Supplement: Statistical Physics
Fitting in a Box

- Counting momentum states with momentum $q$ and de Broglie wavelength
  \[
  \lambda = \frac{\hbar}{q} = \frac{2\pi \hbar}{q}
  \]

- In a discrete volume $L^3$ there is a discrete set of states that satisfy periodic boundary conditions

- We will hereafter set $\hbar = c = 1$

- As in Fourier analysis
  \[
e^{2\pi i x / \lambda} = e^{iqx} = e^{iq(x+L)} \rightarrow e^{iqL} = 1
  \]
Fitting in a Box

- Periodicity yields a discrete set of allowed states

\[ Lq = 2\pi m_i, \quad m_i = 1, 2, 3... \]

\[ q_i = \frac{2\pi}{L} m_i \]

- In each of 3 directions

\[ \sum_{m_xi m_yj m_zk} \rightarrow \int d^3m \]

- The differential number of allowed momenta in the volume

\[ d^3m = \left( \frac{L}{2\pi} \right)^3 d^3q \]
Density of States

- The total number of states allows for a number of internal degrees of freedom, e.g. spin, quantified by the degeneracy factor \( g \).
- Total density of states:

\[
\frac{dN_s}{V} = \frac{g}{V} d^3 m = \frac{g}{(2\pi)^3} d^3 q
\]

- If all states were occupied by a single particle, then particle density

\[
n_s = \frac{N_s}{V} = \frac{1}{V} \int dN_s = \int \frac{g}{(2\pi)^3} d^3 q
\]
Distribution Function

- The distribution function $f$ quantifies the occupation of the allowed momentum states

\[ n = \frac{N}{V} = \frac{1}{V} \int f dN_s = \int \frac{g}{(2\pi)^3} f d^3 q \]

- $f$, aka phase space occupation number, also quantifies the density of particles per unit phase space $dN/(\Delta x)^3(\Delta q)^3$

- For photons, the spin degeneracy $g = 2$ accounting for the 2 polarization states

- Energy $E(q) = (q^2 + m^2)^{1/2}$

- Momentum $\rightarrow$ frequency $q = 2\pi/\lambda = 2\pi\nu = \omega = E$ (where $m = 0$ and $\lambda\nu = c = 1$)
Bulk Properties

- Integrals over the distribution function define the bulk properties of the collection of particles

  - Number density

    \[ n(x, t) \equiv \frac{N}{V} = g \int \frac{d^3q}{(2\pi)^3} f \]

  - Energy density

    \[ \rho(x, t) = g \int \frac{d^3q}{(2\pi)^3} E(q) f \]

    where \( E^2 = q^2 + m^2 \)

  - Momentum density

    \[ (\rho + p)v(x, t) = g \int \frac{d^3q}{(2\pi)^3} q f \]
Bulk Properties

- Pressure: particles bouncing off a surface of area $A$ in a volume spanned by $L_x$: per momentum state

\[ p_q = \frac{F}{A} = \frac{N_{\text{part}}}{A} \frac{\Delta q}{\Delta t} \]

\[ (\Delta q = 2|q_x|, \quad \Delta t = 2L_x/v_x, ) \]

\[ = \frac{N_{\text{part}}}{V} |q_x||v_x| = \frac{N_{\text{part}}}{V} \frac{|q||v|}{3} \]

\[ (v = \gamma mv/\gamma m = q/E) \]

\[ = \frac{N_{\text{part}}}{V} \frac{q^2}{3E} \]
Bulk Properties

- So that summed over occupied momenta states

\[ p(\mathbf{x}, t) = g \int \frac{d^3q}{(2\pi)^3} \frac{|q|^2}{3E(q)} f \]

- Pressure is just one of the quadratic in \( q \) moments, in particular the isotropic one

- The remaining 5 components are the anisotropic stress (vanishes in the background)

\[ \pi^i_j(\mathbf{x}, t) = g \int \frac{d^3q}{(2\pi)^3} \frac{3q^i q_j - q^2 \delta^i_j}{3E(q)} f \]

- We shall see that these are related to the 5 quadrupole moments of the angular distribution
Bulk Properties

- These are more generally the components of the stress-energy tensor

\[ T^\mu_\nu = g \int \frac{d^3 q}{(2\pi)^3} \frac{q^\mu q_\nu}{E(q)} f \]

- 0-0: energy density
- 0-\(i\): momentum density
- \(i - i\): pressure
- \(i \neq j\): anisotropic stress
- In the FRW background cosmology, isotropy requires that there be only a net energy density and pressure
Equilibrium

- Thermal physics describes the equilibrium distribution of particles for a medium at temperature \( T \).

