Apr. 20

Quantum Statistical Mechanics

It is straightforward to extend the formalism that we have built for the statistical mechanics of classical systems to the study of quantum systems. In particular, in the canonical and grand canonical ensembles, earch possible state appears, with a probability proportional to a function of its energy and particle number. The same derivations give the same rules for quantum systems, now using quantum-mechanical formulae for the sum over states and the energy of each state.

I will start with some orientation to the formalism of quantum mechanics. The next few paragraphs will define my notation and review the most basic concepts.

In quantum mechanics, the possible states of a physical system are the states of a Hilbert space $\mathcal{H}$. The Hamiltonian H is an operator on this space. The eigenstates of H are states $|i\rangle$ such that

$$H|i\rangle = E_i |i\rangle$$

These are the states of definite energy. Since H is a self-adjoint operator, these states form a basis for $\mathcal{H}$; that is, any quantum state of the system can be written as

$$|\alpha\rangle = \sum_i |i\rangle\langle i|\alpha\rangle = \sum_i c_{i\alpha} |i\rangle$$

The time evolution of a state is given by solving the equation

$$i \frac{d}{dt} |\alpha(t)\rangle = H |\alpha(t)\rangle$$

This is the *Schrodinger equation.* Any other equation called the Schrödinger equation is a specific realization of this one. The solution of the Schrödinger equation is

$$|\alpha(t)\rangle = e^{-iHt}\,|\alpha(0)\rangle$$

an evolution by a unitary transformation generated by the Hamiltonian. Note that, for the same reasons that I set $k_B = 1$ above, I will set $\hbar = 1$ in my discussion of quantum mechanics.

Observables in quantum mechanics are described by Hermitian operators A. In an eigenstate $|j\rangle$ of A with eigenvalue a_j, the value of A is a_j. In a more general state $|k\rangle$, A does not take a definite value but, rather, experiments measuring A give various values a_j with probabilities p_j. The average value of A is

$$\langle A\rangle = \langle k|A|k\rangle = \sum_{jj'} \langle k|j\rangle \underbrace{\langle j|A|j'\rangle}_{a_j\delta_{jj'}} \langle j'|k\rangle$$

so that

$$\langle A\rangle = \sum_j p_j(k)\, a_j$$

with

$$p_j(k) = |\langle k|j\rangle|^2$$

It is one of the great mysteries of quantum mechanics that, in any given experiment, we always get one of the values a_j.

A vector in the Hilbert space, $|i\rangle$, is called a *pure state.* In statistical mechanics, we typically want to compute averages over a collection of quantum states in which the various states $|i\rangle$ appear with different probabilities p_i. An average over quantum states is called a *mixed state.* (I do not encourage this terminology.)

Such an average is described as follows: In an ensemble in which states $|i\rangle$ appear with probability p_i, the expectation value of an observable A is

$$\langle A \rangle = \sum_i p_i \langle i | A | i \rangle$$

This can be written as

$$\langle A \rangle = \text{trace}\,[\rho A]$$

where ρ is a matrix given by

$$\rho = \sum_i |i\rangle p_i \langle i|$$

We can think of ρ as a Hermitian operator on the Hilbert space. It is called the *density matrix.*

It is interesting to ask the reverse question: Under what circumstances can a Hermitian operator be a density matrix? A density matrix ρ should satisfy the following general properties:

1. ρ should be Hermitian with eigenvalues $0 \le p_i \le 1$.
2. ρ should satisfy $\text{tr}\rho = 1$, corresponding to

$$\sum_i p_i = 1$$

If ρ has one eigenvalue equal to 1 and all others equal to 0, it has the form

$$\rho = |k\rangle\langle k|$$

for some $|k\rangle$. In this case, it represents a *pure state*. Also, in this case, ρ is a projector:

$$\rho^2 = \rho$$

In general for a density matrix

$$0 \leq \rho^2 \leq \rho$$

that is, diagonal matrix elements of ρ^2 are bounded above by the matrix elements of ρ.

