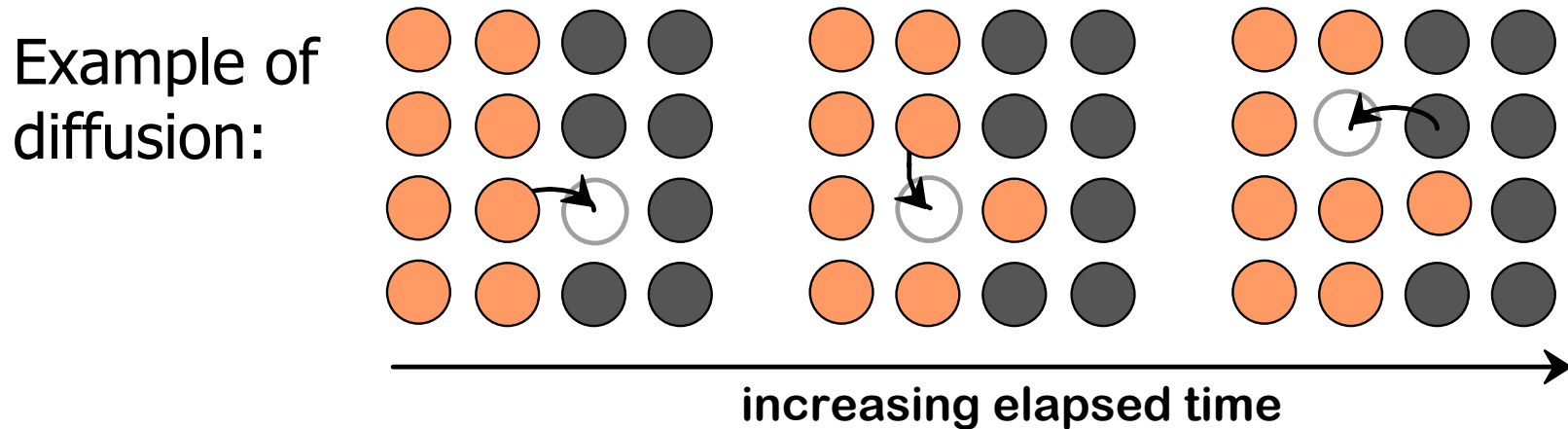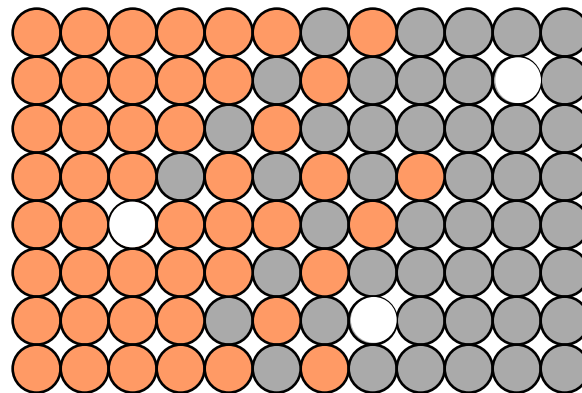# Permeation

- Rate at which a gas or vapor passes through a polymer
- Consists of 3 processes:
  - Absorption of the permeating species into the polymer
  - Diffusion through the polymer
  - Desorption of the permeating species from the polymer surface and removal
- Factors affecting permeability of a polymer:
  - Solubility and diffusivity of the small molecule in the polymer
  - Chain packing and side group complexity, polarity, crystallinity, orientation, fillers, humidity and plasticization

Essential factors for permeation

- Free volume: in order for any molecules to move in a material there must be holes available

