7.1 According to quantum mechanics, the molecules of a diatomic gas possess rotational energy levels:

$$\varepsilon_r = \frac{\hbar^2}{2I} r(r+1), \qquad r = 0,1,2,\ldots$$

(where I is a constant), ε_r being $(2r+1)$-fold degenerate. Write down an expression for the partition function of the rotational motion. Hence find the molar rotational heat capacity of the gas: (i) at low temperatures, (ii) at high temperatures.

For one molecule, the partition function for the rotational motion is:

$$Z_1^{rot}(T,V) = \sum_{r=0}^{\infty} e^{-\beta \varepsilon_r} = \sum_{r=0}^{\infty}(2r+1)e^{-\frac{\hbar^2 \beta}{2I}r(r+1)} = \sum_{r=0}^{\infty}(2r+1)e^{-\frac{\hbar^2}{2IkT}r(r+1)}$$

The low temperature limit is defined by: $kT \ll \frac{\hbar^2}{2I}$

keep just the first two terms...

$$Z_1^{rot}(T,V) = \sum_{r=0}^{\infty}(2r+1)e^{-\frac{\hbar^2}{2IkT}r(r+1)} = 1 + 3e^{-\hbar^2/IkT}$$

$\ln(1+x) \sim x$ if x is small

$$\overline{\varepsilon}^{rot} = -\frac{\partial \ln Z_1^{rot}}{\partial \beta} = -\frac{\partial \ln\left(1+3e^{-\hbar^2/IkT}\right)}{\partial \beta} = -\frac{\partial\left(3e^{-\beta\hbar^2/I}\right)}{\partial \beta} = \frac{3\hbar^2}{I}e^{-\beta\hbar^2 kT} = \frac{3\hbar^2}{I}e^{-\hbar^2/}$$

$$E^{rot} = N\overline{\varepsilon}^{rot} = \frac{R}{k}\overline{\varepsilon}^{rot}$$

$$C_V^{rot} = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{R}{k}\frac{3\hbar^2}{I}e^{-\hbar^2/IkT}\right) = \frac{R}{k}\frac{3\hbar^4}{I^2 kT^2}e^{-\hbar^2/IkT} = 3R\left(\frac{\hbar^2}{IkT}\right)^2 e^{-\hbar^2/IkT}$$

The high temperature limit is defined by: $kT \gg \frac{\hbar^2}{2I}$

convert to an integral: $dx = 2r+1 \Rightarrow x = r^2 + r = r(r+1),\ \ldots$

$$Z_1^{rot}(T,V) = \sum_{r=0}^{\infty}(2r+1)e^{-\frac{\hbar^2}{2IkT}r(r+1)} = \int_0^{\infty} e^{-\frac{\hbar^2}{2IkT}x}dx = \frac{2IkT}{\hbar^2}$$

$$\overline{\varepsilon}^{rot} = -\frac{\partial \ln Z_1^{rot}}{\partial \beta} = -\frac{\partial \ln\left(2IkT/\hbar^2\right)}{\partial \beta} = -\frac{\partial \ln\left(2I\beta/\hbar^2\right)}{\partial \beta} = \frac{2I/\hbar^2}{2I\beta/\hbar^2} = \frac{1}{\beta} = kT$$

$$E^{rot} = N\overline{\varepsilon}^{rot} = \frac{R}{k}\overline{\varepsilon}^{rot} = \frac{R}{k}kT = RT$$

$$C_V^{rot} = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}(RT) = R$$

For carbon monoxide, CO the constant I has the value 1.3×10^{-39} g cm^2. What is the molar rotational heat capacity of carbon monoxide at room temperature?

