FYS4130 Oblig 1

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1.

The known quantities are the input parameters T, V, μ, the functions $S(T,V,\mu)$, $N(T,V,\mu)$, $P(T,V,\mu)$ and all derivatives of these functions with respect to the input parameters, holding the other input parameters constant.

The problem essentially asks to express the specific heat capacity at constant volume in terms of the known quantities.

In the expression for the specific heat capacity at constant volume,

$$c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N},$$

T is known (because it's an input parameter) and N is known (because it's one of the known functions of the input parameters). The only quantity that is not known (explicitly) is the derivative

$$\left(\frac{\partial S}{\partial T}\right)_{V,N},$$

because one of the quantities held constant (N) is not one of the input parameters. This derivative must be expressed in terms of known quantities.

We can write the derivative as a Jacobian,

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{\partial(S,V,N)}{\partial(T,V,N)},$$

and use the chain rule for Jacobians to introduce the input parameters,

$$\frac{\partial(S,V,N)}{\partial(T,V,N)} = \frac{\partial(S,V,N)}{\partial(T,V,\mu)} \Big/ \frac{\partial(T,V,N)}{\partial(T,V,\mu)} = \frac{\partial(S,N,V)}{\partial(T,\mu,V)} \Big/ \frac{\partial(N,V,T)}{\partial(\mu,V,T)}.$$

The Jacobian in the denominator can be written as

$$\frac{\partial(N,V,T)}{\partial(\mu,V,T)} = \left(\frac{\partial N}{\partial \mu}\right)_{V,T}$$

which is a known quantity. The Jacobian in the numerator can be written as

$$\frac{\partial(S,N,V)}{\partial(T,\mu,V)} = \left(\frac{\partial S}{\partial T}\right)_{\mu,V}\left(\frac{\partial N}{\partial \mu}\right)_{T,V} - \left(\frac{\partial S}{\partial \mu}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{\mu,V},$$

where each partial derivative is a known quantity. We thus have

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{\left(\frac{\partial S}{\partial T}\right)_{\mu,V}\left(\frac{\partial N}{\partial \mu}\right)_{T,V} - \left(\frac{\partial S}{\partial \mu}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{\mu,V}}{\left(\frac{\partial N}{\partial \mu}\right)_{V,T}} = \left(\frac{\partial S}{\partial T}\right)_{\mu,V} - \frac{\left(\frac{\partial S}{\partial \mu}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{\mu,V}}{\left(\frac{\partial N}{\partial \mu}\right)_{V,T}},$$

and an expression for the specific heat capacity at constant volume in terms of the known quantities is

$$c_V = \frac{T}{N}\left[\left(\frac{\partial S}{\partial T}\right)_{\mu,V} - \frac{\left(\frac{\partial S}{\partial \mu}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{\mu,V}}{\left(\frac{\partial N}{\partial \mu}\right)_{T,V}}\right].$$

2.

For reference, the standard quantities are given by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}, \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}, \quad c_P = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P,N}, \quad c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N}.$$

The problem text asks to find an expression for $(\partial P \,/\, \partial U)_{G,N}$, but it's probably easier to find an expression for $(\partial U \,/\, \partial P)_{G,N}$ and invert the resulting expression.

$$\left(\frac{\partial U}{\partial P}\right)_{G,N} = \frac{\partial(U,G)}{\partial(P,G)} = \frac{\partial(U,G)}{\partial(T,P)} \Big/ \frac{\partial(P,G)}{\partial(T,P)} = -\frac{\partial(U,G)}{\partial(T,P)} \Big/ \frac{\partial(G,P)}{\partial(T,P)}$$

Since $dG = -SdT + VdP$ we have that

$$\frac{\partial(G,P)}{\partial(T,P)} = \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S,$$

and

$$\frac{\partial(U,G)}{\partial(T,P)} = \left(\frac{\partial U}{\partial T}\right)_{P,N}\left(\frac{\partial G}{\partial P}\right)_{T,N} - \left(\frac{\partial U}{\partial P}\right)_{T,N}\left(\frac{\partial G}{\partial T}\right)_{P,N} = \left(\frac{\partial U}{\partial T}\right)_{P,N} V + \left(\frac{\partial U}{\partial P}\right)_{T,N} S.$$

