Problem Set 5
EPS 528, Science of Complex Systems

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Problem 1.

Solution. If we start with $H = U + pV$, then assuming that pressure is constant, we can write the differential form of enthalpy as

$$dH = dU + p\,dV \Rightarrow \Delta H = \int dH = \int dU + p\int dV = \Delta U + p\int dV, \qquad (1)$$

since p is constant. Furthermore, the first law of thermodynamics gives that $\Delta U = Q + W = \int dQ - \int p\,dV$, while from the second law, $\Delta S \geq \int \frac{dQ}{T} \Rightarrow \int \frac{dQ}{T} \leq 0 \Rightarrow \int dQ \leq 0$, since entropy is constant (i.e., $\Delta S = 0$) and $T > 0$ always. Hence, combining the first and second laws of thermodynamics as they apply to a spontaneous process under constant entropy and constant pressure, we have the inequality $\Delta U \leq 0 - \int p\,dV = -\int p\,dV$. Then, this inequality can be substituted into (1), from which we derive that

$$\Delta H = \Delta U + p\int dV \leq -p\int dV + p\int dV = 0 \Rightarrow \boxed{\Delta H \leq 0}. \qquad (2)$$

(2) demonstrates what we wanted to show: Namely, enthalpy decreases for spontaneous processes under constant entropy and constant pressure. $\square$

Problem 2.

Solution. To calculate the mean (expected value) of any thermodynamic quantity X in a system via the partition function $Z = \sum_i \exp(-\beta E_i)$, we note that $\overline{X} = \sum_i X_i \exp(-\beta E_i)/Z$, where X_i is the value of X associated with the ith microstate of the system. Hence, we can compute $\overline{E^2}$ like

$$\overline{E^2} = \frac{\sum_i E_i^2 \exp(-\beta E_i)}{Z} = \frac{\sum_i E_i\left[E_i \exp(-\beta E_i)\right]}{Z} = \frac{\sum_i E_i\left[-\partial_\beta \exp(-\beta E_i)\right]}{Z}$$

$$= \frac{\sum_i -\left[-\partial_\beta^2 \exp(-\beta E_i)\right]}{Z} = \frac{\sum_i \partial_\beta^2 \exp(-\beta E_i)}{Z} = \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}\sum_i \exp(-\beta E_i) = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}, \quad (3)$$

where we exploited linearity of differentiation, thereby allowing us to move ∂_β^2 outside of the

sum. Furthermore,

$$\overline{(\Delta E)^2} = \frac{\sum_i (\Delta E_i)^2 \exp(-\beta E_i)}{Z} = \frac{\sum_i \left(E_i - \overline{E}\right)^2 \exp(-\beta E_i)}{Z}$$

$$= \frac{\sum_i \left(E_i^2 - 2E_i\overline{E} + \overline{E}^2\right) \exp(-\beta E_i)}{Z} = \frac{\sum_i E_i^2 \exp(-\beta E_i)}{Z} - \frac{\sum_i 2E_i\overline{E} \exp(-\beta E_i)}{Z}$$

$$+ \frac{\sum_i \overline{E}^2 \exp(-\beta E_i)}{Z} = \frac{\sum_i E_i^2 \exp(-\beta E_i)}{Z} - 2\overline{E}\frac{\sum_i E_i \exp(-\beta E_i)}{Z} + \overline{E}^2 \frac{\sum_i \exp(-\beta E_i)}{Z}$$

$$= \frac{\sum_i E_i^2 \exp(-\beta E_i)}{Z} - 2\overline{E}\left(\overline{E}\right) + \overline{E}^2 \frac{Z}{Z} = \frac{\sum_i E_i^2 \exp(-\beta E_i)}{Z} - \overline{E}^2. \tag{4}$$

Hence, combining (3) and (4), we can simplify via chain rule and product rule:

$$\frac{\partial^2 \log Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left[\frac{\partial \log Z}{\partial \beta}\right] = \frac{\partial}{\partial \beta}\left[\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right] = \frac{\partial Z}{\partial \beta}\frac{\partial}{\partial \beta}\left[\frac{1}{Z}\right] + \frac{1}{Z}\frac{\partial}{\partial \beta}\left[\frac{\partial Z}{\partial \beta}\right]$$

$$= \frac{\partial Z}{\partial \beta}\left(-\frac{1}{Z^2}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2$$

$$= \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(-\frac{\partial \log Z}{\partial \beta}\right)^2 = \frac{\sum_i E_i^2 \exp(-\beta E_i)}{Z} - \overline{E}^2 = \overline{(\Delta E)^2} \Rightarrow \boxed{\overline{(\Delta E)^2} = \frac{\partial^2 \log Z}{\partial \beta^2}}.$$

$\square$

Problem 3.

