Assessing transport properties of polymers by experimental techniques and simulation methods

Ulf W. Gedde*
Royal Institute of Technology
School of Chemical Science & Engineering
Fibre & Polymer Technology
SE–100 44 Stockholm, Sweden

gedde@polymer.kth.se

Outline

- Fundamentals, areas of interest
- Experimental methods
- Analysis of experimental data
- Examples
- Simulation

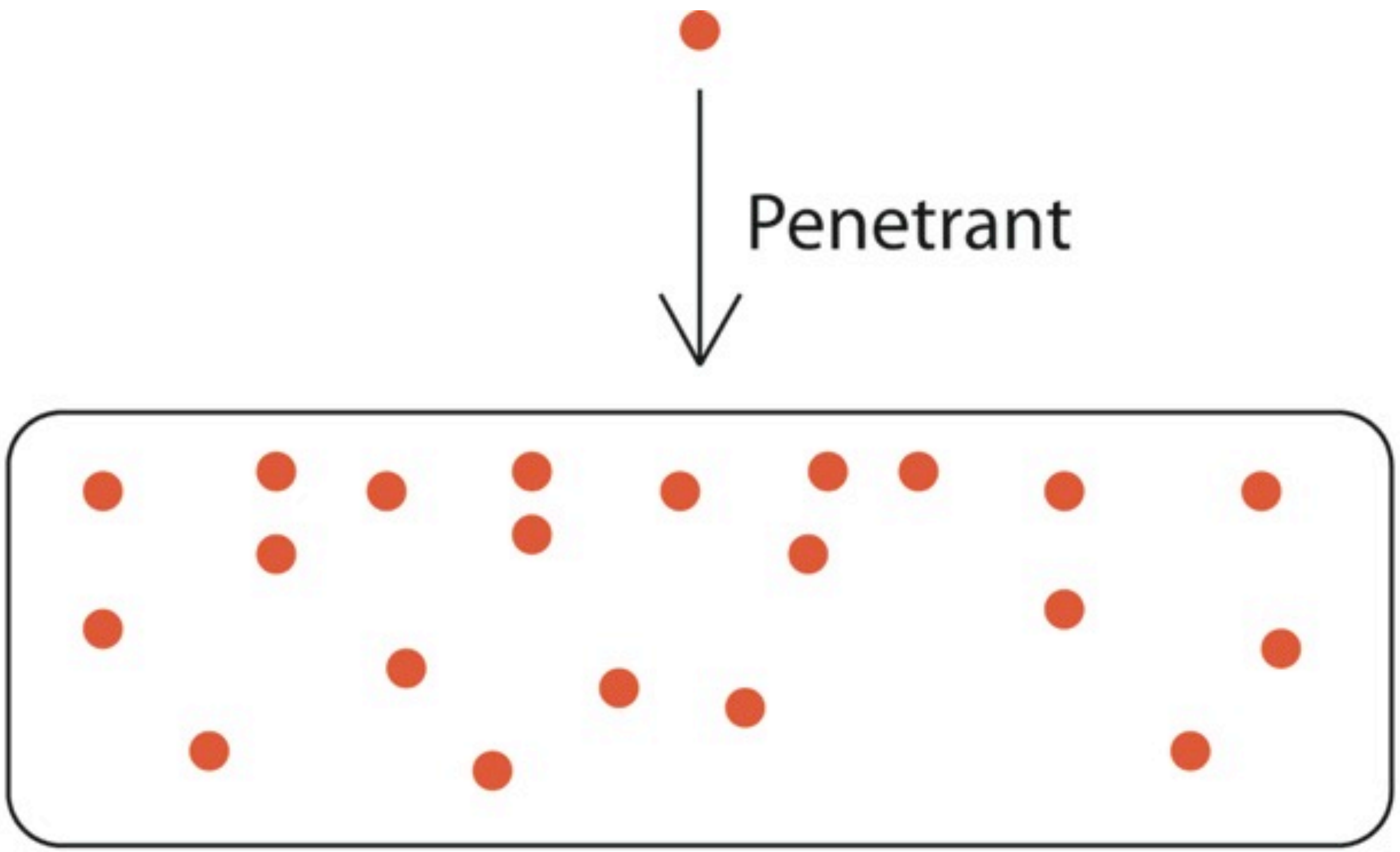
What is it?

Diffusivity (*D*)

Solubility (*S*)

Permeability (*P*= *DS*)

Polymer complexity



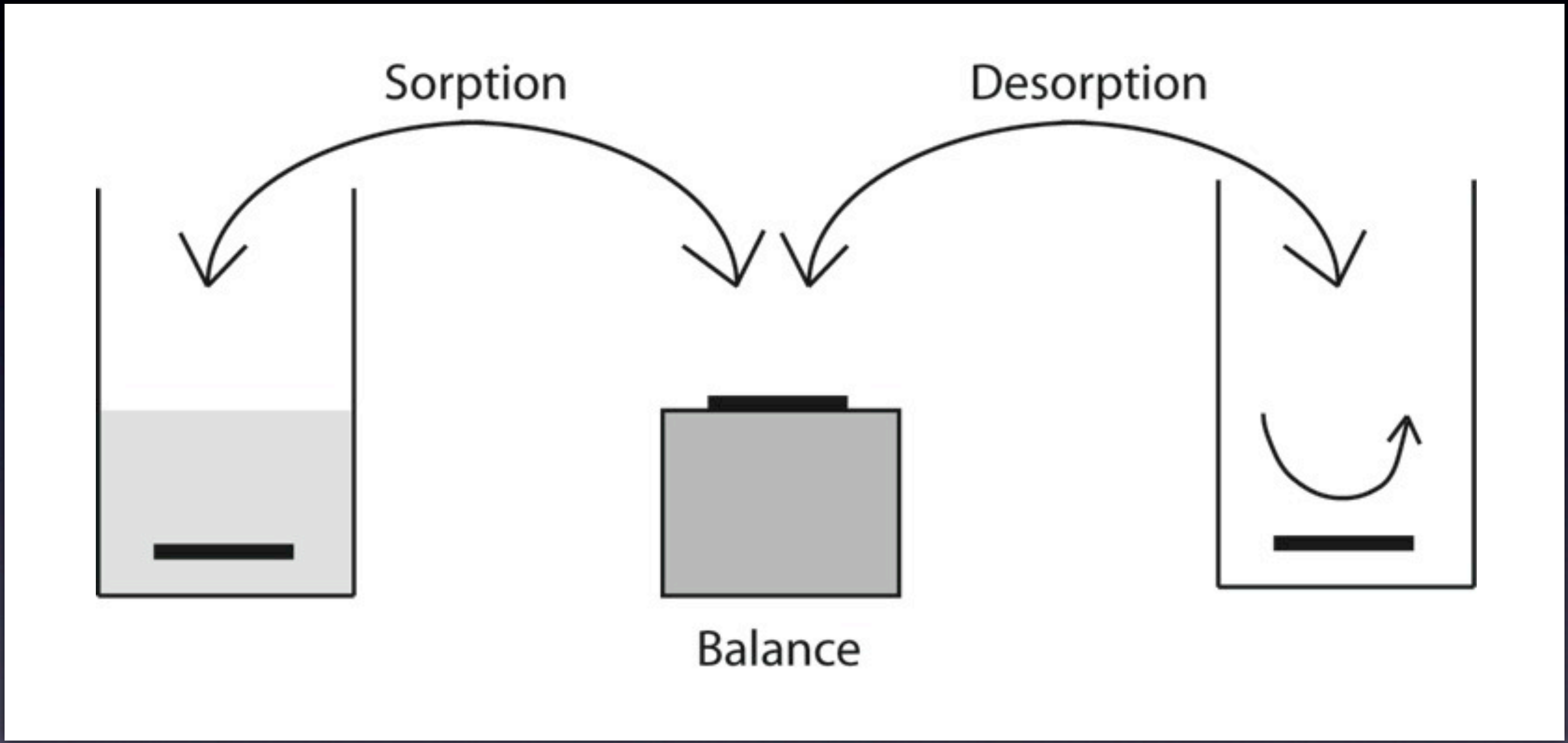
Structure change (increase in free volume, crystal melting, etc))
Swelling (dimensional changes; internal stresses)

Interest areas

- Food packaging
- Long-term performance of hot-water pipes
- Fuel systems
- Slow release of drugs
- PVC cables in nuclear power plants

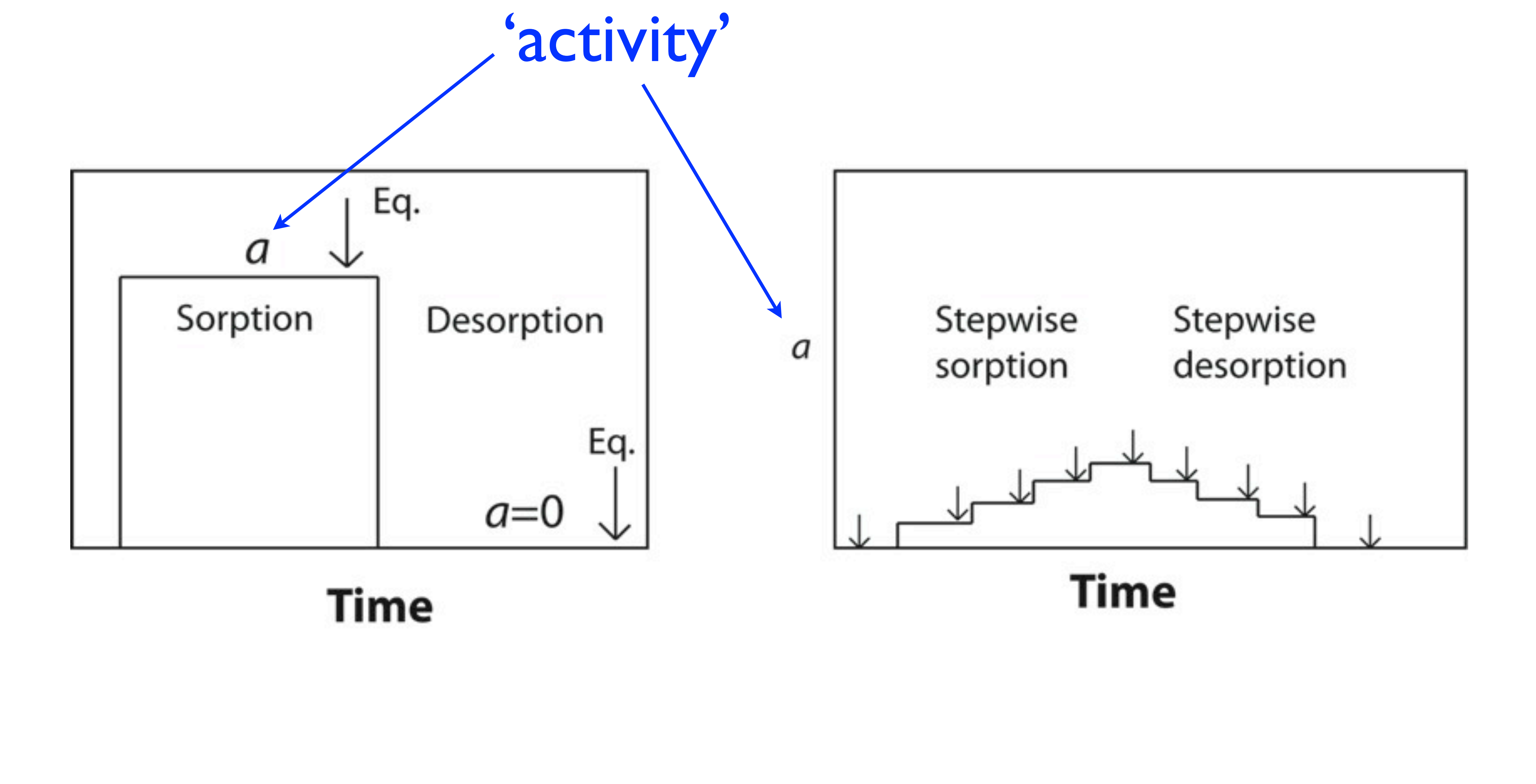
Experiments

Gravimetry

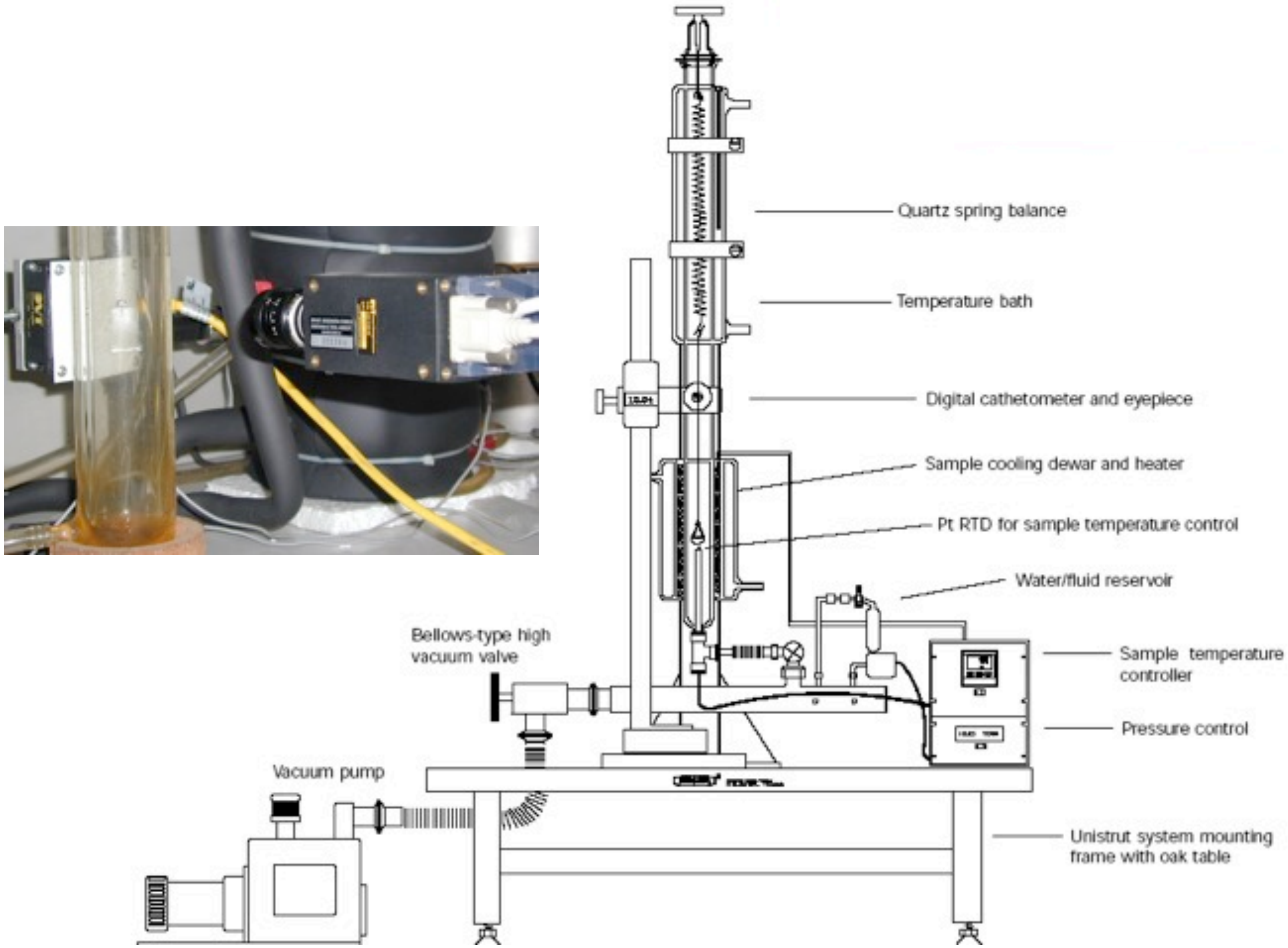


(a) Balance (1–100 μg)
(b) TGA (0.1 μg)
(c) Quartz crystal (1 ng)

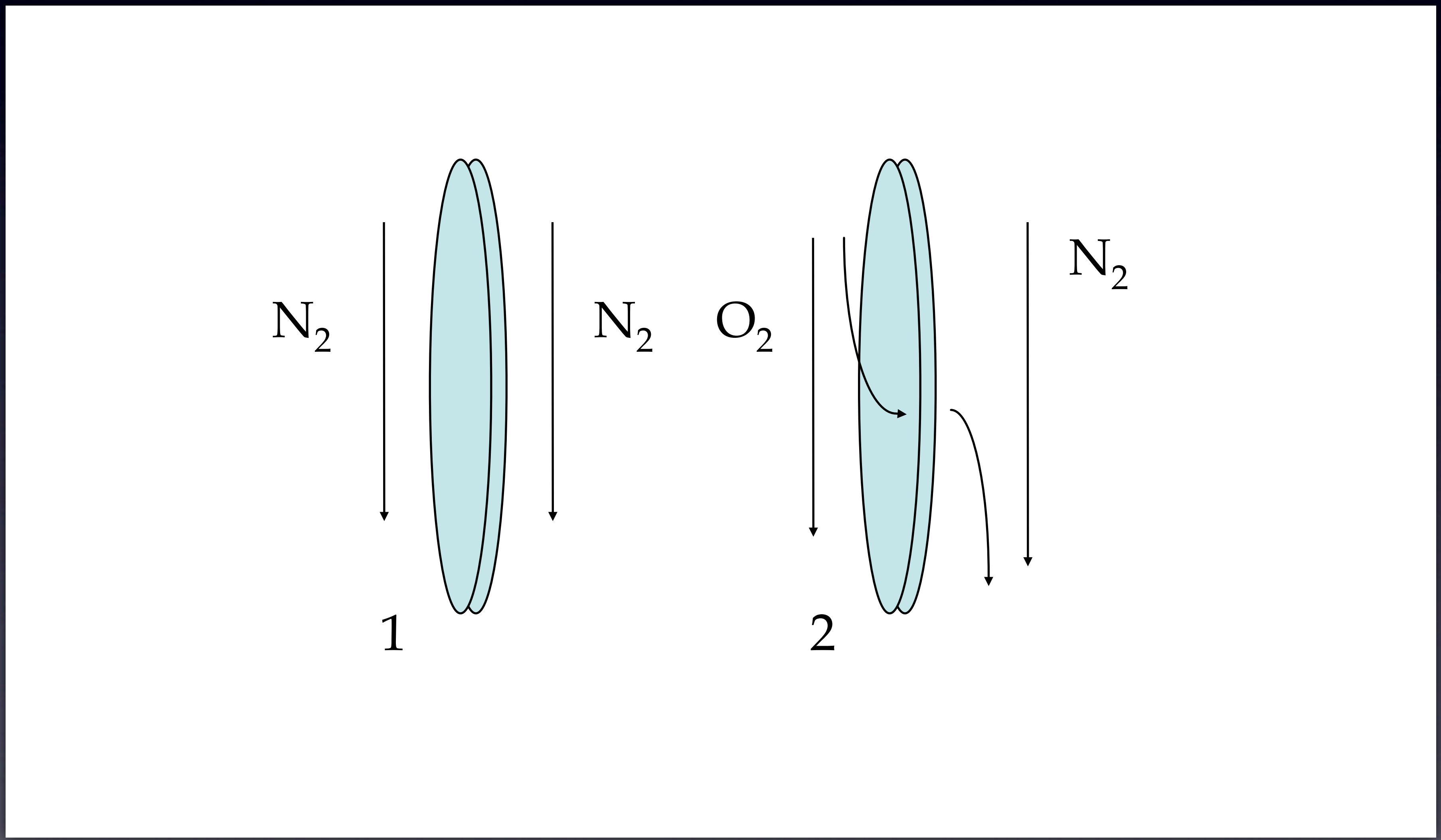
Experiments



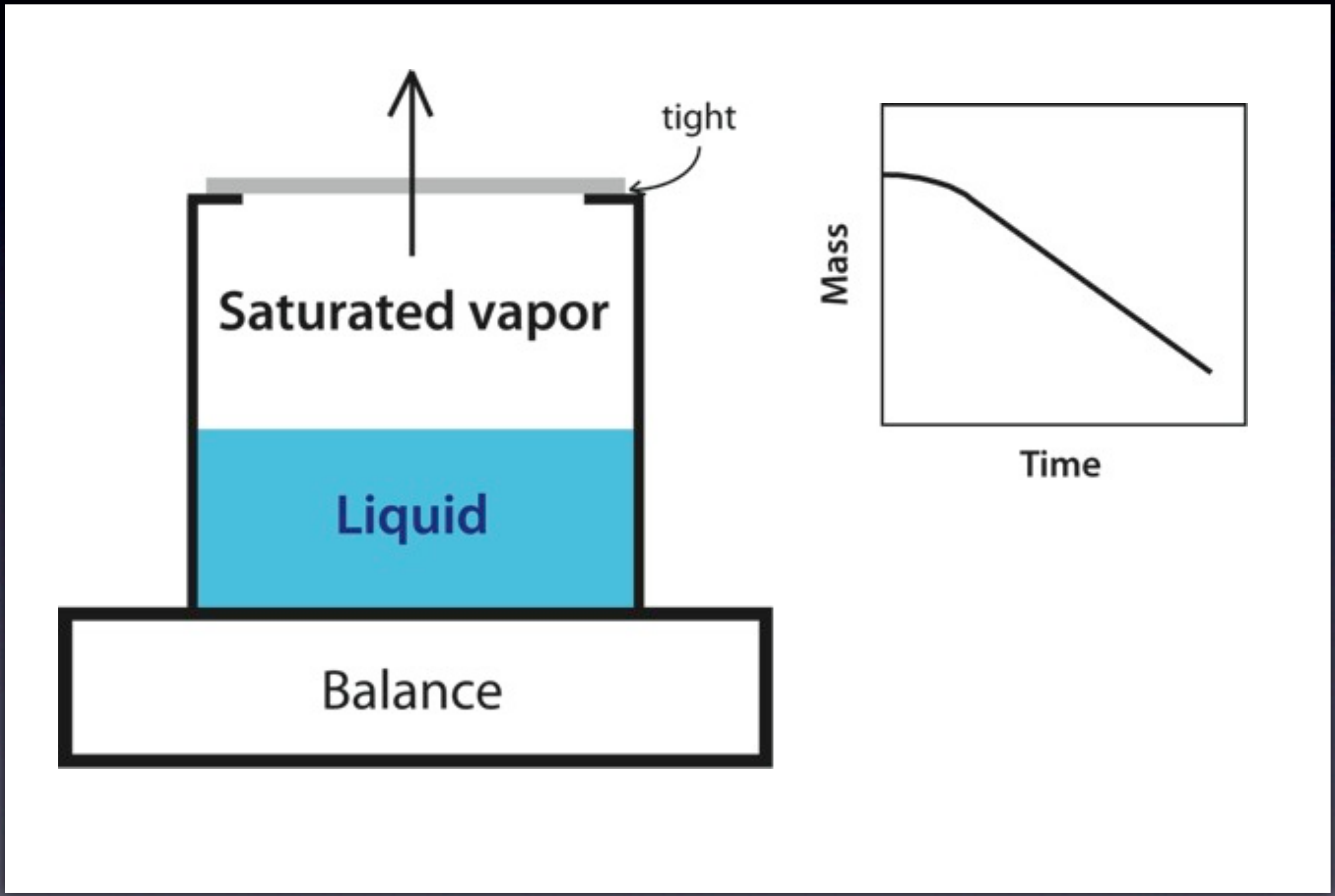
Quartz spring balance



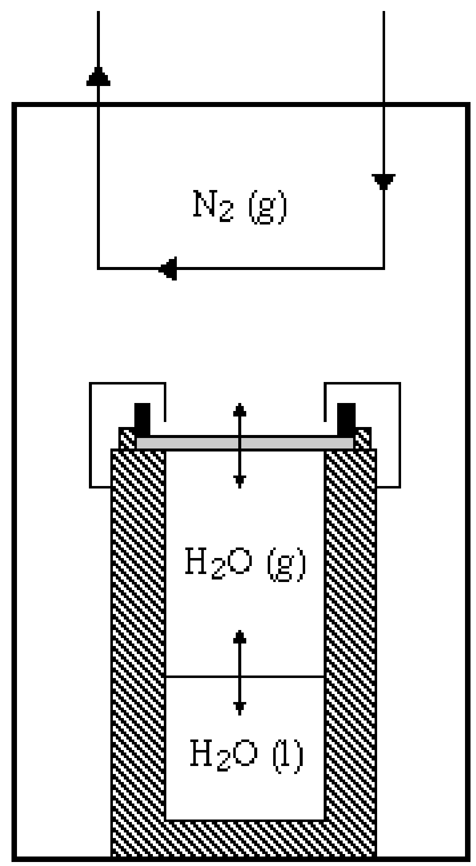
Oxygen transmission



Cup method

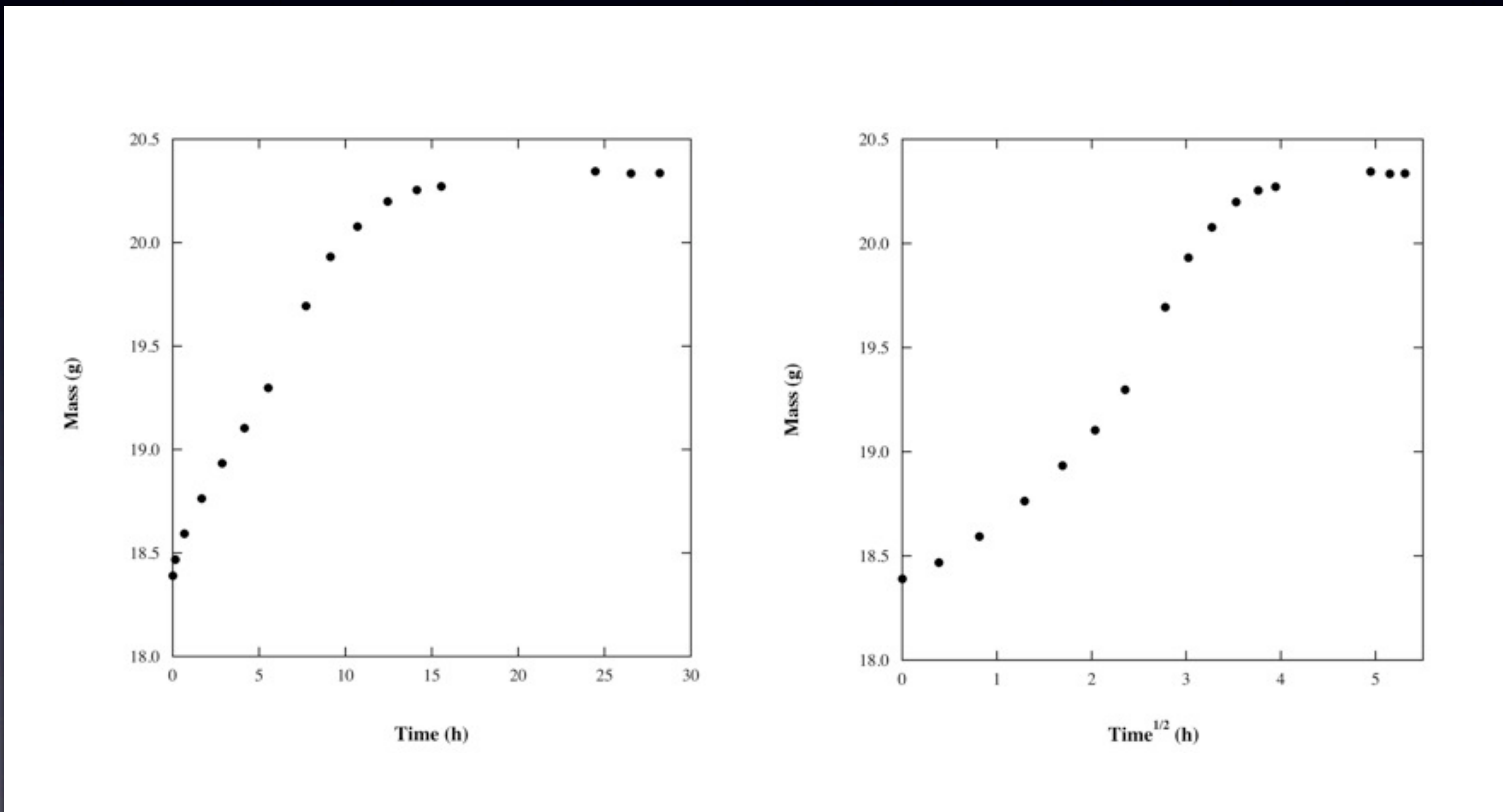


Microcalorimetry

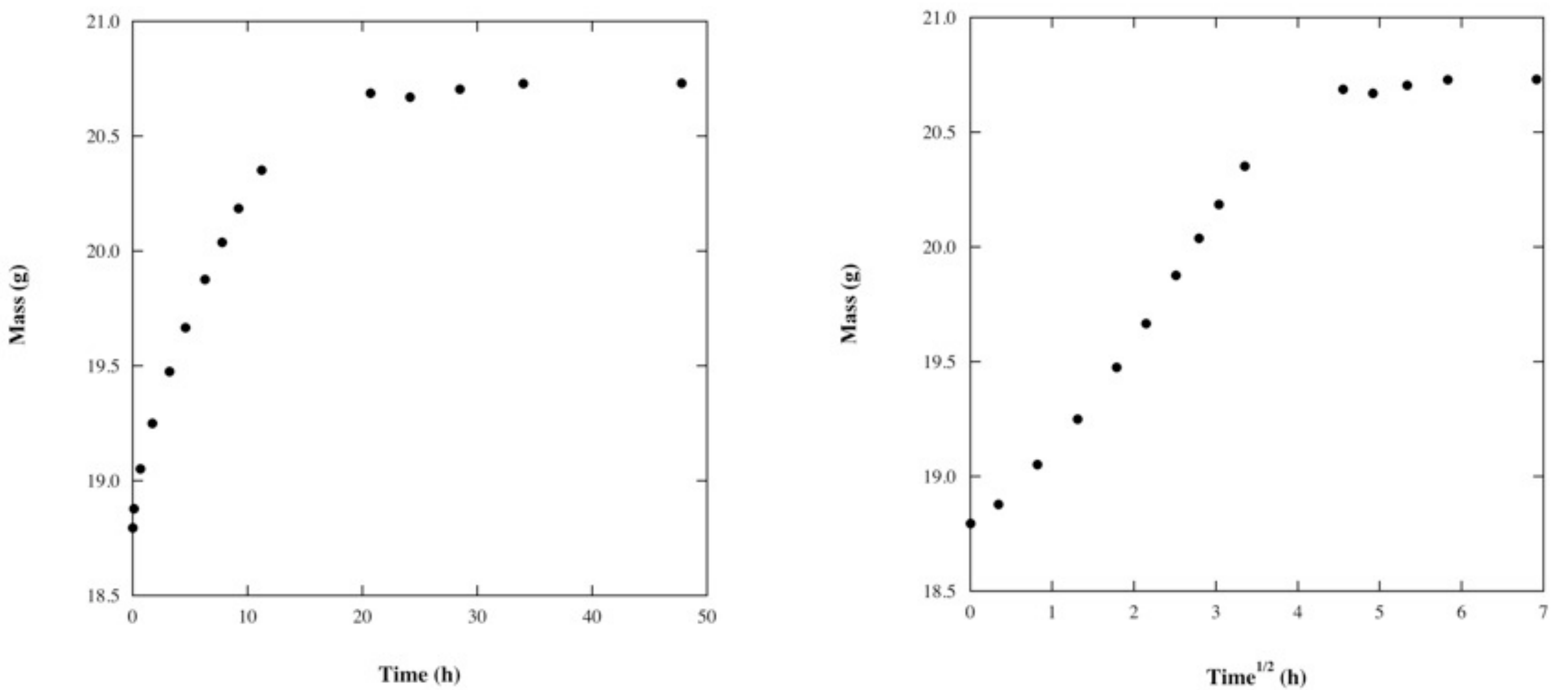


$$Q_o = \frac{P_e M l}{\Delta H_v A \Delta p}$$

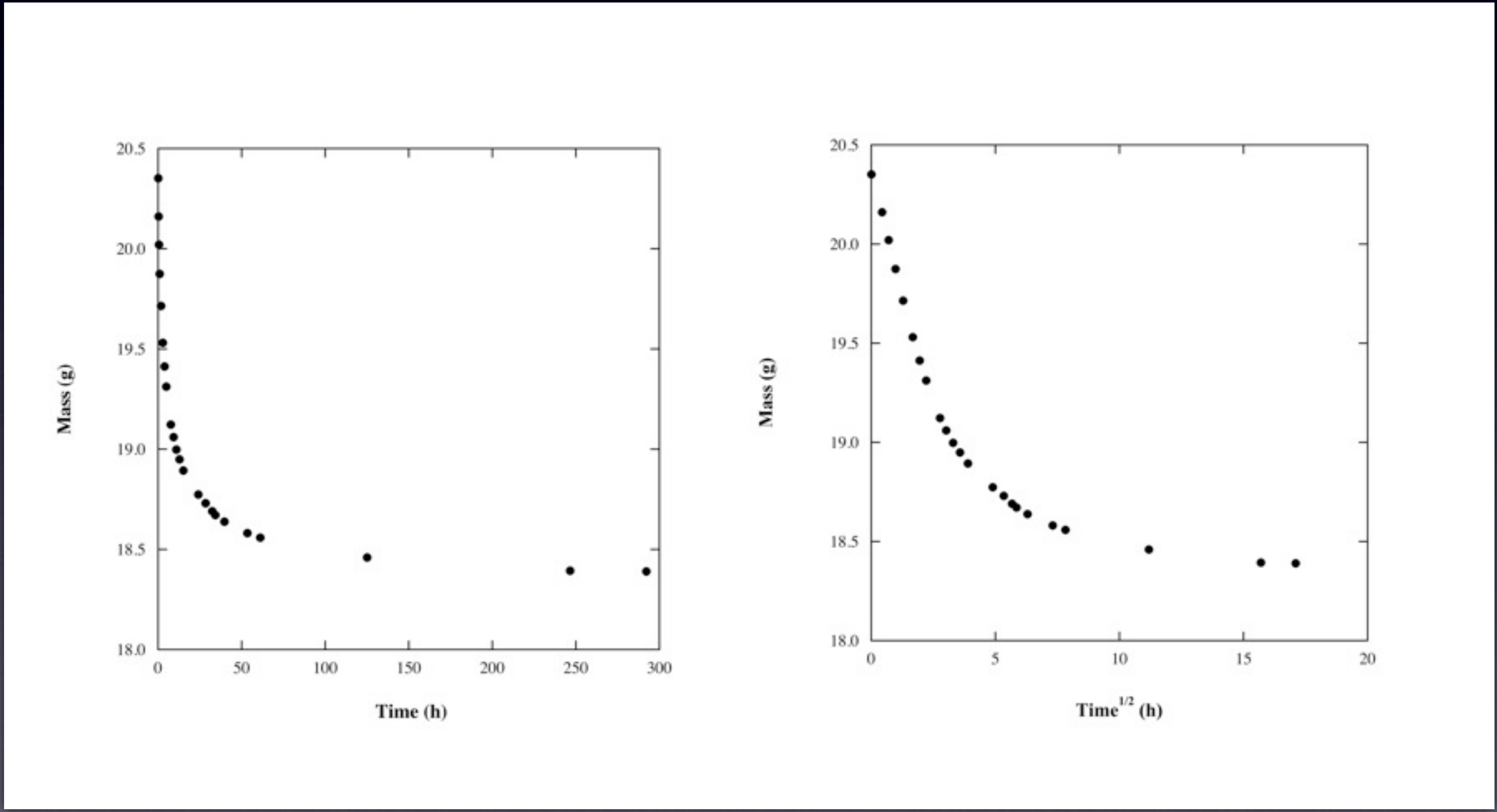
Sorption: PE – hexane



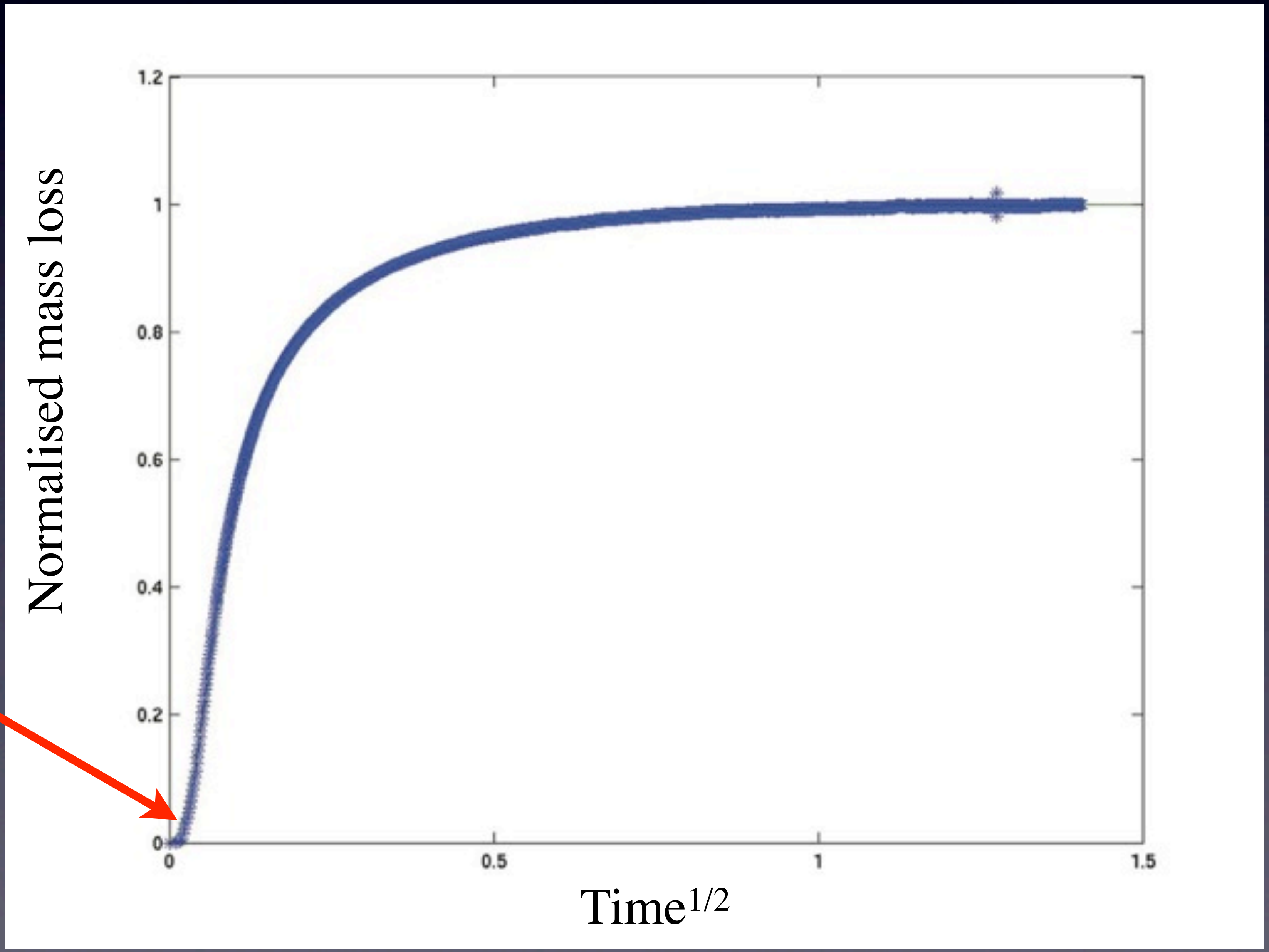
Sorption: NR – hexane



Desorption: PE-hexane



TG- methanol desorption



Initial 'problem'

Calculations
Equations

Overview

- Fickian equations
- Boundary conditions (outer and inner boundaries)
- Starting conditions

Diffusion equations

$$F_x = -D\frac{\partial C}{\partial x}$$

Fick's 1:st law

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

Fick's 2:nd law

$$D(C) = D_0 e^{\alpha C}$$

Exponential equation

$$D_\mathrm{T} = A \times \exp\left(-B_\mathrm{d}/f_2\right) \times \exp\left(\left(B_\mathrm{d} v_1^\mathrm{a}\left(f_1 - f_2\right)\right) \Big/ \left(f_2\left(f_2 + v_1^\mathrm{a}\left(f_1 - f_2\right)\right)\right)\right)$$

Free volume exponential

Outer boundary

$C_b = 0$ — Evaporation, fast

$C_\mathrm{b} = C_{\mathrm{b},0}\mathrm{e}^{-\beta t}$ from $\left(\partial C_\mathrm{b}/\partial t\right) = -\beta C_\mathrm{b}$ — Evaporation, slower low gradient

$$D\left(C_b\right)\left(\frac{\partial C}{\partial x}\right)_{x=0} = F_0 C_b$$

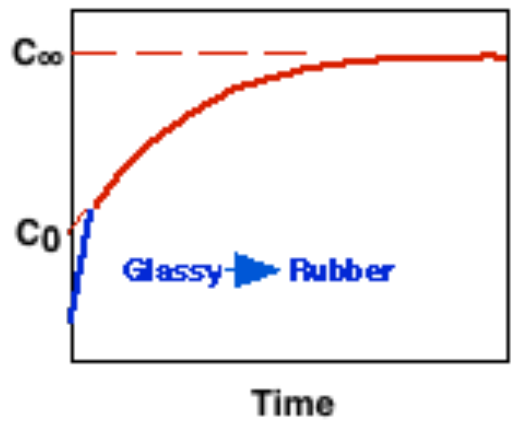
Evaporation, slower Ficks first law

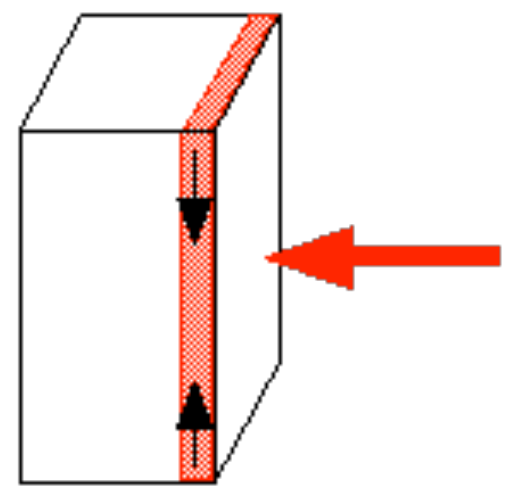
$$D\left(C_b\right)A\left(\frac{\partial C}{\partial x}\right)_{x=0} = V_0 k_r K C_b$$

Towards liquid, slower Ficks first law

Explicit time-dependent boundary conditions

$$C = C_0 + \left(C_\infty - C_0\right)\cdot\left(1 - e^{-t/\tau}\right)$$





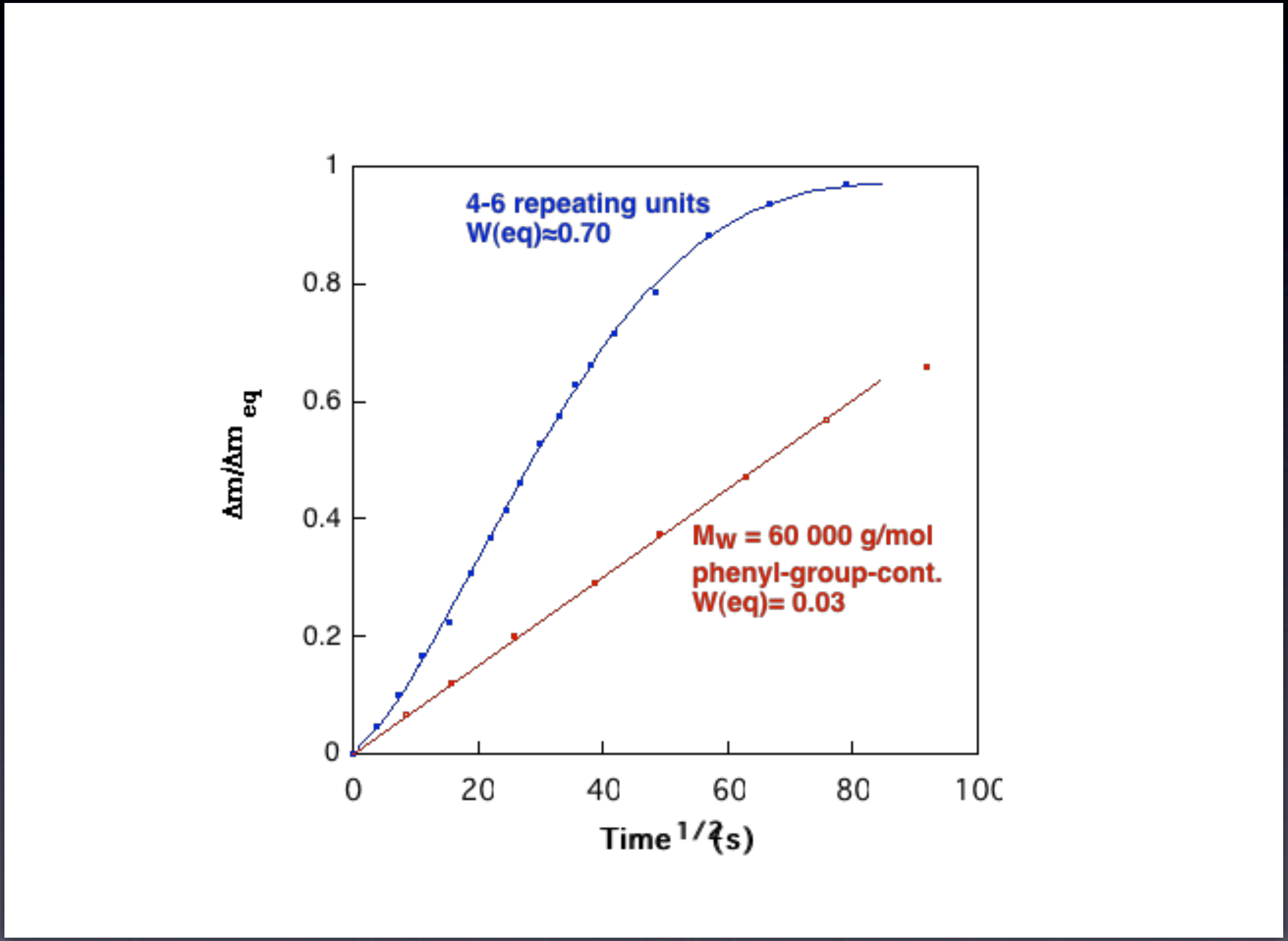
Swelling-induced stresses

$$K_\tau = \sum_{i=1}^{3} \frac{\sigma_i(C)}{\sigma_\Sigma(C)} e^{-\frac{t}{\tau_i(C)}}$$

$$C = C_o + \left(C_\infty - C_o\right)\left(1 - K_\tau\right)$$

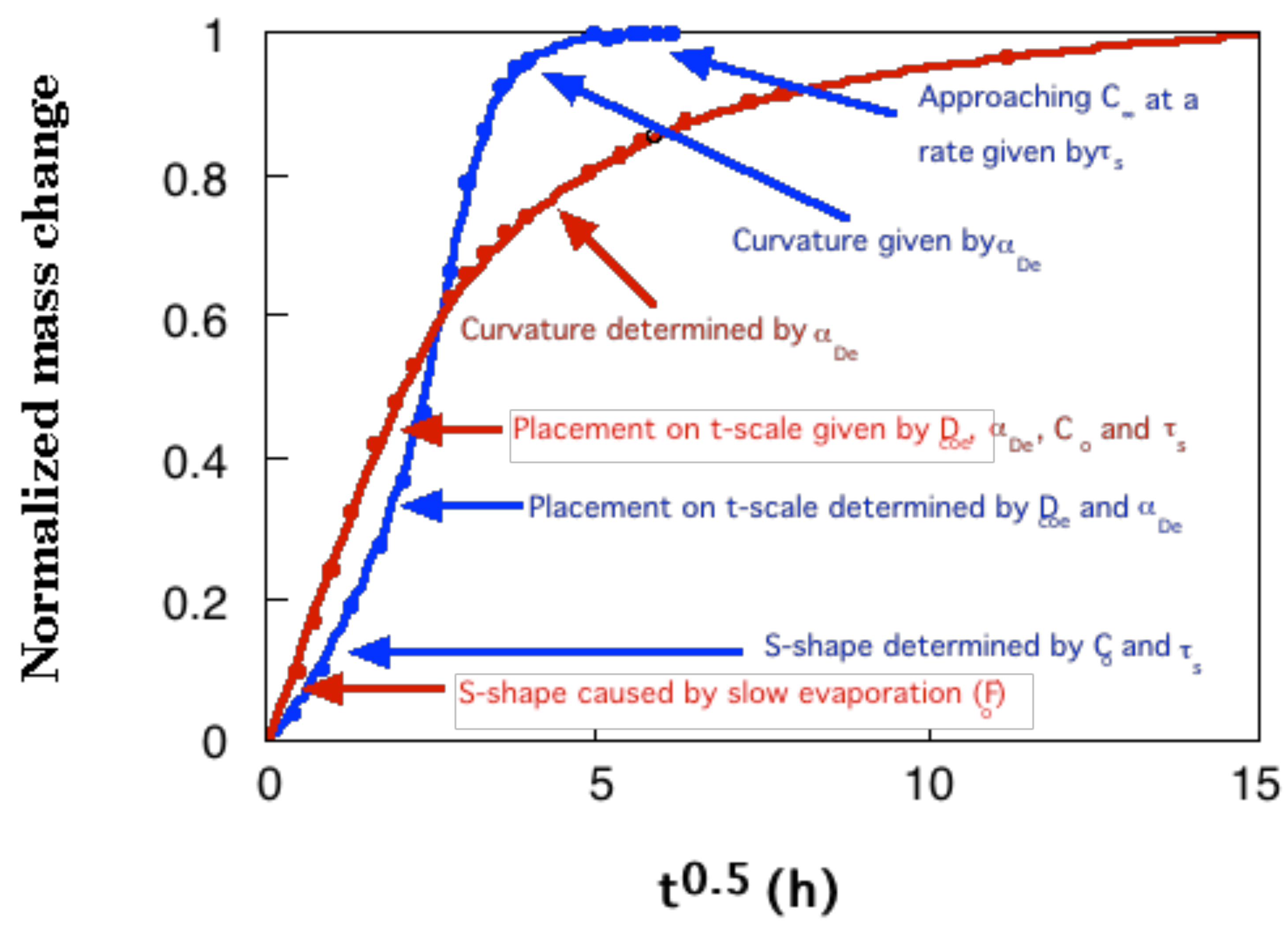
Examples

Sorption: SR – PDMS



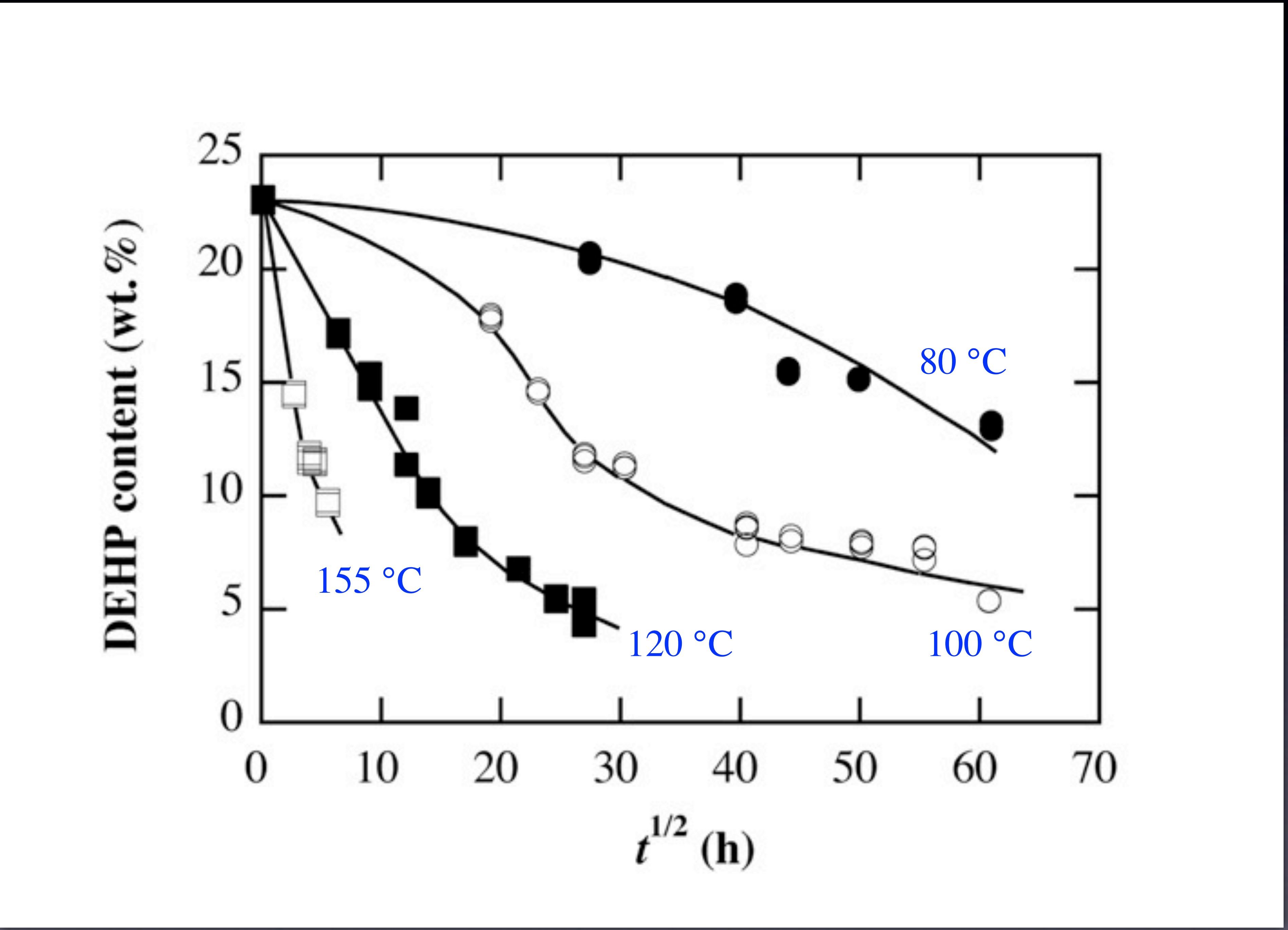
U. W. Gedde, A. Hellebuyck, M. Hedenqvist, *Polym. Eng. Sci.*, **36**, 2077 (1996).

Sorption/desorption



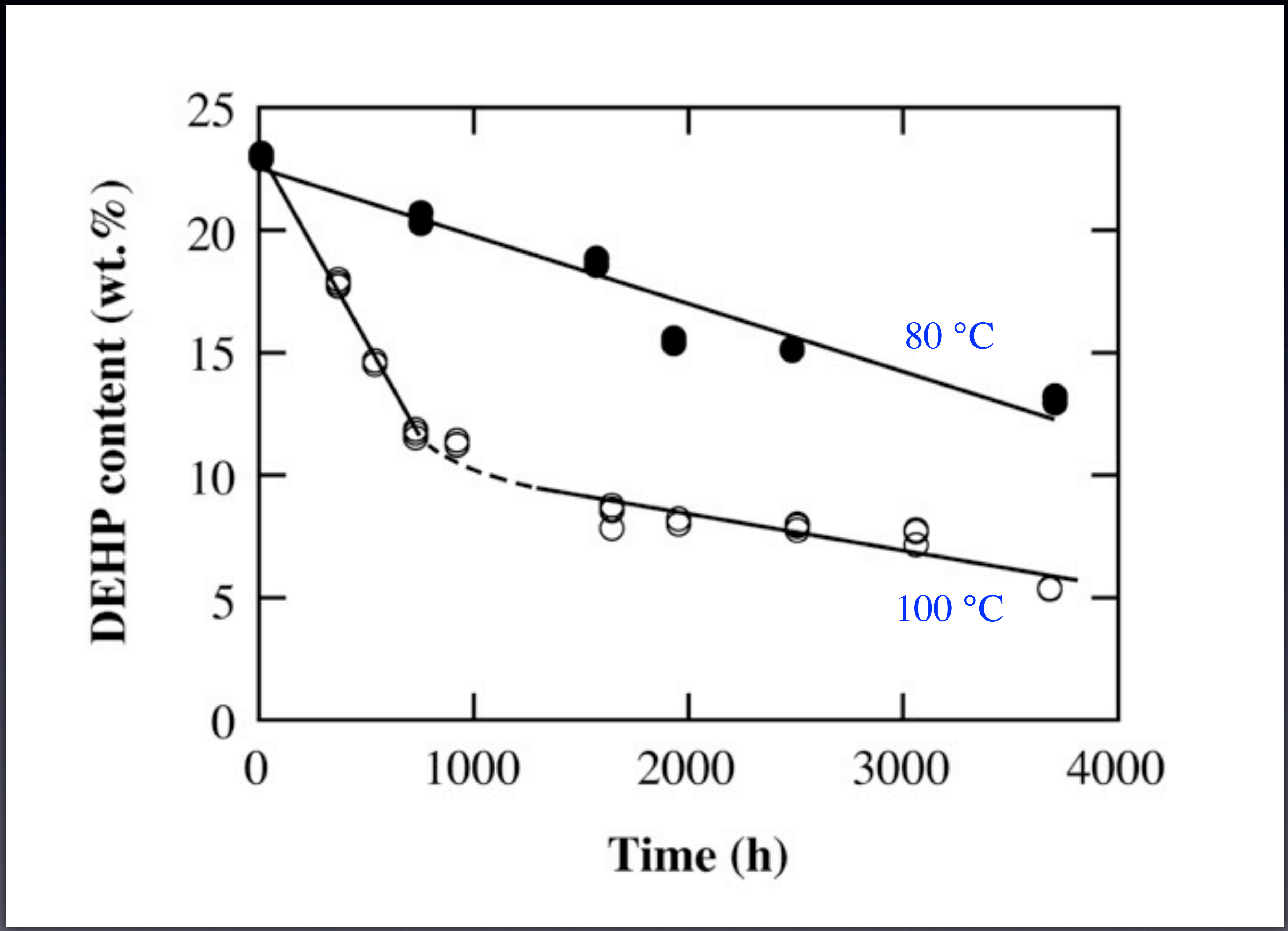
M. S. Hedenqvist, U. W. Gedde, *Polymer*, **40**, 2381 (1999).

DEHP from P-PVC



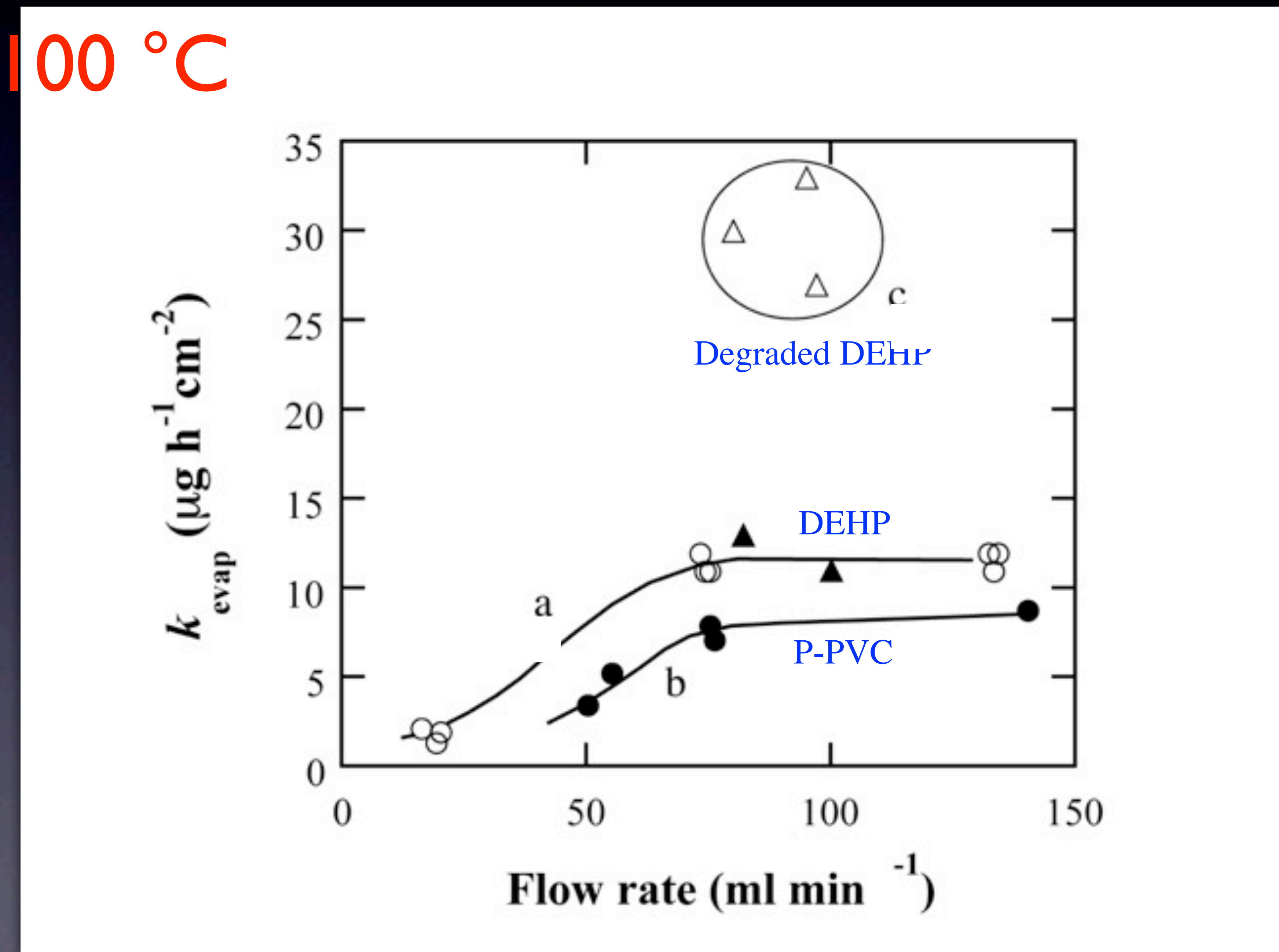
M. Ekelund, B. Azhdar, M.S. Hedenqvist and U. W. Gedde, *Polym. Degrad. Stab.*, 93, 1704 (2008).

PPVC–DEHP



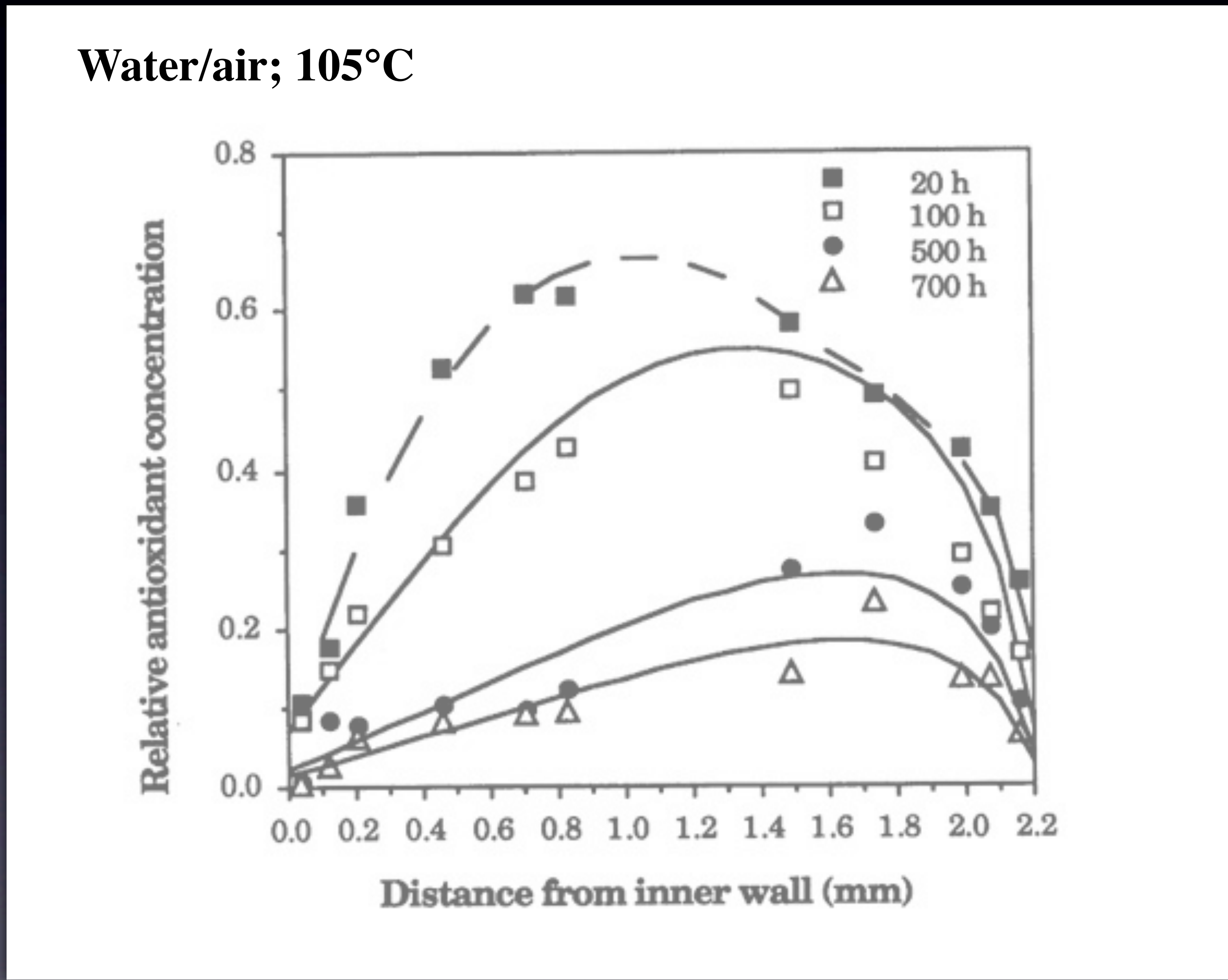
M. Ekelund, B. Azhdar, M.S. Hedenqvist and U. W. Gedde, *Polym. Degrad. Stab.*, 93, 1704 (2008).

