# Molecular Diffusion under Nanometer Scale Confinement during CMP of Nanoporous Films

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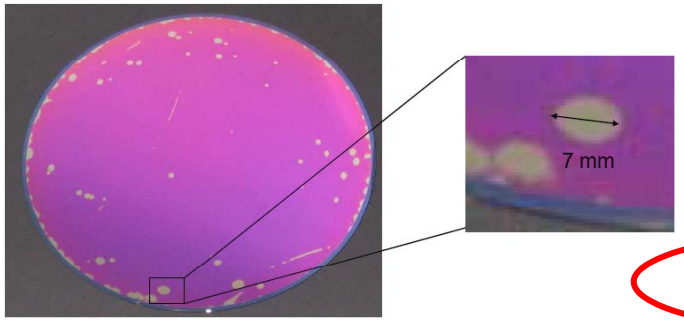
# Road Map for Optimizing CMP of ULK Dielectrics




ULK damage

**CMP Damage**

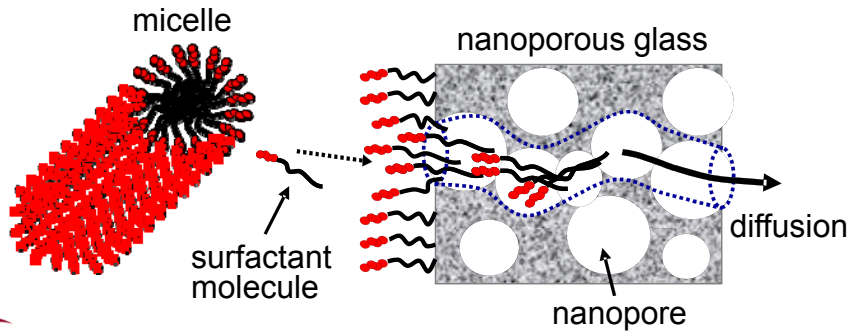
**Defect Evolution**

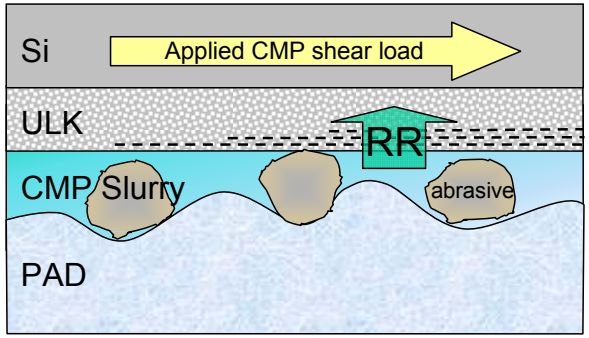
optimizing CMP

**k Increase**

**Diffusion**

**Removal Rate (RR)**

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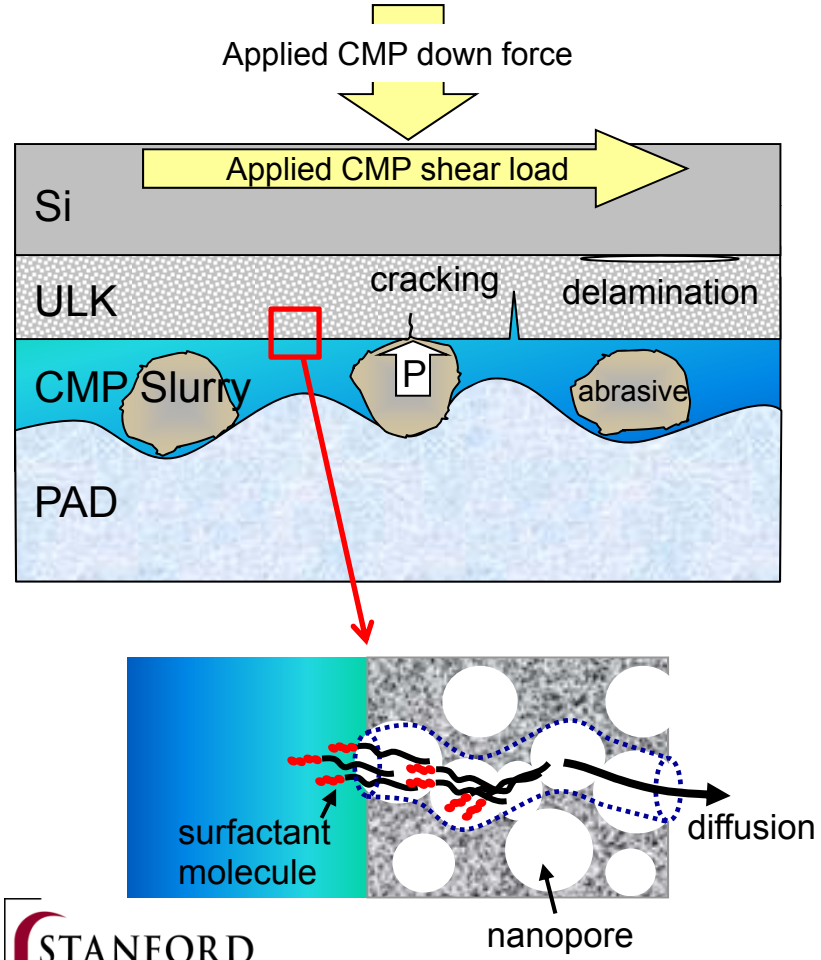
# Diffusion of Solutions into ULK Films

While reducing *k* by increasing porosity, ULK films for Cu interconnects have become more susceptible to diffusion during CMP resulting in increased $k_{eff}$, delamination, cracking, etc.




Fundamental understanding on molecular mobility under nanometer scale confinement is required, because it was found very different from that in the bulk.

