Problem Set 3

1. In general: $\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$

$$C_v = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V$$

For vdW gas:

$$\ln Q = -\ln N! + \frac{3N}{2} \ln\left(\frac{2\pi m k T}{h^2}\right) + N \ln(V - Nb)$$

$$+ \frac{aN^2}{V k_B T}$$

Only a few terms survive differentiation

$$\frac{\partial \ln Q}{\partial T} = \frac{3N}{2}\left(\frac{h^2}{2\pi m k_B T}\right)\left(\frac{2\pi m k_B}{h^2}\right) - \frac{aN^2}{V k_B T^2}$$

$$+k_B T^2 \frac{\partial \ln Q}{\partial T} = \frac{3N}{2}\left(\frac{+k_B T^2}{T}\right) - \frac{aN^2}{V k_B T^2}(k_B T^2)$$

$$\langle E \rangle = \frac{3N k_B T}{2} - \frac{aN^2}{V}$$

ideal gas portion

excluded volume portion

$$C_v = \frac{3N k_B}{2}$$ ← same as ideal gas!

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2. Einstein crystal = 3N non-interacting Harmonic oscillators

only interactions are with their own lattice locations, not with each other

$$E = \sum_{i=1}^{3N} \hbar\omega\left(n_i + \tfrac{1}{2}\right)$$ ← n_i = quantum state of oscillator i

2 continued):

$$q_{ho} = \sum_{v=0}^{\infty} e^{-\beta h\nu(v+\frac{1}{2})}$$

term depends on v

constant term (no v dependence)

$$= \sum_{v=0}^{\infty} \left[e^{-\beta h\nu v} \; e^{-\beta h\nu/2} \right]$$

$$= e^{-\beta h\nu/2} \sum_{v=0}^{\infty} e^{-\beta h\nu v}$$

$$= e^{-\beta h\nu/2} \sum_{v=0}^{\infty} x^{v} \qquad \text{where } x = e^{-\beta h\nu}$$

$$= e^{-\beta h\nu/2} \left(\frac{1}{1-x} \right)$$

$$= e^{-\beta h\nu/2} \left(\frac{1}{1-e^{-\beta h\nu}} \right)$$

$$q_{ho} = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} \qquad \text{Q.E.D.}$$

If we have 3N (distinguishable) oscillators

$$Q = (q_{ho})^{3N} = \left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} \right)^{3N}$$

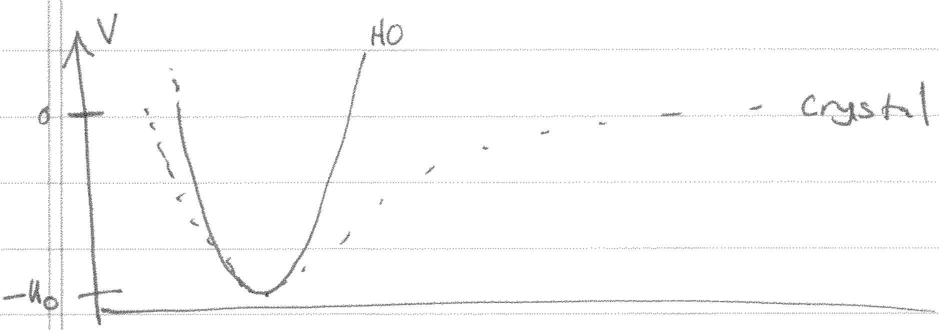
Now, the harmonic oscillator has an equilibrium position which has energy $= 0$, i.e.: $V(x) = \frac{1}{2}k(x-x_0)^2$

when $x = x_0$, $V(x) = \underline{\underline{0}}$

In a crystal this is the lattice energy relative to the infinitely separated atoms:

$$\text{Au}_{(s)} \longrightarrow \text{Au}_{(g)} \qquad \Delta U = \text{lattice energy of Au}_{(s)}$$

2.



So if we re-zero to $-u_0$ this shifts <u>all</u> the energies, and all the boltzmann factors by $e^{+\beta u_0}$

$$Q = e^{\beta u_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^{3N} \qquad QED.$$

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3. $$f_0 = \frac{P_0}{Q} = \frac{e^{-\beta h\nu(0+\frac{1}{2})}}{\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)}$$

$\leftarrow$ Boltzmann factor for $v=0$

$\leftarrow$ full Q

$$f_0 = e^{-\beta h\nu/2}\left(\frac{1-e^{-\beta h\nu}}{e^{-\beta h\nu/2}}\right)$$

$$f_0 = 1-e^{-\beta h\nu} = 1-e^{-h\nu/k_BT} \qquad QED.$$

for N_2 $\quad \tilde{\nu} = 2330\ \text{cm}^{-1}$ $\leftarrow$ $\tilde{\nu}$ is in wavenumbers

speed of light

$$\nu = 2330\ \text{cm}^{-1}\cdot 3.0\times10^{10}\ \frac{\text{cm}}{\text{s}}$$

$$\nu = 6.99\times10^{13}\ \frac{1}{\text{s}}$$

$$\Theta_{vib} = \frac{h\nu}{k_B} = \frac{6.626\times10^{-34}\ \text{J}\cdot\text{s}\quad 6.99\times10^{13}\ \frac{1}{\text{s}}}{1.381\times10^{-23}\ \frac{\text{J}}{\text{K}}}$$

$$= 3354\ \text{K}$$

$$\boxed{\begin{array}{lll} f_0 = 1-e^{-\Theta_{vib}/T}: & 300\text{K}: & f_0 = 0.999986 \\ & 600\text{K}: & f_0 = 0.99626 \\ & 1000\text{K}: & f_0 = 0.9651 \end{array}}$$

4. HCl: $\tilde{\nu} = 2886 \text{ cm}^{-1}$

$\nu = 2886 \text{ cm}^{-1} \times 3.0\times10^{10} \frac{\text{cm}}{\text{s}}$

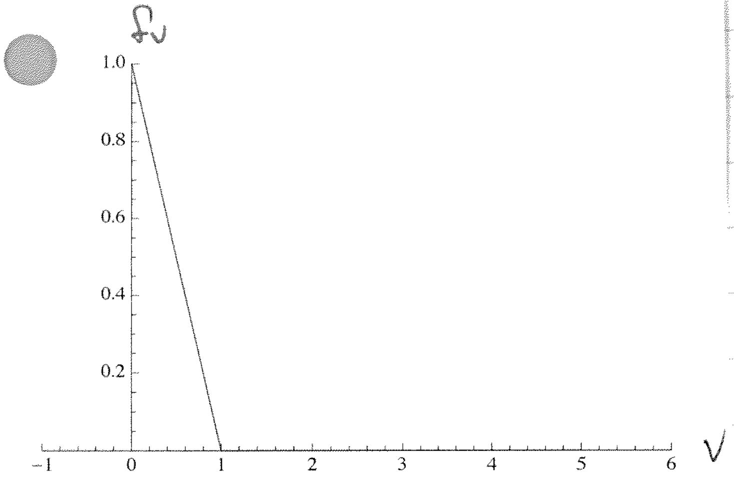
$\nu = 8.58 \times 10^{13} \ \frac{1}{\text{s}}$

$$\Theta_{vib} = \frac{h\nu}{k_B} = \frac{6.626\times10^{-34} \text{ J}\cdot\text{s} \times 8.58\times10^{13}\frac{1}{\text{s}}}{1.381\times10^{-23}\ \frac{\text{J}}{\text{K}}}$$