(a) *Solution.* Considering that each box has N compartments in total and that there are N of each ball type, we only need to consider the number of ways to sort one type of ball, say, blue, because then it would follow that the rest of the compartments must be filled by the other type of ball, in this case, red. However, since we distinguish different compartments, we need to consider the possible arrangements for each box separately, because one box's arrangements can be chosen independently of the other. Hence, it suffices to compute the number of ways for there to be K blue balls in one box and $N - K$ blue balls in the other. For the box with K blue balls, there are $\binom{N}{K}$ ways to choose the compartments for them. Similarly, for the box with $N - K$ blue balls, there are $\binom{N}{N-K} = \binom{N}{K}$ possible choices of compartments. Finally, since we distinguish the boxes, we can either let the left box have K blue balls and the right box have $N - K$ blue balls, or vice-versa, which gives two choices for the boxes. Therefore, we have a total of $\boxed{2\binom{N}{K}^2}$ possible arrangements for the whole system.

$\square$

(b) *Solution.* Assuming that $N \ggg 1$, Stirling's approximation will be extremely accurate with astronomically small error, and in particular, this should especially be the case if $N = 10^6$. For 49%-51% mixing, $K = \frac{49N}{100}$,[1] while for 50%-50% mixing, $K = \frac{N}{2}$, such

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[1]Using $K = \frac{51N}{100}$ would give the same answer in this case.

that the relative likelihood of the latter case with respect to the former is

$$P := \frac{2\left(\frac{N}{\frac{N}{2}}\right)^2}{2\left(\frac{N}{\frac{49N}{100}}\right)^2} = \left[\frac{\left(\frac{N}{\frac{N}{2}}\right)}{\left(\frac{N}{\frac{49N}{100}}\right)}\right]^2 = \left[\frac{\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}}{\frac{N!}{\left(\frac{49N}{100}\right)!\left(\frac{51N}{100}\right)!}}\right]^2 = \left[\frac{\left(\frac{49N}{100}\right)!\left(\frac{51N}{100}\right)!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\right]^2. \tag{5}$$

Then, applying Stirling's approximation, $n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n$, to (5), we further get that

$$\sqrt{P} = \frac{\left(\frac{49N}{100}\right)!\left(\frac{51N}{100}\right)!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \approx \frac{\left(\sqrt{2\pi\left(\frac{49N}{100}\right)}\left(\frac{\frac{49N}{100}}{e}\right)^{\frac{49N}{100}}\right)\left(\sqrt{2\pi\left(\frac{51N}{100}\right)}\left(\frac{\frac{51N}{100}}{e}\right)^{\frac{51N}{100}}\right)}{\left(\sqrt{2\pi\left(\frac{N}{2}\right)}\left(\frac{\frac{N}{2}}{e}\right)^{\frac{N}{2}}\right)\left(\sqrt{2\pi\left(\frac{N}{2}\right)}\left(\frac{\frac{N}{2}}{e}\right)^{\frac{N}{2}}\right)} =$$

$$\frac{\left(\sqrt{\frac{49N}{100}}\left(\frac{49N}{100}\right)^{\frac{49N}{100}}\right)\left(\sqrt{\frac{51N}{100}}\left(\frac{51N}{100}\right)^{\frac{51}{100}N}\right)\left(\frac{1}{e}\right)^{\frac{49N}{100}}\left(\frac{1}{e}\right)^{\frac{51N}{100}}}{\left(\sqrt{\frac{N}{2}}\left(\frac{N}{2}\right)^{\frac{N}{2}}\right)\left(\sqrt{\frac{N}{2}}\left(\frac{N}{2}\right)^{\frac{N}{2}}\right)\left(\frac{1}{e}\right)^{\frac{N}{2}}\left(\frac{1}{e}\right)^{\frac{N}{2}}} = \frac{\left(\frac{49N}{100}\right)^{\frac{49N}{100}+\frac{1}{2}}\left(\frac{51N}{100}\right)^{\frac{51N}{100}+\frac{1}{2}}}{\left(\frac{N}{2}\right)^{N+1}}$$

$$= \frac{49^{\frac{49N}{100}+\frac{1}{2}}51^{\frac{51N}{100}+\frac{1}{2}}\left(\frac{N}{100}\right)^{\frac{49N}{100}+\frac{1}{2}}\left(\frac{N}{100}\right)^{\frac{51N}{100}+\frac{1}{2}}}{\left(\frac{N}{2}\right)^{N+1}} = \frac{49^{\frac{49N}{100}+\frac{1}{2}}51^{\frac{51N}{100}+\frac{1}{2}}}{50^{N+1}} =$$

