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Non-equilibrium integral Doppler anemometric analysis of particle mixtures in a channel flow using an intrinsic hydrodynamic focusing force biased by another force

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ABSTRACT

Integral Doppler anemometric (IDA) analysis of particles exploits the strict correlation between the lateral position and the mean-time longitudinal velocity of a particle in a laminar flow. If the flow velocity profile is known, this correlation enables the transverse concentrational profile of a particle mixture to be measured by registering the Doppler frequency shifts for the particles simultaneously over the whole cross-section of a flow. IDA analysis allows one to detect the particle fractions in a channel flow with a transverse field applied [field-flow fractionation (FFF) arrangement] long before the longitudinal separation, and even before the complete transverse separation of fractions has occurred. This means a sharp decrease in the channel length and analysis time necessary compared with analytical FFF. The theory of IDA analysis is considered, then the intrinsic hydrodynamic lateral focusing force, naturally arising in a channel flow, is biased by another lateral (constant) force of any nature. Such a combination allows one to measure various physico-chemical parameters of particles working in the focusing regime favourable for registration. The theory is considered in a non-diffusive approximation for stationary, but laterally non-equilibrium, conditions. The theoretical relationships are given and the main characteristic features are considered for IDA analysis in a flat channel with Poiseuille or Couette flow for the three main ranges of external lateral force magnitude compared with the intrinsic hydrodynamic focusing force: (1) when two (different) lateral focusing positions still exist for particles; (2) when one lateral focus is left; and (3) when no lateral focusing occurs, and all the particles are drifting towards one wall. The transverse concentration profiles of particles and corresponding IDA spectra are calculated. The non-equilibrium IDA analytical separation of micrometre-size particles in a flow is demonstrated experimentally in the hydrodynamic focusing regime, using gravity as an external biasing force. The necessary channel length was *ca.* 10 cm, the analysis time *ca.* 30 s.

INTRODUCTION

The separation of particles in a flow and transverse external field [field-flow fractionation (FFF)] is a well established method for the analysis of particle mixtures [1,2]. The FFF process results in the formation of separated concentration zones along the channel, each zone corresponding to a certain fraction, which can be detected (or collected) at the outlet of a channel. For inherent physical reasons this process is completed only long after the establishment of a transverse separation of particles in a lateral field. As a consequence, it usually requires a 10–100-fold longer time than the

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process of particle transverse equilibration. For purely analytical purposes it is sufficient to register the transverse separation of particle fractions. Such a possibility is provided by integral Doppler anemometry (IDA) analysis, a recently developed technique for the rapid measurement of the transverse concentration profiles of particles in a laminar flow [3–5]. The basic idea of this method is that the flow velocity profile in a channel sets a definite relationship between the lateral position of a particle and its mean-time velocity along the flow. This local velocity can be measured via the Doppler frequency shift of the scattered light frequency, the corresponding local concentration of particles being measured by the scattered light intensity. Hence the integral Doppler spectrum of particles in a flow, measured from the whole cross-section of a channel, gives the transverse concentration profile of particles, provided that the flow velocity profile is known.

The IDA analysis of particle mixtures in a flow requires, similarly to analytical FFF [1,2], some intrinsic or externally applied force for transverse separation of particles in a channel. However, it differs from the original FFF principle in the role of the flow velocity gradient. In FFF this gradient is necessary for the longitudinal separation of fractions, which completes the whole separation process and precedes the registration procedure. In IDA analysis this gradient is necessary for Doppler registration purposes only, providing the coordinate-velocity sweep of the channel cross-section. Therefore, the registration can be done before the establishment of longitudinal separation of fractions. What is more, in IDA analysis it is not necessary to wait until the completion of the transverse separation of particles, as soon as transient (non-equilibrium) transverse concentration profiles of fractions are distinguished. These two features predetermine the essentially shorter analysis times and channel lengths that can be achieved with the IDA analysis approach compared with analogous FFF analytical schemes. At the same time, the IDA technique requires an optically transparent section of a channel wall, which may present additional difficulties in practical design for some kinds of transverse field. From this point of view it seems very advantageous to use the intrinsic hydrodynamic focusing force, which allows the IDA analytical separation of particles in a flow to be accomplished without application of any external force [6].

The IDA analysis can be implemented in two versions: (a) the non-stationary scheme with instantaneous local probe injection, as in FFF techniques; and (b) the stationary scheme with a time-constant homogeneous concentration distribution of the particle mixture at the channel entrance. The latter version is more suitable for experimental realization, so it was chosen for this work. In the stationary version the measuring channel with the lateral force applied is included in a closed circuit containing the suspension being analysed. This suspension circulates with a constant velocity, and is stirred homogeneously outside the channel. Thus, the stationary concentration distributions of particles in a channel flow are established due to the action of the lateral force and velocity gradient, being specific for each particle fraction. Near the channel entrance these distributions are essentially non-equilibrium relative to the lateral field, while further along the channel they can transform into equilibrium ones, depending on the interrelation between the channel length, flow velocity and force magnitude.

