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Extraparticle Diffusional Effects in Gel Permeation Chromatography. I. Theory

J. A. BIESENBERGER *and* A. OUANO,* *Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030*

Synopsis

A systems approach is applied to the analysis of chromatogram resolution dispersion, or zone broadening, in gel permeation chromatography (GPC). Three possible sources of dispersion are considered; these are: the packed columns; the empty tubing between pump and columns, columns and detector, etc.; and the detection system, viz., the differential refractometer cell. It is shown that empty tubing can contribute significantly to the degree of dispersion and to skewness of elution curves and that this dispersion should depend on molecular weight of solute (polymer) and diameter and length of the tubing. The importance of dispersion in the empty tubing is compared with that in the packed columns and refractometer cell.

THEORY

Generally in GPC, a pulse input of solute in solution with concentration C_0 (g/l.) and width ϵ (sec) is introduced via a sample injection loop into a stream of solvent flowing with volumetric flow rate u. This may be represented as a rectangular pulse with

$$uC_0\epsilon = A$$

and

$$u\epsilon = V_s$$

where A and V_s are weight of solute and volume of solution injected, respectively. If ϵ is sufficiently small, the rectangular pulse may be approximated by an impulse, or delta, function

$$\delta(t) = \begin{cases} 1/\epsilon \text{ for} & 0 \leq t \leq \epsilon \\ 0 \text{ for} & t > \epsilon \text{ and } t < 0 \end{cases}$$

such that

$$\lim_{\epsilon \to 0} uC_0 \int_0^\epsilon \delta(t)dt = A$$

* Present address, General Electric Company, Pittsfield, Massachusetts.

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and

$$\lim_{\epsilon \to 0} u \int_0^{\epsilon} \delta(t)dt = V_s.$$

In this work it is also desirable to consider the introduction of a step input of solute

$$1(t) = \begin{cases} 1 \text{ for } t > 0 \\ 0 \text{ for } t < 0 \end{cases}$$

such that

$$uC_0 \cdot t \cdot 1(t) = A(t)$$

and

$$ut \cdot 1(t) = V_s(t).$$

Since both the packed columns and the empty tubing in GPC are actually cylinders through which solutions flow axially, a differential mass balance in cylindrical coordinates may be used to formulate mathematical models for solute dispersion in both:

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial z} + D_R \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + D_L \frac{\partial^2 c}{\partial z^2} \tag{1}$$

where c = solute concentration at any point and at any time; v = solution velocity at any point (v is, in general, a function of r); and D_R, D_L = dispersion coefficients for the solute in solution in the radial and longitudinal (axial) directions, respectively. This equation refers to a differential element located at any point in a cylinder of radius, R, and length, L. The three terms on the right-hand side describe net convective axial, diffusive radial and diffusive axial transport rates per unit volume, respectively, at any point.

Equation 1 may be specialized in order to describe solute dispersion in either packed columns or empty tubing. For example, when the ratio of column diameter to particle diameter, d_T/d_p, in a packed column exceeds a value of approximately 30, the interstitial solution velocity v may be considered to be uniform across the column diameter[1] and simply equal to the average value $\bar{v}$ everywhere:

$$v = \frac{u}{\pi R^2 \alpha} = \bar{v}$$

where α, the interstitial volume fraction of the column, is

$$\alpha \equiv \frac{V_0}{V_T}$$

and V_T = total volume of the packed column.

It is also well known that $D_R < D_L$ in packed columns.[2] However, for pulse and step input functions of the type used in this work, since plug flow

prevails, $\partial c/\partial r = 0$ in eq. 1 and the packed column dispersion model becomes

$$\frac{\partial c}{\partial t} = -\bar{v}\frac{\partial c}{\partial z} + D_L\frac{\partial^2 c}{\partial z^2}. \tag{2}$$

Equation 2 has been used previously.[3–5]

In empty tubing for a solution under laminar flow conditions

$$v = v_0\left[1 - \left(\frac{r}{R}\right)^2\right] = 2\bar{v}\left[1 - \left(\frac{r}{R}\right)^2\right]$$

where v_0 is the solution velocity at the tube axis. Moreover, $D_R = D_L = D$ where D is the molecular diffusivity of the solute in solution. The dispersion model for the empty tubing then becomes, from eq. 1,

$$\frac{\partial c}{\partial t} = -v_0\left[1 - \left(\frac{r}{R}\right)^2\right]\frac{\partial c}{\partial z} + D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial z^2}\right] \tag{3}$$

Regarding dispersion in the refractometer cell, it is assumed in this work that the cell behaves like a perfectly mixed vessel of volume V_c. This represents the most extreme model of mixing possible (complete backmixing) and a mass balance for the solute gives the cell dispersion model

$$V_c\frac{dc}{dt} = \int_0^R\int_0^{2\pi} c_e v(r) r d\theta dr - uc \tag{4}$$

where c = solute concentration (uniform) in the cell at any time, and c_e = solute concentration at the exit of the empty tubing connected to the entrance of the cell. The two terms on the right-hand side of eq. 4 represent transport rate into the cell from the connecting tubing and transport rate out of the cell, respectively.

To completely describe extraparticle dispersion of a monodispersed solute in a system which consists of all three of the above components, it is necessary to solve at least three consecutive differential equations, with the solution of one being the initial condition for the next, and so on. The initial condition for the first equation may be a rectangular pulse or a step function and the solution of the last (eq. 4) should represent the elution curve as detected by the refractometer. A rectangular pulse input gives the usual GPC elution curve.

It is instructive from a physical viewpoint to consider certain limiting cases of the dispersion models which identify so-called dispersion regimes. These regimes lend themselves to simpler mathematical description and will be introduced here via a characteristic-time approach.

Since a diffusion coefficient is actually defined as a characteristic diffusion length, squared, divided by a characteristic diffusion time, it is reasonable to define $\lambda_R \equiv R^2/D_R$ as a characteristic time associated with radial dispersion and $\lambda_L \equiv L^2/D_L$ as a characteristic time associated with axial dispersion.

Moreover, the following definitions are also appropriate: $\theta \equiv V/u = L/\bar{v}$ is mean residence time in the cylinder and also a characteristic time associated with convective transport through the cylinder where

$$V = \begin{cases} V_0 \text{ for a packed column, its interstitial volume} \\ V_t \text{ for an empty tube, its volume} \end{cases}$$

and $\theta_c \equiv V_c/u$ is mean residence time in the cell and also a characteristic time associated with transport through the cell.

It is now apparent that radial dispersion in the cylinders will be small if

$$\lambda_R \gg \theta \text{ or if } \frac{R^2\bar{v}}{D_R L} \equiv Ta \gg 1$$

and axial dispersion will be small if

$$\lambda_L \gg \theta \text{ or if } \frac{L\bar{v}}{D_L} \equiv Pe_L \gg 1$$

where Pe_L is the well-known longitudinal Peclet number (dimensionless) and Ta is a dimensionless number which is defined in the present work as the Taylor number for reasons which will become apparent. In both cases, as θ becomes large, those mechanisms responsible for dispersion in the cylinder will have more time to occur and therefore will become more pronounced. Thus, dispersion in the cell will become unimportant relative to the cylinder if θ_c is sufficiently small. This criterion may be written as

$$\theta_c \ll \theta$$

or, more precisely,

$$\sigma_c \ll \sigma$$

where σ_c and σ are the standard deviations for cell and cylinder dispersion, respectively.

The Taylor and Peclet numbers as criteria for the importance of radial and axial dispersion may be derived in a more formal way by writing eq. (1) in dimensionless form

$$\frac{\partial c^*}{\partial t^*} = -\frac{v}{\bar{v}}\frac{\partial c^*}{\partial z^*} + \frac{1}{Ta}\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial c^*}{\partial r^*}\right) + \frac{1}{Pe_L}\frac{\partial^2 c^*}{\partial z^{*2}} \tag{5}$$

with the aid of the following dimensionless variables:

$$c^* \equiv \frac{c}{c_0},\ r^* \equiv \frac{r}{R},\ z^* \equiv \frac{z}{L} \text{ and } t^* \equiv \frac{t}{\theta}.$$

The consequences of $Ta \gg 1$ and $Pe_L \gg 1$ are obvious from eq. (5) and the dispersion regimes previously alluded to may now be introduced.

THE PACKED COLUMN

For plug flow in a packed column, the dispersion model, eq. (2), in dimensionless form is

$$\frac{\partial c^*}{\partial t^*} = -\frac{\partial c^*}{\partial z^*} + \frac{1}{Pe_L}\frac{\partial^2 c^*}{\partial z^{*2}} \tag{2a}$$

and after transformation via $x^* = z^* - t^*$, it becomes

$$\frac{\partial c^*}{\partial t^*} = \frac{1}{Pe_L}\frac{\partial^2 c^*}{\partial x^{*2}}. \tag{2b}$$

Its solution for an impulse solute input,[6] evaluated at the column exit ($z^* = 1$), is

$$c^{**} = \sqrt{\frac{Pe_L}{4\pi t^*}} \exp\left\{-\frac{Pe_L}{4t^*}(1 - t^*)^2\right\}$$

where $C^{**} \equiv CV_0/A$.

If dispersion in time of an elution curve represented by this function is small relative to the mean residence time in the column, i.e., if $t^* \approx 1$ with respect to the entire elution curve, then it may be approximated by the Gaussian distribution

$$c^{**} = \sqrt{\frac{Pe_L}{4\pi}} \exp\left\{-\frac{Pe_L}{4}(1 - V_r^*)^2\right\} \tag{6}$$

where $V_r \equiv ut$ is retention volume and $V_r^* \equiv V_r/u\theta = t^*$ is dimensionless retention volume or time. This approximation has previously been discussed.[7]

Clearly the peak value of c^{**}, $c^{**}_{\max}$, in eq. (6) occurs at the mean value of t ($t = \theta$) or V_r ($V_r^* = 1$) and the variance σ^{*2} is given by

$$\sigma^{*2} = \left(\frac{\sigma}{\theta}\right)^2 = \frac{2}{Pe_L} \tag{7}$$

so that σ^* is actually a measure of relative dispersion of the elution curve. Thus, if eq. (6) is to accurately represent dispersion in a packed column it follows that σ^* must be small. More specifically, this criterion may be written as

$$\sigma^{*2} \ll 1 \text{ or}^4\ Pe_L \gg 2.$$

If the elution curve for a pulse solute input is Gaussian, then the elution curve for a step input[6] must be

$$c^* = \frac{1}{2}\left\{1 - \operatorname{erf}\left[\sqrt{\frac{Pe_L}{4V_r^*}}(1 - V_r^*)\right]\right\} \tag{8}$$

where

$$\operatorname{erf}\left[\sqrt{\frac{Pe_L}{4V_r^*}}\,(1 - V_r^*)\right] \equiv \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{\frac{Pe_L}{4V_r^*}}(1 - V_r^*)} \exp\{-\zeta^2\} d\zeta$$

is the error function and $\zeta \equiv \sqrt{Pe_L/4V_r^*}\,(1 - V_r^*)$.

In the design of packed-bed chemical reactors, the criterion $Pe_L > 100$ is sufficient to guarantee that the effects of axial dispersion are negligible. Moveover, engineering correlations[2] for liquids flowing through packed columns with values for the Reynolds number Re_p in excess of approximately 0.1 show that the dimensionless number, another Peclet number,

$$Pe_p \equiv \frac{d_p \bar{v}}{D_L}$$

is virtually independent of Re_p for a given liquid–particle system and that for many Newtonian liquid systems it has a value within the region

$$0.5 < Pe_p < 2. \tag{9}$$

This implies that D_L is proportional to $\bar{v}$ and is so because eddy diffusion is the primary mechanism contributing to axial dispersion. The Reynolds number for packed columns is defined as

$$Re_p = \frac{d_p \bar{v} \rho}{\mu}$$

where ρ = liquid density and μ = liquid viscosity.

As $\bar{v}$ becomes very small, Pe_p decreases in proportion to Re_p ,which indicates that D_L approaches a constant value of the order of the molecular diffusivity, D. Van Deemter et al.[4] have concluded from the data of Simpson and Wheaton[8] for the system ethylene glycol–water with molecular diffusivity of the order of 10^{-5} cm²/sec[9] and particle diameters d_p within the range of 20μ to 200μ that molecular diffusion played a negligible role in axial dispersion even for values of Re_p less than 0.1.

In GPC the following values are typical: u = 1 cc/min, d_p = 50, d_T = 0.307 in., L = 4 ft, and α = 0.35, so that d_T/d_p = 155 and $L/d_p = 2.4 \times 10^4$. Typical approximate values for Re_p and Pe_L, assuming that inequality (9) is still valid, are then approximately

$$Re_p = 0.05 \text{ and } 10^4 < Pe_L < 5 \times 10^4.$$

Thus, it might be reasonable to expect dispersion in the packed column to be small in the relative sense, symmetrical (Gaussian) and insensitive to molecular weight of the solute. The last conclusion is based upon the fact that D for ODCB (in toluene) also has a value of the order of 10^{-5} cm²/sec and D for polymers is even two orders of magnitude smaller. For example, D for polystyrene (in toluene)[10] is of the order of 10^{-7} cm²/sec. This means that eddy diffusivity and not molecular diffusivity probably domi-

nates D_L under typical GPC conditions. If this is the case, then a sample calculation for, say, $V_r = V_0 = 21$ cc using eq. (7) shows that the following approximate values for absolute dispersion σ might be expected:

$$0.1 \text{ min} < \sigma < 0.3 \text{ min}$$

or, in terms of retention volume,

$$0.1 \text{ cc} < \sigma_v < 0.3 \text{ cc}.$$

There is, however, certainly some justification for caution when speculating about eddy diffusion in polymer solutions in view of the fact that polymers, even at low concentrations, not only dramatically affect the viscosity of the solvents in which they are dissolved but may also cause them to exhibit viscoelastic or other non-Newtonian flow behavior. Very little data are available on dispersion in polymer solutions flowing through packed columns. However, there is some evidence[11] that Pe_p is independent of Re_p to values of Re_p as low as 0.03 and that it has a value of approximately 0.2, slightly less than the lower value used in the above example.

The conventional efficiency parameters used in chromatography may also, in modified form, be used to characterize extraparticle dispersion. These are: plate count n, now actually the number of theoretical mixing stages; and $HETP$, now actually the height equivalent to a theoretical mixing stage:

$$n \equiv \left(\frac{\theta}{\sigma}\right)^2 = \frac{Pe_L}{2} \text{ and } HETP \equiv \frac{L}{n} = \frac{2L}{Pe_L}$$

Clearly, when $Pe_p = 2$, the column may be represented by the equivalent model of L/d_p mixers in series, as follows:

$$n = \frac{L}{d_p} \text{ and } HETP = d_p.$$

THE EMPTY TUBING

For typical GPC flow rates, tube diameters and solute concentrations, say, 1 cc/min, 1 mm and 2 g/l. Newtonian laminar flow conditions should prevail with

$$Re = \frac{d_t \bar{v} \rho}{\mu} \sim 30.$$

Dispersion should then depend on the molecular diffusivity of the solute ($D_R = D_L = D$) and therefore on its molecular weight.

It is evident from eq. (5) that two extreme, distinctly different dispersion regimes are possible and that both are subject to simple mathematical analysis. The first will be called the segregated flow regime and the second, the Taylor regime.

The Segregated Flow Regime

This regime is approached when both

$$Ta \equiv \frac{R^2\bar{v}}{DL} \gg 1 \text{ and } Pe \equiv \frac{L\bar{v}}{D} \gg 1$$

and clearly occurs when D is small, as with large molecules. However, it may also occur for constant u when L is small or R is large, and it obeys the simple dispersion model

$$\frac{\partial c^*}{\partial t^*} = -\frac{v}{\bar{v}}\frac{\partial c^*}{\partial z^*} = -2\,[1 - r^{*2}]\frac{\partial c^*}{\partial z^*} \tag{3a}$$

whose solution for a rectangular pulse input, evaluated at the tube exit ($z^* = 1$), is

$$c_e^* = 1\left[t^* - \frac{0.5}{(1 - r^{*2})}\right] - 1\left[t^* - \epsilon^* - \frac{0.5}{(1 - r^{*2})}\right].$$

The elution curve for segregated flow, obtained from

$$c^* = \frac{\int_0^R 2\pi c_e^* v(r) r dr}{\pi R^2 \bar{v}} = 4\int_0^1 c_e^*(1 - r^{*2}) r^* dr^*$$

is, for a rectangular pulse input,

$$c = c_0\left\{\left[1 - \left(\frac{0.5\,\theta}{t}\right)^2\right]1(t - 0.5\,\theta) - \left[1 - \left(\frac{0.5\,\theta}{t - \epsilon}\right)^2\right]1(t - \epsilon - 0.5\,\theta)\right\} \tag{10a}$$

or, in dimensionless form,

$$c^* = \left[1 - \left(\frac{0.5}{V_r^*}\right)^2\right]1(V_r^* - 0.5) - \left[1 - \left(\frac{0.5}{V_r^* - V_s^*}\right)^2\right] \times 1(V_r^* - V_s^* - 0.5) \tag{10b}$$

where $V_s^* \equiv V_s/u\theta = \epsilon^*$ is dimensionless sample injection volume or time.

For a step solute input, the solution of eq. (3a), evaluated at the tube exit, is

$$c_e^* = 1\left[t^* - \frac{0.5}{(1 - r^{*2})}\right]$$

and, therefore, the elution curve is simply

$$c = c_0\left\{\left[1 - \left(\frac{0.5\,\theta}{t}\right)^2\right]1(t - 0.5\,\theta)\right\} \tag{11a}$$

or, in dimensionless form,

$$c^* = \left[1 - \left(\frac{0.5}{V_r^*}\right)^2\right]1(V_r^* - 0.5). \tag{11b}$$

An elution curve represented by eqs. (10a) or (10b) is highly unsymmetrical (skewed). Its peak lies to the left of its mean and it has a long tail.

The Taylor Regime

This regime is approached when

$$Ta \equiv \frac{R^2\bar{v}}{DL} \ll 1 \tag{12}$$

and

$$Pe \equiv \frac{L\bar{v}}{D} \gg 1. \tag{13}$$

The first criterion, inequality (12), which may also be written as

$$\frac{L}{\bar{v}} \gg \frac{R^2}{D}, \tag{12a}$$

is obviously met when D becomes large; however, it is compatible with the second, inequality (13), for constant u only when $R^2 \ll L^2$ or $R \ll L$.

This type of dispersion was first analyzed by Taylor[12] who gave a more precise criterion for its existence than inequality (12a), namely,

$$\frac{L}{\bar{v}} \gg \frac{2R^2}{(3.8)^2 D} \tag{14}$$

and is now commonly referred to as "Taylor axial diffusion." It is called axial diffusion although it is actually a manifestation of the combined effects of a velocity profile and radial molecular diffusion with the virtual absence, or at least comparative unimportance, of true (molecular) axial diffusion. The reason for this is, in essence, the remarkable fact that radial diffusion, if given the opportunity, partially cancels the dispersion effect of the velocity profile in such a way as to give the resultant dispersion the appearance of being genuine axial diffusion; it even obeys the usual axial dispersion model, eqs. (2), (2a), or (2b), with D_L given by[12]

$$D_L = \frac{4R^2\bar{v}^2}{192D}. \tag{15}$$

As a consequence, the elution curve in the Taylor regime for a pulse solute input is symmetrical (Gaussian) and is described by eq. (6) if relative dispersion is small in the sense previously discussed. That this must be the case may be seen by combining inequality (14) with eq. (15), which gives

$$Pe_L \equiv \frac{L\bar{v}}{D_L} \gg 7.$$

Thus, it appears that a system in order merely to qualify for the Taylor regime exhibits small relative dispersion.

An order-of-magnitude calculation for the Taylor regime shows that when Pe_L has a reasonable value of, say, 200, in order for σ_e to have a value comparable to that of one packed column, say, 0.2 cc, it is necessary to have 100 in. (L) of empty tubing when $u = 1$ cc/min and $d_t = 1$ mm. This result is obtained from eq. (7) and requires that D for the solute have a value of approximately 9×10^{-5} cm²/sec, from eq. (15). Furthermore, from inequality (14), ODCB in toluene may just qualify for the Taylor regime in 100 in. of empty tubing; certainly then, polystyrene ($D \sim 10^{-7}$) in toluene will not.

General Case

When dispersion in empty tubing is unsymmetrical and broader than expected of Taylor axial diffusion and yet does not meet the requirements of the segregated flow regime, eq. (3) must be solved for the appropriate input functions. No analytical solution of this equation is available but a numerical method for solving it with the aid of a high-speed digital computer has been developed[13] for step input functions.

It is reasonable to expect polymer solutions flowing through empty tubing to exhibit dispersion between the two regimes and to expect the shape as well as the breadth of this dispersion to be sensitive to molecular weight of the polymer, certainly to a greater degree than in packed columns.

THE REFRACTOMETER CELL

In order to compute the solute concentration "seen" by the detector (refractometer) and include the dispersion caused by the refractometer cell itself, i.e., to simulate as accurately as possible the actual elution curves, it is necessary to substitute the appropriate solution of eq. (1), evaluated at the cell entrance, for c_e in eq. (4) and solve the resulting equation for c. For the special cases considered in this work it is sufficient to replace the entire integral in eq. (4) with $uc(t)$ either from eqs. (6) or (8), if the column is connected directly to the refractometer cell, or from eqs. (10a) or (11a), when tubing is connected to the cell, which is the usual case. The reason for this is that the integration operation is tantamount to cup-averaging[14] the solute concentration issuing from the tubing. For the packed column v is constant and $\partial c/\partial r = 0$ so that cup-averaging is unnecessary. For the empty tubing, the integration has already been performed; in fact, it is precisely the operation used to transform the solutions of eq. (3a), evaluated at the tube exit, into eqs. (10a) and (11a).

Dispersion in the completely backmixed cell model, eq. (4), is given by the simple expression

$$\sigma_c = \frac{V_c}{u} = \theta_c. \tag{16}$$

For a standard Waters Associates refractometer cell ($V_c = 0.07$ cc) and a typical flow rate, $u = 1$ cc/min, dispersion in the cell, $\sigma_c = \theta_c = 0.07$ min, is small relative to that in a typical packed column ($V_0 = 21$ cc) or

empty tube ($V_t \sim 0.02$ cc/in.). Thus, approximate elution curves may be computed directly from eqs. (6) or (8) when little or no tubing is present between column and cell and from eqs. (10b) or (11b) when an appreciable length of tubing is connected to the cell inlet.

It is appropriate at this point to elaborate briefly on the concept of relative dispersion, σ/θ, which has been discussed elsewhere in connection with distribution of residence times in separation processes[7] and molecular weight distributions of polymers.[15,16] It is well known that the standard deviation σ is a measure of absolute breadth or dispersion of any distribution. However, absolute breadth is not always the most appropriate parameter with which to characterize a distribution having a physical origin; the selection of an appropriate parameter depends upon the precise nature of the information desired. For example, the dispersion index

$$D \equiv \frac{\bar{x}_w}{\bar{x}_N} = \frac{\bar{M}_w}{\bar{M}_N} \geqslant 1$$

is used by polymer scientists and engineers to characterize molecular weight dispersion in polymers, where $\bar{x}_N$, $\bar{M}_N$ = number-average degree of polymerization and molecular weight, respectively, and $\bar{x}_w$, $\bar{M}_w$ = weight-average degree of polymerization and molecular weight, respectively.

What is actually desired in this case is a measure of the effect of molecular weight distribution on the physical properties of a polymer. For the same value of absolute molecular weight dispersion, σ_N, this effect will clearly be more pronounced in a polymer having a low average molecular weight, $\bar{x}_N$, than in one having a high average. Hence, a measure of relative dispersion, $\sigma_N/\bar{x}_N$, is actually desired, i.e., absolute breadth of the distribution relative to the mean size of the molecules. Since this is what D actually measures, as seen from the relationship[15]

$$\left(\frac{\sigma_N}{\bar{x}_N}\right)^2 = D - 1$$

it appears to be an appropriate parameter to use in this case.

Similarly, in the design of packed bed reactors or chromatographic columns, a large value for n indicates an efficient reaction or separation column. The reason for this is, again, that relative dispersion $(1/n)$ is the important parameter since it measures dispersion in the column relative to its total reaction or separation capability.

Now, in the case of extraparticle dispersion in GPC columns or in the empty tubing, $2/Pe_L$ characterizes relative dispersion, whereas σ characterizes absolute dispersion. However, the latter quantity is actually what is measured by the detector. Hence, even though Pe_L may be larger for packed GPC columns than for the empty tubing, it is still possible for σ to be larger as well, depending upon the relative values for θ. Thus, the packed column might affect chromatogram resolution more seriously than the empty tubing.

In conclusion, then, when contrasting the dispersion effects of columns versus empty tubing, it is important to compare V_0 and V_t as well as the values for Pe_L.

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