

# Chromatography Band-Broadening (rate theory)

## A. Introduction

1. Band-broadening is a general term used to describe the overall dispersion or widening of a sample peak as it passes through a separation system.



**2. Band-broadening in Chromatography is a result of several effects. These includes diffusion processes, and transfer of solutes between the mobile and stationary phases, etc.**

**3. One goal of chromatographic theory is to relate the width of a solute peak to various physical parameters that describe the chromatographic system used in its separation. Examples of such parameter include linear velocity, column size, diameter of the packing materials, and capacity factors that describe the solute's retention.**

**4. An understanding of how parameters affect band-broadening allows better control of the separation and helps in the designing of improved systems for chromatography.**

## B. Theoretical measures of band-broadening:

1. In chromatographic theory, the width of a peak is usually described in terms of H, the high equivalent of a theoretical plate,

$$H = L/n$$

L = column length

N = number of theoretical plates =  $(t_R/\sigma)^2$

$t_R$  = retention time of the solute

$\sigma$  = standard deviation of the peak (in time units)



Retention: time, volume, **and distance**

2. An alternate expression for n, H may be rewritten directly in terms of standard deviation of a peak when using distance describe retention:

$$N = (L/\sigma)^2$$

$$H = L/(L/\sigma)^2 = \sigma^2/L$$

Where:  $\sigma$  = standard deviation of the peak (in distance units)

$\sigma^2$  = variance of the peak

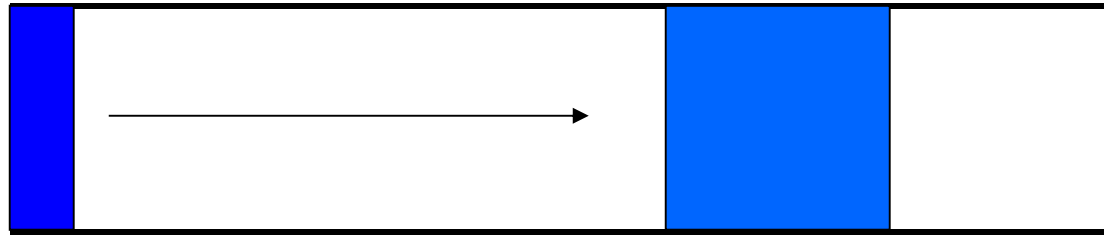
**3. This expression for H is useful since variances ( $\sigma^2$ ) are additive. This means that the total plate height observed for a system ( $H_{\text{tot}}$ ) may be broken down in the sum of variances of plate height for each individual process giving rise to band-broadening.**

$$\begin{aligned} H_{\text{tot}} &= H_1 + H_2 + H_3 + \dots \\ &= (\sigma^2)_1/L + (\sigma^2)_2/L + (\sigma^2)_2/L + \dots \end{aligned}$$

**Where:  $H_1, H_2, H_3$  = plate heights due to processes 1, 2, 3...  
 $(\sigma^2)_1, (\sigma^2)_2, (\sigma^2)_3$  = Variances due to processes 1, 2, 3, ...**

**How can we build rate theory?**

# Chromatographic Band-Broadening and Rate Theory



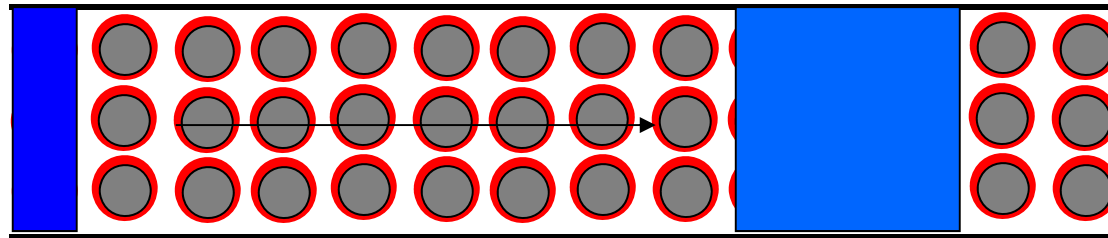
Chromatographic column

## How do we describe band-broadening?

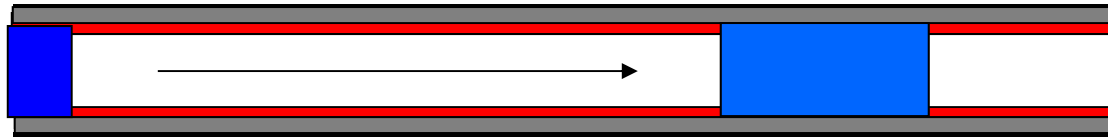
Basic method for problem solving:

1. Understanding the question.
2. Lay out the parameters regarding this question.
3. Try to use concepts and formulas to find the connections.
4. Solving the question.