The theoretical description of IDA particle analysis naturally splits into two independent tasks: (a) the calculation of the particle concentration distribution all over the channel flow for the given temporal and boundary conditions; and (b) the calculation of the corresponding IDA spectra of suspension flow, taking into account the flow velocity profile, measuring geometry, illumination distribution and particle polydispersity. The final expressions for the shape of IDA spectra should contain certain adjustable parameters characteristic of particle fractions, which enable the analytical procedure to be accomplished.

This paper, like the previous one [6], considers IDA particle analysis under non-equilibrium field-flow conditions, *i.e.*, in the process of transverse equilibration of particles in a channel. The non-equilibrium scheme of IDA analysis seems the most advantageous over analogous FFF analytical schemes as far as analysis speed and channel length are concerned. The general theory was developed [6] using a kinematic (non-diffusive) approximation. This approximation is justified for the case of sufficiently large particles (>1 μm size) in the process of transverse equilibration, because diffusion plays a minor role in the transformation of the particle concentration distribution in that case. In this paper we consider two schemes of stationary non-equilibrium IDA particle analysis in a flow which are of most interest for practical applications: (a) with a constant lateral force of any nature; and (b) with the intrinsic hydrodynamic focusing force, biased by a constant lateral force. Analytical separation experiments for the latter case are also presented.

THEORETICAL

Consider a laminar dilute suspension flow in a flat channel of width $2h$. We shall use the dimensionless coordinate system in units of h with the z-axis along the flow, x-axis perpendicular to the channel walls and the origin at the middle of channel inlet. Let $v_z(x) = v_{\|}u(x)$ be the flow velocity profile and $F_x(x) = F_0\varphi(x)$ be the profile of lateral force acting on particles suspended in a flow. Here $v_{\|} > 0$, $F_0 = \pm|F_0|$ are characteristic values and $u(x)$, $\varphi(x) > 0$ are dimensionless profiles. Let μ be a characteristic parameter of particle species and $C_0(\mu, x_0)$ be the corresponding stationary concentration distribution at the channel inlet. Then, in a non-diffusive approximation, the stationary concentration distribution $C(x,z)$ of particles in a channel flow is given by [6]

$$C(x,z) = \int C_0\{\mu, x_0(x,z,\mu)\}C(x,z,\mu)\,\mathrm{d}\mu \tag{1a}$$

$$C(x,z,\mu) = \frac{\varphi\{x_0(x,z,\mu)\}}{\varphi(x)} \tag{1b}$$

$$z = \mu\int_{x_0}^{x}\frac{u(x)}{\varphi(x)}\mathrm{d}x, \qquad \mu = \frac{6\pi\eta a v_{\|}}{F_0} \equiv \frac{v_{\|}}{v_{\perp}} \tag{1c}$$

where a is the particle radius, η is the fluid viscosity and $v_{\perp}$ is the characteristic lateral drift velocity of a particle. Eqn. 1c is the trajectory equation, which connects the actual particle's lateral coordinate x with its starting coordinate x_0 and *vice versa*. Particles are assumed to drift according to Stokes law, and to have the unperturbed local flow velocity in the z direction.

In the following discussion we adopt two restrictions. First, we assume homogeneous concentrational profiles at the inlet of a channel, *i.e.*, $C_0(\mu,x_0)$ being independent of x_0. Second, we consider the particle mixture with a discrete set of fractions, which in turn can be well exemplified by a binary mixture owing to additivity of results:

$$C_0(\mu) = \frac{1}{\sqrt{2\pi}} \cdot \left\{\frac{C_1}{\sigma_1} \cdot \exp\left[-\frac{(\mu-\mu_1)^2}{2\sigma_1}\right] + \frac{C_2}{\sigma_2} \cdot \exp\left[-\frac{(\mu-\mu_2)^2}{2\sigma_2}\right]\right\} \quad (2)$$

Here we assume a Gaussian-type parameter distribution of fractions near mean values μ_1, μ_2, with partial concentrations C_1, C_2 and widths σ_1, σ_2. In such a case the shape of the integral Doppler spectrum $S(\omega,z)$ of suspension flow, registered at some distance z from the channel inlet, is given approximately by [3,6]

$$S(\omega,z) \sim \int a^3\psi(qa)C_0(\mu) \int_{-1}^{1} \frac{\varphi\{x_0(x,z,\mu)\}}{\varphi(x)} \delta[\omega - qv_{\|}u(x)]\mathrm{d}x\mathrm{d}\mu \quad (3)$$

where $\omega = 2\pi f$ is the angular frequency, q and $\psi(qa)$ are the light-scattering vector and indicatrix, respectively, and $\delta[y(x)]$ is the delta-function of $y(x)$.

