量子力学
Quantum mechanics

School of Physics and Information Technology
Shaanxi Normal University

Chapter 5

IDENTICAL PARTICLES

5.4 Quantum Statistical Mechanics

If we have a large number of N particles, in thermal equilibrium at temperature T, what is the probability that a particle would be found to have the specific energy, E_j?

The fundamental assumption of statistical mechanics is that in *thermal equilibrium* every distinct state with the same total energy, E, is equally probable.

The temperature, T, is a measure of the total energy of a system in *thermal equilibrium* in classical mechanics. *What is the new in quantum mechanics?* How to count the distinct states!

Why? Give a example to demonstrate!

5.4.1 An Example

Suppose we have just have three noninteracting particles, A, B, and C, (all of mass m) in the *one*-dimensional infinite square well. The total energy is

where n_A,n_B, and n_C are positive integers. Now suppose, for the sake of argument, that total energy

which is to say,

Thus (n_A,n_B,n_C) can be one of the following:

total

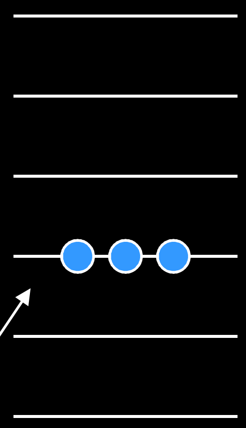
For example, (n_A,n_B,n_C)=(11,11,11) means n_A=11, n_B=11, n_C=11, and A,B,C in the single states

If the particles are distinguishable, the three-particle state is

The total number of probable (n_A,n_B,n_C) is 13.

The most important quantity is the number of particles in each state, that is, the occupation number, N_n, for the single state .

Configuration（排布）: The collection of all *occupation numbers* for a given (3-particle) state we will call the configuration.



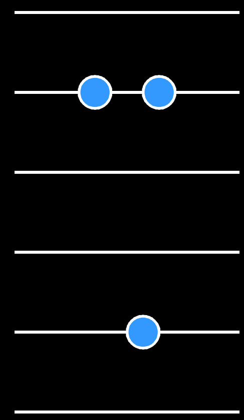
1. *Distinguishable condition:*

If the particles are *distinguishable*, each of these (n_A, n_B, n_C) represents *a* distinct quantum state, and the fundamental assumption of statistical mechanics says that in thermal equilibrium they are all equally likely.

If all the three particles are in , the configuration is

one state

If two are in and one is in , the configuration is



three different states

If two are in and one is in , the configuration is

$N_1 =$

three different states

If one is in , one in , and one is in , the configuration is

six different states

Of course, the last is the most probable configuration, because it can be achieved in six different ways, whereas the middle two occur three ways, and the first only one.

Under the above condition, if we select one of these three particles at random, what is the probability (P_n) of getting a specific (allowed) energy E_n ?

E_1 : Only the third configuration ➡ Probability 3/13

In the third configuration, two particles are in E_1 ➡ Probability 2/3

E_2 :

E_3 :

E_4 :

E_5 : the second configuration ➡ Probability 3/13

In the second configuration, one particle is in E_5 ➡ Probability 1/3

the fourth configuration ➡ Probability 6/13

In the fourth configuration, one particle is in E_5 ➡ Probability 1/3

E_7 : Only the fourth configuration $\Rightarrow$ Probability 6/13

In the fourth configuration, one particle is in E_7 $\Rightarrow$ Probability 1/3

E_{11} : Only the first configuration $\Rightarrow$ Probability 1/13

In the first configuration, three particles are in E_{11} $\Rightarrow$ Probability 3/3

Similarly

We can check this by total probability

$P = P_1$

Above analysis is based on the assumption that the three particles are *distinguishable*!

2. Identical fermions:

For fermions, no two particles are in the same state. This antisymmetrization requirement exclude the configurations where two particles are in the same state. Only the fourth configuration is available now!

