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SPREADING PHENOMENA IN CHROMATOGRAPHIC COLUMNS

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Abstract—An integrodifferential equation of transport of a P-mer through a chromatographic column working on the principle of phase distribution chromatography (PDC) near the theta point of the system polymer/solvent is stated and integrated analytically. Two contributions to the concentration profile are found, representing perturbed Gaussian and superposed Schulz distributions respectively. A spreading function is calculated, containing as its zero term the Tung spreading function known from gel permeation chromatography (GPC). The complete spreading function can be applied to calculate the molecular weight distribution of polymers from the elution curves of PDC measured in the dynamic region of the column (at temperatures substantially less than the theta temperature). It can also be applied to calculate the hydrodynamical–kinetic parameters, characterizing the axial dispersion (spreading effects) in PDC. Since no resolution takes place near the theta point (i.e. beyond the dynamic region of the PDC-column), the results can be used also for other chromatographic columns, e.g. in GPC.

INTRODUCTION

It is well known from numerous experiments with gel permeation chromatography (GPC) that the width of the elution curve obtained by this technique always exceeds the contribution of the molecular weight distribution (MWD) of the injected polymer sample to the width measured e.g. by the variance σ_V^2 of the elution curve. When the nonuniformity $U = \bar{M}_w/\bar{M}_n - 1$ of the sample with a given weight average $\bar{M}_w$ and number average $\bar{M}_n$ of the molecular weight tends to zero, the variance σ_V^2 does not vanish but tends to some limit, usually slightly depending on $\bar{M}_w$. The elution curve then differs slightly from a Gaussian curve. This effect known as *axial dispersion* or *spreading of the concentration profile* takes place to some extent in any chromatographic column. It can especially well be observed in phase distribution chromatography (PDC) because the resolution of the PDC-column depends very sensitively on the column temperature [1–5]. Since the resolution asymptotically vanishes in the neighbourhood (but below) the theta temperature of the system polymer/solvent used, the spreading effect alone can be measured in this range [2, 5]. Hence, unlike the GPC, PDC is especially suited for the investigation of spreading phenomena in chromatographic columns.

The axial dispersion (spreading) represents a rather complex phenomenon, including both hydrodynamic and kinetic effects. It is well known that two kinds of kinetics have to be considered in a chromatographic process: kinetics with high rates (fast kinetics) being a basis for the resolution of the column, and kinetics with low rates (slow kinetics) leading to a tailing of the concentration profile. There are two ways for calculating it: first, the statistical method dealing with the statistics of the molecular exchange between mobile and stationary phase of the column, and second, the analytical method dealing with a balance equation in the mass flow assumed as a continuum.

In the *statistical approach*, the transport of a P-mer through the column is interpreted as an infinite sequence of alternative adsorption and desorption steps of the transported P-mer on the stationary phase. The concentration profile in the neighbourhood of a given flow coordinate at a given time t to $t + dt$ is obtained by summing up over all Poisson-distributed steps, and by recalculating the transport variables to the elution volume and to any of its averages in the profile, eventually. This method has been worked out by Giddings and Eyring [6], Giddings [7], McQuarrie [8] and others.

The *analytical approach* deals with the flow as continuum being governed by a balance equation which describes mathematically both hydrodynamical and kinetical interactions of the transported P-mer with the stationary phase of the column. The concentration profile is then interpreted as an integral of the balance equation satisfying certain time and space boundaries given by the *resolution mechanism* in the column. This method has been applied by Vilenchic and Belenkij [9] in GPC, and by Giddings [10] and others.

It is clear that the concentration profile, calculated by one of these methods, includes both the contribution of the resolution and the contribution of the axial dispersion, when e.g. polymer samples are considered in GPC. The question arises how to separate these two very different contributions to the profile.

The simplest way to separate them is the employment of an empirical statistical analysis of the measured polydisperse elution curve. This method was applied in GPC by Tung [11], Rosen and Provder [12], Hamielec [13] and others. However, the well-known Gram–Charlier series of mathematical statis-

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Dedicated to Professor Dr Oto Wichterle on the occasion of his 70th birthday.

tics obtained in this way represents a purely empirical result, given neither information on the chromatographic process, nor the physical meaning of the calculated statistical momenta. Only its zero term, introduced empirically by Tung [11], and representing a Gaussian function with two variables, can trivially be interpreted as a formal analogy to Fick's second low in a flowing system. But so far no proof has been given that the higher terms in a series for the normalized concentration profile (spreading function) are really Gram terms. The perturbation concept itself cannot give an explanation.

The analytic approach mentioned above has probably as few chances as the statistical when the spreading phenomena in a GPC-column are investigated. On the other hand, the chances are very good when the axial dispersion in the PDC-column is investigated by this method because the resolution of the PDC-column can practically be eliminated at temperatures just below the theta temperature. The spreading effects alone can then be measured and described with high accuracy. This will be shown in the following sections.

TRANSPORT EQUATION OF PDC NEAR THE THETA POINT

Consider the PDC-column [2–5] of length L working just below the theta temperature of the system polymer/solvent. A one-dimensional Cartesian system of coordinates with the origin $0(z)$ fixed at one column end may be situated into the column axis. Let a P-mer be injected at the position $z = 0$ into the column at time $t = 0$. Consider, in addition, an axial flow of this given P-mer through the column, the flow being characterized by some constant elution rate u (cm/sec) and by a local reduced concentration $c(z, t)$ (cm^{-1}) of the transported P-mer at the position $0 \leqq z \leqq L$ and the time $t \geqq 0$. The concentration c may be normalized as follows:

$$\int_0^L c(z, t)\,\mathrm{d}z = 1 \quad \text{for all values of } t. \tag{1a}$$

Since practically no resolution takes place in the column, only the spreading effects are measured at the position $z = L$ and the elution time $t = t_e$. If $c'(z, t)$ is the equilibrium reduced concentration of the P-mer in the stationary phase at (z, t), and j the vector of flow density caused by the axial dispersion in the flow at (z, t), then the mass balance of the P-mer in the column becomes

$$\left(\frac{\partial}{\partial t} + u\frac{\partial}{\partial z}\right)c(z, t) + \frac{\partial c'(z, t)}{\partial t} + \operatorname{div} j = 0. \tag{1b}$$

The first term represents a time variation of c relative to a system of coordinates $0'(z)$ moving with the mass centre of the concentration profile in the flow; the second term represents a local time variation of c' in the flow relative to $0(z)$; the third term contains the vector of flow density which can be written as

$$j = -D' \operatorname{grad} c(z, t) = -D'\frac{\partial c(z, t)}{\partial z}\,\mathrm{e}_z \tag{1c}$$

when a *constant coefficient of (hydrodynamical) axial dispersion* D′ *(cm²/sec)* is introduced into the mass balance equation (1b).

Equation (1c) represents a simplification, but it is necessary for avoiding serious mathematical difficulties in the analytic solution of the problem of spreading. For the same purpose, a linear adsorption–desorption kinetics is assumed, allowing the simple formulation

$$\frac{\partial c'(z, t)}{\partial t} = \lambda c(z, t) - \lambda' c'(z, t) \tag{1d}$$

for the second term of equation (1b). In equation (1d), *λ is the constant coefficient of adsorption and λ' the constant coefficient of desorption* (units: sec^{-1}) of the P-mer on the stationary phase of the PDC-column near the theta point. The balance equation (1b) then reads

$$\frac{\partial c}{\partial t} = D'\frac{\partial^2 c}{\partial z^2} - u\frac{\partial c}{\partial z} - \lambda c + \lambda' c', \tag{2a}$$

$c'(z, t)$ being an integral of the partial differential equation (1d) with fixed $c(z, t)$, λ and λ'. This function is evidently equal to

$$c'(z, t) = \lambda \int_0^t \mathrm{d}\tau\, \mathrm{e}^{\lambda'(\tau - t)} c(z, \tau) \tag{2b}$$

which can easily be checked by differentiating equation (2b) partially with respect to t, and by comparing the result with equation (1d). After inserting equation (2b) into equation (2a), the *integrodifferential equation of transport of a P-mer through a PDC-column working near the theta point* is obtained:

$$\frac{\partial c}{\partial t} = D'\frac{\partial^2 c}{\partial z^2} - u\frac{\partial c}{\partial z} - \lambda c + \lambda\lambda' \int_0^t \mathrm{d}\tau\, \mathrm{e}^{\lambda'(\tau - t)} c(z, \tau). \tag{3a}$$

