Solution: A problem concerning free energy

1. Using $F = E - TS$ and $dE = TdS - pdV + \mu dN$,

$$dF = dE - TdS - SdT = -SdT - pdV + \mu dN \tag{1}$$

reading off S, p, μ

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{2}$$

Energy, Gibbs' Free Energy, and the Grand Potential can be found by writing them in terms of Helmholtz Free Energy and using the results above.
For Energy,

$$E = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{V,N} = -T^2\left(\frac{\partial (F/T)}{\partial T}\right)_{V,N} \tag{3}$$

Gibbs free energy

$$G = F + pV = F - V\left(\frac{\partial F}{\partial V}\right)_{T,N} = -V^2\left(\frac{\partial (F/V)}{\partial V}\right)_{T,N} \tag{4}$$

Grand potential

$$\Omega = F - \mu N = F - N\left(\frac{\partial F}{\partial N}\right)_{T,V} = -N^2\left(\frac{\partial (F/N)}{\partial N}\right)_{T,V} \tag{5}$$

2. From (5) we have

$$\begin{aligned}\Omega = -T\ln Z_{\text{G.C.}} &= F - N\left(\frac{\partial F}{\partial N}\right)_{T,V} \\ &= -T\ln Z_{\text{C}} - N\left(\frac{\partial(-T\ln Z_{\text{C}})}{\partial N}\right)_{T,V} \\ &= -T\ln Z_{\text{C}} + NT\left(\frac{\partial \ln Z_{\text{C}}}{\partial N}\right)_{T,V}\end{aligned} \tag{6}$$

So,

$$\ln Z_{\text{G.C.}} = \ln Z_{\text{C}} - N\left(\frac{\partial \ln Z_{\text{C}}}{\partial N}\right)_{T,V} \tag{7}$$

3. The standard result from statistical mechanics is

$$Z_{\text{G.C.}} = \sum_N e^{-\alpha N} Z_{\text{C}}(N) \tag{8}$$

This differs from 7 due to assumptions made when moving from Free Energy and canonical ensemble to the Grand Potential and grand canonical ensemble. When we move from the grand canonical to canonical and $F(T, v, N)$ we are fixing the particle number to be the average particle number in the grand canonical ensemble, $\bar{N}$. This assumptions becomes more exact in the macroscopic limit $N \to \infty$. As N grows the fluctuations (which go as $\delta N = \sqrt{N}$) become infinitesimally small compared to N. That is $\frac{\delta N}{N} \ll 1$.

Examining $Z_{\mathrm{G.C.}}$ the main contribution is going to come from the region $\bar{N} \pm \delta N$. So,

$$Z_{\mathrm{G.C.}} \approx \delta N \mathrm{e}^{-\alpha \bar{N}} Z_{\mathrm{C}}(\bar{N}) \tag{9}$$

taking the log of both sides,

$$\ln Z_{\mathrm{G.C.}} \approx \ln Z_{\mathrm{C}}(\bar{N}) - \alpha \bar{N} + \ln \delta N \tag{10}$$

$$= \ln Z_{\mathrm{C}}(\bar{N}) - \bar{N} \left(\frac{\partial \ln Z_{\mathrm{C}}}{\partial \bar{N}} \right) + \ln \delta N \tag{11}$$

The last term $\log \delta N$ is negligibly small compared to the rest, so in the macroscopic limit 8 approaches 7.