1)

7.21 Suppose you had a program to simulate the motions of four molecules moving in 2D slowly enough that you could clearly see the velocities of all disks. (Hint: The Piston-Cylinder applet in the DMD module at Etomica.org is an example of such a program when kept in "adiabatic" mode.)

(a) Let the disk interactions be characterized by the ideal gas potential. Describe how the disks would move about. Note that the slow particles would always stay slow, and the fast particles stay fast. Why is that?

(b) Change the potential to "repulsion only" as modeled by a hard disk model. Compare the motions of the "repulsion only" particles to the ideal gas particles. Explain the differences. Which seems more realistic?

(c) Set the potential to "repulsion and attraction," as modeled by the square-well model with $\lambda = 2.0$. Compare the motions of these disks to the "repulsion only" particles and ideal gas particles. Explain the differences.

2)

P8.2 For certain fluids, the equation of state is given by $Z = 1 - b\rho/T_r$

Develop an expression for the enthalpy departure function for fluids of this type.

$$\frac{(H - H^{ig})}{RT} = \int_0^\rho -T\left[\frac{\partial Z}{\partial T}\right]_\rho \frac{d\rho}{\rho} + Z - 1 \qquad 8.24$$

3)

8.7 In Example 8.2 we wrote the equation of state in terms of $Z = f(T,\rho)$. The equation of state is also easy to rearrange in the form $Z = f(T,P)$. Rearrange the equation in this form, and apply the formulas from Section 8.6 to resolve the problem using departures at fixed T and P.

Example 8.2 is given below.

$$\left(\frac{H - H^{ig}}{RT}\right) = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad 8.29$$

$$\left(\frac{S - S^{ig}}{R}\right) = -\int_0^P \left[(Z - 1) + T\left(\frac{\partial Z}{\partial T}\right)_P\right]\frac{dP}{P} \qquad 8.30$$

Example 8.2 Real entropy in a combustion engine

A properly operating internal combustion engine requires a spark plug. The cycle involves adiabatically compressing the fuel-air mixture and then introducing the spark. Assume that the fuel-air mixture in an engine enters the cylinder at 0.08 MPa and 20°C and is adiabatically and reversibly compressed in the closed cylinder until its volume is 1/7 the initial volume. Assuming that no ignition has occurred at this point, determine the final T and P, as well as the work needed to compress each mole of air-fuel mixture. You may assume that C_V^{ig} for the mixture is 32 J/mole-K (independent of T), and that the gas obeys the equation of state,

$$PV = RT + aP$$

where a is a constant with value $a = 187$ cm³/mole. Do not assume that C_V is independent of ρ. Solve using density integrals.

Solution: The system is taken as a closed system of the gas within the piston/cylinder. Because there is no flow, the system is adiabatic, able, and reversible, the entropy balance becomes

$$\frac{dS}{dt} = \sum_{in} S^{in} \dot{m}^{in} - \sum_{out} S^{out} \dot{m}^{out} + \frac{\dot{Q}}{T_{sys}} + \dot{S}_{gen} = 0 \qquad 8.31$$

showing that the process is isentropic. To find the final T and P, we use the initial state to find the initial entropy and molar volume. Then at the final state, the entropy and molar volume are used to determine the final T and P.

This example helps us to understand the difference between departure functions at fixed T and V and departure functions at fixed T and P. The equation of state in this case is simple enough that it can be applied either way. It is valuable to note how the ln(Z) term works out. Fixed T and V is convenient since the volume change is specified in this example, and we cover this as Method I, and then use fixed T and P as Method II.

This EOS is easy to evaluate with either the pressure integrals of Section 8.6 or the density integrals of Section 8.5. The problem statement asks us to use density integrals.[a] First, we need to rearrange our equation of state in terms of $Z = f(T, \rho)$. This rearrangement may not be immediately obvious. Note that dividing all terms by RT gives $PV/RT = 1 + aP/RT$. Note that $V\rho = 1$. Multiplying the last term by $V\rho$, $Z = 1 + aZ\rho$ which rearranges to

$$Z = \frac{1}{1 - a\rho} \qquad\qquad PV = RT + aP$$

Also, we find the density at the two states using the equation of state,

$$\rho = \frac{P}{RT + aP} \Rightarrow \rho_1 = 3.257\text{E-}5 \text{ gmole/cm}^3 \Rightarrow \rho_2 = 2.280\text{E-}4 \text{ gmole/cm}^3$$

