

高分子の結晶化

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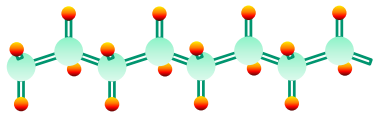
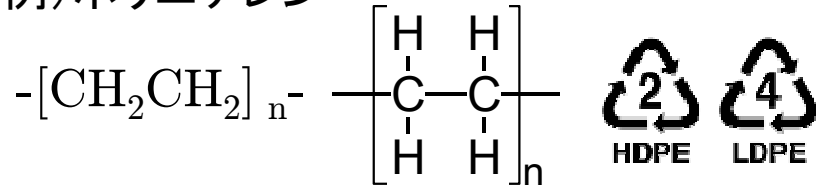
「結晶成長」とは

高分子の折り畳み鎖結晶化機構

標準モデル, 成長様式, 高分子性, 1次核形成, 準安定相の役割

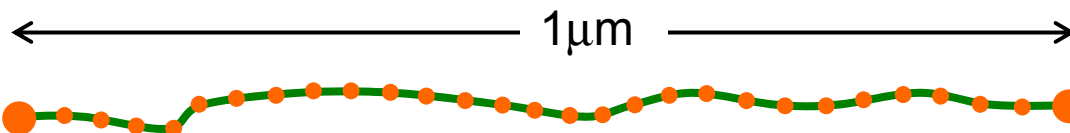
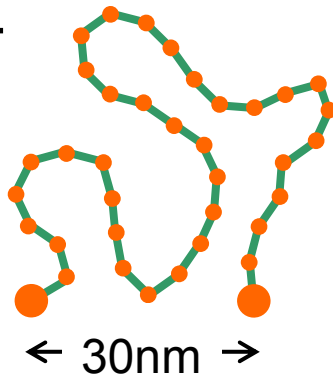
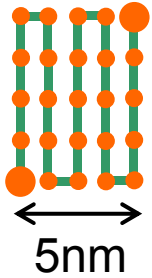
高分子

例) ポリエチレン



0.25nm

$M=10$ 万



プラスチック, 繊維

糸状の分子

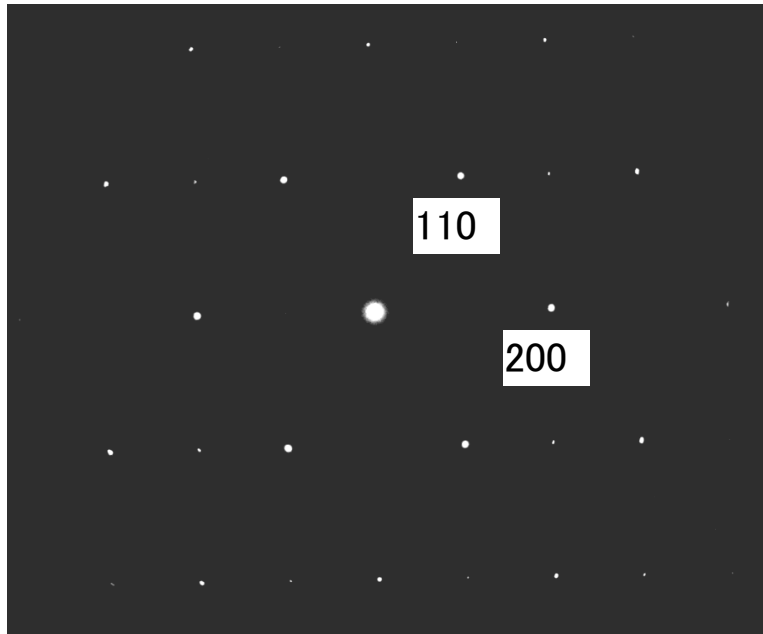
軽い, 配向性, 加工性

紡糸・成形

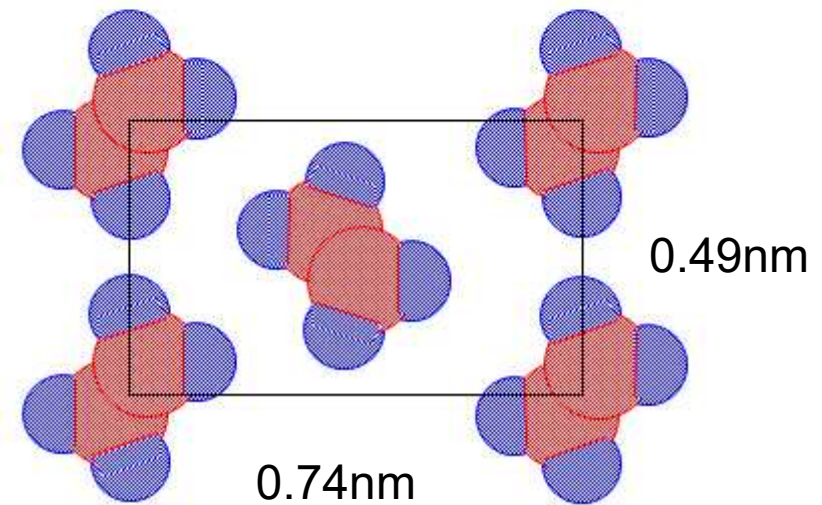
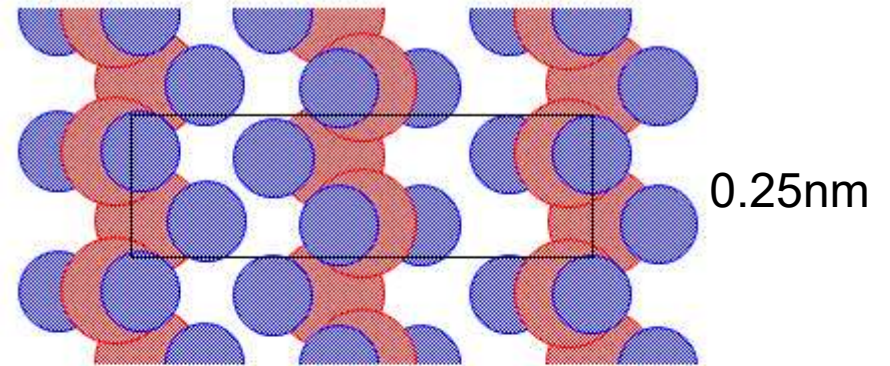
高機能性

エンブラ, 高強度, 耐熱性,
生体適合性(生分解性),
導電性, 圧電性 etc

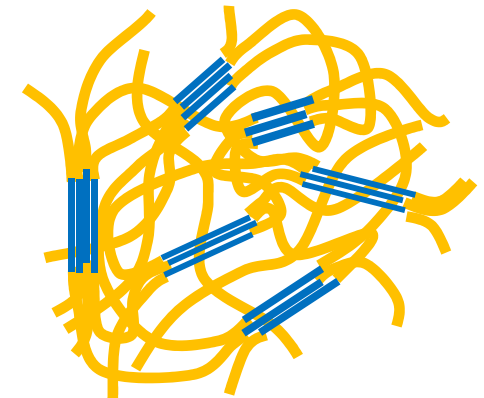
結晶構造



ポリエチレン
透過型電子顕微鏡
電子線回折像

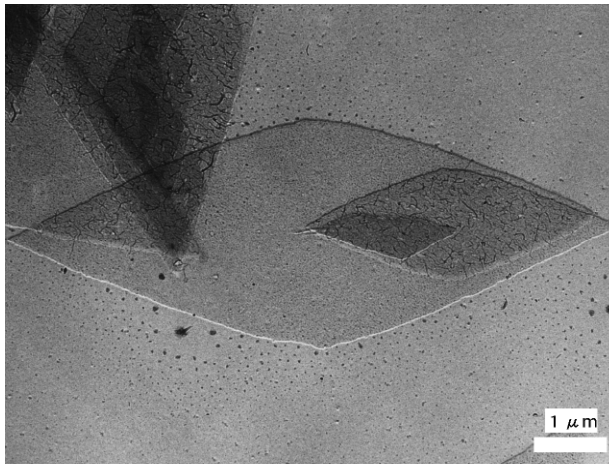


折りたたみ鎖単結晶

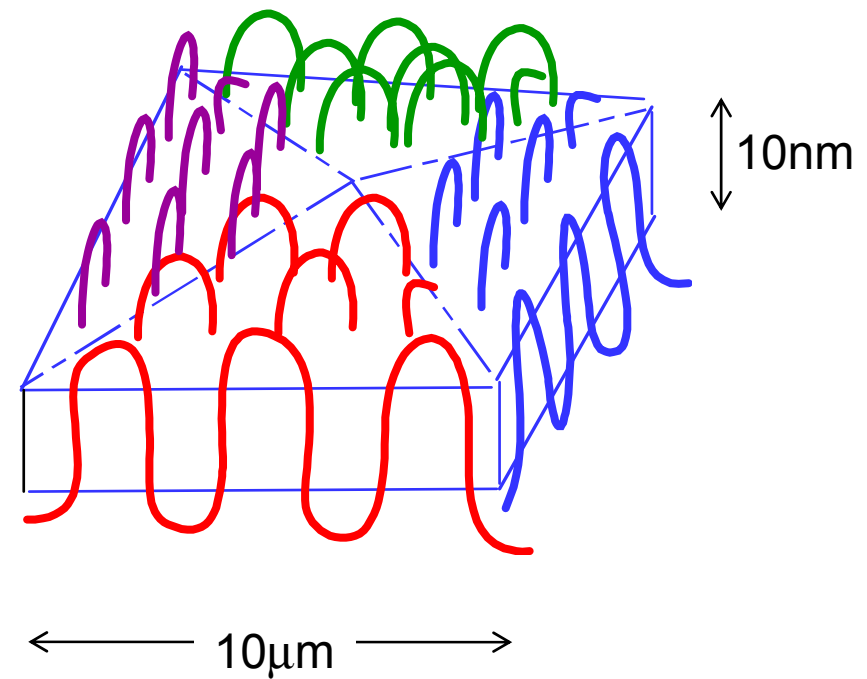
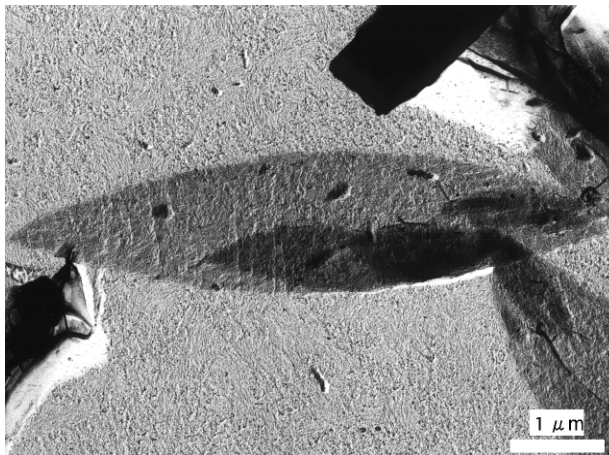


房状ミセルモデル

溶液

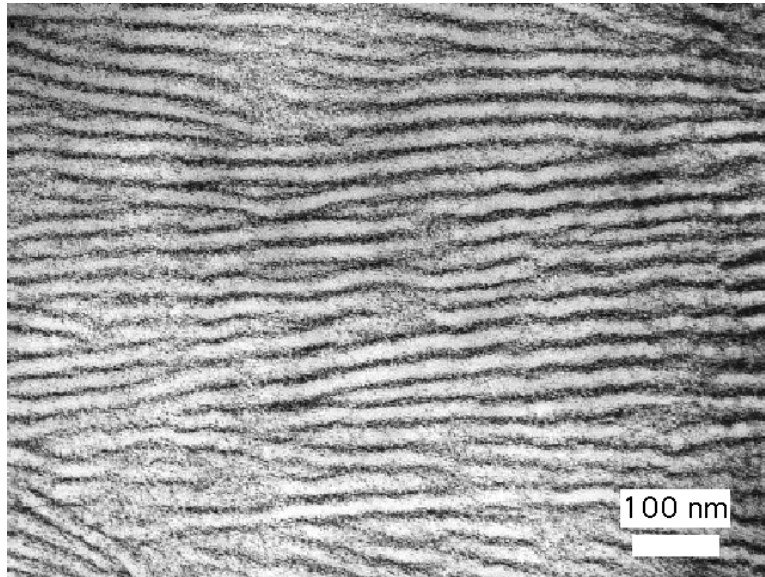


融液

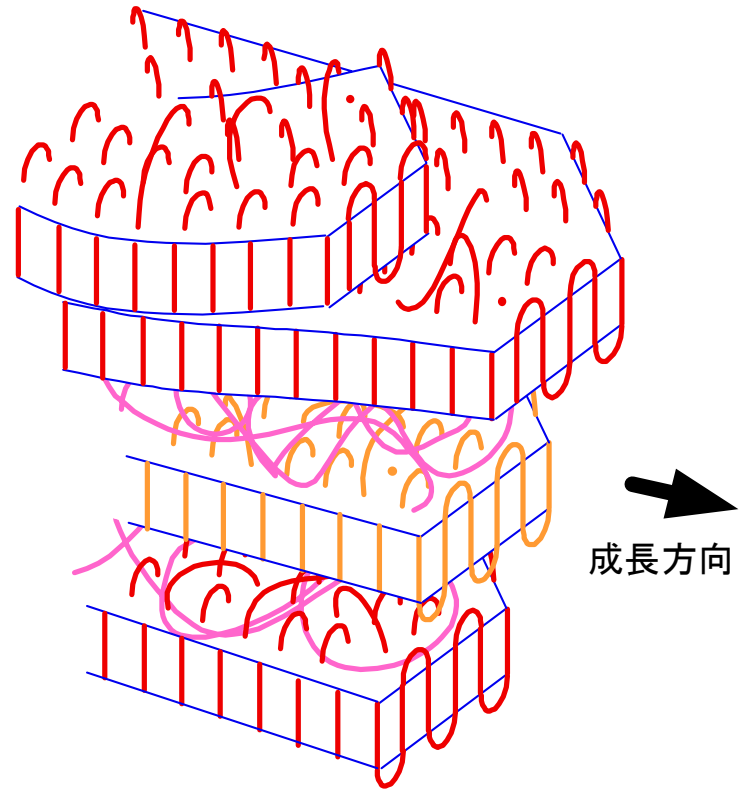


ポリフッ化ビニリデン単結晶
透過型電子顕微鏡像

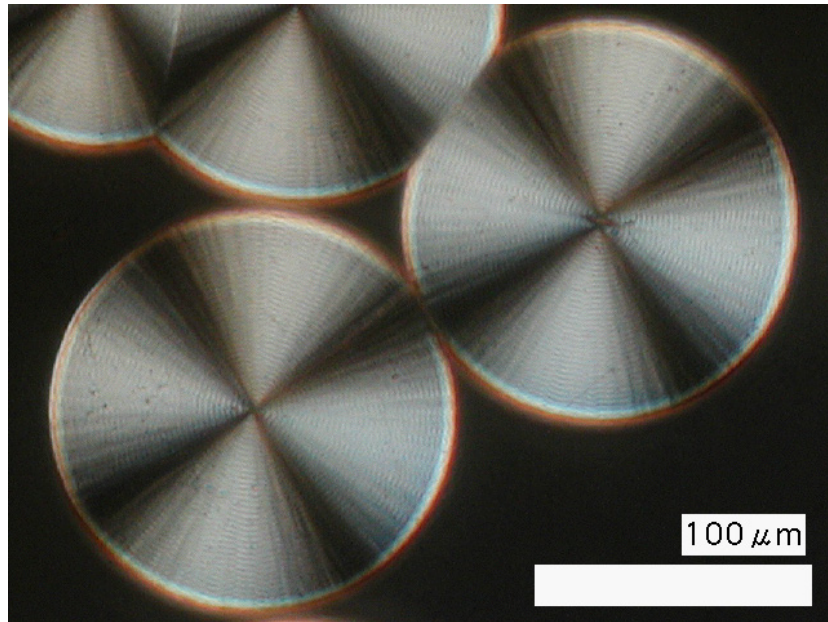
結晶・非晶の積層構造



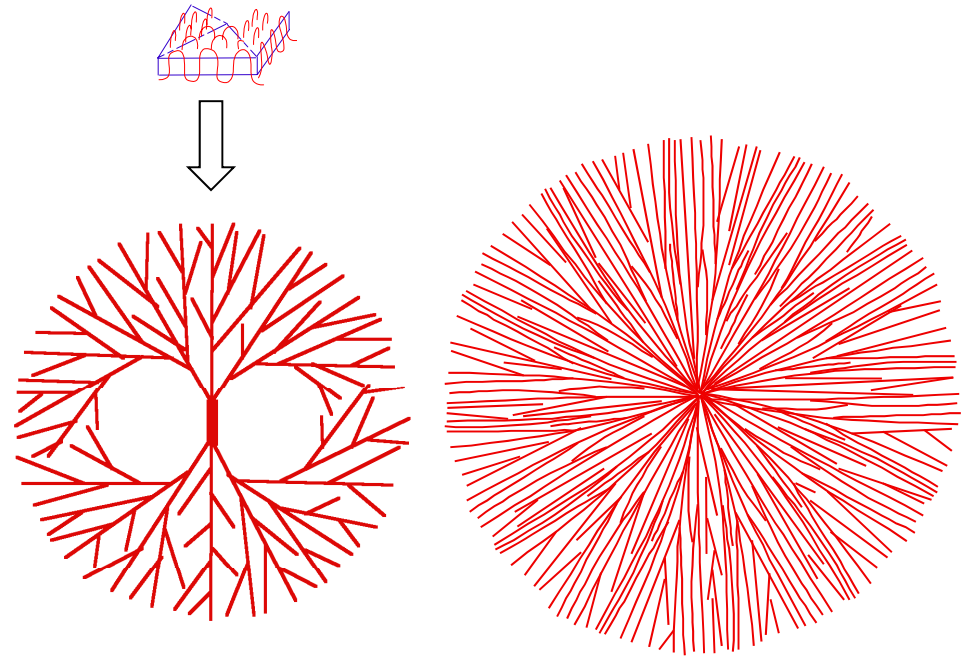
アイソタクティックポリプロピレン
染色後 透過型電子顕微鏡像
山田氏提供 (サンアロマー)



球晶



ポリフッ化ビニリデン球晶
偏光顕微鏡像

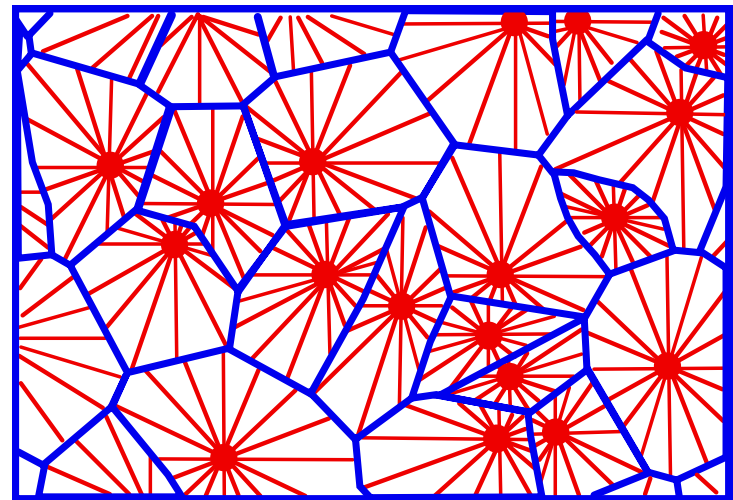
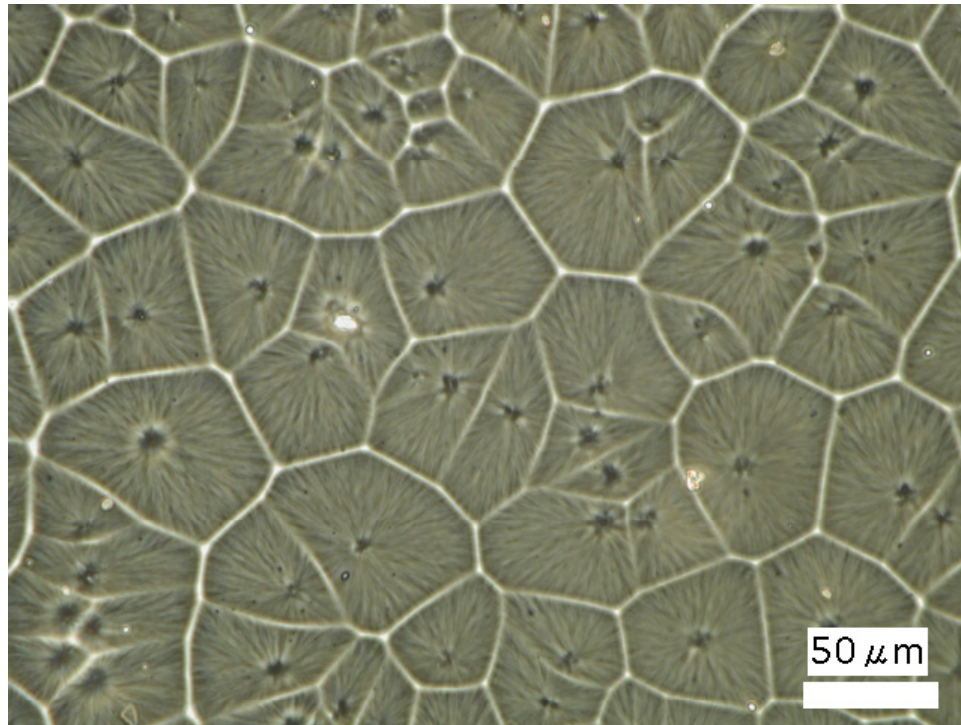


多彩な高次構造形成

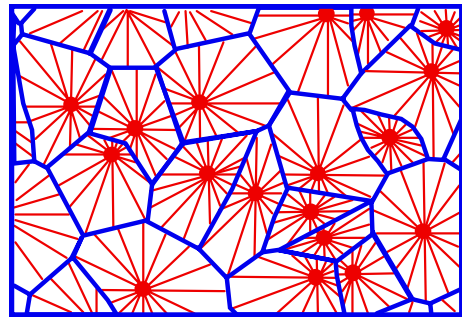


ポリヒドロキシ酪酸 偏光顕微鏡像

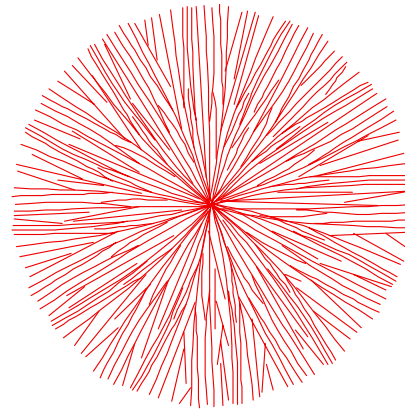
球晶の集合体



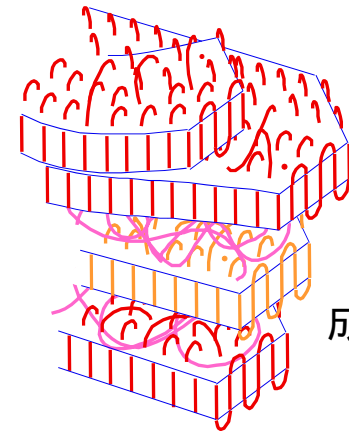
結晶性高分子のつくる階層構造



球晶の集合体



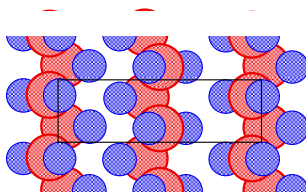
球晶



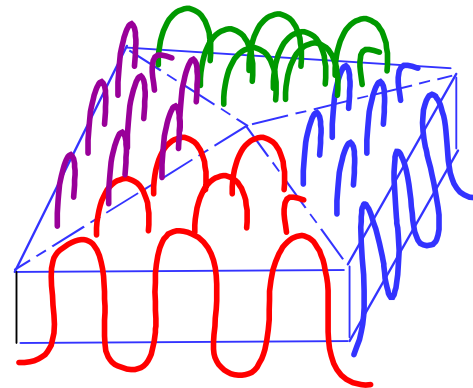
成長方向



結晶・非晶の積層構造



結晶構造



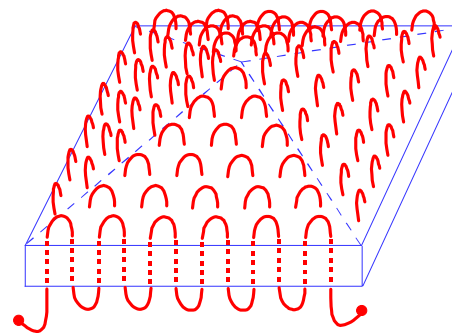
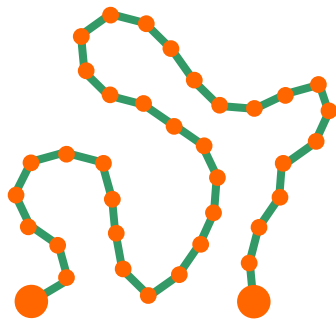
単結晶

折り畳み鎖結晶

説明されるべき特徴

- A) 結晶厚の結晶化温度(過冷却度)依存性
- B) 成長速度の結晶化温度(過冷却度)依存性
- C) 結晶の融解挙動

Sir Charles Frank: "If one could understand enough about the morphology of crystals, he understood essential points of the fundamentals of crystal growth."
"Diamonds are letters sent from the depth of the Earth."
「雪は天から送られた手紙である」中谷宇吉郎



高分子結晶の熱力学

融液—結晶間の $\Delta\mu_{l-c}$ = 融液結晶化の駆動力

混合状態の格子モデル

溶解温度, ブレンドの融点, ランダム共重合体の融点

融点の分子量依存性

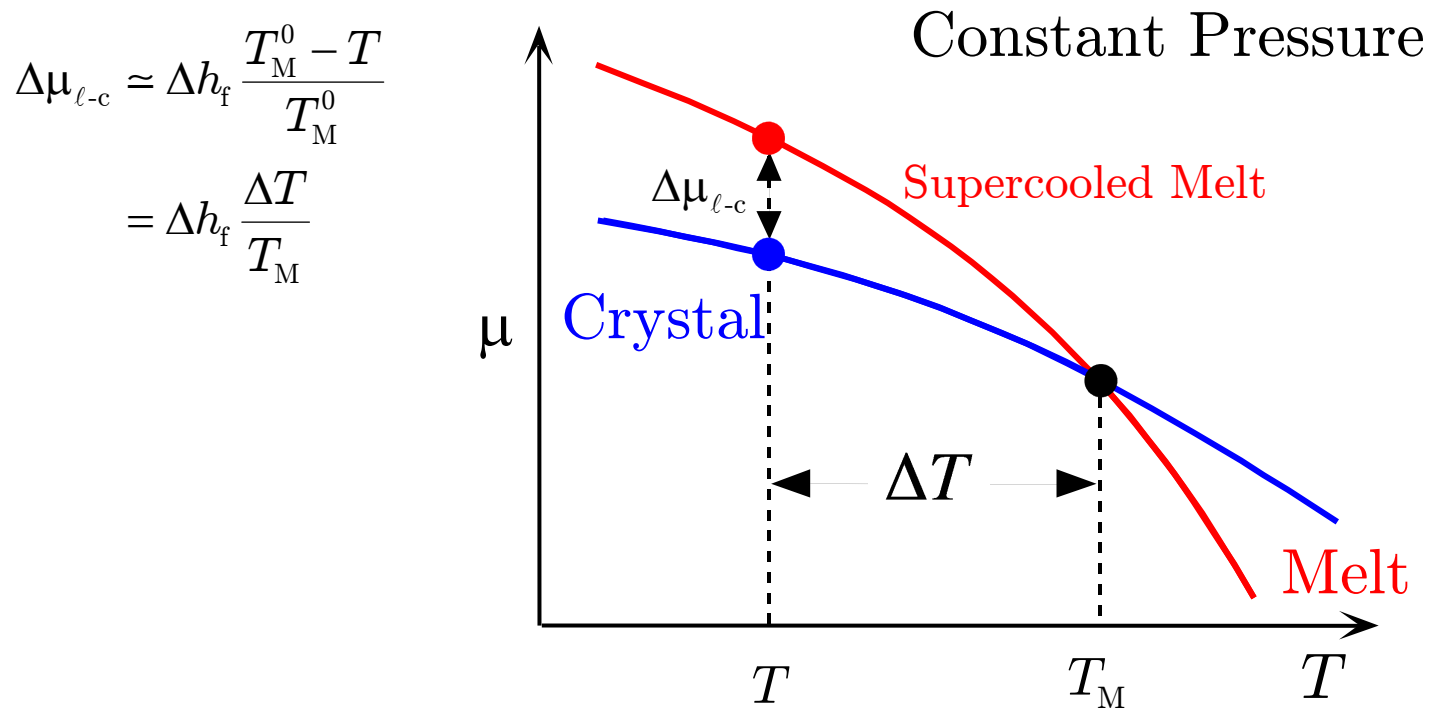
融点の圧力依存性

折り畳み鎖結晶の融点: 平衡融点の決定方法

動的過程

ガラス, ガラス転移

融液—結晶間の $\Delta\mu_{\ell-c}$ = 融液結晶化の駆動力



$$\because \text{At } T_M: \mu_s(T_M) = \mu_\ell(T_M) \Rightarrow h_s(T_M) - T_M s_s(T_M) = h_\ell(T_M) - T_M s_\ell(T_M)$$

$$\Rightarrow h_\ell(T_M) - h_s(T_M) = T_M [s_\ell(T_M) - s_s(T_M)] \Rightarrow \Delta h_f(T_M) = T_M \Delta s_f(T_M)$$

$$\Delta\mu(T) \approx \Delta h_f(T_M) - T \Delta s_f(T_M) \approx \Delta h_f(T_M) \frac{T_M - T}{T_M} = \Delta h_f \frac{\Delta T}{T_M}$$

$\Delta h_f, \Delta s_f$: Const. と仮定

$\Delta\mu_{l-c}$ の補正項

$\Delta h, \Delta s$: Const. のとき, $\Delta\mu_0 \approx \Delta h_f \frac{\Delta T}{T_M}$

実際には, $(\frac{\partial h}{\partial T})_p = T(\frac{\partial s}{\partial T})_p = c_p$

そこで c_p : Const. のとき,

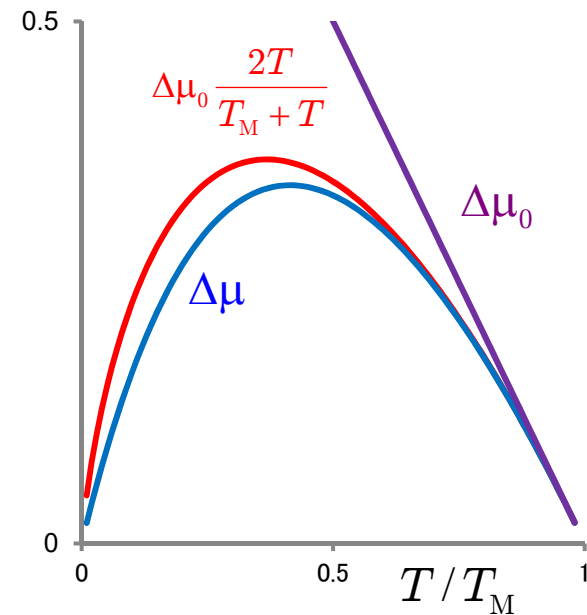
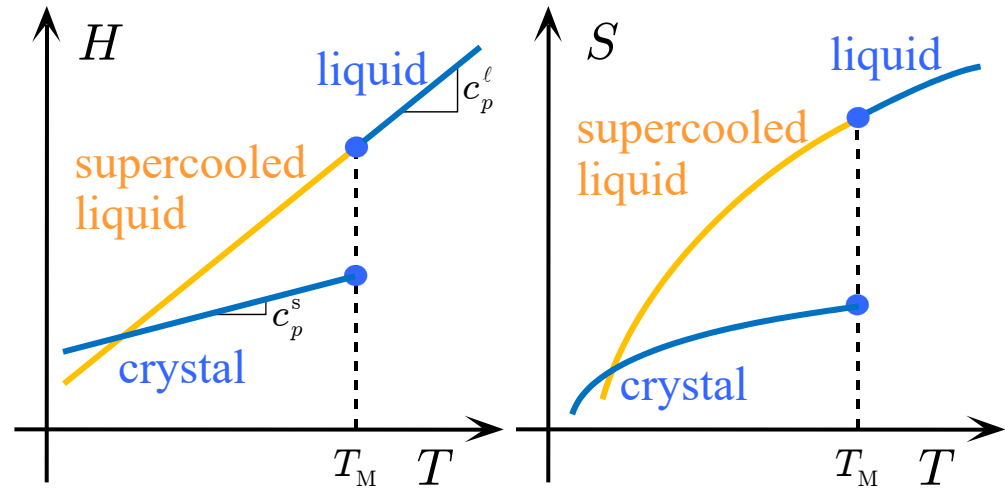
$$h = h_M - \int_T^{T_M} c_p dT = h_M - c_p(T_M - T)$$

$$s = s_M - \int_T^{T_M} \frac{c_p}{T} dT = s_M - c_p \ln \frac{T_M}{T}$$

$$\Delta\mu = \Delta h - T \Delta s = \Delta\mu_0 - \Delta c_p [(T_M - T) - T \ln \frac{T_M}{T}]$$

例えば, $T = 0K$ で, $\Delta h = 0$ のとき,

$$\Delta\mu \cong \Delta\mu_0 f \quad \text{Hoffman: } f \equiv \frac{2T}{T_M + T}$$



Hoffman: J Chem Phys **29** ('58) 1192

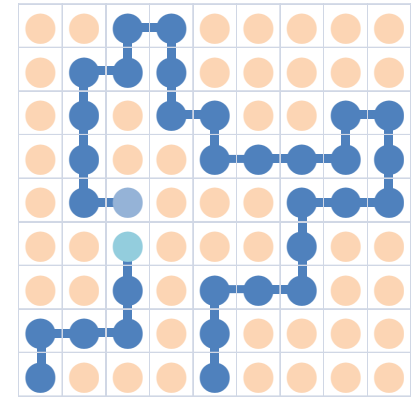
Hoffman, Weeks: J Chem Phys **37** ('62) 1723

混合状態の格子モデル

単分子2成分系の格子モデル

$$W = \frac{N!}{N_A! N_B!} \quad S = k_B \ln W \sim -k_B (N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N})$$

$$U = N_A \Delta \varepsilon (z x_B) = z \Delta \varepsilon \frac{N_A N_B}{N}$$



高分子理想鎖の格子モデル (Flory-Huggins)

高分子鎖は溶媒分子と大きさの等しいセグメント N 個からできているとする。
 N は高分子と溶媒のモル体積の比に等しい。

$$\phi_0 = \frac{n_0}{\Omega}, \quad \phi_1 = \frac{Nn_1}{\Omega}, \quad \Omega = n_0 + Nn_1$$

$$W(n_0, Nn_1) = \frac{1}{n_1! 2^{n_1}} \prod_{j=0}^{n_1-1} (\Omega - Nj) \times [z(1 - \frac{Nj}{\Omega})] \times [(z-1)(1 - \frac{Nj}{\Omega})]^{N-2}$$

頭尾 1つ目 2つ目 3つ目以降

$$S(n_0, Nn_1) = k_B \ln W = k_B (-n_0 \ln \phi_0 - n_1 \ln \phi_1 + n_1 \ln \frac{z(z-1)^{N-2} N}{2e^{N-1}})$$

$$S(0, Nn_1) = k_B n_1 \ln \frac{Nz(z-1)^{N-2}}{2e^{N-1}} \quad S(n_0, 0) = 0$$

$$\Delta S = S(n_0, Nn_1) - S(0, Nn_1) - S(n_0, 0) = -k_B (n_0 \ln \phi_0 + n_1 \ln \phi_1)$$

証明)

$$\begin{aligned}
 W &= \frac{1}{n_1! 2^{n_1}} \prod_{j=0}^{n_1-1} (\Omega - Nj) \times [z(1 - \frac{Nj}{\Omega})] \times [(z-1)(1 - \frac{Nj}{\Omega})]^{N-2} \\
 &= (\delta\Omega)^{n_1} \frac{1}{n_1!} \prod_{j=0}^{n_1-1} (1 - \frac{Nj}{\Omega})^N \quad \delta \equiv \frac{1}{2} z(z-1)^{N-2} \\
 &= (\delta \frac{N^N}{\Omega^{N-1}})^{n_1} \frac{1}{n_1!} \prod_{j=0}^{n_1-1} (\frac{\Omega}{N} - j)^N = (\delta \frac{N^N}{\Omega^{N-1}})^{n_1} \frac{1}{n_1!} \left[\frac{(\Omega/N)!}{(n_0/N)!} \right]^N
 \end{aligned}$$

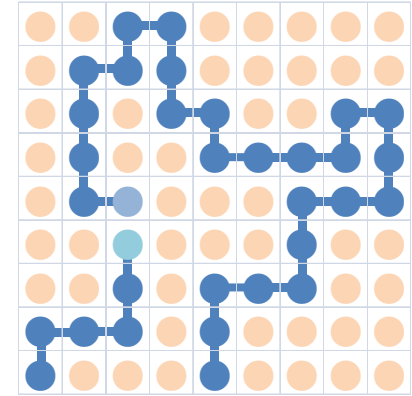
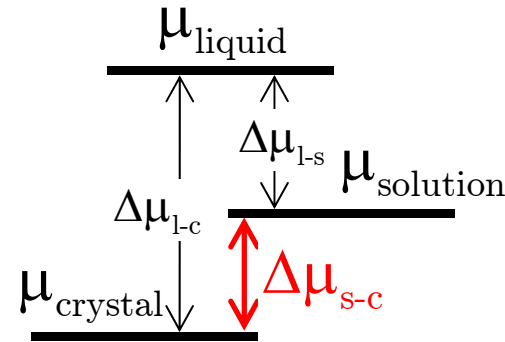
ここで, Stirlingの近似式 $\ln N! \underset{N \gg 1}{\sim} N(\ln N - 1)$

$$\begin{aligned}
 \ln W &\sim n_1 \ln \delta \frac{N^N}{\Omega^{N-1}} - n_1 (\ln n_1 - 1) + N \frac{\Omega}{N} (\ln \frac{\Omega}{N} - 1) - N \frac{n_0}{N} (\ln \frac{n_0}{N} - 1) \\
 &= n_1 \ln \delta + N n_1 \ln N - (N-1) n_1 \ln \Omega - n_1 \ln n_1 + n_1 + \Omega \ln \Omega - \Omega \ln N - \Omega - n_0 \ln n_0 + n_0 \ln N + n_0 \\
 &= n_1 (\ln \delta + 1 - N + \ln N) - n_1 (\ln n_1 - \ln \Omega + \ln N) - n_0 (\ln n_0 - \ln \Omega) + (n_0 + N n_1 - \Omega) (1 + \ln N) \\
 &= n_1 \ln \frac{\delta N}{e^{N-1}} - n_1 \ln \frac{N n_1}{\Omega} - n_0 \ln \frac{n_0}{\Omega} \\
 &= -n_1 \ln \phi_1 - n_0 \ln \phi_0 + n_1 \ln \frac{\delta N}{e^{N-1}} \quad \text{ただし, } \phi_0 = \frac{n_0}{\Omega} \quad \phi_1 = \frac{N n_1}{\Omega} \quad n_0 + N n_1 = \Omega
 \end{aligned}$$

溶解 $\Delta\mu_{s-c} = \text{融解} \rightarrow \text{混合}$

$$\Delta\mu_{l-c} \approx \Delta h_f \frac{T_M^0 - T}{T_M^0}$$

$\Delta\mu_{l-s}$: 格子モデル(Flory-Huggins)



$$\Delta S = -k_B (n_0 \ln \phi_0 + n_1 \ln \phi_1) \quad \Delta U = z \Delta \varepsilon \frac{n_0 N n_1}{\Omega} = \chi k_B T n_0 \phi_1 \quad \chi \equiv \frac{z \Delta \varepsilon}{k_B T}$$

$$\Delta F = \Delta U - T \Delta S = k_B T (n_0 \ln \phi_0 + n_1 \ln \phi_1 + \chi n_0 \phi_1)$$

$$\Delta\mu = \frac{\partial \Delta F}{\partial n_1} = k_B T \left(\frac{n_0}{\phi_0} \frac{\partial \phi_0}{\partial n_1} + \ln \phi_1 + \frac{n_1}{\phi_1} \frac{\partial \phi_1}{\partial n_1} + \chi n_0 \frac{\partial \phi_1}{\partial n_1} \right) = k_B T [\ln \phi_1 - (N-1) \phi_0 + \chi N \phi_0^2]$$

$$\begin{aligned} \therefore \frac{\partial \phi_0}{\partial n_1} &= \frac{\partial}{\partial n_1} \frac{n_0}{n_0 + N n_1} = \frac{-N n_0}{(n_0 + N n_1)^2} & n_0 \frac{\partial \phi_0}{\partial n_1} &= -N \phi_0^2 \\ \frac{\partial \phi_1}{\partial n_1} &= \frac{\partial}{\partial n_1} \frac{N n_1}{n_0 + N n_1} = \frac{N n_0}{(n_0 + N n_1)^2} & n_1 \frac{\partial \phi_1}{\partial n_1} &= \phi_0 \phi_1 \end{aligned}$$

