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Deviations to classical retention theory of field-flow fractionation¹

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Abstract

The classical retention equation in field-flow fractionation (FFF) is based on the assumption of an exponential transversal distribution of the analyte and of a parabolic flow profile. Effects which led to deviations of the retention time from this classical equation have been listed by J.C. Giddings in the last paper of which he is the sole author. The state-of-knowledge about these effects is discussed and the errors on the analyte relative velocity, R , resulting from neglecting these effects are computed in the specific case of 0.5- μm particles experimenting a field force of $1.011 \cdot 10^{-15}$ N in a 200- μm thick channel at room temperature, i.e., for which the basic FFF parameter, λ , is equal to 0.02. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Field-flow fractionation (FFF) encompasses a large variety of methods of separation and characterization of supramolecular compounds (macromolecules, colloids, particles, cells). Although a few studies using a methodological approach resembling that of FFF were previously [1–4] or independently [5–7] performed, the general concept of FFF was invented in the mid-1960s by the late Professor J. Calvin Giddings who envisioned the wide potential

of this new separation method in terms of applications and system variants [8]. According to the classification of separation methods made by Giddings, FFF belongs, as chromatography, to the F(+) class, as both are flow-assisted methods in which the (chemical) potential gradient responsible for retention occurs essentially in directions perpendicular to the main direction of the flow [9]. In both methods, the separation between two species arises from differences in their equilibrium transverse relative concentration gradients as well as from the nonuniformity of the axial flow profile. While in chromatography the nonuniform transverse concentration gradient of an analyte arises from the difference in the standard state chemical potential of that analyte between two phases moving at different velocities (generally a carrier fluid phase and a stationary condensed phase), in FFF a single phase is used and the continuous potential gradient is gener-

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¹Dedicated to the memory of J. Calvin Giddings, a giant in separation science and a man who inspired me and continues to inspire me; with an immense respect for his profound communion with nature and his accomplishments in preserving it for the enjoyment of future generations.

ated by applying a force field, interacting with the analytes, in the direction perpendicular to that of the flow of the carrier liquid.

The various FFF techniques were first developed in Giddings' laboratory, then in an increasing number of laboratories over nearly all continents. J.C. Giddings is, by far, the person who has most contributed to the development of FFF, authoring or co-authoring 30% of the more than 900 papers already published on FFF theory, instrumentation or applications.

A quite interesting feature of FFF, very soon recognized by Giddings after disclosure of the concept [10], is that the retention time of a given analyte can be predicted accurately from first principles, owing to the geometrical simplicity of the separation medium. The classical retention equation, which relates the retention time to the force exerted by the applied field on the analyte molecules or particles, is based on some assumptions. This allows to predict retention and optimize the separation as well as to characterize an unknown analyte from its retention time. Sometimes, however, the experimental operating conditions do not allow the assumptions leading to the classical retention equation to be strictly fulfilled. Then, the accuracy of the separation prediction and/or analyte characterization is impaired. It is therefore important to point out the factors which limit this accuracy in order either to correct them or/and to be aware of this limitation.

In the last article of which he is the sole author, written a few weeks before his death on October 24, 1996, Cal Giddings addressed the "factors influencing accuracy of colloidal and macromolecular properties measured by field-flow fractionation" [11]. He considered two kinds of errors limiting this accuracy: those arising from errors in experimental measurements of retention times and system parameters and those arising from shortcomings of the classical retention equation (model errors). Factors in this second kind of errors are, according to Giddings, due to the neglect of: (1) steric exclusion; (2) lift forces; (3) particle slip; (4) van der Waals forces; (5) electrostatic forces; (6) nonparabolic flow (edge effects and viscosity gradients); and (7) nonuniformity of the field across channel thickness. Retrospectively, this article may be looked at as a message addressed to researchers involved in FFF for de-

veloping an improved theoretical basis of FFF in order to take full profit of the unique advantages of this method for the separation and characterization of supramolecular species. In the following, the main assumptions underlying the classical retention equation are pointed out, then the state-of-knowledge regarding the various factors leading to shortcomings of the classical equation and listed above is discussed.

2. Classical retention equation in FFF

One considers a straight FFF channel of length L , and of rectangular cross-section, with thickness w , and breadth b . The analyte relative velocity, R , is defined as the ratio of the mean velocity of the analyte zone, \mathcal{V} , to the cross-sectional average carrier velocity, $\langle v \rangle$:

$$R \equiv \frac{\mathcal{V}}{\langle v \rangle} \quad (1)$$

The FFF classical retention equation expresses R as a function of the basic FFF parameter, λ , characterizing the analyte as [12]:

$$R_{\text{class}} = 6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right] \quad (2)$$

where R_{class} denotes the classical expression of R . For a straight channel, in steady-state conditions, R is related to the hold-up time, t_o , i.e., the mean residence time of the carrier liquid in the channel, and to the analyte retention time, t_R , i.e., the first moment of the residence time distribution of the analyte in the channel, as:

$$R = \frac{t_o}{t_R} \quad (3)$$

since $t_o = L/\langle v \rangle$ and $t_R = L/\mathcal{V}$ [13]. In previous publications, R has been called retention ratio. However, there seems to be today a general consensus in the FFF community to avoid this term and call R the (analyte) relative velocity in order to eliminate the confusion brought by the use of the term 'retention' (due to the fact that the retention time increases when the retention ratio decreases).

The basic FFF parameter, λ , is an analyte characteristic parameter expressing the strength of the

interaction of the analyte with the applied field. It is defined as:

$$\lambda = \frac{D}{|U_{\text{field}}|w} \quad (4a)$$

where D is the analyte diffusion coefficient and U_{field} the velocity impelled by the field on analyte molecules or particles, or, equivalently, as:

$$\lambda = \frac{kT}{|F_{\text{field}}|w} \quad (4b)$$

where k is the Boltzmann constant, T the absolute temperature and F_{field} the force exerted by the field on one analyte molecule or particle. Note that, for simplification in the following, one describes the individual entities making an analyte as particles, whether these entities are (macro)molecules in solution or particles in suspension. From the value of this force and the field strength, the relevant properties of the analyte, such as molecular weight or particle size, can be accessed. From Eqs. (2), (3), (4a), (4b), the force is obtained from the retention time. When λ is small enough for the coth term in Eq. (1) to be approximated to 1, R becomes equal to $6\lambda - 12\lambda^2$, and F_{field} is given by:

$$|F_{\text{field}}| \approx \frac{4kT}{w \left(1 - \sqrt{1 - \frac{4t_o}{3t_R}} \right)} \quad (5)$$

The error on F_{field} arising from this expression is lower than 1% when t_R is larger than $1.5t_o$, which corresponds to a normal and recommended operating range. Note that, for increasingly large t_R , the limit of F_{field} becomes:

$$\lim_{t_R \gg t_o} |F_{\text{field}}| = \frac{6kT}{w} \frac{t_R}{t_o} \quad (6)$$

However, in order for the error on F_{field} made by using this equation instead of the combination of Eqs. (2)–(4) to be smaller than 1%, t_R must exceed $34 t_o$.

