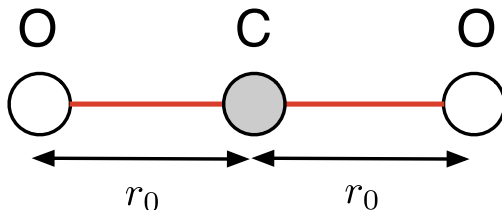# Problem 1.   Carbon Dioxide

Carbon dioxide CO_2 consists of two oxygen atoms $^{16}_{8}O$ (8 protons and 8 neutrons) and a carbon atom $^{12}_{6}C$ as shown below. The spacing between the oxygen and carbon atoms is r_0 as shown below.

Consider CO_2 at room temperature T_0 and atmospheric pressure p_0. Assume that the molecule does not vibrate but only rotates as a whole around its center of mass. The rotations can be treated essentially classically.

(a) The rotational constant of CO_2 is[1], $\Delta \equiv \hbar^2/2I \simeq 0.048\,\text{meV}$. Estimate r_0 and show that your estimate provides a reasonable order of magnitude estimate for Δ. Briefly describe the physical significance of Δ.

(b) Determine the energy per molecule of the gas.

(c) Determine the entropy of the gas.

    (i) Evaluate the result for the S/Nk_B numerically.

    (ii) How would your result change for S/Nk_B if all the mass of CO_2 was concentrated at a single point?

The lowest vibrational mode of CO_2 involves the displacement of the central carbon atom which is opposite to the displacements of the two oxygen atoms – see below. The quantized oscillations of this mode are excited by a photon of energy $E = \hbar\omega = 83\,\text{meV}$.
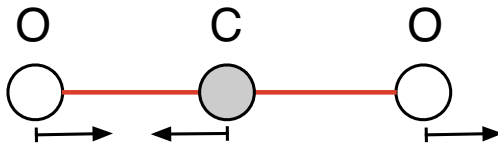
(d) Determine the change in entropy per atom S/Nk_B of part (c) when the first vibrational mode is included. Evaluate this change numerically.

Solution

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[1]Note that the units here are milli electron volts

(a) The typical distance is an $r_0 = 1\,\text{Å}$. The moment of inertia of the molecule is $I = 2Mr_0^2$ where $M = 16m_p^2$ is the mass of the Oxygen nucleus. Then

$$\Delta = \frac{\hbar^2}{2I} = \frac{(\hbar c)^2}{64m_p^2 c^2 r_0^2} = \frac{(1970\,\text{eVÅ})^2}{64(938.MeV)\,1\text{Å}^2} = 0.06\,\text{meV} \tag{1}$$

Our estimate is about 50% too large. Changing $r_0 = 1.15\,\text{Å}$ produces a value of $\Delta \simeq 0.048\,\text{meV}$.

The energy levels of a rigid rotor are

$$\epsilon_J = \Delta\,J(J+1). \tag{2}$$

and the rotational states are labelled by two quantum numbers

$$J = 0, 1, 2, \ldots m = -J \ldots J \tag{3}$$

Thus delta provides the spacing between energy levels. Energy differences of this order of magnitude should be treated quantum mechanicallly.

(b) This is an ideal gas and the equipartition theorem applies

$$\frac{U}{N} = \langle \epsilon \rangle = \frac{3}{2}kT + 2 \times \tfrac{1}{2}kT \tag{4}$$

There are three translational degrees of freedom and two rotational ones.

(c) The partitional function of the gas is

$$Z_N = \frac{1}{N!}Z_1 \tag{5}$$

Its log (or $-\beta F$) is

$$-\beta F = \ln Z_N = \ln Z_1 - N \ln N + N \tag{6}$$

The single particle patition function

$$Z_1 = \sum_{J=0}^{\infty} \sum_{m=-J}^{J} \int \frac{V d^3 p}{(2\pi\hbar)^3} e^{-\beta p^2 - \beta \epsilon_J} \tag{7}$$

The sum over the rotational levels gives

$$Z_1^{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)e^{-\beta\Delta J(J+1)} = \frac{kT}{\Delta} \tag{8}$$

Following the results from lecture

$$Z_1 = V\frac{(2\pi MkT)^{3/2}}{h^3}\frac{kT}{\Delta} \tag{9}$$

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Putting together the ingrediants

$$-\beta F = N\left[\ln(V/N) + \frac{(2\pi MkT)^{3/2}}{h^3} + \ln(kT/\Delta) - N\right] \tag{10}$$