Since it represents a balance equation of the mass flow with axial dispersion (spreading) alone, it must be integrated with time and space boundaries of the *process of injection*:

$$c(z, 0) = \phi(z) \quad c(0, t) = \psi(t) \quad \left.\frac{\partial c}{\partial z}\right|_{z=0} = \eta(t). \tag{3b}$$

For a given P-mer, the axial dispersion is described by the constant set of column parameters $(D', u, \lambda, \lambda')$. It is typcial for equations (3a–b) that $D'(\mathrm{P})$, $u(\mathrm{P})$, $\lambda(\mathrm{P})$ and $\lambda'(\mathrm{P})$ vary only slowly with P, and that the influence of (λ, λ') on $c(z, t)$ is less than that of (D', u). It is evident from equation (3a) that $c(z, t)$ represents a Gaussian function $G(z - ut)$ in an infinitely long column, provided the injection at $z = 0$ and $t = 0$ is infinitely fast and $\lambda = 0$. In this case, the time boundary in equation (3b) represents Dirac's delta functional* (concentration impulse)

$$c(z, 0) = \delta(z) \tag{3c}$$

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*The incorrect notation "delta function" for δ should be omitted because $\delta(x)$ represents the singular kernel of the mapping function $f(x) \mapsto$ number $f(0)$

$$\int_{-\infty}^{\infty} \delta(x) f(x)\,\mathrm{d}x = f(0).$$

Hence, $\delta(x)$ does not represent a usual function (= mapping number→number) but a distribution, i.e. a function–function or shortly functional.

and the space boundaries are omitted. Equation (1a) is then modified to

$$\int_{-\infty}^{+\infty} \delta(z)\,\mathrm{d}z = 1. \tag{3d}$$

INTEGRAL OF THE TRANSPORT EQUATION

In PDC, the injection time is always very short when compared with the elution time. Further, the 4σ-width of the concentration profile is very short in comparison with the column length L. Hence, the time boundary (3c) can be taken instead of $\phi(z)$ in equation (3b) in which both space boundaries can be omitted. The system of equations (3a–b) then reads

$$\frac{\partial c(z,t)}{\partial t} - D'\frac{\partial^2 c(z,t)}{\partial z^2} + u\frac{\partial c(z,t)}{\partial z} + \lambda c(z,t)$$

$$-\lambda\lambda' \int_0^t \mathrm{d}\tau\, \mathrm{e}^{\lambda'(\tau - t)} c(z,\tau) = 0 \tag{4a}$$

$$c(z,0) = \delta(z) \quad -\infty < z < +\infty \quad t \geqq 0.$$

To integrate, the zero on the right-hand side is replaced by the product of delta functionals $\delta(z)\delta(t)$. This is allowed since $z = 0$ at $t = 0$ is valid. In this way, the system of equations (4a) is unified to *one* equation containing the singular time boundary (3c) implicitly:

$$\frac{\partial c}{\partial t} - D'\frac{\partial^2 c}{\partial z^2} + u\frac{\partial c}{\partial z} + \lambda c$$

$$-\lambda\lambda' \int_0^t \mathrm{d}\tau\, \mathrm{e}^{\lambda'(\tau - t)} c(z,\tau) = \delta(z)\delta(t). \tag{4b}$$

To integrate equation (4b), the formal differential operator

$$L(z,t) = \frac{\partial c}{\partial t} - D'\frac{\partial^2 c}{\partial z^2} + u\frac{\partial c}{\partial z} + \lambda c - \delta(z)\delta(t) \tag{5a}$$

is introduced and equation (4b) is written as a formal Abel's integral equation of the first kind

$$L(z,t) = \lambda\lambda' \int_0^t \mathrm{e}^{\lambda'(\tau - t)} c(z,\tau)\,\mathrm{d}\tau. \tag{5b}$$

Now, for all ($\lambda > 0, \lambda' > 0$) the relation

$$\int_0^t \frac{\partial}{\partial t} \mathrm{e}^{\lambda'(\tau - t)} c(z,\tau)\,\mathrm{d}\tau =$$

$$-\lambda' \int_0^t \mathrm{e}^{\lambda'(\tau - t)} c(z,\tau)\,\mathrm{d}\tau = -\frac{1}{\lambda} L(z,t)$$

is valid. Hence,

$$\partial L(z,t)/\partial t + \lambda' L(z,t) - \lambda\lambda' c(z,t) = 0 \tag{5c}$$

is valid according to equation (5b). Inserting equation (5a) into (5c), the partial differential operator of higher order on $c(z,t)$

$$\{\partial^2/\partial t^2 + (\lambda + \lambda')\partial/\partial t - D'\partial^3/\partial t\partial z^2$$

$$+ u\partial^2/\partial t\partial z - \lambda' D'\partial^2/\partial z^2 + \lambda' u\partial/\partial z\} c(z,t)$$

$$= \delta(z)\delta'(t) + \lambda'\delta(z)\delta(t) \tag{6}$$

is obtained, where $\delta'(t) = (\mathrm{d}/\mathrm{d}t)\delta(t)$ is a new singular functional. It can easily be shown that equation (6) holds for all $\lambda \geqq 0$, $\lambda' > 0$ and $D' \geqq 0$. For $\lambda = 0$ and $D' \to 0 + 0$, the concentration impulse $\delta(z - ut)$ follows from equation (6) with $t \geqq 0$; for $t = 0$ it is identical with the boundary (3c). The operator $\lambda' + \partial/\partial t$ with $\lambda' > 0$ is cancelled out when $\lambda = 0$ in equation (6).

To solve equation (6), the right-hand-side functional is represented as a Fourier transform. From the well-known relations

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}\omega\, \mathrm{e}^{-i\omega t}$$

and

$$\delta'(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}\omega(-i\omega)\, \mathrm{e}^{-i\omega t}$$

the functional

$$\delta(z)\delta'(t) + \lambda'\delta(z)\delta(t) =$$

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}k\,\mathrm{d}\omega\, \mathrm{e}^{-ikz}\, \mathrm{e}^{-i\omega t}\, \frac{\lambda' - i\omega}{2\pi} \tag{7a}$$

follows. Hence, the Fourier transform $c_*(k,\omega)$ of the reduced concentration

$$c(z,t) =$$

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}k\,\mathrm{d}\omega\, \mathrm{e}^{-ikz}\, \mathrm{e}^{-i\omega t} c_*(k,\omega) \tag{7b}$$

is introduced, and equations (7a–b) are inserted into equation (6). After performing the differentiations, the expression

$$c_*(k,\omega) =$$

$$\frac{1}{2\pi}\frac{i\omega - \lambda'}{\omega^2 + 2f(k)\omega + \lambda'[\lambda + \lambda' + i2f(k)]} \tag{7c}$$

for the Fourier transform c_* is obtained; it contains the complex function

$$2f(k) = uk + i(D'k^2 + \lambda + \lambda'). \tag{8}$$

After inserting equation (7c) into equation (7b), the reduced concentration profile searched for yields (unit: cm^{-1}):

$$c(z,t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}k\, \mathrm{e}^{-ikz} \tag{9}$$

$$\times \frac{i}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}\omega \frac{(\omega + i\lambda')\,\mathrm{e}^{-i\omega t}}{\omega^2 + 2f(k)\omega + \lambda'[\lambda + \lambda' + i2f(k)]}.$$

In agreement with equation (6), the factor $\omega + i\lambda'$ with any $\lambda' > 0$ cancels out from equation (9) when $\lambda = 0$ is set in equations (8–9); the profile (9) then does not contain λ'.

