Previous lecture

- Migration of a moving grain boundary diffusion source

- Regimes of grain boundary "short-circuit" diffusion for stationary and moving boundaries

- Some grain boundary diffusion mechanisms

- Dislocation core structure and dislocation "short circuits"

Today

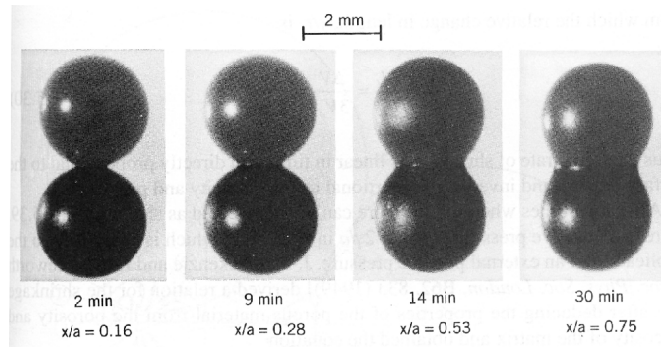- Some phenomena where short-circuits are important

Diffusion in noncrystalline materials

- Gasses and liquids

- Interstitials in metallic glasses and polymers

- Diffusion in network glasses
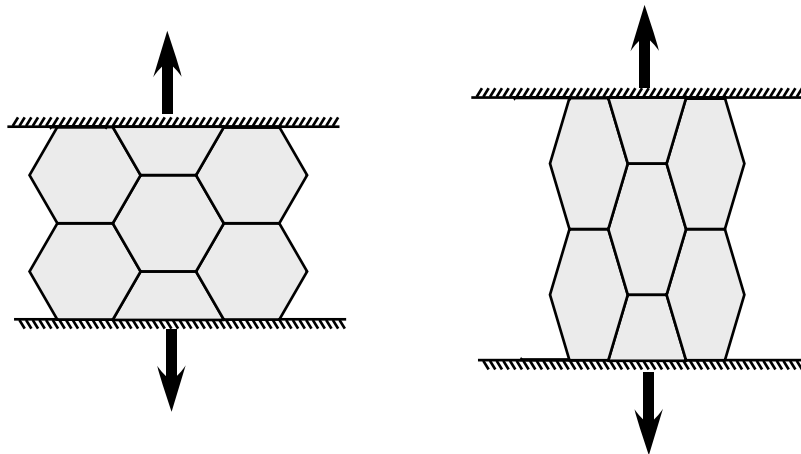
- Diffusion in polymers by reptation

Practical phenomena involving grain boundary diffusion

Sintering

2 mm

| 2 min | 9 min | 14 min | 30 min |
| x/a = 0.16 | x/a = 0.28 | x/a = 0.53 | x/a = 0.75 |

Coble creep

Superplasticity

Diffusion in gasses

•flux of molecules across a plane in a concentration gradient leads to

$$J_x = \frac{1}{6}\bar{v}\left[n(x+l) - n(x-l)\right] = -\frac{1}{3}\bar{v}l$$

where $\bar{v}$ = mean particle velocity

and l = mean free path of particles

so $D = \frac{1}{3}\bar{v}l = \frac{2}{3\sqrt{}}\frac{1}{\bar{p}}_0\sqrt{\frac{(kT)^3}{m}}$

•D varies inversely with p

•D varies as $p^{3/2}$

•Typical D in a gas at STP is 5×10^{-7} m^2/s

Diffusion in liquids

•Distribution of free volume amongst N particles, subject to conservation

$$\frac{N_i}{N} = \frac{1}{\langle v \rangle} \exp \left(- \frac{v^*}{\langle v \rangle} \right)$$