Eq. (2), and subsequently Eq. (5), relies on the assumptions that the equilibrium concentration distribution of the analyte particles in a cross-section is exponential and that the axial particle velocity profile is parabolic and two-dimensional, i.e., Ref. [14]:

$$\frac{c(x/w)}{\langle c \rangle} = \frac{e^{-\frac{x/w}{\lambda}}}{\lambda \left(1 - e^{-\frac{1}{\lambda}} \right)} \quad (7)$$

and

$$v_p(x/w) = v(x/w) \quad (8)$$

with

$$\frac{v(x/w)}{\langle v \rangle} = 6 \left[\frac{x}{w} - \left(\frac{x}{w} \right)^2 \right] \quad (9)$$

where c is the analyte concentration at distance x from the accumulation wall, $\langle c \rangle$ the cross-sectional average analyte concentration, v_p the particle velocity when the particle center is at distance x from the accumulation wall, v the unperturbed carrier velocity at position x . It is worth specifying the conditions to be fulfilled for Eqs. (7)–(9) to be valid. First, assuming that the transverse particle concentration profile is exponential implies that: (a) the particles are like point masses (i.e., they do not exhibit steric interactions with the channel walls); (b) they are non interacting (i.e., the analyte suspension or solution is highly diluted at all positions in the channel); (c) the transversal force experienced by the analyte particles is constant throughout the channel, which itself implies that: (c1) the field force is constant (i.e., the field strength is constant and the experiment occurs in isothermal conditions); (c2) that the flow pattern does not give rise to transversal forces on the particles (i.e., there are no hydrodynamic lift forces); and (c3) that the channel walls do not exert forces on the particles; hence that particle–wall (c31) van der Waals or (c32) electrostatic interactions are negligible. The particles are swept along the channel by the flow of carrier. The particle axial velocity profile is parabolic when: (d) the particles are displaced at the flow velocity (i.e., there is no particle slip) and when the carrier flow itself is parabolic. The latter condition implies a steady state (i.e., not varying with time), fully developed (i.e., far enough from the channel entrance region) laminar flow of; (e) an incompressible isothermal Newtonian fluid (i.e., a carrier fluid with a viscosity constant anywhere in the channel); (f) between two stationary impermeable infinite parallel plates (i.e., in a channel wide enough for the

influence of the small edge walls on the flow profile to be negligible).

It can be seen that there is an almost direct relationship between the factors which, when neglected, lead to measurement errors stated by Giddings and listed in the previous section and the above conditions to be satisfied for fulfilling the classical retention equation. Indeed Giddings factors (1)–(5) correspond, respectively, to conditions (a), (c2), (d), (c31), (c32), factor (6) to conditions (f) and (e), and factor (7) to condition (c1). Although condition (b) for non-interaction of particles was not explicitly stated by Giddings, it may be considered to be implicitly included in his factor (7) as the effect of particle interactions can be regarded as modifying the field [15].

3. Deviations to the classical retention equation

In his paper on factors influencing accuracy of analyte properties measured by FFF, Giddings stated that “more systematic studies of departures from the standard model must be done to further improve the accuracy of measuring properties by FFF” [11]. In the following, one reviews the state-of-knowledge about the various factors leading to deviations from the classical retention equation and influencing the accuracy of analyte properties measured by FFF. In addition, when possible, one strives to provide an estimate of the level of error on R arising from the neglect of the influence of a given factor. This error depends on the kind of factor and on various parameters. It will be evaluated in the case of spherical particles of diameter $d_p = 0.5 \mu\text{m}$ moving in a $200\text{-}\mu\text{m}$ thick channel and experimenting a field force of $1.011 \times 10^{-15} \text{ N}$ at $T = 293 \text{ K}$, which corresponds to $\lambda = 0.02$ and $t_R/t_o = 8.68$ according to the classical retention equation. All the factors listed above can act simultaneously to modify analyte retention from the classical equation. If the effects of the various individual factors are small enough, the deviation of particle retention from the classical value can be assumed to be the sum of deviations arising from the individual factors. Accordingly, the effect of each individual factor is, in most cases, evaluated below as if this factor was acting separately. Whatever the influence of these factors on

analyte equilibrium concentration and velocity profiles, the analyte relative velocity is given by:

$$R = \int_0^1 \frac{c(x/w)}{\langle c \rangle} \frac{v_p(x/w)}{\langle v \rangle} d(x/w) \quad (10)$$

Obviously, inserting Eqs. (7)–(9) into Eq. (10) gives Eq. (2).

Using the Boltzmann distribution law, one can get the concentration profile as:

$$\frac{c(x/w)}{c_{\text{ref}}} = \exp \left[- \frac{W_{\text{tot}}(x) - W_{\text{tot}}(x_{\text{ref}})}{kT} \right] \quad (11)$$

where W_{tot} is the total potential energy of one analyte particle and c_{ref} is the analyte concentration at a reference position x_{ref} . x_{ref} is generally taken at the accumulation wall, but is preferably selected at another position when the concentration at this wall vanishes due to some exclusion effects. $W_{\text{tot}}(x)$ is the sum of the potential energy arising from the applied external field, W_{field} , and that due to other effects, $W_{\text{non-field}}$:

$$W_{\text{tot}}(x) - W_{\text{tot}}(x_{\text{ref}}) = [W_{\text{field}}(x) - W_{\text{field}}(x_{\text{ref}})] + [W_{\text{non-field}}(x) - W_{\text{non-field}}(x_{\text{ref}})] \quad (12)$$

