



COLLEGE OF ARTS AND SCIENCES

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DEPARTMENT OF PHYSICS AND ASTRONOMY

The UNIVERSITY *of* OKLAHOMA

Statistical Mechanics

PHYS 5163 HOMEWORK ASSIGNMENT 5

PROBLEMS: {1,2,3,4}

Due: March 4, 2022 at 6:00 PM

STUDENT

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PROFESSOR

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Problem 1:

In 1906, Berthelot proposed the following equation of state as an improvement of the ideal gas equation of state:

$$\left(P + \frac{a}{kT v^2} \right) (v - v_0) = kT. \quad (1)$$

Here, a and v_0 are substance specific constants (they have to be determined for each substance) and v is equal to V/N , with N being the number of atoms or molecules in the substance. Let us consider a gas that satisfies Berthelot's equation of state as well as the additional condition that the internal energy U approaches $5NkT/2$ in the $v \rightarrow \infty$ limit.

- (a) Determine the Helmholtz free energy \mathcal{A} (your answer will depend on an undetermined constant).

We are working in the canonical ensemble and we demand $U \rightarrow \frac{5}{2}NkT$. We first use the fact that

$$P = - \left(\frac{\partial \mathcal{A}}{\partial V} \right)_{T,N} \quad (\times)$$

We also know that

$$U = A - T \left(\frac{\partial A}{\partial T} \right)_{V,N} \quad (\times \times)$$

Taking our equation of state in (1) and solving for P

$$P = \frac{NK T}{V - V_0} - \frac{a}{k T} \frac{N^2}{V^2}$$

We then put this in (x) and we have

$$\left(\frac{\partial A}{\partial V} \right)_{T,N} = \frac{a}{k T} \frac{N^2}{V^2} - \frac{N K T}{V - V_0} \quad (\times \times \times)$$

Re-arranging (xxx) we then find A to be

$$A = \int \frac{a}{k T} \frac{N^2}{V^2} - \frac{N K T}{V - V_0} dV = - \frac{a}{k T} \frac{N^2}{V} - N K T \log(V - V_0) + N F(N, T)$$

We then put this result into (xx) and we then have

$$\begin{aligned} U &= - \frac{a}{k T} \frac{N^2}{V} - N K T \log(V - V_0) + N F(N, T) - T \cdot \frac{a}{k T^2} \frac{N^2}{V} + N K T \log(V - V_0) - N T \frac{\partial F(N, T)}{\partial T} \\ &= N f(N, T) - N T \left(\frac{\partial f(N, T)}{\partial T} \right)_{V,N} - 2 N \frac{a}{k T} \frac{N}{V} \stackrel{!}{=} \frac{5}{2} N K T \\ &\quad \text{LD goes to zero by assignment} \end{aligned}$$

Problem 1: Continued

We then can solve for $f(N, T)$ with

$$f(N, T) - T \left(\frac{\partial f(N, T)}{\partial T} \right)_{V, N} = \frac{5}{2} kT \Rightarrow \left(\frac{\partial f(N, T)}{\partial T} \right) = \frac{1}{T} f(N, T) - \frac{5}{2} k$$

We then can say

$$f(N, T) = -\frac{5}{2} kT \log(T) + CT$$

The Helmholtz Free Energy is then

$$A = -\frac{\alpha}{kT} \frac{N^2}{V} - NkT \log(V - V_0) - \frac{5}{2} NkT \log(T) + CTN$$

- (b) Determine the specific heat C_V at constant volume

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (2)$$

in terms of T and v .

Potential energy is defined as

$$U = N [f(N, T) - T (\partial f / \partial T)_{V, N} - \alpha / kT N / V]$$

Using our prior definition for $f(N, T)$, U is then

$$U = N [5/2 kT - \alpha / kT N / V]$$

N/V goes to zero by assignment $\therefore U \rightarrow \frac{5}{2} NkT \therefore C_V$ is then

$$C_V = \frac{5}{2} Nk$$

Problem 1: Review

Procedure:

- We first begin by stating the relationship for pressure

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N}$$

where we also use the fact that

$$U = A - T \left(\frac{\partial A}{\partial T} \right)_{V,N}$$

- Take the equation of state in (1) and solve it for P
- Using the prior definitions for P and U we can then create a first order partial differential equation that can be used to solve for the Helmholtz Free Energy with an unknown constant
- We then use the equation for U and find the unknown constant that way
- – We then proceed to use the definition for U that is defined in part (a) with the equation for C_V in (2)

