Calculating the stability of surfaces and interfaces

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This is a brief description of a practical scheme often used to study the stability of surfaces and interfaces within the framework of ab initio thermodynamics. In fact, a surface can be seen as a special case of a heterogeneous interface, which separates two different phases in equilibrium. For a surface, one of these phases would be vapor. In the following, what is said about a surface or interface will, in general, apply to both.

1 Interface and Surface Energy

For an interface- or surface system in thermodynamical equilibrium, the chemical potential of each component must be identical in every phase (equilibrium condition). A consequence of this is the Gibbs phase rule, stating that for a system with π phases and C components in equilibrium, the number of degrees of freedom F is given by

$$F = C - \pi + 2$$

A degree of freedom is an intensive variable that can be varied while still maintaining equilibrium. Our objective is to study the relative stabilities of various surface structures as a function of these variables. Let's assume there are two phases, with a total of three components (atomic species). This gives three degrees of freedom, which can be e.g. temperature, partial pressure of a gas, or chemical composition of a solid phase.

We can describe the stability in terms of the surface free energy σ. The surface free energy for a surface system with area A, where the number and chemical potential of each atomic species are N_i and μ_i, respectively, is defined as

$$\sigma = \frac{1}{A} \left(G(T, P, N_i) - \sum N_i \mu_i(T, P) \right)$$

where G is the Gibbs free energy. For a given temperature T and pressure P, the thermodynamically most stable system minimizes its surface free energy by adapting the composition of the surface region. This may lead to local surface compositions different from bulk compositions, i.e. the surface system has excesses of one or more components. This deviation from stoichiometry affects the free energy via the chemical potentials. Assuming there is only one excess component, the introduced change in free energy from non-stoichiometry can be expressed in terms of the chemical potential of this component. If the system contained an additional solid phase, an additional reference component would be required. Provided that the chemical potentials of the components are known, σ can be evaluated for a set of candidate surfaces to predict the equilibrium structure.

As an example, consider two-phase systems with a binary compound $X_m Y_n$ in contact with, in one case a gas phase Y_2, and in the other case an elemental bulk phase Z at equilibrium.

$$X_m Y_n(bulk) \quad X, Y, Z(interface) \quad Z(bulk)$$
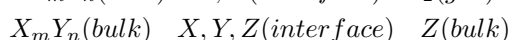
The surface (interface) region may exchange atoms with the bulk and gas phases, which act as reservoirs. Assuming equilibrium in the calculation of the surface free energy, the dependence of the free energy on the intensive variables enters through the chemical potentials. These are equal to the corresponding chemical potential in the bulk phases and therefore can be obtained from bulk calculations. With a few additional

assumptions, their dependence on other intensive variables can be estimated. For example, we use the ideal gas expression to get the pressure dependency.

For the free surface, with X_mY_n as substrate, the surface region may contain a number of Y atoms that differ from that required by stoichiometry. The free surface energy becomes

$$\sigma = \frac{1}{A}\left(G(T,P,N_X,N_Y) - N_X\mu_X(T,P) - N_Y\mu_Y(T,P),\right)$$

The chemical potentials of the X and Y components at the surface are not independent, but related via the equilibrium condition for exchange of atoms with the reservoirs, in this case;

$$\mu_{X_mY_n,bulk} = m\mu_X + n\mu_Y$$

Which allow us to express the free energy in terms of only the chemical potential of the excess quantity Y and the bulk quantity $\mu_{X_mY_n,bulk}$:

$$\sigma = \frac{1}{A}\left(G(T,P,N_X,N_Y) - \frac{N_X}{m}\mu_{X_mY_n,bulk}(T,P) - \left(N_Y - \frac{n}{m}N_X\right)\mu_Y(T,P)\right)$$

For the interface in the example above, the only difference in the expression for the surface free energy is an additional term for the elemental phase Z:

$$\sigma = \frac{1}{A}\left(G(T,P,N_X,N_Y) - \frac{N_X}{m}\mu_{X_mY_n,bulk}(T,P) - \left(N_Y - \frac{n}{m}N_X\right)\mu_Y(T,P) - N_Z\mu_Z(T,P)\right)$$

For μ_Y a simple approach is to allow it to vary between values for which the phases in the system are stable. That is, it can be regarded as a free parameter in the calculations within a specified range, and we will now discuss how limiting values of this interval can be found.

