PHSX 671: Homework #5

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Problem 1

5.1: Determine an equation for the chemical potential of a Van der Waals gas.

Solution:
By equation 5.14 and 5.8:

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{V,N}, \qquad S_{\text{VDW}} = Nk_B\left[\ln\left(\frac{V-bN}{N}\right) + \frac{3}{2}\ln\left(\frac{2m\pi}{\beta h^2}\right) + \frac{5}{2}\right]$$

$$-\left(\frac{\partial S}{\partial N}\right)_{V,P} = -\left[\ln\left(\frac{V-bN}{N}\right) + \frac{3}{2}\ln\left(\frac{2m\pi}{\beta h^2}\right) + \frac{5}{2}\right] + \frac{1}{N}$$

$$\frac{\mu}{T} = -k_B\left[\ln\left(\frac{V-bN}{N}\right) + \frac{3}{2}\ln\left(\frac{2m\pi}{h^2}T\right) + \frac{5}{2}\right] + \frac{k_B}{N}$$

$$\mu = \frac{k_BT}{N} - k_BT\ln\left(\frac{V-bN}{N}\right) + \frac{3T}{2}\ln\left(\frac{2m\pi}{h^2}T\right) + \frac{5k_B}{2}$$

Problem 2

5.2: Determine an equation for C_V for a Van der Waals gas.

Solution:
By equation 5.15 and 5.8:

$$C_V = -\beta\left(\frac{\partial S}{\partial \beta}\right)_V, \qquad S_{\text{VDW}} = Nk_B\left[\ln\left(\frac{V-bN}{N}\right) + \frac{3}{2}\ln\left(\frac{2m\pi}{\beta h^2}\right) + \frac{5}{2}\right]$$

$$-\left(\frac{\partial S}{\partial \beta}\right)_V = \frac{3Nk_B}{2\beta} \implies C_V = \frac{3Nk_B}{2}$$

Problem 3

5.3: Determine an equation for C_P for a Van der Waals gas.

Solution:
By equation 5.17 and 5.8:

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P, \qquad \begin{cases} S_{\text{VDW}} = N\left[\ln\left(\frac{V-bN}{N}\right) + \frac{3}{2}\ln\left(\frac{2m\pi}{\beta h^2}\right) + \frac{5}{2}\right] \\ \left(P + a\frac{N^2}{V^2}\right)(V - bN) = \frac{N}{\beta} \end{cases}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{Nk_BT}{V-bN} - a\frac{N^2}{V^2}\right) = \frac{Nk_B}{V-bN}$$

On my first attempt, I incorrectly solved for V algebraically. Doing this the right way would lead to some cubic equation which I am not equipped to differentiate. A bit of research reminded me of implicit differentiation, which I have not used in a few years.

From the VDW equation: $[P + a(N^2/V^2)][V - bN] = Nk_BT$ Taking the partial derivative with respect for T for constant P to both sides:

$$\begin{aligned} \frac{\partial}{\partial T}\left(P + a\frac{N^2}{V^2}\right)(V - bN) + \left(P + a\frac{N^2}{V^2}\right)\frac{\partial}{\partial T}(V - bN) &= \frac{\partial}{\partial T}(Nk_BT) \\ (V - bN)\left(-2a\frac{N^2}{V^3}\right)\left(\frac{\partial V}{\partial T}\right)_P + \left(P + a\frac{N^2}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P &= Nk_B \\ \left[P + a\frac{N^2}{V^2} - \frac{2N^2a(V-bN)}{V^3}\right]\left(\frac{\partial V}{\partial T}\right)_P &= Nk_B \\ \left(\frac{\partial V}{\partial T}\right)_P &= \frac{Nk_B}{P + a\frac{N^2}{V^2} - \frac{2N^2a(V-bN)}{V^3}} \\ \left(\frac{\partial V}{\partial T}\right)_P &= \frac{Nk_BV^3}{PV^3 - N^2aV + 2N^3ab} \end{aligned}$$

$$C_P = \frac{3}{2}Nk_B + T\left(\frac{Nk_B}{V-bN}\right)\left(\frac{Nk_BV^3}{PV^3 - N^2aV + 2N^3ab}\right)$$

