

AMTH 428 / E&EB 428 / EPS 428/528 / PHYS 428
Assignment #5

Due: 10:30 AM on October 28, 2020

1. (5%) Enthalpy H is another thermodynamic potential. It is defined as $U + pV$, where U , p , and V are internal energy, pressure, and volume, respectively. Show that enthalpy decreases for spontaneous processes under constant entropy and constant pressure, using the two fundamental laws of thermodynamics.
2. (5%) You saw in the class that the mean energy \bar{E} is related to the partition function Z as

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta}. \quad (1)$$

Show that the variance of energy $\sigma^2(E) (\equiv \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2)$ can be expressed as

$$\overline{(\Delta E)^2} = \frac{\partial^2 \ln Z}{\partial \beta^2}. \quad (2)$$

3. Consider two boxes, each with N separate compartments. You also have a bag containing N red balls and N blue balls, and you arrange those balls into the two boxes. Same-color balls are indistinguishable to each other, but we distinguish different compartments; for example, there are N different ways to place one blue ball with $(N - 1)$ red balls in a box. We also distinguish the boxes, e.g., the left box and the right box.
 - (a) (5%) How many different arrangements are possible for having K blue balls and $(N - K)$ red balls in one box and $(N - K)$ blue balls and K red balls in the other?
 - (b) (15%) Compare the total number of possible arrangements for 49%-51% mixing and that for 50%-50% mixing. Using the Stirling's approximation, $n! \sim \sqrt{2\pi n}(n/e)^n$, express the relative likelihood of the latter case with respect to the former. When $N = 10^6$, how many times the equal mixing is more likely to happen than the 49%-51% mixing?
 - (c) (10%) Count up all possible arrangements (or states), from the case of each box containing the same-color balls to the case of 50%-50% mixing. Then, using $S = k \ln \Omega$, where k is the Boltzmann constant and Ω is the total number of states, calculate the entropy associated with this ball mixing, with $N = N_A$, where N_A is the Avogadro number.
4. Some exercises with the van der Waals equation:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT, \quad (3)$$

where v is the molar volume.

- (a) (5%) Solve the equation for the volume, pressure, and temperature at the critical point, i.e., express v_c , p_c , and T_c in terms of a , b , and R . Note that the van der Waals equation is a cubic equation in v , and that all three roots coincide at the critical point.
- (b) (5%) For water, a is $553.6 \text{ L}^2 \text{ kPa mol}^{-2}$, and b is $0.03049 \text{ L mol}^{-1}$ (mind dimensions!). Compute p_c and T_c using your answer to (a) and compare with the actual values (22.064 MPa and 647 K).
- (c) (5%) Let us define the reduced variables as follows: $v' = v/v_c$, $p' = p/p_c$, and $T' = T/T_c$. Express the original equation in terms of the reduced variables. (This reduced version will be useful for the next question.)

(d) (10%) Derive the following scaling: $v_{\text{gas}} - v_{\text{liquid}} \sim (T_c - T)^{1/2}$ as $T \rightarrow T_c$ (or $T' \rightarrow 1$). Note that, at $T' < 1$, there are two stable volumes for the same value of p . Using this fact, you can express T' as a function of v'_{gas} and v'_{liquid} only. Also, near T_c , we can approximate as $v'_{\text{gas}} = 1 + \epsilon/2$ and $v'_{\text{liquid}} = 1 - \epsilon/2$, where $\epsilon \equiv v'_{\text{gas}} - v'_{\text{liquid}}$.

(e) (5%) Also derive the following scaling: $p - p_c \sim (v - v_c)^3$ as $v \rightarrow v_c$.