Introductory Chemical Engineering Thermodynamics

CHAPTER 7

(7.01) The compressibility factor chart provides…

a) Pr = 0.88, the T limit where $Z^o > 0.95$ is Tr = 1.75, T > 220 K
b) Pr = 0.41, the T limit where $Z^o > 0.95$ is Tr = 1.4, T > 425 K
c) Pr = 0.47, the T limit where $Z^o > 0.95$ is Tr = 1.5, T > 775K
Therefore, it can be seen that there isn't any single temperature above which the ideal gas law is valid for all fluids; the temperature depends on the fluid.

(7.02) A container having a volume of 40 L….

option (i) methane
a) methane MW = 16, $T_r = 1.574$,
initial state, Pr = 2.172, $Z^o = 0.85$, $Z^1 = 0.22$, $Z = 0.85 + 0.011(0.22) = 0.85$
$\underline{V} = ZRT/P = 212\ cm^3/mol$
m(kg) = MW*$\underline{V}$/V = 3.02 kg
final state, Pr = 1.086 $Z^o = 0.93$, $Z^1 = 0.04$, $Z = 0.93 + 0.011(0.04) = 0.93$
$\underline{V} = ZRT/P = 463.9\ cm^3/mol$
m(kg) = MW*$\underline{V}$/V = 1.38 kg
1.64 kg lost

b) methane MW = 16. intial state

Current State		Roots		
T (K)	300	Z	V	fugacity
P (MPa)	10		cm^3/gmol	MPa
Z for 1 root region		0.83374	207.95	8.22918

m(kg) = MW*$\underline{V}$/V = 3.078 kg
final state

Current State		Roots		
T (K)	300	Z	V	fugacity
P (MPa)	5		cm^3/gmol	MPa
Z for 1 root region		0.90178	449.846	4.50673

m = 1.423 kg
1.66 kg have been lost.

option (ii) propane
a) Using Z charts, propane, MW = 44, Tr = 0.811
initial state, $Pr = 1.177$, $Z^o = 0.2$, $Z^1 = -0.075$, $Z = 0.2 - 0.152(0.075) = 0.189$
$V = ZRT/P = 94.08$ cm^3/mol
m(kg) = MW*$\underline{V}$/V = 18.7 kg
final state, $Pr = 0.0212$.
$Z^o = 0.98$, $Z^1 = -0.01$, $Z = 0.98 - 0.152(0.01) = 0.98$
$V = ZRT/P = 27201.2$ cm^3/mol
m(kg) = MW*$\underline{V}$/V = 0.065 kg
18.6 kg lost

b) Using PREOS, propane, MW = 44
initial state

Current State	Roots		
T (K) 300 P (MPa) 5	Z	V cm^3/gmol	fugacity MPa
& for 1 root region	0.1675674	83.594048	0.964453

m(kg) = MW*$\underline{V}$/V= 21.054 kg
(PR may not be very accurate for liquids)
final state

Current State	Roots		
T (K) 300 P (MPa) 0.09	Z	V cm^3/gmol	fugacity MPa
answers for three root region	0.9853583	27309.113	0.088698
	0.0094478	261.84412	
	0.0031627	87.654349	0.815113

vapor root is most stable, m = 0.064 kg
21 kg have been lost (PR may not be very accurate for liquids)

iii) butane MW = 58, Tr = 0.706
initial state, a check of the vapor pressure shows that butane is liquid. $Pr = 1.32$, $Z^o = 0.21$, $Z^1 = -0.1$, $Z = 0.21 - 0.193(0.1) = 0.191$
$V = ZRT/P = 95.3$ cm^3/mol
m(kg) = MW*$\underline{V}$/V = 24.3 kg
final state, $Pr = 0.264$, by looking at the Z chart the conditions are close to the vapor pressure. By checking the Antoine equation, the vapor pressure is about 0.26 MPa, therefore n-butane is liquid at 1 MPa, so use the liquid branch on the Z charts. $Z^o = 0.05$, $Z^1 = -0.01$, $Z = 0.05 - 0.193(0.01) = 0.0481$
$V = ZRT/P = 119.9$ cm^3/mol
m(kg) = MW*$\underline{V}$/V = 19.4 kg
4.9 kg lost

initial state

Current State		Roots		
T (K)	300	Z	V	fugacity
P (MPa)	5		cm^3/gmol	MPa
& for 1 root region		0.19084	95.1988	0.29149

m(kg) = MW*$\underline{V}$/V= 24.37 kg

final state

Current State		Roots		
T (K)	300	Z	V	fugacity
P (MPa)	1		cm^3/gmol	MPa
answers for three root region		0.60066	1498.16	0.73299
		0.33151	826.844	
		0.03879	96.761	0.24991

liquid root is more stable, m = 23.97 kg

0.4 kg lost (PR may not be very accurate for liquids)

(7.03) Estimate the liquid density (g/cm3) of propane at 298K and 10 bars...

Gasoline is ~0.692 g/cc.

PREOS$\Rightarrow$ V=86cm3/gmole $\Rightarrow$ ρ = 44/86 = 0.511 g/cm3.

5 gal*1e6cm3/264gal = 18900 cm3 $\Rightarrow$ 10kg $\Rightarrow$ \$20/10kg = \$2/kg

Gasoline is 1gal*1e6cm3/264gal = 3784 cm3

0.692 g/cc*3784cc /1000g/kg = 2.6kg $\Rightarrow$ \$3.75/2.6kg = \$1.44/kg

gasoline ~ 72% of propane cost.

Note: the price of gasoline will vary.

(7.04) From experimental data it is known that at moderate pressures the volumetric equation of state may be written as *PV = RT + BP* ...

Solution

a) B=0 at T_B = 504.67 K

$$dH = CpdT + \left[V - T\left(\frac{\partial V}{\partial V}\right)_P\right]dP \Rightarrow \left(\frac{\partial T}{\partial P}\right)_H = \left[V - T\left(\frac{\partial V}{\partial V}\right)_P\right]/Cp$$

For T_{inv} ;

$$\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H \Rightarrow \frac{V}{T} = \left(\frac{\partial V}{\partial T}\right)_P \;; \qquad PV = RT + BP \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT}$$

$$PV = RT + BP \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} = \frac{V}{T} = \left(\frac{RT}{P} + B\right)/T = \frac{R}{P} + \frac{dB}{dT} \Rightarrow T\frac{dB}{dT} = B$$

From regression we have,

B = -2.691e6* $(1/T)^2$-1.714e4*$(1/T)$+44.53

$T(dB/dT)$=2*2.691e6*$(1/T)^2$+ 1.714e4*$(1/T)$ = B

Solving the quadratic equation, T_{inv}= 959K.

(7.05) Data for hydrogen are given by Dymond and Smith (1969) as:

(a) See figure

(b) Gen'l B equation is inaccurate at low T, but OK near 300K.

B_r=0.083-0.422/$Tr^{1.6}$ +ω(0.139-0.172/$Tr^{4.2}$);

Tr = 300/33 = 9; B = 11 cc/mole

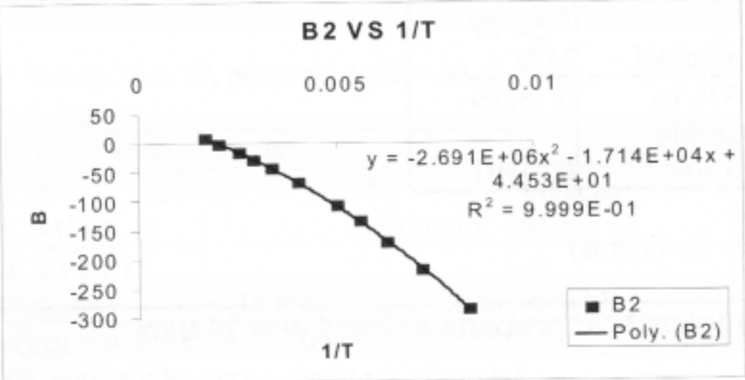
TdB/dT= (1.6(0.422)/$Tr^{1.6}$ + ω 4.2(.172)/$Tr^{4.2}$)RT_c/P_c

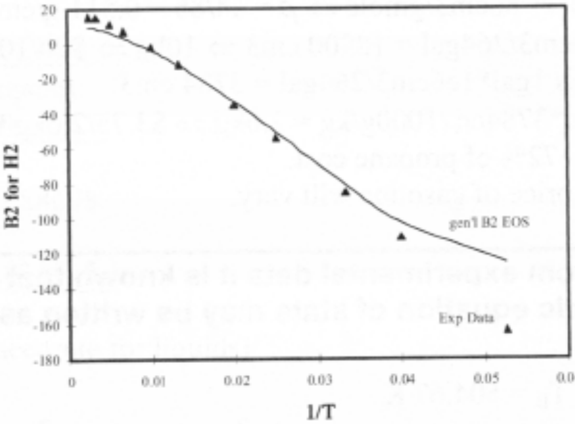
= (0.020 + -0.22*0.00007) 211 = 4.22

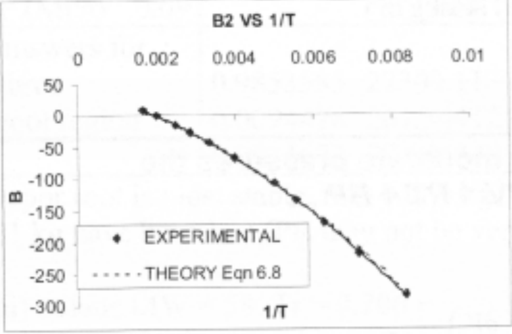
$\Rightarrow$ $dT/dP)_H$ = (TdB/dT - B)/C_P =(4.22-11)cc/mol/(30cc-MPa/mol-K)

$\Rightarrow$ = -0.23 K/MPa

For dP = -30 Mpa, dT= +7K so T_f= 307 K. This is positive, but nowhere near the autoignition temperature.







