## Supplement: Statistical Physics

## Fitting in a Box

- Counting momentum states with momentum $q$ and de Broglie wavelength

$$
\lambda=\frac{h}{q}=\frac{2 \pi \hbar}{q}
$$

- 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

$$
e^{2 \pi i x / \lambda}=e^{i q x}=e^{i q(x+L)} \rightarrow e^{i q L}=1
$$

## Fitting in a Box

- Periodicity yields a discrete set of allowed states

$$
\begin{aligned}
L q & =2 \pi m_{i}, \quad m_{i}=1,2,3 \ldots \\
q_{i} & =\frac{2 \pi}{L} m_{i}
\end{aligned}
$$

- In each of 3 directions

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

- The differential number of allowed momenta in the volume

$$
d^{3} m=\left(\frac{L}{2 \pi}\right)^{3} d^{3} q
$$

## 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:

$$
\frac{d N_{s}}{V}=\frac{g}{V} d^{3} m=\frac{g}{(2 \pi)^{3}} d^{3} q
$$

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

$$
n_{s}=\frac{N_{s}}{V}=\frac{1}{V} \int d N_{s}=\int \frac{g}{(2 \pi)^{3}} d^{3} q
$$

## Distribution Function

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

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

- $f$, aka phase space occupation number, also quantifies the density of particles per unit phase space $d N /(\Delta x)^{3}(\Delta q)^{3}$
- For photons, the spin degeneracy $g=2$ accounting for the 2 polarization states
- Energy $E(q)=\left(q^{2}+m^{2}\right)^{1 / 2}$
- 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

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

- Energy density

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

where $E^{2}=q^{2}+m^{2}$

- Momentum density

$$
(\rho+p) \mathbf{v}(\mathbf{x}, t)=g \int \frac{d^{3} q}{(2 \pi)^{3}} \mathbf{q} f
$$

## Bulk Properties

- Pressure: particles bouncing off a surface of area $A$ in a volume spanned by $L_{x}$ : per momentum state

$$
\begin{aligned}
p_{q}= & \frac{F}{A}=\frac{N_{\text {part }}}{A} \frac{\Delta q}{\Delta t} \\
& \left(\Delta q=2\left|q_{x}\right|, \quad \Delta t=2 L_{x} / v_{x},\right) \\
= & \frac{N_{\text {part }}}{V}\left|q_{x}\right|\left|v_{x}\right|=\frac{N_{\text {part }}}{V} \frac{|q||v|}{3} \\
& (v=\gamma m v / \gamma m=q / E) \\
= & \frac{N_{\text {part }}}{V} \frac{q^{2}}{3 E}
\end{aligned}
$$

## Bulk Properties

- So that summed over occupied momenta states

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

- 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)

$$
\pi_{j}^{i}(\mathbf{x}, t)=g \int \frac{d^{3} q}{(2 \pi)^{3}} \frac{3 q^{i} q_{j}-q^{2} \delta^{i}{ }_{j}}{3 E(q)} f
$$

- 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

$$
T_{\nu}^{\mu}=g \int \frac{d^{3} q}{(2 \pi)^{3}} \frac{q^{\mu} q_{\nu}}{E(q)} f
$$

- 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 import. Number density

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

- 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

$$
G(U, N, V)=\sum_{U_{1}, N_{1}} G_{1}\left(U_{1}, N_{1}, V_{1}\right) G_{2}\left(U-U_{1}, N-N_{1}, V_{2}\right)
$$

- The most likely distribution of $U_{1}$ and $U_{2}$ is given for the maximum $d G / d U_{1}=0$

$$
\left(\frac{\partial G_{1}}{\partial U_{1}}\right)_{N_{1}, V_{1}} G_{2} d U_{1}+G_{1}\left(\frac{\partial G_{2}}{\partial U_{2}}\right)_{N_{2}, V_{2}} d U_{2}=0 \quad d U_{1}+d U_{2}=0
$$

## 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 $\sum_{i} \mu_{i} d N_{i}=0$

## Temperature and Chemical Potential

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

$$
\mu=\left.\frac{\partial F}{\partial N}\right|_{T, V}, \quad F=U-T S
$$

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

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

- Taylor expand

$$
\begin{gathered}
\ln G_{\mathrm{res}}(U-E, N-1, V) \approx \ln G_{\mathrm{res}}(U, N, V)-\frac{E}{T}+\frac{\mu}{T} \\
P \approx \exp [-(E-\mu) / T]
\end{gathered}
$$

- 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

$$
P\left(E_{i}, N_{i}\right) \propto \exp \left[-\left(E_{i}-\mu N_{i}\right) / T\right]
$$

- 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)

$$
P\left(E_{i}, N_{i}\right) \propto \exp \left[-\left(E_{i}-\mu N_{i}\right) / T\right]
$$

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 $t \sim 1 \mathrm{yr}$.