# 1. Understanding the question



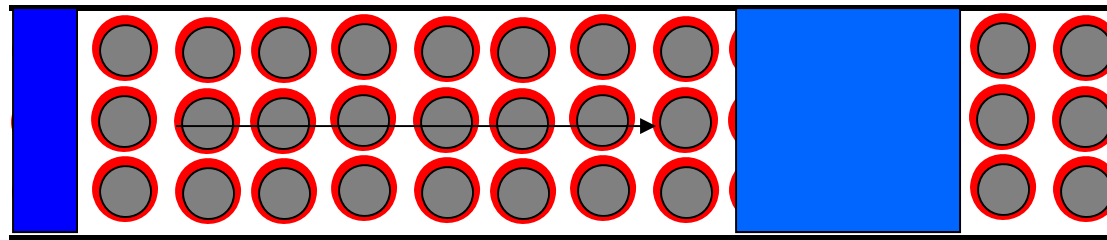
**Packed-bed system**



**Open-tubular system**

**Band-broadening in a chromatographic system!**

## 2. Lay out all the parameters regarding this question



Packed-bed system

### Processes (i.e., parameters) Effect Band-Broadening:

(1) Diffusion

(2) Fluid flow

(3) Equilibrium between stationary phase and mobile phase

### 3. Try to use concepts and formulas to find the connections

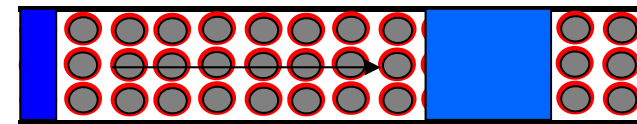
#### Processes:

- (1) Diffusion
- (2) Fluid flow
- (3) Equilibrium between stationary phase and mobile phase

#### A. Analysis of These Process:

(1) Diffusion: (longitudinal)

(2) Flow and Diffusion in mobile phase  
(Eddy or multi-path diffusion)



Packed-bed system

(3) Non-equilibrium (resistance to mass transfer)



**B. Find the connections between these processes:**

**The band-broadening contributes from these processes are additive!  
The sum of the contributes give rise to the total band-broadening**

**We learned in last class!**

**The total plate height observed for a system ( $H_{\text{tot}}$ ) may be broken down in the sum of variances of plate height for each individual process giving rise to band-broadening.**

$$H_{\text{tot}} = H_1 + H_2 + H_3 + \dots = (\sigma^2)_1/L + (\sigma^2)_2/L + (\sigma^2)_2/L + \dots$$

