A one dimensional simple harmonic oscillator is in equilibrium with a heat reservoir at absolute temperature T. Deduce the expression for the partition function of the system. Hence find out the expression for mean energy. What will be the values of average energy in the limiting cases of high and low temperatures? Are they in agreement with classical theory?

Consider a one-dimensional harmonic oscillator at temperature T. If ν is the oscillator frequency, the energy levels available for the oscillator are given by

$$E_n = \left(n + \frac{1}{2}\right) h \upsilon$$
 n = 0, 1, 2, (1)

The mean energy of the oscillator is given by

Where

$$\overline{\mathbf{E}} = kT^2 \frac{\partial \ln Z}{\partial T}$$

$$Z = \sum_{n=0}^{\infty} \exp(-E_n / kT) = e^{-\frac{1}{2}h\upsilon/kT} \sum_{n=0}^{\infty} \exp(-nh\upsilon/kT) = e^{-\frac{1}{2}h\upsilon/kT} \sum_{n=0}^{\infty} \exp(-h\upsilon/kT)^n$$
(2)
(3)

The summation term in the above expression is equivalent to the summation

$$Z = \sum_{n=0}^{\infty} x^{n} = (1-x)^{-1} = 1 + x + x^{2} + x^{3} + \dots$$

$$Z = \frac{e^{-\frac{1}{2}h\nu/kT}}{1-e^{-h\nu/kT}} = \frac{e^{-\frac{1}{2}h\nu/kT}}{1-e^{-h\nu/kT}} = \frac{e^{-\frac{1}{2}h\nu/kT}}{1-\frac{1}{e^{h\nu/kT}}} = \frac{e^{\frac{1}{2}h\nu/kT}}{e^{h\nu/kT} - 1}$$

$$\Rightarrow \ln Z = \frac{1}{2}\frac{h\nu}{kT} - \ln(e^{h\nu/kT} - 1)$$

$$(4)$$

$$\therefore \overline{E} = kT^{2}\frac{\partial}{\partial T} [\frac{1}{2}\frac{h\nu}{kT} - \ln(e^{h\nu/kT} - 1)] = -\frac{1}{2}h\nu - \frac{e^{h\nu/kT}(-h\nu)}{e^{h\nu/kT} - 1}$$

$$\Rightarrow \overline{E} = \frac{-\frac{1}{2}h\nu e^{h\nu/kT} + \frac{1}{2}h\nu + e^{h\nu/kT}(h\nu)}{e^{h\nu/kT} - 1} = \frac{\frac{1}{2}h\nu + \frac{1}{2}h\nu e^{h\nu/kT}}{e^{h\nu/kT} - 1}$$

$$= \frac{h\nu - \frac{1}{2}h\nu + \frac{1}{2}h\nu e^{h\nu/kT}}{e^{h\nu/kT} - 1} = \frac{1}{2}h\nu(e^{h\nu/kT} - 1) + h\nu}{e^{h\nu/kT} - 1} = h\nu \left[\frac{1}{2} + \frac{1}{e^{h\nu/kT}}\right]$$

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(5)



In this case it is possible to neglect the higher order terms in the

Expression of
$$e^{\frac{hv}{kT}}$$

Eq. (5) gives $\overline{E} = hv \left[\frac{1}{2} + \frac{1}{\frac{hv}{kT} + \frac{1}{2} \left(\frac{hv}{kT}\right)^2 + \dots} \right] = hv \left[\frac{1}{2} + \frac{kT}{hv} \left(1 + \frac{1}{2} \frac{hv}{kT} \right)^{-1} \right]$
Using $(1+x)^{-1} = 1 - x + x^2 - x^3 + \dots$

$$\overline{\mathbf{E}} \cong \mathbf{h}\upsilon \left[\frac{1}{2} + \frac{kT}{h\upsilon} \left(1 - \frac{1}{2}\frac{h\upsilon}{kT}\right)\right] = kT$$

This is identical to the classical result, as expected.

2) Low temperature:

$$\frac{h\upsilon}{kT} >> 1$$

In this case,
$$\frac{1}{e^{h\upsilon/kT}-1} \cong \frac{1}{e^{h\upsilon/kT}} = e^{-h\upsilon/kT} \cong 0$$

Therefore, $\overline{E} \cong \frac{1}{2}hv$

This nonvanishing limiting value, called the zero point energy of the oscillator, cannot be explained classically and is due to the uncertainty principle.

Discuss the behavior of the fermi function. Show that the derivative of the fermi function is symmetrical about $E = E_{F}$.

The fermi function is given by:

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$
(1)
where E_F is the fermi energy (this is also called the chemical potential)
where E_F is the fermi energy (this is also called the chemical potential)
If $\frac{E_F}{kT} \ll 0$ then $e^{(E-E_F)/kT} \gg 1$

Therefore, F-D distribution function reduces to M-B function.