Problem 4

5.4: Consider a real gas that is confined within a vertical box of cross-sectional area A. The molecules of this gas will have translational kinetic energy and gravitational potential energy, but no other kinetic or potential energies. You can also assume that the molecules of the gas are indistinguishable. Calculate the partition function for a horizontal slice of this gas between a vertical position of z and $z + dz$ above the bottom of the box.

Solution:

$$Z = \left(\frac{e}{Nh^3}\right)^N Z_K Z_U$$

$$Z_K = \int e^{-\beta K(\bar{p}_1, \bar{p}_2, \dots)}\, d^3p_1\, d^3p_2 \dots d^3p_N$$
$$Z_U = \int e^{-\beta K(\bar{q}_1, \bar{q}_2, \dots)}\, d^3q_1\, d^3q_2 \dots q^3p_N$$

For kinetic energy:

$$\begin{aligned} Z_K &= \left(\int_0^\infty e^{\frac{\beta}{2m}p^2} 4\pi p^2\, dp\right)^N \\ &= \left(2\sqrt{2}\left(\frac{m\pi}{\beta}\right)^{3/2}\right)^N \\ &= \left(\frac{2m\pi}{\beta}\right)^{3N/2} \end{aligned}$$

For gravitational potential energy, we have $\epsilon = mgz$. the $x - y$ integrals give a since its gravitational:

$$\begin{aligned} Z_U &= \left(A\int_z^{z+dz} e^{-\beta mgz}\, dz\right)^N \\ &= \left[\left(-\frac{1}{\beta mg}e^{-\beta mgz}\right)\Bigg|_z^{z+dz}\right]^N = \left[\frac{1}{\beta mg}\left(e^{-\beta mgz} - e^{-\beta mg(z+dz)}\right)\right]^N \end{aligned}$$

$$\begin{aligned} Z &= Z_K Z_U \\ &= A\left(\frac{e}{Nh^3}\right)^N \left(\frac{2m\pi}{\beta}\right)^{3N/2} \left(\frac{1}{\beta mg}\right)^N \left(e^{-\beta mgz} - e^{-\beta mg(z+dz)}\right)^N \end{aligned}$$

Problem 5

5.5: A Van der Waals gas is allowed to freely expand into a vacuum under adiabatic conditions. What is the change in the temperature of the gas following the expansion? Express your answer as a relationship between dT and dV.

Solution:
Walking through the derivation of heat capacity at constant pressure again, we can arrive at an expression for heat in terms of some relevant variables:

$$dE = TdS - PdV = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

We can express dS:

$$\begin{gathered}
dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] dV \\
\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V, \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \\
\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V} \quad \rightarrow \quad \frac{\partial}{\partial V}\left(\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right) = \frac{\partial}{\partial T}\left(\frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]\right) \\
\frac{1}{T}\frac{\partial^2 E}{\partial V \partial T} = -\frac{1}{T^2}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] + \frac{1}{T}\left[\left(\frac{\partial P}{\partial V}\right)_V + \left(\frac{\partial^2 E}{\partial T \partial V}\right)_T\right]
\end{gathered}$$

And since internal energy is also an exact differential, its cross partial derivatives must be equal

$$\begin{gathered}
\frac{\partial^2 E}{\partial V \partial T} = \frac{\partial^2 E}{\partial T \partial V} \quad \rightarrow \quad 0 = -\frac{1}{T^2}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V \\
P + \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V
\end{gathered}$$

We're almost there. Now let's go back to the previously derived equation for dS.

$$\begin{gathered}
dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] dV \\
TdS = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] dV \\
\bar{d}Q = C_V dT + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] dV \\
\underbrace{\bar{d}Q}_{=0} = C_V dT + \underbrace{P + \left(\frac{\partial E}{\partial V}\right)_T}_{=T\left(\frac{\partial P}{\partial T}\right)_V = 0} dV \\
0 = C_V dT
\end{gathered}$$

Adibatic conditions implies that both heat capacity and pressure are zero. As a consequence the pressure differential is also zero. This implies dT must be zero because C_V cannot be zero. Therefore the temperature is constant!