- Expect that the typical energy of a particle by equipartition is \( E \sim T \), so that \( f_{\text{eq}}(E/T, ?) \) in equilibrium.

- Must be a second variable of importance. Number density

\[
  n = g \int \frac{d^3q}{(2\pi\hbar)^3} f_{\text{eq}}(E/T) =? \quad n(T)
\]

- If particles are conserved then \( n \) cannot simply be a function of temperature.

- The integration constant that concerns particle conservation is called the chemical potential. Relevant for photons when creation and annihilation processes are ineffective.
Temperature and Chemical Potential

- Fundamental assumption of statistical mechanics is that all accessible states have an equal probability of being populated. The number of states $G$ defines the entropy $S(U, N, V) = \ln G$ where $U$ is the energy, $N$ is the number of particles and $V$ is the volume.

- When two systems are placed in thermal contact they may exchange energy, particles, leading to a wider range of accessible states

$$G(U, N, V) = \sum_{U_1, N_1} G_1(U_1, N_1, V_1)G_2(U - U_1, N - N_1, V_2)$$

- The most likely distribution of $U_1$ and $U_2$ is given for the maximum $dG/dU_1 = 0$

$$\left(\frac{\partial G_1}{\partial U_1}\right)_{N_1, V_1} G_2 dU_1 + G_1 \left(\frac{\partial G_2}{\partial U_2}\right)_{N_2, V_2} dU_2 = 0 \quad dU_1 + dU_2 = 0$$
Temperature and Chemical Potential

• Or equilibrium requires

\[ \left( \frac{\partial \ln G_1}{\partial U_1} \right)_{N_1,V_1} = \left( \frac{\partial \ln G_2}{\partial U_2} \right)_{N_2,V_2} \equiv \frac{1}{T} \]

which is the definition of the temperature (equal for systems in thermal contact)

• Likewise define a chemical potential \( \mu \) for a system in diffusive equilibrium

\[ \left( \frac{\partial \ln G_1}{\partial N_1} \right)_{U_1,V_1} = \left( \frac{\partial \ln G_2}{\partial N_2} \right)_{U_2,V_2} \equiv -\frac{\mu}{T} \]

defines the most likely distribution of particle numbers as a system with equal chemical potentials: generalize to multiple types of particles undergoing “chemical” reaction → law of mass action

\[ \sum_i \mu_i dN_i = 0 \]
Temperature and Chemical Potential

- Equivalent definition: the chemical potential is the free energy cost associated with adding a particle at fixed temperature and volume

\[ \mu = \frac{\partial F}{\partial N} \bigg|_{T,V}, \quad F = U - TS \]

Free energy: balance between minimizing energy and maximizing entropy \( S \)

- Temperature and chemical potential determine the probability of a state being occupied if the system is in thermal and diffusive contact with a large reservoir at temperature \( T \)
Suppose the system has two states unoccupied $N_1 = 0$, $U_1 = 0$ and occupied $N_1 = 1$, $U_1 = E$ then the ratio of probabilities in the occupied to unoccupied states is given by

$$P = \frac{\exp[\ln G_{\text{res}}(U - E, N - 1, V)]}{\exp[\ln G_{\text{res}}(U, N, V)]}$$

Taylor expand

$$\ln G_{\text{res}}(U - E, N - 1, V) \approx \ln G_{\text{res}}(U, N, V) - \frac{E}{T} + \frac{\mu}{T}$$

$$P \approx \exp[-(E - \mu)/T]$$

This is the Gibbs factor.
Gibbs or Boltzmann Factor

- More generally the probability of a system being in a state of energy $E_i$ and particle number $N_i$ is given by the Gibbs factor

$$P(E_i, N_i) \propto \exp\left[\frac{-(E_i - \mu N_i)}{T}\right]$$

- Unlikely to be in an energy state $E_i \gg T$ mitigated by the number of particles

- Dropping the diffusive contact, this is the Boltzmann factor
Thermal & Diffusive Equilibrium

- A gas in thermal & diffusive contact with a reservoir at temperature $T$

- Probability of system being in state of energy $E_i$ and number $N_i$ (Gibbs Factor)

\[ P(E_i, N_i) \propto \exp\left[-(E_i - \mu N_i)/T\right] \]

where $\mu$ is the chemical potential (defines the free energy “cost” for adding a particle at fixed temperature and volume)

- Chemical potential appears when particles are conserved

- CMB photons can carry chemical potential if creation and annihilation processes inefficient, as they are after $t \sim 1\text{yr.}$
Distribution Function

