1. Consider a molecule with a permanent electric dipole moment $\vec{p}$ placed in an electric field $\vec{\mathcal{E}}$, with $\vec{p}$ aligned either parallel or anti-parallel to $\vec{\mathcal{E}}$.

   (a) Recall that the energy of a dipole in an electric field is given by $E = -\vec{p}\cdot\vec{\mathcal{E}}$, and show that this system has two allowed energy states separated by $2p\mathcal{E}$.

   (b) For simplicity assume a ground state energy of 0 and an excited state energy of $2p\mathcal{E}$ and degeneracies in the ratio $g(2p\mathcal{E})/g(0) = 2/1$. For a collection of N molecules obeying Maxwell-Boltzmann statistics, calculate the ratio of the number of molecules in the excited state to the number in the ground state at temperature T.

   (c) For high T such that $k_BT \gg 2p\mathcal{E}$, the ratio of the number of molecules in the upper state to the number in the lower is 2 to 1. Taking reasonable estimates of $p = 1.0\times10^{-30}\ C\cdot m$ and $\mathcal{E} = 1.0\times10^{6}\ V/m$, find the temperature at which the ratio has fallen by a measurable 10% to 1.9 to 1.

   (d) Calculate the average energy $\overline{E}$ at T and show that $\overline{E}\to 0$ as $T\to 0$ and $\overline{E}\to 4p\mathcal{E}/3$ as $T\to\infty$

   (e) Find E_{totatl} from $\overline{E}$, and show that the heat capacity for this two-level system is

$$C = \left(\frac{Nk_B}{2}\right)\left(\frac{2p\mathcal{E}}{k_BT}\right)^2\left(\frac{e^{2p\mathcal{E}/k_BT}}{(1+\frac{1}{2}e^{2p\mathcal{E}/k_BT})}\right)$$

   (f) Sketch C as a function of $2p\mathcal{E}/k_BT$. Find the value of $2p\mathcal{E}/k_BT$ at which C is a maximum, and explain, in physical terms, the dependence of C on T.

Solution

(a) Let the energy of the parallel case be E_U and the energy of the anti-parallel case be E_D, we then have:

$$\begin{aligned}
E_U &= -\vec{p}\cdot\vec{\mathcal{E}}\\
&= -p\mathcal{E}\cos(0)\\
&= -p\mathcal{E}\\
E_D &= -\vec{p}\cdot\vec{\mathcal{E}}\\
&= -p\mathcal{E}\cos(180)\\
&= p\mathcal{E}\\
\Delta E &= E_D - E_U\\
&= 2p\mathcal{E}
\end{aligned}$$

(b) Let $n(2p\mathcal{E})$ be the number of molecules in the excited state with energy $2p\mathcal{E}$. Then the ration of the number of molecules in the excited state to that in the ground state is:

$$\begin{aligned} \frac{n(2p\mathcal{E})}{n(0)} &= \frac{g(2p\mathcal{E})Ae^{-2p\mathcal{E}/k_BT}}{g(0)Ae^0} \\ &= 2e^{-2p\mathcal{E}/k_BT} \end{aligned} \tag{1}$$

(c) Using Equation (1) we get;

$$\begin{aligned} 1.9 &= 2e^{-2p\mathcal{E}/k_BT} \\ \ln(1.9/2) &= -\frac{2p\mathcal{E}}{k_BT} \\ T &= -\frac{2p\mathcal{E}}{k_B\ln(0.95)} \\ &= -\frac{2\times 1.0\times 10^{-30}\times 1.0\times 10^{6}}{1.38\times 10^{-23}\times -5.13\times 10^{-2}} \\ &= 2.83\ K \end{aligned}$$

(d) the average energy $\overline{E}$ is given by:

$$\begin{aligned} \overline{E} &= \frac{n(2p\mathcal{E})\times(2p\mathcal{E})+n(0)\times 0}{n(2p\mathcal{E})+n(0)} \\ &= \frac{\frac{n(2p\mathcal{E})}{n(0)}\times 2p\mathcal{E}}{\frac{n(2p\mathcal{E})}{n(0)}+1} \end{aligned}$$

using Equation (1), we get:

$$\begin{aligned} \overline{E} &= \frac{2e^{-2p\mathcal{E}/k_BT}\times 2p\mathcal{E}}{2e^{-2p\mathcal{E}/k_B}+1} \\ &= \frac{2p\mathcal{E}}{1+\frac{1}{2}e^{2p\mathcal{E}/k_BT}} \end{aligned}$$

As $T\rightarrow 0$, $e^{2p\mathcal{E}/k_BT}\rightarrow\infty$ and $\overline{E}\rightarrow 0$, and as $T\rightarrow\infty$, $e^{2p\mathcal{E}/k_BT}\rightarrow 1$ and $\overline{E}\rightarrow 4p\mathcal{E}/3$.

(e) The total energy is E_{total} the average energy $\overline{E}$ times the total number of molecules N, i.e.

$$\begin{aligned} E_{total} &= N\overline{E} \\ &= \frac{2Np\mathcal{E}}{1+\frac{1}{2}e^{2p\mathcal{E}/k_BT}} \end{aligned}$$

The heat capacity C is given by:

$$\begin{aligned} C &= \frac{dE_{total}}{dT} \\ &= \frac{\left(\frac{Nk_B}{2}\right)\left(\frac{2p\mathcal{E}}{k_BT}\right)^2 e^{2p\mathcal{E}/k_BT}}{\left(1+\frac{1}{2}e^{2p\mathcal{E}/k_BT}\right)^2} \end{aligned}$$

(f) Let $x = 2p\mathcal{E}/k_BT$, then the heat capacity C becomes:

$$C = \frac{Nk_B x^2 e^x}{2(1+\frac{1}{2}e^x)^2} \tag{2}$$

When $T \to \infty$, $x \to 0$, and we find from Equation (2) that $C \to 0$.

A plot of Equation (2) as $C/(Nk_B/2)$ vs x is shown in Figure (1).