(7.06) N. B. Vargaftik lists the following experimental data…

					Exp	Gen Chart		PREOS	
P	Pr	Z(0)	Z(0.25)	Z(0.177)	V	V=ZRT/P*MW	% Deviation	V (PR)	% Deviation
1.013	0.278	0.9	0.92	0.91416	60.7	57.97198837	4.4942531	58.25066	4.0351645
2.026	0.555	0.85	0.85	0.85	27.79	26.95162232	3.0168323	26.37752	5.0827015
3.546	0.972	0.68	0.7	0.69416	13.36	12.57730296	5.8585108	12.47146	6.6507201
7.091	1.944	0.4	0.42	0.41416	3.818	3.752028201	1.7279151	3.832948	0.3915211

(7.07) Evaluate $(\partial P/\partial V)_T$ for the equation of state: P = RT/(V-b)

$(\partial P/\partial V)_T$ = -RT/(V-b)^2

(7.08) Evaluate $\left(\frac{\partial P}{\partial T}\right)_V$ for the equation of state….

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{3}{2}\frac{a}{T^{5/2}} + \frac{1}{T^{3/2}}\frac{da}{dT}$$

if *a* is constant, then *da/dT* = 0.

Note: This EOS might not make much sense at the ideal gas limit since $P \neq RT/V$ there.

(7.09) Evaluate $(dP/dT)_V$ for the Redlich-Kwong equation…

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} + \frac{a}{2T^{3/2}V(V+b)}$$

(7.10) (a) The derivative….

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = \frac{-\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T}$$

Peng-Robinson equation of state is,

$$P = [RT\rho / (1 - b\rho)] - [a\rho^2 / (1 + 2b\rho - b^2\rho^2)] \quad , \quad \text{since } \rho = 1/V$$

$$P = [RT / (V-b)] - [a / (V^2 + 2bV - b^2)]$$

Where b= constant and a=a(T)

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{1}{(V^2+2bV-b^2)} * \frac{da}{dT}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a(V+b)}{(V^2+2bV-b^2)^2}$$

Therefore,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\frac{-R}{(V-b)} + \frac{1}{(V^2+2bV-b^2)} * \frac{da}{dT}}{\frac{-RT}{(V-b)^2} + \frac{2a(V+b)}{(V^2+2bV-b^2)^2}}$$

$$\text{where} \quad \frac{da}{dT} = \frac{-a_c \kappa \sqrt{\alpha T_r}}{T}$$

(b) Isothermal compressibility of ethylene for *saturated vapor and liquid* at three different conditions. Let's work on condition 1 to show how we can obtain the answer.

With P^{sat}=0.414 MPa, go to the Preos.xls spreadsheet, change to ethylene critical parameters (Tc, Pc, ω). The isothermal compressibility is,

$$\kappa_T = \frac{-1}{V}\left(\frac{\partial P}{\partial V}\right)_T^{-1}$$

We need to find κ_T for both vapor and liquid phases for each given P^{sat}. It's easier to do this using the Preos.xls spreadsheet we already have and creating few more columns as needed. For example, looking at the attached spreadsheet below. The following states are the actual PR saturation properties which are very close the the P,T's in the problem statement. V (vapor) = 3627.219 cm3/mol, calculate a (changes as temp changes) and b (stays constant), calculate $(dP/dV)_T$, and then calculate isothermal compressibility for the vapor phase. For the same given P^{sat}, repeat calculations for liquid phase with V(liquid) = 49.49433 cm3/mole.

$-1/V*[\text{inverse of } (dP/dV)_T]$

Peng-Robinson Equation of State (Pure Fluid)

Properties				
Gas	T_c (K)	P_c (MPa)	ω	R(cm^3MPa/molK)
ethylene	282.4	5.032	0.085	8.314

Current State		Roots					
T (K)	**197.6963**	Z	V	fugacity	rho	(dP/dV)T	iso comp
P (MPa)	**0.414**		cm^3/gmol	MPa	gmol/cm3		$(MPa)^{-1}$
answers for three root region		0.91362	**3627.219**	0.380864	0.000276	-0.0001	2.661320522
		0.06477	257.1479		0.003889	0.015715	
		0.012467	**49.49433**	0.38118	0.020204	-4.93343	0.004095393
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	

Stable Root has a lower fugacity

Intermediate Calculations			
T_r	0.700058	a (MPa cm^6/$gmol^2$)	
P_r	0.082273	586711.4	
κ	0.503782	b (cm^3/gmol)	
α	1.171309	36.30059	
fugacity ratio		A	0.08991
	0.999172	B	0.0091434

To find vapor pressure, or saturation temperatur
see cell A28 for instructions

Properties				
Gas	T_c (K)	P_c (MPa)	ω	R(cm^3MPa/molK)
ethylene	282.4	5.032	0.085	8.314

Current State		Roots					
T (K)	225.9182	Z	V	fugacity	rho	(dP/dV)T	iso comp
P (MPa)	1.16		cm^3/gmol	MPa	gmol/cm3		$(MPa)^{-1}$
answers for three root region		0.81585	1321.033	0.977873	0.000757	-0.00069	1.093353855
		0.127224	206.003		0.004854	0.020406	
		0.034507	55.8737	0.977841	0.017898	-1.92072	0.009318117
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	

Stable Root has a lower fugacity

Intermediate Calculations			
T_r	0.799994	a (MPa cm^6/$gmol^2$)	
P_r	0.230525	555602.7	
κ	0.503782	b (cm^3/gmol)	
α	1.109204	36.30059	
fugacity ratio		A	0.1826836
	1.000033	B	0.0224187

To find vapor pressure, or saturation temperature,
see cell A28 for instructions

Peng-Robinson Equation of State (Pure Fluid)

Properties				
Gas	T_c (K)	P_c (MPa)	ω	R(cm^3MPa/molK)
ethylene	282.4	5.032	0.085	8.314

Current State		Roots					
T (K)	254.161	Z	V	fugacity	rho	(dP/dV)T	iso comp
P (MPa)	2.6		cm^3/gmol	MPa	gmol/cm3		$(MPa)^{-1}$
answers for three root region		0.662306	538.2754	1.943205	0.001858	-0.00274	0.678442653
		0.209071	169.9176		0.005885	0.018271	
		0.083958	68.23502	1.943141	0.014655	-0.46927	0.031229696
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	

Stable Root has a lower fugacity

Intermediate Calculations			
T_r	0.900003	a (MPa cm^6/$gmol^2$)	
P_r	0.516693	527135.2	
κ	0.503782	b (cm^3/gmol)	
α	1.052371	36.30059	
fugacity ratio		A	0.3069429
	1.000033	B	0.0446651

To find vapor pressure, or saturation temperatur
see cell A28 for instructions

In summary,

Tr	T(K)	Isothermal compres = $-(\partial V/\partial P)_T/V$ (MPa^{-1})		P^{sat}(MPa)
		vapor	liquid	
0.7	197.7	2.661	0.004	0.414
0.8	225.9	1.093	0.009	1.16
0.9	254.2	0.678	0.031	2.6

(7.11) When a cubic equation of state gives three real roots…

(a) Ethylene at 250K

T (K)	250	Z	V	fugacity
P (MPa)	1		cm3/gmol	MPa
answers for three		0.886624	1842.848	0.896571
root region		0.063055	131.059	
		0.032857	68.29415	1.703631
T (K)	250	Z	V	fugacity
P (MPa)	3		cm3/gmol	MPa
answers for three		0.506753	351.0956	2.076417
root region		0.347524	240.7763	
		0.093331	64.66268	1.815896
T (K)	250	Z	V	fugacity
P (MPa)	10		cm3/gmol	MPa
answers for three		#NUM!	#NUM!	#NUM!
root region		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		0.281432	58.4956	2.23099
T (K)	250	Z	V	fugacity
P (MPa)	100		cm3/gmol	MPa
answers for three		#NUM!	#NUM!	#NUM!
root region		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		2.176828	45.24537	18.8759

T (K)	250	Z	V	fugacity
P (MPa)	150		cm3/gmol	MPa
answers for three		#NUM!	#NUM!	#NUM!
root region		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		3.131613	43.39371	54.71019
T (K)	250	Z	V	fugacity
P (MPa)	170		cm3/gmol	MPa
answers for three		#NUM!	#NUM!	#NUM!
root region		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		3.506471	42.87176	82.84868
P (MPa)	175		cm3/gmol	MPa
answers for three		3.599716	42.75435	91.83609
root region		-2.32381	-27.6002	
		-3.33209	-39.5758	#NUM!
T (K)	250	Z	V	fugacity
P (MPa)	200		cm3/gmol	MPa
answers for three		4.063553	42.23047	153.0864
root region		-1.51804	-15.7762	
		-5.0383	-52.3605	#NUM!
& for 1 root region		#NUM!	#NUM!	#NUM!