To the potential energies W_{tot} , W_{field} and $W_{\text{non-field}}$, are associated the forces F_{tot} , F_{field} and $F_{\text{non-field}}$, respectively, by means of the following generic relationship:

$$F = - \frac{dW}{dx} \quad (13)$$

where F_{tot} , F_{field} and $F_{\text{non-field}}$ are, respectively, the total force, the field-induced force and the sum of non-field effects exerted on one analyte particle. Eq. (12) becomes then simply:

$$F_{\text{tot}}(x) = F_{\text{field}}(x) + F_{\text{non-field}}(x) \quad (14)$$

The concentration profile can alternatively be expressed in terms of F_{tot} by:

$$\frac{c(w/x)}{c_{\text{ref}}} = \exp \left[+ \frac{w}{kT} \int_{x_{\text{ref}}/w}^{x/w} F_{\text{tot}} d(x/w) \right] \quad (15)$$

When the field force is constant through the channel,

Eq. (15) becomes, using Eqs. (4b) and (14) and noting that $|F_{\text{field}}| = -F_{\text{field}}$:

$$\frac{c(x/w)}{c_{\text{ref}}} = \exp \left[-\frac{1}{\lambda} \left(\frac{x}{w} - \frac{x_{\text{ref}}}{w} \right) + \frac{w}{kT} \int_{x_{\text{ref}}/w}^{x/w} F_{\text{non-field}} d(x/w) \right] \quad (16)$$

As the x -axis is directed from the accumulation wall to the depletion wall, negative non-field forces correspond to an attraction toward the accumulation wall and positive non-field forces to the repulsion away from this wall. The mean concentration is then given by:

$$\frac{\langle c \rangle}{c_{\text{ref}}} = \int_0^1 \frac{c(x/w)}{c_{\text{ref}}} d(x/w) \quad (17)$$

Of course, the relative concentration profile, $c/\langle c \rangle$, to be used in Eq. (10) does not depend on the reference position selected.

3.1. Steric exclusion

Due to their finite size, the particle centers cannot reach the walls but are located at distances comprised between $d_p/2$ and $w-d_p/2$ from the accumulation wall. Accordingly, in Eq. (10), the 0 and 1 limits of integration must be, respectively, changed to α and $1-\alpha$, where α is the reduced particle radius:

$$\alpha = \frac{d_p}{2w} \quad (18)$$

One then obtains, for an exponential concentration profile [16]:

$$R = 6(\alpha - \alpha^2) + 6\lambda(1 - 2\alpha) \left[\coth\left(\frac{1 - 2\alpha}{2\lambda}\right) - \frac{2\lambda}{1 - 2\alpha} \right] \quad (19)$$

The error arising from using the classical retention equation instead of Eq. (19) for the 0.5- μm particles is then -5.9% . In spite of the rather small value of α in the present case ($\alpha = 0.00125$), the error is signifi-

cant. As both α and λ are much lower than 1, the relative error is approximately equal to α/λ . For larger values of the particle size and/or for larger values of the field force, the error becomes still more significant.

For nearly all field types implemented, λ decreases with increasing particle size. For small sizes, R decreases with increasing α . However, for relatively large particle sizes, the steric effect becomes predominant and R increases with increasing α . There is thus a critical particle size, $d_{p,\text{inv}}$, for which R is minimum. This is the steric inversion size. Its value depends on the dependence of λ on d_p , hence on the particular field at hand [17]. Most often, the steric inversion diameter is around 1 μm , but its value can be modified by appropriate adjustment of the operating parameters [18]. Below this critical size, one operates in the Brownian (or normal) retention mode. Operation above this size corresponds to the steric mode. In principle, Eq. (19) describes both modes. However, in almost all practical conditions leading to the steric mode, hydrodynamic lift forces appear and play a dominant role in the control of retention. One therefore describes the corresponding operating mode as the lift mode. Eq. (19) is then of no or little usefulness for describing retention above the so-called steric inversion, but is quite useful in the upper size range of the Brownian operating mode.

3.2. Lift forces

In spite of the fact that the carrier flows in FFF channels at a low channel Reynolds number, hydrodynamic lift forces appear to significantly and dominantly influence the retention behavior of particles larger than about 1 μm [19]. Evidence that these forces are hydrodynamic in nature is provided by the fact that R depends on carrier flow-rate, which is not predicted by the classical or steric Eq. (2) or Eq. (19), respectively. However, the exact nature of these forces is presently not clear. Certainly, they arise from non-linear effects, i.e., such as that effect reflected by the inertial term ($v \cdot \text{grad} v$ term) in the Navier–Stokes momentum balance equation. Indeed, in the opposite case, reversing the flow direction would lead to a reversal of this hydrodynamic lift transversal force, which is not realistic as the direc-

tion of the force on a particle (toward or away from a nearby wall) cannot depend on the direction of the flow.

Lift forces are found to strongly increase with the particle size, as well as with the average carrier flow velocity. The direct computation of the inertial lift force, even for rigid spherical particles, from the Navier–Stokes equation is a problem of formidable complexity which has not been solved in the conditions pertaining in FFF. A tabulated solution when the particle is far from the channel walls was given many years ago by Ho and Leal [20]. It is found that the lift force depends greatly on the particle position in the channel. In addition, this force pushes particles away from the walls as well as away from the channel center, so that there are three positions where the lift force vanishes in the channel, corresponding approximately to $x/w=0.2$ and 0.8 , which are equilibrium particle positions in absence of an applied external field, and to $x/w=0.5$, which is an unstable equilibrium position. One can approximate the tabulated function by the following expression:

$$F_{Li} = k_{Li} \frac{\rho_i d_p^4 \langle v \rangle^2}{w^2} \left(0.2 - \frac{x}{w}\right) \left(0.5 - \frac{x}{w}\right) \left(0.8 - \frac{x}{w}\right) \quad (20)$$

where ρ_i is the carrier density. The value of the dimensionless constant k_{Li} is obtained by fitting the Ho and Leal tabulated data to Eq. (20). It depends on the range of x/w values used for this fit. Thus, one gets k_{Li} equal to 48.3, 46.0, or 47.6 for x/w ranges of 0.01–0.99, 0.10–0.90, 0.01–0.19, respectively. A value of 52.6 was previously given [21]. Owing to the approximate nature of Eq. (20), k_{Li} can be taken as equal to 50.

