chemical potential calculation

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1 Insertions

We first perform insertions onto a lattice starting for an initial configuration. This initial configuration has type $t(\sigma)$ at each site σ. The solution has atom types $\alpha \in \mathcal{A}$ and the atomic fraction of α in the solution is x_α.

Then, to calculate chemical potentials, we first note that, given a system with free energy G°, we can add an extra atom of type α, yielding a free energy:

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

So:

$$G_\beta - G_\alpha = \mu_\beta - \mu_\alpha \tag{2}$$

which then measures the free energy difference from swapping an α atom to an β atom. Then, approximating (at 0 K and 0 bar) the free energy as internal energy yields:

$$\left\langle E_\sigma^{(\beta)} - E_\sigma^{(\alpha)} \right\rangle = \mu_\beta - \mu_\alpha \tag{3}$$

where $E_\sigma^{(\alpha)}$ is the energy of the lattice with an atom of type α at site σ. Additionally, we can form an Euler equation for the reference configuration:

$$\frac{1}{N} E_\sigma^{(t(\sigma))} = \sum_\alpha \mu_\alpha x_\alpha \tag{4}$$

where N is the number of sites in the lattice. For an alloy with k elements, we can form $\frac{1}{2}k(k-1)$ equations for each α-β pair. So, including the Euler equation below, we can form a system of $\frac{1}{2}k(k-1)+1$ equations, which forms either a fully determined system for $k = 2$, or an overdetermined system for $k > 2$. Both cases can be solved using least squares.

2 Fitting

We have multiple data points, i.e. a set of chemical potentials for each composition, by creating multiple solutions with specified compositions. Then, the free energy density is (assuming a regular solution model):

$$f = f^\circ + \sum_\alpha \mu_\alpha^\circ c_\alpha + \sum_{\alpha \neq \beta} \Omega_{\alpha\beta} c_\alpha c_\beta \tag{5}$$

where f° is a reference free energy, μ_α° is a reference chemical potential of species α, c_α is the number density of species α, and $\Omega_{\alpha\beta}$ is the heat of mixing between α and β. The chemical potential of α is then:

$$\mu_\alpha = \frac{\partial f}{\partial c_\alpha} = \mu_\alpha^\circ + \sum_{\beta \neq \alpha} \Omega_{\alpha\beta} c_\beta \tag{6}$$

Or, in terms of atomic fractions x_β:

$$\mu_\alpha = \mu_\alpha^\circ + \sum_{\beta \neq \alpha} A_{\alpha\beta} x_\beta \tag{7}$$

where v is the atomic volume and $A_{\alpha\beta} = v\Omega_{\alpha\beta}$.