Chemistry 410B Exam 2 Spring 2009
Solutions

1. **40 points.**

   (a) The van der Waals b coefficient for $\mathrm{CCl_2F_2}$ is $0.0998\,\mathrm{L\,mol^{-1}}$. Estimate R_{LJ}. **Solution:**

   $$b \approx \frac{2\mathcal{N}_A \pi R_{\mathrm{LJ}}^3}{3} \qquad R_{\mathrm{LJ}} \approx \left(\frac{3b}{2\mathcal{N}_A\pi}\right)^{1/3} = \boxed{4.3\,\text{Å}}.$$

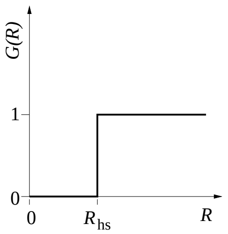
   (b) Give the value of each probability for a rotating linear molecule:

   i. $\lim_{T\to 0} \mathcal{P}(J=0) = \boxed{1}$ (all molecules in ground state.)

   ii. $\lim_{T\to 0} \mathcal{P}(J=4) = \boxed{0}$ (all molecules in ground state.)

   iii. $\lim_{T\to \infty} \mathcal{P}(J=4) = \boxed{0}$ (molecules equally spread over all states.)

   (c) Sketch the pair correlation function for a hard sphere potential.



   (d) Identify each of the following particles as a fermion ("F") or boson ("B").

   i. electron $\boxed{\mathrm{F}}$

   ii. $^{235}\mathrm{U}$ nucleus $\boxed{\mathrm{F}}$

   iii. $^{235}\mathrm{U}$ neutral atom $\boxed{\mathrm{B}}$

   iv. $^{19}\mathrm{F}^-$ ion $\boxed{\mathrm{F}}$

   v. $^{1}\mathrm{H}_2$ molecule $\boxed{\mathrm{B}}$

2. Calculate the pressure in bar of 1210 mol krypton in a 150.0 L container at 298 K, if $a = 2.325\,\mathrm{L^2\,m\bar{o}l^{-2}}$ and $b = 0.0396\,\mathrm{L\,mol^{-1}}$. **Solution:**

$$\begin{aligned}
RT &= \left(P + \frac{a}{V_m^2}\right)(V_m \;-\; b) \\
P &= \frac{RT}{V_m - b} - \frac{a}{V_m^2} \\
&= \frac{(0.083145\,\mathrm{bar\,L\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{(150.0\,\mathrm{L}/1210\,\mathrm{mol}) - 0.0396\,\mathrm{L\,mol^{-1}}} - \frac{2.325\,\mathrm{L^2\,m\bar{o}l^{-2}}}{(150.0\,\mathrm{L}/1210\,\mathrm{mol}))^2} \\
&= \boxed{142\,\mathrm{bar}}.
\end{aligned}$$

   The ideal gas pressure would be 200 bar.

3. Find the integral approximation to the vibrational partition function for a degenerate bend in a linear molecule, where $E_{\mathrm{vib}} = \omega_e v$ and $g_{\mathrm{vib}} = v + 1$. **Solution:** For the integral approximation, we replace the sum by an integral and multiply by the volume element dv, which effectively has

a value of 1:

$$\begin{aligned}
q_{\text{vib}} &= \sum_0^\infty (v+1)\, e^{-\omega_e v/(k_B T)} \approx \int_0^\infty (v+1)\, e^{-\omega_e v/(k_B T)}\, dv \\
&= \int_0^\infty v\, e^{-\omega_e v/(k_B T)}\, dv + \int_0^\infty e^{-\omega_e v/(k_B T)}\, dv \\
&= \frac{1}{\omega_e^2/(k_B T)^2} + \frac{1}{\omega_e/(k_B T)} = \frac{(k_B T)^2 + \omega_e (k_B T)}{\omega_e^2}.
\end{aligned}$$

In the limit that $k_B T \gg \omega_e$, this simplifies to $(k_B T/\omega_e)^2$, which is the same result predicted in the high-temperature limit from multiplying together the two partitiion functions for each bending mode, $q_{\text{vib}}(1) q_{\text{vib}}(2)$.

4. For a crystal where each vibrational mode can absorb a finite amount of energy per mode,

$$\epsilon(T) = \frac{\epsilon_0 k_B T}{\epsilon_0 + k_B T},$$

(a) find an equation for C_{Vm}; (b) find $\lim_{T\to 0} C_{Vm}$; (c) find $\lim_{T\to\infty} C_{Vm}$. **Solution:** There are still $3N$ vibrational modes, as in the Einstein theory, so the molar energy will be $E_m = 3\mathcal{N}_A \epsilon(T)$. To get the heat capacity, we'll take the derivative with respect to temperature:

$$\begin{aligned}
C_{Vm} &= \left(\frac{\partial E_m}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{3\mathcal{N}_A \epsilon_0 k_B T}{\epsilon_0 + k_B T}\right) \\
&= 3\mathcal{N}_A k_B \epsilon_0 \left[\frac{1}{\epsilon_0 + k_B T} - \frac{T}{(\epsilon_0 + k_B T)^2}\right] = \frac{3R\epsilon_0}{\epsilon_0 + k_B T}\left[1 - \frac{T}{\epsilon_0 + k_B T}\right] \\
\lim_{T\to 0} C_{Vm} &= \frac{3R\epsilon_0}{\epsilon_0 + 0}\left[1 - \frac{0}{\epsilon_0 + 0}\right] = \boxed{3R} \\
\lim_{T\to\infty} C_{Vm} &= \lim_{T\to\infty} \frac{3R\epsilon_0}{k_B T}\left[1 - \frac{T}{k_B T}\right] = \boxed{0}.
\end{aligned}$$