STATISTICAL MECHANICS OF DIATOMIC GASES

1- For monatomic gas, whose molecules have three degrees of freedom of translatory motion, the internal energy and the specific heat of one mole of gas are $u = \dfrac{3}{2}RT$, and $c_V = \left(\dfrac{\partial u}{\partial T}\right)_V = \dfrac{3}{2}R$, respectively.

The energy does not depend upon the volume.

2- A molecule is a stable compound of two like or different atoms.

3- The nature of forces that leads to the formation of a molecule from isolated atoms is treated in quantum mechanics.

4- The energy of the molecule is made up of:
   i.   The translation kinetic energy of its center of mass E_{trans}.
   ii. Energy of excitation of the atomic electrons in the molecule E_e.
   iii. Energy of vibration of the nuclei along the axis joining them, E_{vib}, and
   iv. The rotational kinetic energy due to the rotational motion of the atoms about the center of mass of the molecule, E_{rot}. Thus

$$E = E_{trans} + E_e + E_{rot} + E_{vib}$$

The translational motion of a diatomic molecule is not quantized. All the other kinds of internal motion of the molecule are quantized, i.e. E_e, E_{rot}, and E_{vib} assume a discrete series of values.

Approximations:

I-   Assume that the three kind of internal motion of molecule are independent of one another.

II- The influence of vibrational motion on rotation can be neglected. i.e. the moments of inertial of molecules stay constant.

III- $\Delta E_e \approx 1\,\text{eV} \approx 10^4\,\text{K}$ i.e. very high temperature is required to produce a substantial number of molecules in excited electronic states. This is why we are neglecting the contribution of the electronic states.

IV- Because of $\Delta E_{vib} \approx 10^{-3}\,\text{eV}$ to $10^{-1}\,\text{eV}$, $\Delta E_{rot} \approx 10^{-4}$ then it is easy to find a few vibrational and rotation states at room temperature.
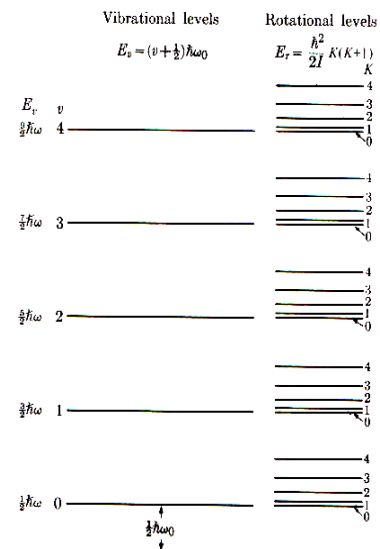
Fig. 8.13 Vibrational excitation of diatomic molecules leads to the excitation of many rotational levels corresponding to each vibrational level, thus resulting in the fine structure of the vibrational levels.

Vibrational modes:

For an oscillator with mass *m* and angular frequency $\omega = 2\pi f$, the Hamiltonian in three dimensions is:

$$H(\mathbf{p},\mathbf{q}) = \underbrace{\frac{\mathbf{p}^2}{2m}}_{\text{Kinetic energy}} + \underbrace{\frac{1}{2}m\omega^2\mathbf{q}^2}_{\text{Potential energy}}$$

and the vibrational energy level is given by:

$$\varepsilon_j = (j + \frac{1}{2})\hbar\omega, \qquad j = 0,1,2,\cdots$$

Note That:
- The energies are equally spaced, i.e. $\Delta\varepsilon_j = \hbar\omega$,
- The ground state has "zero point" energy equal to $\hbar\omega/2$,
- The states are non-degenerate, i.e. $g_j = 1$ for all j.

Prof. Dr. I. Nasser   Phys540, T172   1-Mar-18

Diatomic_Gas   (Ashly H. Carter chapter 15)

- The partition function: (use the geometric series summation $\sum\limits_{v=0}^{\infty} e^{-vb} = \dfrac{1}{1-e^{-b}}$)

$$z_{vib} = \sum_v e^{-\beta\,\varepsilon_v} = e^{-a}\sum_v e^{-v(2a)} = \frac{e^{-a}}{1-e^{-2a}} = \frac{1}{e^a - e^{-a}} = (2\sinh a)^{-1}, \qquad a = \frac{\theta_{vib}}{2T}, \quad \theta_{vib} = \frac{\hbar\omega}{k_B}$$

Note that: the value of θ_{vib} (has a units of temperature K) separates between the quantum and classical regions.

Example: If you know that $\hbar\omega = 0.29$ eV for N_2, then [Note: $1\text{eV} = 1.6\times10^{-19}$ J , $k_B = 1.38\times10^{-23}\ \frac{\text{J}}{\text{K}}$]

$$\theta_{vib} = \frac{\hbar\omega}{k_B} = \frac{0.29\times1.6\times10^{-19}\ \text{J}}{1.38\times10^{-23}\ \frac{\text{J}}{\text{K}}} = 3362\ \text{K}.$$

So, any temperature less than or equal 3362 K will be in quantum region, and any temperature greater than 3362 K will be in classical region.
H.W. Calculate θ_{vib} for H_2, O_2, and Cl_2.

- We shall also be concerned with the occupation numbers, or with $P_i = N_i / N$, the fraction of the total number of particles with energy ε_j. The Boltzmann distribution for $g_i = 1$ is

$$P_j = \frac{N_j}{N} = \frac{e^{-\beta\varepsilon_j}}{z_{vib}} = e^{-\beta\varepsilon_j}e^a(1-e^{-2a}) = (1-e^{-2a})e^{-\beta\varepsilon_j+a}$$
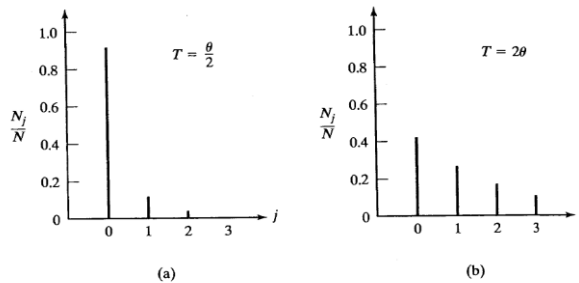
The exponent of the term outside the parentheses can be written

$$-\beta\varepsilon_j + a = -\frac{1}{k_BT}(j+\tfrac{1}{2})\frac{h\nu}{k_BT} + \frac{h\nu}{2k_BT} = -j\frac{h\nu}{k_BT} = -ja = -j\frac{\theta_{vib}}{T}$$

Thus

$$P_j = \frac{N_j}{N} = (1 - e^{-\frac{\theta_{vib}}{T}})e^{-j\frac{\theta_{vib}}{T}}$$

A sketch of the last equation for two temperatures shows that the lower the temperature, the more rapidly the occupation numbers decrease with j (Figure 15.1). At higher temperatures, more particles populate the higher energy levels.
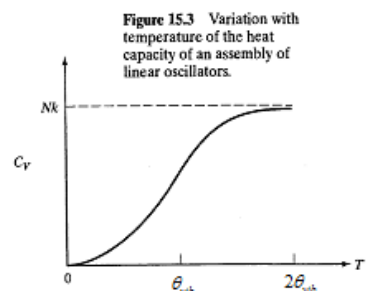

Figure 15.1 Fractional occupation numbers for quantized linear oscillators with (a) $T = \theta/2$, and (b) $T = 2\theta$.

- The single particle partition function leads to a heat capacity of

$$C_{vib} = \left(\frac{\partial U_{vib}}{\partial T}\right)_{V,N} = Nk_B\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{\left(e^{\theta_{vib}/T}-1\right)^2}$$

This heat capacity decays exponentially as $T \ll \theta_{vib}$ and tends to zero as $T \to 0$, and tends to R per mole as $T \gg \theta_{vib}$,

Figure 15.3 Variation with temperature of the heat capacity of an assembly of linear oscillators.