Now we can discuss the averages over quantum states corresponding to the canonical and grand canonical ensembles. These correspond to averaging with specific choices of the density matrix: For the canonical ensemble,

$$\rho = \frac{\sum_i |i\rangle e^{-\beta E_i} \langle i|}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta H}}{Z}$$

taken over the Hilbert space of states of states with a specific value of the particle number. The denominator of this expression is the canonical partition function

$$Z = \sum_i e^{-\beta E_i} = \operatorname{tr} e^{-\beta H}$$

Then the canonical average of an observable O is given by

$$\langle O \rangle = \operatorname{tr} \rho O = \frac{\operatorname{tr} O e^{-\beta H}}{\operatorname{tr} e^{-\beta H}}$$

For the grand canonical ensemble, the density matrix is given by

$$\rho = \frac{e^{-\beta(H-\mu N)}}{\Xi}$$

The denominator of this expression is the grand partition function

$$\Xi = \mathrm{tr}\, e^{-\beta(H-\mu N)}$$

In classical mechanics, the canonical average is time-independent. This is also true in quantum mechanics,

$$\begin{aligned} \rho(t) &= \sum_i |i(t)\rangle \frac{e^{-\beta E_i}}{Z} \langle i(t)| \\ &= \sum_i e^{-iHt} |i\rangle e^{-\beta E_i} \langle i| e^{+iHt} / Z \\ &= e^{-iHt} e^{-\beta H} e^{+iHt} / Z \quad = \quad e^{-\beta H}/Z = \rho \end{aligned}$$

The final line follows because H commutes with itself. A similar argument can be made for the grand canonical partition function if particle number is conserved, $[H, N] = 0$.

In classical statistical mechanics, we were able to compute some important averages by differentiating the log of the partition function. The same formulae hold in quantum statistical mechanics. For example,

$$E = \langle H \rangle = \frac{\mathrm{tr}\, H e^{-\beta H}}{Z} = -\frac{\partial}{\partial \beta} \log Z$$

As we did in classical statistical mechanics, we define the Helmholtz free energy F by

$$Z = e^{-\beta F} \quad \text{or} \quad F = -T \log Z$$

Then, if the entropy is defined as

$$F = E - TS \quad \text{or} \quad S = -\beta(F - E)$$

we can compute the entropy by

$$\begin{aligned} E - F &= \operatorname{tr} H e^{-\beta H}/Z + \frac{1}{\beta} \log Z \\ &= -\frac{1}{\beta} \operatorname{tr} [\rho \, [-\beta H - \log Z]] \\ &= -T \operatorname{tr} [\rho \, (\log \rho)] \end{aligned}$$

Then finally

$$S = -\operatorname{tr} \rho \log \rho$$

Representing the trace as a sum over eigenstates of ρ,

$$S = -\sum_i p_i \log p_i$$

This is exactly the Shannon expression for the entropy of an ensemble.

In quantum mechanics, the computation of quantum averages is ultimately a sum over discrete states. If there is a unique state $|0\rangle$ of lowest energy, the *ground state*, then as the temperature $T \to 0$ ($\beta \to \infty$),

$$\rho \to |0\rangle\langle 0|$$

Then ρ tends to a pure state at $T = 0$ and $S \to 0$ as $T \to 0$. This statement is sometimes called the *zeroth law of thermodynamics.*

The simplest example of a quantum system is a 2-state system. An example of such a system is single spin in a magnetic field. For this problem, the Hamiltonian is

$$\mathcal{H} = -\mu h \sigma^3 \qquad \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and its eigenstates are

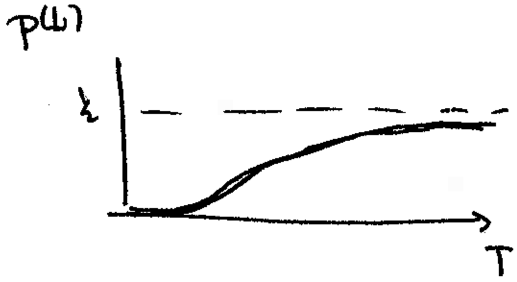
$$E = -\mu h : \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\uparrow\rangle \qquad E = +\mu h : \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\downarrow\rangle$$

The canonical density matrix is

$$\rho = \frac{e^{+\beta\mu h} |\uparrow\rangle\langle\uparrow| + e^{-\beta\mu h} |\downarrow\rangle\langle\downarrow|}{e^{\beta\mu h} + e^{-\beta\mu h}}$$

The state $|\uparrow\rangle$ is the ground state. The probability of being in the *excited state* $|\downarrow\rangle$ is

$$p(\downarrow) = \frac{1}{1 + e^{+2\beta\mu h}}$$



This expression has the behavior:

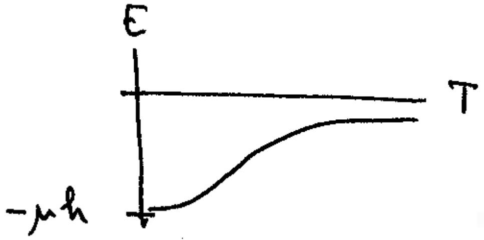
$$T \to 0 \text{ or } \beta \to \infty \qquad p(\downarrow) \sim e^{-2\beta\mu h} \to 0$$

$$T \to \infty \text{ or } \beta \to 0 \qquad p(\downarrow) \to \tfrac{1}{2}$$

The thermal energy of the single-spin system as a function of temperature is

$$E = \langle H \rangle = -\mu h \, \frac{e^{\beta\mu h} - e^{-\beta\mu h}}{e^{\beta\mu h} + e^{-\beta\mu h}}$$

$$\text{or} \qquad E = -\mu h \tanh(\beta\mu h)$$



From this, we can derive the specific heat

$$C_V = \frac{\partial E}{\partial T} = -\frac{1}{T^2}\frac{\partial E}{\partial \beta} \Rightarrow C_V = \left(\frac{\mu h}{T}\right)^2 \frac{1}{\cosh^2 \beta\mu h}$$

The single-spin system is perhaps a little too simple. The next most simple—and perhaps more illustrative—example is the harmonic oscillator. For this system, the eigenvalues of H are

$$E = \hbar\omega\,(n + \tfrac{1}{2}) \qquad n = 0, 1, 2, \ldots$$

For this sytem (with $\hbar = 1$ henceforth), the partition function is

$$Z = \sum_{n=0}^{\infty} e^{-\beta\omega(n+\frac{1}{2})}$$

$$= e^{-\beta\omega/2}\left(1 + e^{-\beta\omega} + e^{-2\beta\omega} + \ldots\right)$$

The sum here is a geometric series that is easily summed

$$Z = e^{-\beta\omega/2} \frac{1}{1 - e^{-\beta\omega}}$$

$$= \frac{1}{2 \sinh \beta\omega/2}$$

The thermal energy is then

$$E = -\frac{\partial}{\partial\beta} \log Z = \frac{\omega}{2} \frac{\cosh \beta\omega/2}{\sinh \beta\omega/2}$$

or

$$E = \frac{\omega}{2} \coth \frac{\beta\omega}{2}$$

so that, for the extreme values of temperature

$$T \to 0 \qquad \beta \to \infty \qquad E \to \frac{\omega}{2} + \mathcal{O}(e^{-\beta\omega})$$

$$T \to \infty \qquad \beta \to 0 \qquad E \to \frac{\omega}{2} \frac{2}{\beta\omega} = \frac{1}{\beta}$$

Note that the latter case is just

$$E \to T$$

and that this result is dimensionally correct without the need for $\hbar$. The correspondence principle says that the same result should be true in classical mechanics, and this result is exactly that of the classical equipartition theorem. For large T, with $\hbar\omega \ll T$, the quantum levels are so close together that we can ignore their discreteness. For low T, on the other hand, the discreteness is essential,

$$E = \frac{\omega}{2} + \omega e^{-\beta\omega} + \cdots$$

The specific heat of the harmonic oscillator is

$$C_v = -\frac{1}{T^2}\frac{\partial}{\partial\beta}E = \left(\frac{\omega}{2T}\right)^2 \frac{1}{\sinh^2 \beta\omega/2}$$

Note the interesting formal similarity to the expression for a two-level system.

There is one more simple quantum system that is important to study. This is the rigid rotor

with moment of inertia I. The Hamiltonian is

$$\mathcal{H} = \frac{L^2}{2I}$$

The energy eigenvalues are

$$E_l = \frac{\hbar^2 l(l+1)}{2I}$$

with multiplicity

$$(2\ell+1)$$

Then the partition function is

$$Z = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\beta \ell(\ell+1)/2I}$$

For low T or $\beta \rightarrow \infty$,

$$Z = 1 + 3\, e^{-\beta/I} + 5\, e^{-3\beta/I} + \cdots$$

$$E = 3\frac{\hbar^2}{I}\, e^{-\beta/I} + 15\, \frac{\hbar^2}{I}\, e^{-3\beta/I} + \cdots$$

For high T, we can again argue that the levels are very close together and we can ignore their discreteness. In this limit, we can approximate the sum in Z by an integral,

$$Z \approx \int_0^{\infty} d\ell\ (2\ell+1)\ e^{-\beta \ell(\ell+1)/2I}$$

$$= \int_0^{\infty} dL^2\ e^{-\beta L^2/2I} \qquad L^2 = \ell^2+\ell$$

Then $\qquad = \qquad 2I/\beta$

$$E = -\frac{\partial}{\partial\beta}\log Z \cong \frac{1}{\beta} = T$$

This is again the result of the equipartition theorem for a system with two degrees of freedom described by quadratic Hamiltonians. Rotations have three degrees of freedom, but for a rigid rotor, there is no significance to rotations about the axis of the rotor.