Key Concepts:

- Since we are not told anything about our chemical potential μ , we know we are working in the Canonical Ensemble
- We use Maxwell relationships to relate Thermodynamic properties that can be derived with the aide of Statistical Mechanics
- With the aide of these Maxwell equations we can create a differential equation that will allow us to solve for the desired quantity that we are asked for
- Using the definition for internal energy U we can find the unknown constant comes from our partial differential equation
- – Since we have found an expression for the Helmholtz Free Energy A we can find the specific heat at constant volume C_V by expressing our internal Energy U in terms of A
- Since A is explicitly dependent upon T , U is then implicitly dependent upon T and we can then use equation (2) to calculate the specific heat

Variations:

- We can be given a different gas that has a different equation of state
 - * We would use the same procedure but the small details of what each expression would evaluate to would be slightly different
 - * It should be noted that if we are enforcing $U \rightarrow \frac{5}{2}NkT$ then we should get the same specific heat at the end as well
- We could be asked to find C_V through different means
 - * We then would backtrack to (a) so that this new equation could be used
- We could be asked to find a different quantity
 - * This would require us to use a different equation to find this quantity

Problem 2:

In Problem 1, we determined the pressure and internal energy of a substance governed by Berthelot's equation of state, subject to the condition $U \rightarrow 5NkT/2$ for $v \rightarrow \infty$.

- (a) What are the units of a and v_0 that enter into Berthelot's equation of state? Use your result to rewrite the pressure and internal energy per particle as dimensionless quantities (denote the dimensionless pressure by \tilde{P} and the dimensionless internal energy per particle by $\tilde{\epsilon}$).

Note: In the process, you will have to define a dimensionless volume \tilde{v} and a dimensionless temperature \tilde{T} (or more precisely, Boltzmann constant times temperature).

Berthelot's equation on the right hand side has units of

$$[kT] = \frac{J}{\text{mol K}} \cdot K = \frac{J}{\text{mol}}$$

We know that $[v_0] = \text{m}^3$, so that means

$$\left[\frac{a}{kT v^2} \right] = \text{Pa} = \frac{N}{\text{m}^2} = \frac{\text{kg}}{\text{m s}^2}$$

Doing some unit algebra we find

$$[a] = kT v^2 \frac{N}{\text{m}^2} = \frac{J}{\text{mol K}} \cancel{K} \cdot (m^3)^2 \frac{N}{\text{m}^2} = J \cdot N \text{m} \cdot m^3 = J^2 \cdot m^3 \checkmark$$

\hookrightarrow omit, arbitrary

Berthelot's equation re-arranged for P is

$$P = \frac{kT}{V - V_0} - \frac{a}{kT v^2} \quad (*)$$

We then write out for what variable do we divide by which to make $(*)$ dimensionless

$$V \rightarrow V_0$$

$$kT \rightarrow \sqrt{a/V_0}$$

$$P \rightarrow \sqrt{a/V_0^3}$$

Equation $(*)$ then becomes

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V}-1} - \frac{1}{\tilde{T}\tilde{V}^2}$$

Problem 2: Continued

where

$$\tilde{P} = \frac{P}{\sqrt{\frac{a}{V_0^3}}} , \quad \tilde{v} = \frac{v}{V_0} , \quad \tilde{T} = \frac{kT}{\sqrt{\frac{a}{V_0}}} .$$

Doing the same for \mathcal{E} we have

$$\mathcal{E} = \frac{U}{N} = - \frac{\partial a}{V k T} + \frac{5}{2} k T$$

which dimensionlessly is

$$\tilde{\mathcal{E}} = - \frac{\partial}{\tilde{T} \tilde{v}} + \frac{5}{2} \tilde{T}$$

where $\tilde{\mathcal{E}} = \mathcal{E} / \sqrt{a/V_0}$. This then means finally

$$\boxed{\tilde{P} = \frac{\tilde{T}}{\tilde{v}-1} - \frac{1}{\tilde{T} \tilde{v}^2}, \quad \tilde{\mathcal{E}} = - \frac{\partial}{\tilde{T} \tilde{v}} + \frac{5}{2} \tilde{T}}$$

- (b) Determine the critical dimensionless temperature \tilde{T}_c , which is obtained by enforcing

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{v}} \right)_T = 0 \quad (3)$$

and

$$\left(\frac{\partial^2 \tilde{P}}{\partial \tilde{v}^2} \right)_T = 0 \quad (4)$$

Explain how Eq. (3) relates to the isothermal compressibility. Explain whether or not

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{v}} \right)_T > 0 \quad (5)$$

and

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{v}} \right)_T < 0 \quad (6)$$

are physical.