- Continuous path through the polymer

Example of diffusion:
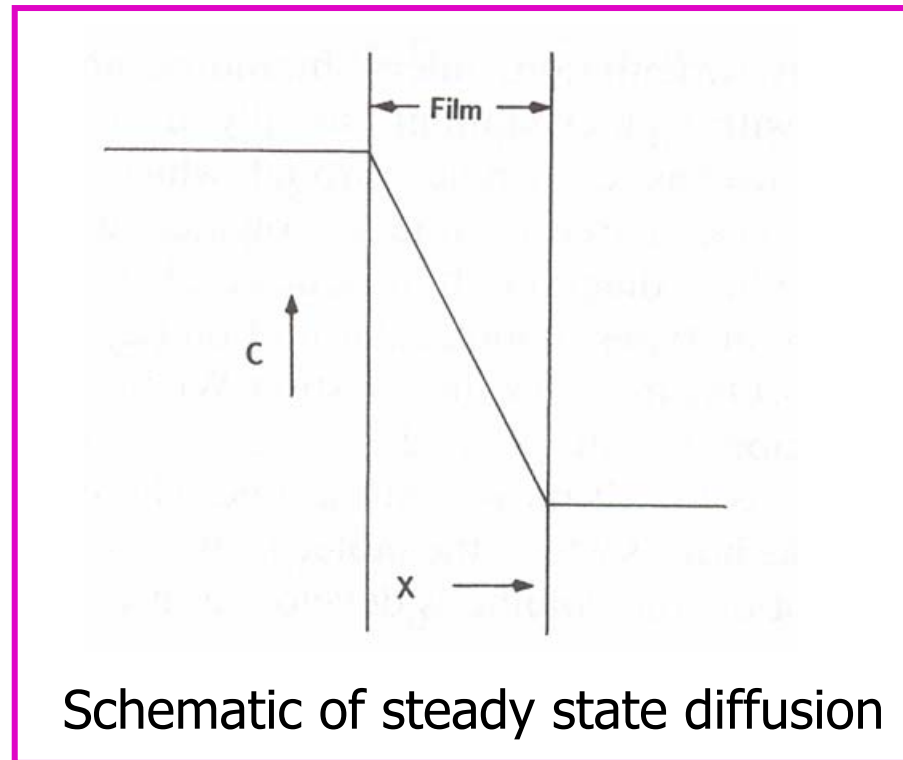

increasing elapsed time

After some time:

Fick's Laws

- Steady State:

$$J = -D \frac{\partial c}{\partial x}$$

- Unsteady state:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial c}{\partial x} \right]$$


Schematic of steady state diffusion

J is the flux of permeant [=] (mass/area/time)

D is the diffusivity: it depends on polymer, diffusing species, temperature and in some cases on concentration c.
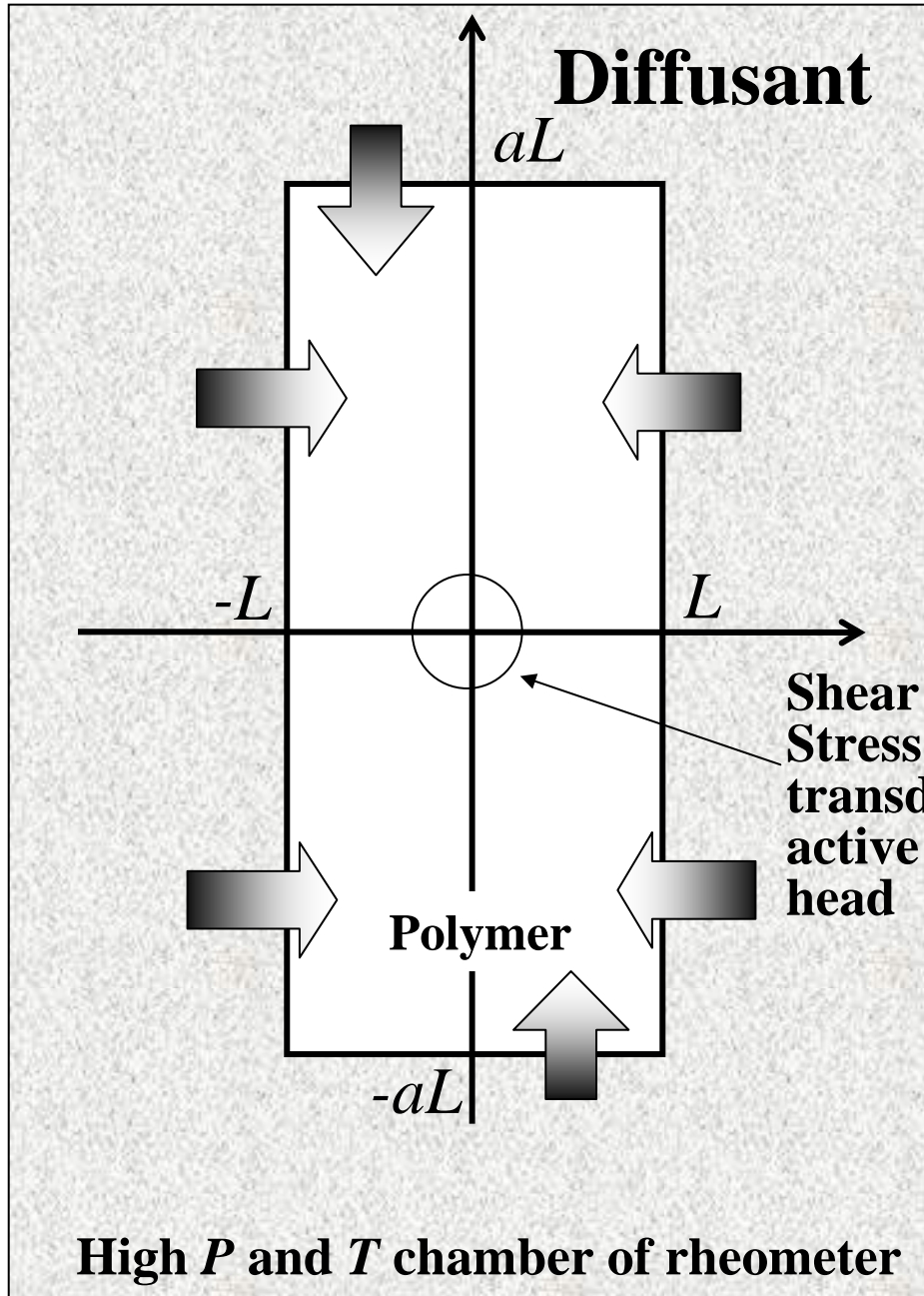
Example of diffusion in a rubbery polymer