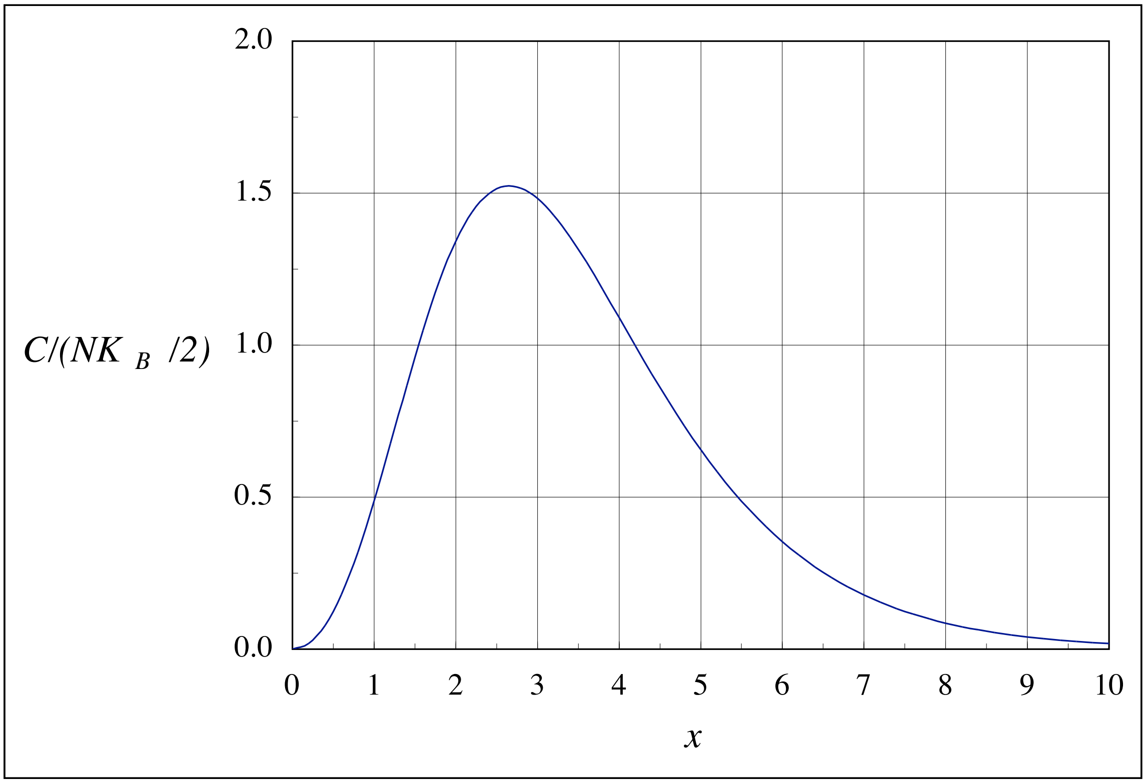

Figure 1:

Equation (2) can be written as:

$$\begin{aligned} C &= \frac{Nk_B x^2 e^x}{2(1+\frac{1}{2}e^x)^2} \\ &= \left(\frac{Nk_B}{2}\right)\frac{x^2 e^x}{1+e^x+\frac{1}{4}e^{2x}} \\ &= \left(\frac{Nk_B}{2}\right)\frac{x^2}{e^{-x}+1+\frac{1}{4}e^x} \\ &= \left(\frac{Nk_B}{2}\right)\frac{x^2}{1+e^{-x}+\frac{1}{4}e^x} \\ &= \left(\frac{Nk_B}{2}\right)\frac{1}{\frac{1}{x^2}\left(1+e^{-x}+\frac{1}{4}e^x\right)} \qquad (3) \\ \frac{C}{\frac{1}{2}Nk_B} &= \frac{1}{\frac{1}{x^2}\left(1+e^{-x}+\frac{1}{4}e^x\right)} \qquad (4) \end{aligned}$$

Now, using $e^x = 1 + x + x^{/2!} + x^3/3! + \cdots$ and $e^{-x} = 1 - x + x^2/2! - x^3/3! + \cdots$ in Equation (4) we get:

$$\begin{aligned} \frac{C}{\frac{1}{2}Nk_B} &= \frac{1}{\frac{1}{x^2}\left(1+e^{-x}+\frac{1}{4}e^x\right)} \\ &= \frac{1}{\frac{1}{x^2}\left[1+(1-x+x^2/2!-x^3/3!+\cdots)+\frac{1}{4}(1+x+x^2/2!+x^3/3!+\cdots)\right]} \\ &= \frac{1}{\left(\frac{2}{x^2}-\frac{1}{x}+\frac{1}{2}-\frac{x}{3!}+\cdots\right)+\frac{1}{4}\left(\frac{2}{x^2}+\frac{1}{x}+\frac{1}{2}+\frac{x}{3!}+\cdots\right)} \qquad (5) \end{aligned}$$

As $T \to 0$, $x \to \infty$ and the right hand side of Equation (5) $\to 0$, i.e. $C \to 0$ as $T \to 0$ and as $T \to \infty$.

To find the value of $2p\mathcal{E}/k_BT$ at which C is maximum, we set the derivative of Equation (2) to zero, i.e.

$$\begin{aligned} \frac{dC}{dx} &= 0 \\ &= \frac{Nk_B}{2}\left[\frac{2xe^x}{(1+\frac{1}{2}e^x)^2}+\frac{x^2e^x}{(1+\frac{1}{2}e^x)^2}-\frac{x^2e^x}{(1+\frac{1}{2}e^x)^3}\right] \\ &= \frac{Nk_B}{2}\,\frac{x^2e^x}{(1+\frac{1}{2}e^x)^2}\left[2+x-\frac{xe^x}{(1+\frac{1}{2}e^x)}\right] \qquad (6) \end{aligned}$$

The condition for maximum C is obtained from Equation (6) as:

$$\begin{aligned}
0 &= 2 + x - \frac{xe^x}{(1 + \frac{1}{2}e^x)} \\
&= 2 + e^x + x + \frac{1}{2}xe^x - xe^x \\
\frac{2+x}{x-2} &= \frac{1}{2}e^x \qquad (7)
\end{aligned}$$

we can find the solution of Equation (7) by plotting the two functions: $y = \frac{x+2}{x-2}$ and $y = \frac{1}{2}e^x$ on the same graph and locate the point of intersection. The plot of the two functions is shown in Figure (2). The two curves intersect at $x \approx 2.65$, so