Quantity	Formula	$T \to 0$	$T \to \infty$
Partition function	$Z_{vib} = z_{vib}{}^N = (2\sinh a)^{-N}$	0?	$(\dfrac{k_B T}{\hbar \omega})^N$
Helmholtz free energy	$F = -k_B T \ln Z_{vib} = N k_B T \ln(2\sinh a)$	0?	$F = N k_B T \ln(\beta \hbar \omega)$
Entropy	$S = -\left(\dfrac{\partial F}{\partial T}\right)_{V,N} = N k_B \left[a \coth a - \ln(a \sinh a)\right]$	0	$S = N k_B \left[1 - \ln(\beta \hbar \omega)\right]$
Internal energy	$U_{vib} = -\left(\dfrac{\partial \ln Z_{vib}}{\partial \beta}\right)_{V,N} = N \hbar w \left[\dfrac{1}{2} + \dfrac{1}{e^{2a}-1}\right]$	0	$2 \times \dfrac{1}{2} \times N k_B T = nRT$
Pressure	$P = \dfrac{N}{\beta}\left(\dfrac{\partial \ln(z)}{\partial V}\right)_{T,N}$		$N k_B T / V = nRT / V$
Vibrational heat capacity	$C_{vib} = \left(\dfrac{\partial U_{vib}}{\partial T}\right)_{V,N} = \left(\dfrac{\partial U_{vib}}{\partial \beta}\right)_{V,N}\left(\dfrac{\partial \beta}{\partial T}\right)_{V,N}$ $= N k_B \left(\dfrac{\theta_{vib}}{T}\right)^2 \dfrac{e^{\theta_{vib}/T}}{\left(e^{\theta_{vib}/T}-1\right)^2}$	$Nk\left(\dfrac{\theta_{vib}}{T}\right)^2 e^{-\theta_{vib}/T}$	$N k_B = nR$

Substance	$\theta_{vib} = \dfrac{\hbar \omega}{k_B}$ (K)	$\theta_{rot} = \dfrac{\hbar^2}{2I k_B}$ (K)
H_2	6140	85.4
O_2	2239	2.1
N_2	3362	2.9
Cl_2	810	0.0347

Example: If you know that $\hbar \omega = 0.29$ eV for N_2, calculate c_{vib} per mole at $T = 1000$ K . [Note: any temperature less than 3362 K, will be in quantum region, $k_B = 1.38 \times 10^{-23} \ \frac{J}{K}$]

 Answer: From the above table, it was found that 1000 K $< \theta_{vib}(N_2)$. Consequently, 1000 K will be in the quantum region. Then, use $a = \dfrac{3362}{1000} = 3.362$

We can have

$$c_{vib} = R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{\left(e^{\theta_{vib}/T}-1\right)^2} = 8.31 \, a^2 \frac{e^a}{\left(e^a - 1\right)^2} = 3.49 \text{ J mole}^{-1} \text{ K}^{-1}$$

This is in excellent agreement with the experimental value, 3.43 J mole^{-1} K^{-1}, and away from the classical value $c_{vib} = R = 8.314$ JK^{-1}mol^{-1} .

Rotational modes:

Classically, the kinetic energy of rotation is:

$$\text{K.E.} = \frac{1}{2} I \omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$

Using the relation $m_1 r_1 = m_2 r_2$, $r_o = r_1 + r_2$, then the moment of inertia about an axis through the center of mass of a diatomic molecule is:

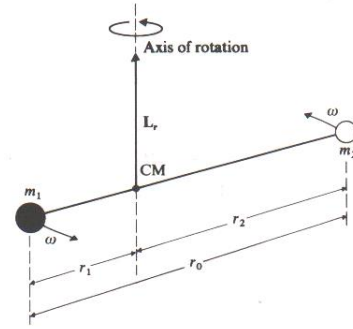$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_o^2, \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Fig. 8.8 Rotational motion of a diatomic molecule about an axis through the center of mass.