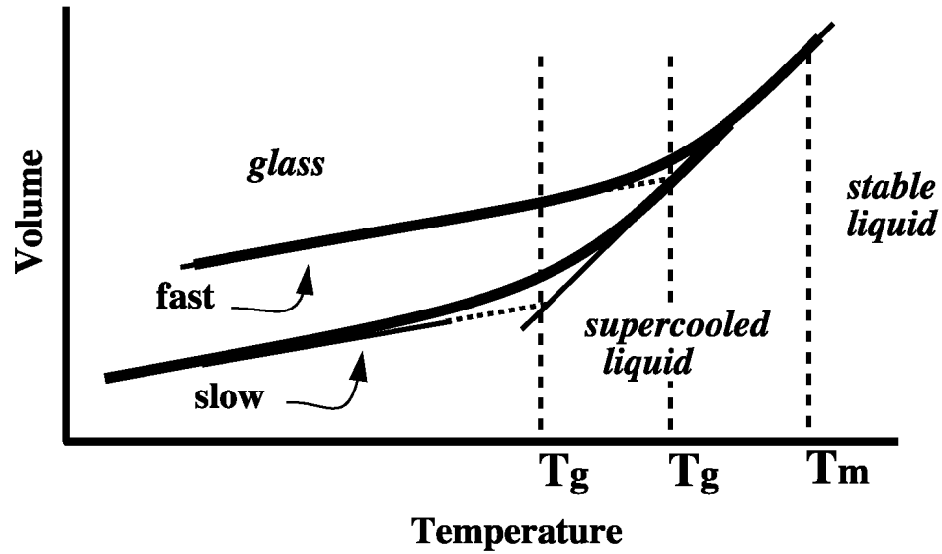where $\langle v \rangle$ is the average free volume and v^* is the critical free volume, $v^* \approx 10 \langle v \rangle$

•Using relation for D over distribution of free volumes,

$$D = \int_{v^*} D(v) p(v)\, dv \quad \text{one can show that}$$

$$D = D(v^*) \exp \left(- \frac{v^*}{\langle v \rangle} \right) = ga(v^*) \langle u \rangle \exp \left(- \frac{v^*}{\langle v \rangle} \right)$$

and thus in liquids $D \sim T^{3/2}$

The glass transition; free volume

• Flowable liquid above glass transition, rigid glass below

• More free volume when glass is cooled rapidly

Diffusion in amorphous metals

•Self-diffusion has these characteristics
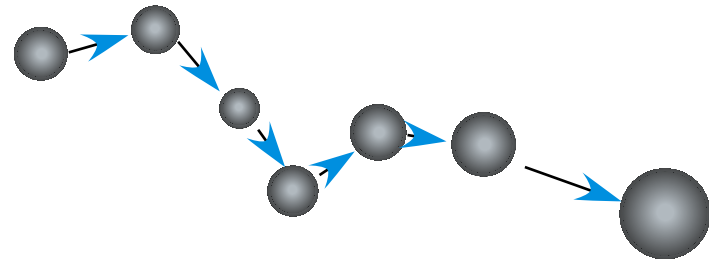> After a quench, D relaxes to a constant value
> If T is changed in the amorphous state, D changes instantanously
> No isotope effect
> D obeys an Arrhenius law
> Activation volume must be very small

> *Implication:* self-diffusion must occur
> by a cooperative mechanism, such as
> a ring mechanism, or motion of a
> chain-like groups of atoms

•Diffusion of small impurity atoms
> The distribution of free volume in the amorphous structure means that there
>> is a distribution of "traps" in which the impurity atoms reside.
> The traps fill up with Fermi-Dirac statistics, and D can be modelled as