As a check, the simple case $\lambda = 0$ (no adsorption) is first investigated. In this case, $2f(k) = uk + i(D'k^2 + \lambda')$ follows from equation (8) so that the inner integral in equation (9) reduces to

$$J(0) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{\omega + uk + iD'k^2} \quad -\infty < k < \infty. \tag{10a}$$

It is calculated by means of the residuum theorem and Jordan's lemma in the complex plane $\omega := \mathrm{Re}(\omega) + i\,\mathrm{Im}(\omega)$.The integrand has a pole of order 1 at the position $\omega_1 = -uk - iD'k^2$ in the halfplane $\mathrm{Im}(\omega) < 0$ for $k \neq 0$, and in the origin for $k = 0$. The residuum at $\omega = \omega_1$ is equal to $\exp(-D'tk^2) \times \exp(iutk)$. When the contour from Appendix A1 is chosen and Jordan's lemma is applied, the residuum theorem yields the reduced concentration profile

$$c(z, t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk\, e^{-i(z-ut)k}\, e^{-D'tk^2}$$

$$= \frac{1}{\sqrt{2\pi}} \mathscr{F}\{e^{-D'tk^2}; z - ut\} \tag{10b}$$

according to Appendix A1 and equation (9). This well-known Fourier transform represents a Gaussian function with the variable mean ut and the variance $2D't$ as can easily be seen from equations (13a–c):

$$c(z, t) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(z-\bar{z})^2/(2\sigma^2)} \qquad [10c)$$

with

$$\bar{z} = ut \quad \text{and} \quad \sigma^2 = 2D't. \tag{10d}$$

Tung's spreading function follows immediately from equation (10c) when z and $\bar{z}$ are recalculated to elution volume V and its mathematical expectation $\bar{V}$(P) in the elution curve without tailing, respectively. Only *hydrodynamical interactions* of the P-mer with the stationary phase of the column are considered here since $\lambda = 0$.

The investigation of the general case of *hydrodynamical–kinetic interactions* ($\lambda > 0$, $\lambda' > 0$) is much more complicated. The inner integral in equation (9) now reads

$$J(\lambda, \lambda') = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \frac{(\omega + i\lambda')\, e^{-i\omega t}}{\omega^2 + 2f(k)\omega + \lambda'[\lambda + \lambda' + i2f(k)]} \tag{11a}$$

with the complete complex function (8). The integrand has now two poles of order 1 at the positions

$$\omega_{1,2} = -f \mp \sqrt{(f - i\lambda')^2 - \lambda\lambda'} \tag{11b}$$

in the halfplane $\mathrm{Im}(\omega) < 0$ or in the origin as can be seen from Fig. 3 in Appendix A1. The corresponding residua are equal to

$$\mathrm{Res}_{1,2} = \frac{-(f - i\lambda') \mp \sqrt{(f - i\lambda')^2 - \lambda\lambda'}}{\mp 2\sqrt{(f - i\lambda')^2 - \lambda\lambda'}} \times \exp\{itf \pm it\sqrt{(f - i\lambda')^2 - \lambda\lambda'}\} \tag{11c}$$

as can be seen from Appendix A2. It can be proved by calculating the variation of the argument $\arg(\omega - \omega_1) + \arg(\omega - \omega_2)$ along the contour from Appendix A1 that both poles (11b) must be considered. Since the mathematical behaviour of these poles is very different, the contribution of ω_1 and that of ω_2 to the integral (11a) must be investigated separately.

(A) CONTRIBUTION OF POLE ω_1 TO THE INTEGRAL

If only the pole $\omega = \omega_1$ [sign − in equation (11b)] is considered, then the integral (11a) can be calculated by means of the residuum theorem and Jordan's lemma as shown in Appendix A2. According to equation (9), the concentration profile related to ω_1 is obtained as the Fourier transform

$$c_1(z, t) = \frac{e^{-\lambda t}}{\sqrt{2\pi}} \mathscr{F}\{e^{-D'tk^2}F(k, t; \lambda); \quad z - ut\} \tag{12a}$$

with

$$F(k, t; \lambda) = \frac{\xi + \sqrt{\xi^2 + 4\lambda\lambda' t^2}}{2\sqrt{\xi^2 + 4\lambda\lambda' t^2}} \times \exp\left[\tfrac{1}{2}\sqrt{\xi^2 + 4\lambda\lambda' t^2} - \tfrac{1}{2}\xi\right] \tag{12b}$$

and

$$\xi = D't(ik)^2 + ut(ik) + (\lambda' - \lambda)t. \tag{12c}$$

The complex function (12b) has the property

$$F(k, t; 0) = 1 = F(k, 0; \lambda). \tag{12d}$$

Hence, the Tung-profile (10c) follows from equation (12a) in the limit $\lambda \to 0$ for any $\lambda' > 0$, as can be easily seen from equation (10b). The ansatz

$$F(k, t; \lambda) := \sum_{n=0}^{\infty} \alpha_n(t; \lambda)(ik)^n \tag{12e}$$

with any coefficients α_n having the property

$$\alpha_n(t; 0) = \alpha_n(0; \lambda) = \delta_{n0} = \begin{cases} 1 & \text{for} \quad n = 0 \\ 0 & \phantom{\text{for}} \quad n \neq 0 \end{cases} \tag{12f}$$

yields the concentration profile

$$c_1(z, t) = \frac{e^{-\lambda t}}{\sqrt{2\pi}} \sum_{n=0}^{\infty} \alpha_n \mathscr{F}\{e^{-D'tk^2}(ik)^n; \quad z - ut\} \tag{12g}$$

for all $\lambda \geqq 0$ in equation (12a). The series (12g) contains the well-known Fourier transform [14]

$$\mathscr{F}\{e^{-a^2k^2}(ik)^v; \kappa\} = (a\sqrt{2})^{-v-1} \times \exp[-(\kappa^2)/(8a^2)]D_v\left(\frac{\kappa}{a\sqrt{2}}\right), \quad \mathrm{Re}(a) > 0,\ \mathrm{Re}(v) > -1 \tag{13a}$$

in which $D_v(\zeta)$ is the parabolic–cylindrical function of order v. Since $v = n = 0, 1, 2, \ldots$ in equation (12g), $D_n(\zeta)$ reduces to the weighted Hermite polynomial $\mathrm{H}_n(\zeta/\sqrt{2})$:

$$D_n(\zeta) = e^{-\zeta^2/4}2^{-n/2}\mathrm{H}_n(\zeta/\sqrt{2}) \tag{13b}$$

with

$$\mathrm{H}_n(\zeta) = (-1)^n e^{\zeta^2}\frac{d^n}{d\zeta^n}e^{-\zeta^2}. \tag{13c}$$

Thus, the reduced concentration profile $c_1(z, t)$ related to the pole ω_1 represents a Fourier series in orthogonal Hermite polynomials, the first term being [due to $\mathrm{H}_0(\zeta) = 1$] a Gaussian function when λ tends to zero:

$$c_1(z, t) = \frac{e^{-\lambda t}}{\sigma\sqrt{2\pi}}e^{-(z-\bar{z})^2/(2\sigma^2)} \times \sum_{n=0}^{\infty}\frac{\alpha_n}{(\sigma\sqrt{2})^n}\mathrm{H}_n\left(\frac{z-\bar{z}}{\sigma\sqrt{2}}\right). \tag{14}$$

The mathematical expectation $\bar{z}$ of z in this series and the corresponding variance σ^2 are defined by equation (10d); hence, they are related to the leading Gaussian term in the series (14).

To obtain the *spreading function* $C_1(z, \bar{z})$ *related to the pole* ω_1, the profile (14) must be normalized in analogy to equation (1a):

$$C_1(z, \bar{z}) = c_1(z, t)\Big/\int_{-\infty}^{+\infty} c_1(z, t)\,dz. \tag{15}$$

If the well-known orthogonality relation for the Hermite polynomials

$$\int_{-\infty}^{+\infty} e^{-\zeta^2}\mathrm{H}_n(\zeta)\mathrm{H}_m(\zeta)\,d\zeta = 2^n n!\sqrt{\pi}\delta_{mn} \tag{16a}$$

with the Kronecker-delta $\delta_{mn} = 1$ for $m = n$ and $= 0$ for $m \neq n$ is applied to equation (14), then the norm

$$\int_{-\infty}^{+\infty} c_1(z, t)\,dz = \alpha_0 e^{-\lambda t} \tag{16b}$$

is found; it is equal to 1 for $\lambda = 0$, as predicted by equation (12f). Inserting equations (14) and (16b) into equation (15), one obtains the spreading function

$$C_1(z, \bar{z}) = \frac{1}{\sigma\sqrt{2\pi}}e^{-(z-\bar{z})^2/(2\sigma^2)} \times \left[1 + \sum_{n=1}^{\infty}\frac{\alpha_n}{\sigma^n\alpha_0}\mathrm{He}_n\left(\frac{z-\bar{z}}{\sigma}\right)\right] \tag{17}$$

with the modified Hermite polynomials

$$\mathrm{He}_n(\zeta) = 2^{-n/2}\,\mathrm{H}_n(\zeta/\sqrt{2}). \tag{18}$$

The spreading function (17) represents a surface, since z and $\bar{z}$ are independent variables: $\bar{z} = ut$ can be related to the position of the mass centre in the profile at time t; z describes any point of this profile. The Tung term $n = 0$ describes the influence of hydrodynamical interactions upon the profile related to the pole ω_1, and the higher terms the influence of kinetic interactions giving the tail of the profile. The series (17) can be interpreted as a *Gram–Charlier series* of mathematical statistics when $\alpha_1 = 0$ is presumed in equation (12e).

To calculate the Fourier coefficients $\alpha_n(t; \lambda)$ of the orthogonal series (17), the series (12e) must be stated. When no restrictions on (λ, λ') are allowed, the complex function (12b) must be expanded into a Taylor series in (ik). If the tailing of the concentration profile is not too large, then the square root

$$\sqrt{\xi^2 + 4\lambda\lambda' t^2} = \xi\left(1 + \frac{4\lambda\lambda' t^2}{\xi^2}\right)^{1/2}$$

from equation (12b) can be expanded into the harmonic series

$$(1 + x)^m = 1 + \frac{m}{1!}x + \frac{m(m-1)}{2!}x^2 + \ldots.$$

with $m = 1/2$ and $|x| = |4\lambda\lambda' t^2/\xi^2| \leqq 1$ for all $-\infty < k < \infty$. According to equation (12c), the relation

$$\left|\frac{4\lambda\lambda' t^2}{\xi^2}\right| = \frac{4\lambda\lambda'}{(\lambda' - \lambda - D'k^2)^2 + (uk)^2} \leqq \frac{4\lambda\lambda'}{(\lambda' - \lambda)^2}$$

is valid for all k. Hence, the convergence condition $|x| \leqq 1$ leads to the restriction

$$\lambda'/\lambda + \lambda/\lambda' \geqq 6 \tag{19}$$

on (λ, λ') in the chromatographic process. However, this restriction is always permissible if the tailing of the profile is not too large, e.g. as found in PDC and GPC. If condition (19) is satisfied, then the expansion of the square root yields the useful approximation

$$F(k, t; \lambda) \approx 1 + \frac{\lambda\lambda' t^2}{1!}\xi^{-1} + \frac{(\lambda\lambda' t^2)^2}{2!}\xi^{-2} + \ldots \tag{20a}$$

containing the complex functions

$$\xi^{-n}(ik) = \xi^{-n}(0) + \sum_{v=1}^{\infty}\left.\frac{d^v\xi^{-n}}{d(ik)^v}\right|_{k=0}\frac{(ik)^v}{v!} \qquad n = 1, 2, \ldots \tag{20b}$$

calculated from equation (12c). After introducing the dimensionsless parameters

$$\Omega = \lambda\lambda' t^2 \quad \text{and} \quad \Lambda = (\lambda' - \lambda)t, \tag{21}$$

calculating the derivatives in equation (20b) from equation (12c), inserting equation (20b) into equation (20a) and comparing the result with equation (12e), the following Fourier coefficients are obtained:

$$\begin{aligned}
\alpha_0 &= \mathrm{e}^{\Omega/\Lambda}\\
\alpha_1 &= \bar{z}\frac{\mathrm{d}\alpha_0}{\mathrm{d}\Lambda}\\
\alpha_2 &= \frac{\bar{z}}{2}\frac{\mathrm{d}\alpha_1}{\mathrm{d}\Lambda}+\frac{\sigma^2}{2\bar{z}}\alpha_1\\
\alpha_3 &= \frac{\bar{z}}{3}\frac{\mathrm{d}\alpha_2}{\mathrm{d}\Lambda}-\frac{\sigma^2}{6}\frac{\mathrm{d}\alpha_1}{\mathrm{d}\Lambda}+\frac{\sigma^2}{\bar{z}}\alpha_2-\frac{\sigma^4}{2\bar{z}^2}\alpha_1 \qquad (22a)\\
&\vdots
\end{aligned}$$

The coefficient α_k obviously has the dimension cm^k, in agreement with equation (17). Performing finally the differentiations in the recurrence relations (22a), the quotients required in equation (17) are obtained:

$$\begin{aligned}
\frac{\alpha_1}{\alpha_0} &= -\frac{\bar{z}\Omega}{\Lambda^2}\\
\frac{\alpha_2}{\alpha_0} &= \frac{\Omega}{2\Lambda^2}\left[\frac{\bar{z}^2}{\Lambda}\left(2+\frac{\Omega}{\Lambda}\right)-\sigma^2\right]\\
\frac{\alpha_3}{\alpha_0} &= \frac{\Omega\bar{z}}{\Lambda^3}\left[\sigma^2\left(1+\frac{\Omega}{4\Lambda}\right)\right.\\
&\qquad \left.-\frac{\bar{z}^2}{\Lambda}\left(\frac{\Omega^2}{6\Lambda^2}+\frac{\Omega}{\Lambda}+1\right)\right] \qquad (22b)\\
&\vdots
\end{aligned}$$

From the first equation of the system (22a) and from equations (21) and (22b), it can easily be seen that the coefficients (22a) have the property (12f). The condition (19) now reads

$$\Omega/\Lambda^2 \leqq 0.25. \qquad (22c)$$

The quotients (22b) exhibit an especially simple form if the additional condition

$$\Omega/|\Lambda| \gg 1 \qquad (23a)$$

is satisfied. In this case, the dimensionless quotients

$$\frac{\alpha_n}{\sigma^n\alpha_0} = \frac{(-1)^n}{n!}\left(\frac{\Omega\bar{z}}{\Lambda^2\sigma}\right)^n \quad n \geqq 1 \qquad (23b)$$

follow from the system of equations (22b). The series (17) then converges very quickly if $\Omega\bar{z}/(\Lambda^2\sigma) \leqq 0.9$ is valid. In general, this is a relatively strong restriction on (λ, λ') in any chromatographic process. It can be accepted in PDC near the theta point where experiments give a value nearly 0.8 indicating only a slight tailing of the eluogram due to kinetic interactions of the transported P-mer with the stationary phase of the column. The same behaviour can be presumed in GPC.

(B) CONTRIBUTION OF POLE ω_2 TO THE INTEGRAL

If only the pole $\omega = \omega_2$ [sign + in equation (11b)] is considered, then the calculation from Section A must be performed with $+\surd$ instead with $-\surd$, as can be easily seen from equations (11b, c). This yields the concentration profile related to the pole ω_2

$$c_2(z, t) = -\frac{\mathrm{e}^{-\lambda t}}{\sqrt{2\pi}}\,\mathscr{F}\{\mathrm{e}^{-D'tk^2}G(k, t; \lambda); z-ut\} \qquad (24a)$$

with

$$G(k, t; \lambda) = \frac{\xi-\sqrt{\xi^2+4\lambda\lambda' t^2}}{2\sqrt{\xi^2+4\lambda\lambda' t^2}} \times \exp\left[-\frac{1}{2}\sqrt{\xi^2+4\lambda\lambda' t^2}-\frac{1}{2}\xi\right] \qquad (24b)$$

and ξ from equation (12c). The complex function (24b) has the obvious property

$$G(k, t; 0) = 0 \quad \text{for all} \quad t \geqq 0 \qquad (24c)$$

which must be skilfully utilized. If the condition (19) is satisfied, then the function (24b) can be approximated as

$$G(k, t; \lambda) \approx -\lambda\lambda' t^2\,\mathrm{e}^{-\xi}\xi^{-2}\,\mathrm{e}^{-\lambda\lambda' t^2/\xi} \qquad t \geqq 0. \qquad (25a)$$

It contains the strong oscillating factor

$$\mathrm{e}^{-\xi} = \mathrm{e}^{+D'tk^2}\,\mathrm{e}^{(\lambda-\lambda')t}\,\mathrm{e}^{-iutk},$$

as can be easily seen from equation (12c). Therefore, if the ansatz

$$G(k, t; \lambda) := \sum_{n=0}^{\infty}\alpha_n'(ik)^n$$

were applied in analogy to equation (12e), then an extremely slowly convergent Gram–Charlier series would be obtained which would not be applicable. What is to do shows the Fourier transform in equation (24a). It contains the product

$$\mathrm{e}^{-\lambda t}\,\mathrm{e}^{-D'tk^2}\,\mathrm{e}^{-izk}\,\mathrm{e}^{+iutk} = \mathrm{e}^{-izk}\,\mathrm{e}^{-\lambda' t}\,\mathrm{e}^{\xi}$$

which eliminates the inconvenient factor $\exp(-\xi)$ in equation (25a). Within this useful approximation, the concentration profile (24a), related to the pole ω_2, reads

$$c_2(z, t) = \frac{\lambda\lambda' t^2\,\mathrm{e}^{-\lambda' t}}{\sqrt{2\pi}} \times \mathscr{F}\{\xi^{-2}\,\mathrm{e}^{-\lambda\lambda' t^2/\xi}; z\}. \qquad (25b)$$

It vanishes for $\lambda = 0$ at all $t \geqq 0$, as expected according to equation (24c).

