

Quiz 17

Philip Cherian

April 9, 2024

In a previous quiz we showed that excluded volume leads to an increase in free energy. Let us now see what effect interactions between the molecules of a gas has on the free energy. Consider a van der Waals gas with an internal energy and equation of state given by

$$U = C_V T - \frac{aN^2}{V} \quad \text{and} \quad \left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T. \quad (1)$$

(a) We will first try to find $S(T, V)$ for such a system. Show that

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{Nk_B}{V - Nb}. \quad (2)$$

Hint: The fastest way to prove the second equation is to first prove a Maxwell relation. [6]

- (b) Use the above two results to find $S(T, V)$ for the van der Waals gas. Compare your result to the “excluded-volume” gas ($a = 0, b \neq 0$). What do you see? [2]

- (c) Using the fact that $F(T, V, N) = U - TS$, find F for the given system. Does a decrease or increase the free energy of the system? [2]