Exam #1 Review Questions

What follows is a sampling of questions of the sort you can expect on Exam #1. The exam will consist of 5-8 questions like these, with a mix designed to test your understanding of basic concepts and your ability to do simple calculations and derivations. (Note that some of the questions below require data of the sort tabulated in the topic summaries. I would supply all necessary data in the exam.)

1. Based on the idea of corresponding states, at what \( T \) and \( P \) would you expect propane to behave most similarly to Ar at 200 K and 200 bar?

2. The Carnahan-Starling equation,

\[
Z = \frac{PV}{RT} \approx \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} \quad \text{where} \quad y = \frac{b_0}{4V} \quad \text{(and} \quad b_0 = \frac{2\pi N_A \sigma^3}{3})
\]

provides an excellent approximation to the equation of state of a hard-sphere fluid at all densities. What are the 1st and 2nd virial coefficients, \( B_2(V) \) and \( B_3(V) \), predicted by this equation of state? [Hint: \((1 + x)^{-3} = 1 - 3x + 6x^2 - 10x^3 + 15x^4 + \ldots \quad \text{for} \quad |x| < 1.]\]

3. The energies of a rigid rotor in 2-dimensions are described by the equation:

\[
\varepsilon_J = \frac{\hbar^2 J^2}{2I} \quad J = 0, 1, 2, \ldots
\]

The states are non-degenerate.

(a) Write an expression for the partition function \( Q(N,T) \) of a collection of \( N \) non-interacting but indistinguishable rotors of this sort.

(b) Assuming that one can make the high-temperature approximation and convert the sum to an integral, evaluate \( Q(N,T) \) explicitly.

(c) What is the energy and heat capacity of this system? [Hint: \( \int_0^\infty e^{-ax^2} \, dx = \left(\frac{\pi}{4a}\right)^{1/2} \).]

4. For a diatomic molecule in equilibrium, there is often a maximum in the population of molecules as a function of rotational quantum number \( J \), whereas the population of vibrational levels always decreases with the vibrational quantum number \( v \). Why is there such a difference?
5. The vibrational temperature of Br$_2$ is 463 K. Above what temperature does the population of Br$_2$ molecules in vibrationally excited states (i.e. $n>0$) exceed 10%?

6. Is the value of the classical partition function of the rigid rotor that one calculates using the high temperature (or classical) approximation greater than or less than the exact value? Explain.

7. M&S (p. 66) describe the law of corresponding states to mean that “all gases have the same properties if they are compared at corresponding conditions (same values of $P_R$, $V_R$, and $T_R$).” Does the term “properties” here extend to thermal properties? For example, does the law imply that all gases have the same heat capacity when viewed under corresponding conditions? Explain.

8. M&S (Eqs. 4.39-4.40) write expressions for the molecular partition function and molar energy of an ideal gas of diatomic molecules which are equivalent to:

$$q(V, T) = \frac{V}{A^3} \cdot \frac{T}{e^{\Theta_{\text{rot}}/k_BT}} e^{-\Theta_{\text{vib}}/k_BT} e^{D_e/k_BT}$$

$$\Lambda = \left( \frac{h^2}{2\pi m k_BT} \right)^{1/2} \quad (5-1)$$

$$\bar{U} = \frac{3}{2} RT + RT + R \frac{\Theta_{\text{vib}}}{2} + R \frac{\Theta_{\text{vib}} e^{-\Theta_{\text{vib}}/k_BT}}{1 - e^{-\Theta_{\text{vib}}/k_BT}} - N_A D_e$$

These expressions depend on the choice M&S make for the zero of energy, which they take to be the energy of separated atoms at rest. How would these two expressions change if instead one took the zero of energy to be the energy of the lowest quantum state of the molecule (i.e. the ground electronic state and with the translational, rotational, and vibrational quantum numbers taking their lowest values)?

9. To what extent would you expect the triple-point parameters of a substance to serve as reducing variables for corresponding states correlations?

10. The ratio of Lennard-Jones parameters of Ar and C(CH$_3$)$_4$ (“np”) derived from 2$^{\text{nd}}$ virial coefficient data is $\sigma_{\text{np}}/\sigma_{\text{Ar}} = 1.98$. The ratio of critical temperatures of these two fluids is $T_{c_{\text{np}}}/T_{c_{\text{Ar}}} = 2.88$. Interpret this observation based on corresponding states ideas.
11. The graph below shows $B_{2V}(T)$ data for He, Ar, Kr, and Xe scaled by the appropriate Lennard-Jones parameters. In this reduced representation the data for Ar, Kr, and Xe nearly coincide, whereas the He data deviate substantially from the correlation established by remaining data. Explain this behavior.

![Graph showing $B_{2V}(T)$ data for He, Ar, Kr, and Xe scaled by Lennard-Jones parameters.]

12. The heat capacity of an ideal gas of linear molecules is given by M&S as:

$$
\frac{C_v}{Nk_B} = \frac{3}{2} + \frac{2}{2} + \frac{3n-5}{2} \left( \Theta_{\text{vib}}^{(i)} \right)_T \left( \frac{e^{-\Theta_{\text{vib}}^{(i)}/T}}{1-e^{-\Theta_{\text{vib}}^{(i)}/T}} \right)
$$

(M&S 4.59)

(a) What molar heat capacity does this equation predict for Cl$_2$(g) at 5000 K?

(b) What is the limiting value of $C_v$ of a diatomic molecule like Cl$_2$(g) predicted by this equation as $T \to \infty$.

(c) The experimental heat capacity of Cl$_2$ at 5000 K is $C_v = 31.912$ J K$^{-1}$ mol$^{-1}$. Discuss the approximations inherent in Eq. 4.59 that might be responsible for the deviation between the calculated and experimental values of $C_v$ at this high temperature.

13. For the three molecules depicted below (all planar) construct a table summarizing the following quantities:

- i) the rotational symmetry number
- ii) the number of vibrational modes
- iii) the limiting $T \to \infty$ value of the molar heat capacity $C_v / R$

![Molecules O$_3$, BF$_3$, C$_{10}$H$_8$]
14. At 300 K and 375 bar the compressibility factor of CH₄(g) is 1.0. What, if anything, does this information imply about the intermolecular interactions of CH₄ under these conditions?

15. Parameters of the Lennard-Jones potential of Ar, obtained from fits to 2nd virial coefficient data, are $\epsilon/k_B = 120$ K and $\sigma = 3.41$ Å. Use this information, together with the critical properties of Ar and CCl₄, to estimate Lennard-Jones parameters for CCl₄.

16. Which of the potentials illustrated below would give rise to corresponding states behavior? Explain your reasoning.

Note that $\sigma, \epsilon, R, K,$ and $a$ are to be considered molecule-specific parameters.