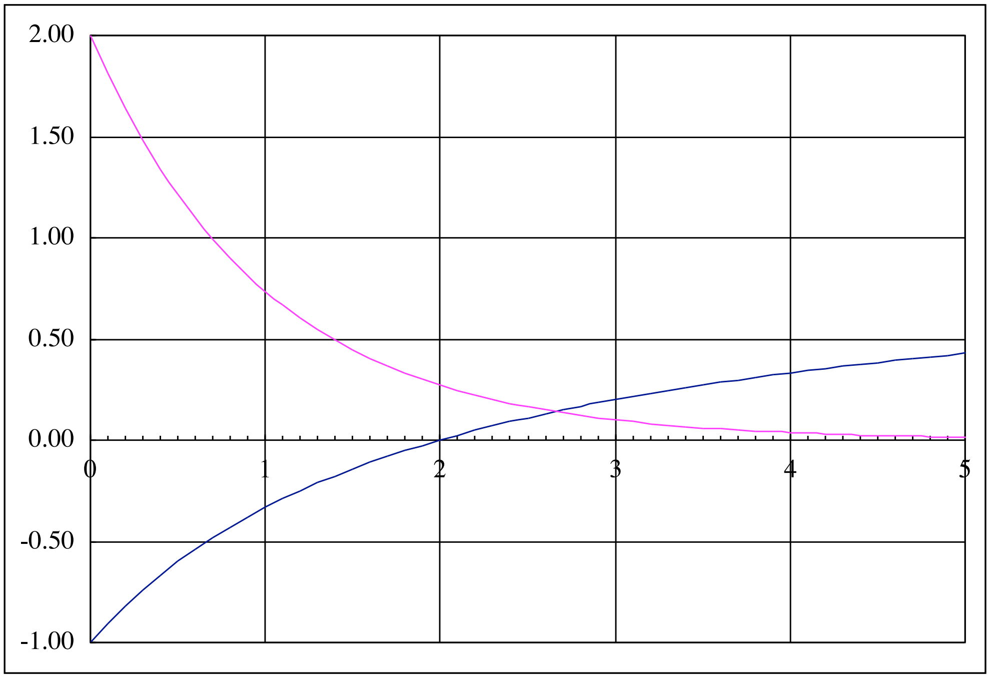

Figure 2:

this is the value of $2p\mathcal{E}/k_BT$ at which C is maximum. The temperature at which

C is maximum is then given by:

$$\begin{aligned} 2.65 &= \frac{2p\mathcal{E}}{k_B T} \\ T &= \frac{2p\mathcal{E}}{2.65 k_B} \\ &= 0.0547\ K \end{aligned}$$

---

2. The rotational motion of molecules has an effect on the equilibrium separation of the nuclei, a phenomenon known as "bond stretching". To model this effect, consider a diatomic molecule with reduced mass μ, oscillator frequency $\omega_\circ$, and internuclear separation $R_\circ$ when the angular momentum is zero. The effective potential energy for nonzero values of ℓ is then

$$U_{eff}(r) = \frac{1}{2}\mu\omega_\circ^2(r - R_\circ)^2 + \ell(\ell+1)\,\frac{\hbar^2}{2\mu r^2} \tag{8}$$

   (a) Minimize the effective potential $U_{eff}(r)$ to find an equation for the equilibrium separation of the nuclei, R_ℓ, when the angular momentum is ℓ. Solve this equation approximately, assuming $\ell \ll \mu\omega_\circ R_\circ^2/\hbar$.

   (b) Near the corrected equilibrium point, R_ℓ, the effective potential again is nearly harmonic and can be written approximately as

$$U_{eff}(r) \approx \frac{1}{2}\mu\omega_\circ^2(r - R_\ell)^2 + U_\circ \tag{9}$$

   Find expressions for the corrected oscillator frequency ω and the energy offset $U_\circ$ by matching U_{eff} and its first two derivatives at the equilibrium point R_ℓ. Show that the fractional change in frequency is given by

$$\frac{\Delta\omega}{\omega_\circ} \approx \frac{3\ell(\ell+1)\hbar^2}{2\mu^2\omega_\circ^2 R_\circ^4}$$

Solution

(a) At the equilibrium separation R_ℓ, the effective potential energy U_{eff} is minimum,

$$\begin{aligned} 0 &= \left.\frac{dU_{eff}}{dr}\right|_{R_\ell} \\ &= \mu\omega_\circ^2(R_\ell - R_\circ) - \frac{\ell(\ell+1)\hbar^2}{\mu R_\ell^3} \\ R_\ell &= R_\circ + \left[\frac{\ell(\ell+1)\hbar^2}{\mu^2\omega_\circ^2}\right]\left(\frac{1}{R_\ell^3}\right) \end{aligned} \tag{10}$$

when $\ell \ll \mu\omega_\circ R_\circ/\hbar$, the second tern on the right hand side of Equation (10) is small and is only a small correction to $R_\circ$, which is the equilibrium separation at zero angular momentum. For a small angular momentum, ℓ, then R_ℓ is very close to $R_\circ$. We then can replace R_ℓ in the second term in Equation (10) by $R_\circ$.

$$R_\ell \approx R_\circ + \left[\frac{\ell(\ell+1)\hbar^2}{\mu^2\omega_\circ^2}\right]\left(\frac{1}{R_\circ^3}\right) \tag{11}$$

(b) From Equation (8) we see that the energy offset $U_\circ$, is the effective potential energy at R_ℓ,

$$\begin{aligned} U_\circ &= U_{eff}(R_\ell) \\ &= \frac{1}{2}\mu\omega_\circ^2\left[R_\circ + \frac{\ell(\ell+1)\hbar^2}{\mu^2\omega_\circ^2}\frac{1}{R_\ell^3} - R_\circ\right]^2 + \frac{\ell(\ell+1)\hbar^2}{2\mu R_\ell^2} \\ &= \frac{\ell(\ell+1)\hbar^2}{2\mu R_\ell^2}\left[\frac{\ell(\ell+1)\hbar^2}{\mu\omega_\circ^2}\frac{1}{R_\ell^4} + 1\right] \end{aligned} \tag{12}$$