高分子 1 本当たりの量が計算された。溶媒と高分子構造単位のもル体積を v_0, v_u として、1 本の高分子の構造単位数 $N v_0 / v_u$ で割ることで、構造単位 1 モル当たりの量とする。

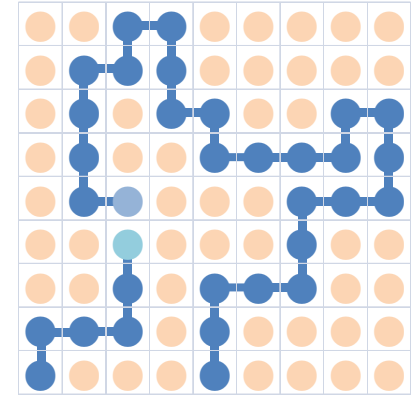
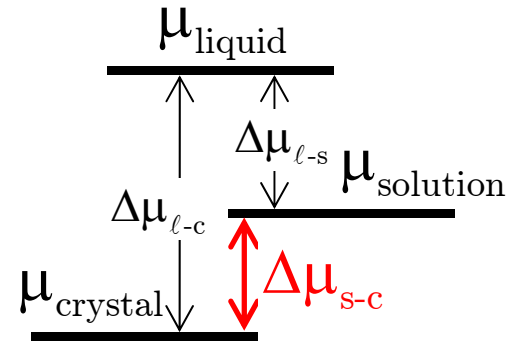
$$\Delta\mu_{l-s} = \frac{-\Delta\mu}{N v_0 / v_u} = -k_B T \frac{v_u}{v_0} \left[\frac{\ln \phi_1}{N} - \left(1 - \frac{1}{N}\right) \phi_0 + \chi \phi_0^2 \right] \approx -k_B T \frac{v_u}{v_0} (-\phi_0 + \chi \phi_0^2) \text{ for } N \gg 1$$

Mandelkern: “Crystallization of Polymers”

溶解 $\Delta\mu_{s-c} = \text{融解} \rightarrow \text{混合}$

$$\Delta\mu_{\ell-c} \approx \Delta h_f \frac{T_M^0 - T}{T_M^0}$$

$$\Delta\mu_{\ell-s} \approx -k_B T \frac{v_u}{v_0} (-\phi_0 + \chi \phi_0^2) \text{ for } N \gg 1$$

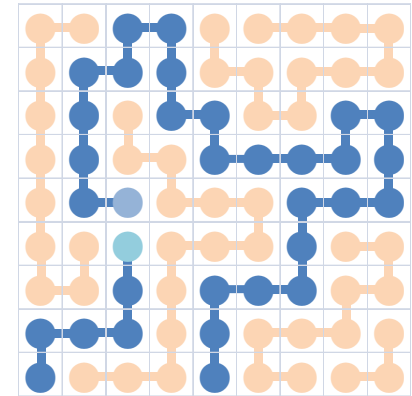
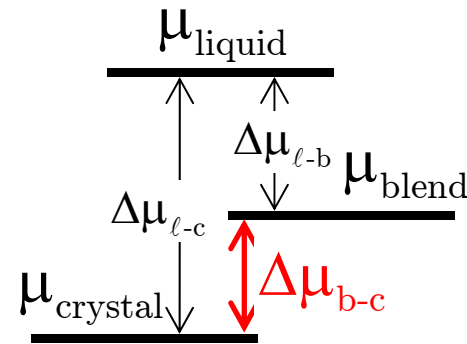


溶解温度 T_d で $\Delta\mu_{s-c} = 0$ から, $\Delta\mu_{\ell-c} = \Delta\mu_{\ell-s} \quad \therefore \Delta h_f \frac{T_M^0 - T_d}{T_M^0} = -RT_d \frac{v_u}{v_0} (-\phi_0 + \chi \phi_0^2)$

$$\Delta h_f \left(\frac{1}{T_d} - \frac{1}{T_M^0} \right) = R \frac{v_u}{v_0} (\phi_0 - \chi \phi_0^2)$$

希薄溶液 ($\phi_0 \sim 1$) では, $\Delta h_f \left(\frac{1}{T_d} - \frac{1}{T_M^0} \right) = R \frac{v_u}{v_0} (1 - \chi)$

高分子ブレンドの融点 西-Wangの式



$\Delta\mu_{\ell-b}$: 格子モデル(Flory-Huggins)

$$\phi_0 = \frac{N_0 n_0}{N_0 n_0 + N_1 n_1} \quad \phi_1 = \frac{N_1 n_1}{N_0 n_0 + N_1 n_1}$$

$$\Delta F = k_B T (n_0 \ln \phi_0 + n_1 \ln \phi_1 + \chi N_0 n_0 \phi_1)$$

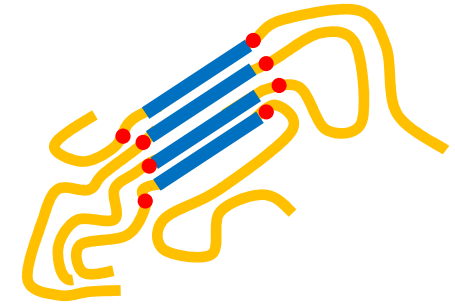
$$\Delta\mu = \frac{\partial \Delta F}{\partial n_1} = k_B T \left[\ln \phi_1 - \left(\frac{N_1}{N_0} - 1 \right) \phi_0 + \chi N_1 \phi_0^2 \right]$$

$$\Delta\mu_{\ell-b} = \frac{-\Delta\mu}{N_1 v_0 / v_u} = -k_B T \frac{v_u}{v_0} \left[\frac{\ln \phi_1}{N_1} - \left(\frac{1}{N_0} - \frac{1}{N_1} \right) \phi_0 + \chi \phi_0^2 \right] \approx -k_B T \frac{v_u}{v_0} \chi \phi_0^2 \quad \text{for } N_0, N_1 \gg 1$$

溶解温度 T_d で $\Delta\mu_{s-c} = 0$ から, $\Delta\mu_{\ell-c} = \Delta\mu_{\ell-b}$

$$\therefore \Delta h_f \frac{T_M^0 - T_M}{T_M^0} = -R T_M \frac{v_u}{v_0} \chi \phi_0^2 \Rightarrow \Delta h_f \left(\frac{1}{T_M} - \frac{1}{T_M^0} \right) = -R \frac{v_u}{v_0} \chi \phi_0^2$$

ランダム共重合体の融点 Floryの式



X_A : ランダム共重合体中の結晶性(A)成分のモル分率

ζ : A成分連鎖からなる結晶の厚さ(長さ)

$$\zeta \Delta h_f \frac{T_M^0 - T_M}{T_M^0} - T_M [-R \ln(X_A)^\zeta] = 0$$

$$\therefore \Delta h_f \left(\frac{1}{T_M} - \frac{1}{T_M^0} \right) = -R \ln X_A$$

Flory: J Chem Phys **17** ('49) 223

Mandelkern: "Crystallization of Polymers"

Helfand, Lauritzen: Macromolecules **6** ('73) 631

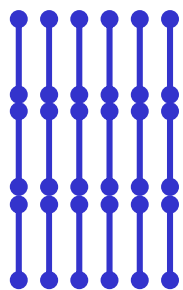
融点の分子量依存性

Broadhurst, Flory-Vrij

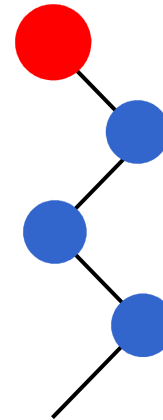
$$T_M(n) = \frac{\Delta h_f}{\Delta s_f} = \frac{n \Delta h_f^0 + \Delta h_f^e}{n \Delta s_f^0 + \Delta s_f^e}$$

$$= T_M(\infty) \frac{n + a}{n + b + c \ln n}$$

$$a < 0, b > 0, c > 0$$



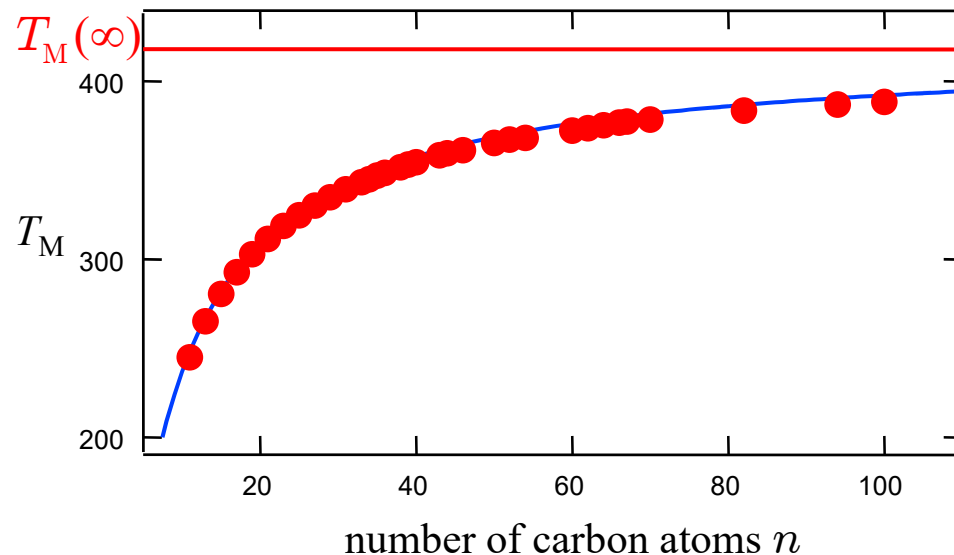
結晶内: 末端同士1通り
 溶融体: ランダム n 通り



$$\Delta \mu_f = \Delta h_f - T \Delta s_f$$

$$\Delta h_f = n \Delta h_f^0 + \Delta h_f^e$$

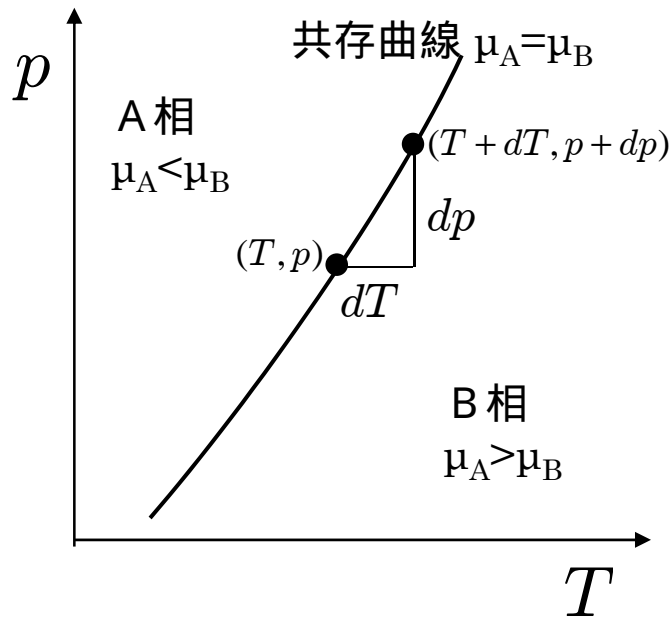
$$\Delta s_f = n \Delta s_f^0 + \Delta s_f^e$$



融点

圧力依存性 Clapeyron Clausius の式

共存曲線の接線： $\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$ ただし、 $L = \text{潜熱}$.

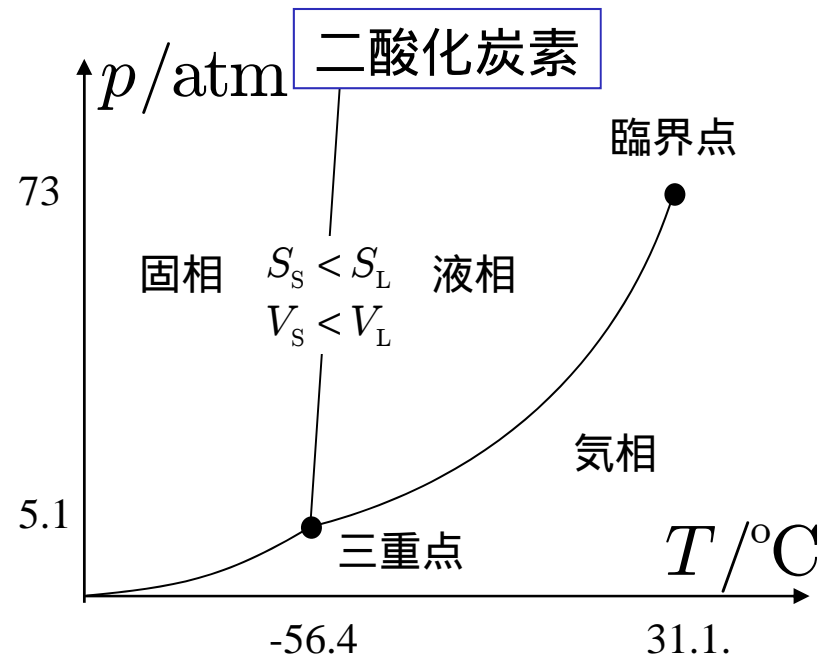
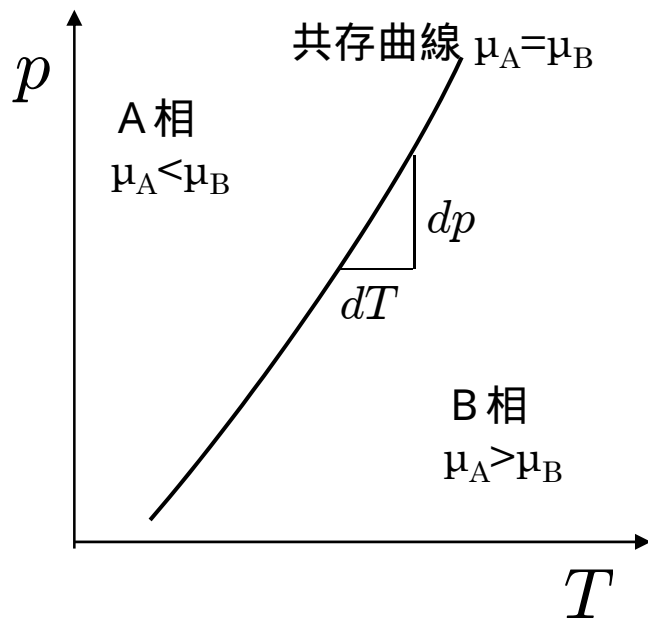


$$\begin{cases} \mu_A(T, p) = \mu_B(T, p) \\ \mu_A(T + dT, p + dp) = \mu_B(T + dT, p + dp) \end{cases}$$
$$\left(\frac{\partial \mu_A}{\partial T}\right)_p dT + \left(\frac{\partial \mu_A}{\partial p}\right)_T dp = \left(\frac{\partial \mu_B}{\partial T}\right)_p dT + \left(\frac{\partial \mu_B}{\partial p}\right)_T dp$$
$$-s_A dT + v_A dp = -s_B dT + v_B dp$$
$$\frac{dp}{dT} = \frac{s_B - s_A}{v_B - v_A} = \frac{\Delta s}{\Delta v} = \frac{L}{T \Delta v}$$

融点

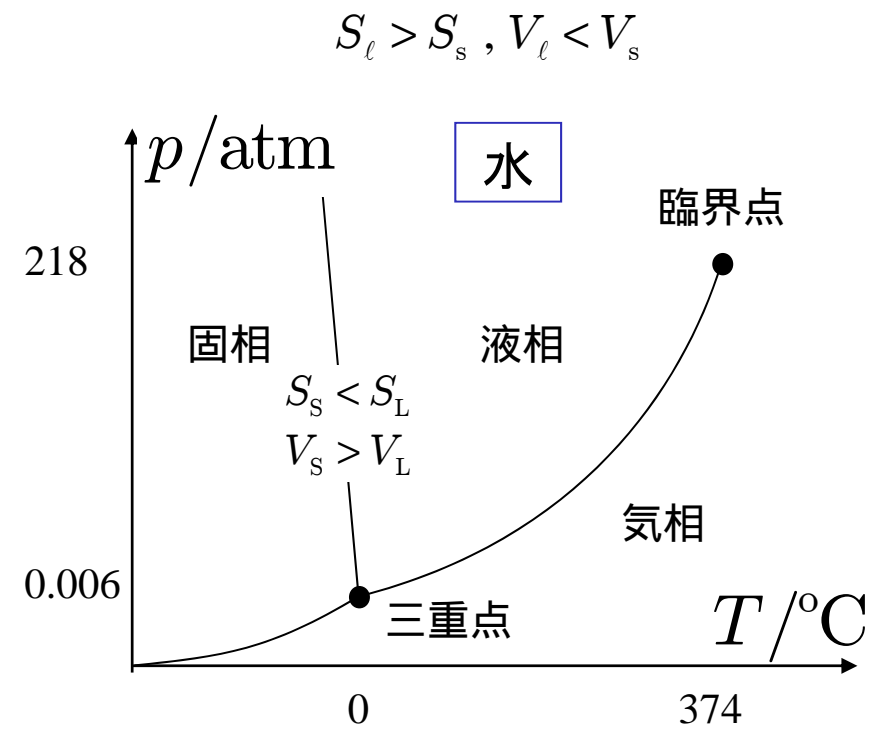
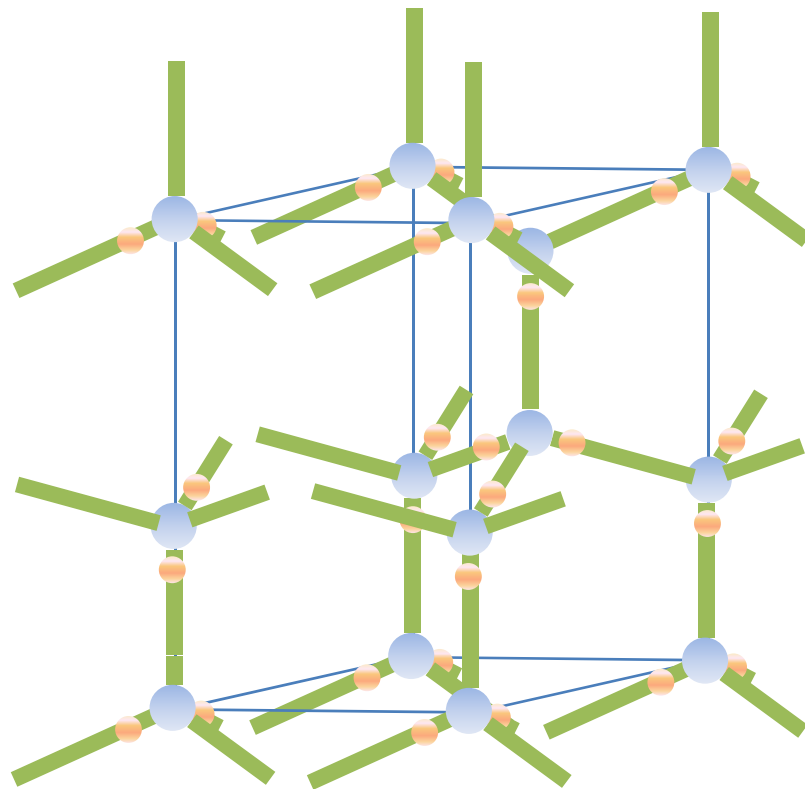
圧力依存性 Clapeyron Clausius の式

共存曲線の接線： $\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$ ただし、 L = 潜熱.



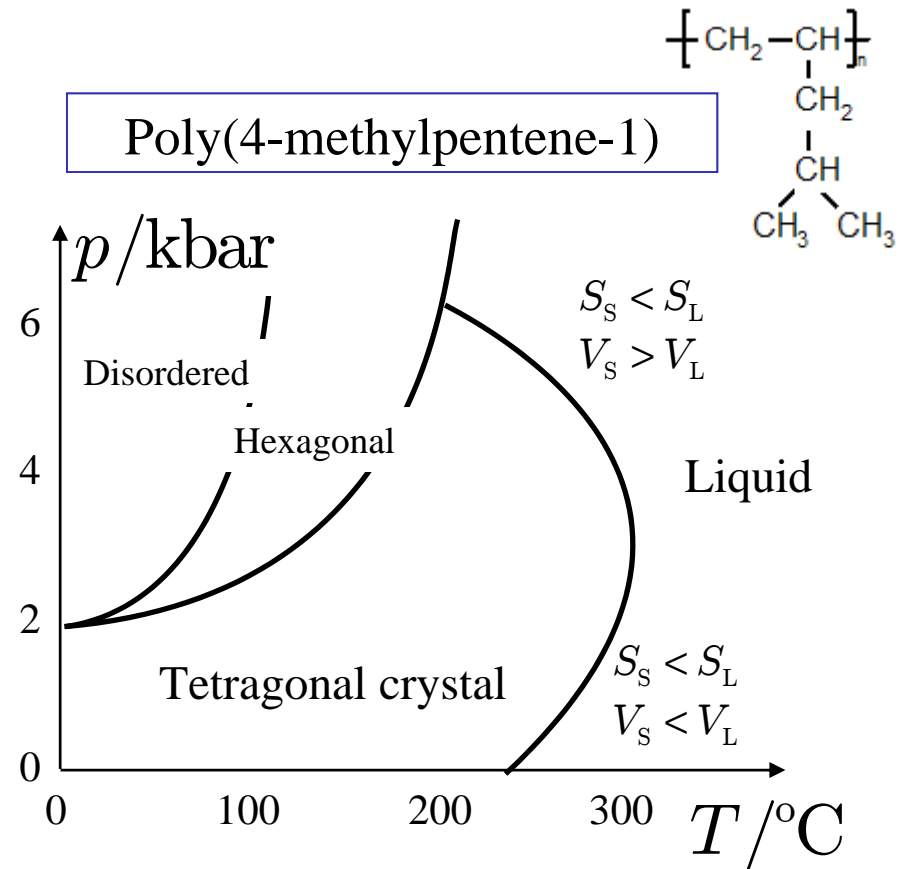
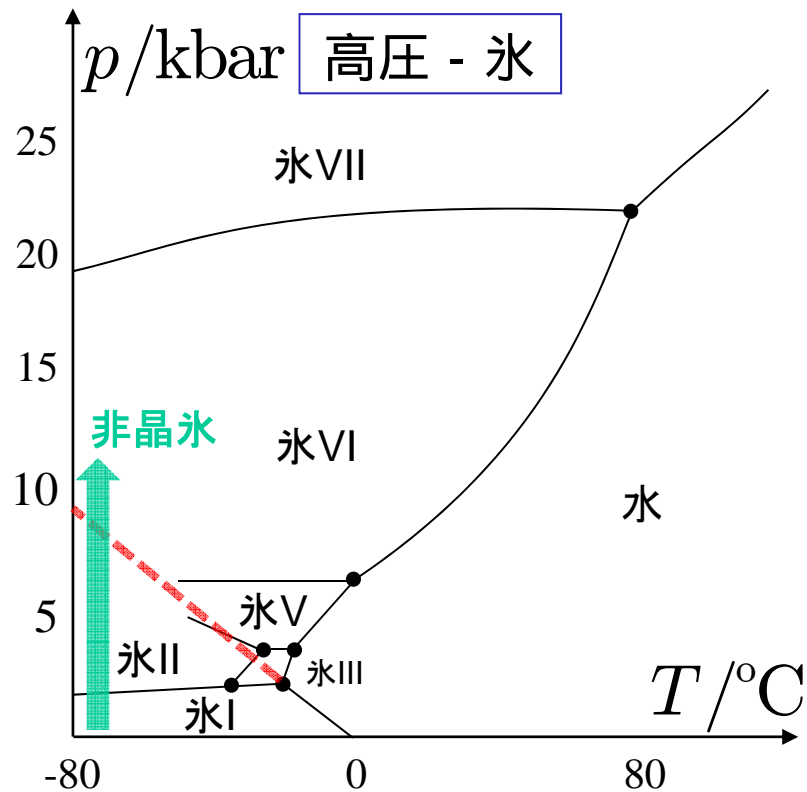
融点

圧力依存性 Clapeyron Clausius の式



融点

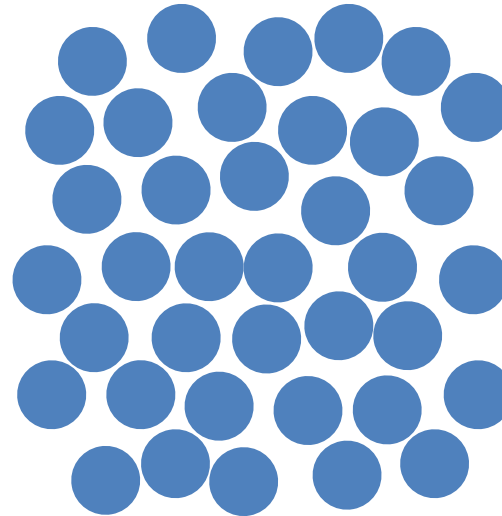
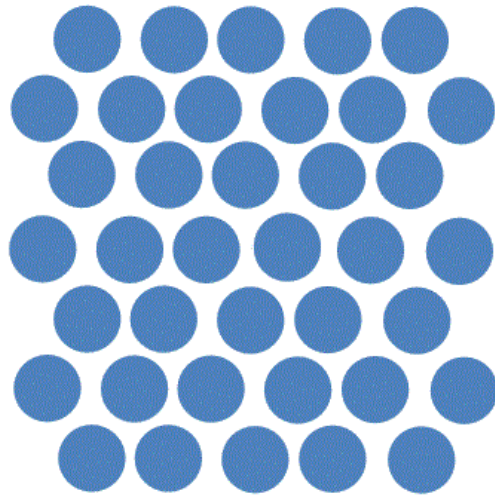
圧力依存性 Clapeyron Clausius の式



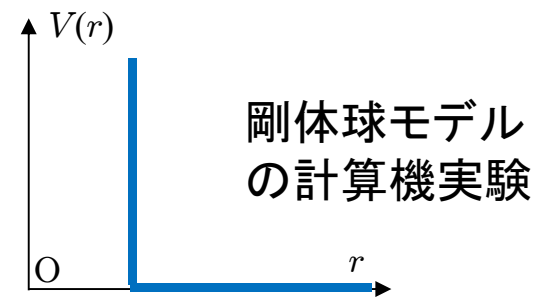
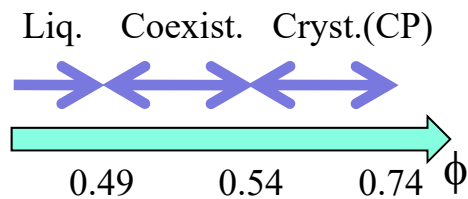
Entropically Favored Ordering

$$S_{\text{crystal}} > S_{\text{liquid}}$$

$$S = S_{\text{vibrational}} + S_{\text{configurational}}$$



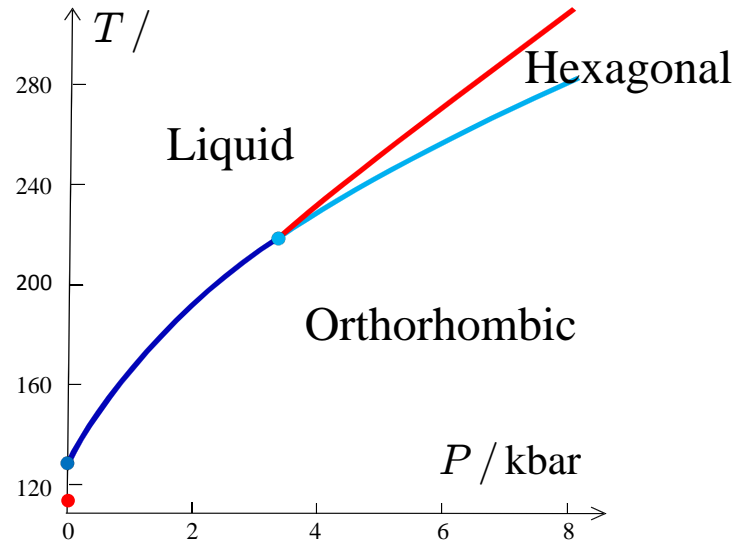
ラテックス球の
2次元結晶化



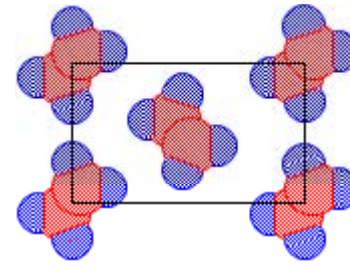
PMMA colloidal suspension ($2.3\mu\text{m}$, $\phi \approx 0.6$)
Weeks: Soft Jammed Materials 2007

Alder & Wainwright: *Phys Rev* 127 (62) 359

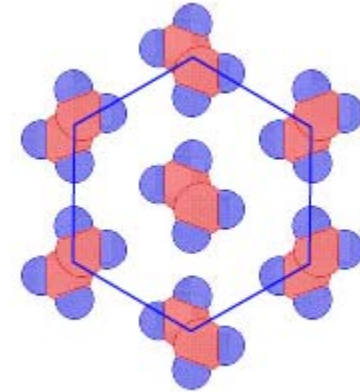
Polyethylene 高温高压下



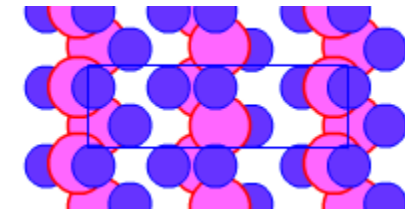
Orthorhombic



Hexagonal



Sliding Diffusion



Wunderlich, Arakawa:

J Polym Sci **A2** ('64) 3697

Bassett, Block, Piermarini:

J Appl Phys **45** ('74) 4146

Hikosaka: Polymer **28** ('87) 1257

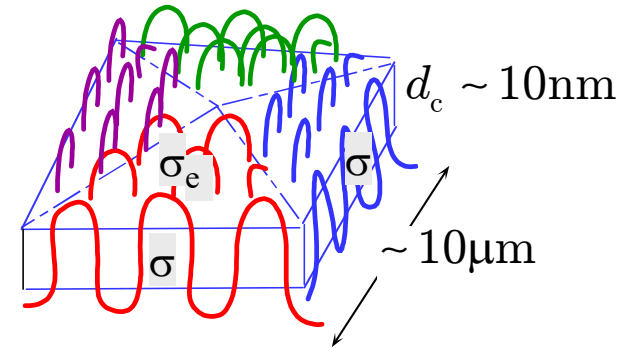
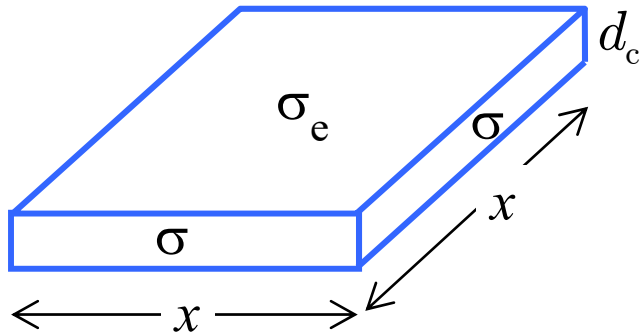
Rastogi, Hikosaka, Kawabata, Keller:

Macromolecules **24** ('91) 6384

高压(PE伸びきり鎖結晶)

折り畳み鎖結晶の融点：Gibbs-Thomsonの式（サイズ効果）

$$\Delta\mu = \mu_2 - \mu_1 = \gamma \frac{2v_1}{R}, \quad v_1: 1 \text{ 相内での分子 1 個の体積}$$



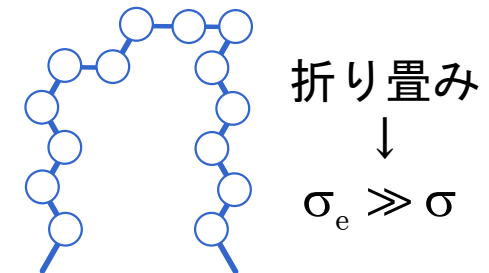
$$\Delta G = 4x d_c \sigma + 2x^2 \sigma_e - x^2 d_c \Delta\mu$$

$$= x^2 (4\sigma d_c/x + 2\sigma_e - d_c \Delta\mu) = 0$$

$$\Delta\mu = \Delta h_f \frac{T_M^0 - T}{T_M^0}$$

伸びきり鎖の平衡融点

表面自由エネルギー(J/m²) σ, σ_e



Gibbs-Thomsonの式 $d_c/x \ll 1$

$2\sigma_e - d_c \Delta\mu \cong 0$ 折り畳み鎖結晶と融液の平衡

$$@T_M: T_M = T_M^0 - \frac{C}{d_c}, \quad C = \frac{2\sigma_e T_M^0}{\Delta h_f} \quad \text{折り畳み鎖結晶の融点}$$

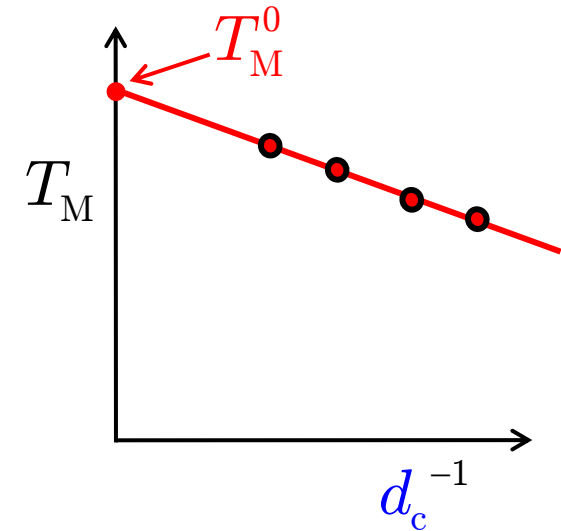
$$@T_c: d_c \geq d_c^* = \frac{2\sigma_e}{\Delta\mu(T_c)} = \frac{C}{T_M^0 - T_c} \quad \text{結晶厚さの下限}$$

伸びきり鎖結晶の平衡融点 T_M^0 の決定法

Gibbs-Thomsonプロット

$$T_M = T_M^0 - \frac{C}{d_c}, \quad C = \frac{2\sigma_e T_M^0}{\Delta h_f}$$

T_M と d_c のデータセットが必要



簡便法 (Hoffman-Weeksプロット)

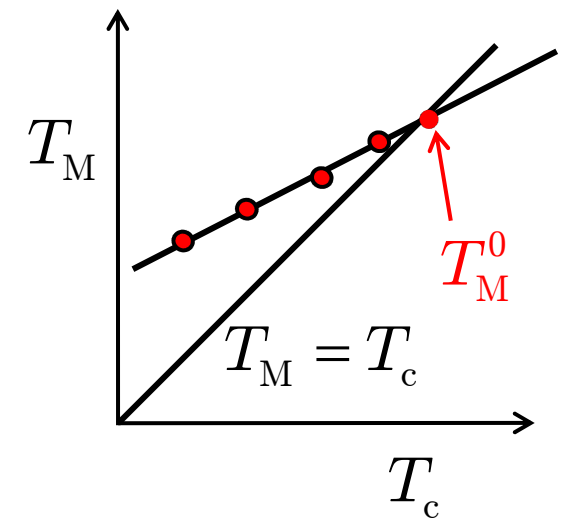
もし $T_c \rightarrow T_M^0$, なら $T_M \rightarrow T_M^0$ であろう。

T_M と T_c のデータセットが必要

融液結晶化時の厚化成長では,

$$d_c = \gamma d_c^* = \gamma \frac{C}{T_M^0 - T_c}$$

$$\therefore T_M = T_M^0 \left(1 - \frac{T_M^0 - T_c}{\gamma T_M^0}\right) \Rightarrow T_M = \frac{1}{\gamma} T_c + \left(1 - \frac{1}{\gamma}\right) T_M^0$$

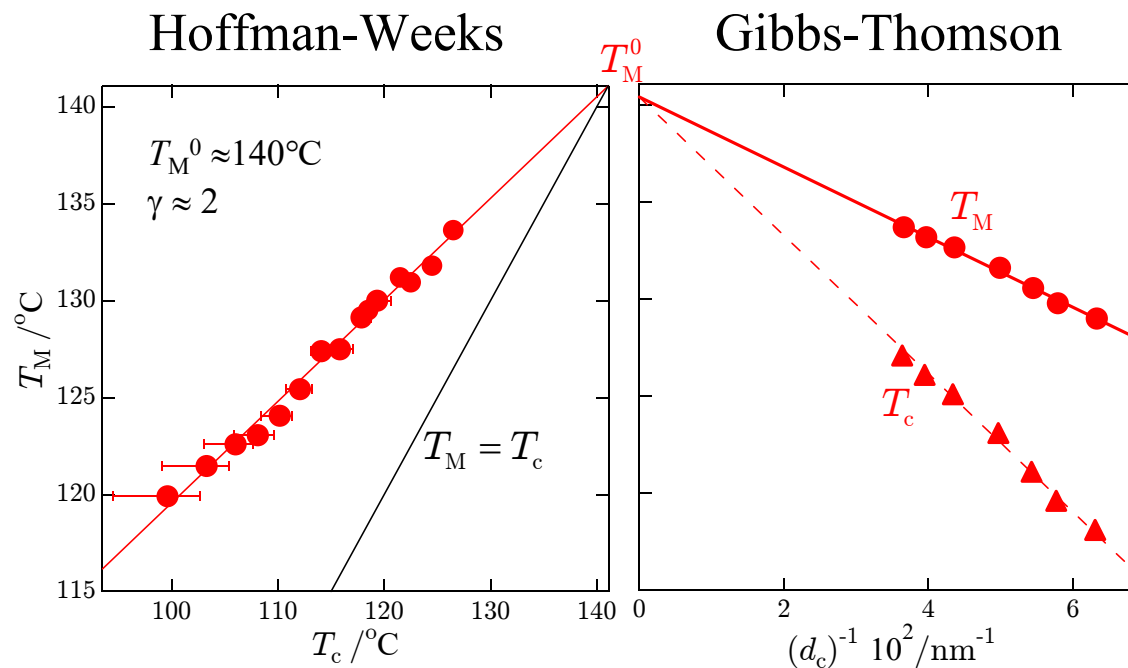


T_M の決定法

顕微鏡法などによる融解の直接観察, 熱測定

問題点: ピーク幅, 再組織化・再結晶化, 複数ピーク, 昇温速度依存性

T_M^0 の決定法: ポリエチレンの例



問題点のうち, 再組織化・再結晶化の影響は高速昇温により回避できる。

ピーク帰属は昇温速度依存性により, その昇温速度依存性は融解キネティクスとして定量的に評価できる。

動的過程：素過程の進行速度

Arrhenius の式

反応速度 k :

$$k = A \exp\left[-\frac{Q}{RT}\right] = A \exp\left[-\frac{Q/N_A}{kT}\right]$$

Q : 1 モル当たりの活性化エネルギー

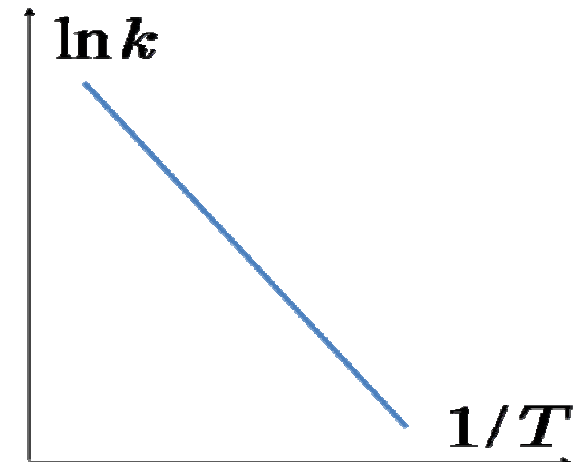
$R = N_A k_B$: 気体定数

N_A : Avogadro 定数

k_B : Boltzmann 定数

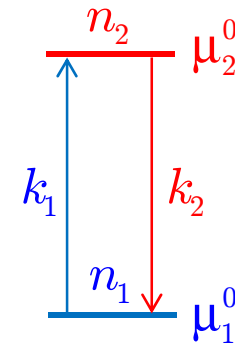
Q/N_A : 分子 1 個当たりの活性化エネルギー

A : 頻度因子



動的過程：素過程の進行速度

Eyring の反応速度論



等温等圧: $G = (\mu_1^0 + k_B T \ln[\frac{n_1}{n_1 + n_2}]) n_1 + (\mu_2^0 + k_B T \ln[\frac{n_2}{n_1 + n_2}]) n_2$

$N = n_1 + n_2$ 一定で G 最小: $0 = \Delta G = (\mu_1^0 + k_B T \ln[\frac{n_1}{n_1 + n_2}]) \Delta n - (\mu_2^0 + k_B T \ln[\frac{n_2}{n_1 + n_2}]) \Delta n$

平衡定数: $K = \frac{n_2}{n_1} = \exp[-\frac{\mu_2^0 - \mu_1^0}{k_B T}] (= \frac{k_1}{k_2})$

