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INTEGRAL DOPPLER ANEMOMETRY AND ANALYTICAL FIELD-FLOW FRACTIONATION

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SUMMARY

Doppler anemometry is extensively used for velocity profile determination in channels. In this context, the dimensions of the laser light scattering volume are smaller than those of the channel cross-section. An alternative approach is possible when the scattering volume is comparable with or exceeds the transverse dimension of the channel so that the scattered light contains integral information on particle velocity distributions in the channel. In the most interesting case the distribution of the particle concentrations is inhomogeneous across the channel, due to some transverse force. In this case, the shape of the Doppler spectrum depends upon the energy of the particle interaction with the transverse field. This should allow the use of integral Doppler anemometry (IDA) for evaluating particle parameters, which determine the strength of this interaction. Situations are considered where the transverse force presses particles against the channel wall or focuses them in regions with different flow velocities. It is shown that the speed of the analysis is the most important advantage of IDA over conventional field-flow fractionation. In the former case, the duration of analysis practically coincides with the characteristic time to establish a Bolzmann equilibrium in the transverse field. In the latter case, this duration strongly depends on the differences between the relevant parameters of the particles being separated and is usually 10^2 to 10^3 times greater than the time for equilibration. Some results of preliminary experiments are presented.

INTRODUCTION

One of the promising and intensively developing methods of particle separation is transverse field-flow fractionation (FFF)[1–3]. In FFF, the fluid carrying the substances to be separated passes through a flat channel while a transverse force is applied across the channel, and particles concentrate near one of its walls. The average width of the near-wall layers formed is different for different fractions, and this allows their separation due to a velocity gradient in the laminar flow. One of the modifications of FFF is focusing field-flow fractionation, in which particles with different physicochemical properties are focused in different regions of the channel cross-section. Since the flow velocities are different in these regions, such particles can also be separated at the outlet of the column.

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The main disadvantage of FFF is the relatively long analysis time, which diminishes the productivity of the method and results in excessive dilution of the initial sample as well as in increased column length. This disadvantage is a consequence of the principle itself. Indeed, the initial sample must be separated in space into several fractions, but this process might take a long time in the case of comparatively small differences in average particle velocities. At the same time, the average fraction velocities are established considerably more rapidly, approximately during the time, τ_0, of particle equilibration in a transverse field. That means that analytical FFF can be accomplished much more rapidly than is the case with existing columns, if the flow velocities of the fractions are recorded.

This could be achieved by laser Doppler anemometry, in which the velocity of particle motion can be measured by the Doppler frequency shift of the scattered light. The possibility of applying laser Doppler anemometry as a method of measuring the particle concentration distribution in the transverse field in FFF is considered in the present paper. The realization of this approach in the case of a Bolzmann-type concentration distribution permits the evaluation of the parameters determining particle interaction with the force field and to accomplish analytical particle separation.

THEORETICAL

Let us consider an ensemble of identical point scatterers, moving in laminar flow in a flat channel with a width of 2 h. We shall denote as $u(x)$ the flow-velocity profile of the channel, and as $w(x)$ the normalized by unity distribution function of the scatterer concentration in the transverse force field. (The x-axis is perpendicular to the channel walls, the z-axis is oriented along the flow, and the origin of the coordinates is near the wall, where the particles are concentrated.) We shall assume that the diameter of the probing laser beam exceeds the channel width.

The recording of Doppler spectra of scattered laser radiation is usually accomplished in the heterodyne mode, by mixing with a reference laser beam on the input window of a photodetector and recording the beat frequency, ω (ref. 4). (In our case the homodyne as well as the heterodyne mode is possible as a result of a whole set of Doppler frequencies which can be mixed with each other.) The power frequency spectrum, $S(\omega)$, of the current fluctuations of the recording photodetector in the heterodyne mode is given by[4]

$$S(\omega) = \int_{-\infty}^{+\infty} [g(t)\exp(i\omega_g t) + g^*(t)\exp(-i\omega_g t)]\exp(i\omega t)\mathrm{d}t \qquad (1)$$

where ω_g is the heterodyne frequency, $g(t)$ is the correlation function of the scattered radiation amplitude, $g^*(t)$ is the complex conjugate of $g(t)$ and t is the time. Constant factors as well as frequency-independent terms are omitted from eqn. 1, since we are interested only in the shape of the Doppler spectra.

