Correlations in the Landau theory

To understand the effect of correlations, we must go beyond the uniform phase and include fluctuations. Here, we focus on the case with $h(\vec{x})=0$.

Let $\quad m(\vec{x}) = m + \varphi(\vec{x})$, where $\varphi(\vec{x})$ represents small spatial fluctuations in the local order parameter $m(\vec{x})$.

$$= \begin{cases} \varphi(\vec{x}) & \text{for } t \geq 0 \\ \pm\sqrt{\dfrac{a_0}{4u_0}}\,|t|^{1/2} & \text{for } t<0 \ (t\to 0) \end{cases}$$

$$\Rightarrow \Psi = \frac{1}{2}|\nabla m(\vec{x})|^2 - \beta\, m(\vec{x})\, h(\vec{x}) + \frac{a_0 t}{2} m^2(\vec{x}) + u_0 m^4(\vec{x})$$

$$= \begin{cases} \dfrac{1}{2}|\nabla \varphi|^2 + \dfrac{a_0 t}{2}\varphi^2 + u_0\varphi^4, & \text{for } t \geq 0 \\[2mm] \dfrac{1}{2}|\nabla \varphi|^2 + \dfrac{a_0 t}{2}\left(\pm\sqrt{\dfrac{a_0}{4u_0}}|t|^{1/2}+\varphi\right)^2 + u_0\left(\pm\sqrt{\dfrac{a_0}{4u_0}}|t|^{1/2}+\varphi\right)^4, & \text{for } t<0 \end{cases}$$

$$\simeq \begin{cases} \dfrac{1}{2}|\nabla \varphi|^2 + \dfrac{a_0 t}{2}\varphi^2, & \text{for } t \geq 0 \\[2mm] \dfrac{1}{2}|\nabla \varphi|^2 - \dfrac{a_0^2 t^2}{8u_0} + \dfrac{a_0^2 t^2}{16 u_0} \pm a_0\sqrt{\dfrac{a_0}{4u_0}}\,t|t|^{1/2}\varphi \pm 4u_0\dfrac{a_0^{3/2}}{8 u_0^{3/2}}|t|^{3/2}\varphi + \dfrac{a_0 t}{2}\varphi^2 \\[2mm] \qquad\qquad -\dfrac{6\,a_0}{4}t\varphi^2, & t>0 \end{cases}$$

$$= \begin{cases} \dfrac{1}{2}|\nabla \varphi|^2 + \dfrac{a_0 t}{2}\varphi^2, & \text{for } t \geq 0 \\[2mm] \dfrac{1}{2}|\nabla \varphi|^2 - \dfrac{a_0^2 t^2}{16u_0} - a_0 t\varphi^2, & \text{for } t<0 \end{cases}$$

$$\therefore \quad \Psi = \Psi_{\text{uniform}} + \Psi_{\text{fluctuation}}$$

where $\quad \Psi_{\text{fluctuation}} = \dfrac{1}{2}|\nabla \varphi|^2 + \dfrac{\varphi^2}{2\xi^2}$, where $\xi^2 = \begin{cases} \dfrac{1}{a_0 t}, & \text{for } t \geq 0 \\[2mm] \dfrac{-1}{2a_0 t}, & \text{for } t<0 \end{cases}$

$$\therefore \quad Z = Z_{uniform} \; Z_{fluctuation}$$

$$Z_{fluctuation} \propto Tr \; e^{-\beta H_{fluc}[\varphi(\vec{x})]}$$

$$\beta H_{fluc}[\varphi(\vec{x})] = \int d^d x \; \Psi_{fluc}(\vec{x})$$

Let's go to Fourier space.

$$\varphi_{\vec{k}} = \frac{1}{(2\pi)^{d/2}} \int d^d x \; \varphi(\vec{x}) \; e^{i\vec{k}\cdot\vec{x}} \qquad \text{and} \quad \varphi(\vec{x}) = \frac{1}{(2\pi)^{d/2}} \int d^d k \; \varphi_{\vec{k}} \; e^{-i\vec{k}\cdot\vec{x}}$$

