

$$10.5 \quad \text{By H.1c, } \frac{\partial x}{\partial y} \Big|_z \frac{\partial y}{\partial z} \Big|_x \frac{\partial z}{\partial x} \Big|_y = -1 \Rightarrow \left. \frac{\partial T}{\partial P} \right|_H = -\frac{-1}{\left. \frac{\partial P}{\partial H} \right|_T \left. \frac{\partial H}{\partial T} \right|_P}$$

$$\text{By H.1a, } \left. \frac{\partial x}{\partial y} \right|_z = \left. \frac{\partial y}{\partial x} \right|_z \Rightarrow \left. \frac{\partial T}{\partial P} \right|_H = -\frac{\left. \frac{\partial H}{\partial P} \right|_T}{\left. \frac{\partial H}{\partial T} \right|_P}$$

$$dH = TdS + VdP + \mu dN > 0 \quad (\text{assume } N = \text{constant}).$$

$$\Rightarrow \left. \frac{\partial H}{\partial P} \right|_T = T \left. \frac{\partial S}{\partial P} \right|_T + V = -T \left. \frac{\partial V}{\partial T} \right|_P + V \quad \text{where the last step was by H.1b-a}$$

$$\text{By 1.3.18, } C_p = \left. \frac{\partial H}{\partial T} \right|_P \Rightarrow \left. \frac{\partial T}{\partial P} \right|_H = \frac{T \left. \frac{\partial V}{\partial T} \right|_P - V}{C_p} \quad (1)$$

$$\text{By 10.21, } \frac{Pv}{kT} = \sum_{i=1}^{\infty} a_i(T) \left(\frac{\lambda^3}{v} \right)^{i-1} \approx a_1(T) + a_2(T) \left(\frac{\lambda^3}{v} \right) + \dots = 1 + a_2(T) \left(\frac{\lambda^3}{v} \right)$$

$$\Rightarrow v = \frac{kT}{P} + \frac{a_2 \lambda^3 kT}{Pv},$$

Now, I'm going to make the (sketchy?) substitution $\frac{kT}{Pv} \approx 1$, by 10.21, again.

$$\Rightarrow v = \frac{kT}{P} + a_2 \lambda^3 \Rightarrow V = \frac{NkT}{P} + Na^2 \lambda^3$$

Plug V into (1), and get:

$$\left. \frac{\partial T}{\partial P} \right|_H = - \left[\cancel{-\frac{NkT}{P}} - T \frac{\partial}{\partial T} Na_2 \lambda^3 + \cancel{\frac{NkT}{P}} + Na^2 \lambda^3 \right] \frac{1}{C_p} = -\frac{N}{C_p} \left[-T \frac{\partial (a_2 \lambda^3)}{\partial T} + a_2 \lambda^3 \right]$$

$$\Rightarrow \left. \frac{\partial T}{\partial P} \right|_H = \frac{N}{C_p} \left(T \frac{\partial (a_2 \lambda^3)}{\partial T} - a_2 \lambda^3 \right) \quad \checkmark$$

Let's compute $\left. \frac{\partial T}{\partial P} \right|_H$ for the given interparticle interaction.

i) $U(r) = \infty, 0 < r < D$: $(a_2 = \frac{2\pi}{\lambda^3} \int_0^\infty (1 - e^{-U(r)/kT}) r^2 dr \text{ by 10.3.1})$

$$a_2 = \frac{2D^3\pi}{3\lambda^3} \Rightarrow \left. \frac{\partial T}{\partial P} \right|_H = \frac{N}{C_p} \left(\frac{2D^3\pi}{3} \left(T \frac{\partial \lambda^3}{\partial T} \frac{1}{\lambda^3} - \frac{\lambda^3}{\lambda^3} \right) \right) = \boxed{-\frac{2ND^3\pi}{3CP}}$$

ii) $U(r) = -U_0, D < r < r_1$, $a_2 = \frac{2\pi}{3\lambda^3} (e^{U_0/kT} - 1)(D^3 - r_1^3)$

(This is the only T-dependent regime) $\Rightarrow \left. \frac{\partial T}{\partial P} \right|_H = \frac{N}{C_p} \left(T \frac{\partial}{\partial T} \left(\frac{2\pi}{3} (e^{U_0/kT} - 1)(D^3 - r_1^3) \right) \right) - \frac{2\pi}{3} (e^{U_0/kT} - 1)(D^3 - r_1^3) \quad \checkmark$

$$\Rightarrow \boxed{\left. \frac{\partial T}{\partial P} \right|_H = \frac{2N\pi}{3C_p kT} (D^3 - r_1^3) (kT - e^{U_0/kT} (kT + U_0))}$$

iii) $U(r) = 0, r > r_1$ $\Rightarrow a_2 = 0 \Rightarrow \boxed{\left. \frac{\partial T}{\partial P} \right|_H = 0}$ temp limit?

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