In calculating $g(t)$ we shall assume that the spatial scale of inhomogeneities in the scattering particle concentrations greatly exceed the wavelength of the laser radiation. In this approximation, $g(t)$ is given by the sum of independent contributions from individual scatterers[4], which in our particular case means integration over the

channel cross-section with the weight function, $w(x)$. To obtain the average contribution from a single scatterer, we shall use as in ref. 4, the solution of the diffusion equation, namely the equation of convective diffusion in a force field[5]. Solving this equation by the Fourier method with the above-mentioned assumptions on the scale of spatial inhomogeneity of the system, we finally obtain:

$$g(t) = \exp(-Dq^2|t| + i\omega_0 t)\int_0^{2h} w(x)\exp\left\{i\left[P_e \cdot \frac{D}{2h} \cdot q_x + u(x)q_z\right]t\right\}dx \qquad (2)$$

Here, $q = 2k_0\sin(\theta/2)$ is the absolute value of the scattering wavenumber, $\vec{q} = \vec{k}_0 - \vec{k}_s$, $\vec{k}_0$ and ω_0 are the wavenumber and frequency of the incident wave respectively, $\vec{k}_s$ is the wavenumber of the scattered wave under observation angle θ, D is the particle diffusion coefficient; the quantity $P_e = \partial W/\partial x \cdot h/kT$ characterizes the transverse force field, $W(x)$. Typically for FFF, $P_e \cdot D/2h \ll u(x)$, so that the corresponding term in the exponent of eqn. 2 can be neglected.

Substituting eqn. 2 in eqn. 1 we obtain

$$S(\omega) \approx \int_0^{2h} w(x)\left\{\frac{1}{[\omega + \Delta\omega + u_z(x)q_z]^2 + (Dq^2)^2} + \frac{1}{[\omega - \Delta\omega - u_z(x)q_z]^2 + (Dq^2)^2}\right\}dx \qquad (3)$$

where $\Delta\omega = \omega_g - \omega_0$. Since the flow velocity profile, $u(x)$, is usually known, eqn. 3 permits the calculation of the parameters of $w(x)$ and the value of D from the Doppler spectra measured in the heterodyne mode.

In case of negligibly small diffusive broadening of Doppler spectra (the quantitative criterion is given below), the expressions for $S(\omega)$ can be obtained in explicit form. This is a consequence of the fact that in the limit of $D \to 0$, Lorentzian curves in eqn. 3 transform into δ-functions of the relevant arguments, and the integration procedure is simplified. (For $D = 0$ this follows directly from eqns. 1 and 2.) It is expedient to carry out further analyses for the two most easily achieved velocity profiles, namely Poiseuille and Couette profiles. The former describes a laminar flow in a channel with the stationary walls under a given pressure drop across the channel length; the latter describes the flow in a channel with one wall moving parallel to the other with velocity, u_0.

Couette profile

(a) $u(x) = u_0 \cdot x/2h$. The particles are concentrated near the stationary wall. In this case, owing to the δ-function, the integration in eqn. 3 is actually reduced to the linear substitution of the variable x for the variable ω in $w(x)$ according to the equation $\omega \pm (\Delta\omega + u_0 q_z \cdot x/2h) = 0$. Thus, the frequency dependence of $S(\omega)$ for the heterodyne detection coincides with the spatial dependence of the particle concentration in the cross-section of a channel. In particular, for an exponential distribution, $w(x) \approx \exp(-P_e \cdot x/h)$, typical for FFF, we have:

$$S(\omega) \approx \frac{P_e}{|u_0 q_z|}\left[\exp\left(-P_e \cdot \frac{\omega \mp |\Delta\omega|}{|u_0 q_z|}\right) \cdot \theta(\omega \mp |\Delta\omega|) \cdot \theta(|u_0 q_z| \pm |\Delta\omega| - \omega) + \right.$$

$$\left. \exp\left(P_e \cdot \frac{\omega \pm |\Delta\omega|}{|u_0 q_z|}\right) \cdot \theta(-\omega \mp |\Delta\omega|) \cdot \theta(\omega \pm |\Delta\omega| + |u_0 q_z|)\right] \tag{4}$$

The upper signs before $\Delta\omega$ in eqn. 4 hold for $\Delta\omega q_z u_0 > 0$, the lower ones for $\Delta\omega q_z u_0 < 0$, $\theta(x)$ is the so-called step function: $\theta(x) = 0$ for $x < 0$, $\theta(x) = 1$ for $x \geqslant 0$. The introduction of the θ functions in eqns. 3 and 4 is formally necessary for a transition from the finite to the infinite integration limits, while dealing with the expressions containing δ-functions. Physically, it is a consequence of the sharp cut-offs of the Doppler spectra in the absence of diffusive broadenings.

(b) $u(x) = u_0(1 - x/2h)$. The particles are concentrated near the moving wall. The expression for $S(\omega)$ can be obtained from the corresponding formula 4 by multiplying by $\exp(-P_e)$ and reversing the exponent signs.