All that remains is to find the derivatives $(\partial U \,/\, \partial T)_{P,N}$ and $(\partial U \,/\, \partial P)_{T,N}$. Since $dU = TdS - PdV$ we have that

$$\left(\frac{\partial U}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N} - P\left(\frac{\partial V}{\partial T}\right)_{P,N} = Nc_P - PV\alpha,$$

and

$$\left(\frac{\partial U}{\partial P}\right)_{T,N} = T\left(\frac{\partial S}{\partial P}\right)_{T,N} - P\left(\frac{\partial V}{\partial P}\right)_{T,N} = -T\left(\frac{\partial V}{\partial T}\right)_{P,N} - P\left(\frac{\partial V}{\partial P}\right)_{T,N} = -TV\alpha + PV\kappa_T$$

where I've used that $-SdT + VdP$ is an exact differential to obtain the Maxwell relation $(\partial S \,/\, \partial P)_{T,N} = -(\partial V \,/\, \partial T)_{P,N}$. Thus,

$$\frac{\partial(U,G)}{\partial(T,P)} = \left(\frac{\partial U}{\partial T}\right)_{P,N} V + \left(\frac{\partial U}{\partial P}\right)_{T,N} S = (Nc_P - PV\alpha)V + (P\kappa_T - T\alpha)VS.$$

Now we can put everything together,

$$\left(\frac{\partial U}{\partial P}\right)_{G,N} = -\frac{\partial(U,G)}{\partial(T,P)} \Big/ \frac{\partial(G,P)}{\partial(T,P)} = \frac{(Nc_P - PV\alpha)V + (P\kappa_T - T\alpha)VS}{S},$$

and invert the expression to get

$$\left(\frac{\partial P}{\partial U}\right)_{G,N} = \frac{S\,/\,V}{Nc_P - PV\alpha + (P\kappa_T - T\alpha)S}.$$

3

$$F = T\left[N_x \ln\left(\alpha l b^2 \frac{N_x}{V}\right) + N_y \ln\left(\alpha l b^2 \frac{N_y}{V}\right) + N_z \ln\left(\alpha l b^2 \frac{N_z}{V}\right) + \gamma l b^2 \frac{N_x N_y + N_y N_z + N_z N_x}{V}\right]$$

a)

Simply substituting $lb^2\widetilde{V}$ for V in the expression of the Helmholtz free energy gives

$$\frac{F}{T} = N_x \ln\left(\alpha l b^2 \frac{N_x}{lb^2\widetilde{V}}\right) + N_y \ln\left(\alpha l b^2 \frac{N_y}{lb^2\widetilde{V}}\right) + N_z \ln\left(\alpha l b^2 \frac{N_z}{lb^2\widetilde{V}}\right) + \gamma l b^2 \frac{N_x N_y + N_y N_z + N_z N_x}{lb^2\widetilde{V}}$$

$$= N_x \ln\left(\alpha \frac{N_x}{\widetilde{V}}\right) + N_y \ln\left(\alpha \frac{N_y}{\widetilde{V}}\right) + N_z \ln\left(\alpha \frac{N_z}{\widetilde{V}}\right) + \gamma \frac{N_x N_y + N_y N_z + N_z N_x}{\widetilde{V}}.$$

b)

A main result from the course book is that, at equilibrium, the Helmholtz free energy is minimized with respect to any extensive quantity of the system, subject to the constraints. The volume is held constant, while N_x, N_y, N_z are allowed to vary as long as they satisfy $N_x + N_y + N_z = N$. Therefore, the equilibrium Helmholtz free energy is given by

$$F_{\text{eq}} = \min_{N_x, N_y, N_z} F \;:\; N = N_x + N_y + N_z.$$

The constraint can be used to eliminate N_z so that the Helmholtz free energy can be expressed in terms of two free variables N_x, N_y.