## Diffusion Controlling Factors

- Molecular weight, structure and polarity
- Pore size
- Porogen removal
- Temperature

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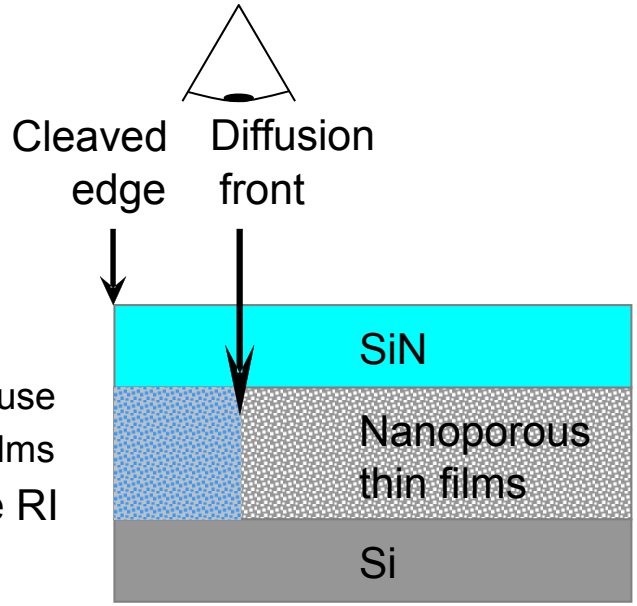
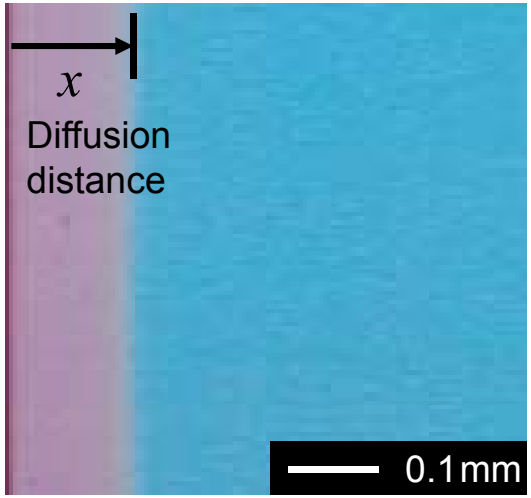
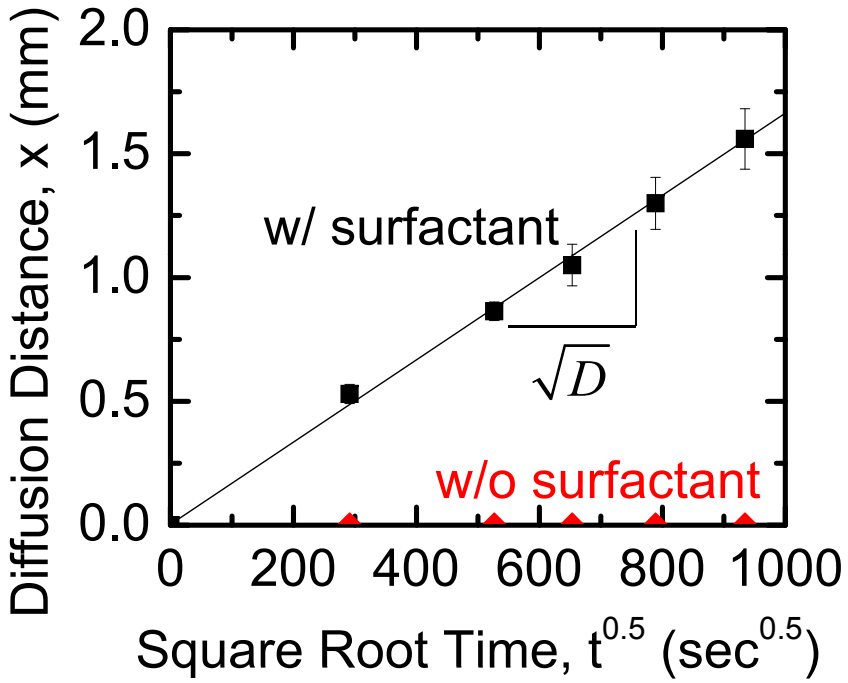
# Lateral Diffusion Technique




Solutions diffuse into porous films → change RI




*Diffusion of 0.1wt% surfactant solution in MSSQ (d ~ 2.1 nm)*




Fickian diffusion: $x = \sqrt{Dt}$

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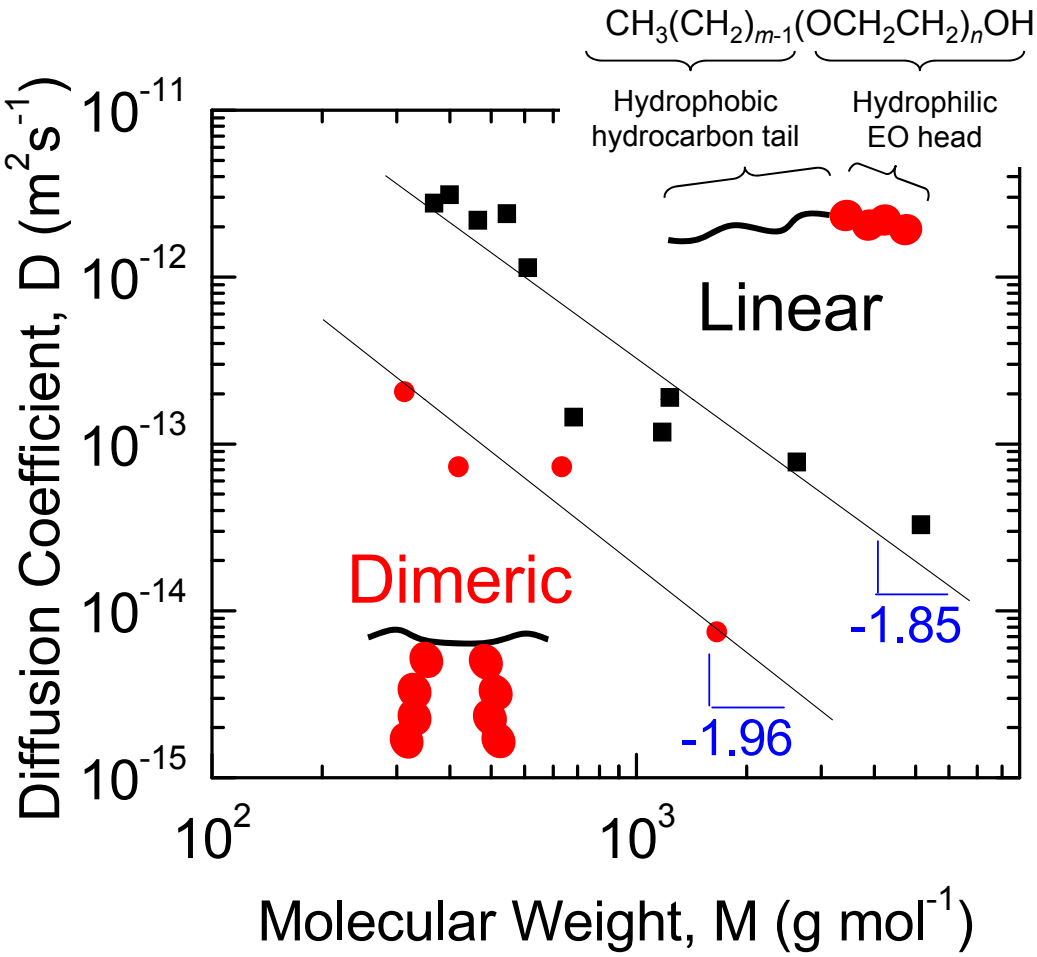
T. Kim, K. Mackie, Q. Zhong, M. Peterson, T. Konno, and R. H. Dauskardt, Nano Letters, 9(6), 2427-2432, 2009.