Eqns. 1 and 3 give the necessary relationships between particle parameters a and μ and the shape of appropriate IDA spectra. They should be further specified for given profiles of lateral force and flow velocities.

Homogeneous lateral force, $\varphi(x) = 1$

This case is of special interest, being both practically important and easily tractable. To avoid unnecessary complications, let us assume that μ has the same sign for all particle fractions. In that case, owing to the action of lateral force, all the particles are gradually displaced to the channel wall lying at $x = \mathrm{sign}(\mu)$. This means that for each particle fraction there exists the characteristic boundary trajectory $x = x_m(z,\mu)$. It starts from the point $x_0 = -\mathrm{sign}(\mu)$, $z_0 = 0$ and defines the position along the channel of a sharp edge of concentration distribution of this fraction: $C(x,z) \equiv 0$ (in a non-diffusive approximation!) for $x < x_m(z,\mu)$ if $\mu > 0$, or for $x > x_m(z,\mu)$ if $\mu < 0$. This trajectory's equation is obtained by substitution of $x_0 = -\mathrm{sign}(\mu)$ into eqn. 1c and has the following forms for plane Poiseuille and Couette flows, respectively:

$$u(x) = 1 - x^2: \quad z = \frac{1}{3} \cdot |\mu| \cdot [2 + (3x_m - x_m^3)\mathrm{sign}(\mu)] \quad (4a)$$

$$u(x) = \frac{1}{2}(1 + x): \quad z = \frac{1}{4} \cdot |\mu| \cdot [2 + (2x_m + x_m^2 - 1)\mathrm{sign}(\mu)] \quad (4b)$$

The shapes of these boundary trajectories are shown in Fig. 1a for two values of $|\mu|$. Note that the trajectories are strongly dependent on $|\mu|$. In the case of Couette flow they also depend on the sign of μ (direction of the lateral force) owing to the lack of central-plane symmetry.

The final point, $x_m = \text{sign}(\mu)$, $z = z_f$, of the boundary trajectory defines the effective distance from the channel inlet corresponding to the particles quasi-equilibration in the lateral field. From eqns. 4 we obtain the general expressions for z_f in the case of Poiseuille (P) and Couette (C) flows, and also equations specified for sedimentation–flotation non-equilibrium FFF (NEFFF), tested experimentally in this work:

$$u(x) = 1 - x^2: \quad (z_f)_P = \frac{4}{3}|\mu| = \frac{8\pi\eta a v_{\parallel}}{|F_0|}; \quad (z_f)_P = \frac{6\eta v_{\parallel}}{a^2 g|\rho_1 - \rho_0|} \tag{5a}$$

$$u(x) = \frac{1}{2}(1 + x): \quad (z_f)_C = \frac{3}{4}(z_f)_P = |\mu| \tag{5b}$$

The shape of the transverse concentration profile which enters the expression for the IDA spectrum (eqn. 3) is determined by eqn. 1a. It shows that for $\varphi(x) = $ constant and a strictly monodisperse fraction this profile has (in a non-diffusive approximation!) a step-like shape at any $z < z_f$ and regardless of the flow velocity profile. The edge position of this step is determined by the boundary trajectory $x = x_m(z,\mu)$, described by eqns. 4. This is accompanied by (mathematical) singularity in $C(x,z)$ at the opposite wall of a channel. In reality, such singularity and the sharp edge at $x = x_m(z,\mu)$ are smeared more the greater is the distance z from the channel inlet, owing to particle

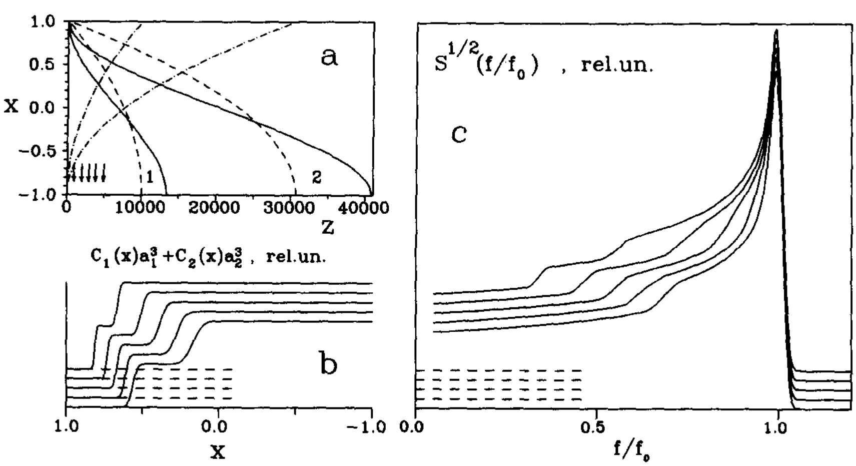

Fig. 1. (a) Boundary trajectories for a binary mixture of particles in a channel flow with a constant lateral force, calculated for plane Poiseuille (———) and Couette flows. – – –, The force is directed to the stationary channel wall; —·—·—, to the moving wall. Fractionation parameter: (1) $\mu_1 = -1 \cdot 10^4$; (2) $\mu_2 = -3.1 \cdot 10^4$. (b) Transverse profiles of a stationary volumetric concentration of a binary particle mixture in a plane Poiseuille flow, calculated for several distances z along the channel [marked by arrows in (a)]. Curves are shifted vertically for clearness. $(\sigma_1/|\mu_1|) = (\sigma_2/|\mu_2|) = 0.05$; $C_1a_1^3 = C_2a_2^3$. (c) Integral Doppler spectra of suspension flow, corresponding to the concentrational profiles in (b). $C_1 = 0.16$, $C_2 = 0.84$.