$$\frac{F}{T} = N_x \ln\left(\alpha\frac{N_x}{\widetilde{V}}\right) + N_y \ln\left(\alpha\frac{N_y}{\widetilde{V}}\right) + (N - N_x - N_y)\ln\left(\alpha\frac{N - N_x - N_y}{\widetilde{V}}\right)$$

$$+\gamma\frac{N_x N_y + (N - N_x - N_y)(N_x + N_y)}{\widetilde{V}}$$

At equilibrium (or any extremum), the partial derivatives of F with respect to N_x and N_y vanishes.

$$\frac{1}{T}\frac{\partial F}{\partial N_x} = \ln\left(\alpha\frac{N_x}{\widetilde{V}}\right) + N_x \cdot \frac{1}{\alpha\frac{N_x}{\widetilde{V}}} \cdot \alpha\frac{1}{\widetilde{V}} - \ln\left(\alpha\frac{N - N_x - N_y}{\widetilde{V}}\right)$$

$$+(N - N_x - N_y) \cdot \frac{1}{\alpha\frac{N - N_x - N_y}{\widetilde{V}}} \cdot \left(-\alpha\frac{1}{\widetilde{V}}\right) + \gamma\frac{N_y - (N_x + N_y) + (N - N_x - N_y)}{\widetilde{V}}$$

$$= \ln\left(\alpha\frac{N_x}{\widetilde{V}}\right) - \ln\left(\alpha\frac{N - N_x - N_y}{\widetilde{V}}\right) + \gamma\frac{N - 2N_x - N_y}{\widetilde{V}} = 0$$

$$\frac{1}{T}\frac{\partial F}{\partial N_y} = \ln\left(\alpha\frac{N_y}{\widetilde{V}}\right) - \ln\left(\alpha\frac{N - N_x - N_y}{\widetilde{V}}\right) + \gamma\frac{N - N_x - 2N_y}{\widetilde{V}} = 0$$

Now we have two equations with two unknowns,

$$\ln\left(\alpha\frac{N - N_x - N_y}{\widetilde{V}}\right) = \ln\left(\alpha\frac{N_x}{\widetilde{V}}\right) + \gamma\frac{N - 2N_x - N_y}{\widetilde{V}},$$

$$\ln\left(\alpha\frac{N-N_x-N_y}{\widetilde{V}}\right) = \ln\left(\alpha\frac{N_y}{\widetilde{V}}\right) + \gamma\frac{N-N_x-2N_y}{\widetilde{V}},$$

which can be combined to

$$\ln\left(\alpha\frac{N_x}{\widetilde{V}}\right) + \gamma\frac{N-2N_x-N_y}{\widetilde{V}} = \ln\left(\alpha\frac{N_y}{\widetilde{V}}\right) + \gamma\frac{N-N_x-2N_y}{\widetilde{V}},$$

$$\ln\left(\alpha\frac{N_x}{\widetilde{V}}\right) - \gamma\frac{N_x}{\widetilde{V}} = \ln\left(\alpha\frac{N_y}{\widetilde{V}}\right) - \gamma\frac{N_y}{\widetilde{V}},$$

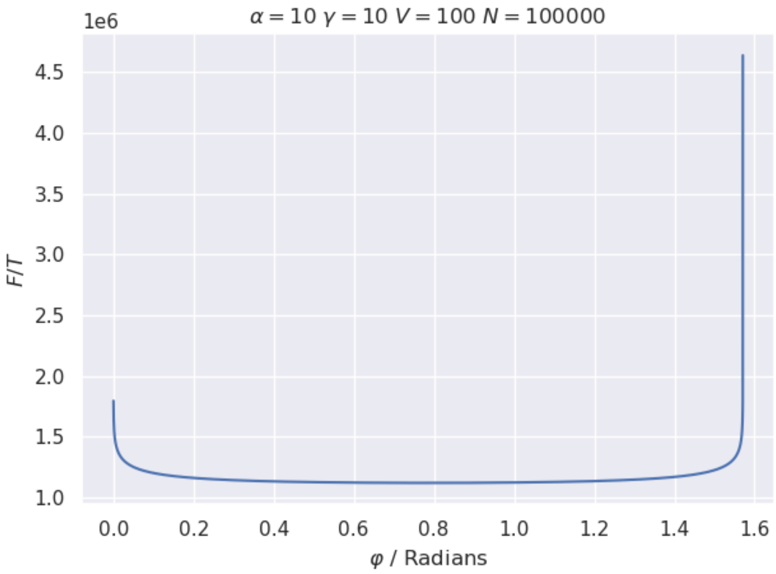
$$\ln\left(\frac{N_x}{N_y}\right) = \gamma\frac{N_x-N_y}{\widetilde{V}}.$$