The rotational energy level is given by:

$$\varepsilon_r = \frac{L^2}{2I} = \frac{l(l+1)}{2I}\hbar^2, \qquad\qquad l = 0, 1, 2, \cdots,$$

Where, $I = \mu r_o^2$, μ is the reduced mass, r_o is the equilibrium distance between the nuclei, and I is the moment of inertia of the molecule relative to a perpendicular axis passing through the center of mass and l determining the angular momentum of the molecule relative to the center of mass with its degeneracy $g_l = (2l+1)$.

The partition function:

$$z_{rot} = \sum_l g_i e^{-\beta \varepsilon_l} = \sum_l (2l+1) e^{-\beta \varepsilon_l} = \sum_l (2l+1) e^{-l(l+1)\theta_{rot}/T}, \qquad \theta_{rot} = \frac{\hbar^2}{2Ik_B}$$

A- Low temperatures, $T \ll \theta_{rot}$, we just take the first two terms in the series leading to

Figure 15.4 Variation with temperature of the heat capacity of an assembly of rigid rotators.

$$z_{rot} = \sum_l (2l+1) e^{-\beta \varepsilon_l} = 1 + 3 e^{-2\theta_{rot}/T},$$

$$U_{rot} = 6 N k_B \theta_{rot} e^{-2\theta_{rot}/T},$$

$$C_{V,rot} = 3 N k_B \left(\frac{2\theta_{rot}}{T}\right)^2 e^{-2\theta_{rot}/T}$$
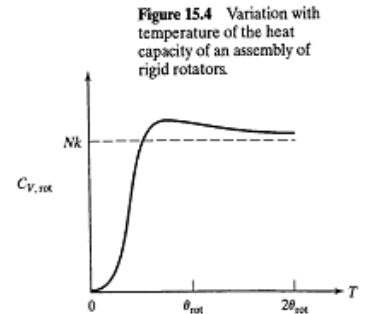

B- High temperatures: At high temperature, $T \gg \theta_{rot}$, a very large number of rotational states are occupied. Also, the spacing of the rotational levels becomes very small compared with the thermal energy, and we may compute z_{rot} by replacing the summation by integration. We also substitute $2l$ for $2l+1$ and l^2 for $l(l+1)$. Then

$$Z_{rot,classical} \approx \int_0^\infty dl (2l+1) e^{-l(l+1)\theta_{rot}/T} \approx \int_0^\infty 2l e^{-l^2 \theta_{rot}/T} dl = \frac{T}{\theta_{rot}},$$

which leads to internal energy of $N k_B T$ and a heat capacity of R per mole due to rotations.

Example: Calculate θ_{rot} for the diatomic nitrogen. [$M = 14.008$ amu]

Answer: The mass of a single nitrogen atom is $m = \dfrac{14.008}{6.023 \times 10^{26}} = 2.325 \times 10^{-26}$ kg,

the reduced mass is $\mu = m/2 = 1.163 \times 10^{-26}$ kg, and the moment of inertia of a molecule is

$$I = \mu r^2 = 1.163 \times 10^{-26} \text{ kg} \times \left(1.0976 \times 10^{-10}\right)^2 \text{ m}^2 = 14 \times 10^{-47} \text{ kg.m}^2,$$

$$\theta_{rot} = \frac{h^2}{8\pi^2 I k_B} = \frac{\left(6.625\times 10^{-36}\right)^2 \text{J}^2\text{s}^2}{8\pi^2 \times 14\times 10^{-47}\,\text{kg.m}^2 \times 1.38\times 10^{-23}\,\dfrac{\text{J}}{\text{molecule.K}}} = 2.88\ \text{K}$$

Example: Calculate the partition function for the hydrogen molecule at 300 K, given that the moment of inertia for molecule is $I = 6.29\times 10^{-48}$ kg.m^2.