The first and second derivative of the dimensionless pressure is

$$\frac{\partial \tilde{P}}{\partial \tilde{v}} = - \frac{\tilde{T}}{(\tilde{v}-1)^2} + \frac{2}{\tilde{T} \tilde{v}^3} = 0 \quad , \quad \frac{\partial^2 \tilde{P}}{\partial \tilde{v}^2} = \frac{2\tilde{T}}{(\tilde{v}-1)^3} - \frac{6}{\tilde{T} \tilde{v}^4} = 0$$

Problem 2: Continued

We can then say

$$\frac{\partial}{\tilde{T}_c \tilde{V}_c^3} = \frac{\tilde{T}_c}{(\tilde{V}_c - 1)^2} \quad , \quad \frac{\partial \tilde{T}_c}{(\tilde{V}_c - 1)^3} = \frac{b}{\tilde{T}_c \tilde{V}_c^4}$$

Dividing the two equations we find $\tilde{V}_c = 3 \therefore \tilde{T}_c = \sqrt{81a7}$. Algebraically

$$T_c = \sqrt{\frac{8a}{27k^2v_0}}$$

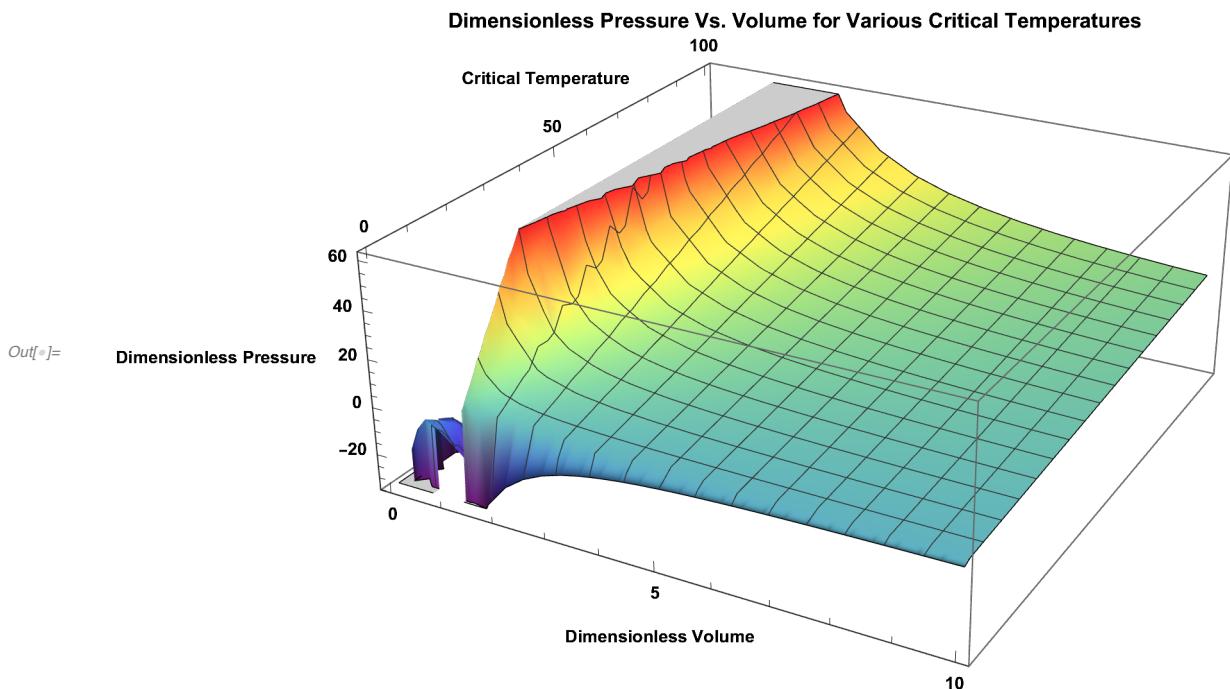
- (c) Plot isotherms in a \tilde{P} versus \tilde{v} diagram. Include the equation of state for $\tilde{\tau} = \tilde{\tau}_c$, $\tilde{\tau} < \tilde{\tau}_c$ and $\tilde{\tau} > \tilde{\tau}_c$. Do you encounter negative \tilde{P} ? Does this bother you?