## Distribution Function

- Mean occupation of the state in thermal equilibrium

$$
f \equiv \frac{\sum N_{i} P\left(E_{i}, N_{i}\right)}{\sum P\left(E_{i}, N_{i}\right)}
$$

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 $N_{i}=0,1$

$$
\begin{aligned}
f & =\frac{P(E, 1)}{P(0,0)+P(E, 1)} \\
& =\frac{e^{-(E-\mu) / T}}{1+e^{-(E-\mu) / T}} \\
& =\frac{1}{e^{(E-\mu) / T}+1}
\end{aligned}
$$

- In the non-relativistic, non-degenerate limit

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

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

$$
f=e^{-(m-\mu) / T} e^{-q^{2} / 2 m T}=e^{-(m-\mu) / T} e^{-m v^{2} / 2 T}
$$

## Bose-Einstein Distribution

- For bosons each state can have multiple occupation,

$$
\begin{aligned}
f & =\frac{\frac{d}{d \mu / T} \sum_{N=0}^{\infty}\left(e^{-(E-\mu) / T}\right)^{N}}{\sum_{N=0}^{\infty}\left(e^{-(E-\mu) / T}\right)^{N}} \quad \text { with } \sum_{N=0}^{\infty} x^{N}=\frac{1}{1-x} \\
& =\frac{1}{e^{(E-\mu) / T}-1}
\end{aligned}
$$

- Again, non relativistic distribution is Maxwell-Boltzmann

$$
f=e^{-(m-\mu) / T} e^{-q^{2} / 2 m T}=e^{-(m-\mu) / T} e^{-m v^{2} / 2 T}
$$

with a spatial number density

$$
\begin{aligned}
n & =g e^{-(m-\mu) / T} \int \frac{d^{3} q}{(2 \pi)^{3}} e^{-q^{2} / 2 m T} \\
& =g e^{-(m-\mu) / T}\left(\frac{m T}{2 \pi}\right)^{3 / 2}
\end{aligned}
$$

## Ultra-Relativistic Bulk Properties

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

$$
\begin{aligned}
n_{\text {boson }} & =g T^{3} \frac{\zeta(3)}{\pi^{2}} \quad \zeta(n+1) \equiv \frac{1}{n!} \int_{0}^{\infty} d x \frac{x^{n}}{e^{x}-1} \\
n_{\text {fermion }} & =\frac{3}{4} g T^{3} \frac{\zeta(3)}{\pi^{2}}
\end{aligned}
$$

- Energy density

$$
\begin{array}{r}
\rho_{\text {boson }}=g T^{4} \frac{3}{\pi^{2}} \zeta(4)=g T^{4} \frac{\pi^{2}}{30} \\
\rho_{\text {fermion }}=\frac{7}{8} g T^{4} \frac{3}{\pi^{2}} \zeta(4)=\frac{7}{8} g T^{4} \frac{\pi^{2}}{30}
\end{array}
$$

- Pressure $q^{2} / 3 E=E / 3 \rightarrow p=\rho / 3, w_{r}=1 / 3$


## 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

$$
\frac{D f}{D t}=\left[\frac{\partial}{\partial t}+\frac{d \mathbf{q}}{d t} \frac{\partial}{\partial \mathbf{q}}+\frac{d \mathbf{x}}{d t} \frac{\partial}{\partial \mathbf{x}}\right] f=0
$$

Expanding universe: de Broglie wavelength of particles "stretches"

$$
q \propto a^{-1}
$$

- Homogeneous and isotropic limit

$$
\frac{\partial f}{\partial t}+\frac{d q}{d t} \frac{\partial f}{\partial q}=\frac{\partial f}{\partial t}-H(a) \frac{\partial f}{\partial \ln q}=0
$$

- Implies energy conservation: $d \rho / d t=-3 H(\rho+p)$


## Boltzmann Equation

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

$$
\frac{D f}{D t}=C[f]
$$

- 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:

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

- Matrix element $M$, assumed T [or CP] invariant
- (Lorentz invariant) phase space element

$$
\int d(\text { phase space })=\Pi_{i} \frac{g_{i}}{(2 \pi)^{3}} \int \frac{d^{3} q_{i}}{2 E_{i}}
$$

- Energy conservation: $(2 \pi)^{4} \delta^{(4)}\left(q_{1}+q_{2}+\ldots\right)$


## Boltzmann Equation

- Emission - absorption term involves the particle occupation of the various states
- For concreteness: take $f$ to be the photon distribution function
- Interaction $\left(\gamma+\sum i \leftrightarrow \sum \mu\right)$; sums are over all incoming and outgoing other particles