diffusion and polydispersity. Whereas the diffusion can be reasonably neglected in the case of sufficiently large particles, the degree of polydispersity does not correlate *a priori* with the size (or some other parameters) of the particles. Therefore, in view of the strong μ dependence of the boundary trajectories (see Fig. 1a and eqns. 4), the inherent polydispersity of any real particle system should necessarily be taken into account in the theory. This necessity, in turn, additionally justifies the use and extends the application range of the non-diffusive approximation adopted here.

Fig. 1b and c show transverse concentration profiles and corresponding IDA spectra for a binary mixture of particles (eqn. 2) in a Poiseuille flow, calculated according to eqns. 1–3. For a negligibly small instrumental broadening of a Doppler line, the relationships between the IDA spectrum and the concentration profile are as follows:

Poiseuille flow, $u(x) = 1 - x^2$:

$$S(\omega,z) \sim \frac{1}{\sqrt{1 - \dfrac{\omega}{\omega_0}}} \int a^3\psi(qa)C_0(\mu)\left[C\left\{\sqrt{1 - \frac{\omega}{\omega_0}}, z,\mu\right\} + C\left\{-\sqrt{1 - \frac{\omega}{\omega_0}}, z,\mu\right\}\right]\mathrm{d}\mu \quad (6a)$$

Couette flow, $u(x) = \frac{1}{2}(1 + x)$:

$$S(\omega,z) \sim \int a^3\psi(qa)C_0(\mu)C\left\{\left(2\frac{\omega}{\omega_0} - 1\right), z,\mu\right\}\mathrm{d}\mu \quad (6b)$$

Here $\omega_0 = qv_{\parallel}$. Eqns. 6 show that [in view of the weak $\psi(qa)$ dependence on a] the shape of the IDA spectrum is related to the profile of the volumetric concentration of the particles, a^3C. This relationship reduces to simple changes of variables, specified by the corresponding spatial dependence of flow velocity. The central-plane symmetry of Poiseuille flow leads to additional summation of concentration profiles over "positive" ($0 \leqslant x \leqslant 1$) and "negative" ($-1 \leqslant x \leqslant 0$) halves of a channel. This feature should be taken into account in the course of $C(x,z)$ reconstruction from the measured spectra, because $C(x,z)$ has no central-plane symmetry. In the case of Couette flow the relationship mentioned is especially simple. Here the shape of the IDA spectrum replicates the shape of $C(x,z)$ owing to the linear connection between the Doppler frequency and the lateral coordinate of a particle, which is especially convenient for the measurements.

Hence Fig. 1 illustrates situations for both Poiseuille and Couette flows. Together with eqns. 1 and 4, it shows that for the discrete set of fractions in a particle mixture in a channel flow with a constant lateral force, the stationary non-equilibrium transverse concentration profiles and the corresponding IDA spectra have characteristic shoulders corresponding to each fraction. This gives the possibility of analytical fractionation of a mixture relative to the parameter μ, which contains the size and some other relevant parameter of a particle (see eqns. 1 and 5). The corresponding values of μ can be found from the measured shoulders' positions $x_m(z,\mu)$ and the known registration position z, using eqns. 4 and, for a more precise evaluation, eqns. 1. Fig. 1a and eqns. 4 enable one to optimize the separation conditions by choosing the appropriate z and $v_{\|}$. The use of Couette flow in IDA particle analysis with a constant lateral force is obviously preferable to Poiseuille flow owing to the much simpler data processing.

Combination of intrinsic hydrodynamic and constant external force

A particle in a channel flow undergoes the action of intrinsic focusing hydrodynamic force, acting in a lateral direction [5–10]. In the case of Poiseuille flow there are two symmetrical non-central focusing positions, $\pm x_f$, the exact value $0 < |x_f| < 1$ being dependent on the ratio a/h [6,8,9], whereas in Couette flow the focusing position is the central plane of a channel [10]. The characteristic magnitude of this focusing force depends strongly on a/h, giving the possibility of using this force for the analytical fractionation of particles in a flow [6]. The combination of this force with the second (external) lateral force of any physical nature opens up a very promising possibility of analytical fractionation of particles relative to various parameters, using an efficient and precise focusing regime of IDA registration.