• Mean occupation of the state in thermal equilibrium

\[ f \equiv \frac{\sum N_i P(E_i, N_i)}{\sum P(E_i, N_i)} \]

where the total energy is related to the particle energy as
\[ E_i = N_i E \] (ignoring zero pt)

• Density of (energy) states in phase space makes the net spatial density of particles

\[ n = g \int \frac{d^3 p}{(2\pi)^3} f \]

where \( g \) is the number of spin states
Fermi-Dirac Distribution

• For fermions, the occupancy can only be \( N_i = 0, 1 \)

\[
f = \frac{P(E, 1)}{P(0, 0) + P(E, 1)}
\]

\[
e^{-\frac{(E-\mu)}{T}}
\]

\[
= \frac{1}{1 + e^{-\frac{(E-\mu)}{T}}}
\]

\[
= \frac{1}{e^{\frac{(E-\mu)}{T}} + 1}
\]

• In the non-relativistic, non-degenerate limit

\[
E = \left( q^2 + m^2 \right)^{1/2} \approx m + \frac{1}{2m} q^2
\]

and \( m \gg T \) so the distribution is Maxwell-Boltzmann

\[
f = e^{-\frac{(m-\mu)}{T}} e^{-\frac{q^2}{2mT}} = e^{-\frac{(m-\mu)}{T}} e^{-\frac{mv^2}{2T}}
\]
Bose-Einstein Distribution

• For bosons each state can have multiple occupation,

\[ f = \frac{d}{d\mu/T} \sum_{N=0}^{\infty} \frac{(e^{-(E-\mu)/T})^N}{\sum_{N=0}^{\infty} (e^{-(E-\mu)/T})^N} \quad \text{with} \quad \sum_{N=0}^{\infty} x^N = \frac{1}{1 - x} \]

\[ = \frac{1}{e^{(E-\mu)/T} - 1} \]

• Again, non relativistic distribution is Maxwell-Boltzmann

\[ f = e^{-\frac{(m-\mu)}{T}} e^{-\frac{q^2}{2mT}} = e^{-\frac{(m-\mu)}{T}} e^{-\frac{mv^2}{2T}} \]

with a spatial number density

\[ n = g e^{-\frac{(m-\mu)}{T}} \int \frac{d^3q}{(2\pi)^3} e^{-\frac{q^2}{2mT}} \]

\[ = g e^{-\frac{(m-\mu)}{T}} \left( \frac{mT}{2\pi} \right)^{3/2} \]
Ultra-Relativistic Bulk Properties

- Chemical potential $\mu = 0$, $\zeta(3) \approx 1.202$

- Number density

$$ n_{\text{boson}} = gT^3 \frac{\zeta(3)}{\pi^2} \quad \zeta(n + 1) \equiv \frac{1}{n!} \int_0^\infty dx \frac{x^n}{e^x - 1} $$

$$ n_{\text{fermion}} = \frac{3}{4} gT^3 \frac{\zeta(3)}{\pi^2} $$

- Energy density

$$ \rho_{\text{boson}} = gT^4 \frac{3}{\pi^2} \zeta(4) = gT^4 \frac{\pi^2}{30} $$

$$ \rho_{\text{fermion}} = \frac{7}{8} gT^4 \frac{3}{\pi^2} \zeta(4) = \frac{7}{8} gT^4 \frac{\pi^2}{30} $$

- Pressure $q^2/3E = E/3 \rightarrow p = \rho/3$, $w_r = 1/3$
Boltzmann Equation

• Interactions or “collisions” between particles drive the various distributions to equilibrium through the Boltzmann equation

• Boltzmann equation is also known as the particle transport or radiative transfer equation

• Composed of two parts: the free propagation or Liouville equation and the collisions
Liouville Equation

- Liouville theorem: phase space distribution function is conserved along a trajectory in the absence of particle interactions

\[ \frac{Df}{Dt} = \left[ \frac{\partial}{\partial t} + \frac{dq}{dt} \frac{\partial}{\partial q} + \frac{dx}{dt} \frac{\partial}{\partial x} \right] f = 0 \]

Expanding universe: de Broglie wavelength of particles “stretches”

\[ q \propto a^{-1} \]

- Homogeneous and isotropic limit

\[ \frac{\partial f}{\partial t} + \frac{dq}{dt} \frac{\partial f}{\partial q} = \frac{\partial f}{\partial t} - H(a) \frac{\partial f}{\partial \ln q} = 0 \]