For diatomic molecules with identical atoms at the two ends, for example, N_2 and O_2, there is an additional subtlety. Since the ends are identical, the rotational wavefunction must be *symmetric* under reversal of the orientation of the rotor. Spherical harmonics of even ℓ are symmetric; spherical harmonics of odd ℓ are antisymmetric. So we must sum over even ℓ only. The expansion of the partition function for low T becomes

$$Z = 1 + 5e^{-3\beta/I} + \cdots$$

and for high T

$$Z \approx \frac{1}{2}\int_0^\infty d\ell\ (2\ell+1)\ e^{-\beta\ell(\ell+1)/2I}$$

The high-temperature limit

$$E \to T$$

is not affected.

For a diatomic molecule at room temperature, I argued in a previous lecture that the vibrational excitations obey

$$\frac{\hbar\omega}{T} \gg 1$$

while the rotational excitations obey

$$\frac{\hbar^2}{2IT} \ll 1$$

We have now justified the statements from quantum statistical mechanics needed to prove the formula for γ in a gas of diatomic molecules.

I will now apply the rules of quantum statistical mechanics to the statistics of an ideal gas. I will assume that the gas is composed of structureless atoms with no internal degrees of freedom.

The state of an atom is then described by the values of its momenta. To apply the rules, it is simplest to make the momenta discrete, so that we can perform the sum over states by counting. If we put the gas in the large box, the discretization of states depends on the boundary conditions at the wall of the box. The terms in the free energy that grow like the volume, as opposed to terms proportional to the surface area, are independent of the particular boundary conditions chosen. It is convenient, then, to make the boundary conditions as simple as possible. Here, and later in the course, I will take advantage of this freedom by chosing to work in a cubic box with periodic boundary conditions. Then

$$V = L^3$$

and the quantized momenta are

$$p^i = \frac{2\pi}{L} n^i \qquad i = x, y, z \qquad n^i = 0, \pm 1, \pm 2, \ldots$$

The energy of a single atom is

$$\frac{p^2}{2m} = \frac{1}{2m}\left(\frac{2\pi}{L}\right)^2 \left[(n^x)^2 + (n^y)^2 + (n^z)^2\right]$$

Since these states are discrete, we can sum over them in a simple way,

$$\sum_{n^x n^y n^z}$$

In the limit $L \to \infty$, these discrete states become very closely spaced, and we can replace the sum by an integral

$$\sum_{n^x n^y n^z} = \int dn^x dn^y dn^z = \int \left(\frac{L}{2\pi}\right)^3 d^3p = V \int \frac{d^3p}{(2\pi)^3}$$

This expression for summing over single-particle states is exactly

$$\int \frac{d^3q\, d^3p}{(2\pi\hbar)^3}$$

This calculation then supports the choice of phase space volume or normalization used in our classical calculations.

To describe an ideal gas of N atoms, we must place these N atoms into the discrete states. This is most easily done by allowing N to fluctuate (negligibly) by $\sqrt{N}$ and applying the grand canonical ensemble. In that formalism, we allow any number of particles to be in the box, weighting each particle by

$$e^{\beta\mu}$$

At the end of the calculation, we will adjust the chemical potential μ to make $\langle N \rangle$ come out to the desired number.

Now the question arises: When we put particles into each discrete quantum state, how do we count situations in which several particles are put into the same quantum state? In quantum mechanics, particles of the same type must be treated as *identical.* But it turns out that quantum mechanics still allows two answers distinct to this question, depending on the *intrinsic spin* of the particle.

- For particles of *integer* spin ($s = 0, 1, 2, \cdots$), we are allowed to put *any number* of particles into a given quantum state. However, we must treat these particles as *indistinguishable*; that is, the situation in which n particles are put into a given state is counted as one quantum state of the n=particle system. This counting is called *Bose-Einstein statistics*; the particles themselves are called *bosons.* The method of counting follows from the fact that particles of integer spin are described by wavefunctions that are *symmetric* under interchange of a pair of particles.
- For particles of *half-integer* spin ($s = \frac{1}{2}, \frac{3}{2}, \cdots$), we are allowed to put *at most one* particle into a given quantum state. However, we must treat these particles as *indistinguishable*; that is, the situation in which n particles are put into a given state is counted as one quantum state of the n=particle system. This counting is called *Fermi-Dirac statistics*; the particles themselves are called *fermions.* The method of counting follows from the fact that particles of integer spin are described by wavefunctions that are *antisymmetric* under interchange of a pair of particles.