A comparison of equation (25b) with equation (12g) shows that the mathematical behaviours of the poles ω_1 and ω_2 are very different: Whereas the pole ω_1 leads to a Fourier transform at the point $z-ut$ giving perturbed Gaussian profiles, the pole ω_2 leads to a Fourier transform at the point z not giving such profiles directly. We shall see that $c_2(z, t)$ completely vanishes for $\lambda' > \lambda$ in the condition (19) if $z > 0$ is valid relative to $0(z)$. In the opposite case $\lambda' < \lambda$ in (19), $c_2(z, t)$ represents superposed gamma-profiles at $|z|$ and t which can be transformed into a product containing exponential and modified Bessel functions. Within the approximations being used, these profiles play a role only along a short way in the column, i.e. for small values of ut; they can then be expanded into a Gram–Charlier series and be added to the main result (14). The third case $\lambda = \lambda'$ is omitted since it is not compatible with the restriction (19).

To calculate the Fourier transform (25b), the exponential function is expanded into a Taylor series:

$$\mathrm{e}^{-\lambda\lambda' t^2/\xi} = \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\left(\frac{\lambda\lambda' t^2}{\xi}\right)^n. \qquad (26a)$$

Inserting ξ from equation (12c) into equation (26a), and equation (26a) into equation (25b), the Fourier transform

$$\mathscr{F}\{\xi^{-2}\,\mathrm{e}^{-\lambda\lambda' t^2/\xi}; z\} = \sum_{n=0}^{\infty} \frac{(-\lambda\lambda' t^2)^n}{n!\sqrt{2\pi}} \times \int_{-\infty}^{+\infty} \frac{\mathrm{e}^{-ikz}}{[-D'tk^2 + iutk + (\lambda' - \lambda)t]^{n+2}}\,\mathrm{d}k \tag{26b}$$

is obtained because the series (26a), multiplied by ξ^{-2}, has a majorant at $k = 0$ so that it converges uniformly and so can be integrated term by term. The complex integral in equation (26b) is calculated by means of Jordan's lemma and residuum theorem in the complex plane $k := \mathrm{Re}(k) + i\,\mathrm{Im}(k)$. The integrand has two poles of order $n + 2$ in the zeros $k_{1,2}$ of the complex quadratic polynomial

$$\mathrm{P}_2(k) = -D'tk^2 + iutk + (\lambda' - \lambda)t.$$

They read

$$k_{1,2} = i\,\frac{u \mp \sqrt{u^2 - 4D'(\lambda' - \lambda)}}{2D'} \tag{26c}$$

so that

$$\mathrm{P}_2(k) = -D't(k - k_1)(k - k_2) \tag{26d}$$

is valid. Since the integrand is analytic at all other points k of the complex plane, there are two possibilities for choosing the contour, both depending on $\mathrm{sign}(\lambda' - \lambda)$.

If $\mathrm{sign}(\lambda' - \lambda) = +1$, i.e. if $\lambda' > \lambda$ is valid in equation (26c), then both poles $k_{1,2}$ lie on the positive imaginary axis. Hence, $z > 0$ and a contour along the real axis from $+\mathrm{R}$ to $-\mathrm{R}$ and along the halfcircle $|k| = \mathrm{R}$ in the lower halfplane $\mathrm{Im}(k) < 0$ is chosen for

$$\lambda' > \lambda \quad \text{and} \quad z > 0. \tag{27a}$$

Since the integrand is analytic in the whole area confined by the contour, the integral vanishes along them according to the residuum theorem. Furthermore, the function $\chi(k) = 1/\mathrm{P}_2^{n+2}(k)$ converges uniformly to zero in the lower complex halfplane $\mathrm{Im}(k) < 0$ and on the real axis if $|k| = \mathrm{R} \to \infty$. Hence, the integral also vanishes along the halfcircle $\mathrm{R} = \infty$ for $z > 0$ according to Jordan's lemma. Thus, the integral in the Fourier transform (26b) is equal to zero when the case (27a) is considered. Defining the *spreading function* $C_2(z, \bar{z})$ *related to the pole* ω_2 in analogy to equation (15) for $c_2 > 0$ and $C_2 \equiv c_2$ for $c_2 = 0$, the relation.

$$C_2(z, \bar{z}) = 0 \tag{27b}$$

is obtained in case (27a). In this case, the complete axial dispersion (spreading) in the column is caused by the pole $\omega = \omega_1$ as shown in section A.

If $\mathrm{sign}(\lambda' - \lambda) = -1$, i.e. if $0 < \lambda' < \lambda$ is valid in equation (26c), then the pole $k = k_1$ lies on the negative imaginary axis, and the pole $k = k_2$ on the positive imaginary axis. Applying Jordan's lemma and residuum theorem for $z > 0$ on $k = k_1$ [halfplane $\mathrm{Im}(k) < 0$], and for $z < 0$ on $k = k_2$ [halfplane $\mathrm{Im}(k) > 0$], and assuming

$$0 < \lambda' < \lambda \tag{28a}$$

in both cases, the integral in equation (26b)

$$\int_{-\infty}^{+\infty} f(k)\,\mathrm{d}k = +2\pi i \operatorname*{Res}_{k=k_2} f(k)$$

$$= \frac{+2\pi i}{(n+1)!} \lim_{\substack{k \to k_2 \\ z<0}} \frac{\mathrm{d}^{n+1}}{\mathrm{d}k^{n+1}} [f(k)(k - k_2)^{n+2}] \tag{28b}$$

for $z < 0$, and

$$\int_{-\infty}^{+\infty} f(k)\,\mathrm{d}k = -2\pi i \operatorname*{Res}_{k=k_1} f(k)$$

$$= \frac{-2\pi i}{(n+1)!} \lim_{\substack{k \to k_1 \\ z>0}} \frac{\mathrm{d}^{n+1}}{\mathrm{d}k^{n+1}} [f(k)(k - k_1)^{n+2}]$$

for $z > 0$ is obtained. Calculating the $n + 1$ th derivatives by means of the well-known Leibniz rule, inserting the integrals from the the system of equations (28b) into equation (26b), and equation (26b) into equation (25b), one obtains the concentration profile related to the pole ω_2 under the condition (28a)

$$c_2(z, t) = \sum_{n=0}^{\infty} \sum_{m=0}^{n+1} \beta_{nm} \frac{\lambda'^{n+1}}{\Gamma(n+1)} t^n \mathrm{e}^{-\lambda' t} \times \frac{\gamma^{n-m+2}}{\Gamma(n-m+2)} |z|^{n-m+1} \mathrm{e}^{-\gamma|z|} \tag{28c}$$

with

$$\gamma = \frac{\sqrt{u^2 - 4D'(\lambda' - \lambda)} - u\,\mathrm{sign}(z)}{2D'} > 0 \tag{28d}$$

and

$$\beta_{nm} = \frac{(n+m+1)!}{(n+1)!m!} \left[\frac{\lambda}{\gamma\sqrt{u^2 - 4D'(\lambda' - \lambda)}}\right]^n \times \left[\frac{D'\gamma}{\sqrt{u^2 - 4D'(\lambda' - \lambda)}}\right]^m \frac{\lambda}{\gamma^2[u^2 - 4D'(\lambda' - \lambda)]}$$

