic probability	3
1.2	Criteria for equilibrium	3
1.3	Correlation to Thermodynamics	5
1.4	Example: ideal gas equation	6
2	Phase Space, Ensemble and Liouville's Theorem	7
2.1	Phase Space and Ensemble	7
2.2	Liouville's Theorem	7
3	Classical Counting	9
3.1	Stirling Approximation of $N!$ for large N	9
3.2	Boltzmann Counting	11
3.3	Boltzmann distribution function	13
3.3.1	Correlation to known quantities	14
3.3.2	Calculate C_V	16
3.3.3	Calculate average Energy	16
3.4	Applications	17
3.4.1	Equation of state (gas equation)	17
3.4.2	Equipartition of energy	18
3.4.3	Interaction of Radiation with Matter	20
3.5	Degenerate levels (states)	22
4	Quantum mechanical counting	27
4.1	Pauli exclusion principle	27
4.2	Boltzmann distribution	28
4.3	Fermi-Dirac distribution	28
4.4	Bose-Einstein distribution	29
4.5	Summarize FD and BE	29
4.6	Sign of μ	32
4.7	Radiation Laws	34

1 Introduction and Boltzmann's hypothesis

Statistical Mechanics is a microscopic theory of Thermodynamics, i.e. Mechanics (classical and qm) of very large (statistical) number of particles.

1.1 Thermodynamic probability

The state of a system is described by the thermodynamic probability Ω i.e. the total number of possible configurations (microstates) the particles in the system can have to achieve a given outer state (macrostate). The more freedom (possibilities) the particles have, the likelier the state.

Equilibrium is the most probable state i.e.

$$\Omega_{equil} = \Omega_{max} \quad (1.1)$$

In thermodynamic Systems: $\Omega = \Omega(N, E, V)$

1.2 Criteria for equilibrium

Take two systems A_1 and A_2 with states $\Omega_1(N_1, E_1, V_1)$ and $\Omega_2(N_2, E_2, V_2)$. A_1 and A_2 interact and achieve equilibrium. The compound system has state $\Omega^{(0)} = \Omega_1 \Omega_2$

Energy exchange

N_1, N_2, V_1, V_2 are constant

$$E^{(0)} = E_1 + E_2 = const$$

As we have equilibrium $\delta\Omega^{(0)} = 0$. As the state only depends on the energy E_1 (or E_2 as they are dependent), we get $\delta\Omega^{(0)} = \frac{\partial\Omega^{(0)}}{\partial E_1} \delta E_1 = 0$

$$\frac{\partial\Omega^{(0)}}{\partial E_1} \Big|_{\bar{E}_1, \bar{E}_2} = \left(\frac{\partial\Omega_1}{\partial E_1} \Omega_2 \right)_{\bar{E}_1, \bar{E}_2} + \left(\frac{\partial\Omega_2}{\partial E_1} \Omega_1 \right)_{\bar{E}_1, \bar{E}_2} = 0$$

where \bar{E}_1, \bar{E}_2 are the energies of A_1 and A_2 in equilibrium.

$$\frac{\partial\Omega_1}{\partial E_1} \Big|_{\bar{E}_1} \Omega_2(\bar{E}_2) + \Omega_1(\bar{E}_1) \frac{\partial\Omega_2}{\partial E_1} \Big|_{\bar{E}_2} = 0$$

We can replace the partial derivative for E_1 as $\frac{\partial}{\partial E_1} = \frac{\partial E_2}{\partial E_1} \frac{\partial}{\partial E_2} = -\frac{\partial}{\partial E_2}$

$$\begin{aligned}\frac{\partial \Omega_1}{\partial E_1} \Big|_{\bar{E}_1} \Omega_2(\bar{E}_2) - \Omega_1(\bar{E}_1) \frac{\partial \Omega_2}{\partial E_2} \Big|_{\bar{E}_2} &= 0 \\ \frac{1}{\Omega_1(\bar{E}_1)} \frac{\partial \Omega_1}{\partial E_1} \Big|_{\bar{E}_1} - \frac{1}{\Omega_2(\bar{E}_2)} \frac{\partial \Omega_2}{\partial E_2} \Big|_{\bar{E}_2} &= 0\end{aligned}$$

or

$$\beta_1 \equiv \frac{\partial}{\partial E_1} \ln \Omega_1 \Big|_{\bar{E}_1} = \frac{\partial}{\partial E_2} \ln \Omega_2 \Big|_{\bar{E}_2} \equiv \beta_2 \quad (1.2)$$

i.e. in equilibrium $\beta_1 = \beta_2$

$\beta = \frac{\partial}{\partial E} \ln \Omega$ is equilibrium parameter (must be related to T by 0th law)

Boltzmann's hypothesis

Take a look at the entropy: $\Delta S^{(0)} = \Delta S_1 + \Delta S_2$

$$\begin{aligned}\Delta S^{(0)} &= \frac{\partial S_1}{\partial E_1} \Delta E_1 + \frac{\partial S_2}{\partial E_2} \Delta E_2 \\ &= \frac{\partial S_1}{\partial E_1} (-\Delta E) + \frac{\partial S_2}{\partial E_2} (\Delta E)\end{aligned}$$

Assuming that heat is flowing from A_1 to A_2 . The second Law tells us $\Delta S > 0$, i.e.

$$\begin{aligned}\Delta E \left(-\frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} \right) &> 0 \\ \frac{\partial S_2}{\partial E_2} &> \frac{\partial S_1}{\partial E_1}\end{aligned}$$

Recall the Maxwell relation: $\frac{\partial U}{\partial S} = T$, therefore

$$\begin{aligned}\frac{1}{T_2} &> \frac{1}{T_1} \\ T_1 &> T_2\end{aligned}$$

Combine $\frac{\partial}{\partial E} \ln \Omega = \beta$ and $\frac{\partial E}{\partial S} = T$

$$\frac{\partial}{\partial E} \ln \Omega \frac{\partial E}{\partial S} = \beta T = \frac{\partial \ln \Omega}{\partial S}$$

According to Boltzmann this is constant

$$\frac{\partial S}{\partial \ln \Omega} = \frac{1}{\beta T} \equiv k \quad (1.3)$$

with a universal constant k (later Boltzmann's constant). Integrating yields

$$S + S_0 = k \ln \Omega$$

The choice of $S_0 = 0$ (suggested by Planck) leads to

$$S = k \ln \Omega \quad (1.4)$$

If all "particles" are confined to one state then $\Omega = 1$ (impossible), $S = k \ln 1 = 0$. Impossibility of attaining $T = 0$ from 3rd Law.

Exchange of Volume

E_1, E_2, N_1, N_2 are constant. Similar calculus leads to

$$\eta \equiv \frac{\partial}{\partial V} \ln \Omega \quad (1.5)$$

is fixed for A_1, A_2 in equilibrium

Exchange of Particles

E_1, E_2, V_1, V_2 are constant

$$\zeta \equiv \frac{\partial}{\partial N} \ln \Omega \quad (1.6)$$

is fixed in equilibrium

1.3 Correlation to Thermodynamics

The quantities

$$\beta = \frac{\partial}{\partial E} \ln \Omega \quad \eta = \frac{\partial}{\partial V} \ln \Omega \quad \zeta = \frac{\partial}{\partial N} \ln \Omega$$

must be related to thermodynamic coordinates (i.e. same values for equilibrium). To see this, we compare the differentials for $\ln \Omega$. On the one hand we have

$$\begin{aligned} d \ln \Omega &= \frac{\partial \ln \Omega}{\partial E} dE + \frac{\partial \ln \Omega}{\partial V} dV + \frac{\partial \ln \Omega}{\partial N} dN \\ &= \beta dE + \eta dV + \zeta dN \end{aligned}$$

On the other hand we have

$$d \ln \Omega = \frac{1}{k} dS$$

The first Law was $TdS = dE + PdV - \mu dN$, so we get

$$\begin{aligned} d \ln \Omega &= \frac{1}{kT} dE + \frac{P}{kT} dV - \frac{\mu}{kT} dN \\ d \ln \Omega &= \beta dE + \eta dV + \zeta dN \end{aligned}$$

Therefore

$$\beta = \beta \quad \eta = \frac{P}{kT} \quad \zeta = \frac{-\mu}{kT} \quad (1.7)$$

and in equilibrium: $T_1 = T_2, P_1 = P_2, \mu_1 = \mu_2$

1.4 Example: ideal gas equation

As an application we can derive the ideal gas equation

1. The gas consist of non-interacting, non-overlapping "particles"
2. The probability of any particle to occupy a certain state is the same for all particles

The possibilities for one particle are proportional to V . The possible states for N particles are proportional to V^N , i.e. $\Omega \propto V^N = cV^N$

$$\eta = \frac{\partial}{\partial V} \ln \Omega = \frac{\partial}{\partial V} (\ln c + \ln V^N) = \frac{N}{V}$$

as $\eta = \frac{P}{kT}$ we get

$$\begin{aligned}\frac{N}{V} &= \frac{P}{kT} \\ PV &= NkT\end{aligned}$$

2 Phase Space, Ensemble and Liouville's Theorem

2.1 Phase Space and Ensemble

Usual configuratoin space: $(x, y, z) = \vec{q}$

Usual momentum space: $(p_x, p_y, p_z) = \vec{p}$

For a N "particle" system the phase space is (\vec{q}_i, \vec{p}_i) with $i = 1 \dots 3N$

Ensemble: collection of all states of a system over all time, i.e. a mental copy of all states