We consider below the more complicated case of Poiseuille flow, with the obvious extension to Couette flow. In the former case, as was pointed out previously [6], the intrinsic hydrodynamic force can be well approximated by the equation

$$F_x = F_0\varphi(x); F_0 = \frac{9\pi}{4}v_{\|}^2 \cdot \frac{\rho_0 a^2}{1 - x_f^2}\left(\frac{a}{h}\right)^2; \varphi(x) = x(x_f^2 - x^2) \tag{7}$$

Combining eqn. 7 with some constant external force F_e, we obtain from eqn. 1 the following trajectory equation:

$$z = \mu \int_{x_0}^{x} \frac{1 - x^2}{x(x_f^2 - x^2) + \lambda} \mathrm{d}x \tag{8}$$

where $\lambda = (F_e/F_0)$. Hence, the particle fraction is now characterized by two parameters, μ and λ. The first contains the size of a particle (eqn. 7), and the second contains the combination of size and some other particle parameter, which is relevant for the external field. Integrating eqn. 8, we obtain

$$\frac{z}{\mu} = A\ln\left(\frac{x - x_1}{x_0 - x_1}\right) + B\ln\left(\frac{x - x_2}{x_0 - x_2}\right) + C\ln\left(\frac{x - x_3}{x_0 - x_3}\right) \tag{9}$$

where

$$x_1 = \frac{2}{\sqrt{3}} x_f \cos\left[\frac{1}{3}\arcsin\left(\frac{\lambda}{\beta}\right) - \frac{5\pi}{6}\right]$$

$$x_2 = \frac{2}{\sqrt{3}} x_f \cos\left[\frac{1}{3}\arcsin\left(\frac{\lambda}{\beta}\right) + \frac{\pi}{2}\right]$$

$$x_3 = \frac{2}{\sqrt{3}} x_f \cos\left[\frac{1}{3}\arcsin\left(\frac{\lambda}{\beta}\right) - \frac{\pi}{6}\right]$$

$$\beta^{-1} = \frac{3\sqrt{3}}{2x_f^3} \qquad x_f > 0$$

$$A = (x_1^2 - 1)(x_1 - x_2)^{-1}(x_1 - x_3)^{-1}$$

$$B = (1 - x_2^2)(x_1 - x_2)^{-1}(x_2 - x_3)^{-1}$$

$$C = (x_3^2 - 1)(x_1 - x_3)^{-1}(x_2 - x_3)^{-1}$$

Here for $\lambda > \beta$ the roots x_1, x_2 and x_3 are complex, but the whole expression for z always remains real. Eqns. 8 and 9 show that, depending on the relative magnitude λ of the external force, three qualitatively different focusing regimes are possible: (1) if $0 \leqslant |\lambda| < \beta$, then there are two lateral focusing positions, x_1 and x_3, which are the initial (at $F_e = 0$) focusing positions, shifted from $\pm x_f$ owing to external force; (2) if $\beta < |\lambda| < (1 - x_f^2)$, then only one focusing position is left, *e.g.*, x_3 for $\lambda > 0$; (3) if $(1 - x_f^2) < |\lambda|$, then the external force is dominating, and the particles are drifting to the appropriate wall. The latter regime is similar to the case of a constant lateral force, considered above.

All three focusing regimes are illustrated by Figs. 2 and 3, where the corresponding boundary trajectories (eqn. 9, $x_0 = 1$) and transverse concentrational profiles (eqns. 1 and 9) are plotted for a single fraction of particles (eqn. 2 with a single term). Note that the concentration profiles are plotted as the sums of profiles, computed for $0 \leqslant x \leqslant 1$ and $-1 \leqslant x \leqslant 0$. This is done according to the form in which they enter the IDA spectrum of Poiseuille suspension flow (eqn. 6a), and in which they are evaluated from the measured spectra. As Fig. 3 shows, in the first regime a transverse concentration profile of each fraction has two characteristic peaks, in the second regime a peak and a shoulder and in the third regime only a shoulder. The

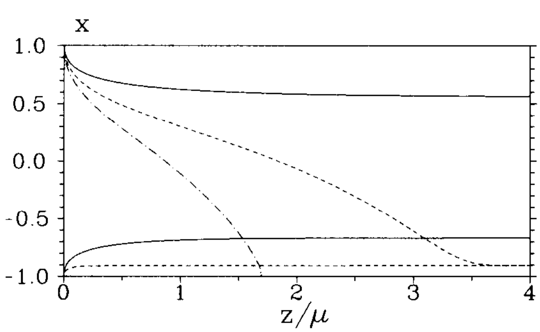

Fig. 2. Boundary trajectories for a single fraction of particles in a plane Poiseuille flow, calculated for three characteristic examples of the ratio between the constant external and intrinsic hydrodynamic lateral forces: ———, $0 < |\lambda| < \beta$; – – –, $\beta < |\lambda| < (1 - x_f^2)$; —·—·—, $-|\lambda| > (1 - x_f^2)$. $x_f = 0.62$; $\lambda = 0.04, 0.4$ and 0.8, respectively. These trajectories give the positions of concentration peaks and shoulders.

