6.1 Introduction

- In the previous lecture, we talked about the dynamics of polymer chains in the melt (polymer only) and dilute solution (polymer minority component)
- But, when the polymer is the majority component, what can we say about the motion of the solvent?
- In particular, we are interested in the degree to which the solvent permeates the polymer, how much is absorbed and how fast it can move through the sample
- Restrict attention to mainly amorphous structures
  - Rubbery polymers (extensively studied since Graham 1866)
  - Glassy polymers: more complicated
  - Semi-crystalline polymers: crystallites embedded in matrix
6.2 Motivation for studying diffusion in polymers

- Important for many design applications

<table>
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<th>Application</th>
<th>Penetrant</th>
<th>Design goal</th>
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<td>packaging additives</td>
<td>gas, moisture</td>
<td>high barrier</td>
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<td>gas separation</td>
<td>plasticizers, dyes</td>
<td>high barrier</td>
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<td>analytical chemistry</td>
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<td>monomer removal</td>
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<td>polymer electrolytes</td>
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<td>controlled release</td>
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<tr>
<td></td>
<td>biomolecules</td>
<td>high selectivity</td>
</tr>
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6.3 Macroscopic manifestations

- Sorption isotherm
- Diffusivity as a function of temperature
- Solubility and diffusivity of various gases in natural rubber
- Permeability of various gases in natural rubber
- Permeability of various gases in different polymers
6.4 Sorption isotherm for CO$_2$ in PET at 25°C

- Typical curve shape for a glassy polymer

![Sorption isotherm graph]

6.5 Solubility and diffusivity of gases in rubber

- Diffusivity drops with penetrant size (Stokes)
- Solubility increases with penetrant size (condensation)

![Solubility and diffusivity graph]
6.6 Permeability of gases in rubber

- Minimum due to combined low solubility and diffusivity

6.7 Permeability of gases in various polymers

- Similar trends for a wide range of polymers
6.8.1 Revision of diffusion theory

- Linear flux-force relationship

\[ J = -A \frac{dX}{dx} \]

where \( A \) is some phenomenological coefficient and \( X \) is a potential

- When \( X \) is concentration, gives **Fick’s first law**

\[ J = -D \frac{dC}{dx} \]

where \( D \) is the **diffusion coefficient**

6.8.2 Revision of diffusion theory

- Concentration of penetrant proportional to pressure on polymer (**Henry’s law**)

\[ C = kp \]

where \( k \) is a solubility coefficient and \( p \) is the vapour pressure of penetrant

- Steady state **permeability** = flux/pressure gradient:

\[ P = Dk = \text{Diffusivity} \times \text{Solubility} \]

- In an ideal system, solubility and diffusivity are constant
- When they are concentration dependent, the behaviour is usually called ‘anomalous’
6.9 Solution-diffusion model

- Treat permeation as a three stage process

1. Adsorption onto polymer surface
2. Diffusion through bulk polymer
3. Desorption into external phase

6.10.1 Sorption

- Rubbery polymers – ideal behaviour
- Glassy polymers – anomalous behaviour via the dual mode sorption mechanisms
  - Adsorption in microvoids (‘holes’), $c_h$
  - Ordinary dissolution, $c_d$

$$c_h = kp + c'_h bp/(1 + bp)$$

$b$ is a hole affinity constant
6.10.2 Sorption

- Reason for the microvoids is that free volume is frozen into structure at the glass transition
- Solubility given by enthalpy of dissolution $\Delta H_s$
- Above $T_g$, there is endothermic chain separation
- Below $T_g$, exothermic heat of absorption

6.11 Macroscopic diffusion

- Fick’s second law
  \[
  \frac{dc}{dt} = -\frac{dJ}{dx} = -D \frac{d^2c}{dx^2}
  \]
- Activated process $\Rightarrow$ Arrhenius behaviour:
  \[
  D = D_0 \exp\left(-\frac{E_a}{RT}\right)
  \]
- Effect of glass transition is changes in slope
- $E_a$(rubber) > $E_a$(glass)
- Rubber: penetrant must create channels, activate chains
- Glass: penetrant moves through holes, local activation
6.12 Arrhenius plots for O₂ and Ar in PVA