(b) n-Hexane at 400 K and 0.2, 0.5, 1, 10, 100, 130 and 150 MPa

Current State		Roots		
T (K)	400	Z	V cm³/gmol	fugacity MPa
P (MPa)	0.2			
answers for three root region		0.946254383	15735.21	0.189735
		0.037706718	627.0229	
		0.009486155	157.7447	0.401982
& for 1 root region		#NUM!	#NUM!	#NUM!

Current State		Roots		
T (K)	400	Z	V cm³/gmol	fugacity MPa
P (MPa)	0.5			
answers for three root region		0.855530656	5690.629	0.436354
		0.104442282	694.7059	
		0.023645203	157.2779	0.407734
& for 1 root region		#NUM!	#NUM!	#NUM!

Current State		Roots		
T (K)	400	Z	V cm³/gmol	fugacity MPa
P (MPa)	1			
answers for three root region		0.640342159	2129.643	0.744715
		0.279828175	930.6494	
		0.047065948	156.5314	0.417466
& for 1 root region		#NUM!	#NUM!	#NUM!

Current State		Roots		
T (K)	400	Z	V cm³/gmol	fugacity MPa
P (MPa)	10			
answers for three root region		#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		0.442719785	147.2393	0.628824

Current State		Roots		
T (K)	400	Z	V	fugacity
P (MPa)	100		cm^3/gmol	MPa
answers for three root region		#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		3.767887939	125.312	22.756

Current State		Roots		
T (K)	400	Z	V	fugacity
P (MPa)	130		cm^3/gmol	MPa
answers for three root region		4.807383647	122.9873	69.69454
		-2.430283147	-62.1739	
		-5.636383889	-144.196	#NUM!
& for 1 root region		#NUM!	#NUM!	#NUM!

Current State		Roots		
T (K)	400	Z	V	fugacity
P (MPa)	150		cm^3/gmol	MPa
answers for three root region		5.493297991	121.797	145.4783
		-1.695907157	-37.6015	
		-7.71194859	-170.989	#NUM!
& for 1 root region		#NUM!	#NUM!	#NUM!

(c) argon at 420K.

Current State		Roots		
T (K)	420	Z	V	fugacity
P (MPa)	0.1		cm^3/gmol	MPa
answers for three root region		#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		0.999887	34914.86	0.099989

Current State		Roots		
T (K)	420	Z	V	fugacity
P (MPa)	2		cm^3/gmol	MPa
answers for three root region		#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	
		#NUM!	#NUM!	#NUM!
& for 1 root region		0.998154	1742.717	1.99588

Current State		Roots		
T (K)	420	Z	V	fugacity
P (MPa)	3		cm^3/gmol	MPa
answers for three root region		0.99755	1161.108	2.991218
		-0.00694	-8.07384	
		-0.00773	-9.00137	#NUM!
& for 1 root region		#NUM!	#NUM!	#NUM!

Current State		Roots		
T (K)	420	Z	V	fugacity
P (MPa)	5		cm^3/gmol	MPa

answers for three root region	0.996962	696.2541	4.978272
	-0.00798	-5.57362	
	-0.01751	-12.2313	#NUM!
& for 1 root region	#NUM!	#NUM!	#NUM!

The correct root switches from being the single root to the largest real root. When three real roots exist at this temperature and the higher pressures, the smallest real root isn't a "liquid". The value is less than zero in this case, and must be disregarded. It doesn't represent a real fluid.

By looking at the columns listing fugacity, we see that the largest real root (vapor) is the most stable at 1 MPa, but at 3 MPa the smallest real root is more stable (liquid). For the calculations between 10 MPa and 170 MPa, the equation of state gives only one real root (liquid). For the calculations at 175 MPa and 200 MPa, the largest real root is the only meaningful root, and it represents a *liquid* phase. The other roots are meaningless.

Therefore, it is not accurate to say that the largest real root will always represent a vapor phase.

(7.12) Plot P_r vs ρ_r for the PR EOS with T_r = [0.7,0.9,1.0] …

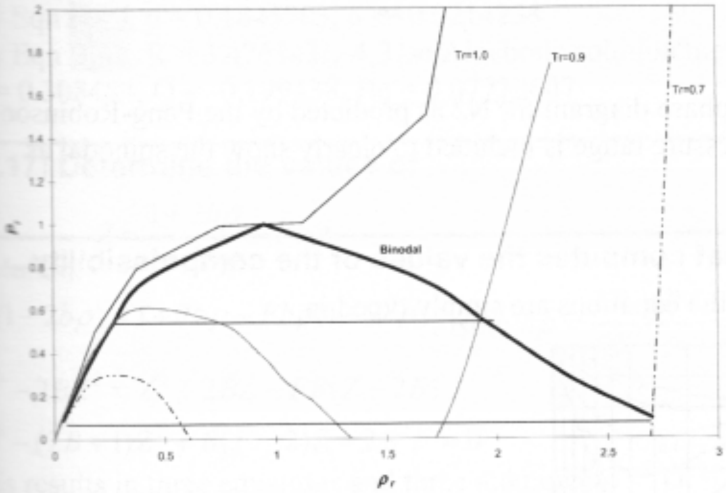
FYI: Z*bρ=Pb/RT = Pr*.0778/Tr ⇒ Pr=Z*bρ*Tr/0.0778;

Note: *a/bRT*=0.45724*α/(0.0778*Tr). So, getting Z vs. bρ is ez.

bρ = 0.0778*R*Tc*ρ/Pc. Zc=Pc/(ρc*R*Tc)⇒ρc*Zc=Pc/(R*Tc)

⇒ bρ = ρ*0.0778/(ρc*Zc) ⇒ ρ_r = bρ*Zc/0.0778

⇒ Suggestion: compute Z for bρ=[0,0.1,0.2,…,0.9] and convert to Pr as above.



(7.13) Plot the spinodal for the PR EOS

For the saturation curve refer to HW 7.12. For the spinodal curve, a simple (and acceptable) approach is to simply connect the dots from the extrema of the P_r vs. ρ_r plot.

A more sophisticated analysis would be to derive the expression for the derivative and set it to zero using the solver to determine the density at a given T_r. An advantage of this approach is that tabulating the derivatives at each temperature is useful for visualizing the critical point determination. Applying central difference rule to the analytical first derivative generally suffices to determine where $(\partial P/\partial \rho)_T = (\partial^2 P/\partial \rho^2)_T = 0$.

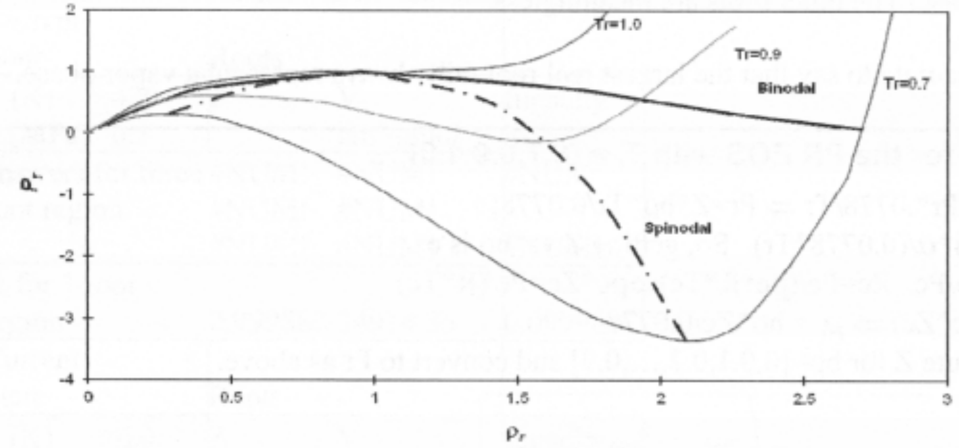
$$bP = \frac{RTb\rho}{1-b\rho} - \left(\frac{a}{b}\right)\frac{(b\rho)^2}{1+2b\rho-(b\rho)^2} \Rightarrow$$

$$\left(\frac{\partial bP}{\partial b\rho}\right)_T = \frac{RT}{1-b\rho} + \frac{RTb\rho}{(1-b\rho)^2} - \frac{2\left(\frac{a}{b}\right)b\rho}{1+2b\rho-(b\rho)^2} + \frac{\left(\frac{a}{b}\right)(b\rho)^2(2-2b\rho)}{(1+2b\rho-(b\rho)^2)^2}$$

$$= \frac{RT}{(1-b\rho)^2} - \frac{2\left(\frac{a}{b}\right)(b\rho)(1+2b\rho-(b\rho)^2) - 2\left(\frac{a}{b}\right)(b\rho)^2 + 2\left(\frac{a}{b}\right)(b\rho)^3}{(1+2b\rho-(b\rho)^2)^2}$$

Pr = bP/RT*RT/bPc = (bP/RT) *(RTc/Pc)/(.0778RTc/Pc) * Tr = bP/RTc*Tr/.0778

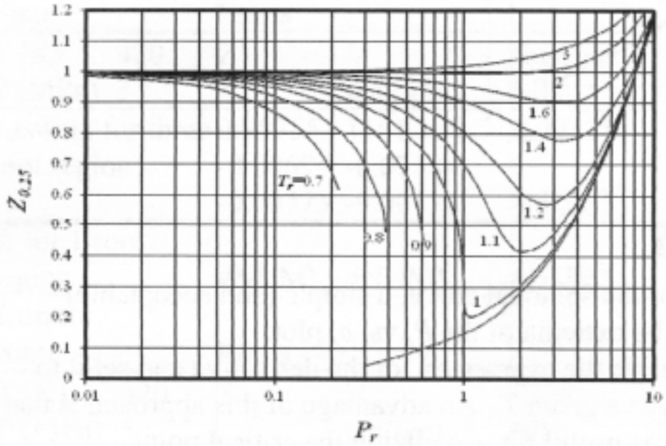
$\rho_r = b\rho/b\rho_c = b\rho/(.0778RTc/Pc*Pc/RTc\ /Zc) = b\rho*0.0778/0.292$



Pressure vs. density projection of the phase diagram for N2 as predicted by the Peng-Robinson (1976) equation of state. Negative pressure range is included to clearly show the spinodal as locus of extrema.