$$\frac{49^{\frac{49N}{100}+\frac{1}{2}}51^{\frac{51N}{100}+\frac{1}{2}}}{50^{\frac{49N}{100}+\frac{1}{2}}50^{\frac{51N}{100}+\frac{1}{2}}} = \left(\frac{49}{50}\right)^{\frac{49N}{100}+\frac{1}{2}}\left(\frac{51}{50}\right)^{\frac{51N}{100}+\frac{1}{2}} = \sqrt{\frac{2499}{2500}}\left(\frac{49}{50}\right)^{\frac{49N}{100}}\left(\frac{51}{50}\right)^{\frac{51N}{100}}$$

$$= \sqrt{\frac{2499}{2500}}\left[\left(\frac{49}{50}\right)^{\frac{49}{100}}\left(\frac{51}{50}\right)^{\frac{51}{100}}\right]^N \Rightarrow \boxed{P \approx \frac{2499}{2500}\left[\left(\frac{49}{50}\right)^{\frac{49}{100}}\left(\frac{51}{50}\right)^{\frac{51}{100}}\right]^{2N}}. \tag{6}$$

Then, plugging in $N = 10^6$ into (6) and using Wolfram Alpha to compute P, we find that in the situation described in the problem, $\boxed{P \approx 5.36045986 \times 10^{173}}$. Hence, even for N not that large (say, compared to Avogadro's number), the likelihood of equal mixing is astronomically larger than even a 49%-51% split. □

(c) *Solution.* From part (a), we define $\Omega\left(K\right) = 2\left(\frac{N}{K}\right)^2$, i.e., the total number of arrangements where we have $N - K$ balls of one color in one box and K in the other. If each box contains the same color balls, then either the left box has all N red balls and the right box all N blue balls, or vice-versa. This gives only two possible arrangements. If we suddenly started to mix up the balls and eventually reached the case of 50%-50% mixing (the "equilibrium" state), then using part (a) and Stirling's approximation again, the number of possible arrangements would increase from $\Omega\left(0\right) = 2\left(\frac{N}{0}\right)^2 = 2$ to $\Omega\left(\frac{N}{2}\right) = 2\left(\frac{N}{\frac{N}{2}}\right)^2$. Adding up over all possible arrangements in this range,

$$\Omega = \sum_{K=0}^{N/2}\Omega\left(K\right) = 2\sum_{K=0}^{N/2}\left(\frac{N}{K}\right)^2. \tag{7}$$

For there to be exactly 50%-50% mixing, we have to assume that N is even, such that "$\frac{N}{2}$ balls" makes any physical sense. Of course, if N is large enough, then even when

N is odd, it will be *very*, very close to an even number, and hence, we can just force N to be even. By a well-known combinatorial identity,[2]

$$\sum_{l=0}^{n-1}\binom{2n}{l}^2 = \frac{1}{2}\left[\binom{4n}{2n} - \binom{2n}{n}^2\right] \Rightarrow \sum_{K=0}^{N/2-1}\binom{N}{K}^2 = \frac{1}{2}\left[\binom{2N}{N} - \binom{N}{N/2}^2\right]$$

$$\Rightarrow \sum_{K=0}^{N/2}\binom{N}{K}^2 = \sum_{K=0}^{N/2-1}\binom{N}{K}^2 + \binom{N}{N/2}^2 = \frac{1}{2}\left[\binom{2N}{N} - \binom{N}{N/2}^2\right] + \binom{N}{N/2}^2$$

$$= \frac{1}{2}\left[\binom{2N}{N} + \binom{N}{N/2}^2\right], \tag{8}$$

and combining (7) with (8), we find that $\boxed{\Omega = \binom{2N}{N} + \binom{N}{N/2}^2}$. Furthermore, applying Stirling's approximation again to this formula for Ω, we can approximate

$$\Omega = \binom{2N}{N} + \binom{N}{N/2}^2$$

$$\approx \frac{\sqrt{4\pi N}\left(\frac{2N}{e}\right)^{2N}}{\sqrt{2\pi N}\left(\frac{N}{e}\right)^N \sqrt{2\pi N}\left(\frac{N}{e}\right)^N} + \left(\frac{\sqrt{2\pi N}\left(\frac{N}{e}\right)^N}{\sqrt{\pi N}\left(\frac{N}{2e}\right)^{N/2}\sqrt{\pi N}\left(\frac{N}{2e}\right)^{N/2}}\right)^2$$

$$= \frac{2^{2N}}{\sqrt{N\pi}} + \frac{2^{2N+1}}{N\pi} = \frac{2^{2N}}{\sqrt{N\pi}}\left(1 + \frac{2}{\sqrt{N\pi}}\right) \Rightarrow \boxed{\Omega \approx \frac{2^{2N}}{\sqrt{N\pi}}\left(1 + \frac{2}{\sqrt{N\pi}}\right).} \tag{9}$$

