Chemical potential profile

Jacob Jeffries

February 2024

1 Chemical Potentials at Equilibrium

Consider a reference system with free energy G° over domain Ω. Then, adding one atom of type α yields a system with a new free energy:

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

Or, adding a type of α' instead:

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

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

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

Assuming 0 K and 0 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 α occupying site σ, and $\langle \cdot \rangle_\Omega$ indicates averaging over the domain Ω. Additionally, we have the Euler equation (at 0 K and 0 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 σ 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_α is the atomic fraction of type α.

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 Ω is the entire spatial domain). Then, we can solve for the chemical potential in each subdomain ω with:

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