**Where:  $H_1, H_2, H_3$  = plate heights due to processes 1, 2, 3...**

**$(\sigma^2)_1, (\sigma^2)_2, (\sigma^2)_3$  =Variances due to processes 1, 2, 3, ...**

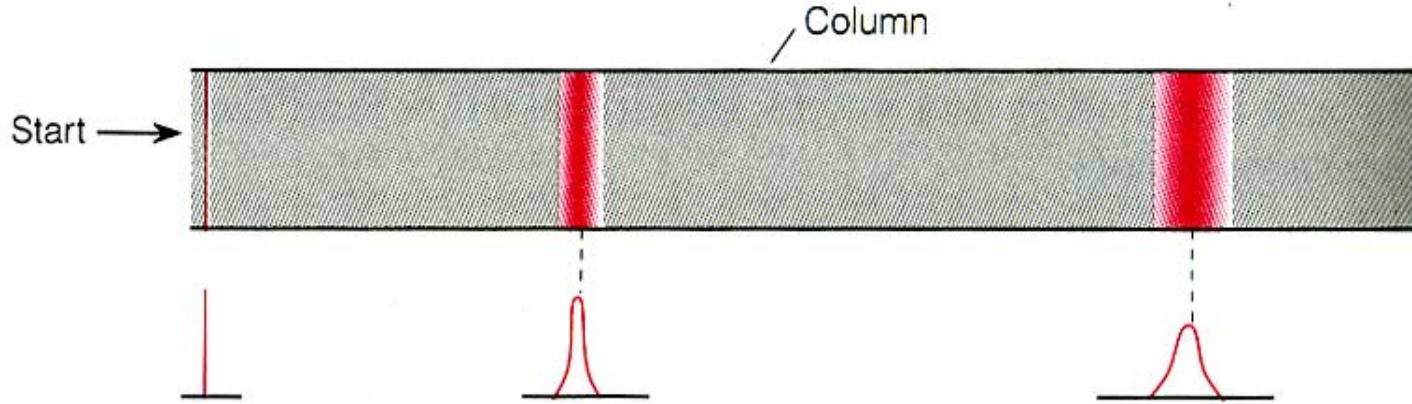
$$H_{\text{tot}} = H_L + H_E + H_R$$

**(1) Diffusion: (longitudinal)  $H_L$**

**(2) Flow and Diffusion in mobile phase (Eddy or multi-path diffusion)  $H_E$**

**(3) Non-equilibrium (resistance to mass transfer)  $H_R$**

# (1) Diffusion: (longitudinal)



$$C_x = C_0 \left( \frac{1}{2\sqrt{\pi Dt}} \right) e^{-x^2/4Dt}$$

$$\sigma^2 = 2Dt = 2D\left(\frac{L}{u}\right)$$

$$H_L = (\sigma^2)_L/L = 2D_m/u$$

Packed bed

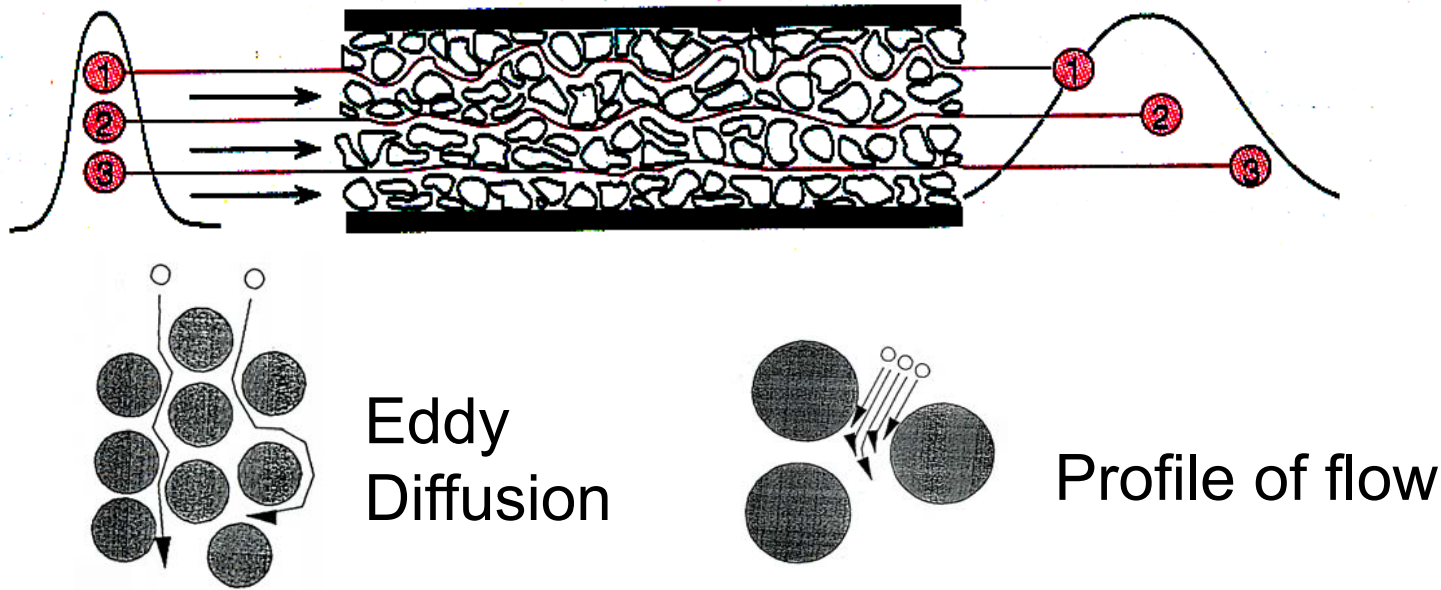
$$H_L = (\sigma^2)_L/L = 2D_m/[u(1+\epsilon_p/\epsilon_e)]$$