Finally, we can calculate the entropy associated with this ball mixing by using the formula $S = k\log\Omega$ and (9), from which we get that

$$S \approx k\log\left[\frac{2^{2N}}{\sqrt{N\pi}}\left(1 + \frac{2}{\sqrt{N\pi}}\right)\right] = k\log\frac{2^{2N}}{\sqrt{N\pi}} + k\log\left(1 + \frac{2}{\sqrt{N\pi}}\right)$$

$$= k\log 2^{2N} - k\log\sqrt{N\pi} + k\log\left(1 + \frac{2}{\sqrt{N\pi}}\right)$$

$$= 2Nk\log 2 - \frac{k}{2}\log(\pi N) + k\log\left(1 + \frac{2}{\sqrt{N\pi}}\right). \tag{10}$$

When $N \gg 1$, then $\frac{2}{\sqrt{N\pi}} \ll 1$, whence it becomes apparent that we can use the approximation $\log(1 + x) = x + \mathcal{O}(x^2) \approx x$. With this, (10) becomes

$$S \approx 2Nk\log 2 - \frac{k}{2}\log(\pi N) + \frac{2k}{\sqrt{N\pi}}$$

$$\Rightarrow \boxed{S \approx k\left(2N\log 2 - \frac{1}{2}\log(\pi N) + \frac{2}{\sqrt{N\pi}}\right),} \tag{11}$$

where (11) is correct with an $\mathcal{O}(N^{-1})$ error. Finally, letting $N = N_A = 6.02214 \times$

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[2]For a reference, see https://www2.karlin.mff.cuni.cz/~slavik/papers/identities3.pdf.

10^{23} mol^{-1}, (11) becomes

$$S \approx \left(1.38065 \times 10^{-23} \text{ J K}^{-1}\right) \left[2 \left(6.02214 \times 10^{23} \text{ mol}^{-1}\right) \log 2\right.$$

$$\left. -\frac{1}{2} \log \left(\pi \left(6.02214 \times 10^{23} \text{ mol}^{-1}\right)\right) + \frac{2}{\sqrt{\left(6.02214 \times 10^{23} \text{ mol}^{-1}\right) \pi}}\right]$$

$$\Rightarrow \boxed{S \approx 11.5263.} \tag{12}$$

(12) suggests that, if we are dealing with very large numbers, then it may be wiser to deal with entropy rather than merely the total number of states, since the entropy returns values which are much more appropriate in terms of magnitude. $\qquad\square$

Problem 4.

(a) *Solution.* At first, we should write the van der Waals equation in a standard cubic form in v like $p(v) = a_3 v^3 + a_2 v^2 + a_1 v + a_0$. We do this below:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \Rightarrow \left(pv^2 + a\right)(v - b) = RTv^2 \Rightarrow pv^3 - bpv^2 + av - ab = RTv^2$$

$$\Rightarrow pv^3 - (RT + bp)v^2 + av - ab = 0. \tag{13}$$

Every cubic equation has three roots, and we can solve for these roots explicitly. By Cardano's formula,[3] a cubic polynomial of the form $Ax^3 + Bx^2 + Cx + D$ has roots $x_* = S + T - \frac{B}{3A}$ and $x_\pm = -\frac{S+T}{2} - \frac{B}{3A} \pm \frac{i\sqrt{3}}{2}(S - T)$, where $S = \left(R + \sqrt{Q^3 + R^2}\right)^{1/3}$, $T = \left(R - \sqrt{Q^3 + R^2}\right)^{1/3}$, $Q = \frac{3AC - B^2}{9A^2}$, and $R = \frac{9ABC - 27A^2D - 2B^3}{54A^3}$. In particular, we observe that the roots $x_\pm$ coincide when $S = T$, and in turn, this double root coincides with x_* when $S + T - \frac{B}{3A} = -\frac{S+T}{2} - \frac{B}{3A} \Rightarrow S + T = -\frac{S+T}{2} \Rightarrow S = -T$, in which case the triple root is $x = -\frac{B}{3A}$. This occurs when $S = T = 0$, or more specifically,

$$S = T = 0 \Rightarrow \left(R + \sqrt{Q^3 + R^2}\right)^{1/3} = \left(R - \sqrt{Q^3 + R^2}\right)^{1/3} = 0$$