$$kT = \left(1.38 \cdot 10^{-23} JK^{-1}\right)\left(300K\right) = 4.14 \cdot 10^{-21} J$$

$$\frac{h^2}{2I} = \frac{\left(1.055 \cdot 10^{-34} Js\right)^2}{2 \cdot 1.3 \cdot 10^{-39} \, gcm^2} = \frac{\left(1.055 \cdot 10^{-34} Js\right)^2}{2 \cdot 1.3 \cdot 10^{-39} \, gcm^2 \, 10^{-3} \, kg/g \, 10^{-4} \, m^2/cm^2} \stackrel{68 \ \ 2 \ \ 2}{=} \frac{1.11 \cdot 10^{-} \ \ J \ \ s}{2.6 \cdot 10^{-46} \, kg \, m^2} = 4.2 \cdot 10^{-23} J$$

$$kT > \frac{h^2}{2I}$$

$$C_V^{rot} = R$$

3

7.2 A diatomic molecule may to a good approximation be considered as vibrating in 1D simple harmonic motion with circular frequency ω. According to quantum mechanics such a system possesses an infinite set of non-degenerate energy levels with energy $\hbar\omega\left(r+\frac{1}{2}\right)$, $r=0,1,2,\cdots,\infty$. Obtain expressions for the vibrational partition function and the vibrational heat capacity. What are the high and low temperature limits of this heat capacity?

$$Z_1^{vib}(T,V)=\sum_{r=0}^{\infty}e^{-\beta\varepsilon_r}=\sum_{r=0}^{\infty}e^{-\beta\hbar\omega\left(r+\frac{1}{2}\right)}=e^{-\beta\hbar\omega/2}\sum_{r=0}^{\infty}e^{-\beta\hbar\omega r}=e^{-\beta\hbar\omega/2}\frac{1}{1-e^{-\beta\hbar\omega}}=\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

$$\overline{\varepsilon}^{vib}=-\frac{\partial\ln Z_1^{vib}}{\partial\beta}=-\frac{1}{Z_1^{vib}}\frac{\partial Z_1^{vib}}{\partial\beta}=-\frac{\left(1-e^{-\beta\hbar\omega}\right)}{e^{-\beta\hbar\omega/2}}\left(\frac{(-\hbar\omega/2)e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}-\frac{(-\hbar\omega e^{-\beta\hbar\omega})e^{-\beta\hbar\omega/2}}{\left(1-e^{-\beta\hbar\omega}\right)^2}\right)$$

$$\overline{\varepsilon}^{vib}=\frac{\left(1-e^{-\beta\hbar\omega}\right)}{e^{-\beta\hbar\omega/2}}\left(\frac{(\hbar\omega/2)e^{-\beta\hbar\omega/2}}{\left(1-e^{-\beta\hbar\omega}\right)}-\frac{\hbar\omega e^{-\beta\hbar\omega}e^{-\beta\hbar\omega/2}}{\left(1-e^{-\beta\hbar\omega}\right)^2}\right)=\frac{\hbar\omega}{2}-\frac{\hbar\omega e^{-\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)}=\hbar\omega\left(\frac{1}{2}-\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$$

$$E^{vib}=N\overline{\varepsilon}^{vib}=\frac{R}{k}\overline{\varepsilon}^{vib}=\frac{R}{k}\hbar\omega\left(\frac{1}{2}-\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)=\frac{R\hbar\omega}{k}\left(\frac{1}{2}-\frac{1}{e^{\hbar\omega/kT}-1}\right)$$

$$C_V^{vib}=\left(\frac{\partial E}{\partial T}\right)_V=\frac{\partial}{\partial T}\left(\frac{R\hbar\omega}{k}\left(\frac{1}{2}-\frac{1}{e^{\hbar\omega/kT}-1}\right)\right)=\frac{R\hbar\omega}{k}\frac{\hbar\omega e^{\hbar\omega/kT}/kT^2}{\left(e^{\hbar\omega/kT}-1\right)^2}$$

$$C_V^{vib}=R\left(\frac{\hbar\omega}{kT}\right)^2\frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}$$

$$\frac{\hbar\omega}{kT}\gg 1 \qquad C_V^{vib}=R\left(\frac{\hbar\omega}{kT}\right)^2\frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}\right)^2}=R\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/kT}$$

$$\frac{\hbar\omega}{kT}\ll 1 \qquad C_V^{vib}=R\left(\frac{\hbar\omega}{kT}\right)^2\frac{1-\hbar\omega/kT}{\left(1-\hbar\omega/kT-1\right)^2}=R\left(1-\hbar\omega/kT\right)=R$$

Obtain the molecular vibrational heat capacity of N2 at 1000K given that the vibrational level spacing $\hbar\omega$ is 0.3 eV.

