工業反応装置特論

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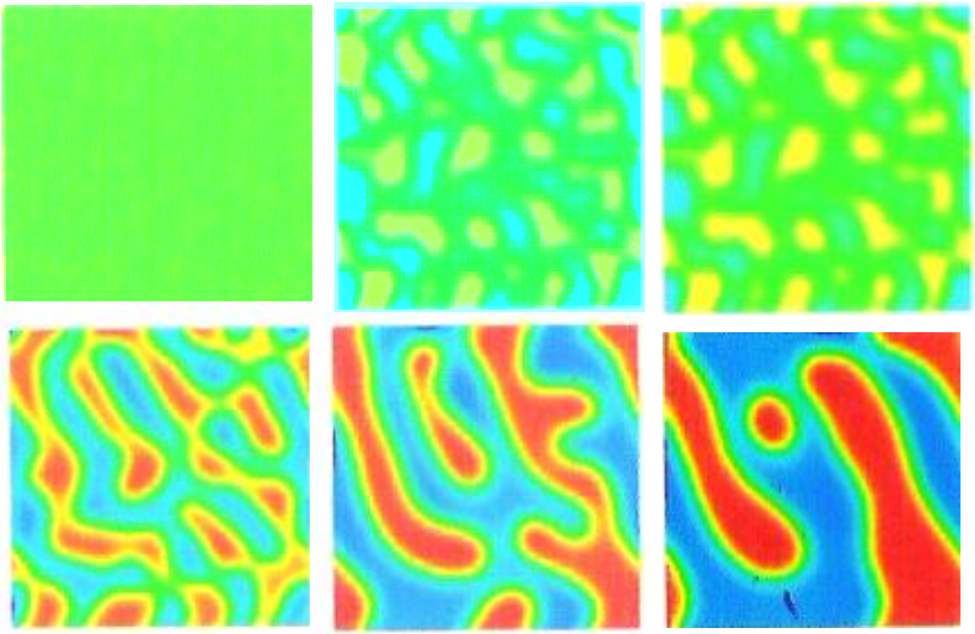
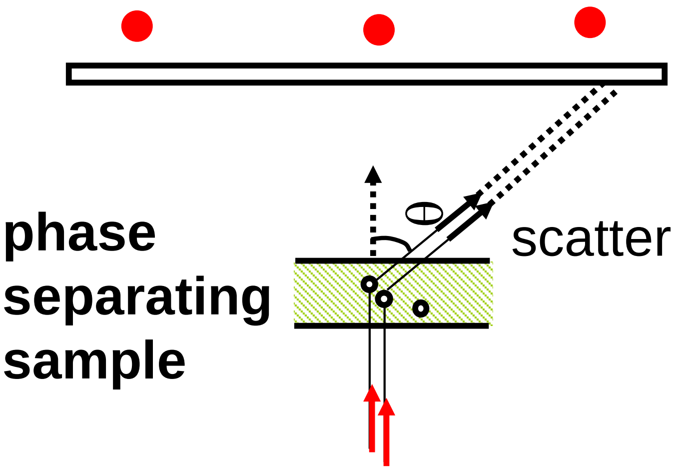
周期的な相構造



