Statistical Physics: Workshop Problems 5

(1) (a) From the hint, or otherwise, note that

$$\int_{-\infty}^{\infty} dx \, \exp[-b\,x^2] = \sqrt{\frac{\pi}{b}}$$

$$(\text{derivative wrt } b) \Rightarrow \int_{-\infty}^{\infty} dx \, x^2 \, \exp[-b\,x^2] = \frac{1}{2}\sqrt{\frac{\pi}{b^3}}.$$

Using the Boltzmann distribution and these standard integrals, the average energy for x is

$$\langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} dx \, a\,x^2 \, \exp[-\beta\,a\,x^2]}{\int_{-\infty}^{\infty} dx \, \exp[-\beta\,a\,x^2]} = a\,\frac{1}{2}\sqrt{\frac{\pi}{(\beta\,a)^3}}\sqrt{\frac{\beta\,a}{\pi}} = \frac{k_{\mathrm{B}}T}{2}$$

where β is the inverse temperature, $\beta = 1/(k_{\mathrm{B}}T)$.

(b) Since the energy is additive, the internal energy will be

$$U = N\eta\frac{k_{\mathrm{B}}T}{2}.$$

(2) (a) For the Ne atoms, the energy of each atom is (translational kinetic energy)

$$(1/2)mv_x^2 + (1/2)mv_y^2 + (1/2)mv_z^2$$

so there are three degrees of freedom. The internal energy and heat capacity are therefore

$$U = \frac{3}{2}Nk_{\mathrm{B}}T \Rightarrow C_V = \frac{dU}{dT} = \frac{3}{2}Nk_{\mathrm{B}}.$$

(b) For the O_2 molecules, the energy due to translational kinetic energy of the centre of mass is as above. There is additionally rotational motion with energy

$$(1/2)I\omega_1^2 + (1/2)I\omega_2^2$$

where I is the moment of inertia for the two rotations about the centre of the diatomic molecule. The moment of inertia for rotation around axis connecting the two atoms is zero, so we have two degrees of freedom in the energy due to rotations, therefore

$$U = \frac{3+2}{2}Nk_{\mathrm{B}}T \Rightarrow C_V = \frac{dU}{dT} = \frac{5}{2}Nk_{\mathrm{B}}.$$

(c) Finally, the O_2 molecule is vibrating along the diatomic bond. The energy of one simple harmonic oscillator has two degrees of freedom defined by the kinetic a potential energies

$$\frac{1}{2}mv^2 + \frac{1}{2}kx^2.$$

The energy U and heat capacity associated with vibrations is therefore

$$U = \frac{2}{2}Nk_{\mathrm{B}}T \Rightarrow C_V = \frac{dU}{dT} = Nk_{\mathrm{B}}.$$

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(d) For the O_2 molecules, the total energy due to translations, rotations and vibrations is at high temperatures

$$U = \frac{3+2+2}{2}Nk_BT \Rightarrow C_V = \frac{dU}{dT} = \frac{7}{2}Nk_B$$

(3) (a)

$$
\begin{aligned}
Z_1^{\text{vibr}} &= \sum_{n=0}^{\infty} \exp[-\beta(n+1/2)\hbar\omega] \\
&= \exp\left[\frac{-\beta\hbar\omega}{2}\right] \sum_{n=0}^{\infty} \exp[-\beta\hbar\omega n] \\
&= \frac{\exp\left[\frac{-\beta\hbar\omega}{2}\right]}{1 - \exp[-\beta\hbar\omega]} \\
&= \frac{\exp\left[\frac{\beta\hbar\omega}{2}\right]}{\exp[\beta\hbar\omega] - 1}
\end{aligned}
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(b)

$$
\begin{aligned}
U^{\text{vibr}} &= -N\frac{\partial \ln Z_1}{\partial\beta} = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega \exp[\beta\hbar\omega]}{\exp[\beta\hbar\omega] - 1} \\
\Rightarrow C_V^{\text{vibr}} &= \frac{\partial U^{\text{vibr}}}{\partial T} = \frac{Nk_B\hbar^2\omega^2\beta^2 \exp(\beta\hbar\omega)}{(\exp(\beta\hbar\omega) - 1)^2}
\end{aligned}
$$

The high temperature limits are $U^{\text{vibr}} \simeq Nk_BT$ and $C_V^{\text{vibr}} \simeq Nk_B$. These results are the same as the vibrational contributions to U and C_V in (2) for $\eta = 2$.

(c) A straightforward substitution gives

$$C_V^{\text{vibr}} = \frac{Nk_B(T^{\text{vibr}}/T)^2 \exp(T^{\text{vibr}}/T)}{(\exp(T^{\text{vibr}}/T) - 1)^2}.$$

(d) $T^{\text{vibr}} = h\nu/k_B = 2200K \Rightarrow T^{\text{vibr}}/T = 2200/293 = 7.51$. So the heat capacity is

$$C_V^{\text{vibr}} = \frac{Nk_B(T^{\text{vibr}}/T)^2 \exp(T^{\text{vibr}}/T)}{(\exp(T^{\text{vibr}}/T) - 1)^2} = \frac{Nk_B 7.51^2 \exp 7.51}{(\exp 7.51 - 1)^2} = 0.0310 Nk_B.$$

At room temperature $C_V = 5/2Nk_B$ so the percentage is 0.0310/2.5=1.24%.