Time average of all states \equiv Ensemble average

Density function $\rho(\vec{q}_i, \vec{p}_i, t)$, ρ is the density of points in phase-space. The volume-integral is a norm (not normalized)

$$\int \rho(\vec{q}_i, \vec{p}_i, t) d^{3N} \vec{q} d^{3N} \vec{p} = norm \geq 0$$

The ensemble average of a physical quantity f is the 1st momentum of f with respect to the density ρ

$$\langle f \rangle = \frac{\int f(\vec{q}_i, \vec{p}_i) \rho(\vec{q}_i, \vec{p}_i, t) d\tau}{\int \rho(\vec{q}_i, \vec{p}_i, t) d\tau}$$

with the volume-element in phase-space $d\tau$

Equilibrium:

$$\frac{\partial \rho}{\partial t} = 0 \quad \text{stationary ensemble} \quad (2.1)$$

2.2 Liouville's Theorem

Criterion for equilibrium: $\frac{\partial \rho}{\partial t} = 0$ must be satisfied

Continuity equation $\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0$. Here we have $\rho(\vec{q}_i, \vec{p}_i, t)$. The velocity (time-rate-change) of "points" in phase-space is $\vec{v} = (\dot{\vec{q}}_i, \dot{\vec{p}}_i)$. The current at a point in phase-space is $\vec{J} = \rho \vec{v}$. So we get the continuity equation.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad (2.2)$$

$\nabla = \left(\frac{\partial}{\partial \vec{q}_i}, \frac{\partial}{\partial \vec{p}_i} \right)$, therefore

$$\begin{aligned}\nabla(\rho \vec{v}) &= \sum_{i=1}^N \left[\frac{\partial}{\partial \vec{q}_i}(\rho \dot{\vec{q}}_i) + \frac{\partial}{\partial \vec{p}_i}(\rho \dot{\vec{p}}_i) \right] \\ &= \sum_i \left[\left(\frac{\partial \rho}{\partial \vec{q}_i} \dot{\vec{q}}_i + \rho \frac{\partial \dot{\vec{q}}_i}{\partial \vec{q}_i} \right) + \left(\frac{\partial \rho}{\partial \vec{p}_i} \dot{\vec{p}}_i + \rho \frac{\partial \dot{\vec{p}}_i}{\partial \vec{p}_i} \right) \right]\end{aligned}$$

Now Hamilton's equation of motion are

$$\dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{q}_i} \quad \dot{\vec{q}}_i = \frac{\partial H}{\partial \vec{p}_i}$$

using this we get

$$\begin{aligned}\nabla(\rho \vec{v}) &= \sum_i \left[\left(\frac{\partial \rho}{\partial \vec{q}_i} \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i} \frac{\partial H}{\partial \vec{q}_i} \right) + \rho \left(\frac{\partial}{\partial \vec{q}_i} \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_i} \frac{\partial H}{\partial \vec{q}_i} \right) \right] \\ &= \sum_i \left(\frac{\partial \rho}{\partial \vec{q}_i} \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i} \frac{\partial H}{\partial \vec{q}_i} \right) \\ &= \{\rho, H\}_{P.B.}\end{aligned}$$

with the Poisson-Brackets. Therefore the continuity equation gives Liouville's Theorem

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\}_{P.B} \quad (2.3)$$

1. $\frac{\partial \rho}{\partial t} = 0$ if ρ is independent of (\vec{q}_i, \vec{p}_i) i.e. constant energy, Microcanonical ensemble
2. $\frac{\partial \rho}{\partial t} = 0$ if $\rho = \rho([H])$, Canonical ensemble

3 Classical Counting

3.1 Stirling Approximation of $N!$ for large N

Ω = number of microstates. e.g. N particles (identical), total number of arrangements $N!$. if N_i particles have energy E_i then $N_i!$ arrangements are identical. then $\Omega = \frac{N!}{\prod_i N_i!}$
 When $N \gg 1$ then $N!$ can be expressed analytically: Integral representation of $n!$:

$$n! = \int_0^\infty x^n e^{-x} dx \equiv \int_0^\infty f(x, n) dx$$

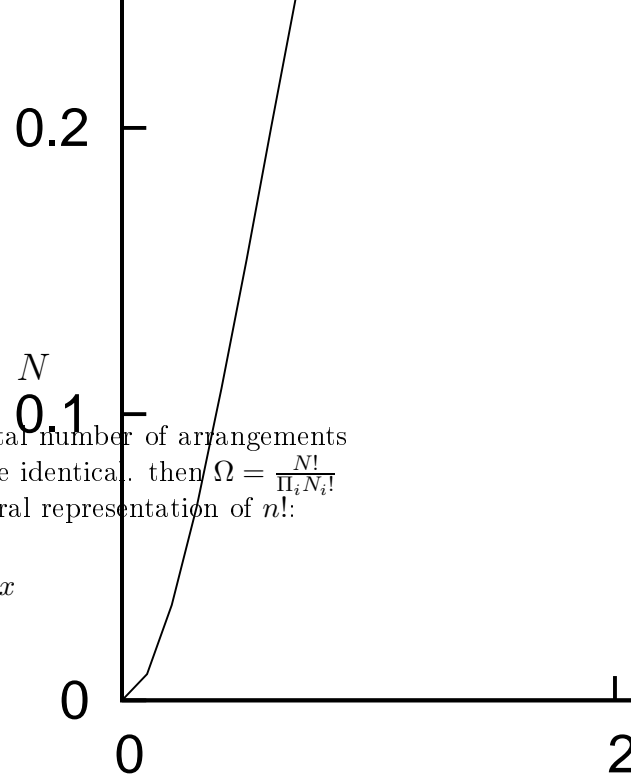


Figure 3.1: Plot of $f(x, 2)$

$$\begin{aligned} f(x, n) &= x^n e^{-x} \\ f'(x, n) &= nx^{n-1} e^{-x} - x^n e^{-x} \\ &= x^n e^{-x} \left(\frac{n}{x} - 1 \right) \\ f'(n, n) &= 0 \\ f''(n, n) &= -n^{n-1} e^{-n} < 0 \end{aligned}$$

f is peaked around $x = n$, i.e. $n!$ receives most contribution from small range of x around $x = n$. Approximate:

$$n! \approx \int_0^\infty f_{approx}(x, n) dx$$

$$\begin{aligned} f_{approx}(x, n) &= f(n, n) + (x - n)f'(n, n) + \frac{(x - n)^2}{2!}f''(n, n) + \dots \\ &= n^n e^{-n} + 0 + \frac{(x - n)^2}{2!}(-n^{n-1}e^{-n}) + \dots \\ &= n^n e^{-n} \left(1 - \frac{(x - n)^2}{2n} + \dots \right) \\ &\approx n^n e^{-n} \left(1 - \frac{(x - n)^2}{2n} + \frac{1}{2!} \left(-\frac{(x - n)^2}{2n} \right)^2 + \dots \right) \\ f_{approx}(x, n) &= n^n e^{-n} e^{-\left(\frac{x-n}{\sqrt{2n}}\right)^2} \end{aligned}$$

Therefore

$$\begin{aligned} n! &\approx n^n e^{-n} \int_0^\infty e^{-\left(\frac{x-n}{\sqrt{2n}}\right)^2} dx \\ &= n^n e^{-n} \underbrace{\sqrt{2n} \int_{-n}^\infty e^{-y^2} dy}_{\propto \sqrt{\pi}} \\ n! &\approx n^n e^{-n} \sqrt{2n\pi} \end{aligned} \tag{3.1}$$

In the Boltzmann-Hypothesis $S = k \ln \Omega$ so we need to approximate $\ln n!$:

$$\begin{aligned} \ln n! &= \ln n^n e^{-n} \sqrt{2n\pi} \\ &= n \ln n - n \ln e + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi \\ &\approx \left(n + \frac{1}{2} \right) \ln n - n \\ \ln n! &\approx n \ln n - n \end{aligned} \tag{3.2}$$

Example. Hooke's Law: $F = -kx$

Model: N links (each of unit length), length L of the chain, $N \gg L$, i.e. lot of creases.

$$\begin{aligned} \# \text{ of backward links} &= \frac{N + L}{2} \\ \# \text{ of forward links} &= \frac{N - L}{2} \end{aligned}$$

As Ω is the number of microstates possible to achieve a given outward state, we have

$$\Omega = \frac{\text{Total number of arrangements of Links}}{(\# \text{ of arr. of forward l.})(\# \text{ of arr. of backward l.})}$$

$$\Omega = \frac{N!}{\left(\frac{N+L}{2}\right)! \left(\frac{N-L}{2}\right)!}$$

So we get:

$$\begin{aligned} S &= k \ln \Omega = k \left[\ln N! - \ln \left(\frac{N+L}{2}! \right) - \ln \left(\frac{N-L}{2}! \right) \right] \\ &= k \left\{ N \ln N - N - \left(\frac{N+L}{2} \right) \ln \left(\frac{N+L}{2} \right) + \left(\frac{N+L}{2} \right) - \left(\frac{N-L}{2} \right) \ln \left(\frac{N-L}{2} \right) + \left(\frac{N-L}{2} \right) \right\} \\ S &= k \left\{ N \ln N - \left(\frac{N+L}{2} \right) \ln \left(\frac{N+L}{2} \right) - \left(\frac{N-L}{2} \right) \ln \left(\frac{N-L}{2} \right) \right\} \\ &= k \left\{ \left(\frac{N+L}{2} \right) \ln N + \left(\frac{N-L}{2} \right) \ln N - \left(\frac{N+L}{2} \right) \ln \left(\frac{N+L}{2} \right) - \left(\frac{N-L}{2} \right) \ln \left(\frac{N-L}{2} \right) \right\} \\ &= k \left\{ \left(\frac{N+L}{2} \right) \left[\ln N - \ln \left(\frac{N+L}{2} \right) \right] + \left(\frac{N-L}{2} \right) \left[\ln N - \ln \left(\frac{N-L}{2} \right) \right] \right\} \\ &= -\frac{k}{2} \left\{ (N+L) \ln \frac{N+L}{2N} + (N-L) \ln \frac{N-L}{2N} \right\} \end{aligned}$$

