PHYS301
Homework 9 solutions

Spring 2026

Due: April 20th

Contents

Problem 1 [12 points]

Consider a Van der Waals monoatomic gas of N particles of mass m in a volume V and at temperature T. Its equation of state is given by

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = Nk_B T \tag{1}$$

where a, b are constants that depend on the nature of the gas.

a) Show that the entropy of this gas is given by

$$S = Nk_B \left[\ln\left(\frac{V - Nb}{\lambda_Q^3 N}\right) + \frac{5}{2}\right] \tag{2}$$

where

$$\lambda_Q = \frac{h}{\sqrt{2\pi m k_B T}} \tag{3}$$

b) Show that the average energy of this gas is

$$\langle E \rangle = \frac{3}{2}Nk_B T - \frac{N^2 a}{V} \tag{4}$$

c) Consider the isotherms (curves of constant T in a P vs V plane) of the Van der Waals equation of state. There is a critical temperature T_C at which

$$\left.\frac{\partial P}{\partial V}\right|_{T=T_c} = 0, \quad \left.\frac{\partial^2 P}{\partial V^2}\right|_{T=T_c} = 0 \tag{5}$$

Compute T_c, as well as the corresponding pressure P_c and volume V_c.

d) Rewrite the van der Waals equation of state in terms of the dimensionless variables

$$t \equiv \frac{T}{T_c}, \quad p \equiv \frac{P}{P_c}, \quad v \equiv \frac{V}{V_c} \tag{6}$$

Note how the constants a, b disappear. In terms of these new variables, all gases look the same. This is known as the law of corresponding states.

e) Compute the so-called universal compressibility ratio

$$\frac{P_c V_c}{Nk_B T_c} \tag{7}$$

for the van der Waals gas. Experimental values for real gases range from around 0.28 to 0.3. How does the van der Waals prediction compare with these numbers?

a) Let's start by recalling the total partition function

$$Z_{\text{tot}}(N,V,T) \approx Z_{\text{ideal}}\left(1+\frac{N}{2V}\int d^3r f(r)+\cdots\right)^N \tag{8}$$

Where the ideal gas partition function is

$$Z_{\text{ideal}} = \frac{V^N}{N!\lambda_Q^{3N}} \tag{9}$$

and the integral is related to the second virial coefficient, which we found to be:

$$\begin{aligned} B_2(T) &= -\frac{1}{2}\int d^3r f(r) \\ &= b - \frac{a}{k_BT} \end{aligned} \tag{10}$$

With this in mind, the total partition function follows

$$\begin{aligned} Z_{\text{vdW}} &= Z_{\text{ideal}}\left(1-\frac{N}{V}B_2(T)\right)^N \\ &= Z_{\text{ideal}}\left(1-\frac{N}{V}\left(b-\frac{a}{k_BT}\right)\right)^N \\ &= Z_{\text{ideal}}\left(1+\frac{N}{V}\left(\frac{a}{k_BT}-b\right)\right)^N \end{aligned} \tag{11}$$

Which allows us to compute the Helmholtz Free Energy[1]

$$\begin{aligned} F_{\text{vdW}} &= -k_BT\ln Z_{\text{vdW}} \\ &= -kT\ln(Z_{\text{ideal}}) - k_BTN\ln\left(1+\frac{N}{V}\left(\frac{a}{k_BT}-b\right)\right) \\ &= F_{\text{ideal}} - k_BTN\ln\left(1+\frac{N}{V}\left(\frac{a}{k_BT}-b\right)\right) \end{aligned} \tag{12}$$

Which is expected: As $a, b \to 0$, we should recover the ideal gas results. The entropy is then computed directly as

$$\begin{aligned} S_{\text{vdW}} &= -\left(\frac{\partial F_{\text{vdW}}}{\partial T}\right)_V \\ &= -\left(\frac{\partial F_{\text{ideal}}}{\partial T}\right)_V + \left(\frac{\partial}{\partial T}k_BTN\ln\left(1+\frac{N}{V}\left(\frac{a}{k_BT}-b\right)\right)\right)_V \\ &= Nk_B\left[\ln\left(\frac{V}{N\lambda_Q^3}\right)+\frac{5}{2}\right] + k_BN\frac{\partial}{\partial T}T\ln\left(1+\frac{N}{V}\left(\frac{a}{k_BT}-b\right)\right) \\ &= Nk_B\left[\ln\left(\frac{V}{N\lambda_Q^3}\right)+\frac{5}{2}\right] + k_BN\left(-\frac{a}{a+k_BT\left(\frac{V}{N}-b\right)} + \ln\left[1+\left(\frac{a}{k_BT}-b\right)\frac{1}{V/N}\right]\right) \end{aligned} \tag{13}$$

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[1] Here I left Z_{ideal} symbolic since we know what its entropy and energy are.