Cahn-Hilliard方程式の解の一例

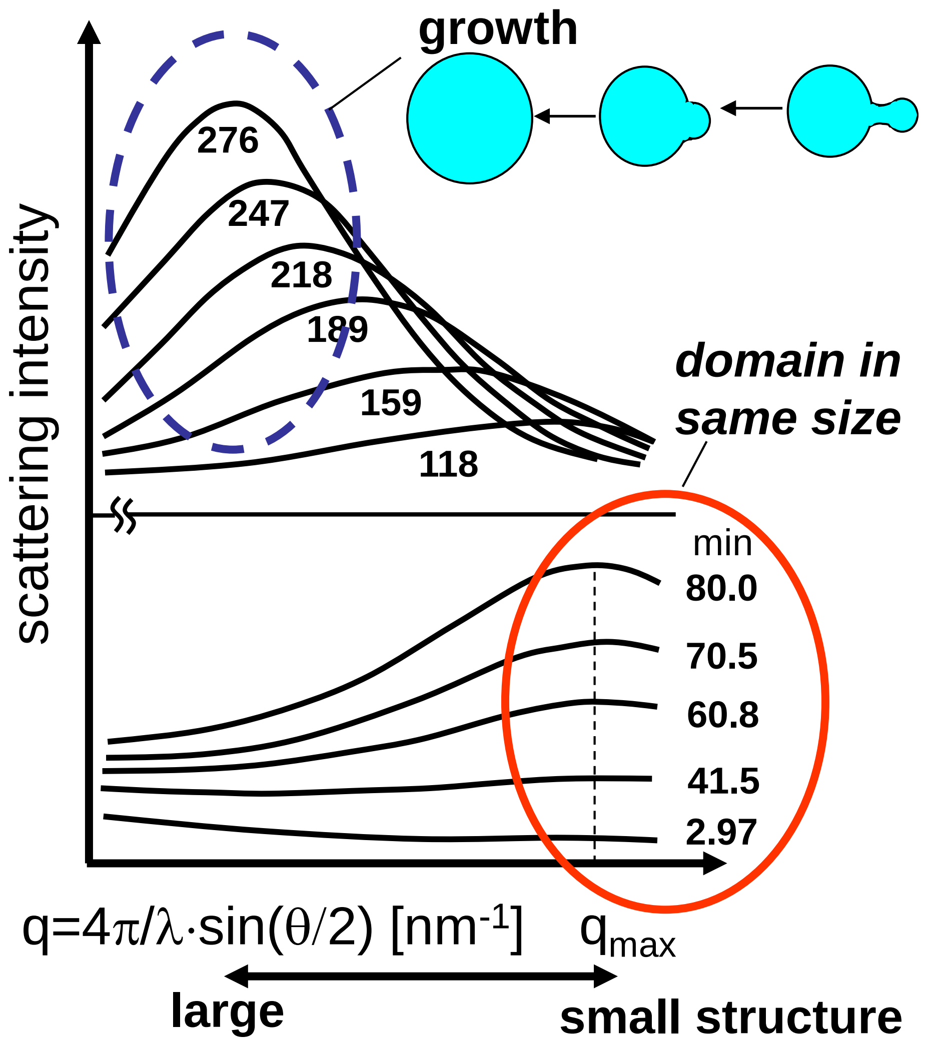
LIGHT SCATTERING EXPERIMENT

1. set sample in beam path



2. measure θ to calculate q

(Izumitani and Hashimoto., J. Chem. Phys., 83, 3694, 1985)



Q. 揃ったサイズの構造が初期に
生成する。このサイズを理論予測するには？

SOLUTION OF CH EQUATION (1)

*E*quation for binary solution

$$\frac{\partial \phi_1}{\partial t} = \frac{\partial}{\partial z}\left[M \frac{\partial}{\partial z}\left\{ \frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) - \kappa_1 \frac{\partial^2}{\partial z^2}\phi_1 \right\}\right] \quad (1)$$

ϕ_1 : volume fraction of component 1

g : free energy of mixing in homogeneous systems $\frac{g}{RT} = \frac{\phi_1 \ln \phi_1}{N_1} + \frac{\phi_2 \ln \phi_2}{N_2} + \chi_{12}\phi_1\phi_2 \quad (2)$

簡単のため濃度がある平均値$\overline{\phi_1}$の周りでわずかにのみ変化すると仮定し

次の近似を導入する

$$\frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) \approx \frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right)\Bigg|_{\overline{\phi_1}} + \frac{\partial^2}{\partial {\phi_1}^2}\left(\frac{g}{RT}\right)\Bigg|_{\overline{\phi_1}} (\phi_1 - \overline{\phi_1}) \quad (3)$$

$\overline{\phi_1}$を混合自由エネルギーの極大値の組成にとれば

$$\frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right)\Bigg|_{\overline{\phi_1}} = 0 \quad (4)$$

SOLUTION OF CH EQUATION (2)