# Effects of Molecular Weight and Structure




Increasing *M* and branch #

↓

Decreasing *D*

*Diffusion of 0.1wt% surfactant solution in MSSQ (d ~ 2.1 nm)*

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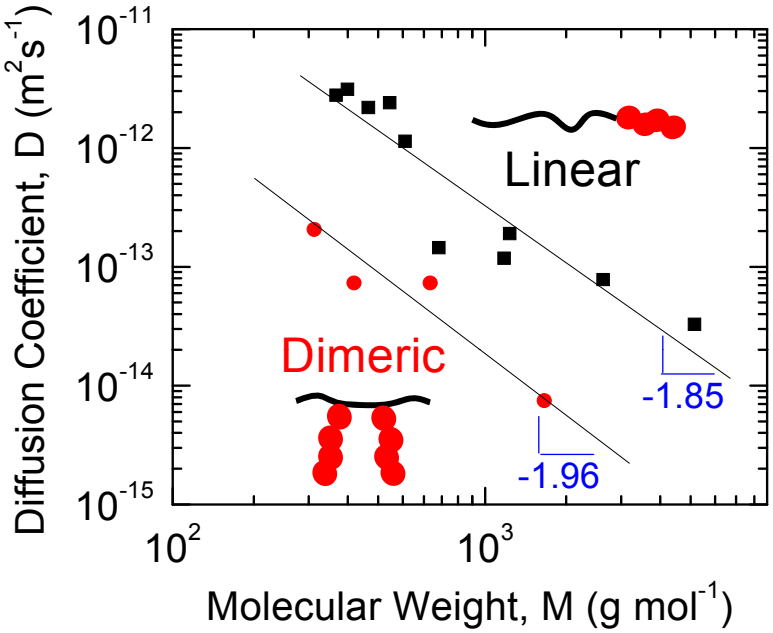
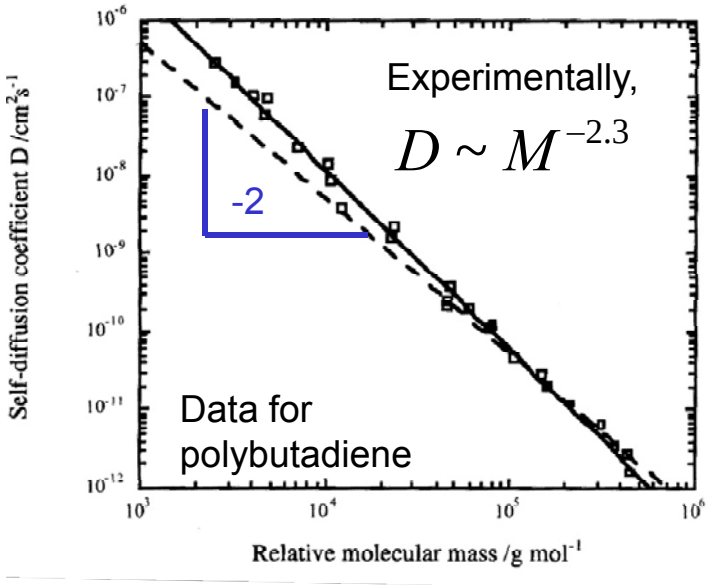
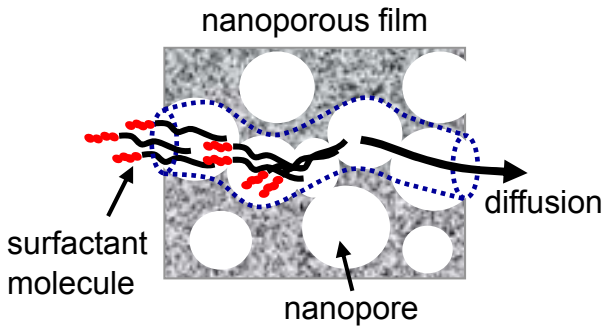
# Molecular Reptation under Nanoconfinement

$$D \sim M^{-\alpha}$$ α = 2 polymer reptation theory

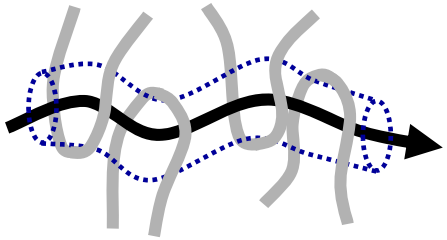



Jones, *Soft Condensed Matter*, p. 92, 2002




Static tube by
Interconnected nanopores



Dynamic tube by
polymer entanglement

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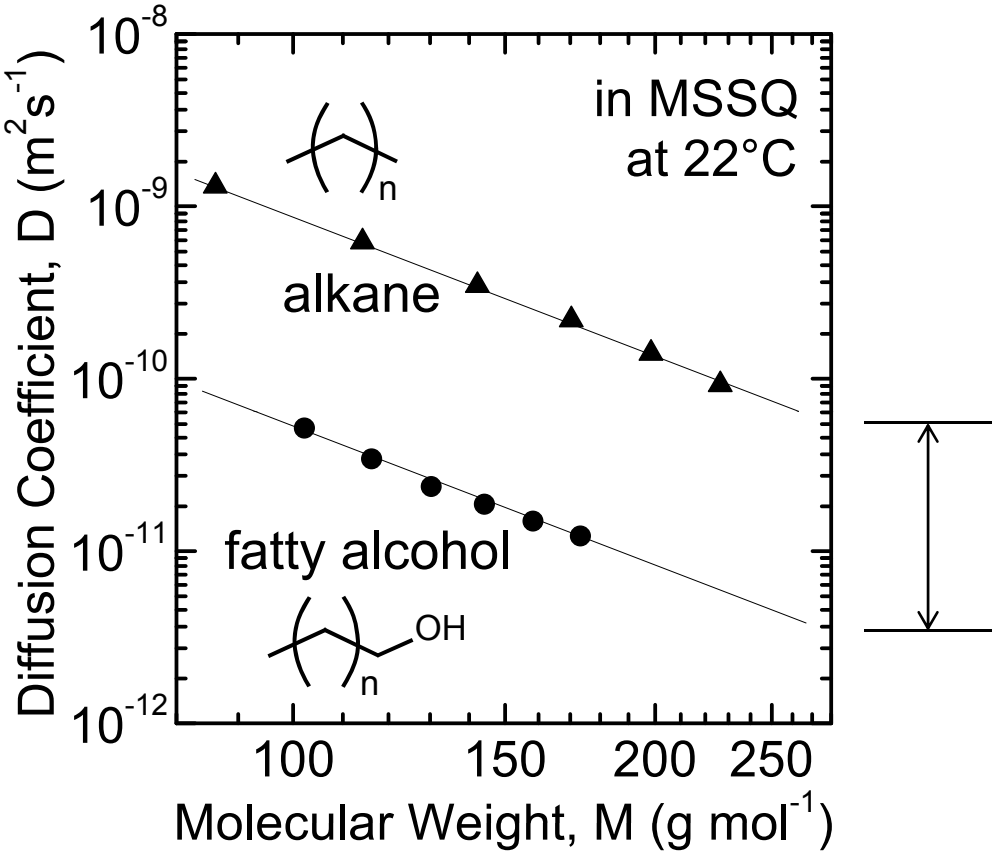
# Effect of Molecular Polarity