E_1 :

E_5 : Only one configuration ⇨ Probability 1

In the fourth configuration, one particle is in E_5 ⇨ Probability 1/3

E_7 : In this configuration, one particle is in E_7 ⇨ Probability 1/3

E_{17} : In this configuration, one particle is in E_{17} ⇨ Probability 1/3

3. *Identical bosons:*

For bosons, each configuration enables one state, so

E_1 : The third configurations ⇨ Probability 1/4

In this configuration, two particles are in E_1 ⇨ Probability 2/3

E_5 : the second configuration ⇨ Probability 1/4

In the second configuration, one particle is in E_5 ⇨ Probability 1/3

the fourth configuration ⇨ Probability 1/4

In the fourth configuration, one particle is in E_5 ⇨ Probability 1/3

Similarly

Conclusion:

(1) This example shows that the nature of the particles determines the counting properties, or the statistical properties! The number of internal distinct states is different and the probability of getting specific energy is different too.

(2) This example gives a system of three particles. If the number of particles in huge, we can conclude: The distribution of individual particle energies, at equilibrium, is simply their distribution in the most *probable configuration*.

5.4.2 The General Case

Now consider an arbitrary potential, for which one particle energies are

with degeneracies

Suppose we put N particles (all with the same mass) into this potential; we are interested in the configuration

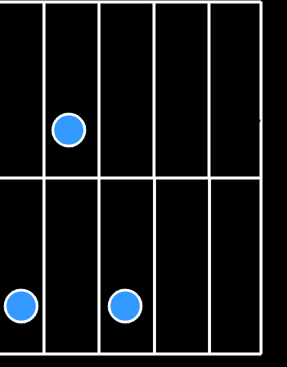
for which there are N_1 particles with energy E_1, N_2 particles with energy E_2, and so on.

Now we consider general question: *how many distinct states correspond to this particular configuration?*

The answer: *The number of the distinct states* $Q(N_1, N_2, N_3, \ldots\ldots)$ *depends on whether the particles are distinguishable, identical fermions, or identical bosons.*

1. *Distinguishable particles*:

(1) Choose N_1 from N for energy bin: the *binomial coefficient*



(2) Arrangement of the N_1 particles within the bin on the degenerate d_1 states:

(3) Thus the number of ways to put N_1 particles, selected from a total population of N, into a bin containing d_1 distinct option, is

(4) The same goes for energy bin E_2, of course, except that there are now only N-N_1 particles left to work with:

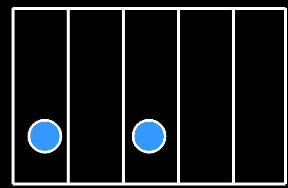
(5) Finally, it follows that

2. *Identical fermions:*

(1) The particles are identical.

(2) The antisymmetrization requires that only one particle can occupy any given state.

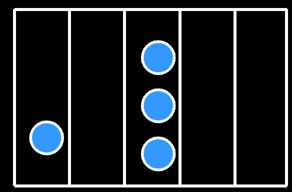
Here we pick N_1 draws from d_1 draws to locate particles.

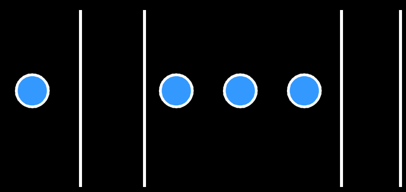


3. *Identical bosons:*

(1) The particles are identical.

(2) Although the wave function of the *N*-particle state is symmetry, more than one particles can occupy the draws in certain bin.





5.4.3 The Most Probable Configuration

In thermal equilibrium, every state with a given total energy E and a given particle number N is equally likely. So the most probable configuration $(N_1, N_2, N_3, \ldots\ldots)$ is the one that can be achieved in the largest number of different ways—— it is that particular configuration for which $Q(N_1,N_2,N_3,\ldots\ldots..)$ is a ***maximum***, subject to the constraints

The problem of maximizing a function $F(x_1, x_2, x_3,\ldots\ldots)$ of several variables, subject to the constraints $f\,(x_1, x_2, x_3,\ldots\ldots)=0$, $f\,(x_1, x_2, x_3,\ldots\ldots)=0$, etc., is most conveniently handled by the method of **Lagrange multipliers**. We introduce the new function and set all its derivatives equal to zero:

In our case it's a little easier to work with the logarithm of Q, instead of Q itself——this turns the products into sums. Since the logarithm is a monotonic function of its argument, the maxima of Q and $\ln(Q)$ occur at the same point. So we let

where α and β are the Lagrange multipliers.