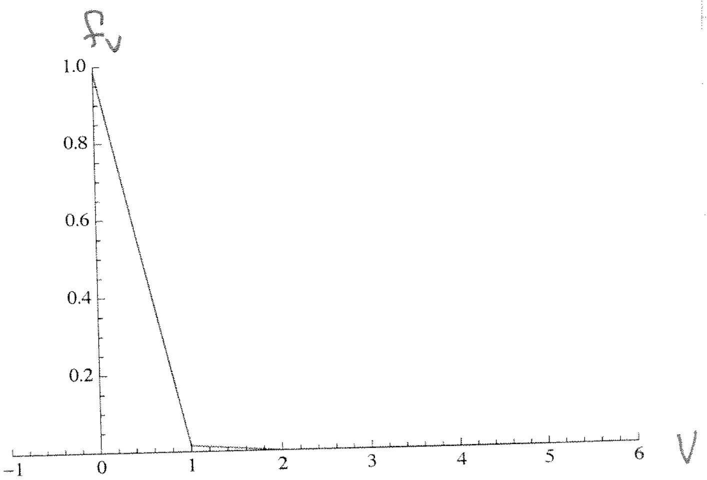
$\Theta_{vib} = 4118 \text{ K}$

$$f_i = e^{-\beta h\nu(v_i+\frac{1}{2})}\left(\frac{1-e^{-\beta h\nu}}{e^{-\beta h\nu/2}}\right)$$

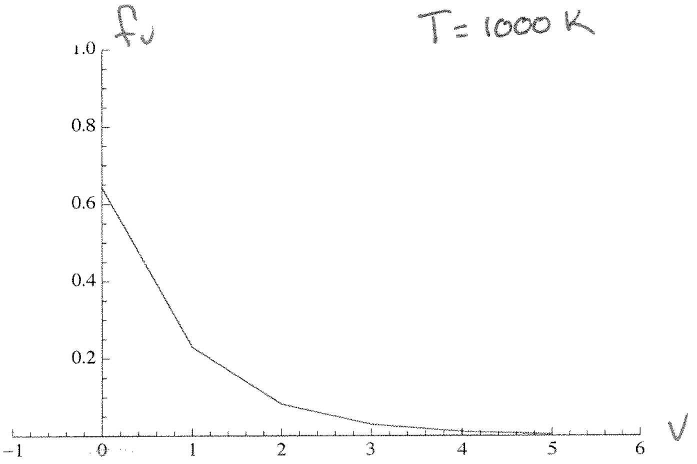
$$f_i = e^{-\Theta_{vib} v_i/T}\left(1-e^{-\Theta_{vib}/T}\right) \longleftarrow$$ this is the formula we use:



T = 300 K



T = 1000 K



T = 4000 K

5) $T_{tr} = \dfrac{\hbar^2 2\pi}{M L^2 k_B}$

The translational partition function in 1D is

$$q_{tr}(V,T) = \sqrt{\frac{2\pi m k_B T}{h^2}}\, L$$

← if we rearrange this by pulling L into the $\sqrt{\ }$ and using $\hbar = \frac{h}{2\pi}$

$$q_{tr}(V,T) = \sqrt{\frac{m k_B T L^2}{2\pi \hbar^2}}$$

$$q_{tr}(V,T) = \sqrt{\frac{T}{T_{tr}}}$$

← T_{tr} is a way of understanding the temperature at which the number of states becomes significantly populated

That is if $T \ll T_{tr}$, q is small & only the ground state is populated

if $T \gg T_{tr}$ q is large & many states are populated.

In this case: $M = 20.1797 \frac{g}{mol} \times \frac{1}{6.022 \times 10^{23} \frac{1}{mol}} \times \frac{1\ kg}{1000\ g}$

$$T_{tr} = \frac{(1.055 \times 10^{-34}\ J \cdot s)^2 (2)(\pi)}{3.35 \times 10^{-26}\ kg\ (10^{-3} m)^2\ 1.381 \times 10^{-23}\ JK^{-1}}$$

$$\boxed{T_{tr} = 1.5116 \times 10^{-13}\ K}$$

← pretty darned low, so many states will be populated at room temp.