In the case of focusing field-flow fractionation and for a Boltzmann equilibrium in a transverse field, the probability of particle localization in the plane with the coordinate x is given by

$$w(x) = \frac{\sqrt{P_e}}{\sqrt{\pi}h} \cdot \exp\left[-P_e \cdot \frac{(x - x_0)^2}{h^2}\right] \tag{5}$$

where x_0 is the focusing point position. The normalizing factor in eqn. 5 is calculated assuming the effective width of the transverse concentration distribution is small, compared with the distance from its centre to the channel walls, *i.e.*, for $(P_e)^{-\frac{1}{2}} \ll 1 - |\xi_0|$ where $\xi_0 = x_0/h$ is the focusing parameter.

In this case, we obtain the following expression for the frequency spectrum

$$S(\omega) \approx \frac{2\sqrt{P_e}}{\sqrt{\pi}|u_0 q_z|} \cdot \exp\left[-4P_e\left(\frac{\omega - \omega_0}{u_0 q_z}\right)^2\right] \tag{6}$$

where $\omega_0 = \frac{|u_0 q_z|}{2}(1 + \xi_0)$. The linear dependence of velocity (and, therefore, Doppler frequency) on the coordinate results in a shape of the integral spectrum which is similar to that of the transverse concentration distribution of the scatterers.

Poiseuille profile: $u(x) = 2u_0 \cdot \frac{x}{h}(1 - \frac{x}{2h})$

The symmetry of the velocity profile leads to the summation of Doppler frequencies with the weight factors, $w(x) + w(x - 2h)$, so that the Doppler spectrum generally does not immediately represent the concentration distribution of the scatterers. When $w(x) \approx \exp(-P_e \cdot x/h)$, we obtain:

$$S(\omega) \approx P_e \frac{\exp\left(-\frac{P_e}{2}\right)}{|u_0 q_z|} \left\{ \mathrm{Ch}\left[\frac{P_e}{2}\left(1 - \frac{\omega \mp |\Delta\omega|}{|u_0 q_z|}\right)^{1/2}\right]\left(1 - \frac{\omega \mp |\Delta\omega|}{|u_0 q_z|}\right)^{-1/2} \cdot \right.$$

$$\theta(\omega \mp |\Delta\omega|) \cdot \theta(|u_0 q_z| \pm |\Delta\omega| - \omega) +$$

$$\mathrm{Ch}\left[\frac{P_e}{2}\left(1 + \frac{\omega \pm |\Delta\omega|}{|u_0 q_z|}\right)^{\frac{1}{2}}\right]\left(1 + \frac{\omega \pm |\Delta\omega|}{|u_0 q_z|}\right)^{-\frac{1}{2}} \cdot$$

$$\left. \theta(-\omega \mp |\Delta\omega|) \cdot \theta(\omega \pm |\Delta\omega| + |u_0 q_z|) \right\} \tag{7}$$

The upper signs before $\Delta\omega$ in eqn. 7 hold for $\Delta\omega q_z u_0 > 0$ and the lower ones for $\Delta\omega q_z u_0 < 0$. Consider the case $P_e \gg 1$, which is typical of FFF. The moving particles are localized in the thin near-wall layer with a width of the order of h/P_e, so that the corresponding Doppler frequencies are in the range of $|\omega \pm \Delta\omega| \approx |u_0 q_z / P_e| \ll |u_0 q_z|$. Here, eqn. 7 is transformed into eqn. 4. In the opposite case, $P_e \to 0$, corresponding to an uniform distribution of scattering particles in a flow, we obtain the Doppler spectrum characteristic of the Poiseuille profile of flow velocities in a flat channel.

In the case of a focusing transverse force, we obtain the following expression for the frequency spectrum

$$S(\omega) \approx \frac{\sqrt{P_e}}{2\sqrt{\pi}|u_0 q_z|} \cdot \frac{\exp\left[-P_e\left(\sqrt{1 - \frac{\omega}{\omega_0}} + \xi_0\right)^2\right] + \exp\left[-P_e\left(\sqrt{1 - \frac{\omega}{\omega_0}} - \xi_0\right)^2\right]}{\sqrt{1 - \frac{\omega}{\omega_0}}} \tag{8}$$

where $\omega_0 = |u_0 q_z|$. Depending on the focusing plane position, *i.e.*, upon the sign of ξ_0, one of the terms in the numerator of eqn. 8 is resonant, while the other term monotonously decreases with the frequency. For $\sqrt{P_e} \gg 1$, the non-resonant term is negligible small, and the position of the maximum of $S(\omega)$ is determined by the condition $\omega_0 = |q_z(1 - \xi_0^2)u_0|$. With due account of this fact, eqn. 8 can be rewritten in the form:

$$S(\omega) \approx \frac{\sqrt{P_e}}{2\sqrt{\pi}|\xi_0 u_0 q_z|} \cdot \exp\left[-P_e\left(\frac{\omega - \omega_0}{2\xi_0 u_0 q_z}\right)^2\right] \tag{9}$$

