Derivation of the formula relating chemical potentials and chemical concentrations

We consider a lattice model with Ω sites at thermal equilibrium (canonical ensemble). We denote the number of each species of ligand by L_i and from statical physics we have that chemical potential of each is $\mu_i = \frac{\partial F}{\partial L_i}$ with $F = U - TS$. We have $U = \sum_i L_i \epsilon_i$ with the ϵ_i being the inherent chemical energies per molecule of each ligand type. And finally we have $S = \mathrm{k}\ln(W)$ with W being the number of lattice microstates for any particular set of L_i given by $W = \binom{\Omega}{L_1 \; L_2 \; \ldots}$. Now we can calculate

$$\mu_i = \epsilon_i - \mathrm{k}T\frac{\partial}{\partial L_i}\ln(W) \tag{1}$$

but first approximate using Stirling's approximation

$$\begin{aligned}
\ln(W) = \ln\left(\binom{\Omega}{L_1 \;\; L_2 \;\; \cdots}\right) &= \ln\left(\frac{\Omega!}{L_1!L_2!\cdots(\Omega - L_1 - L_2 - \cdots)!}\right) & (2)\\
&= \ln(\Omega!) - \ln(L_1!) - \ln(L_2!) - \cdots - \ln((\Omega - L_1 - L_2 - \cdots)!) & (3)
\end{aligned}$$

now assuming all the individual L_i and $(\Omega - L_1 - L_2 - \cdots)$ are large we get to

$$\begin{aligned}
\ln(W) \simeq\ & \Omega\ln(\Omega) - \Omega - L_1\ln(L_1) + L_1 - L_2\ln(L_2) + L_2 - \cdots & (4)\\
& - (\Omega - L_1 - L_2 - \cdots)\ln((\Omega - L_1 - L_2 - \cdots)) + (\Omega - L_1 - L_2 - \cdots) & (5)\\
=\ & \Omega\ln(\Omega) - L_1\ln(L_1) - L_2\ln(L_2) - \cdots - (\Omega - L_1 - L_2 - \cdots)\ln((\Omega - L_1 - L_2 - \cdots)) & (6)\\
=\ & \Omega\ln\left(\frac{\Omega}{\Omega - L_1 - L_2 - \cdots}\right) - L_1\ln\left(\frac{L_1}{\Omega - L_1 - L_2 - \cdots}\right) - \cdots & (7)\\
=\ & -\Omega\ln\left(1 - \frac{L_1 + L_2 + \cdots}{\Omega}\right) - L_1\ln\left(\frac{L_1}{\Omega - L_1 - L_2 - \cdots}\right) - \cdots & (8)\\
& & (9)
\end{aligned}$$

now there's two alternative methods I want to try

0.1 Approximate first

Approximate by saying $\frac{L_1 + L_2 + \cdots}{\Omega}$ is small or in other words $\Omega \gg L_1 + L_2 + \cdots$ to get

$$\begin{aligned}
\ln(W) \simeq\ & -\Omega\left(-\frac{L_1 + L_2 + \cdots}{\Omega}\right) - L_1\ln\left(\frac{L_1}{\Omega}\right) - \cdots & (10)\\
=\ & L_1 + L_2 + \cdots - L_1\ln\left(\frac{L_1}{\Omega}\right) - \cdots & (11)\\
=\ & L_1\left(1 - \ln\left(\frac{L_1}{\Omega}\right)\right) - \cdots & (12)\\
& & (13)
\end{aligned}$$

this leads to

$$\begin{aligned}
\mu_i =\ & \epsilon_i - \mathrm{k}T\frac{\partial}{\partial L_i}\ln(W) & (14)\\
\simeq\ & \epsilon_i - \mathrm{k}T\left(1 - \ln\left(\frac{L_i}{\Omega}\right) + L_i\frac{-1}{\frac{L_i}{\Omega}}\frac{1}{\Omega}\right) = \epsilon_i + \mathrm{k}T\ln\left(\frac{L_i}{\Omega}\right) & (15)
\end{aligned}$$

0.2 The full version

Or just stick through with the pretty gross expressions to calculate

$$\frac{\partial}{\partial L_i}\ln(W) = \frac{\partial}{\partial L_i}\left(-\Omega\ln\left(1-\frac{L_1+L_2+\cdots}{\Omega}\right)-\sum_j L_j\ln\left(\frac{L_j}{K}\right)\right) \quad \text{with} \quad K=\Omega-L_1-L_2-\cdots \tag{16}$$

$$= -\Omega\frac{1}{1-\frac{\Omega-K}{\Omega}}(-\frac{1}{\Omega})-\frac{\partial}{\partial L_i}\sum_j L_j\ln\left(\frac{L_j}{K}\right) \tag{17}$$

$$= \frac{\Omega}{\Omega-\Omega+K}-\sum_j\left(\delta_{ij}\ln\left(\frac{L_j}{K}\right)+L_j\frac{\partial}{\partial L_i}\ln\left(\frac{L_j}{K}\right)\right) \tag{18}$$

$$= \frac{\Omega}{K}-\ln\left(\frac{L_i}{K}\right)-\sum_j L_j\frac{K}{L_j}\frac{\partial}{\partial L_i}\frac{L_j}{K} \tag{19}$$

$$= \frac{\Omega}{K}-\ln\left(\frac{L_i}{K}\right)-\sum_j K\left(\frac{\delta_{ij}}{K}+L_j\frac{-1}{K^2}(-1)\right) \tag{20}$$

$$= \frac{\Omega}{K}-\ln\left(\frac{L_i}{K}\right)-\sum_j \delta_{ij}+L_j\frac{1}{K} \tag{21}$$

$$= -1+\frac{\Omega-\sum_j L_j}{K}-\ln\left(\frac{L_i}{K}\right) \tag{22}$$

$$= -\ln\left(\frac{L_i}{K}\right) \tag{23}$$

$$\tag{24}$$

which is beautiful as it agrees perfectly and gives a simple expression for

$$\mu_i = \epsilon_i - \mathrm{k}T\frac{\partial}{\partial L_i}\ln(W) = \epsilon_i + \mathrm{k}T\ln\left(\frac{L_i}{\Omega-L_1-L_2-\cdots}\right) \tag{25}$$

0.3 Relation to concentration

In our simplified lattice model it seems clear that $\frac{L_i}{\Omega}$ is some measure of a concentration. I'm not entirely sure how to relate it to a "real" experimental concentration but I'm sure it's possible, maybe worth doing sometime.