Phase transitions in material science

First-order phase transition
Second-order phase transition

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Ehrenfest classification

Paul Ehrenfest classified phase transitions based on the behavior of the thermodynamic free energy. Phase transitions were labeled by the lowest derivative of the free energy that is discontinuous at the transition. *First-order phase transitions* exhibit a discontinuity in the first derivative of the free energy with respect to some thermodynamic variable. The various solid/liquid/gas transitions are classified as first-order transitions because they involve a discontinuous change in density, which is the (inverse of the) first derivative of the free energy with respect to pressure. *Second-order phase transitions* are continuous in the first derivative (the order parameter, which is the first derivative of the free energy with respect to the external field, is continuous across the transition) but exhibit discontinuity in a second derivative of the free energy.

First-order phase transitions

First-order phase transitions involve a latent heat. During such a transition, a system either absorbs or releases a fixed (and typically large) amount of energy per volume. During this process, the temperature of the system will stay constant as heat is added: the system is in a "mixed-phase regime" in which some parts of the system have completed the transition and others have not. Familiar examples are the melting of ice or the boiling of water (the water does not instantly turn into vapor, but forms a mixture of liquid water and vapor bubbles). Imry and Wortis showed that quenched disorder can broaden a first-order transition. That is, the transformation is completed over a finite range of temperatures, but phenomena like supercooling and superheating survive and hysteresis is observed on thermal cycling.

Second-order phase transitions

Examples of second-order phase transitions include the ferromagnetic phase transition in materials such as iron, where the magnetization, which is the first derivative of the free energy with respect to the applied magnetic field strength, increases continuously from zero as the temperature is lowered below the Curie temperature. The magnetic susceptibility, the second derivative of the free energy with the field, changes discontinuously. Under the Ehrenfest classification scheme, there could in principle be third, fourth, and higher-order phase transitions. However, in practice we are limited to first- and second-order transitions in known materials.

Second-order phase transitions

Second-order phase transitions are also called *continuous phase transitions*. Other examples of second-order phase transitions are the superconducting transition and the superfluid transition. In contrast to viscosity, thermal expansion and heat capacity of amorphous materials show a relatively sudden change at the glass transition temperature which enables accurate detection using differential scanning calorimetry measurements. Lev Landau gave a theory of second-order phase transitions. Apart from isolated, simple phase transitions, there exist transition lines as well as multi-critical points, when varying external parameters like the magnetic field or composition.

Liquid-glass transition

The liquid-glass is observed in many polymers and supercooled liquids below the melting point of the crystalline phase. This is not a typical transition between thermodynamic ground states: it is widely believed that the true ground state is always crystalline. Glass is a quenched disorder state, and its entropy, density, and so on, depend on the thermal history. Therefore, the glass transition is primarily a dynamic phenomenon: on cooling a liquid, internal degrees of freedom successively fall out of equilibrium.

Temperature dependence of thermodynamic quantities