Define $\kappa = \frac{N+L}{2N}$, $\Rightarrow \frac{N-L}{2N} = 1 - \kappa$

$$S = -kN \{ \kappa \ln \kappa + (1 - \kappa) \ln(1 - \kappa) \}$$

In 1 dimension, Force = Pressure. The Maxwell-relation was $P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial L}\right)_T$ with $F = U - TS = -TS$ as $U = \text{const}$ since microcanonical ensemble

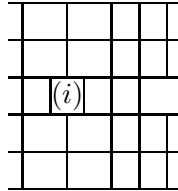
$$\begin{aligned} P &= \frac{\partial}{\partial L} (kNT \{ \kappa \ln \kappa + (1 - \kappa) \ln(1 - \kappa) \}) \\ &= kNT \{ \ln \kappa + 1 + (-1) \ln(1 - \kappa) + (-1) \} \frac{1}{2N} \\ &= \frac{kT}{2} \{ \ln \kappa - \ln(1 - \kappa) \} \\ &= \frac{kT}{2} \ln \frac{N+L}{N-L} \\ P &= \frac{kT}{2} \ln \left(\frac{1 + \frac{L}{N}}{1 - \frac{L}{N}} \right) \end{aligned}$$

As $\frac{L}{N} \ll 1$ expand around $\frac{L}{N} = 0$: $\ln \frac{1+x}{1-x} = 2x + \frac{2}{3}x^3 + \dots$

$$P = \frac{kT}{N} L$$

3.2 Boltzmann Counting

Phase space:



phase cell, labeled by E_i , with N_i particles in it. The total number of particles is N , $N = \sum_i N_i$, $E = \sum_i N_i E_i$

$$\begin{aligned} \text{No. of microstates} &= \frac{\text{No. of arrangements of } N \text{ particles}}{\text{No. of indistinguishable arrangements}} \\ \Omega &= \frac{N!}{\prod_i (N_i!)} \end{aligned} \quad (3.3)$$

$$\begin{aligned} S &= k \ln \frac{N!}{\prod_i (N_i!)} \\ &= k \left[\ln N! - \ln \left(\prod_i (N_i!) \right) \right] \\ &= k \left[\ln N! - \sum_i \ln N_i! \right] \end{aligned}$$

But $N \gg 1$ and $N_i \gg 1$, therefore approximation with Sterling

$$\begin{aligned} S &= k \left[N \ln N - N - \sum_i (N_i \ln N_i - N_i) \right] \\ &= k \left[N \ln N - \sum_i (N_i \ln N_i) \right] \end{aligned}$$

It is convenient to introduce $\omega_i = \frac{N_i}{N}$, i.e. $\sum \omega_i = 1$

$$\begin{aligned} S &= k \left[N \ln N - \sum_i (N \omega_i \ln (N \omega_i)) \right] \\ &= kN \left[\ln N - \sum_i (\omega_i \ln N + \omega_i \ln \omega_i) \right] \\ &= kN \left[\ln N - \ln N \sum_i \omega_i - \sum_i \omega_i \ln \omega_i \right] \\ S &= -kN \sum_i \omega_i \ln \omega_i \end{aligned} \quad (3.4)$$

For equilibrium we have $S_{eq} = S_{max}$, i.e. $\delta S = 0$ with respect to variation $\delta \omega_i$

$$\delta S = \sum_i \frac{\partial S}{\partial \omega_i} \delta \omega_i$$

$\delta \omega_i$ are arbitrary variations of the function $\omega(E_i)$ subject to the constraints:

$$1. \sum_i E_i \omega_i = \text{const}$$

$$2. \sum_i \omega_i = 1$$

i.e. set

$$\delta S + \lambda_1 \delta E + \lambda_2 \delta N = 0$$

i.e. vary

$$\mathcal{S} = S + \lambda_1 \underbrace{\sum_i N_i E_i}_{S_1} + \lambda_2 \underbrace{\sum_i N_i}_{S_2}$$

- $\frac{\partial S}{\partial \omega_i} = -kN \frac{\partial}{\partial \omega_i} \left(\sum_j \omega_j \ln \omega_j \right) = -kN(\ln \omega_i + 1)$

$$\delta S = \sum_i \frac{\partial S}{\partial \omega_i} \delta \omega_i = -kN \sum_i (\ln \omega_i + 1) \delta \omega_i$$

- $\frac{\partial S_1}{\partial \omega_i} = \frac{\partial}{\partial \omega_i} N \sum_j E_j \omega_j = N E_i$

$$\delta S_1 = N \sum_i E_i \delta \omega_i$$

- $\frac{\partial S_2}{\partial \omega_i} = \frac{\partial}{\partial \omega_i} N \sum_j \omega_j = N$

$$\delta S_2 = N \sum_i \delta \omega_i$$

$$\begin{aligned} \delta S &= -kN \sum_i (\ln \omega_i + 1) \delta \omega_i + \lambda_1 N \sum_i E_i \delta \omega_i + \lambda_2 N \sum_i \delta \omega_i \\ &= N \sum_i [-k(\ln \omega_i + 1) + \lambda_1 E_i + \lambda_2] \delta \omega_i \end{aligned}$$

for arbitrary $\delta \omega_i$, therefore

$$-k(\ln \omega_i + 1) + \lambda_1 E_i + \lambda_2 = 0 \quad \forall i$$

i.e

$$\begin{aligned} \ln \omega_i &= -\alpha + \beta E_i \\ \omega_i &= e^{-\alpha + \beta E_i} \end{aligned} \tag{3.5}$$

We had $1 = \sum_i \omega_i$ i.e. $1 = \sum_i \omega_i = e^{-\alpha} \sum_i e^{\beta E_i}$ i.e.

$$\begin{aligned} e^\alpha &= \sum_i e^{-\beta E_i} \geq 0 \\ e^\alpha &= Z(\beta) \end{aligned} \tag{3.6}$$

$Z(\beta)$ is called "partition function"

3.3 Boltzmann distribution function

The Boltzmann distribution function is then given by

$$f_B(E_i) = \frac{e^{-\beta E_i}}{Z} \quad Z = \sum_i e^{-\beta E_i} \tag{3.7}$$

or for continuous energy spectrum

$$f_B(E) = \frac{e^{-\beta E}}{Z} \quad Z = \int e^{-\beta E} dE \tag{3.8}$$

3.3.1 Correlation to known quantities

The entropy was $S = -kN \sum_i \omega_i \ln \omega_i$ i.e.

$$\begin{aligned}
 S &= -kN \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i - \ln Z) \\
 &= kN \left(\frac{\beta}{Z} \sum_i E_i e^{-\beta E_i} + \frac{\ln Z}{Z} \underbrace{\sum_i e^{-\beta E_i}}_{=Z} \right) \\
 &= kN \left(\frac{\beta}{Z} \sum_i E_i e^{-\beta E_i} + \ln Z \right)
 \end{aligned}$$

$$\sum_i E_i e^{-\beta E_i} = -\frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} = -\frac{\partial}{\partial \beta} Z \text{ i.e.}$$

$$S = kN \left(-\frac{\beta}{Z} \frac{\partial Z}{\partial \beta} + \ln Z \right)$$

Total energy

$$\begin{aligned}
 E &= \sum_i N_i E_i = N \sum_i E_i \omega_i = N \sum_i E_i \frac{e^{-\beta E_i}}{Z} = \\
 &= \frac{N}{Z} \sum_i E_i e^{-\beta E_i} = \frac{N}{Z} \sum_i -\frac{\partial}{\partial \beta} e^{-\beta E_i} = -\frac{N}{Z} \frac{\partial Z}{\partial \beta} \\
 E &= -\frac{N}{Z} \frac{\partial Z}{\partial \beta} \tag{3.9}
 \end{aligned}$$

together we get

$$\begin{aligned}
 S &= kN \left(-\frac{\beta}{Z} \frac{\partial Z}{\partial \beta} + \ln Z \right) = \\
 &= k \left(-N\beta \frac{1}{Z} \frac{\partial Z}{\partial \beta} + N \ln Z \right) \\
 S &= k(\beta E + N \ln Z) \tag{3.10}
 \end{aligned}$$

Relate β

Correlate the new β to known quantities: S applied to Thermodynamics:

$$S = k\beta U + kN \ln Z(\beta)$$

$dS(U, \beta) = \frac{\partial S}{\partial U} dU + \frac{\partial S}{\partial \beta} d\beta$. Calculate dS :

$$\begin{aligned}
 dS &= k\beta dU + \left(kN \frac{1}{Z} \frac{\partial Z}{\partial \beta} + kU \right) d\beta = k\beta dU + (kU - kU) d\beta = \\
 &= k\beta dU
 \end{aligned}$$

The relevant Maxwell Relation is $\left(\frac{\partial U}{\partial S}\right)_{N,V} = \frac{1}{T}$, i.e. $k\beta = \frac{1}{T}$ i.e. the "new" β is our "old" β .