It is amazing that, in Nature, the spin of a particle correctly dictates its statistics. Photons have $s = 1$. They thus obey Bose-Einstein statistics. Then they can form macroscopic electromagnetic fields, in which many photons occupy the same state. Electrons have $s = \frac{1}{2}$. They thus obey Fermi-Dirac statistics. They thus obey the Pauli exclusion principle. It is this fact that is responsible for the stability of atoms and the rigidity of matter.

This connection between spin and statistics can be proved as a theorem in relativistic quantum field theory. Thus, it is a consequence—a very non-obvious one—of the principles of special relativity and locality. The proof is not simple and is well beyond the scope of this course.

I will now compute the basic properties of quantum ideal gases for each case of the statistics. In both cases, particles can exist in several spin states. Let g be the number of these states. For a *massive* particle

$$g = (2s+1)$$

However, for a *massless* particle, the number of possible spin states can be smaller. Notably, a *photon* ($s = 1$) and a graviton ($s = 2$) both have only 2 allowed spin states, corresponding in both cases to left- and right-handed polarization.

For atoms obeying Bose-Einstein (BE) statistics, the grand partition function is

$$\Xi_{BE} = \sum_{\substack{\text{possible multi-particle}\\ \text{states}}} e^{-\beta \sum_j (E_j - \mu)}$$

j = # of particles.

To compute this, we can look at one state at a time and sum the weights for the each possible case of the number of particles occupying that state. Then

$$\Xi_{BE} = \prod_{\text{1-particle states } i} \left(1 + e^{-\beta E_i} e^{\beta\mu} + e^{-\beta\cdot 2E_i} e^{2\beta\mu} + \dots\right)$$

$$= \prod_{\text{1-particle states } i} \frac{1}{1 - e^{-\beta(E_i-\mu)}}$$

so that

$$\log \Xi_{BE} = \sum_{\text{states } i} -\log\left(1 - e^{-\beta(E_i-\mu)}\right)$$

The sum over states, including spin states, can be written as

$$\sum_{\text{states } i} = g \sum_{n^x n^y n^z} = gV \int \frac{d^3p}{(2\pi)^3}$$

Using this formula, and recalling that $\Phi = -T \log \Xi$, we find

$$\Phi_{BE} = T \cdot g \cdot V \cdot \int \frac{d^3p}{(2\pi)^3} \log\left(1 - e^{-\beta(E_i-\mu)}\right)$$

For Fermi-Dirac (FD) statistics, we truncate the sum over the number of particles in each state at $n = 1$. However, this gives a formula very similar to the one in the BE case,

$$\Xi_{FD} = \prod_{\text{states } i} \left(1 + e^{-\beta E_i} e^{\beta\mu}\right)$$

so that

$$\Phi_{FD} = T \cdot g \cdot V \cdot \int \frac{d^3p}{(2\pi)^3} \left(-\log\left(1 + e^{-\beta(E_i-\mu)}\right) \right)$$

To make sense of these equations, we need to determine μ. If the number of atoms is fixed, μ must be adjusted so that the equation

$$N = -\frac{\partial \Phi}{\partial \mu}\Big|_{V,T}$$

is satisfied. This gives

$$\text{BE}: \qquad N = gV \int \frac{d^3p}{(2\pi)^3} \frac{1}{e^{\beta(E-\mu)} - 1}$$

$$\text{FD}: \qquad N = gV \int \frac{d^3p}{(2\pi)^3} \frac{1}{e^{\beta(E-\mu)} + 1}$$

We can read from these equations the average number of particles occupying a quantum state with energy E_i,

$$\text{BE}: \qquad n(i) = \frac{1}{e^{\beta(E_i-\mu)} - 1}$$

$$\text{FD}: \qquad n(i) = \frac{1}{e^{\beta(E_i-\mu)} + 1}$$

As we might have expected, in the FD case, $0 \le n_{FD} \le 1$. in the BE case, however, n_{BE} can be as large as one wishes. For $\beta(E_i - \mu) \gg 1$, in *both* cases

$$n \to e^{-\beta(E_i - \mu)}$$

This gives the simpler formula

$$N = gV \int \frac{d^3p}{(2\pi)^3} \, e^{-\beta E(p)} e^{\beta\mu}$$

which coincides with the formula we wrote for a *classical* ideal gas with chemical potential μ.

