Exam #1 Solutions

1. (10 points) Use the generalized compressibility diagram provided on the last page to estimate over what range of pressures Ar at room temperature conforms to the ideal gas law to within ±20%.

Assume that room temperature is 298 K. The critical temperature of Ar is $T_c = 150.95$ K so that the reduced temperature being considered is $rT = 298/151 = 1.97 \sim 2$. The isotherm corresponding to this reduced temperature is shown in red on the correlation diagram to the right. Ideal volumetric behavior in this representation corresponds to a compressibility factor of $Z = 1$. Greater than 20% deviation is not observed for the $T_r = 2$ isotherm until a pressure of ~11 in reduced units. For Ar, $P_c = 49.3$ bar so that this reduced pressure corresponds to $P = P_r \cdot P_c = 540$ bar.

Thus, at room temperature Ar can be described to within 20% accuracy using the ideal gas e.o.s. over the pressure range 0 → 540 bar.

Aside: That the ideal gas law should be reasonably accurate up to this extreme pressure might seem strange. However it should be remembered that at a temperature of ~2$T_c$ such a high pressure does not mean high densities. In the present case, a pressure of 540 bar corresponds to a reduced density of 1.4 – high but still far from liquid like.

2. (15 points) The 2nd virial coefficient of Kr can be represented by the equation:

$$B_2(T) / \text{cm}^3 \text{mol}^{-1} = 31.70 - 1.298 \times 10^4 (K / T) - 3.327 \times 10^6 (K / T)^2$$

Use this expression and corresponding states ideas to estimate the 2nd virial coefficient of O₂ at 298 K.

There are two ways that one could make this estimate. In either case the essential idea is that under corresponding conditions, which, in the case of viral data (the $P=0$ limit), means the same reduced temperatures, the reduced virial coefficients of the two gases should be equal. For reducing variables, one can either use the Lennard-Jones parameters listed in Table 2.7, which was my original intention, or one could equally well use the critical parameters listed in the 1st table of the data sheet. The relevant values are tabulated below.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\varepsilon / k_B / K$</th>
<th>$b_0 / \text{cm}^3 \text{mol}^{-1}$</th>
<th>$T_c / K$</th>
<th>$\overline{V_c} / \text{cm}^3 \text{mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>118</td>
<td>57.9</td>
<td>154.6</td>
<td>73.4</td>
</tr>
<tr>
<td>Kr</td>
<td>164</td>
<td>70.9</td>
<td>209.4</td>
<td>91.2</td>
</tr>
</tbody>
</table>

Calculations using both methods are outlined below:
i) Using LJ parameters: Here the correspondence is:

\[ B_{O_2}^*(T^*) = B_{Kr}^*(T^*) = B^*(T^*) \]

where \( T^*_x \equiv \frac{k_b T}{\varepsilon_x} \) and \( B_x^* = B_x / b_{0x} \).

The virial coefficient of \( O_2 \) at 298 K can therefore be estimated from

\[ B_{O_2}(T) \approx b_{0o2} \cdot B^*(T^*) = k_b T_0 / \varepsilon_{o2} \]

where \( B^*(T^*) \) is obtained from the parameterization of experimental Kr data via:

\[ B^*[T^* = T \cdot (k_b / \varepsilon_{o2})] = B[T_{Kr} = T^* \cdot (\varepsilon_{Kr} / k_b)] / b_{0Kr} \]

Using the tabulated information, a temperature of 298 K corresponds to a reduced temperature of \( T^* = 298 K / 118 K = 2.52 \) for \( O_2 \). For Kr, this reduced temperature corresponds to a real temperature of \( T_{Kr} = 164 K \cdot 2.52 = 413.3 K \). Using the parameterization of \( B(T) \) provided for Kr, at this temperature:

\[ B_{Kr}(413.3K) = -19.17 \text{ cm}^3 \text{ mol}^{-1} \] and \( B^*(T^*) = -19.17 / 70.9 = -0.272 \)

Finally, the virial coefficient of \( O_2 \) desired is:

\[ B_{O_2}(298 K) = -0.272 \cdot 57.9 \text{ cm}^3 \text{ mol}^{-1} = -24.7 \text{ cm}^3 \text{ mol}^{-1} \]

ii) Using critical parameters: Here the correspondence is:

\[ B_{O_2}^*(T_r) = B_{Kr}^*(T_r) = B^*(T_r) \]

where \( T_r \equiv T / T_{cx} \) and \( B_x^* = B_x / \sqrt{V_{cx}} \).