$$kT=\left(1.38\cdot 10^{-23}JK^{-1}\right)\left(1000K\right)=1.38\cdot 10^{-20}J$$

$$\hbar\omega=0.3eV\frac{1.60217646\times 10^{-19}\ J}{1eV}=4.8\cdot 10^{-20}J$$

$$\frac{\hbar\omega}{kT}=\frac{1.38\cdot 10^{-20}J}{4.8\cdot 10^{-20}J}=0.2875$$

$$C_V^{vib}=R\left(\frac{\hbar\omega}{kT}\right)^2\frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}=R\left(0.2875\right)^2\frac{e^{0.2875}}{\left(e^{0.2875}-1\right)^2}=R\left(0.2875\right)^2\frac{1.333}{0.1109}=0.9935R\sim R$$

3

7.3 At its normal boiling point (NBP) of 630 K, saturated mercury vapour is monatomic and satisfies the perfect gas laws. Calculate the entropy per mole of saturated mercury vapour at its NBP.

The Latent Heat of Vapourization of mercury at its NBP is 5.93x104 J mol-1. Hence find the entropy per mole of liquid mercury at 630 K and 1 atm. (Atomic weight of mercury is 200.6).

$$\ln P = \frac{5}{2}\ln T + \frac{5}{2} + \ln\left[k^{5/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right] - \frac{S_{vapour}}{Nk}$$

$$S_{vapour} = Nk\left\{\frac{5}{2}\ln T + \frac{5}{2} + \ln\left[k^{5/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right] - \ln P\right\}$$

$$S_{vapour} = R\left\{\frac{5}{2}\ln 1000K + \frac{5}{2} + \ln\left[\left(1.38\cdot 10^{-23}\,JK^{-1}\right)^{5/2}\left(\frac{2\pi 200.6K}{\left(6.626\cdot 10^{-34}\,Js\right)^2}\right)^{3/2}\right] - \ln\left(101325Pa\right)\right\}$$

$$S_{vapour} = 190\ JK^{-1}mol^{-1}$$

$$S_{liquid} = S_{vapour} - \frac{L}{T} = 190\ JK^{-1}mol^{-1} - \frac{5.93\cdot 10^4\,Jmol^{-1}}{1000K} = 96\ JK^{-1}mol^{-1}$$

7.4 Consider a perfect gas of particles in the extreme relativistic range (i.e. the kinetic energy E of a particle and its momentum P are related by E=c|p|). Find theh Helmholtz free energy and hence the heat capacity at constant volume for this gas.

$$F = F_{tr} + F_{int}$$

$$F_{tr} = -NkT\ln\frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$F_{int} = -NkT\ln Z_{int}(T)$$

$$F = -NkT\ln\frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} - NkT\ln Z_{int}(T) = -NkT\ln\frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} - NkT\ln\left\{\sum_{i=1}^{N}e^{-\beta\varepsilon_\alpha^{int}}\right\}$$

$$F = -NkT\ln\frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} - NkT\ln\left\{\sum_{i=1}^{N}e^{-\beta p_i c}\right\}$$

$$F = -NkT\ln\frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} - NkT\ln\left\{V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\int_0^\infty p^2 dpe^{-\beta pc}\right\} = -NkT\ln\left\{\frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\int_0^\infty p^2 dpe^{-\beta pc}\right\}$$

$$F = 3NkT = 3RT$$

$$Cv = 3R$$

7.5 For a gas obeying the Maxwell velocity distribution obtain:

$$N = \sum_i \bar{n}_i = e^{\beta\mu}\sum_i e^{-\beta\varepsilon_i} = e^{\beta\mu}\sum_i e^{-\beta\left(\varepsilon_s^{tr}+\varepsilon_\alpha^{int}\right)} = e^{\beta\mu}\underbrace{\sum_\alpha e^{-\beta\varepsilon_\alpha^{int}}}_{Z_1^{int}}\underbrace{\sum_\alpha e^{-\beta\varepsilon_s^{tr}}}_{\substack{Z_1^{int}=\\V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}(2s+1)}} = e^{\beta\mu}Z_1^{int}V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}(2s+1)$$