(7.14) Develop a spreadsheet that computes the values of the compressibility…

Solution: This is a spreadsheet where the equations are simply typed in.



(7.15) Solve for the parameters at the critical point for the SRK EOS...

$Z^3 - Z^2 + (A-B^2-B)Z - AB = 0 = Z^3 - 3ZcZ^2 + 3Zc^2Z - Zc^3$;

$\Rightarrow Zc = 1/3$; $Zc^3 = AB \Rightarrow A = 1/27B$; $A-B^2-B = 3Zc^2 = 1/3 \Rightarrow 1/27 - B^3 - B^2 = B/3$

Solving analytically: $R = (-2/27)^2/4$; $P = (1/27+\sqrt{R})^{1/3}$; $Q = (1/27-\sqrt{R})^{1/3}$;

$B = P - 1/3 = 0.086640349966$; $A = 0.437480233536$

(7.16) Show that $B_C = bP_C/RT_c = 0.07780$ for the Peng Robinson…

The problem asks us to write a cubic in B_C we will work for that form.

Comparing Eqn B.51 and Eqn 7.25, the term for a_2 gives

$3Zc = 1 - Bc$, or $Zc = (1/3)(1 - Bc)$ (1)

the term for a_1 gives

$3Zc^2 = Ac - 3Bc^2 - 2Bc$ (2)

the term for a_0 gives

$Zc^3 = AcBc - Bc^2 - Bc^3$ (3)

In order to get a cubic in Bc, we need to eliminate Zc and Ac by substitution. Squaring Eqn (1)

$Zc^2 = (1/9)(1 - 2Bc + Bc^2)$ (4)

Cubing Eqn (1)

$Zc^3 = (1/27)(1 - 3Bc + 3Bc^2 - Bc^3)$ (5)

Plugging (4) into (2)

$Ac = (1/3)(1 - 2Bc + Bc^2) + 3Bc^2 + 2Bc = 1/3 + (4/3)Bc + (10/3)\ Bc^2$ (6)

Plugging (5) and (6) into (3)

$(1/27)(1 - 3Bc + 3Bc^2 - Bc^3) - (1/3 + (4/3)Bc + (10/3)\ Bc^2)Bc + Bc^2 + Bc^3 = 0$

Simplifying

$Bc^3 + (3/32)Bc^2 + (3/16)Bc + (-1/64) = 0$

By Eqn B.40, $p = 0.1845703$, $q = -0.0214233$

By Eqn B.41, $R = 3.476143E-4$, Use Algebraic solution method,

$P = 0.308484$, $Q = -0.199438$, $\underline{Bc = 0.07779607}$

(7.17) Determine the values of ….

Solution: $$Z = \frac{1+2b\rho}{1-2b\rho} - Fb\rho$$

$Z(1-2b\rho) = 1 + 2b\rho - Fb\rho(1-2b\rho)$, Note $b\rho = \frac{bP}{RT}\frac{\rho RT}{P} = \frac{B}{Z}$

$$Z^3 - 2BZ^2 = Z^2 + 2BZ - FB(Z-2B)$$

$$Z^3 - (2B+1)Z^2 + B(F-2)Z - 2B^2F = 0$$

this results in three equations and three unknowns

$$(2B_c + 1) = 3Z_c$$

$$B_c(F_c - 2) = 3Z_c^2$$

$$2B_c^2F_c = Z_c^3$$

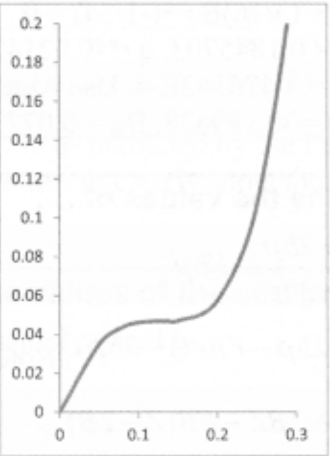
We can use Excel solver to solve simultaneously, or we can manipulate to obtain $-8Z_c^3 - 6Z_c^2 + 6Z_c - 1 = 0$, which results in $Z_c = 0.25, 0.36603, -1.366$, of which only 0.36603 makes sense.

The values are: $Z_c = 0.36603$, $B_c = (3*Z_c-1)/2 = 0.04903$, $F_c = Z_c^3/(2*B_c^2) = 10.196$

(7.18) Consider the equation of state…

Solution: We seek $(\partial P/\partial \eta_P)_T = 0$ and $(\partial^2 P/\partial \eta_P{}^2)_T = 0$.
$\eta Z = bP/RT \Rightarrow$ it suffices for $(\partial \eta Z/\partial \eta_P)_T = 0$ and $(\partial^2 \eta Z/\partial \eta_P{}^2)_T = 0$.
$\eta Z = \eta_P + (4\,\eta_P\hat{}2 - 2\eta_P\hat{}3)/(1-\eta_P)\hat{}3 - \eta_P\hat{}2\,\beta\varepsilon$
$d(\eta Z)/d\,\eta_P = 1+(8{*}\,\eta_P - 6\eta_P\hat{}2)/(1-\eta_P)\hat{}3+(12\,\eta_P\hat{}2 - 6\eta_P\hat{}3)/(1-\eta_P)\hat{}4 - 2{*}\eta_P\beta\varepsilon$
$d^2(\eta Z)/d\,\eta_P{}^2 = (8 - 12\eta_P)/(1-\eta_P)\hat{}3 + 3{*}(8{*}\,\eta_P - 6\eta_P\hat{}2)/(1-\eta_P)\hat{}4$
$+(24\,\eta_P - 18\eta_P\hat{}2)/(1-\eta_P)\hat{}4 + (48\,\eta_P\hat{}2 - 24\eta_P\hat{}3)/(1-\eta_P)\hat{}5 - 2\beta\varepsilon$
Solving $d(\eta Z)/d\eta_P = d^2(\eta Z)/d\,\eta_P{}^2 = 0$, changing $\beta\varepsilon, \eta_p \Rightarrow \beta\varepsilon = 10.601$, $\eta_P = 0.1304$, Zc = 0.359
Hint: We can easily evaluate $(\partial^2 \eta Z/\partial \eta_P{}^2)_T$ by numerical differentiation of $(\partial \eta Z/\partial \eta_P)_T$.
The answers are the same to 4 sig figs. This approach works for non-cubic EOS's as well.
Zc =0.359=>ρc=Pc/(0.359*R*Tc), b=0.1304/ρc, a=bRTc/10.601
b. This value of Zc is very high so only nearly spherical molecules will be close.
Hint: to get an approximation, we can guess values of βε until ηZ vs η shows the flat inflection. This works for any EOS (incl. non-cubic) and is an easy extension of HW7.12 or 7.13 where the local maxima and minima can be inferred by plotting.

eta	Z	eta*Z	d(etaZ)/dEta	d2(etaZ)/dEta2
0.0	1.0000	0.0000	1.0000	
0.05	0.6974	0.0349	0.4248	
0.08	0.5464	0.0437	0.1793	
0.1	0.4611	0.0461	0.0686	
0.12	0.3900	0.0468	0.0085	
0.123	0.3806	0.0468	0.0044	
0.124	0.3776	0.0468	0.0033	-0.9270
0.125	0.3746	0.0468	0.0023	-0.7726
0.126	0.3716	0.0468	0.0016	-0.6170
0.127	0.3687	0.0468	0.0009	-0.4602
0.128	0.3658	0.0468	0.0005	-0.3021
0.129	0.3630	0.0468	0.0002	-0.1428
0.13	0.3602	0.0468	0.0000	0.0178
0.131	0.3574	0.0468	0.0000	0.1797
0.132	0.3547	0.0468	0.0002	0.3429
0.133	0.3521	0.0468	0.0005	0.5074
0.15	0.3135	0.0470	0.0323	
0.2	0.2860	0.0572	0.4705	
0.25	0.4238	0.1059	1.6253	
0.3	0.7934	0.2380	3.8854	



(7.19) The ESD equation of state is given by..

(a) Develop three equations relating Z_c, Z_c^2, and Z_c^3 to the k_1, Y, B, c, q.
(b) To simplify the algebra, define $a \equiv 4c\,k_1 + 1.9(9.5q - k_1)$. Rearrange the equation for Z_c^3 to solve for Y in terms of Z_c, a, and B. Evaluate your expression at $B = 0.03$, $Z_c = 0.34$, and $c = 1.3$.

(c) Eliminate Y from the equation for Z_c by substituting the expression for Y in terms of Z_c, a, and B. Rearrange the equation for Z_c to obtain a quadratic equation in B. Solve the quadratic for B. Evaluate your expression at $Z_c = 0.34$, and $c = 1.3$. Reevaluate your expression for Y at the new value of B.

(e) Use the results from (d) to solve for Z_c from your expression for Z_c^2.

(f) Guess a new value for Z_c and repeat (d) and (e) until $Z_c^{calc} = Z_c^{guess}$.