- Studying the effect of dissolved CO_2 on viscosity of HDPE

- The CO_2 was diffused into the sample in the rheometer where only the edges of the rectangular sample were exposed to the gas

- Measurement of stress was performed at the center of the sample ⟹ needed to know when the concentration of the diffusant in the center of the sample had reached the solubility.

Gas diffuses in on the sides of the sample but not on the top or bottom.
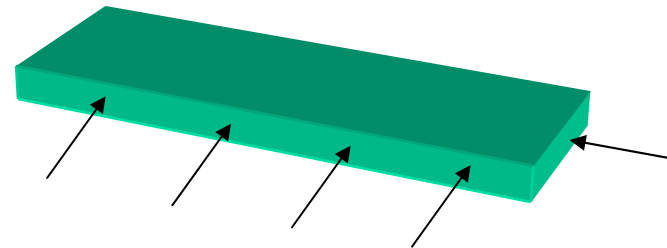
Reference: Effects of Pressure and Supercritical Fluids on the Viscosity of Polyethylene, Park and Dealy, Macromolecules 2006, 39, 5438-5452

Diffusant

aL

$-L$ L

Shear
Stress
transducer
active
head

Polymer

$-aL$

High P and T chamber of rheometer

Diffusion and Saturation

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right)$$

Fick's Model

Saturation Time Prediction

Solution to 2D-Fick's Diffusion Model: Prediction of Level of Saturation

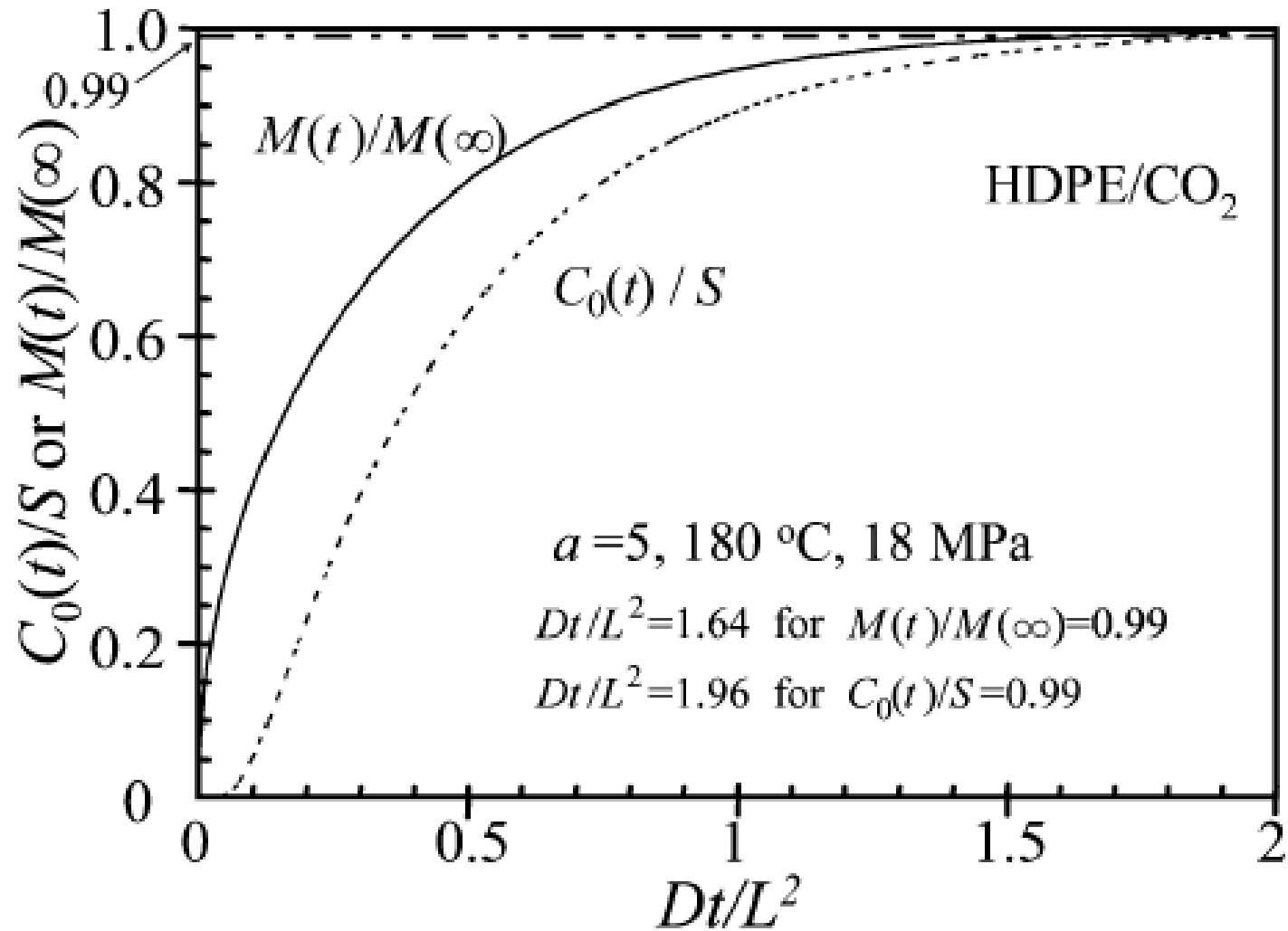Dimensionless center concentration with time:

$$\frac{C(0,0,t)}{S} = 1 - \left\{ \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4L^2} \right] \right\} \left\{ \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} \exp\left[\frac{-D(2m+1)^2 \pi^2 t}{4(aL)^2} \right] \right\}$$

Relative amount absorbed by polymer with time to the absorbed quantity after infinite time:

$$\frac{M(t)}{M(\infty)} = 1 - \left\{ \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4L^2} \right] \right\}$$

$$\times \left\{ \sum_{m=0}^{\infty} \frac{8}{(2m+1)^2 \pi^2} \exp\left[\frac{-D(2m+1)^2 \pi^2 t}{4(aL)^2} \right] \right\}$$

$\dfrac{C(0,0,t)}{S}$ and $\dfrac{M(t)}{M(\infty)}$ will be 0 at $t = 0$ and 1 after saturation. (S is solubility.)

Results of Fick's analysis

The plot shows $C_0(t)/S$ or $M(t)/M(\infty)$ on the y-axis versus Dt/L^2 on the x-axis.

Curves labelled $M(t)/M(\infty)$ and $C_0(t)/S$.

HDPE/CO_2

$a = 5$, 180 °C, 18 MPa

$Dt/L^2 = 1.64$ for $M(t)/M(\infty) = 0.99$

$Dt/L^2 = 1.96$ for $C_0(t)/S = 0.99$

Validation of Fick's analysis

In order to monitor the diffusion, viscosity measurements were taken every few minutes. The CO2 causes a decrease in viscosity, as long as the concentration of CO2 in the middle of the sample is changing then the viscosity will change. When saturation is reached the viscosity reaches η_∞ and remains constant.

Viscosity at time t

$$\eta_R(t) \equiv \frac{\eta(t) - \eta(0)}{\eta(\infty) - \eta(0)}$$

Relative viscosity

Viscosity w/o CO_2

Viscosity at saturation

Saturation with CO_2: Prediction and Data

Legend:
- —— $M(t)/M(\infty)$
- --- $C(0,0,t)/S$
- ▪ η_R: with CO_2
- ● η_R: w/o CO_2