We, are, however, interested in the opposite limit where

$$\frac{\mathbf{E}_{\mathrm{F}}}{\mathrm{kT}} >> 0$$

 \mathbf{T}

In this case E << E_F, then $\frac{E - E_F}{kT} \ll 0$ So that F(E) =1 On the other hand, E >> E_F, then $\frac{E - E_F}{kT} >> 0$ So that $f(E) = e^{(E - E_F)/kT}$ falls off exponentially like a classical M-B distribution. If $E = E_F$, then $f(E) = \frac{1}{2}$ The transition region in which f(E) goes from a value close to unity to a value close to zero corresponds to an energy interval of the order of kT about $E=E_{F}$

In the limit T \rightarrow 0, the transition region is infinitesimally narrow and f(E) is given by the step function.

$$f(E) = \begin{cases} 0 & E < E_F \\ 1 & E > E_F \end{cases}$$

The derivative of the fermi function $f'(E) = \frac{\partial f(E)}{\partial E}$

is symmetrical about $E = E_F$. To see this, we obtain from eq (1)

$$f'(E) = \frac{e^{(E-E_F)/kT} (E_F/kT)}{(e^{(E-E_F)/kT} + 1)^2}$$

$$= (\frac{E_F}{kT}) \frac{e^{(E-E_F)/kT}}{(e^{2(E-E_F)/kT} + 2e^{(E-E_F)/kT} + 1)}$$

$$= (\frac{E_F}{kT}) \frac{1}{(e^{(E-E_F)/kT} + e^{-(E-E_F)/kT} + 2)}$$
(2)

Now in eq (2), if we replace $(E-E_F)$ by $-(E-E_F)$, the expression for f'(E) does not change. Therefore, f'(E) is symmetrical about $E = E_F$.

Plot the Fermi function at different temperatures and explain the significance

The significance of the plot is as follows: At absolute zero the fermi gas is in ground state. Since the Pauli exclusion principle requires that there be no more than one fermion per state, all the lowest states will be occupied until the fermions are all accommodated. The fermi level, in this case, is simply the highest occupied state and above this energy level all the states are unoccupied.



At a slightly higher temperature, T_1 , thermal energy excites the fermions. But the fermions lying well below the fermi level cannot absorb thermal energy because if they did so, they would move to a higher level which would be already occupied, and hence the exclusion principle would be violated.

Therefore, only those electrons close to the fermi level can be excited since the level above EF are empty. The shape of the plot is thus only slightly distorted about $E=E_F$. In a still higher temperature T_2 , even more fermions can be excited, the plot is further distorted about $E=E_F$.

Problems Related to Statistical Mechanics

Problem 1: Calculate the relative number of atoms of hydrogen gas present in ground state and first excited state at room temperature and at very high temperature of 5000 K. Assume M-B statistics to hold good for the hydrogen gas.

Maxwell-Boltzmann Distribution Jaw: $n_i = \frac{g_i}{\rho^{\alpha} \rho^{E_i/kT}}$

In the ground state i = 1, there are two possible electron configuration. Similarly, the first excited state i = 2, there are eight possible electron configuration.

$$n(E_{1}) = \frac{g(E_{1})}{e^{\alpha}e^{E_{1}/kT}} \quad \text{where, } g(E_{1}) = 2, E_{1} = -13.6 \text{ eV} = -13.6 \times 1.6 \times 10^{-19} \text{ J}$$
$$n(E_{2}) = \frac{g(E_{2})}{e^{\alpha}e^{E_{2}/kT}} \quad \text{where, } g(E_{1}) = 8, E_{2} = -3.4 \text{ eV} = -3.4 \times 1.6 \times 10^{-19} \text{ J}$$

$$: \frac{n(E_2)}{n(E_1)} = \frac{g(E_2)}{g(E_1)} e^{(E_1 - E_2)/kT} = \frac{8}{2} e^{-10.2/kT}$$

At room temperature T = (25 + 273) = 298 K

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Therefore, the hydrogen atom at higher temperature is greatly increased.

Problem 2: In a system in thermal equilibrium at absolute temperature T, two states with energy difference 4.83×10⁻²¹ J occur with relative probability e². Deduce the temperature.

According to the M-B distribution law, the probability of a particle for having an energy E is given by:



$$\Rightarrow T = \frac{4.83 \times 10^{-21}}{1.38 \times 10^{-38} \ln(e^2)} = 175 \, K$$

Problem 3: There are a large number of particles each of mass 0.1 gm all lying in a box at an equilibrium temperature 300 K. Calculate the probability that any of them will spontaneously fly to a height 1 Å. Assume that they obey M-B statistics. (k = 1.38×10^{-23} J/K)

The probability of a particle for having an energy E is given by:

$$n(E) = \frac{2\pi}{\left(\pi kT\right)^{3/2}} \sqrt{E}e^{-E/kT}$$

In order to fly to a height 1 Å, the particle must have the energy

E = mgh =
$$0.1 \times 10^{-3} \times 9.8 \times 10^{-10}$$
 J = 9.8×10^{-14} J kT = 1.38×10^{-23} J/K $\times 300$ K = 4.14×10^{-21} J

$$\frac{E}{kT} = \frac{9.8 \times 10^{-14}}{4.14 \times 10^{-21}} = 2.37 \times 10^{7}$$
$$\therefore e^{-E/kT} = e^{-2.37 \times 10^{7}} \approx 0$$

So the probability is almost zero.