Noting, $\eta Z = B$

$$Z = 1+\frac{4c\eta}{1-1.9\eta}-\frac{9.5qY\eta}{1+k_1Y\eta} = 1+\frac{4cB}{Z-1.9B}-\frac{9.5qYB}{Z+k_1YB}$$

$$Z(Z-1.9B)(Z+k1YB) = (Z-1.9B)(Z+k1YB)+4cB(Z+k1YB)-9.5qYB(Z-1.9B)$$

$$Z^3+Z^2B(k_1Y-1.9)-Z*1.9k_1YNB^2-[Z^2+ZB(k_1Y-1.9)-1.9k_1YB^2]-4cB(Z+k1YB)+9.5qYB(Z-1.9B)=0$$

$$Z^3-Z^2[1-B(k_1Y-1.9)]+Z[9.5qYB-4cB-B(k_1Y-1.9)-1.9k_1YB^2]-[4cB^2k_1Y+9.5qYB^2*1.9-1.9k_1YB^2]$$

$$=Z^3-3Z^2[Zc]+3Z[Zc^2]-Zc^3=0$$

Equating like coefficients gives:

$3Zc = 1\text{-}B(k_1Y\text{-}1.9)$;

$3Z_c^2 = [9.5qYB-4cB-B(k_1Y-1.9)-1.9k_1YB^2]$

$Zc^3 = aB^2Y$ where $a = 4ck_1 + 1.9(9.5q\text{-}k_1) \approx 34.22$ cf. 15.112, 114, 115

(b) Substitute $Y= Zc^3/(aB^2) \approx 1.28 \Rightarrow 3Zc = 1\text{-}B[k_1Zc^3/(aB^2)\text{-}1.9]$

(c) $(1.9)B^2+B(3Zc-1)-k_1Zc^3/a=0 \Rightarrow 2(1.9)B=\left[(3Zc-1)+\sqrt{(3Zc-1)^2+4(1.9)k_1Zc^3/a}\right]$; $B=0.038 \Rightarrow Y = 0.7775$

(d) $Z_c^{calc}\sqrt{3}=\sqrt{9.5qYB-4cB-B(k_1Y-1.9)-1.9k_1YB^2}$

(e) $Z_c^{calc}\sqrt{3}=\sqrt{3}*Z_c^{guess}$?; If not, go to 1.

Guessing $Zc \sim 0.34$, and solving by successive substitution gives:

c	k1	q	Zc	a	Y	B	ZcCalc	ZcErr	eok	bCc_mol
1.30E+00	1.7745	1.571428	0.33375	34.22013	1.048837	0.032184	0.333743	6.9469E-06	210.9	15.02
					3Zc-1 =	0.00125				
					Dscrm =	0.014653	0.334153			
					Numer =	0.122298				

Z

c = 0.33375; $Bc = 0.0322$; $Yc = 1.049$; $\varepsilon/k = 211$ K; $b = 15$ cc/mole

---

(7.20) Compute the time to collision for four purely repulsive disks …

Solution:

a. $v_1^2 = v^2+v^2/2.414^2 = 1.17\ v^2$; $v_2^2 = v^2+v^2$; $v_3^2 = v^2/2+v^2/2 = v_4^2$;

$\langle v^2\rangle = v^2*(1.17+2+1+1)/4 = 5.17v^2/4 = 1.29\ v^2$; NOTE: $N_A*m = MW$

Eq. 1.22 (2D) 298= 0.040/(2*8.314)*1.29 $v^2 \Rightarrow v = 310$ m/s(*3600/1500~744 mi/hr)

b. $v_{tot}^x = v*(1\text{-}1+1/1.414\text{-}1/1.414) = 0$; $v_{tot}^y = v*(1/2.414+1\text{-}1/1.414\text{-}1/1.414) = 0$. If they didn't sum to zero, it would mean the center of mass was flying through space.

c. See below

d. See below

d. the highlighted values are the ones of interest.

Sample calc for 4-2 collision:

$r^x_{ij0}=(0.25-0.75)L = -2.5$nm; $u^x_{ij0}=v(-1+1/1.414)= -90.8$ m/s; $u^y_{ij0}=v(1+1/1.414)= 529.2$ m/s

b_{ij}=(0*-90.8)+(-2.5*529.2) = -1323; v_{ij}^2 = 90.8^2+529.2^2 = 288300m^2/s^2

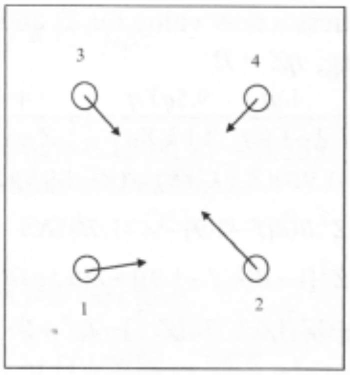
$D_{ij} = 1323^2$-288300*($0^2+2.5^2 - 0.4^2$) = -5398 => No collision b/c $D_{ij} < 0$.

boxLen = 5; v =310 t[=]ns

i	x_i	y_i	v_i^x	v_i^y	t_i^W	t_i^E	t_i^N	t_i^S
1	1.25	1.25	310	128.4	-0.0034	0.0115	0.0276	-0.00818
2	3.75	1.25	-310	310	0.0115	-0.0034	0.0115	-0.00339
3	1.25	3.75	219.2	-219.2	-0.0048	0.0162	-0.0048	0.0162
4	3.75	3.75	-219.20	-219.20	0.0162	-0.0048	-0.0048	0.0162

ij	$r_{ij}^x{}_0$	$r_{ij}^y{}_0$	$u_{ij}^x{}_0$	$u_{ij}^y{}_0$	b_{ij}	u_{ij}^2	D_{ij}	t_{ij}^c
21	-2.5	0	620	-181.6	-1550	417376	-139322	Na
31	0	-2.5	90.8	347.6	-869.02	129076	-30873	Na
32	2.5	-2.5	-529.2	529.2	-2646	560112	89618	0.003388
34	2.5	0	-438.4	0	-1096	192200	30752	0.003421
41	-2.5	-2.5	529.2	347.6	-2192	400888	-141960	0.003889
42	0	-2.5	-90.8	529.2	-2192	400888	-141960	0.003889

(c)



3+2 is the soonest. This is a head-on collision, so $v_2^f = -v_2^i$ and $v_3^f = -v_3^i$.

(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.

(7.22) Suppose you had a program to simulate the motions of N molecules...

Access http://rheneas.eng.buffalo.edu/etomica/modules/swmd/ and link to the 2D DMD Applet. Keep the simulation in "adiabatic" mode throughout. Apply a density of 2.86E-6 mol/m2

a. Run all 3 potentials for 1000ps. Report the temperature, density, and pressure, including the standard error of each. the ideal gas equation.

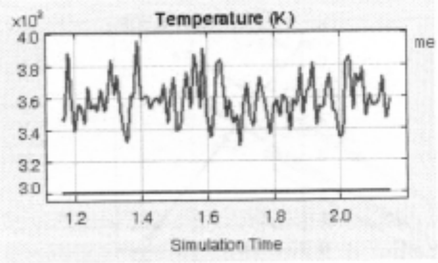
FYI: 43 disks gives the correct density(2.856). From IG EOS: Pig(300) = 71.28

Potential	T(K)	t_{sim} (ps)	P(bar-nm)
IG	300±1.5E-6	22555	71.24±0.0
HS	300±1.4E-6	13115	117.0±0.09
SW	289.2±0.59	10135	49.37±0.19

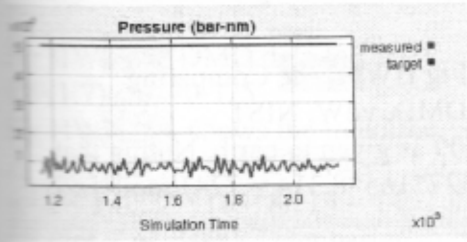
The SW result may fluctuate depending on the T and initialization. Basically, the repulsive and attractive effects are canceling at this density and temperature. The small difference between large numbers makes it difficult to reliably compute the exact value of pressure.

b. Sketch the T vs t for each potential. Explain

For HS and IG, the temperature cannot change because the potentials do not permit a similar exchange. The T for the SW model fluctuates as molecules bond and dissociate, exchanging potential for kinetic.



FYI:



c. How should the internal energy vary for each potential?

ANS. U-Uig = 0 for IG and HS because they cannot overlap or exchange potential energy. (U-Uig)/RT = -2596/(8.314*289)= -1.08 for the SW fluid (λ=2.0, ε/k=1500/8.314=180K) at this density.