Now, on to the error estimate:

5 continued): 1-D PF:

$$q(L,T) = \int_0^\infty e^{-\beta n^2 h^2/8mL^2}\,dn$$

we solve the integral expression to get

$$= \sqrt{\frac{2\pi m k_B T}{h^2}}\,L$$

The real partition function,

$$q_{trans} = \sum_{n=1}^{\infty} e^{-\beta n^2 h^2/8mL^2}$$

was the series, so the difference is the Euler-Mac series!

$$= \sum_{n=1}^{\infty} e^{-bn^2}$$

where $b = \frac{\beta h^2}{8mL^2}$

$$\frac{dq}{dn} = -2bne^{-bn^2}$$

$$\frac{d^2q}{dn^2} = -2be^{-bn^2} + 4b^2n^2e^{-bn^2}$$

$$\frac{d^3q}{dn^3} = 4b^2ne^{-bn^2} - 8b^3n^3e^{-bn^2}$$

So Euler-Mac says:

$$q_{trans} = \sum_{n=1}^{\infty} e^{-bn^2} \approx \underset{\text{this is our } q_{trans}}{\int_0^\infty e^{-bn^2}\,dn} + \frac{1}{2}e^{-b} - \frac{1}{12}\left(-2b\,e^{-b}\right) + \frac{1}{720}\left(4b^2e^{-b} - 8b^3e^{-b}\right)$$

$$q_{trans} = \sqrt{\frac{2\pi mL^2 k_B T}{h^2}} + \left(\frac{1}{2} + \frac{1}{6}b + \frac{1}{180}b^2 - \frac{1}{90}b^3\right)e^{-b}$$

To 1st order in b, this is

$$\underset{\text{The "real" } q_{trans}}{q_{trans}} = \underset{\text{what we use}}{\sqrt{\frac{2\pi mL^2 k_B T}{h^2}}} + \underbrace{\left[\frac{1}{2} + \frac{h^2}{48mL^2 k_B T} + O(b^2)\right]e^{-h^2/8mL^2k_BT}}_{\text{The error to 1st order in } b,\ \Delta q_{trans}}$$

The error will be significant when

$$\frac{\Delta q_{trans}(\text{real})}{q_{trans}(\text{approx})} > 10^{-3} \text{ or so}$$

So; when

$$\frac{\left[\frac{1}{2}+\frac{h^2}{48mL^2k_BT}\right]e^{-h^2/8mL^2k_BT}}{\sqrt{\frac{2\pi mL^2k_BT}{h^2}}} > 10^{-3}$$

Using Mathematica, the temperature at which this happens for Neon is:

3.78×10^{-8} K ← very low!

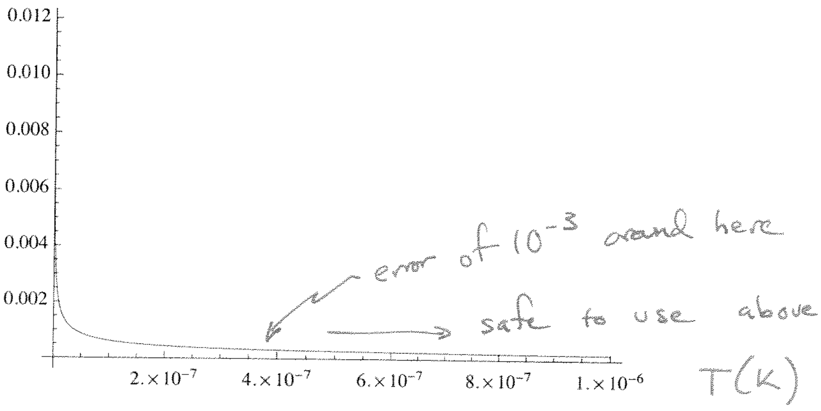
So, for any lab-relevant temperature, the integral approximation that gave us

$$q_{trans}=\sqrt{\frac{2\pi mk_BT}{h^2}}\,L$$

is valid!