Stokes-Einstein relation

$$D \sim \frac{k_B T}{\eta}$$

$$\frac{D_{alkane}}{D_{fatty\,alcohol}} = 17 \cong \frac{\eta_{fatty\,alcohol}}{\eta_{alkane}}$$

Viscosity, $\eta$ (mPa·s) @ 21°C

heptanol = 6.759

octane = 0.537

M ~ 115 g/mol

Increasing molecular polarity
→ Decreasing *D*

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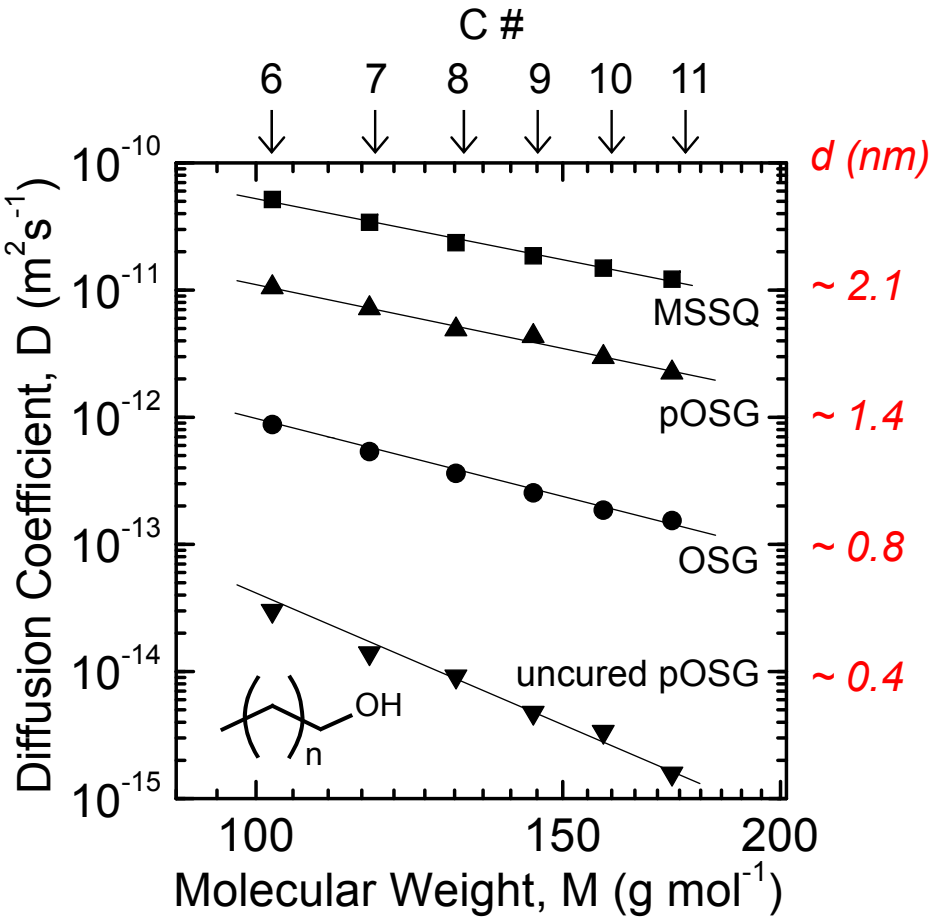
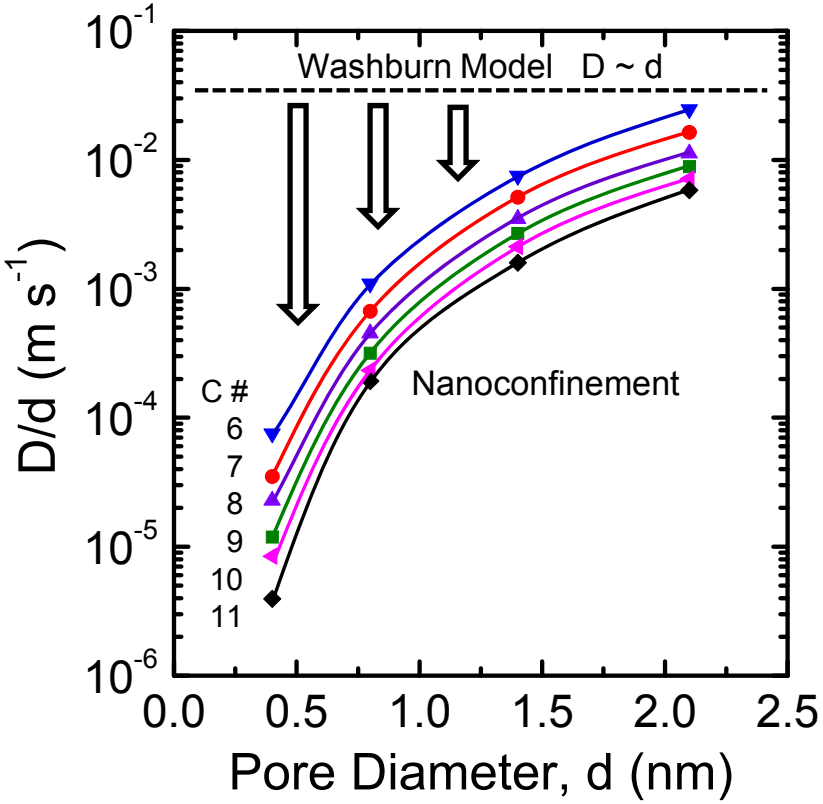
# Effect of Pore Size




*D* ↓ with *d* ↓

*D* decreases more significantly than the continuum-based prediction.