Inserting Eq. (20) in Eq. (16), then in Eqs. (10) and (17), allows to compute R . The error on relative velocity of the 0.5- μm particles made by neglecting the lift force is found equal to $-4 \times 10^{-4}\%$, -0.043% and -4.2% for $\langle v \rangle$ equal to 0.001, 0.01 and 0.1 m/s, respectively. Apart for the last case, which corresponds to unusually fast analytical conditions, the error is negligible. However, Eq. (20) shows that the inertial lift force increases very significantly for increasing particle size, so this error on R also increases with d_p . In the case of an average

flow velocity of 0.01 m/s, the error becomes -0.7 and -11% for particle diameters of 1 and 2 μm , respectively, when keeping the field force constant.

As mentioned above, the inertial lift force approximated by Eq. (20) has been computed for particles relatively far away from the accumulation wall, which does not correspond to the situation encountered in FFF channels where the field force pushes particles in close vicinity to this wall. Attempts to determine lift forces in these conditions by analysis of retention of a large number of data for different particle sizes, flow velocities and field strengths have been performed. It was found that, in order to account for the observed degree of retention, an additional lift force, called near-wall lift force, has to be added to the inertial force of Eq. (20). This force, F_{Ln-w} , is expressed by:

$$F_{Ln-w} = k_{Ln-w} \frac{\eta d_p^3 \langle v \rangle}{w^2 \left(\frac{x}{w} - \frac{d}{2w}\right)} \quad (21)$$

where η is the carrier dynamic viscosity [22]. However, the value of the dimensionless constant k_{Ln-w} appears to vary by nearly two orders of magnitude as a function of the models used to compute it [22,23] and to be strongly dependent on the carrier viscosity [24], so that the possibility is not ruled out that this empirical near-wall lift force is an artifact, due to other effects such as electrostatic and van der Waals interactions [25].

Certainly, there is a need for a better fluid mechanical characterization of the inertial lift force in the FFF typical conditions, i.e., in the vicinity of the accumulation wall, from the fundamental Navier–Stokes equation. This will allow first to have a robust retention theory in the lift mode of operation, which is presently lacking, and second to better isolate and investigate the other factors which lead to deviations from the classical retention theory.

3.3. Particle slip

It is generally assumed that particles in a flow are displaced at the unperturbed carrier velocity at their center of gravity (i.e., the flow velocity when particles are absent), as expressed by Eq. (8). This is

only an approximation as the particles generally lag behind the fluid. The slip velocity, v_{slip} , such that:

$$v_{\text{slip}}(x) = v_p(x) - v(x) \quad (22)$$

has been computed for a rigid particle in an unbounded fluid (i.e., far away from walls) and found equal to $d_p^2(\nabla^2 v)/24$ where $\nabla^2 v$ is the Laplacian of the unperturbed carrier velocity at the sphere center, whatever the velocity field [26]. It is seen that the slip velocity is associated to the curvature of the velocity profile and vanishes for a Couette flow (linear shear flow). In the case of the Poiseuille flow occurring in the FFF channel, one gets from Eq. (9):

$$v_{\text{slip}} = -2\alpha^2 \langle v \rangle \quad (23)$$

It is independent of the position in the channel since the curvature of the flow profile is constant for a parabolic flow. Inserting this expression in Eqs. (21) and (10), together with Eqs. (7) and (9), one gets:

$$R = R_{\text{class}} - 2\alpha^2 \quad (24)$$

The error made by neglecting this slip velocity for 0.5- μm particles in a 200- μm thick channel is only 0.003% which is negligible.

However, this correction applies in an unbounded fluid while, in FFF, particles are forced to move close to the accumulation wall. The fluid mechanical computation, using the Navier–Stokes equation, of the axial velocity of a sphere in these conditions is a difficult problem which has been solved in various limiting situations which are not always pertaining to the FFF situation (such as neglecting inertial effects, or assuming a linear shear flow). A limiting expression for a particle very close to the wall has been given in the lubrication situation as [27]:

$$\frac{v_p(x)}{v(x)} = \frac{1}{0.660 - 0.269 \ln\left(\frac{2x - d_p}{d_p}\right)} \quad (25)$$

after correction for a numerical error [22]. According to this expression, v_p goes to 0 when the particle surface approaches the wall and v_p/v becomes equal to 1 when $x = 0.641 d_p$.

One can compute the particle velocity by using Eq. (25) for x smaller than $0.641 d_p$ and the Faxen correction, Eq. (23), for x larger than this value. Neglecting this slip velocity correction results to an

error of 0.023% in the value of R given by Eq. (19). This effect appears then negligible for the 0.5- μm particles.

This is not really surprising as Eq. (25) indicates a slow decrease of v_p/v as the particle surface approaches the wall. Indeed v_p becomes equal to $v/2$ when the distance from the particle surface to the wall is equal to $0.0034 d_p$, which in our case is equal to 17 Å. One is then at the level of molecular distances for which a basic assumption that the fluid is a continuum fluid, which underlies the Navier–Stokes equation, no longer applies. Furthermore, the molecular nature of the wall and particle surfaces as well as small asperities appearing in these surfaces modify the plane–sphere geometry of the system and the fluid mechanical behavior at this scale. The computation of the particle velocity, as well as of the lift force, in this situation is an open problem which requires establishing the basis of a new physics between that of the quantum mechanics and that of the fluid mechanics of continuous media.

3.4. Van der Waals forces

Van der Waals forces between two macroscopic bodies, like a solid wall and a rigid particle, are the result of the summation of all interactions between individual molecules which make these two bodies. While, the potential energy associated with the interaction between two individual molecules decreases very fast with increasing intermolecular distance, as the sixth power of the reciprocal of this distance, the overall interaction force between two macroscopic bodies has a much longer range of action. This force, called van der Waals force, has been computed for various geometries. In FFF, one is concerned by the particle–wall as well as the particle–particle interactions. The latter depend on analyte volume fraction and become negligible at high dilution. The van der Waals particle–wall interaction force, $F_{\text{vdW,p-w}}$, depends on the particle size and distance from the wall [28]a. It is given by:

$$F_{\text{vdW,p-w}} = -\frac{4}{3} \frac{A_{132} d_p^3}{(4x^2 - d_p^2)^2} \quad (26)$$

Its limiting value when the particle surface approaches the wall becomes:

$$\lim_{x \rightarrow d_p/2} F_{\text{vdW,p-w}} = -\frac{A_{132}d_p}{3(2x - d_p)^2} \quad (27)$$

This force decreases with increasing distance of the particle surface to the wall only as the square of the reciprocal of this distance. In Eqs. (26) and (27), A_{132} is the Hamaker constant, the value of which depends on the nature of the sphere material (1), of the wall material (2), and of the suspending medium (3). When the van der Waals force is dominated by dispersion interactions, it can be approximated by [29]:

$$A_{132} \approx \pm \sqrt{A_{131}A_{232}} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (28)$$

where A_{ii} and A_{iji} are Hamaker constants for two bodies of material i interacting in vacuum and suspending medium j , respectively. In fact, A_{132} is not truly a constant as its value decreases at large particle–wall distances due to a retardation effect.