$$\eta_R \equiv \frac{\eta(0)-\eta(t)}{\eta(0)-\eta(\infty)}$$

$$\dot{\gamma} = 0.63\,\text{s}^{-1}$$

HDPE with CO_2
180°C, 18MPa (2600 psi)
$D=9\times10^{-5}\text{cm}^2/\text{s}$

99% Satu. time

Y-axis: $M(t)/M(\infty)$, $C(0,0,t)/S$, or η_R

X-axis: t (min)
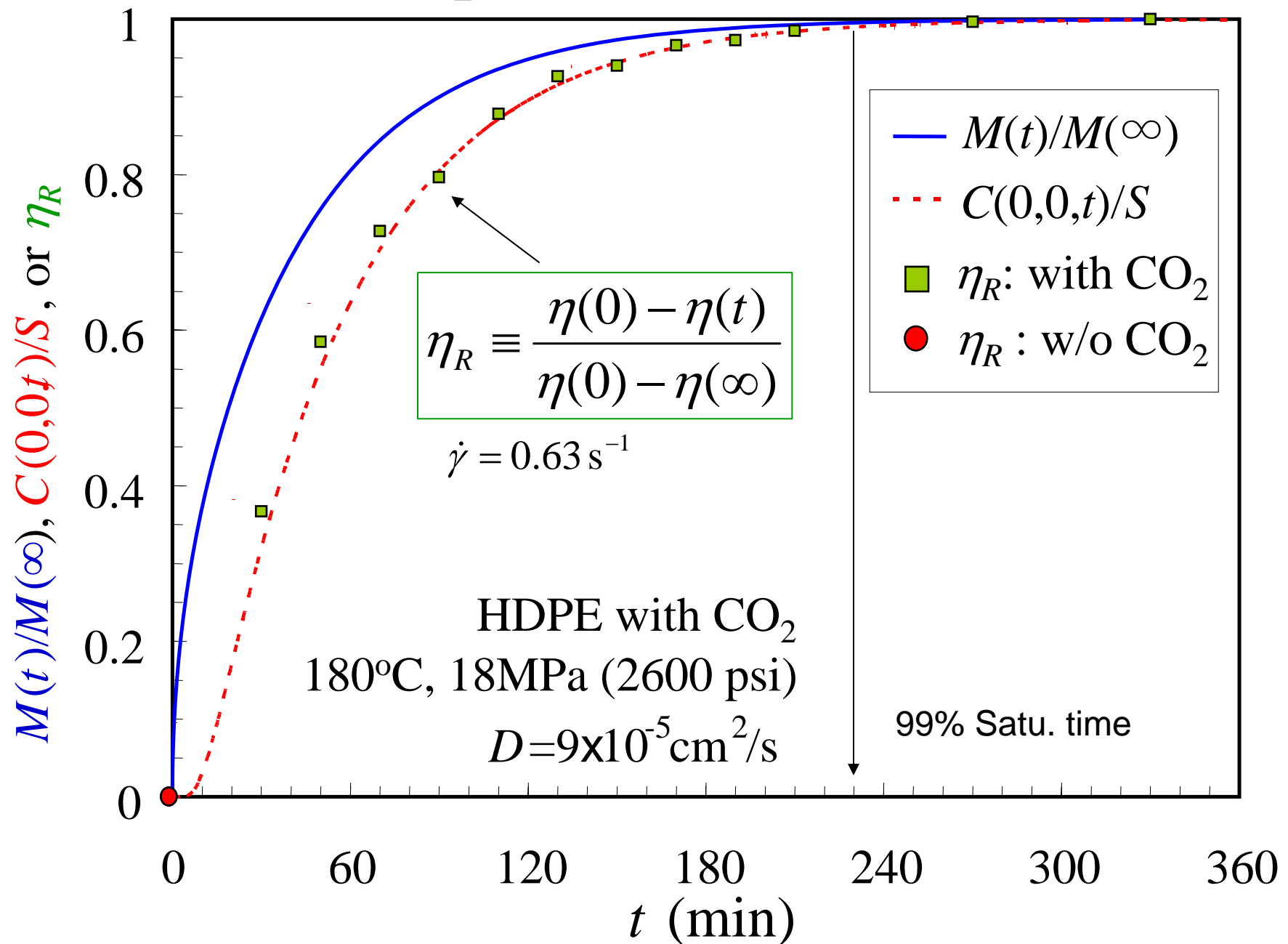
Effect of continuous shearing on diffusion
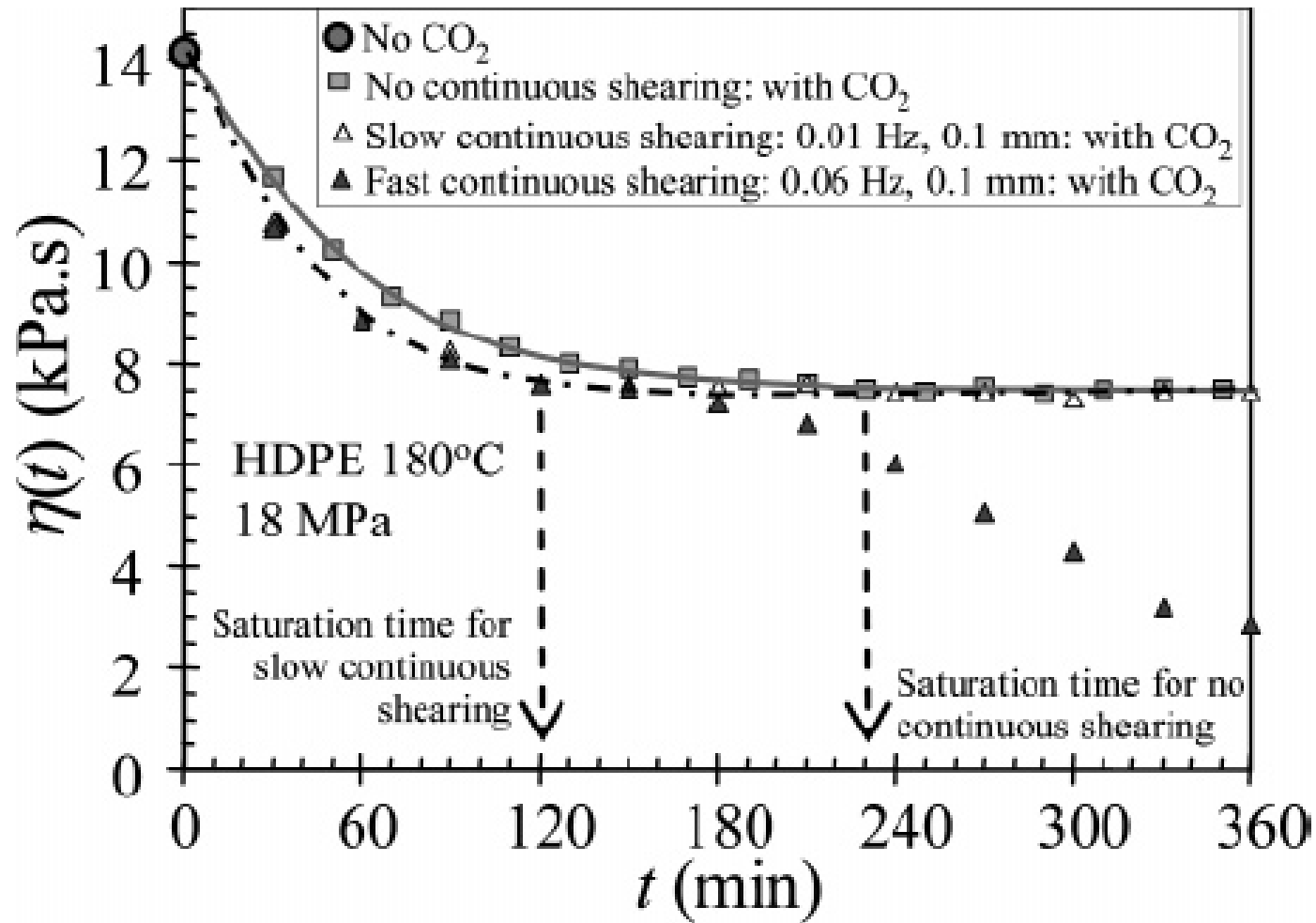
Permeability