1. ***Distinguishable particles*****:**

Assuming the relevant occupation numbers (N_n) are large, we can invoke **stirling's approximation**:

It follows that

The most probable occupation numbers, for distinguishable particles, are

2. Identical fermions:

Assume $N_n >> 1$ and $d_n >> N_n$, so the **stirling's approximation** applies

The most probable occupation numbers, for identical fermions, are

3. *Identical bosons:*

Assuming $N_n >> 1$ and using **stirling's approximation**

$d_n >> 1$

$\Rightarrow$

5.4.4 Physical significance of α and β

The parameters α and β came into the story as Lagrange multipliers, associated with the total number of particles and the total energy.

Mathematically, they are determined by substituting the most probable occupation numbers N_n back into the constraints.

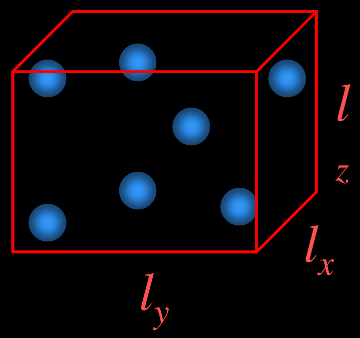
$\Rightarrow$ α and β

To carry out the summation, E_n and d_n should be know for particular potential.

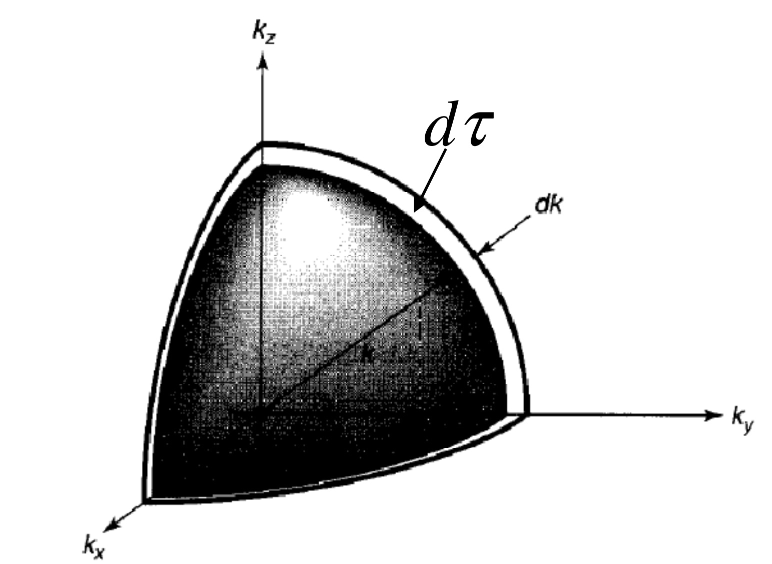
By using **an example** to do this: *ideal gas*

Idea gas: a large number of noninteracting particles, all with the same mass, in the three dimensional infinite square well—— a box!

We know that the allowed energies of the particle are



where



A shell of thickness *dk* contains a volume

so the "degeneracy" is (the number of electron states in the shell)

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

For distinguishable particles, the first constraint becomes

In the *k*-space, the sum will be converted into an integral, treating *k* as a continuous variable, then

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdot \cdots \cdot (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

so

The second constraint becomes

Or, putting in :

The average kinetic energy of an atom at temperature *T*, in classical mechanic, is

Boltzmann constant

This suggests that ***β*** is related to the temperature:

Different substances in thermal equilibrium with one another have the same value of ***β*** , and which can be adopted as s definition of *T*.