相分離が生じるときgは濃度に対して上の凸の曲線であり

$$\frac{\partial^2 g}{\partial \phi_1^{\ 2}} < 0$$であることに注意して$$P \equiv -\frac{\partial^2}{\partial \phi_1^{\ 2}}\left(\frac{g}{RT}\right)\Bigg|_{\overline{\phi_1}}$$とおけば(3)(4)より

$$\frac{\partial}{\partial z}\frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) = -P\frac{\partial}{\partial z}(\phi_1 - \overline{\phi_1}) = -P\frac{\partial \phi_1}{\partial z} \quad (5)$$

(3)(5)を(1)に代入すれば

$$\frac{\partial \phi_1}{\partial t} = M\frac{\partial}{\partial z}\left(-P\frac{\partial \phi_1}{\partial z} - \kappa_1\frac{\partial^3}{\partial z^3}\phi_1\right)$$

$$\therefore \quad \frac{\partial \phi_1}{\partial t} = -M\left(P\frac{\partial^2 \phi_1}{\partial z^2} + \kappa_1\frac{\partial^4 \phi_1}{\partial z^4}\right) \quad (6)$$

SOLUTION OF CH EQUATION (3)

Stability analysis (安定性解析、無限に小さな濃度ゆらぎを考える)

$$\phi_1 = \overline{\phi_1} + \varepsilon(t, x) \quad (7)$$

波長λの理想的sin波

平均値　　**変動成分**

$$\varepsilon(t, x) = \varepsilon_0 \exp(st) \sin(\frac{z}{\lambda}) \quad (8)$$

s>0ならゆらぎ発達（不安定、相分離）
s<0ならゆらぎ消滅（安定）　　**s=0は中立条件**

SOLUTION OF CH EQUATION (4)

(7)(8)より

$$\frac{\partial \phi_1}{\partial t} = 0 + \varepsilon_0 \sin(\frac{z}{\lambda}) \frac{\partial}{\partial t} \exp(st) = \varepsilon_0 \sin(\frac{z}{\lambda}) s \exp(st)$$

$$\frac{\partial \phi_1}{\partial z} = 0 + \varepsilon_0 \exp(st) \frac{1}{\lambda} \cos(\frac{z}{\lambda})$$

$$\frac{\partial^2 \phi_1}{\partial z^2} = -\varepsilon_0 \exp(st) \frac{1}{\lambda^2} \sin(\frac{z}{\lambda})$$

$$\frac{\partial^3 \phi_1}{\partial z^3} = -\varepsilon_0 \exp(st) \frac{1}{\lambda^3} \cos(\frac{z}{\lambda})$$

$$\frac{\partial^4 \phi_1}{\partial z^4} = \varepsilon_0 \exp(st) \frac{1}{\lambda^4} \sin(\frac{z}{\lambda})$$

これらを用いれば(6)は

$$\varepsilon_0 \sin(\frac{z}{\lambda}) s \exp(st) = -M \left[P \left\{ -\varepsilon_0 \exp(st) \frac{1}{\lambda^2} \sin(\frac{z}{\lambda}) \right\} + \kappa_1 \left\{ \varepsilon_0 \exp(st) \frac{1}{\lambda^4} \sin(\frac{z}{\lambda}) \right\} \right]$$

$$= \varepsilon_0 \exp(st) M \sin(\frac{z}{\lambda}) \left[P \left(\frac{1}{\lambda^2} \right) - \kappa_1 \left(\frac{1}{\lambda^4} \right) \right]$$

SOLUTION OF CH EQUATION (5)

整理すれば

$$s = M\left\{P\left(\frac{1}{\lambda^2}\right) - \kappa_1\left(\frac{1}{\lambda^4}\right)\right\} \quad (9)$$

