1. 40 points.

(a) The van der Waals \( b \) coefficient for \( \text{CCl}_2\text{F}_2 \) is \( 0.0998 \text{ L mol}^{-1} \). Estimate \( R_{\text{LJ}} \). \textbf{Solution:}

\[
b \approx \frac{2N_A \pi R_{\text{LJ}}^3}{3}, \quad R_{\text{LJ}} \approx \left( \frac{3b}{2N_A \pi} \right)^{1/3} = 4.3 \text{ Å}.
\]

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

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

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

iii. \( \lim_{T \to \infty} \mathcal{P}(J = 4) = 0 \) (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 \( \boxed{\text{F}} \)

ii. \( ^{235}\text{U} \) nucleus \( \boxed{\text{F}} \)

iii. \( ^{235}\text{U} \) neutral atom \( \boxed{\text{B}} \)

iv. \( ^{19}\text{F}^- \) ion \( \boxed{\text{F}} \)

v. \( ^1\text{H}_2 \) molecule \( \boxed{\text{B}} \)

2. Calculate the pressure in bar of 1210 mol krypton in a 150.0 L container at 298 K, if \( a = 2.325 \text{ L}^2 \text{ mol}^{-2} \) and \( b = 0.0396 \text{ L mol}^{-1} \). \textbf{Solution:}

\[
RT = \left( P + \frac{a}{V_m^2} \right) (V_m - b)
\]

\[
P = \frac{RT}{V_m^2} - \frac{a}{V_m^2}
\]

\[
= \frac{(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(150.0 \text{ L}/1210 \text{ mol}) - 0.0396 \text{ L mol}^{-1}} - \frac{2.325 \text{ L}^2 \text{ mol}^{-2}}{(150.0 \text{ L}/1210 \text{ mol})^2}
\]

\[
= 142 \text{ bar}.
\]

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 \( E_{\text{vib}} = \omega_v v \) and \( g_{\text{vib}} = v + 1 \). \textbf{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:

\[
q_{\text{vib}} = \sum_{v=0}^{\infty} (v + 1) e^{-\omega_e v / (k_B T)} \approx \int_0^\infty (v + 1) e^{-\omega_e v / (k_B T)} dv
\]

\[
= \int_0^\infty v e^{-\omega_e v / (k_B T)} dv + \int_0^\infty e^{-\omega_e v / (k_B T)} dv
\]

\[
= \frac{1}{\omega_e^2 (k_B T)^2} + \frac{1}{\omega_e (k_B T)} = \frac{(k_B T)^2 + \omega_e (k_B T)}{\omega_e^2}.
\]

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 partition 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 \(C_V m\); (b) find \(\lim_{T \to 0} C_V m\); (c) find \(\lim_{T \to \infty} C_V m\). **Solution:** There are still 3N vibrational modes, as in the Einstein theory, so the molar energy will be \(E_m = 3N_A \epsilon(T)\). To get the heat capacity, we’ll take the derivative with respect to temperature:

\[
C_V m = \left(\frac{\partial E_m}{\partial T}\right)_V = \frac{\partial}{\partial T} \left(\frac{3N_A \epsilon_0 k_B T}{\epsilon_0 + k_B T}\right)
\]

\[
= 3N_A k_B \epsilon_0 \left[\frac{1}{\epsilon_0 + k_B T} - \frac{T}{(\epsilon_0 + k_B T)^2}\right] = \frac{3R \epsilon_0}{\epsilon_0 + k_B T} \left[1 - \frac{T}{\epsilon_0 + k_B T}\right]
\]

\[
\lim_{T \to 0} C_V m = \frac{3R \epsilon_0}{\epsilon_0 + 0} \left[1 - \frac{0}{\epsilon_0 + 0}\right] = 3R
\]

\[
\lim_{T \to \infty} C_V m = \lim_{T \to \infty} \frac{3R \epsilon_0}{k_B T} \left[1 - \frac{T}{k_B T}\right] = 0.
\]