Now we can switch from cartesian coordinates N_x, N_y, N_z to cylindrical coordinates $N_x = r\cos\varphi,\ N_y = r\sin\varphi,\ N_z = N_z$.

$$-\ln(\tan\varphi) = \gamma r\frac{\cos\varphi-\sin\varphi}{\widetilde{V}}$$

$$r = -\frac{\widetilde{V}}{\gamma}\frac{\ln(\tan\varphi)}{\cos\varphi-\sin\varphi}$$

Here $0 \le \varphi \le \dfrac{\pi}{2}$ so that N_x, N_y are positive and $N_x + N_y = r(\cos\varphi + \sin\varphi) \le N$. The program plot_helmholtz.py on GitHub plots the Helmholtz free energy in the range $0 \le \varphi \le \dfrac{\pi}{2}$.



The plot shows that F is seemingly a convex function of φ in the given range and for the selected values of the parameters $\alpha, \gamma, \widetilde{V}, N$. But I've looked at several plots with different parameter values and F seems to be a convex function of φ in general. It also seems like F is always minimized at $\varphi = \pi / 4$ (see plot_helmholtz.py on GitHub if you want to try for yourself). I could substitute N_x and N_y for φ in the expression of F and differentiate (twice) with respect to φ, which should reveal that $\varphi = \pi / 4$ is a global minimum, but I'd rather not. So I'll just make a conjecture that F is minimized at $\varphi = \pi / 4$.

$r(\pi / 4)$ is given by

$$r\left(\frac{\pi}{4}\right) = -\frac{\widetilde{V}}{\gamma} \lim_{\varphi \to \pi/4} \frac{\ln(\tan\varphi)}{\cos\varphi - \sin\varphi} = -\frac{\widetilde{V}}{\gamma} \lim_{\varphi \to \pi/4} \frac{\frac{1}{\tan\varphi}\frac{1}{\cos^2\varphi}}{-\sin\varphi - \cos\varphi}$$

$$= \frac{\widetilde{V}}{\gamma} \lim_{\varphi \to \pi/4} \frac{\frac{\cos\varphi}{\sin\varphi}\frac{1}{\cos^2\varphi}}{\sin\varphi + \cos\varphi} = \frac{\widetilde{V}}{\gamma} \lim_{\varphi \to \pi/4} [(\sin\varphi + \cos\varphi)\sin\varphi\cos\varphi]^{-1}$$

$$= \frac{\widetilde{V}}{\gamma}\left[2 \cdot \frac{\sqrt{2}}{2} \cdot \frac{\sqrt{2}}{2} \cdot \frac{\sqrt{2}}{2}\right]^{-1} = \frac{\widetilde{V}}{\gamma}\left[\frac{\sqrt{2}}{2}\right]^{-1} = \frac{\widetilde{V}}{\gamma}\frac{2}{\sqrt{2}} = \frac{\widetilde{V}}{\gamma}\frac{2\sqrt{2}}{2} = \sqrt{2}\frac{\widetilde{V}}{\gamma}$$

so $N_x = N_y = \sqrt{2}\frac{\widetilde{V}}{\gamma} \cdot \frac{\sqrt{2}}{2} = \frac{\widetilde{V}}{\gamma}$. Substituting $\widetilde{V} / \gamma$ for N_x, N_y in the expression of F

gives the equilibrium Helmholtz free energy.