Average Energy

Calculate the average energy per particle, i.e. the first moment of E_i with respect to $f_B(E_i)$:

$$\begin{aligned}\langle U \rangle &= \sum E_i \frac{e^{-\beta E_i}}{Z} = -\frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \\ &= \frac{U}{N}\end{aligned}$$

Refine notation $\langle U \rangle = -\frac{\partial}{\partial \beta} \ln Z$

Now readjust notation:

$Z_N = Z_1^N$ where Z_1 is the partition function per "particle"

$$\begin{aligned}U &= N \langle U \rangle = -N \frac{\partial}{\partial \beta} \ln Z_1 = -\frac{\partial}{\partial \beta} \ln Z_1^N = -\frac{\partial}{\partial \beta} \ln Z_N \\ U &= \sum N_i U_i = N \sum_i \omega_i U_i = N \left(-\frac{\partial}{\partial \beta} \ln Z_1 \right) = -\frac{\partial}{\partial \beta} \ln Z_N\end{aligned}$$

Thermodynamics:

$$S = k\beta U + k \ln Z_N$$

Relate α

Helmholtz: $F = U - TS = U - T \left(\frac{1}{T} U + k \ln Z_N \right) = -\frac{1}{\beta} \ln Z_N$

$$F = -\frac{1}{\beta} \ln Z_N$$

Maxwell relations (involving the potential F)

$$\begin{aligned}S &= -\left(\frac{\partial F}{\partial T}\right)_{N,V} = \frac{\partial}{\partial T} (kT \ln Z_N) = \\ &= k \ln Z_N + kT \frac{\partial}{\partial T} \ln Z_N = k \ln Z_N - \frac{1}{T} \frac{\partial}{\partial \beta} \ln Z_N = \\ &= k\beta U + k \ln Z_N \quad \text{nothing new} \\ P &= -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{1}{\beta} \left(\frac{\partial}{\partial V}\right)_{N,T} \ln Z_N \quad \text{useful} \\ \mu &= \left(\frac{\partial F}{\partial N}\right)_{V,T} = -\frac{1}{\beta} \left(\frac{\partial}{\partial N}\right)_{V,T} \ln Z_N = -\frac{1}{\beta} \ln Z_1 = -\frac{1}{\beta} \ln e^\alpha = -\frac{\alpha}{\beta}\end{aligned}$$

α is a chemical potential.

3.3.2 Calculate C_V

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = - \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \left(\frac{\partial}{\partial \beta} \ln Z_N \right) = \frac{1}{kT^2} \frac{\partial^2}{\partial \beta^2} \ln Z_N = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z_N$$

$$C_V = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z_N \quad (3.11)$$

3.3.3 Calculate average Energy

In the Boltzmann distribution, E ranges from 0 to ∞ . Consider a system at energy E and calculate the derivation ΔE from E (at any observation). Estimate $\frac{\Delta E}{\langle E \rangle}$. If this is very small, the microcanonical ensemble is equivalent to the canonical ensemble.

$$\begin{aligned} \langle E \rangle &= \int E f(E) dE = \int E \frac{e^{-\beta E}}{Z} dE \\ &= \frac{1}{Z} \int E e^{-\beta E} dE = - \frac{1}{Z} \frac{\partial}{\partial \beta} \int e^{-\beta E} dE \\ \langle E \rangle &= - \frac{1}{Z} \frac{\partial Z}{\partial \beta} \end{aligned} \quad (3.12)$$

$$\begin{aligned} (\Delta E)^2 &= \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 - 2E \langle E \rangle + \langle E \rangle^2 \rangle = \\ &= \int E^2 f(E) dE - 2 \langle E \rangle \int E f(E) dE + \langle E \rangle^2 \int f(E) dE = \\ &= \int E^2 f(E) dE - 2 \langle E \rangle^2 + \langle E \rangle^2 = \\ &= \frac{1}{Z} \int E^2 e^{-\beta E} dE - \langle E \rangle^2 = \\ &= \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} \int e^{-\beta E} dE - \langle E \rangle^2 = \\ &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \langle E \rangle^2 = \\ &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \\ &= \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) - \left(\frac{\partial}{\partial \beta} \frac{1}{Z} \right) \frac{\partial Z}{\partial \beta} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \\ &= \frac{\partial^2}{\partial \beta^2} \ln Z + \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \\ &= \frac{\partial^2}{\partial \beta^2} \ln Z \end{aligned}$$

Recall from (3.11) $C_V = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z$, i.e.

$$(\Delta E)^2 = \frac{C_V}{k\beta^2} \quad (3.13)$$

i.e.

$$\frac{\Delta E}{\langle E \rangle} = \frac{\sqrt{kT^2 C_V}}{\langle E \rangle}$$

3.4 Applications

3.4.1 Equation of state (gas equation)

In canonical ensemble (Boltzmann distribution):

$$P = - \left(\frac{\partial F}{\partial V} \right)_{N,T} = kT \left(\frac{\partial}{\partial V} \right)_{N,T} \ln Z_N$$

1. Ideal gas (recall $\Omega \propto V^N$). Energy spectrum is continuous, $f(E) = \frac{e^{-\beta E}}{Z}$, $E = \frac{|\vec{p}|^2}{2m}$
i.e. $V(x) = 0$, no forces.

$$\begin{aligned} Z_1 &= \int e^{-\beta E} d\tau = \int e^{-\beta E} dq dp = \\ &= \int e^{-\beta \frac{p^2}{2m}} dq dp = V \int e^{-\beta \frac{p^2}{2m}} dp = \\ &= V \sqrt{\frac{2m\pi}{\beta}} \end{aligned}$$

This yields a pressure of

$$\begin{aligned} P &= kT \left(\frac{\partial}{\partial V} \right)_{N,T} \ln Z_N = kT \left(\frac{\partial}{\partial V} \right)_{N,T} N \ln Z_1 = \\ &= NkT \frac{\partial}{\partial V} \ln \left(V \sqrt{\frac{2m\pi}{\beta}} \right) = \\ &= NkT \frac{\partial}{\partial V} \left(\ln V + \ln \sqrt{\frac{2m\pi}{\beta}} \right) = \\ &= \frac{NkT}{V} \end{aligned}$$

2. non-ideal Gas, e.g. VdW

$$Z_1 = \int e^{-\beta E} d\tau$$

$$E = \frac{p^2}{2m} + W(q)$$

$$\begin{aligned}
Z_1 &= \int e^{-\beta \frac{p^2}{2m}} dp \int e^{-\beta W(q)} dq \\
&= \sqrt{\frac{2m\pi}{\beta}} \int e^{-\beta W(q)} dq \\
&= \sqrt{\frac{2m\pi}{\beta}} \left(\int dq - \int dq + \int e^{-\beta W(q)} dq \right) \\
&= \sqrt{\frac{2m\pi}{\beta}} \left(V + \int e^{-\beta W(q)} - 1 dq \right) \\
&= \sqrt{\frac{2m\pi}{\beta}} V \left(1 + \frac{1}{V} \int e^{-\beta W(q)} - 1 dq \right)
\end{aligned}$$

$$\begin{aligned}
P &= - \left(\frac{\partial F}{\partial V} \right)_{N,T} = NkT \left(\frac{\partial}{\partial V} \right)_{N,T} \ln Z_1 = \\
&= NkT \frac{\partial}{\partial V} \left[\ln \sqrt{\frac{2m\pi}{\beta}} + \ln V + \ln \left(1 + \frac{c}{V} \right) \right] \\
&= NkT \left(\frac{1}{V} + \frac{\partial}{\partial V} \ln \left(1 + \frac{c}{V} \right) \right) \\
&= NkT \left(\frac{1}{V} - \frac{c}{V^2} + \frac{c^2}{V^3} + \dots \right)
\end{aligned}$$

3.4.2 Equipartition of energy

- For a free particle with mass m in 1 dimension we had $Z_1 = \sqrt{\frac{2m\pi}{\beta}} V$. The average energy is

$$\begin{aligned}
\langle E \rangle &= - \frac{\partial}{\partial \beta} \ln Z_1 \\
&= - \frac{\partial}{\partial \beta} \left(\ln \sqrt{2m\pi} V - \frac{1}{2} \ln \beta \right) \\
&= \frac{1}{2\beta} = \frac{1}{2} kT
\end{aligned}$$

- For a 3 dimensional ideal gas the exact energy is $E = \frac{|\vec{p}|^2}{2m}$.

$$\begin{aligned}
Z_1 &= \int e^{-\beta E} d^3q d^3p \\
&= \left(\frac{2m\pi}{\beta} \right)^{3/2} V
\end{aligned}$$

Therefore the average energy is

$$\begin{aligned}\langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_1 = -\frac{\partial}{\partial \beta} \left(\ln V + \frac{3}{2} \ln 2m\pi - \frac{3}{2} \ln \beta \right) \\ &= \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} kT\end{aligned}$$

Equipartition: $\frac{1}{2}kT$ per degree of freedom.

- Gas of SHO: $E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$

$$\begin{aligned}Z_1 &= \int e^{-\beta \left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 \right)} dp dq \\ &= \int e^{-\beta \frac{p^2}{2m}} dp \int e^{-\frac{\beta}{2}m\omega^2 q^2} dq \\ &= \sqrt{\frac{2m\pi}{\beta}} \sqrt{\frac{2\pi}{\beta m\omega^2}} \\ Z_1 &= \frac{2\pi}{\omega\beta}\end{aligned}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_1 = kT = \left(\frac{1}{2} + \frac{1}{2} \right) kT$$

Heating bulk system by radiation \equiv system of oscillators (ω being the frequency of the radiation).

$$C_V = N \left(\frac{\partial}{\partial T} \right)_V \langle E \rangle = \frac{\partial}{\partial T} NkT = Nk = \text{const}$$

but this is not experimentally observed.