Problem 5 continued on next page...

Problem 6

5.6: Show that for a gas in n dimensions, whose single-particle energy is described by $\epsilon = p^\alpha$, that $\frac{C_P}{C_V} = 1 + \frac{\alpha}{n}$.

Solution:

$$\begin{aligned} Z_T &= \int \cdots \int \exp\left(-\beta p^a\right) \, d^n p \\ &= \int \cdots \int \exp\left(-\beta p^a\right) \, p^{n-1} dp \int d\Omega n \\ E &= -\frac{\partial}{\partial \beta} \ln(Z) \\ &= \frac{\int_0^\infty p^{n-1+a} \exp\left(-\beta p^a\right) \, dp}{\int_0^\infty p^{n-1} \exp(-\beta p^a) \, dp} \end{aligned}$$

Transforming to n-D spherical coordinates gives $p^{n-1}dp$ times the jacobian $(d\Omega n)$. This luckily vanishes when we go from the partition function to energy thanks to it being in the numerator and denominator. If we set $u = -\beta p^\alpha$, this is a ratio of gamma functions, where $\Gamma\left(\frac{n}{a}\right) = \left(\frac{1}{\beta}\right) \frac{\Gamma\left(\frac{n+a}{a}\right)}{\Gamma\left(\frac{n}{a}\right)}$. Then,

$$E = k_B T \frac{n}{\alpha}, \quad E_N = N k_B T \frac{n}{a}$$

$$\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T}\right)_V = \frac{n N k_B}{\alpha} \\ C_P &= C_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

Since there is no specified potential, this should be an ideal gas. In this case, we have already derived the right hand side of the sum for C_P,

$$\begin{aligned} C_P &= C_V + \left(\frac{N k_B T}{PV}\right) N k_B T \\ &= C_V + N k_B T \\ &= \frac{n N k_B}{\alpha} + N k_B T \end{aligned}$$

Then we have the ratio:

$$\begin{aligned} \frac{C_P}{C_V} &= \frac{\frac{n N k_B}{T} + N k_B T}{\frac{n N k_B}{\alpha}} \\ &= 1 + \frac{\alpha}{n} \end{aligned}$$

Equation of State / Explicit Solution:
Halfway in, I use our ideal gas solution, but the solution can be explicitly determined using the parition function to (1) find equation of state, then (2) taking partial derivatives:

(1) Equation of state:

Problem 6 continued on next page...

As with the ideal gas, we need a partition function over space to get volume. Since there is no potential it is just $Z_U = V^N$.

$$\begin{aligned} S &= \ln(Z_T Z_U) + \beta \bar{E} \\ &= \ln[\Gamma(n/a)] - (n/a)\ln(\beta) + \ln\left(\int d\Omega_n\right) + \ln(V^N) + N\beta\frac{n}{a} \end{aligned}$$

Now,

$$\begin{aligned} \beta P &= \left(\frac{\partial S}{\partial V}\right)_{E,N} \\ \beta P &= \frac{N}{V} \end{aligned}$$

(2) Partial derivatives & heat capacity:

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V &= k_B \frac{N}{V} \\ \left(\frac{\partial V}{\partial T}\right)_P &= k_B \frac{N}{P} \\ C_P &= C_V + T k_B^2 \left(\frac{N}{V}\right)\left(\frac{N}{P}\right) \\ &= \frac{nNk_B}{a} + Nk_B T \qquad \text{(since } VP = N/\beta) \end{aligned}$$

Which matches the solution from before.