詳細釣り合いの原理: $n_1 k_1 = n_2 k_2$

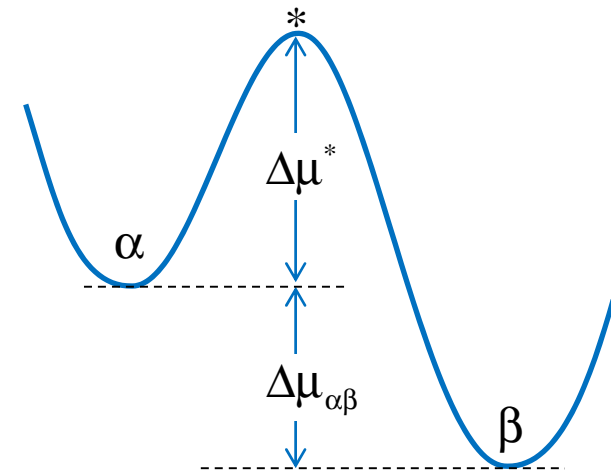
反応速度 k :

$$k_{\alpha \rightarrow \beta} \sim \frac{k_B T}{h} \exp[-\frac{\Delta \mu^*}{k_B T}]$$

$$k_{\beta \rightarrow \alpha} \sim \frac{k_B T}{h} \exp[-\frac{\Delta \mu^* + \Delta \mu_{\alpha\beta}}{k_B T}]$$

$\Delta \mu^*$: 分子 1 個当たりの活性化自由エネルギー

$\Delta \mu_{\alpha\beta}$: 分子 1 個当たりの $\alpha - \beta$ 間の自由エネルギー差



動的過程：素過程の進行速度

Eyring の反応速度論

例) 粘度 η : $\tau = \eta \dot{\gamma}$

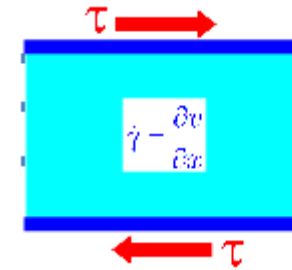
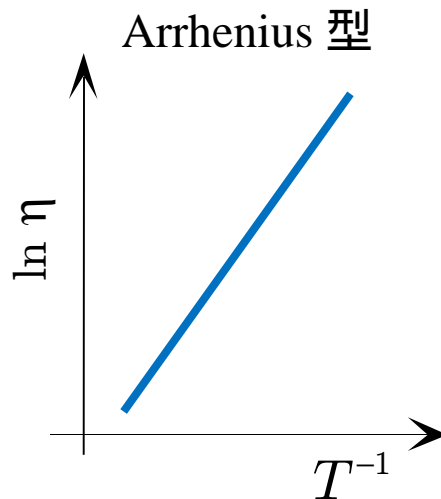
$$k_f - k_b \sim \frac{k_B T}{h} e^{-\frac{\Delta\mu^*}{k_B T}} (1 - e^{-\frac{\Delta w}{k_B T}}) \sim \frac{1}{h} e^{-\frac{\Delta\mu^*}{k_B T}} \Delta w$$

$$\Delta w = (\tau a^2) a = \tau v_s$$

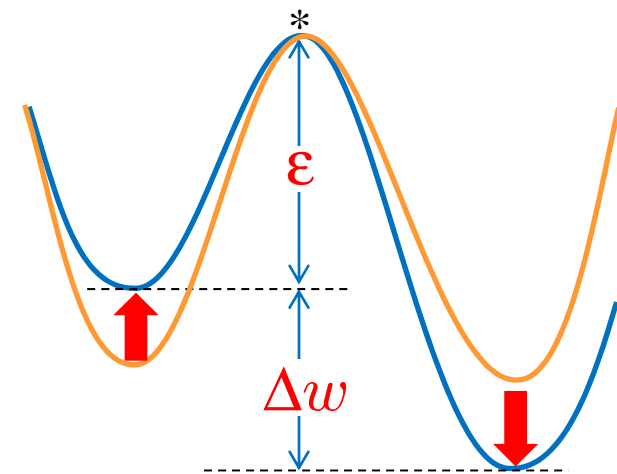
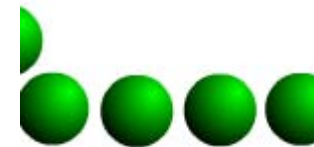
$$\frac{\partial v}{\partial x} = \frac{a(k_f - k_b)}{a} \sim \frac{v_s}{h} e^{-\frac{\Delta\mu^*}{k_B T}} \tau$$

$$\eta = \frac{h}{v_s} \exp\left[\frac{\Delta\mu^*}{k_B T}\right]$$

$$\ln \eta = \ln \frac{h}{v_s} + \frac{\Delta\mu^*}{k_B} T^{-1}$$



$$\tau = \eta \dot{\gamma}$$



Eyring: “絶対反応速度論”

ガラス, ガラス転移

ガラス

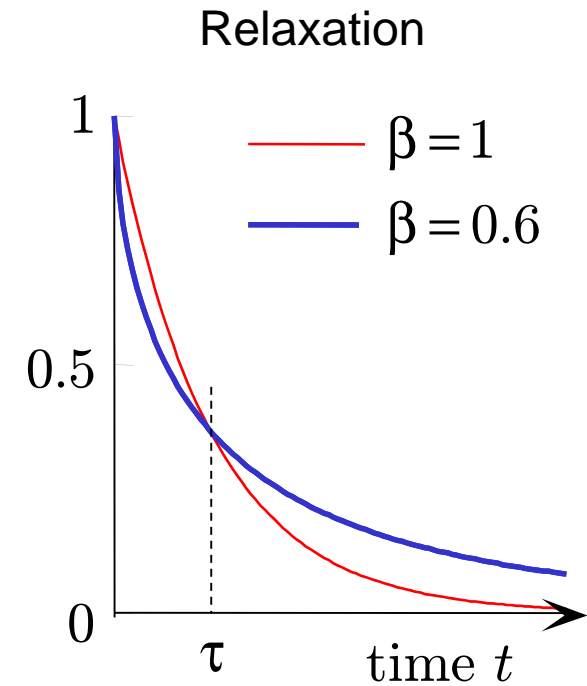
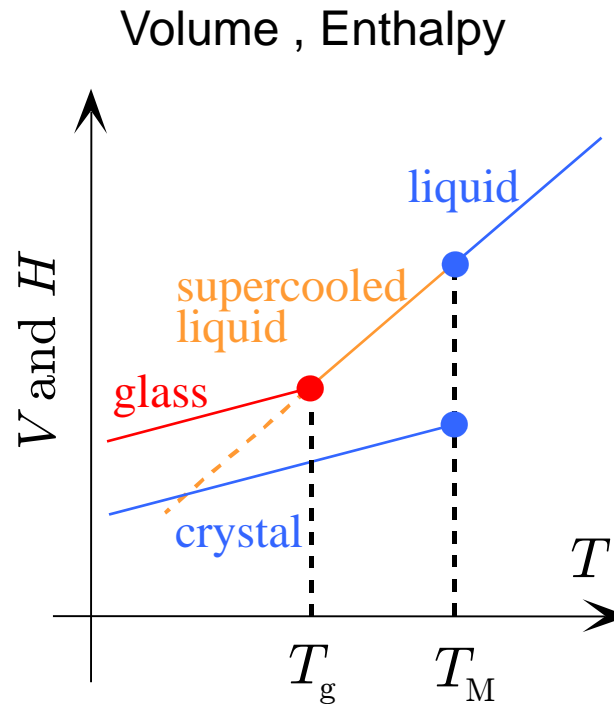
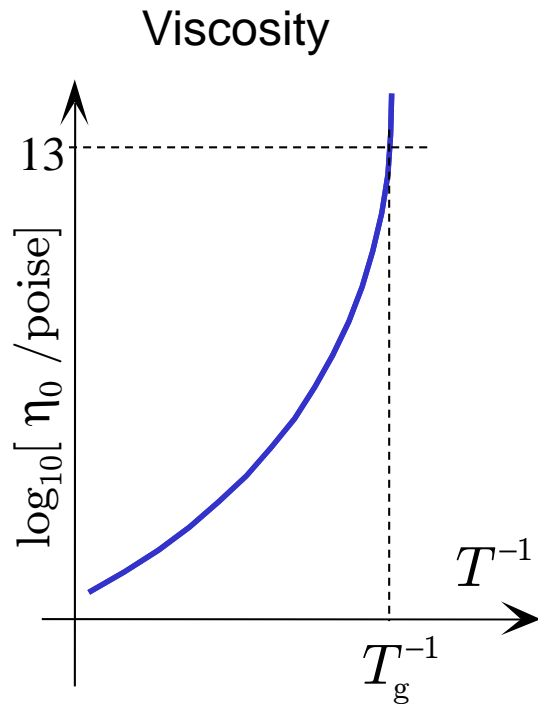
- 長距離秩序なし(液体), 流動性なし(固体)
- 分子鎖全体の形態 ~ 溶融状態(ランダムコイル)



ガラス転移

- 溶融体を降温して(過冷却すると)流動性を失い, 固化する。
- 高分子鎖のミクロブラウン運動(高分子鎖の部分鎖の熱運動に起因するセグメント運動)が凍結される(運動を特徴づける時間がマクロな時間スケール(例 100秒)になる)。
- 動的な転移(緩和現象)であり, 熱力学的な相転移ではない。
- ガラス転移に伴い, 降温(昇温)時の体積やエンタルピー変化に異常が現れる(膨張率や熱容量に階段状の変化が現れる)。

ガラス, ガラス転移



非 Arrhenius 型

Vogel-Flucher 則

$$\eta \propto \exp\left[\frac{C}{T - T_0}\right]$$

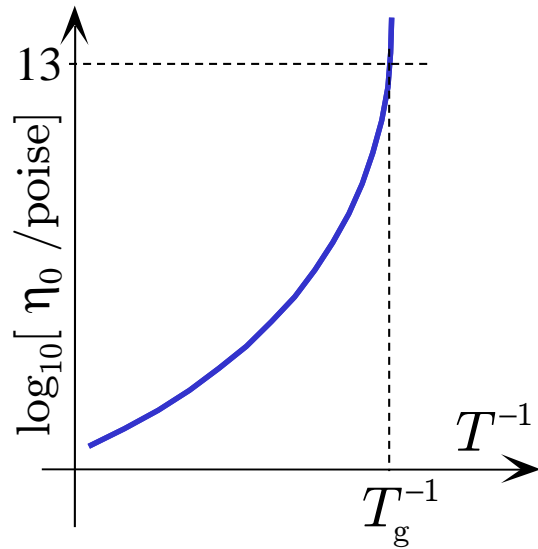
Kohlrausch
-Williams-Watts

$$\exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$$

$$0 < \beta < 1$$

ガラス, ガラス転移

Viscosity η



Vogel-Fulcher-Tamman則

$$\eta_0 = A \exp\left[\frac{U^*}{R(T - T_0)}\right]$$

$$= A \exp\left\{\frac{U^*}{R[T - (T_g - c_2)]}\right\}$$

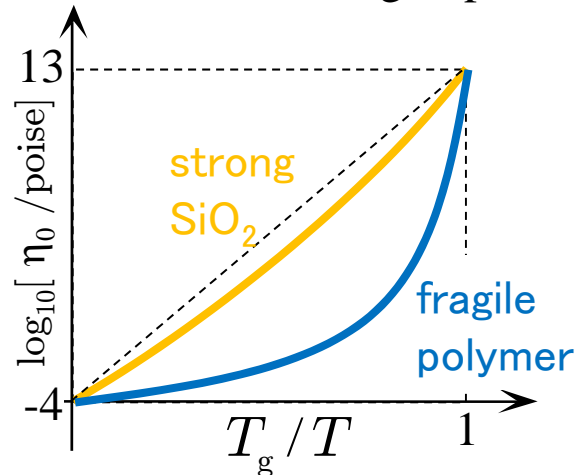
$$a_T = \frac{\eta_0(T)}{\eta_0(T_g)}$$

$$\log_{10} a_T = \frac{\log_e a_T}{\log_e 10} = -\frac{U^*}{2.303c_2R} \frac{T - T_g}{T - T_g + c_2}$$

$$= -c_1 \frac{T - T_g}{T - T_g + c_2} \quad \text{WLF則}$$

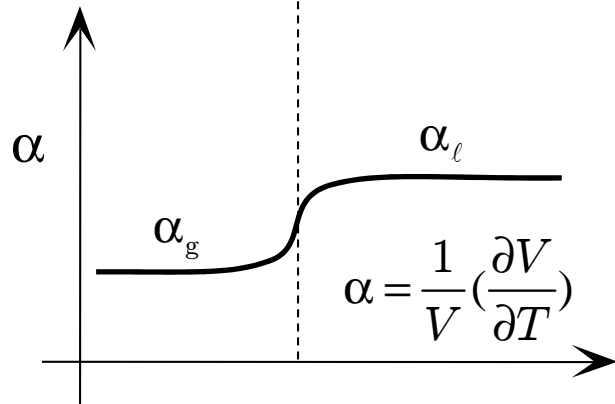
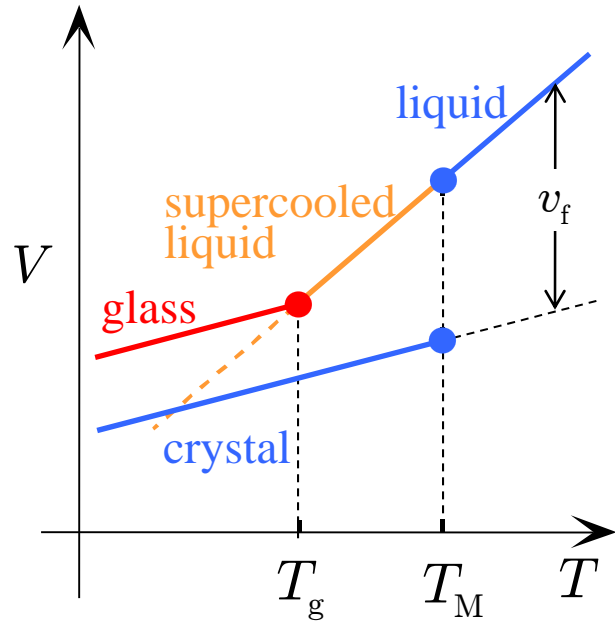
$$c_1 = \frac{U^*}{2.303c_2R}$$

非Arrhenius 性 Angell plot



ガラス, ガラス転移

Volume V



自由体積モデル(現象論)

分子(占有体積 v_0)のまわりの

自由体積 $v_f = v - v_0$ の変化に伴う,

ミクロブラウン運動の易動度の変化(凍結)。

自由体積分率の変化 $f = \frac{v_f}{v_0} = f_g + \alpha_f(T - T_g)$

Doolittle の粘度式 $\eta \propto \exp\left[\frac{B}{f}\right]$

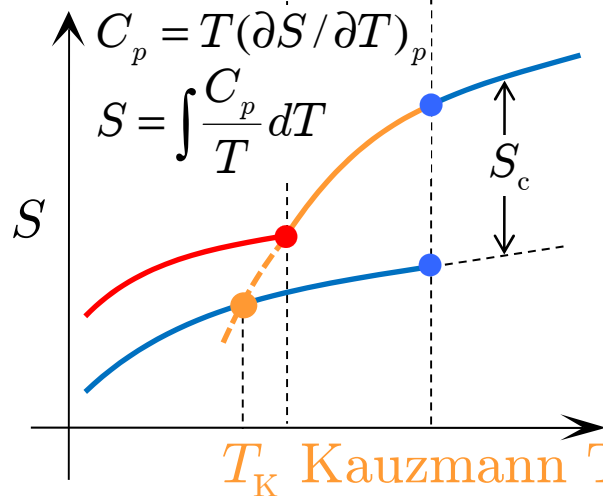
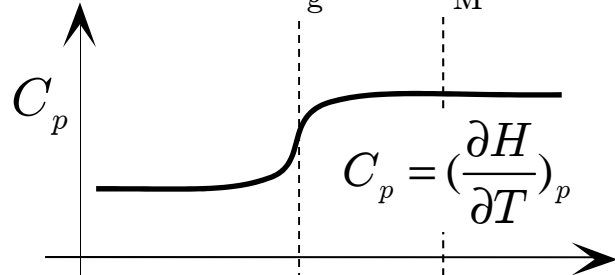
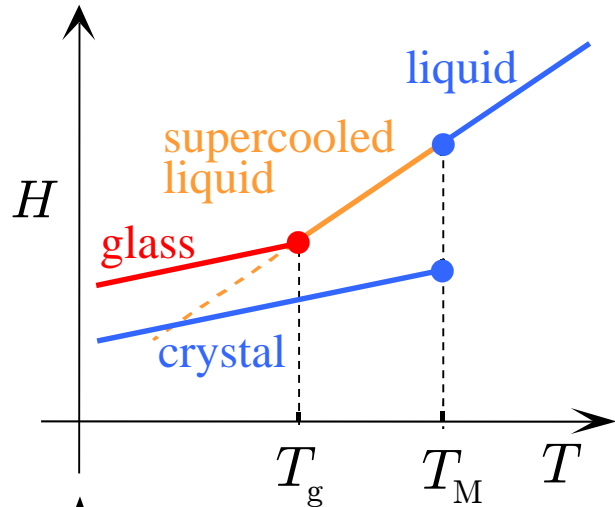
自由体積 f が大きい方が粘度が小さい。

$$\ln\left[\frac{\eta(T)}{\eta(T_g)}\right] = B\left[\frac{1}{f(T)} - \frac{1}{f(T_g)}\right] = -\frac{(B/f_g)(T - T_g)}{(T - T_g) + (f_g/\alpha_f)}$$

WLF則

ガラス, ガラス転移

Enthalpy H



配位エントロピーモデル(現象論)

温度の低下に伴い, 分子鎖の配位の凍結が起こる。

(配位エントロピー $-S_c$ の低下)

分子運動がより協同的になる。

(協同再配置領域CRRが大きくなる)。

$$\text{粘度 } \eta \propto \exp\left[\frac{\Delta\mu}{kT} z^*\right]$$

$\Delta\mu$: 1粒子(モノマー)当たりの運動の活性化エネルギー

z^* : CRRの粒子数

$$S_c = N^* s_c^* \quad , \quad N z^* = N_A \quad \text{全粒子数}$$

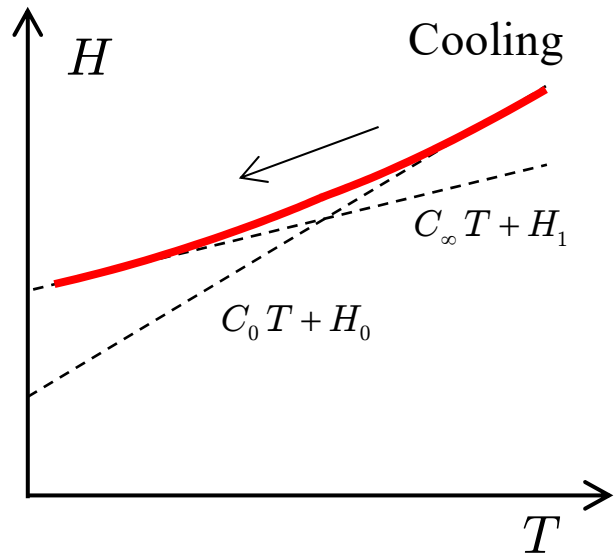
N^* : CRRの総数, $s_c^* = k \ln 2$: CRRの配位エントロピー

$$\therefore z^* = N_A \frac{s_c^*}{S_c} \Rightarrow \eta \propto \exp\left[\frac{D}{T S_c}\right]$$

$$S_c = \int_{T_K}^T \frac{\Delta C_p}{T} dT \sim \Delta C_p \ln\left[\frac{T}{T_K}\right]$$

$$\ln\left[\frac{\eta(T)}{\eta(T_g)}\right] = D \Delta C_p \left[\frac{1}{T \ln[T/T_K]} - \frac{1}{T_g \ln[T_g/T_K]} \right] \sim \text{WLF則}$$

ガラス, ガラス転移 Heat capacity C

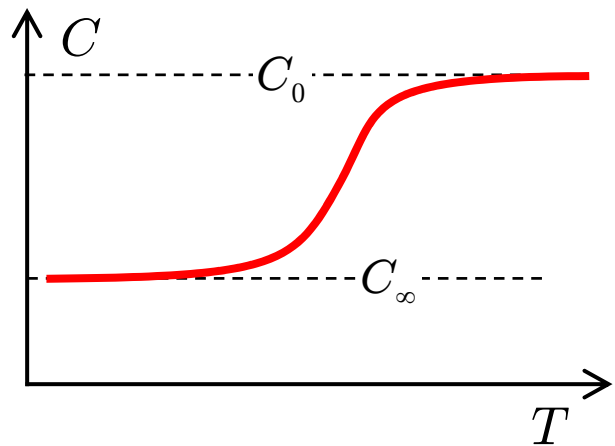


Hutchinson-Kovacs の Kinetic モデル

$$\frac{dH}{dt} = C_\infty \frac{dT}{dt} - \frac{1}{\tau} (H - H_{eq})$$

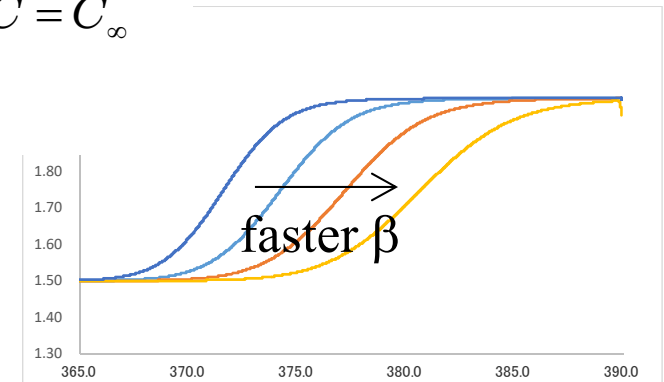
$$T = T_0 - \beta t \Rightarrow C - C_\infty = \frac{1}{\beta \tau} (H - H_{eq})$$

$$\begin{cases} \text{for } T \gg T_{g\beta}, \beta\tau \ll 1 & \therefore H = H_{eq} = C_0 T + H_0 \Rightarrow C = C_0 \\ \text{for } T \ll T_{g\beta}, \beta\tau \gg 1 & \therefore C = C_\infty \end{cases}$$

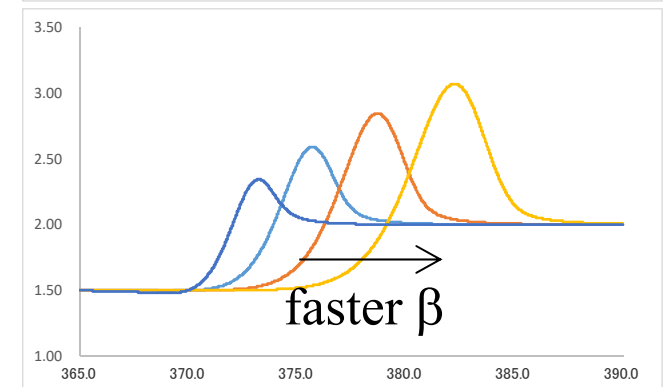


@ $T \sim T_{g\beta}$, $\beta\tau_{g\beta} \approx 2-3K$

Cooling



Heating

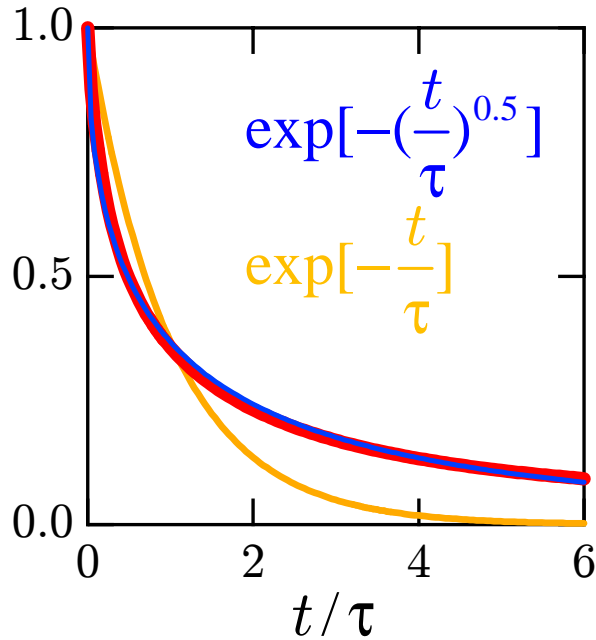


ガラス, ガラス転移

Relaxation

$$\ln\left[\frac{\tau_{\text{HN}}}{\tau_{\text{KWW}}}\right] = f(\beta)$$

$$\alpha \gamma \sim \beta$$



緩和時間の分布 (動的不均一性)

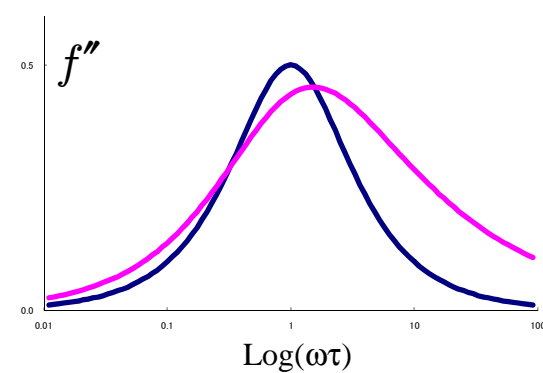
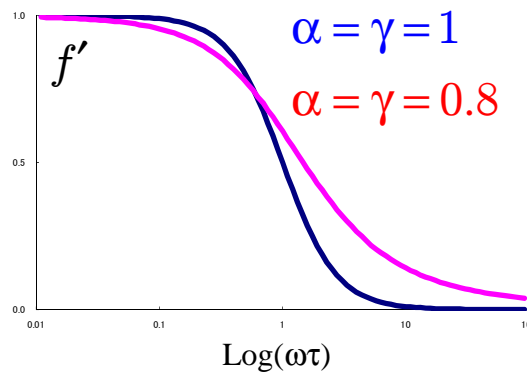
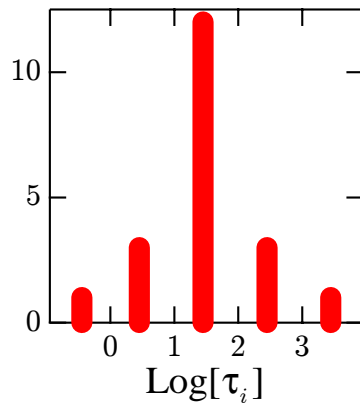
Stretched exponential function

Kohlrausch-Williams-Watts

$$\sum_i p_i \exp\left[-\frac{t}{\tau_i}\right] \approx \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \quad 0 < \beta < 1$$

Havriliak-Negami relaxation

$$\sum_i p_i \frac{1}{1+i\omega\tau} \approx \frac{1}{[1+(i\omega\tau)^\alpha]^\gamma} = f' - i f'' \quad 0 < \alpha, \gamma < 1$$



「結晶成長」とは

「結晶」とは

理想的成長 (Normal Growth) : 融液, 溶液, 気相

表面キネティクス

理想的成長 (Normal Growth) $V = \frac{a}{\tau} = K \frac{\Delta\mu}{k_B T}$

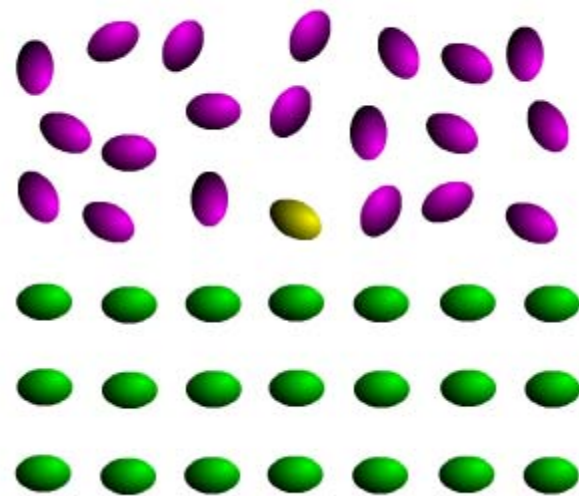
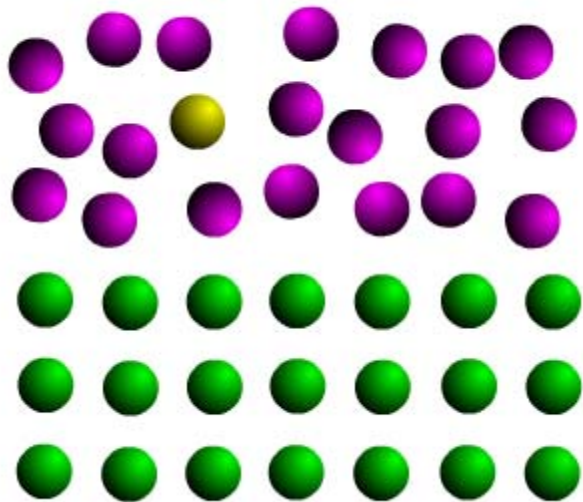
融液からの結晶化： $1 - e^{-\Delta\mu/k_B T} \approx \Delta\mu/k_B T$

$$V = a \cdot \nu e^{-E_d/k_B T} e^{-\Delta S/k_B T} \cdot [1 - e^{-\Delta\mu/k_B T}] \approx K_T \frac{T_M - T}{T_M} \quad \text{Wilson-Frenkel 則}$$

ただし, $\frac{\Delta\mu}{k_B T} \cong \frac{\Delta h}{k_B T} \frac{T_M - T}{T_M}$, $K_T = \frac{k_B T}{\pi a^2 \eta} \frac{\Delta h}{k_B T} e^{-\Delta S/k_B T}$

ここで, $a^2 = 6D\tau_0$, $\frac{1}{\tau_0} = \nu e^{-E_d/k_B T}$, $D = \frac{k_B T}{6\pi\eta a}$ Einstein-Stokes 則

$$\Rightarrow a \nu e^{-E_d/k_B T} = \frac{k_B T}{\pi a^2 \eta}$$



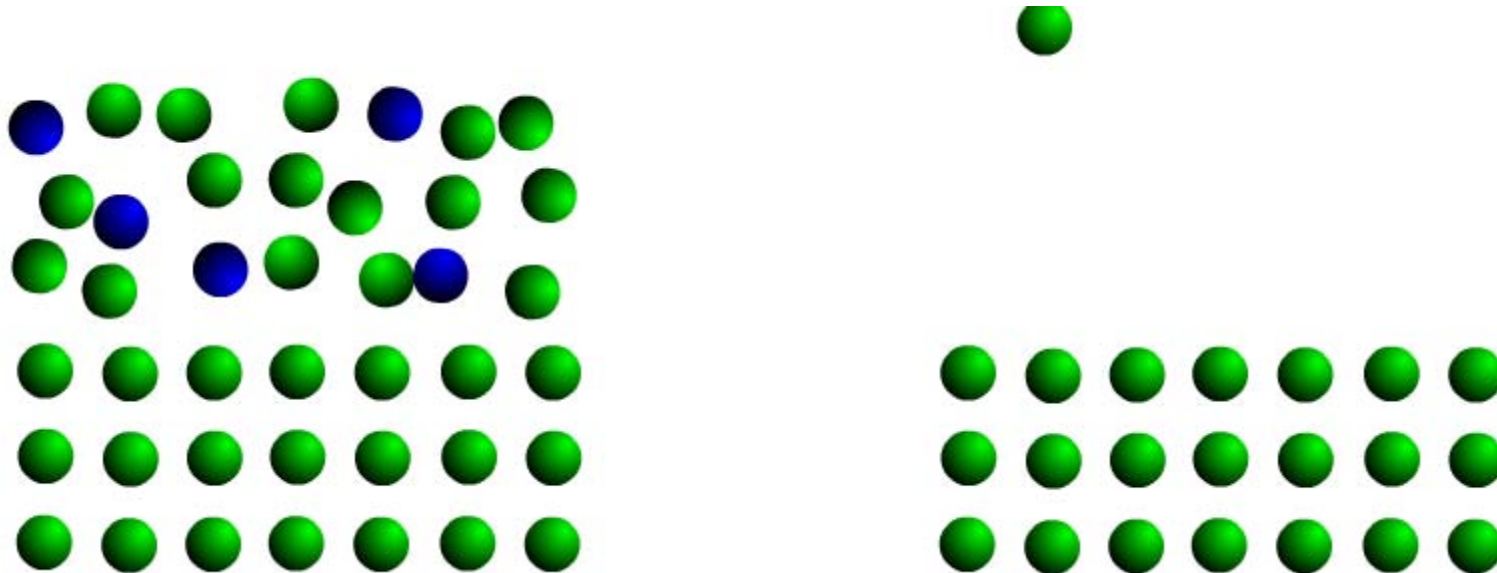
理想的成長 (Normal Growth) $V = \frac{a}{\tau} = K \frac{\Delta\mu}{k_B T}$

溶液からの結晶化：

$$V = a \cdot \nu e^{-E_{\text{des}}/k_B T} \cdot v_s [C - C_{\text{eq}}(T)] = a v_s \nu e^{-E_{\text{des}}/k_B T} [C - C_{\text{eq}}(T)]$$

気相からの結晶化：

$$V = a \cdot a^2 \left[\frac{P}{\sqrt{2\pi m k_B T}} - \frac{P_{\text{eq}}}{\sqrt{2\pi m k_B T}} \right] = \frac{v_s}{\sqrt{2\pi m k_B T}} (P - P_{\text{eq}}) \quad \text{Hertz-Knudsen 則}$$



表面(2次元)核形成

$\Delta\mu$: 駆動力/ J m^{-3}

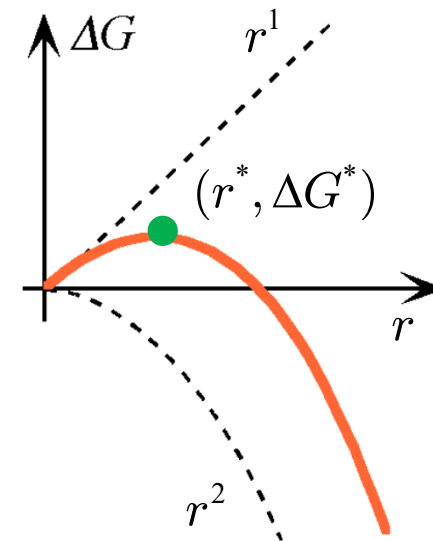
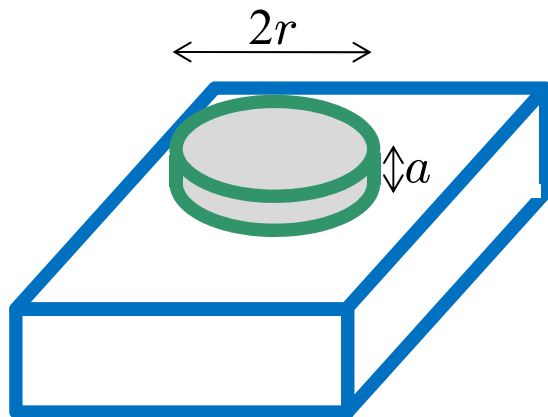
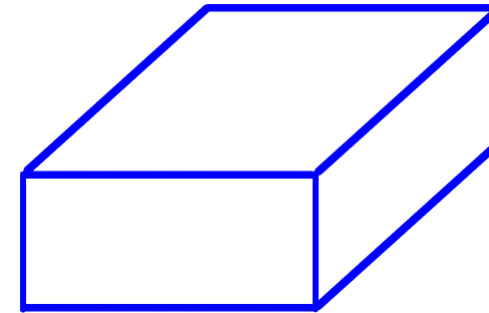
σ : 表面自由エネルギー/ J m^{-2}

2次元核: $\Delta G = -\pi r^2 a \Delta\mu + 2\pi r a \sigma$

臨界核: $0 = \frac{\partial \Delta G}{\partial r} = -2\pi r^* a \Delta\mu + 2\pi a \sigma$

臨界核半径: $r^* = \frac{\sigma}{\Delta\mu}$, 臨界核: $\Delta G^* = \frac{\pi a \sigma^2}{\Delta\mu}$

核形成頻度: $I_c = I_0 \exp\left[-\frac{\Delta G^*}{k_B T}\right] = I_0 \exp\left[-\frac{\pi a \sigma^2}{\Delta\mu k_B T}\right]$



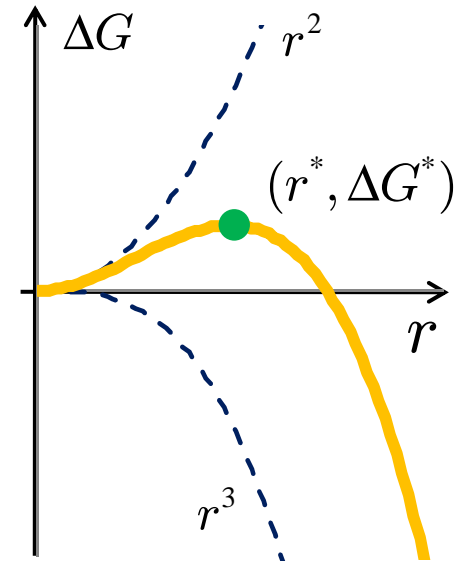
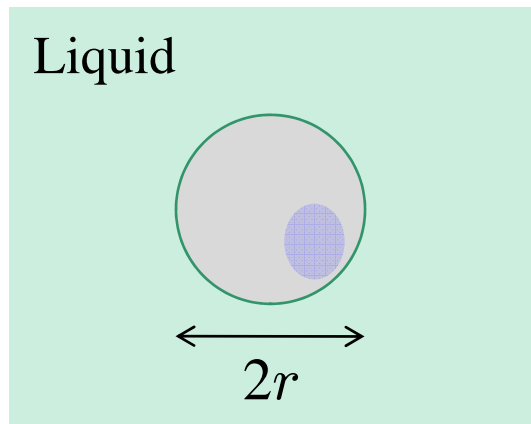
補) 1次核形成

$$1 \text{ 次核: } \Delta G = -\Delta\mu \frac{4}{3} \pi r^3 + \sigma 4\pi r^2$$

$$\text{臨界核: } 0 = \frac{\partial \Delta G}{\partial r} = -4\pi\Delta\mu r^2 + 8\pi\sigma r$$

$$\text{臨界核半径: } r^* = \frac{2\sigma}{\Delta\mu}, \quad \text{臨界核: } \Delta G^* = \frac{16\sigma^3}{3\Delta\mu^2}$$

$$\text{核形成頻度: } I_c = I_0 \exp\left[-\frac{\Delta G^*}{k_B T}\right] = I_0 \exp\left[-\frac{16\sigma^3}{3\Delta\mu^2 k_B T}\right]$$



核形成-成長様式: $V = \frac{a}{\tau}$

核形成頻度 $I_c = I_0 \exp\left[-\frac{\pi a \sigma^2}{\Delta\mu k_B T}\right]$ (単位面積当たり)

ステップ前進速度 $v = K \frac{\Delta\mu}{k_B T}$

$\frac{1}{\tau} = I_c A_k$, $\pi(v\tau)^2 = A_k \Rightarrow$ 被覆面積 $A_k = \left(\frac{\pi v^2}{I_c}\right)^{1/3}$

単一核成長様式 $A_k \gg A$ ($I_c^2 A^3 / v^2 \ll 1$)

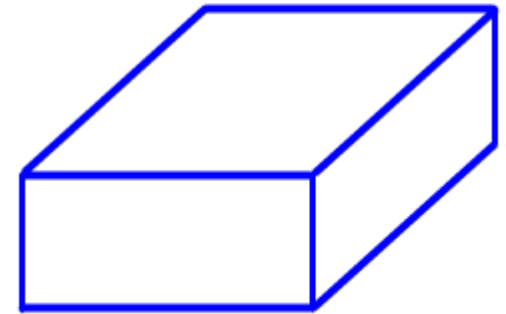
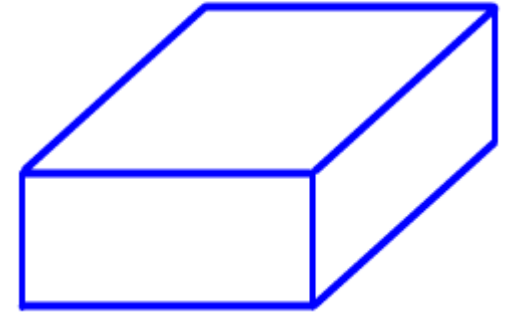
$$\frac{1}{\tau} = I_c A$$

$$V \sim a I_c A = a I_0 A \exp\left[-\frac{\pi a \sigma^2}{\Delta\mu k_B T}\right]$$