(7.23) Sphere and disk collisions can be expressed in vector notation…

a. vector formula for $\|\mathbf{r}_{21}\|^2 = [\mathbf{r}_2° + t^*\mathbf{v}_2 - \mathbf{r}_1° - t^*\mathbf{v}_1]^2 = [\mathbf{r}_{21}° + t\Delta\mathbf{v}_{21}]^2 = (\mathbf{r}_{21}°)^2+2t$ $\mathbf{r}_{21}°\bullet\mathbf{v}_{21}+(t\mathbf{v}_{21})^2$.

b. cf. Eqn. 7.35 => Distance from north wall: L-$\mathbf{r}\bullet\mathbf{y}$; south: $\mathbf{r}\bullet\mathbf{y}$; east: L-$\mathbf{r}\bullet\mathbf{x}$; west: $\mathbf{r}\bullet\mathbf{x}$; $\mathbf{r} \equiv \mathbf{r}° + t^*\mathbf{v}$

c. Assume reference frame of Fig 7.8. Then $v_2^f/v= r_{21}c/\sigma$, meaning that the direction of molecule 1 after collision is given by the vector between centers ($r_{21}c$) at collision time (t_{21}^c) where t_{21}^c is the time when $\|\mathbf{r}_{21}\|^2 = \sigma^2$. Adapting this perspective to the Eqns. 7.29-7.44 gives: $\Delta\mathbf{v}_2 = (\mathbf{r}_{21}^c\bullet \mathbf{v}_{21})\, \mathbf{r}_{21}^c$; Conservation laws give: $\Delta\mathbf{v}_1 = -(\mathbf{r}_{21}^c\bullet \mathbf{v}_{21})\, \mathbf{r}_{21}^c/\sigma^2$.

d. e.g. colliding with east or west wall: $\underline{\Delta\mathbf{v} = -2\,(\mathbf{v}\bullet\mathbf{x})\,\mathbf{x}}$.

(7.24) Now we explore the σ parameter with λ=2.0…

(a) Plot Z vs. η_P for CS vs. Erpenbeck and Wood… See Fig HW7.24a below.

(b) What value do you obtain for Z^{HS}(CS) at $\eta = 0.392$?

$Z^{HS}(CS) = 1 + 4\eta(1-\eta/2)/(1-\eta)^3 = 1 + 4*0.392*(1-0.392/2)/(1-0.392)^3 = 6.609$

(c) What value of σ(nm) corresponds to η = 0.392 at 22.14mol/L?

$0.392 = \eta = b\rho = b$*0.02214mol/cm3 => b = 0.392/0.02214 = 17.71cm^3/mol

$b = N_A\pi\sigma^3/6$ = 602E21molec/mol*π(σnm)3/(6*1E21nm^3/cm^3) => σ=0.383nm

(d) What value of $\beta\varepsilon$ corresponds to the boiling temperature? (e) What ε(J/mol)?

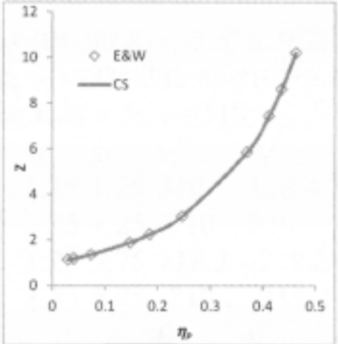


Fig HW7.24a DMD for HS: E&W vs. CS

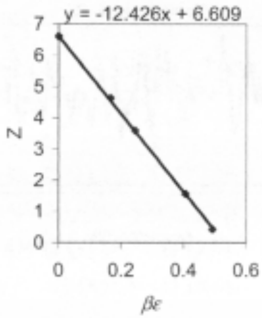


Fig HW7.24c DMD for SW(2.0)@η=0.392

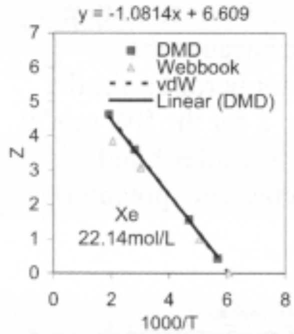


Fig HW7.24de Comparing DMD, vdW, NIST

Fig HW7.24c, shows the trendline setting the intercept to 6.609 as given in partb. Noting that $Z_L^{sat} \approx 0$, $\beta\varepsilon^{sat} = 0.527 = \varepsilon/RT^{sat}(22.14) = \varepsilon/(R*165) \Rightarrow \varepsilon = 0.527*165*8.314 = 724$J/mol=>$\varepsilon/k$ =87K

(d) Plot Z vs. 1000/T comparing to NIST(fluid properties)… ANS. See Fig HW7.24de

(e) Calc a,b for vdW and compare. ANS. $1/(1-\eta^{vdW}) = 6.609 \Rightarrow \eta^{vdW} = 0.849 \Rightarrow$ b=38.3cm3/mol; $Z_L = 6.609\text{-}a\eta/(bR165) = 0 \Rightarrow a$=409498(J-cm^3/mol^2). See Fig HW7.24de

(f) Simulate at 20.0 mol/L using σ,ε from partc and compare to NIST.
FYI: Vbox=27nm3
0.020 mol/cm3 => DMD(325molecules)
=> P = 515±15 bar at T=238±1K =>Z=1.303
η = 0.392*20/22.14 = 0.354
=> ZHS(CS) = 5.33 => Fig HW7.24f
(g) Use a,b from part e and compare vdW to NIST.
VDW => η^{vdW} = 0.849*20/22.14 = 0.767
=> Z(vdW) = 4.29-409498/(38.3*R*T);
=> ZL=0@Tsat = 230 =>Fig HW7.24f

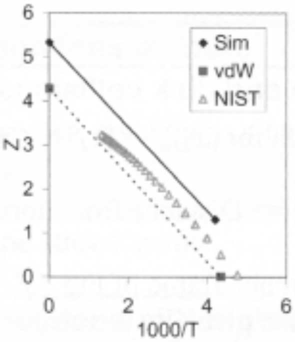


Fig HW7.24f

(h) Neither is perfect. Suggest how to improve.
λ=2.0 is not optimal. Repeating with λ= 1.7 gives nearly perfect prediction of Z_L at ρ=0.02mol/cm^3. This shows that details of potential model affect the macroscopic properties with high sensitivity. Conversely, macroscopic properties combined with DMD can infer details of molecular interactions like an "atomic force nanoscope."

(7.25) Now we explore the σ,ε parameters with λ=1.7…

(a) What value do you obtain for Z^{HS}(CS) at $\eta_P = 0.375$?
$Z^{HS}(\text{CS}) = 1 + 4\eta_P(1\text{-}\eta_P/2)/(1\text{-}\eta_P)^3 = 1 + 4*0.375*(1\text{-}0.375/2)/(1\text{-}0.375)^3 = 5.992$
(b) What value of σ(nm) corresponds to $\eta_P = 0.375$ at 22.14mol/L?
$0.375 = \eta_P = b\rho = b*0.02214$mol/cm3 => $b = 0.375/0.02214 = 16.94$ cm^3/mol
$b = N_A\pi\sigma^3/6$ = 602E21molec/mol*π(σnm)^3/(6*1E21nm^3/cm^3) => σ=0.3773nm
(c) What value of $\beta\varepsilon$ corresponds to the boiling temperature? What ε(J/mol)?

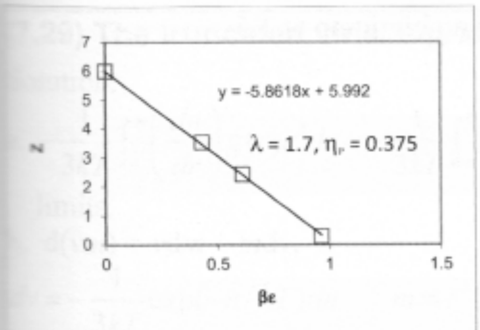


Fig HW7.25c DMD data for SW(1.7)@η_P=0.375

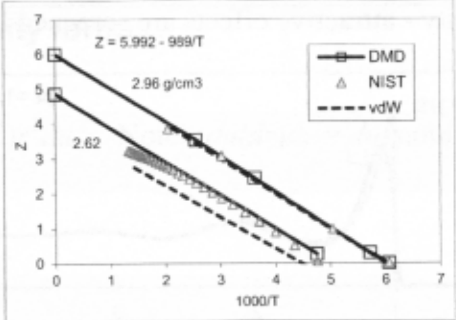


Fig HW7.25df Comparing DMD, vdW, NIST

Fig HW7.25c, shows the trendline. Setting the y-intercept to 5.992 as given in partb. Noting that $Z_L^{sat} \approx 0$, $\beta\varepsilon^{sat} = 5.992/5.8618 = 1.0222 = \varepsilon/RT^{sat}(22.14) = \varepsilon/(R*165)$

=> $\varepsilon = 1.0222 *165*8.314 = 1402$ J/mol=>ε/k =169K.

(d) Plot Z vs. 1000/T comparing to NIST(fluid properties)…

ANS. See Fig HW7.25df at 2.96 g/cm3

(e) **Calc a,b for vdW and compare**. ANS. $1/(1-\eta^{vdW}) = 5.992 \Rightarrow \eta^{vdW} = 0.8333 \Rightarrow$

b=37.64cm3/mol; $Z_L = 5.992 - a\eta/(bR165) = 0 \Rightarrow a$=376195(J-cm^3/mol^2). See Fig HW7.25df

(f) Simulate at 20.0 mol/L using σ,ε from partc and compare to NIST.

FYI: Vbox=27nm^3

(0.020 mol/cm3)*602*27 => DMD(325molecules)

=> P = 90.3±4 bar at T=210±1K =>Z=0.257

η = 0.375*20/22.14 = 0.3377

=> ZHS(CS) = 5.33 => Fig HW7.25df

(g) Use a,b from part e and compare vdW to NIST.