SEE NEXT PAGE

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In[6]:= a = 1;
b = 1;
g = 1;
P[v_, t_] =  $\frac{gt}{v-b} - \frac{a}{tv^2}$ ;
Plot3D[P[v, t], {v, 0, 10}, {t, 0.01, 100}, ColorFunction -> "Rainbow",
PlotLabel -> "Dimensionless Pressure Vs. Volume for Various Critical Temperatures",
AxesLabel -> {"Dimensionless Volume", "Critical Temperature",
"Dimensionless Pressure"}, LabelStyle -> Directive[Bold, Black]]

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Problem 2: Review

Procedure:

- - First begin by performing dimensional analysis on the quantities that are asked of us to examine
 - Rearrange the equation of state to be an equation for pressure
 - Make the following variables dimensionless (v, kT, P) by dividing by the units of each variable in the context of our problem
 - * For example, since kT is in units of Joules, we must divide this quantity by Joules (That is defined by $\sqrt{a/v_0}$ since this quantity [J])
 - * Repeat the above for all quantities in the equation of state
 - Do the same for the internal energy per particle (\mathcal{E}/N)
- - Perform the derivatives on the dimensionless pressure equation and then solve for the critical volume v_c
 - Plug this value for v_c back into the equation for T_c that was found with the derivative equations
 - Plot the quantities in a graph to show the different values at different points

Key Concepts:

- - Creating dimensionless equations allows us to create plots of equations of states for specific cases pertaining to macro variables in our system
 - To create a dimensionless equation, one must divide through by the unit of the equation one is solving for in the context of the quantities given in a problem
 - We create the constraint that both the first and second derivative of the dimensionless pressure must be zero, in doing this we create a way to find the critical temperature and critical volume of our system due to the pressure being extremized in each case
 - Using the equation for critical temperature that was found in part (b) we can then move on to plotting the pressure for different values of the critical temperature

Variations:

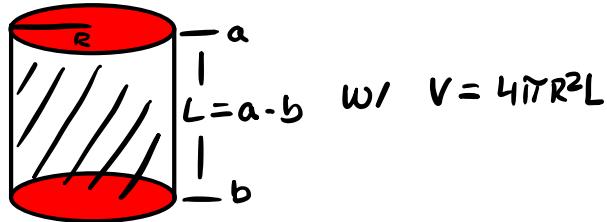
- - We can be given a different initial equation of state
 - * This would change the small details of what each expression evaluates to etc but it would not change the overall procedure
 - We could be given a different constrain to find our critical temperature
 - * This would only change the math of what the expressions evaluate to but the same procedure of finding v_c and then T_c would be the same
 - We could be given a different set of conditions to plot
 - * This would just change the constraints that are applied in Mathematica

Problem 3:

A gas consisting of N identical classical particles is confined inside a cylinder of length $L = a - b$ and with volume $V = \pi R^2 L$, i.e., the particles' coordinates are restricted by $b < z < a$ and $x^2 + y^2 = R^2$. The particles do not interact with each other and the motion of a single particle is governed by the Hamiltonian $\mathcal{H} = \frac{\vec{p}^2}{2m} + Kz$, where K is a constant. Let us assume that the gas is in equilibrium.

- (a) Calculate the partition function of the gas.

We begin by drawing a picture because physics is tolerable with pictures.



We will calculate the canonical partition function with,

$$Q_N(T, V) = \frac{1}{N! h^{3N}} \int_T \int_T e^{-\beta(\frac{\vec{p}^2}{2m} + Kz)} d^{3N} \vec{p} d^{3N} z$$

For our system we see

$$\begin{aligned} Q_N(T, V) &= \frac{1}{N! h^{3N}} \int_0^\infty \left(e^{-\frac{\beta \vec{p}^2}{2m}} \right)^{3N} d\vec{p} \int_b^a \int_0^{\pi R} \int_0^R \left(n e^{-\beta K z} \right)^N dr dz dz \\ &= \frac{1}{N!} \left(\frac{2m\pi}{h^2 \beta} \right)^{3N/2} \left(\frac{\pi R^2}{2\beta K} \right)^N (e^{-\beta K b} - e^{-\beta K a})^N \end{aligned}$$

Our partition function is then

$$Q_N(T, V) = \frac{1}{N!} \left(\frac{2m\pi}{h^2 \beta} \right)^{3N/2} \left(\frac{\pi R^2}{2\beta K} \right)^N (e^{-\beta K b} - e^{-\beta K a})^N$$

- (b) Determine the pressure P_a of the gas on the wall at $z = a$.