Answer:

a) Using the classical expression: $z_{rot,classical} = \dfrac{T}{\theta_{rot}} = \dfrac{300}{\theta_{rot}}$, where

$$\theta_{rot} = \frac{h^2}{8\pi^2 I k_B} = \frac{\left(6.625\times 10^{-36}\right)^2 \text{J}^2\text{s}^2}{8\pi^2 \times 6.29\times 10^{-48}\,\text{kg.m}^2 \times 1.38\times 10^{-23}\,\dfrac{\text{J}}{\text{molecule.K}}} = 64.03\ \text{K}$$

Note that $64.03\ \text{K} < 85.4\ \text{K}$, so we have to treat it using the quantum expression. But, we are going to treat it classically also to see the difference.

i- Using the classical expression:

$$z_{rot,classical} = \frac{300}{64.03} = 4.69$$

ii- Using the quantum expression $z_{rot} = \sum_{l=0}^{\infty} (2l+1)e^{-l(l+1)\theta_{rot}/T}$, one finds:

$$z_{rot} = \sum_{l=0}^{\infty} (2l+1)e^{-l(l+1)\theta_{rot}/T} = 1.000 + 3e^{-2\times 64.03/300} + 5e^{-6\times 64.03/300} + \cdots$$
$$= 1.000 + 1.958 + 1.389 + 0.540 + 0.126 + \cdots$$
$$= 5.001$$

Comments:

1- The contribution due to each rotational level goes through a maximum at $l = 1$ and then decay rapidly, becoming negligible by $l = 6$.
2- This decreasing is mainly due to the factor $-l(l+1)$ in the exponent.
3- The difference between the classical and quantum results is due replacing a summation by an integral when quantization is still significant at this temperature.

15.6 Use the data of Table 15.1 to determine r_o, the equilibrium distance between the nuclei, for
(a) an H$_2$ molecule;
(b) a CO molecule.

Answer:

$$\theta_{rot} = \frac{\hbar^2}{2Ik}, \text{ where } I = \mu r_0^2, \text{ and } \mu \text{ is the reduced mass, } \mu = \frac{m_1 m_2}{m_1 + m_2}.$$

Then, $\theta_{rot} = \dfrac{\hbar^2}{2\mu r_0^2 k}$, and $r_0 = \dfrac{\hbar}{\sqrt{2\mu k \theta_{rot}}}$

a) For H$_2$, $\mu = \dfrac{m}{2}$, so $r_0 = \dfrac{\hbar}{\sqrt{mk\theta_{rot}}}$

Then, $r_0 = \dfrac{1.054 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{(1 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})(1.38 \times 10^{-23} \text{ J/K})(85.4 \text{ K})}}$

$r_0 = 7.54 \times 10^{-11} \text{ m} = 0.754 \text{ Å}$

b) For CO, $\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{(12 \text{ amu})(16 \text{ amu})}{12 \text{ amu} + 16 \text{ amu}} = 6.857 \text{ amu}$

Then, $r_0 = \dfrac{\hbar}{\sqrt{2\mu k \theta_{rot}}} = \dfrac{1.054 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2(6.857 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})(1.38 \times 10^{-23} \text{ J/K})(2.8 \text{ K})}}$

$r_0 = 1.12 \times 10^{-10} \text{ m} = 1.12 \text{ Å}$

Summary
The single particle partition function

$$E = E_{trans} + E_e + E_{rot} + E_{vib}$$

$$E = E_{trans} + E_e \gg E_{vib} \gg E_{rot}$$

$$z = z_{tr} \times z_e \times z_{rot} \times z_{vib} = V\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \times z_e \times z_{rot} \times z_{vib}$$

$$C_V = C_{V,tr} + C_{V,rot} + C_{V,vib}$$

$$= 3\left(\frac{1}{2}Nk_B\right) + 2\left(\frac{1}{2}Nk_B\right) + 2Nk_B\left[\frac{1}{2}\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{\left(e^{\theta_{vib}/T} - 1\right)^2}\right]$$

Note: Regarding C_V, $C_{V,e}$ will be neglected at low temperature, because the energy difference $E_e \gg E_{vib} \gg E_{rot}$.