VDW => η^{vdW} = 0.8333*20/22.14 = 0.753

=> Z(vdW) = 4.045-376195/(38.3*R*T);

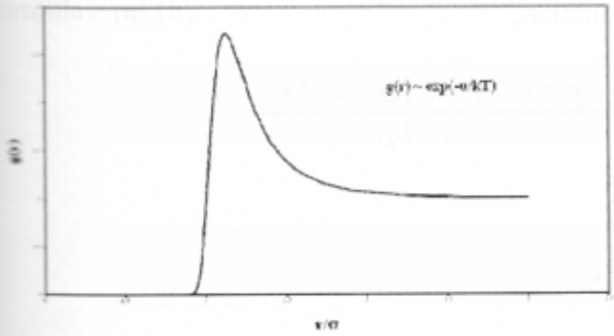
=> ZL=0@Tsat = 230 =>Fig HW7.25df at 2.62g/cm

(h) Compare to 7.24.

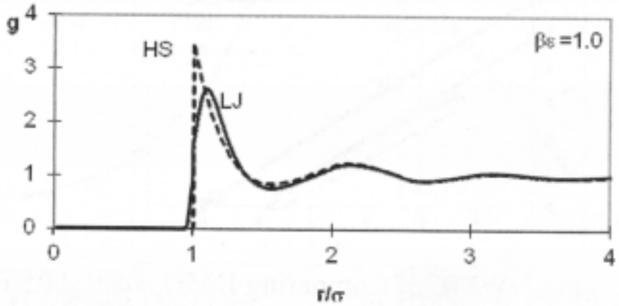
This is not required but it is interesting to note that the results at λ=2.0 are not nearly as accurate as at λ=1.7. This shows that details of potential model affect the macroscopic properties with high sensitivity. Conversely, macroscopic properties combined with DMD can infer details of molecular interactions like an "atomic force nanoscope."

(7.26) The discussion in the chapter…

(a) low density its mirror image of u(r)



(b) high density - attractive effects are screened like SW but no big jump at 1.5.



$$g(\sigma^+) = \frac{1}{1-2b\rho} + \frac{2.5F}{1+Fb\rho}$$

$$g(1.5\sigma^+) = \frac{1}{1-0.176b\rho} + \frac{2.5F}{1+11.39b\rho}$$

$$Z = 1 + 4b\rho\left(\frac{1}{1-2b\rho} + \frac{2.5F}{1+Fb\rho} - 1.5^3\left[1-\exp(-\varepsilon/kT)\right]\left\{\frac{1}{1-0.176b\rho} + \frac{2.5F}{1+11.39Fb\rho}\right\}\right)$$

(7.27) Suppose that a reasonable approximation to the radial distribution…

$$g(\sigma^+) = \frac{1}{1-2b\rho} + \frac{2.5F}{1+Fb\rho}$$

$$g(1.5\sigma^+) = \frac{1}{1-0.176b\rho} + \frac{2.5F}{1+11.39b\rho}$$

$$Z = 1 + 4b\rho\left\{\frac{1}{1-2b\rho} + \frac{2.5F}{1+Fb\rho} - 1.5^3[1-\exp(-\varepsilon/kT)]\left(\frac{1}{1-0.176b\rho} + \frac{2.5F}{1+11.39Fb\rho}\right)\right\}$$

For ($\varepsilon/kT = 1$ and $\rho N_A\sigma^3 = 0.6$)
$F = 1.7183$, $b\rho = 0.314 \Rightarrow Z = 3.44$.

(7.28) Suppose that a reasonable approximation to the radial distribution …

We may use the generalized equation in the math appendix for the compressibility factor for the square-well potential,
$Z = 1 + 4b\rho\{g(\sigma^+) - \lambda^3[1-\exp(-\varepsilon/kT)]g(\lambda\sigma^-)\}$
Evaluating for the proposed radial distribution function,
The term in {} becomes

$$\frac{\exp(\varepsilon/kT) - \lambda^3(1-\exp(-\varepsilon/kT))\exp(\varepsilon/kT)}{1-b\rho} = \frac{\exp(\varepsilon/kT) - \lambda^3(\exp(\varepsilon/kT)-1)}{1-b\rho}$$

$$Z = 1 + \frac{4b}{1-b\rho}\lambda^3\left[1 + \left(\frac{1-\lambda^3}{\lambda^3}\right)\exp\left(\frac{\varepsilon}{RT}\right)\right]$$

(7.29) The truncated virial equation (density form)...

Solution:

a. $-\frac{1}{3kT}\int_0^\infty \left(\frac{du}{dr}\right) g(r) r^3 dr = -\frac{1}{3kT}\int_\infty^0 \exp(-u/kT) r^3 du$, Note: $(du/dr)dr = du$, note change in limits.

b. $d(vm) = v\,dm + m\,dv$,

$dv = -\frac{1}{3kT}\exp(-u/kT)du \qquad m = r^3$

$v = \frac{1}{3}\exp(-u/kT) \qquad dm = 3r^2 dr$

where the initial integral is $\int m\,dv$. Therefore

$$\frac{1}{3}\int_0^\infty d(r^3\exp(-u/kT)) = \int_0^\infty \exp(-u/kT) r^2 dr - \frac{1}{3kT}\int_0^\infty \left(\frac{du}{dr}\right)\exp(-u/kT) r^3 dr$$

$$= \int_0^\infty \exp(-u/kT) r^2 dr - \frac{1}{3kT}\int_0^\infty \left(\frac{du}{dr}\right) g(r) r^3 dr$$

c. The left hand side integrates to $\frac{r^3}{3}\exp(-u/kT)$ which is equal to $r^3/3$ at the upper limit, and zero at the lower limit. This is equivalent to the integral $\int_0^\infty r^2 dr$. Making this substitution, and combining, we have for low density

$$\int_0^\infty [1-\exp(-u/kT)] r^2 dr = -\frac{1}{3kT}\int_0^\infty \left(\frac{du}{dr}\right)\exp(-u/kT) r^3 dr = -\frac{1}{3kT}\int_0^\infty \left(\frac{du}{dr}\right) g(r) r^3 dr$$

(7.30) The virial coefficient can be related...

$$B = \frac{2}{3}\pi N_A \sigma^3 \lambda^3 \left[1 + \left(\frac{1-\lambda^3}{\lambda^3}\right)\exp\left(\frac{\varepsilon}{kT}\right)\right]$$

The column labeled "error" is $(B - B_{calc})^2$ The number at the bottom is the sum. Excel has some difficulty when the parameters that it adjusts are of very different magnitude. Therefore, the ε/k, σ and λ values are converted within the formulas. (a),(b)

square-well for Argon

e/k	100.336786
sigma (Angstroms)	3.02E+00
R =λ=	1.66713034

T(K)	B (cm3/mole)	Bcalc	error
85	-251	-250.8232	0.031272
100	-183.5	-183.9142	0.171553
150	-86.2	-85.72345	0.227101
200	-47.4	-47.65327	0.064147
250	-27.9	-27.68634	0.045652
300	-15.5	-15.44565	0.002954
400	-1	-1.252471	0.063741
500	7	6.710946	0.083552
600	12	11.80222	0.039117
700	15	15.33599	0.112888
800	17.7	17.93146	0.053575
900	20	19.91826	0.006682
			0.902235

c.

Square-well for propane

e/k	421.6414736
sigma (Angstroms)	3.81E+00
R	1.460117412

T(K)	B (cm3/mole)	Bcalc	error
250	-584	-577.1549	46.85524
260	-526	-527.3067	1.707365
270	-478	-483.9469	35.36558
285	-424	-428.6789	21.89236
300	-382	-382.6763	0.457426
315	-344	-343.8879	0.012577
330	-313	-310.809	4.800685
350	-276	-273.6815	5.37564
375	-238	-235.8533	4.608132
400	-208	-205.1563	8.086404
430	-177	-175.2599	3.027925
470	-143	-143.894	0.799275
500	-124	-125.0083	1.016632
550	-97	-99.80619	7.874705
			141.8799

(7.31) One suggestion for a simple pair potential is the triangular potential…

Derive the second virial coefficient and fit the parameters to the virial coefficient data for argon.

Integral to evaluate is of the form

$$B = 2\pi N_A \int_0^\infty \left(r^2 - r^2 \exp[ar+b]\right) dr = 2\pi N_A \left.\frac{r^3}{3}\right|_\sigma^{\lambda\sigma} - 2\pi N_A \int_0^\infty \left(r^2 \exp[ar+b]\right) dr$$

where $a = \varepsilon / [\sigma(1-\lambda)kT]$, $b = -\varepsilon\lambda / [(1-\lambda)kT]$

integrate by parts

dx = exp(ar+b)dr $\qquad$ v = r^2

x = exp(ar+b)/a $\qquad$ dv = 2rdr

second integral becomes

$$\frac{r^2 e^{ar+b}}{a} - \int_\sigma^{\lambda\sigma} \frac{2r}{a} e^{ar+b} dr$$

Integrate by parts again

integrate by parts

dx = exp(ar+b)dr $\qquad$ v = r

x = exp(ar+b)/a $\qquad$ dv = dr

Now the integral becomes

$$\frac{r^2 e^{ar+b}}{a} - \frac{2re^{ar+b}}{a^2} + \frac{2}{a^2} \int_\sigma^{\lambda\sigma} e^{ar+b} dr$$

performing the last integration, the desired integral is

$$\left(\frac{r^2}{a}-\frac{2r}{a^2}+\frac{2}{a^3}\right)e^{ar+b}\Big|_{\sigma}^{\lambda\sigma}$$

inserting variables for the a and b

$$=\left[\frac{\lambda^2(1-\lambda)}{\varepsilon/kT}-\frac{2\lambda(1-\lambda)^2}{(\varepsilon/kT)^2}+\frac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\right]\sigma^3-\left[\frac{(1-\lambda)}{\varepsilon/kT}-\frac{2(1-\lambda)^2}{(\varepsilon/kT)^2}+\frac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\right]\sigma^3 e^{\varepsilon/kT}$$