成長可能なゆらぎの臨界波長λ_cは(9)から

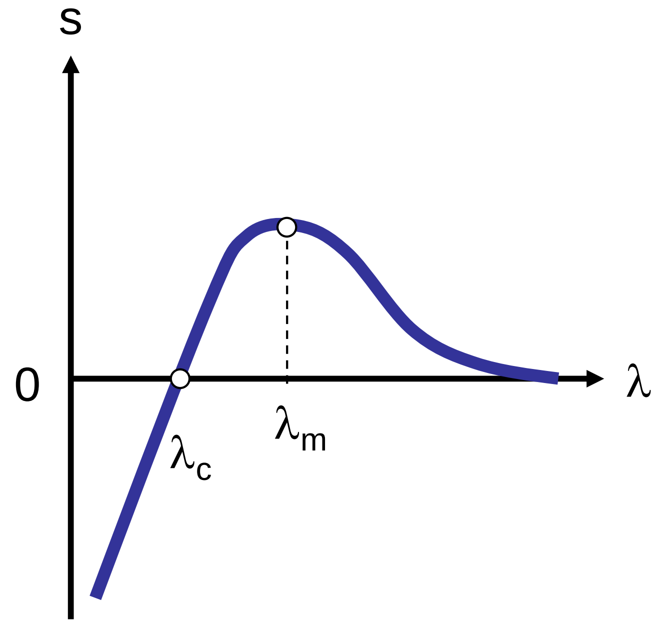
$$0 = M\left\{P\left(\frac{1}{\lambda_c^{\,2}}\right) - \kappa_1\left(\frac{1}{\lambda_c^{\,4}}\right)\right\}$$

$$\lambda_c^{\,2} = \frac{\kappa_1}{P}$$

$$\therefore \lambda_c = \sqrt{\frac{\kappa_1}{P}}$$

界面エネルギの大きさに対応
(κ_1の単位はm^2)

界面のない均一場の
自由エネルギに対応



$\lambda < \lambda_c$の小さなゆらぎは消滅($s < 0$)

$\lambda = \lambda_m$のゆらぎが選択的に成長

２つのエネルギのバランスでサイズが決定される

SOLUTION OF CH EQUATION (6)

最大成長波長λ_mでは

$$\left.\frac{ds}{d\lambda}\right|_{\lambda=\lambda_m} = 0$$

(9)から

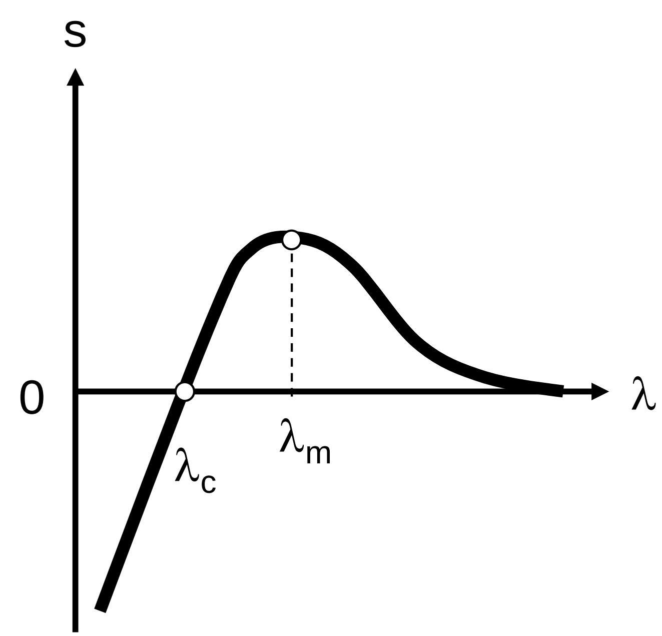
$$\frac{ds}{d\lambda} = M\left\{P(-2)\left(\frac{1}{\lambda^3}\right) + 4\kappa_1\left(\frac{1}{\lambda^5}\right)\right\}$$だから

$$M\left\{P(-2)\left(\frac{1}{\lambda_m{}^3}\right) + 4\kappa_1\left(\frac{1}{\lambda_m{}^5}\right)\right\} = 0$$

整理すれば

$$-P + 2\kappa_1\frac{1}{\lambda_m{}^2} = 0$$

$$\therefore \lambda_m = \sqrt{\frac{2\kappa_1}{P}} = \sqrt{2}\lambda_c \quad (10)$$



$\lambda < \lambda_c$の小さなゆらぎは消滅$(s < 0)$

$\lambda = \lambda_m$のゆらぎが選択的に成長

SOLUTION OF CH EQUATION (7)