- Relativistic ideal gas: (only kinetic energy), $E = c\sqrt{m^2c^2 + |\vec{p}|^2}$

$$\begin{aligned}Z_1 &= \int e^{-\beta E} d^3p d^3q = V \int e^{-\beta c\sqrt{m^2c^2 + p^2}} p^2 dp \sin \theta_p d\theta_p d\phi_p = \\ &= V 4\pi \int_0^\infty p^2 e^{-\beta c\sqrt{m^2c^2 + p^2}} dp\end{aligned}$$

Now take massless particles: $m = 0$

$$\begin{aligned}
Z_1 &= 4\pi V \int p^2 e^{-\beta cp} dp = \\
&= 4\pi V \int \left(-\frac{1}{\beta c}\right) p^2 \frac{d}{dp} e^{-\beta cp} dp = \\
&= -\frac{4\pi V}{\beta c} \left(0 - \int 2p e^{-\beta cp} dp\right) = \\
&= \frac{8\pi V}{\beta c} \int p \left(-\frac{1}{\beta c}\right) \frac{d}{dp} e^{-\beta cp} dp = \\
&= -\frac{8\pi V}{\beta^2 c^2} \left(0 - \int e^{-\beta cp} dp\right) = \\
&= \frac{8\pi V}{\beta^3 c^3}
\end{aligned}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_1 = -\frac{\partial}{\partial \beta} (-3 \ln \beta) = \frac{3}{\beta} = 3kT$$

3.4.3 Interaction of Radiation with Matter

Radiation \equiv e.m. waves with frequency ω

Matter \equiv atoms, molecules, oscillator model with Hooke's constants given by ω of the radiation

Classically: ω has continuous spectrum i.e. from SHO

$$\begin{aligned}
Z_1 &= \int e^{-\beta E} d^3p d^3q = \left(\frac{2\pi}{\omega\beta}\right) \\
\Rightarrow \langle E \rangle &= \frac{1}{2}kT + \frac{1}{2}kT
\end{aligned}$$

$$U = N \langle E \rangle = NkT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk = \text{const} \quad \text{not observed}$$

Planck's Hypothesis: Energy has discrete spectrum (in the context of radiation interacting with microscopic matter). Energy is absorbed in discrete packets ("quanta")

$$E_n = n\hbar\omega$$

So we get

$$Z_1 = \sum_n e^{-\beta \hbar \omega} = \sum_{n=0}^{\infty} \left(e^{-\beta \hbar \omega}\right)^n = \frac{1}{1 - e^{-\beta \hbar \omega}}$$

i.e.

$$\begin{aligned}\langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_1 = \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta \hbar \omega}) = \\ &= \frac{\hbar \omega}{1 - e^{-\beta \hbar \omega}} e^{-\beta \hbar \omega} = \\ &= \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}\end{aligned}$$

$$\begin{aligned}C_V &= N \frac{\partial \langle E \rangle}{\partial T} = N \hbar \omega \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \frac{1}{e^{\beta \hbar \omega} - 1} = \\ &= -\frac{N \hbar \omega}{k T^2} \frac{-1}{(e^{\beta \hbar \omega} - 1)^2} \hbar \omega e^{\beta \hbar \omega} = \\ &= N \hbar^2 \omega^2 k \beta^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \quad T \text{ dependent}\end{aligned}$$

Examine the limits for $T \gg 1$ (i.e. $\beta \ll 1$) and $T \ll 1$ (i.e. $\beta \gg 1$)

- $T \gg 1, \beta \ll 1$, classical limit

$$\langle E \rangle = \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \approx \frac{\hbar \omega}{\beta \hbar \omega} = \frac{1}{\beta} = kT$$

As for the classical SHO (equipartition)

- $T \ll 1, \beta \gg 1$, qm limit

$$\langle E \rangle = \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \approx \frac{\hbar \omega}{e^{\beta \hbar \omega}}$$

$$\begin{aligned}C_V &= N \frac{\partial \langle E \rangle}{\partial T} = N \hbar \omega \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} e^{-\beta \hbar \omega} = \\ &= -N \hbar \omega k \beta^2 (-\hbar \omega) e^{-\beta \hbar \omega} = \\ C_V &= N \hbar^2 \omega^2 k \beta^2 e^{-\beta \hbar \omega}\end{aligned}$$

i.e. $C_V \xrightarrow{T \rightarrow 0} 0$ as 3rd Law and agrees with experimental result

Note. Calculate with correct qm energy: $E = (n + \frac{1}{2}) \hbar \omega$

$$\begin{aligned}Z_1 &= e^{-\beta \frac{\hbar \omega}{2}} \frac{1}{1 - e^{-\beta \hbar \omega}} \langle E \rangle = -\frac{\partial}{\partial \beta} \ln e^{-\beta \frac{\hbar \omega}{2}} + \frac{\partial}{\partial \beta} \ln (1 - e^{-\beta \hbar \omega}) = \\ &= \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}\end{aligned}$$

with the zero point energy $\frac{\hbar \omega}{2}$

Einstein specific heat

$$\begin{aligned}
 C_V &= \frac{\partial}{\partial T} \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right) = \\
 &\stackrel{\theta = \frac{\hbar\omega}{k}}{=} k\theta \frac{\partial}{\partial T} \left(\frac{1}{e^{\frac{\theta}{T}} - 1} \right) = \\
 &= \frac{k\theta^2}{T^2} \frac{e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}} - 1 \right)^2}
 \end{aligned}$$

For system with a range of frequencies sum up all contribution, given the density function

$$\rho = \rho(\theta)$$

$$\text{Einstein: } \rho_E(\theta) = \delta_D(\theta - \theta_E)$$

$$\begin{aligned}
 C_V^{tot} &= \int C_V(\theta, T) \rho_E(\theta) d\theta = \\
 &= C_V(\theta_E, T)
 \end{aligned}$$

$$\text{Debye: } \rho_D = \begin{cases} 1 & \theta \leq \theta_D \\ 0 & \theta > \theta_D \end{cases}$$

$$\begin{aligned}
 C_V^{tot} &= k \int_0^{\theta_D} \frac{\theta^2}{T^2} \frac{e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}} - 1 \right)^2} d\theta = \\
 &= k \int_0^{x_D} \frac{x^2 e^x}{(e^x - 1)^2} T dx = \\
 &= kT \int_0^{x_D} \underbrace{\frac{x^2 e^x}{(e^x - 1)^2} dx}_{\xrightarrow{x_D \rightarrow \infty} \frac{\pi^2}{3}}
 \end{aligned}$$

$$C_V^{Debye} = kT \cdot \text{const}$$

3.5 Degenerate levels (states)

e.g. more than one state with energy E . Boltzmann distribution

$$Z_1 = \int e^{-\beta E} d\mu(E)$$

$d\mu(E) = dE$ maybe, but not necessary. Typically $d\mu(E) = g(E)dE$ where $g(E)$ = no. of states/unit energy range.

Recall equipartition:

$$Z_1 = \int e^{-\beta E} d^3p d^3q = V \int e^{-\beta \frac{p^2}{2m}} d^3p = \left(\frac{2m\pi}{\beta} \right)^{3/2} V$$

But

$$Z_1 = \int e^{-\beta E} dE d^3q = V \int e^{-\beta E} dE = \frac{V}{\beta} \quad \text{incorrect}$$

So

$$Z_1 = \left(\frac{2m\pi}{\beta} \right)^{3/2} V = \int g(E) e^{-\beta E} dE d^3q$$

Invert to find $g(E)$

$$g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} \frac{Z_1(\beta)}{V} d\beta = \frac{(2m\pi)^{3/2}}{2\pi i} \int \frac{e^{\beta E}}{\beta^{3/2}} d\beta$$

Use the result $\frac{1}{2\pi i} \int_{s' - i\infty}^{s' + i\infty} \frac{e^{sx}}{s^{n+1}} ds = \begin{cases} \frac{x^n}{n!} & x > 0 \\ 0 & x \leq 0 \end{cases}$. As $E > 0$

$$g(E) = (2m\pi)^{3/2} \frac{E^{1/2}}{\left(\frac{1}{2}\right)!}$$

Alternative: Count no. of states of energies up to E : $M(E)$. The number of states is proportional to the volume of a ball in state space.

$$M(E) \propto \frac{4\pi}{3} p^3$$

with $p = \sqrt{2mE}^{1/2}$ we get

$$M(E) \propto \frac{4\pi}{3} (2m)^{3/2} E^{3/2}$$

The number of states per unit energy range is

$$\frac{dM}{dE} \propto E^{1/2}$$

same result

Example. 1. Artificial example: $E_n = n\hbar\omega$ (QM SHO) with degeneracy $g(E_n) = n$

$$\begin{aligned} Z_1 &= \sum_n n e^{-\beta n\hbar\omega} = \\ &= \sum_n -\frac{1}{\hbar\omega} \frac{\partial}{\partial \beta} e^{-\beta n\hbar\omega} = \\ &= -\frac{1}{\hbar\omega} \frac{\partial}{\partial \beta} \sum_n \left(e^{-\beta\hbar\omega} \right)^n = \\ &= -\frac{1}{\hbar\omega} \frac{\partial}{\partial \beta} \frac{1}{1 - e^{-\beta\hbar\omega}} = \\ &= \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \end{aligned}$$

$$\begin{aligned}
\langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_1 = -\frac{\partial}{\partial \beta} (-\beta \hbar \omega) + 2 \frac{\partial}{\partial \beta} \ln (e^{-\beta \hbar \omega} - 1) = \\
&= \hbar \omega + \frac{2}{e^{-\beta \hbar \omega} - 1} (-\hbar \omega) e^{-\beta \hbar \omega} = \\
&= \hbar \omega \left(1 - \frac{2e^{-\beta \hbar \omega}}{e^{-\beta \hbar \omega} - 1} \right) = \\
&= \hbar \omega \left(1 - \frac{2}{1 - e^{\beta \hbar \omega}} \right) = \\
&= 2\hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right)
\end{aligned}$$