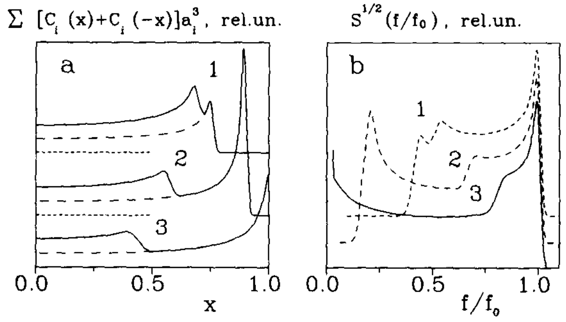

Fig. 3. (a) Transverse profiles of a stationary volumetric concentration of a single fraction of particles (summed over two halves of a channel), calculated for a plane Poiseuille flow for the three main regimes of combined action of a constant external and intrinsic hydrodynamic lateral forces. $\mu = -1.24 \cdot 10^4$; $(\sigma/|\mu|) = 0.07$; $z = 4 \cdot 10^3$; $x_f = 0.62$. (1) $\lambda = 0.086$; (2) $\lambda = 0.38$; (3) $\lambda = 0.76$. (b) Integral Doppler spectra of suspension flow, corresponding to the concentration profiles in (a).

positions of these features are determined by the boundary trajectories (eqn. 9 and Fig. 2) corresponding to the mean μ and λ values in the appropriate eqn. 2, written for a single fraction.

The case of Couette flow, where the intrinsic hydrodynamic force has only one (central-plane) focusing position [10], corresponds qualitatively to the second and third focusing regimes of Poiseuille flow.

Fig. 3b shows the IDA spectra of suspension flow calculated for the concentration profiles in Fig. 3a. They evidently retain all characteristic peaks and shoulders mentioned for concentration profiles. That makes unnecessary the procedure of complete reconstruction of $C(x,z)$ from $S(\omega,z)$ in order to evaluate the μ and λ parameters. This can be done by measuring the spectral positions of peaks and shoulders only, with the subsequent scaling according to $x = \sqrt{1-(\omega/\omega_0)}$.

As eqn. 9 shows, the evaluation of μ and λ can be done in two ways. If the x_f value is known beforehand, then it is sufficient to measure the positions of two peaks (or peak and shoulder) in the presence of an external force. However, the experiments showed that, contrary to theoretical predictions [10], the position of x_f for very narrow channels depends on the ratio of particle size to channel width (a/h) [6,8,9]. In such a case the additional measurements of a concentration peak's position are necessary under the same flow conditions, but in the absence of external force. That gives three sets of (x_m,z) values for determining of x_f, μ and λ from eqn. 9.

EXPERIMENTAL

For the present experiments the simplest possible arrangement was used, with gravity as an additional external force. For this purpose the flat glass channel (y–z plane) was placed horizontally, whereas in the previous experiments [4–6] its central plane was vertical, the z-axis being horizontal. The laser beams and the scattered light were rotated by 90° before and after the channel, respectively, in order not to change the remainder of the optical and registration set-up [4,5]. The channel width $2h$ was 180 μm, channel length 250 mm and the third dimension was 8 mm. The flow velocity at the axis was about 1 cm/s. The measured samples were dilute suspensions (10^5–10^7 particles/cm^3) of human erythrocytes ($a_1 \approx 3{,}5$ μm) and latex particles ($a_2 = 2$ μm) in a standard phosphate-buffered saline at pH 7.3–7.5.

Fig. 4a shows the measured IDA spectra of a pure latex suspension, a pure erythrocyte suspension and their mixture. Fig. 4b shows the volumetric concentrational profiles (summed over upper and lower parts of a channel), reconstructed from these spectra using eqn. 6a. The spectra and profiles of pure suspensions have two characteristic features, namely the peak and the shoulder, which shift systematically with a change of either registration point along the channel or flow velocity. The spectra, measured for mixtures, seem to be the superpositions of spectra measured for pure components (Fig. 4), the heights of peaks and shoulders following the corresponding concentrations of species in a mixture.