$$D^* = D_0 \frac{(1-c)^2}{c} \exp\left(-\frac{\mu - G_0}{kT}\right)$$

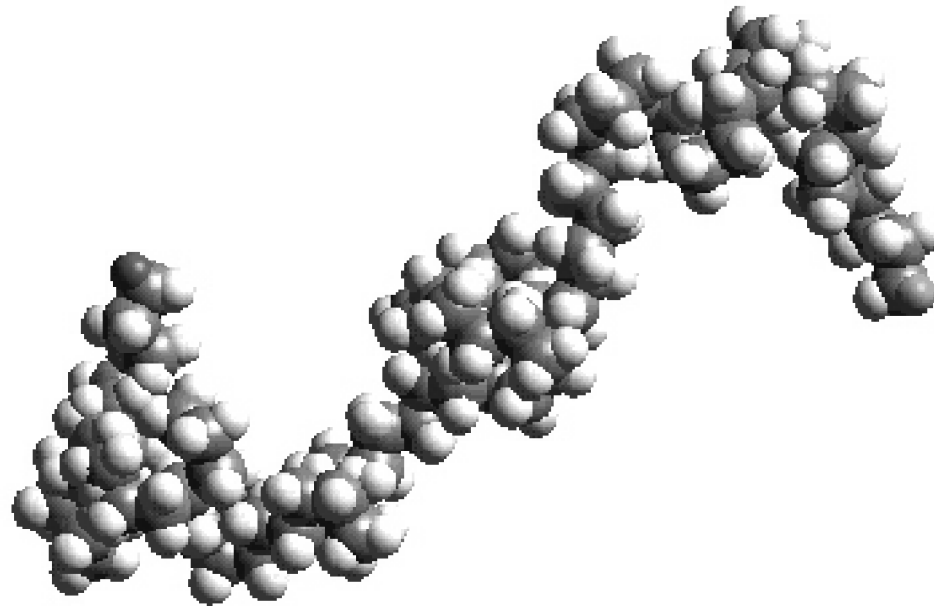A similar relation holds for diffusion of small impurity species in polymers.

Diffusion in amorphous metals - experiments on H in $Pd_{80}Si_{20}$

- D increases strongly with hydrogen concentration, consistent with distribution of traps
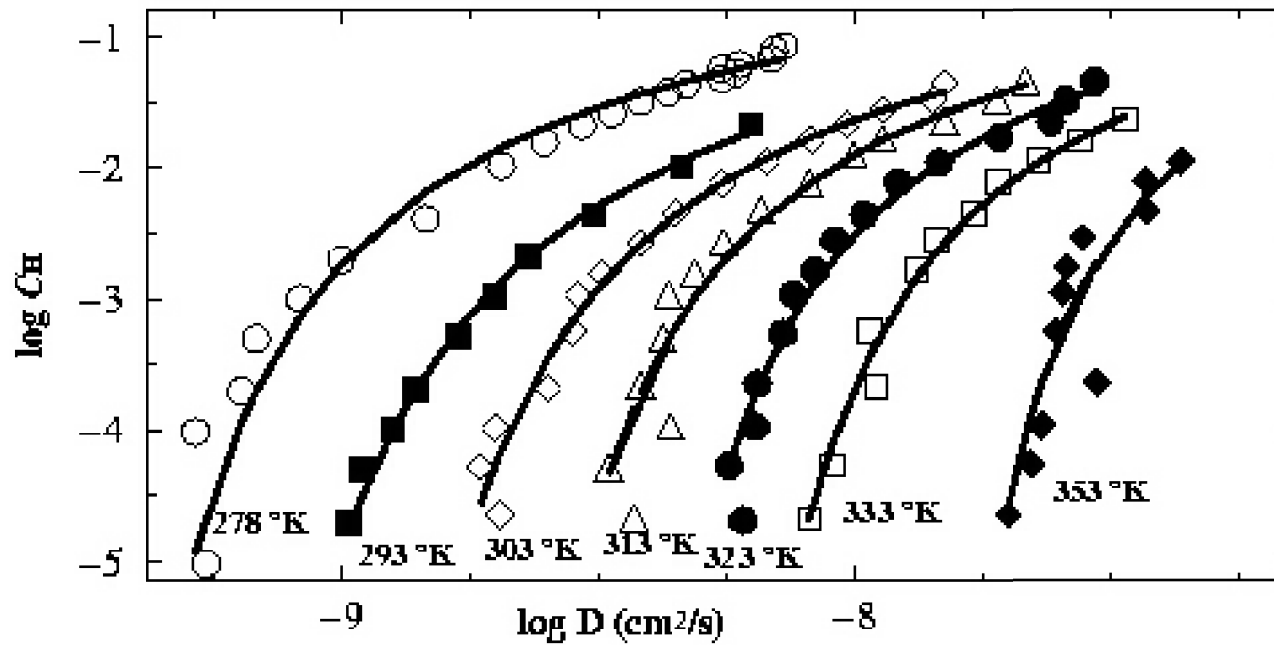
Diffusion in amorphous polymers

- single molecule of polyethylene with $n = 50$ is a self-avoiding random walk

- dilute solution of polymers in a solvent: polymer molecules diffuse by *Brownian motion*.