Then

It is customary to replace ***α*** by the so-called **chemical potential**, By using the **chemical potential**, we can rewrite the most probable number of particles in a particular (one-particle) state with energy ε :

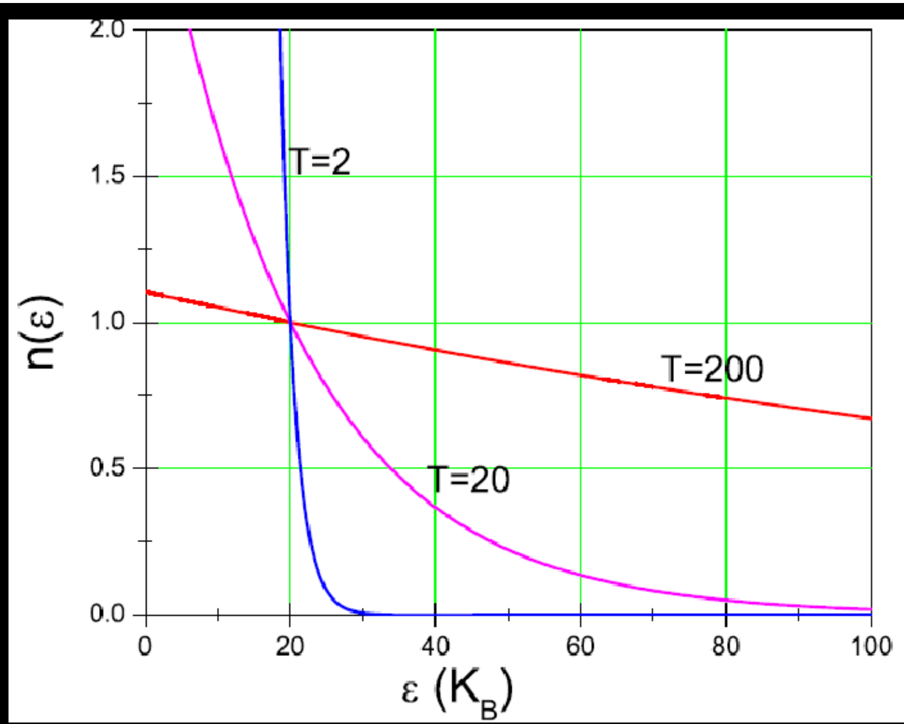
Maxwell-Boltzmann distribution

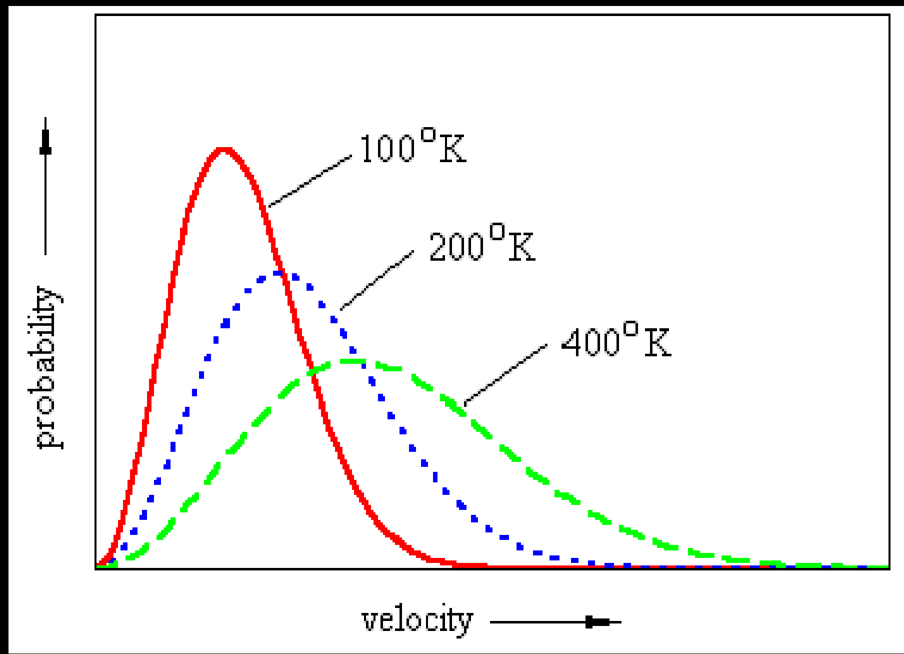
Fermi-Dirac distribution

Bose-Einstein distribution

The Maxwell-Boltzmann distribution is the classical result, for distinguishable particles; the Fermi-Dirac distribution applies to identical fermions, and the Bose-Einstein distribution is for identical bosons.