The profile (28c) is superposed from gamma-distributions in t and $|z|$ of the shape

$$\frac{b^{n+1}}{\Gamma(n+1)} x^n \mathrm{e}^{-bx}$$

well-known from polymer kinetics as Schulz-distribution. Here it is the result of Poisson-distributed alternative adsorption–desorption steps since the double series (28c) can be transformed into modified Bessel functions[*] I_k, well-known from the theory of chromatography. The profile plays a role only along a short way in the column when the

---

[*] $c_2(z, t) = \exp(-\lambda' t - \gamma|z|)\,(X/Y) I_1(X)$ + higher terms follows, with two functions $X(|z|, t; \lambda, \lambda')$ and $Y(t; \lambda, \lambda')$.

factors in the exponential functions are large enough, as is usually true. It vanishes completely for $\lambda = 0$ since then $\beta_{nm} = 0$ for all n and m. For small values of λ, the factor (28d) reduces to

$$\gamma \approx \left(\frac{\lambda - \lambda'}{D'}\right)^{1/2} > 0 \tag{28e}$$

showing that γ can be large in comparison with 1 because D' is very small.

Since the experiments show that the restriction (27a) is valid in PDC (and GPC), the spreading function $C_2(z, \bar{z})$ related to the concentration (28c) is not specified here. Instead, the relation (27b) is applied. The total spreading function $C(z, \bar{z}) = C_1(z, \bar{z}) + C_2(z, \bar{z})$ of the column then follows from equations (17) and (27b):

$$C(z, \bar{z}) = \frac{1}{\sigma\sqrt{2\pi}} \exp[-(z-\bar{z})^2/(2\sigma^2)] \times \left[1 + \sum_{n=1}^{\infty} \frac{\alpha_n}{\sigma^n \alpha_0} \mathrm{He}_n\left(\frac{z-\bar{z}}{\sigma}\right)\right]. \tag{29}$$

This is a quickly convergent Fourier series, if it is interpreted as a Gram–Charlier series [$\alpha_1 := 0$ in equation (12e)], or if $\alpha_n/(\sigma^n\alpha_0)$ is defined by equation (23b) under the conditions (22c), (23a) and (27a) on (λ, λ'). Both interpretations can be used in PDC and GPC.

APPLICATION TO PDC

When V_0 is the free volume of the PDC-column, L its length, $q = V_0/L$ its free cross section, σ_0^2 the variance of the leading Gaussian function in the perturbed elution curve, and $\bar{V}(\mathrm{P})$ the position of the corresponding maximum for a given P-mer transported through the column near the theta point, the relations $V = qz$, $\bar{V}(\mathrm{P}) = q\bar{z}$ and $\sigma_0^2 = q^2\sigma^2$ are valid. This follows from the invariance of the argument in the modified Hermite polynomials from equation (29): $(z-\bar{z})/\sigma = (V/-\bar{V})/\sigma_0$. Setting $K(V, \bar{V}) = C(z, \bar{z})/q$ and $\beta_n = q^n\alpha_n$, the spreading function (29) transforms to

$$K(V, \bar{V}) = \frac{1}{\sigma_0\sqrt{2\pi}} \exp[-(V-\bar{V})^2/(2\sigma_0^2)] \times \left[1 + \sum_{n=1}^{\infty} \frac{\beta_n}{\sigma_0^n \beta_0} \mathrm{He}_n\left(\frac{V-\bar{V}}{\sigma_0}\right)\right]. \tag{30}$$

The first term of this series is the *Tung spreading function* [11] as used in GPC. There are two interpretations of the higher terms in equation (30).

When $K(V, \bar{V})$ should be applied to the computation of the MWD from PDC-measurements in the dynamic region of the column [2–5], equation (30) is interpreted as a *Gram–Charlier series* with

$$\beta_1 := 0. \tag{31}$$

This means that the first two terms in the series (12e) are assumed to be real. Since the coefficients $\beta_n/(\sigma_0^n\beta_0)$ with $n \geqq 2$ in equation (30) are directly calculated from the elution curves measured near the theta point, no information on (λ, λ') is given here. For a given P-mer, the measured elution curve $D(V)$ represents an intersection of the surface (30) by the plane $\bar{V}(\mathrm{P}) = \text{const.}$, predicted by the calibration curve of the column:

$$D(V) := K(V; \bar{V}). \tag{32}$$

On the other hand, it is well-known from mathematical statistics that the Gram–Charlier series for the curve (32) reads

$$D(V) = \sum_{n=0}^{\infty} \frac{\gamma_n}{\sigma_0\sqrt{2\pi}\, n!} \times \exp[-(V-\bar{V})^2/(2\sigma_0^2)]\, \mathrm{He}_n\left(\frac{V-\bar{V}}{\sigma_0}\right), \tag{33a}$$

with the Fourier coefficients*

$$\gamma_n = \int_{-\infty}^{+\infty} D(V)\, \mathrm{He}_n\left(\frac{V-\bar{V}}{\sigma_0}\right) \mathrm{d}V \tag{33b}$$

related to the basis of modified Hermite polynomials defined by equations (18) and (13c) and calculated from the well-known recurrence relations

$$\mathrm{He}_0(\zeta) = 1 \qquad \mathrm{He}_1(\zeta) = \zeta \tag{33c}$$

$$\mathrm{He}_n(\zeta) = \zeta\, \mathrm{He}_{n-1}(\zeta) - (n-1)\, \mathrm{He}_{n-2}(\zeta), \qquad n \geqq 2.$$

Since $\gamma_0 = 1$ and $\gamma_1 = 0$ is valid in equation (33a), the series (30) and (33a) can directly be compared, if the intersection (32) of the surface (30) is considered. This comparison gives the coefficients

$$\frac{\beta_n}{\sigma_0^n\beta_0} = \frac{\gamma_n}{n!} \qquad n = 2, 3, \ldots \tag{34}$$

The coefficients γ_n in equation (34) can directly be computed from the measured curve (32) normalized to one:

$$\int_{-\infty}^{+\infty} D(V)\, \mathrm{d}V = 1. \tag{35a}$$

Calculating namely $\mathrm{He}_n(\zeta)$ from the recurrence relations (33c) for $n = 2,3,4,\ldots$ and inserting them into equation (33b), the relations

$$\gamma_2 = \mu_2'/\sigma_0^2 - 1 \qquad \gamma_3 = \mu_3'/\sigma_0^3$$

$$\gamma_4 = \mu_4'/\sigma_0^4 - 6\,\mu_2'/\sigma_0^2 + 3 \ldots \tag{35b}$$

are obtained which contain the central statistical momenta of $D(V)$ relative to $\bar{V}$

$$\mu_n' = \int_{-\infty}^{+\infty} (V-\bar{V})^n D(V)\, \mathrm{d}V \qquad n \geqq 2. \tag{35c}$$

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*This can be easily proved by inserting equation (33a) into equation (33b) and by applying equations (18) and (16a). Since the elution curve (32) is normalized to 1, the coefficients $\gamma_0 = 1$ and $\gamma_1 = 0$ follow from equation (33b) because $\mathrm{He}_0(\zeta) = 1$ and $\mathrm{He}_1(\zeta) = \zeta$ is valid according to equations (18) and (13c).

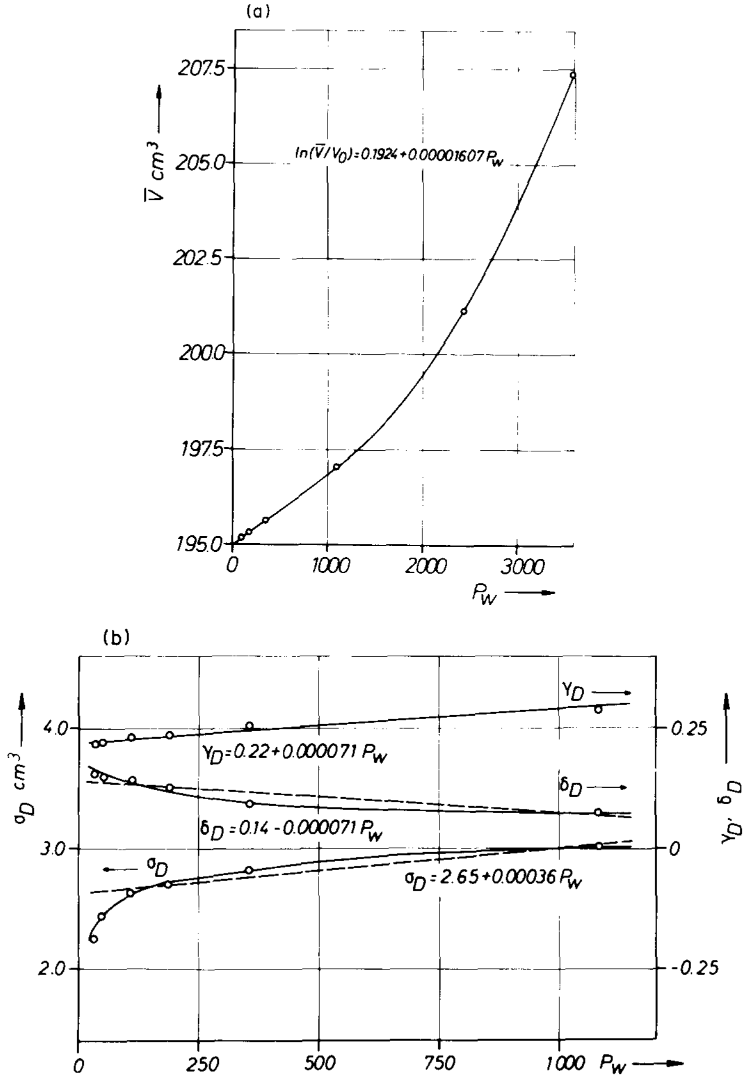

Fig. 1. (a–b) Dependence of the measured elution volume $\bar{V}=\bar{V}_D(\mathrm{P})$ (in cm^3, Fig. 1a), and of the standard deviation σ_D (in cm^3), skewness γ_D, and kurtosis δ_D (Fig. 1b) on the weight-average of the polymerization degree $\bar{P}_w$ of a very narrowly distributed sample, injected into a PDC-column [2] at 28° (polystyrene/cyclohexane, theta temperature 34°).

The quantities $\bar{V}$ and σ_0^2 in these relations represent the maximum and the variance, respectively, of the leading Gaussian function in the elution curve (32). However, the directly accessible quantities are the mathematical expectation

$$\bar{V}_D=\int_{-\infty}^{+\infty} VD(V)\,\mathrm{d}V \qquad (35\mathrm{d})$$

of the elution volume in the perturbed curve (32), and the corresponding variance

$$\sigma_D^2=\int_{-\infty}^{+\infty}(V-\bar{V}_D)^2 D(V)\,\mathrm{d}V>\sigma_0^2. \qquad (35\mathrm{e})$$

Hence the relations between $(\bar{V},\sigma_0^2)$ and $(\bar{V}_D,\sigma_D^2)$ must be found. The first problem is simple: From equations (35d), (32), (30), (18) and (16a) with

$\mathrm{H}_0(\zeta)=1$ and $\mathrm{H}_1(\zeta)=2\zeta$

$$\bar{V}_D=\bar{V}+\beta_1/\beta_0 \qquad (35\mathrm{f})$$

follows, giving $\bar{V}=\bar{V}_D$ according to equation (31). The second problem is a numerical one; it is treated below. After setting $\bar{V}=\bar{V}_D$ in equation (35c) and defining the variance σ_D^2, the skewness γ_D, and the kurtosis δ_D of the elution curve (32) according to the well-known statistical relations

$$\sigma_D^2=\mu_2' \qquad \gamma_D=\mu_3'/\sigma_D^3 \qquad \delta_D=\mu_4'/\sigma_D^4-3, \qquad (36)$$

the coefficients (35b) are obtained as

$$\gamma_2=(\sigma_D/\sigma_0)^2-1 \qquad \gamma_3=\gamma_D(\sigma_D/\sigma_0)^3$$
$$\gamma_4=(\delta_D+3)(\sigma_D/\sigma_0)^4-6(\sigma_D/\sigma_0)^2+3\ldots \qquad (37\mathrm{a})$$

The spreading function (30) then transforms to

$$K(V, \bar{V}_D) = \frac{1}{\sigma_0\sqrt{2\pi}} \exp[-(V - \bar{V}_D)^2/(2\sigma_0^2)] \times \left[1 + \frac{\gamma_2}{2}\mathrm{He}_2\left(\frac{V - \bar{V}_D}{\sigma_0}\right) + \frac{\gamma_3}{6}\mathrm{He}_3\left(\frac{V - \bar{V}_D}{\sigma_0}\right) + \frac{\gamma_4}{24}\mathrm{He}_4\left(\frac{V - \bar{V}_D}{\sigma_0}\right) + \dots\right] \qquad (37b)$$

The variance σ_0^2 of the leading Gaussian term can be found by a nonlinear fit of the measured elution curve (32), normalized according to equation (35a), to the function (37b) with a given constant $\bar{V}_D$ and given coefficients (37a). However, experience shows that practically always $\sigma_D \approx \sigma_0$ is valid in PDC near the theta point. Hence, the quantities (36) can be inserted into equation (37b):

$$\sigma_0 = \sigma_D \qquad \gamma_2 = 0 \qquad \gamma_3 = \gamma_D \qquad \text{and} \qquad \gamma_4 = \delta_D. \qquad (37c)$$

This ansatz may be useful also in GPC when measurements on the same polymer in PDC and GPC are available, i.e. when the MWD of the polymer is known.

Measurements, performed with the polystyrene/cyclohexane–PDC-column [2] at 28°, yield the following dependencies of mathematical expectation of V, standard deviation, skewness and kurtosis of the elution curve on the degree of polymerization P of the injected sample:

$$\begin{aligned} \ln(\bar{V}_D/160.54) &= 0.1924 + 1.607\cdot 10^{-5}\,\mathrm{P} \\ \sigma_D &= 2.65 + 3.6\cdot 10^{-4}\,\mathrm{P\ cm^3} \\ \gamma_D &= 0.22 + 7.1\cdot 10^{-5}\,\mathrm{P} \\ \delta_D &= 0.14 - 7.1\cdot 10^{-5}\,\mathrm{P} \end{aligned} \qquad (38)$$

These functions are obtained from a linear regression of the measured curves shown in Figs 1a and 1b. The corresponding spreading surface was computed according to equations (37b), (37c) and (38). Its axonometric computer plot can be seen in Fig. 2. The axis $\bar{V}(\mathrm{P}) = \bar{V}_D(\mathrm{P})$ specifies nearly the maximum of the section of a plane with the spreading surface $D = K[V, \bar{V}(\mathrm{P})]$ for a fixed degree of polymerization P predicted by the calibration curve of the column. This intersection physically represents a monodisperse elution curve for this P-mer. The axis V specifies the elution volume in this elution curve as a result of the axial dispersion (spreading) in the column for this P-mer. By varying $\bar{V}(\mathrm{P})$, the spreading surface is obtained. It was used as a *kernel of a Fredholm integral equation* for the computation of the MWD of very narrowly distributed polystyrenes from PDC-measurements in the dynamic region of the column (e.g. at 15° for samples with $\mathrm{P}_w \approx 1000$). The results have been published [5]. The corresponding theory will be published separately [15].