The particle–wall van der Waals force is seen to diverge as the particle approaches the wall. Considered alone, the van der Waals interaction leads to an infinite concentration at the wall contact, which corresponds to adhesion and infinite retention, according to Eq. (13) or Eq. (15) since A_{132} is positive for solid materials interacting in liquids. However, fortunately, in practice, attractive van der Waals forces can be compensated by repulsive electrostatic forces.

3.5. Electrostatic forces

When a solid body is placed in contact with an electrolytic solution, its surface becomes charged. This surface charge leads to an electric potential distribution, and thus to the redistribution of ions, within the solution in the vicinity of the solid surface. The ionic concentration maldistribution extends to some characteristic distance from the surface, called the double-layer thickness or Debye length, $1/\kappa$, with κ given by [28]b:

$$\kappa = \left(\frac{e^2 \sum_i z_i^2 n_{i,b}}{\epsilon_0 \epsilon_r kT} \right)^{1/2} = \left(\frac{2000 \mathcal{F}^2}{\epsilon_0 \epsilon_r \mathcal{R}T} \right)^{1/2} \sqrt{I} \quad (29)$$

with

$$I = \frac{1}{2} \sum_i z_i^2 c_{i,b} \quad (30)$$

where e is the elementary charge, ϵ_0 the permittivity of the vacuum, ϵ_r the relative permittivity (or dielectric constant) of the solution, \mathcal{F} the Faraday constant, \mathcal{R} the molar gas constant, $n_{i,b}$ the bulk number concentration of ions of type i and of valence z_i , and $c_{i,b}$ their molar concentration (in mol l⁻¹) in the bulk. I is the ionic strength of the solution. Note that the form of Eq. (29) corresponds to the SI unit system (MKSA electrostatic unit system). It is interesting to note that κ depends on the ionic strength of the solution and on the temperature, but is independent on the surface charge or surface potential. In an aqueous solution of ionic strength equal to 10⁻⁴ M, $1/\kappa$ is typical of the order of 30 nm at room temperature.

When two solid bodies are immersed in an electrolytic solution, the potential distribution around each of them leads to an electrostatic interaction between these bodies. Such is the case in FFF when solid analyte particles suspended in an electrolytic solution migrate in the vicinity of the accumulation wall. Accordingly, analyte particles experience a net force, which is repulsive when the wall and particle surface bear charges of the same sign. The analytical computation of this electrostatic particle–wall interaction force is difficult. It has been attempted in some particular geometries under some limiting assumptions. For a plane–sphere geometry and for relatively large distances (compared to $1/\kappa$) to the wall, the electrostatic interaction force, $F_{\text{es,p-w}}$, is given by [30,31]:

$$F_{\text{es,p-w}} = 32\pi\epsilon_0\epsilon_r\kappa d_p \left(\frac{kT}{e} \right)^2 \tanh\left(\frac{e\psi_p}{4kT} \right) \times \tanh\left(\frac{e\psi_w}{4kT} \right) e^{-\kappa(2x-d_p)/2} \quad (31)$$

where ψ_w and ψ_p are the wall and particle surface electric potentials, respectively.

The expressions for the van der Waals and electrostatic forces can be inserted in Eq. (16) to obtain the resulting concentration distribution of the analyte. Then, with help of Eq. (8), Eq. (9) and Eq. (17), the

analyte relative velocity R is derived from Eq. (10). For the case of an aqueous suspension of 0.5- μm polystyrene latex particles in an FFF channel with stainless steel walls, for which $A_{132} = 2.5 \cdot 10^{-20}$ J, $\psi_p = -0.08$ V and $\psi_w = -0.025$ V [32], one finds that the error on R , relative to that given by the steric Eq. (19), resulting from the neglect of van der Waals and electrostatic particle–wall interactions amounts to -3.8% for an ionic strength of 10^{-4} M. As the error is negative, the R value given by Eq. (19) is lower than that obtained by taking into account van der Waals and electrostatic interactions. This means that the effect of the repulsive electrostatic particle–wall interactions dominates that of the van der Waals interactions. This tendency is more pronounced in a carrier solution of lower ionic strength, since the screening of the electrostatic repulsion occurs then on a larger distance, according to Eq. (29) for $1/\kappa$, and the relative error on R becomes -13.9% for $I = 10^{-5}$ M. However, the opposite trend is observed on increasing ionic strength. Indeed, for $I = 5 \times 10^{-4}$ M, 10^{-3} M and 2×10^{-3} M, the relative error on R becomes $+1.4$, $+4.7$ and $+11.9\%$, respectively. Then, the attractive effect of the van der Waals forces dominates that of the electrostatic forces. Some caution must however, be exerted when using these values due to the assumptions underlying Eq. (31).

Acknowledging that both van der Waals and electrostatic forces modify the analyte equilibrium concentration profiles in the immediate vicinity of the accumulation walls and decrease rapidly to 0 over a distance which is small in comparison of λw , Williams et al. modified the steric retention Eq. (19) as follows:

$$R = 6(\alpha - \alpha^2) + 6\lambda(1 - 2\alpha - 2\lambda) \left(1 + \frac{\delta_w}{\lambda w}\right) \quad (32)$$

where the parameter δ_w is a distance defined by [33]:

$$\delta_w = \int_{d_p/2}^{\infty} \left[1 - \exp\left(-\frac{1}{kT} \int_x^{\infty} (F_{vdw}(x) + F_{es}(x)) dx\right) \right] dx \quad (33)$$

Although the computation of δ_w from Eq. (33) suffers from the same limitations as those of Eq. (31), its value can be determined from retention data of standard analytes. δ_w is believed to have the potential to be a universal constant, for a given carrier liquid, channel wall material and particle material system [33].

3.6. Nonparabolic flow

The classical FFF retention equation is based on the assumption that the particle velocity profile is parabolic, which in practice implies that, first, the particle velocity is equal to the unperturbed flow velocity at the same position (i.e., that the slip velocity is negligible), and, second, that the flow velocity profile is itself parabolic. The slip velocity has been discussed in Section 3.3. The hypothesis of a parabolic flow profile relies on assumptions of a two-dimensional flow geometry and of a constant viscosity. Edge effects and viscosity gradients would therefore lead to deviations from the classical retention equation.