In the limit for $T \gg 1, \beta \ll 1$

$$\begin{aligned}
\langle E \rangle &\approx 2\hbar \omega \left(\frac{1}{2} + \frac{1}{\beta \hbar \omega} \right) = \hbar \omega + \frac{2}{\beta} \\
C_V &= N \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial}{\partial T} 2NkT = 2Nk = \text{const} \quad \text{classical limit}
\end{aligned}$$

2. SHO with degeneracy $g(n) = n^2$

$$\begin{aligned}
Z_1 &= \sum_n g(n) e^{-\beta n \hbar \omega} = \sum_n n^2 e^{-\beta n \hbar \omega} = \\
&= \sum_n \frac{1}{\hbar^2 \omega^2} \frac{\partial^2}{\partial \beta^2} e^{-\beta n \hbar \omega} = \\
&= \frac{1}{\hbar^2 \omega^2} \frac{\partial^2}{\partial \beta^2} \sum_n \left(e^{-\beta \hbar \omega} \right)^n = \\
&= \frac{1}{\hbar^2 \omega^2} \frac{\partial^2}{\partial \beta^2} \frac{1}{1 - e^{-\beta \hbar \omega}} = \\
&= -\frac{1}{\hbar \omega} \frac{\partial}{\partial \beta} \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} = \\
&= -\frac{1}{\hbar \omega} \left(\frac{-\hbar \omega e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} - 2 \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^3} (-1) (-\hbar \omega) e^{-\beta \hbar \omega} \right) = \\
&= \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} + 2 \frac{e^{-\beta \hbar \omega} e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^3} = \\
&= \frac{e^{-\beta \hbar \omega} (1 - e^{-\beta \hbar \omega}) + 2 e^{-\beta \hbar \omega} e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^3} = \\
&= \frac{e^{-\beta \hbar \omega} - e^{-\beta \hbar \omega} e^{-\beta \hbar \omega} + 2 e^{-\beta \hbar \omega} e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^3} = \\
&= \frac{e^{-\beta \hbar \omega} + e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^3} = \\
&= e^{-\beta \hbar \omega} \frac{1 + e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^3}
\end{aligned}$$

$$\begin{aligned}
\langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_1 = -\frac{\partial}{\partial \beta} \left[-\beta \hbar \omega + \ln (1 + e^{-\beta \hbar \omega}) - 3 \ln (1 - e^{-\beta \hbar \omega}) \right] = \\
&= \hbar \omega - \frac{1}{1 + e^{-\beta \hbar \omega}} e^{-\beta \hbar \omega} (-\hbar \omega) + 3 \frac{1}{1 - e^{-\beta \hbar \omega}} (-1) e^{-\beta \hbar \omega} (-\hbar \omega) = \\
&= \hbar \omega \left(1 + \frac{e^{-\beta \hbar \omega}}{1 + e^{-\beta \hbar \omega}} + 3 \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \right) = \\
&= \hbar \omega \left(1 + \frac{1}{e^{\beta \hbar \omega}} + \frac{3}{e^{\beta \hbar \omega} - 1} \right)
\end{aligned}$$

Classical Limit: $T \gg 1, \beta \ll 1$

$$\begin{aligned}
\langle E \rangle &\xrightarrow{T \gg 1} \hbar\omega \left(1 + \frac{1}{2 + \beta\hbar\omega} + \frac{3}{\beta\hbar\omega} \right) = \\
&\approx \hbar\omega \left(1 + \frac{1}{2} + \frac{3}{\hbar\omega} kT \right) = \\
&= 3\hbar\omega \left(\frac{1}{2} + \frac{kT}{\hbar\omega} \right) \\
C_V &= N \frac{\partial \langle E \rangle}{\partial T} = 3k = \text{const}
\end{aligned}$$

3. QM rotator: $E_l = \langle H \rangle = \frac{l(l+1)\hbar^2}{2I}$, ($H = \frac{|\vec{L}|^2}{2I}$). There are $2l+1$ values of m for each l i.e. each E_l is $(2l+1)$ fold degenerate

$$\begin{aligned}
Z_1 &= \sum_i g(l) e^{-\beta E_l} = \sum_l (2l+1) e^{-\beta l(l+1) \frac{\hbar^2}{2I}} = \\
&= \sum_l (2l+1) e^{-\theta l(l+1)\beta}
\end{aligned}$$

- a) $T \ll 1, \beta \gg 1$ extreme QM limit, i.e. we can truncate to $l = 0, 1, 2$

$$Z_1 = 1 + 3e^{-2\theta\beta} + 5e^{-6\theta\beta}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_1 = 6\theta \frac{e^{-2\theta\beta} + 5e^{-6\theta\beta}}{1 + 3e^{-2\theta\beta} + 5e^{-6\theta\beta}}$$

i.e. $\langle E \rangle$ is T dependent and $C_V \xrightarrow{T \rightarrow 0} 0$ agrees with 3rd law

- b) $T \gg 1, \beta \ll 1$ so we must include high l (no truncation); we can treat l as a continuous variable and replace the sum by an integration.

$$\begin{aligned}
Z_1 &= \int_0^\infty (2l+1) e^{-l(l+1)\theta\beta} dl = \int_0^\infty \frac{1}{-\theta\beta} \frac{\partial}{\partial l} e^{-l(l+1)\theta\beta} dl = \\
&= -\frac{1}{\theta\beta} \left[e^{-l(l+1)\theta\beta} \right]_0^\infty = \\
&= \frac{1}{\theta\beta} = \frac{kT}{\theta}
\end{aligned}$$

$$\begin{aligned}
\langle E \rangle &= -\frac{\partial}{\partial \beta} \ln \frac{1}{\theta\beta} = \frac{\partial}{\partial \beta} \ln(\theta\beta) = \frac{1}{\theta\beta} \theta = \\
&= \frac{1}{\beta} = kT \\
C_V &= k = \text{const}
\end{aligned}$$

4 Quantum mechanical counting

4.1 Pauli exclusion principle

No two Fermions can occupy the same state.

If particles are identical then the state function $\psi(x_1, x_2)$ also describes the system with x_1 and x_2 interchanged. i.e.

$$|\psi(x_1, x_2, \dots, x_N)|^2 = |\psi(x_2, x_1, \dots, x_N)|^2$$

or

$$\psi(x_1, x_2, \dots, x_N) = \pm \psi(x_2, x_1, \dots, x_N)$$

i.e. there are two types of (identical) particles in QM

- ψ is symmetric under interchange, BOSONS, integer spin, e.g. γ, g, π
- ψ is antisymmetric under interchange, FERMIONS, half-integer spin, e.g. e^-, p, n

Then if we put two (identical) Fermions in the same state

$$\begin{aligned}\psi(x_1, x_2, \dots, x_N) &= -\psi(x_1, x_1, \dots, x_N) \\ \psi(x_1, x_1, \dots, x_N) &= 0\end{aligned}$$

i.e. no two Fermions can occupy the same state.

Now counting dictated by QM.

1. No two Fermions in a state, i.e. 0 or 1 particle per state (cannot use Stirling approximation)
2. Fermions & Bosons cannot be labeled (indeterministic)

In phase space, a phase cell contains $N_i \gg 1$ particles of energy E_i . Divide each cell into $G > N$ elementary cells, $n_i = \frac{N_i}{G}$ can be small. For the Boltzmann hypothesis, we need the thermodynamic probability Ω . Define:

Ω_α = thermodynamical probability of each elementary phase-cell

$\tilde{\Omega}_i$ = thermodynamical probability of i-th phase cell

$$\Omega_\alpha = \sqrt[G]{\tilde{\Omega}_i}$$

since each one of the G elementary phase cells is equally likely to be occupied by a particle

0. Recover Boltzmann distribution (Classical counting, deterministic)
1. Fermi-Dirac distribution (antisymmetric under interchange)
2. Bose-Einstein distribution (symmetric under interchange)

4.2 Boltzmann distribution

$$\tilde{\Omega}_i = \frac{G^{N_i}}{N_i!}$$

, as $N_i \gg 1$ approximate with Stirling.

$$\begin{aligned}\ln N_i! &= N_i \ln N_i - N_i \\ N_i! &= e^{N_i \ln N_i - N_i} \\ &= N_i^{N_i} e^{-N_i}\end{aligned}$$

Use $N_i = Gn_i$

$$\begin{aligned}\tilde{\Omega}_i &= \frac{G^{Gn_i} e^{Gn_i}}{(Gn_i)^{Gn_i}} = \left(\frac{Ge}{Gn_i} \right)^{Gn_i} = \left(\frac{e}{n_i} \right)^{Gn_i} \\ \Rightarrow \Omega_i &= \sqrt[G]{\tilde{\Omega}_i} = n_i^{-n_i} e^{n_i} \\ \Rightarrow \Omega &= \prod_i \Omega_i = \prod_i n_i^{-n_i} e^{n_i}\end{aligned}$$

