統計物理学I 小テスト(4/22) 解答例.

(1). Gibbsの自由エネルギーの全微分表現は,

$$dG = -SdT + VdP + \sum_i \mu_i dN_i \quad -(i)$$

(2).

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\{N_i\}} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\{N_i\}} dP + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{P,T,\{N_j\}(j\neq i)} dN_i \quad -(ii)$$

(i), (ii) を比較すると,

$$\left(\frac{\partial G}{\partial T}\right)_{P,\{N_i\}} = -S, \quad \left(\frac{\partial G}{\partial P}\right)_{T,\{N_i\}} = V, \quad \left(\frac{\partial G}{\partial N_i}\right)_{P,T,\{N_j\}(j\neq i)} = \mu_i$$

であり, 自由エネルギーに関する2階微分を考えると, (相転移点以外では一般にO.K).

$$\left(\frac{\partial^2 G}{\partial P \partial T}\right)_{\{N_i\}} = -\left(\frac{\partial S}{\partial P}\right)_{T,\{N_i\}}, \quad \left(\frac{\partial^2 G}{\partial T \partial P}\right)_{\{N_i\}} = \left(\frac{\partial V}{\partial T}\right)_{P,\{N_i\}}$$

より

$$-\left(\frac{\partial S}{\partial P}\right)_{T,\{N_i\}} = \left(\frac{\partial V}{\partial T}\right)_{P,\{N_i\}}$$

が示された。他の関係も同様にして,

$$\left(\frac{\partial G}{\partial N_i \partial T}\right)_{P,\{N_j\}(i\neq j)} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P\{N_j\}(i\neq j)}, \quad \left(\frac{\partial G}{\partial T \partial N_i}\right)_{P,\{N_j\}(i\neq j)} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\{N_i\}}$$

$$\Rightarrow \quad -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,\{N_j\}(i\neq j)} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\{N_i\}}$$

$$\left(\frac{\partial G}{\partial N_i \partial P}\right)_{\{N_j\}(i\neq j)} = \left(\frac{\partial V}{\partial N_i}\right)_{P,T,\{N_j\}(i\neq j)}, \quad \left(\frac{\partial^2 G}{\partial P \partial N_i}\right)_{T,\{N_j\}(i\neq j)} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\{N_i\}}$$

$$\Rightarrow \quad \left(\frac{\partial V}{\partial N_i}\right)_{P,T,\{N_j\}(i\neq j)} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\{N_i\}}$$