For the grand canonical ensemble,

$$-\frac{\partial}{\partial\beta} \log \Xi = \langle E - \mu N \rangle$$

Applying this to the partition functions for the quantum idea gases, we find

$$-\frac{\partial}{\partial\beta} \log \Xi_{BE} = gV \int \frac{d^3p}{(2\pi)^3} \frac{E-\mu}{e^{\beta(E-\mu)} - 1}$$

and similarly for Ξ_{FD}. Adding the formula for N from above, we find the expressions for the energy of the gas

$$\text{BE}: \qquad E = gV \int \frac{d^3p}{(2\pi)^3} \frac{E(p)}{e^{\beta(E(p)-\mu)} - 1}$$

$$\text{FD}: \qquad E = gV \int \frac{d^3p}{(2\pi)^3} \frac{E(p)}{e^{\beta(E(p)-\mu)} + 1}$$

In both cases, this expression has the form

$$E = gV \int \frac{d^3p}{(2\pi)^3} \; E(p)\, n(p)$$

as expected from our intuition.

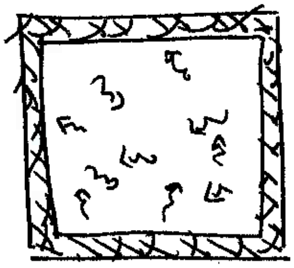
I have shown that the quantum ideal gas formulae reduce to the formula for a classical gas in the limit of low density. In the limit of high density, these gases show new phenomena. I will describe these in detail in the next lecture.

There is one interesting variant of this theory to discuss, the statistical mechanics of relativistic particles. In particular, it is sometimes a good approximation to ignore the rest mass of a particle and write the formula for its energy as

$$E = c|\vec{p}|$$

The rest of the lecture will be devoted to analyzing this situation.

I will begin with the statistical mechanics of *photons.* These are BE particles with $g = 2$. The ideal gas of photons corresponds to the following physical situation: An oven is regulated to stay at a fixed temperature T, and it can radiate photons into its interior. The gas of photons then comes into thermal equilibrium with the inner walls of the oven.



The radiation spectrum in the oven is called *black-body radiation* at temperature T. The same spectrum of photons is radiated into space from a hot surface, provided that the material from which the surface is made does not have significant frequency dependence in the photon emission probability. A body for which the transition rate for emitting photons depends significantly on the frequency or energy of the photons is called a *grey body.*

The population of energy levels in the cavity of the oven can be computed from the formulae for BE statistics. Photons can be freely created and distroyed, so, in equilibrium, they have chemical potential $\mu = 0$. This condition determines the number density of photons in equilibrium.

The BE ideal gas formulae for $\mu = 0$ and a relativistic energy spectrum

$$E = cp$$

are

$$N = gV \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{e^{\beta cp} - 1}$$

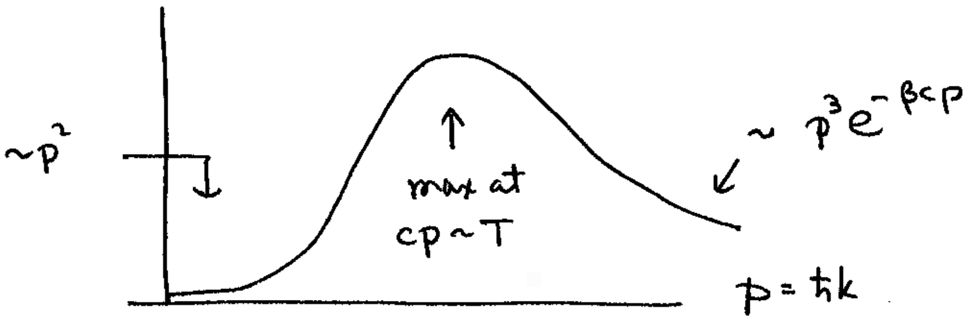
$$E = gV \int \frac{d^3p}{(2\pi\hbar)^3} \frac{cp}{e^{\beta cp} - 1}$$

where p is the photon momentum, related to the wavenumber and wavelength of the mode of electromagnetic radiation by $p = \hbar k = 2\pi\hbar/\lambda$. I will evaluate the formula for E more explicitly.

$$E/V = g \frac{1}{8\pi^3} 4\pi \int_0^\infty dp\, p^2 \frac{cp}{e^{\beta cp} - 1}$$

$$\text{or} \quad E/V = \int_0^\infty dp \frac{g}{2\pi^2} \frac{cp^3}{e^{\beta cp} - 1}$$

This spectrum is the famous *Planck distribution* It behaves as



This distributions shows explicitly how the *color* of a hot black body shifts from red to blue-white as its temperature T increases.

