Date: 2023 Feb 4

Critical temperature

(1) $$p\,v = kT$$

$$\left(p + \frac{a}{v^2}\right)(v-b) = kT$$

$$a = kT_c\, b$$

(2) $$p = \frac{kT}{v-b} - \frac{a}{v^2}$$

$$= \frac{kT}{v-b} - \frac{kT_c}{b}\left(\frac{b}{v}\right)^2$$

$$\frac{p}{(kT_c/b)} = \frac{kT}{kT_c}\,\frac{1}{\left(\frac{v}{b}-1\right)} - \left(\frac{b}{v}\right)^2$$

$$\tilde{v} = \frac{v}{b}$$

$$\tilde{t} = \frac{kT}{kT_c}$$

(3) $$\tilde{p} = \frac{p}{kT_c/b}$$

$$\tilde{p} = \frac{\tilde{t}}{\tilde{v}-1} - \frac{1}{\tilde{v}^2}$$

$v \to \infty$ $\quad \tilde{p} = \frac{\tilde{t}}{\tilde{v}}$

ideal gas

$v \to 1^+$ $\quad \tilde{p} = \frac{\tilde{t}}{(\tilde{v}-1)}$

(4) $$\frac{\partial \tilde{p}}{\partial \tilde{v}} = -\frac{\tilde{t}}{(\tilde{v}-1)^2} + \frac{2}{\tilde{v}^3}$$

$$\frac{\partial \tilde{p}}{\partial \tilde{v}} = 0 \qquad -\tilde{t}\,\tilde{v}^3 + 2(\tilde{v}-1)^2 = 0$$

$$\tilde{t}\,\tilde{v}^3 - 2\tilde{v}^2 + 4\tilde{v} - 2 = 0$$

5 Cubic equation

$$a x^3 + b x^2 + c x + d = 0$$

$$\Delta = 18\,abcd - 4b^3 d + b^2 c^2 - 4ac^3 - 27a^2 d^2$$

$\Delta > 0 \Rightarrow$ three real roots

$\Delta < 0 \Rightarrow$ one real root

6 $a = \tilde{t}$ $\quad b = -2$ $\quad c = +4$ $\quad d = -2$

$$\Delta = 18\,\tilde{t}\,(-2)(4)(-2) - 4(-2)^3(-2) + (-2)^2(4)^2 - 4\tilde{t}(4)^3 - 27\,\tilde{t}^2(-2)^2$$

$$= 288\tilde{t} - \cancel{64} + \cancel{64} - 256\tilde{t} - 108\tilde{t}^2$$

$$= 32\tilde{t} - 108\tilde{t}^2$$

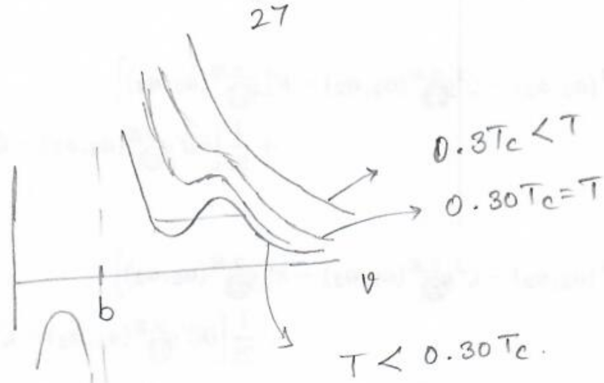
$$= \tilde{t}\,(32 - 108\tilde{t}) = 4\tilde{t}\,(8 - 27\tilde{t})$$

$$\frac{8}{27} = 0.30$$

$$\Delta < 0 \Rightarrow \frac{8}{27} < \tilde{t}$$

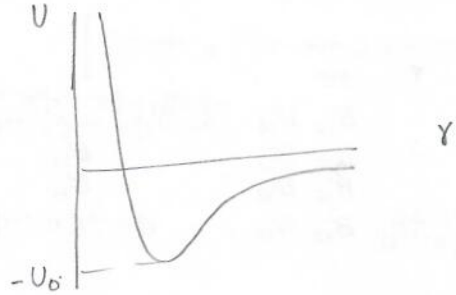
$$\frac{8}{27} kT_c < kT$$

7



The third root is for $v < b$!

(8)



(9)

$$Z(P,V,T) = \frac{1}{\Lambda^{3N}} \frac{1}{N!} \int d^3 r_1 \cdots \int d^3 r_N \; e^{-\frac{1}{kT}\sum_{i<j} U(|\vec{r}_i - \vec{r}_j|)}$$

length

$$\left.\begin{array}{l}\text{Probability that the} \\ \text{system is at} \\ \text{position } \vec{r}_1, \vec{r}_2, \ldots \vec{r}_N\end{array}\right\} = \frac{\frac{1}{\Lambda^{3N}} \frac{1}{N!} \; e^{-\frac{1}{kT}\sum_{i<j} U(|\vec{r}_i - \vec{r}_j|)}}{Z}$$

(10)

$$Z = \frac{V^N}{N!} \; e^{+N \frac{U_0}{kT}} = \left(\frac{V}{N}\right)^N e^{N \frac{U_0}{kT}}$$

$$F = -kT \ln Z = -kT\left[N \ln v + N \frac{U_0}{kT}\right]$$

$$= -NkT \ln v - N U_0$$

$$S = -\frac{\partial F}{\partial T} = Nk \ln v$$

$$P = -\frac{\partial F}{\partial V} = NkT \frac{1}{v} \frac{1}{N} = \frac{kT}{v}$$

(11) van der Waals

$$Z = (v-b)^N \, e^{N \frac{U_0}{kT} \frac{kT_c}{\cancel{U_0}} \frac{b}{v}}$$

$$= (v-b)^N \, e^{N \frac{U_0}{kT} \frac{a}{v}}$$

$$\frac{U_0}{kT} \longrightarrow \frac{U_0}{kT} \frac{v_0}{v}$$

$U_0 v_0 = a$
$= kT_c b$

$$F = -kT \ln Z$$

$$= -kT \left[N \ln(v-b) + N \frac{U_0}{kT} \frac{a/U_0}{v} \right]$$

$$= -NkT \left[\ln(v-b) + \frac{kT_c}{kT} \frac{b}{v} \right]$$

$$S = -\frac{\partial F}{\partial T} = Nk \ln(v-b)$$

$$F = -NkT \ln(v-b) - NkT_c \frac{b}{v}$$

$$P = -\frac{\partial F}{\partial V} = \frac{NkT}{(v-b)} \frac{1}{N} + NkT_c \frac{b}{v^2} \frac{(-1)}{N}$$

$$= \frac{kT}{v-b} - kT_c \frac{b}{v^2}$$

(12) van der Waals (excluded volume)

(1) $v \longrightarrow v - b$

(2) $\frac{U_0}{kT} \longrightarrow \frac{U_0}{kT} \frac{v_0}{v} = \frac{kT_c}{kT} \frac{b}{v}$