Problema 1: Gas de Van der Waals

Ecuación de estado:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT. \tag{1}$$

(a) La transición de fase ocurre cuando

$$\frac{\partial p}{\partial v} = 0 \tag{2}$$

$$\frac{\partial^2 p}{\partial v^2} = 0 \tag{3}$$

Despejando la presión,

$$p = \frac{RT}{v - b} - \frac{a}{v^2}. \tag{4}$$

Derivando una vez e igualando a cero

$$\frac{\partial p}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \quad \Leftrightarrow \quad RTv^3 = 2a(v-b)^2. \tag{5}$$

Derivando nuevamente

$$\frac{\partial^2 p}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \quad \Leftrightarrow \quad 2RTv^4 = 6a(v-b)^3. \tag{6}$$

Dividiendo 6 por 5,

$$2v = 3(v - b) \quad \Leftrightarrow \quad v_c = 3b. \tag{7}$$

Reemplazando v_c en 6,

$$T_c = \frac{2a(2b)^2}{R(3b)^3} = \frac{8}{27}\frac{a}{Rb} \tag{8}$$

y reemplazando T_c y v_c en 4,

$$p_c = \frac{8}{27}\frac{a}{b}\frac{1}{2b} - \frac{a}{9b^2} = \frac{a}{27b^2}. \tag{9}$$

Una relación que resulta útil es

$$\frac{p_c v_c}{T_c} = \frac{3}{8}R. \tag{10}$$

(b) Partiendo de 4,

$$(\pi+1)p_c = \frac{R(t+1)T_c}{(\omega+1)v_c - b} - \frac{a}{(\omega+1)^2 v_c^2} \tag{11}$$

$$\pi+1 = \frac{(t+1)(RT_c/p_c v_c)}{(\omega+1) - b/v_c} - \frac{a}{(\omega+1)^2 p_c v_c^2} \tag{12}$$

$$\pi+1 = \frac{8(t+1)}{3(\omega+1)-1} - \frac{3}{(\omega+1)^2} \tag{13}$$

$$\pi = \frac{4(t+1)}{\frac{3}{2}\omega+1} - \frac{3}{(\omega+1)^2} - 1 \tag{14}$$

(c) Para hacer la aproximación, defino la función

$$f(\pi,\omega,t) = \frac{4(1+t)}{1+\frac{3}{2}\omega} - \frac{3}{(1+\omega)^2} - \pi - 1 \tag{15}$$

y realizo una expansión de Taylor en torno a $(\pi,\omega,t) = (0,0,0)$.

$$\frac{\partial f}{\partial \pi} = -1 \tag{16}$$

$$\frac{\partial f}{\partial \omega} = -\frac{6(1+t)}{1+\frac{3}{2}\omega} + \frac{6}{(1+\omega)^3} \tag{17}$$

$$\frac{\partial f}{\partial t} = \frac{4}{1+\frac{3}{2}\omega} \tag{18}$$

$$\frac{\partial^2 f}{\partial t \partial \omega} = -\frac{6}{(1+\frac{3}{2}\omega)^2} \tag{19}$$

$$\frac{\partial^2 f}{\partial \omega^2} = 18\left[\frac{(1+t)}{(1+\frac{3}{2}\omega)^3} - \frac{1}{(1+\omega)^4}\right] \tag{20}$$

$$\frac{\partial^3 f}{\partial \omega^3} = 18\left[-\frac{9}{2}\frac{(1+t)}{(1+\frac{3}{2}\omega)^4} + \frac{4}{(1+\omega)^5}\right] \tag{21}$$

Teniendo en cuenta que las derivadas de orden superior con respecto a π se anulan, la expresión queda

$$\begin{aligned} f(\pi,\omega,t) = {} & f(0,0,0) \\ & + \frac{\partial f}{\partial \pi}\Big|_0 \pi + \frac{\partial f}{\partial \omega}\Big|_0 \omega + \frac{\partial f}{\partial t}\Big|_0 t \\ & + \frac{1}{2}\frac{\partial^2 f}{\partial \omega^2}\Big|_0 \omega^2 + \frac{\partial^2 f}{\partial t \omega}\Big|_0 t\omega + \frac{1}{6}\frac{\partial^3 f}{\partial \omega^3}\Big|_0 \omega^3 \\ & + \mathcal{O}(t\omega^2, \omega^4). \end{aligned} \tag{22}$$

Evaluando las derivadas, se obtiene

$$f(\pi,\omega,t) = -\pi + 4t - 6t\omega + \frac{3}{2}\omega^3 + \mathcal{O}(t\omega^2,\omega^4) \tag{23}$$

Luego,

$$\pi = 4t - 6t\omega + \frac{3}{2}\omega^3 + \mathcal{O}(t\omega^2,\omega^4) \tag{24}$$

d) La construcción de Maxwell implica la igualdad

$$\int_{v_l}^{v_g} p dv = p_0(v_g - v_l), \tag{25}$$

donde $p_0 = p(v_g) = p(v_l)$.
Utilizando las variables reducidas, se tiene que

$$\int_{v_l}^{v_g} p dv = p_0(v_g - v_l) \tag{26}$$

$$\int_{\omega_1}^{\omega_2} (1+\pi)p_c v_c d\omega = (1+\pi_0)p_c(\omega_2 - \omega_1)v_c \tag{27}$$

$$\int_{\omega_1}^{\omega_2} \pi d\omega = \pi_0(\omega_2 - \omega_1), \tag{28}$$

donde $\pi_0 = \pi_0(\omega_2) = \pi_0(\omega_1)$
Utilizando la expresión aproximada dada por la ecuación 24 e integrando,

$$\begin{aligned} 4t(\omega_2 - \omega_1) - 3t(\omega_2^2 - \omega_1^2) + \frac{3}{8}(\omega_2^4 - \omega_1^4) &= \pi_0(\omega_2 - \omega_1) \\ 4t - 3t(\omega_2 + \omega_1) + \frac{3}{8}(\omega_2 + \omega_1)(\omega_2^2 + \omega_2\omega_1 + \omega_1^2) &= \pi_0. \end{aligned} \tag{29}$$

Por otro lado,

$$\begin{aligned} \pi_0(\omega_2) &= \pi_0(\omega_1) \\ -6t\omega_2 + \frac{3}{2}\omega_2^3 &= -6t\omega_1 + \frac{3}{2}\omega_1^3 \\ \omega_2^3 - \omega_1^3 &= 4t(\omega_2 - \omega_1) \\ \omega_2^2 + \omega_2\omega_1 + \omega_1^2 &= 4t. \end{aligned} \tag{30}$$

Reemplazando 30 en 29,

$$\begin{aligned} 4t - 3t(\omega_2 + \omega_1) + \frac{3}{2}t(\omega_2 + \omega_1) &= \pi_0 \\ 4t - \frac{3}{2}t(\omega_2 + \omega_1) &= \pi_0 \end{aligned} \tag{31}$$

Evaluando π_0 en ω_2, se tiene

$$-\frac{3}{2}t(\omega_2+\omega_1) = -6t\omega_2 + \frac{3}{2}\omega_2^3 \tag{32}$$

$$-t(\omega_2+\omega_1) = -4t\omega_2 + \omega_2^3 \tag{33}$$

$$3t\omega_2 - \omega_2^3 = t\omega_1 \tag{34}$$