▶ Q1

We're given the van der Waals equation of state in (33) and the free energy F in (38).

Relevant equations:

$$U = F + \sigma\tau$$
$$\sigma = -\frac{\partial F}{\partial \tau}_{V,N}$$
$$p = -\frac{\partial F}{\partial V}_{\tau,N}$$

We're also given pressure in (39)

$$p = \frac{N\tau}{V - Nb} - \frac{N^2 a}{V^2}$$

(a)

$$F_{\mathrm{vdW}} = -N\tau\left[\ln\left(\frac{n_Q(V-Nb)}{N}\right) + 1\right] - \frac{N^2 a}{V}$$

Note that n_Q depends on τ, so let's use n'_Q independent of τ

$$\begin{aligned}
F_{\mathrm{vdW}} &= -N\tau\left[\ln\left(\tau^{3/2}\frac{n'_Q(V-Nb)}{N}\right) + 1\right] - \frac{N^2 a}{V} \\
\sigma = -\frac{\partial F}{\partial \tau} &= N + N\frac{\partial}{\partial \tau}\tau\ln\left(\tau^{3/2}\frac{n'_Q(V-Nb)}{N}\right) \\
&= N + N\frac{\partial}{\partial \tau}\left[\tau\ln\left(\tau^{3/2}\right) + \tau\ln\left(\frac{n'_Q(V-Nb)}{N}\right)\right] \\
&= N + N\ln(\tau^{3/2}) + \frac{3}{2} + N\ln\left(\frac{n'_Q(V-Nb)}{N}\right) \\
&= N + N\ln\left(\frac{n_Q(V-Nb)}{N}\right) + N \times 3/2 \\
&= N\left(\ln\left[\frac{n_Q(V-Nb)}{N}\right] + 5/2\right)
\end{aligned}$$

(b)

$$\begin{aligned}
U = F + \sigma\tau = N\tau\left[\ln\left[\frac{n_Q(V-Nb)}{N}\right] + \frac{5}{2} - \ln\left[\frac{n_Q(V-Nb)}{N}\right] - 1\right] - \frac{N^2 a}{V} \\
= \frac{3}{2}N\tau - N^2 a/V
\end{aligned}$$

(c) From p above

$$\begin{aligned}
p &= \frac{N\tau}{V - Nb} - \frac{N^2 a}{V^2} \\
H(\tau, p, V) &= \frac{3}{2}N\tau - \frac{N^2 a}{V} + pV
\end{aligned}$$

How do we get $N\tau$ out of pV? It's in the equation of state...

In [46]:
```
import sympy as sp
p, N, V, a, b, tau = sp.symbols('p N V a b tau')
```

```
eos = (p+N**2*a/V**2)*(V-N*b)
eos.expand()
```

Out[46]: $$-\frac{N^3ab}{V^2} + \frac{N^2a}{V} - Nbp + Vp$$

Since we know the result we're going for, we can add in $N\tau$ and subtract out the above from H

$$H(\tau, p, V) = \frac{5}{2}N\tau - \frac{2N^2a}{V} + Nbp - \frac{N^3ab}{V^2}$$

To finish, we just have to check some equalities:

$$Nbp - \frac{N^3ab}{V^2} = \frac{N^2b\tau}{V}$$
$$-\frac{2N^2a}{V} - \frac{N^3ab}{V^2} = \frac{-2Nap}{\tau}$$

For both of these, plugging in our formula for p and simplifying will yield our equation of state

$$\tau = \frac{pV}{N} - \frac{Na}{V}$$

proving the equality.

▶ Q2

(a) The only complexity of this problem compared to the example is finding $Z = \sum_n e^{\frac{-n\hbar\omega+\epsilon_0}{\tau}}$, only with a new n

$$
\begin{aligned}
Z &= \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{\frac{-\sqrt{n_x^2+n_y^2+n_z^2}\hbar\omega+\epsilon_0}{\tau}} \\
&= \frac{1}{8}\int_0^\infty 4\pi n^2 e^{\frac{-n\hbar\omega+\epsilon_0}{\tau}} dn \\
&= \frac{\pi e^{\epsilon_0/\tau}}{2}\left[\frac{2\tau^3}{\hbar^3\omega^3}\right] = \pi e^{\frac{\epsilon_0}{\tau}}\left(\frac{\tau}{\hbar\omega}\right)^3
\end{aligned}
$$

We are trying to find the pressure when the solid and gas are in equilibrium

$$\lambda_g = \lambda_s$$

As in (10.30), we'll use the ideal gas approximation for λ_g

$$\lambda_g = \frac{n}{n_Q} = \frac{p}{\tau n_Q} = \frac{p}{\tau}\left(\frac{2\pi\hbar^2}{M\tau}\right)^{3/2}$$