$Flory-Huggins$式を用いれば

$$\frac{\partial^2}{\partial \phi_1{}^2}\left(\frac{g}{RT}\right)=\frac{\partial}{\partial \phi_1}\left[\frac{\ln \phi_1}{N_1}+\frac{1}{N_1}-\frac{\ln(1-\phi_1)}{N_2}-\frac{1}{N_2}+\chi_{12}(1-2\phi_1)\right]$$

$$=\frac{1}{N_1\phi_1}+\frac{1}{N_2(1-\phi_1)}-2\chi_{12}$$

$$\left.\frac{\partial^2}{\partial \phi_1{}^2}\left(\frac{g}{RT}\right)\right|_{\overline{\phi}_1}=\frac{1}{N_1\overline{\phi}_1}+\frac{1}{N_2(1-\overline{\phi}_1)}-2\chi_{12}$$

$$\therefore P=-\left\{\frac{1}{N_1\overline{\phi}_1}+\frac{1}{N_2(1-\overline{\phi}_1)}-2\chi_{12}\right\} \quad (11)$$

(10)に代入すると

$$\lambda_m=\sqrt{\frac{2\kappa_1}{2\chi_{12}-\frac{1}{N_1\overline{\phi}_1}-\frac{1}{N_2(1-\overline{\phi}_1)}}}$$

Example:

$\kappa_1=1\times10^{-8}m^2, \chi_{12}=3, N_1=N_2=1000, \overline{\phi}_1=0.5$なら

$$\lambda_m=\sqrt{\frac{2(1\times10^{-8})}{2(3)-\frac{1}{(1000)(0.5)}-\frac{1}{(1000)(0.5)}}}=57.8\ \mu m$$

Report 9 Analytical solution of Cahn-Hilliard equation

氏名

Consider an immiscible blend of polymer 1 and polymer 2. The local volume fraction of component i (i=1, 2) is ϕ_i. The time variation of ϕ_1 is expressed as the Cahn-Hilliard equation (1), where κ_1 represents a constant that attributed to interfacial energy, g the Gibbs free energy of mixing, M the constant, R the gas constant, t the time, T the absolute temperature, z the coordinate along the molecular motion.

Q1. Derive Eq. (3) from Eq. (1) using the approximation Eq. (2).

$$\frac{\partial \phi_1}{\partial t} = \frac{\partial}{\partial z}\left[M \frac{\partial}{\partial z}\left\{ \frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) - \kappa_1 \frac{\partial^2}{\partial z^2}\phi_1 \right\}\right] \quad (1)$$

$$\frac{\partial}{\partial z}\frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) \approx \frac{\partial^2}{\partial \phi_1^2}\left(\frac{g}{RT}\right)\Bigg|_{\overline{\phi_1}} \frac{\partial}{\partial z}\phi_1 \equiv -P\frac{\partial}{\partial z}\phi_1 \quad (2)$$

$$\frac{\partial \phi_1}{\partial t} = -M\left(P\frac{\partial^2 \phi_1}{\partial z^2} + \kappa_1 \frac{\partial^4 \phi_1}{\partial z^4}\right) \quad (3)$$

Q2. Derive Eq. (5) by substituting Eq. (4) into Eq. (3).

$$\phi_1 = \overline{\phi_1} + \varepsilon_0 \exp(st)\sin\left(\frac{z}{\lambda}\right) \quad (4)$$

$$s = M\left\{ P\left(\frac{1}{\lambda^2}\right) - \kappa_1\left(\frac{1}{\lambda^4}\right)\right\} \quad (5)$$

Q3. Derive Eq. (6) for the wavelength of the composition fluctuation, λ_m, at which the growth rate, s, shows a maximum.

$$\lambda_m = \sqrt{\frac{2\kappa_1}{P}} \quad (6)$$

Q4. Flory-Huggins equation gives Eq. (4) for the constant P.

$$P = -\left\{ \frac{1}{N_1\overline{\phi_1}} + \frac{1}{N_2(1-\overline{\phi_1})} - 2\chi_{12} \right\} \quad (7)$$

Calculate and plot λ_m against T [K] using Eqs. (6) and (7), where

$$T = 273 \sim 423K、\kappa_1 = 1\times 10^{-16} m^2, \chi_{12}N = \left(\frac{500}{T}\right)^4, N_1 = N_2 = 1000, \overline{\phi_1} = 0.5$$