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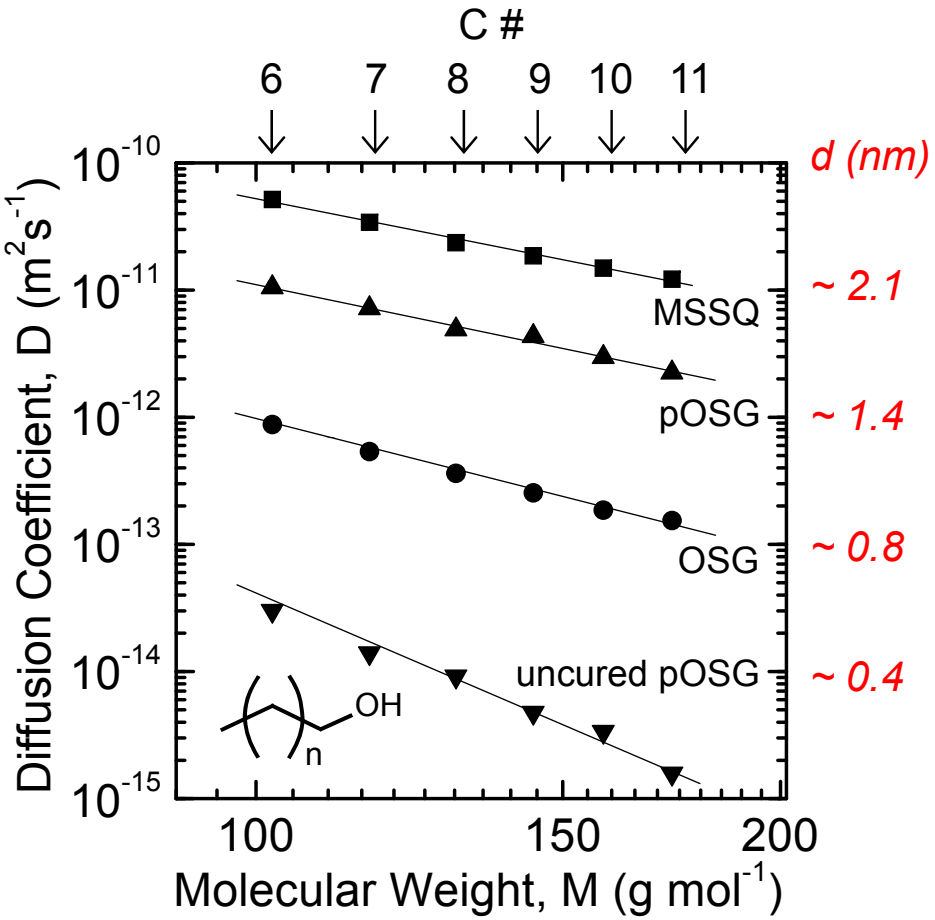
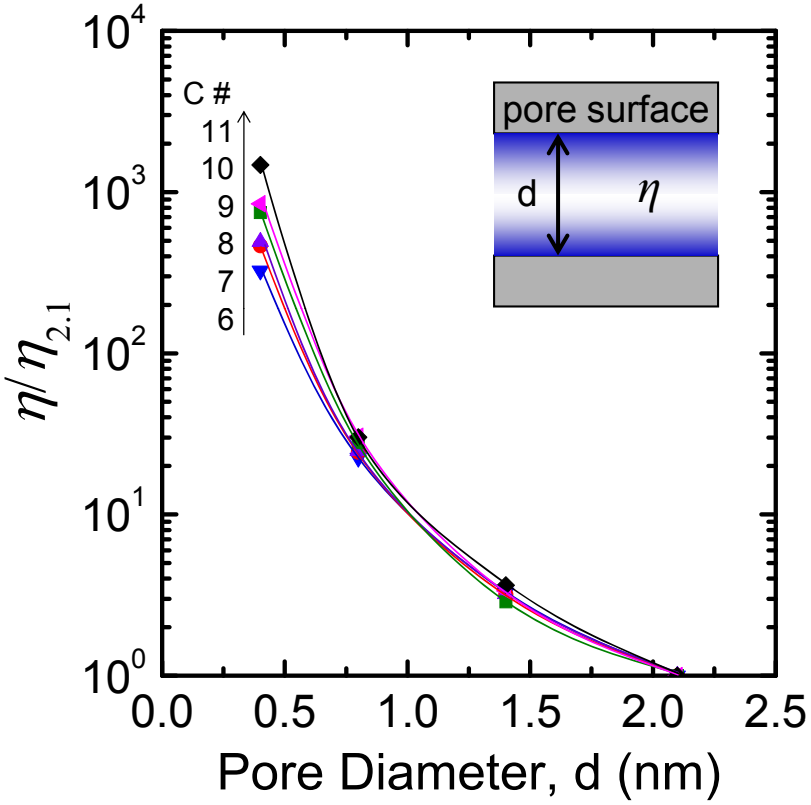
# Nanoconfinement Induced Viscosity Rise