$$\frac{F_{\text{eq}}}{T} = \frac{2\widetilde{V}}{\gamma}\ln\left(\alpha\frac{\widetilde{V}/\gamma}{\widetilde{V}}\right) + \left(N - \frac{2\widetilde{V}}{\gamma}\right)\ln\left(\alpha\frac{N - \frac{2\widetilde{V}}{\gamma}}{\widetilde{V}}\right) + \gamma\frac{\left(\frac{\widetilde{V}}{\gamma}\right)^2 + \left(N - \frac{2\widetilde{V}}{\gamma}\right)\frac{2\widetilde{V}}{\gamma}}{\widetilde{V}}$$

$$= \frac{2\widetilde{V}}{\gamma}\ln\left(\frac{\alpha}{\gamma}\right) + \left(N - \frac{2\widetilde{V}}{\gamma}\right)\ln\left(\frac{\alpha}{\gamma}\frac{N - \frac{2\widetilde{V}}{\gamma}}{\widetilde{V}/\gamma}\right) + \frac{\widetilde{V}}{\gamma} + 2\left(N - \frac{2\widetilde{V}}{\gamma}\right)$$

$$= 2\kappa\ln\left(\frac{\alpha}{\gamma}\right) + (N - 2\kappa)\ln\left(\frac{\alpha}{\gamma}\frac{N - 2\kappa}{\kappa}\right) + 2\kappa + 2(N - 2\kappa)$$

where $\kappa \equiv \widetilde{V}/\gamma$. Since $dF = -SdT - PdV + \mu dN$ the pressure is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\frac{1}{lb^2}\left(\frac{\partial F}{\partial \widetilde{V}}\right)_{T,N} = -\frac{1}{lb^2\gamma}\left(\frac{\partial F}{\partial \kappa}\right)_{T,N},$$

where

$$\frac{1}{T}\left(\frac{\partial F}{\partial \kappa}\right)_{T,N} = 2\ln\left(\frac{\alpha}{\gamma}\right) - 2\ln\left(\frac{\alpha}{\gamma}\frac{N - 2\kappa}{\kappa}\right) + (N - 2\kappa)\cdot\frac{1}{\frac{\alpha}{\gamma}\frac{N-2\kappa}{\kappa}}\cdot\frac{\alpha}{\gamma}\frac{-2\kappa - (N - 2\kappa)}{\kappa^2} + 2 - 4$$

$$= 2\ln\left(\frac{\alpha}{\gamma}\right) - 2\ln\left(\frac{\alpha}{\gamma}\frac{N - 2\kappa}{\kappa}\right) - \frac{N}{\kappa} - 2 = 2\ln\left(\frac{\alpha}{\gamma}\right) - 2\ln\left(\alpha\frac{N - 2\widetilde{V}/\gamma}{\widetilde{V}}\right) - \frac{\gamma N}{\widetilde{V}} - 2$$

$$= 2\ln\left(\frac{\alpha}{\gamma}\right) - 2\ln\left(\frac{\alpha N}{\widetilde{V}} - \frac{2\alpha}{\gamma}\right) - \frac{\gamma N}{\widetilde{V}} - 2.$$

Putting it all together gives

$$P = \frac{2T}{lb^2\gamma}\left[\ln\left(\frac{\alpha N}{\widetilde{V}} - \frac{2\alpha}{\gamma}\right) - \ln\left(\frac{\alpha}{\gamma}\right) + \frac{\gamma N}{2\widetilde{V}} + 1\right] = \frac{2T}{lb^2\gamma}\left[\ln\left(\gamma\frac{N}{\widetilde{V}} - 2\right) + \frac{\gamma N}{2\widetilde{V}} + 1\right]$$

$$= \frac{2T}{lb^2\gamma}\left[\ln\left(lb^2\gamma\frac{N}{V} - 2\right) + \frac{lb^2\gamma}{2}\frac{N}{V} + 1\right] = \frac{2T}{lb^2\gamma}\left[\ln\left(lb^2\gamma n - 2\right) + \frac{lb^2\gamma n}{2} + 1\right]$$

which shows that the pressure increases as more rods are added to a fixed volume.

