Set 3: Thermal Physics

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 $E \sim kT$, so that f(E/kT, ?) in equilibrium
- Must be a second variable of import. Number density

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

- 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) = k 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, leading to a wider range of accessible states

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

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

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

Temperature and Chemical Potential

• Or equilibrium requires

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

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

• Likewise define a chemical potential μ for a system in diffusive equilibrium

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

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

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V}, \quad F = U - TS$$

free energy: balance between minimizing energy and maximizing entropy ${\cal S}$

• 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 N₁ = 0, U₁ = 0 and occupied N₁ = 1, U₁ = E then the ratio of probabilities in the occupied to unoccupied states is given by

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

• Taylor expand

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

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

• 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

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

- Unlikely to be in an energy state E_i >> kT mitigated by the number of particles
- Dropping the diffusive contact, this is the Boltzmann factor

Mean Occupation

• Mean occupation in thermal equilibrium

$$f = \langle N \rangle = \frac{\sum_{i} N_i P(E_i, N_i)}{\sum P(E_i, N_i)}$$

- Take E_i = N_iE where E is the particle energy (zero point drops out)
- For fermions: occupancy $N_i = 0, 1$

$$f = \frac{P(E,1)}{P(0,0) + P(E,1)} = \frac{\exp[-(E-\mu)/kT]}{1 + \exp[-(E-\mu)/kT]}$$
$$= \frac{1}{\exp[(E-\mu)/kT] + 1}$$
 Fermi-Dirac Distribution

• $T \to 0, f \to [e^{\pm \infty} + 1]^{-1}$ ($E > \mu, f = 0$); ($E < \mu, f = 1$), occupied out to a sharp energy or Fermi surface with $\delta E = kT$

Bose-Einstein Distribution

• For bosons:

$$\sum_{i} P[E_i, N_i] = \sum_{N_i=0}^{\infty} \exp[-N_i(E-\mu)/kT] = \sum_{N_i=0}^{\infty} [e^{-(E-\mu)/kT}]^{N_i}$$
$$= \frac{1}{1 - e^{-(E-\mu)/kT}}$$

$$\sum_{i} N_{i} P[E_{i}, N_{i}] = \sum_{N_{i}=0}^{\infty} N_{i} \exp[-N_{i}(E-\mu)/kT]$$
$$= \frac{\partial}{\partial \mu/kT} \sum_{N_{i}=0}^{\infty} [e^{-(E-\mu)/kT}]^{N_{i}}$$
$$= \frac{\partial}{\partial \mu/kT} \left(\frac{1}{1-e^{-(E-\mu)/kT}}\right) = \frac{e^{-(E-\mu)/kT}}{(1-e^{-(E-\mu)/kT})^{2}}$$

Bose-Einstein Distribution

• Bose Einstein distribution:

$$f = \frac{\sum_{i} N_i P[E_i, N_i]}{\sum_{i} P[E_i, N_i]} = \frac{1}{e^{(E-\mu)/kT} - 1}$$

For $E - \mu \gg kT$, $f \to 0$. For $E - \mu < kT \ln 2$, f > 1, high occupation (Bose-Einstein condensate).

• General equilibrium distribution

$$f = \frac{1}{e^{(E-\mu)/kT} \pm 1}$$

+ = fermions, - = bosons

• μ alters the number of particles at temperature T

Maxwell Boltzmann Distribution

• In both cases, if $(E - \mu) \gg kT$ (including rest mass energy), then

 $f = e^{-(E-\mu)/kT}$

- A non-degenerate gas of particles mean occupation $f \ll 1$
- For non relativistic particles

$$E = (q^2c^2 + m^2c^4)^{1/2} = mc^2(1 + q^2/m^2c^2)^{1/2}$$
$$\approx mc^2(1 + q^2/2m^2c^2) = mc^2 + \frac{1}{2}mv^2$$

$$f = e^{-(mc^2 - \mu)/kT} e^{-mv^2/2kT}$$

• A non-relativistic, non-degenerate gas of particles

• When particles can be freely created and destroyed $\mu \to 0$ and for bosons this is the black body distribution

$$f = \frac{1}{e^{E/kT} - 1}$$

• Specific intensity

$$I_{\nu} = B_{\nu} = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$

• At low frequencies $h\nu \ll kT$ (Rayleigh Jeans)

$$\exp(h\nu/kT) - 1 \approx 1 + h\nu/kT - 1 = h\nu/kT$$
$$B_{\nu} = \frac{2h\nu^3}{c^2}\frac{kT}{h\nu} = 2\frac{\nu^2}{c^2}kT$$

independent of h (classical, many photon limit)