Combining all together:

$$B=2\pi N_A\sigma^3\left[\frac{\lambda^3}{3}-\left(\frac{\lambda^2(1-\lambda)}{\varepsilon/kT}-\frac{2\lambda(1-\lambda)^2}{(\varepsilon/kT)^2}+\frac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\right)\right.$$

$$\left.+\left(\frac{(1-\lambda)}{\varepsilon/kT}-\frac{2(1-\lambda)^2}{(\varepsilon/kT)^2}+\frac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\right)\exp\left(\frac{\varepsilon}{kT}\right)\right]$$

Using Excel to fit parameter values by minimizing the sum of errors, $\Sigma(B - B_{calc})^2$

Triangular Potential

e/k (K)	154.7212
σ(A)	3.035509
R	1.911652

Intermediate Calcs

(1-R) -0.91165

T(K)	Bexpt	Bcalc	error	e/kT
85	-251	-250.911	0.00796	1.82025
100	-183.5	-183.573	0.005306	1.547212
150	-86.2	-85.6677	0.283387	1.031475
200	-47.4	-47.7864	0.149337	0.773606
250	-27.9	-27.8662	0.001142	0.618885
300	-15.5	-15.6182	0.013963	0.515737
400	-1	-1.36657	0.13437	0.386803
500	7	6.659918	0.115656	0.309442
600	12	11.80534	0.037893	0.257869
700	15	15.38381	0.14731	0.22103
800	17.7	18.01613	0.099939	0.193402
900	20	20.03356	0.001126	0.171912

$$B=2\pi N_A\int_0^\infty\left(r^2-r^2\exp[ar+b]\right)dr=2\pi N_A\frac{r^3}{3}\Big|_{\sigma}^{\lambda\sigma}-2\pi N_A\int_0^\infty\left(r^2\exp[ar+b]\right)dr \quad a=\varepsilon/[\sigma(1-\lambda)kT]$$

$$b=-\varepsilon\lambda/[(1-\lambda)kT] \quad \frac{r^2e^{ar+b}}{a}-\int_{\sigma}^{\lambda\sigma}\frac{2r}{a}e^{ar+b}dr \quad \frac{r^2e^{ar+b}}{a}-\frac{2re^{ar+b}}{a^2}+\frac{2}{a^2}\int_{\sigma}^{\lambda\sigma}e^{ar+b}dr \quad \left(\frac{r^2}{a}-\frac{2r}{a^2}+\frac{2}{a^2}\right)e^{ar+b}\Big|_{\sigma}^{\lambda\sigma}$$

$$=\left[\frac{\lambda^2(1-\lambda)}{\varepsilon/kT}-\frac{2\lambda(1-\lambda)^2}{(\varepsilon/kT)^2}+\frac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\right]\sigma^3-\left[\frac{(1-\lambda)}{\varepsilon/kT}-\frac{2(1-\lambda)^2}{(\varepsilon/kT)^2}+\frac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\right]\sigma^3 e^{\varepsilon/kT}$$

$$B=2\pi N_A\sigma^3\left[\frac{\lambda^3}{3}-\left(\begin{array}{l}\dfrac{\lambda^2(1-\lambda)}{\varepsilon/kT}-\dfrac{2\lambda(1-\lambda)^2}{(\varepsilon/kT)^2}+\\ \dfrac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\end{array}\right)+\left(\begin{array}{l}\dfrac{(1-\lambda)}{\varepsilon/kT}-\dfrac{2(1-\lambda)^2}{(\varepsilon/kT)^2}+\\ \dfrac{2(1-\lambda)^3}{(\varepsilon/kT)^3}\end{array}\right)\exp\left(\frac{\varepsilon}{kT}\right)\right]$$

(7.32) (Doesn't appear in textbook).

The attractive contribution to the compressibility factor is shown below. Derive an expression for the attractive contribution to the compressibility factor for fluids that can be accurately represented by a) square well potential b) Sutherland potential. Evaluate each of the expressions at $\rho N_A \sigma^3 = 1$ and $\varepsilon/kT = 1$

SOLUTION

$$Z^{att} = -\frac{\rho N_A}{6kT}\int_{\sigma}^{\infty} r\frac{d}{dr}u(r)g4\pi r^2 dr$$

$$g = 1 + \frac{\rho N_A \sigma^6 \varepsilon}{r^3 kT}$$

a) Square Well Potential

$$u(r) = \infty \quad \sigma \geq r$$

$$= -\varepsilon \quad \sigma < r < 1.5\sigma$$

$$= 0 \quad r \geq 1.5\sigma$$

$$y(r) = \exp(\frac{u}{kT})g(r)$$

$$\frac{\partial}{\partial r}\exp(\frac{u}{kT}) = -\frac{1}{kT}\exp(-\frac{u}{kT})\frac{\partial u}{\partial r}$$

$$Z^{att} = -\frac{\rho N_A}{6kT}\int r\frac{du(r)}{dr}y(r)\exp(-\frac{u}{kT})4\pi r^2 dr$$

$$= -\frac{\rho N_A}{6kT}\int_{\sigma}^{\infty} rkT\frac{d}{dr}(\exp(-\frac{u}{kT}))y(r)4\pi r^2 dr$$

$$\therefore Z^{att} = \frac{\rho}{6kT}.kT\int_{\sigma}^{\infty}\frac{d}{dr}\exp(\frac{u}{kT})y(r)4\pi r^3 dr$$

$$= \frac{\rho}{6}\int_{\sigma}^{\infty}\frac{d}{dr}\exp(-\frac{u}{kT})y(r)4\pi r^3 dr$$

From Appendix B

$$\exp(-\frac{u}{kT}) = \exp(\frac{\varepsilon}{kT})H(r-\sigma) + \left[\exp(\frac{\varepsilon}{kT}) - 1\right][1 - H(r - \lambda\sigma)]$$

Integrating we get,

$$\frac{d}{dr}\exp(-\frac{u}{kT}) = \exp(\frac{\varepsilon}{kT})\delta(r-\sigma) + \left[\exp(\frac{\varepsilon}{kT}-1)\right][1-\delta(r-\lambda\sigma)]$$

Substituting in the Z^{att} term we get,

$$Z^{att} = \frac{\rho N_A}{6}\int_{\sigma}^{1.5\sigma}\left[\delta(r-\sigma)y(r)\exp(\frac{\varepsilon}{kT}) - \delta(r-1.5\sigma)y(r)\left[\exp\left(\frac{\varepsilon}{kT}-1\right)\right]\right]4\pi r^3 dr$$

$$= \frac{N_A\rho}{6}\left[y(\sigma)\exp(\frac{\varepsilon}{kT}) - 1.5^3 y(1.5\sigma)(\exp(\frac{\varepsilon}{kT}-1))\right]4\pi\sigma^3$$

$$= \frac{N_A\rho 4\pi\sigma^3}{6}\left[y(\sigma)\exp(\frac{\varepsilon}{kT}) - 1.5^3 y(1.5\sigma)(\exp(\frac{\varepsilon}{kT}-1))\right]$$

$$= \frac{N_A\rho 4\pi\sigma^3}{6}\left[g(\sigma^+) - 1.5^3 g(1.5\sigma^-)(1-\exp(-\frac{\varepsilon}{kT})\right]$$

$$g(\sigma^+) = 2$$

$$g(\lambda\sigma^-) = 1 + \frac{1}{1.5^3} = 1.296$$

$$Z^{att} = -\frac{N_A\rho 4\pi\sigma^3}{6}(2.80)$$

$$Z^{att} = -\frac{4\pi}{6}(2.80) = -5.863$$

b) For the Sutherland Potential

$$Z^{att} = \frac{\rho N_A}{6kT}\int_{\sigma}^{\infty} r\frac{du(r)}{dr}g.4\pi r^2 dr$$

$$u(r) = \infty \quad r \le \sigma$$

$$= -\varepsilon\left(\frac{\sigma}{r}\right)^6 \quad r > \sigma$$

$$\frac{d(u(r))}{dr} = \frac{6\varepsilon\sigma^6}{r^7}$$

$$Z^{att} = -\frac{\rho N_A}{6kT}\int_{\sigma}^{\infty} r.\frac{6\varepsilon\sigma^6}{r^7}\left(1+\frac{\rho N_A\sigma^6\varepsilon}{r^3kT}\right)4\pi r^2 dr$$

$$= -\frac{4\pi N_A\rho\varepsilon\sigma^6}{kT}\int_{\sigma}^{\infty}\left(\frac{1}{r^4}+\frac{\rho N_A\sigma^6\varepsilon}{r^7kT}\right)dr$$

$$= -\frac{4\pi N_A\rho\varepsilon\sigma^6}{kT}\left[-\frac{1}{3r^3}-\frac{\rho N_A\sigma^6\varepsilon}{6r^6kT}\right]_{\sigma}^{\infty}$$

$$= -\frac{4\pi N_A\rho\varepsilon\sigma^6}{kT}\left[\frac{1}{3\sigma^3}-\frac{\rho N_A\varepsilon}{6kT}\right]$$

$$= -\frac{4\pi N_A\rho\varepsilon\sigma^3}{3kT}-\frac{4\pi\rho^2\varepsilon^2 N_A{}^2\sigma^6}{6k^2T^2} = -\frac{4\pi\rho\sigma^3}{2}N_A = -2\pi$$