- Implies energy conservation: \( d\rho/dt = -3H(\rho + p) \)
Boltzmann Equation

- Boltzmann equation says that Liouville theorem must be modified to account for collisions

\[ \frac{Df}{Dt} = C[f] \]

- Heuristically

\[ C[f] = \text{particle sources} - \text{sinks} \]

- Collision term: integrate over phase space of incoming particles, connect to outgoing state with some interaction strength
Boltzmann Equation

- Form:

\[ C[f] = \frac{1}{E} \int d(\text{phase space}) [\text{energy-momentum conservation}] \times |M|^2 [\text{emission} - \text{absorption}] \]

- Matrix element \( M \), assumed T [or CP] invariant

- (Lorentz invariant) phase space element

\[ \int d(\text{phase space}) = \Pi_i \frac{g_i}{(2\pi)^3} \int \frac{d^3 q_i}{2E_i} \]

- Energy conservation: \( (2\pi)^4 \delta^{(4)}(q_1 + q_2 + ...) \)
Boltzmann Equation

- Emission - absorption term involves the particle occupation of the various states
- For concreteness: take $f$ to be the photon distribution function
- Interaction ($\gamma + \sum_i \leftrightarrow \sum_\mu$); sums are over all incoming and outgoing other particles
- $[\text{emission-absorption}] + = \text{boson}; - = \text{fermion}$

$$\Pi_i \Pi_\mu f_\mu (1 \pm f_i)(1 \pm f) - \Pi_i \Pi_\mu (1 \pm f_\mu) f_i f$$
Boltzmann Equation

- **Photon Emission:** $f_\mu (1 \pm f_i)(1 + f)$
  
  $f_\mu$: proportional to number of emitters
  
  $(1 \pm f_i)$: if final state is occupied and a fermion, process blocked; if boson the process enhanced
  
  $(1 + f)$: final state factor for photons: “1”: spontaneous emission (remains if $f = 0$); “$+f$”: stimulated and proportional to the occupation of final photon

- **Photon Absorption:** $-(1 \pm f_\mu)f_if$
  
  $(1 \pm f_\mu)$: if final state is occupied and fermion, process blocked; if boson the process enhanced
  
  $f_i$: proportional to number of absorbers
  
  $f$: proportional to incoming photons
Boltzmann Equation

- If interactions are rapid they will establish an equilibrium distribution where the distribution functions no longer change

\[ C[f_{eq}] = 0 \]

- Solve by inspection

\[
\Pi_i \Pi_\mu f_\mu (1 \pm f_i)(1 \pm f) - \Pi_i \Pi_\mu (1 \pm f_\mu) f_i f = 0
\]

- Try \( f_a = (e^{E_a/T} \mp 1)^{-1} \) so that \( (1 \pm f_a) = e^{-E_a/T} (e^{E_a/T} \mp 1)^{-1} \)

\[
e^{-\sum (E_i + E)/T} - e^{-\sum E_\mu /T} = 0
\]

and energy conservation says \( E + \sum E_i = \sum E_\mu \), so identity is satisfied if the constant \( T \) is the same for all species, i.e. are in thermal equilibrium.
Boltzmann Equation

• If the interaction does not create or destroy particles then the distribution

\[ f_{eq} = \left( e^{(E-\mu)/T} \mp 1 \right)^{-1} \]

also solves the equilibrium equation: e.g. a scattering type reaction

\[ \gamma E + i \rightarrow \gamma E' + j \]

where \( i \) and \( j \) represent the same collection of particles but with different energies after the scattering

\[ \sum (E_i - \mu_i) + (E - \mu) = \sum (E_j - \mu_j) + (E' - \mu) \]

since \( \mu_i = \mu_j \) for each particle

• Not surprisingly, this is the Fermi-Dirac distribution for fermions and the Bose-Einstein distribution for bosons
Boltzmann Equation

- More generally, equilibrium is satisfied if the sum of the chemical potentials on both sides of the interaction are equal, \( \gamma + i \leftrightarrow \nu \)

\[
\sum \mu_i + \mu = \sum \mu_\nu
\]

i.e. the law of mass action is satisfied

- If interactions that create or destroy particles are in equilibrium then this law says that the chemical potential will vanish: e.g.