$$\bar{n}(p) = e^{\beta\mu}e^{-\beta\left(\varepsilon_s^{tr}+\varepsilon_\alpha^{int}\right)} = e^{\beta\mu}e^{-\beta\varepsilon_s^{tr}}\sum_\alpha e^{-\beta\varepsilon_\alpha^{int}} = e^{\beta\mu}e^{-\beta\varepsilon_s^{tr}}Z_1^{int} = e^{\beta\mu}Z_1^{int}e^{-\beta p^2/2m}$$

$$dN = \bar{n}(p)\frac{V4\pi p^2 dp}{h^3}(2s+1) = e^{\beta\mu}Z_1^{int}e^{-\beta p^2/2m}\frac{V4\pi p^2 dp}{h^3}(2s+1)$$

$$P(p)\,dp = \frac{dN}{N} = \frac{e^{\beta\mu}Z_1^{int}e^{-\beta p^2/2m}\dfrac{V4\pi p^2 dp}{h^3}(2s+1)}{e^{\beta\mu}Z_1^{int}V\left(\dfrac{2\pi mkT}{h^2}\right)^{3/2}(2s+1)} = \frac{4\pi}{(2\pi mkT)^{3/2}}e^{-\beta p^2/2m}p^2 dp = \sqrt{\frac{2}{\pi}}\frac{1}{(mkT)^{3/2}}e^{-\beta p^2/2m}p^2 dp$$

$$p = mv$$

$$P(v)\,dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}e^{-mv^2/2kT}v^2 dv$$

The most probable speed for the molecules:

$$P(v)\,dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}e^{-mv^2/2kT}v^2$$

$$\left.\frac{dP(v)}{dv}\right|_{v=max} = 0$$

$$-\sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}e^{-mv_{max}^2/kT}v_{max}^2\left(mv_{max}/kT\right) + \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}e^{-mv^2/kT}2v_{max} = 0$$

$$v_{max}^2\left(mv_{max}/kT\right) = 2v_{max}$$

$$v_{max} = 2\frac{kT}{m}$$

The most probable kinetic energy:

$$T_{max} = \frac{1}{2}mv_{max}^2 = \frac{1}{2}\left(2\frac{kT}{m}\right)^2 = 2\left(\frac{kT}{m}\right)^2$$

The average speed of the molecules is:

$$P(v)\,dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2} e^{-mv^2/2kT} v^2\,dv$$

$$\langle v\rangle = \int_0^\infty v P(v)\,dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\int_0^\infty e^{-mv^2/2kT} v^3\,dv$$

$$x = mv^2/2kT \Rightarrow v^2 = 2kTx/m,\qquad dx = mv/kT\,dv \Rightarrow dv = kT/mv\,dx$$

$$\langle v\rangle = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\int_0^\infty e^{-x} v^3\, kT/mv\,dx = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\left(\frac{kT}{m}\right)\int_0^\infty e^{-x} v^2\,dx$$

$$\langle v\rangle = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{1/2}\int_0^\infty e^{-x}\left(\frac{2kT}{m}\right)x\,dx = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{1/2}\left(\frac{2kT}{m}\right)\int_0^\infty e^{-x} x\,dx$$

$$\langle v\rangle = 2\sqrt{\frac{2}{\pi}}\left(\frac{kT}{m}\right)^{1/2}\int_0^\infty e^{-x} x\,dx$$

$$\frac{\Gamma(n+1)}{a^{n+1}} = \int_0^\infty e^{-ax} x^n\,dx$$

$$\Gamma(n+1) = n\Gamma(n)$$

$$\Gamma(\tfrac12) = \sqrt{\pi}$$

3

$$\langle v\rangle = 2\sqrt{\frac{2}{\pi}}\left(\frac{kT}{m}\right)^{1/2}\Gamma(2) = \sqrt{\frac{8}{\pi}}\left(\frac{kT}{m}\right)^{1/2} \sim 1.6\left(\frac{kT}{m}\right)^{1/2}$$

