水と高分子材料の分子動力学計算による研究

- 膨潤と脆化の分子機構 -

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ポリマーの力学特性に及ぼす水の影響

ポリエステル、ポリアミド、・・・・

・環境と平衡にある膨潤状態での使用が前提

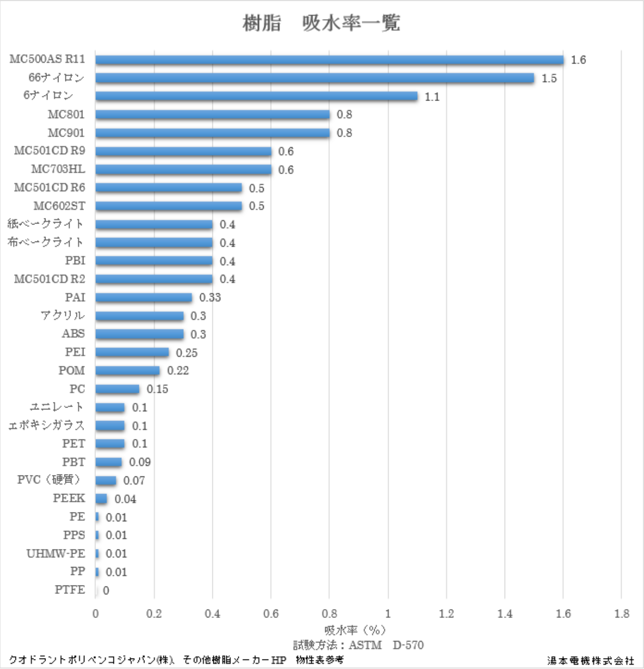
漁具、繊維、構造材料、・・・・

0.5 ~ 2 wt%

力学特性は、長期的に劣化、脆化
水の存在により加速

Possible Origins of Embrittlement

1. Crystallization
2. Hydrolysis
3. Disentanglement
4. Hydrogen bonds
5. Physical aging = densification



https://www.yumoto.jp/material-onepoint/plastic-the-water-absorbent

水による劣化の加速

・広く樹脂、繊維に共通な劣化因子として本質的に重要
・にもかかわらず、詳細は不明。分子機構の解明が必要

膨潤と脆化の分子機構

１．PLAの水による膨潤
２．脆化の分子機構

PLA中の水の自由エネルギー解析

Widom equation and test particle insertion method

Widom equation in its original form for chemical potential of pure liquid

NVT

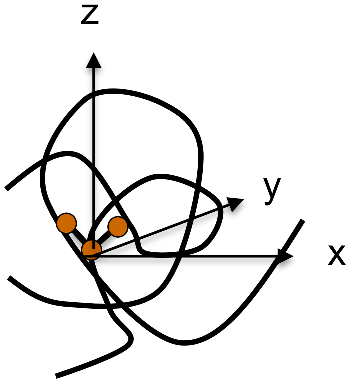
Widom (1963)

$$\begin{aligned}\mu^{\mathrm{ex}} &= \left(\frac{\partial F^{\mathrm{ex}}}{\partial N}\right)_{V,T} \\ &= F^{\mathrm{ex}}(N+1,V,T) - F^{\mathrm{ex}}(N,V,T) \\ &= kT\ln\frac{VZ_N(V,T)}{Z_{N+1}(V,T)} \\ &= -kT\ln\left\langle \exp\left\{-\beta v^{N+1}(\boldsymbol{r}^N)\right\}\right\rangle_N\end{aligned}$$

N→∞ : rigorous
N=N : free energy of transfer from vacuum

Center of mass of the (N+1)th particle is fixed at (0,0,0).

Free energy of transfer of a solute with rotational degrees of freedom **Ω** from vacuum to inside of the system of interest



$$\Delta G = -kT\ln\left\langle \exp\left\{-\beta V(\boldsymbol{r}_0,\boldsymbol{\Omega}_0;\boldsymbol{R}^N)\right\}\right\rangle_{\boldsymbol{R}^N}$$

1. canonical importance sampling

Adams (1974)

$$\left\langle \exp\left\{-\beta V(\boldsymbol{r},\boldsymbol{\Omega};\boldsymbol{R}^N)\right\}\right\rangle_{\boldsymbol{r},\boldsymbol{\Omega};\boldsymbol{R}^N}$$

: random sampling (inefficient)

$$\Downarrow$$

$$\left\langle \iint 1\cdot\exp\left\{-\beta V(\boldsymbol{r},\boldsymbol{\Omega};\boldsymbol{R}^N)\right\}d\boldsymbol{r}\,d\boldsymbol{\Omega}\right\rangle_{\boldsymbol{R}^N}$$

: canonical ensemble

Efficient and rigorous sampling

2. Multi-particle simultaneous sampling

Interactions

$$V(\boldsymbol{R}^N,\boldsymbol{r}^n,\boldsymbol{\Omega}^n)=V_N(\boldsymbol{R}^N)+V_n(\boldsymbol{R}^N,\boldsymbol{r}^n,\boldsymbol{\Omega}^n)$$

$$V_N(\boldsymbol{R}^N)=\sum_{I>J}^{N}\sum_{J}^{N}V_{IJ}(\boldsymbol{R}_I,\boldsymbol{R}_J)$$: environment-environment interaction

$$V_n(\boldsymbol{R}^N,\boldsymbol{r}^n,\boldsymbol{\Omega}^n)=\sum_{i}^{n}\sum_{\alpha_i}^{m_i}\sum_{J}^{N}V_{\alpha_i J}(\boldsymbol{r}_{\alpha_i},\boldsymbol{R}_J)$$: solute-environment interaction

MD

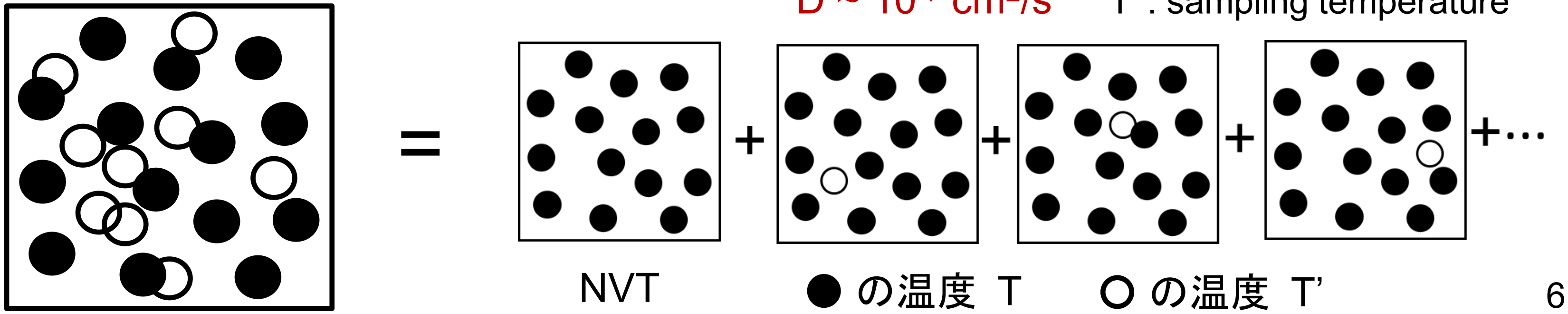
$$\ddot{\boldsymbol{R}}_I=\frac{\boldsymbol{F}_I}{M_I}\qquad \boldsymbol{F}_I=-\frac{dV_N(\boldsymbol{R}^N)}{d\boldsymbol{R}_I}$$

$$\ddot{\boldsymbol{r}}_{\alpha_i}=\frac{\boldsymbol{F}_{\alpha_i}}{m_{\alpha_i}}\qquad \boldsymbol{F}_{\alpha_i}=-\frac{dV_n(\boldsymbol{R}^N,\boldsymbol{r}^n,\boldsymbol{\Omega}^n)}{d\boldsymbol{r}_{\alpha_i}}$$

$\boldsymbol{r}_{\alpha_i}$: atom α of solute molecule i
$\boldsymbol{R}_I$: environmental molecule I
n : number of solute molecules
m_i: number of atoms of the solute molecule i
N : number of atoms of the environmental molecules

T : temperature of interest
T' : sampling temperature

D ~ 10^{-7} cm^2/s



● の温度 T ○ の温度 T'

Efficient and rigorous sampling

3. High temperature sampling : single-particle distribution

$$\rho(\boldsymbol{r}) \propto \left\langle \exp\left(-\frac{V(\boldsymbol{r};\boldsymbol{R}^N,\boldsymbol{\Omega})}{kT'}\right)\right\rangle_{\boldsymbol{R}^N,\boldsymbol{\Omega}}$$

$$\Delta F(\boldsymbol{r}) = -kT' \ln\frac{\rho(\boldsymbol{r})}{\rho(\boldsymbol{r}^0)} + \underline{\Delta F(\boldsymbol{r}^0)}$$

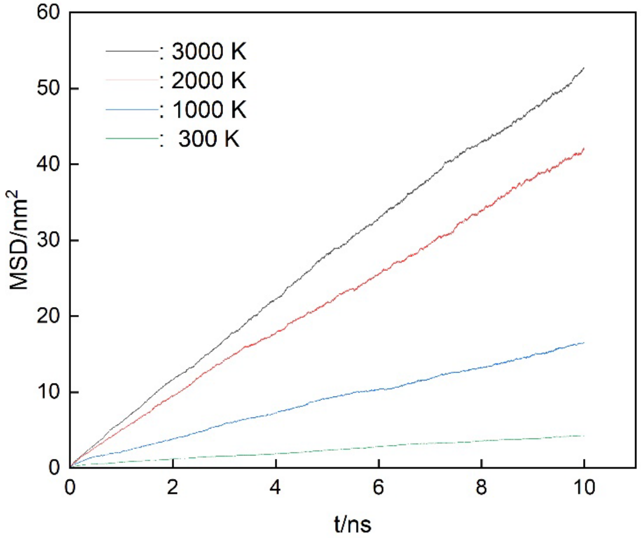
Free energy of transfer
from vacuum to a particular position $\boldsymbol{r}^0$

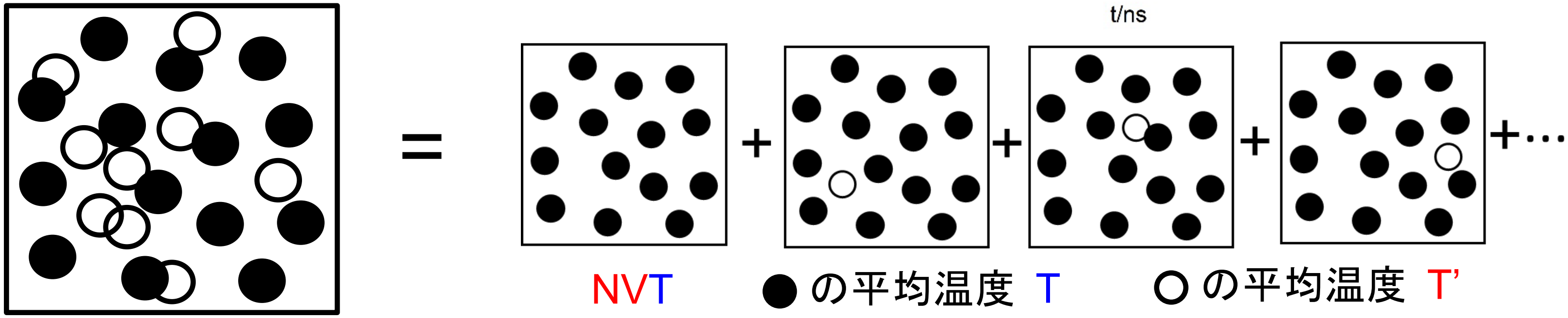
$$\Delta U(\boldsymbol{r}) \approx \left\langle V(\boldsymbol{r};\boldsymbol{R}^N,\boldsymbol{\Omega})\right\rangle_{\boldsymbol{R}^N,\boldsymbol{\Omega}}$$

$$\Delta S(\boldsymbol{r}) = \frac{-\Delta F(\boldsymbol{r}) + \Delta U(\boldsymbol{r})}{T}$$

T : temperature of interest

T’ : sampling temperature





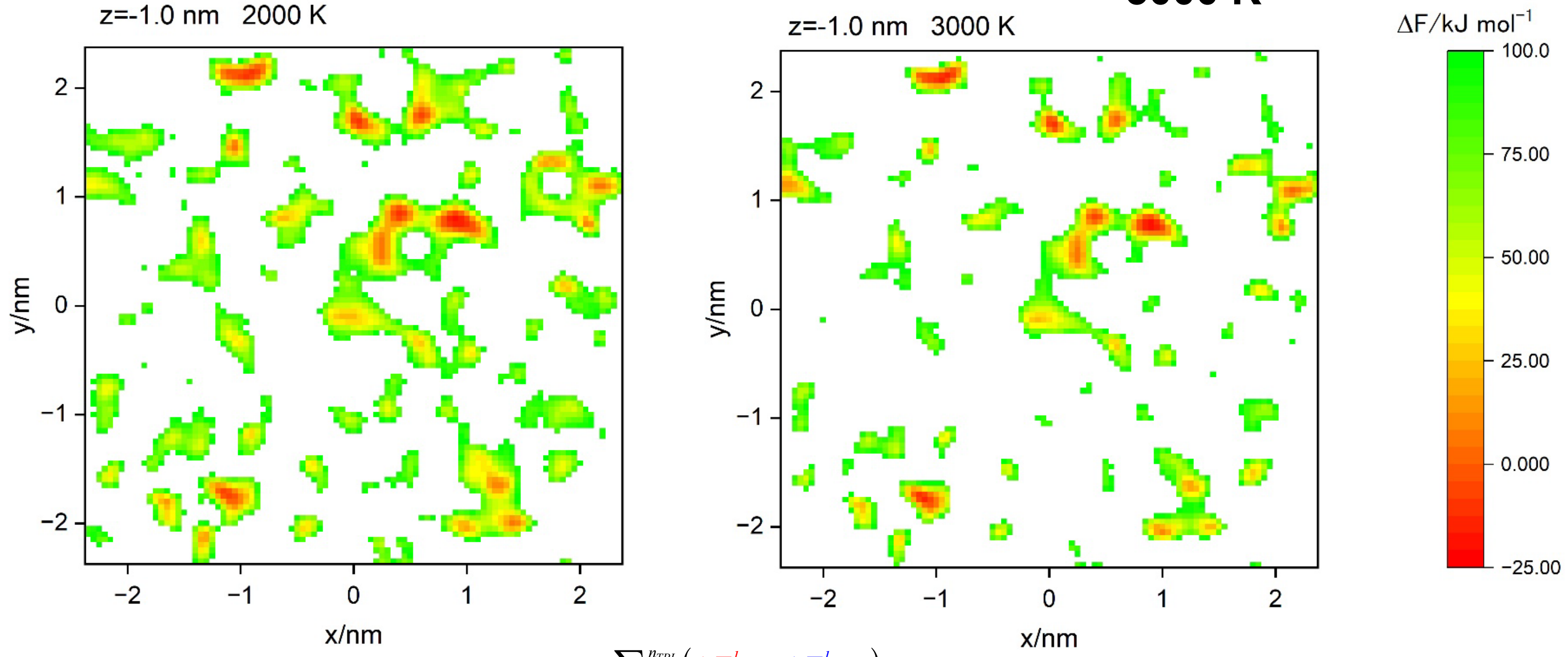
NVT ● の平均温度 T ○ の平均温度 T’

3D map

300 KのPLA中の水の膨潤

サンプリング温度　2000 K

3000 K



$$\Delta F_{g\to p}(i,j,k)=\frac{\sum_{l=1}^{n_{TPI}}\left(\Delta F_{TPI}^{l}+\Delta F_{Widom}^{l}\right)}{n_{TPI}}$$

100×100×100の3D精密地図

ΔFの平均値

2000 K　　-17.72 kJ/mol

(3000 K　　-20.68 kJ/mol)

expl.　　-13.7 kJ/mol
(溶解度)

気相分子密度を1200倍に濃縮 (低密度極限)

実際は
240倍

$$\left\langle \exp\left\{-\beta\Delta F_{g\to p}\right\}\right\rangle=\frac{\sum_{i}\sum_{j}\sum_{k}\exp\left\{-\beta\Delta F_{g\to p}(i,j,k)\right\}}{n_{mesh}}$$

$$\left\langle \Delta F_{g\to p}\right\rangle=-kT\ln\left\langle \exp\left\{-\beta\Delta F_{g\to p}\right\}\right\rangle$$

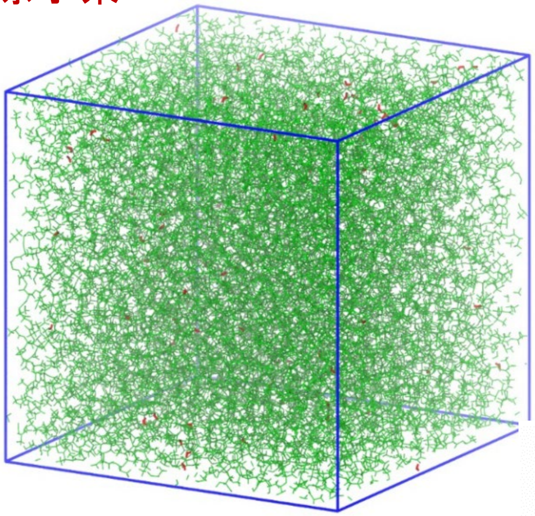
飽和蒸気圧では、MDセル中に
気相で0.09個、高分子相で22個

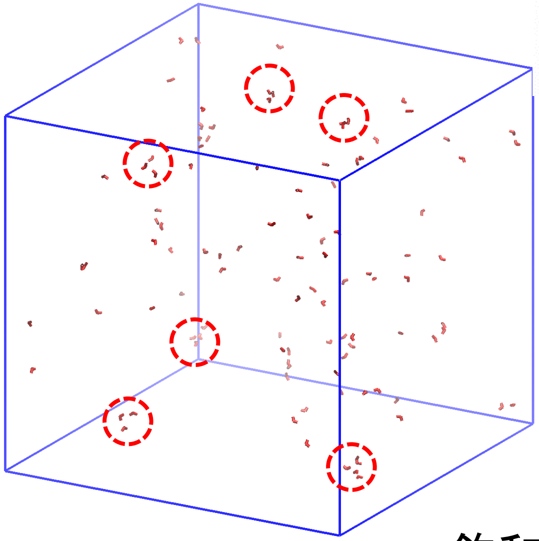
比較的高密度

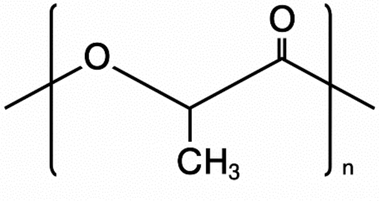
PLAの膨潤

水

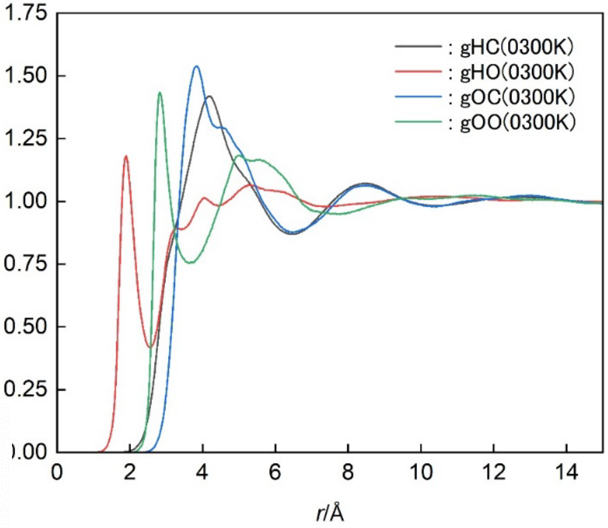
200万原子系

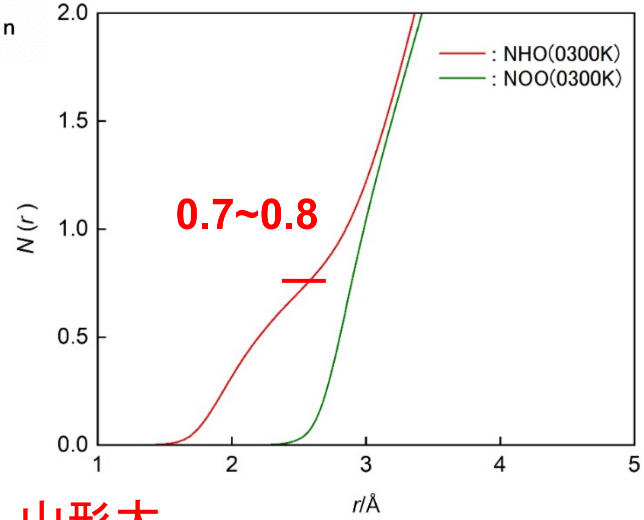






water-polymer RDF





飽和濃度　0.5wt%　山形大

膨潤と脆化の分子機構

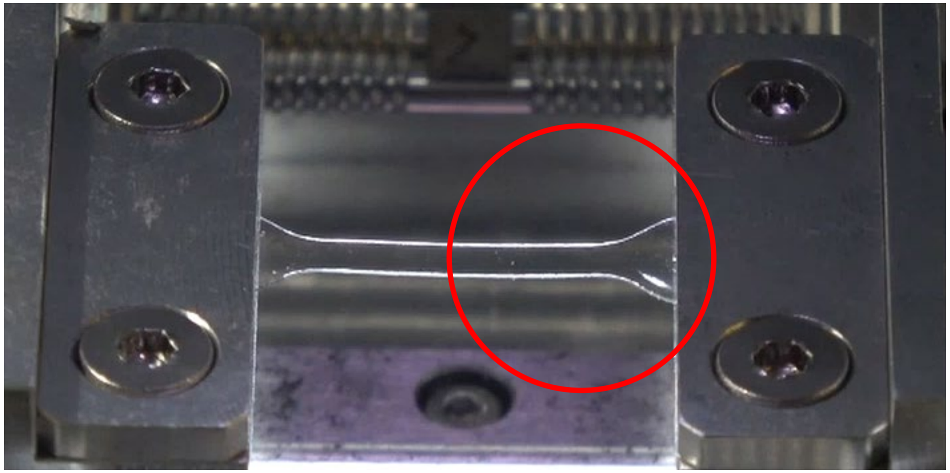
１． PLA中の膨潤
２． 脆化の分子機構

膨潤したPLAが示す力学的性質の変化と
その分子機構

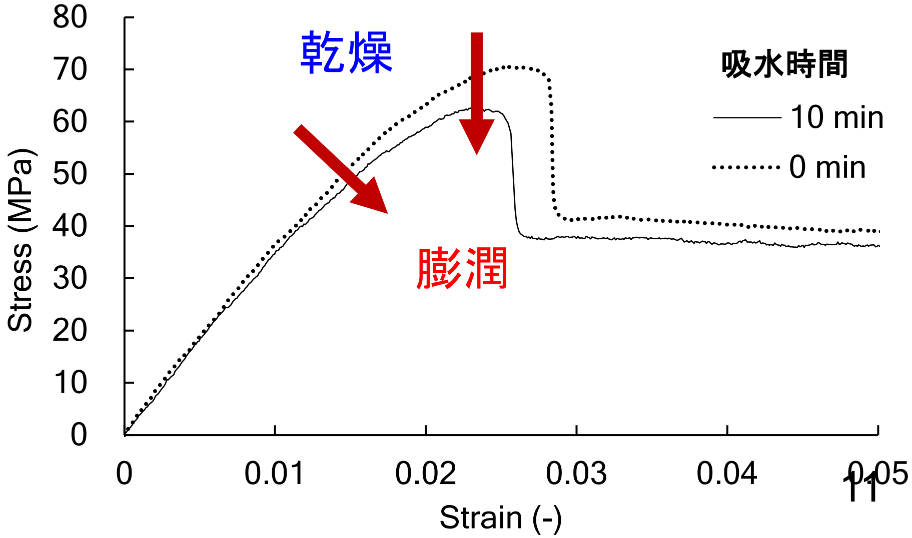
膨潤したPLAの短時間挙動

山形大 実験

膨潤直後（10分後）



引張速度1 mm/min
画像16倍速



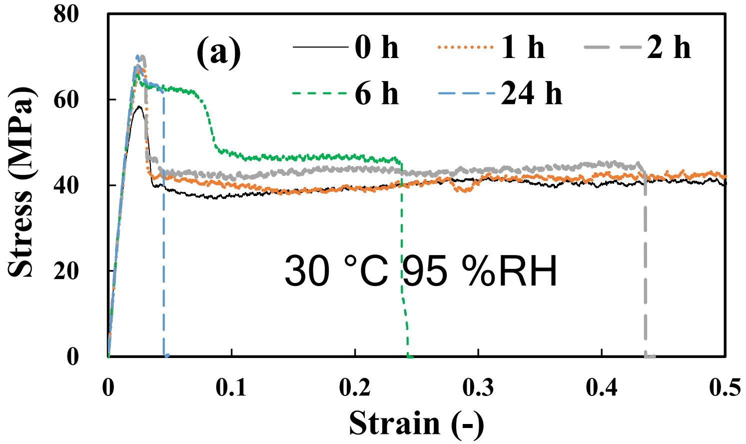
弾性率、降伏応力ともに低下

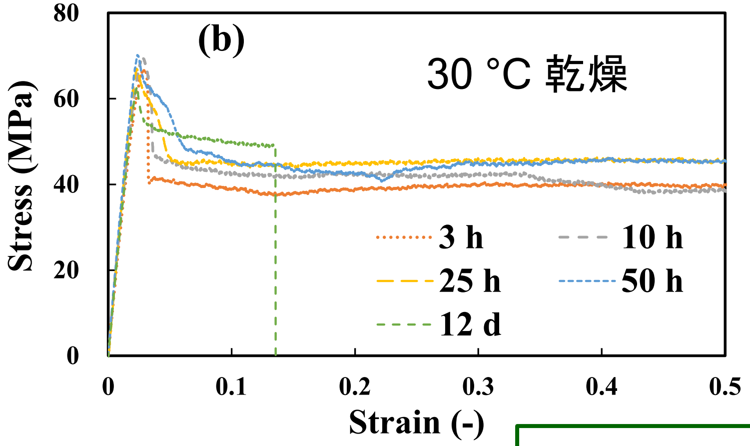
3970 MPa → 3550 MPa

70.7 MPa → 62.6 MPa

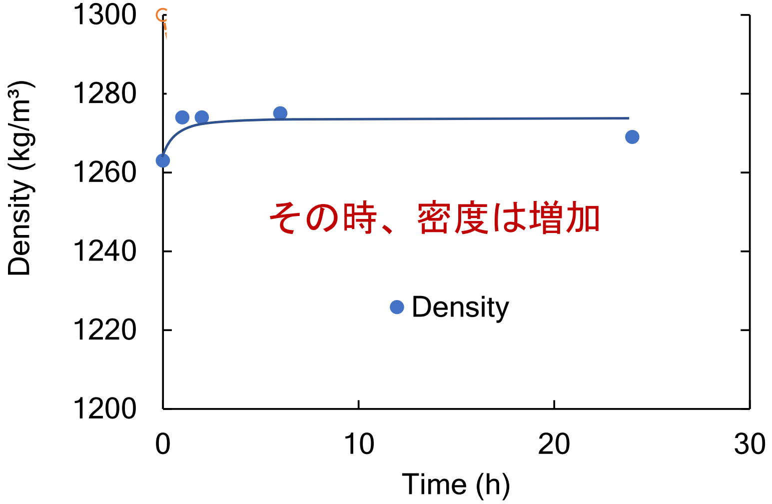
可塑化の方向

膨潤したPLAの長時間挙動





山形大　小林先生、伊藤（浩）先生



その時、密度は増加

膨潤により、時間とともに
- 弾性率、降伏応力が増加
- 延性から脆性に転移
- 時間オーダーの変化
- 水の含有率が低いほど、速度は遅い

乾燥状態だと週オーダーで脆化

脆化の方向

Possible Origins of Embrittlement

- ✕ 1. Crystallization　X線で観察されない
- ✕ 2. Hydrolysis　1日だと百万本の結合に1本
- ✕ 3. Disentanglement　考えにくい
- ✕ 4. Hydrogen bonds　考えにくい
- 5. Physical aging = densification

・老化による脆化

短時間挙動と長時間挙動が逆の方向

矛盾なく説明できる分子機構はどのようなものか

A hypothesis (1)

two effects of water on PLA

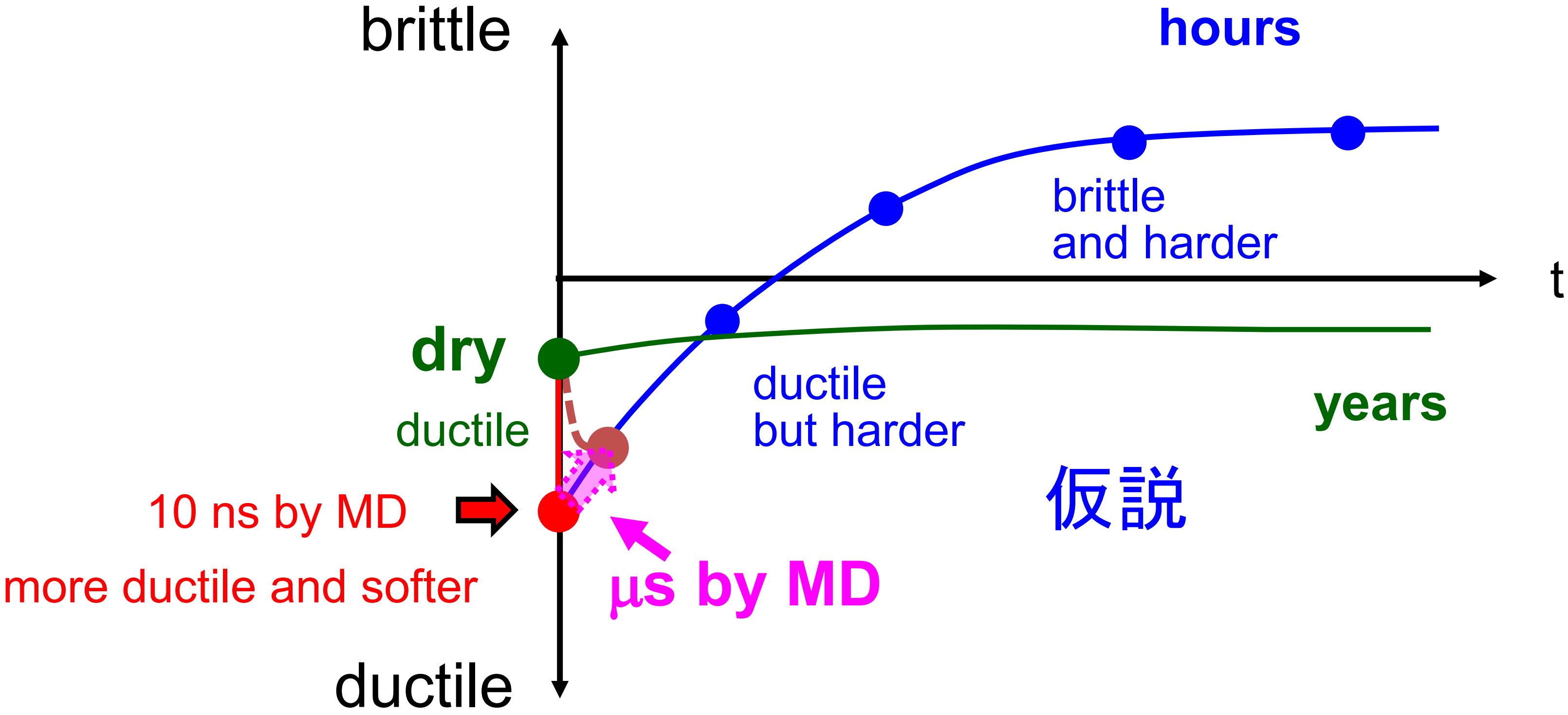
1. 延伸方向に沿った自由エネルギー障壁の低下

   plasticizer, 溶媒、潤滑、……

   応答時間不要、水分子浸透の直後から機能

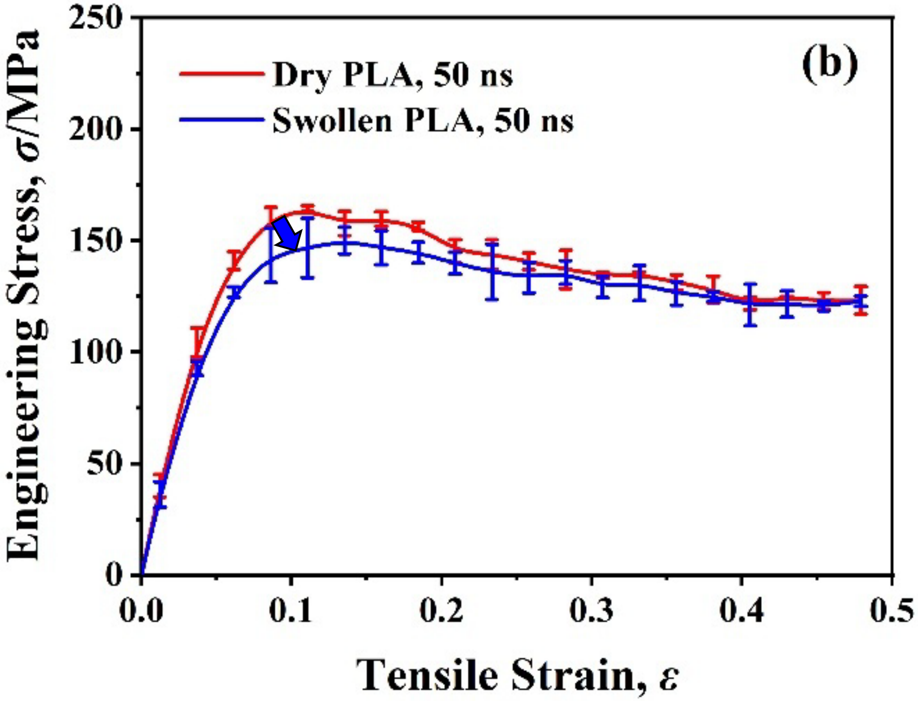
2. 安定構造に向けた、構造変化速度の加速

   高分子構造が変化するための応答時間が必要



MD計算

SS curve of swallen PLA



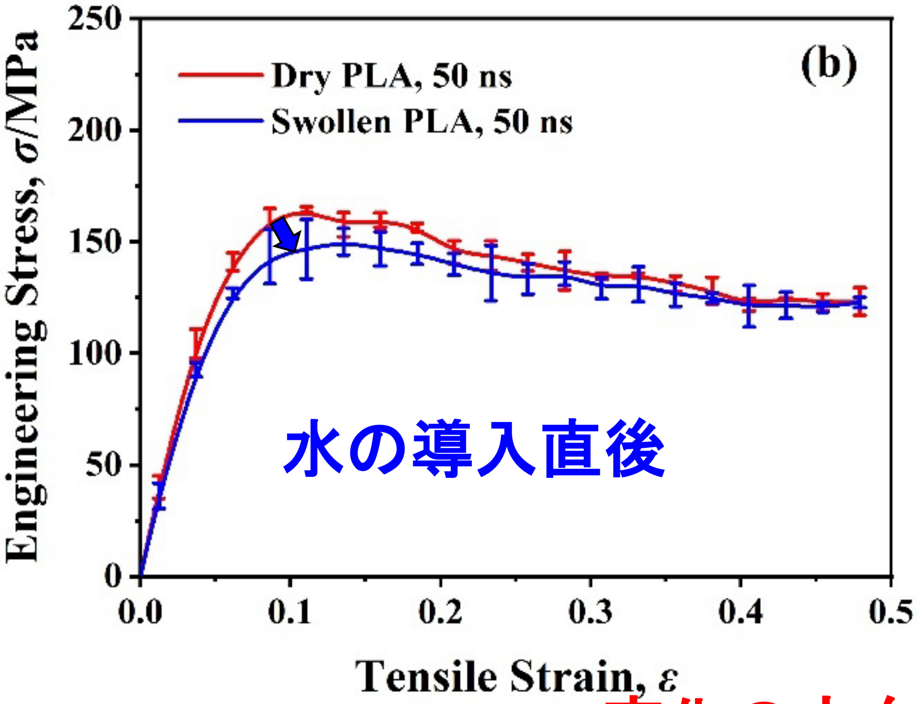
水の導入直後

変化の方向
- 弾性率が小さくなる
- 降伏応力が小さくなる

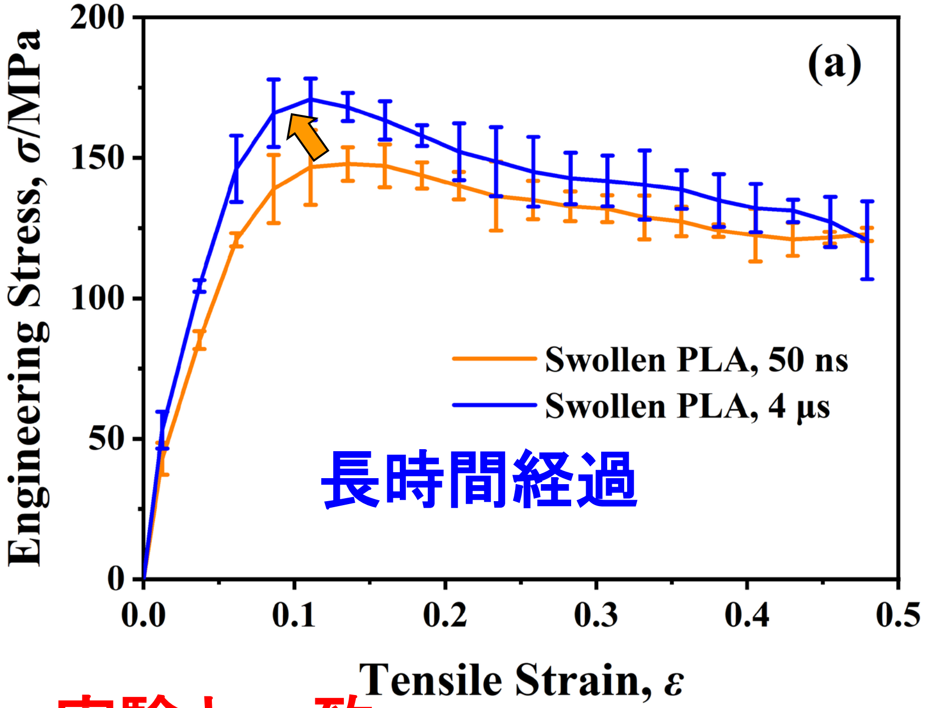
実験と一致

System	PLA, no water (320K)	Swollen PLA (50 ns, 320K)
Young’s modulus (MPa)	2500	2200
Yield stress (MPa)	163	148
Yield strain	0.11	0.12

SS curve of swallen PLA



水の導入直後



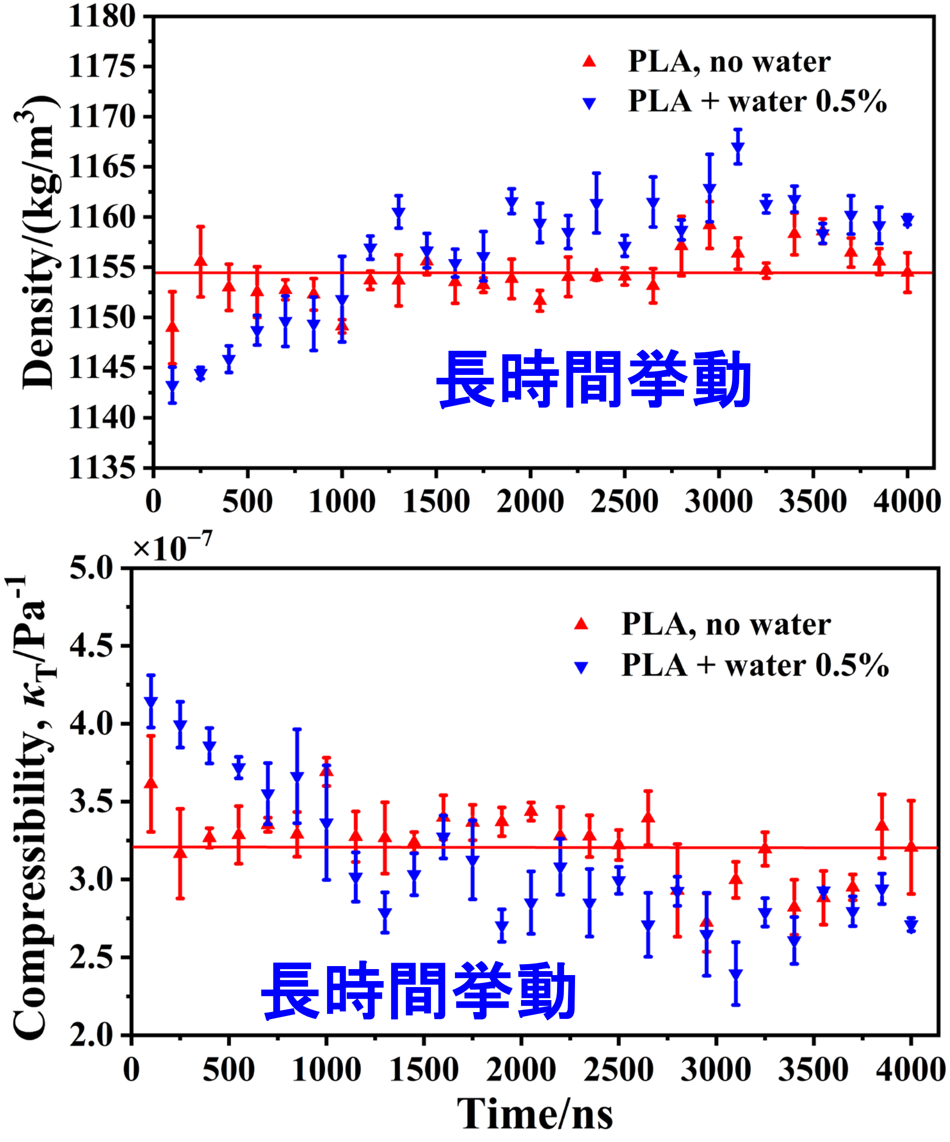
長時間経過

変化の方向　実験と一致

System	PLA, no water (320K)	Swollen PLA (50 ns, 320K)	Swollen PLA (4000 ns, 320K)
Young’s modulus (MPa)	2500	2200	2500
Yield stress (MPa)	163	148	172
Yield strain	0.11	0.12	0.10

Long-time collective properties　計算

ガラス転移点直下の温度で計算、平衡化を加速



密度 → 増加

等温圧縮率 → 減少

硬くなる

実験と一致

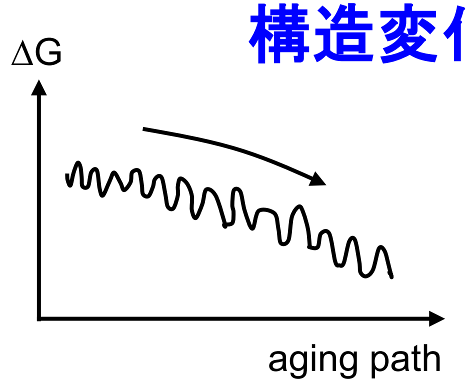
- A quick shrink is observed in Swollen PLA;
- A clear decrease is observed in Isothermal compressibility, i.e., the deviation in volume, indicating the hardening behavior;

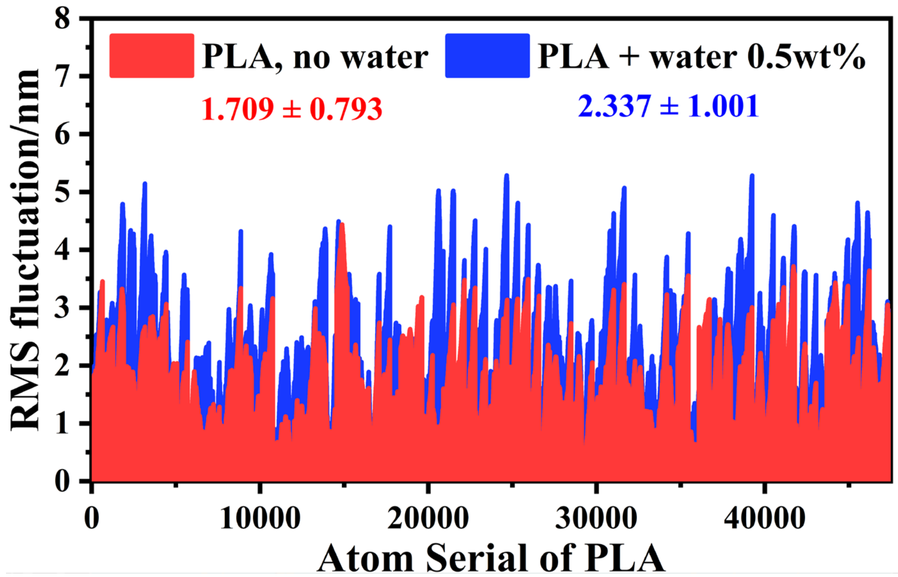
$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{\sigma_V}{kTV} = \frac{\langle V^2\rangle - \langle V\rangle^2}{kT\langle V\rangle}$$

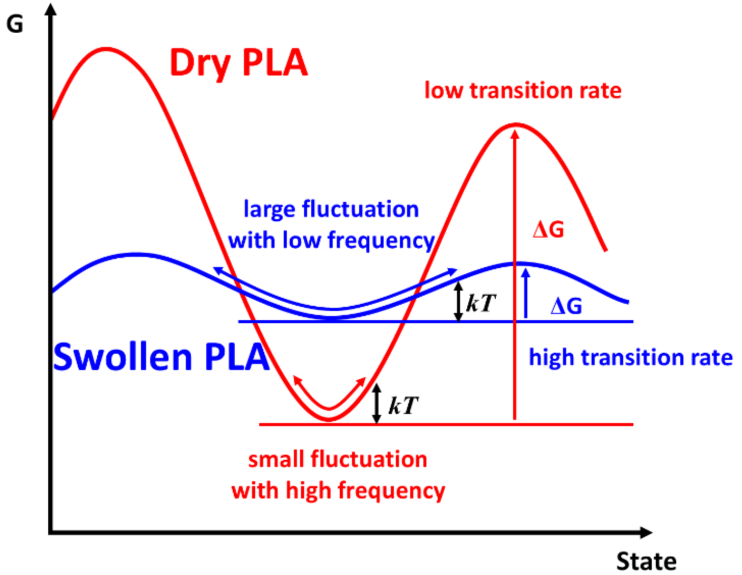
Short-time single-particle properties (1)

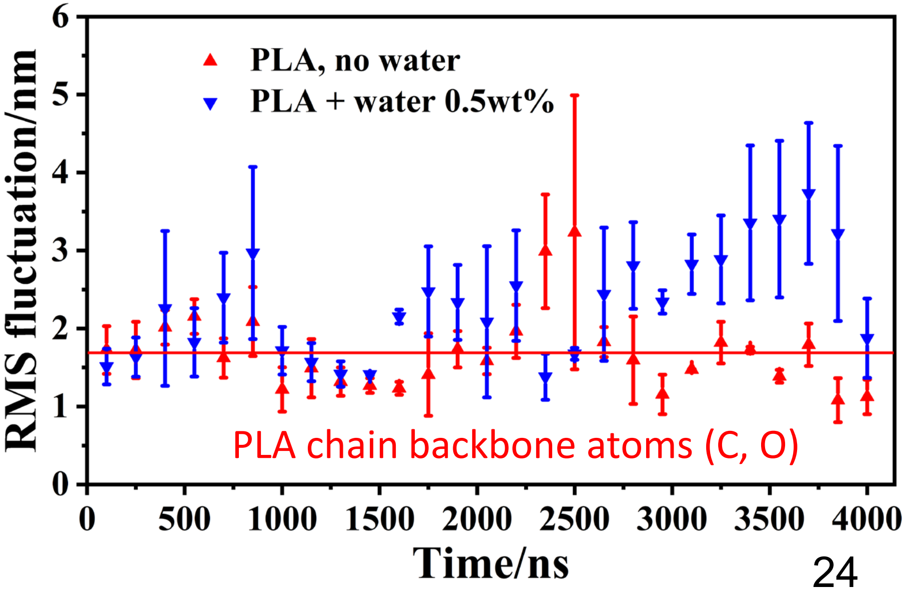
RMSF of the atoms

安定構造へ向けた構造変化のし易さ

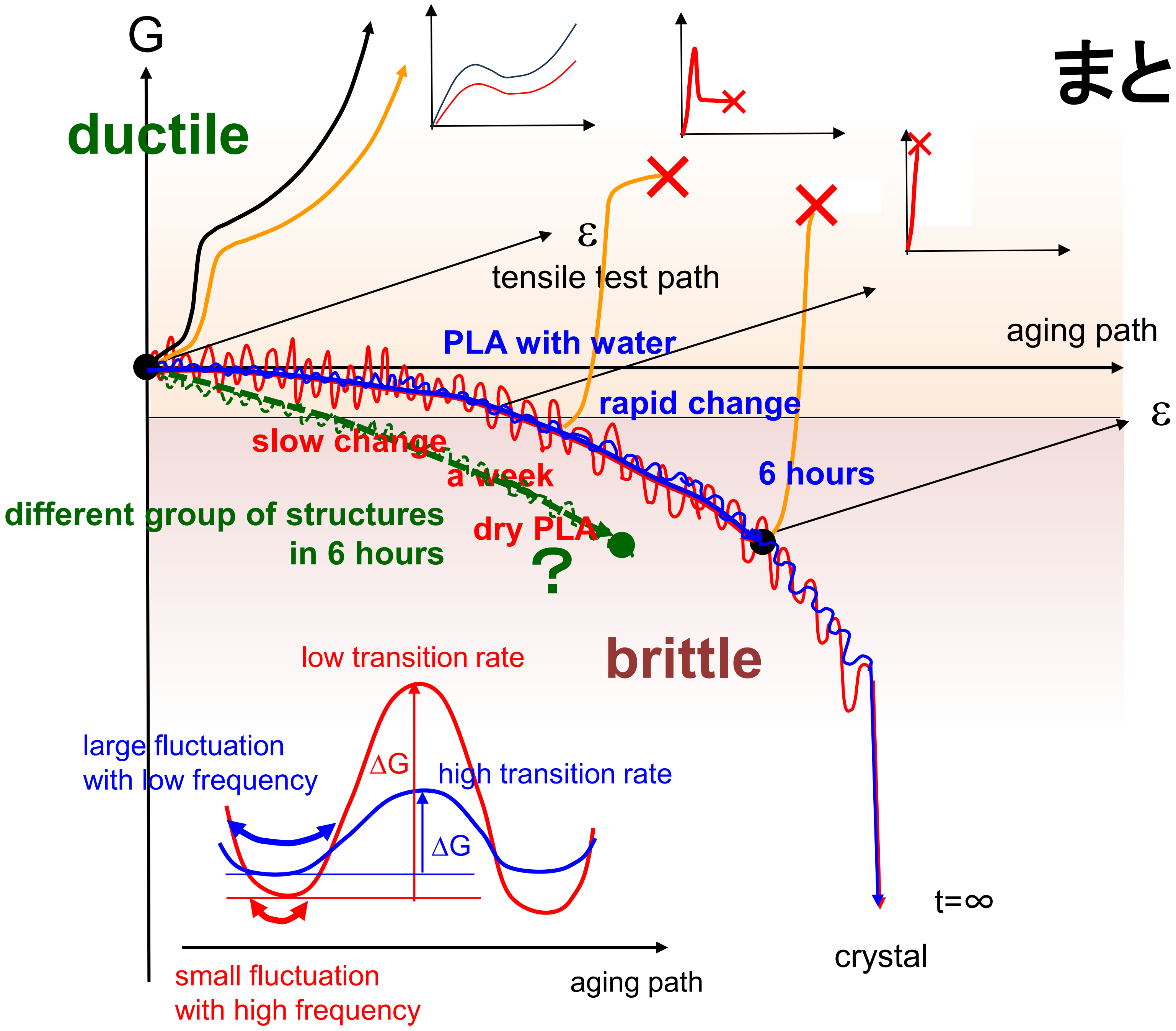








まとめ



G

ductile

ε

tensile test path

aging path

PLA with water

rapid change

ε

slow change

a week

6 hours

different group of structures
in 6 hours

dry PLA

?

brittle

low transition rate

large fluctuation
with low frequency

ΔG

high transition rate

ΔG

t=∞

crystal

small fluctuation
with high frequency

aging path

Thank you!