\( \gamma + e^- \rightarrow 2\gamma + e^- \)

\[
\mu_e + \mu = \mu_e + 2\mu \rightarrow \mu = 0
\]

so that the chemical potential is driven to zero if particle number is not conserved in interaction
Maxwell Boltzmann Distribution

- For the nonrelativistic limit \( E = m + \frac{1}{2}q^2/m \), nondegenerate limit \( (E - \mu)/T \gg 1 \) so both distributions go to the Maxwell-Boltzmann distribution

\[
f_{eq} = \exp\left[-\frac{(m - \mu)}{T}\right] \exp\left(-\frac{q^2}{2mT}\right)
\]

- Here it is even clearer that the chemical potential \( \mu \) is the normalization parameter for the number density of particles whose number is conserved.

- \( \mu \) and \( n \) can be used interchangably
Poor Man’s Boltzmann Equation

- Non expanding medium

\[ \frac{\partial f}{\partial t} = \Gamma (f - f_{eq}) \]

where \( \Gamma \) is some rate for collisions

- Add in expansion in a homogeneous medium

\[ \frac{\partial f}{\partial t} + \frac{dq}{dt} \frac{\partial f}{\partial q} = \Gamma (f - f_{eq}) \]

\( q \propto a^{-1} \rightarrow \frac{1}{q} \frac{dq}{dt} = -\frac{1}{a} \frac{da}{dt} = H \)

\[ \frac{\partial f}{\partial t} - H \frac{\partial f}{\partial \ln q} = \Gamma (f - f_{eq}) \]

- So equilibrium will be maintained if collision rate exceeds expansion rate \( \Gamma > H \)
Non-Relativistic Bulk Properties

- Number density

\[ n = g e^{-(m-\mu)/T} \frac{4\pi}{(2\pi)^3} \int_0^{\infty} q^2 dq \exp\left(-\frac{q^2}{2mT}\right) \]

\[ = g e^{-(m-\mu)/T} \frac{2^{3/2}}{2\pi^2} (mT)^{3/2} \int_0^{\infty} x^2 dx \exp\left(-x^2\right) \]

\[ = g \left(\frac{mT}{2\pi}\right)^{3/2} e^{-(m-\mu)/T} \]

- Energy density \( E = m \rightarrow \rho = mn \)

- Pressure \( q^2/3E = q^2/3m \rightarrow p = nT \), ideal gas law
Ultra-Relativistic Bulk Properties

- Chemical potential $\mu = 0$, $\zeta(3) \approx 1.202$
- Number density

$$n_{\text{boson}} = gT^3 \frac{\zeta(3)}{\pi^2} \quad \zeta(n + 1) \equiv \frac{1}{n!} \int_0^\infty \frac{x^n}{e^x - 1} \, dx$$

$$n_{\text{fermion}} = \frac{3}{4} gT^3 \frac{\zeta(3)}{\pi^2}$$

- Energy density

$$\rho_{\text{boson}} = gT^4 \frac{3}{\pi^2} \zeta(4) = gT^4 \frac{\pi^2}{30}$$

$$\rho_{\text{fermion}} = \frac{7}{8} gT^4 \frac{3}{\pi^2} \zeta(4) = \frac{7}{8} gT^4 \frac{\pi^2}{30}$$

- Pressure $q^2/3E = E/3 \rightarrow p = \rho/3$, $w_r = 1/3$
**Entropy Density**

- First law of thermodynamics

\[ dS = \frac{1}{T} (d\rho(T)V + p(T)dV) \]

so that

\[ \frac{\partial S}{\partial V} \bigg|_T = \frac{1}{T} [\rho(T) + p(T)] \]

\[ \frac{\partial S}{\partial T} \bigg|_V = \frac{V}{T} \frac{d\rho}{dT} \]

- Since \( S(V, T) \propto V \) is extensive

\[ S = \frac{V}{T} [\rho(T) + p(T)] \quad \sigma = \frac{S}{V} = \frac{1}{T} [\rho(T) + p(T)] \]
Entropy Density

- Integrability condition \( dS/dVdT = dS/dTdV \) relates the evolution of entropy density

\[
\frac{d\sigma}{dT} = \frac{1}{T} \frac{d\rho}{dT}
\]

\[
\frac{d\sigma}{dt} = \frac{1}{T} \frac{d\rho}{dt} = \frac{1}{T} \left[ -3(\rho + p) \right] \frac{d\ln a}{dt}
\]

\[
\frac{d\ln \sigma}{dt} = -3 \frac{d\ln a}{dt} \quad \sigma \propto a^{-3}
\]

comoving entropy density is conserved in thermal equilibrium

- For ultra relativistic bosons \( s_{\text{boson}} = 3.602n_{\text{boson}} \); for fermions factor of \( 7/8 \) from energy density.

\[
g_* = \sum_{\text{bosons}} g_b + \frac{7}{8} \sum g_f
\]