Course: Statistical Mechanics / Review of thermodynamics / Phase transitions and phase diagrams

Experimentally, any element or compound can be found, depending on the thermodynamic conditions in which it is, in different phases. When we say that a system is in a particular phase we mean that its physical properties (like density or magnetization) are uniform. We have also seen that the states of equilibrium for a thermodynamic system are minima of appropriate thermodynamic potentials. Let us consider for example a $PVT$ system and its Gibbs free energy $G(T, P)$; the molar Gibbs free energy will be:

$$g(T, P) = \frac{G(T, P)}{N}$$

and we can describe the thermodynamic properties of the system in $(g, T, P)$ space. Let us suppose for example that the system can be found in two phases $\alpha$ and $\beta$ (for example liquid and solid), and call $g_\alpha$ and $g_\beta$ their respective molar Gibbs potentials; then for given values of $T$ and $P$ the stable phase will be that with the lowest value of $g$ : for example, if we have $g_\alpha(T, P) < g_\beta(T, P)$ then the system will be in phase $\alpha$ . Therefore there will be regions in $(T, P)$ space were the most stable phase will be $\alpha$ and others in which it will be $\beta$ . A phase diagram is a representation of these regions in the appropriate parameter space (for the $PVT$ system we are considering, $(T, P)$ space). If we now plot the values of $g$ as a function of $T$ and $P$ in $(g, T, P)$ space for every phase of the system, we can determine the regions where the two phases will be the stable ones, namely we can determine the phase diagram of the system, as shown in the following figure:
Stability of phases

The very interesting region of this space (and the one on which we will focus our attention in this section) is the line where the surfaces of the two phases intersect: along this the two phases coexist, and when the system crosses it we say that it undergoes a phase transition.

Obviously, what we have stated can be generalized to systems which exhibit an arbitrary number of phases [1].

For a $PVT$ system the phase diagram can be represented by a surface in $PVT$ space described by a state equation like $f(P,V,T) = 0$ (with $f$ a function depending on the particular system considered). In this case it is more useful to consider the projection of this surface on $(T,P)$ and $(V,P)$ planes. Generally these projections look like those shown in the following figures:
Projection of the phase diagram of a PV T system in $(T, P)$ space.

Projection of the phase diagram of a PV T system in $(V, P)$ space.

(there are however notable exceptions, like water for example). In particular, PV T systems are generally characterized by the existence of a triple point (see Gibbs phase rule) and a critical point in the $(T, P)$ phase diagram (in the first figure these are determined, respectively, by the temperatures $T_t$ and $T_c$). The existence of a critical point has a very intriguing consequence: since the liquid-
gas coexistence line ends in a point, this means that a liquid can continuously be transformed in a gas (or vice versa), and in such a way that the coexistence of liquid and gaseous phases is never encountered[2].

Obviously, our considerations are valid also for different thermodynamic systems. For example, if we consider a magnetic system and its \((T,H)\) phase diagram (where \(H\) is the external magnetic field[3]), then we find another critical point as shown in the following figure:

\[
\begin{array}{c}
H \\
\uparrow pos. \text{ magn.} \\
\downarrow neg. \text{ magn.} \\
T_c \quad T \\
\end{array}
\]

In this case when \(T > T_c\) the system is paramagnetic, namely it has no spontaneous magnetization when \(H = 0\); when \(T < T_c\) however, the system is magnetic and its magnetization can be positive (the total magnetic dipole moment \(\vec{M}\) points upwards) or negative (it points downwards), and depends on the sign of \(H\).

The same system in \((H,M)\) space can be represented for different values of the temperature as in the following figure:

\[
\begin{array}{c}
M \\
\downarrow \quad T = T_c \\
\uparrow \quad T > T_c, T < T_c \\
H \\
\end{array}
\]

In particular, we can see that when \(T < T_c\) the magnetization \(M\) has a jump discontinuity at \(H = 0\).

1. There are however constraints on how many phases can coexist at a given temperature and pressure, see Gibbs phase rule.
2. It can be legitimately asked if such a point exists also for the solid-liquid transition. As far as we know this doesn’t happen, and a reasonable explanation for this has been given by Landau: critical points can exist only between phases that differ quantitatively and not qualitatively. In the case of liquid and gas, in fact, the two phases have the same internal symmetry (both are invariant under continuous spatial translations) and differ only for the mean distance between the particles, while the solid and liquid phases have qualitatively different internal symmetries (solids are invariant only under discrete spatial translations).

3. For simplicity, we are supposing that the real magnetic field \( \vec{H} \), which is a vector, is directed along an axis, for example the vertical axis, so that we can consider only its magnitude \( H \) and thus treat it as a scalar.
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