The total heat capacity

$$C_V = C_{V,tr} + C_{V,rot} + C_{V,vib}$$

$$= \frac{3}{2}Nk_B + Nk_B + Nk_B\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{\left(e^{\theta_{vib}/T} - 1\right)^2}$$

For most diatomic molecules the separation between the rotational energy levels is much less than $k_B T_{room}$, but the separation between vibrational levels is much greater than $k_B T_{room}$. This means that the heat capacity at room temperature is typically $5R/2$ per mole: with $3R/2$ coming from the translational heat capacity and the other R from the rotations. At room temperature the vibrational contributions are small, only coming into play at higher temperature.
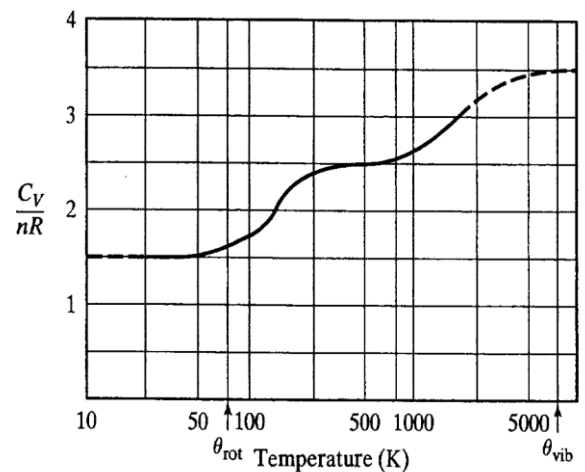
Figure 15.5 Values of C_V/nR for hydrogen (H$_2$) as a function of temperature. The temperature scale is logarithmic. (Adapted from *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*, 3rd edition, by F.W. Sears and G.L. Salinger, Addison-Wesley, 1975.)

Appendix

Simple Harmonic Oscillator

Consider a one dimensional harmonic oscillator with mass m and frequency v.
a) Write down the Hamiltonian.
b) Use the vibrational energy

$$E_n = (n + \tfrac{1}{2})hv, \qquad n = 0,1,2,\cdots$$

to calculate the classical partition function.

c) Calculate the quantum partition function. Show that in the limit of $\dfrac{hv}{k_B T} \to 0$ this result reduces to that

found classically in part (b).

d) Use the quantum mechanical partition function to calculate the internal energy, entropy, and the heat capacity of a system consisting of N such oscillator as a function of temperature.

Answer:
a) In one dimension, the Hamiltonian of the system is given by:

$$\hat{H}(p_x, q_x) = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2 \hat{q}_x^2, \qquad \omega = 2\pi v$$

b) classically the partition function for single oscillator is:

$$Z_{sp} = Z_{trans} Z_{vibr} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta H} \frac{dp_x dq_x}{h} = \frac{1}{h} \underbrace{\int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x}_{\sqrt{\frac{2\pi m}{\beta}}} \underbrace{\int_{-\infty}^{\infty} e^{-\frac{\beta m \omega^2 x^2}{2}} dx}_{\sqrt{\frac{2\pi}{\beta m \omega^2}}}$$

$$= \frac{1}{h}\sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{\beta m \omega^2}} = \frac{1}{\beta \hbar \omega}, \qquad \hbar = \frac{h}{2\pi}$$