The entropy is

$$\frac{S}{k} = -\beta F + \beta U \tag{11}$$

$$= N\left[\ln(n_Q/n) + \frac{7}{2} + \ln(kT/\Delta)\right] \tag{12}$$

where we have introduced the quantum concentration $\frac{(2\pi MkT)^{3/2}}{h^3}$

(i) Let us group terms

$$\frac{S}{Nk} = \left[\left(\ln(n_Q/n) + \frac{5}{2}\right) + \left(1 + \ln(kT/\Delta)\right)\right] \tag{13}$$

The first term is the Sackur-Tetrode result for a mono-atomic gas. The second term is the the diatomic gas. Carefully evaluating

$$\log(n_Q/n) = 16.1 \tag{14}$$
$$\log(T/\Delta) = 6.25 \tag{15}$$

So we have

$$\frac{S}{Nk} = \left[\left(18.6\right) + \left(7.25\right)\right] = 23.8 \tag{16}$$

(ii) Well we would just have the Sackur Tetrode result of 18.6

(d) This is more than I intendend. The vibrational mode is adds to the partition function

$$Z_1 = Z_{1\text{trans}} Z_{1\text{rot}} Z_{\text{vib}} \tag{17}$$

The log of the partition function is changed by the vibrational contribution

$$\Delta \log Z_1 = \log Z_{\text{vib}} = -\log(1 - e^{-\beta\hbar\omega}) \tag{18}$$

where we hav recalled the partition function of the oscillator

$$Z_{\text{vib}} = \frac{1}{1 - e^{-\beta\hbar\omega}} \tag{19}$$

The energy of the oscillator is

$$\langle\epsilon\rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \tag{20}$$

So we have from a single oscillator

$$S_{\text{vib}} = -\log(1 - e^{-\beta\hbar\omega}) + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} \tag{21}$$

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So we have

$$\frac{\Delta S}{Nk} = -\log(1 - e^{-\beta\hbar\omega}) + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} \tag{22}$$

Substuting $\beta\hbar\omega = 3.32$ we find

$$\frac{\Delta S}{Nk} = 0.16 \tag{23}$$

which is quite small compared to the classical results

Problem 2.   Hot Gluon Plasma

(a) We have

$$Z_{G1} = \sum_n e^{-\beta(\varepsilon_1 n - \mu n)} = \frac{1}{1 - e^{-\beta(\varepsilon_1 - \mu)}} = \frac{1}{1 - e^{\beta\mu}e^{-\beta\epsilon}} \tag{24}$$

The mean number is

$$\langle n \rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln Z_{G1} = \frac{e^{\beta\mu}e^{-\beta\epsilon}}{1 - e^{\beta\mu}e^{-\beta\epsilon}} \tag{25}$$

$$= \frac{1}{e^{\beta(\varepsilon_1 - \mu)} - 1} \tag{26}$$

(b) The total number of gluons in a volume V is

$$N_g = g\int \frac{V d^3p}{(2\pi\hbar)^3}\frac{1}{e^{\beta(\varepsilon - \mu)} - 1} \tag{27}$$

where $g = 16$ is the degeracy. Integrating over the angles the density of gluons is

$$n_g = \frac{g}{2\pi^2}\frac{1}{\hbar^3}\int_0^\infty p^2 dp\frac{1}{e^{cp/kT} - 1} \tag{28}$$

Introducing a dimensionless momentum $u = p/(kT/c)$ as motivated by the exponent

$$e^{-\beta cp/kT} \equiv e^{-u} \tag{29}$$

we find

$$n_g = \frac{g}{2\pi^2}\left(\frac{kT}{\hbar c}\right)^3 \int_0^\infty u^2 du\frac{1}{e^u - 1} \tag{30}$$

So the density is

$$n_g = \frac{g}{2\pi^2}\left(\frac{kT}{\hbar c}\right)^3 2.404 \tag{31}$$

(c) The wavelength of the gluon

$$\langle\lambda\rangle = \left\langle\frac{h}{p}\right\rangle \tag{32}$$

$$\langle\lambda\rangle = \frac{g\int \frac{V d^3p}{(2\pi\hbar)^3}\frac{1}{e^{\beta(\varepsilon - \mu)} - 1}\frac{h}{p}}{g\int \frac{V d^3p}{(2\pi\hbar)^3}\frac{1}{e^{\beta(\varepsilon - \mu)} - 1}} \tag{33}$$

All constants cancel between the numerator and denominator

$$\langle\lambda\rangle = \frac{\int_0^\infty p^2 dp\frac{1}{e^{cp/kT} - 1}\frac{h}{p}}{\int_0^\infty p^2 dp\frac{1}{e^{cp/kT} - 1}} \tag{34}$$