多核成長様式 $A_k \ll A$ ($I_c^2 A^3 / v^2 \gg 1$)

$$\frac{1}{\tau} = I_c A_k = (\pi I_c v^2)^{1/3}$$

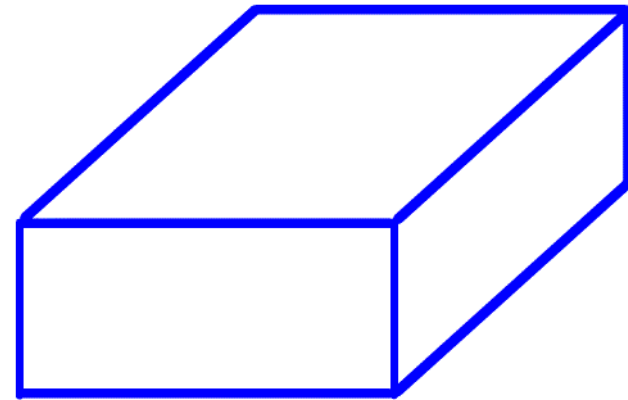
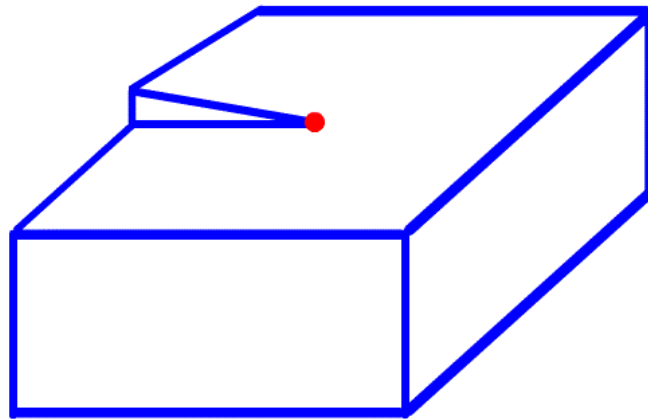
$$V \sim a (I_c v^2)^{1/3} = a I_0^{1/3} \left(K \frac{\Delta\mu}{k_B T}\right)^{2/3} \exp\left[-\frac{\pi a \sigma^2}{3 \Delta\mu k_B T}\right]$$



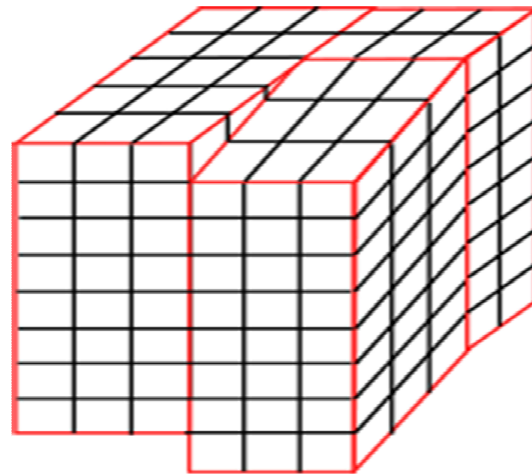
らせん転位による結晶成長

F.C.Frank
(1949)

<http://home.hiroshima-u.ac.jp/atoda/Figs/crystalgrowth.html>



らせん転位



表面キネティクス $V = \frac{a}{\tau}$

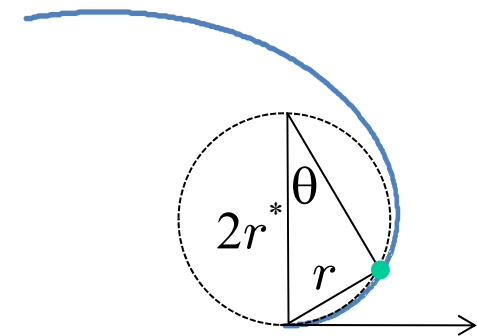
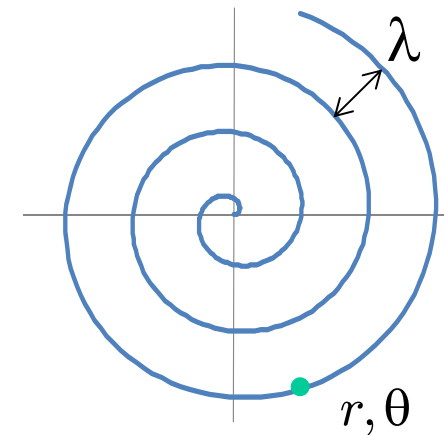
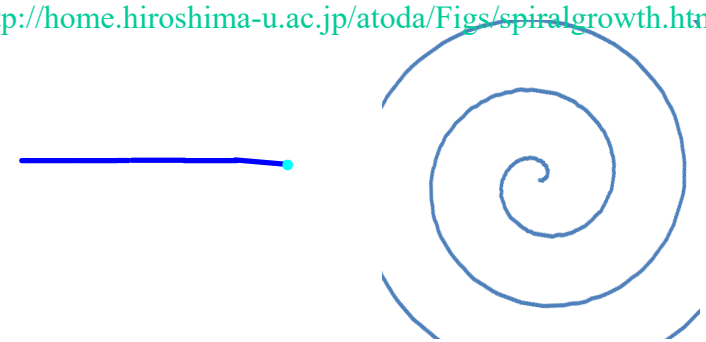
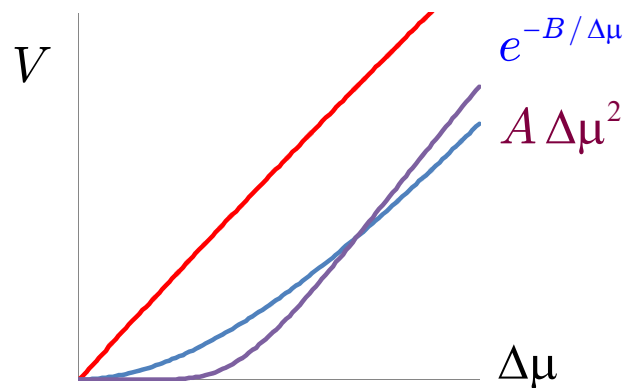
らせん転位による渦巻成長: Frank

$$v = v_0 \left(1 - \frac{r^*}{r}\right), \quad v_0 \equiv K \frac{\Delta\mu}{k_B T}, \quad r^* = \frac{\sigma}{\Delta\mu}$$

アルキメデスらせん $r \approx 2r^* \theta$ による成長
ステップ間隔 $\lambda \approx 4\pi r^* \rightarrow \lambda \approx 19r^*$

$$\tau = \frac{\lambda}{v_0}$$

$$V = \frac{a}{(\lambda/v_0)} = \frac{a}{19} \frac{\Delta\mu}{\sigma} \left(K \frac{\Delta\mu}{k_B T}\right) = \frac{aK}{19\sigma k_B T} \Delta\mu^2$$



$$r = 2r^* \sin \theta \sim 2r^* \theta$$

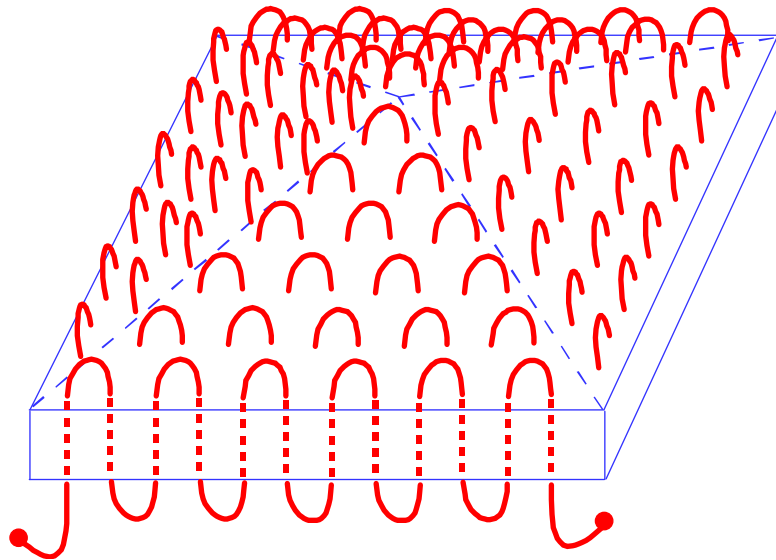
高分子の折り畳み鎖結晶化機構

標準モデル

折り畳み鎖結晶

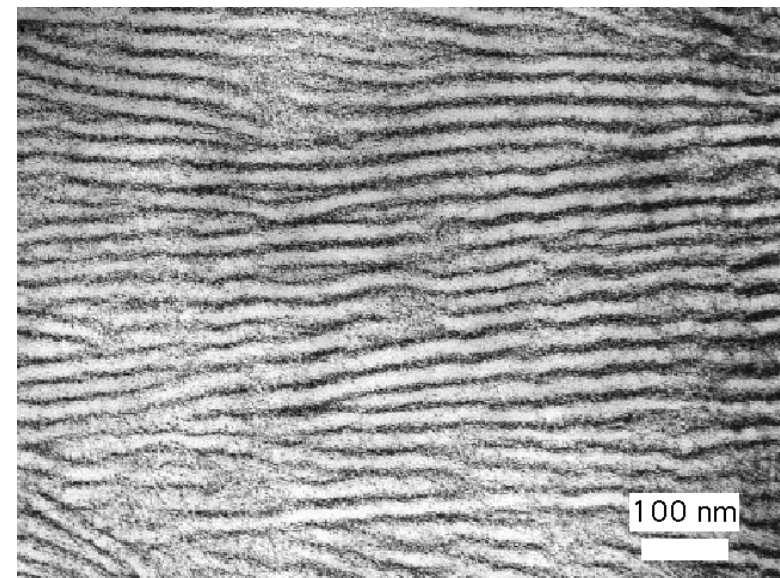
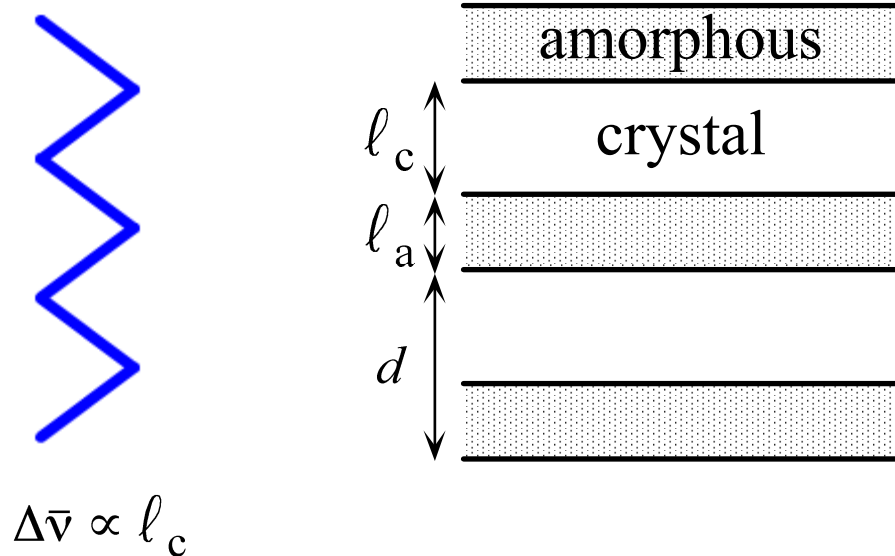
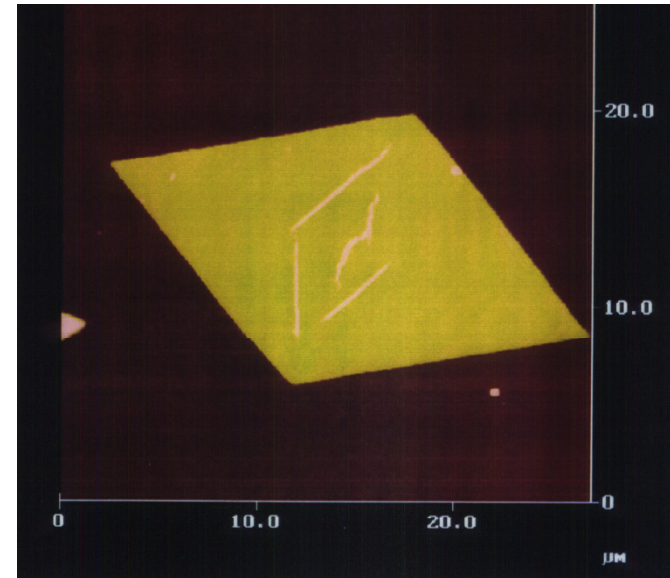
説明されるべき特徴

- A) 結晶厚の結晶化温度(過冷却度)依存性
- B) 成長速度の結晶化温度(過冷却度)依存性



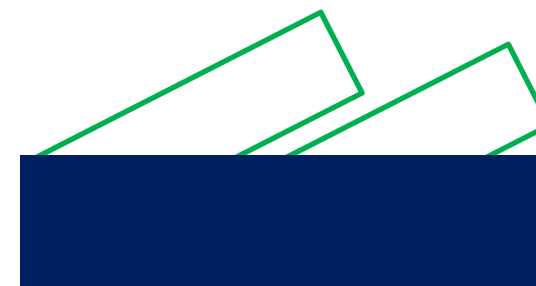
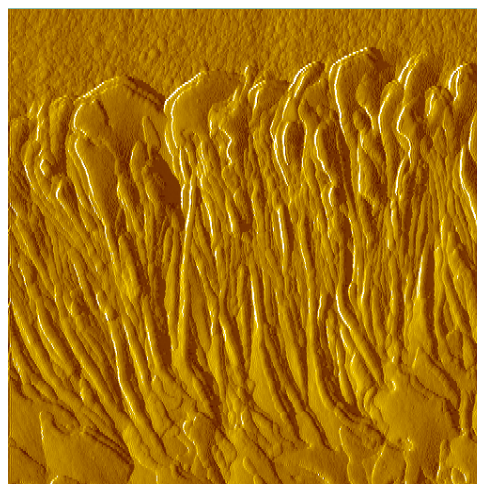
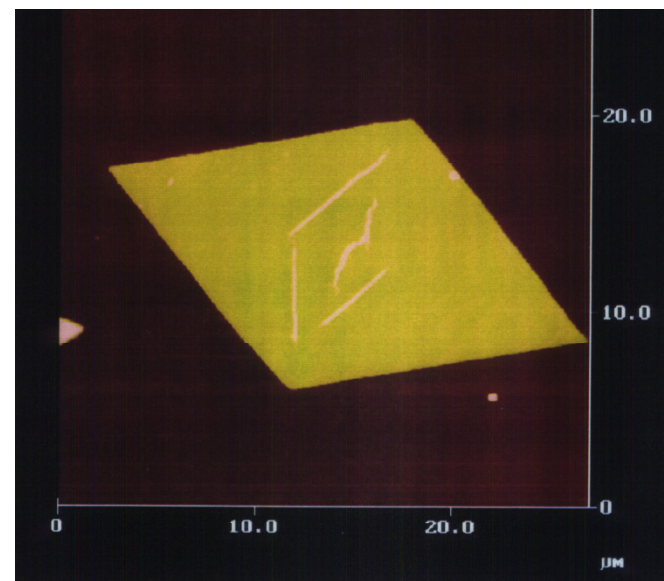
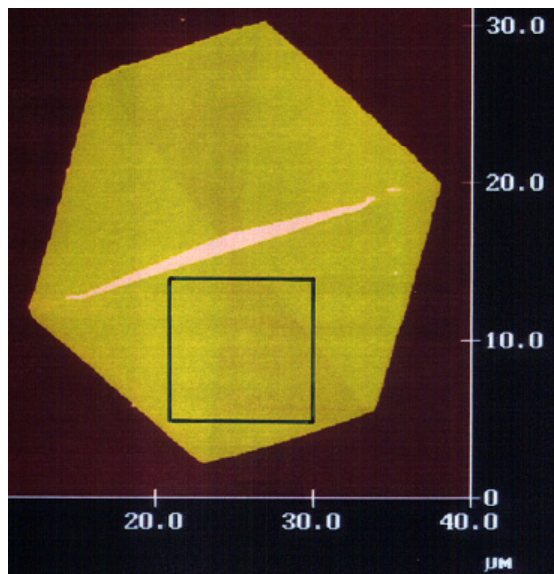
結晶の厚さの測定法

- 原子間力顕微鏡(AFM)
- 電子顕微鏡
- 小角散乱($2 d \sin \theta = \lambda$)
- ラマン散乱(LAM)



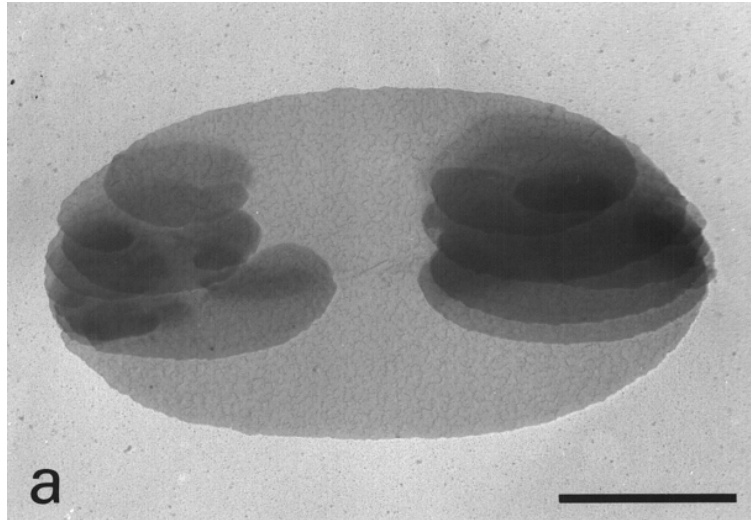
結晶の厚さの測定法

- 原子間力顕微鏡(AFM)

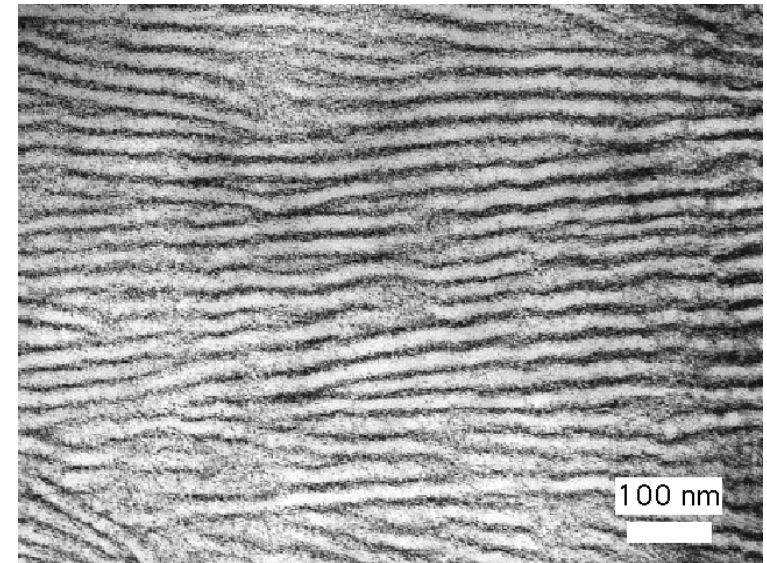


結晶の厚さの測定法

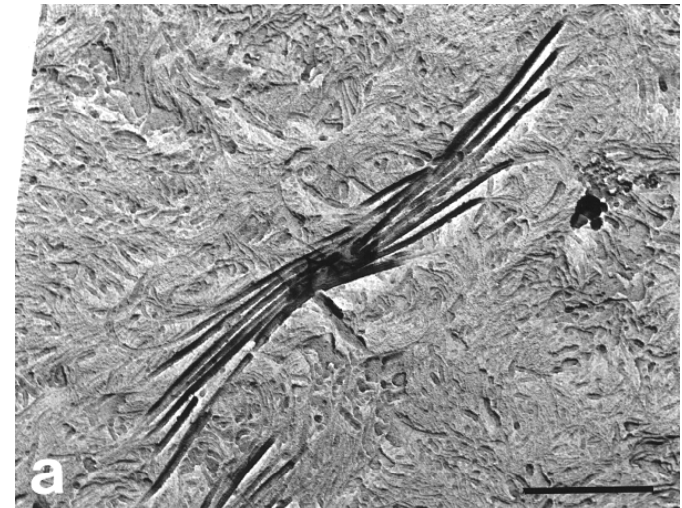
- 電子顕微鏡(TEM)



Shadowing Pt-Pd

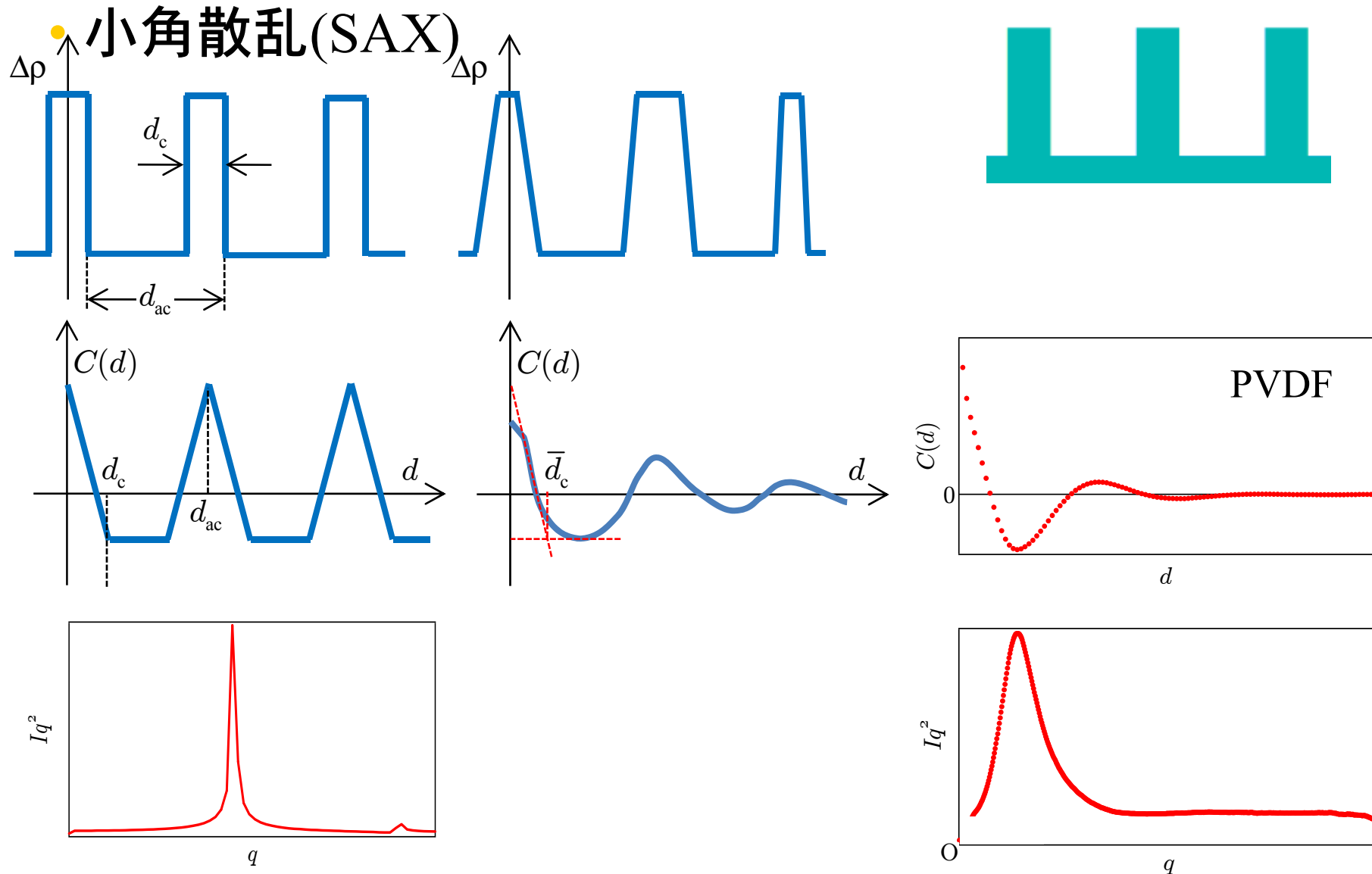


Staining RuO_4

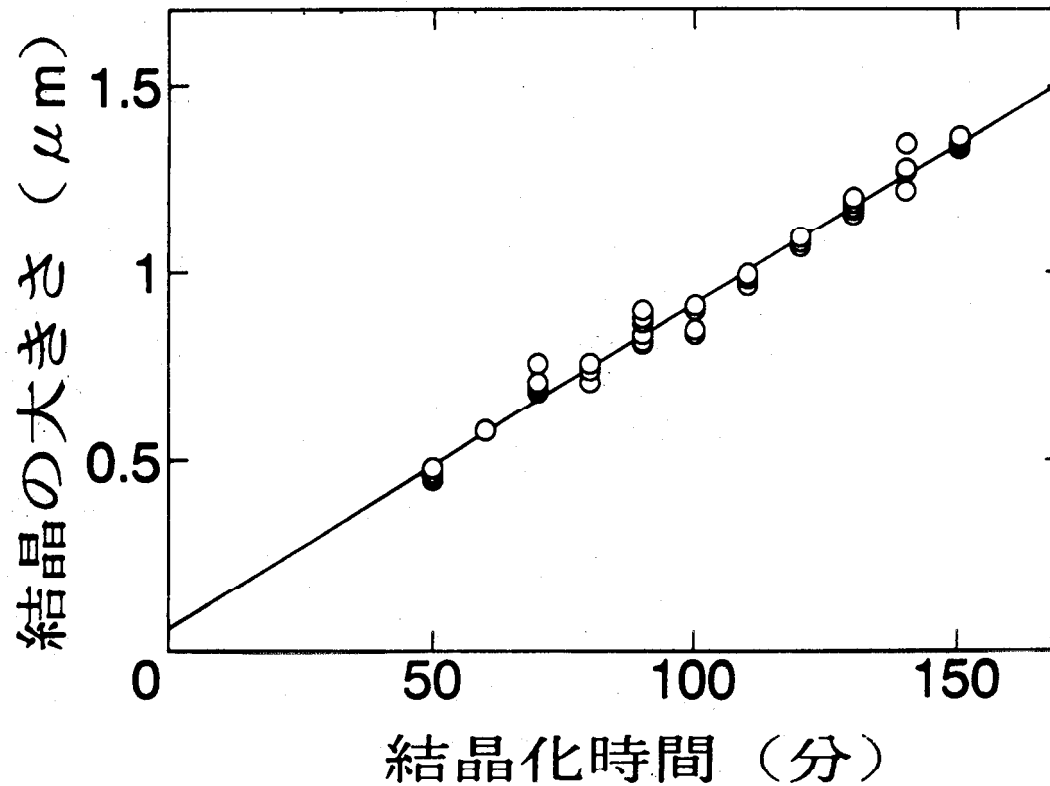


過マンガン酸エッチング+ Replica
Bassett et al.

結晶の厚さの測定法

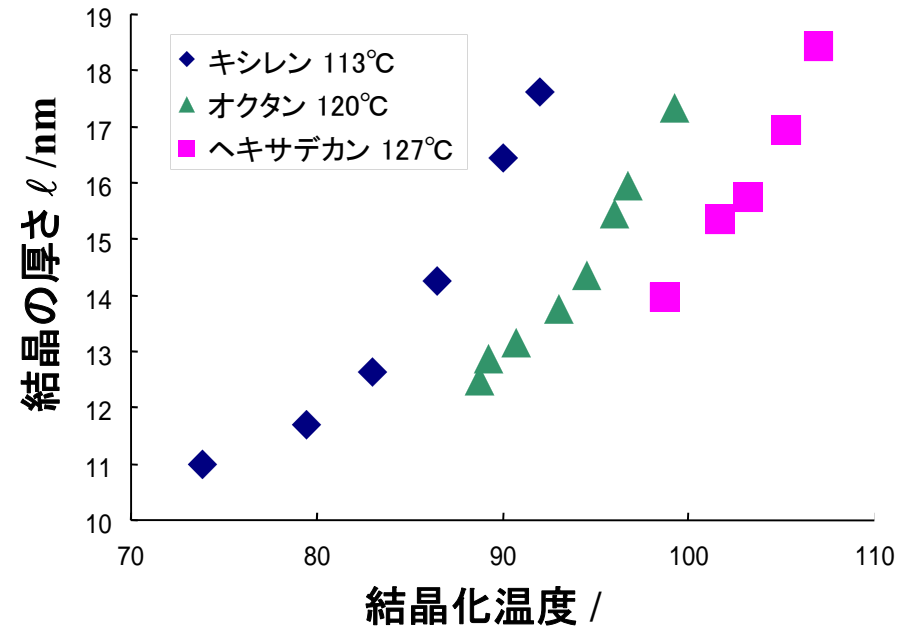
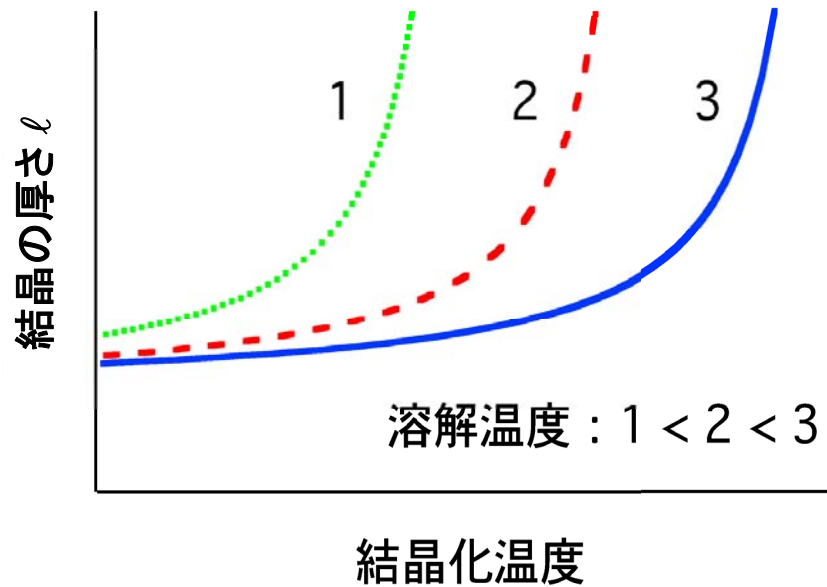


結晶成長速度の測定

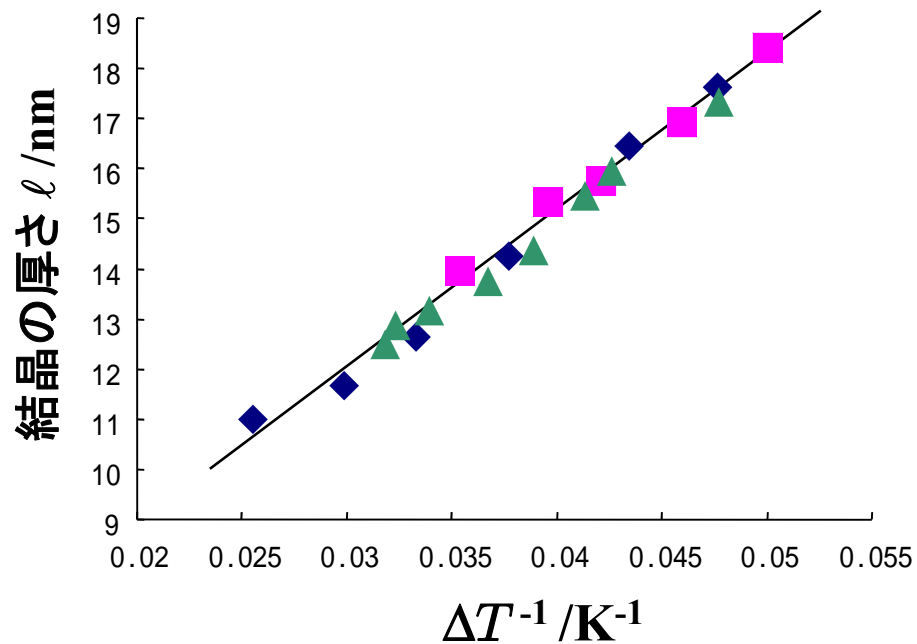
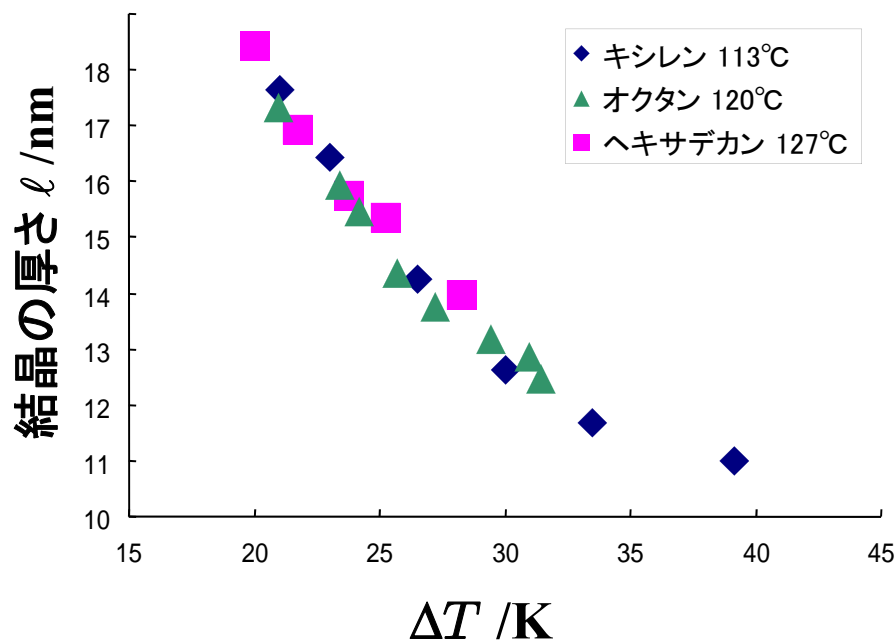


結晶の大きさの結晶化時間による変化. 結晶化条件は, 溶媒 octane, 濃度 1.0×10^{-5} wt%, 温度 92.1°C .

結晶厚の結晶化温度 T_c 依存性

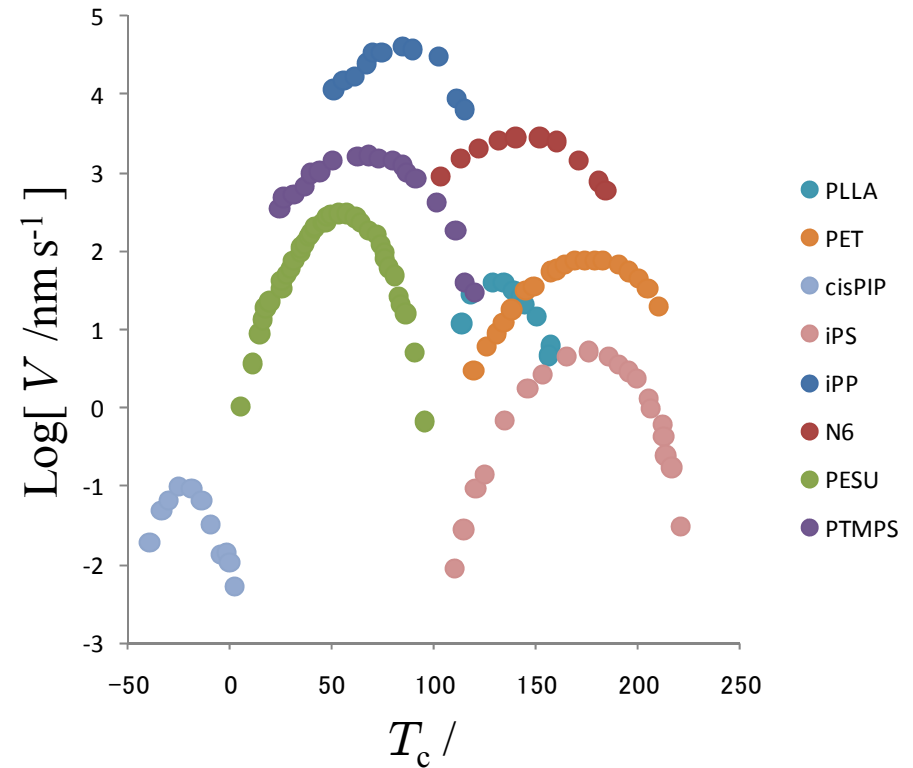
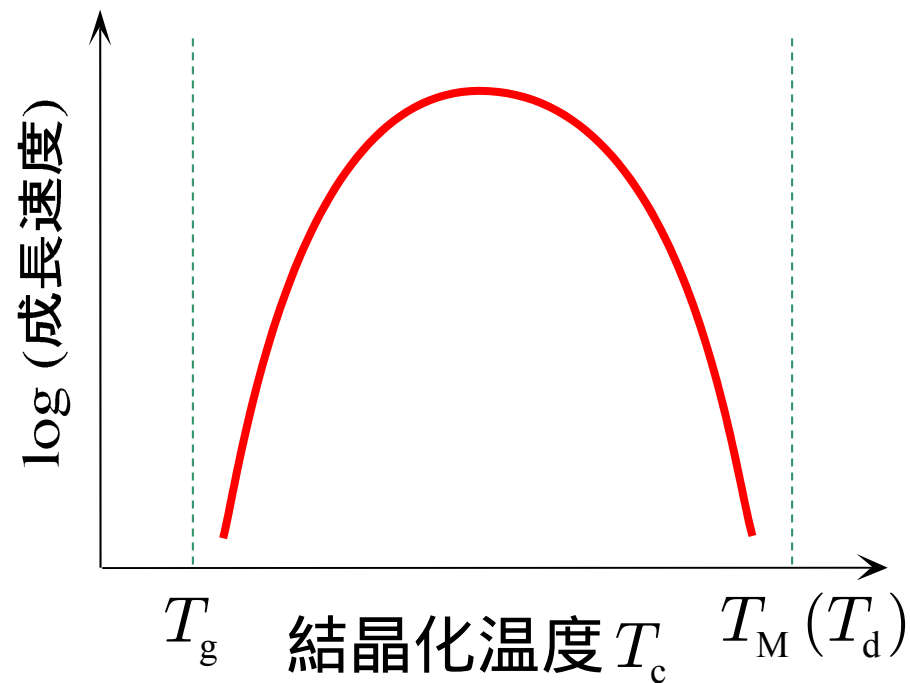


結晶厚の過冷却度 ΔT 依存性

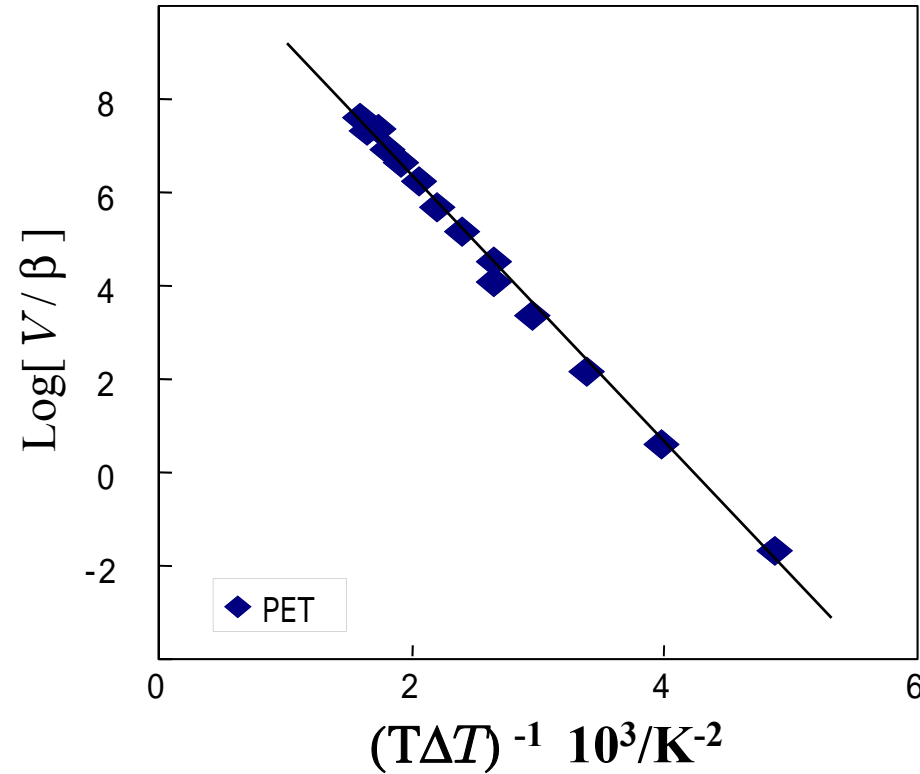


$$l = \delta l + \frac{A}{\Delta T} \quad , \quad \Delta T = T_M - T_c$$

成長速度の結晶化温度 T_c 依存性



成長速度の過冷却度 ΔT 依存性



$$V \propto \beta \exp\left[-\frac{K}{T \Delta T}\right] \quad , \quad \beta : \text{高分子の易動度}$$

成長速度式中の易動度 β

Growth from the melt

$$V \propto \beta \exp\left[-\frac{K}{T\Delta T}\right]$$

$$\beta \propto \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \propto \eta^{-1}$$

Vogel-Fulcher-Tamman

$$T_\infty = T_g - 50 \pm 5 \text{ K}$$

$$U^* = 4100 \text{ cal/mol}$$

$$a_T = \exp\left[-\frac{c_1(T-T_0)}{c_2 + T - T_0}\right]$$

WLF

β' for crystallization

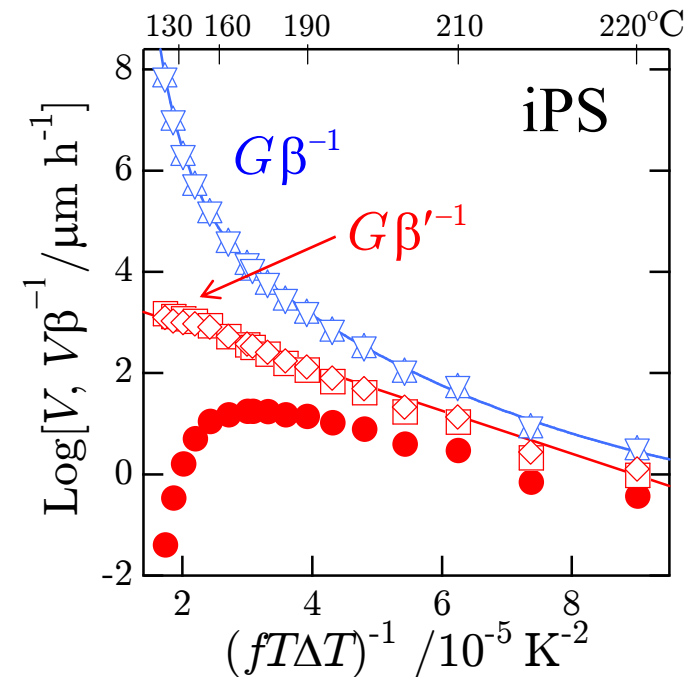
$$\beta' \propto \exp\left[-\frac{U^{*'}}{R(T-T'_\infty)}\right] \neq \eta^{-1}$$

$$T'_\infty = T_g - 30 \text{ K}$$

$$U^{*'} = 1500 \text{ cal/mol}$$

Growth from solution

$$\beta \propto \exp\left[-\frac{U^*}{RT}\right] \quad \text{Arrhenius}$$



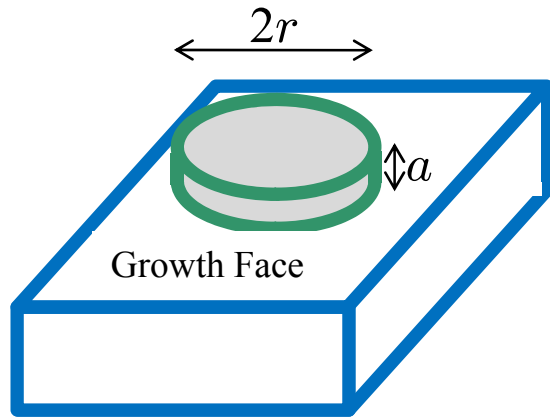
Hoffman, Davis, Lauritzen:

Treatise on Solid State Chemistry, 1976, Vol 3, Chap 7

標準モデル: 表面核形成律速モデル

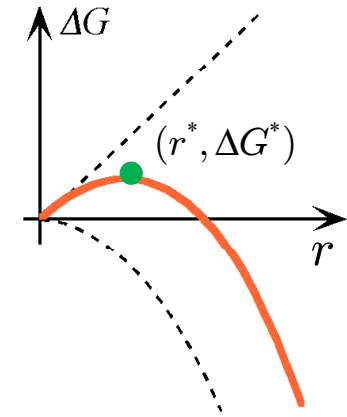
Lauritzen - Hoffmanモデル

Point, 彦坂モデル

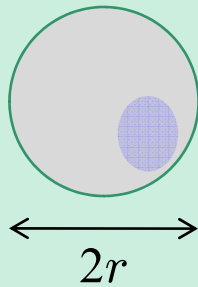


2次核(表面核)

$$\Delta G = -\pi r^2 a \Delta\mu + 2\pi r a \sigma$$



Liquid



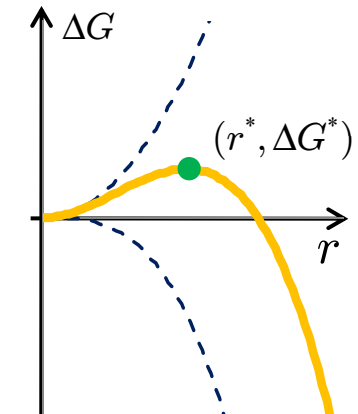
1次核

$$\Delta G(r) = -\Delta\mu \frac{4}{3} \pi r^3 + \sigma 4\pi r^2$$

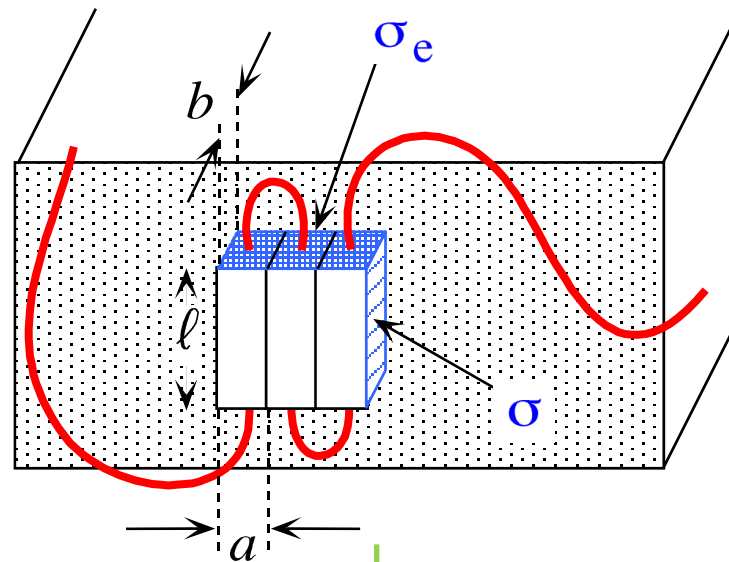
臨界核: $0 = \frac{\partial \Delta G}{\partial r^*} = -4\pi \Delta\mu r^2 + 8\pi \sigma r$

$$r^* = \frac{2\sigma}{\Delta\mu}$$

$$\Delta G^* = \frac{16\sigma^3}{3\Delta\mu^2}$$



標準モデル



表面核：

$$\Delta G(n, l) = -\Delta\mu(nabl) + 2\sigma_e(nab) + 2\sigma(bl)$$

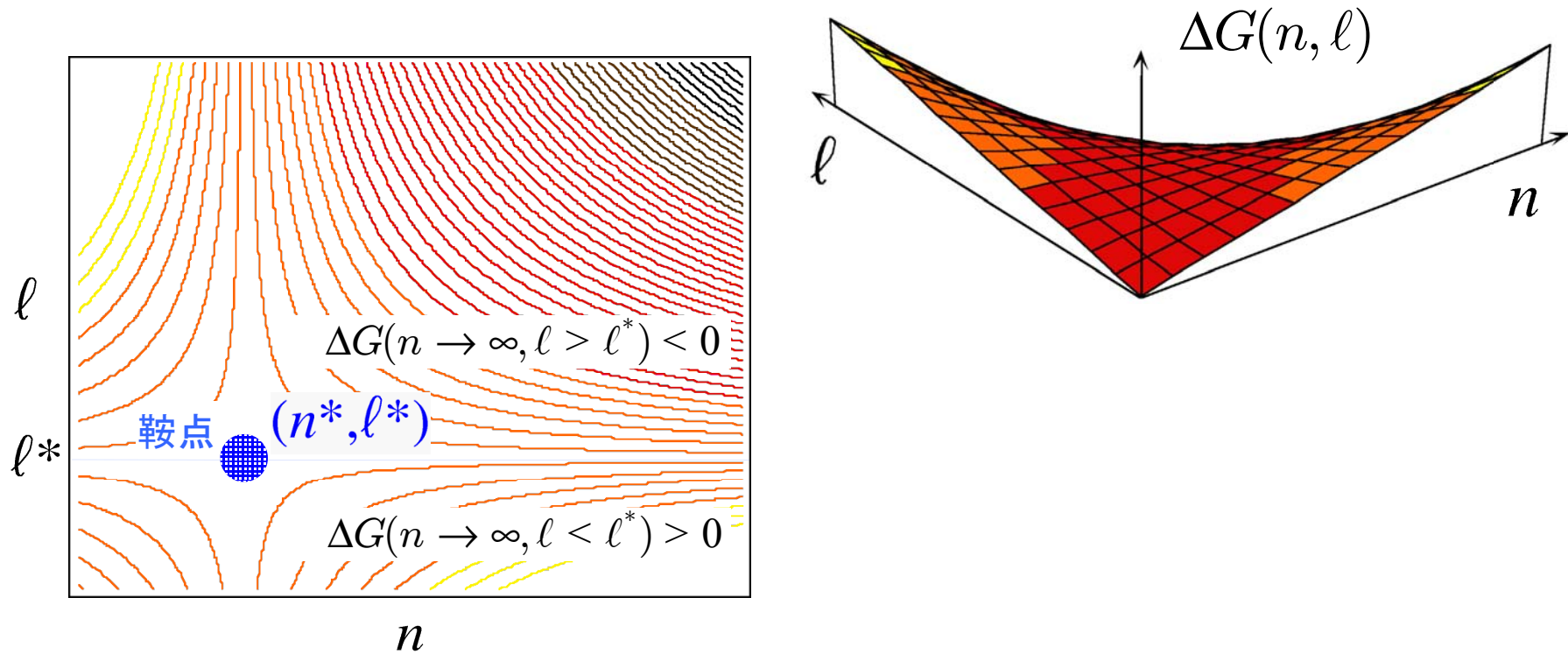
$$\Delta\mu = \Delta h_f \frac{\Delta T}{T_M}$$

ラメラ厚の下限

$$\Delta G(1, l) = -\Delta\mu(abl^*) + 2\sigma_e(ab) < 0$$

$$\Rightarrow \boxed{l > l^* \equiv \frac{2\sigma_e}{\Delta\mu} = \frac{A}{\Delta T}}$$

自由エネルギー曲面



$$\Delta G = -\Delta\mu(nabl) + 2\sigma_e(nab) + 2\sigma(bl)$$

$$\text{臨界核: } 0 = \frac{\partial\Delta G}{\partial n^*} = -abl^* \Delta\mu + 2\sigma_e ab$$

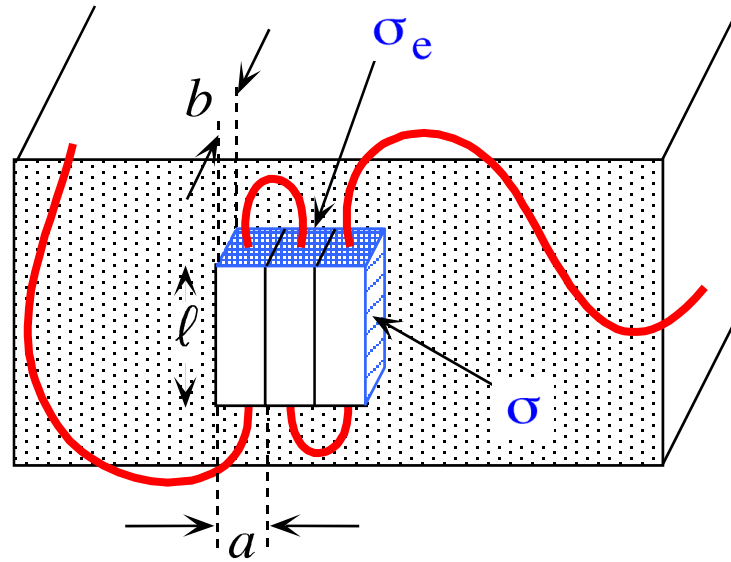
$$0 = \frac{\partial\Delta G}{\partial l^*} = -n^* ab\Delta\mu + 2\sigma b$$

$$an^* = \frac{2\sigma}{\Delta\mu}$$

$$l^* = \frac{2\sigma_e}{\Delta\mu} = \frac{A}{\Delta T}$$

$$\Delta G^* = \frac{4b\sigma\sigma_e}{\Delta\mu}$$

高分子結晶の表面核形成

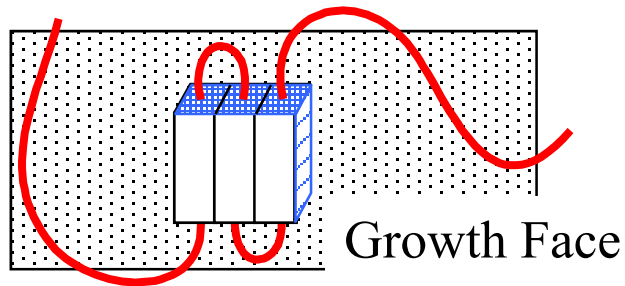


$$an^* = \frac{2\sigma}{\Delta\mu} \quad \ell^* = \frac{2\sigma_e}{\Delta\mu} = \frac{A}{\Delta T} \quad \Delta G^* = \frac{4b\sigma\sigma_e}{\Delta\mu}$$

$$I_c = I_0 \exp\left[-\frac{\Delta G^*}{k_B T}\right] = I_0 \exp\left[-\frac{4b\sigma\sigma_e}{\Delta\mu k_B T}\right] = I_0 \exp\left[-\frac{K}{T\Delta T}\right]$$

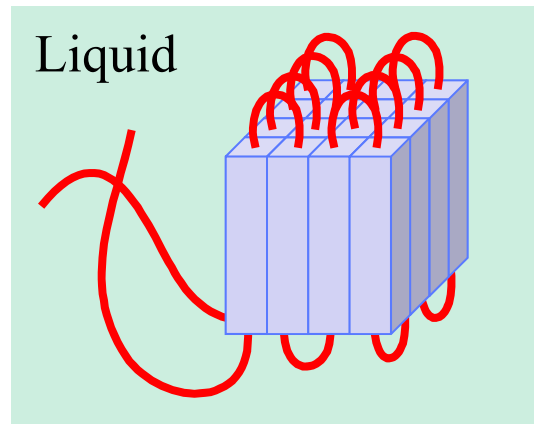
$$A = \frac{2\sigma_e T_M}{\Delta h_f} \quad K = \frac{4b\sigma\sigma_e T_M}{k_B \Delta h_f} \quad \because \Delta\mu \cong \Delta h_f \frac{\Delta T}{T_M}$$

補) 高分子結晶の1次核形成



2次核(表面核)

$$\Delta G(n, l) = -\Delta\mu(nabl) + 2\sigma_e(nab) + 2\sigma(bl)$$



1次核 $x \equiv na = mb$

$$\Delta G(n, l) = -\Delta\mu x^2 l + 2\sigma_e x^2 + 4\sigma xl$$

臨界核: $0 = \frac{\partial \Delta G}{\partial l^*} = -\Delta\mu x^2 + 4\sigma x$

$$0 = \frac{\partial \Delta G}{\partial x^*} = -2\Delta\mu xl + 4\sigma_e x + 4\sigma l$$

$$x^* = n^* a = m^* b = \frac{4\sigma}{\Delta\mu} \quad l^* = \frac{4\sigma_e}{\Delta\mu}$$

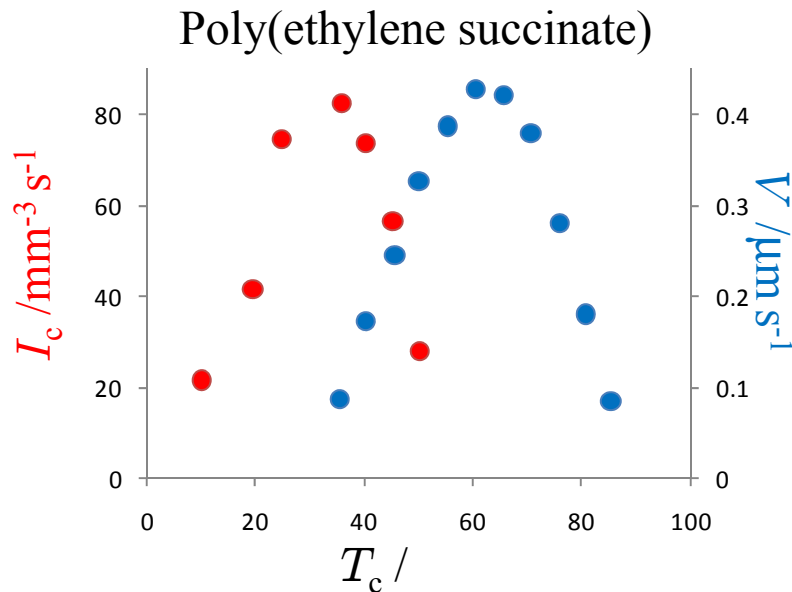
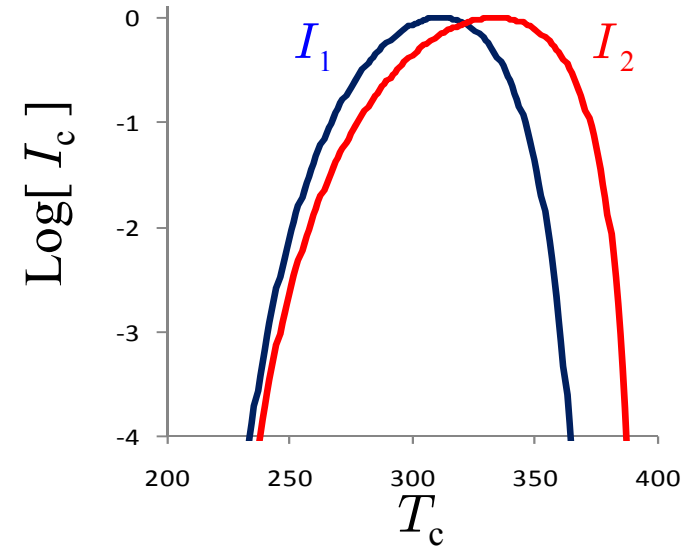
$$\Delta G^* = \frac{32\sigma^2\sigma_e}{\Delta\mu^2}$$

補) 1次核と表面核

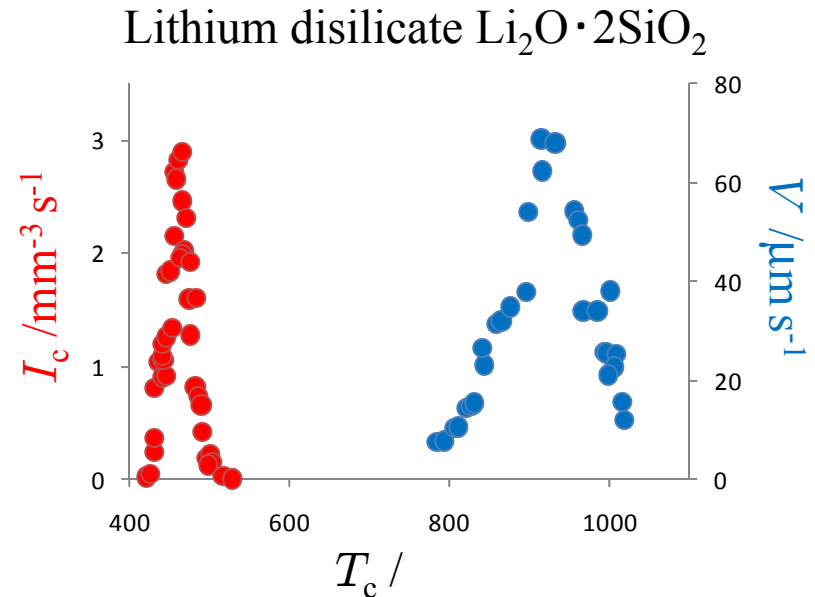
1次核: $I_c^1 \propto \beta \exp\left[-\frac{16\sigma^3}{3k_B T (\Delta\mu)^2}\right]$

表面核: $I_c^2 \propto \beta \exp\left[-\frac{\pi a \sigma^2}{k_B T} \frac{1}{\Delta\mu}\right] \propto V$

$\beta \propto \exp\left[-\frac{U^*}{R(T - T_\infty)}\right]$ $\Delta\mu = \frac{\Delta h_f}{T_M} \Delta T$



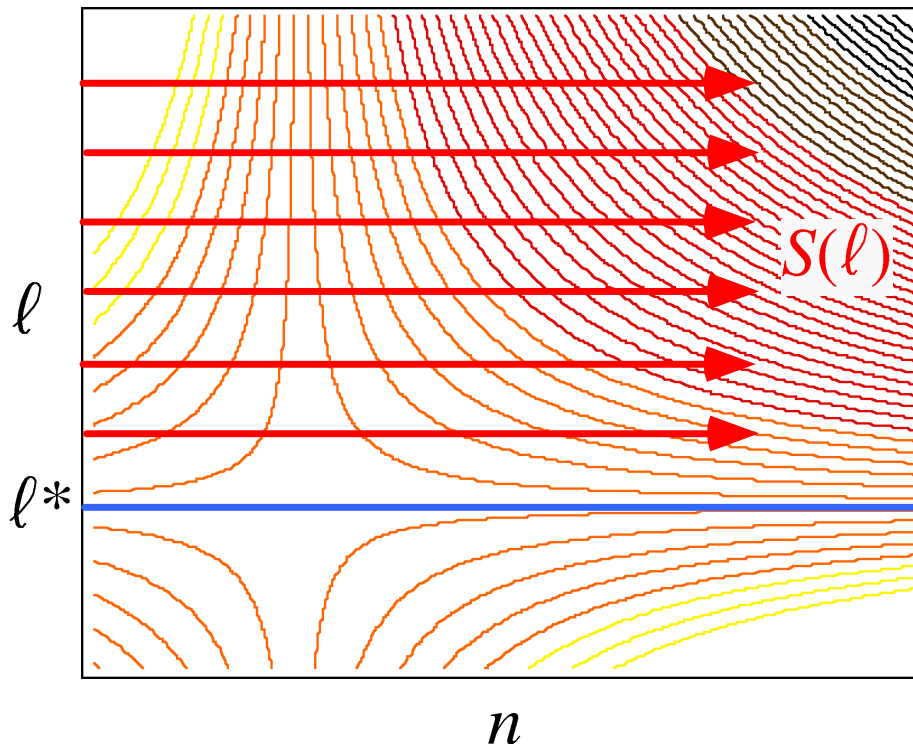
Umemoto, Hayashi, Kawano, Kikutani, Okui:
J Macromol Sci **B42** ('03) 421



Fokin *et al.*: J Non Cryst Solid **351** ('05) 1491
Matusita, Tashiro: J Ceram Soc Jpn **81** ('73) 500

Lauritzen & Hoffman の標準モデル

<http://home.hiroshima-u.ac.jp/atoda/Figs/models.html>

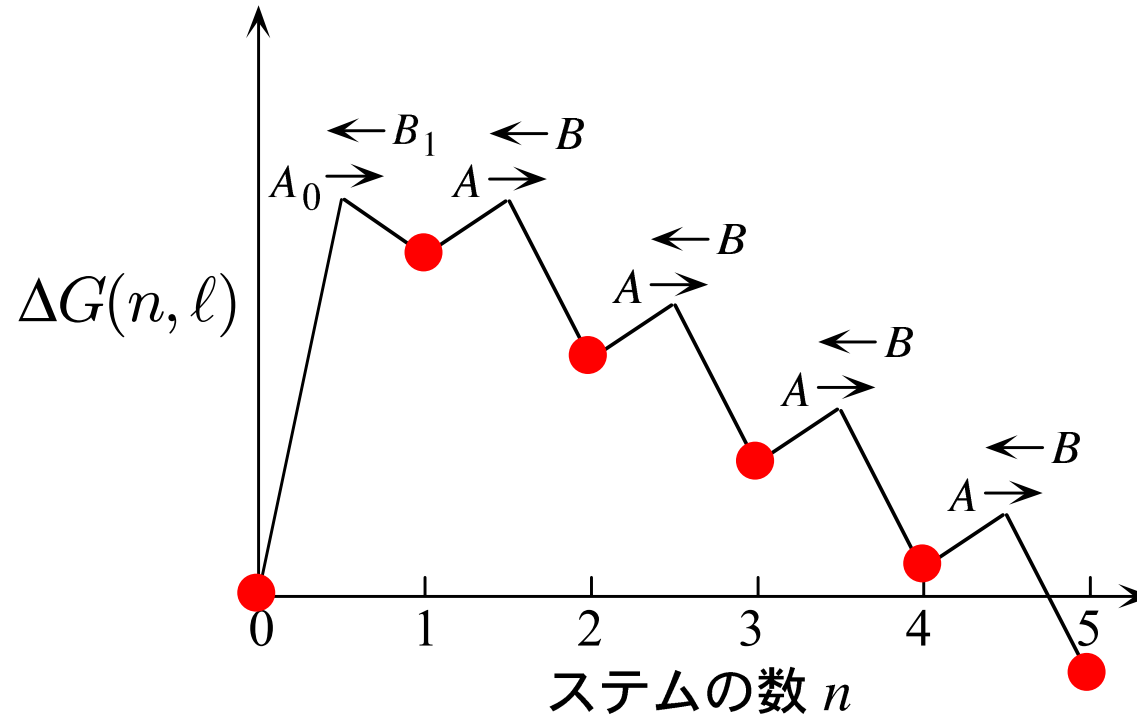


標準モデル
by Lauritzen & Hoffman

$$I = \int_{l^*}^{\infty} S(l) dl, \quad \langle l \rangle = \frac{\int_{l^*}^{\infty} l S(l) dl}{\int_{l^*}^{\infty} S(l) dl}$$

Hoffman JD, Davis GT, Lauritzen, Jr, JI,
"Treatise on Solid State Chemistry"
Plenum Press, 1976, Vol 3, Chap 7.

自由エネルギー変化

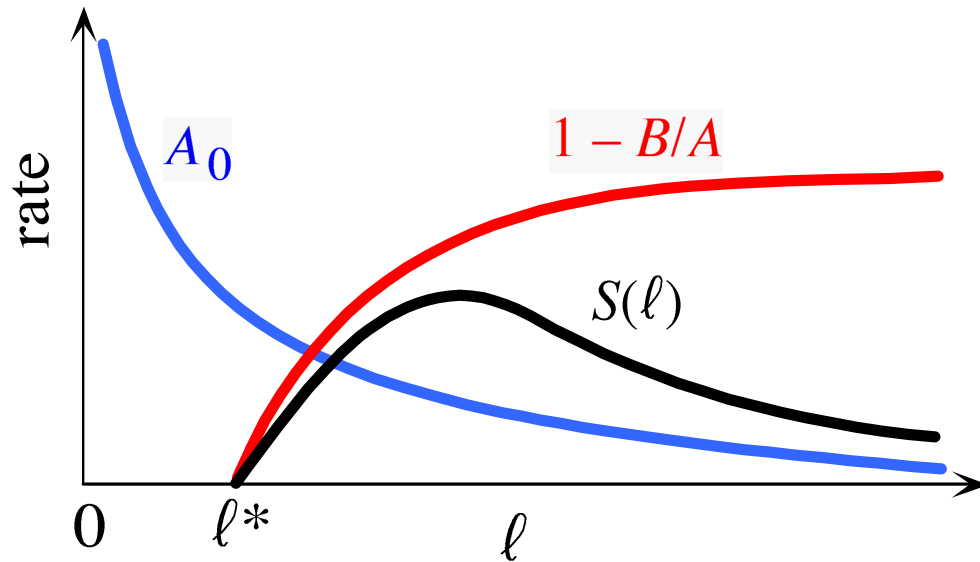


$$A_0 = \beta \exp\left[-\frac{2 b \ell \sigma - a b \ell \Delta\mu}{k T}\right]$$

$$B_1 = A = \beta$$

$$B = \beta \exp\left[\frac{2 a b \sigma_e - a b \ell \Delta\mu}{k T}\right]$$

流れの厚さに対する分布・結晶化速度



$$\Delta\mu \cong \Delta h_f \frac{T_M - T}{T_M} = \Delta h_f \frac{\Delta T}{T_M}$$

定常解 : $S(l) \propto A_0 (1 - B/A)$

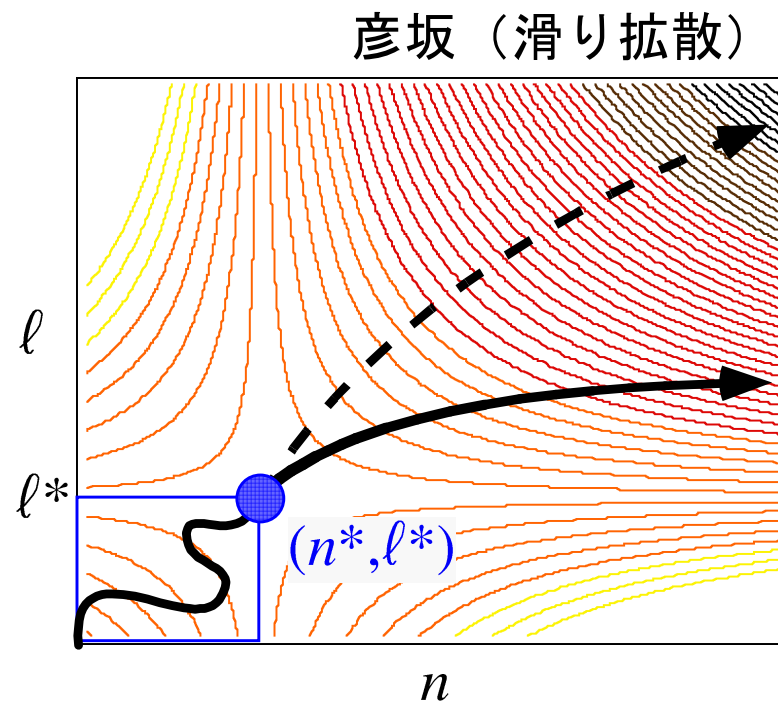
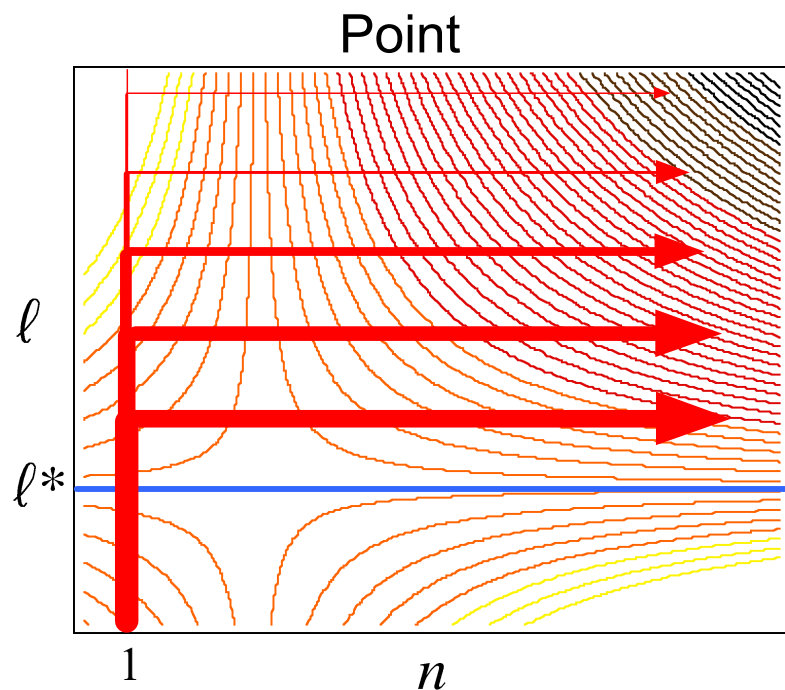
$$\langle l \rangle \cong \frac{k_B T / b}{2 \sigma - a \Delta\mu} + \frac{2 \sigma_e}{\Delta\mu} = \delta l(\Delta T) + \frac{A}{\Delta T}$$

$$I \propto \exp\left[-\frac{4 b \sigma \sigma_e}{k_B T \Delta\mu}\right] = \exp\left[-\frac{K}{T \Delta T}\right]$$

$$A \equiv \frac{2 \sigma_e T_M}{\Delta h_f}, \quad K \equiv \frac{4 b \sigma \sigma_e T_M}{k_B \Delta h_f}$$

修正モデル

<http://home.hiroshima-u.ac.jp/atoda/Figs/models.html>



Point による
修正モデル

古典的核形成 + 滑り拡散
モデル (by 彦坂)

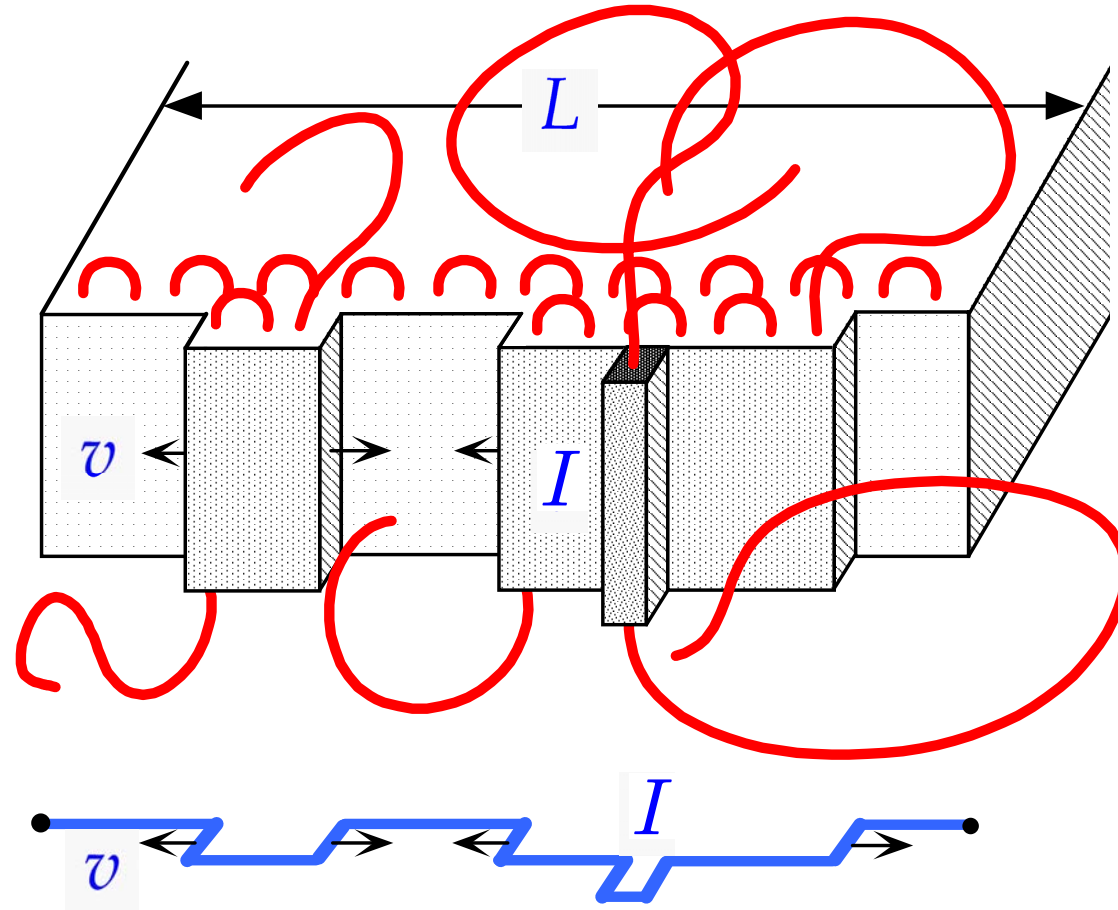
Point JJ, *Macromol*, **12**, 1979, 770.

Hikosaka M, *Polymer*, **31**, 1990, 458

高分子の折り畳み鎖結晶化機構

成長様式

結晶成長様式



結晶成長様式

成長速度

$$V \approx \begin{cases} bIL & \text{for } IL^2 / 2v \ll 1 \\ b\sqrt{2Iv} & \text{for } IL^2 / 2v \gg 1 \end{cases}$$

$$\frac{1}{\tau} = I L_k, \quad 2v\tau = L_k \Rightarrow \text{被覆長 } L_k = \left(\frac{2v}{I}\right)^{1/2}$$

単一核成長様式 $L_k \gg L$ ($IL^2 / 2v \ll 1$)

$$\frac{1}{\tau} = I L$$

$$V \sim b I L$$

多核成長様式 $L_k \ll L$ ($IL^2 / 2v \gg 1$)

$$\frac{1}{\tau} = I L_k = (2Iv)^{1/2}$$

$$V \sim b(2Iv)^{1/2}$$

単一核
成長様式

多核
成長様式

結晶成長様式

表面核形成頻度

$$I \propto \beta \exp\left[-\frac{K}{T \Delta T}\right]$$

ステップ伝搬速度

$$v \propto \beta (1 - \exp[-A\Delta T])$$

~ 一定 for ΔT 高分子結晶化

$$z = \frac{IL^2}{2v} \propto L \exp\left[-\frac{K}{T \Delta T}\right]$$

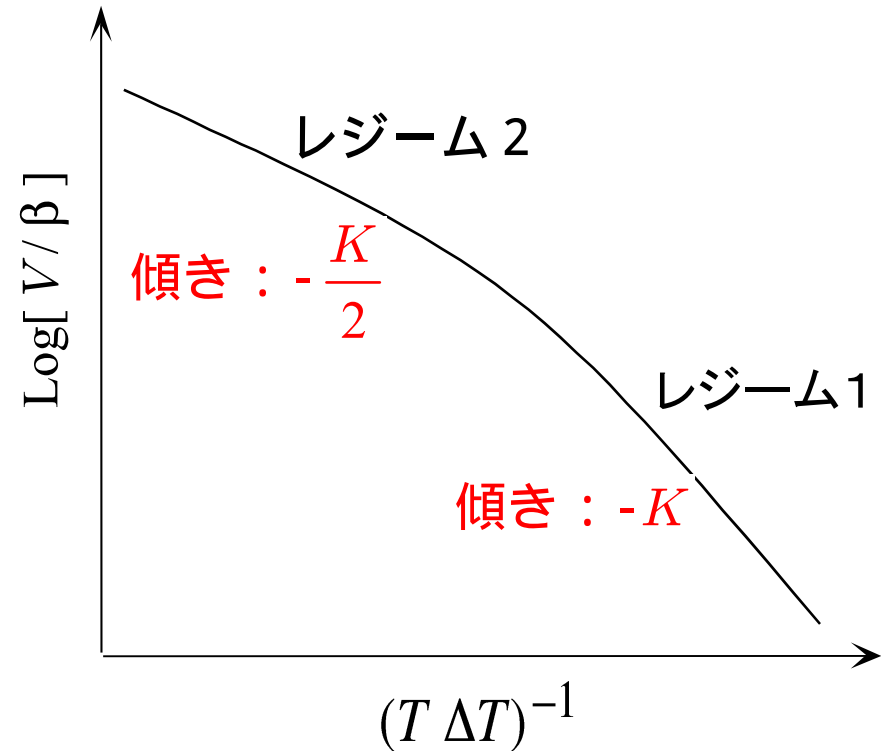
単一核成長様式 $z \ll 1$ ΔT 低

$$V = b I L \propto L \exp\left[-\frac{K}{T \Delta T}\right]$$

多核成長様式 $z \gg 1$ ΔT 高

$$V = b (2Iv)^{1/2} \propto \exp\left[-\frac{K/2}{T \Delta T}\right]$$

レジーム転移



結晶成長様式

表面核形成頻度

$$I \propto \beta \exp\left[-\frac{K}{T \Delta T}\right]$$

ステップ伝搬速度

$$v \propto \beta (1 - \exp[-A\Delta T])$$

~ 一定 for ΔT 高分子結晶化

$$z = \frac{IL^2}{2v} \propto L \exp\left[-\frac{K}{T \Delta T}\right]$$

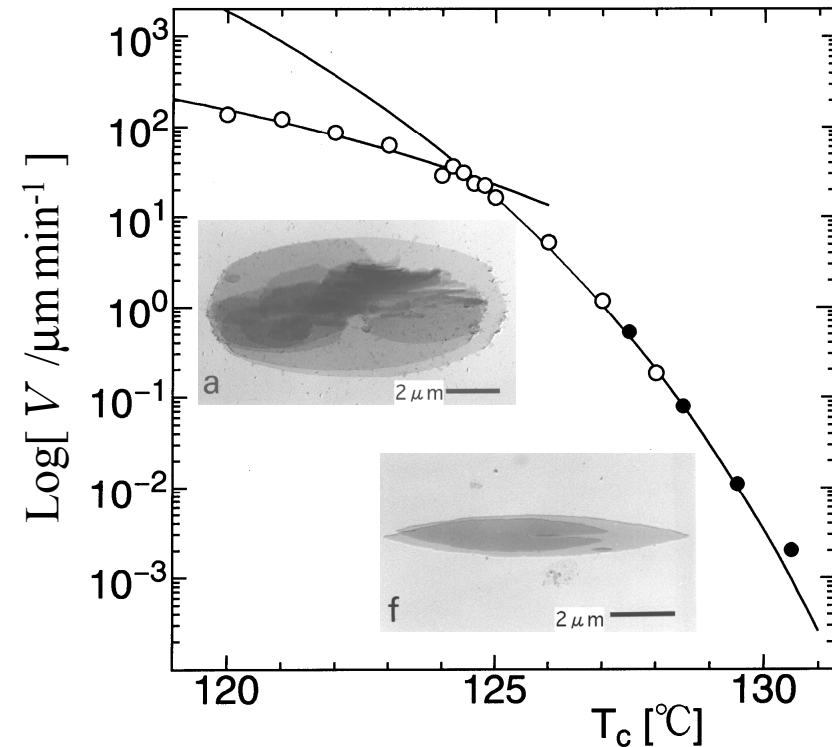
単一核成長様式 $z \ll 1$ ΔT 低

$$V = b I L \propto L \exp\left[-\frac{K}{T \Delta T}\right]$$

多核成長様式 $z \gg 1$ ΔT 高

$$V = b (2Iv)^{1/2} \propto \exp\left[-\frac{K/2}{T \Delta T}\right]$$

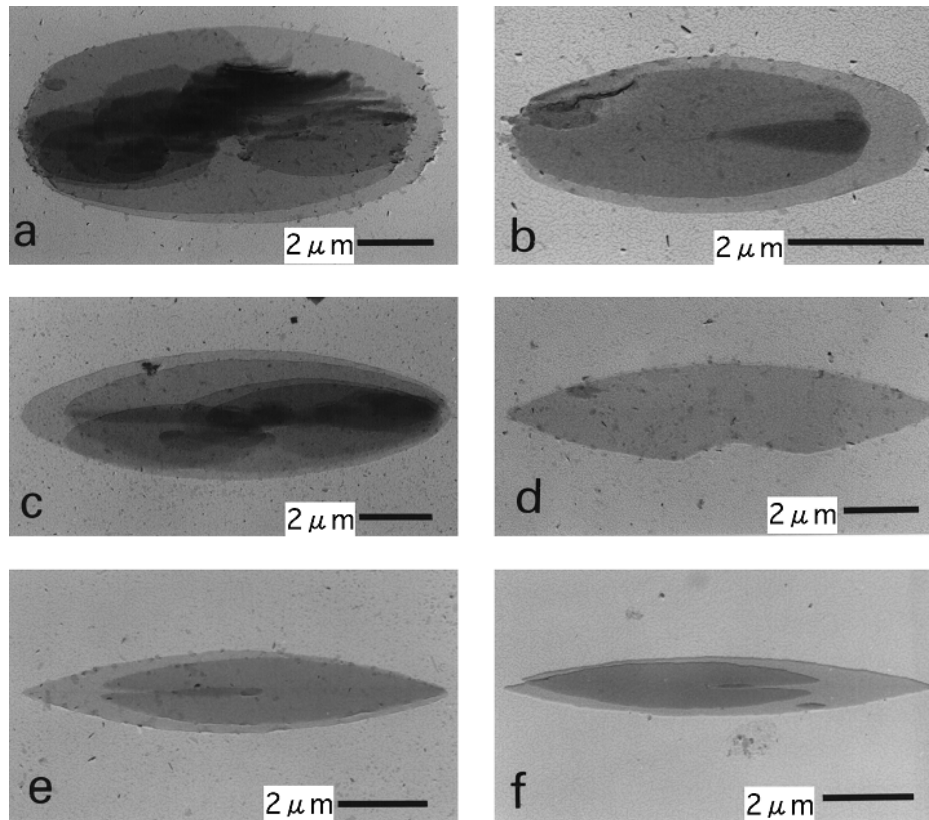
レジーム転移
(polyethylene)



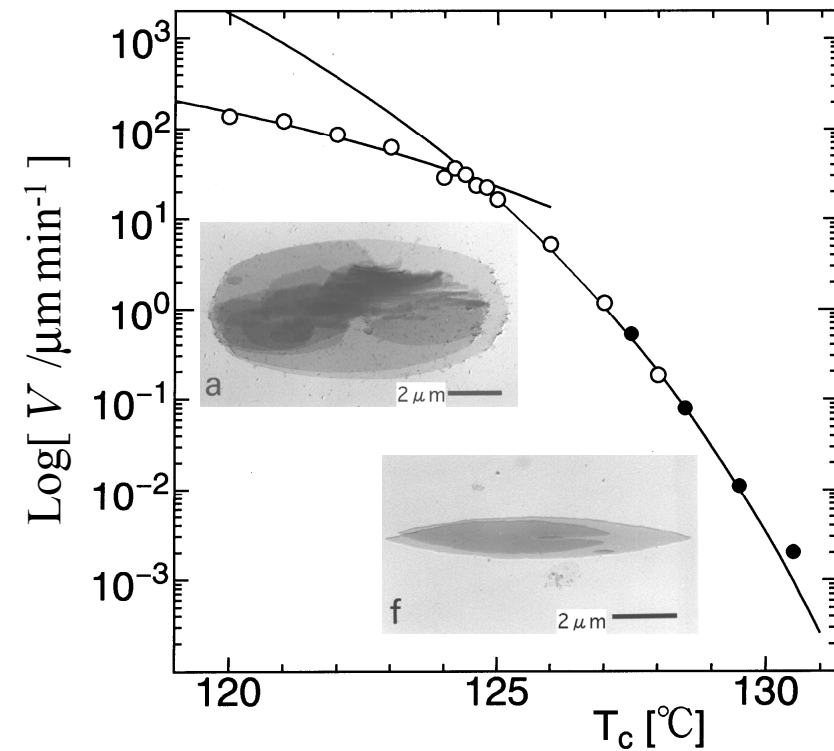
Hoffman, Frolen, Ross, Lauritzen: J Res Nat Bur Stand **79A** ('75) 671

Toda: Colloid Polym Sci **270** ('92) 667

結晶成長様式



レジーム転移 (polyethylene)

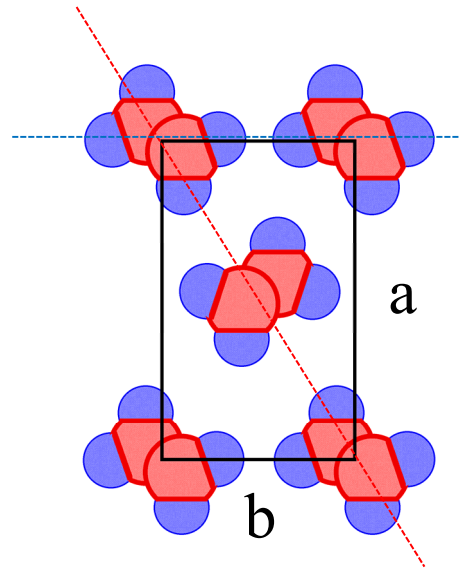
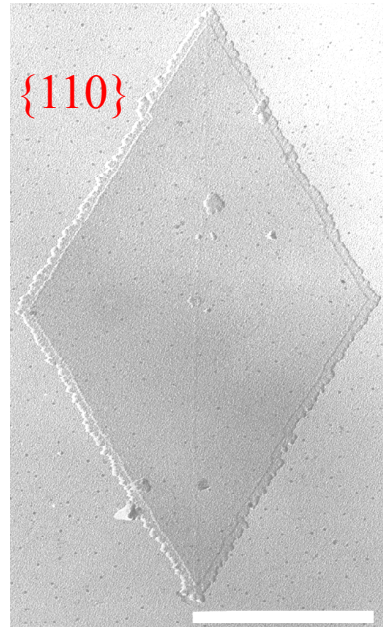


Hoffman, Frolen, Ross, Lauritzen: J Res Nat Bur Stand **79A** ('75) 671

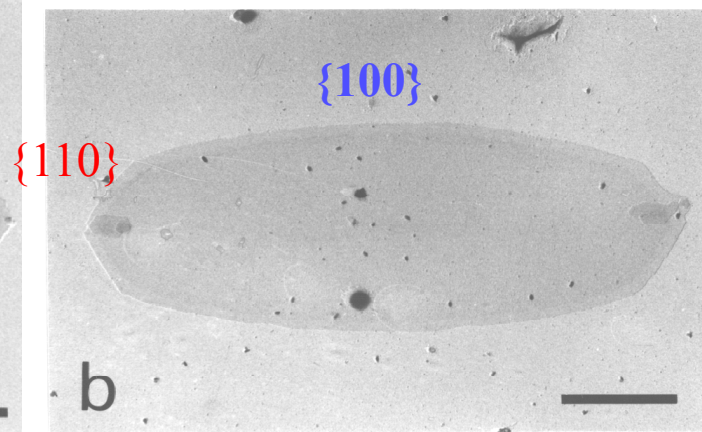
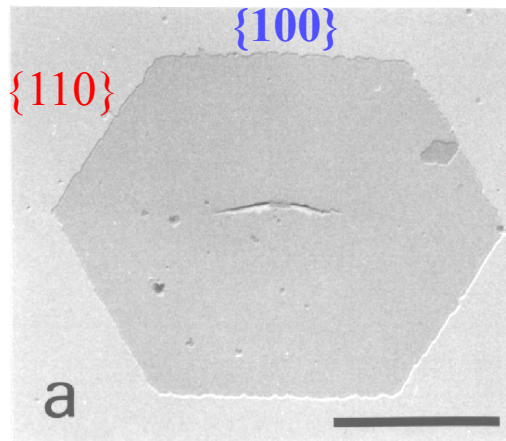
Toda: Colloid Polym Sci **270** ('92) 667

Toda: Faraday Disc **95** ('93) 129

結晶の成長形

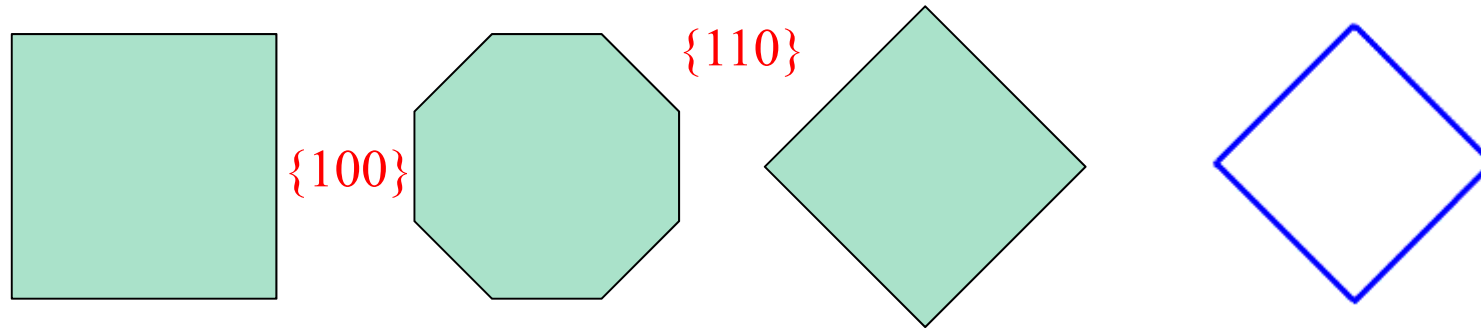


Polyethylene by TEM

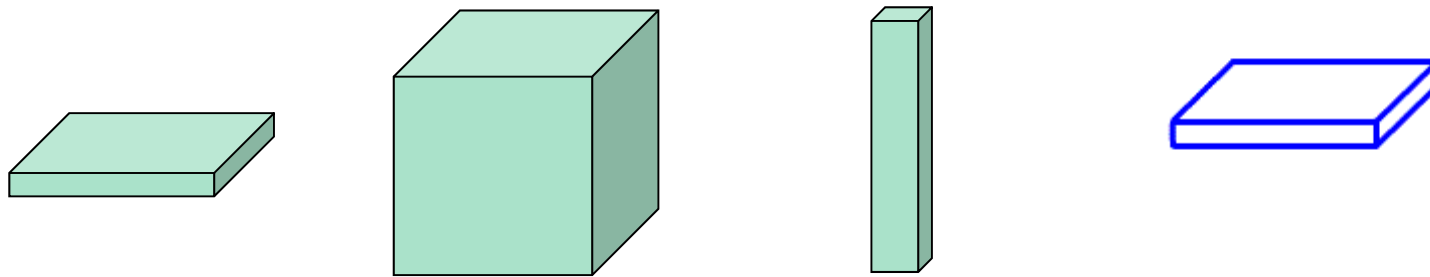


結晶の成長形

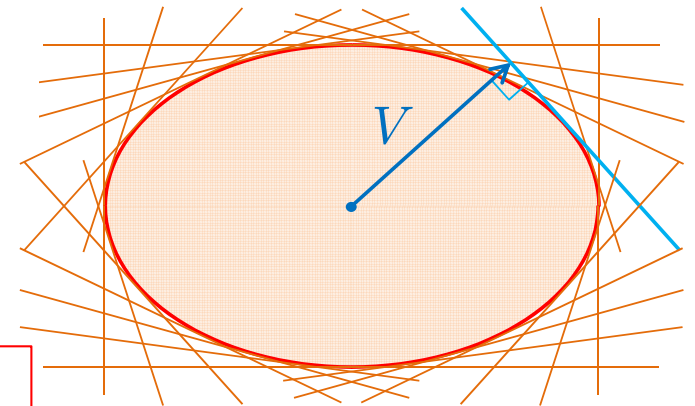
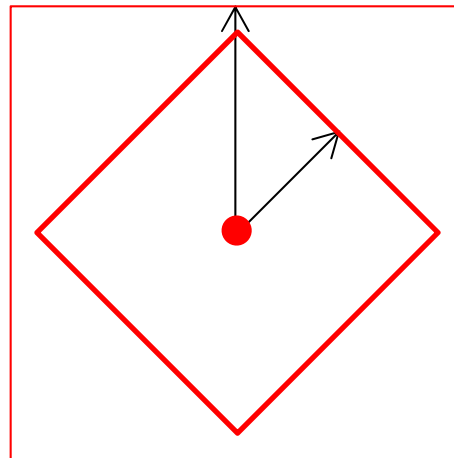
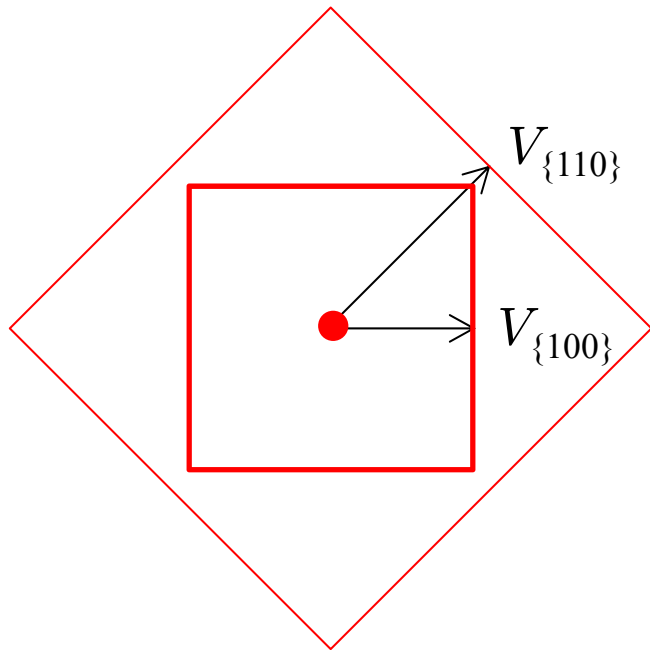
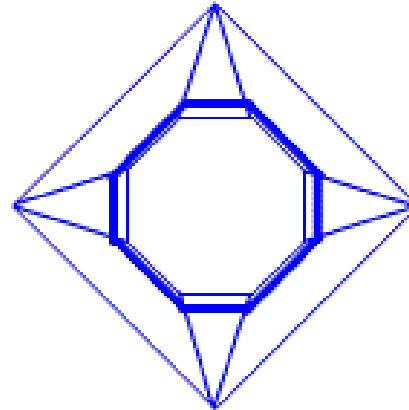
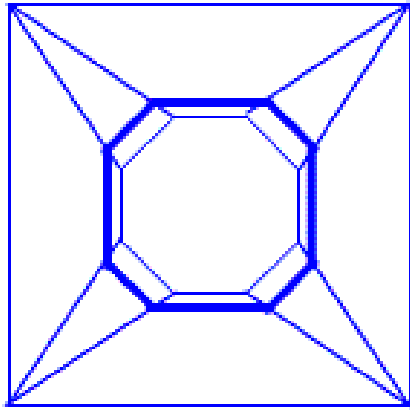
晶相変化



晶癖変化

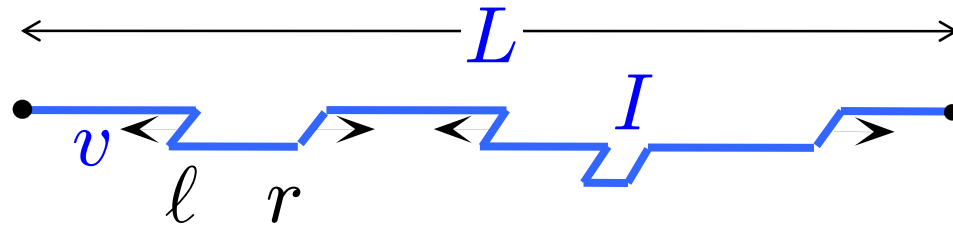


結晶の成長形



Envelope

瀬戸-Frank モデル

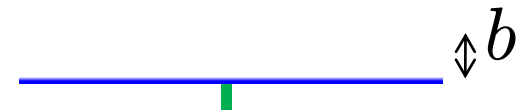


l, r : 左右に進むステップの線密度

成長速度 : $G = b \frac{1}{\tau} = b v (l + r)$

$$\begin{cases} \frac{\partial l}{\partial t} - v \frac{\partial l}{\partial x} = +I - 2v \langle l r \rangle \\ \frac{\partial r}{\partial t} + v \frac{\partial r}{\partial x} = +I - 2v \langle l r \rangle \end{cases}$$

対生成 対消滅



瀬戸-Frank モデル

定常解 ($\frac{\partial \ell}{\partial t} = \frac{\partial r}{\partial t} = 0$)

$$-v \frac{\partial \ell}{\partial x} = v \frac{\partial r}{\partial x} = +I - 2v\ell r \quad \& \quad \ell\left(\frac{L}{2}\right) = r\left(-\frac{L}{2}\right) = 0$$



$$\ell + r = 2c \quad \frac{\partial \ell}{\partial x} = -\frac{I}{v} + 4c\ell - 2\ell^2$$

$$\ell - c = \sqrt{(I/2v) - c^2} \tan[-2x\sqrt{(I/2v) - c^2}]$$

$$c = \sqrt{(I/2v) - c^2} \tan[L\sqrt{(I/2v) - c^2}]$$

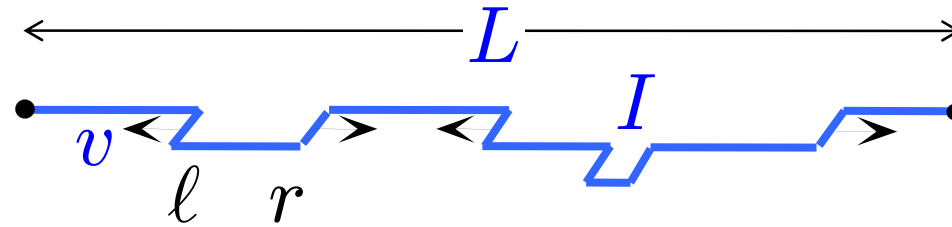
$$\simeq (IL/2v)[1 - (IL^2/3v) + \dots] \quad \text{for } IL^2/2v \ll 1$$

$$\simeq \sqrt{I/2v}[1 - (\pi^2 v/4IL^2) + \dots] \quad \text{for } IL^2/2v \gg 1$$

成長速度 : $G = 2bv(\ell + r) = 2bvc$

$$\simeq \begin{cases} bIL & \text{for } IL^2/2v \ll 1 \\ b\sqrt{2Iv} & \text{for } IL^2/2v \gg 1 \end{cases}$$

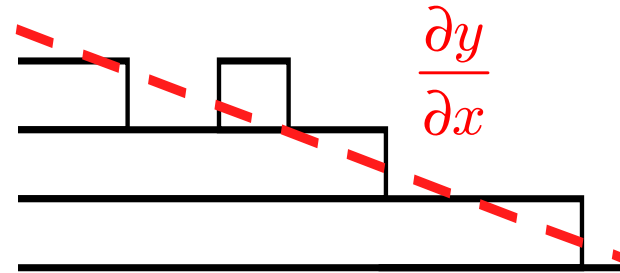
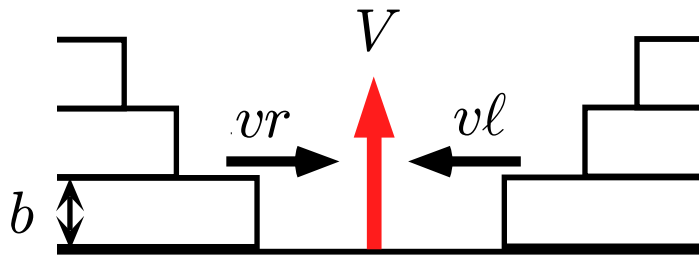
瀬戸-Frank-Mansfield モデル



l, r : 左右に進むステップの線密度

速度 : $V = b \frac{1}{\tau} = b v (\ell + r)$

傾き : $\frac{\partial y}{\partial x} = b(\ell - r)$



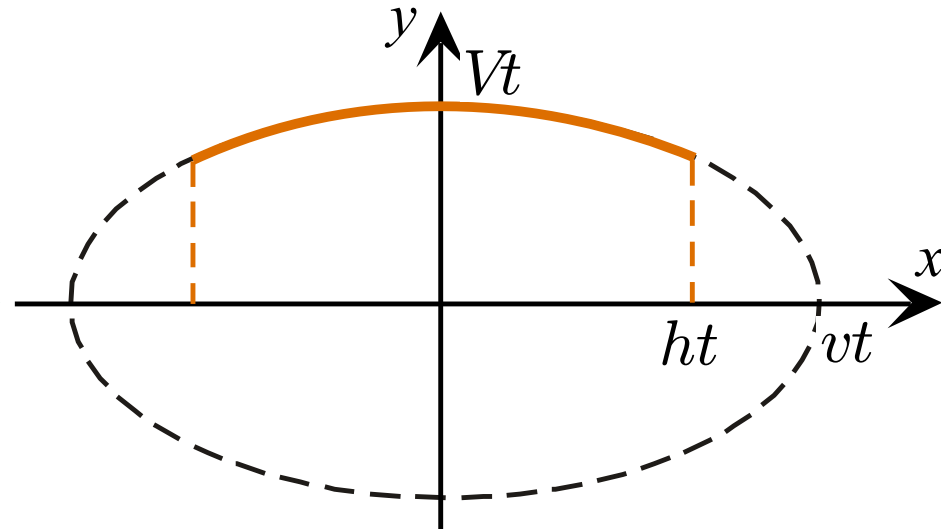
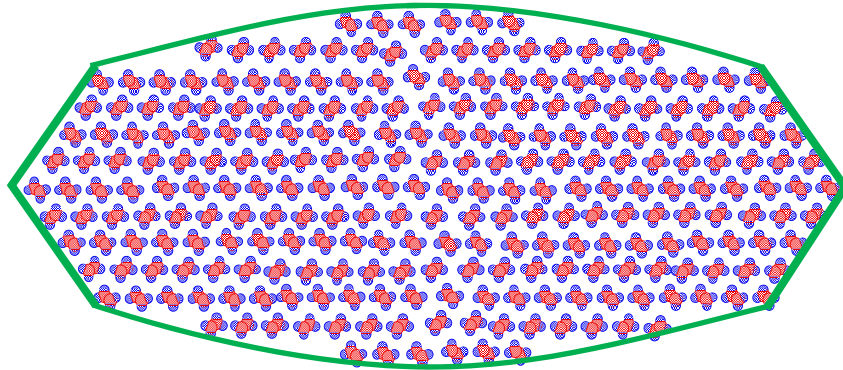
境界条件 :

$$L = 2 h t$$



$$\ell(2 h t) = r(-2 h t) = 0$$

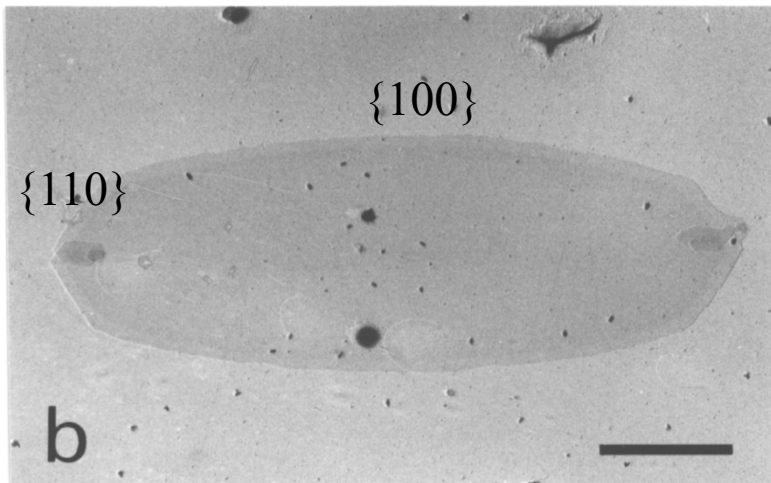
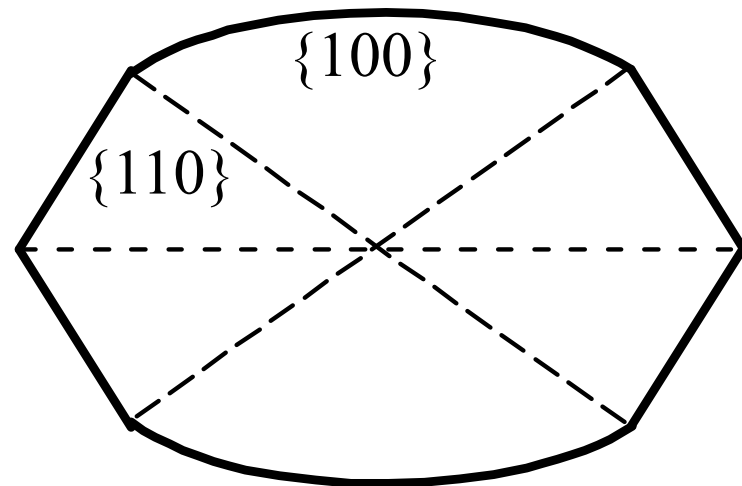
瀬戸-Frank-Mansfield モデル $t \gg 1$



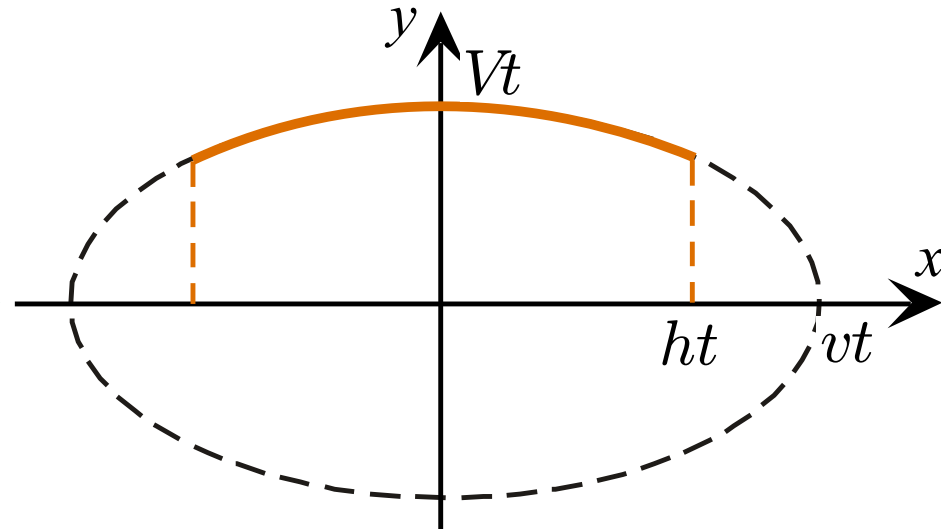
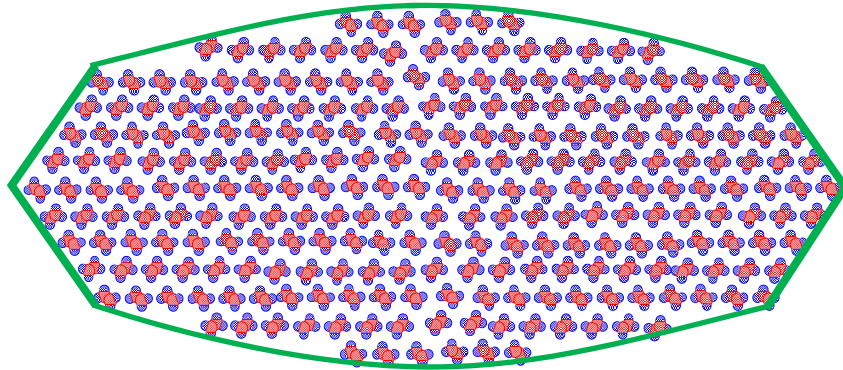
Part of ellipse

$$y = V t [1 - (x / vt)^2]^{1/2}$$

$$v > h$$



瀬戸-Frank-Mansfield モデル $t \gg 1$

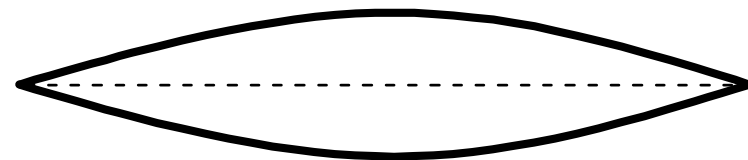


Part of ellipse

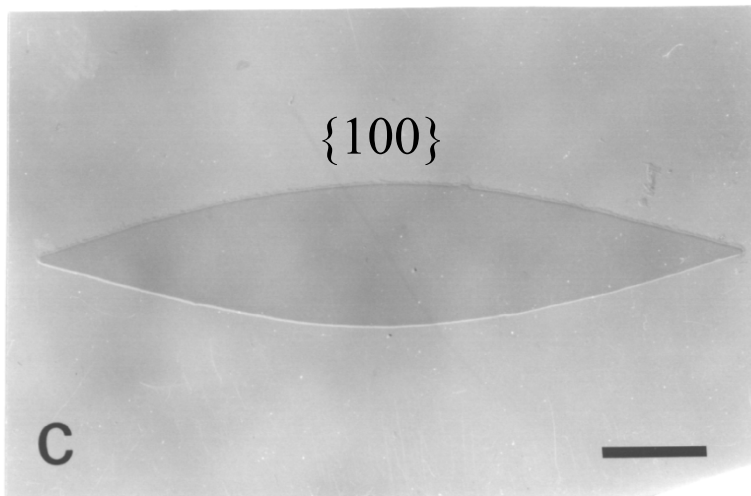
$$y = V t [1 - (x / vt)^2]^{1/2}$$

$$v < h$$

{100}のみ



レンズ型結晶

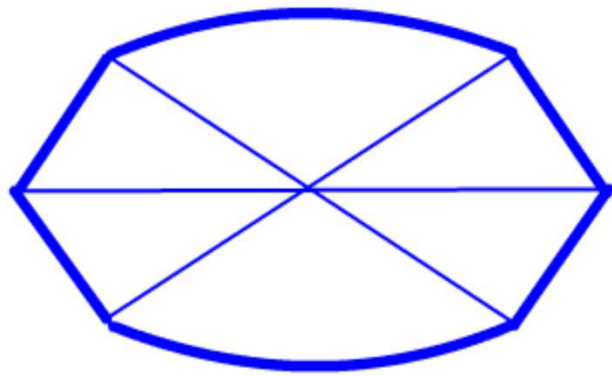


単一核成長様式 $z \ll 1$ ΔT 低

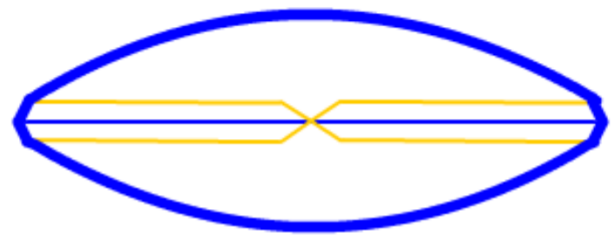
$$V = b I L \propto L \exp\left[-\frac{K}{T \Delta T}\right]$$

多核成長様式 $z \gg 1$ ΔT 高

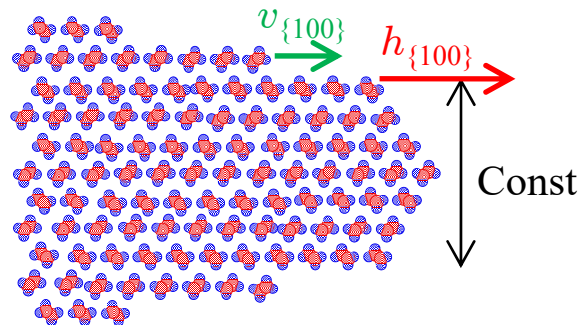
$$V = b(2Iv)^{1/2} \propto \exp\left[-\frac{K/2}{T \Delta T}\right]$$



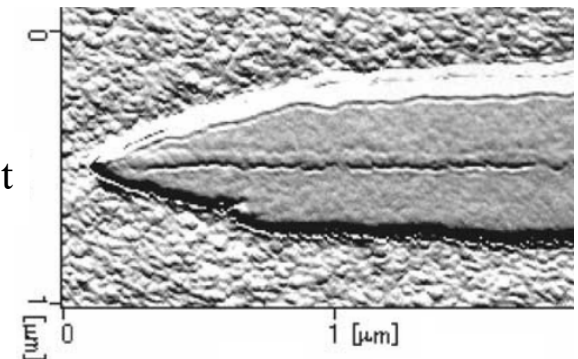
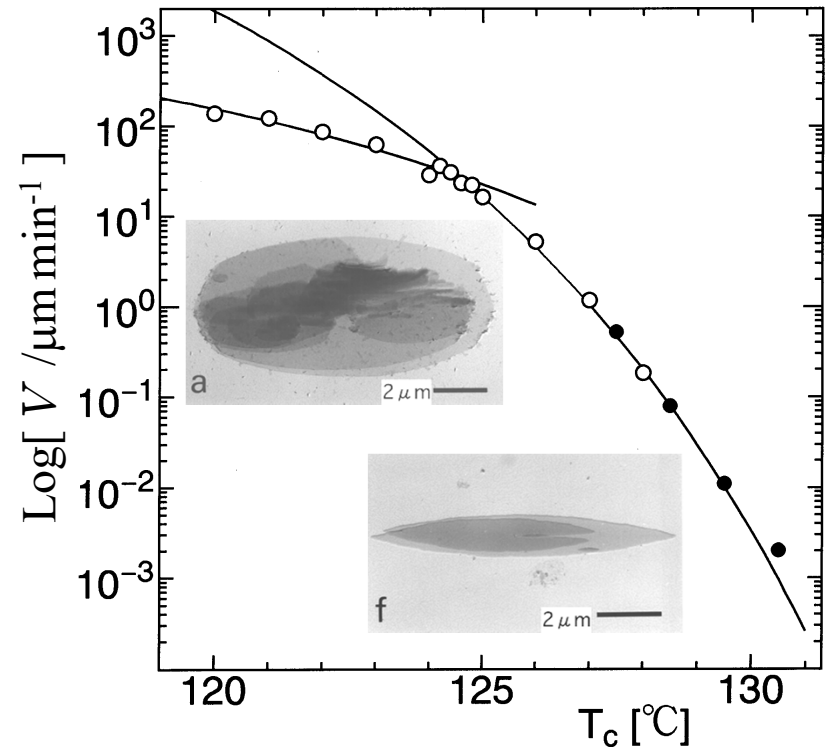
$$V \propto (2Iv)^{1/2}$$



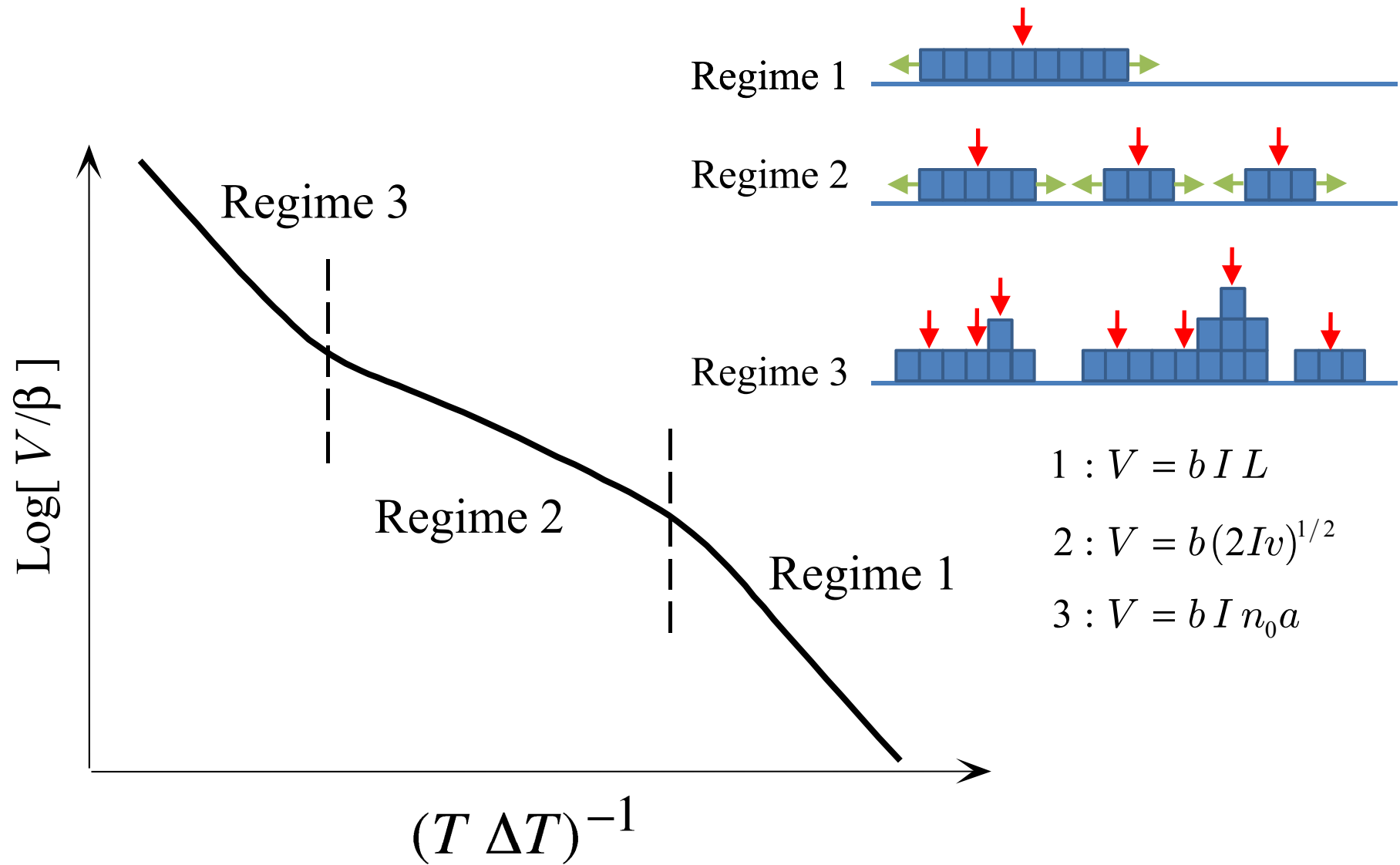
$$V \propto I L$$



レジーム転移 (polyethylene)

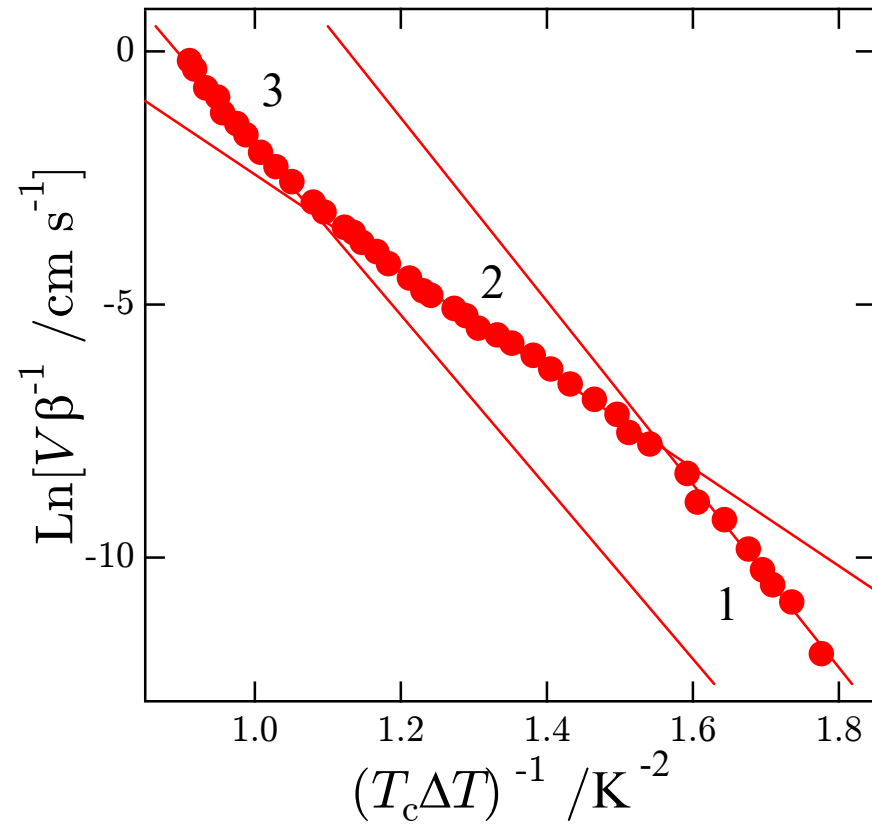
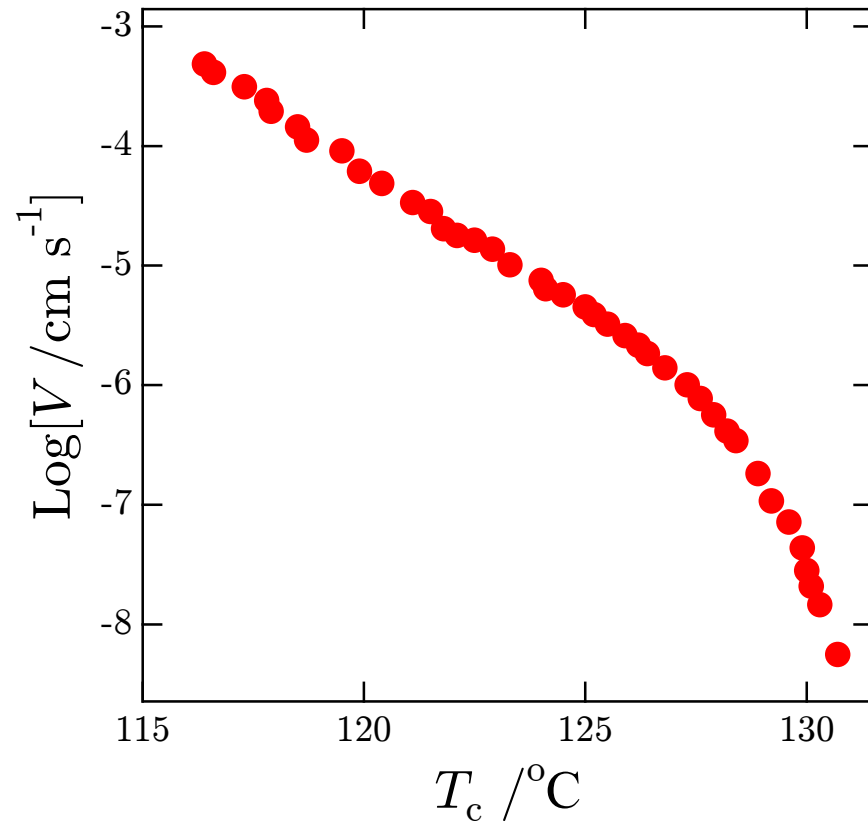


Regime 1, 2, 3

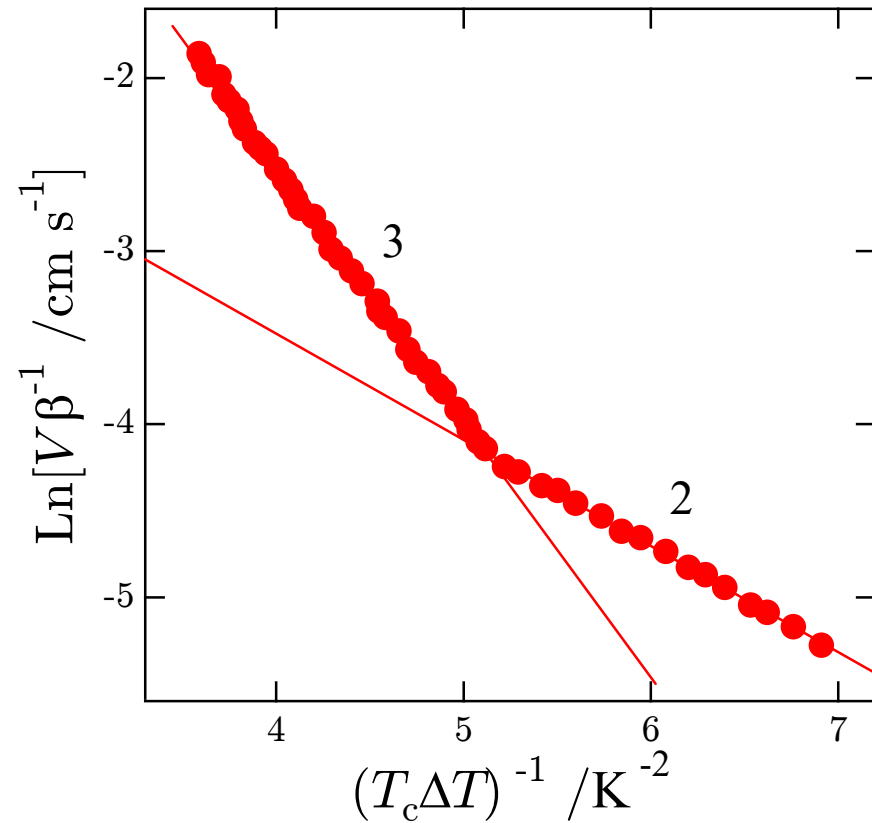
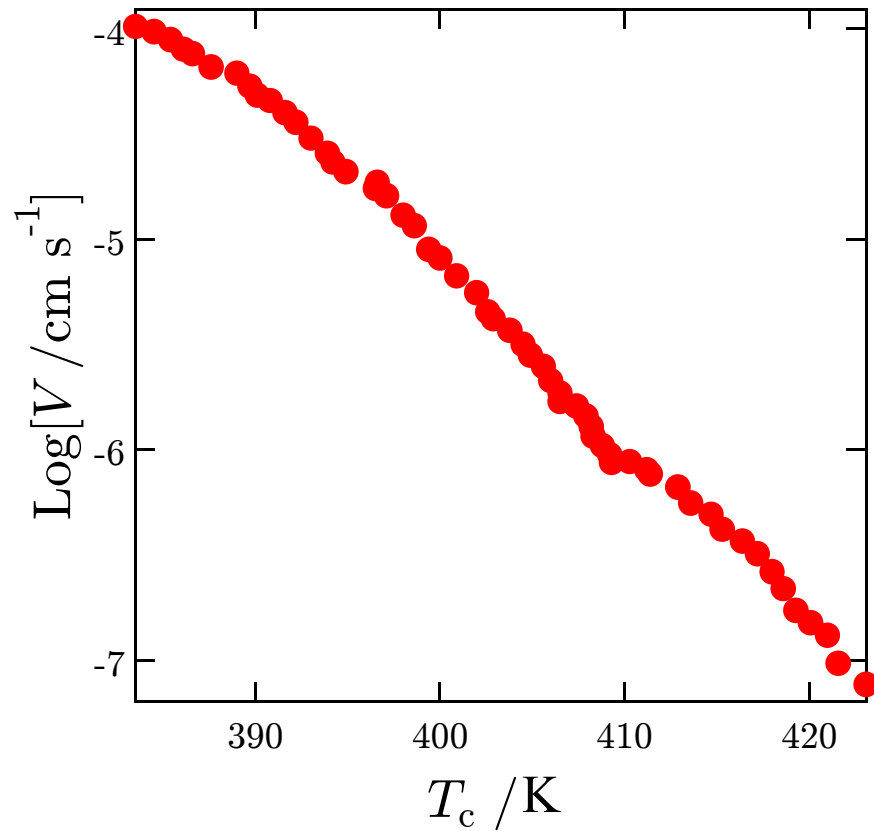


Regime 1, 2, 3 transition

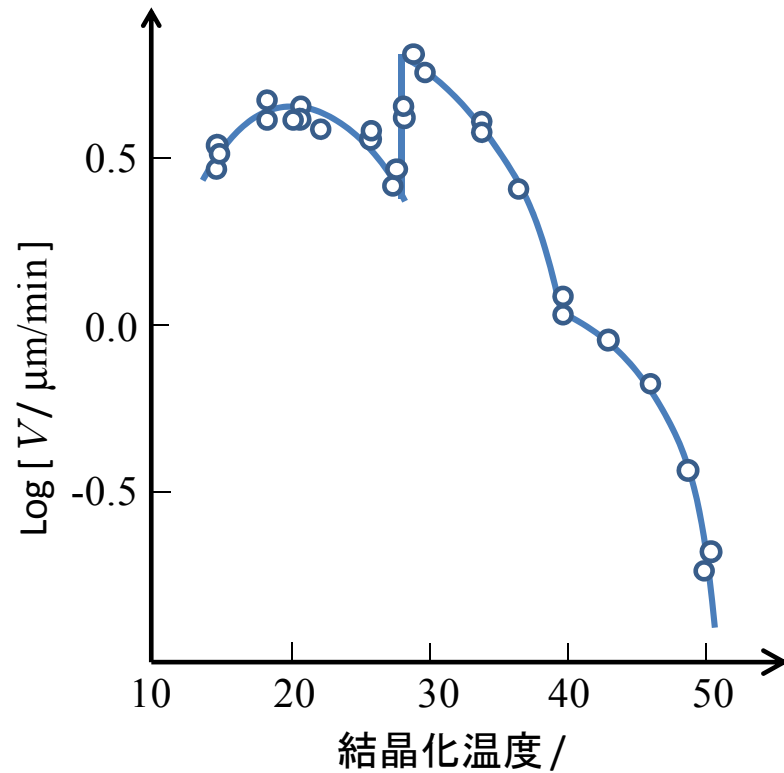
PE



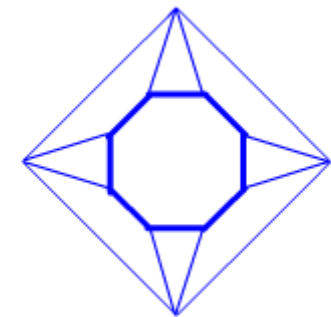
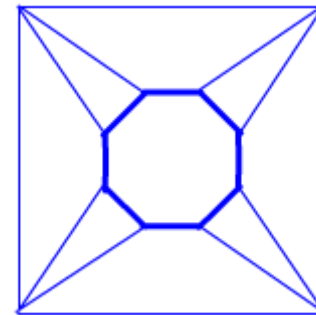
Regime 1, 2, 3 transition iPP



成長速度の ΔT 依存性変化の原因1

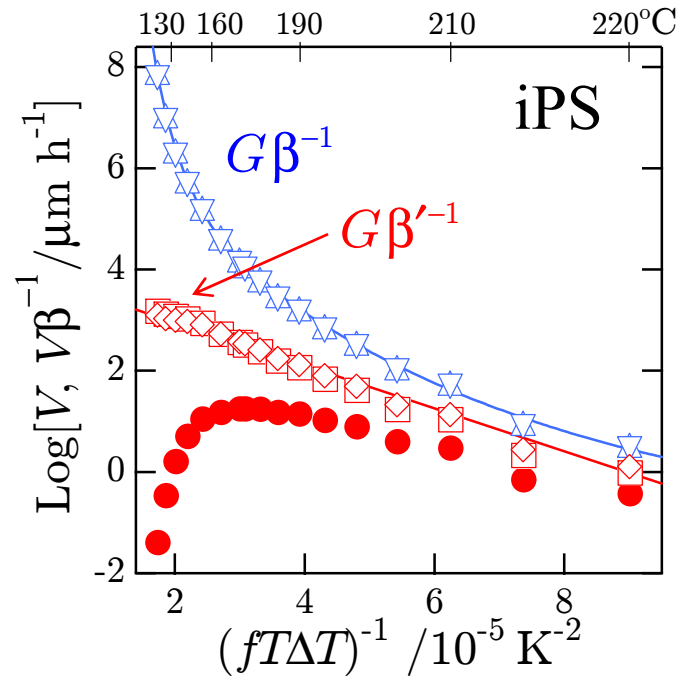


1. 成長結晶相の変化(不連続変化)
2. 成長軸の変化(傾きの変化)



ポリエチレンアジペートの球晶成長 $M=9900$
Takayanagi: Mem Fac Eng Kyushu Univ 16 ('57) 111

成長速度の ΔT 依存性変化の原因2



易動度の $\beta(T)$

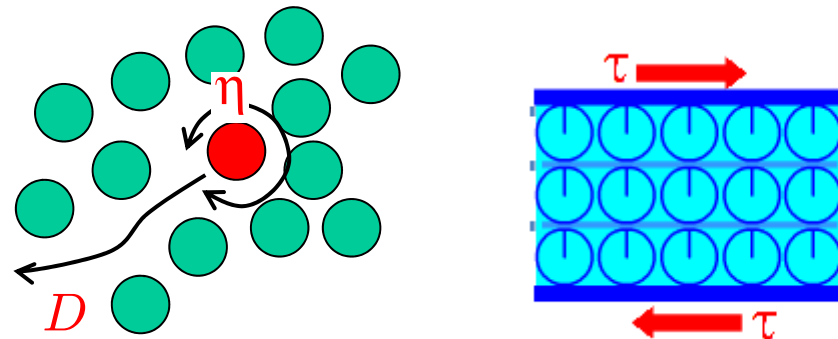
$$G \propto \beta(T) \exp\left[-\frac{K}{T \Delta T}\right]$$

$$\beta(T) \propto \exp\left[-\frac{U^*}{R(T - T_\infty)}\right] \propto \eta^{-1}(T)$$

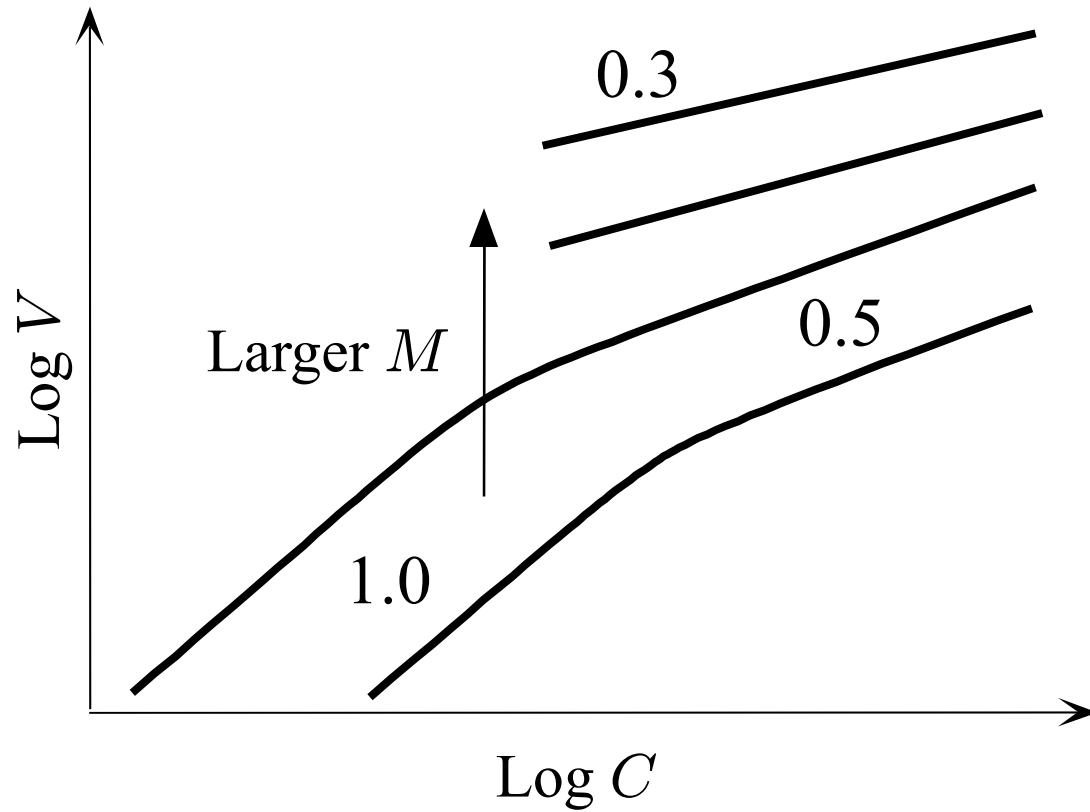
$$\beta'(T) \propto \exp\left[-\frac{U'^*}{R(T - T'_\infty)}\right] \neq \eta^{-1}(T)$$

Breakdown of Einstein's relation near T_g

$$D > \frac{kT}{6\pi\eta r_{SE}} \text{ for } T < T_B \cong 1.2T_g$$



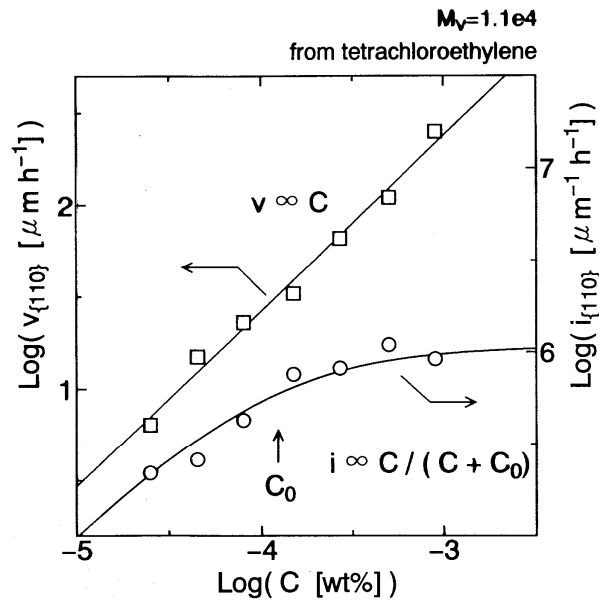
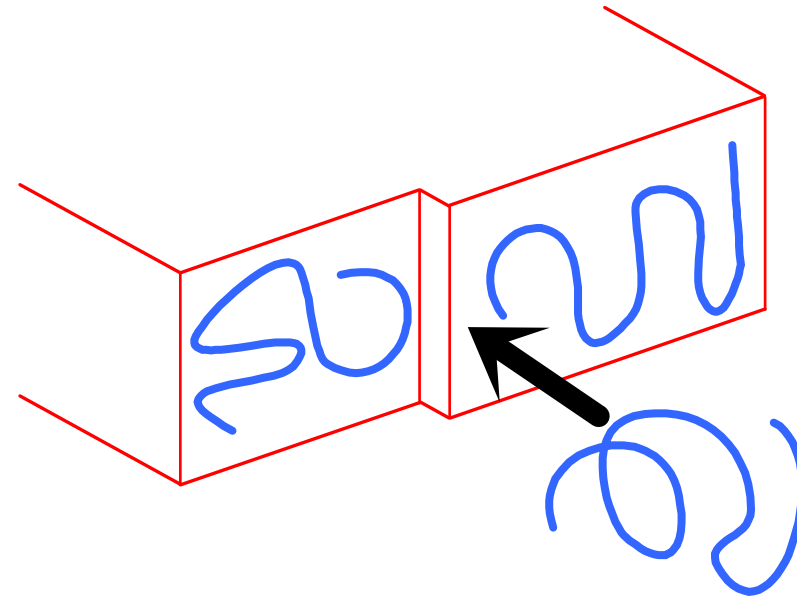
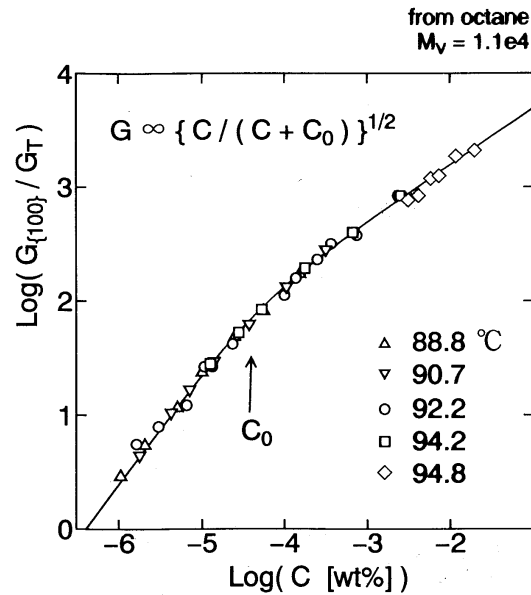
成長速度の濃度依存性



$$V \propto C^\gamma$$

$$I(C) \quad v(C)$$

成長速度の濃度依存性



$$I(C) \propto \frac{C}{C + C_0}, \quad v(C) \propto C$$

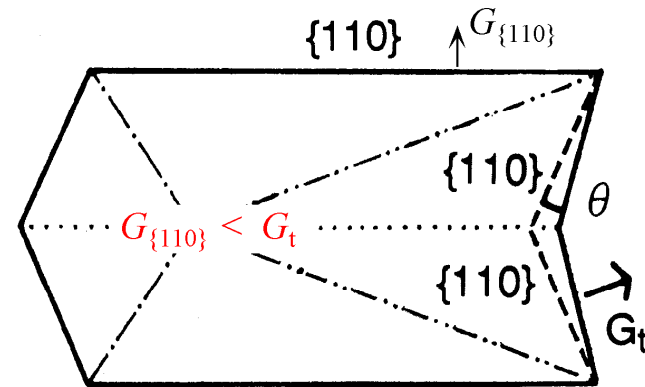
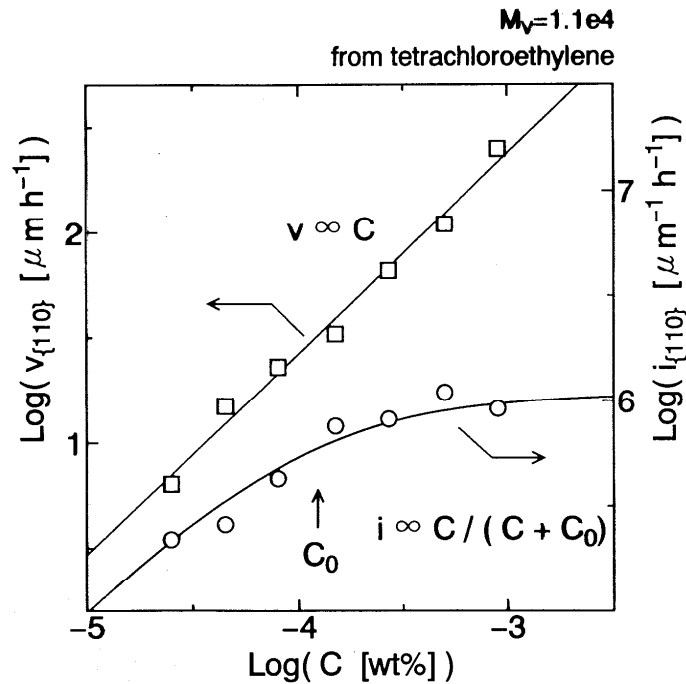
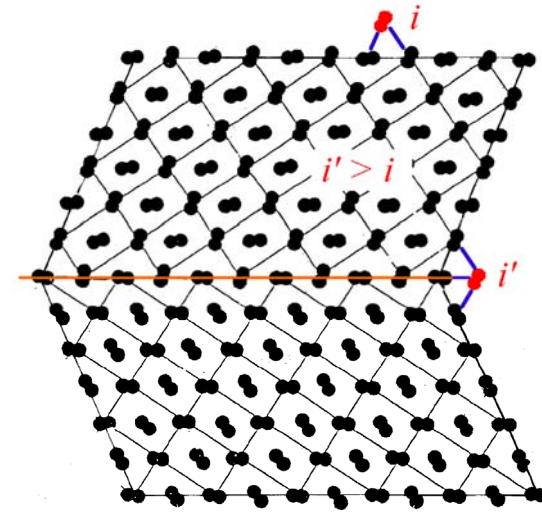
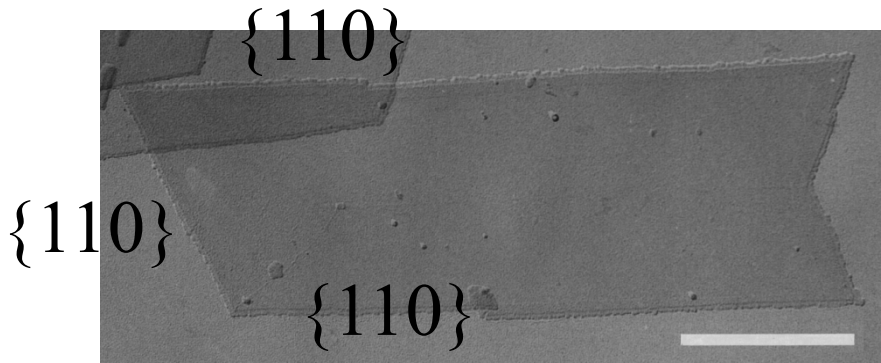
等温吸着式

$$C_0 \propto \exp[-A M]$$

$$V \propto [I v]^{1/2} \propto \left[\frac{C^2}{C + C_0} \right]^{1/2}$$

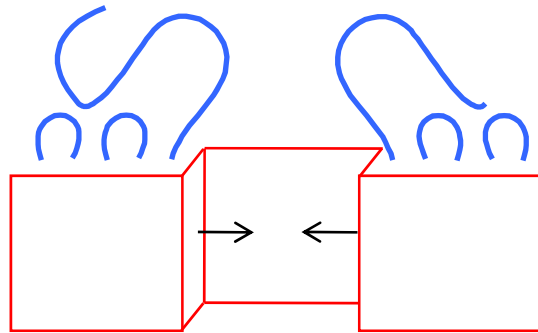
ポリエチレン単結晶（{110}双晶）

Polyethylene by TEM (1 μ m)



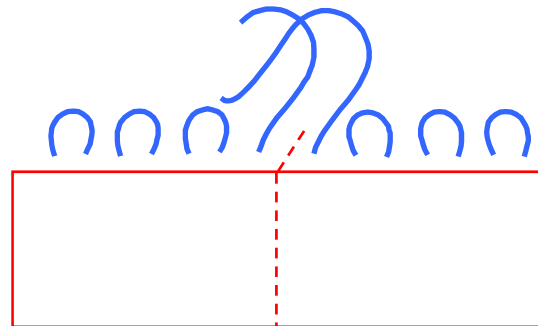
$$G_{\{110\}}, G_t, \theta \Rightarrow i', i, v$$

成長速度の濃度・分子量依存性



$$V \propto C^\gamma \quad \gamma < 0.5$$

$10^{-3} M_w$	15.7	25.2	61.6	83.9	195
γ	0.52	0.42	0.38	0.36	0.24

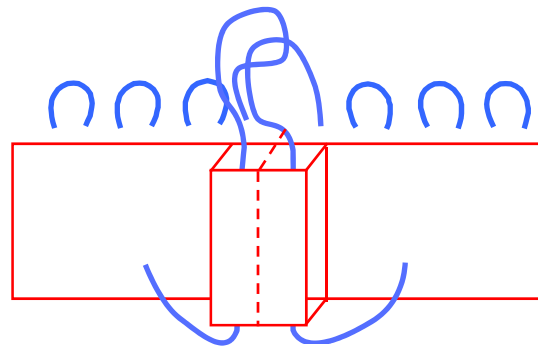


$$V \propto [I v(C)]^{1/2} \propto C^{1/2}$$

$$V \propto [I_{\text{cilia}} I v(C)]^{1/3} \propto C^{1/3}$$

$$V \propto [I_{\text{cilia}} I'_{\text{cilia}} I v(C)]^{1/3} \propto C^{1/4}$$

⋮



I_{cilia}

高分子の折り畳み鎖結晶化機構

高分子性

高分子性

分子量依存性

$$1 \text{ 次核形成頻度: } I \propto I_0 \beta \exp\left[-\frac{C}{T\Delta T^2}\right]$$

$$\beta \propto \exp\left[-\frac{U^*}{R(T - T_\infty)}\right]$$

$$\text{結晶成長速度: } V \propto G_0 \beta \exp\left[-\frac{K}{T\Delta T}\right]$$

$$\begin{cases} \Delta T = T_M(M) - T_c \\ T_\infty = T_g(M) - 30 \text{ K} \end{cases}$$

$$T_M(M) \text{ , } T_g(M_n) = T_g^\infty - \frac{A}{M_n} \text{ (Fox-Flory)}$$

$$I_0 \propto M^{-\alpha} \quad G_0 \propto M^{-\beta}$$

$$\eta_0 \propto M^{3.4}, \quad D^{-1} \propto M^2 \quad \text{for } M > M_e$$

$$\zeta \propto M^1$$

$$\text{Hoffman: } G(\Delta T) \propto M^{-1.3}$$

Polymer 23 ('82) 656

$$\text{彦坂: } G(\Delta T) \propto M^{-1.8} \text{ (FCC)} \propto M^{-0.7} \text{ (ECC)}$$

Polym J 31 ('99) 749

$$I(\Delta T) \propto M^{-1} \text{ (ECC)}$$

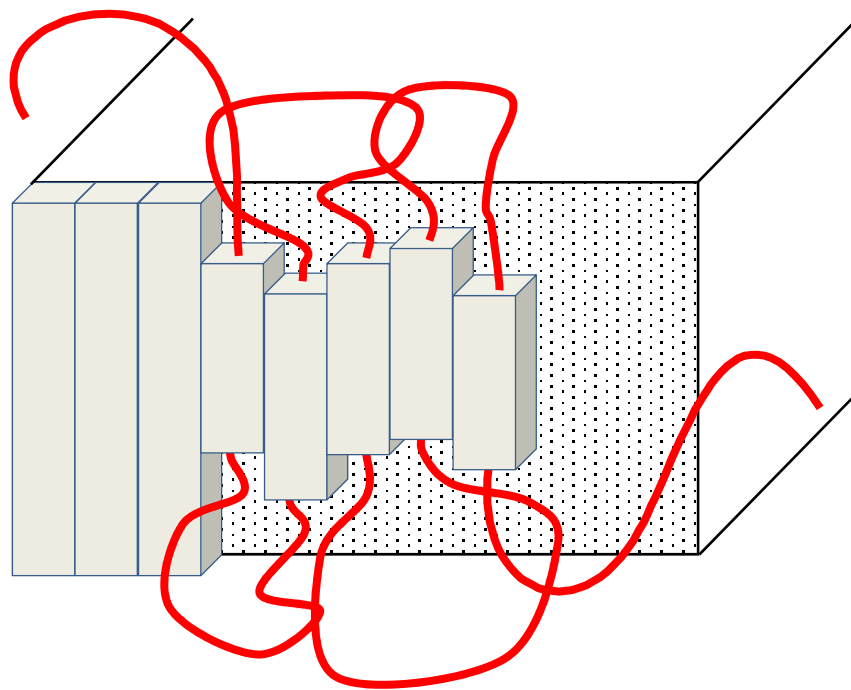
$$\text{奥居: } G_{\max} \propto M^{-0.5}$$

Polymer 46 ('05) 8790

高分子性

Molecular Nucleation

Wunderlich: Farad Disc Roy Soc Chem 68 (79) 239



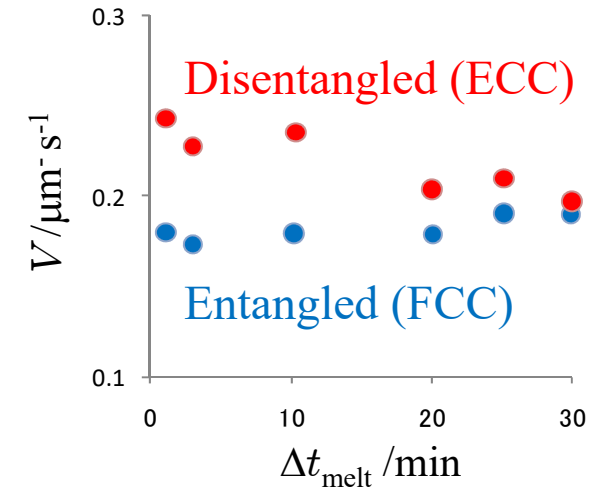
高分子性

絡み合い

1. Melt memory effects of heterogeneous nucleation
2. Crystal Growth Rate V

補) Gel spinning:

chain orientation with minimum intermolecular entanglements



PE: $T_{\text{melt}} = 160^\circ\text{C}$, $T_c = 123^\circ\text{C}$

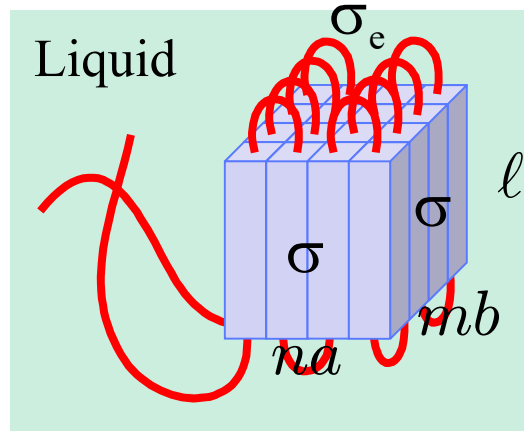
Psarski, Piorkowska, Galeski:

Macromol 33('00)916

高分子の折り畳み鎖結晶化機構

1次核形成

高分子結晶の1次核形成



$$x \equiv na = mb$$

Homogeneous

$$\Delta G(n, l) = -\Delta\mu x^2 l + 2\sigma_e x^2 + 4\sigma xl$$

$$\text{臨界核: } 0 = \frac{\partial \Delta G}{\partial l} = -\Delta\mu x^2 + 4\sigma x$$

$$0 = \frac{\partial \Delta G}{\partial x} = -2\Delta\mu xl + 4\sigma_e x + 4\sigma l$$

$$x^* = n^* a = m^* b = \frac{4\sigma}{\Delta\mu} \quad l^* = \frac{4\sigma_e}{\Delta\mu}$$

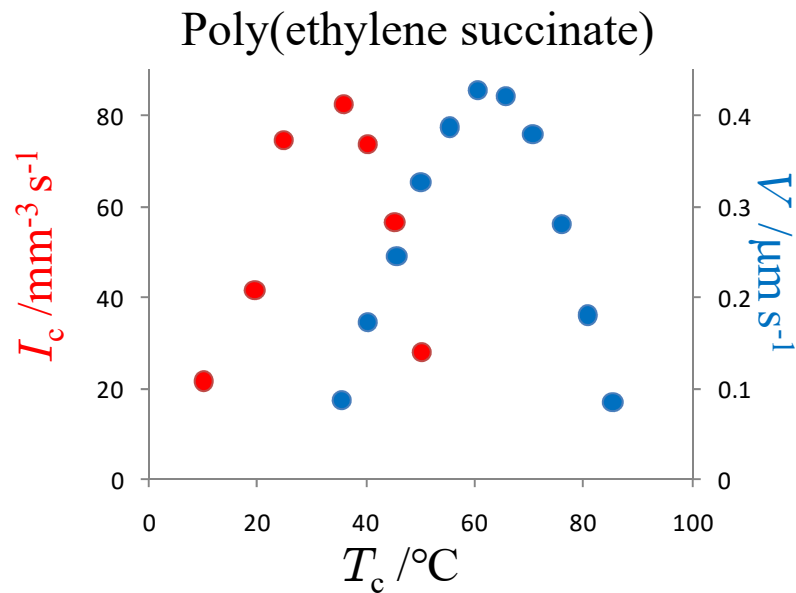
$$\Delta G^* = \frac{32\sigma^2\sigma_e}{\Delta\mu^2}$$

高分子結晶の1次核形成

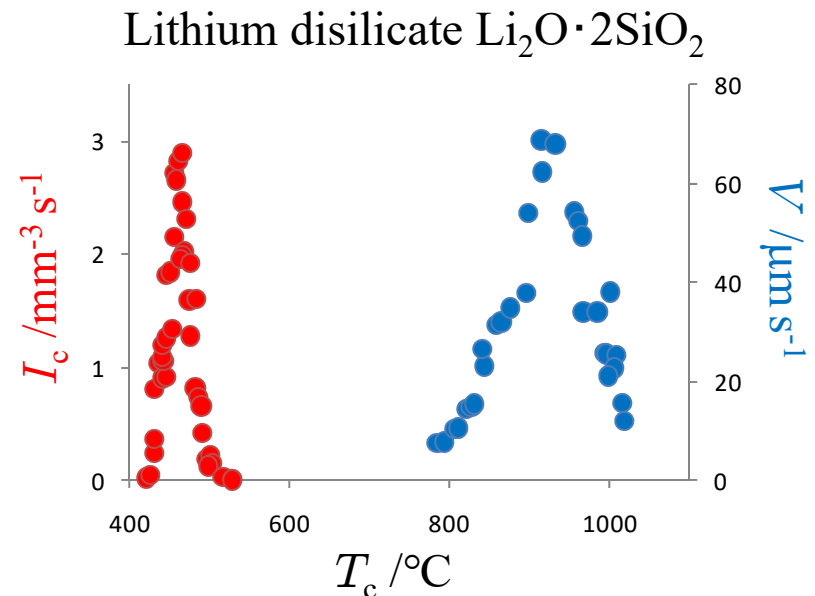
$$1 \text{ 次核: } I_c^1 \propto \beta \exp\left[-\frac{16\sigma^3}{3k_B T (\Delta\mu)^2}\right]$$

$$\text{表面核: } I_c^2 \propto \beta \exp\left[-\frac{\pi a \sigma^2}{k_B T} \frac{1}{\Delta\mu}\right] \propto V$$

$$\beta \propto \exp\left[-\frac{U^*}{R(T - T_\infty)}\right] \quad \Delta\mu = \frac{\Delta h_f}{T_M} \Delta T$$

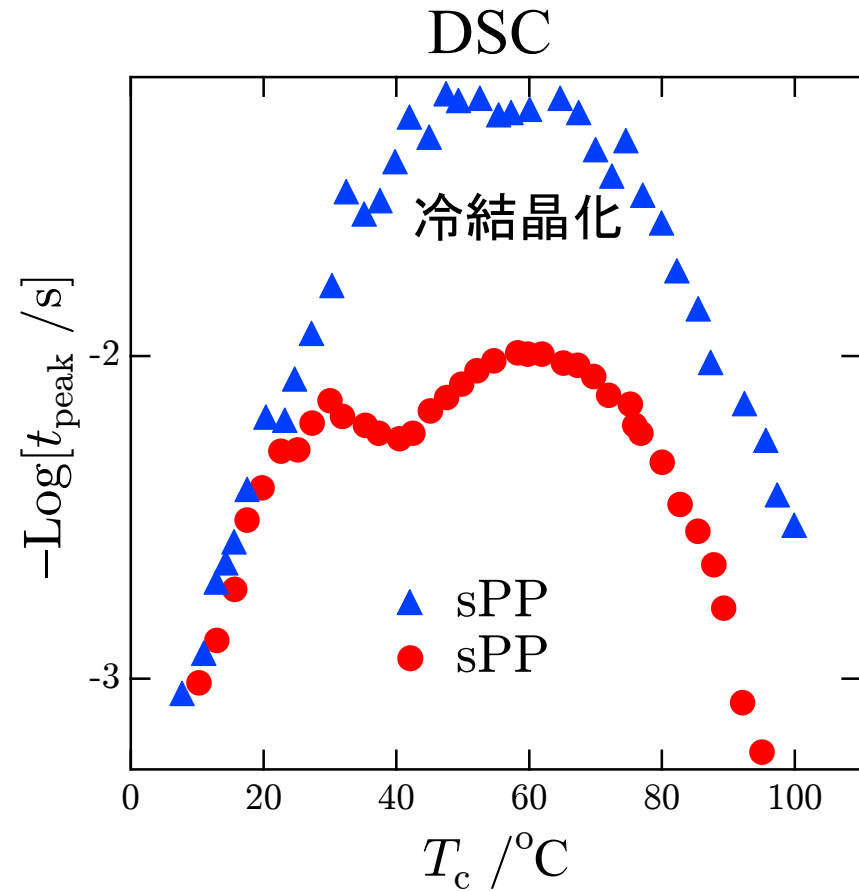
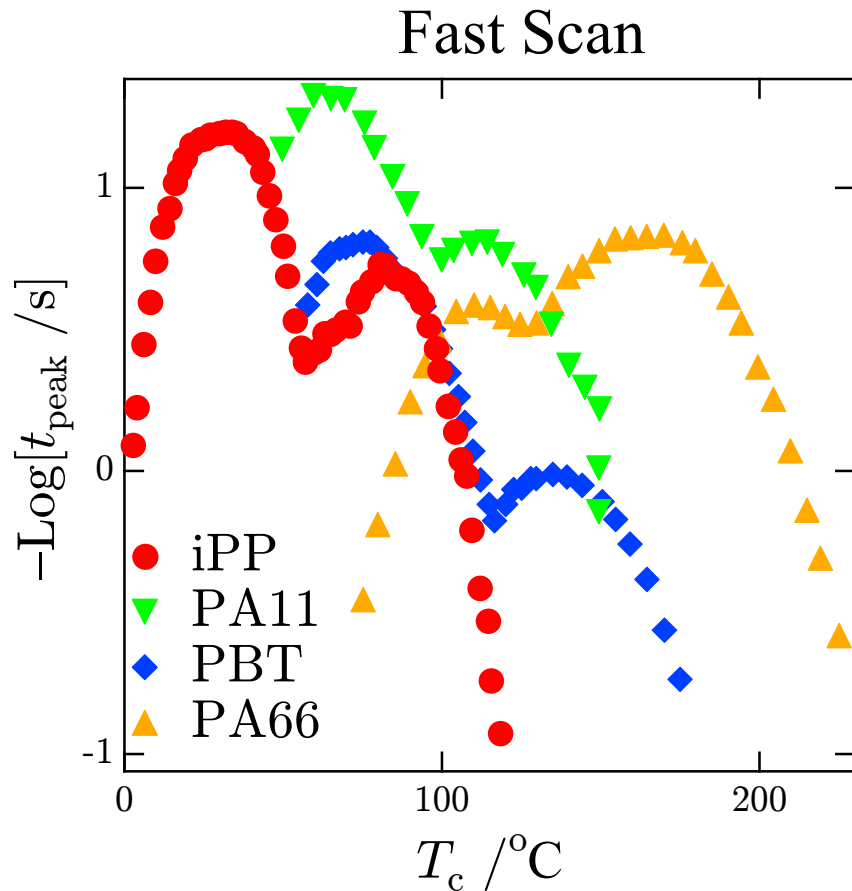