- "good" solvents: chains more spread out and $R_h \sim N^{3/5} b$

- "theta" solvents: chains more compact and $R_h \sim \sqrt{N} b$

•*D* for polymer molecules in dilute solution is given by
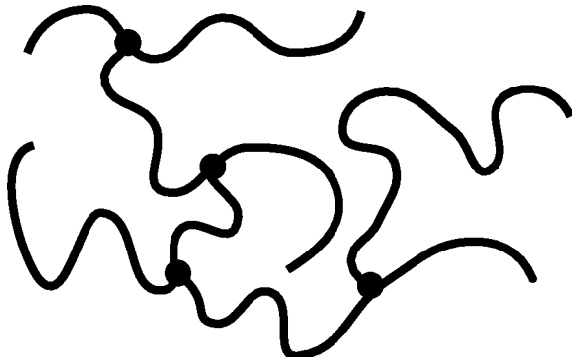
$$D \sim \frac{kT}{6 \quad R_h}$$

Diffusion in polymer melts

•large number of long chains -> *entanglements*

•molecules move by "slithering" mechanism called *reptation*
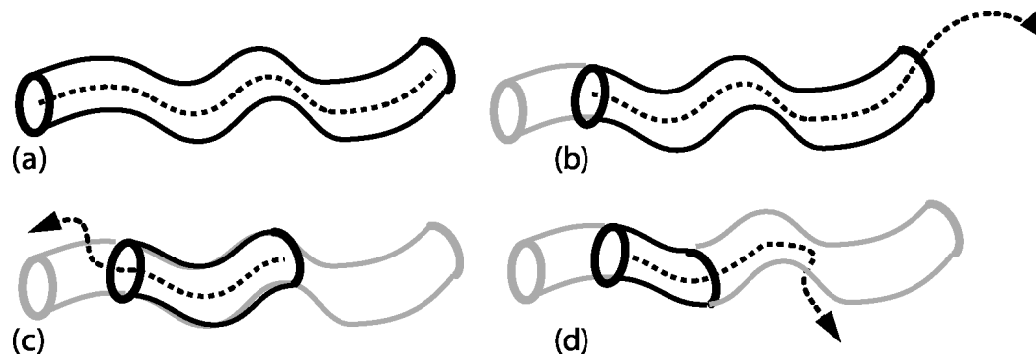
Reptation model

- jump frequency n will be inversely proportional to N $= \dfrac{0}{N}$

- reptation time for complete destruction of tube $_{rep} \quad \dfrac{N^2}{} = \dfrac{N^3}{0}$

- self-diffusivity of a chain in the melt is thus

$$D = \frac{r^2}{6} \quad \frac{Nb^2}{6 \, _{rep}} \quad \frac{b^2 \, _0}{6N^2}$$

References for additional study:

Diffusion in gases:

F. Reif, *Fundamentals of statistical and thermal physics*, McGraw-Hill, 1977, pp. 484–486 on "Calculation of the coefficient of self-diffusion for a dilute gas."

D.A. McQuarrie, *Statistical Mechanics*, Harper & Row, 1973 pp. 358–365 on "Elementary kinetic theory of transport in gases."

Fractals:

Allen & Thomas, *The Structure of Materials*, pp. 74-80.

Molecular dimensions in polymer melts and solutions; reptation:

T.P. Lodge, N.A. Rotstein, and S. Proger, "Dynamics of entangled Polymer Liquids: Do linear Chains Reptate?" in *Advances in Chemical Physics*, Vol. LXXIX, Johh Wiley & Sons, 1990, pp. 1–26.