- Shows changes in $D$ around $T_g$

![Image of Arrhenius plots for O₂ and Ar in PVA]

6.13 Free volume theory of diffusion

- Molecules can only diffuse through free volume

- Probability of finding a hole $\sim \exp(-B / v_f)$, where $B$ depends on the volume needed by the penetrant and $v_f$ is the fractional free volume

- Diffusion depends on penetrant mobility:

$$D = RTA_f \exp(-B / v_f)$$
6.14 Microscopic picture of diffusion

- Related to the autocorrelation function of penetrant currents. If different particles are uncorrelated (low concentration, short-ranged interactions):

\[ D = \frac{1}{3} \int \langle v(t)v(0) \rangle dt \]  

(Green-Kubo)

- For long times, equivalent to

\[ D = \frac{1}{6t} \left\langle [R(t) - R(0)]^2 \right\rangle \]  

(Einstein)

- Assumes a random walk: no memory
- Correlated motions give rise to anomalous diffusion (restricted motion or conformational changes due to the environment)

6.15 Time lag measurement of diffusion

- Starting with a membrane of thickness \( l \) free of penetrant
- Apply a penetrant pressure on one side, and measure the flow \( Q_t \)
- In the steady state: \( Q_t = \frac{Dc}{l} \left( t - \frac{l^2}{6D} \right) \)

\[ \frac{Q_t}{lc} \]

\[ \theta = \frac{t^2}{6D} \]
6.16 Pressure decay measurement of diffusion

- Polymer sample is put in a closed, fixed volume
- After evacuation, penetrant gas is applied at a certain pressure. Pressure in the chamber then decreases due to mass uptake $M_t$ by the polymer, according to

\[
\frac{M_t}{M_\infty} = 4 \frac{D t}{\pi l^2}
\]

6.17.1 Computer simulation of diffusion

- Construct an atomistic scale model of the bulk material including the gas molecules
- Simulate the behaviour of the system for sufficient time to observe diffusion
- Analyse to obtain the mean square displacement (MSD) of the gas molecules
- The self diffusion coefficient (equivalent to the diffusivity for low concentrations of solute) can be obtained from curve of MSD versus time
- Example: diffusion of nitrogen gas through polydimethylsiloxane (PDMS)
6.17.2 Building a model

- Take some $N_2$ and a PDMS chain…

6.17.3 Building a model

- Pack them (RIS) into a box with periodic boundaries to an appropriate density…
6.17.4 Calculating mean-squared displacement

- Evolve system in time, and observe penetrant motion

![Diagram of a system with molecules and a grid]

6.17.5 Calculating mean-squared displacement

- Looking at motion of a single penetrant molecule projected onto a plane, can see more clearly

![Diagram of motion in a plane with coordinates x (Å) and y (Å)]
6.17.6 Calculating mean-squared displacement

- MSD plot confirms the jump diffusion mechanism
- Average over many molecules and long times to obtain $D$ from Einstein formula

Summary of M6 Part 1

- In these last six lectures, we have discussed a number of key issues in polymer physics
- I will try to summarise the most important concept of each lecture in one bullet point!!
- Here goes…
- Although a freely jointed chain of uncorrelated segments is sufficient to differentiate between polymers and simple molecules, correct account of the couplings between the torsional degrees of freedom is required to distinguish between conformations of chemically dissimilar polymers
- Polymer coils in the melt or at their $\Theta$-point adopt ideal conformations, but in a good solvent they are expanded
Summary of M6 Part 1

- In general, different polymers are immiscible unless there are strongly favourable enthalpic interactions
- The phase diagram and morphologies of a binary diblock copolymer are governed by balance between interfacial forces and chain entropy, but allow mixing of chemically dissimilar polymers on a microscopic scale
- Diffusion of polymers is governed by their molecular weight and concentration, with abrupt changes in scaling behaviour at critical values of these
- Permeability of polymers by solvents can be explained on the basis of their diffusivity and solubility, and the structure of the polymer matrix

Endings, and new beginnings...

Professor Andrew Keller (1926–1999)