①
$$\int d^d x \; \varphi^2(\vec{x}) = \frac{1}{(2\pi)^d} \int d^d x \int d^d k_1 \int d^d k_2 \; \varphi_{\vec{k}_1} \varphi_{\vec{k}_2} \; e^{-i\vec{k}_1\cdot\vec{x}} \; e^{-i\vec{k}_2\cdot\vec{x}}$$

$$= \int d^d k_1 \int d^d k_2 \; \varphi_{\vec{k}_1} \varphi_{\vec{k}_2} \; \delta(\vec{k}_1 + \vec{k}_2) \qquad \therefore \quad \frac{1}{(2\pi)^d} \int d^d x \; e^{-i\vec{k}\cdot\vec{x}} = \delta(\vec{k})$$

$$= \int d^d k \; \varphi_{\vec{k}} \varphi_{-\vec{k}}$$

$$= \int d^d k \; |\varphi_{\vec{k}}|^2$$

②
$$\int d^d x \; |\nabla\varphi|^2 = \frac{1}{(2\pi)^d} \int d^d x \int d^d k_1 \int d^d k_2 \; \varphi_{\vec{k}_1} \varphi_{\vec{k}_2} \; e^{-i\vec{k}_1\cdot\vec{x}} \; e^{-i\vec{k}_2\cdot\vec{x}} \; (-i\vec{k}_1)\cdot(-i\vec{k}_2)$$

$$= -\int d^d k_1 \int d^d k_2 \; \varphi_{\vec{k}_1} \varphi_{\vec{k}_2} \; \delta(\vec{k}_1 + \vec{k}_2) \; \vec{k}_1 \cdot \vec{k}_2$$

$$= \int d^d k \; \varphi_{\vec{k}} \varphi_{-\vec{k}} \; k^2$$

$$= \int d^d k \; |\varphi_{\vec{k}}|^2 \; k^2$$

$$\Rightarrow \int d^d x \; \Psi_{fluc}(\vec{x}) = \int d^d k \; \frac{k^2 + \xi^{-2}}{2} \; |\varphi_k|^2$$

$$\Rightarrow Z_{fluc} \propto Tr \; e^{-\int d^d k \left(\frac{k^2 + \xi^{-2}}{2}\right)|\varphi_{\vec{k}}|^2} \qquad \text{(Gaussian factors)}$$

$$\therefore \langle \varphi_{\vec{k}} \rangle = 0 \qquad \text{and} \qquad \langle |\varphi_{\vec{k}}|^2 \rangle \propto \frac{1}{k^2 + \xi^{-2}}$$

$$\int d^d k \; e^{-i\vec{k}\cdot\vec{x}} \langle |\varphi_{\vec{k}}|^2 \rangle = \frac{1}{(2\pi)^d} \int d^d k \; d^d x_1 d^d x_2 \; e^{-i\vec{k}\cdot(\vec{x}+\vec{x}_1-\vec{x}_2)} \langle \varphi(\vec{x}_1)\varphi(\vec{x}_2)\rangle$$

$$= \int d^d x_1 \, d^d x_2 \; \langle \varphi(\vec{x}_1)\varphi(\vec{x}_2)\rangle \, \delta(\vec{x}+\vec{x}_1-\vec{x}_2)$$

$$= \int d^d x_1 \langle \varphi(\vec{x}_1)\varphi(\vec{x}_1+\vec{x})\rangle$$

$$= V G(\vec{x}) \qquad \text{where } \langle \varphi(\vec{x}_1)\varphi(\vec{x}_1+\vec{x})\rangle \text{ is independent}$$
$$\text{of } \vec{x}_1 \text{ (translational symmetry)}.$$

$$\Rightarrow G(\vec{x}) \propto \frac{1}{V} \int d^d k \; \frac{e^{-i\vec{k}\cdot\vec{x}}}{k^2 + \xi^{-2}} \sim \frac{e^{-|\vec{x}|/\xi}}{|\vec{x}|^{d-2}} \quad \text{as} \quad |\vec{x}| \to \infty$$