The first tern inside the square brackets on the right of Equation (12) is small and can be ignored, we then have:

$$U_\circ \approx \frac{\ell(\ell+1)\hbar^2}{2\mu R_\ell^2}$$

The force constant K is related to the frequency ω of molecular vibration and the effective potential energy U_{eff} by:

$$\begin{aligned} K &= \mu\omega^2 \\ &= \frac{d^2U_{eff}}{dr^2} \end{aligned}$$

So, it is posible to relate the frequency at angular momentum state $\omega_\circ$ to the frequency at a state of zero angular momentum $\omega_\circ$, by taking the second derivative of Equation (8) and equate it to $\mu\omega_\ell$,

$$\begin{aligned} \frac{d^2U_{eff}}{dr^2} &= \mu\omega_\circ^2 + \frac{3\ell(\ell+1)\hbar^2}{\mu R_\ell^4} \\ &= \mu\omega_\ell^2 \\ \omega_\ell^2 &= \omega_\circ^2 + \frac{3\ell(\ell+1)}{\mu R_\ell^4} \end{aligned}$$

Since $R_\ell \approx R_\circ$ and for $\ell \ll \mu\omega_\circ R_\circ/\hbar$, we than can write:

$$\omega_\ell^2 \approx \omega_\circ^2 + \frac{3\ell(\ell+1)}{\mu R_\circ^4}$$

The second term on the right is small and $\omega_\ell \approx \omega_\circ$, so

$$\begin{aligned} \omega_\ell^2 - \omega_\circ^2 &= (\omega_\ell - \omega_\circ)(\omega_\ell + \omega_\circ) \\ &\approx 2\omega_\circ\Delta\omega \end{aligned}$$

the fractional change is then;

$$\frac{\Delta\omega}{\omega_\circ} \approx \frac{3\ell(\ell+1)\hbar^2}{2\mu^2\omega_\circ^2 R_\circ^4}$$

3. To obtain a more clearly defined picture of the Fermi-Dirac distribution, consider a system of 20 Fermi-Dirac particles sharing 94 units of energy. By drawing diagrams like Figure (3), show that there are nine different microstates. Using

$$\overline{n_j} = n_{j1}p_1 + n_{j2}p_2 + \cdots$$

calculate and plot the average number of particles in each energy level from 0 to $14E$. Locate the Fermi energy at 0 K on your plot from the fact that electrons at 0 K fill all the levels consecutively up to the Fermi energy. (At 0 K the system no longer has 94 units of energy, but has the minimum amount of $90E$.)

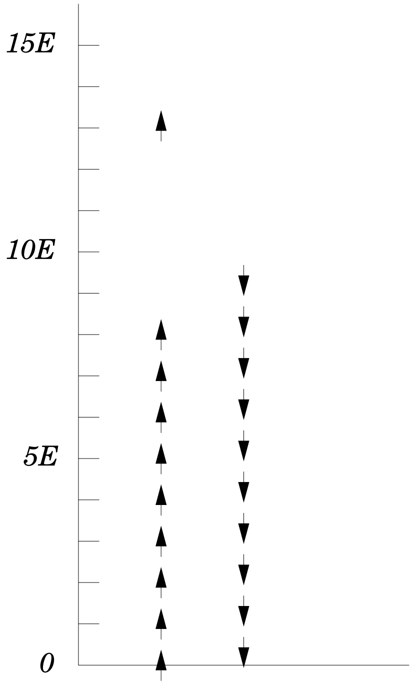

Figure 3: One of the nine equally probable micro-states for 20 Fermi-Dirac particles with a total energy of $94E$

Solution

Figure (4) shows all possible arrangements. It should be noted that filling the lowest 10 level takes only 90 units of energy. In addition, keeping the total energy limited to 94 units it is not possible to promote any particle from the first six levels, because any of these particles can only go levels that are already occupied. So we restricted

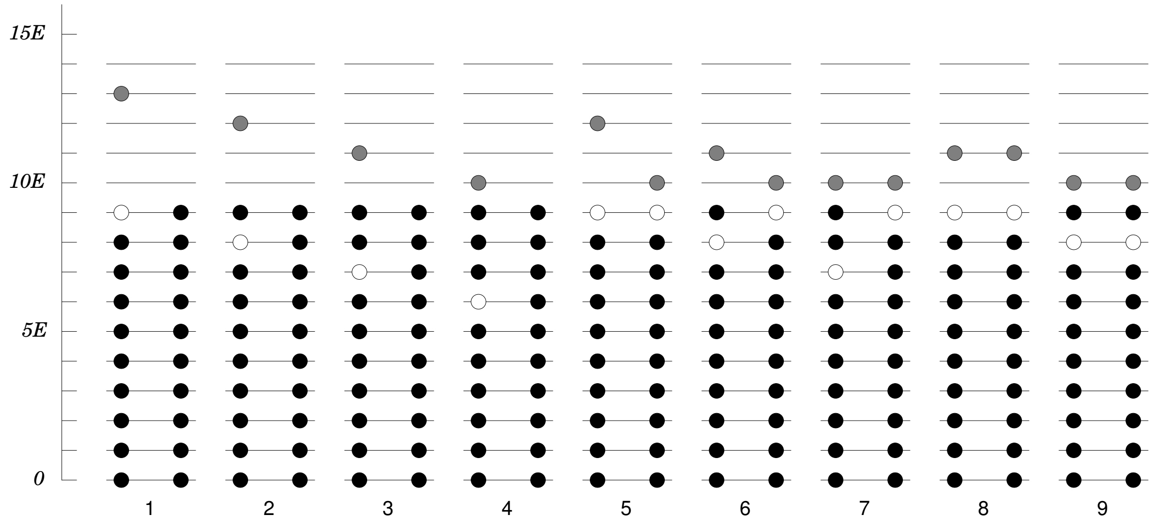

Figure 4: All possible equally probable micro-states for 20 Fermi-Dirac particles with a total energy of $94E$. Open circles represent the original locations of the grey ones.