Let's now take the $V/N \gg 1$ limit, so that

$$S_{\text{vdW}} \approx Nk_B \left[\ln\left(\frac{V}{N\lambda_Q^3}\right) + \frac{5}{2}\right] + k_B N\left(-\frac{Na}{k_B T V} + \left(\frac{a}{k_B T} - b\right)\frac{N}{V}\right) \tag{14}$$

Where we use the fact that $\ln(1+x) \simeq x$ when $x \ll 1$. We see that the terms with a will cancel each other out, and we are left with:

$$\begin{aligned} S_{\text{vdW}} &\approx Nk_B \left[\ln\left(\frac{V}{N\lambda_Q^3}\right) + \frac{5}{2}\right] - k_B \frac{N^2}{V} b \\ &= Nk_B \left(\left[\ln\left(\frac{V}{N\lambda_Q^3}\right) + \frac{5}{2}\right] - \frac{N}{V} b\right) \\ &\approx Nk_B \left(\left[\ln\left(\frac{V}{N\lambda_Q^3}\right) + \frac{5}{2}\right] + \ln\left(1 - \frac{N}{V} b\right)\right) \qquad (!) \\ &= Nk_B \left[\ln\left(\frac{V}{N\lambda_Q^3} \cdot \left(1 + \frac{N}{V} b\right)\right) + \frac{5}{2}\right] \\ &= Nk_B \left[\ln\left(\frac{V - Nb}{\lambda_Q^3 N}\right) + \frac{5}{2}\right] \end{aligned} \tag{15}$$

Where in Eq. (!) we use the fact that $\ln(1-x) \approx -x$ for small x (in reverse).

b) Similar to part (a), we compute $\langle E \rangle$ from definition:

$$\begin{aligned} \langle E_{\text{vdW}} \rangle &= -\frac{\partial}{\partial \beta} \ln(Z_{\text{vdW}}) \\ &= -\frac{\partial}{\partial \beta} \ln(Z_{\text{ideal}}) - N\frac{\partial}{\partial \beta} \ln\left(1 + \frac{N}{V}\left(\frac{a}{k_B T} - b\right)\right) \\ \text{(Using the ideal gas result)} \qquad &= \frac{3}{2} N k_B T - N \frac{\partial}{\partial \beta} \ln\left(1 + \frac{N}{V}(a\beta - b)\right) \\ &= \frac{3}{2} N k_B T - \frac{aN^2}{V\left(1 + \frac{N}{V}(a\beta - b)\right)} \\ &\approx \frac{3}{2} N k_B T - \frac{N^2 a}{V} \end{aligned} \tag{16}$$

c) Observe that pressure P in Eq. 1 can be isolated

$$P = \frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2} \tag{17}$$

The first and second derivatives of Eq. 17 can be computed directly

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_T &= -\frac{Nk_B T}{(V - Nb)^2} + \frac{2N^2 a}{V^3} \\ \left(\frac{\partial^2 P}{\partial V^2}\right)_T &= \frac{2Nk_B T}{(V - Nb)^3} - \frac{6N^2 a}{V^4} \end{aligned} \tag{18}$$

Setting them two zero yields the relations:

$$\begin{aligned} &\text{(i)} \qquad \frac{Nk_BT}{(V-Nb)^2} = \frac{2N^2a}{V^3} \\ &\text{(ii)} \qquad \frac{2Nk_BT}{(V-Nb)^3} = \frac{6N^2a}{V^4} \end{aligned} \tag{19}$$

Diving one of the other removes the T-dependence, allowing us to solve for V (in this case, V_c)

$$\begin{aligned} \frac{\left(\frac{Nk_BT}{(V-Nb)^2}\right)}{\left(\frac{2Nk_BT}{(V-Nb)^3}\right)} &= \frac{\left(\frac{2N^2a}{V^3}\right)}{\left(\frac{6N^2a}{V^4}\right)} \\ \frac{1}{2}(V-Nb) &= \frac{2}{6}V \\ 3V - 3NB &= 2V \\ V &= 3Nb \end{aligned} \tag{20}$$