There are three stability conditions for the Helmholtz free energy, one of which is

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} \leq 0$$

which can be expressed in terms of the density $n = N\,/\,V$ as

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = -\frac{n}{V}\left(\frac{\partial P}{\partial n}\right)_{T,N} \to \left(\frac{\partial P}{\partial n}\right)_{T,N} \geq 0.$$

$$\left(\frac{\partial P}{\partial n}\right)_{T,N} = \frac{2T}{lb^2\gamma}\left(\frac{lb^2\gamma}{lb^2\gamma n - 2} + \frac{lb^2\gamma}{2}\right) \geq 0$$

This further leads to the condition

$$\frac{lb^2\gamma}{lb^2\gamma n - 2} + \frac{lb^2\gamma}{2} \geq 0 \to \frac{1}{lb^2\gamma n - 2} \geq -\frac{1}{2}.$$

Assuming $lb^2\gamma n > 2$ we further have

$$1 \geq -\frac{lb^2\gamma n - 2}{2} \to 2 \geq -lb^2\gamma n + 2 \to 0 \geq -lb^2\gamma n \to n \geq 0$$

which always holds. The assumption $lb^2\gamma n < 2$ leads to $n \leq 0$ which is impossible to satisfy.

It's tempting to say that when the particle density becomes low enough, the system becomes unstable. However, violation of the inequality $lb^2\gamma n > 2$ does *not* signal a phase transition. It can be written on the equivalent form

$$lb^2\gamma n > 2 \ \rightarrow N > \frac{2V}{lb^2} = \frac{2\widetilde{V}}{\gamma} = N_x + N_y$$

so there is no new insight behind the inequality $lb^2\gamma n > 2$. So the stability condition $(\partial P \,/\, \partial V)_{T,N} \leq 0$ is always satisfied.

Another stability condition is

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \leq 0.$$

Since $F \propto T$ when treating V and N as constants, the second derivative vanishes. So this one is always satisfied.

The third one is not listed in Chp. 16 in the course book, since it assumes that the number of particles of the system is constant. In this problem this is not the case, so in the spirit of Eq. (16.16) I propose that (since N is an extensive quantity like V)

$$\left(\frac{\partial^2 F}{\partial N^2}\right)_{T,N} \geq 0$$

is a stability condition. The first and second derivatives of the equlibrium Helmholtz free energy with respect to N are

$$\frac{1}{T}\left(\frac{\partial F}{\partial N}\right)_{T,V} = \ln\left(\frac{\alpha}{\gamma}\frac{N-2\kappa}{\kappa}\right) + (N-2\kappa)\cdot\frac{1}{\frac{\alpha}{\gamma}\frac{N-2\kappa}{\kappa}}\cdot\frac{\alpha}{\gamma\kappa} + 2 = \ln\left(\frac{\alpha}{\gamma}\frac{N-2\kappa}{\kappa}\right) + 3$$

$$\frac{1}{T}\left(\frac{\partial^2 F}{\partial N^2}\right)_{T,N} = \frac{1}{\frac{\alpha}{\gamma}\frac{N-2\kappa}{\kappa}}\cdot\frac{\alpha}{\gamma\kappa} = \frac{1}{N-2\kappa}.$$

which leads to the condition

$$N - 2\kappa > 0$$

$$N > \frac{2\widetilde{V}}{\gamma} = N_x + N_y$$

which is always satisfied. So in conclusion, there are no phase transitions as the number of particles is increased. Unless I made a mistake, which is about as probable as the second law of thermodynamics at any given time.

c)

Since $dG = -SdT + VdP + \mu dN$, at constant N and T we have $dG = VdP$ and thus

$$G = \int_0^P V(P)dP.$$

The pressure in terms of the volume is given by

$$P = \frac{2T}{lb^2\gamma}\left[\ln\left(lb^2\gamma\frac{N}{V} - 2\right) + \frac{lb^2\gamma}{2}\frac{N}{V} + 1\right]$$

which is a strictly decreasing function, but not easily invertible. But I'll use the assumption given in the problem text that the concentration is low and taylor expand the natural log ($\ln x \approx x - 1,\ x \ll 1$),

$$\ln\left(lb^2\gamma\frac{N}{V} - 2\right) \approx lb^2\gamma\frac{N}{V} - 3,$$

and write the pressure in terms of volume as

$$P = \frac{2T}{lb^2\gamma}\left[lb^2\gamma\frac{N}{V} - 3 + \frac{lb^2\gamma}{2}\frac{N}{V} + 1\right] = \frac{2T}{lb^2\gamma}\left[\frac{3}{2}lb^2\gamma\frac{N}{V} - 2\right].$$