Here's a plot of the error of this integral approximation vs. temperature

relative error of $\sqrt{\frac{2\pi mk_BT}{h^2}}\,L$



error of 10^{-3} around here

→ safe to use above here

6.a) A harmonic oscillator has frequency $\omega = \sqrt{\frac{k}{\mu}}$ where the potential is $V(r) = \frac{1}{2} k (r - r_e)^2$

To find the frequency, we need only take the second derivative:

$$\frac{\partial V}{\partial r} = k(r - r_e)$$

$$\frac{\partial^2 V}{\partial r^2} = k = \mu \omega^2$$

Additionally, the angular frequency, ω, is related to the frequency by a factor of 2π:

$$\omega = 2\pi\nu$$

Therefore

$$\left(\frac{\partial^2 V}{\partial r^2}\right)_{r=r_e} = \mu 4\pi^2\nu^2$$

equivalent harmonic frequency

reduced mass

second derivative

taken at equilibrium bond length

For the morse oscillator

$$U(r) = D_e \left(1 - e^{-b(r-r_e)}\right)^2$$

$$\frac{\partial U}{\partial r} = 2D_e \left(1 - e^{-b(r-r_e)}\right)\left(b e^{-b(r-r_e)}\right)$$

$$\frac{\partial^2 U}{\partial r^2} = 2D_e\left[\left(b e^{-b(r-r_e)}\right)^2 - \left(1 - e^{-b(r-r_e)}\right) b^2 e^{-b(r-r_e)}\right]$$

When $r = r_e$

$$\left(\frac{\partial^2 U}{\partial r^2}\right)_{r=r_e} = 2D_e\left[b^2 - (0) b^2\right]$$

$$\left(\frac{\partial^2 U}{\partial r^2}\right)_{r=r_e} = 2D_e b^2 = \mu 4\pi^2\nu$$

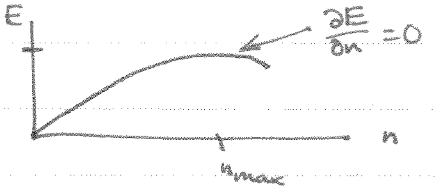
$$b^2 = \frac{\mu 4\pi^2\nu^2}{2D_e}$$

or $\boxed{b = \sqrt{\frac{\mu 2\pi^2}{D_e}}\,\nu}$

6 b) $\bar{\omega} = 4320\ \text{cm}^{-1}$

$$\nu = 4320\ \text{cm}^{-1} \times 2.99\times10^{10}\ \frac{\text{cm}}{\text{s}} = \boxed{1.29\times10^{14}\ \frac{1}{s} = \nu}$$

n_{max} is the highest energy before E vs. n turns over



or: $\left(\frac{\partial E}{\partial n}\right)_{n=n_{max}} = 0$

$$\frac{\partial E}{\partial n} = h\nu - x_e h\nu\, 2(n+\tfrac{1}{2}) = 0$$

$$2x_e h\nu (n+\tfrac{1}{2}) = h\nu$$

$$2x_e (n_{max}+\tfrac{1}{2}) = 1$$

$$(n_{max}+\tfrac{1}{2}) = \frac{1}{2x_e}$$

$$\boxed{n_{max} = \frac{1}{2x_e} - \frac{1}{2}}$$

so if we figure out x_e, we've got n_{max}

Likewise: $2x_e = \frac{1}{n_{max}+\frac{1}{2}}$

$x_e = \frac{1}{2n_{max}+1}$ ← If we get n_{max} we've also got x_e

N_{max} is also the last state below dissociation:

When $n = 0$, $E_0 = \frac{h\nu}{2} - x_e h\nu \left(\frac{1}{4}\right)$

when $n = n_{max}$, $E_{n_{max}} = h\nu(n_{max}+\tfrac{1}{2}) - h\nu x_e (n_{max}+\tfrac{1}{2})^2$

