Stanley's derivation of the van der Waals critical quantities

See H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, OUP 1971, p 71-72.

Van der Waals equation of state is:

$$\left(p + a\frac{N^2}{V^2}\right)(V - Nb) = NkT. \tag{1}$$

The critical point is specified by

$$\frac{\partial p}{\partial V} = 0, \quad \frac{\partial^2 p}{\partial V^2} = 0. \tag{2}$$

By evaluating the derivatives, setting them equal to zero, and solving the simultaneous equations, one obtains the critical quantities $p_\mathrm{c}, V_\mathrm{c}$ and T_c.

Stanley gives a simpler derivation without the use of calculus. This starts from writing the van der Waals equation as

$$V^3 - \frac{N(bp + kT)}{p}V^2 + \frac{aN^2}{p}V - \frac{abN^3}{p} = 0. \tag{3}$$

This is a cubic equation so in general there there will be three roots for $V(p, T)$ But at the critical point these roots coalesce to the single value V_c. in other words, at the critical point the cubic

$$V^3 - \frac{N(bp_\mathrm{c} + kT_\mathrm{c})}{p_\mathrm{c}}V^2 + \frac{aN^2}{p_\mathrm{c}}V - \frac{abN^3}{p_\mathrm{c}} = 0 \tag{4}$$

will factorise as

$$(V - V_\mathrm{c})^3 = 0. \tag{5}$$

Let us expand this out:

$$V^3 - 3V_\mathrm{c}V^2 + 3V_\mathrm{c}^2V - V_\mathrm{c}^3 = 0. \tag{6}$$

Then by comparing the coefficients of Eqs. (4) and (6) we see

$$3V_\mathrm{c} = \frac{N(bp_\mathrm{c} + kT_\mathrm{c})}{p_\mathrm{c}} \tag{7}$$

$$3V_\mathrm{c}^2 = \frac{aN^2}{p_\mathrm{c}} \tag{8}$$

$$V_\mathrm{c}^3 = \frac{abN^3}{p_\mathrm{c}}. \tag{9}$$

From (1.8) and (1.9) we solve for p_c and v_c to get

$$p_\mathrm{c} = \frac{a}{27b^2} \tag{10}$$

$$V_\mathrm{c} = 3Nb \tag{11}$$

and substituting these into Eq. (7) gives

$$kT_\mathrm{c} = \frac{8a}{27b}. \tag{12}$$