Maxwell-Boltzmann distribution

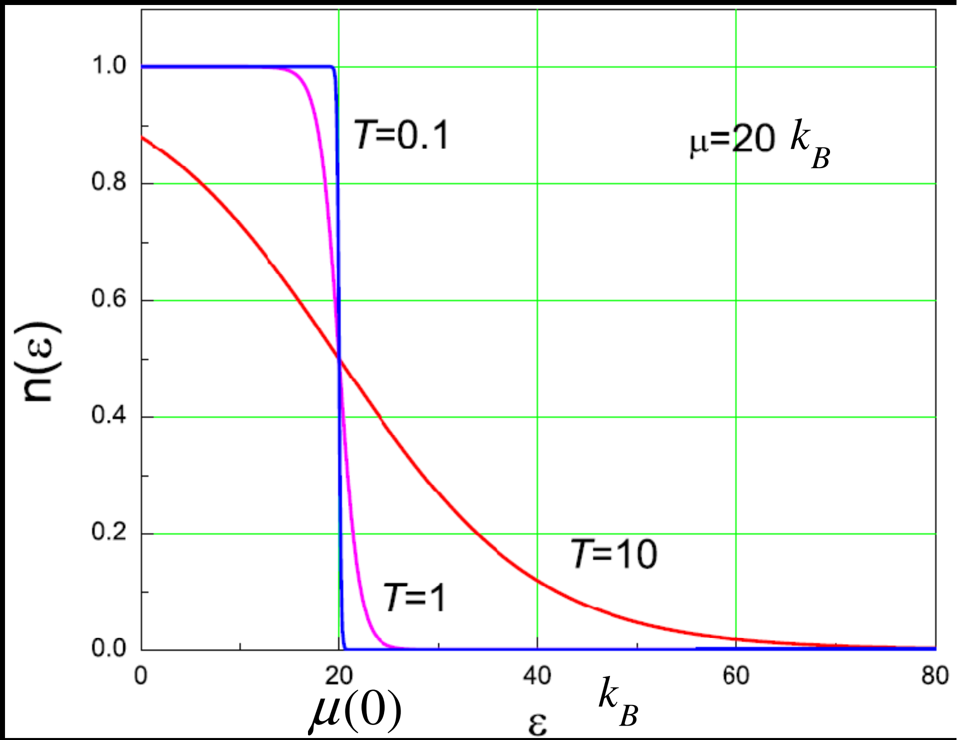




$n(v) = e$

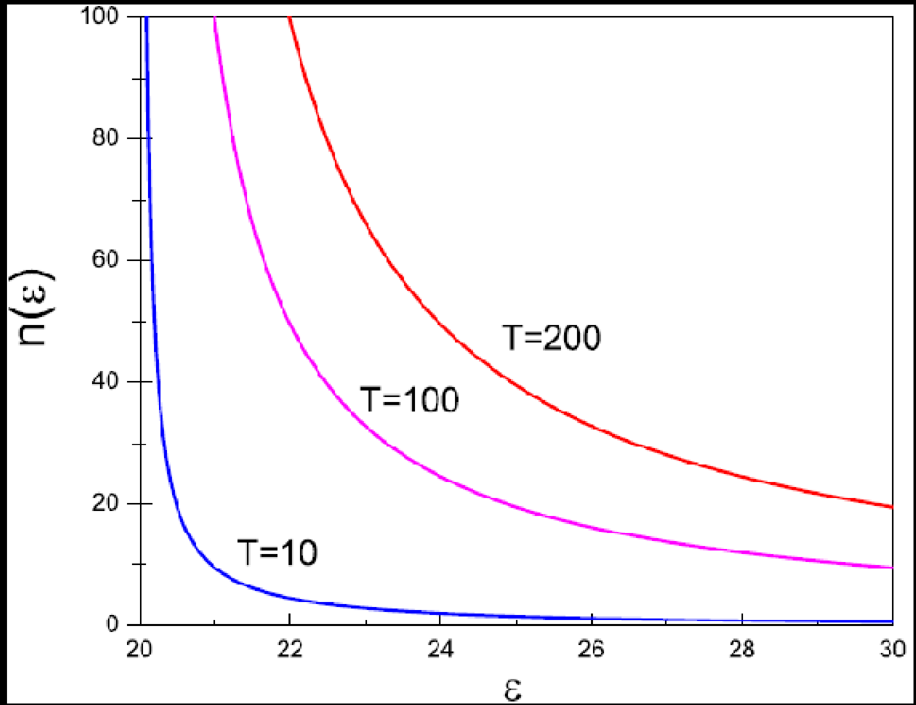
The Fermi-Dirac distribution has a particularly simple behavior as :

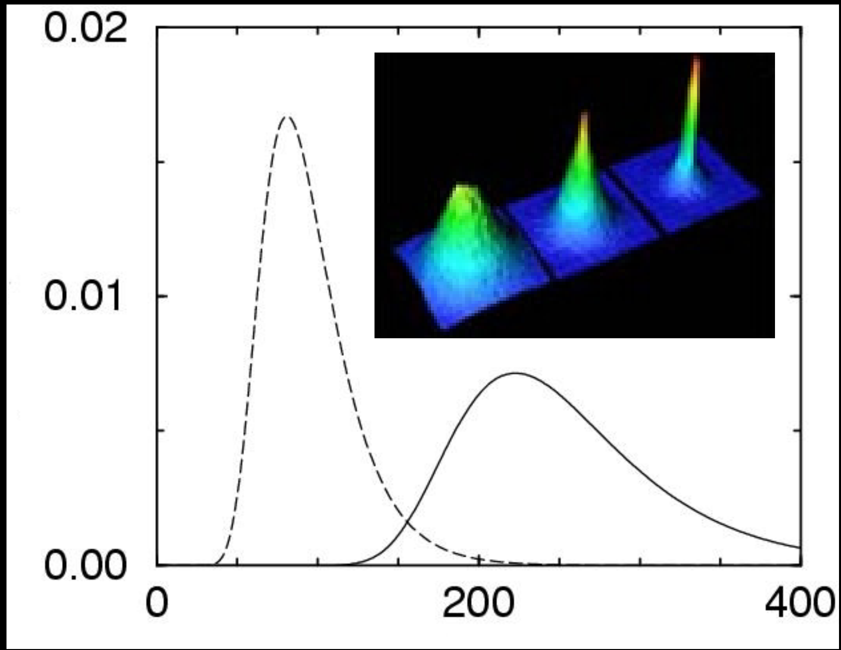
As



All states are filled, up to an energy $\mu(0)$, and none are occupied for energies above $\mu(0)$. Evidently the chemical potential at absolute zero is precisely the Fermi energy:

Bose-Einstein distribution





Returning to the special case of an ideal gas, for distinguishable particles we found that the total energy at temperature *T* is

and the chemical potential is

5.4.5 The Blackbody Spectrum

Photons (quantum of the electromagnetic field) are identical bosons with spin 1, but they are very special, because they are massless particles, and hence intrinsically relativistic. There are four properties belong to nonrelativistic quantum mechanics:

(1) Energy:

(2) Wave number:

(3) Spin: two spin states occur, $m=1$ or -1.

(4) The number of the photons are not conserved:

For free photons in a box of volume V, d_k is given by

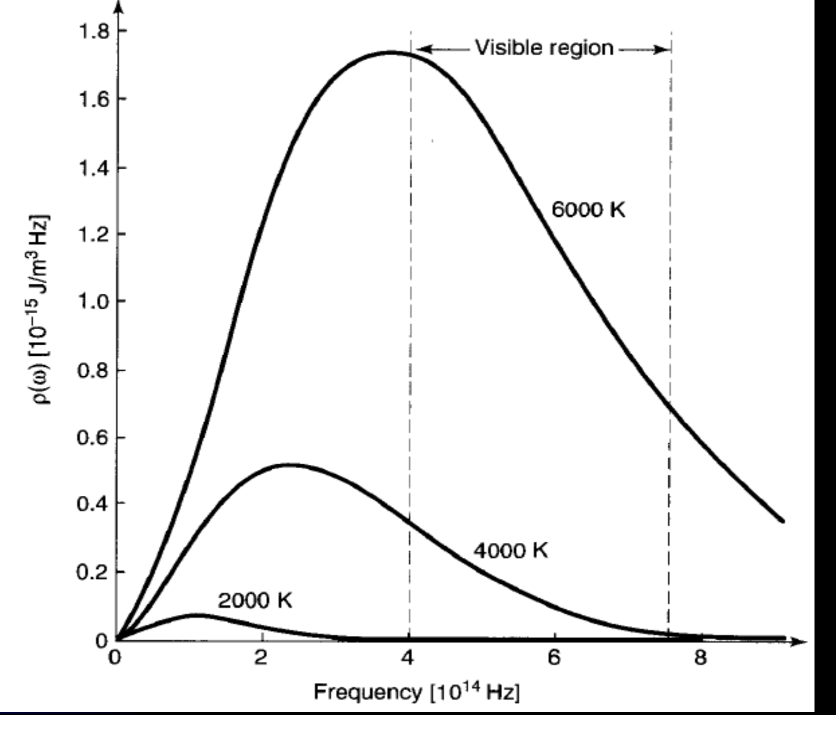
multiplied by 2 for two spin states, and expressed in terms of