• Commit your favorite blackbody to memory: e.g. 3K, $\nu \sim 100$ GHz, $\lambda \sim 0.3$ cm, $h\nu \sim 0.0004$ eV



Cosmic Microwave Background

• FIRAS observations



- $B_{\nu} \propto \nu^2$ would imply an ultraviolet catastrophy $S = \int B_{\nu} d\nu$
- At high frequencies $h\nu \gg kT$ (Wien tail)

$$\exp(h\nu/kT) - 1 \approx e^{h\nu/kT}$$

$$B_{\nu} = \frac{2h\nu^3}{c^2} e^{-h\nu/kT}$$

exhibits the Boltzmann suppression, particle nature of light

• Scaling with T

$$\frac{\partial B_{\nu}}{\partial T} = \frac{2h\nu^3}{c^2} \frac{\partial f}{\partial T} = \frac{2h\nu^3}{c^2} \left(\frac{-1}{(e^{h\nu/kT} - 1)^2}\right) \frac{-h\nu}{kT^2} > 0$$

so that specific intensity at all ν increases with T

• Setting $\partial B_{\nu}/\partial \nu = 0$ defines the maximum $h\nu_{\rm max} = 2.82kT$

• Surface Brightness

$$S = \int_0^\infty B_\nu d\nu = \frac{2h}{c^2} \int_0^\infty \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu$$
$$= \frac{2h}{c^2} \left(\frac{kT}{h}\right)^4 \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{2\pi^4 k^4}{15c^2 h^3} T^4 \equiv \frac{\sigma_B T^4}{\pi}$$

where $\sigma_B = 2\pi^5 k^4 / 15c^2 h^3$ is the Stephan-Boltzmann constant and the π accounts for the emergent flux at the radius R of a uniform sphere where angles up to the $\pi/2$ tangent can be viewed

$$F \equiv \int S \cos \theta d\Omega = S \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos \theta \sin \theta d\theta = \pi S$$

• Energy density

$$u = \int \frac{B_{\nu}}{c} d\nu d\Omega = \frac{4\pi}{c} \frac{\sigma_B T^4}{\pi} = \frac{4\sigma_B}{c} T^4$$

• Number density

$$n = 2 \int d\Omega \frac{1}{c^3} \int \nu^2 d\nu \frac{1}{e^{h\nu/kT} - 1}$$
$$= \frac{8\pi}{c^3} \left(\frac{kT}{h}\right)^3 \int_0^\infty \frac{x^2 dx}{e^x - 1} = \frac{16\pi\zeta(3)}{c^3} \left(\frac{kT}{h}\right)^3$$
$$= \frac{2\zeta(3)}{\pi^2 c^3} \left(\frac{kT}{\hbar}\right)^3$$

where $\zeta(3) \approx 1.202$

Effective Temperature

- Common to quantify the specific intensity I_{ν} with an equivalent temperature T that a black body would have
- Brightness temperature: match specific intensity $I_{\nu} = B_{\nu}(T_B)$ to define a frequency dependent brightness temperature, most commonly matched in the Rayleigh-Jeans approximation

$$I_{\nu} = B_{\nu} \Big|_{\rm RJ} = \frac{2\nu^2}{c^2} k T_B, \quad T_B = \frac{c^2}{2\nu^2 k} I_{\nu}$$

- Color temperature: match peak intensity to black body peak $k\nu_{\rm max} = 2.82kT_{\rm color}$ - ambiguous since depends on measuring a representative frequency range - useful if the source is unresolved so that only flux and not I_{ν} measured
- Effective temperature: match total flux to that of black body requires measuring all frequencies or bolometric measurement: $F = \sigma_B T_{eff}^4$