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Introducing the dimensionless variable as before

$$\langle \lambda \rangle = \left(\frac{hc}{kT} \right) \frac{\int_0^\infty u^2 du \frac{1}{e^u - 1} \frac{1}{u}}{\int_0^\infty u^2 du \frac{1}{e^u - 1}} \tag{35}$$

$$= \left(\frac{hc}{kT} \right) \frac{\pi^2/6}{2.404} \tag{36}$$

$$= \left(\frac{hc}{kT} \right) 0.684 \tag{37}$$

(d) To determine the distribution of wavelengths $\mathrm{d}n_g/\mathrm{d}\lambda$ of the gluons within gas, we use Eq. (28) but don't do the last integral

$$\mathrm{d}n_g = \frac{g}{2\pi^2\hbar^3} \frac{p^2 \mathrm{d}p}{e^{cp/kT} - 1} \tag{38}$$

recognizing that

$$p = \frac{h}{\lambda} \tag{39}$$

and effecting the change of variables

$$\mathrm{d}p = \frac{h}{\lambda^2} \mathrm{d}\lambda \tag{40}$$

We find

$$\mathrm{d}n_g = \frac{g}{2\pi^2} (2\pi)^3 \frac{\mathrm{d}\lambda}{\lambda^4} \frac{1}{e^{hc/\lambda kT} - 1} \tag{41}$$

Or simplifying the constants

$$\mathrm{d}n_g = 4\pi g \frac{1}{e^{hc/\lambda kT} - 1} \frac{\mathrm{d}\lambda}{\lambda^4} \tag{42}$$

Problem 3. N electrons and N sites

(a) There are four states labelled $s = 0$, $s = 1u$, $s = 1d$, and $s = $ "*double*". The labels are irrelevant

state s	E_s	N_s
0	0	0
1u	0	1
1d	0	1
double	Δ	2

The grand partition function is

$$Z_G = 1 + e^{\beta\mu} + e^{\beta\mu} + e^{2\beta\mu}e^{-\beta\Delta} \tag{43}$$

$$= 1 + 2z + z^2 e^{-\beta\Delta} \tag{44}$$

where $z \equiv e^{\beta\mu}$ is known as the fugacity.

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(b) From the problem statement there is on average one electron per site $\langle n \rangle = 1$. The chemical potential is such that this condition (one per site) is fulfilled.

We evaluate the mean number of particles in a site as follows:

$$\langle n \rangle = \sum_{states} P_s N_s \tag{45}$$

The probability of being in a state is

$$P_s = \frac{e^{\beta \mu N_s} e^{-\beta E_s}}{Z_G} \tag{46}$$

leading to

$$\langle n \rangle = \frac{2z + 2z^2 e^{-\beta \Delta}}{1 + 2z + z^2 e^{-\beta \Delta}} \tag{47}$$

Requiring that $\langle n \rangle = 1$ yields

$$\langle n \rangle = \frac{2z + 2z^2 e^{-\beta \Delta}}{1 + 2z + z^2 e^{-\beta \Delta}} = 1 \tag{48}$$

Or

$$1 = z^2 e^{-\beta \Delta} \tag{49}$$

So we find

$$z = e^{\beta \Delta / 2} \quad \text{or} \quad \mu = \Delta/2 \tag{50}$$

(c) The energy is the derivative of the partition function at fixed z

$$\langle \epsilon \rangle = \sum_s P_s E_s \tag{51}$$

We evaluate this at $z = e^{\beta \Delta / 2}$ noting that

$$z^2 e^{-\beta \Delta} = 1 \tag{52}$$

So

$$\langle \epsilon \rangle = \sum_s P_s E_s = \frac{\Delta}{1 + 2e^{\beta \mu} + 1} = \frac{\Delta}{2 + 2e^{\beta \mu}} \tag{53}$$

The heat capacity is harder than I intended and was not graded. Let us not immediately set $\mu = \Delta/2$

$$\langle \epsilon \rangle = \frac{\Delta z^2 e^{-\beta \Delta}}{1 + 2z + z^2 e^{-\beta \Delta}} \tag{54}$$

Evaluating the heat capacity

$$C = \left(\frac{\partial \langle \epsilon \rangle}{\partial T} \right)_N = -k\beta^2 \left(\frac{\partial \langle \epsilon \rangle}{\partial \beta} \right)_N \tag{55}$$