So

$$V_c = 3Nb \tag{21}$$

With this unknown found, we can solve for T_c using equation (i):

$$\begin{aligned} T_c &= \frac{2N^2a}{V_c^3} \cdot \frac{(V_c - Nb)^2}{Nk_B} \\ &= \frac{2Na}{(3Nb)^3} \cdot \frac{(3Nb-Nb)^2}{k_B} \\ &= \frac{2Na2^2N^2b^2}{3^3N^3b^3k_B} \\ &= \frac{8a}{27bk_B} \end{aligned} \tag{22}$$

Using Eq. 17 with $V = V_c$ and $T = T_c$, we see that

$$\begin{aligned} P_c &= P(T_c, V_c) \\ &= \frac{Nk_BT_c}{V_c - Nb} - \frac{N^2a}{V_c^2} \\ &= \frac{Nk_B}{3Nb - Nb} \cdot \frac{8a}{27bk_B} - \frac{N^2a}{(3Nb)^2} \\ &= \frac{a}{27b^2} \end{aligned} \tag{23}$$

We see that T_c, P_c and V_c only depend on the parameters a, b inherent to the a given gas.

d) Using the substitutions

$$V \to vV_c = v3Nb, \quad P \to pP_c = p\frac{a}{27b^2}, \quad T \to tT_c = t\frac{8a}{27bk_B} \tag{24}$$

The Van der Waals equation becomes

$$\begin{aligned} \left(P+\frac{1}{V^2}N^2a\right)(V-Nb) &= Nk_BT \\ \left(p\frac{a}{27b^2}+\frac{1}{(v3Nb)^2}N^2a\right)(v3Nb-Nb) &= Nk_Bt\frac{8a}{27bk_B} \\ \frac{a}{b}\left(\frac{p}{27}+\frac{1}{9v^2}\right)N(3v-1) &= \frac{a}{b}Nt\frac{8}{27} \\ \left(p+\frac{3}{v^2}\right)(3v-1) &= 8t \end{aligned} \tag{25}$$

Where any dependence of a, b is completely gone.

e) Computing the ratio using the values found in part (c) yields

$$\begin{aligned} \frac{P_cV_c}{Nk_BT_c} &= \frac{\frac{a}{27b^2}\cdot 3Nb}{Nk_B\frac{8a}{27bk_B}} \\ &= \frac{3}{8} = 0.375 \end{aligned} \tag{26}$$

This value is slightly higher then the experimental range. Further, observe how it is constant regardless of what a and b are. ■

Problem 2 [5 points]

Consider the Dieterici equation of state for a gas of N particles in volume V and temperature T

$$P = \frac{Nk_BT}{V - Nb} e^{-aN/Vk_BT} \tag{27}$$

where a, b are constants.

a) Compute the temperature, pressure, and volume T_c, P_c, and V_c at the critical point.

b) Compute the compressibility ratio $(P_cV_c)/(Nk_BT_c)$ for this gas. Is this number closer to the experimentally measured values mentioned in question 1(e)? Can you explain why that is? Hint: Consider how the Van der Waals equation of state is a limiting case of the Dieterici one.

a) Following the same procedure as in problem 1, the critical point is defined through the derivatives

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_T &= 0 \\ \left(\frac{\partial^2 P}{\partial V^2}\right)_T &= 0 \end{aligned} \tag{28}$$

Note that this definition is equivalent to

$$\begin{aligned} \left(\frac{\partial \ln P}{\partial V}\right)_T &= 0 \\ \left(\frac{\partial^2 \ln P}{\partial V^2}\right)_T &= 0 \end{aligned} \tag{29}$$

Which is more convenient[2] given the shape of P. Observe that

$$\ln P = \ln(Nk_BT) - \ln(V - Nb) - \frac{aN}{Vk_BT} \tag{30}$$

Hence

$$\begin{aligned} \left(\frac{\partial \ln P}{\partial V}\right)_T &= -\frac{1}{V - Nb} + \frac{aN}{k_BTV^2} \\ \left(\frac{\partial^2 \ln P}{\partial V^2}\right)_T &= \frac{1}{(V - Nb)^2} - \frac{2aN}{k_BTV^3} \end{aligned} \tag{31}$$

Setting both of them equal to zero yields the two relations

$$\begin{aligned} &\text{(i)} \quad k_BT_cV_c^2 = aN(V_c - Nb) \\ &\text{(ii)} \quad k_BT_cV_c^3 = 2aN(V_c - Nb)^2 \end{aligned} \tag{32}$$

for variables T, V at their critical values. Since we have two equations, we can use them to eliminate one of the variables, namely T (divide equation (ii) by equation (i)):

$$V_c = 2(V_c - Nb) \tag{33}$$

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[2] It is true that we can take the derivatives on P, but they will not be as short/compact as those coming from $\ln P$.