6 b. continued):

$$\Delta E = E_{max} - E_0 = h\nu n_{max} + \frac{h\nu}{2} - h\nu x_e \left(n_{m\cdot}^2 + n_{max} + \frac{1}{4}\right) - \frac{h\nu}{2} + h\nu_{xe}\left(\frac{1}{4}\right)$$

$$\Delta E = h\nu n_{max} - h\nu x_e n_{max}^2 - h\nu x_e n_{max}$$

This is <u>also</u>

$$D_0 = h\nu n_{max} - h\nu x_e n_{max}^2 - h\nu x_e n_{max}$$

Plugging in x_e:

$$D_0 = h\nu\left(n_{max} - \frac{n_{max}^2}{2n_{max}+1} - \frac{n_{max}}{2n_{max}+1}\right)$$

$$D_0 = h\nu n_{max}\left(1 - \frac{n_{max}}{2n_{max}+1} - \frac{1}{2n_{max}+1}\right)$$

$$= h\nu n_{max}\left(\frac{2n_{max}+1 - n_{max} - 1}{2n_{max}+1}\right)$$

$$= h\nu n_{max}\left(\frac{n_{max}}{2n_{max}+1}\right)$$

$$D_0 = h\nu \frac{n_{max}^2}{2n_{max}+1}$$

$$\frac{D_0}{h\nu} = \frac{n^2}{2n+1}$$

$$n^2 = \frac{D_0}{h\nu}(2n+1)$$

$$n^2 - \frac{2D_0}{h\nu} n - \frac{D_0}{h\nu} = 0$$

$$n = \frac{\frac{2D_0}{h\nu} \pm \sqrt{\frac{4D_0^2}{h^2\nu^2} + 4\frac{D_0}{h\nu}}}{2}$$

$$n_{max} = \frac{D_0}{h\nu} \pm \sqrt{\frac{D_0^2}{h^2\nu^2} + \frac{D_0}{h\nu}}$$

6b continued) $D_0 = 103.2 \frac{\text{kcal}}{\text{mol}} \times \frac{1000 \text{ cal}}{1 \text{ kcal}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} \times \frac{1}{6.022 \times 10^{23} \frac{1}{\text{mol}}}$

$$D_0 = 7.17 \times 10^{-19} \text{ J}$$

$$\frac{D_0}{h\nu} = \frac{7.17 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \times 1.29 \times 10^{14} \frac{1}{s}}$$

$$\frac{D_0}{h\nu} = 8.388$$

$$n_{max} = 8.388 \pm \sqrt{77.535 + 8.388}$$

$$= 8.388 \pm 9.269 \quad \longleftarrow \text{ only one of these make sense}$$

$$= 17.66 \quad \longrightarrow \quad 17 \text{ is the largest integer}$$

$$\boxed{\begin{aligned} n_{max} &= 17 \\ x_e &\cong \frac{1}{35} = 2.86 \times 10^{-2} \\ \nu &= 1.29 \times 10^{14} \frac{1}{s} \end{aligned}}$$

6c) There are a couple of ways to do this, but this is what I started in class:

$$q = \sum_{n=0}^{n_{max}} e^{-\beta h\nu(n+\frac{1}{2}) + \beta h\nu x_e(n+\frac{1}{2})^2}$$

$$q = \sum_{n=0}^{n_{max}} e^{-\beta h\nu(n+\frac{1}{2})} e^{\beta h\nu x_e(n+\frac{1}{2})^2}$$

Now: $e^{\beta h\nu x_e(n+\frac{1}{2})^2} \approx 1 + \beta h\nu x_e (n+\tfrac{1}{2})^2 + \frac{\beta^2 h^2 \nu^2 x_e^2}{4}(n+\tfrac{1}{2})^4 + \ldots$

Taylor series

6c continued):