- [emission-absorption] $+=$ boson; $-=$ fermion

$$
\Pi_{i} \Pi_{\mu} f_{\mu}\left(1 \pm f_{i}\right)(1 \pm f)-\Pi_{i} \Pi_{\mu}\left(1 \pm f_{\mu}\right) f_{i} f
$$

## Boltzmann Equation

- Photon Emission: $f_{\mu}\left(1 \pm f_{i}\right)(1+f)$
$f_{\mu}$ : proportional to number of emitters
$\left(1 \pm f_{i}\right)$ : 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: $-\left(1 \pm f_{\mu}\right) f_{i} f$
$\left(1 \pm f_{\mu}\right)$ : 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 $C\left[f_{\mathrm{eq}}\right]=0$
- Solve by inspection

$$
\Pi_{i} \Pi_{\mu} f_{\mu}\left(1 \pm f_{i}\right)(1 \pm f)-\Pi_{i} \Pi_{\mu}\left(1 \pm f_{\mu}\right) f_{i} f=0
$$

- $\operatorname{Try} f_{a}=\left(e^{E_{a} / T} \mp 1\right)^{-1}$ so that $\left(1 \pm f_{a}\right)=e^{-E_{a} / T}\left(e^{E_{a} / T} \mp 1\right)^{-1}$

$$
e^{-\sum\left(E_{i}+E\right) / T}-e^{-\sum E_{\mu} / T}=0
$$

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

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

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

$$
\gamma_{E}+i \rightarrow \gamma_{E^{\prime}}+j
$$

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

$$
\sum\left(E_{i}-\mu_{i}\right)+(E-\mu)=\sum\left(E_{j}-\mu_{j}\right)+\left(E^{\prime}-\mu\right)
$$

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

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

- 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

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

where $\Gamma$ is some rate for collisions

- Add in expansion in a homogeneous medium

$$
\begin{aligned}
\frac{\partial f}{\partial t}+\frac{d q}{d t} \frac{\partial f}{\partial q} & =\Gamma\left(f-f_{\mathrm{eq}}\right) \\
\quad( & \left.q \propto a^{-1} \rightarrow \frac{1}{q} \frac{d q}{d t}=-\frac{1}{a} \frac{d a}{d t}=H\right) \\
\frac{\partial f}{\partial t}-H \frac{\partial f}{\partial \ln q} & =\Gamma\left(f-f_{\mathrm{eq}}\right)
\end{aligned}
$$

- So equilibrium will be maintained if collision rate exceeds expansion rate $\Gamma>H$


## Non-Relativistic Bulk Properties

- Number density

$$
\begin{aligned}
n & =g e^{-(m-\mu) / T} \frac{4 \pi}{(2 \pi)^{3}} \int_{0}^{\infty} q^{2} d q \exp \left(-q^{2} / 2 m T\right) \\
& =g e^{-(m-\mu) / T} \frac{2^{3 / 2}}{2 \pi^{2}}(m T)^{3 / 2} \int_{0}^{\infty} x^{2} d x \exp \left(-x^{2}\right) \\
& =g\left(\frac{m T}{2 \pi}\right)^{3 / 2} e^{-(m-\mu) / T}
\end{aligned}
$$

- Energy density $E=m \rightarrow \rho=m n$
- Pressure $q^{2} / 3 E=q^{2} / 3 m \rightarrow p=n T$, ideal gas law


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- Number density

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n_{\text {fermion }} & =\frac{3}{4} g T^{3} \frac{\zeta(3)}{\pi^{2}}
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- Energy density

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\begin{array}{r}
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\end{array}
$$

- Pressure $q^{2} / 3 E=E / 3 \rightarrow p=\rho / 3, w_{r}=1 / 3$


## Entropy Density

- First law of thermodynamics

$$
d S=\frac{1}{T}(d \rho(T) V+p(T) d V)
$$

so that

$$
\begin{array}{r}
\left.\frac{\partial S}{\partial V}\right|_{T}=\frac{1}{T}[\rho(T)+p(T)] \\
\left.\frac{\partial S}{\partial T}\right|_{V}=\frac{V}{T} \frac{d \rho}{d T}
\end{array}
$$

- 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 $d S / d V d T=d S / d T d V$ relates the evolution of entropy density

$$
\begin{aligned}
\frac{d \sigma}{d T} & =\frac{1}{T} \frac{d \rho}{d T} \\
\frac{d \sigma}{d t} & =\frac{1}{T} \frac{d \rho}{d t}=\frac{1}{T}[-3(\rho+p)] \frac{d \ln a}{d t} \\
\frac{d \ln \sigma}{d t} & =-3 \frac{d \ln a}{d t} \quad \sigma \propto a^{-3}
\end{aligned}
$$

comoving entropy density is conserved in thermal equilibrium

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

$$
g_{*}=\sum_{\text {bosons }} g_{b}+\frac{7}{8} \sum g_{f}
$$