Method I. In terms of fixed T and V, $\left(\frac{\partial Z}{\partial T}\right)_\rho = 0$; $Z - 1 = \frac{1}{1 - a\rho} - \frac{1 - a\rho}{1 - a\rho} = \frac{a\rho}{1 - a\rho}$

$$\frac{(S - S^{ig})_{TV}}{R} = \int_0^\rho \left[-T\left[\frac{\partial Z}{\partial T}\right] - (Z - 1)\right]\frac{d\rho}{\rho} = -a\int_0^\rho \frac{d\rho}{1 - a\rho} = \ln(1 - a\rho)$$

$$dS^{ig} = (C_P^{ig}/T)dT - (R/P)dP$$

$$S_2 - S_1 = (S - S^{ig})_{TV,2} + (S_2^{ig} - S_1^{ig}) - (S - S^{ig})_{TV,1}$$

$$= R\cdot[\ln(1 - 187\cdot2.28\text{E-}4) + \{(C_V/R)\ln(T_2/T_1) + \ln(V_2/V_1)\} - \ln(1 - 187\cdot3.257\text{E-}5)]$$

$$\Delta S/R = 0 = -0.04357 + 32/8.314\cdot\ln(T_2/293.15) - \ln(7) + 0.00611 = 0 \Rightarrow T_2 = 490.8 \text{ K}$$

Example 8.2 Real entropy in a combustion engine (Continued)

Method II. In terms of T and P,

$$Z = \frac{1}{1-a\rho}$$

$$\frac{(S-S^{ig})}{R} = \int_0^\rho \left[-T\left[\frac{\partial Z}{\partial T}\right]-(Z-1)\right]\frac{d\rho}{\rho} + \ln Z$$

$$= -a\int_0^\rho \frac{d\rho}{1-a\rho} + \ln Z = \ln(1-a\rho) + \ln\left[\frac{1}{1-a\rho}\right] = 0$$

Since the departure is zero, it drops out of the calculations.

$S_2 - S_1 = S_2^{ig} - S_1^{ig} = C_p\ln(T_2/T_1) - R\ln(P_2/P_1)$. However, since we are given the final volume, we need to calculate the final pressure. Note that we cannot insert the ideal gas law into the pressure ratio in the last term even though we are performing an ideal gas calculation; we must use the pressure ratio for the real gas.

$$\Delta S = C_p\ln(T_2/T_1) - R\ln\left[\frac{RT_2}{V_2-a}/\frac{RT_1}{V_1-a}\right] = (C_p-R)\ln(T_2/T_1) - R\ln\left(\frac{V_1-a}{V_2-a}\right)$$

Now, if we rearrange, we can show that the result is the same as Method I:

$$\Delta S = C_V\ln(T_2/T_1) + R\ln(V_2/V_1) + R\ln\left(\frac{1-a\rho_2}{1-a\rho_1}\right)$$

$$= R\ln(1-a\rho_2) + C_V\ln(T_2/T_1) + R\ln(V_2/V_1) - R\ln(1-a\rho_1)$$

This is equivalent to the equation obtained by Method I and $T_2 = 490.8$ K.

Finally, $P_2 = \frac{RT_2}{V_2-a} = \frac{8.314(490.8)}{1/2.28\times10^{-4}-187} = 0.972$ MPa

$W = \Delta U = (U-U^{ig})_2 + C_V\Delta T - (U-U^{ig})_1 = 0 + C_V\Delta T - 0 = 6325$ J/mole

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a. The solution to the problem using pressure integrals is left as homework problem 8.7.

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(7.21) Suppose you had a program to simulate the motions of four..

Solution:
a. The ideal gas molecules run right over each other. Because their potential is simply point masses, they can never collide or alter each other's velocities.
b. The hard sphere molecules collide like billiard balls
c. The SW molecules collide similar to HS, but "do-si-do" and stick together.

2)
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(P8.2) $Z = 1 - b\rho/T_r$

Depature function $\Rightarrow \left(\dfrac{H-H^{ig}}{RT}\right) = \int_0^\rho -T\left[\dfrac{\partial Z}{\partial T}\right]_\rho \dfrac{d\rho}{\rho} + Z - 1 \ldots\ldots\ldots$Eqn. 8.24

$\Rightarrow \left(\dfrac{H-H^{ig}}{RT}\right) = \int_0^\rho -T_r\left[\dfrac{b\rho}{T_r^2}\right]\dfrac{d\rho}{\rho} - \dfrac{b\rho}{T_r} = \dfrac{-T_r b\rho}{T_r^2} - \dfrac{b\rho}{T_r} = -\dfrac{2b\rho}{T_r}$

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(8.07) In **example 8.2**, we wrote the equation of state in terms of Z...

$$\frac{PV}{RT} = 1 + \frac{aP}{RT} \qquad (Z-1) = \frac{aP}{RT} \qquad \left(\frac{\partial Z}{\partial T}\right)_P = -\frac{aP}{RT^2}$$

$$\frac{S-S^{ig}}{R} = -\int_0^P \left[(Z-1) + T\left(\frac{\partial Z}{\partial T}\right)_P\right]\frac{\partial P}{P} = 0$$

Rest of the problem is the same!

$$\frac{H-H^{ig}}{RT} = \int_0^P -T\left(\frac{\partial Z}{\partial T}\right)_P \frac{\partial P}{P}$$

$$= \int_0^P \frac{aP}{RT}\frac{\partial P}{P} = \frac{aP}{RT}$$