$$\Rightarrow \boxed{\eta = 0}$$

$$\xi \sim |t|^{-1/2} \quad \Rightarrow \quad \boxed{\nu = 1/2}$$

Ginzburg criterion

$$\frac{G(\xi)}{G(0)} \sim \frac{1}{\xi^{d-2} m^2} \sim \frac{|t|^{d/2-1}}{|t|} = |t|^{(d-4)/2}$$
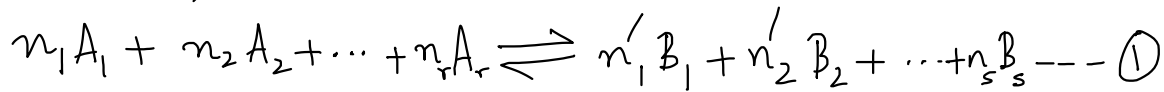
$\Rightarrow$ The correlations decay if $d > 4$.

$d = 4$ is the upper critical dimension of the above theory.

[There is also a lower critical dimension below which fluctuations destroy the ordered phase.]

CHEMICAL EQUILIBRIUM

Consider the reaction

$$n_1 A_1 + n_2 A_2 + \cdots + n_r A_r \rightleftharpoons n_1' B_1 + n_2' B_2 + \cdots + n_s' B_s \quad --- \text{①}$$

When such a reaction achieves chemical equilibrium, its Gibbs free energy attains its minimum value and stops changing.

Let μ_X be the chemical potential of X $(X \in \{A_i, B_i\})$, and N_X be the number of X molecules at equilibrium.

$$\therefore \quad G = \sum_{i=1}^{r} \mu_{A_i} N_{A_i} + \sum_{i=1}^{s} \mu_{B_i} N_{B_i}$$

$$\Delta G = 0 \implies \sum_{i=1}^{r} \mu_{A_i} \Delta N_{A_i} + \sum_{i=1}^{s} \mu_{B_i} \Delta N_{B_i} = 0 \quad --- \text{②}$$

where we have assumed the chemical potentials don't vary since we fix the temperature and pressure.

In the reaction ①, when n_1 molecules of A_1 are consumed, so are n_2 molecules of A_2, ... Simultaneously n_1' molecules of B_1, n_2' molecules of B_2, ..., are produced.

$$\implies \frac{\Delta N_{A_1}}{\Delta N_{A_2}} = \frac{n_2}{n_1} \; , \cdots \quad , \quad \frac{\Delta N_{B_i}}{\Delta N_{A_1}} = - \frac{n_i'}{n_1}$$

$$\implies \Delta N_{A_i} = \frac{n_i}{n_1} \Delta N_{A_1} \quad \text{and} \quad \Delta N_{B_i} = -\frac{n_i'}{n_1} \Delta N_{A_1}$$

Plugging these into Eq. ②, we get,

$$\sum_{i=1}^{r} n_i \mu_{A_i} - \sum_{i=1}^{s} n_i' \mu_{B_i} = 0 \quad --- \text{③}$$

For a mixture of ideal gases,

$$\mu_i = k_B T \ln P_i + \chi_i(T)$$

where P_i = partial pressure of ith component = $P[A_i]/\rho$, $[A_i]$ being the concentration of A_i

$$\chi_i = -k_B T \ln\left[k_B T / \lambda_i^3 \sum_{j=0}^{\infty} g_{ij} e^{-\varepsilon_{ij}/k_B T} \right]$$

where $\lambda_i = \sqrt{\dfrac{2\pi\hbar^2}{m_i k_B T}}$

$\{\varepsilon_{i0}, \varepsilon_{i1}, \ldots\}$ are the static energy levels of molecule i, and $\{g_{i0}, g_{i1}, \ldots\}$ are the degeneracies.

If $\varepsilon_{i1} - \varepsilon_{i0} \gg k_B T$, then $\chi_i = -k_B T \ln\left[\dfrac{k_B T \, g_{i0}}{\lambda_i^3}\right] + \varepsilon_{i0}$