DEHP loss rate



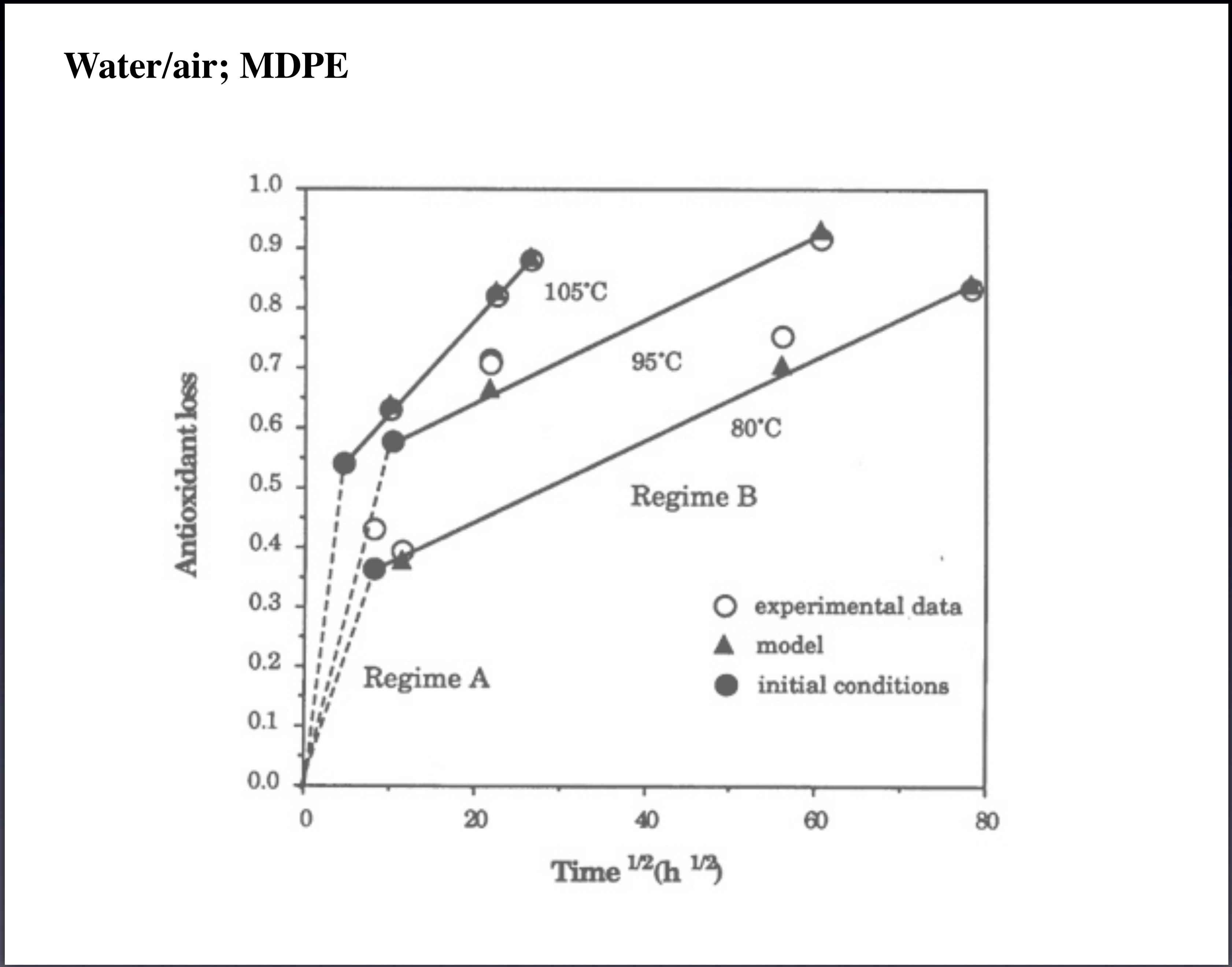
M. Ekelund, B. Azhdar, U.W. Gedde, Polym. Degrad. Stab., submitted (2010)

Antioxidant loss



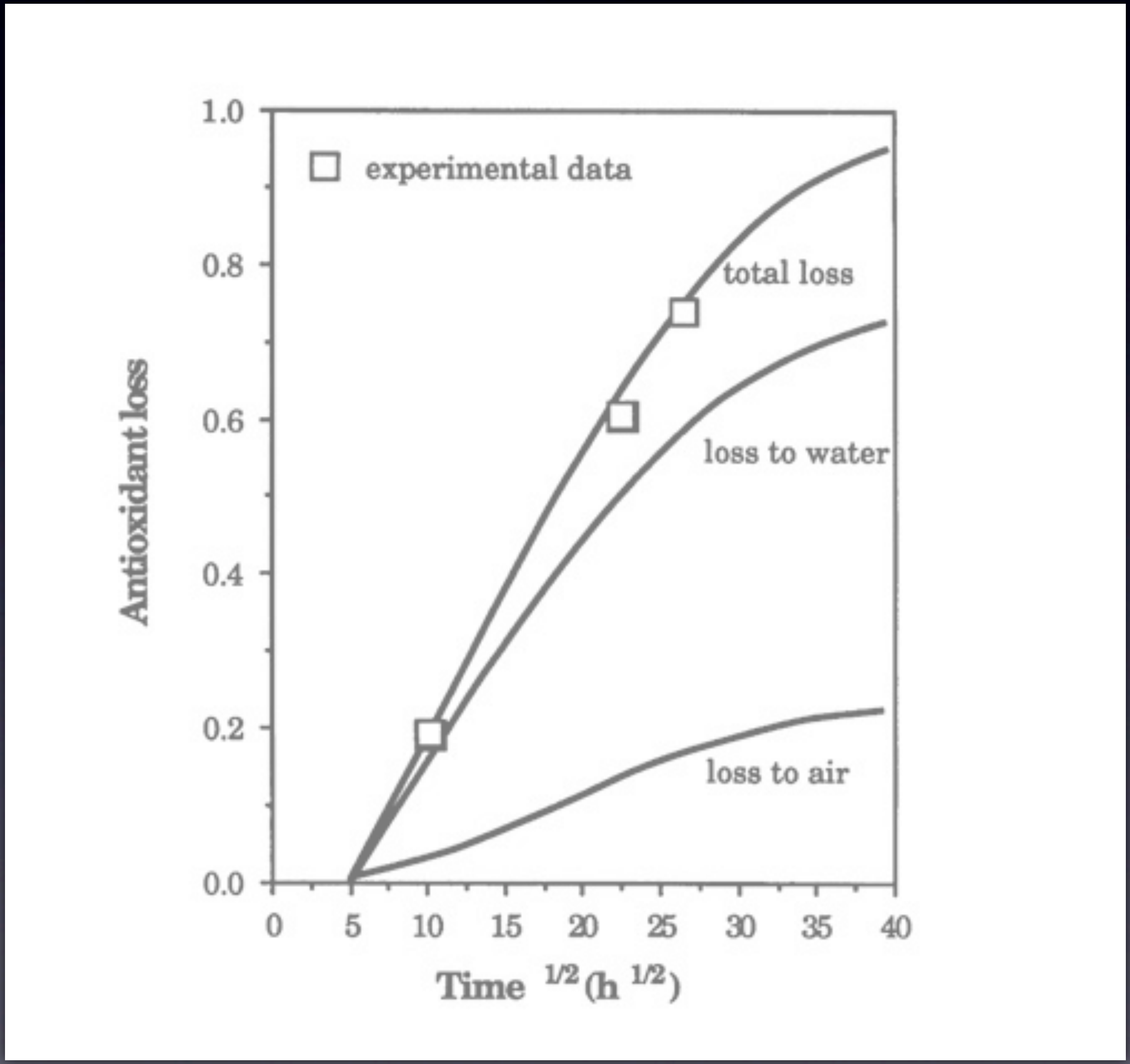
G.D. Smith K. Karlsson, U.W. Gedde, Polym. Eng. Sci. 1992;32:658.

Antioxidant loss



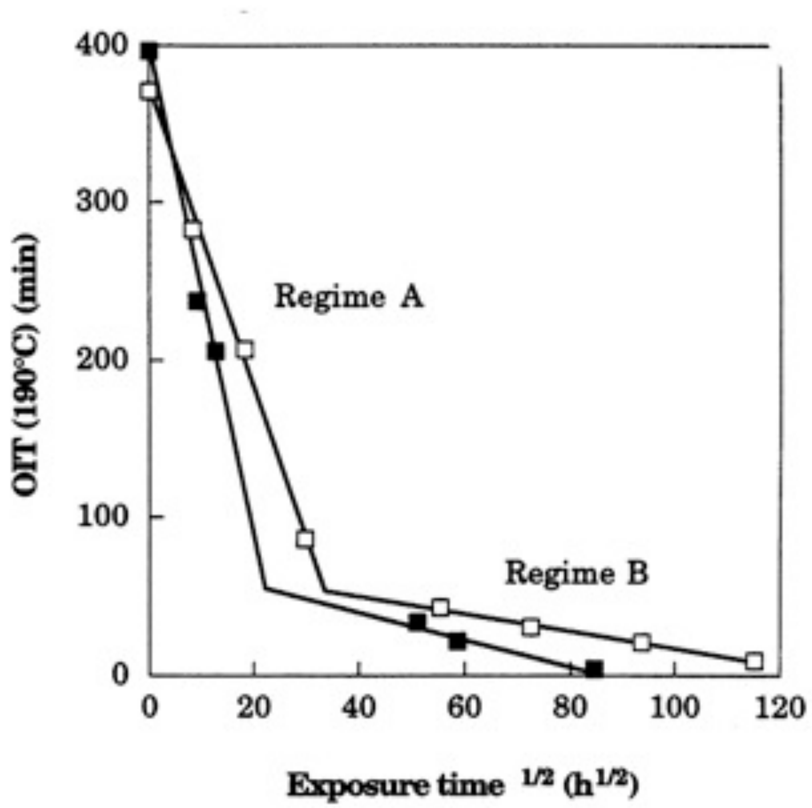
G.D. Smith K. Karlsson, U.W. Gedde, Polym. Eng. Sci. 1992;32:658.

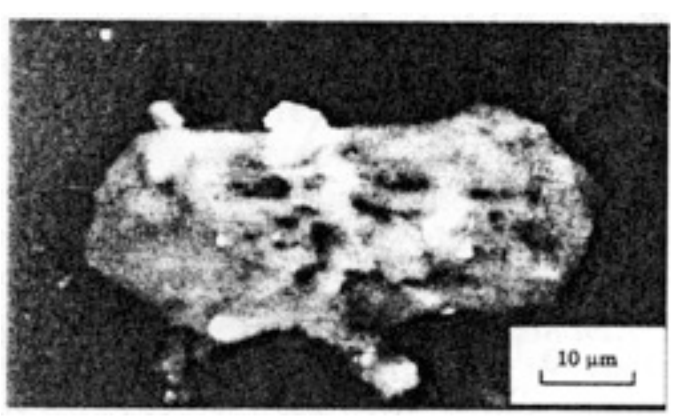
Loss to different media

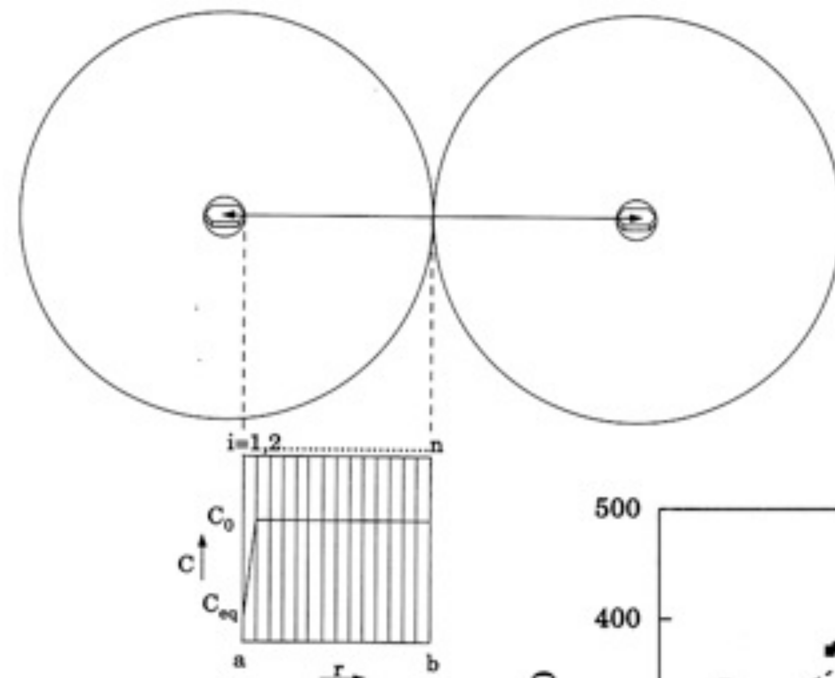


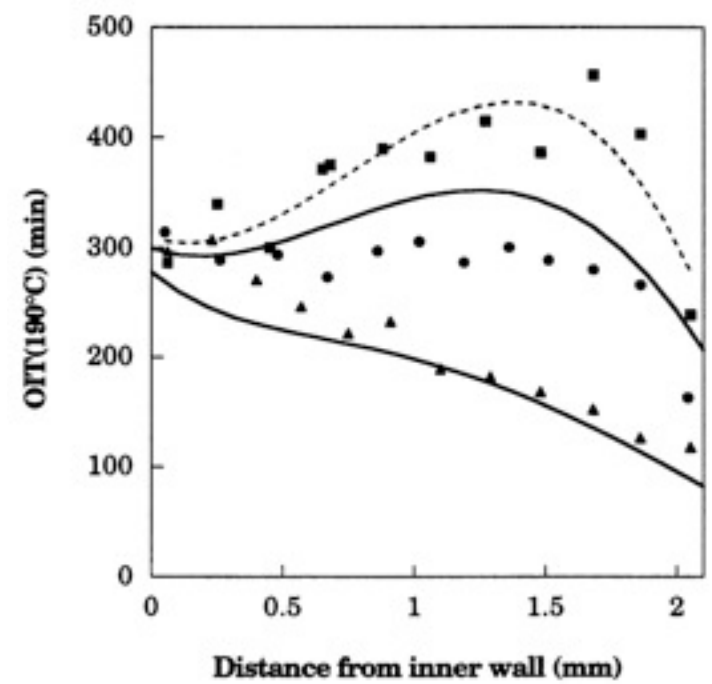
G.D. Smith K. Karlsson, U.W. Gedde, Polym. Eng. Sci. 1992;32:658.

Internal precipitation









J. Viebke, M. Hedenqvist, U. W. Gedde, *Polym. Eng. Sci.*, **36**, 2896 (1996).

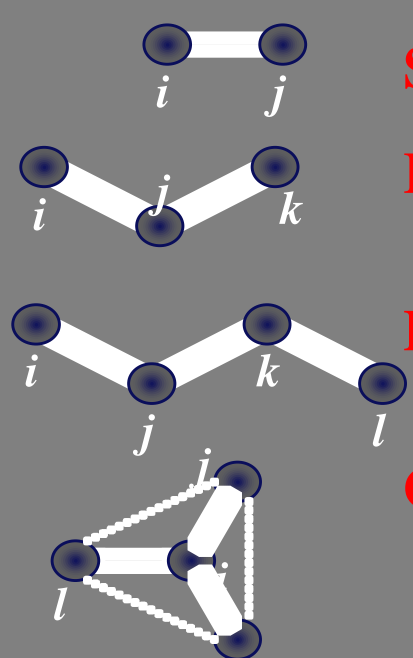
Simulation

MD simulation

$$\mathbf{f}_i = -\nabla_{\mathbf{r}_i} V$$

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$$

Calculate forces
Move atoms
Temp. & Pressure
REPEAT

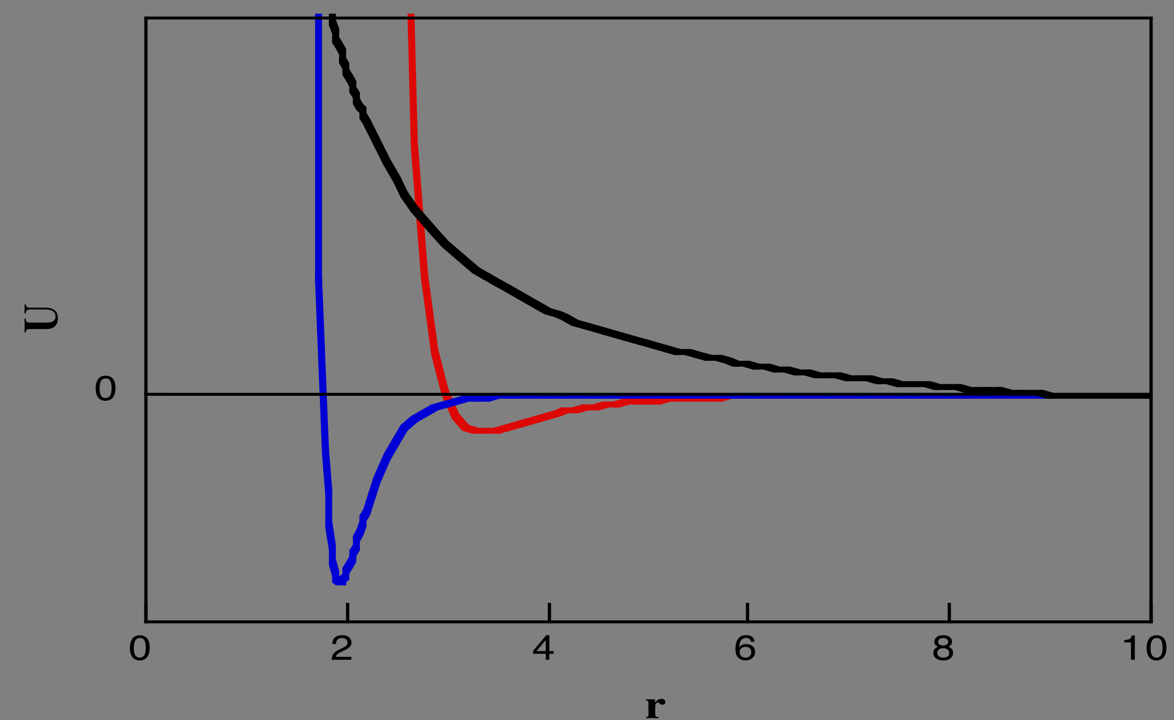


Stretch

Bend

Dihedral (torsions)