The theory presented in this paper can also be used for calculating the set of parameters $(D', u, \lambda, \lambda')$ from elution curves of PDC measured near the theta point. In this case, the Fourier series (30) cannot be interpreted as a Gram–Charlier series because $\beta_1 \neq 0$ is now required in equation (12e). Hence, the $m + 2$

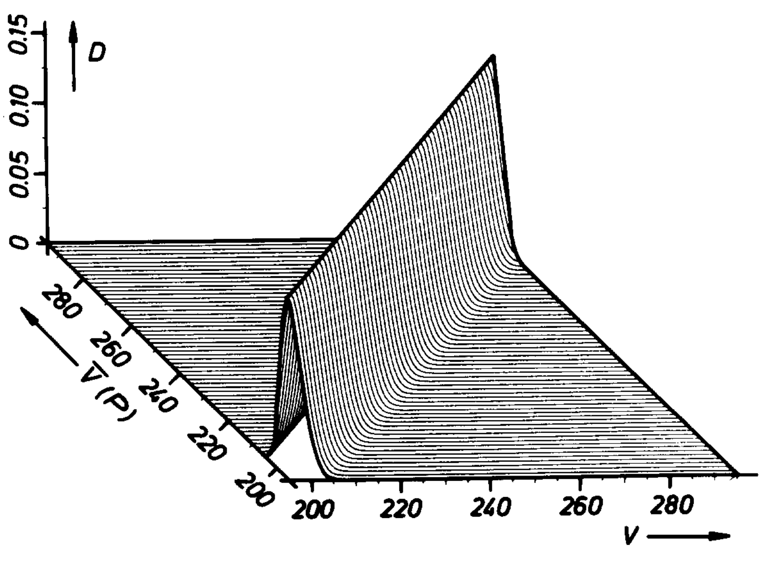

Fig. 2. PDC-spreading surface $D = K(V, \bar{V})$. Axis $\bar{V} = \bar{V}_D(\mathrm{P})$ (in cm³) specifies nearly the maximum of the section of a plane $\bar{V}$ = const. with the spreading surface D for a fixed degree of polymerization predicted by the calibration curve of the column. Axis V (in cm³) specifies the elution volume in this section (monodisperse elution curve) as a result of the axial dispersion (spreading) in the column for this P. The surface D is calculated from PDC-measurements at 28° as indicated in Figs 1a–b. (The axonometric computer plot is taken from [5]; courtesy Hüthig & Wepf—Verlag Basel–Heidelberg–New York.)

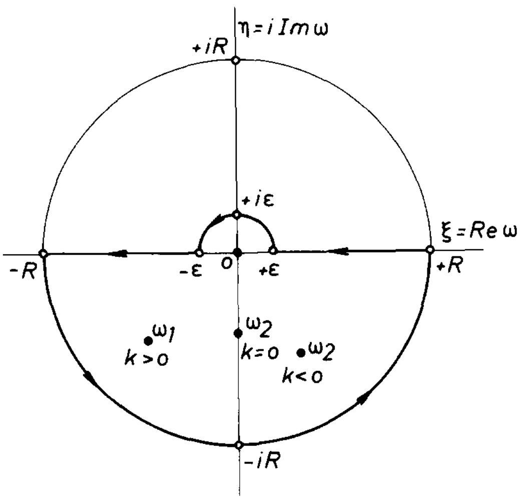

Fig. 3. Choice of the contour in the residual theorem applied in Appendices 1 and 2.

parameters $\bar{V} \neq \bar{V}_D$, $\sigma_0 < \sigma_D$, $\beta_1/\beta_0, \ldots \beta_m/\beta_0$ with a suitable m must be computed from the measured elution curves (32) by means of a nonlinear Gaussian fit to the spreading function (30). In the next step, a nonlinear Gaussian fit of $(D', u, \lambda, \lambda')$ to the set $\beta_1/\beta_0, \ldots, \beta_m/\beta_0$ found above must be performed, u being used for checking the calculations, since it can be directly measured. Both numerical problems are rather complicated, except for the simple case of equation (23b). It reads now

$$\frac{\beta_n}{\sigma_0^n \beta_0} = \frac{(-1)^n}{n!}\left(\frac{\Omega \bar{V}}{\Lambda^2 \sigma_0}\right)^n \tag{39}$$

with Ω and $\Lambda > 0$ from equation (21) under the conditions (22c) and (23a). The difficulties arise from the fact that the corresponding functional matrices are ill-conditioned to inversion. These calculations will be published separately [16].

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Dedication—The first systematical investigations of the possibility to calculate the molecular weight distributions of polymers from different methods like light scattering, chromatography, ultracentrifuge, etc. were performed by the author in the Institute of Macromolecular Chemistry in Prague many years ago. At this blissful time, I had the pleasure and privilege of working in collaboration with Professor Oto Wichterle and his team. Since then I have kept this time in my heart. This paper, dedicated to Professor Wichterle, is a greeting from Mainz to Prague. I add my best wishes to the Jubilar for the years to come in life and science.

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APPENDIX A1

When the integrand in the integral (10a) is designated by $g(\omega) = \phi(\omega)/\psi(\omega)$, pole and residuum follow from the well-known relations $\psi(\omega_1) = 0$ and $\operatorname{Res} g = \phi(\omega_1)/\psi'(\omega_1)$ with $\psi'(\omega) = d\psi/d\omega = 1$, respectively. Choosing the contour according to Fig. 3, the residuum theorem reads

$$\int_{+R}^{+\varepsilon} d\omega\, g(\omega) + \int_{\substack{|\omega|=\varepsilon \\ 0<\arg\omega<\pi}} d\omega\, g(\omega) + \int_{-\varepsilon}^{-R} d\omega\, g(\omega)$$

$$+ \int_{\substack{|\omega|=R \\ \pi<\arg\omega<2\pi}} d\omega\, g(\omega) = 2\pi i \operatorname*{Res}_{\omega=\omega_1} g(\omega). \tag{A1-1}$$

The following estimate for the second integral is valid:

$$\left| \int_{\substack{|\omega|=\varepsilon \\ 0<\arg\omega<\pi}} d\omega\, g(\omega) \right| \leqq \frac{|e^{-i\omega t}|\pi\varepsilon}{|\varepsilon - u|k| - D'k^2|}$$

$$= \begin{cases} \pi & \text{for} \quad k = 0 \\ 0(\varepsilon) & \quad k \neq 0 \end{cases}.$$

Hence, if $\varepsilon \to 0$ and $R \to \infty$ in Fig. 3 then the residuum theorem (A1-1) yields the integral (10a) as

$$\int_{-\infty}^{+\infty} d\omega\, g(\omega) = \int_{\substack{|\omega|=R\to\infty \\ \pi<\arg\omega<2\pi}} d\omega\, g(\omega) - 2\pi i \operatorname*{Res}_{\omega=\omega_1} g(\omega). \tag{A1-2}$$

Now, the complex function $\chi(\omega) = 1/\psi(\omega) \to 0$ uniformly in the halfplane $\text{Im}(\omega) < 0$ and on the real axis of Fig. 3 if $|\omega| = R \to \infty$. Its majorant $k = k_0$ has namely the property

$$\lim_{R\to\infty} |\chi(\omega)| \leqq \lim_{R\to\infty} \frac{1}{|R - u|k_0| - D'k_0^2|} = 0.$$

Since $t > 0$ is valid in equation (10a), the contour integral in equation (A1-2) vanishes according to the well-known Jordan's lemma:

$$\lim_{R\to\infty} \int_{\substack{|\omega|=R \\ \pi<\arg\omega<2\pi}} e^{-i\omega t}\chi(\omega)\, d\omega = 0. \tag{A1-3}$$

APPENDIX A2

The contour from Fig. 3 is chosen and the calculation is performed in analogy to Appendix A1. This time, the estimates

$$\left| \int_{\substack{|\omega| = \varepsilon \\ 0 < \arg\omega < \pi}} \mathrm{d}\omega \, g(\omega) \right| \leqq \frac{|\mathrm{e}^{-i\omega t}|(\varepsilon + \lambda')\pi\varepsilon}{|\varepsilon^2 - |2f|\varepsilon - \lambda'|\lambda + \lambda' + i2f||}$$

$$= \begin{cases} -\pi\lambda'/(\lambda + \lambda') & \\ & \text{for} \\ 0(\varepsilon) & \end{cases} \begin{matrix} k = 0 \\ \\ k \neq 0 \end{matrix}$$

and

$$\lim_{\mathrm{R}\to\infty} |\chi(\omega)|$$

$$\leqq \lim_{\mathrm{R}\to\infty} \frac{\mathrm{R} + \lambda'}{|\mathrm{R}^2 - |2f(k_0)|\mathrm{R} - \lambda'|\lambda + \lambda' + i2f(k_0)||} = 0$$

are valid, giving equations (12a–c) and (24a–b) in analogy to equations (A1-1–3). The function $\xi(ik)$ is introduced by setting
$it(f \pm \surd) = it(2f - i\lambda') + (1/2)2it \times (\pm\sqrt{-f + i\lambda'})$ in the exponent of the residua, and by multiplying and dividing the fraction for exp with $2it$.