3.6.1. Edge effects

In laminar flow conditions, the velocity vectors in a straight FFF channel are all oriented in the direction of the channel axis, z . However, because of the presence of the small edge walls, the flow profile is not only dependent on x , the axis along the channel thickness, but also on y , the axis along the channel breadth. In isothermal conditions, the velocity profile of a Newtonian fluid in a channel of rectangular cross-section with walls at $x=0$, $x=w$, $y=-b/2$ and $y=+b/2$, is given by [34]:

$$v(x,y) = \frac{w^2}{2\eta} \frac{\Delta P}{L} \left[\frac{x}{w} - \frac{x^2}{w^2} - \frac{8}{\pi^3} \sum_{n=10}^{\infty} \frac{1}{(2n+1)^3} \times \frac{\cosh(2n+1) \frac{\pi y}{w}}{\cosh(2n+1) \frac{\pi b}{2w}} \sin(2n+1) \frac{\pi x}{w} \right] \quad (34)$$

from which one gets

$$\begin{aligned} \langle v \rangle &\equiv \frac{1}{bw} \int_0^w \int_{-b/2}^{+b/2} v(x,y) dy dx \\ &= \frac{w^2}{12\eta} \frac{\Delta P}{L} \left[1 - \frac{192}{\pi^5} \frac{w}{b} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \right. \\ &\quad \left. \times \tanh\left(\frac{(2n+1)\pi b}{2w}\right) \right] \end{aligned} \quad (35)$$

where ΔP is the pressure drop along the channel. From Eq. (7), Eq. (8), Eq. (10), Eq. (34) and Eq. (35), the analyte relative velocity is given by [35]:

$R =$

$$\frac{6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right] - \frac{96}{\pi^3} \frac{w}{b} \lambda \coth\left(\frac{1}{2\lambda}\right) \sum_{n=0}^{\infty} \frac{\tanh\left(\frac{(2n+1)\pi b}{2w}\right)}{(2n+1)^3 [1 + (2n+1)^2 \pi^2 \lambda^2]}}{1 - \frac{192}{\pi^5} \frac{w}{b} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh\left(\frac{(2n+1)\pi b}{2w}\right)} \quad (36)$$

The denominator of Eq. (36) can be approximated by $1 - 0.630w/b$, with an error smaller than 0.4% for an aspect ratio, b/w larger than 2 [21]. Then, Eq. (36) can be written:

$$R = \frac{\left\{ 6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right] \right\} \left(1 - J \frac{w}{b} \right)}{(1 - 0.630w/b)} \quad (37)$$

J is an edge-correction factor which depends on λ and to a lesser extent on w/b . It has been computed by Giddings and Schure who found that J goes from 0.630 for λ infinite (unretained solute) to 0.543 for λ equal to 0 [36]. Taking $J=0.55$ as a mean J value in the useful 0–0.2 range of λ values, one gets:

$$R = \left\{ 6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right] \right\} (1 + 0.08w/b) \quad (38)$$

As, in practice, the aspect ratio of FFF channels lies in the range 40–200, the error made on the classical retention equation by neglecting the edge effect is about -0.04 to -0.2% , which can generally be considered as negligible.

3.6.2. Viscosity gradients

When the carrier viscosity is not constant across the channel thickness, but becomes dependent on the distance to the walls, the laminar, steady-state, two-

dimensional velocity profile of a Newtonian fluid is given by [37]:

$$v(x) = -\frac{\Delta P}{L} \left(\int_0^x \frac{x}{\eta} dx - \frac{\int_0^w \frac{x}{\eta} dx}{\int_0^w \frac{dx}{\eta}} \int_0^x \frac{dx}{\eta} \right) \quad (39)$$

The knowledge of the viscosity profile, $\eta(x)$, is required to integrate this equation. Obviously, when η is constant, one retrieves the Poiseuille parabolic profile. In practice, the carrier viscosity might depend on x because the carrier fluid is a binary, or polynary, fluid or still a diphasic, or multiphasic, carrier, one (or more) constituent(s) of which become(s) nonuniformly distributed as a result of its (or their) interaction(s) with the applied field, which happens in FFF with secondary chemical equilibria or in focusing FFF. These techniques have rarely been implemented. So, most often, a viscosity gradient is encountered in thermal FFF because of the temperature dependence of viscosity. Then, the viscosity profile depends on the carrier nature and on the temperatures of the hot and cold walls. Eq. (39) can be solved analytically only for special analytical expressions of the viscosity–temperature relationship and of the temperature profile. For instance, a polynomial regression of $1/\eta$ vs x leads to an analytical expression of $v(x)$, then of R for an exponential concentration profile.

Alternatively, the velocity profile can be obtained by numerically solving Eq. (39) for the specific $\eta(T)$ and $T(x)$ relationships at hand and a regression of the relative flow profile, $v/\langle v \rangle$, according to some polynomial expression can be searched for. As the analyte is essentially concentrated near the accumulation wall (which is generally the cold wall in thermal FFF), the flow profile needs to be accurately described especially near this wall. Accordingly, it has been proposed to approximate the exact relative velocity profile by a third-degree polynomial profile which has the same slope as the exact one near the cold wall [38]. Then, this third-degree polynomial relative velocity profile depends on one adjustable parameter, ν , called flow distortion parameter, which is such that the ratio of the slope of the exact velocity profile near the accumulation wall to that the

parabolic profile is equal to $1 + \nu$. The approximate relative velocity profile is then given as:

$$\frac{v}{\langle v \rangle} = 6 \left[(1 + \nu) \frac{x}{w} - (1 + 3\nu) \left(\frac{x}{w} \right)^2 + 2\nu \left(\frac{x}{w} \right)^3 \right] \quad (40)$$

It can be shown that ν is given by

$$\nu = -1 - \frac{1}{6\eta(0)} \frac{\int_0^1 \frac{x/w}{\eta} d(x/w) / \int_0^1 \frac{d(x/w)}{\eta}}{\int_0^1 \left[\int_0^{x/w} \frac{x/w}{\eta} d(x/w) - \int_0^1 \frac{x/w}{\eta} d(x/w) \int_0^{x/w} \frac{d(x/w)}{\eta} / \int_0^1 \frac{d(x/w)}{\eta} \right] d(x/w)} \quad (41)$$

where $\eta(0)$ is the viscosity at the temperature of the accumulation wall. An empirical expression allowing to estimate ν as a function of the cold wall and hot wall temperatures and of the nature of the carrier liquid has been derived [39]. Typically, ν lies in the -0.2 to -0.1 range.