To evaluate the complete integral over p, set $x = \beta cp$. Then

$$\frac{E}{V} = \frac{g}{2\pi^2} \frac{1}{c^3 \beta^4} \left[\int_0^\infty dx \; \frac{x^3}{e^x - 1} \right]$$

The value of the integral in the bracket is $\pi^4/15$; I will prove that in a moment. Then

$$\frac{E}{V} = g \frac{\pi^2}{30} T^4 \frac{1}{(\hbar c)^3}$$

This is often written (putting $g = 2$ for definiteness)

$$\frac{E}{V} = 4\sigma T^4 / c$$

where

$$\sigma = \frac{\pi^2}{60 \hbar^3 c^2}$$

is the *Stefan-Boltzmann constant.*

In a similar way, we can compute the grand potential,

$$\Phi = gTV \int \frac{d^3p}{(2\pi\hbar)^3} \log\left(1 - e^{-\beta cp}\right)$$

$$= \frac{gVT^4}{c^3} \frac{4\pi}{8\pi^2} \int_0^\infty dx \; x^2 \log\left(1 - e^{-x}\right)$$

Integrate by parts,

$$\Phi = -\frac{gV}{c^3} T^4 \frac{1}{2\pi^2} \int_0^\infty dx \, \frac{x^3}{3} \frac{1}{e^x-1}$$

This is the same integral that we found just above, and so

$$\Phi = -gV \frac{\pi^2}{90} T^4 \frac{1}{(\hbar c)^3}$$

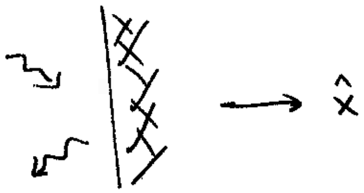
Since $\Phi = -pV$, the pressure of a photon gas is

$$p = g \frac{\pi^2}{90} T^4 \frac{1}{(\hbar c)^3} = \frac{1}{3} E/V$$

The relation

$$p = \frac{1}{3} \frac{E}{V}$$

is a standard result for relativistic particles. To derive it in a simpler way, we can repeat the argument that I gave in the first lecture on the ideal gas, but now for particles that travel at the speed of light. Consider the elastic reflection of particles from a wall perpendicular to $\hat{x}$ in a time interval Δt,



and compute the momentum transferred in this time interval. This is

$$\Delta P_x = \int_{p_x>0} \frac{d^3p}{(2\pi)^3}\, g\, n(p) \left[c\, \frac{p_x}{p}\, \Delta t \right] (\text{Area}) \cdot 2p_x$$

Note that I have taken c instead of the value p/m that we had earlier, as the velocity of a gas particle. Since

$$\left\langle c\, \frac{p_x^2}{p} \right\rangle = \frac{1}{3} \langle cp \rangle = \frac{1}{3} \langle E(p) \rangle$$

we find

$$\frac{\text{Force}}{\text{Area}} = \frac{1}{2} \cdot 2 \cdot \int \frac{d^3p}{(2\pi)^3}\, g\, n(p)\, E(p) \cdot \frac{1}{3}$$

or, finally,

$$P = \frac{1}{3} \frac{E}{V}$$

From the value of Φ, we can obtain the entropy of a photon gas by the relation

$$S = - \left. \frac{\partial \Phi}{\partial T} \right|_V$$

The result is

$$S = g V \cdot \frac{2\pi^2}{45}\, T^3\, \frac{1}{(\hbar c)^3}$$

This would be a good time to pause and evaluate the integral that arises in the computation of E and Φ. A more general form of this integral is

$$\int_0^\infty dx \quad x^{n-1} \, \frac{1}{e^x - 1}$$

We can evaluate this by expanding the denominator and integrating term by term,

$$\int_0^\infty dx \; x^{n-1} \frac{1}{e^x-1} = \int_0^\infty dx \; x^{n-1} \left(e^{-x} + e^{-2x} + e^{-3x} + \cdots \right)$$

$$= \int_0^\infty dy \; y^{n-1} e^{-y} \cdot \left[1 + \frac{1}{2^n} + \frac{1}{3^n} + \cdots \right]$$

The result is

$$\int_0^\infty dx \; x^{n-1} \frac{1}{e^x-1} = \Gamma(n) \, \zeta(n)$$

where $\Gamma(n)$ is the familiar Gamma function

$$\Gamma(n) = (n-1)!$$

and $\zeta(n)$ is the *Riemann zeta function*

$$\zeta(n) = \sum_{m=1}^\infty \frac{1}{m^n}$$

Some values of $\zeta(n)$ are

$$\zeta(2) = \frac{\pi^2}{6} = 1.64493..$$

$$\zeta(3) = 1.20206..$$

$$\zeta(4) = \frac{\pi^4}{90} = 1.08232..$$

Then, as a special case,

$$\int_0^\infty dx \quad x^3 \frac{1}{e^x-1} = 3! \cdot \zeta(4) = \frac{\pi^4}{15}$$