to promoting particles from levels with energies 6 - 9 units. The probability of each micro-state is then 1/9. The first six states $(0-5E)$ have 2 particles each, so,

$$\begin{aligned}\overline{n}_{0E}\text{ through }\overline{n}_{5E} &= \frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2\\ &+ \frac{1}{9}\times 2+\frac{1}{9}\times 2\\ &= 2.00\end{aligned}$$

$$\begin{aligned}\overline{n}_{6E} &= 8\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)\\ &= 1.89\\ \overline{n}_{7E} &= 7\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)\\ &= 1.78\\ \overline{n}_{8E} &= 6\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)\\ &= 1.55\\ \overline{n}_{9E} &= 4\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)\\ &= 1.22\\ \overline{n}_{10E} &= \left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 2\right)\\ &= 0.777\end{aligned}$$

$$\begin{aligned}
\overline{n}_{11E} &= \left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)\\
&= 0.444\\
\overline{n}_{12E} &= \left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)\\
&= 0.222\\
\overline{n}_{13E} &= \left(\frac{1}{9}\times 1\right)\\
&= 0.111\\
\overline{n}_{14E} &= 0.00
\end{aligned}$$

The plot of $n_{ave} = \overline{n}$ vs energy states is shown in Figure (5). At 0 K all low energy levels are full, that is all levels from $0E$ up to $9E$, so the Fermi energy is then $9E$ as shown in Figure (5).

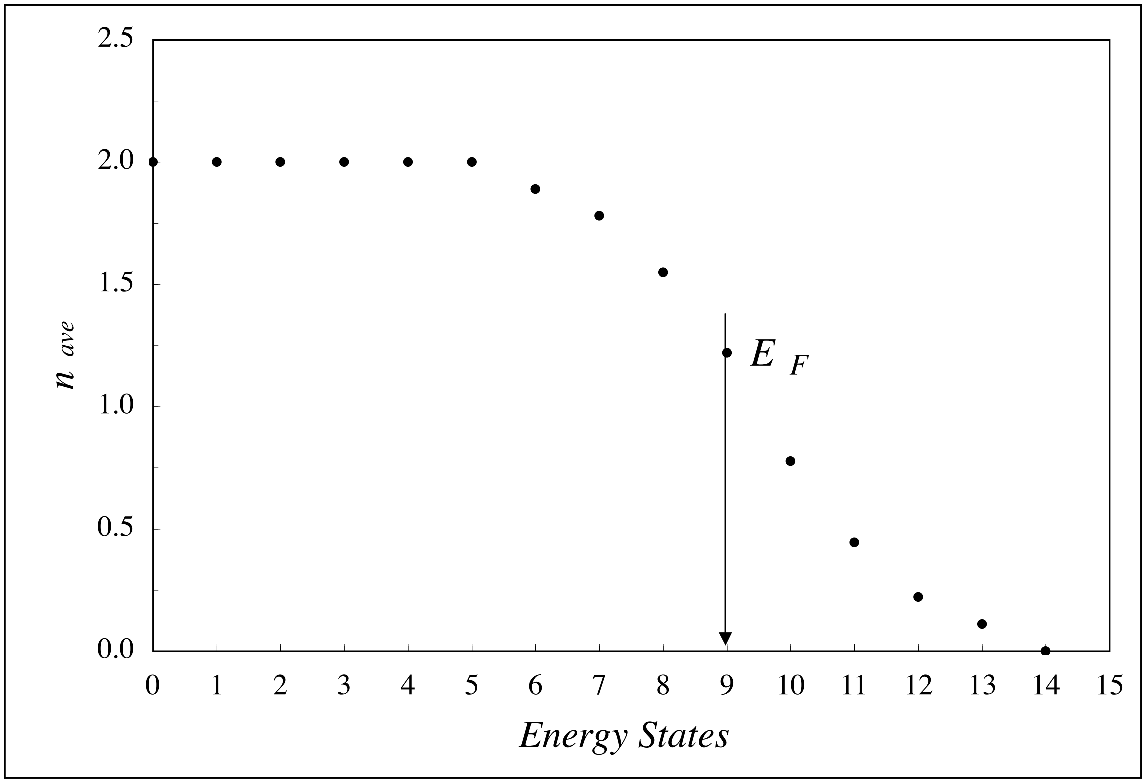

Figure 5:

4. The Fermi energy of aluminum is 11.63 eV.
   (a) Assuming that the free electron model applies to aluminum, calculate the number of free clcctrons per unit volume at low temperatures.
   (b) Determine the valence of aluminum by dividing the answer found in part (a) by the number of aluminum atoms per unit volume as calculated from the density and the atomic weight. Note that aluminum has a density of 2.70 g/cm^3.

Solution

(a) The free electron density n is related to the Fermi energy E_F through:

$$\begin{aligned} E_F &= \left(\frac{h^2}{2m_e}\right)\left(\frac{3n}{8\pi}\right)^{2/3} \\ n &= \left(\frac{8\pi}{3}\right)\left(\frac{2m_e E_F}{h^2}\right)^{3/2} \\ &= \left(\frac{8\pi}{3}\right)\left(\frac{2 \times 9.11 \times 10^{-31} \times 11.63 \times 1.6 \times 10^{-19}}{(6.625 \times 10^{-34})^2}\right)^{3/2} \\ &= 1.80 \times 10^{29} \text{ free electrons}/m^3 \end{aligned}$$

(b) The number of atoms/m^3 n' can be calculated using the density ρ, Avogadro's number N_A, and the molecular mass M:

$$\begin{aligned} n' &= \frac{\rho N_A}{M} \\ &= \frac{2.7 \times 6.02 \times 10^{23}}{27} \\ &= 6.02 \times 10^{22} \text{ atoms}/cm^3 \\ &= 6.02 \times 10^{28} \text{ atoms}/m^3 \end{aligned}$$