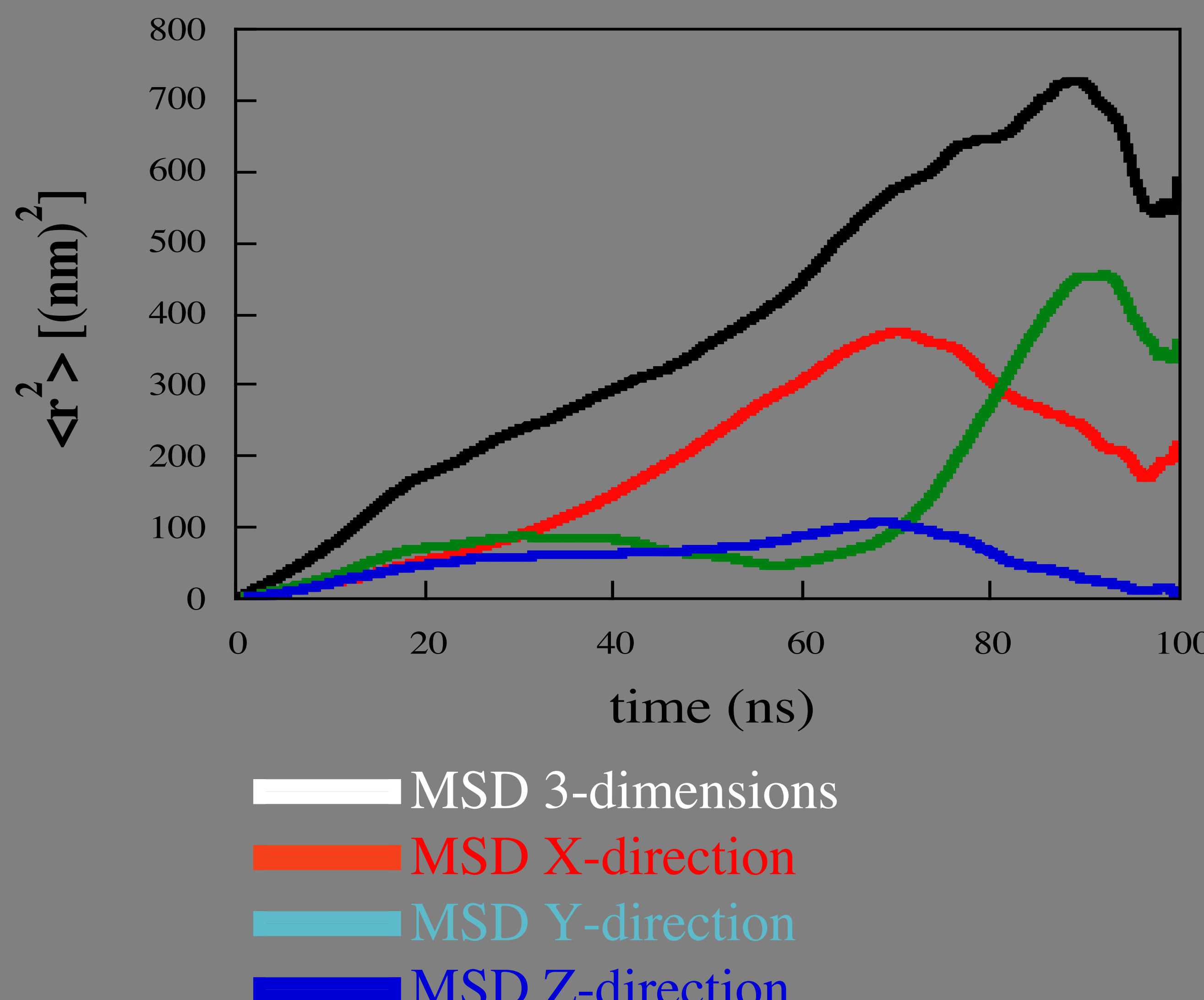
Out of plane

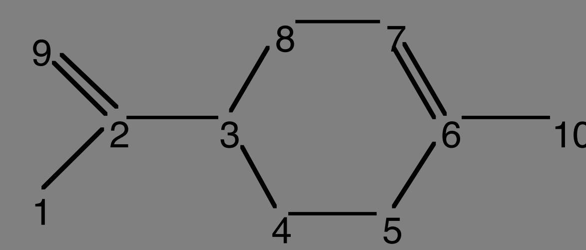


- Lennard-Jones potential between all* atoms
- H-bond: strong with short range
- Electrostatic between all charged atoms

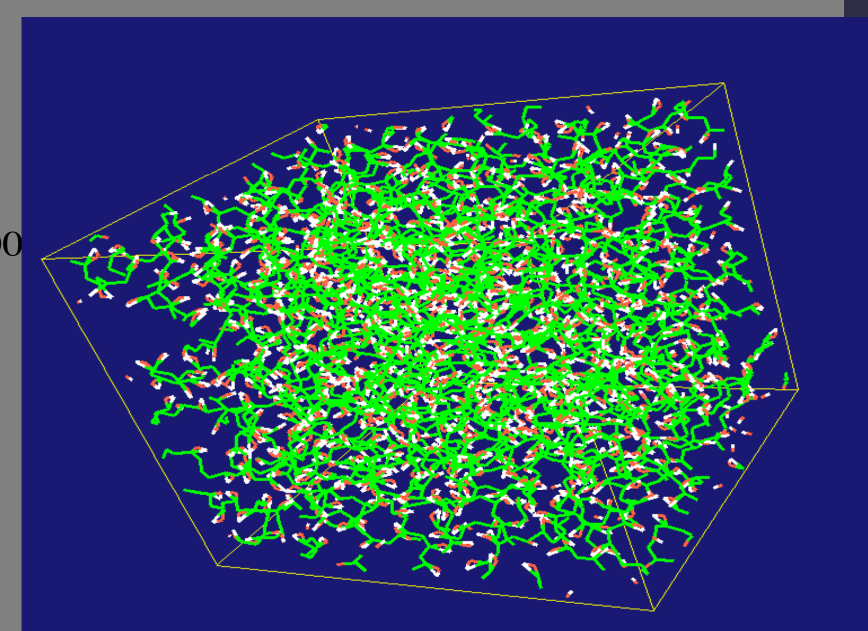
* Except H-bond

Limonene in PE



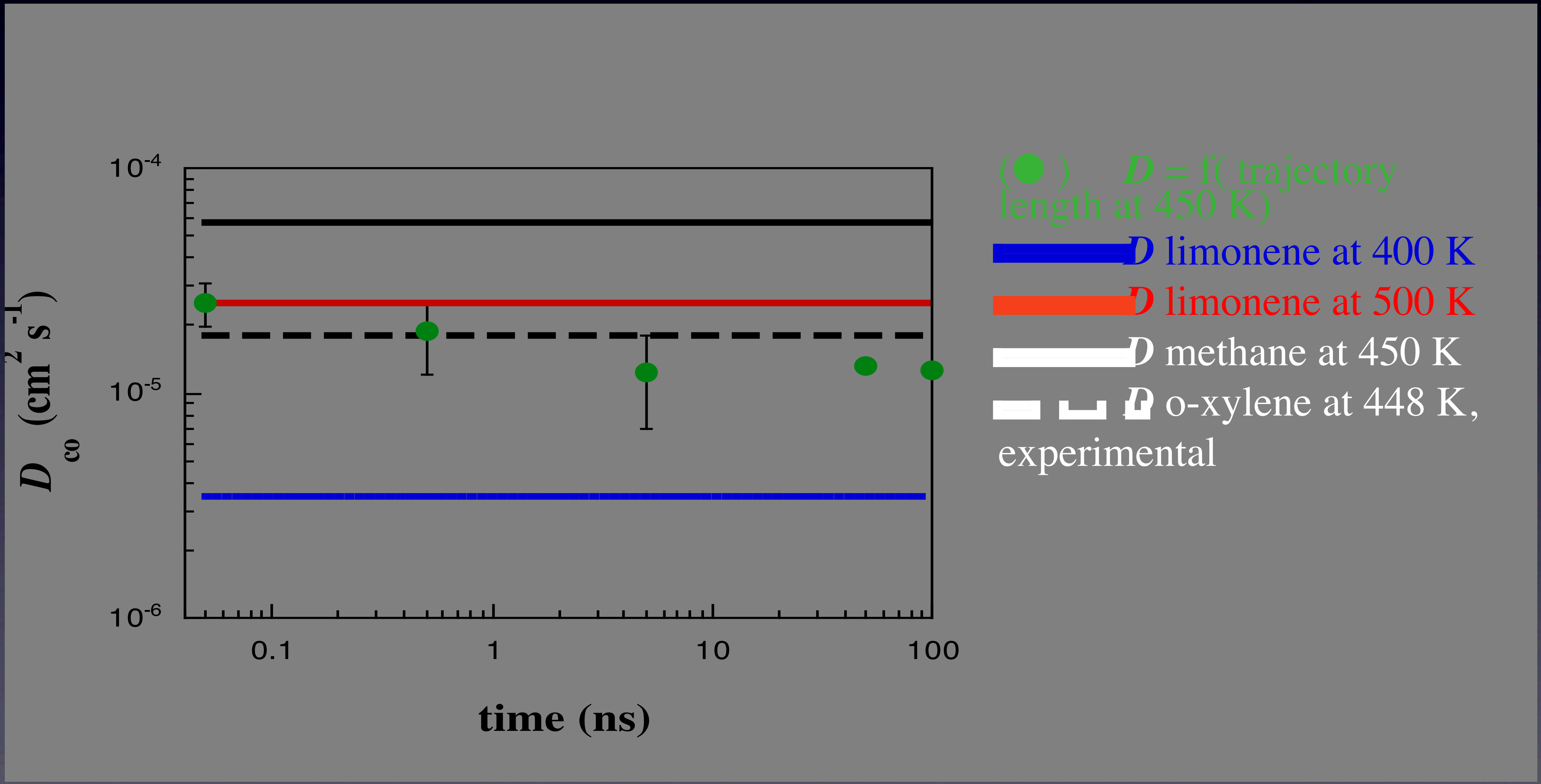


Limonene



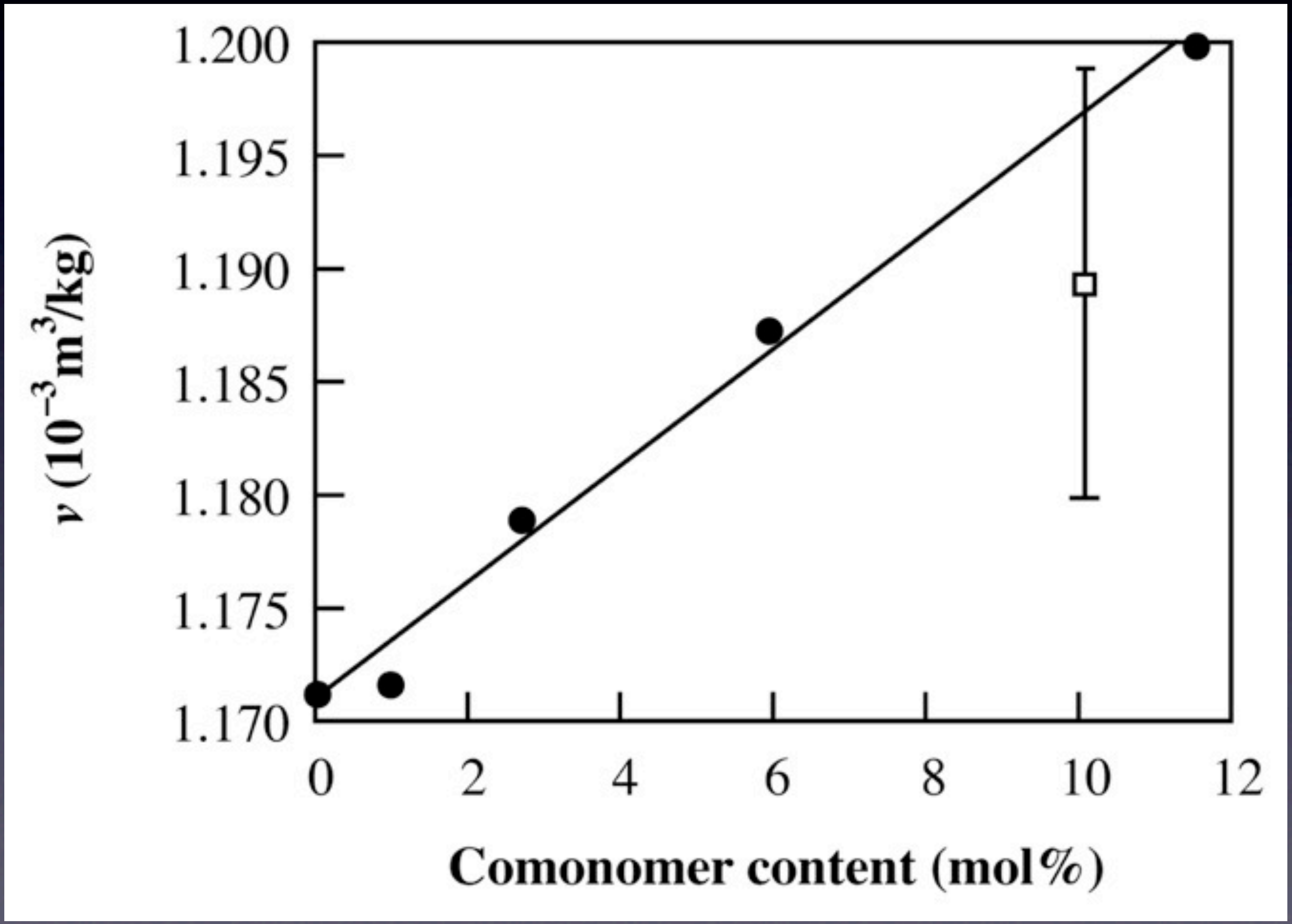
G. E. Karlsson, T. S. Johansson, U. W. Gedde, M. S. Hedenqvist, *Macromolecules*, **35**, 7453 (2002).

D prediction



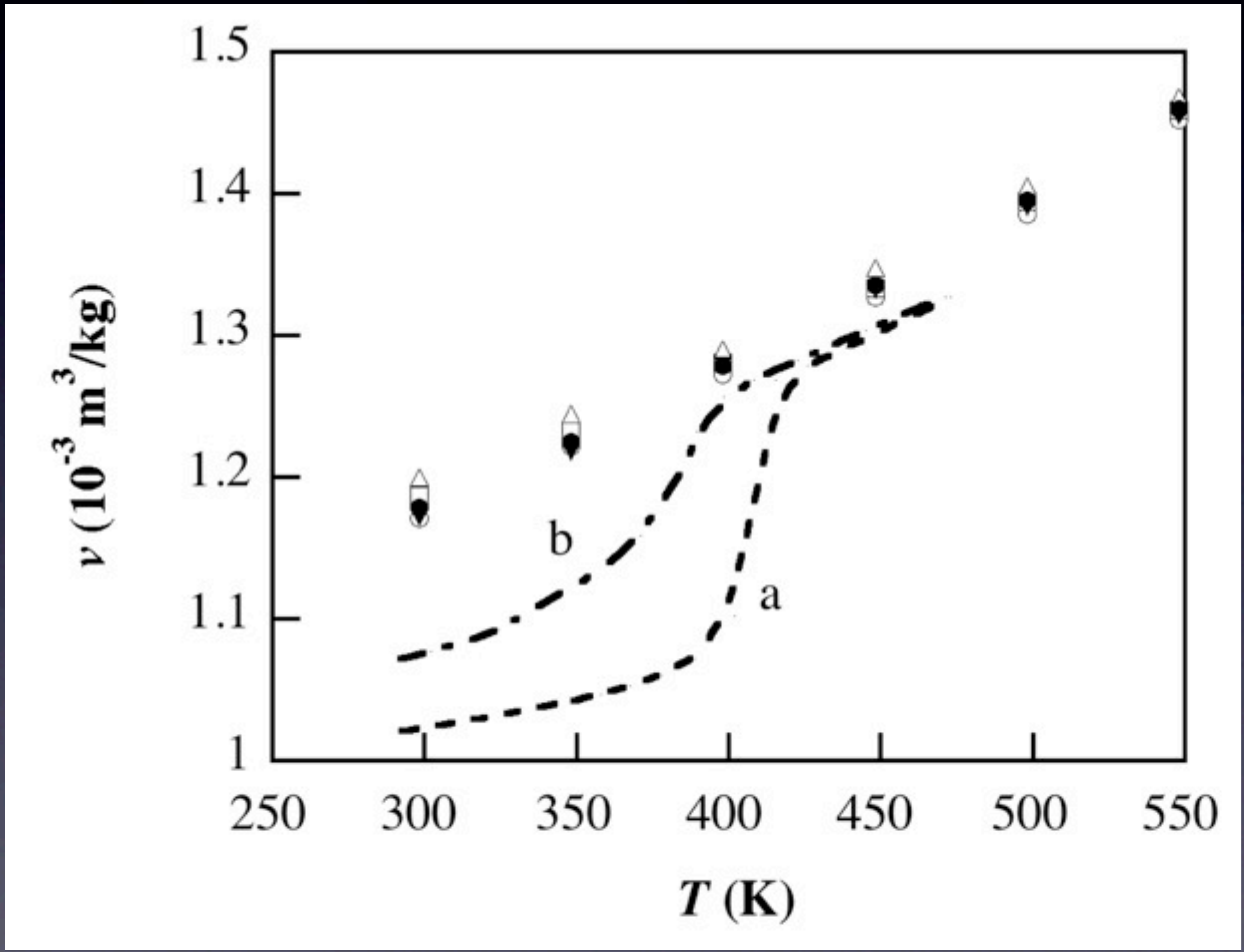
G. E. Karlsson, T. S. Johansson, U. W. Gedde, M. S. Hedenqvist, *Macromolecules*, **35**, 7453 (2002).

Poly(ethylene-*co*-octene)s



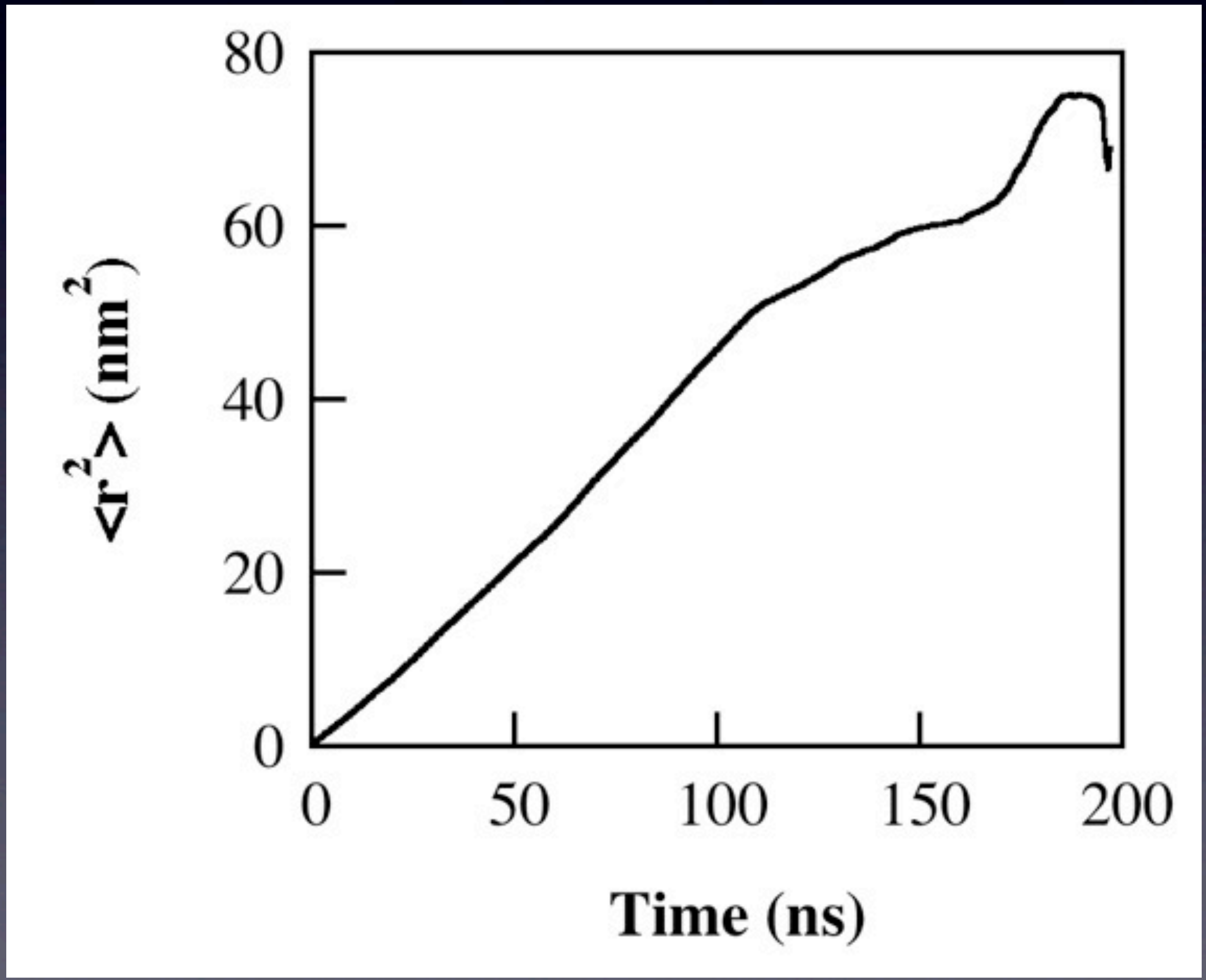
A. Mattozzi, M. S. Hedenqvist, U. W. Gedde, Polymer, **48**, 5174 (2007).

Isobaric data



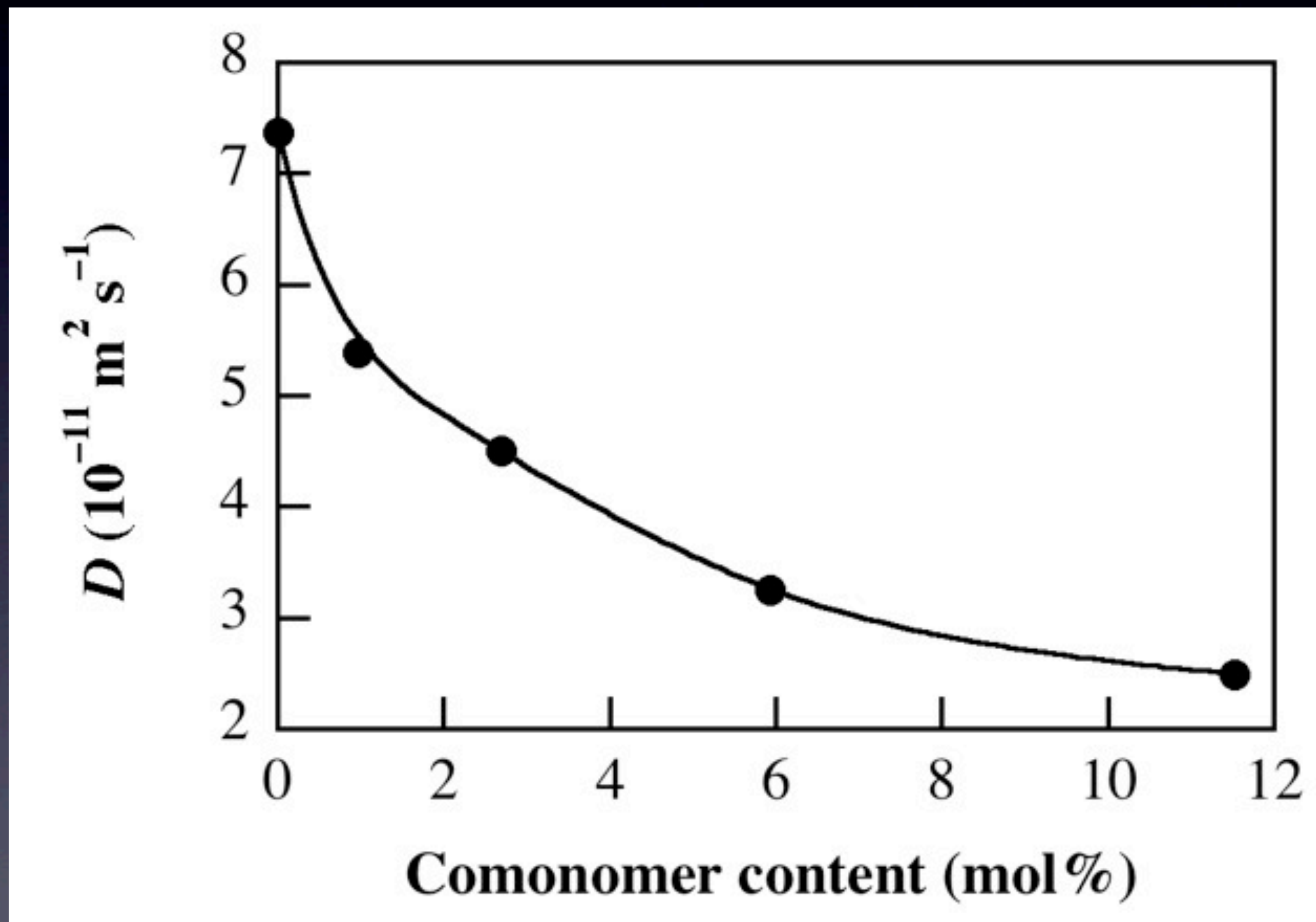
A. Mattozzi, M. S. Hedenqvist, U. W. Gedde, Polymer, **48**, 5174 (2007).

Penetrant random walk statistics



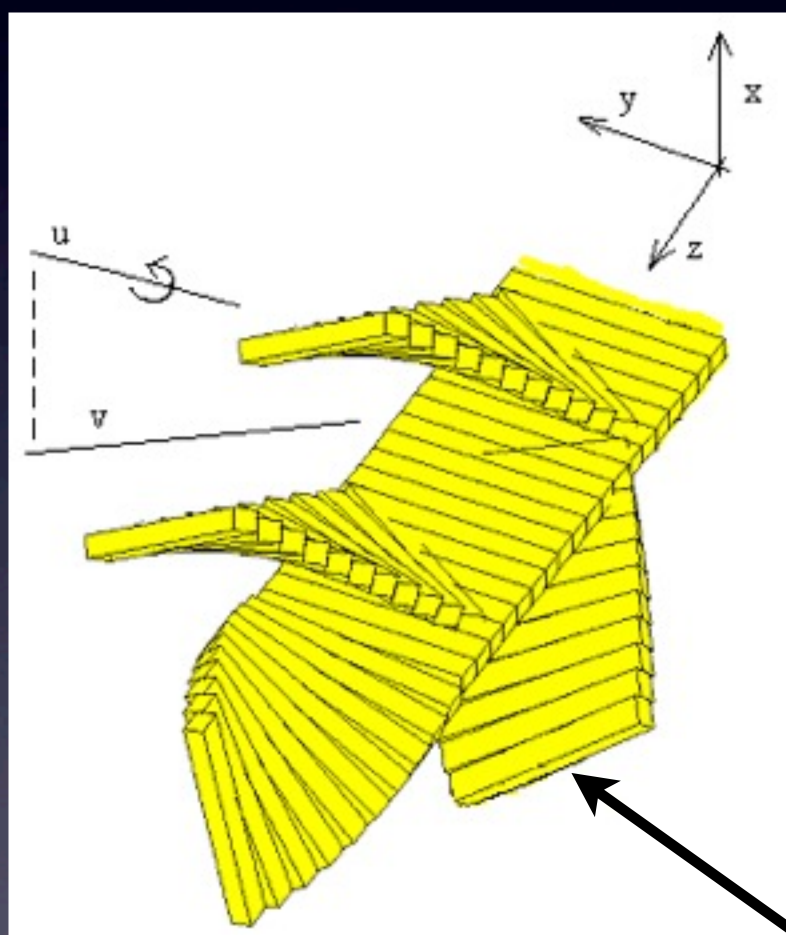
A. Mattozzi, M. S. Hedenqvist, U. W. Gedde, Polymer, **48**, 5174 (2007).

D predictions

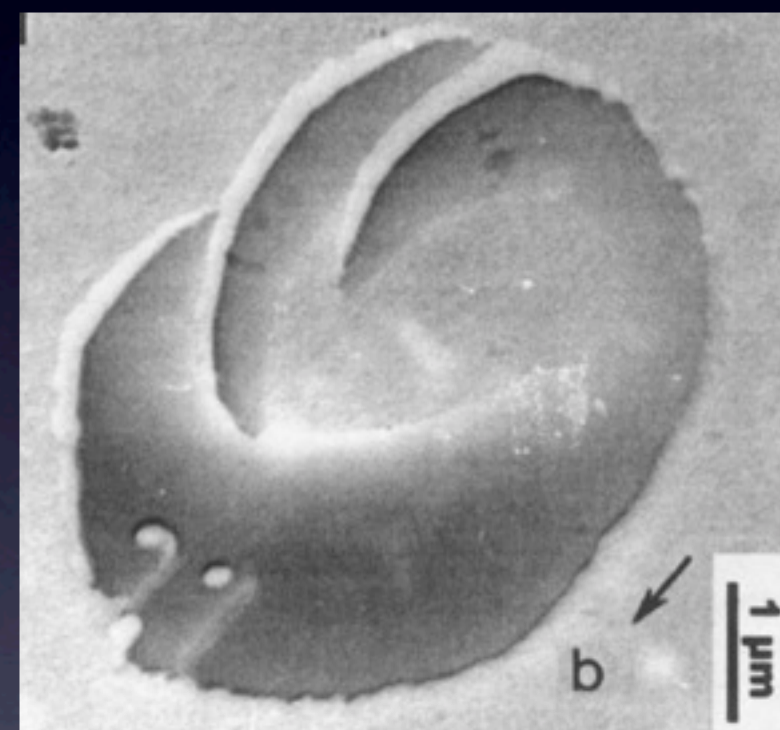


A. Mattozzi, M. S. Hedenqvist, U. W. Gedde, Polymer, **48**, 5174 (2007).

Spherulite growth

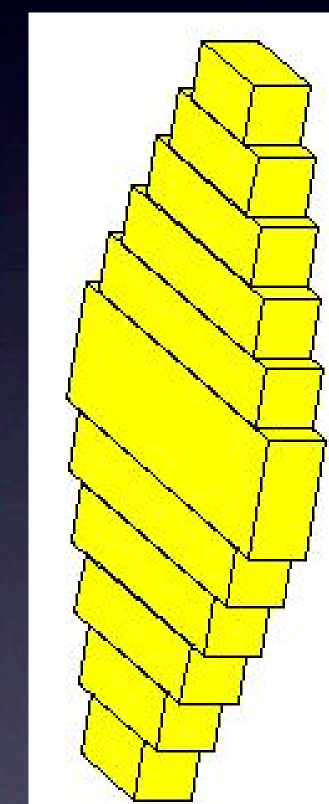


Branching and splaying



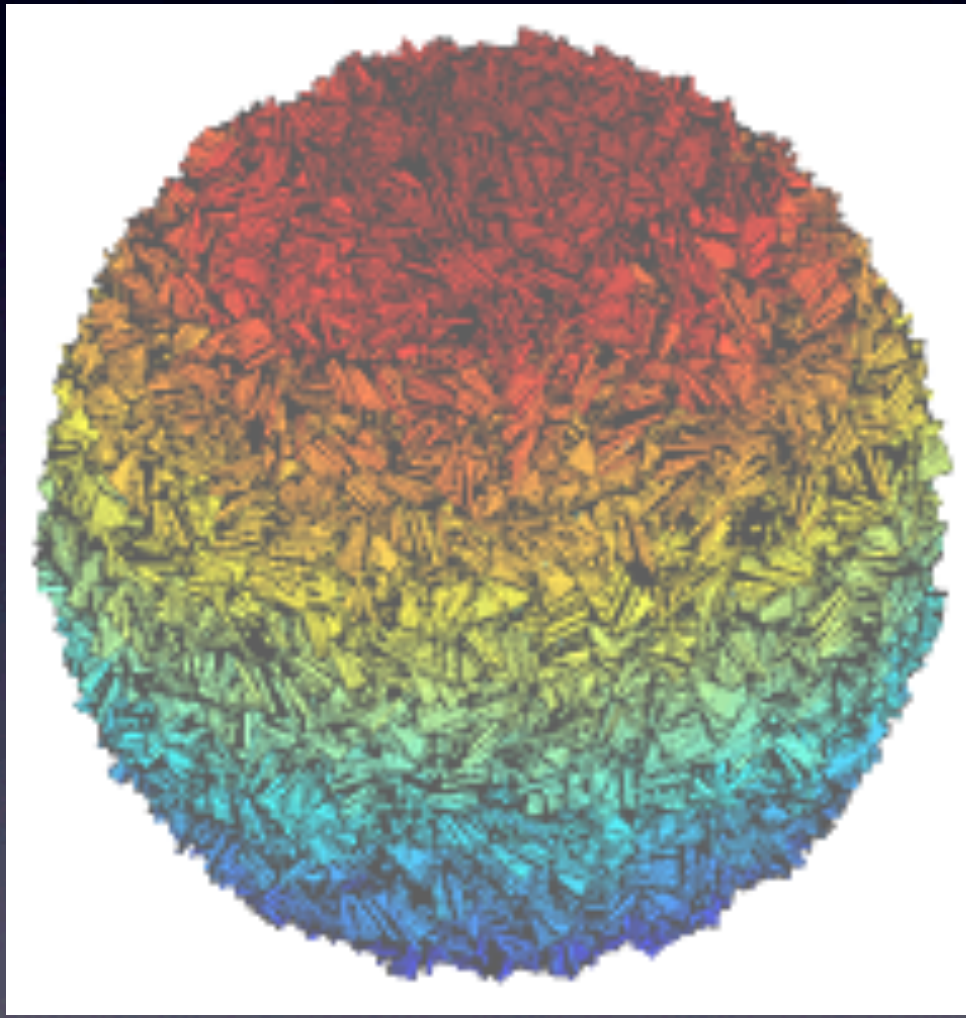
Patel D, Bassett DC. Polymer 2002;43:3795.

Crystal aspect ratio (AR)



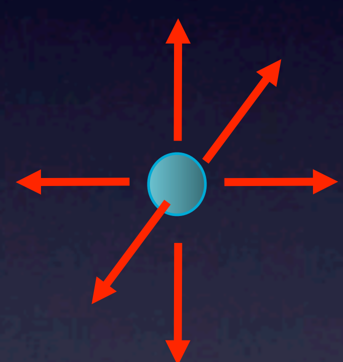
Simultaneous growths along a,b and c-axes

Built spherulite

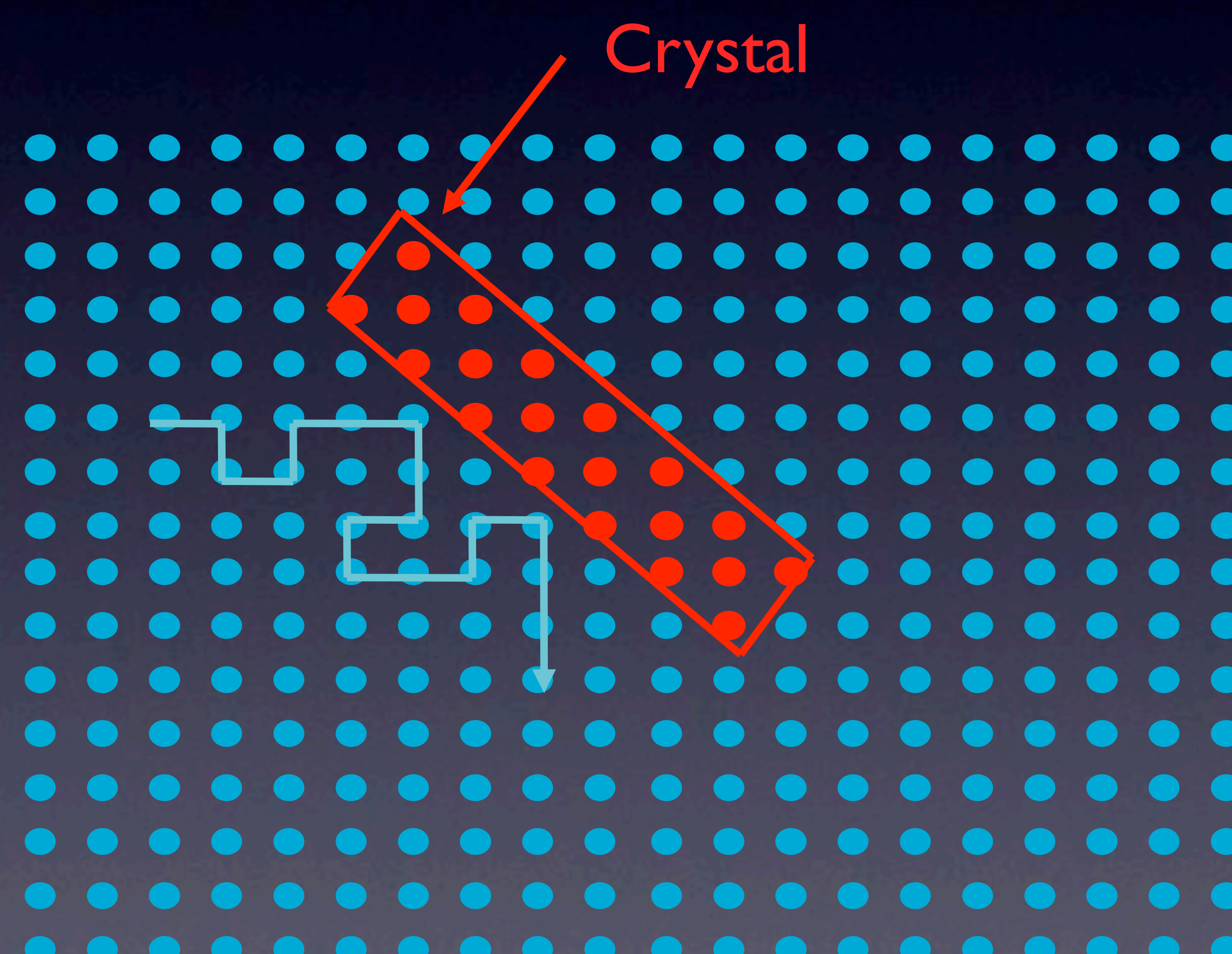


- First generation: on-lattice random-walk
- Second generation: off-lattice; new strategy for avoiding crystal collisions, 100–1000 times faster

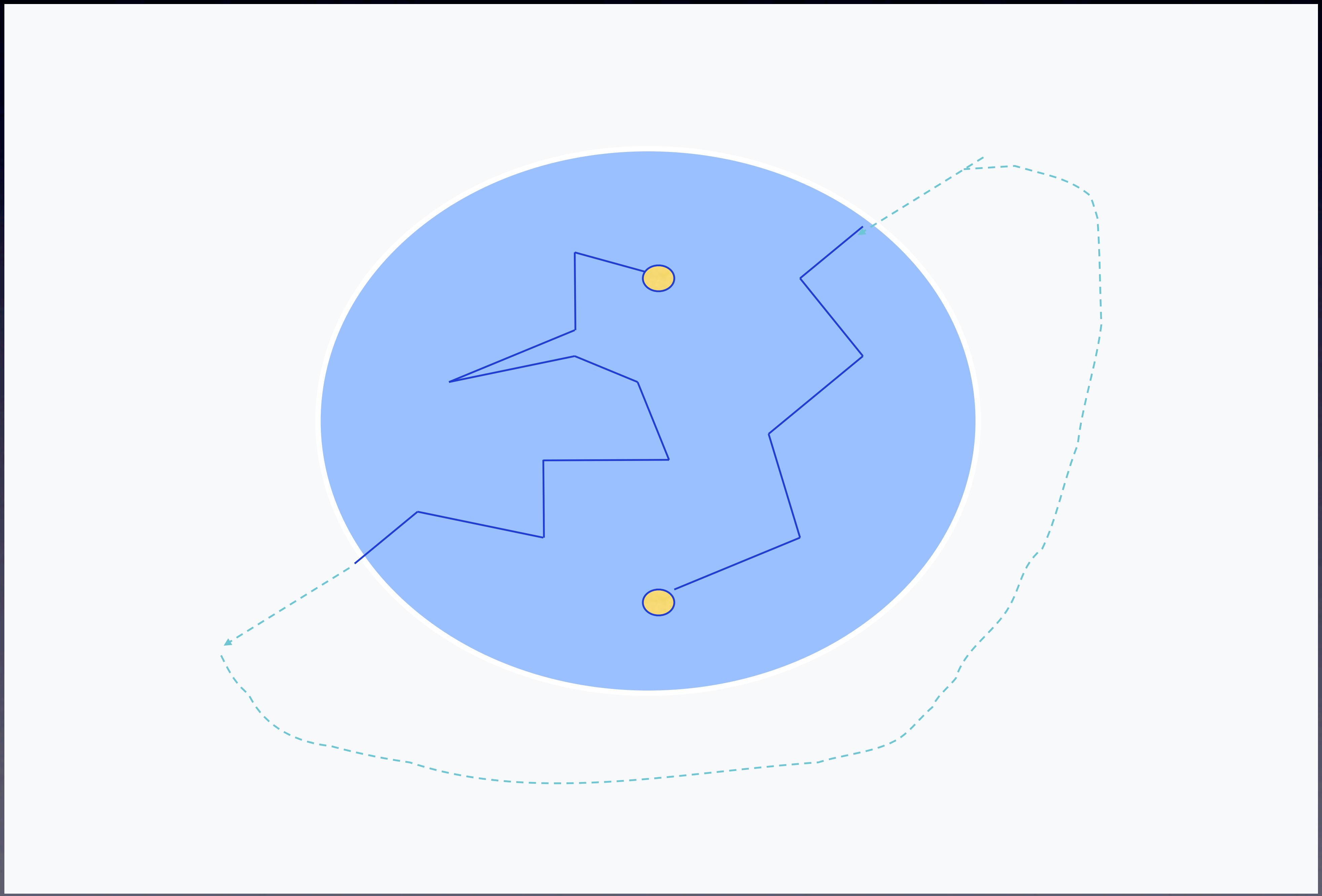
Random walk on-lattice model



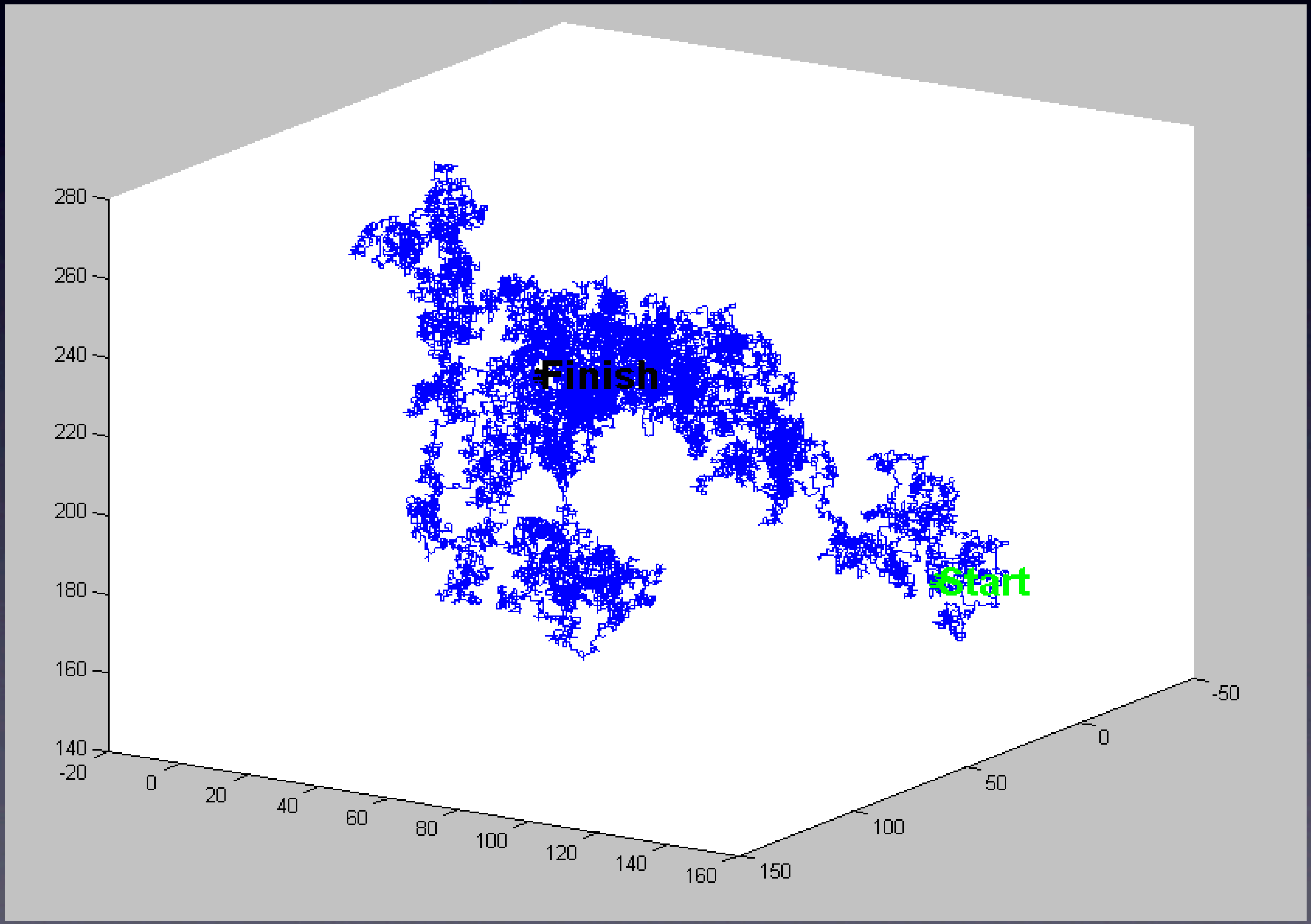
Orthogonal lattice



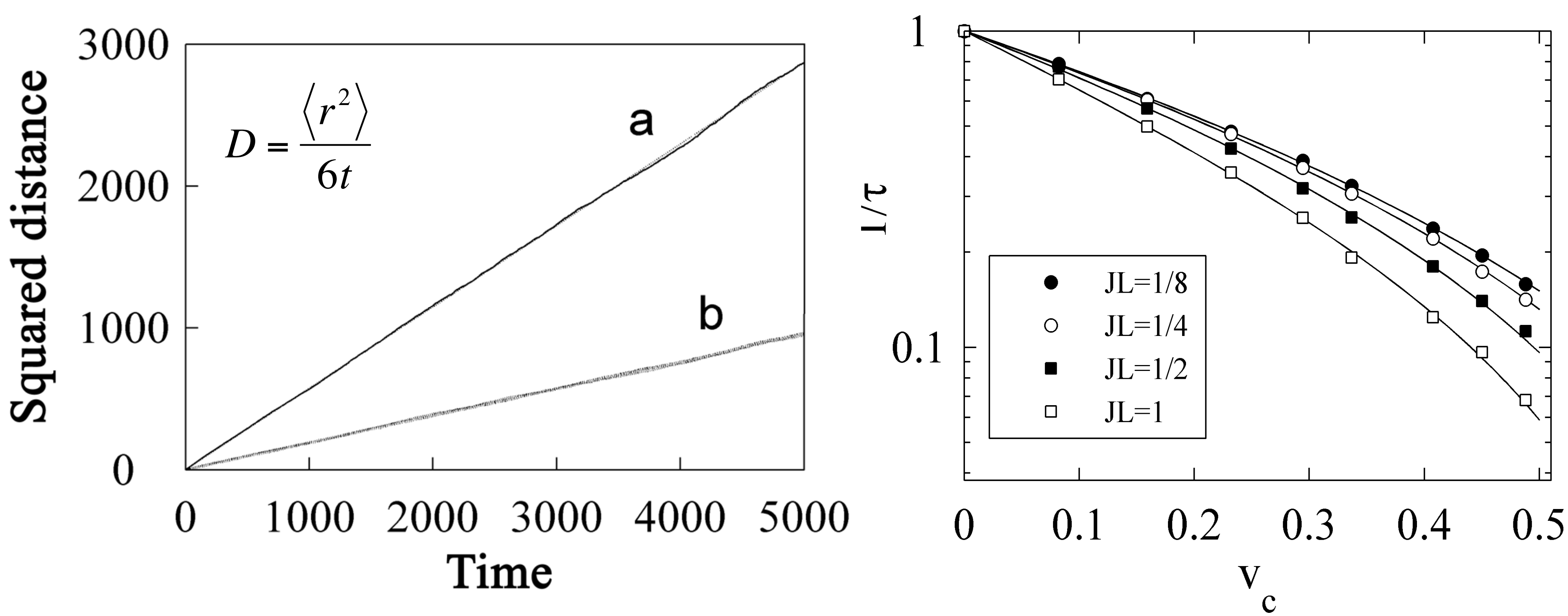
Periodic boundary conditions



Penetrant trajectory

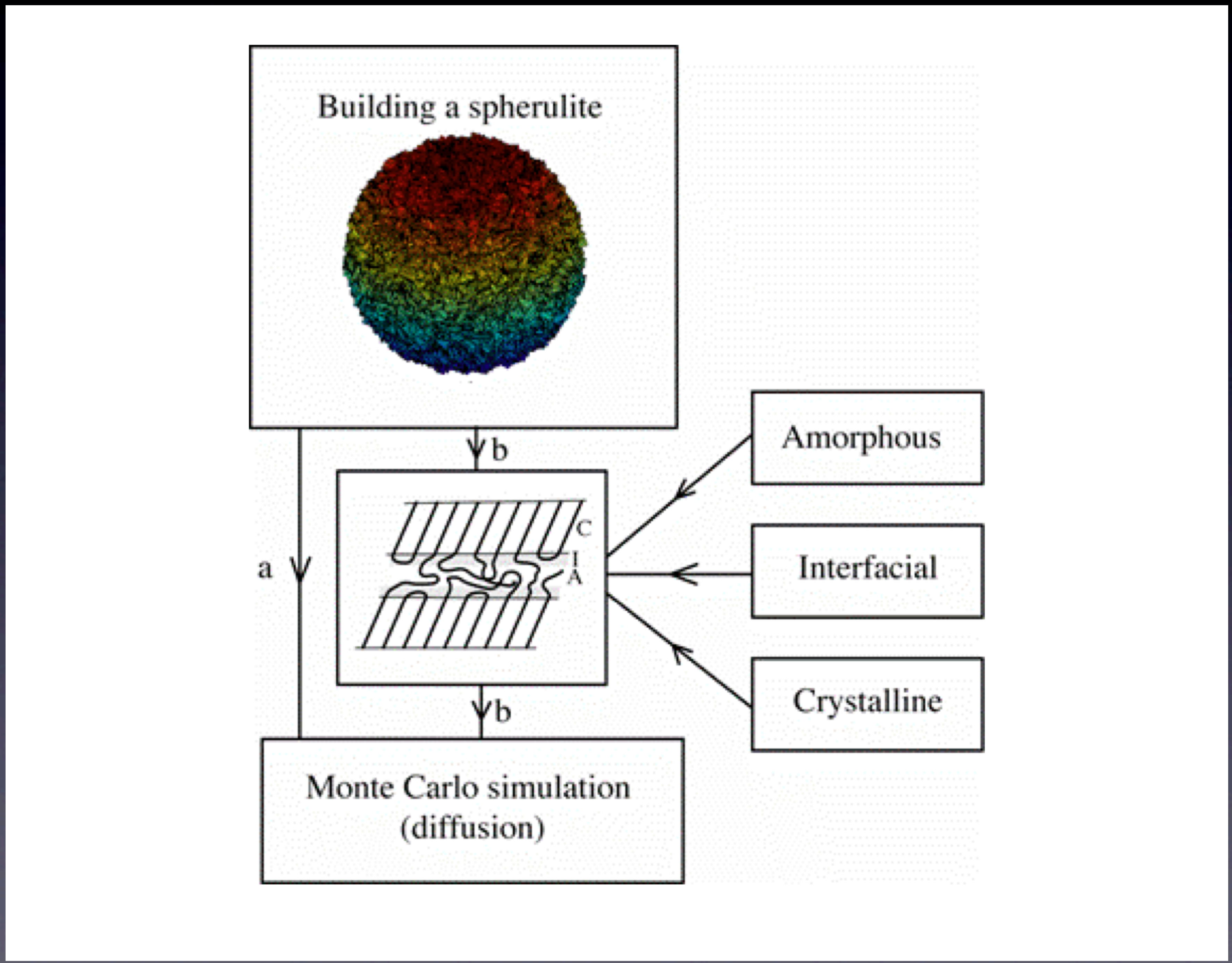


How to obtain D



F. Nilsson, U. W. Gedde and M. S. Hedenqvist, *Eur. Polym. J.*, 45, 3409–3417 (2009).

Multiscale simulation



F. Nilsson, U. W. Gedde and M. S. Hedenqvist, *Eur. Polym. J.*, 45, 3409–3417 (2009).