Stopping at 1st order in x_e, we have:

$$q \approx \sum_{n=0}^{n_{max}} e^{-\beta h\nu(n+\frac{1}{2})}\left(1+\beta h\nu x_e\left(n+\tfrac{1}{2}\right)^2\right)$$

$$\approx \overbrace{\frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}}} + \overbrace{\beta h\nu x_e\, e^{-\theta_{vib}/2T}\sum_{n=0}^{\infty}\left(n+\tfrac{1}{2}\right)^2 e^{-\theta_{vib}n/T}}$$

Here we've assumed $n_{max}\to\infty$

Using $\sum_{n=0}^{\infty} n x^n = \frac{x}{(1-x)^2}$ and $\sum_{n=0}^{\infty} n^2 x^n = \frac{x^2+x}{(1-x)^3}$

We get:

$$\sum_{n=0}^{\infty}\left(n+\tfrac{1}{2}\right)e^{-\theta_{vib}n/T} = \frac{e^{-2\theta_{vib}/T}+e^{-\theta_{vib}/T}}{\left(1-e^{-\theta_{vib}/T}\right)^3} + \frac{e^{-\theta_{vib}/T}}{\left(1-e^{-\theta_{vib}/T}\right)^2} + \frac{1}{4\left(1-e^{-\theta_{vib}/T}\right)}$$

$$= \frac{2e^{-\theta_{vib}/T}}{\left(1-e^{-\theta_{vib}/T}\right)^3} + \frac{1}{4\left(1-e^{-\theta_{vib}/T}\right)}$$

And:

$$q_{vib} = \frac{e^{-\theta_{vib}/2T}}{\left(1-e^{-\theta_{vib}/T}\right)}\left\{1+\beta\nu x_e h\left(\frac{1}{4}+2\left(\frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}}\right)^2\right)\right\}$$

$$\boxed{q_{vib}^{Morse} = q_{vib}^{HO}\left[1+\beta\nu x_e h\left(\frac{1}{4}+2\left(q_{vib}^{HO}\right)^2\right)\right]}$$

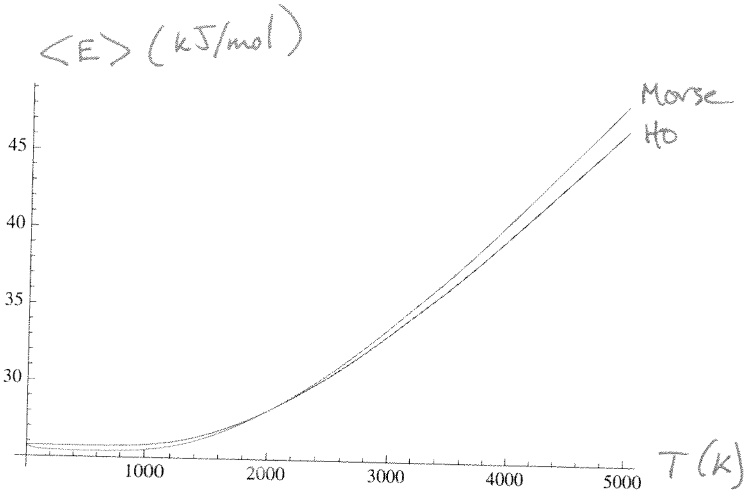
$\langle E\rangle = \left(\frac{\partial \ln q^{Morse}}{\partial \beta}\right) \leftarrow$ we need $\ln q^{Morse}$