The rms of the molecules is:

$$P(v)\,dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2} e^{-mv^2/2kT} v^2\,dv$$

$$\langle v^2\rangle = \int_0^\infty v^2 P(v)\,dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\int_0^\infty e^{-mv^2/2kT} v^4\,dv$$

$$x = mv^2/2kT \Rightarrow v^2 = 2kTx/m,\quad dx = mv/kT\,dv \Rightarrow dv = kT/mv\,dx$$

$$\langle v^2\rangle = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\int_0^\infty e^{-mv^2/2kT} v^4\,dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\left(\frac{kT}{m}\right)\int_0^\infty e^{-x} v^3\,dx$$

$$\langle v^2\rangle = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{1/2}\int_0^\infty e^{-x}\left(\frac{2kT}{m}\right)^{3/2} x^{3/2}\,dx = (2)^{3/2}\sqrt{\frac{2}{\pi}}\left(\frac{kT}{m}\right)\int_0^\infty e^{-x} x^{3/2}\,dx = 4\sqrt{\frac{1}{\pi}}\left(\frac{kT}{m}\right)\int_0^\infty e^{-x} x^{3/2}\,dx$$

$$\langle v^2\rangle = 4\sqrt{\frac{1}{\pi}}\left(\frac{kT}{m}\right)\Gamma(\tfrac52) = 4\sqrt{\frac{1}{\pi}}\left(\frac{kT}{m}\right)(\tfrac32)(\tfrac12)\Gamma(\tfrac12) = 4\sqrt{\frac{1}{\pi}}\left(\frac{kT}{m}\right)(\tfrac32)(\tfrac12)\sqrt{\pi} = 3\left(\frac{kT}{m}\right)$$

$$v_{rms} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}$$

The mean kinetic energy of the particles is:

$$\langle T \rangle = \left\langle \frac{1}{2}mv^2 \right\rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m3\left(\frac{kT}{m}\right) = \frac{3}{2}kT$$

7.9 A diatomic molecule consists of atoms of masses M1 and M2, whose position coordinates are r1 and r2. The atoms interact through an attractive potential V(|r1-r2|). Show how the energy of the molecule decomposes into translational, vibrational, and rotational parts.
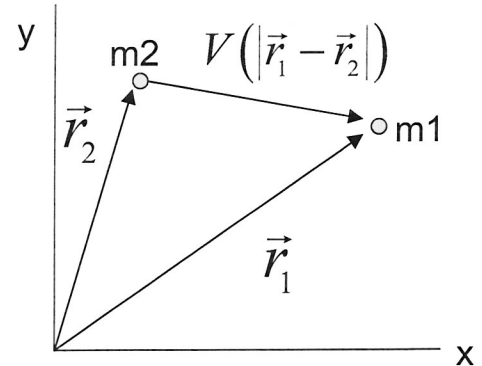
The 2-Particle system:

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V\left(\left|\vec{r}_1 - \vec{r}_2\right|\right)$$

$\vec{r} = \vec{r}_1 - \vec{r}_2$ relative coordinate of the total momentum

$\hat{P}_{total} = \hat{p}_1 + \hat{p}_2$ the total momentum

$\hat{p}_{rel} = \frac{m_1\hat{p}_1 - m_2\hat{p}_2}{m_1 + m_2}$ and $\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$ with $M = m_1 + m_2$

$$\hat{H} = \underbrace{\frac{\hat{P}^2}{2M}}_{\substack{\hat{H}_{CM} = \text{Center of Mass} \\ \text{for Particle in free space}}} + \underbrace{\frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})}_{\hat{H}_{rel} = \text{Relative Hamiltonian}}$$

The relative Hamiltonian can be broken into the rotational and vibrational components by decomposing the relative momentum term into angular and radial parts and by doing a Taylor expansion of the potential.

$$\frac{\hat{p}_{rel}^2}{2\mu} = \frac{\hat{p}_\theta^2}{2\mu r^2} + \frac{\hat{p}_\phi^2}{2\mu r^2 \sin^2\theta} + \frac{\hat{p}_r^2}{2\mu} = \frac{\hat{L}^2}{2I} + \frac{\hat{p}_r^2}{2\mu}$$

$$\hat{H} = \underbrace{\frac{\hat{P}^2}{2M}}_{\substack{\hat{H}_{CM} = \text{Center of Mass} \\ \text{for Particle in free space}}} + \underbrace{\frac{\hat{L}^2}{2I}}_{\substack{\text{Rotational} \\ \text{Energy}}} + \underbrace{\frac{\hat{p}_r^2}{2\mu} + V(\vec{r})}_{\substack{\text{Vibrational} \\ \text{Energy}}}$$