DISCUSSION AND CONCLUSIONS

Comparison of volumetric concentration profiles, reconstructed from the measured IDA spectra (Fig. 4), with the theoretical curves (Figs. 2 and 3) shows that the measurements were done in the second focusing regime. In this regime lateral focusing occurs in the nearest vicinity of the lower channel wall only, giving a pronounced narrow peak in the IDA spectrum. In the upper half of a channel the sedimentation force outweighs the focusing hydrodynamic force, and the particles gradually sink to the lower focusing plane. The latter process is analogous to the case of a constant lateral force (eqns. 4 and 5 and Fig. 1), and gives a shoulder in the concentration profile and IDA spectrum (Fig. 4). This shoulder is more distinct and steep for erythrocytes (at $x \approx 0.42$) than for latex (at $x \approx 0.69$), which gives evidence for the higher degree of polydispersity of the latex suspension. In the case of the pure latex suspension, apart from the main shoulder (at $x \approx 0.69$), there is the smaller second shoulder at $x \approx 0.4$. This corresponds to the pairs of latex particles which were

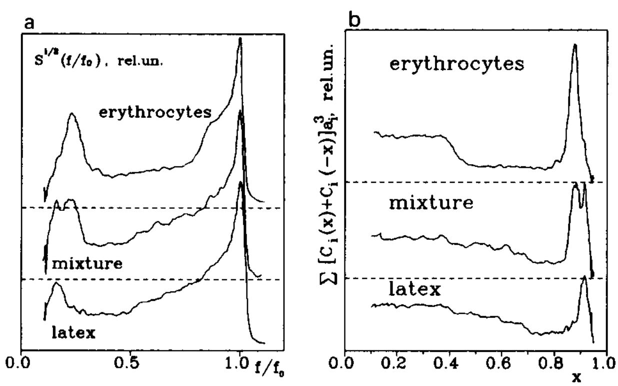

Fig. 4. (a) Integral Doppler spectra of channel flows of suspensions of erythrocytes and latex, and of their mixture ($C_1/C_2 \approx 0.15$), measured at $z = 2 \cdot 10^3$ ($zh = 180$ mm) and $v_{\parallel} = 0.86$ cm/s. (b) Transverse volumetric concentration profiles of particles in suspension flows, reconstructed from the corresponding IDA spectra. The formation of concentration peaks is due to the focusing hydrodynamic force, whereas their shift is due to gravity.

also detected in a small amount in the suspension on microscopic examination. With the mixtures the peaks and shoulders corresponding to the individual components can be distinctly resolved and correspond in position to those in the profiles of the pure suspensions. The values of size and material density of fractions evaluated from the measured IDA spectra using eqns. 7–9 agree with their known values.

Hence the experimental data show that, under the measuring conditions, the lateral focusing and the lateral separation of different particle fractions occur in a channel flow owing to the combined action of the intrinsic focusing hydrodynamic force and gravity. The separation occurs under laterally non-equilibrium conditions, which is evidenced by the presence of shoulders along with the peaks in the concentration profiles. These experiments demonstrate the possibility of non-equilibrium sedimentation–flotation IDA analysis of particle mixtures. The experimental set-up is characterized by an extremely simple channel design and a very short analysis time; the registration can be started 1 min after switching on the circulation of suspension, and takes *ca.* 30 s. The analysis can be done either in a constant force regime or in a focusing force regime. As Figs. 1, 3 and 4 show, the latter gives a better resolution of fractions owing to the formation of very narrow concentration peaks. The positions of these peaks in units of channel half-width h can be measured from IDA spectra with great accuracy and reproducibility, characteristic of laser Doppler anemometry [11], so the absolute error depends mainly on the absolute evaluation of $2h$. The evaluation of characteristic parameters of fractions can be done from the measured positions of peaks and shoulders, using the boundary trajectory diagrams in Figs. 1 and 2 and eqns. 4, 5 and 9. These diagrams can also be used for optimization of IDA analysis. The key optimization parameters are the coordinate z_R of IDA spectrum registration and the separation parameter of fraction μ, defined by eqns. 1 (see also eqns. 5). As Figs. 1 and 2 show, by varying z_R it is possible to obtain a better resolution of fractions in the preselected range of μ values, whereas by varying the flow velocity $v_{\parallel}$ and fluid viscosity η which enter the μ expressions it is possible to shift the entire set of μ values of the mixture being analysed. The parameter μ also defines the effective distance along the channel, which corresponds to equilibration of the particle fraction in a constant lateral field (eqns. 5). As Fig. 1 shows, the optimum range of IDA registration positions z_R (*i.e.*, the necessary channel length) is less than *ca.* 0.5 μ_{min} h, where μ_{min} is the minimum μ value for a mixture of fractions. This applies also to the externally biased hydrodynamic focusing force (eqns. 7–9). In the present experiments with gravity as a biasing lateral force, the necessary channel length was *ca.* 10 cm. Using centrifugation instead of gravity (although it requires a special optical design), it is possible to work with channels several centimetres long (see eqns. 5), the analysis time being several tens of seconds. For comparison, in high-speed versions of FFF analysis (thermal and steric) the analysis time is *ca.* 5 min and in sedimentation FFF it is *ca.* 30 min, typical channel lengths being several tens of centimetres [2]. It is interesting also to compare our experiments with the original sedimentation–flotation focusing field-flow fractionation experiments [12,13]. These experiments were done in a standard FFF regime, *i.e.*, under laterally equilibrium conditions. First, to create the focusing conditions and to obtain an efficient longitudinal separation of particles at the end of a channel, a specially designed density gradient of the carrier fluid and a modulated cross-section of a channel should be used [12,13]. This is not necessary in a non-equilibrium registration regime with the use of intrinsic hydrodynamic force.

