# Chemical potential profile

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## 1  Chemical Potentials at Equilibrium

Consider a reference system with free energy $G^\circ$ over domain $\Omega$. Then, adding one atom of type $\alpha$ yields a system with a new free energy:

$$G = G^\circ + \mu_\alpha \tag{1}$$

Or, adding a type of $\alpha'$ instead:

$$G' = G^\circ + \mu_{\alpha'} \tag{2}$$

Therefore, the free energy difference between the system with one extra $\alpha$ atom and one extra $\alpha'$ atom is:

$$G' - G = \mu_{\alpha'} - \mu_\alpha \tag{3}$$

Assuming $0\,\mathrm{K}$ and $0\,\mathrm{bar}$, we can equate this to a difference in internal energy, therefore:

$$\mu_{\alpha'} - \mu_\alpha = \left\langle E_\sigma^{(\alpha')} - E_\sigma^{(\alpha)} \right\rangle_\Omega \tag{4}$$

where $E_\sigma^{(\alpha)}$ is the energy of the lattice with an atom of type $\alpha$ occupying site $\sigma$, and $\langle \cdot \rangle_\Omega$ indicates averaging over the domain $\Omega$. Additionally, we have the Euler equation (at $0\,\mathrm{K}$ and $0\,\mathrm{bar}$):

$$u = \sum_\alpha x_\alpha \mu_\alpha \tag{5}$$

where $u$ is the potential energy per atom of some reference configuration. If we have a reference configuration defined by a map $t$, where $t(\sigma)$ is the type occupying site $\sigma$ in the reference configuration, then:

$$\frac{1}{N} \left\langle E_\sigma^{(t(\sigma))} \right\rangle_\Omega = \sum_\alpha x_\alpha \mu_\alpha \tag{6}$$

where $N$ is the number of lattice sites and $x_\alpha$ is the atomic fraction of type $\alpha$.

The equations from 4 and 6 form either a perfectly determined system or an overdetermined system, and can thus by solved with least-squares for chemical potentials.

## 2 Chemical Potentials at Non-Equilibrium

Instead, we assume that the chemical potentials vary over subdomains $\omega \subseteq \Omega$ (where $\Omega$ is the entire spatial domain). Then, we can solve for the chemical potential in each subdomain $\omega$ with:

$$
\begin{aligned}
\mu_{\alpha'}(\omega) - \mu_\alpha(\omega) &= \frac{|\omega|}{|\Omega|} \left\langle E_\sigma^{(\alpha')} - E_\sigma^{(\alpha)} \right\rangle_\omega \\
\sum_\alpha x_\alpha(\omega) \mu_\alpha(\omega) &= \frac{1}{N} \frac{|\omega|}{|\Omega|} \left\langle E_\sigma^{(t(\sigma))} \right\rangle_\omega
\end{aligned}
\tag{7}
$$

where $|\Omega| = \int d\Omega$ is the volume of the domain $\Omega$. Here, the volume rescaling is necessary or else the cohesive energy of the subdomain $\omega$ is overestimated.