$\vec{r}_0 = $ equilibrium distance

$$\hat{H} = \underbrace{\frac{\hat{P}^2}{2M}}_{\substack{\hat{H}_{CM} = \text{Center of Mass} \\ \text{for Particle in free space}}} + \underbrace{\frac{\hat{L}^2}{2I}}_{\substack{\text{Rotational} \\ \text{Energy}}} + \underbrace{\frac{\hat{p}_r^2}{2\mu} + V(\vec{r}_0) + \frac{1}{2}(\vec{r} - \vec{r}_0)V''(\vec{r}_0)}_{\substack{\text{Vibrational} \\ \text{Energy}}}$$

The equipartition theorem holds that the translational component has 3 degrees of freedom, the rotational component has 2 degrees of freedom and the vibrational has 1 degree of freedom, with each degree of freedom contributing ½ kT to the total energy. The equipartition theorem energy is 3kT so the molar heat capacity is 3R.

7.10 A polyatomic molecule consists of n atoms, each possessing three degrees of freedom (treat each as a point mass neglecting the internal energy). Divide the degrees of freedom of the molecule into translational, rotational, and vibrational degrees: 1) for a nonlinear molecule, 2) for a linear molecule:
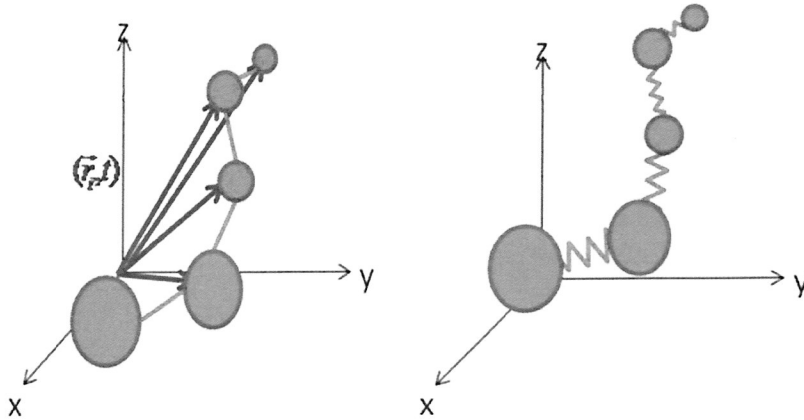
The non-linear molecule has 3N degrees of freedom. These can be regarded as 3 degrees of translational freedom of the center of mass, and 2 degrees of rotational freedom about the CM (1 degree of rotational freedom if the molecule is linear).
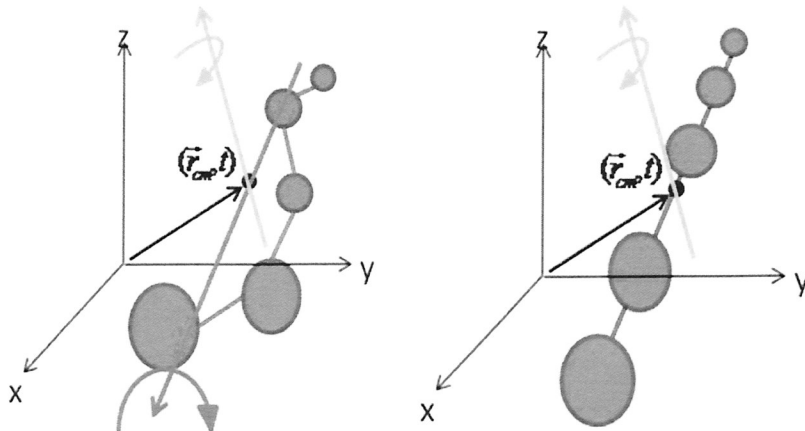

And the number of independent vibrational modes is:

1) $F_v = 3N-(3+2)=3N-5$

2) $F_v = 3N-(3+1) = 3N-6$

The rotational and translational modes are always contributing to the total heat, but the vibrational modes are not always excited since they are on the order of eV and room temperature is about 1/40 eV. The heat capacities are then still $3/2R$ for the translational component, $\frac{1}{2}R$ for the rotational component of linear and R for the rotational component of non-linear molecules, and about 0 for the vibrational components. Thus the heat capacities are 2R and 5/2R for linear and nonlinear.