The valence of aluminum is then:

$$\begin{aligned} \frac{n}{n'} &= \frac{1.80 \times 10^{29}}{6.02 \times 10^{28}} \\ &= 3 \end{aligned}$$

---

5. A one-dimensional model for the electronic energy of a diatomic homonuclear molecule is described by the potential well and barrier shown in Figure (6). In the simplest case, the barrier width is shrunk to zero ($w \to 0$) while the barrier height increases without limit ($U \to \infty$) in such a way that the product Uw approaches a finite value S called the barrier strength. Such a barrier $-$ known as a delta function barrier $-$ can be shown to produce a discontinuous slope in the wavefunction at the barrier site $L/2$ given by

$$\left.\frac{d\psi}{dx}\right|_{L/2^+} - \left.\frac{d\psi}{dx}\right|_{L/2^-} = \frac{2mS}{\hbar^2}\psi(L/2) \tag{13}$$

Solve the wave equation in the well subject to this condition to obtain expressions for the energies of the ground state and first excited state as functions of the barrier strength S. Examine carefully the limits $S \to 0$ and $S \to \infty$ and comment on your findings.

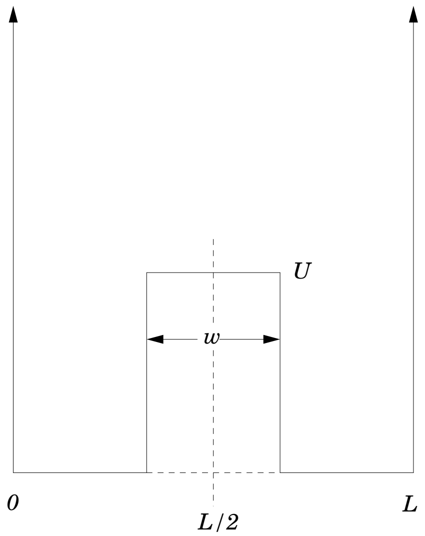

Figure 6:

Solution

To the left and to the right of the barrier location the wave function *psi* is that of a free particle with a wave number k given by:

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{14}$$

so the wave functions are:

$$\begin{aligned} \psi^-(x) &= A\sin(kx) + B\cos(kx) & 0 \le x \le \frac{L}{2} \qquad (15) \\ \psi^+(x) &= F\sin(kx) + G\cos(kx) & \frac{L}{2} \le x \le L \qquad (16) \end{aligned}$$

The infinite walls at $x = 0$ and $x = L$ requires that $\psi^-(0) = \psi^+(L) = 0$. using these boundary conditions in Equations (15) and (16) we get:

$$\begin{aligned} 0 &= A \times 0 + B \\ B &= 0 \qquad (17) \\ 0 &= F\sin(kL) + G\cos(kL) \\ G &= -F\tan(kL) \qquad (18) \end{aligned}$$

Using Equations (17) and (18) in Equations (15) and (16) we get:

$$\begin{aligned} \psi^-(x) &= A\sin(kx) & 0 \le x \le \frac{L}{2} \qquad (19) \\ \psi^+(x) &= F\{\sin(kx) - \tan(kL)\cos(kx)\} \\ &= F\left\{\sin(kx) - \left(\frac{\sin(kL)}{\cos(kL)}\right)\cos(kx)\right\} \\ &= \left(\frac{F}{\cos(kL)}\right)\{\sin(kx)\cos(kL) - \cos(kx)\sin(kL)\} \\ &= C\sin(kx - kL) & \frac{L}{2} \le x \le L \qquad (20) \end{aligned}$$

The waves can be either symmetric or antisymmetric at the middle point. Let us examine each case separately.

(A) Antisymmetric Case: If the waves are antisymmetric at the middle point then the wave functions on either side of the mid-point must vanish at the mid-point, i.e.

$$\psi^\pm(L/2) = 0 \qquad (21)$$

This also means that the barrier has no effec on the wave functions and consequently the slope at the mid-point is continuous.

$$\begin{aligned} \frac{d\psi^-}{dx} &= Ak\cos(kx) \\ \frac{d\psi^+}{dx} &= Ck\cos(kx - kL) \end{aligned}$$

at the mid point the two slopes are equal, so we get:

$$\begin{aligned} Ak\cos(kL/2) &= Ck\cos(kL/2 - kL) \\ Ak\cos(kL/2) &= Ck\cos(-kL/2) \\ Ak\cos(kL/2) &= Ck\cos(kL/2) \\ A &= C \end{aligned}$$

To satisfy the condition in Equation (21), we must put $kL/2 = n\pi$. Using this in Equation (14) we can get the energy E for the antisymmetric case as:

$$\begin{aligned} E_n &= \frac{(\hbar k)^2}{2m} \\ &= \frac{\pi^2\hbar^2}{2m(L/2)^2}\, n^2 \qquad\qquad n = 1, 2, \cdots \end{aligned} \tag{22}$$

(B) Symmetric Case Sine the waves are symmetric around the mid-point, the two wave function must be equal at that point, i.e.

$$\begin{aligned} A\sin(kL/2) &= C\sin(kL/2 - kL) \\ &= C\sin(-kL/2) \\ &= -C\sin(kL/2) \\ A &= -C \end{aligned} \tag{23}$$

It is given that the slopes of the two functions at the mid-point are different and the difference is given by Equation (13) from which and Equation (23) we get:

$$\begin{aligned} Ck\cos(kL/2 - kL) - Ak\cos(kL/2) &= \frac{2mS}{\hbar^2} A\sin(L/2) \\ Ck\cos(-kL/2) - Ak\cos(kL/2) &= \frac{2mS}{\hbar^2} A\sin(L/2) \\ -Ak\cos(kL/2) - Ak\cos(kL/2) &= \frac{2mS}{\hbar^2} A\sin(L/2) \\ -2k\cos(kL/2) &= \frac{2mS}{\hbar^2} \sin(L/2) \\ \tan(kL/2) &= -\frac{2\hbar^2}{mSL}\left(\frac{kL}{2}\right) \\ \tan(x) &= -\alpha x \end{aligned} \tag{24}$$

where $x = kL/2$ and $\alpha = 2\hbar^2/mSL$. The roots of Equation (24) can be found graphically by plotting the functions $y = \tan(x)$ and $y = -\alpha x$ and determining the values of x at the points of intersections of the two functions as shown in Figure (7).