Another similar integral that will be relevant for us is

$$\int_0^\infty dx \quad x^{n-1} \frac{1}{e^x+1}$$

We can evaluate this integral in the same way,

$$\begin{aligned}\int_0^\infty dx\, x^{n-1} \frac{1}{e^x+1} &= \int_0^\infty dx\, x^{n-1} \left(e^{-x} - e^{-2x} + e^{-3x} - e^{-4x} + \dots\right) \\ &= \left(\int_0^\infty dy\, y^{n-1} e^{-y}\right)\left(1 - \frac{1}{2^n} + \frac{1}{3^n} - \dots\right) \\ &= \Gamma(n)\left[\left(1 + \frac{1}{2^n} + \frac{1}{3^n} + ..\right) - \frac{2}{2^n}\left(1 + \frac{1}{2^n} + \frac{1}{3^n} + ..\right)\right]\end{aligned}$$

The final result is

$$\int dx \quad x^{n-1} \cdot \frac{1}{e^x+1} = \Gamma(n)\, \zeta(n) \left(1 - \frac{1}{2^{n-1}}\right)$$

In working out the energy, entropy, and pressure of photons, we only used the properties that photons are relativistic BE particles with $g = 2$. The results we derived will then be valid for any other type of relativistic BE particle. They also apply to other particles that have an energy-momentum relation

$$E = cp$$

for any fixed value of c. For example, sound waves in a crystal have a linear dispersion relation. When the system of vibrations is quantized, the quanta are particles called *phonons* with

$$E = c_s p$$

where c_s is the speed of sound. Often, phonons are particles of spin zero, but in most cases there are 3 modes of oscillation corresponding to the three axes along which an atom in a crystal can vibrate. Then phonons obey the formulae above with

$$g = 3$$

If we have electrons or other FD particles at a very high temperature so that $T \gg mc^2$, it is a good approximation to ignore the mass of the particle and approximate $E \approx cp$. Then we can work out the thermodynamic properties of a system of these particles from a set of formulae similar to those above, generalized to the FD case.

We meet conditions where the temperature is much higher than the electron mass in the early universe. In this environment, electrons and positrons are pair-produced through processes such as

$$\gamma + \gamma \rightleftarrows e^- + e^+$$

If this reaction runs to equilibrium,

$$\mu(e^+) + \mu(e^-) = 0$$

If the density of e^+ and e^- due to this pair-production is much greater than the density due to the absolute number of electrons, then

$$n(e^+) \approx n(e^-)$$

and so $\mu(e^+) \approx \mu(e^-)$. Then it is a good approximation to set

$$\mu(e^+) \approx \mu(e^-) \approx 0$$

Today, there is a finite density of electrons in the universe, and there are almost no positrons. However, in the very early universe when $T \gg m_e c^2$, a much larger density of electrons and positrons was produced thermally. The thermal densities completely overwhelmed the net excess of electrons, such that

$$\frac{n(e^-) - n(e^+)}{n(e^-) + n(e^+)} \sim 10^{-10}$$

At this time in the early universe, it was a good approximation to take $\mu(e^-) = 0$. The electron-positron system has $g = 4$, two particles, with two spin states each.

For a relativistic FD gas with $\mu = 0$, the formulae for E, S, and p can be worked out in the same way as for the BE case discussed above. The final formulae are the same, with the substitution of the FD distribution for the BE distribution. Then, for the energy,

$$E = gV \int \frac{d^3p}{(2\pi)^3} \frac{cp}{e^{\beta c p}+1}$$

The integral evaluates to

$$E = gV \frac{1}{2\pi^2 c^3 \beta^4} \int_0^1 dx \, \frac{x^3}{e^x+1}$$

so that, finally,

$$E = gV \frac{T^4}{2\pi^2 c^3} \frac{\pi^4}{15} \cdot \frac{7}{8}$$

The relations between E, S, and p are exactly the same as in the BE case. Then, to summarize both cases,

$$\frac{E}{V} = g \frac{\pi^2}{30} T^4 \frac{1}{(\hbar c)^3} \cdot \begin{cases} 1 & \text{BE} \\ 7/8 & \text{FD} \end{cases}$$

with

$$P = \frac{1}{3}\frac{E}{V} \qquad S = \frac{4}{3}\frac{E}{T}$$

These formulae are also summarized by writing the following formula for the effective number of degrees of freedom in a relativistic gas,

$$g = \sum_{\text{bosons}} g_b + \frac{7}{8} \sum_{\text{fermions}} g_f$$