2 Range of Chemical Potential

The chemical potentials, of components X and Y, have to be lower than the Gibbs free energy of respective bulk phases. Otherwise pure bulk phases of X and Y would start precipitate out of the compound, and the $\mu_{X_m,Y_n,bulk}$ phase would not be stable. Thus,

$$\mu_X(T,P) \leq g_{X,bulk}(T,P) \quad \text{and} \quad \mu_Y(T,P) \leq g_{Y,bulk}(T,P) \tag{1}$$

Furthermore, the chemical potentials are related to Gibbs free energy of the bulk phase $\mu_{X_m,Y_n,bulk}$,

$$m\mu_X(T,P) + n\mu_Y(T,P) = g_{X_mY_n,bulk}(T,P) - \frac{m}{n}g_{X,bulk}(T,P)\,\mu_{X_m,Y_n,bulk},$$

or, using (1),

$$\mu_Y(T,P) = \frac{1}{n}g_{X_m}$$

So that

$$\mu_Y(T,P) - g_{Y,bulk}(T,P) \geq \frac{1}{n}g_{X_mY_n,bulk}(T,P) - \frac{m}{n}g_{X,bulk}(T,P) - g_{Y,bulk}(T,P) = \frac{1}{n}\Delta G_f(T,P)$$

$\Delta G_f(T,P)$ is the Gibbs free energy of formation of the $\mu_{X_m,Y_n,bulk}$ phase.

The previous inequalities establish natural limiting values of the Y chemical potential.

Since for a pure system the chemical potential is equal to the Gibbs energy per particle, we can write this interval for $\mu_Y(T,P)$ as;

$$\frac{1}{n}\Delta G_f(T,P) << \mu_Y(T,P) - \mu_{Y,bulk}(T,P) \leq 0$$

In reality, it is possible that other stable phases exist within this range. If such phases are known, the interval can be adjusted to the limits given by their stability range.

In cases where the standard state of the component Y is a gas, it is appropriate to use the partial pressure of the gas as an intensive variable. Assuming i:math:Y to be a diatomic ideal gas with known chemical potential at standard pressure P^0, we can evaluate the chemical potential at any other pressure using the ideal gas expression

$$\mu_Y(T,P_{Y_2}) = \mu_Y(T,P^0) + \tfrac{1}{2}k_B\log\frac{P_{Y_2}}{P^0}$$

In principle, the free energy of a gas molecule can be calculated; however, in many cases computations are more precise for solid compounds than for gases. A way to exploit this fact is to consider a thermodynamic cycle corresponding to the formation of a solid compound where Y is involved. One then uses tabulated thermodynamical data to assess the free energy. For example, we can consider the reaction

$$mX(g) + \frac{n}{2}Y_2(g) \rightarrow X_mY_n(s)$$

at standard pressure P^0 and temperature T, where the Gibbs free energy of formation is given as

$$g_{X_mY_n,bulk}(T,P^0) = m\mu_X(T,P^0) + \frac{n}{2}\mu_Y(T,P^0) + \Delta g_f(T,P^0)$$

Any cycle can be used as long as the heat of formation $\Delta G_f(T^0, P^0)$ is available from thermodynamical tables.

3 Using Density-Functional Theory as Input

So far, the formalism has been based on Gibbs free energies as given by

$$G = E + PV - TS$$

where all quantities have their usual thermodynamic meaning. In general, total energies from DFT correspond to the electronic contribution to Helmholtz free energies at zero temperature, neglecting zero-point vibrations.

Using the energies from DFT as an estimate for the Gibbs free energy, the main approximation we make is to ignore the vibrational modes of the lattice. This approximation should be better for interfaces, where the vibrational contributions to the free energy should be close to the reference bulk systems due to similarity in atomic densities. For solids, the pressure-volume term is normally small and can be neglected in most cases [1].

It is recommended to use the heat of formation as given by Job.out in *MedeA* as a measure of the internal energy of the structure rather than the VASP energy. The difference is that using the heat of formation for the internal energy corresponds to expressing the energy with respect to the constituting elements in their standard state, while the VASP energy is based on the non-spin polarized energy of the atomic states. We recommend using *MedeA*'s heat of formation, as this quantity is more physical; in particular, it can be compared to experimental values and contains information about the compound's stability.

[1] M W Finnis, A Y Lozovoi, and A Alavi, "The Oxidation of NiAl: What Can We Learn From Ab Initio Calculations?", Ann. Rev. Mater. Res. **35**, 167-207 (2005).

DOCUMENTATION