We can calculate the the pressure of our gas with

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} \quad (*)$$

Where

$$A = -kT \log(Q_N).$$

Problem 3: Continued

Since the only aspect of our volume that is changing we can write as

$$P_a = -\frac{1}{\pi R^2} \left(\frac{\partial A}{\partial a} \right)_{N,T}$$

Which for our system is

$$P_a = -\frac{1}{\pi R^2} \left(\frac{\partial}{\partial a} \right)_{N,T} \log(c^*(e^{-\beta k b} - e^{-\beta k a})) = \frac{1}{\pi R^2} \cdot N \cdot \frac{\beta k e^{-\beta k a}}{e^{-\beta k b} - e^{-\beta k a}}$$

We then say the pressure at a is

$$P_a = \frac{N \beta k}{\pi R^2} \frac{1}{e^{\beta k L} - 1}$$

$$L = a - b$$

- (c) Determine the pressure P_b of the gas on the wall at $z = b$.

The pressure at b will be the negative at a due to symmetry \therefore

$$P_b = \frac{N \beta k}{\pi R^2} \frac{1}{1 - e^{-\beta k L}}$$

- (d) Compare the pressures P_a and P_b in the limit $KL \gg kT$. Explain.

If we let $KL \gg kT$, $e^{-\beta k L} \rightarrow 0 \therefore$ we can see that $P_a < P_b$ and this is due to a having a higher potential and a lower density

Problem 3: Review

Procedure:

- Begin by solving for the Classical Canonical Partition function with

$$Q_N(T, V) = \frac{1}{N!h^{3N}} \int \int e^{-\beta \mathcal{H}} d^{3N}\vec{p} d^{3N}q$$

with the Hamiltonian that is given to us

- Calculate the pressure of our gas with

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N,T}$$

where A is our classical Helmholtz Free Energy

- Since the only component of our volume that is changing is the height we can write our equation for pressure as then

$$P_{x_i} = - \frac{1}{\pi R^2} \left(\frac{\partial A}{\partial x_i} \right)_{N,T}$$

- Using the fact that our cylinder is symmetric, we can then just say $P_a = -P_b$
- Evaluate the limit and discuss what this means in terms of potential and density for the location of our cylinder

Key Concepts:

- Since we are working the Canonical Ensemble, we solve for our Classical Partition function create a bridge between Statistical Mechanics and Thermodynamics
- Using the Maxwell equation for pressure we can determine what the pressure of our cylinder of gas is at a and b
- Since our cylinder is symmetric we can generally say that $P_a = -P_b$
- If $\frac{kL}{KT} \gg 1$ then this means that $e^{-\beta kL} \rightarrow 0$ and this then means that at location a we will have a higher potential and a lower density and this implies that $P_a < P_b$

Variations:

- We can be given a different Hamiltonian
 - * This will change what our partition function will evaluate to but it will not change the methodology of how to proceed for the rest of the problems
- We could be asked to find a different quantity instead of pressure
 - * We would then use a different Maxwell equation to find this quantity
- We could be asked to find the pressure at a different spot other than a or b
 - * We would then evaluate our derivative at a different point with the same method
- This part will essentially have the same variations as part (b)
- We could be asked to evaluate a different limit
 - * This would impact what happens to our density and potential and thus it would change what the pressures are at this point
- We could be asked to find a limit for a different quantity
 - * This would change what Maxwell equation we use and our overall final expression. The same methodology would hold just with different equations of quantities

Problem 4:

This problem investigates the properties of the van der Waals equation of state,

$$(v - b) \left(P + \frac{a}{v^2} \right) = kT, \quad (7)$$

where a and b are substance specific constants and $v = V/N$.

- (a) Show that the van der Waals equation of state reduces to the ideal gas equation of state in the ultralow density limit and derive the leading-order correction to the ideal gas equation of state in the low density limit.

We first start with re-arranging the van der Waals equation of state

$$(v - b)(P + a/v^2) = kT \Rightarrow \frac{PV}{kT} = -\frac{a}{kTV} + \frac{1}{1 - bv} = -\frac{a}{kTV} + 1 + bn$$

Taking the above and re-arranging

$$\frac{PV}{kT} = 1 + (b - a/kT)n + \dots$$

So we can clearly see that when $kT = a/b$ we recover the ideal gas



- (b) For neon, the following holds:

$$b - \frac{a}{kT} \rightarrow 1.3 \times 10^{-5} \frac{\text{m}^3}{\text{mol}} \text{ for } T \rightarrow \infty \quad (8)$$

and

$$b - \frac{a}{kT} \rightarrow 0 \text{ for } T \rightarrow 125 \text{ K} \quad (9)$$

Using these relations, determine a and b for neon.