Let the points of intersection be x_n, this gives us:

$$\begin{aligned} k_n &= \frac{2x_n}{L} \\ E_n &= \frac{\hbar^2 k_n^2}{2m} \end{aligned} \tag{25}$$

Only values of x_n (and k_n) larger than zero should be considered, since the wave function is symmetric and $k = 0$ makes the wave functions vanish everywhere.

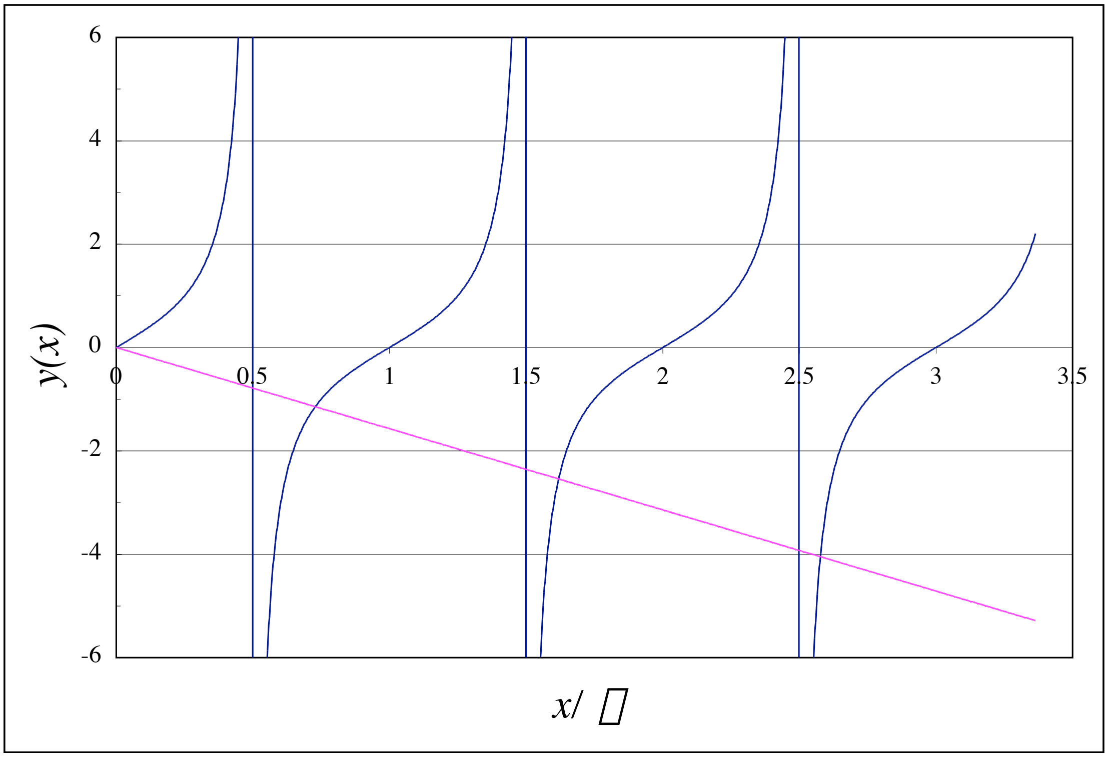

Figure 7:

Now if $S \to \infty$, the the slope α of the straight line $y = -\alpha x$ becomes zero, the line lies on the x-axis, and will intersect with $\tan(x)$ at $x_n = n\pi$ with $n = 1, 2, 3, \cdots$. The energy levels E_n corresponding to various waves are then given by:

$$E_n = \frac{\pi^2\hbar^2}{2m(L/2)^2}\, n^2 \qquad\qquad n = 1, 2, 3, \cdots \tag{26}$$

Equations (22) and (26) are identical, that is the energy levels of the asymmetric case and the symmetric case with $S = \infty$ are degenerate.

If $S = 0$, then $\alpha = \infty$ and the line becomes vertical and can intercept the $\tan(x)$ curve at $x_n = (n + \frac{1}{2})\pi$ with $n = 0, 1, 2, 3, \cdots$. the energy levels E_n are then given by:

$$E_n = \frac{\pi^2\hbar^2}{2mL^2}\,(n + \frac{1}{2})^2 \qquad\qquad n = 0, 1, 2, 3\cdots \tag{27}$$

The ground state energy is then given by:

$$E_\circ = \frac{\pi^2\hbar^2}{4mL^2}$$

and the first state is;

$$E_1 = \frac{9\pi^2\hbar^2}{4mL^2}$$

6. As a model for a diatomic molecule, consider two identical point masses m connected by a rigid massless rod of length $R_\circ$. Suppose that this molecule rotates about an axis perpendicular to the rod through its midpoint. Use the Bohr quantization rule for angular momentum to obtain the allowed rotational energies in this approximation. Compare your result with the correct quantum mechanical treatment of this model.