$$\Rightarrow R + \sqrt{Q^3 + R^2} = R - \sqrt{Q^3 + R^2} = 0 \Rightarrow R = \sqrt{Q^3 + R^2} = 0$$

$$\Rightarrow R = Q = 0 \Rightarrow \frac{9ABC - 27A^2D - 2B^3}{54A^3} = \frac{3AC - B^2}{9A^2} = 0$$

$$\Rightarrow 9ABC = 27A^2D + 2B^3, \quad 3AC = B^2. \tag{14}$$

In particular, if we apply the relationships between the variables in (14) in the case of (13) when $v = v_c$, $p = p_c$, and $T = T_c$,

$$-9p_c \left(RT_c + bp_c\right) a = -27p_c^2 ab - 2\left(RT_c + bp_c\right)^3, \tag{15}$$

$$3p_c a = \left(RT_c + bp_c\right)^2. \tag{16}$$

Solving (16) for T_c, we find that $T_c = \frac{-bp_c \pm \sqrt{3ap_c}}{R}$, and since $a, b, p, R > 0$, we must

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[3]For a reference, see https://brilliant.org/wiki/cardano-method/.

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have the positive root, or $T_c = \frac{\sqrt{3ap_c} - bp_c}{R}$. Then, substituting this relation into (15),

$$-9p_c \left(\sqrt{3ap_c} - bp_c + bp_c \right) a = -27p_c^2 ab - 2 \left(\sqrt{3ap_c} - bp_c + bp_c \right)^3$$

$$\Rightarrow -9p_c \left(\sqrt{3ap_c} \right) a = -27p_c^2 ab - 2 \left(\sqrt{3ap_c} \right)^3$$

$$\Rightarrow -9\sqrt{3}p_c^{3/2} a^{3/2} = -27p_c^2 ab - 6\sqrt{3}p_c^{3/2} a^{3/2} \Rightarrow 27p_c^2 ab = 3\sqrt{3}p_c^{3/2} a^{3/2}$$

$$\Rightarrow \sqrt{p_c} = \frac{\sqrt{3a}}{9b} \Rightarrow \boxed{p_c = \frac{a}{27b^2}.} \tag{17}$$

Substituting (17) into our expression for T_c above, we further find that

$$T_c = \frac{\sqrt{3a}\frac{\sqrt{3a}}{9b} - b\frac{a}{27b^2}}{R} = \frac{\frac{a}{3b} - \frac{a}{27b}}{R} = \frac{8a}{27bR} \Rightarrow \boxed{T_c = \frac{8a}{27bR}.} \tag{18}$$

Finally, from earlier, the triple root at $v = v_c$ is

$$v_c = -\frac{B}{3A} = \frac{RT_c + bp_c}{3p_c} = \frac{RT_c}{3p_c} + \frac{b}{3} = \frac{R\frac{8a}{27bR}}{3\frac{a}{27b^2}} + \frac{b}{3} = \frac{\frac{8}{27}}{\frac{1}{9b}} + \frac{b}{3} = 3b \Rightarrow \boxed{v_c = 3b.} \tag{19}$$

$\square$

(b) *Solution.* Using the parameters $a = 553.6$ L^2 kPa mol^{-2} and $b = 0.03049$ L mol^{-1}, we can compute p_c and T_c using (17) and (18), respectively:

$$p_c = \frac{553.6}{27 \left(0.03049\right)^2} \text{ kPa} \approx 22055.52848 \text{ kPa} \approx 22.056 \text{ MPa} \Rightarrow \boxed{p_c \approx 22.056 \text{ MPa.}}$$

$$\tag{20}$$

$$T_c = \frac{8 \left(553.6\right)}{27 \left(0.03049\right) \left(8.314\right)} \text{ K} \approx 647.0753557 \text{ K} \Rightarrow \boxed{T_c \approx 647.08.} \tag{21}$$

Our critical pressure in (20) matches the actual value up to four significant figures (so, excluding the last decimal place given), while our critical temperature in (21) matches the actual value up to three significant figures (so, for *all* given decimal places). The *relative* error is probably about the same in both cases, $\sim 10^{-4} = 0.01\%$. Also, given the hydrogen bonding present between water molecules, water has relatively high intermolecular forces (which causes it to deviate heavily from ideal gas behavior), yet our results in this part suggest that the van der Waals equation still yields immense accuracy in capturing the thermodynamics of water near the critical point.[4] $\square$

