[tex175] Critical singularities of van der Waals gas

Start from the van der Waals equation of state,

$$\left(\bar{p}+\frac{3}{\bar{V}^2}\right)(3\bar{V}-1)=8\bar{T},$$

in reduced units,

$$\bar{p}\doteq\frac{p}{p_c},\quad \bar{V}\doteq\frac{V}{V_c},\quad \bar{T}\doteq\frac{T}{T_c},\quad \bar{\rho}_l\equiv\frac{\rho_l}{\rho_c},\qquad p_c=\frac{a}{27b^2},\quad V_c=3nb,\quad T_c=\frac{8a}{27bR}.$$

Introduce small deviations from the critical values,

$$\bar{p}\doteq 1+\pi,\quad \bar{V}\doteq 1+\omega,\quad \bar{T}\doteq 1+\tau$$

and write the equation of state in the from $\pi=\pi(\tau,\omega)$.
(a) Determine the critical exponent δ from the critical isotherm, $\pi(0,\omega)$.
(b) Determine the critical exponent γ from the isothermal compressibility, $\kappa_T\doteq -V^{-1}(\partial V/\partial p)_T$.
(c) To calculate the critical exponent β expand the function $\pi(\tau,\omega)$ to third-order in both variables. The shape of the coexistence curve near the critical point is determined by the the function $\omega_s(-\tau_s)$ inferred from solution of $\pi(-\tau,\omega)=\pi(-\tau,-\omega)$.
(d) To calculate the exponent α find the discontinuity of the heat capacity C_p at the critical point. Hint: Use $C_p-C_V=TV\alpha_p^2/\kappa_T$, which is nonzero only below T_c.

Solution: