Chapter 18. Concentration distributions in solids and in laminar flow

- Shell mass balances, boundary conditions
- Diffusion through a stagnant film
- Diffusion with heterogeneous and homogeneous chemical reaction
- Diffusion into a falling liquid film (gas absorption, solid dissolution)
- Diffusion and chemical reaction inside a porous catalyst
- Diffusion in a three-system component gas

Concentration distributions in solids and in laminar flow

- Flux N_A : moles of A per unit area per unit time (system fixed in space)

$$\underset{\substack{\text{combined}\\ \text{flux}}}{N_{Az}} = \underset{\substack{\text{molecular}\\ \text{flux}}}{-c\mathscr{D}_{AB}\frac{\partial x_A}{\partial z}} + \underset{\substack{\text{convective}\\ \text{flux}}}{x_A(N_{Az} + N_{Bz})}$$

- A relationship between N_A and N_B is needed.

Chemical reaction

- Reaction rate: chemical reaction constant

Homogeneous reaction	Heterogeneous reaction
$R_A = k_n''' c_A^n$	$N_{Az}\big\|_{\text{surface}} = k_n'' c_A^n\big\|_{\text{surface}}$
It is included in the mass balance	It is included as a boundary condition

18.1 Shell mass balance and boundary conditions

- Balance

$$\begin{Bmatrix}\text{rate of}\\ \text{mass of}\\ A\text{ in}\end{Bmatrix} - \begin{Bmatrix}\text{rate of}\\ \text{mass of}\\ A\text{ out}\end{Bmatrix} + \begin{Bmatrix}\text{rate of production of}\\ \text{mass of } A \text{ by}\\ \text{homogeneous reaction}\end{Bmatrix} = 0$$

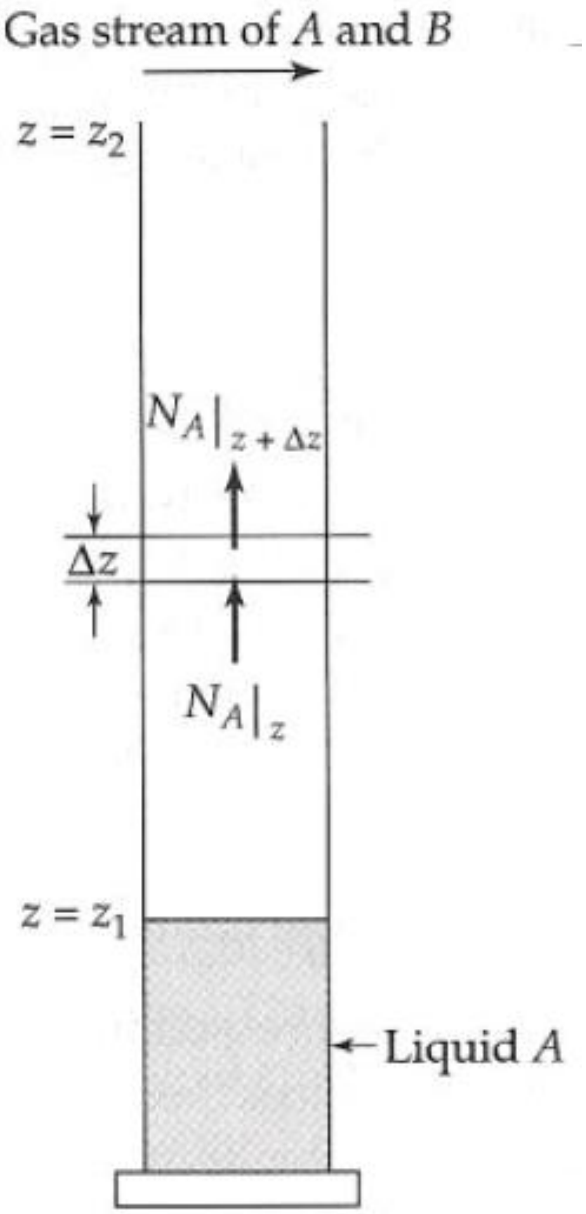
- Specified concentration at a surface
- Specified mass flux at a surface
- At the surface:

$$N_{A0} = k_c(c_{A0} - c_{Ab})$$

- Chemical reaction at the surface

18.2 Diffusion Through a stagnant gas film

- Liquid A is evaporating into gas B.
- Constant level for liquid A
- A stream of gas mixture A and B flows slowly on the top.
- A and B are ideal gases
- Plug flow



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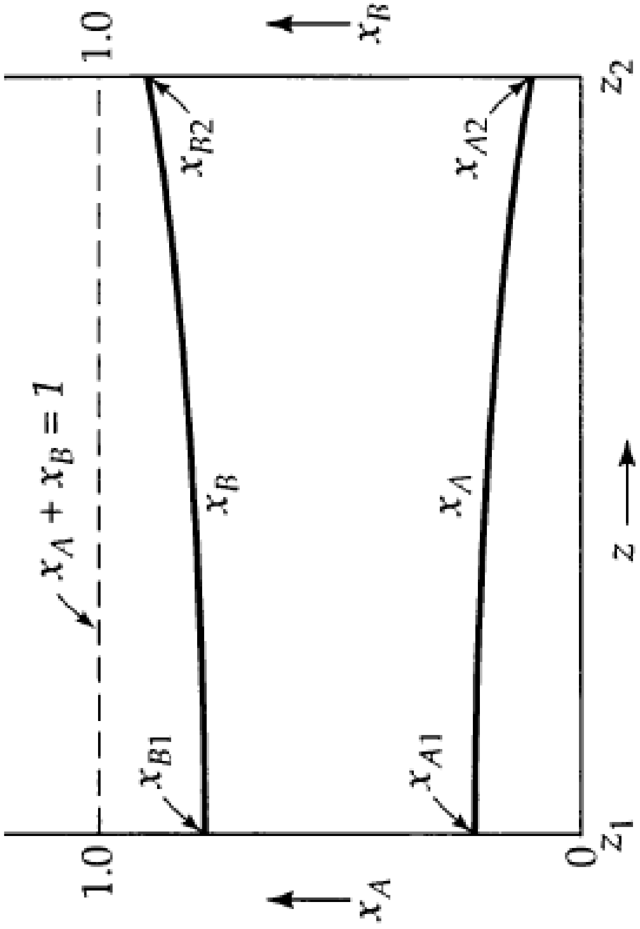
Concentration profiles



- x_{A1} equilibrium concentration at interface p_A^{vap}/p

- Boundary conditions BC1 and BC2

$$\text{at } z = z_1, \qquad x_A = x_{A1}$$
$$\text{at } z = z_2, \qquad x_A = x_{A2}$$

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Equations

- B is stationary $$\mathbf{N}_A = x_A(\mathbf{N}_A + \mathbf{N}_B) - c\mathcal{D}_{AB}\nabla x_A$$
- Using $N_{Bz}=0$ $$N_{Az} = -\frac{c\mathcal{D}_{AB}}{1-x_A}\frac{dx_A}{dz}$$
- Mass balance $$SN_{Az}|_z - SN_{Az}|_{z+\Delta z} = 0 \quad \Rightarrow \quad -\frac{dN_{Az}}{dz} = 0$$
- Introducing N_{Az} $$\frac{d}{dz}\left(\frac{c\mathcal{D}_{AB}}{1-x_A}\frac{dx_A}{dz}\right) = 0$$

Equations

- Integrating

$$\frac{1}{1 - x_A} \frac{dx_A}{dz} = C_1$$

- Integrating, again
  - (no concentration as boundary condition)

$$-\ln(1 - x_A) = C_1 z + C_2$$

- Using BCs 1 and 2

$$\left(\frac{1 - x_A}{1 - x_{A1}}\right) = \left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)^{\frac{z - z_1}{z_2 - z_1}}$$

Other calculations

- For x_B

$$x_B = 1 - x_A$$

- Avg. conc. of B in the tube

$$\frac{x_{B,\text{avg}}}{x_{B1}} = \frac{\int_{z_1}^{z_2} (x_B/x_{B1})dz}{\int_{z_1}^{z_2} dz} = \frac{\int_0^1 (x_{B2}/x_{B1})^{\zeta}\, d\zeta}{\int_0^1 d\zeta} = \left.\frac{(x_{B2}/x_{B1})^{\zeta}}{\ln(x_{B2}/x_{B1})}\right|_0^1$$

- Rewriting

$$x_{B,\text{avg}} = \frac{x_{B2} - x_{B1}}{\ln(x_{B2}/x_{B1})}$$

Rate of mass transfer at the liquid-gas interface

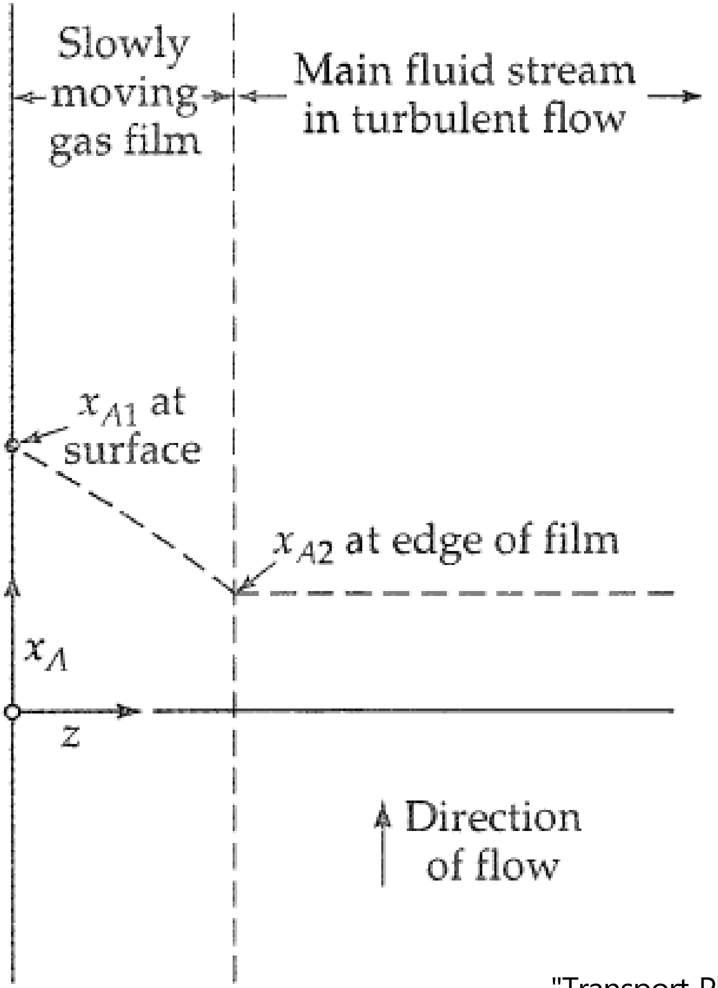
- Rate of evaporation

$$N_{Az}\big|_{z=z_1} = -\frac{c\mathcal{D}_{AB}}{1-x_{A1}}\frac{dx_A}{dz}\bigg|_{z=z_1} = +\frac{c\mathcal{D}_{AB}}{x_{B1}}\frac{dx_B}{dz}\bigg|_{z=z_1} = \frac{c\mathcal{D}_{AB}}{z_2-z_1}\ln\left(\frac{x_{B2}}{x_{B1}}\right)$$

- Using the previous result

$$N_{Az}\big|_{z=z_1} = \frac{c\mathcal{D}_{AB}}{(z_2-z_1)(x_B)_{\ln}}(x_{A1}-x_{A2})$$

Experimental determination of diffusivities



- Film model for mass transfer
  - Near the surface is a slowly moving film
  - Substance A diffuses through this film
  - Sharp transition from stagnant film to a well mixed fluid
  - Concentration gradient only in the film (linear)

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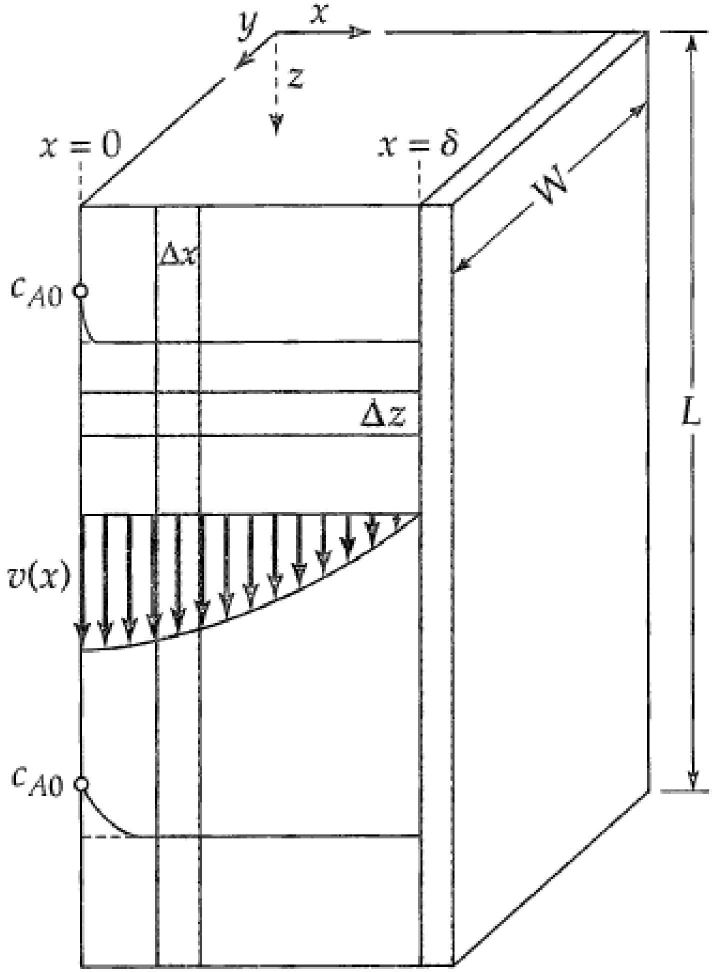
18.5 Diffusion into a falling liquid film (gas absorption)



- Forced convection mass transfer
- Absorption of gas A by a laminar film liquid B
- A slightly soluble in B
- Small penetration distance compared with film thickness
- Ex. Absorption of Oxygen in water

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Equations

- Velocity profile

$$v_z(x) = v_{\max}\left[1 - \left(\frac{x}{\delta}\right)^2\right]$$

- C varies with x and z Mass balance over a element of volume ($\Delta x \, \Delta z \, W$)

$$N_{Az}|_z \, W\Delta x - N_{Az}|_{z+\Delta z} \, W\Delta x + N_{Ax}|_x \, W\Delta z - N_{Ax}|_{x+\Delta x} \, W\Delta z = 0$$

$$\Rightarrow \quad \frac{\partial N_{Az}}{\partial z} + \frac{\partial N_{Ax}}{\partial x} = 0$$

- Introducing N_{Ax} and N_{Az} and

$$N_{Az} = \underline{-\mathscr{D}_{AB}\frac{\partial c_A}{\partial z}} + x_A(N_{Az} + N_{Bz}) \approx c_A v_z(x)$$

$$N_{Ax} = -\mathscr{D}_{AB}\frac{\partial c_A}{\partial x} + \underline{x_A(N_{Ax} + N_{Bx})} \approx \mathscr{D}_{AB}\frac{\partial c_A}{\partial x}$$

$$\Rightarrow \quad v_z \frac{\partial c_A}{\partial z} = \mathscr{D}_{AB}\frac{\partial^2 c_A}{\partial x^2}$$

Equations

- Inserting the velocity profile $$v_{\max}\left[1-\left(\frac{x}{\delta}\right)^2\right]\frac{\partial c_A}{\partial z} = \mathscr{D}_{AB}\frac{\partial^2 c_A}{\partial x^2}$$
- Boundary conditions $$\text{at } z = 0, \quad c_A = 0 \qquad \text{at } x = 0, \quad c_A = c_{A0}$$ $$\text{at } x = \delta, \quad \frac{\partial c_A}{\partial x} = 0$$
- For short contact times $$v_{\max}\frac{\partial c_A}{\partial z} = \mathscr{D}_{AB}\frac{\partial^2 c_A}{\partial x^2}$$
- New BCs $$\text{at } z = 0, \quad c_A = 0 \qquad \text{at } x = 0, \quad c_A = c_{A0}$$ $$\text{at } x = \infty, \quad c_A = 0$$
- The solution is $$\frac{c_A}{c_{A0}} = 1 - \operatorname{erf}\frac{x}{\sqrt{4\mathscr{D}_{AB}z/v_{\max}}} = \operatorname{erfc}\frac{x}{\sqrt{4\mathscr{D}_{AB}z/v_{\max}}}$$

Equations

- Local mass flux

$$N_{Ax}\big|_{x=0} = -\mathscr{D}_{AB}\frac{\partial c_A}{\partial x}\bigg|_{x=0} = c_{A0}\sqrt{\frac{\mathscr{D}_{AB}v_{\max}}{\pi z}}$$

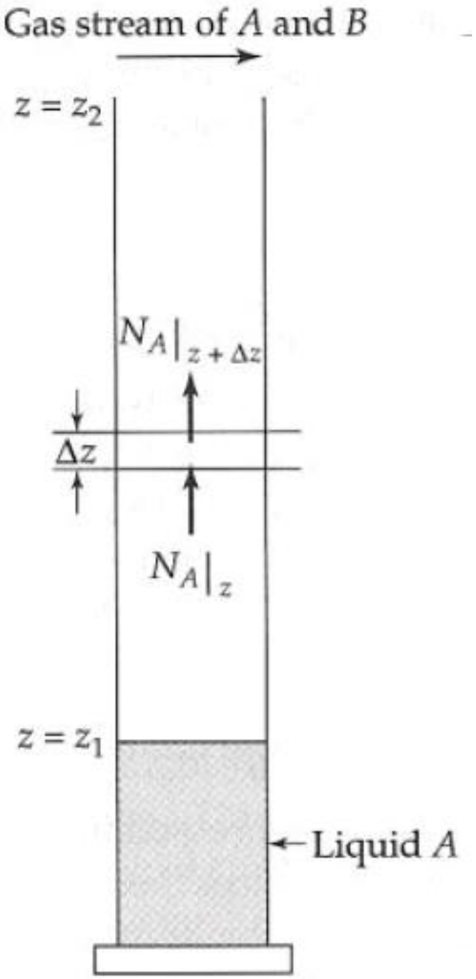
- Total molar flow of A across the surface at x=0

$$\begin{aligned} W_A &= \int_0^W \int_0^L N_{Ax}\big|_{x=0}\,dz\,dy \\ &= Wc_{A0}\sqrt{\frac{\mathscr{D}_{AB}v_{\max}}{\pi}}\int_0^L \frac{1}{\sqrt{z}}\,dz \\ &= WLc_{A0}\sqrt{\frac{4\mathscr{D}_{AB}v_{\max}}{\pi L}} \end{aligned}$$

18.8 Diffusion in a three-component system

- Diffusion through a stagnant gas film (§18.2, two gases) is extended to three components
- Water (species 1) is evaporating into air (a mixture of nitrogen (species 2) and oxygen (species 3)
- Mass balances

$$\frac{dN_{\alpha z}}{dz} = 0 \qquad \alpha = 1, 2, 3$$



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18.8 Diffusion in a three-component system

- Species 2 and 3 are not moving

$$N_{2z} = 0 \text{ and } N_{3z} = 0$$

- Using Maxwell-Stefan equations.
  - Two concentrations are needed, since

$$x_1 + x_2 + x_3 = 1$$

  - Then

$$\frac{dx_2}{dz} = \frac{N_{1z}}{c\mathscr{D}_{12}} x_2; \qquad \frac{dx_3}{dz} = \frac{N_{1z}}{c\mathscr{D}_{13}} x_3$$

18.8 Diffusion in a three-component system

- Note: D_{23} is not included (no relative motion between 2 and 3
- Integrating from a arbitrary z to L

$$\int_{x_2}^{x_{2L}} \frac{dx_2}{x_2} = \frac{N_{1z}}{c\mathcal{D}_{12}} \int_z^L dz; \qquad \int_{x_3}^{x_{3L}} \frac{dx_3}{x_3} = \frac{N_{1z}}{c\mathcal{D}_{13}} \int_z^L dz$$

- Mole fraction profiles for nitrogen and oxygen

$$\frac{x_2}{x_{2L}} = \exp\left(-\frac{N_{1z}(L-z)}{c\mathcal{D}_{12}}\right); \qquad \frac{x_3}{x_{3L}} = \exp\left(-\frac{N_{1z}(L-z)}{c\mathcal{D}_{13}}\right)$$

- Mol fraction profile for water vapour

$$x_1 = 1 - x_{2L}\exp\left(-\frac{N_{1z}(L-z)}{c\mathcal{D}_{12}}\right) - x_{3L}\exp\left(-\frac{N_{1z}(L-z)}{c\mathcal{D}_{13}}\right)$$

Concentration profile

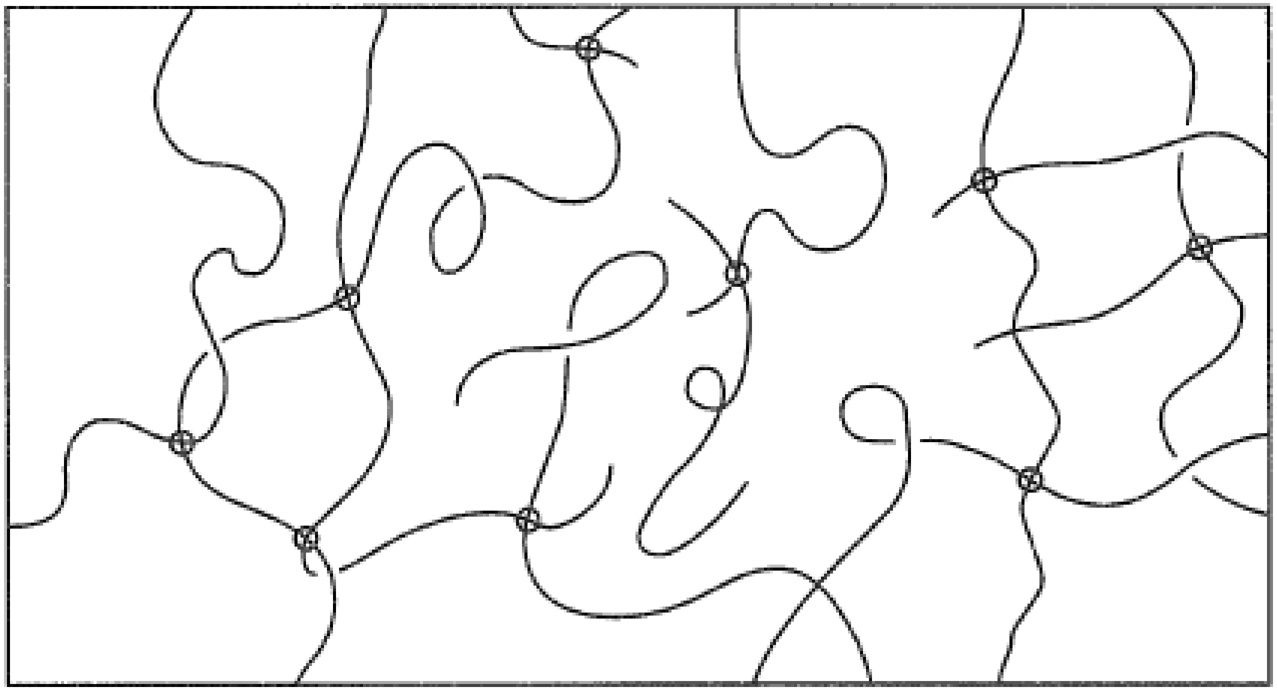
- N_{1z} is determined from BC at z=0
- Transcendental equation for N_{1z}.

$$x_{10} = 1 - x_{2L}\exp\left(-\frac{N_{1z}L}{c\mathscr{D}_{12}}\right) - x_{3L}\exp\left(-\frac{N_{1z}L}{c\mathscr{D}_{13}}\right)$$

Molecular theories for polymeric liquids

- Theories. There are two classes
  - Network theories
  - Single-molecule theories
- Network theories
  - Developed to describe rubber behaviour
  - Extended to describe molten polymer, concentrated solutions
  - Assumptions about formations and rupturing of junctions are done

Network theories. A polymer network formed by temporary junctions (circles)



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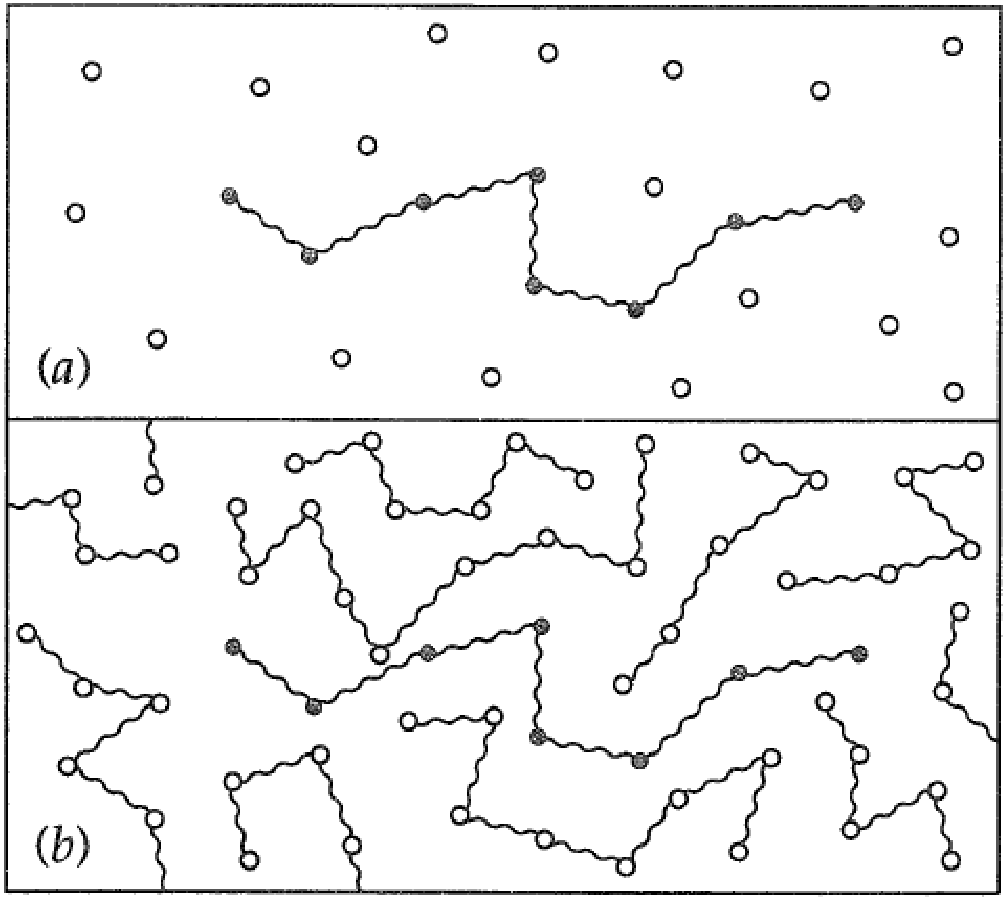
The single-molecule theories

- Developed to describe polymers in very diluted solutions
  - i.e., infrequent polymer-polymer interactions.
- Polymers are represent by “bead springs”
- Theory can extent to molten polymers and concentrated solutions

The single-molecule bead spring models.
a) dilute polymer solutions
b) polymer melt without solvent



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