Combining Eq. (40) for the relative velocity profile and Eq. (7) for the relative concentration profile, one gets the analyte relative velocity from Eq. (10) which gives [40]:

$$R = 6\lambda \left\{ \nu + (1 - 6\lambda\nu) \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right] \right\} \quad (42)$$

When λ is small enough for the coth term to be approximated by 1, this becomes

$$R = 6(1 + \nu)\lambda - 12(1 + 3\nu)\lambda^2 + 72\nu\lambda^3 \quad (43)$$

For $\lambda=0.02$, the error resulting from the neglect of the flow distortion due to the viscosity gradient amounts to $+10.2\%$, $+16.0\%$ and $+22.6\%$ for ν equal, respectively, to -0.1 , -0.15 and -0.2 . Accordingly, gross errors in analyte characterization can result from the neglect of this viscosity effect in thermal FFF.

3.7. Nonuniformity of the field across channel thickness

If the force exerted by the field on one analyte particle is not constant across the channel thickness, the λ parameter itself is not constant, according to

Eq. (4b). Then, the analyte transversal equilibrium concentration profile is no longer exponential and R is no longer given by Eq. (2) which is based on the assumption of the exponential distribution of the analyte described by Eq. (7). More precisely, Eq. (4b) states that the non-constancy of λ is associated to a variation of F_{field}/T across the channel thickness. Alternatively, according to Eq. (4a), this can be viewed as a variation of D/U_{field} , i.e., of U_{field} and/or D .

Such a field force nonuniformity arises in sedimentation FFF because the centrifugal acceleration, and hence the field force, is proportional to the distance of the particle to the channel rotation axis. If R_o is the curvature radius of the outer wall of the channel, the relative variation of F_{field} , and hence of λ , is equal to w/R_o . In typical sedimentation channels, this ratio is of the order of 0.1 – 0.3% and the corresponding effect on R is negligible. Variations of F_{field} across the channel thickness, or more precisely of F_{field}/T according to Eq. (4b), also arise in thermal FFF. In this technique indeed, separation occurs as a function of the analyte Soret coefficient, s_T , which, like other physicochemical transport parameters, depends on temperature. The variation of s_T with T is unknown as nearly all experimental data on thermodiffusion have up to now been handled under the Boussinesq approximation, i.e., assuming that all physicochemical transport parameters are constant (except the density in thermogravitational experiments). In previous works, thermal FFF retention data have been interpreted by means of the constant- λ assumption and the resulting λ value was associated with either the cold wall temperature or the temperature at the position of the center-of-gravity of the analyte concentration exponential distribution [41,42]. This procedure is not coherent since, on one hand, λ is assumed constant hence independent of temperature, and, on the other hand, one recognizes that its value must be associated to a specific temperature.

An attempt was made to take into account the variation of λ across the channel thickness by assuming that the temperature dependence of s_T follows a quadratic law [43]. Together with the expression of the temperature profile, $T(x)$, obtained by solving the Fourier law of heat conduction, the variation of λ with x was obtained as:

$$\lambda = \frac{1}{(s_T + \gamma)w \frac{dT}{dx}} \quad (44)$$

where γ is the thermal expansion coefficient of the carrier liquid. The coefficients of the quadratic s_T - T relationship of a given analyte were obtained by a simplex optimization procedure of fitting experimental retention data obtained in various cold wall temperature conditions [43]. This procedure requires at least three experiments to be performed in different temperature conditions. It cannot be applied to single thermal FFF retention data.

To allow to take into account the variation of λ for treating single retention data, the following approach was developed [44]. Since the temperature profile in a thermal FFF is approximately linear, one can expect the rate of variation of λ within the thermal FFF channel to be relatively uniform. Accordingly, one can take into account the dependence of λ with distance from the accumulation wall in thermal FFF by writing:

$$\lambda = \lambda_o \left(1 + \beta \frac{x}{w} \right) \quad (45)$$

where λ_o is the value of λ at the accumulation wall and β the relative variation of λ across the channel thickness, which must be larger than -1 . The analyte relative velocity for a so-called 'linear- λ ' profile and the third-degree polynomial velocity profile given of Eq. (40) has been computed [44]. It is given, for $\beta\lambda_o \neq 1/4, 1/3, 1/2$ or 1 by

$$R = 6 \sum_{i=0}^3 a_i \frac{1 - \beta\lambda_o}{1 - (i+1)\beta\lambda_o} \frac{1 - (1 + \beta) \frac{(i+1)\beta\lambda_o - 1}{\beta\lambda_o}}{1 - (1 + \beta) \frac{\beta\lambda_o - 1}{\beta\lambda_o}} \quad (46)$$

with

$$a_0 = - \left(\frac{1 + \nu}{\beta} + \frac{1 + 3\nu}{\beta^2} + \frac{2\nu}{\beta^3} \right) \quad (47a)$$

$$a_1 = \frac{1 + \nu}{\beta} + \frac{2(1 + 3\nu)}{\beta^2} + \frac{6\nu}{\beta^3} \quad (47b)$$

$$a_2 = - \left(\frac{1 + 3\nu}{\beta^2} + \frac{6\nu}{\beta^3} \right) \quad (47c)$$

$$a_3 = \frac{2\nu}{\beta^3} \quad (47d)$$

Alternative expressions of R are obtained when $\beta\lambda_o = 1/4, 1/3, 1/2$ or 1 [44]. In practice, λ_o and β are not known and, obviously, these two parameters cannot be determined from a single experimental measurement of R . Nevertheless, an apparent λ value, λ_{app} , defined as the λ value of a hypothetical (constant- λ) exponential concentration profile which would give the same analyte relative velocity, R , as the actual experimental one can be determined by solving Eq. (42) for λ , given R and ν . Then, it was shown that the distance from the accumulation wall, x_{eq} , for which λ of the actual linear- λ profile is equal to λ_{app} is, with a good approximation, given by [44]:

$$\frac{x_{eq}}{w} = 2\lambda_{app} - 2.1365(1 + 2\nu)\lambda_{app}^2 - 6.1678(2 - \nu)\lambda_{app}^3 \quad (48)$$

The Soret coefficient is then obtained from Eq. (44) in which λ_{app} is used for λ and the temperature at x_{eq} used to compute γ and dT/dx . Accordingly, λ_o and β are not known from a single R measurement, but a specific λ value, λ_{app} , is obtained at a specific position within the channel, x_{eq} , i.e., at the corresponding temperature, $T_{eq} = T(x_{eq})$. If determinations of R for a given analyte are performed in different cold and/or hot wall temperature conditions, λ values are obtained at different T_{eq} . This allows to determine the temperature dependence of the Soret coefficient without any prior hypothesis on the analytical form of this dependence. It was found that s_T decreases with increasing temperatures and that, depending on the range of temperatures investigated and on the polymer-solvent system, this variation can be represented by a linear or quadratic relationship [45]. Thus, thermal FFF appears to be a very useful physicochemical tool for investigating the Soret coefficients of polymer and colloidal materials and their temperature dependence.