And so the entropy is

$$S = k \ln \Omega = k \ln \prod_i \Omega_i = k \sum_i \ln \Omega_i = k \sum_i (-n_i \ln n_i + n_i) = -k \sum_i (n_i \ln n_i - 1)$$

Previous version $S = -k \sum_i \omega_i \ln \omega_i$ with $\omega_i = \frac{N_i}{N}$

4.3 Fermi-Dirac distribution

$$\tilde{\Omega}_i = \frac{G!}{(G - N_i)! N_i!}$$

As $G \gg 1, N_i \gg 1$ approximate with Sterling

$$\begin{aligned}\tilde{\Omega}_i &= \frac{e^{-G} G^G}{e^{N_i - G} (G - N_i)^{G - N_i} e^{-N_i} N_i^{N_i}} = \frac{G^G}{(G - N_i)^{G - N_i} N_i^{N_i}} = \\ &= \frac{G^G}{(G - Gn_i)^{(G - Gn_i)} (Gn_i)^{Gn_i}} = \frac{G^G}{G^{G - Gn_i} (1 - n_i)^{G - Gn_i} G^{Gn_i} n_i^{Gn_i}} = \\ &= \frac{G^G}{G^G (1 - n_i)^{G - Gn_i} n_i^{Gn_i}} = \frac{1}{(1 - n_i)^{G - Gn_i} n_i^{Gn_i}} = \\ &= [n_i^{-n_i} (1 - n_i)^{n_i - 1}]^G \\ \Rightarrow \Omega_i &= \sqrt[G]{\tilde{\Omega}_i} = n_i^{-n_i} (1 - n_i)^{n_i - 1}\end{aligned}$$

So the entropy is

$$\begin{aligned} S &= k \ln \prod_i \Omega_i = k \sum_i \ln \Omega_i = k \sum_i [-n_i \ln n_i + (n_i - 1) \ln(1 - n_i)] = \\ &= -k \sum_i [n_i \ln n_i + (1 - n_i) \ln(1 - n_i)] \end{aligned}$$

4.4 Bose-Einstein distribution

In Bose statistics any number of particles (A) in given state B . States B and particles A are not individually labeled. Assign each particle A to the state on their left

$$BAABAAABABAABB...$$

How many possibilities are there? We have $G + N_i$ "particles" to distribute, the left-most particle has to be a B , so G possibilities for this, the rest can choose freely, i.e. $(G + N_i - 1)!$ possible arrangements. As the particles are indistinguishable $N_i!$ are the same, as the states are indistinguishable, $G!$ are the same. So we get

$$\begin{aligned} \tilde{\Omega}_i &= \frac{G(G + N_i - 1)}{G!N_i!} = \frac{(G + N_i - 1)!}{(G - 1)!N_i!} \\ &\approx \frac{(G + N_i)!}{G!N_i!} = \frac{e^{-G-N_i}(G + N_i)^{G+N_i}}{e^{-G}G^G e^{-N_i}N_i^{N_i}} = \\ &= \frac{(G + G n_i)^{G+G n_i}}{G^G (G n_i)^{G n_i}} = \frac{G^G G^{G n_i} (1 + n_i)^{G+G n_i}}{G^G G^{G n_i} n_i^{G n_i}} = \\ &= \frac{(1 + n_i)^{G+G n_i}}{n_i^{G n_i}} = \\ &= [(1 + n_i)^{1+n_i} n_i^{-n_i}]^G \\ \Rightarrow \Omega_i &= (1 + n_i)^{1+n_i} n_i^{-n_i} \end{aligned}$$

i.e. the entropy is

$$\begin{aligned} S &= k \ln \prod_i \Omega_i = k \sum_i \ln [(1 + n_i)^{1+n_i} n_i^{-n_i}] = \\ &= k \sum_i [(1 + n_i) \ln(1 + n_i) - n_i \ln n_i] = \\ &= -k \sum_i [n_i \ln n_i - (1 + n_i) \ln(1 + n_i)] \end{aligned}$$

4.5 Summarize FD and BE

Define $\Omega_i^{(FD)} = \Omega_i^{(+)}$, $\Omega_i^{(BE)} = \Omega_i^{(-)}$. $\Omega_i^{(\pm)} = n_i^{-n_i} (1 \mp n_i)^{n_i \mp 1}$

$$S^{(\pm)} = k \ln \prod_i \Omega_i^{(\pm)} = k \sum_i [-n_i \ln n_i + (n_i \mp 1) \ln(1 \mp n_i)]$$

Use calculus of variation:

$$\delta S = \sum \frac{\partial S}{\partial n_i} \delta n_i$$

subject to the constraints of fixed energy and fixed number of particles.

$$\delta S + \lambda_1 \delta E + \lambda_2 \delta \left(\sum_i N_i \right) = 0$$

$$\delta E = \sum_i E_i \delta n_i, \quad \delta N = \sum_i \delta n_i$$

$$\begin{aligned} \frac{\partial S}{\partial n_i} &= k \frac{\partial}{\partial n_i} \left\{ \sum_i [-n_i \ln n_i + (n_i \mp 1) \ln(1 \mp n_i)] \right\} = \\ &= k \left[-\ln n_i - 1 + \ln(1 \mp n_i) \mp \frac{(n_i \mp 1)}{1 \mp n_i} \right] = \\ &= k \left[\ln \frac{1 \mp n_i}{n_i} - 1 \mp \frac{\mp(1 \mp n_i)}{1 \mp n_i} \right] = \\ &= k \ln \frac{1 \mp n_i}{n_i} = \\ \delta S &= -k \sum_i \ln \frac{n_i}{1 \mp n_i} \end{aligned}$$

i.e.

$$\sum_i \delta n_i \left[-k \ln \frac{n_i}{1 \mp n_i} + \lambda_1 E_i + \lambda_2 \right] = 0$$

δn_i being arbitrary (subject to the constraints imposed)

$$-k \ln \frac{n_i}{1 \mp n_i} + \lambda_1 E_i + \lambda_2 = 0 \quad \forall i$$

i.e.

$$\begin{aligned} \ln \frac{n_i}{1 \mp n_i} &= -(\alpha + \beta E_i) \\ n_i &= (1 \mp n_i) e^{-(\alpha + \beta E_i)} \\ n_i(1 \pm e^{-(\alpha + \beta E_i)}) &= e^{-(\alpha + \beta E_i)} \\ n_i &= \frac{e^{-(\alpha + \beta E_i)}}{1 \pm e^{-(\alpha + \beta E_i)}} \\ n_i &= \frac{1}{e^{\alpha + \beta E_i} \pm 1} \end{aligned}$$

or with continuous spectrum

$$f(E) = \frac{1}{e^{\alpha + \beta E} \pm 1}$$

Evaluate S :

$$\begin{aligned}
S &= k \sum_i [-n_i \ln n_i + (n_i \mp 1) \ln(1 \mp n_i)] = \\
&= -k \sum_i [n_i (\ln n_i - \ln(1 \mp n_i)) \pm \ln(1 \mp n_i)] = \\
&= -k \sum_i \left[n_i \ln \frac{n_i}{1 \mp n_i} \pm \ln(1 \mp n_i) \right] = \\
&= -k \sum_i [-(\alpha + \beta E_i) n_i \pm \ln(1 \mp n_i)] = \\
&= k \left[\alpha \sum_i n_i + \beta \sum_i E_i n_i \mp \sum_i \ln(1 \mp n_i) \right] = \\
&= k \left[\alpha N + \beta E \mp \sum_i \ln(1 \mp n_i) \right]
\end{aligned}$$

If we now proceed like before to employ the Maxwell Relation $(\frac{\partial U}{\partial S})_{N,V} = T \Rightarrow (\frac{\partial S}{\partial U})_{N,V} = \frac{1}{T}$, we meet an obstacle. The term $\sum_i \ln(1 \mp n_i)$ is not independent of E , so β cannot be identified as before. %beginalign* Here, we proceed with the alternative path of subjecting the Helmholtz free energy $F = U - TS$ to the variational principle. Note that now T appears explicitly so we do not need the Lagrange multiplier to fix the energy. Using only the constraint fixing the number of particles, we arrive at exactly the same result, without having to identify β . To identify the corresponding Lagrange multiplier α , recall the Maxwell Relation $(\frac{\partial F}{\partial N})_{T,V} = \mu$,

$$\begin{aligned}
F &= U - TS = U - Tk \left[\alpha N + \beta U \mp \sum_i \ln(1 \mp n_i) \right] = \\
&= -kT\alpha N \pm kT \sum_i \ln(1 \mp n_i)
\end{aligned}$$

i.e.

$$\begin{aligned}
\mu &= \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT\alpha \\
\alpha &= -\beta\mu
\end{aligned}$$

i.e. the FD/BE distribution is:

$$f_{\pm}(E) = \frac{1}{e^{\beta(E-\mu)} \pm 1} \quad (4.1)$$

$$f_{\pm}(E) = \frac{1}{e^{\beta(E-E_0)} \pm 1} \quad (4.2)$$

$$E_0 = \mu = \mu(T).$$

$$\begin{aligned} F &= NE_0 \pm \sum_i \ln \left(1 \mp \frac{1}{e^{\beta(E-E_0)} \pm 1} \right) = NE_0 \pm \sum_i \ln \left(\frac{e^{\beta(E-E_0)}}{e^{\beta(E-E_0)} \pm 1} \right) = \\ &= NE_0 \mp \sum_i \ln \left(1 \pm e^{\beta(E_0-E)} \right) \end{aligned}$$

Note. If you don't take the G^{th} root you get a better result for S and do not have to cheat on E and N . For more realistic considerations you can even take G_i being the number of states for each energy level. The result is the same

4.6 Sign of μ

1. Bose-Einstein: $f_{BE} = \frac{1}{e^{\beta(E-\mu)} - 1}$. Suppose we calculate the number of particles, it has to be > 0

$$N = \int \frac{g(E)}{e^{\beta(E-\mu)} - 1} > 0$$

i.e. $e^{\beta(E-\mu)} > 1$ for arbitrary E i.e. $e^{-\beta\mu} > 1$

$$\mu < 0 \quad \forall T \quad (4.3)$$

See Figure 4.1 for plot.