The virial coefficient of \( O_2 \) at 298 K can therefore be estimated from

\[ B_{O_2}(T) \approx \sqrt{V_{e02}} \cdot B^*(T_r = T / T_{e02}) \]

where \( B^*(T_r) \) is obtained from the parameterization of experimental Kr data via:

\[ B^*[T_r = T / T_{e02}] = B[T_{Kr} = T_r \cdot T_{cKr}], \sqrt{V_{cKr}} \]

A temperature of 298 K corresponds to a reduced temperature of \( T_r = 298 K / 154.6 K = 1.93 \) for \( O_2 \). For Kr, this reduced temperature corresponds to a real temperature of \( T_{Kr} = 209.4 K \cdot 1.93 = 403.6 K \). Using the parameterization of \( B(T) \) provided for Kr, at this temperature:

\[ B_{Kr}(403.6K) = -20.89 \text{ cm}^3 \text{ mol}^{-1} \] and \( B^*(T_r) = -20.89 / 91.2 = -0.229 \)

Here the estimate for the virial coefficient of \( O_2 \) is:

\[ B_{O_2}(298 K) = -0.229 \cdot 73.4 \text{ cm}^3 \text{ mol}^{-1} = -16.8 \text{ cm}^3 \text{ mol}^{-1} \]

The experimental value of \( B_2(298.15) \) for \( O_2 \) is -16.5 cm³ mol⁻¹. In this case at least the estimate obtained using the critical parameters is much closer to the experimental value.
3. (10 points) The acentric factors of methane, ethane, CO2, and HF are 0.008, 0.098, 0.225, and 0.372, respectively. Rationalize these values in terms of the nature of the intermolecular interactions present in the various fluids.

The acentric factor ($\omega$) is an empirical measure of the extent to which the $P(\bar{V},T)$ e.o.s. of a fluid departs from that of the prototypical simple fluid Ar. The conformity ($\omega$~0) or lack of conformity in volumetric properties reflects an underlying similarity or dissimilarity of the effective intermolecular potential governing the interactions between molecules of a given fluid and the simple spherical (“centric”) interactions operative in Ar.

The interactions between two CH4 molecule are nearly spherically symmetric and resemble those between two Xe atoms. This similarity which is reflected in the value of $\omega$ of CH4 being close to zero. Although the nature of the interactions between C2H6 molecules is essentially the same as between CH4 molecules, i.e. in both cases only dispersion interactions are important, the shape of C2H6 is much less spherical and its effective intermolecular potential therefore deviates more from that of a rare gas atom, resulting in a larger value of $\omega$. CO2 is also far from spherical in shape. In addition, although not dipolar, it possesses important electrical (quadrupole-quadrupole) interactions that make its interactions even less similar to those of a rare-gas atom, which is the reason for its larger value of $\omega$. Finally, HF possesses a large dipole moment and is capable of forming strong hydrogen bonds between molecules. Its large value of $\omega$ reflects the substantial differences in its interactions compared to simple spherical systems. These differences mean that HF displays $P(\bar{V},T)$ behavior which departs significantly from that of rare-gas like fluids.

4. (30 points) The states and energies of a model 4-bead chain are enumerated below:

<table>
<thead>
<tr>
<th>conformation</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>straight</td>
<td>0</td>
</tr>
<tr>
<td>single bend</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>double bend</td>
<td>$2\varepsilon$</td>
</tr>
</tbody>
</table>

(a) What is the partition function $q_{\text{conf}}(T)$ associated with the conformations of such a chain, and what are the probabilities of finding the chain in the various conformations (i.e. having 0, 1, or 2 bends)?