7.11 Carbon dioxide (CO2) is a linear molecule and it possesses 4 vibrational modes. The vibrational temperatures $\Theta vib = \hbar\omega/k$ of these modes are 3360 K, 1890 K, 954 K, and 954 K (degenerate). Use figure 6.5 to estimate the molar heat capacity at constant volume of the CO2 at 312K.
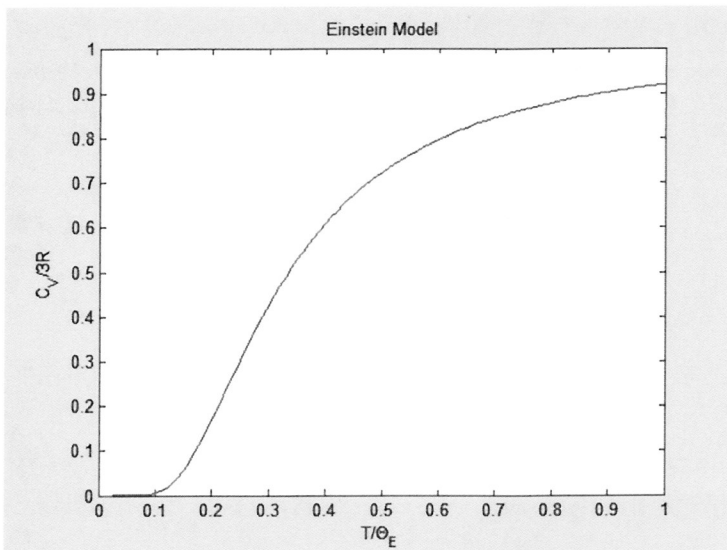
Matlab plot generated with this code (note that x-axis is 1/x, that is T/Θ_E).

```
gcf = figure(3);
hold off;t = zeros(101);Cv = zeros(101);
for i=0:100
    x=100.0/i;
    t(i+1)=1/x;
    Cv(i+1) = x*x*exp(x)/(exp(x)-1)^2;
end
plot(t,Cv,'color','b');
ylim([0 1]);
xlim([0 1]);
title(['Einstein Model']);
ylabel('C_V/3R');
xlabel('T/\Theta_E');
x=954.0/312.0;
t=1/x;
Cv = x*x*exp(x)/(exp(x)-1)^2
x=1890.0/312.0;
t=1/x;
Cv = x*x*exp(x)/(exp(x)-1)^2
x=3360.0/312.0;
t=1/x;
Cv = x*x*exp(x)/(exp(x)-1)^2
```

The results are:

Cv(954 @ 312) = 0.4838R, Cv (1890 @ 312) = 0.0863R, Cv(3360@ 312) = 0.0024R

Cv = Cv(Translational) + Cv(Rotational) + 2* Cv(954 @ 312)+ Cv (1890 @ 312)+ Cv(3360@ 312)

Cv =5/2R +1.0563R=3.5563R

6.7 Kittel

$$F = -kT \ln Z$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{kT \, \partial Z / \partial V}{Z} = \frac{kT \, \partial\left(\sum_s E_s e^{-E_s/kT}\right)/\partial V}{Z}$$

$$P = -\frac{\sum_s \left(\partial E_s / \partial V\right)_N e^{-E_s/kT}}{Z}$$

$$\left(\partial E_s / \partial V\right) = -\frac{2}{3}\frac{E_s}{V} = -\frac{2}{3}\frac{U}{V}$$

$$P = \frac{\sum_s \frac{2}{3}\frac{U}{NV} e^{-E_s/kT}}{Z} = \frac{2U \sum_s e^{-E_s/kT}}{3VZ} = \frac{2UZ}{3VZ} = \frac{2U}{3V}$$