2. Fermi-Dirac $f_{FD} = \frac{1}{e^{\beta(E-\mu)} + 1}$

$$\begin{aligned} N &= \int \frac{g(E)}{e^{\beta(E-\mu)} + 1} dE = \\ &= e^{\beta\mu} \int \frac{g(E)}{e^{\beta E} + e^{\beta\mu}} dE \end{aligned}$$

If $\mu < 0$ ($\mu = -a^2$)

$$N = e^{-\beta a^2} \int \frac{g(E)}{e^{\beta E} + e^{-\beta a^2}} dE$$

Consider now $T \rightarrow 0$, i.e. $\beta \rightarrow \infty$. Then $\int \frac{g(E)}{e^{\beta E} + e^{-\beta a^2}} dE \rightarrow \int \frac{g(E)}{e^{\beta E}} dE = I < \infty$ which is convergent, i.e.

$$N = e^{-\beta a^2} I \xrightarrow{T \rightarrow 0} 0$$

which is absurd, i.e.

$$\mu(T=0) > 0 \quad (4.4)$$

See Figure 4.2 for plot.

For $T = 0$ the distribution function is the Heaviside step-function (Figure 4.3)

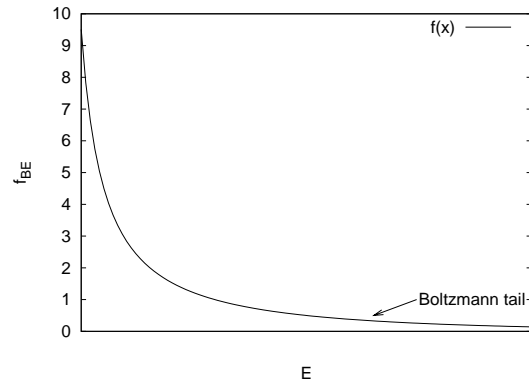


Figure 4.1: Bose-Einstein distribution

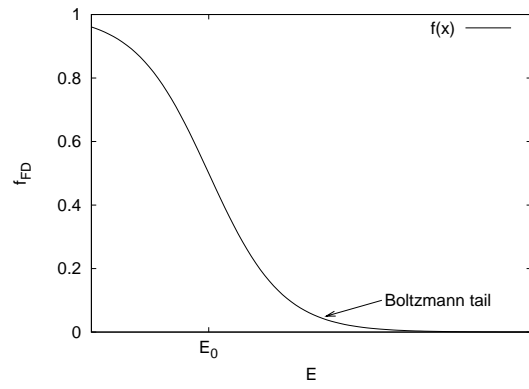


Figure 4.2: Fermi-Dirac distribution for $T > 0$

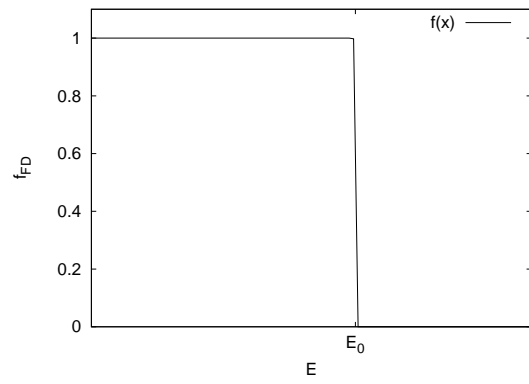


Figure 4.3: Fermi-Dirac distribution for $T = 0$

4.7 Radiation Laws

Photon gas ($E = \hbar\omega$ (QM)) obeys Bose-Einstein statistics $f(E) = \frac{1}{e^{\beta(E-E_0)} - 1}$. Photons are superrelativistic, i.e. their number is not fixed, i.e. the Lagrangian multiplier α fixing N is zero. $\alpha = 0 \Rightarrow E_0 = \mu = 0$. The total energy is

$$U = \int E f(E) d\tau$$

$d\tau$ is the volume-element in phase space, i.e. $d\tau = d^3x 4\pi p^2 dp$. Because of the uncertainty relation we cannot make both dx and dp infinitesimally small, so we have to divide by \hbar^3

$$U = \frac{4\pi V}{\hbar^3} \int E f(E) p^2 dp$$

As for radiation holds $p = \frac{E}{c} = \frac{\hbar\omega}{c}$ we change variables to get

$$U = \frac{4\pi V}{\hbar^3} \frac{\hbar^3}{c^3} \int \hbar\omega f(\hbar\omega) \omega^2 d\omega$$

In order to account for the two possible polarisations we have to multiply by 2. The energy/unit volume is

$$\frac{U}{V} = \frac{8\pi\hbar}{c^3} \int \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega$$

1. Rayleigh -Jeans: energy/unit volum/frequency for long wavelength

$$\epsilon = \frac{8\pi\hbar}{c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \approx \frac{8\pi\hbar}{c^3} \frac{\omega^3}{\beta\hbar\omega} = \frac{8\pi}{\beta c^3} \omega^2$$

2. Wien's law: energy/unit volume/frequency for small wavelength

$$\epsilon = \frac{8\pi\hbar}{c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \approx \frac{8\pi\hbar}{c^3} \frac{\omega^3}{e^{\beta\hbar\omega}} = \frac{8\pi\hbar}{c^3} \omega^3 e^{-\beta\hbar\omega}$$

3. Stefan's Law: energy dependence on T

$$\begin{aligned} \frac{U}{V} &= \frac{8\pi\hbar}{c^3} \int \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega = \\ &= \frac{8\pi\hbar}{c^3} \frac{1}{(\beta\hbar)^4} \int \frac{x^3}{e^x - 1} dx = \\ &= \frac{8\pi k^4}{c^3 \hbar^3} T^4 \int \frac{x^3}{e^x - 1} dx = \\ \frac{U}{V} &= \frac{8\pi k^4}{c^3 \hbar^3} \frac{\pi^4}{15} T^4 = \sigma_{S-B} T^4 \end{aligned}$$

Example. Consider a superrelativistic radiation gas of Bosons/Fermions and give

$$g(E) = \begin{cases} 1 & 0 \leq E \leq E_D \\ 0 & E > E_D \end{cases}$$

Calculate C_V and discuss the limits.

$$U = \int_0^{E_D} \frac{E}{e^{\beta E} \pm 1} dE =$$

- QM Limit, $\beta \gg 1$

$$\begin{aligned} U &= \int_0^{E_D} \frac{E}{e^{\beta E} \pm 1} dE \approx \int_0^{E_D} \frac{E}{e^{\beta E}} dE = \\ &= \int_0^{E_D} E e^{-\beta E} dE = \\ &= \left[-\frac{E}{\beta} e^{-\beta E} \right]_0^{E_D} + \frac{1}{\beta} \int_0^{E_D} e^{-\beta E} dE = \\ &= -\frac{E_D e^{\beta E_D}}{\beta} + \frac{1}{\beta^2} [1 - e^{-\beta E_D}] = \\ U &= -\frac{1}{\beta^2} [(E_D \beta + 1)e^{-\beta E_D} - 1] \approx k^2 T^2 \end{aligned}$$

i.e.

$$C_V \propto T \xrightarrow{T \rightarrow 0} 0$$

as expected of QM C_V

- Classical Limit, $\beta \ll 1$

1. BE:

$$U = \int_0^{E_D} \frac{E}{e^{\beta E} - 1} dE \approx \int_0^{E_D} \frac{E}{\beta E} dE = \frac{E_D}{\beta} = E_D kT$$

i.e.

$$C_V = E_D k = \text{const}$$

2. FD:

$$\begin{aligned} U &= \int_0^{E_D} \frac{E}{e^{\beta E} + 1} dE \approx \int_0^{E_D} \frac{E}{2 + \beta E} dE = \frac{1}{\beta} \int_0^{\beta E_D} \frac{x}{2 + x} dx = \\ &= \frac{1}{\beta} \int_0^{\beta E_D} \left(1 - \frac{2}{2 + x} \right) dx = \frac{1}{\beta^2} [x - 2 \ln(2 + x)]_0^{\beta E_D} = \\ &= \frac{1}{\beta^2} [\beta E_D - 2 \ln(2 + \beta E_D) + 2 \ln(2)] = \\ &= \frac{1}{\beta^2} \left[\beta E_D - 2 \ln \frac{2 + \beta E_D}{2} \right] = \\ U &= E_D kT - 2k^2 T^2 \ln \left(1 + \frac{E_D}{2kT} \right) \end{aligned}$$

$$\begin{aligned}
C_V &= \frac{\partial U}{\partial T} = E_D k - 2k^2 T \left\{ 2 \ln \left(1 + \frac{E_D}{2kT} \right) + \frac{T}{1 + \frac{E_D}{2kT}} \left(-\frac{E_D}{2kT^2} \right) \right\} = \\
&= E_D k - 2k^2 T \left\{ 2 \ln \left(1 + \frac{E_D}{2kT} \right) - \frac{E_D}{2kT + E_D} \right\}
\end{aligned}$$

i.e. C_V is T dependent which is absurd.