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Since this derivative is at fixed N should hold fixed

$$ze^{-\beta\Delta/2} = 1 \tag{56}$$

which followed from the condition that $\langle n \rangle = 1$. Differentiatiating

$$\partial_\beta z\, e^{-\beta\Delta/2} - ze^{-\beta\Delta/2}\Delta/2 = 0 \tag{57}$$

Or

$$\partial_\beta z = z\tfrac{1}{2}\Delta \tag{58}$$

After differentiating z we may set it to its $\beta\Delta/2$. Thus

$$\partial_\beta(z^2 e^{-\beta\Delta}) = 2z^2 e^{-\beta\Delta}\tfrac{1}{2}\Delta - z^2 e^{-\beta\Delta}\Delta = 0 \tag{59}$$

Doing the algebra we find

$$-\frac{\partial\langle\epsilon\rangle}{\partial\beta} = \frac{\Delta z^2 e^{-\beta\Delta}}{(1 + 2z + z^2 e^{-\beta\Delta})^2} z\Delta \tag{60}$$

Setting $z = e^{\beta\Delta/2}$ we find

$$C = -k_B\beta^2\frac{\partial\epsilon}{\partial\beta} = k_B\frac{(\beta\Delta)^2 e^{\beta\Delta/2}}{(2 + 2^{\beta\Delta/2})^2} \tag{61}$$

Problem 4. Graphene

(a) The number of electrons is determined by integrating up to the fermi momentum

$$N_e = g\int_{p<p_F}\frac{A d^2 p}{(2\pi\hbar)^2} \tag{62}$$

The integral is just the area of a circle in momentum space πp_F^2. Then

$$n_e = \frac{N_e}{A} = \frac{g\pi p_F^2}{4\pi^2\hbar^2} \tag{63}$$

So we find

$$p_F = \hbar\sqrt{\frac{n_e 4\pi}{g}} \tag{64}$$

The fermi energy is the energy for particles with momentum p_F

$$\epsilon_F = c_0 p_F = \hbar c_0\sqrt{\frac{n_e 4\pi}{g}} \tag{65}$$

Evaluating this numerically with $g = 2$ and $\hbar c_0 = 197\,\text{eV}\cdot\text{nm}/300$ gives

$$\epsilon_F = 0.37\,\text{eV} \tag{66}$$

The temperature is approximate $kT = 0.025\,\text{eV}$. So the fermi energy is only about ten times larger than the temperature, and there could be corrections to the zero temperature result. However ten is a big number and so the zero temperature result is a good guide, even quantitatively.

(b) The average debroglie wavelength is

$$\langle \lambda \rangle = \frac{g \int_{p<p_F} \frac{A d^2 p}{(2\pi\hbar)^2} \frac{h}{p}}{g \int_{p<p_F} \frac{A d^2 p}{(2\pi\hbar)^2}} \tag{67}$$

And so we have

$$\langle \lambda \rangle = \frac{\int_0^{p_F} p \, dp \frac{h}{p}}{\int_0^{p_F} p \, dp} = \frac{h p_F}{\frac{1}{2}p_F^2} = \frac{2h}{p_F} = \frac{4\pi\hbar}{p_F} \tag{68}$$

So we see putting $g = 2$

$$\langle \lambda \rangle = C_0 n_e^{-1/2} \qquad C_0 = \frac{4\pi}{\sqrt{(4\pi/g)}} \simeq 5.01 \tag{69}$$

Thus $\lambda = 0.80 \, n_e^{-1/2}$ is of order the interparticle spacing $n_e^{-1/2}$.

(c) The energy of the gas is

$$U = g \int_{p<p_F} \frac{A d^2 p}{(2\pi\hbar)^2} c_0 p \tag{70}$$

So we find

$$\frac{U}{A} = \frac{g}{2\pi\hbar^2} \int_0^{p_F} p \, dp \, c_0 p = \frac{g}{2\pi\hbar^2} c_0 \frac{1}{3} p_F^3 \tag{71}$$

We note that this can be written

$$\frac{U}{A} = \frac{2}{3} n_e \epsilon_F \tag{72}$$

Or

$$U = \frac{2}{3} N \epsilon_F \tag{73}$$

(d) Determine the pressure due to the carrier electrons. The energy can be written

$$U = C_0 A p_F^3 = C_1 A^{-1/2} \tag{74}$$

where C_0 and C_1 etc denote a constant. Then

$$p = -\left(\frac{\partial U}{\partial A}\right) = \frac{1}{2} C_1 A^{-3/2} = \frac{1}{2} \frac{U}{A} = \frac{1}{3} n_e \epsilon_F \tag{75}$$

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