

chemical potential calculation

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1 Insertions

We first perform insertions onto a lattice starting from 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:

$$G_\beta = G^\circ + \mu_\beta \quad (1)$$

So:

$$G_\beta - G_\alpha = \mu_\beta - \mu_\alpha \quad (2)$$

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

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

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:

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

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

The free energy per atom is, at 0 K and 0 bar:

$$g = \sum_{\alpha \in \mathcal{A}} \mu_\alpha x_\alpha \quad (5)$$

where \mathcal{A} is the set of alloying elements. Then, assuming a regular solution model:

$$g = \sum_{\alpha \in \mathcal{A}} \mu_{\alpha}^{\circ} x_{\alpha} + \sum_{(\alpha, \beta) \in \mathcal{C}_2(\mathcal{A})} \Omega_{\alpha\beta} x_{\alpha} x_{\beta} \quad (6)$$

where $\mathcal{C}_2(\mathcal{A})$ denotes the size-2 combinations of \mathcal{A} , i.e. every unique pair of alloying elements. This corresponds to chemical potentials:

$$\mu_{\alpha} = \frac{\partial g}{\partial x_{\alpha}} = \mu_{\alpha}^{\circ} + \sum_{\beta \in \mathcal{A} \setminus \{\alpha\}} \Omega_{\alpha\beta} x_{\beta} \quad (7)$$

where $\Omega_{\alpha\beta} = \Omega_{\beta\alpha}$ is symmetric, and $\Omega_{\alpha\alpha} = 0$.

The naive approach, given data consisting of a bunch of chemical potentials as a function of composition, would be to directly fit the data to (7). However, this approach does not (and cannot) account for the necessary constraints on $\Omega_{\alpha\beta}$ using traditional linear regression methods.

Of course, one can instead come up with some loss function and simply optimize it using some minimization scheme, but then we miss valuable information on the fit, such as hypothesis tests and the root-mean-square-error of the fit.

So, instead, given the data of chemical potentials and compositions, we reduce our data to instead calculate g using (6), and fit that reduced data to the regular solution model in (7), since adding interaction terms in a multiple linear regression model is quite standard.