The volume in terms of pressure is then

$$V = \frac{3lb^2\gamma NT}{lb^2\gamma P + 4T},$$

and the Gibbs free energy is

$$G = 3lb^2\gamma NT \int_0^P \frac{dP}{lb^2\gamma P + 4T} = 3lb^2\gamma NT \cdot \left[\frac{\ln\left(lb^2\gamma P + 4T\right)}{lb^2\gamma}\right]_0^P$$

$$= 3NT \cdot \left[\ln\left(lb^2\gamma P + 4T\right)\right]_0^P = 3NT \ln\left(\frac{lb^2\gamma P + 4T}{4T}\right).$$

The two stability conditions for the Gibbs free energy (at constant N) are

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \leq 0, \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \leq 0.$$

Taking the first and second derivative with respect to pressure:

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = 3NT \cdot \frac{4T}{lb^2\gamma P + 4T} \cdot \frac{lb^2\gamma}{4T} = \frac{3lb^2\gamma NT}{lb^2\gamma P + 4T}$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} = -\frac{3lb^2\gamma NT}{\left(lb^2\gamma P + 4T\right)^2} \cdot lb^2\gamma = -\frac{3\left(lb^2\gamma\right)^2 NT}{\left(lb^2\gamma P + 4T\right)^2}$$

So the first stability condition is always satisfied. Taking the first and second derivative with respect to temperature:

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = 3N \ln\left(\frac{lb^2\gamma P + 4T}{4T}\right) + 3NT \cdot \frac{4T}{lb^2\gamma P + 4T} \cdot \frac{16T - 4lb^2\gamma P - 16T}{16T^2}$$

$$= 3N \ln\left(\frac{lb^2\gamma P + 4T}{4T}\right) - \frac{3lb^2\gamma NP}{lb^2\gamma P + 4T}$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} = 3N \cdot \frac{4T}{lb^2\gamma P + 4T} \cdot \frac{16T - 4lb^2\gamma P - 16T}{16T^2} + \frac{3lb^2\gamma NP}{\left(lb^2\gamma P + 4T\right)^2} \cdot 4$$

$$= -\frac{3lb^2\gamma NP}{T\left(lb^2\gamma P + 4T\right)} + \frac{12lb^2\gamma NP}{\left(lb^2\gamma P + 4T\right)^2}$$

We thus require that

$$-\frac{3lb^2\gamma NP}{T\left(lb^2\gamma P + 4T\right)} + \frac{12lb^2\gamma NP}{\left(lb^2\gamma P + 4T\right)^2} \leq 0$$

$$\frac{12lb^2\gamma NP}{\left(lb^2\gamma P + 4T\right)^2} \leq \frac{3lb^2\gamma NP}{T\left(lb^2\gamma P + 4T\right)}$$

$$\frac{4}{lb^2\gamma P + 4T} \leq \frac{1}{T}$$

$$4T \leq lb^2\gamma P + 4T$$

$$P \geq 0$$

which is always true. So there are no phase transitions when the pressure is changed either. Again, unless I've made a mistake.

4 a)

We learned in FYS2160 that the number of ways one can distribute M quanta over N

oscillators (or M cookies over N people or whatever) is given by

$$\Omega(N, M) = \frac{(M+N-1)!}{M!(N-1)!}.$$

This is justified by the classic "stars and bars" graphical representation, where one draws M stars separated by $N-1$ bars, for a total of $M+N-1$ symbols. Then one asks, in how many ways can you separate M stars by $N-1$ bars, or, in how many ways can you let $N-1$ out of $M+N-1$ symbols be bars? That is given by

$$\binom{M+N-1}{N-1} = \frac{(M+N-1)!}{M!(N-1)!}.$$

b)