(c) *Solution.* In these reduced variables, $v' = v/v_c \Rightarrow v = v_c v' = 3bv'$, $p' = p/p_c \Rightarrow p = p_c p' = \frac{p'a}{27b^2}$, and $T' = T/T_c \Rightarrow T = T_c T' = \frac{8aT'}{27bR}$. Hence, substituting this transformation into the van der Waals equation,

$$\left(p + \frac{a}{v^2} \right) \left(v - b \right) = RT \Rightarrow \left(\frac{p'a}{27b^2} + \frac{a}{\left(3bv'\right)^2} \right) \left(3bv' - b \right) = R\frac{8aT'}{27bR} = \frac{8aT'}{27b}$$

$$\Rightarrow \frac{a}{b} \left(\frac{p'}{27} + \frac{1}{9 \left(v'\right)^2} \right) \left(3v' - 1 \right) = \frac{8aT'}{27b} \Rightarrow \boxed{\left(p' + \frac{3}{\left(v'\right)^2} \right) \left(3v' - 1 \right) = 8T'.} \tag{22}$$

$\square$

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[4]In fact, for $T > T_c$ as well, the van der Waals equation still remains very accurate for most fluids and gases.

(d) *Solution.* As noted in the question, near T_c, there are two stable volumes for the same value of p, and hence, the same value of p', such that, by using (22), we can write that

$$\left(p' + \frac{3}{\left(v'_{\text{gas}}\right)^2}\right)\left(3v'_{\text{gas}} - 1\right) = 8T', \tag{23}$$

$$\left(p' + \frac{3}{\left(v'_{\text{liquid}}\right)^2}\right)\left(3v'_{\text{liquid}} - 1\right) = 8T'. \tag{24}$$

[5] We can solve for T' such that both (23) and (24) are simultaneously satisfied. Since p' is the same in both cases, this entails solving for p' in both equations, then setting the resultant equations equal to each other. We do this below:

$$\left(p' + \frac{3}{\left(v'_{\text{gas}}\right)^2}\right)\left(3v'_{\text{gas}} - 1\right) = 8T' \Rightarrow p' + \frac{3}{\left(v'_{\text{gas}}\right)^2} = \frac{8T'}{3v'_{\text{gas}} - 1}$$

$$\Rightarrow p' = \frac{8T'}{3v'_{\text{gas}} - 1} - \frac{3}{\left(v'_{\text{gas}}\right)^2} = \frac{8T'}{3v'_{\text{liquid}} - 1} - \frac{3}{\left(v'_{\text{liquid}}\right)^2}$$

$$\Rightarrow T'\left(\frac{8}{3v'_{\text{gas}} - 1} - \frac{8}{3v'_{\text{liquid}} - 1}\right) = \frac{3}{\left(v'_{\text{gas}}\right)^2} - \frac{3}{\left(v'_{\text{liquid}}\right)^2}$$

$$\Rightarrow T'\left(\frac{8\left(3v'_{\text{liquid}} - 1\right) - 8\left(3v'_{\text{gas}} - 1\right)}{\left(3v'_{\text{gas}} - 1\right)\left(3v'_{\text{liquid}} - 1\right)}\right) = \frac{3\left[\left(v'_{\text{liquid}}\right)^2 - \left(v'_{\text{gas}}\right)^2\right]}{\left(v'_{\text{gas}}\right)^2\left(v'_{\text{liquid}}\right)^2}$$

$$= \frac{3\left(v'_{\text{liquid}} - v'_{\text{gas}}\right)\left(v'_{\text{liquid}} + v'_{\text{gas}}\right)}{\left(v'_{\text{gas}}\right)^2\left(v'_{\text{liquid}}\right)^2}$$

$$\Rightarrow T' = \frac{3\left(v'_{\text{liquid}} - v'_{\text{gas}}\right)\left(v'_{\text{liquid}} + v'_{\text{gas}}\right)}{\left(v'_{\text{gas}}\right)^2\left(v'_{\text{liquid}}\right)^2}\frac{\left(3v'_{\text{gas}} - 1\right)\left(3v'_{\text{liquid}} - 1\right)}{8\left(3v'_{\text{liquid}} - 1\right) - 8\left(3v'_{\text{gas}} - 1\right)}$$

$$= \frac{\left(v'_{\text{liquid}} - v'_{\text{gas}}\right)\left(v'_{\text{liquid}} + v'_{\text{gas}}\right)}{8\left(v'_{\text{gas}}\right)^2\left(v'_{\text{liquid}}\right)^2}\frac{\left(3v'_{\text{gas}} - 1\right)\left(3v'_{\text{liquid}} - 1\right)}{v'_{\text{liquid}} - v'_{\text{gas}}}$$

$$= \frac{\left(3v'_{\text{gas}} - 1\right)\left(3v'_{\text{liquid}} - 1\right)\left(v'_{\text{liquid}} + v'_{\text{gas}}\right)}{8\left(v'_{\text{gas}}\right)^2\left(v'_{\text{liquid}}\right)^2}. \tag{25}$$