6.9 Kittel

$$Z_n = 1 + \lambda Z_{\text{int}} e^{-\beta\varepsilon_n} = 1 + \lambda\left(e^{-\beta\varepsilon} + e^{-\beta(\varepsilon+d)}\right)e^{-\beta\varepsilon_n}$$

$$Z = \prod_n \left(1 + \lambda Z_{\text{int}} e^{-\beta\varepsilon_n}\right)$$

$$\langle N \rangle = \lambda \frac{\partial \ln Z}{\partial \lambda} = \lambda \frac{\partial \sum_n^\infty \ln\left(1 + \lambda Z_{\text{int}} e^{-\beta\varepsilon_n}\right)}{\partial \lambda} = \sum_n^\infty \frac{\left(Z_{\text{int}} e^{-\beta\varepsilon_n}\right)}{\left(1 + \lambda Z_{\text{int}} e^{-\beta\varepsilon_n}\right)}$$

$$\langle N \rangle \sim \lambda Z_{\text{int}} \sum_n^\infty e^{-\beta\varepsilon_n} = \lambda Z_{\text{int}} Z_1 = \lambda Z_{\text{int}} n_Q V$$

$$\lambda = \frac{N}{V Z_{\text{int}} n_Q} = \frac{n}{Z_{\text{int}} n_Q} \Rightarrow \mu = kT \ln\left(\frac{n}{Z_{\text{int}} n_Q}\right)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \Rightarrow F = NkT\left\{\ln\left(\frac{n}{Z_{\text{int}} n_Q}\right) - 1\right\}$$

$$F = NkT\left\{-\ln\left(\frac{n_Q}{n}\right) - \ln\left(Z_{\text{int}}\right) - 1\right\}$$

$$S = -\left(\frac{\partial F}{\partial (kT)}\right)_{V,N} = N\left\{\ln\left(\frac{Z_{\text{int}} n_Q}{n}\right) + \frac{5}{2} + \frac{\varepsilon}{kT} + \frac{d/kT}{e^{d/kT}+1}\right\}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N}{V} kT$$

$$Cp = kT\left(\frac{\partial S}{\partial (kT)}\right)_P = N\left\{\frac{5}{2} + \frac{e^{d/kT}\left(d/kT\right)^2}{\left(e^{d/kT}+1\right)^2}\right\}$$

6.12 Chemical potential of 2D monatomic gas.

$$f(p)dp = \frac{A2\pi \, pdp}{h^2}(2s+1)$$

$$s = 0$$

$$n = \frac{A2\pi \, pdp}{h^2}$$

$$N = e^{\beta\mu} \int_0^\infty e^{-\beta p^2/2m} f(p)dp = e^{\beta\mu} \int_0^\infty e^{-\beta p^2/2m} \frac{A2\pi \, pdp}{h^2} = e^{\beta\mu} \frac{A2\pi}{h^2} \int_0^\infty e^{-\beta p^2/2m} pdp$$

$$x^2 = \beta p^2/2m \Rightarrow p^2 = (2m/\beta)x^2$$

$$xdx = \beta \, pdp/2m \Rightarrow pdp = (m/\beta)dx$$

$$N = e^{\beta\mu} \frac{A2\pi m}{\beta h^2} \int_0^\infty e^{-x^2} dx = e^{\beta\mu} \frac{A\pi m}{\beta h^2}\sqrt{\pi}$$

$$e^{\beta\mu} = \frac{N\beta h^2}{Am(\pi)^{3/2}}$$

$$\mu = \frac{1}{\beta}\ln\left(\frac{N\beta h^2}{Am(\pi)^{3/2}}\right)$$

U = kT (there are 2 degrees of freedom in a 2D monatomic gas – each contributes 1/2kT to total energy).

Entropy:

$$N = e^{\beta\mu} \frac{A(\pi)^{3/2} m}{\beta h^2}$$

$$\ln Z = N \ln \frac{A2\pi m}{N\beta h^2}$$

$$F = -kT \ln Z = -kTN \ln \frac{A2\pi mkT}{Nh^2}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{A,N} = kN \ln \frac{A2\pi mkT}{Nh^2} + kTN \frac{Nh^2}{A2\pi mkT} \frac{A2\pi mk}{Nh^2}$$

$$S = kN \ln \frac{A2\pi mkT}{Nh^2} + kN$$

$$S = kN\left[\ln \frac{A2\pi mkT}{Nh^2} + 1\right]$$