Hence

$$V_c = 2Nb \tag{34}$$

Plugging this back into eq. (i) or (ii), we find that the critical temperature is

$$\begin{aligned}\text{(starting from eq. (i))} \quad T_c &= \frac{aN(V_c - Nb)}{k_B V_c^2} \\ &= \frac{aN(2Nb - Nb)}{k_B (2Nb)^2} \\ &= \frac{a}{4bk_B}\end{aligned} \tag{35}$$

Now that we have V_c and T_c, we can plug them back into $P(V,T)$ to find P_c:

$$\begin{aligned}P_c &= P(V_c, T_c) \\ &= \frac{Nk_BT_c}{V_c - Nb} e^{-aN/V_c k_B T_c} \\ &= \frac{a}{4bk_B}\frac{Nk_B}{Nb}\exp\left(-\frac{aN}{k_B}\frac{1}{2Nb}\frac{4bk_B}{a}\right) \\ &= \frac{a}{4b^2}\exp(-2)\end{aligned} \tag{36}$$

b) The compressibility ratio follows directly

$$\begin{aligned}\frac{P_cV_c}{Nk_BT_c} &= \frac{a}{4b^2}\exp(-2)\, 2b\frac{4b}{a} \\ &= 2\exp(-2) \\ &\approx 0.27\end{aligned} \tag{37}$$

independent of the values of a, b. We see that this value falls a little short from the experimental range quoted in problem 1.e, making it smaller than the van der Waals universal compressibility but nonetheless closer to the desired range. In the same way that the van der Waals equation of state can be thought of as a correction to the ideal gas, we see that the Dieterici equation of state has further corrections on top of the van der Waals terms. This is directly seen if we expand the exponential in the Dieterici equation around 0. To be precise, the van der Waals equation has linear corrections, while the Dieterici equation contains higher order corrections.

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Problem 3 [3 points]

Consider the Clausius-Clapeyron equation for a first-order phase transition between a liquid and a gas phase

$$\frac{dP}{dT} = \frac{L}{T(v_{\text{gas}} - v_{\text{liquid}})} \tag{38}$$

where L is the specific heat, and $v \equiv V/N$. Under the assumption that L is constant, $v_{\text{gas}} \gg v_{\text{liquid}}$, and $PV = Nk_BT$, solve the above equation to determine the shape of the liquid-gas interface in the P vs T phase diagram.

In the limit that $v_{\text{gass}} \gg v_{\text{liquid}}$, we have

$$v_{\text{gas}} - v_{\text{liquid}} \simeq v_{\text{gas}} \tag{39}$$

So

$$\frac{dP}{dT} = \frac{L}{Tv_{\text{gas}}} \tag{40}$$

Using the ideal gas law $Pv = k_BT$, it follows that

$$v_{\text{gas}} = k_BT/P \tag{41}$$

Plugging this into the differential equation yields

$$\frac{dP}{dT} = \frac{L}{k_B} \cdot \frac{P}{T^2} \tag{42}$$

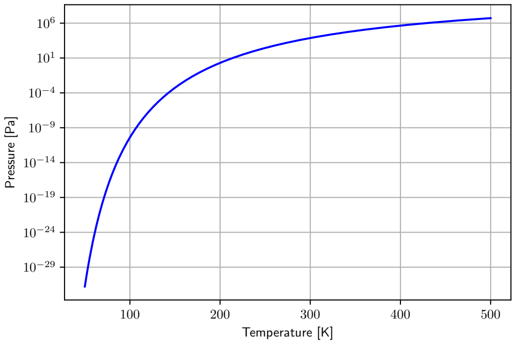
This differential equation can be solved by separation of variables:

$$\begin{aligned} \frac{dP}{P} &= \frac{L}{k_B}\frac{dT}{T^2} \\ \text{(integrating...)} \qquad \ln P &= -\frac{L}{k_B}\frac{1}{T} + \text{const.} \end{aligned} \tag{43}$$

We solve for P using exponentiation:

$$P(T) = P_0 \exp\left(-\frac{L}{k_BT}\right) \tag{44}$$

Where we absorbed the integration constant as a multiplicative factor. Using standard values, we can plot this function:



Observing that this matches reference diagrams. ■