We start by applying boundary conditions

$$\lim_{T \rightarrow \infty} \left(b - \frac{a}{kT} \right) \rightarrow 1.3 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}, \quad \lim_{T \rightarrow 125 \text{ K}} \left(b - \frac{a}{kT} \right) = 0 \therefore a = b k T$$

We find a for neon to be

$$a = 1.38 \times 10^{-23} \frac{\text{J}}{\text{mol K}} (1.3 \times 10^{-5}) \frac{\text{m}^3}{\text{mol}} (125 \text{ K}) = 2.24 \times 10^{-26} \frac{\text{J} \cdot \text{m}^3}{(\text{mol})^2}$$

Therefore for neon we have

$$a = 2.24 \times 10^{-26} \frac{\text{J} \cdot \text{m}^3}{(\text{mol})^2}, \quad b = 1.3 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}$$

Problem 4: Continued

- (c) Determine the critical volume v_c and critical temperature T_c for neon from the conditions

$$\left(\frac{\partial P}{\partial v} \right)_T = 0 \quad (10)$$

and

$$\left(\frac{\partial^2 P}{\partial v^2} \right)_T = 0 \quad (11)$$

First we massage Van der Waals equation,

$$Pv + \frac{a}{v} - Pb - \frac{ab}{v^2} = kT \quad \therefore \quad P(v-b) = kT + \frac{ab}{v^2} - \frac{a}{v} \Rightarrow P = \frac{1}{(v-b)} \left(kT + \frac{1}{v} \left(\frac{ab}{v} - a \right) \right)$$

we now start taking derivatives

$$\left(\frac{\partial P}{\partial v} \right)_T = \frac{kT}{(v-b)^2} - \frac{2a}{v^3} = 0 \quad \therefore \quad \left(\frac{\partial^2 P}{\partial v^2} \right)_T = \frac{2kT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

We can now say

$$kT = \frac{2a(v-b)^2}{v^3} \quad \text{and} \quad kT = \frac{3a(v-b)^3}{v^4} \quad \therefore \quad \frac{2a(v-b)^2}{v^3} = \frac{3a(v-b)^3}{v^4}$$

Now solving for v we have

$$\frac{2}{3} = \frac{(v-b)}{v} \quad \therefore \quad 2v = 3v - 3b \Rightarrow v = 3b \quad (*)$$

We put (*) into (10)

$$\frac{kT}{4b^2} - \frac{\partial a}{\partial T b^3} = 0 \quad \frac{kT}{4b^2} = \frac{\partial a}{\partial T b^3} \quad \therefore \quad T = \frac{8a}{\partial T b} = 36.9957 \text{ K} , \quad v = 3.9 \times 10^{-5} \text{ m}^3$$

So for neon we have

$v_c = 3.9 \times 10^{-5} \text{ m}^3 , \quad T_c = 36.996 \text{ K}$

These values are in line with the experimental values

Problem 4: Review

Procedure:

- - Begin by rearranging the equation of state to resemble an ideal gas as close as possible
 - Apply limiting conditions to this newly found equation to show that it will go to the equation for an ideal gas in the right limit
- - Apply the limits that are given to us in the problem statement to find values for a and b
- - Rearrange Van der Waals equation for pressure and perform the derivatives in equations (10) and (11)
 - Determine the critical volume algebraically from the derivatives in the previous step

Key Concepts:

- - In the correct ratio for a/b the Van der Waals equation of state will simplify to the ideal gas equation of state
 - Applying the boundary conditions given to us will allow us to assign values to the quantities a and b
 - Through Calculus of variations we can find the critical volume of our system by taking the derivatives of P in equations (10) and (11)

Variations:

- - We of course can be given a different equation of state
 - * This then changes the small details of the problem but not the overall procedure
 - We could be asked to evaluate a different limit
 - * This then requires slightly different math but the overall procedure is the same
- - The limits for our quantities could change slightly
 - * This then impacts what our exact values of the quantities evaluate to but not how we evaluate them
- - We could be asked to find a different critical value
 - * We then would use a different Maxwell equation with the same procedure as before