- Permeability coefficient, P = volume of vapour passing through a unit area of polymer per unit time, with a unit pressure difference across the sample

$$P = \frac{(\text{quantity of permeant}) \times (\text{film thickness})}{(\text{area}) \times (\text{time}) \times (\text{pressure drop across the film})}$$

- Solubility coefficient, S = volume of vapour per unit volume of polymer per unit pressure

$$P = D \cdot S$$

$$\text{Units of } P = \frac{cm^3 \times cm}{cm^2 \times s \times Pa}$$

$$\text{Units of } D = cm^2/s$$

$$\text{Units of } S = \frac{cm^3 (273.15K; \ 1.013 \times 10^5 \, Pa)}{cm^3 \times Pa}$$

Permeability Data

Table 4.5 Permeability in polymers at 25°C (70)

Polymer	Permeant	$P \times 10^{13}$	$P_0 \times 10^7$	ΔE
Polyethylene (LDPE)	O_2	2.2	66.5	42.7
	N_2	0.73	329	49.9
	CO_2	9.5	62	38.9
	H_2O	68	48.8	33.5
cis-1,4-Polybutadiene	N_2	14.4	0.078	21.3
	He	24.5	0.0855	20.3
Poly(ethyl methacrylate)	O_2	0.889	2.1	36.4
	CO_2	3.79	0.435	28.9
Poly(ethylene terephthalate)[a]	O_2	0.0444	0.227	37.7
(amorphous)	CO_2	0.227	0.00021	27.0
	CH_4	0.0070	0.9232	24.7
Poly(vinylidene chloride)[b]	N_2	0.00070	900	70.3
	O_2	0.00383	825	66.6
	CO_2	0.0218	24.8	51.5
	H_2O	7.0	863	46.1
Cellulose	H_2O	18900	—	—

[a] Major component of plastic soft drink bottles.
[b] Major component of Saran®.
Units: P, P_0 = cm³ (273 K; 1×10^5 Pa) $\times$ (cm/cm²) $\times$ s⁻¹ $\times$ Pa⁻¹.
   ΔE = kJ/mol.

$$P = P_0 \exp\left(\frac{-\Delta E}{RT}\right)$$

Effect of permeant size

The diffusion rate decreases with permeant size.
Example from previous table for LDPE:

Permeant	$P \times 10^{13}$	Size of permeant
O_2	2.2	0.346 nm
N_2	0.73	0.364 nm
CO_2	9.5	0.33 nm
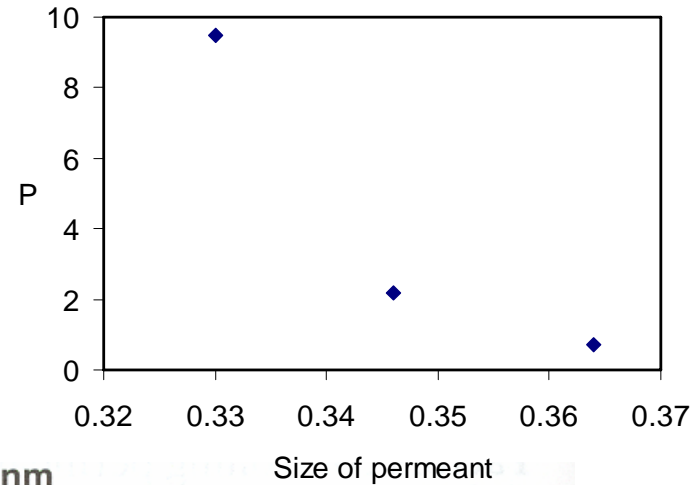
Table 4.6 Kinetic diameters[a] of various permeants (72), nm

Molecule	Diameter	Molecule	Diameter
He	0.26	C_2H_4	0.39
H_2	0.289	Xe	0.396
NO	0.317	C_3H_8	0.43
CO_2	0.33	$n\text{-}C_4H_{10}$	0.43
Ar	0.34	CF_2Cl_2	0.44
O_2	0.346	C_3H_6	0.45
N_2	0.364	CF_4	0.47
CO	0.376	$i\text{-}C_4H_{10}$	0.50
CH_4	0.38		

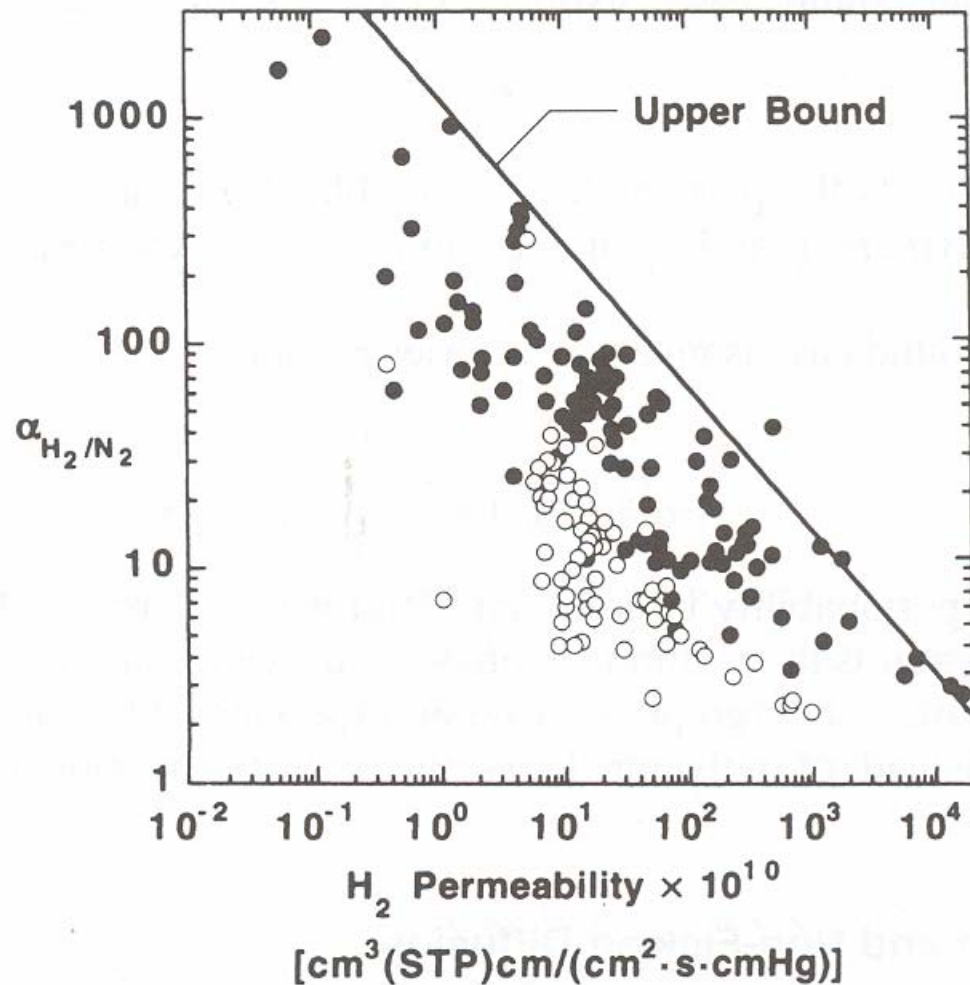# Permeation in glassy polymers vs rubbery polymers

