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:

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

So:

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

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

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

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-α' 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, we can fit the chemical potentials as a function of concentration:

$$\mu_\alpha = \mu_\alpha^\circ + \sum_\beta A_{\alpha\beta}(x_\beta - x_\beta^\circ) \tag{5}$$

where μ_α° and $A_{\alpha\beta}$ are fitting parameters and x_α° is some reference concentration. Then, without loss of generality, we can always set $x_\beta^\circ = 0$, since:

$$\mu_\alpha = \mu_\alpha^\circ + \sum_\beta A_{\alpha\beta} x_\beta^\circ + \sum_\beta A_{\alpha\beta} x_\beta \tag{6}$$

where $\mu_\alpha^\circ + \sum_\beta A_{\alpha\beta} x_\beta^\circ$ is a constant. So, setting $x_\beta^\circ = 0$, we fit:

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

This can be achieved with multivariate multiple linear regression. Note that, though, there are only $k-1$ independent variables since $\sum_\alpha x_\alpha = 1$. So, one element γ must be excluded from the fit for unique $A_{\alpha\beta}$'s. Therefore:

$$\mu_\alpha = \mu_\alpha^\circ + \sum_{\beta \neq \gamma} A_{\alpha\beta} x_\beta \tag{8}$$

The function `lm` in `R` automatically excludes columns to enforce linear independence between independent variables.