Umemoto, Hayashi, Kawano, Kikutani, Okui:
J Macromol Sci **B42** ('03) 421



Fokin *et al.*: J Non Cryst Solid **351** ('05) 1491
Matusita, Tashiro: J Ceram Soc Jpn **81** ('73) 500

熱測定：等温結晶化



Fast Scan Calorimetry

iPP: Schawe, *J. Therm Anal Calor*, **116** (2014) 1165

PA11: Mollova, Androsch, Mileva, Schick, Benhamida, *Macromolecules* **46** (2013) 828

PBT: Androsch, Rhoades, Stolte, Schick, *Euro Polym J* **66** (2015) 180

PA66: Rhoades, Williams, Androsch, *Thermochim Acta* **603** (2015) 103

DSC

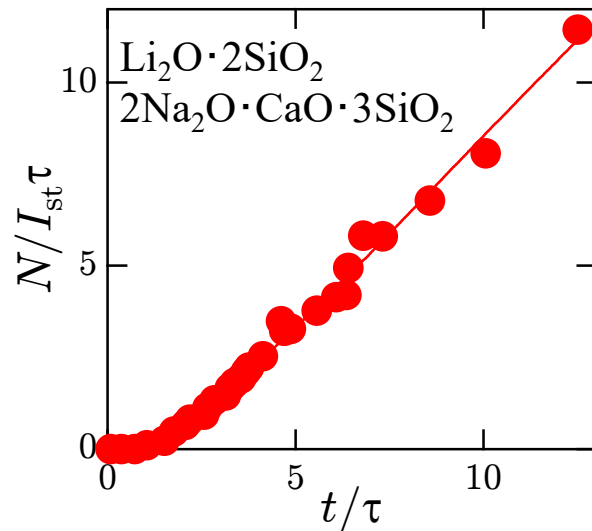
Supaphola, Spruiell, *Polymer* **42** (2001) 699

高分子結晶の1次核形成

$$I(t) = I_{\text{st}} \left[1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp\left(-\frac{m^2 t}{\tau}\right) \right]$$

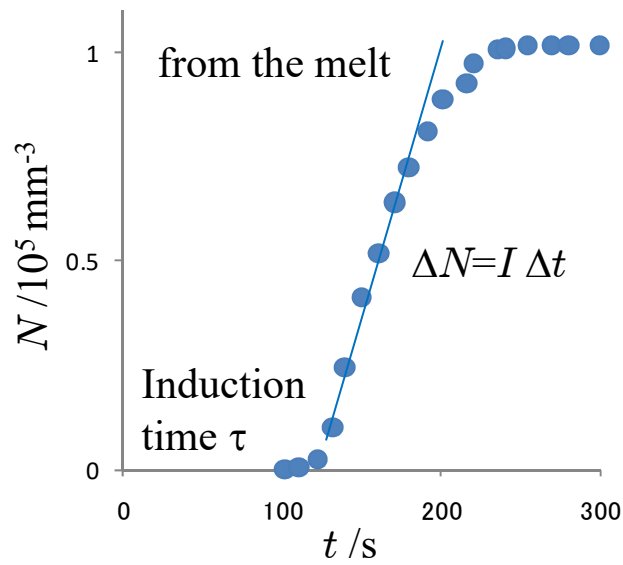
$$N(t) \sim I_{\text{st}} \left(t - \frac{\pi^2 \tau}{6} \right) \quad \text{for } t \rightarrow \infty$$

$$t_{\text{ind}} = \frac{\pi^2}{6} \tau = \frac{\pi^2}{6} \cdot \frac{16h}{\pi} \frac{\sigma}{\Delta G^{*2} a^4} \exp\left[\frac{\Delta G_{\eta}}{k_{\text{B}} T}\right] \propto \frac{1}{\beta \Delta G^{*2}} \quad I_{\text{st}} \propto \beta \exp\left[-\frac{\Delta G^*}{k_{\text{B}} T}\right]$$

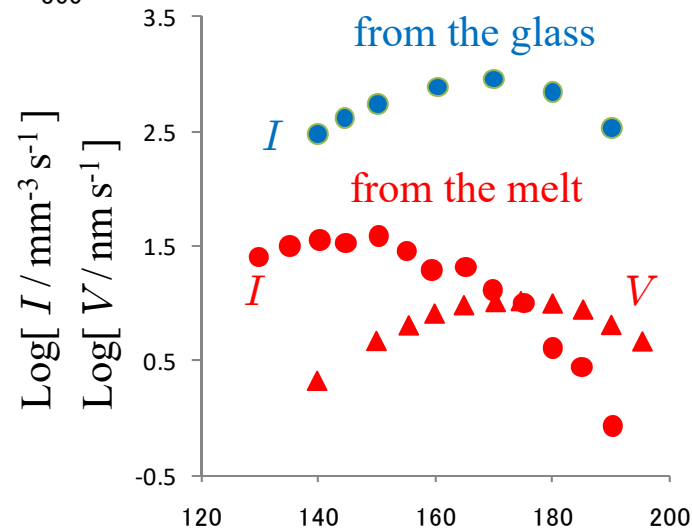
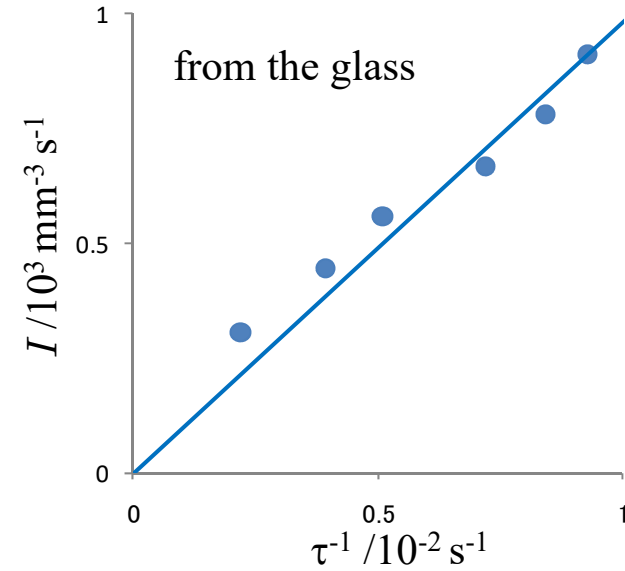


Fokin, Nikolay, Yuritsyn, Zanotto:
in “Nucleation Theory and Applications”

高分子結晶の1次核形成



it-Polystyrene



高分子結晶の1次核形成

均一核:

$$\Delta G^* = \frac{32\sigma^2\sigma_e}{\Delta\mu^2}$$

不均一核:

$$y^* = m^*b = \frac{2\Delta\sigma}{\Delta\mu}$$

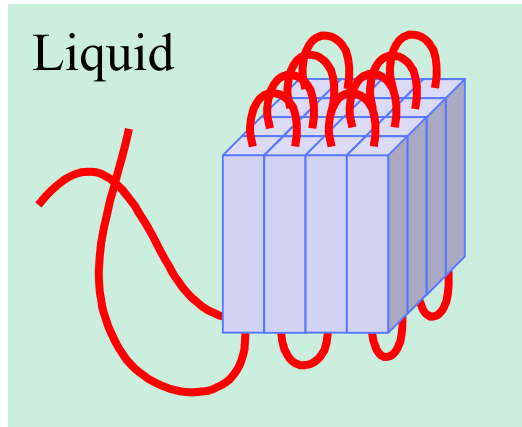
for $m^* > 1$ ($b\Delta\mu < 2\Delta\sigma$)

$$\Delta G_H^* = \frac{16\sigma\sigma_e\Delta\sigma}{\Delta\mu^2}$$

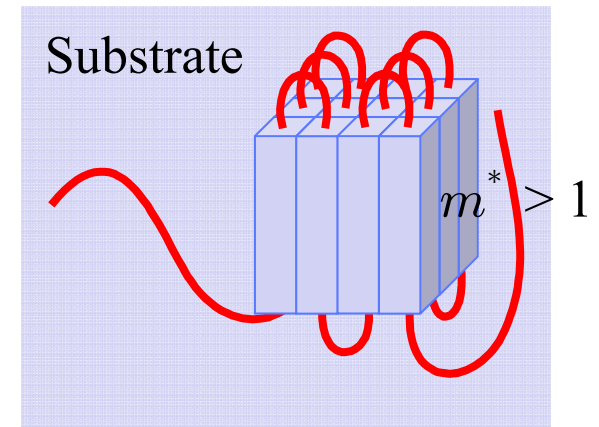
for $m^* < 1$ ($b\Delta\mu > 2\Delta\sigma$)

$$\begin{aligned} \Delta G_H^* &= \frac{4b\sigma\sigma_e}{\Delta\mu - \Delta\sigma/b} \\ &\sim \frac{4b\sigma\sigma_e}{\Delta\mu} \end{aligned}$$

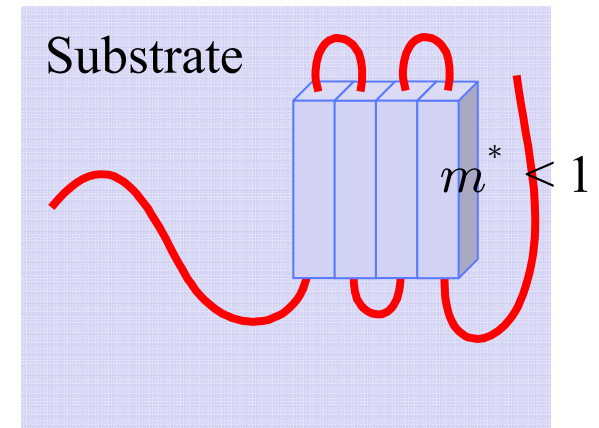
for $b\Delta\mu \gg \Delta\sigma$



均一核

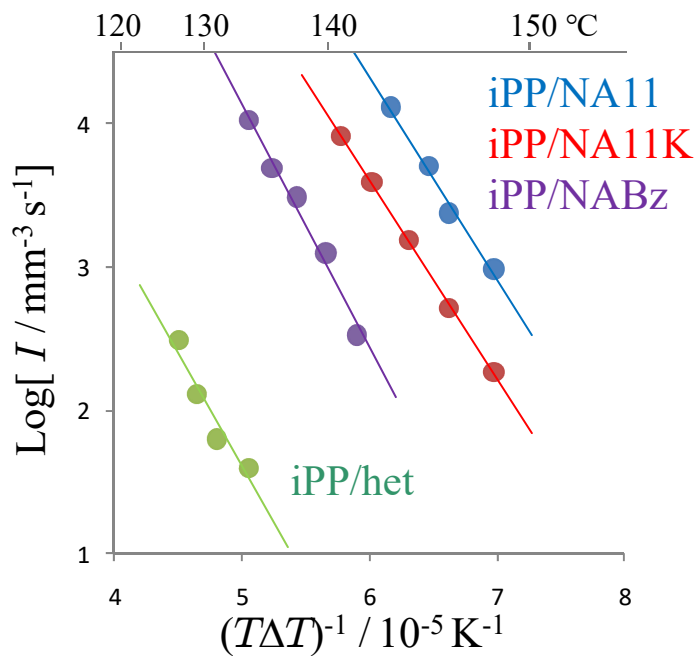
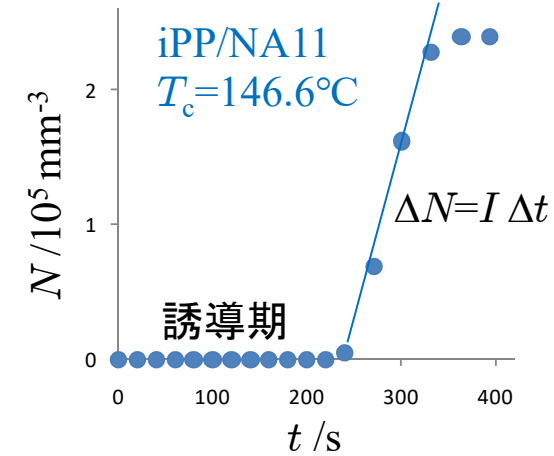


不均一核



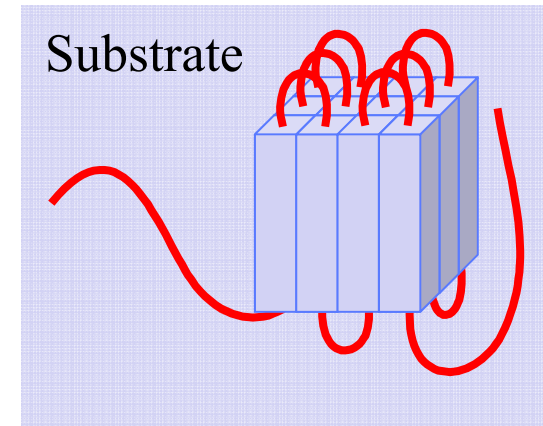
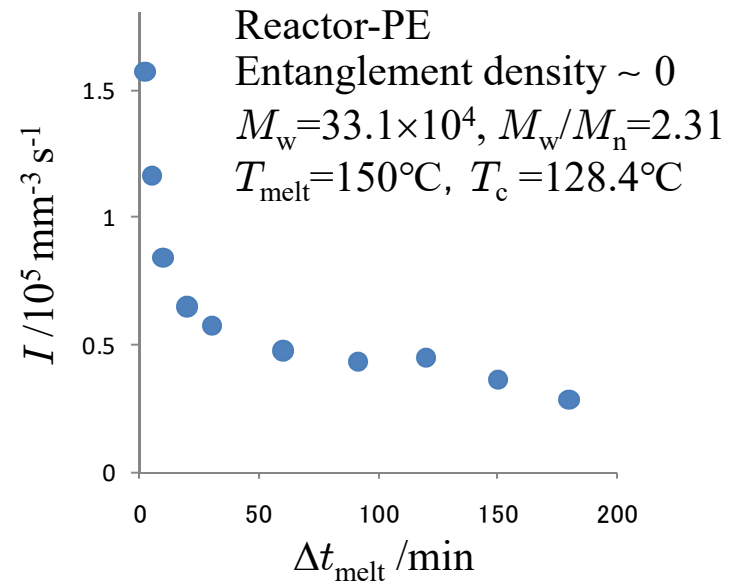
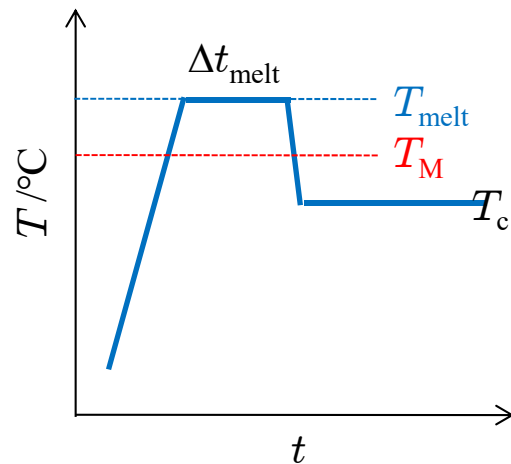
高分子結晶の1次核形成

核剤の効果(不均一核)



高分子結晶の1次核形成

不均一核(融液記憶効果)



1. Activity of heterogeneity
2. Entanglements

高分子の折り畳み鎖結晶化機構

準安定状態の役割

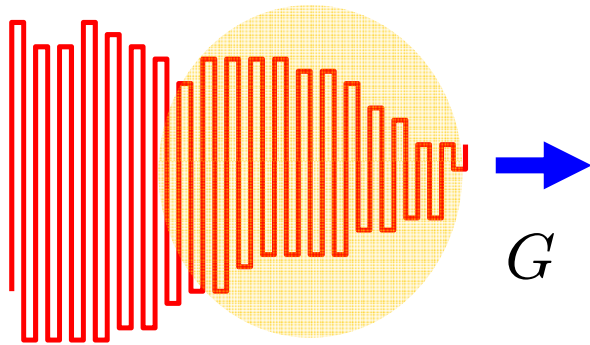
結晶成長先端の形態(計算機実験)

エントロピー障壁・Pinning モデル

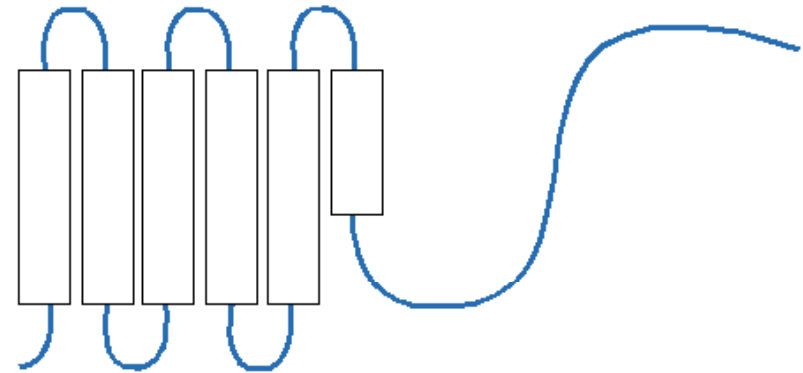
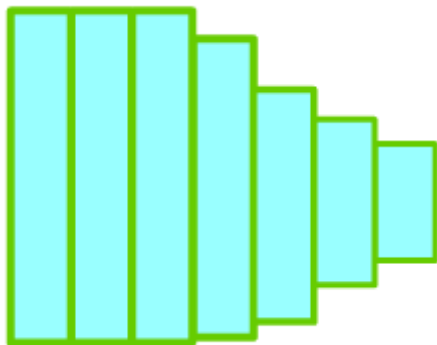
Keller-Strobl モデル

梶モデル 相分離

エントロピー障壁モデル



Pinning
 $\Delta S > 0$
 準安定

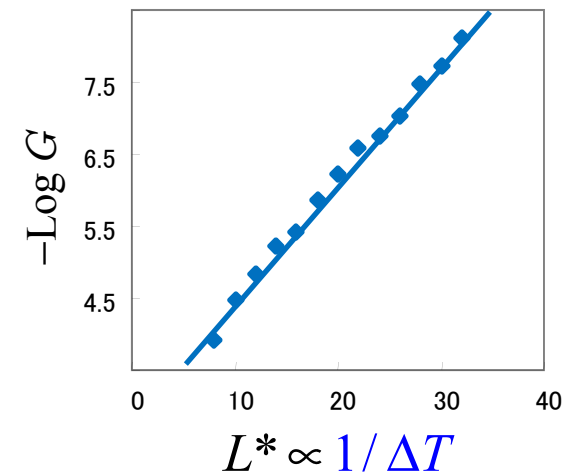


エントロピー障壁：

$$\Delta S \propto \ell^* = A / \Delta T$$

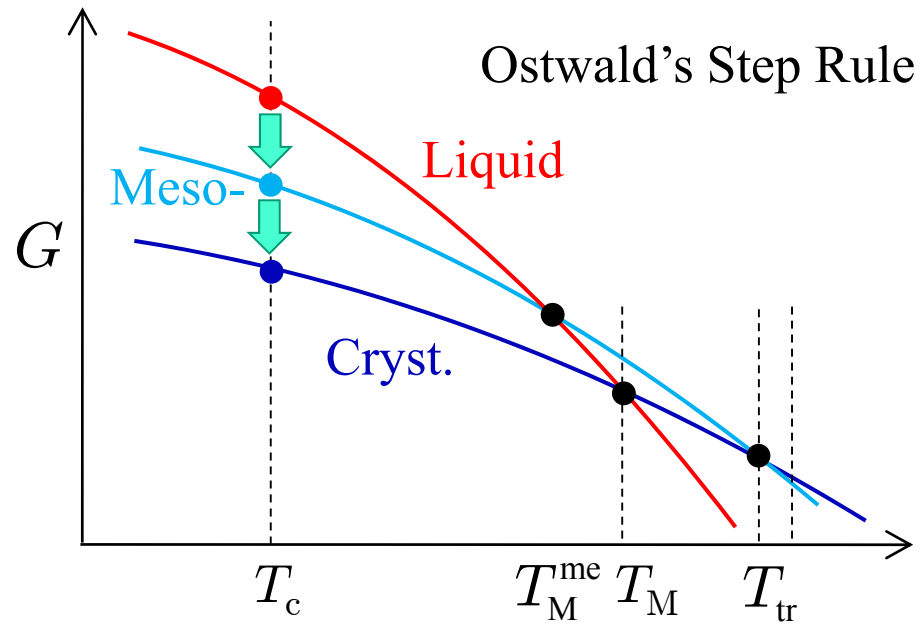
$$G \propto \exp[-\Delta S / k_B]$$

$$\propto \exp[-C / \Delta T]$$



Sadler, DM: Nature **326** (1987) 174
 Doye & Frenkel: Phys Rev Lett **81**('98) 2160
 Toda: J Chem Phys 18 ('03) 8446

準安定相



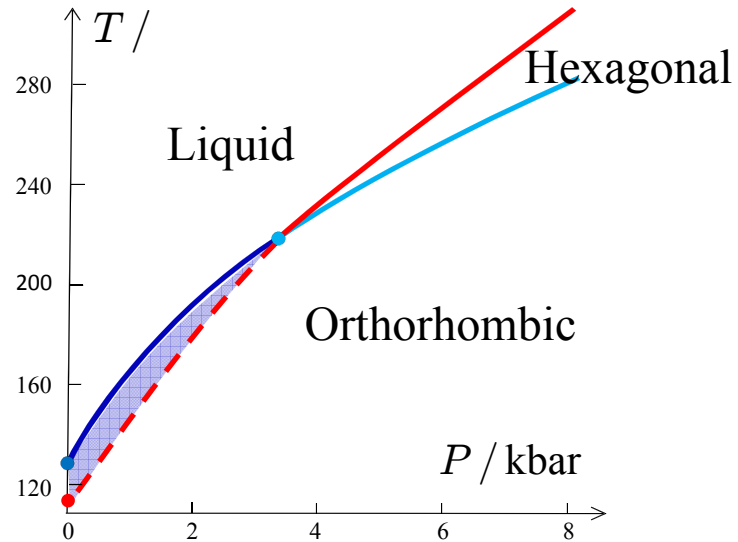
$$S^{cryst} < S^{meso} < S^{melt}$$

$$\sigma^{cryst-melt} > \sigma^{meso-melt}$$

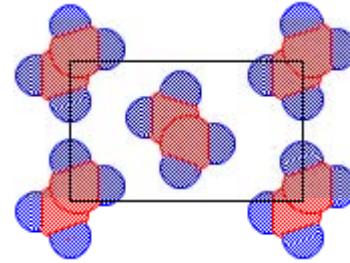
$$G^{cryst-melt} < G^{meso-melt}$$

PE	orthorhombic	hexagonal
PVDF-TrFE	orthorhombic	hexagonal
i-PB1	trigonal	tetragonal
i-PP	monoclinic	meso

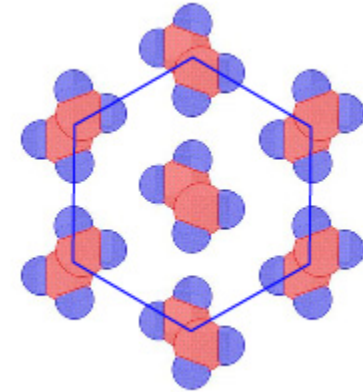
準安定相(例:PE 高温高压下)



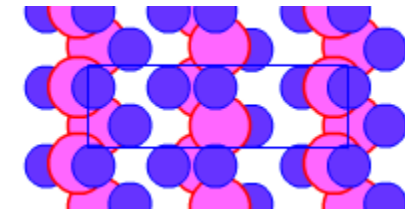
Orthorhombic



Hexagonal



Sliding Diffusion



Wunderlich, Arakawa:

J Polym Sci **A2** ('64) 3697

Bassett, Block, Piermarini:

J Appl Phys **45** ('74) 4146

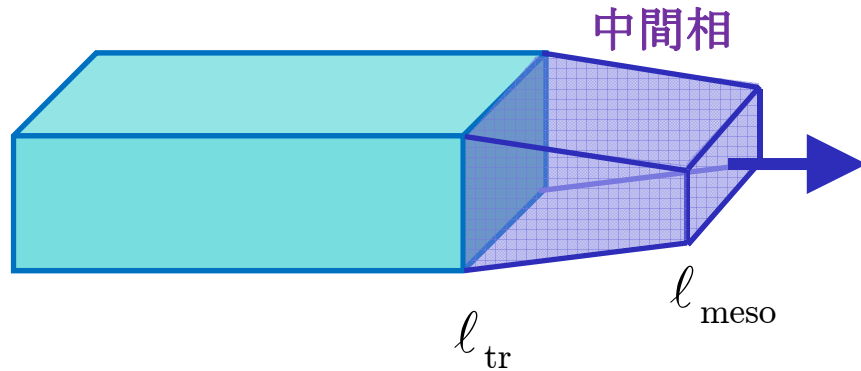
Hikosaka: Polymer **28** ('87) 1257

Rastogi, Hikosaka, Kawabata, Keller:

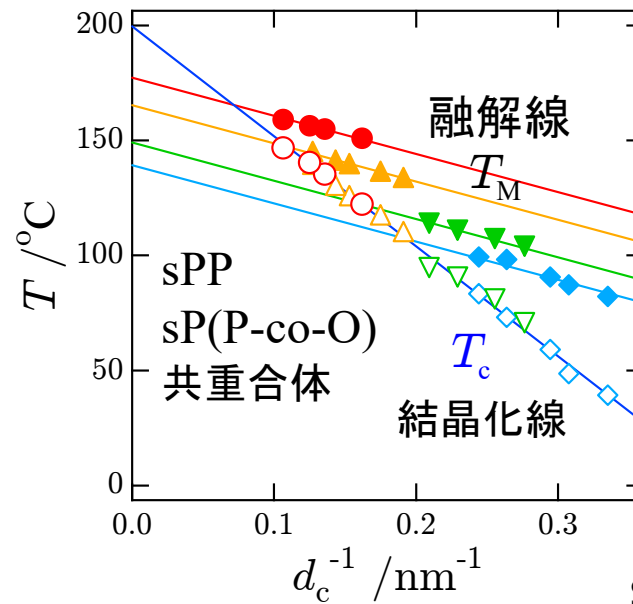
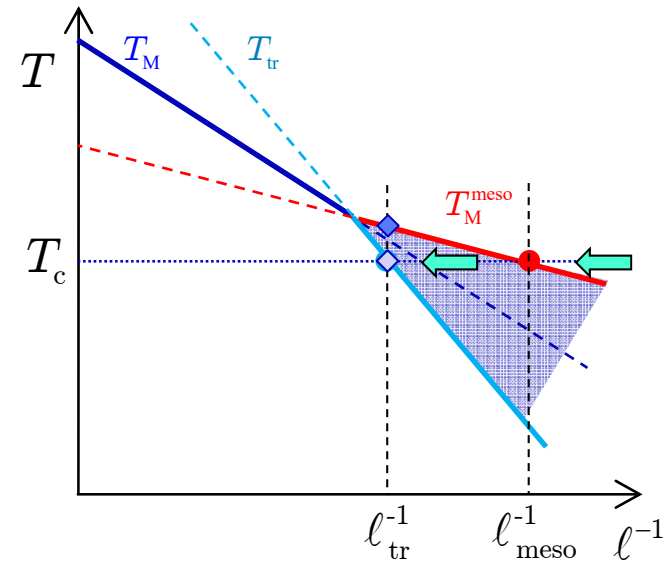
Macromolecules **24** ('91) 6384

高压(PE伸びきり鎖結晶)

成長先端の準安定相?



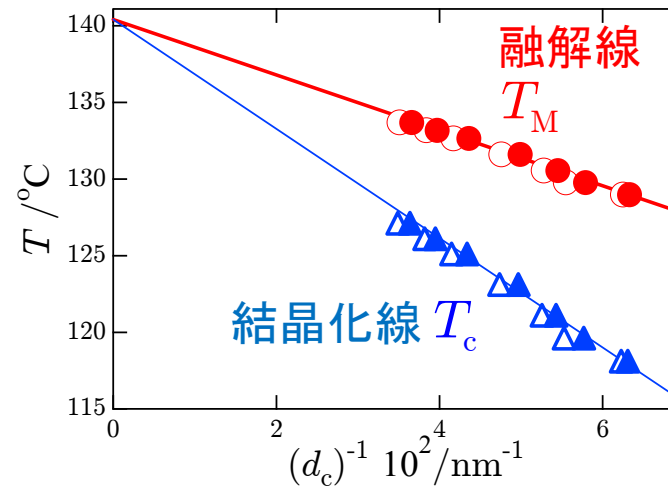
Keller et al : J Mater Sci 29 (1994) 2579



Strobl : Eur. Phys. J. E3 (2000) 165

融解線と結晶化線

Gibbs-Thomson

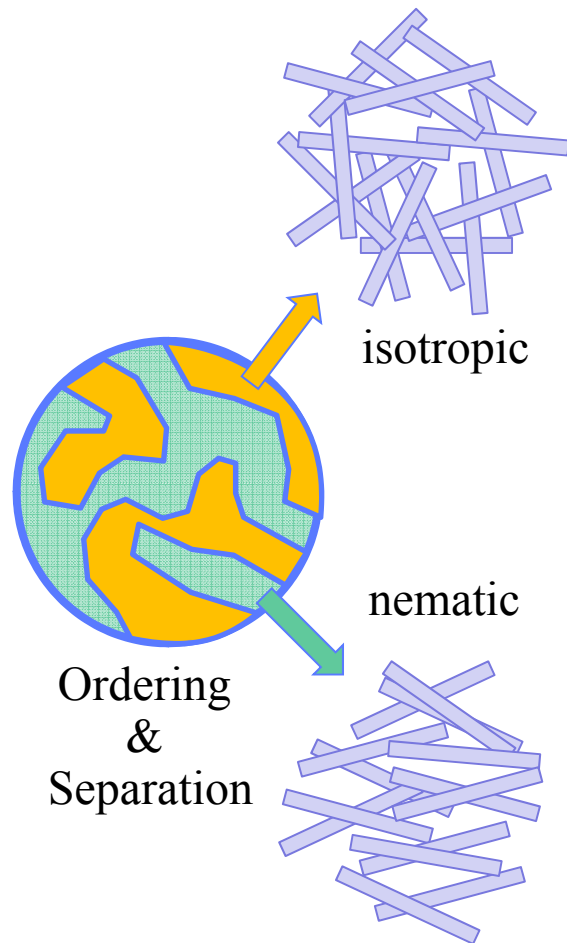


G-Tプロット (融解線)

$$T_M = T_M^0 - \frac{C}{d_c}, \quad C = \frac{2\sigma_e T_M^0}{\Delta h_f}$$

結晶化線 $T_c = T_M^0 - \frac{1}{\gamma} \frac{C}{d_c}$

準安定相の役割



「1次核形成」前の誘導期

密度とコンフォメーションのカップリング

過冷却液体

→ ミクロ相分離(準安定)

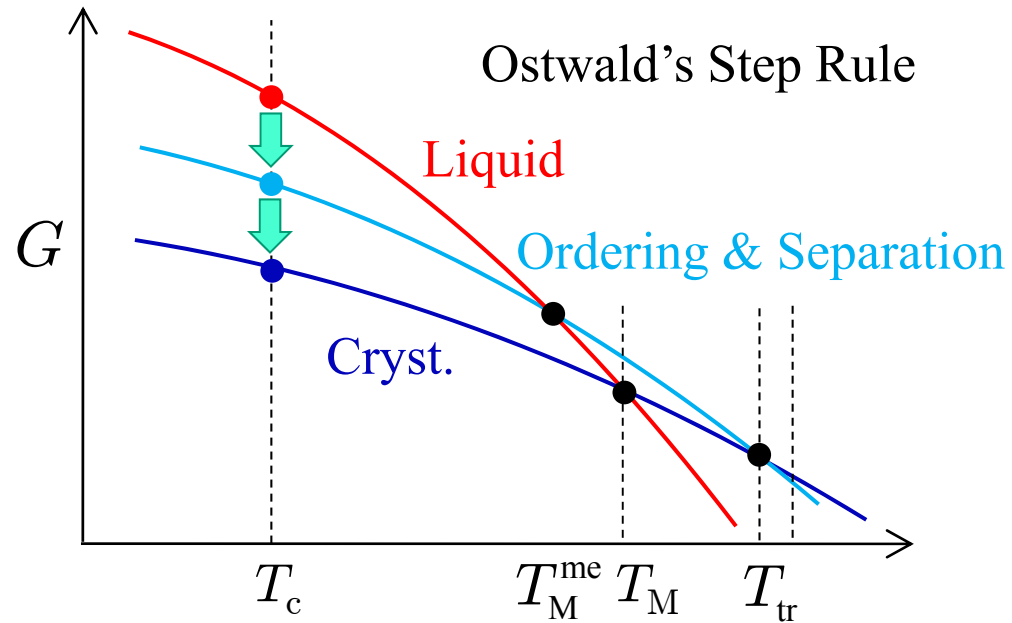
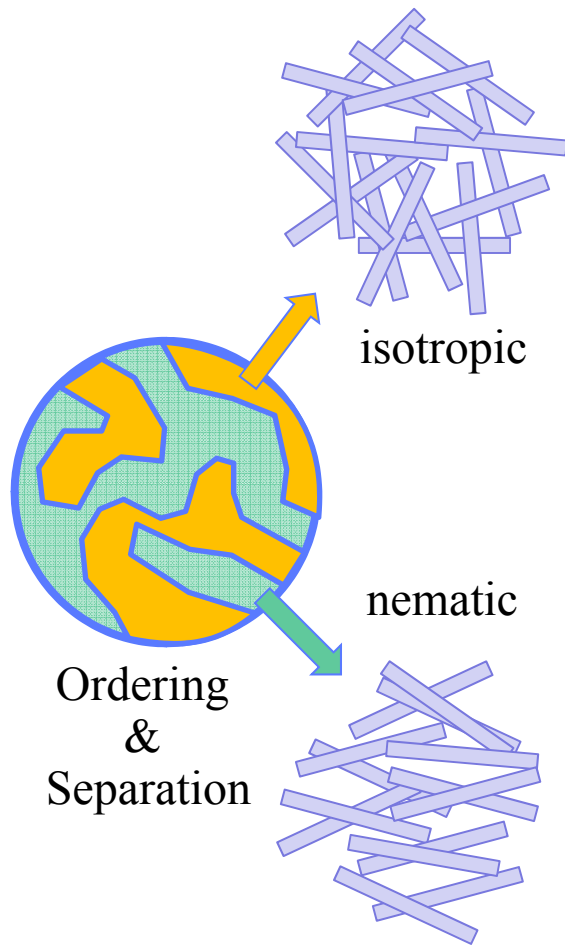
→ 1次核形成の可能性

光散乱

X線小角散乱

X線広角回折

準安定相の役割



$$S^{\text{cryst}} < S^{\text{meso}} < S^{\text{melt}}$$

$$\sigma^{\text{cryst-melt}} > \sigma^{\text{meso-melt}}$$

$$G^{\text{cryst-melt}} < G^{\text{meso-melt}}$$

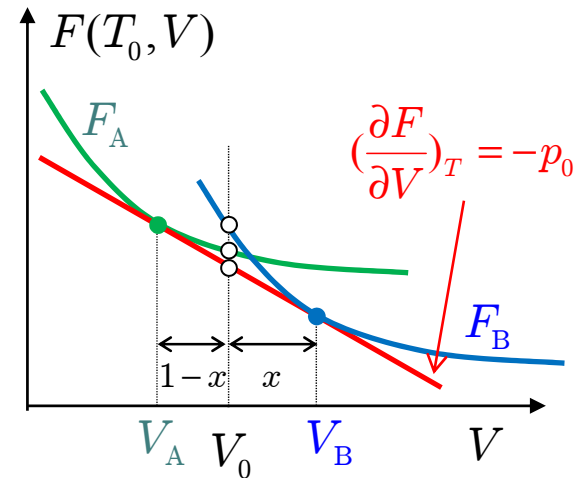
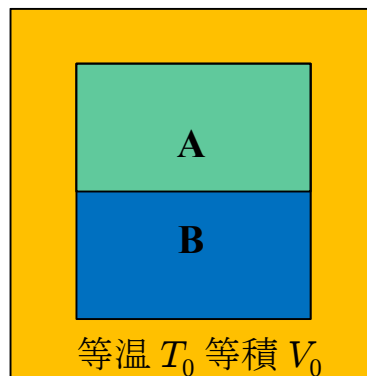
PE	orthorhombic	hexagonal
PVDF-TrFE	orthorhombic	hexagonal
i-PB1	trigonal	tetragonal
i-PP	monoclinic	meso

相分離 1 : 2相共存

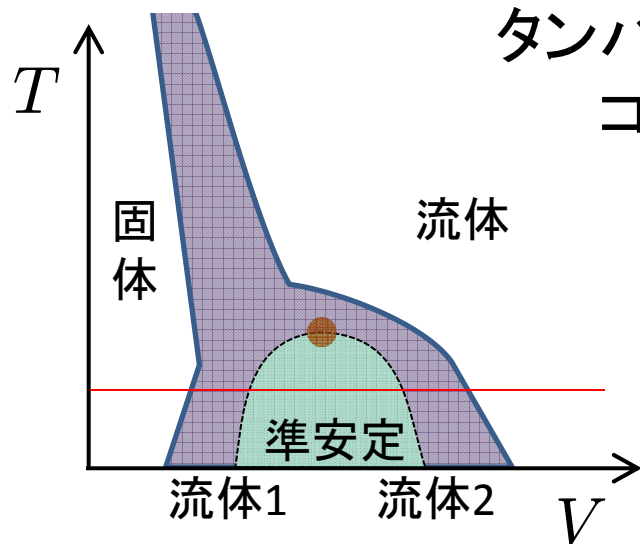
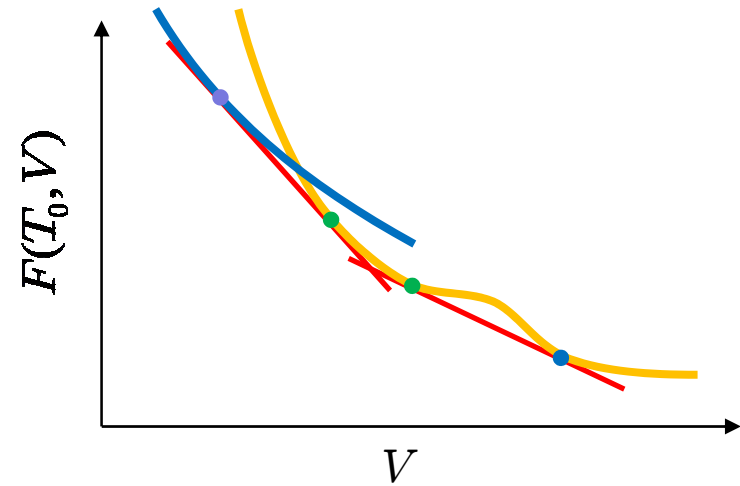
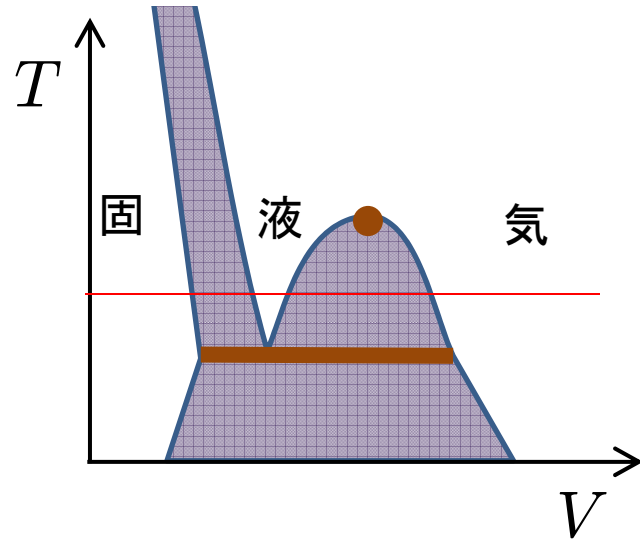
相転移点 (p_0, T_0) で、一定体積 V_0 ($V_A < V_0 < V_B$) 下での A-B 2相の共存

$$\mu_A(T_0, p_0) = \mu_B(T_0, p_0) \quad \mu = f + p_0 v \quad p_0 = -\frac{f_A - f_B}{v_A - v_B} = -\frac{\partial f_A}{\partial V} = -\frac{\partial f_B}{\partial V}$$

$$F(T, V) = U - TS \quad dF = S dT - p dV \quad \left(\frac{\partial F}{\partial V}\right)_T = -p < 0 \quad \left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\frac{\partial p}{\partial V} > 0$$



相分離3: 気相-液相-固相



タンパク質の結晶
コロイド系