Solution

The angular momentum L of this system is:

$$\begin{aligned} L &= mv\frac{R_\circ}{2} + mv\frac{R_\circ}{2} \\ &= mvR_\circ \end{aligned}$$

According Bohr's theory the angular momentum must be multiples of $\hbar$, i.e.

$$\begin{aligned} L &= mvR_\circ \\ &= n\hbar \\ v &= \frac{n\hbar}{mR_\circ} \qquad\qquad n = 1, 2, 3, \cdots \end{aligned}$$

The energy of rotation E_B according to Bohr's theory is then:

$$\begin{aligned} E_B &= \frac{1}{2}mv^2 + \frac{1}{2}mv^2 \\ &= m\left(\frac{n\hbar}{mR_\circ}\right)^2 \\ &= \frac{\hbar^2}{mR_\circ^2}\, n^2 \qquad\qquad n = 1, 2, \cdots \end{aligned} \tag{28}$$

Energy of rotation E_Q according to a correct quantum mechanical treatment is given by:

$$E_Q = = \left(\frac{\hbar^2}{2I_{cm}}\right) \{\ell(\ell+1)\}$$

Where I_{cm} is the moment od inertia about the center of mass,

$$\begin{aligned} I_{cm} &= m\left(\frac{R_\circ^2}{2}\right)^2 + m\left(\frac{R_\circ^2}{2}\right)^2 \\ &= \frac{1}{2}mR_\circ^2 \\ E_Q &= \left(\frac{\hbar^2}{mR_\circ^2}\right) \{\ell(\ell+1)\} \qquad\qquad \ell = 0, 1, 2, \cdots \end{aligned} \tag{29}$$

Comparing Equations (28) and (29) we see that $\ell(\ell+1)$ replaces n^2 in the Bohr result. However, the two expression are indistinguishable for large ℓ and n, but they disagree markedly for small values of ℓ or n. In particular, E_Q can be zero while E_B has a minimum value of $\hbar^2/mR_\circ^2$, when $n = 1$.

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7. Silver has a density of $1.05 \times 10^3 kg/m^3$ and a resistivity of $1.60 \times 10^{-8} \Omega \cdot m$ at room temperature.

   (a) On the basis of the classical free-electron gas model, and assuming that each silver atom contributes one electron to the electron gas, calculate the average time between collisions of the electrons.

   (b) Calculate the mean free path from τ and the electron's thermal velocity.

   (c) How does the mean free path compare to the lattice spacing?

Solution

(a) The average time τ between collisions in an electron gas is:

$$\tau = \frac{m_e}{ne^2\rho}$$

where m_e is the mass of the electron ($9.11 \times 10^{-31}\,kg$) n is number of electrons in the gas per m^3, ρ is the resistivity ($1.60 \times 10^{-8}\,\Omega \cdot m$), and e ($1.6 \times 10^{-19}\,C$) is the electronic charge. n can be calculated from Avogadro's number (6.02×10^{23}), the density of silver ($1.05\ g/cm^3$), the atomic number of silver (108), and the number of electrons each silver atom contributes the electron gas (1),

$$\begin{aligned} n &= 1 \times 6.02 \times 10^{23} \times \frac{1.05}{108}\,\text{electrons}/cm^3 \\ &= 5.85 \times 10^{22}\,\text{electrons}/cm^3 \\ &= 5.85 \times 10^{28}\,\text{electrons}/m^3 \end{aligned}$$

The mean time τ is then:

$$\begin{aligned} \tau &= \frac{9.11 \times 10^{-31}}{1.60 \times 10^{-8} \times 5.85 \times 10^{28} \times (1.6 \times 10^{-19})^2} \\ &= 3.80 \times 10^{-14}\,s \end{aligned}$$

(b) the mean free path L is given by:

$$L = v_{rms}\tau$$

The root mean square speed of electrons at a temperature $T\,K$ can be calculated from:

$$\begin{aligned}
\frac{1}{2}m_e v_{rms}^2 &= \frac{3}{2}k_B T \\
v_{rms} &= \sqrt{\frac{3k_B T}{m_e}} \\
&= \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{9.11 \times 10^{-31}}} \\
&= 1.2 \times 10^5\, m/s
\end{aligned}$$

The mean free path is then:

$$\begin{aligned}
L &= v_{rms}\tau \\
&= 1.2 \times 10^5 \times 3.80 \times 10^{-14} \\
&= 4.6 \times 10^{-9}\, m
\end{aligned}$$

8. Assuming that conduction electrons in silver are described by the Fermi free-electron gas model with $E_F = 5.48 eV$, repeat the calculations of Problem 7.

Solution

It is possible to replace v_{rms} by v_F:

(a) The average time between collision is:

$$\begin{aligned} \tau &= \frac{m_e}{ne^2\rho} \\ &= \frac{\sigma m_e}{ne^2} \end{aligned} \tag{30}$$

where $\sigma = 1/\rho$ is the conductivity and ρ is the resistivity, m_e is the mass of the electron, e is the electron's charge, and n is the number of electrons per unit volume.

$$\begin{aligned} \sigma &= \frac{1}{\rho} \\ &= \frac{1}{1.6 \times 10^{-8}} \\ &= 6.25 \times 10^{7}\ (\Omega \cdot m)^{-1} \end{aligned} \tag{31}$$

Let A_v be Avogadro's number (particles/mol), d the density (g/cm^3) and M the molar mass. Assuming that there is one free electron per atom, then the free electron density is:

$$\begin{aligned} n &= \frac{A_v d}{M} \\ &= \frac{6.02 \times 10^{23} \times 10.5}{108} \\ &= 5.85 \times 10^{22}\ e/cm^3 \\ &= 5.85 \times 10^{28}\ e/m^3 \end{aligned} \tag{32}$$

Using Equations (31) and (32) in Equation (30) we get

(b)

(c)

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9. The natural line width emitted by a collection of Cr^{3+} ions in ruby in thermal equilibrium at 290 K is about 0.4 nm for the 694.4-nm line. This is the thermal line width. Show that the emission from a ruby laser is much more monochromatic than 694.4 ± 0.2 nm if laser emission is confined to a single cavity mode. Take the length of the ruby between polished faces to be 10 cm, $n = 1.8$, and $dn/d\lambda = 0$.

Solution

The laser operation is confined to a single mode, the laser line width will be equal to the change in wavelength between adjacent lines.

$$\begin{aligned}
|\Delta\lambda| &= \frac{\lambda^2}{2L(n - \lambda\, dn/d\lambda)} \\
&= \frac{(694.4)^2}{2 \times 10 \times 10^7 \times 1.8} \\
&= 1.34 \times 10^{-3}\ nm
\end{aligned}$$

So:

$$\lambda_{laser} = 694.4 \pm 0.001\ nm$$

So the condition:

$$L = m\,\frac{\lambda}{2n}$$

restricts the laser wavelength to about 1/200 of the thermal line width.