(1a) Since $G = \mu N$ we have $\left.\frac{G}{N}\right|_{v=v_e} = \mu|_{v=v_e} = \mu|_{v=v_g} = \left.\frac{G}{N}\right|_{v=v_g}$

(1b) Note that $G = F(T,V) + PV$

$$0 = \left.\frac{G}{N}\right|_{v=v_e} - \left.\frac{G}{N}\right|_{v=v_g} = \frac{1}{N}\int_{v_g}^{v_e} \frac{\partial G}{\partial v}\,dv = \int_{v_g}^{v_e} \frac{\partial G}{\partial V}\,dv$$

$$= \int_{v_g}^{v_e} \left(\underbrace{\frac{\partial F}{\partial V}}_{=-P} + P + V\frac{\partial P}{\partial V} \right) dv = \int_{v}^{v_e} V\frac{\partial P}{\partial V}\,dv$$

$$= \int_{v_g}^{v_e} v\frac{\partial P}{\partial v}\,dv = vP\Big|_{v_g}^{v_e} - \int_{v_g}^{v_e} P\,dv = v_e P_{eq} - v_g P_{eq} - \int_{v_g}^{v_e} P\,dv$$

$$= \int_{v_g}^{v_e} (P_{eq} - P)\,dv$$

The integral is the difference of the shaded areas, so they must be equal.

(2a) just substitute $T = T_c T_r$, $v = v_c v_r$, $P = P_c P_r$ and simplify

---

(2b) Let $P_r = P_r(T_r, v_r)$. We know that $\frac{\partial P_r}{\partial v_r}(1,1) = \frac{\partial^2 P_r}{\partial v_r^2}(1,1) = 0$,

and we can compute $\frac{\partial^3 P_r}{\partial v_r^3} = \frac{72}{v_r^5} - \frac{1296\,T_r}{(3v_r - 1)^4}$

$$\rightarrow \frac{\partial^3 P_r}{\partial v_r^3}(1,1) = 72 - \frac{1296}{16} = -9$$

Expanding in a Taylor series at $T_r = 1$ and near $v_r = 1$ we get

$$P_r \sim P_r(1,1) + \frac{1}{3!}\frac{\partial^3 P_r}{\partial v_r^3}(1,1)\,(v_3-1)^3 = 1 - \frac{3}{2}(v_3-1)^3$$

so $$P_r - 1 \sim -\frac{3}{2}(v_r-1)^3 \quad \Rightarrow \quad v_3 - 1 \sim -\left(\frac{2}{3}(P_r-1)\right)^{1/3}$$

(2c) First note that $$\frac{\partial}{\partial P} = \frac{1}{P_c}\frac{1}{\partial P_r} \quad \rightarrow \quad K_T = -\frac{1}{v}\frac{\partial v}{\partial P_r} = \frac{1}{v_r}\frac{\partial v_r}{\partial P_r}$$

Let $P_r^*(T_r) = P_r(T_r, 1)$

Then $$K_T\Big|_{v_r=1} = -\frac{\partial v_r}{\partial P_r}(T_r, P_r^*(t)) = -\left(\frac{\partial P_r}{\partial v_r}(T_r,1)\right)^{-1}$$

$$\frac{\partial P_r}{\partial v_r}\Big|_{v_r=1} = 6(1-T_r) = -6t \quad \Rightarrow \quad K_T\Big|_{v_r=1} = \frac{1}{P_c}\frac{1}{6t}$$

(2d) We have $$\frac{8(1+t)}{2-3x} - \frac{3}{(1-x)^2} = \frac{8(1+t)}{2+3y} - \frac{3}{(1+y)^2} \sim \frac{8T_r}{2+3x} - \frac{3}{(1+x)^2}$$

Solving for t we get

$$8(1+t) \sim \frac{\dfrac{3}{(1-x)^2} - \dfrac{3}{(1+x)^2}}{\dfrac{1}{2-3x} - \dfrac{1}{2+3x}} = \frac{12x}{(1-x^2)^2}\,\frac{4-9x^2}{6x}$$

$$= \frac{8-18x^2}{(1-x^2)^2} \sim (8-18x^2)(1+2x^2) \sim 8-2x^2$$

$$\Rightarrow \quad t \sim -\frac{x^2}{4} \quad \Rightarrow \quad x \sim \sqrt{-2t} \quad (t \to 0^-)$$

So $v_\ell - 1 \sim -\sqrt{-2t}$ and $v_g - 1 \sim \sqrt{-2t}$

2e

- $$\left(\frac{\partial u}{\partial v}\right)_T = \frac{\partial F}{\partial v} + T\frac{\partial S}{\partial v} = -P - T\frac{\partial^2 F}{\partial v \partial T} = -P + T\frac{\partial P}{\partial T}$$

$$S = -\frac{\partial F}{\partial T}$$

- Integrating $\left(\frac{\partial u}{\partial v}\right)_T$ from ∞ to V we get

$$U(T, v) = U_0(T) + N\int_\infty^v \left(\frac{\partial u}{\partial v}\right)_T dv$$

Since $U(T, v) \sim U_0(T)$ $(v \to \infty)$ and the Van der Waals gas behaves like the ideal gas as $v \to \infty$, we must have $U_0(T) = \frac{3}{2}N\kappa T$

- $$P = \frac{\kappa T}{v-b} - \frac{a}{v^2} \Rightarrow \frac{\partial P}{\partial T} = \frac{\kappa}{v-b}$$

$$\left(\frac{\partial u}{\partial v}\right)_T = -P + T\frac{\partial P}{\partial T} = -\frac{\kappa T}{v-b} + \frac{a}{v^2} + \frac{\kappa T}{v-b} = \frac{a}{v^2}$$

$$\Rightarrow U(T, v) = U_0(T) + N\int_\infty^v \frac{a}{v^2}\, dv = \frac{3}{2}N\kappa T - \frac{Na}{v}$$

$$\Rightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}N\kappa = \text{const} \Rightarrow C_V \sim \frac{3}{2}N\kappa\, |t|^0$$