

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 Attempt #2:

By equation 5.14 and 5.8:

$$\begin{aligned}\frac{\mu}{T} &= - \left(\frac{\partial S}{\partial N} \right)_{V,N}, \quad S_{\text{VDW}} = Nk_B \left[\ln \left(\frac{V - bN}{N} \right) + \frac{3}{2} \ln \left(\frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \\ - \left(\frac{\partial S}{\partial N} \right)_{V,P} &= - \left[\ln \left(\frac{V - bN}{N} \right) + \frac{3}{2} \ln \left(\frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] + \frac{1}{N} \\ \frac{\mu}{T} &= -k_B \left[\ln \left(\frac{V - bN}{N} \right) + \frac{3}{2} \ln \left(\frac{2m\pi}{h^2 T} \right) + \frac{5}{2} \right] + \frac{k_B}{N}\end{aligned}$$

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

Problem 2

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

Solution:

By equation 5.15 and 5.8:

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

Problem 3

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

Solution Attempt #2:

By equation 5.17 and 5.8:

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

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

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

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

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

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:

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

$$Z_K = \int e^{-\beta K(p_1, p_2, \dots)} d^3 p_1 d^3 p_2 \dots d^3 p_N$$

$$Z_U = \int e^{-\beta K(q_1, q_2, \dots)} d^3 q_1 d^3 q_2 \dots d^3 q_N$$

For kinetic energy:

$$Z_K = \left(\int_0^\infty e^{\frac{\beta}{2m} p^2} 4\pi p^2 dp \right)^N$$

$$= \left(2\sqrt{2} \left(\frac{m\pi}{\beta} \right)^{3/2} \right)^N$$

$$= \left(\frac{2m\pi}{\beta} \right)^{3N/2}$$

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

$$Z_U = \left(A \int_z^{z+dz} e^{-\beta mgz} dz \right)^N$$

$$= \left[\left(-\frac{1}{\beta mg} e^{-\beta mgz} \right) \Big|_z^{z+dz} \right]^N = \left[\frac{1}{\beta mg} \left(e^{-\beta mgz} - e^{-\beta mg(z+dz)} \right) \right]^N$$

$$Z = Z_K Z_U$$

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

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 Attempt #2:

But for an adiabatic system, $Q = 0$, so we can use the first law of thermodynamics to say:

$$dE = -PdV$$

And if I have a way to express dE , I could work out an expression for dV/dT . In working with heat capacity, we found:

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

So,

$$\begin{aligned} \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT &= -PdV \\ \left(\frac{\partial E}{\partial T}\right)_V \frac{dT}{dV} &= - \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right] \\ \frac{dV}{dT} &= - \frac{\left(\frac{\partial E}{\partial T}\right)_V}{\left(\frac{\partial E}{\partial V}\right)_T + P} \end{aligned}$$

Looking through my notes again, I realize that:

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V, \quad \left(\frac{\partial E}{\partial V}\right)_T + P = T \left(\frac{\partial P}{\partial T}\right)_V$$

So,

$$\frac{dV}{dT} = - \frac{C_V}{T \left(\frac{\partial P}{\partial T}\right)_V}$$

Earlier in problem #3 I used the equation of state for a VDW gas to find

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

Which makes the expression dV/dT :

$$\frac{dV}{dT} = - \frac{C_V}{T \left(\frac{Nk_B}{V - bN}\right)}$$

Which can be simplified using $C_V = \frac{3Nk_B}{2}$ and a touch of algebra:

$$\frac{dV}{dT} = - \frac{(3Nk_B)(V - bN)}{TNk_B}$$

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:

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

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 $\Gamma(\frac{n}{a}) = (\frac{1}{\beta})^{\frac{n}{a}} \frac{\Gamma(\frac{n+a}{a})}{\Gamma(\frac{n}{a})}$. 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 ,

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

Then we have the ratio:

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

Equation of State / Explicit Solution:

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

(1) Equation of state:

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:

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

Which matches the solution from before.