As suggested in the problem, we can approximate $v'_{\text{gas}} = 1 + \frac{\varepsilon}{2}$ and $v'_{\text{liquid}} = 1 - \frac{\varepsilon}{2}$ for $0 < \varepsilon \ll 1$. Then, $v'_{\text{liquid}} + v'_{\text{gas}} = 1 + \frac{\varepsilon}{2} + 1 - \frac{\varepsilon}{2} = 2$, and substituting these into (25),

$$T' = \frac{\left(3v'_{\text{gas}} - 1\right)\left(3v'_{\text{liquid}} - 1\right)\left(v'_{\text{liquid}} + v'_{\text{gas}}\right)}{8\left(v'_{\text{gas}}\right)^2\left(v'_{\text{liquid}}\right)^2} = \frac{2\left(3\left(1 + \frac{\varepsilon}{2}\right) - 1\right)\left(3\left(1 - \frac{\varepsilon}{2}\right) - 1\right)}{8\left(1 + \frac{\varepsilon}{2}\right)^2\left(1 - \frac{\varepsilon}{2}\right)^2}$$

$$= \frac{\left(2 + \frac{3\varepsilon}{2}\right)\left(2 - \frac{3\varepsilon}{2}\right)}{4\left(1 + \frac{\varepsilon}{2}\right)^2\left(1 - \frac{\varepsilon}{2}\right)^2} = \frac{16 - 9\varepsilon^2}{16 - 8\varepsilon^2 + \varepsilon^4} = \left(1 - \frac{9\varepsilon^2}{16}\right)\frac{1}{1 - \frac{\varepsilon^2}{2} + \frac{\varepsilon^4}{16}}. \tag{26}$$

The rational function in (26) can be expanded in terms of ε using the usual geometric series approximation $\frac{1}{1-x} = 1 + x + x^2 + \mathcal{O}\left(x^3\right)$, which converges when $|x| < 1$. In

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[5]Note that T' is the same for both (23) and (24) because, as given in the problem, there are two stable volumes for the same value of p near T_c. Namely, in reduced variables, these volumes are v'_{gas} and v'_{liquid}.

particular, if we let $x = \frac{\varepsilon^2}{2} - \frac{\varepsilon^4}{16}$, then (26) can be expanded like

$$T' = \left(1 - \frac{9\varepsilon^2}{16}\right)\left(1 + \frac{\varepsilon^2}{2} - \frac{\varepsilon^4}{16} + \left(\frac{\varepsilon^2}{2}\right)^2 + \mathcal{O}\left(\varepsilon^6\right)\right)$$

$$= \left(1 - \frac{9\varepsilon^2}{16}\right)\left(1 + \frac{\varepsilon^2}{2} + \frac{3\varepsilon^4}{16} + \mathcal{O}\left(\varepsilon^6\right)\right) = 1 - \frac{\varepsilon^2}{16} - \frac{3\varepsilon^4}{32} + \mathcal{O}\left(\varepsilon^6\right)$$

$$\Rightarrow 1 - T' = \frac{\varepsilon^2}{16} + \frac{3\varepsilon^4}{32} + \mathcal{O}\left(\varepsilon^6\right). \tag{27}$$

Finally, rewriting (27) in terms of the original variables,

$$1 - T' = \frac{\varepsilon^2}{16} + \frac{3\varepsilon^4}{32} + \mathcal{O}\left(\varepsilon^6\right) \Rightarrow 1 - \frac{T}{T_c}$$

$$= \frac{\left(v'_{\text{gas}} - v'_{\text{liquid}}\right)^2}{16} + \frac{3\left(v'_{\text{gas}} - v'_{\text{liquid}}\right)^4}{32} + \mathcal{O}\left(\left(v'_{\text{gas}} - v'_{\text{liquid}}\right)^6\right)$$

$$= \frac{\left(\frac{v_{\text{gas}}}{v_c} - \frac{v_{\text{liquid}}}{v_c}\right)^2}{16} + \frac{3\left(\frac{v_{\text{gas}}}{v_c} - \frac{v_{\text{liquid}}}{v_c}\right)^4}{32} + \mathcal{O}\left(\left(\frac{v_{\text{gas}} - v_{\text{liquid}}}{v_c}\right)^6\right)$$