(b) At what temperature does the probability finding the chain with a single bend exceed the probability of it being straight?

(c) Write an expression for the average energy of the chain. How does this average energy behave in the limits of $T \to 0$ and $T \to \infty$?

(d) Use the results of (d) to sketch the average energy and heat capacity of the chain versus temperature. (No need to calculate anything – just depict the qualitative behavior.)

(a) The partition function is:

$$q_{\text{conf}}(\beta) = 1 + 3e^{-\beta \varepsilon} + e^{-2\beta \varepsilon}$$
and the probabilities of finding a 0-, 1-, or 2-bend conformation are:

\[
p_0 = \frac{1}{q} \quad p_1 = \frac{3e^{-\beta \epsilon c}}{q} \quad p_2 = \frac{e^{-2\beta \epsilon c}}{q}
\]

(b) The probability of a single bend conformer relative to a straight chain is:

\[
p_1 / p_0 = 3e^{-\beta \epsilon c}
\]

We want to find \( T \) (or \( \beta \)) such that \( p_1 / p_0 > 1 \) which means \( 3e^{-\beta \epsilon c} > 1 \). This condition occurs for

\[
\beta \epsilon < \ln 3 \quad \text{or} \quad T > \left( \frac{\epsilon / k_B}{\ln 3} \right) = 0.91(\epsilon / k_B)
\]

(c) The average energy is given by:

\[
< E_{\text{conf}} > = -\frac{d \ln q_{\text{conf}}}{d \beta} = \frac{1}{q_{\text{conf}}}(3e^{-\beta \epsilon c} + 2e^{-2\beta \epsilon c})
\]

i) as \( T \to 0, \beta \to \infty, e^{-\beta \epsilon c} \to 0, q_{\text{conf}} \to 1 \) so that \(< E > \to 0\)

ii) as \( T \to \infty, \beta \to 0, e^{-\beta \epsilon c} \to 1, q_{\text{conf}} \to 5 \) so that \(< E > \to \frac{1}{2}(3\epsilon + 2\epsilon) = \epsilon\)

(d) The sketches I made are shown on the following page. The main thing I was looking for in these plots was a correct depiction of the low and high temperature limiting behavior. The energy limits are described above. As discussed in class, the heat capacity will go to zero both at high and low temperatures for a system such as this where there are a finite number of energy states available.

In my sketches I show steps in \(< E >\) to indicate first randomization of population between 0 and 1-bend chains and then incorporation of 2-bond chains. I wasn’t sure how well defined these two steps would be, so I programmed the equations into Mathcad to find out how close my guess was. As illustrated below, the energies of 1- and 2-bend chains are apparently not different enough to produce the 2-level structure I depicted in \(< E >\) or the resulting double-peaked structure in \(C_V\) I’d sketched. (The energies need to differ by 5-10-fold for this type of structure to be obvious.)
5. (5 points) **What is the correct value of the rotational partition function of HCl at 0 K? Explain your answer.**

The classical rotational partition function of a diatomic molecule like HCl is \( q_{\text{rot}} = T / \Theta_{\text{rot}} \). If one used this expression one would predict that \( q_{\text{rot}} \to 0 \) as \( T \to 0 \), but this would be incorrect. This expression for \( q_{\text{rot}} \) is a high-temperature approximation, which is not valid as \( T \to 0 \). For the correct answer one must look at the expression for \( q_{\text{rot}} \) before making the high-temperature approximation:

\[
q_{\text{rot}} = \sum_{J=0}^{\infty} (2J + 1) \exp(-J(J+1)\Theta_{\text{rot}} / T)
\]

\[
= 1 + 3 \cdot \exp(-2\Theta_{\text{rot}} / T) + 5 \cdot \exp(-6\Theta_{\text{rot}} / T) \ldots
\]

As \( T \to 0 \) only the 1\(^{\text{st}}\) term of this series survives and this term yields the correct limiting behavior \( q_{\text{rot}} \to 1 \) as \( T \to 0 \) (i.e. there is effectively a single rotational state available at 0K, the ground rotational state, \( J=0 \)).

6. (20 points) **The partition function of a hard-sphere gas of mass \( m \) and size parameter \( b \) can be written:**

\[
Q(N,V,T) \equiv \frac{1}{N!} \frac{(V - Nb)^N}{\Lambda^{3N}} \quad \text{with} \quad \Lambda = \left( \frac{h^2}{2\pi mk_b T} \right)^{1/2}
\]

(a) Derive expressions for the average energy and heat capacity of such a gas.

(b) Show that this \( Q \) leads to the expected volumetric equation of state \( P(V - N_b b) = RT \).

(c) How would you expect the partition function and the answers to part (a) to change if the gas were 2-dimensional rather than 3-dimensional?
(a) The average energy is determined from the partition function by:

\[ <E> = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \]

To perform the necessary differentiations we can focus only on the temperature dependence of \( Q \) and write:

\[ Q = c\Lambda^{-3N} = c'T^{3N/2} \]

where \( c \) and \( c' \) are independent of temperature. Thus,

\[ \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = \frac{\partial}{\partial T} \left\{ \frac{3N}{2} \ln(T) + \ln(c') \right\}_{N,V} = \frac{3N}{2T} \]

The energy is therefore

\[ <E> = \frac{3}{2} Nk_B T \]

The heat capacity is related to the energy by \( C_V = (\partial <E>/\partial T)_{N,V} \) so that

\[ C_V = \frac{3}{2} Nk_B \]

It should not be a surprise at this point that these energetic quantities are the same as those of an ideal gas.

(b) The pressure is given by

\[ P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} \]

Focusing on the volume dependence, \( Q \) can be written:

\[ \ln Q = N \ln(V - Nb) + \ln c \]

where \( c \) is independent of \( V \). Differentiation yields:

\[ P = k_B T \left( \frac{\partial}{\partial V} N \ln(V - Nb) \right)_{N,T} = \frac{Nk_B T}{(V - Nb)} \]

Rearranging and writing this expression and substituting \( N = nN_A \) and \( V = n\bar{V} \), and using \( N_A k_B = R \) provides the desired result

\[ P(\bar{V} - N_A b) = RT \]

(c) Except for the replacement of \( V \) by \( (V-Nb) \), the partition function of this hard-sphere gas is identical to the partition function of an ideal monatomic gas. Based on the derivation of the ideal gas partition function, it is reasonable to assume that the \( \Lambda^{3N} \) term here arises from treating translational motions using the particle-in-a-box model. In the ideal gas the translational partition function is a product of
three partition functions, one each for motion in the $x$, $y$, and $z$ directions. If one were to use the same development for a 2-dimensional system, one of these partition functions would be absent and instead of $\Lambda^3N$ one would have $\Lambda^2N$. The energy and heat capacity would then be:

$$<E> = Nk_B T, \quad \text{and} \quad C_V = Nk_B$$

7. (10 points) The heat capacity of CO$_2$ (g) is smaller than that of H$_2$O (g) at low temperatures but the opposite is true at temperatures higher than about 300 K. Explain why such behavior is expected.

CO$_2$ is a linear molecule whereas H$_2$O is bent. Although both molecules have 9 nuclear degrees of freedom, the geometric difference means that CO$_2$ has one fewer rotational and one more vibrational mode than does H$_2$O. At temperatures where translations and rotations have reached their classical limits (which is well below 300 K) but where vibrational degrees of freedom are inactive (i.e. $C_{\text{vib}} \sim 0$) the heat capacity of CO$_2$ should be less than that of H$_2$O by the contribution of 1 rotational degree of freedom to $C_V$, $\frac{1}{2}R$ (i.e. under these conditions $C_V$ (H$_2$O)$\sim 3R$ whereas $C_V$ (CO$_2$)$\sim \frac{5}{2}R$). Once vibrational modes become active this deficit will be made up and ultimately CO$_2$ will have the higher heat capacity ($\frac{13}{2}R$ versus $6R$) by virtue of the fact that vibrational degrees of freedom contribute 1 $R$ each to $C_V$ whereas rotational modes contribute only $\frac{1}{2}R$. 