Thermodynamics of materials

23. Phase Equilibrium of Single-Component Materials III

Kunok Chang
kunok.chang@khu.ac.kr

Kyung Hee University

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Landau Theory of Phase Transitions

- Any phase transition can be characterized by physically well-defined other parameters that distinguish the parent and new transformed phases.
- An order parameter is typically defined to zero in the high-temperature phase and has a finite value in the low-temperature phase.
- Example: Compositional phase separation etc.

Landau Theory of Phase Transitions

- For a phase transition described by a single order parameter η, we can express the free energy density as

$$f(\eta) = f(0) + \left(\frac{\partial f}{\partial \eta}\right)_0 \eta + \frac{1}{2}\left(\frac{\partial^2 f}{\partial \eta^2}\right)_0 \eta^2 + \frac{1}{3!}\left(\frac{\partial^3 f}{\partial \eta^3}\right)_0 \eta^3 + \frac{1}{4!}\left(\frac{\partial^4 f}{\partial \eta^4}\right)_0 \eta^4 + \cdots$$

considering the symmetry of the system, we vanish all odd-order terms,

$$f(\eta) = f(0) + \frac{1}{2}\left(\frac{\partial^2 f}{\partial \eta^2}\right)_0 \eta^2 + \frac{1}{4!}\left(\frac{\partial^4 f}{\partial \eta^4}\right)_0 \eta^4 + \cdots$$

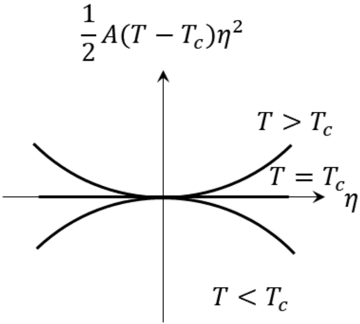
keeping terms up to fourth order,

$$f(\eta) - f(0) = \frac{1}{2}\left(\frac{\partial^2 f}{\partial \eta^2}\right)_0 \eta^2 + \frac{1}{4!}\left(\frac{\partial^4 f}{\partial \eta^4}\right)_0 \eta^4$$

- If we assume only the coefficient in the first term is temperature-dependent,

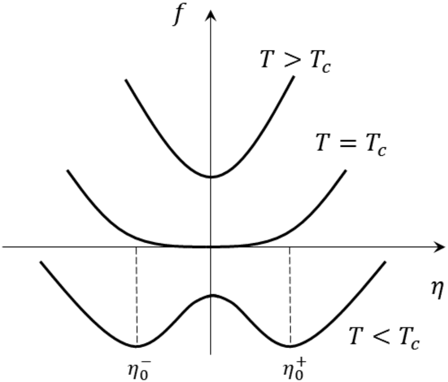
$$f(\eta) - f(0) = \frac{A(T - T_c)}{2}\eta^2 + \frac{B}{4}\eta^4$$

where A and B are positive coefficients, and T_c is the critical temperature for the phase transition.



- When $B = 0$, and $T < T_c$, the parent phase with $\eta = 0$ is unstable since a finite value of order parameter η has a lower energy density.

- When $B \neq 0$,



- At temperatures higher than T_c, the state with $\eta = 0$ has the lowest free energy density and this the stable state.
- Below T_c the states with finite values of the order parameter, η_0^- and η_0^+, are the stable phases. For minimizing free energy,

$$\left.\frac{\partial f(\eta)}{\partial \eta}\right|_{\eta_0} = A(T - T_c)\eta_0 + B\eta_0^3 = 0$$

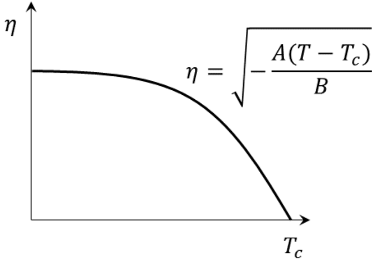
proceed to

$$\eta_0^+ = \sqrt{-\frac{A(T - T_c)}{B}} \qquad \eta_0^- = -\sqrt{-\frac{A(T - T_c)}{B}}$$

- At $T = T_c$,

$$\eta_0^+ = \eta_0^- = 0 \qquad \left.\frac{\partial f(\eta)}{\partial \eta}\right|_{\eta_0} = 0$$

Landau Theory of Phase Transitions



- Schematic dependence of η_0^+ as a function of temperature. The magnitude of order parameter gradually goes to zero as the temperature approaches to the critical temperature, i.e., there is no jump in the order parameter value at the transition temperature.
- A phase transition at which the order parameter value is continuous is called a second-order phase transition or simply a continuous transition.

- To describe a first-order phase transition, it is necessary to add either a cubic or a sixth-order term. Let's first look at the $\eta^2 - \eta^3 - \eta^4$ free energy density model,

$$f(\eta) - f(0) = \frac{A(T - T_c)}{2}\eta^2 - \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4$$

- To obtain the equilibrium order parameter,

$$\left.\frac{\partial f(\eta)}{\partial \eta}\right|_{\eta_0} = A(T - T_c)\eta_0 - B\eta_0^2 + C\eta_0^3 = 0$$

the solutions are

$$\eta_{0,1} = 0$$

$$\eta_{0,2} = \frac{B + \sqrt{B^2 - 4AC(T - T_c)}}{2C}$$

$$\eta_{0,3} = \frac{B - \sqrt{B^2 - 4AC(T - T_c)}}{2C}$$

Landau Theory of Phase Transitions

- At the critical temperature T_c,

$$\eta_{0,1} = 0 \qquad \eta_{0,2} = \frac{B}{C} \qquad \eta_{0,3} = 0$$

- At the transition temperature T_0,

$$B^2 - 4AC(T_0 - T_c) = 0 \rightarrow T_0 = T_c + \frac{B^2}{4AC}$$

Landau Theory of Phase Transitions