$\epsilon_p$ : intraparticle porosity  
 $\epsilon_e$ : interparticle porosity  
 $D_m$ : solute diffusion coefficient in mobile phase.  
 $u$ : linear velocity of flow

**Larger the  $D_m$ , larger the  $H_L$ !**  
**Larger the  $u$ , smaller the  $H_L$ !**

**Longitudinal Diffusion: Why?**  
 is significant in GC  
 but has much less effect in LC

## 2) Flow and Diffusion in mobile phase (Eddy or multi-path diffusion) $H_E$



$$H_E = \left[ \frac{2\lambda d_p^{1+x}}{(D_m)^x} \right] u^x$$

$\lambda$ : column packing factor (0.5~1.5)

$d_p$ : average size of the filling particles

$D_m$ : solute diffusion coefficient in mobile phase

$u$ : linear velocity

$x$ : constant of system (0 ~ 1/3)

In general,  $x=0$  for GC. And  $x=1/3$  for LC

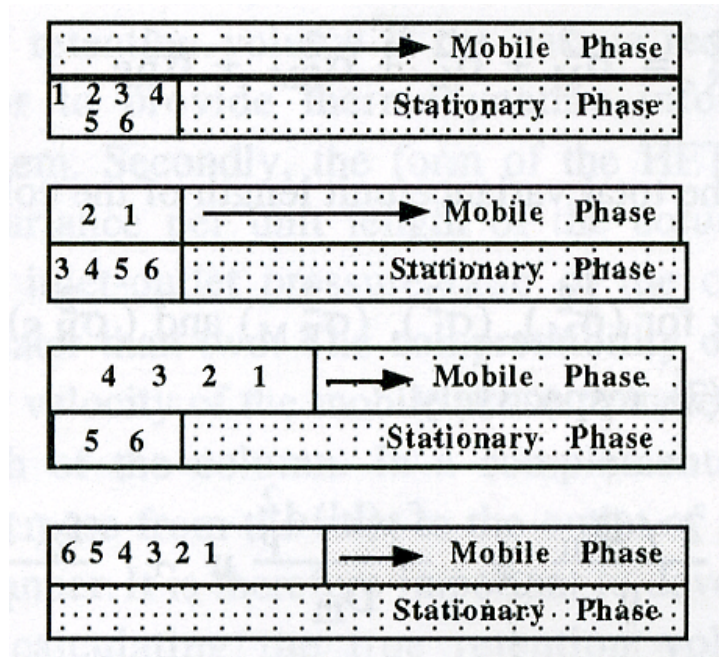
*Smaller the  $d_p$ , smaller the  $H_E$ !*

*The effects from  $D_m$  and  $u$  is opposite to those for  $H_L$ !*

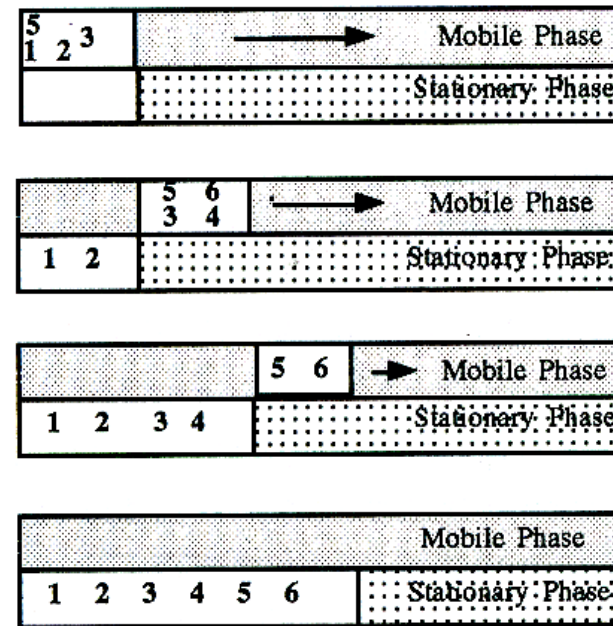
**Every thing has two sides!**

### (3) Non-equilibrium (resistance to mass transfer) $H_R$ (I)

From a kinetic standpoint, achieving equilibrium between mobile and stationary phases needs time (diffusion limitation)!



From stationary phase to mobile phase



From mobile phase to stationary phase

Resistance to mass transfer lead to slightly non-equilibrium between mobile and stationary phases.

### (3) Non-equilibrium (resistance to mass transfer) $H_R$ (II)

#### (1) Resistance to mass transfer from stationary phase to mobile phase

$$H_s = q_s \left( \frac{k}{(1+k)^2} \right) \left( \frac{d_f^2}{D_s} \right) u$$

**k**: capacity factor  
**d<sub>f</sub>**: thickness of stationary phase  
**D<sub>s</sub>**: solute diffusion coefficient in stationary phase.  
**q<sub>s</sub>**: shape factor for the stationary phase coating (2/3 for a thin layer on the support).  
**u**: linear velocity of flow

#### (2) Resistance to mass transfer from mobile phase to stationary phase

$$H_M = f(k) \left( \frac{d_p^2}{D_m} \right) u$$

**f(k)**: a function of k, increasing with k  
**d<sub>p</sub>**: average size of the filling particles  
**D<sub>m</sub>**: solute diffusion coefficient in mobile phase  
**u**: linear velocity

(3)  $H_R = H_S + H_M$  → Less effect on GC

# Final Solution for the Question (I)

$$H_{\text{tot}} = H_L + H_E + H_R = H_L + H_E + H_S + H_M$$

$$\left( \frac{2}{1 + \epsilon_p / \epsilon_e} \right) \left( \frac{D_m}{u} \right) + \left[ 2\lambda d_p^{1+x} \right] \left( \frac{u^x}{(D_m)^x} \right) + q_s \left( \frac{k}{(1+k)^2} \right) \left( \frac{d_f^2}{D_s} \right) u + f(k) \left( \frac{d_p^2}{D_m} \right) u$$

	$H_{\text{tot}} =$	$H_L$	+	$H_E$	+	$H_S$	+	$H_M$
$u \uparrow$		$\downarrow$		$\uparrow$		$\uparrow$		$\uparrow$
$D \uparrow$		$\uparrow$		$\downarrow$		$\downarrow$		$\downarrow$
$d_p \uparrow$		-		$\uparrow$		-		$\uparrow$
$d_f \uparrow$		-		-		$\uparrow$		-
$k \uparrow$						$\downarrow$		$\uparrow$

## Final Solution for the Question (II)

$$H_{\text{tot}} = H_L + H_E + H_R = H_L + H_E + H_S + H_M$$

$$\left( \frac{2}{1 + \epsilon_p / \epsilon_e} \right) \left( \frac{D_m}{u} \right) + \left[ 2\lambda d_p^{1+x} \right] \left( \frac{u^x}{(D_m)^x} \right) + q_s \left( \frac{k}{(1+k)^2} \right) \left( \frac{d_f^2}{D_s} \right) u + f(k) \left( \frac{d_p^2}{D_m} \right) u$$

$$H_{\text{tot}} = A + B/u + (C_S + C_M)u \quad (\text{For GC, van Deemter equation})$$

$$H_{\text{tot}} = Au^{1/3} + B/u + (C_S + C_M)u \quad (\text{For LC, Knox equation})$$

Basic method for problem solving:

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## How does Mother Nature Optimize Conflict Parameters?

$$\begin{aligned} H_{\text{tot}} &= A + B/u + (C_S + C_M)u \\ &= A + B/u + Cu \end{aligned} \quad (\text{van Deemter equation})$$

*Is there a minimum for  $H_{\text{tot}}$ ?*

$$\frac{d H_{\text{tot}}}{d u} = ? \quad (\text{inflexion?})$$

$$\frac{d^2(H_{\text{tot}})}{d^2(u)} = ? \quad (\text{minimum or maximum?})$$

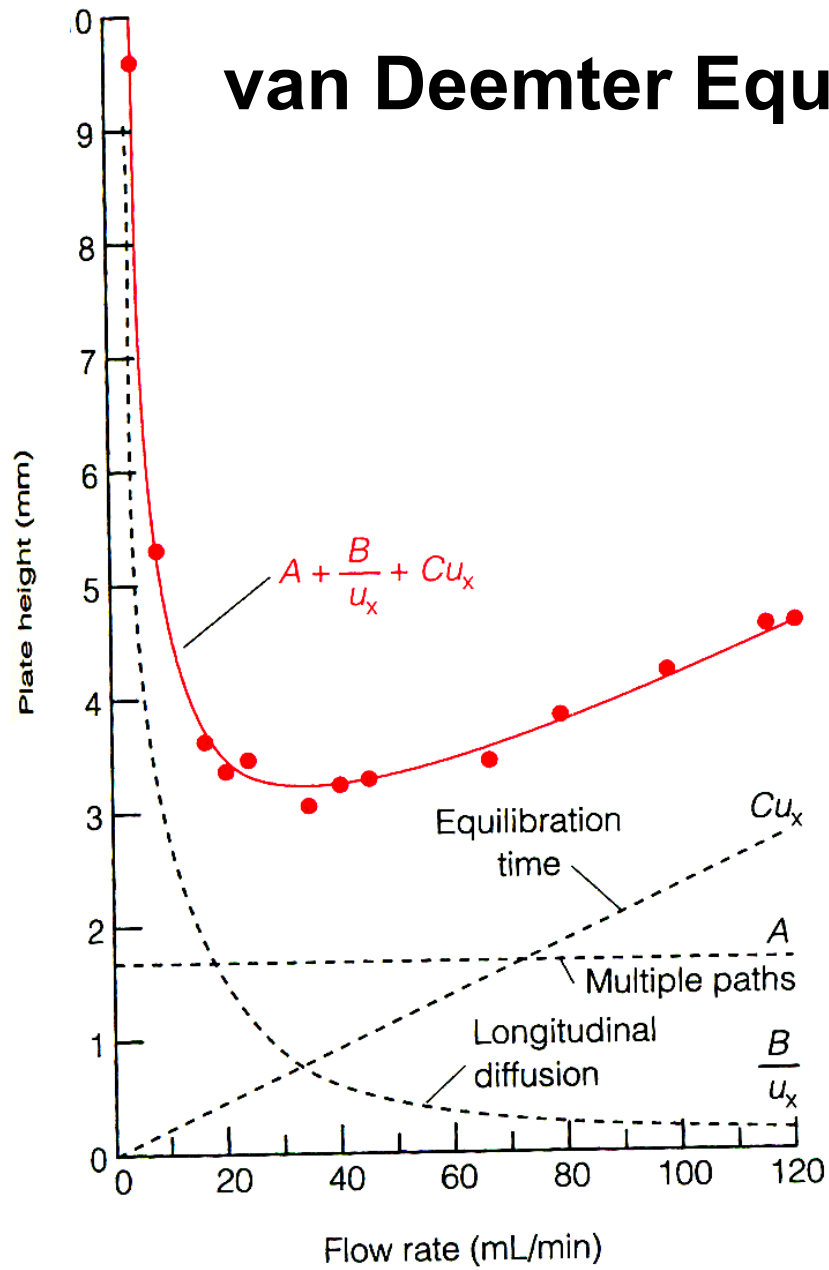
**Good news: there is a minimum for  $H_{\text{tot}}$ .**

$$H_{\text{tot}} = A + 2*(BC)^{1/2}$$

$$u_{\text{opt}} = (B/C)^{1/2}$$



# van Deemter Equation



a. Chromatography Parameters:  $t_R$ ,  $t_M$ ,  $V_R$ ,  $V_M$ ,  $t_R'$ ,  $V_R'$ ,  $W_b$ ,  $W_h$ .

b. Solute Retention:  $k$ ,  $k = t_R'/t_M$        $t_R' = k t_M$        $t_R = (k+1) t_M$

c. Efficiency of Chromatography and Plate Theory:  $N$  and  $H$

$$N = (t_R / \sigma_t)^2$$

d. Measures of Solute Separation:  $\alpha$ ,  $R_s$

e. Fundamental factors affecting resolution:

$$R_s = \frac{t_{R2} - t_{R1}}{(W_{b2} + W_{b1})/2}$$

f. Einstein diffusion equation:

$t_d = d^2/(2D)$       Where,  $t_d$  = average time required to diffuse a distance  $d$   
 $d$  = distance of travel

g: flow on open tube:  $R_e = \rho u d_p / \eta$   
flow on packed bed:  $R_e = \rho u d_p / \eta$

h. Hagen-Poiseuille Equation and Darcy Equation.

i. band-broadening

**Read Chapter 2 in “The Essence of Chromatography”**