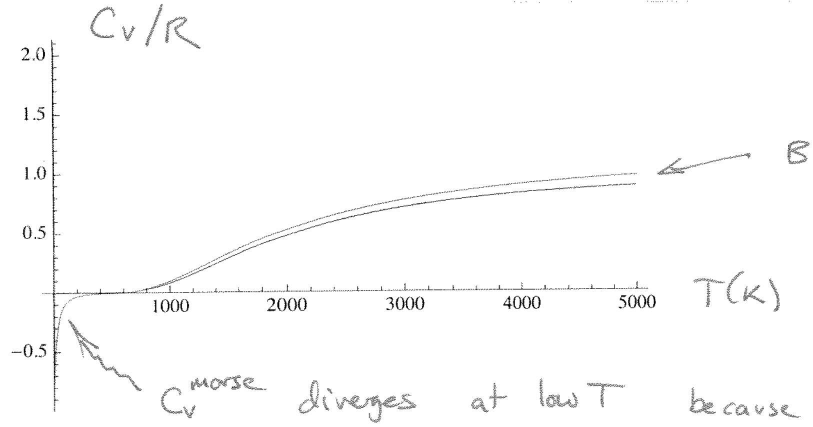
6c continued)

$$\ln q^{morse} = \ln q^{HO} + \ln\left(1 + \beta \nu x_e h \left[\frac{1}{4} + 2\left(q^{HO}\right)^2\right]\right)$$

$$\frac{\partial \ln q^{morse}}{\partial \beta} = \frac{\partial \ln q^{HO}}{\partial \beta} + \frac{1}{1 + \beta \nu x_e h \left(\frac{1}{4} + 2 q_{HO}^2\right)} \left(\nu x_e h \left(\frac{1}{4} + 2 q_{HO}^2\right) + \beta \nu x_e h \, 4 q_{HO} \frac{\partial q_{HO}}{\partial \beta}\right)$$

Since this gets ugly quickly, we turn to mathematica:





Both converge to $C_v = R$

C_v^{morse} diverges at low T because levels get very close together

```
# A simple Morse oscillator code to predict the average energy and heat
# capacity for a morse approximation to H2 by summing up over all allowed
# states of the system:

import math

nmax = 17         # derived in the solution set
xe = 1.0 / 35.0   # likewise
nu = 1.29e14      # and this
h = 6.626e-34     # Planck's constnat
kb = 1.381e-23    # Boltzmann's constant
Na = 6.022e23     # Avogadro's number

def eMorse(n):
    em = h * nu * (n + 0.5) * (1.0 + xe * (n + 0.5))
    return em

Tmin = 1.0
Tmax = 5000.0
ntemps = 5000

E0 = eMorse(0)

Qtots = []  # create an array to store the partition functions
Eners = []  # create an array to store the energies

for i in range(ntemps):
    T = Tmin + (Tmax-Tmin)*float(i)/float(ntemps)
    beta = 1.0 / (kb * T)

    # first get the total partition function:
    qtot = 0.0
    for n in range(nmax):
        # to prevent underflow, we'll set the energy scale relative to the
        # zero-point energy (that way, q will always be >= 1 even at low T)
        qtot = qtot + math.exp(-beta * (eMorse(n)-E0))

    Qtots.append(qtot)
    # next compute the average energy
    eave = 0.0
    for n in range(nmax):
        eave = eave + eMorse(n) * math.exp(-beta * (eMorse(n)-E0))

    # normalize by the partition function
    eave = eave / qtot

    Eners.append(eave)

# now, after we're done computing energies, we can compute the heat
# capacities
for i in range(ntemps):
    T = Tmin + (Tmax-Tmin)*float(i)/float(ntemps)
    dT = (Tmax-Tmin)/float(ntemps)

    if (i == 0):
        # use a forward difference approximation at the start:
        Cv = (Eners[i+1] - Eners[i]) / dT
    elif (i == ntemps-1):
        # use a backward difference approximation at the end:
        Cv = (Eners[i] - Eners[i-1]) / dT
    else:
        # use a centered difference approximation everywhere else:
        Cv = (Eners[i+1]-Eners[i-1]) / (2.0 * dT)

    # return energy values in kJ / mol, Cv in units of R
    print "%f\t%f\t%f\t%f" % (T, Qtots[i], Eners[i] * Na / 1000.0, Cv / kb)
```

Morse Oscillator model for H2

Exact sum of states