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

\[ \sum_{m_{x,i} m_{y,j} m_{z,k}} \rightarrow \int d^3m \]

• 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:

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

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

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

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

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

- $f$, 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

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

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

• 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)

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

• 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

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

- 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 $f_{eq}(E/T, \gamma)$ in equilibrium
- Must be a second variable of import. Number density

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

- 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 \( \rightarrow \) 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 \( T \)
Gibbs or Boltzmann Factor

- 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

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

- 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)

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

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 $N_i = 0, 1$

\[
f = \frac{P(E, 1)}{P(0, 0) + P(E, 1)} = \frac{e^{-(E-\mu)/T}}{1 + e^{-(E-\mu)/T}} = \frac{1}{e^{(E-\mu)/T} + 1}
\]

- In the non-relativistic, non-degenerate limit

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

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

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

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

with a spatial number density

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

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

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

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

- Form:

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

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

- (Lorentz invariant) phase space element

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

- Energy conservation: \((2\pi)^4 \delta^{(4)}(q_1 + q_2 + \ldots)\)
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:** \(- (1 \pm f_\mu)f_i f \)
  - \( (1 \pm f_\mu) \): 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

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

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

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

- 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

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

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

- Add in expansion in a homogeneous medium

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

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

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

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

- Number density

\[ n = g e^{-(m-\mu)/T} \frac{4\pi}{(2\pi)^3} \int_{0}^{\infty} q^2 dq \exp(-q^2/2mT) \]

\[ = g e^{-(m-\mu)/T} \frac{2^{3/2}}{2\pi^2} (mT)^{3/2} \int_{0}^{\infty} x^2 dx \exp(-x^2) \]

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

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

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

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

- Number density

\[
\begin{align*}
  n_{\text{boson}} &= gT^3 \frac{\zeta(3)}{\pi^2} \\
  n_{\text{fermion}} &= \frac{3}{4} gT^3 \frac{\zeta(3)}{\pi^2}
\end{align*}
\]

- Energy density

\[
\begin{align*}
  \rho_{\text{boson}} &= gT^4 \frac{3}{\pi^2} \zeta(4) = gT^4 \frac{\pi^2}{30} \\
  \rho_{\text{fermion}} &= \frac{7}{8} gT^4 \frac{3}{\pi^2} \zeta(4) = \frac{7}{8} gT^4 \frac{\pi^2}{30}
\end{align*}
\]

- 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

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

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

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

\[
S = \frac{V}{T} [\rho(T) + p(T)] \quad \sigma = S/V = \frac{1}{T} [\rho(T) + p(T)]
\]
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 relativisitc bosons $s_{\text{boson}} = 3.602n_{\text{boson}}$; for fermions factor of $7/8$ from energy density.

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