In fact, the variation of λ with x may actually not be linear across the whole channel thickness. Nevertheless, this linear- λ retention model can still be applied provided that β is taken as $\ln\lambda/d(x/w)$ near the accumulation wall since it is in this region that

the analyte is concentrated and, thus, that the description of the λ profile needs to be the most accurate. If $\lambda_0=0.02$, $\nu=-0.15$ and $\beta=0.5$, these two last values being typical for a temperature drop of 50 K across the thermal FFF channel, the error made on the analyte relative velocity by neglecting the nonuniformity of the field force, which is the relative difference between Eq. (42) and Eq. (46), amounts to -1.9% . In spite of the fact that λ_0 is rather small and the analyte highly compressed in the narrow temperature region near the accumulation wall, this error is relatively significant. It is expected to increase, in absolute value, when the analyte particle cloud extends to a wider part of the channel cross-section, i.e., when λ_0 increases, since the difference between the mean effective λ and λ_0 then increases. Indeed, for $\lambda_0=0.1$, the error on R amounts to -6.6% .

4. Conclusion

The various sources of error limiting the accuracy of supramolecular properties measured by FFF, which were listed by Giddings, arising from shortcomings of the classical retention equation have been discussed. The resulting errors on the analyte relative velocity have been evaluated in the case of $0.5\text{-}\mu\text{m}$ particles experimenting a field force of $1.011 \cdot 10^{-15}$ N in a $200\text{-}\mu\text{m}$ thick channel at room temperature. Although the numerical values of the errors have been computed for a quite specific case and may greatly vary when changing operating conditions, they give an estimate of the relative importance of the investigated effects.

If edge effects can generally be neglected, performing accurate determinations of properties of colloidal particles suspended in an electrolyte solution requires that one takes into account the steric and colloidal (van der Waals and electrostatic) interactions with the accumulation wall. In the case of thermal FFF, one needs to take into account the effects of flow distortion and of field nonuniformity resulting from the applied temperature gradient.

Furthermore, the influence of hydrodynamic lift forces and the effect of particle slip are not presently well characterized in conditions prevailing in FFF.

There is a need for fundamental fluid mechanics studies for understanding and predicting the behavior of colloidal materials flowing near a wall. As discussed above, this might require the development of a new fundamental physics tool to investigate fluid dynamics at the molecular scale.

5. Symbols

a_i	coefficient of Eqs. (47a)–(47d)
A_{132}	Hamaker constant
b	channel breadth
c	analyte concentration
$c_{i,b}$	bulk molar concentration of ions of type i
c_{ref}	analyte concentration at the reference position
$\langle c \rangle$	cross-sectional average analyte concentration
d_p	particle diameter
$d_{p,\text{inv}}$	steric inversion particle diameter
D	analyte diffusion coefficient
e	elementary charge ($=1.602189 \cdot 10^{-19}$ C)
F_{field}	force exerted by the applied field on one analyte molecule or particle
\mathcal{F}	Faraday constant ($=96485.31$ C mol $^{-1}$)
F_{Li}	inertial lift force acting on one analyte particle
$F_{\text{Ln-w}}$	empirical near-wall lift force acting on one analyte particle
$F_{\text{non-field}}$	sum of the forces acting on one analyte particle other than the field force
F_{tot}	total force exerted on one analyte particle
$F_{\text{vdW,p-w}}$	particle–wall van der Waals force acting on one analyte particle
I	ionic strength of the electrolytic solution
J	edge-correction factor
k	Boltzmann constant ($=1.38066 \cdot 10^{-23}$ J K $^{-1}$)
k_{Li}	constant in the inertial lift force Eq. (19)
$k_{\text{Ln-w}}$	constant in the empirical near-wall lift force Eq. (20)
L	channel length
$n_{i,b}$	bulk number concentration of ions of type i
Δp	pressure drop along the channel
R	analyte relative velocity

R_o	curvature radius of the outer wall of the sedimentation FFF channel
\mathcal{R}	molar gas constant (= 8.31451 J mol ⁻¹ K ⁻¹)
s_T	Soret coefficient
t_o	hold-up time
t_R	retention time of an analyte
T	absolute temperature
T_{eq}	temperature at the equivalent position
U_{field}	velocity impelled by the field on the analyte
v	carrier velocity
v_p	particle velocity
$\langle v \rangle$	mean carrier velocity
\bar{v}	mean velocity of the analyte zone
w	channel thickness
W	potential energy of one analyte particle
W_{field}	potential energy of one particle arising from the applied field
$W_{non-field}$	potential energy of one particle arising from effects others than that due to the field
x	distance from the accumulation wall
x_{eq}	equivalent position (distance from the accumulation wall) for a linear- λ profile
x_{ref}	reference position in the channel
z_i	valence of ions of type i
α	reduced particle radius
β	relative rate of variation of λ across channel thickness
δ_w	parameter, with dimension of a length, characterizing particle–wall interactions
ϵ_o	permittivity of the vacuum (= 8.854188 10 ⁻¹² F m ⁻¹)
ϵ_r	relative permittivity of the solution (or dielectric constant)
η	carrier dynamic viscosity
$\eta(0)$	carrier viscosity at the accumulation wall
κ	reciprocal of the Debye length (or double layer thickness)
λ	basic FFF parameter
λ_{app}	apparent λ value for a linear- λ profile
λ_o	λ parameter at the accumulation wall
ν	flow distortion parameter
ρ_l	carrier density
ψ_p	electric potential at the particle surface
ψ_w	electric potential at the wall surface

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