Free volume is much lower in glassy polymers than in rubbery polymers therefore diffusion tends to be slower
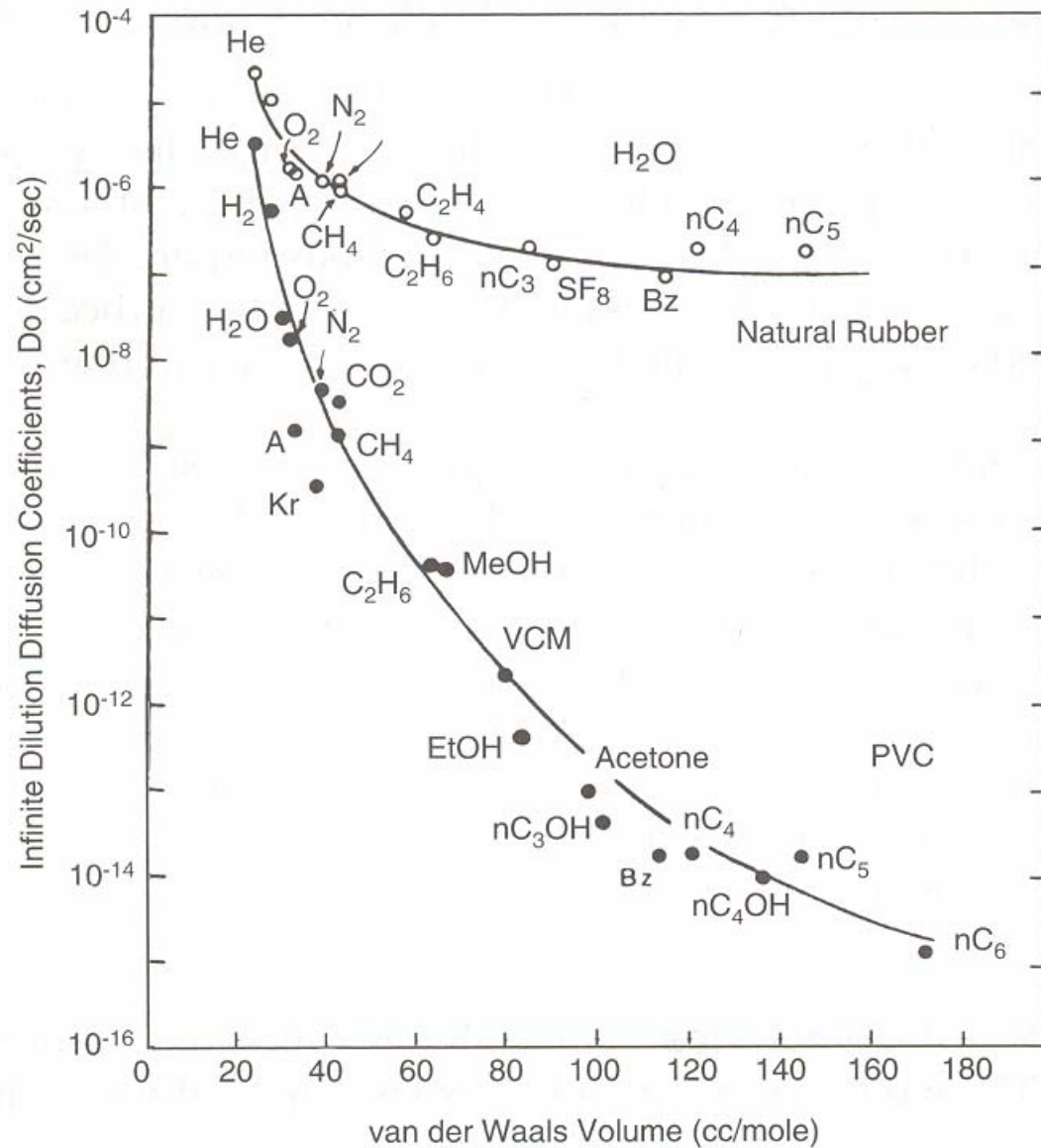
Permselectivity of polymer membranes and gas separations

If the permeabilities of 2 gases in one polymer are different then this polymer may be used to separate the gases to some extent. This is property of the polymer described by the gas selectivity, $\alpha_{A/B}$.

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

Open circles are for rubbery polymers and closed circles are for glassy polymers. Upper bound is an empirical relation.

Gas permeability in polymer blends

- The gas permeability in polymer blends where one component is dispersed in the other component will fall in between upper and lower bounds defined by the parallel and series models respectively

Upper bound:
$$P_b = \phi_1 P_1 + \phi_2 P_2$$

Lower bound:
$$P_b = \frac{P_1 P_2}{\phi_1 P_1 + \phi_2 P_2}$$

The permeability of a blend can be maximized if the continuous phase is made up of the polymer with the higher permeability.