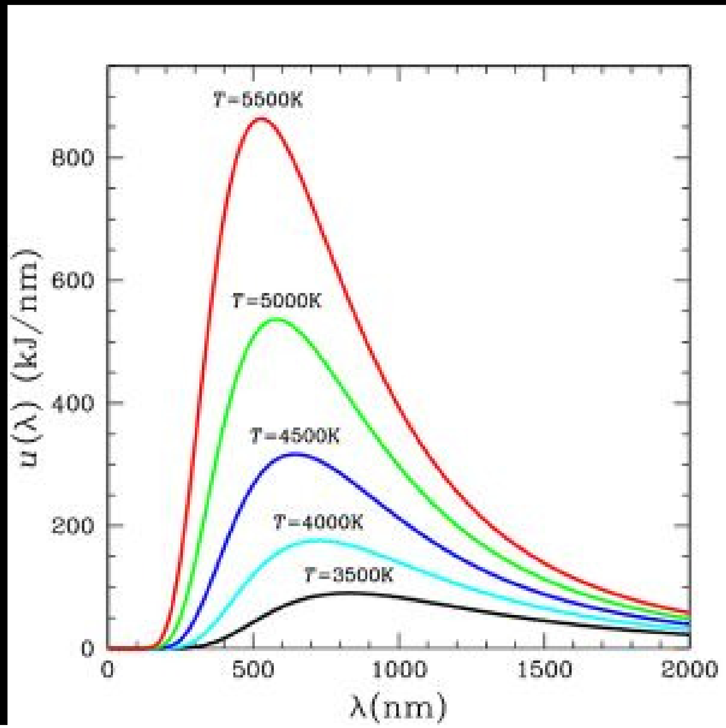
So the energy density,

That is

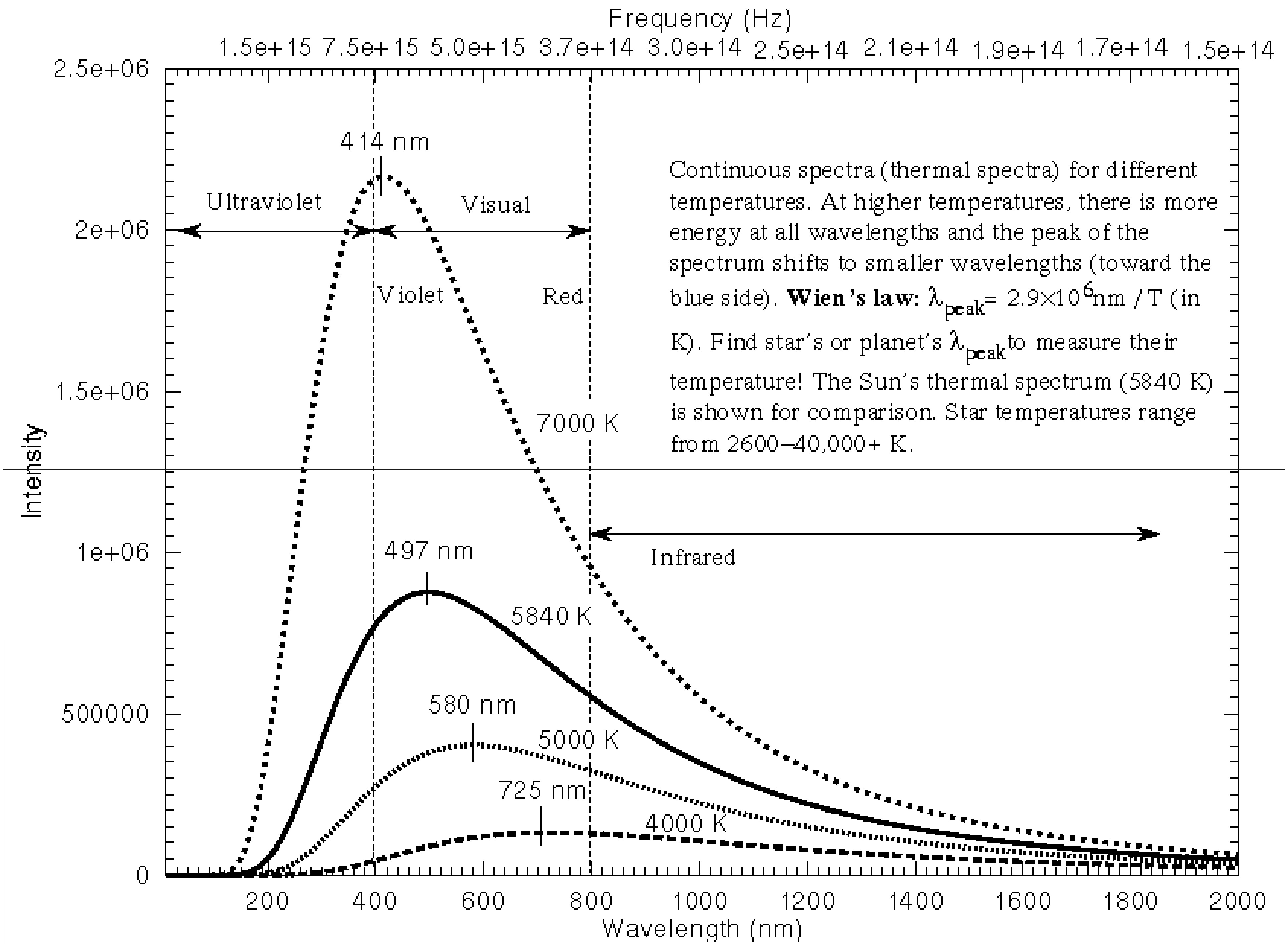
We introduce energy density per unit frequency:

This is **Plank's famous formula** for the blackbody spectrum, giving the energy per unit volume, per unit frequency, for an electromagnetic field in equilibrium at temperature *T*.





T=5500K
T=5000K
T=4500K
T=4000K
T=3500K
u(λ) (kJ/nm)
λ(nm)
0
200
400
600
800
500
1000
1500
2000



Frequency (Hz)
1.5e+15 7.5e+15 5.0e+15 3.7e+14 3.0e+14 2.5e+14 2.1e+14 1.9e+14 1.7e+14 1.5e+14
2.5e+06
2e+06
1.5e+06
1e+06
500000
0
Intensity
414 nm
Ultraviolet
Visual
Violet
Red
7000 K
497 nm
5840 K
580 nm
5000 K
725 nm
4000 K
Infrared
200 400 600 800 1000 1200 1400 1600 1800 2000
Wavelength (nm)
Continuous spectra (thermal spectra) for different temperatures. At higher temperatures, there is more energy at all wavelengths and the peak of the spectrum shifts to smaller wavelengths (toward the blue side). **Wien's law:** $\lambda_{peak} = 2.9\times10^6 nm / T$ (in K). Find star's or planet's λ_{peak} to measure their temperature! The Sun's thermal spectrum (5840 K) is shown for comparison. Star temperatures range from 2600–40,000+ K.