For λ_s, we need to assume a small solid volume and apply (10.28)

$$
\begin{aligned}
\mu_s &= F_s + pv_s \simeq F_s = -\ln Z \\
\lambda_s \equiv e^{\mu_s/\tau} &= \frac{1}{Z} = \frac{e^{-\epsilon_0/\tau}}{\pi}\left(\frac{\hbar\omega}{\tau}\right)^3
\end{aligned}
$$

This gives our pressure as

$$
\begin{aligned}
\lambda_g &= \lambda_s \\
\frac{p}{\tau}\left(\frac{2\pi\hbar^2}{M\tau}\right)^{3/2} &= \frac{e^{-\epsilon_0/\tau}}{\pi}\left(\frac{\hbar\omega}{\tau}\right)^3 \\
p &\simeq \left(\frac{M}{2\pi}\right)^{3/2}\frac{\omega^3}{\tau^{1/2}}e^{-\epsilon_0/\tau}
\end{aligned}
$$

(b) Using (10.18) we have

$$
\begin{aligned}
L = \tau^2\frac{d}{d\tau}\ln p &= \tau^2\frac{d}{d\tau}\left[\ln\left(\frac{e^{-\epsilon_0/\tau}}{\tau^{1/2}}\right) + \left(\ln\left(\frac{M}{2\pi}\right)^{3/2}\omega^3\right)\right] \\
&= \frac{2\epsilon_0 - \tau}{2} = \epsilon_0 - \frac{1}{2}\tau
\end{aligned}
$$

The question actually asks for us to explain *why* this is the case. We're able to use (10.18) thanks to the various assumptions we made earlier. Latent heat decreases with temperature because

▶ Q3

▶ Q4

Rather than recalculating the phonon energy at low temperatures, we'll use our previous result

$$U(\tau) \simeq \frac{3\pi^4 N\tau^4}{5(k_B\theta)^3} \tag{4.46}$$

$$C_V = \frac{12\pi^4 N}{5}\left(\frac{\tau}{k_B\theta}\right)^3 \tag{4.47}$$

The free energy density is

$$F \equiv U - \tau\sigma \tag{3.35}$$

$$f = \frac{F}{V} = \frac{U}{V} - \tau\frac{\sigma}{V}$$

leaving σ as the last value to find. We actaully have a formula for entropy from heat capacity

$$\sigma(\tau) - \sigma(0) = \int_0^\tau \frac{C_V(\tau)}{\tau} d\tau \tag{6.39}$$

$$\sigma(\tau) = \frac{12\pi^4 N}{5(k_B\theta)^3}\int_0^\tau \tau^2 d\tau = \frac{4\pi^4 N\tau^3}{5(k_B\theta)^3}$$

$$f = \frac{3\pi^4 N\tau^4}{5V(k_B\theta)^3} - \frac{4\pi^4 N\tau^4}{5V(k_B\theta)^3}$$

Now to clean things up

$$\theta = \frac{\hbar v}{k_B}\left(6\pi^2 n\right)^{1/3}$$

$$f = -\frac{n\pi^4\tau^4}{5(6\pi^2 n\hbar^3 v^3)} = -\frac{\pi^2\tau^4}{30v^3\hbar^3}$$

(b) Since α is stable at low temperature, we know $U_\alpha(0) < U_\beta(0)$, and $U_\beta(0) - U_\alpha(0)$ is positive. We know that τ_c^4 must be positive, so v_β must be less than v_α.

The only energies here are the ground state energy $U(0)$ and phonon energy f, so the transition occurs when

$$U_\alpha(0) + f_\alpha(\tau) = U_\beta(0) + f_\beta(\tau)$$

These are equal at $\tau = \tau_c$, so we know a solution exists, and exists only when $v_\beta < v_\alpha$

(c) Since we have phonon entropy and τ_c, we need only find $\Delta\sigma$

$$L = \tau\Delta\sigma = \sigma_\beta(\tau_c) - \sigma_\alpha(\tau_c)$$

$$= \left[\frac{2\pi^2\tau_c^4}{15\hbar^3}\left(v_\beta^{-3} - v_\alpha^{-3}\right)\right]$$

$$= \frac{2\pi^2}{15\hbar^3}\left[\frac{30\hbar^3}{\pi^2}\frac{U_\beta(0) - U_\alpha(0)}{v_\beta^{-3} - v_\alpha^{-3}}\left(v_\beta^{-3} - v_\alpha^{-3}\right)\right]$$

$$= 4\left[U_\beta(0) - U_\alpha(0)\right]$$