*D* ↓ with *d* ↓

$\eta$ ↑ with *d* ↓

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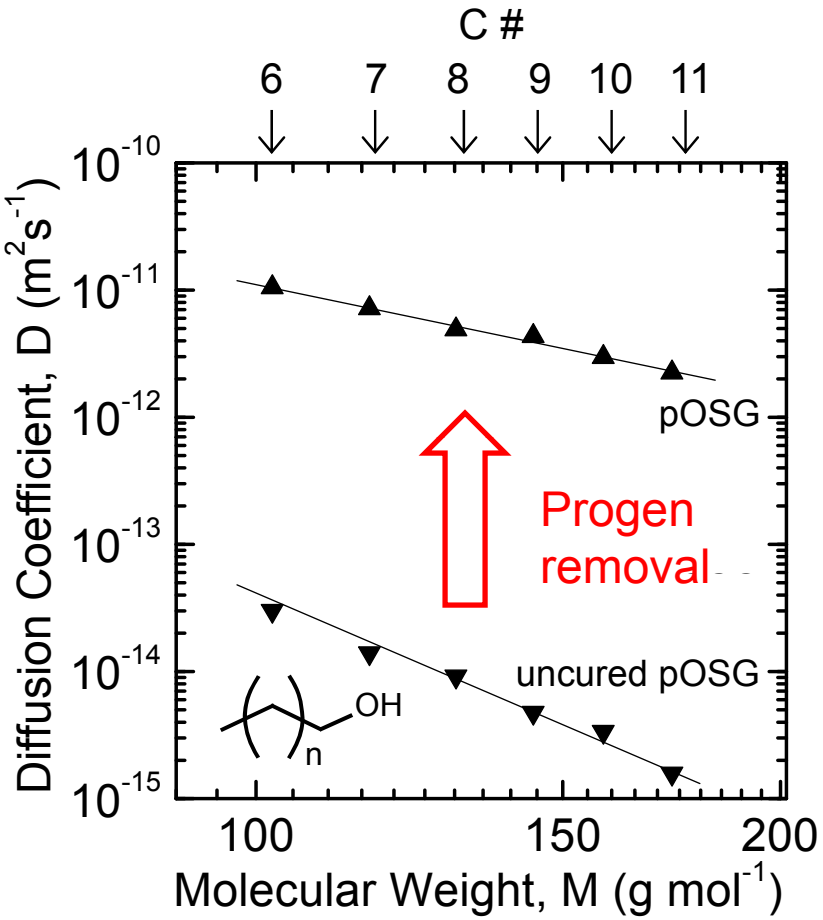
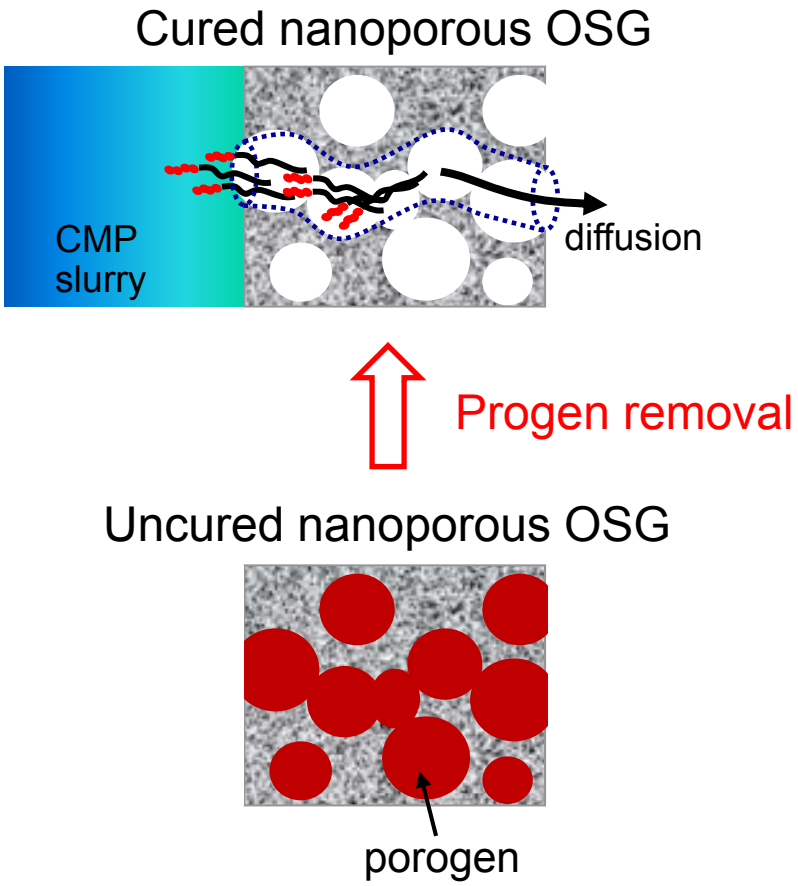
# Effect of Porogen Removal




## Implications for CMP at Advanced Technology Nodes

- Current: Curing ULK → CMP polishing
- Suggest: CMP polishing → Curing ULK to minimize diffusion of CMP slurries.

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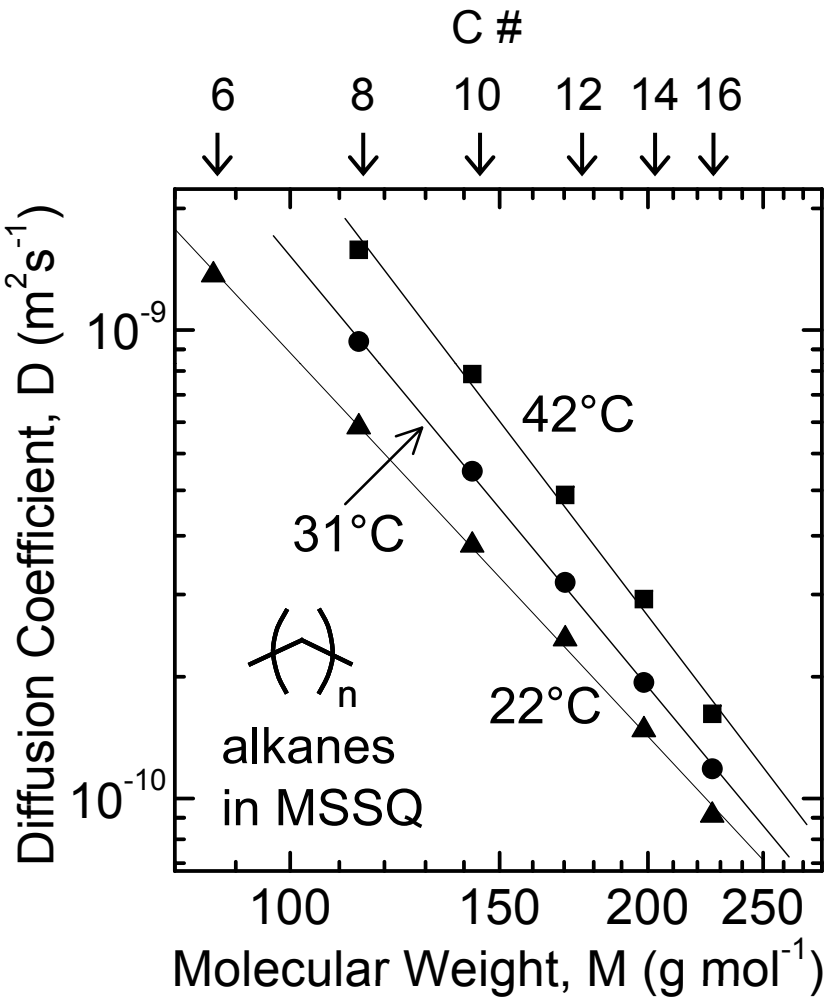
# Effect of Temperature




*D* ↓ with *T* ↓ and *M* ↑

The diffusivities in MSSQ were lower than those in the bulk by at least a factor of three.

