Thermal Equilibrium

Basics

- *Thermal equilibrium* is a central concept in thermodynamics. It describes the unique state of an ensemble of particles (i.e. the atoms of an crystal) that the system assumes by itself sooner or later (and later can mean really, really late) for a given set of intrinsic parameters (e.g., temperature, pressure, chemical potential) and extrinsic parameters (e.g., volume, entropy, number of particles).
  - The state of the system is unambiguously described by a state function which is called a **thermodynamic potential** and there are several thermodynamic potentials that can be used for a system description.
  - Whereas in principle *any* thermodynamic potential can be used for *any* situation (because they are related by a so-called **Legendre transformation**); it is useful to use specific thermodynamic potentials for specific systems.
- Depending on the kind of "contact" between the system under consideration and the environment (e.g. totally isolated, energy flow permitted, particle flow permitted, and so on), typical situations are:
- *Constant volume **V**, temperature **T**, and number of particles **N***.
  - The proper thermodynamic potential is the **free energy *F*(*V, T, N*)** (sometimes called **Helmholtz energy**).
- *Constant pressure **p**, constant temperature **T**, and constant particle (= atom) number **N***
  - This is the situation typical for a crystal. The appropriate thermodynamic potential is the **free enthalpy *G(p, T, N)*** (sometimes called **Gibbs energy**).
- The free enthalpy (defined as $G = H - TS$) with H = enthalpy of the system and S = entropy is thus the most important thermodynamic potential when considering defects.
  - Thermal equilibrium for this case then simply means a state with an (absolute) minimum of the free enthalpy of the crystal.