The entropy is given by

$$S = k \ln \Omega(N, M) = k \ln\left[\frac{(M+N-1)!}{M!(N-1)!}\right]$$

$$= k \ln(M+N-1)! - k \ln M! - k \ln(N-1)!$$

Assuming large N and E (and thus M) we can use Stirling's formula $\ln N! \approx N \ln N - N$

$$S / k \approx \ln(M+N)! - \ln M! - \ln(N)!$$

$$\approx (M+N)\ln(M+N) - (M+N) - M \ln M + M - N \ln N + N$$

$$= (M+N)\ln(M+N) - M \ln M - N \ln N$$

The temperature can be found from

$$\frac{1}{kT} = \frac{1}{k}\left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{k}\left(\frac{\partial S}{\partial M}\right)_N \left(\frac{\partial M}{\partial E}\right)_N$$

where

$$\frac{1}{k}\left(\frac{\partial S}{\partial M}\right)_N = \ln(M+N) + (M+N)\cdot\frac{1}{(M+N)}\cdot 1 - \ln M - M\cdot\frac{1}{M}$$

$$= \ln(M+N) - \ln M = \ln\left(\frac{M+N}{M}\right) = \ln\left(1+\frac{N}{M}\right),$$

and

$$E = \hbar\omega\sum_i^N (n_i + 1/2) = \hbar\omega\left(\sum_i^N n_i + \sum_i^N 1/2\right) = \hbar\omega\left(M + \frac{N}{2}\right)$$

giving $(\partial M / \partial E)_N = 1/\hbar\omega$. The temperature in terms of the energy is thus

$$\frac{1}{kT} = \frac{1}{\hbar\omega}\ln\left(1+\frac{N}{M}\right) = \frac{1}{\hbar\omega}\ln\left(1+\frac{N}{E/\hbar\omega - N/2}\right)$$

which can be inverted to find the energy in terms of temperature:

$$e^{\hbar\omega/kT} - 1 = \frac{N}{E/\hbar\omega - N/2}$$

$$\frac{E}{\hbar\omega} - \frac{N}{2} = \frac{N}{e^{\hbar\omega/kT} - 1}$$

$$E = \frac{N\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{N\hbar\omega}{2}$$

Since $S/k = (M+N)\ln(M+N) - M\ln M - N\ln N$, the entropy in terms of energy is

$$S/k = \left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)\ln\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right) - \left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)\ln\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right) - N\ln N,$$

and so the entropy in terms of temperature is

$$S \,/\, k = \left(\frac{N}{e^{\hbar\omega/kT}-1}+\frac{N}{2}+\frac{N}{2}\right)\ln\left(\frac{N}{e^{\hbar\omega/kT}-1}+\frac{N}{2}+\frac{N}{2}\right)$$

$$-\left(\frac{N}{e^{\hbar\omega/kT}-1}+\frac{N}{2}-\frac{N}{2}\right)\ln\left(\frac{N}{e^{\hbar\omega/kT}-1}+\frac{N}{2}-\frac{N}{2}\right)-N\ln N$$

$$=\left(\frac{N}{e^{\hbar\omega/kT}-1}+N\right)\ln\left(\frac{N}{e^{\hbar\omega/kT}-1}+N\right)-\frac{N}{e^{\hbar\omega/kT}-1}\ln\left(\frac{N}{e^{\hbar\omega/kT}-1}\right)-N\ln N$$

$$=\frac{Ne^{\hbar\omega/kT}}{e^{\hbar\omega/kT}-1}\ln\left(\frac{Ne^{\hbar\omega/kT}}{e^{\hbar\omega/kT}-1}\right)-\frac{N}{e^{\hbar\omega/kT}-1}\ln\left(\frac{N}{e^{\hbar\omega/kT}-1}\right)-N\ln N$$

$$=\frac{N}{1-e^{-\hbar\omega/kT}}\ln\left(\frac{N}{1-e^{-\hbar\omega/kT}}\right)-\frac{N}{e^{\hbar\omega/kT}-1}\ln\left(\frac{N}{e^{\hbar\omega/kT}-1}\right)-N\ln N$$

c)

Since $E=\dfrac{N\hbar\omega}{e^{\hbar\omega/kT}-1}+\dfrac{N\hbar\omega}{2}$ the heat capacity is

$$C=\left(\frac{\partial E}{\partial T}\right)_N=\frac{-N\hbar\omega\cdot e^{\hbar\omega/kT}\cdot\left(-\frac{\hbar\omega}{kT^2}\right)}{\left(e^{\hbar\omega/kT}-1\right)^2}$$

$$=\frac{N}{k}\left(\frac{\hbar\omega}{T}\right)^2\frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}$$