Consequently, for *N*-oscillator system we get

$$Z_N = (Z_{sp})^N = \left(\frac{1}{\beta \hbar \omega}\right)^N$$

$$F = -k_B T \ln Z_N = Nk_B T \ln(\beta \hbar \omega)$$

H.W. prove the following thermodynamic quantities

$$\mu = k_B T \ln(\beta \hbar \omega)$$

$$P = 0$$

$$S = Nk_B \left[\ln(\beta \hbar \omega) + 1\right]$$

$$U = Nk_B T = 2\left(\tfrac{1}{2} Nk_B T\right) \qquad \text{(Equipartition theorem)}$$

$$C_P = C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} = Nk_B$$

c) In quantum mechanics, since the energy levels is $E_n = (n + \tfrac{1}{2})hv$, the partition function is given by

7

$$Z_{sp} = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-a} \sum_{n=0}^{\infty} e^{-2na} = \frac{e^{-a}}{1-e^{-2a}} = \frac{1}{e^a - e^{-a}} = (2\sinh a)^{-1}, \qquad a = \frac{\beta \hbar \omega}{2}.$$

In the limit $a \to 0 \quad \Rightarrow \quad e^a - e^{-a} = (1 + a + \cdots) - (1 - a + \cdots) = 2a = \beta \hbar \omega$, then $Z_{sp} = \dfrac{1}{\beta \hbar \omega}$, which

is the same result as in part b.

d) For N-independent particles

$$Z_N = (Z_{sp})^N = (2\sinh a)^{-N}$$

Writing $\beta = 1/k_B T$ we could obtain the following results:

$$F = -k_B T \ln Z_N = Nk_B T \ln(2\sinh a) = Nk_B T \ln\left[\frac{e^{-a}}{1-e^{-2a}}\right] = Nk_B T\left[a + \ln\left(1 - e^{-2a}\right)\right]$$

$$= N\left[\frac{1}{2}\hbar\omega + \frac{1}{\beta}\ln\left(1 - e^{-2a}\right)\right]$$

$$U = -\frac{\partial}{\partial \beta}\ln Z = N\left(\frac{\hbar\omega}{2}\right)\coth a = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{2a}-1}\right]$$

$$C_P = C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} = Nk_B \frac{e^{2a}}{\left(e^{2a}-1\right)^2}(2a)^2$$

$$S = \frac{U - F}{T} = Nk_B\left[a\coth a - \ln(2\sinh a)\right]$$

H.W. prove that in the limit of $a \to 0$ the internal energy will be: $U = \dfrac{1}{2}\hbar\omega + 2\left(\frac{1}{2}Nk_B T\right)$.

15-9. Using the relation

$$P = \frac{N}{\beta}\left(\frac{\partial \ln(z)}{\partial V}\right)_{T,N}$$

show that the equation of state of a diatomic gas is the same as that of a monatomic gas.

Answer:

$P = NkT\left(\dfrac{\partial \ln Z}{\partial V}\right)_T$.   Where $Z = Z_{trans}Z_{rot}Z_{vib}$, so $\ln Z = \ln Z_{trans} + \ln Z_{rot} + \ln Z_{vib}$

        Z_{rot} and Z_{vib} do not depend on volume, so $P = NkT\left(\dfrac{\partial \ln Z}{\partial V}\right)_T = NkT\left(\dfrac{\partial \ln Z_{trans}}{\partial V}\right)_T$.

        $Z_{trans} = V\left(\dfrac{2\pi mkT}{h^2}\right)^{3/2}$, so $\ln Z_{trans} = \ln V + \dfrac{3}{2}\ln\left(\dfrac{2\pi mkT}{h^2}\right)$

        $P = NkT\left(\dfrac{\partial \ln Z_{trans}}{\partial V}\right)_T = NkT\left(\dfrac{\partial \ln V}{\partial V}\right)_T = \dfrac{NkT}{V}$.   So,   <u>$PV = NkT$</u>