The slope is increasing with *T*, which is opposite to the trend in the bulk.

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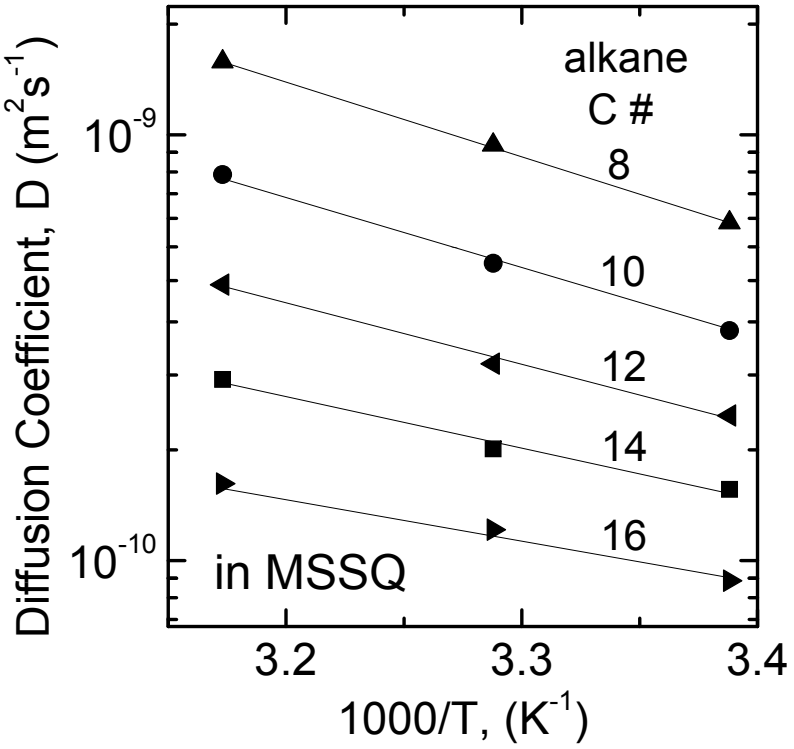
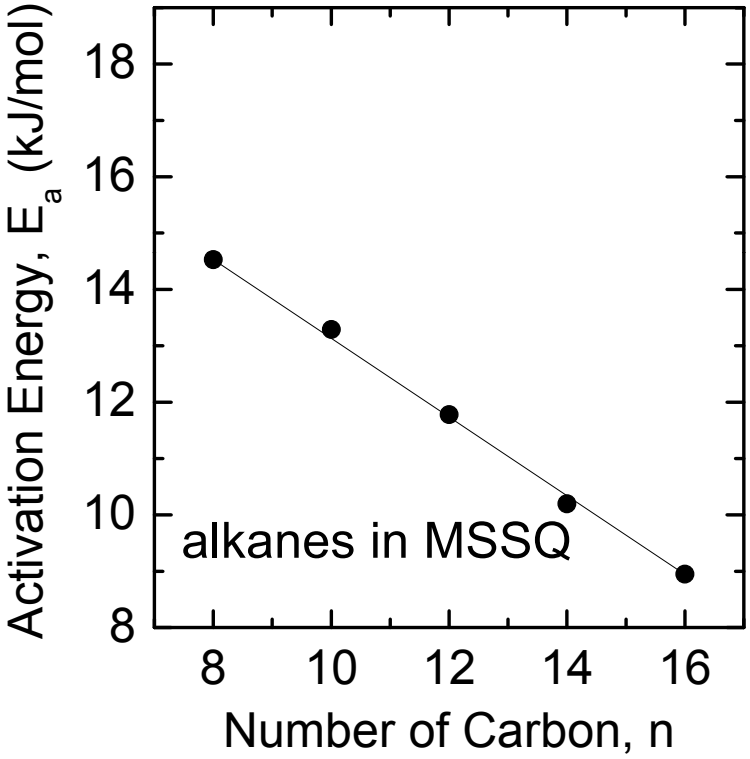
# Activation Energy for Diffusion

## Arrhenius Plot




## $E_a$ vs. Chain Length




$$D = D_o \exp\left(\frac{-E_a}{k_B T}\right)$$

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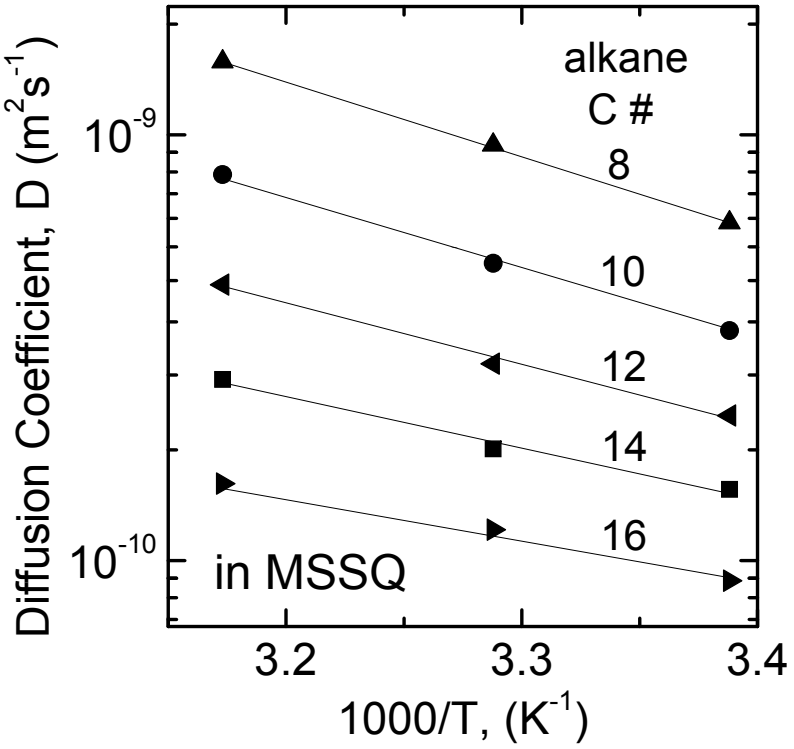