Second, in the non-equilibrium scheme the registration position is obviously closer to the channel entrance, so the necessary channel length is considerably lower.

The experimental results obtained here and the theory developed demonstrate two possible general schemes of non-equilibrium IDA particle analysis: (1) using an externally applied lateral force, similar to conventional FFF schemes [1,2]; (2) using combinations of external fields of various natures with the intrinsic hydrodynamic focusing force. The second scheme seems very promising, because it gives the possibility of measuring various physico-chemical parameters of particles in a favourable focusing regime of IDA registration. For practical design of experimental set-ups it is essential that the intrinsic hydrodynamic force, and gravity, cannot be simply "switched" on and off. However, the former is strongly dependent on the $v_{\|}$ and a/h (eqn. 7), so it can be made negligibly small by using an appropriately wide channel and a sufficiently low flow velocity. The action of gravity can be either included in calculations or compensated for by matching the carrier fluid density ρ_0 or eliminated by using perpendicular forces geometry.

The theory of IDA analysis, developed in a non-diffusive approximation, proved to be efficient for (a) general qualitative analysis of a separation process in various experimental set-ups, with different kinds of lateral forces and flow velocities; (b) optimization purposes; and (c) quantitative evaluation of experimental data (for micrometre-size particles and, in some instances, for submicrometre-size particles). The use of a convective diffusion equation in the theory is not so important in the wide field of applications of non-equilibrium IDA analysis. The main reasons are first that the early stages of lateral equilibration of particles usually need to be considered, and second that the polydispersity of any real particle system in many instances plays the major role compared with diffusion in the smearing of concentration profiles in these stages.

In conclusion, it is necessary to point out that the method of IDA analysis does not involve the use of a laser Doppler anemometer as just another particle detector in FFF. It is based on another principle of analytical fractionation of particles under field-flow conditions, which does not require the preliminary longitudinal separation of fractions and, what is more, allows one to do the analysis even before the completion of the transverse separation of fractions. These features give major advantages in terms of analysis duration and necessary channel length. IDA analysis also gives the possibility, which is unattainable in conventional FFF, of performing mixture analyses in a continuous injection regime, when no longitudinal separation of fractions occurs in a channel. This is a very promising possibility, *e.g.*, for on-line product monitoring (indicative FFFF [6]). As for the choice of the detector in IDA, it is dictated primarily by the necessity to register the spatial dependence of particle velocity in a flow, which is the basic idea of the IDA method. In principle, this can also be done using some other physical phenomena, *e.g.*, by ultrasound scattering. However, at present such detectors are not at hand for this particular application, so the laser Doppler anemometer remains the only usable detector for IDA particle analysis. On the other hand, the laser Doppler anemometer can also be used for registration of particle fractions in conventional FFF schemes, where these fractions are separated longitudinally. However, owing to the non-stationary time conditions in FFF, such applications have specific features which are beyond the scope of the stationary analysis presented in this paper, and will be the subject of a future publication.

SYMBOLS

a	radius of a particle
$C(x,z)$	concentration of particle mixture in a flow
$C(x,z,\mu)$	concentration of particle fraction in a flow
$C_0(\mu)$	stationary homogeneous concentration at the channel entrance
C_1, C_2	relative concentrations of fractions in a binary mixture
$F_x(x)$ and F_0	lateral force and its magnitude
F_e	external biasing lateral force
f	frequency in Hz
g	acceleration due to gravity (or to centrifugal force)
h	half-width of a flat channel
q	laser light scattering wavenumber
$S(\omega,z)$	IDA power spectrum at a distance z from the entrance
$u(x)$	dimensionless velocity profile of a channel flow
$v_{\parallel}$	maximum flow velocity
x	lateral coordinate of a particle (in units of h)
x_0	lateral coordinate of a particle at the channel entrance
x_f	lateral position of the focusing point
$x_m(z,\mu)$	boundary trajectory of a particle fraction
z	particle coordinate along the flow (in units of h)
z_f	effective distance, corresponding to lateral equilibration
z_R	position of registration of IDA spectrum
β	$2x_f^3/3\sqrt{3}$
η	fluid viscosity
$\lambda = (F_e/F_0)$	characteristic ratio between external biasing and intrinsic hydrodynamic forces
μ	characteristic separation parameter of a particle fraction
ρ_0	fluid density
ρ_1	particle material density
σ	effective width of Gaussian distribution of particle fraction over parameter μ
$\varphi(x)$	dimensionless profile of lateral force
$\psi(qa)$	light scattering indicatrix
$\omega = 2\pi f$	cyclic frequency; $\omega_0 = qv_{\parallel} = 2\pi f_0$

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