$$= \frac{\left(v_{\text{gas}} - v_{\text{liquid}}\right)^2}{16v_c^2} + \frac{3\left(v_{\text{gas}} - v_{\text{liquid}}\right)^4}{32v_c^4} + \mathcal{O}\left(\left(\frac{v_{\text{gas}} - v_{\text{liquid}}}{v_c}\right)^6\right)$$

$$\Rightarrow T_c - T = T_c\left[\frac{\left(v_{\text{gas}} - v_{\text{liquid}}\right)^2}{16v_c^2} + \frac{3\left(v_{\text{gas}} - v_{\text{liquid}}\right)^4}{32v_c^4} + \mathcal{O}\left(\left(\frac{v_{\text{gas}} - v_{\text{liquid}}}{v_c}\right)^6\right)\right]$$

$$\Rightarrow T_c - T \approx \frac{T_c}{16v_c^2}\left(v_{\text{gas}} - v_{\text{liquid}}\right)^2 \Rightarrow \boxed{v_{\text{gas}} - v_{\text{liquid}} \approx \frac{4v_c}{\sqrt{T_c}}\sqrt{T_c - T}.} \tag{28}$$

(28) holds whenever $|v_{\text{gas}} - v_{\text{liquid}}| \ll v_c \iff 0 < \varepsilon \ll 1$ and demonstrates the scaling property $v_{\text{gas}} - v_{\text{liquid}} \sim \sqrt{T_c - T}$ whenever $T \approx T_c$ and $v \approx v_c$. $\qquad\square$

(e) *Solution.* Firstly, we can solve for $p' = p'(v', T')$ using (22):

$$\left(p' + \frac{3}{(v')^2}\right)(3v' - 1) = 8T' \Rightarrow p' + \frac{3}{(v')^2} = \frac{8T'}{3v' - 1} \Rightarrow p' = \frac{8T'}{3v' - 1} - \frac{3}{(v')^2}. \tag{29}$$

In particular, when $T' = 1$, i.e., $T = T_c$, (29) becomes

$$p'(v', 1) = \frac{8}{3v' - 1} - \frac{3}{(v')^2}, \tag{30}$$

and Taylor expanding (30) about the critical point $v' = 1$, i.e., $v = v_c$,

$$p'(v', 1) = p'(1, 1) + \left.\frac{\partial p'}{\partial v'}\right|_{v'=1} (v' - 1) + \left.\frac{\partial^2 p'}{\partial v'^2}\right|_{v'=1} \frac{(v' - 1)^2}{2}$$

$$+ \left.\frac{\partial^3 p'}{\partial v'^3}\right|_{v'=1} \frac{(v' - 1)^3}{6} + \mathcal{O}\left((v' - 1)^4\right) = \frac{8}{3 - 1} - 3$$

$$+6 \left[\frac{1}{(v')^3} - \frac{4}{(3v' - 1)^2}\right]_{v'=1} (v' - 1) + \left[\frac{144}{(3v' - 1)^3} - \frac{18}{(v')^4}\right]_{v'=1} \frac{(v' - 1)^2}{2}$$

$$+ \left[\frac{72}{(v')^5} - \frac{1296}{(3v' - 1)^4}\right]_{v'=1} \frac{(v' - 1)^3}{6} + \mathcal{O}\left((v' - 1)^4\right)$$

$$= 1 + 6(0)(v' - 1) + (18 - 18)\frac{(v' - 1)^2}{2} + \left(72 - \frac{1296}{2^4}\right)\frac{(v' - 1)^3}{6}$$

$$+ \mathcal{O}\left((v' - 1)^4\right) = 1 - 9\frac{(v' - 1)^3}{6} + \mathcal{O}\left((v' - 1)^4\right)$$

$$\Rightarrow p'(v', 1) - 1 = -\frac{3}{2}(v' - 1)^3 + \mathcal{O}\left((v' - 1)^4\right). \tag{31}$$

Finally, rewriting (31) in terms of the original variables,

$$\frac{p(v, T_c)}{p_c} - 1 = -\frac{3}{2}\left(\frac{v}{v_c} - 1\right)^3 + \mathcal{O}\left(\left(\frac{v}{v_c} - 1\right)^4\right)$$

$$= -\frac{3}{2v_c^3}(v - v_c)^3 + \mathcal{O}\left(\left(\frac{v - v_c}{v_c}\right)^4\right) \Rightarrow \boxed{p(v, T_c) - p_c \approx -\frac{3}{2v_c^3}(v - v_c)^3.} \tag{32}$$

(32) holds whenever $|v - v_c| \ll v_c$ and demonstrates the scaling property $p - p_c \sim (v - v_c)^3$ whenever $T \approx T_c$ and $v \approx v_c$. $\qquad\square$