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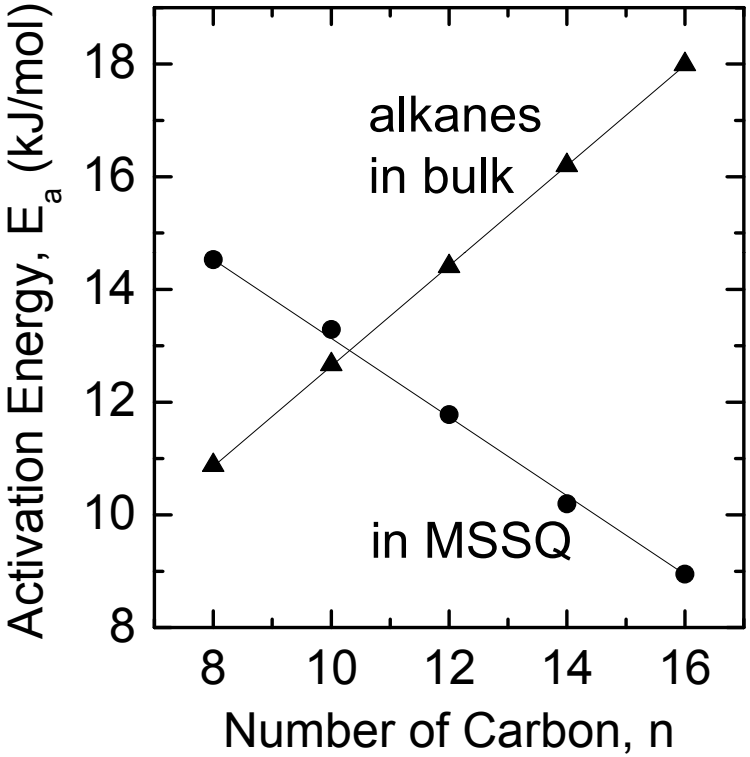


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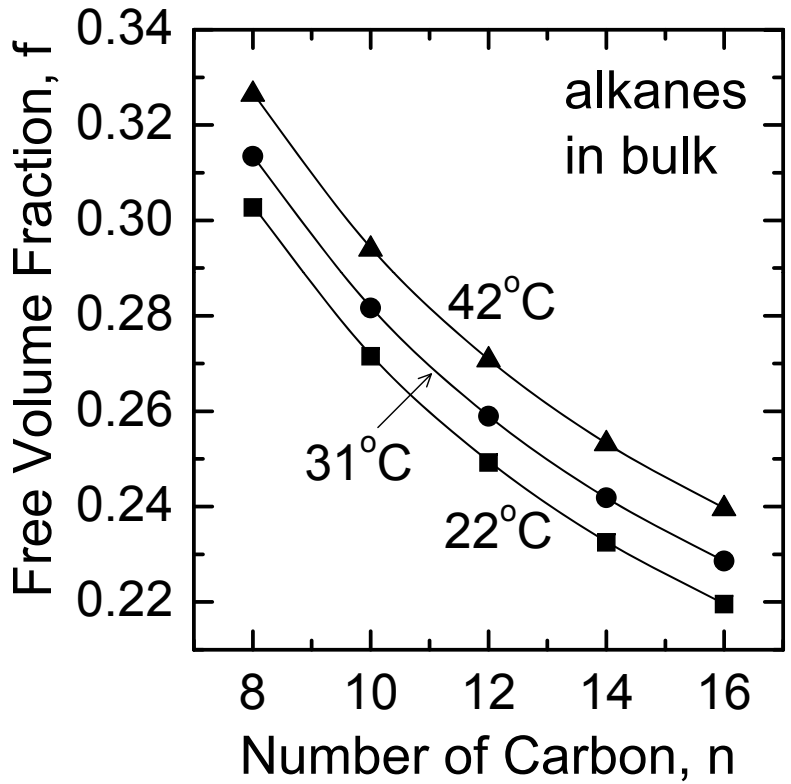
# Free Volume Theory of Diffusion

## Free Volume vs. Chain Length

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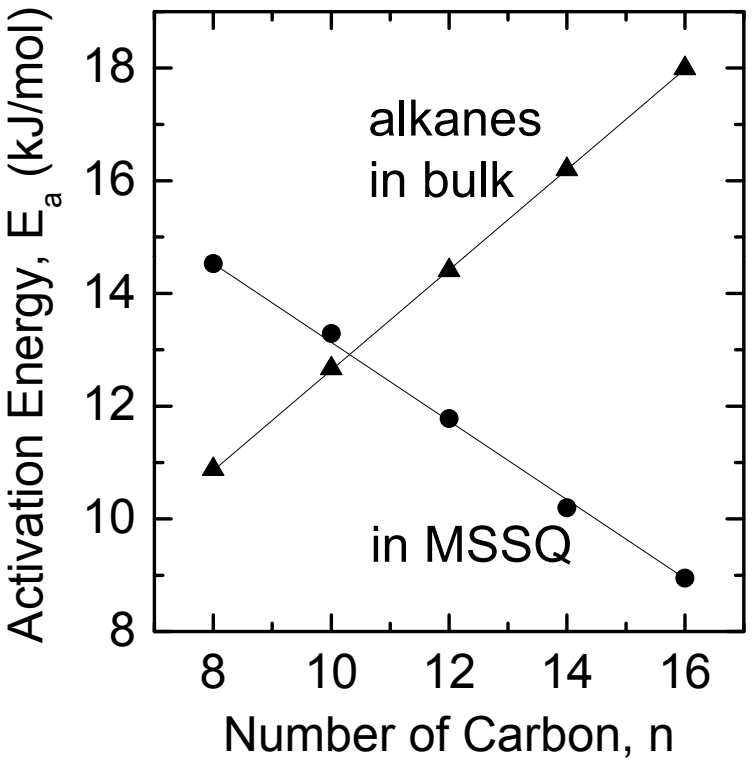


Two ends of a linear chain molecule give rise to free volume into which segments of adjacent molecules can move. Therefore $f \downarrow$ with $T \downarrow$ and $M \uparrow$ resulting in $E_a \uparrow$ in the bulk. However, $E_a \downarrow$ under nanoscale confinement, possibly implying $f \uparrow$ with $M \uparrow$.

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# Conclusions

## Diffusion Controlling Factors

- Molecular weight, structure and polarity
  - $D \downarrow$ with $M \uparrow$, branch # $\uparrow$, and polarity $\uparrow$
- Pore size
  - $D \downarrow$ with $d \downarrow$
- Porogen removal
  - $D \downarrow$ with porogen
- Temperature
  - $D \downarrow$ with $T \downarrow$

## Effects of Nanoconfinement

- Molecular reptation
- $\eta \uparrow$ with $d \downarrow$
- $E_a \downarrow$ with $M \uparrow$