Now let us consider the influence of diffusive broadening on the shape of the Doppler spectra. From eqns. 4 and 7, the width of these spectra $\geqslant |u_0 q_z| \cdot P_e^{-1}$, where $P_e = Fh/kT$, F is the force acting on the particle and kT is the thermal energy. Diffusive broadening of the spectra is of the order of Dq^2, thus for $u_0 \geqslant DP_e k_0 \mathrm{Sin}\theta$ it can be neglected. For typical values of the relevant parameters, $D \approx 10^{-7}$ cm^2 s^{-1}, $P_e \approx$

10, $k_0 \approx 10^4$ cm^{-1} and $\theta \approx 10°$, this condition holds well starting from velocities $u_0 \geqslant 10^{-2}$ cm s^{-1}. Another cause of spectral broadening is the finite time the moving particles are present within the volume illuminated by the laser beam: $\Delta t \approx l P_e u_0^{-1}$, $\delta\omega \approx \Delta t^{-1}$. It is clear that this broadening can be neglected, if the corresponding dimension, l, of the illuminated volume greatly exceeds the laser wavelength.

If several kinds of particles are present in the flow, then the integral Doppler spectrum is determined by the sum of the relevant expressions in eqns. 4, 6, 7 and 9 taking due account of the relative particle concentrations defining the intensity of each peak. Of course, this poses a number of problems in interpreting the integral Doppler anemometry (IDA) data, which are less difficult in the case of focusing FFF.

EXPERIMENTAL

The fundamental difference between IDA and the other optical recording techniques including quasi-elastic light scattering[6] now being used in FFF is the detection of fractions in the separation column itself. This makes a number of specific demands on cell design. First, the hydrodynamic channel of the cell must be transparent to visual light, the walls must be optically perfect either along the whole length, or at least in the region of the flow where particle redistribution in the transverse force field is obvious enough for recording. Secondly, for a given flow velocity chosen from the considerations of separation efficiency in the transverse field, the mutual orientation of the flow velocity vectors, incident light vector and light vector scattered in the direction of the photodetector must ensure the optimum range of Doppler frequencies recorded. Thirdly, the optical set-up for cell illumination must be optimal as far as the adjustment procedure and the minimization of specific artifacts in Dop-

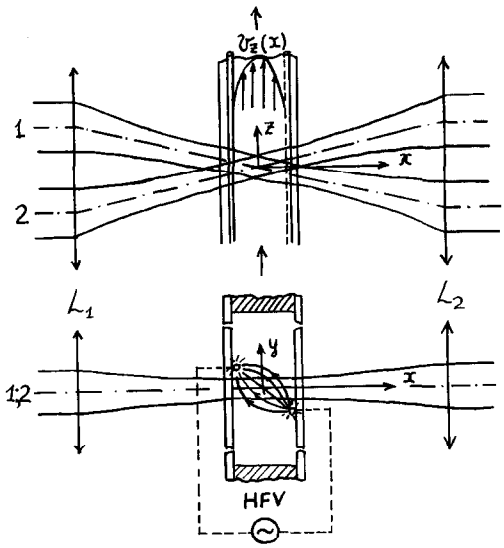


Fig. 1. Diagram of the measuring cell and measurement geometry. L_1 and L_2 are lensen, 1 and 2 are laser beams, and HFV = high frequency voltage.

pler anemometry are concerned. In our experiments, we used a new type of cell, where separation was expected to occur on the basis of dielectrophoresis. Dielectrophoresis is a directed motion of electrically neutral, polarizable particles in a spatially inhomogeneous high-frequency electric field[7]. As is the case with stationary electric and magnetic fields, this motion is due to the forces acting on dipoles in the inhomogeneous field. A flat hydrodynamic channel of the cell (Fig. 1) with a cross-section ≈ 8 mm $\times$ 0.25 mm and a length of ≈ 70 mm is formed by two polished glass plates with a thickness of ≈ 1 mm, separated by spacers. Isolated wire electrodes, 0.040 mm in diameter, are stretched inside the channel along the mid-lines of the wall, being separated by a distance of about 0.5 mm, as shown in Fig. 1. The electrodes are connected to a sinusoidal voltage generator with an amplitude of up to 25 V and a frequency of up 10 MHz. Doppler spectra are recorded, using the differential set-up[8], with an helium–neon laser, photodiode, bandpass preamplifier, radiofrequency spectrum analyzer and XY recorder. The relationship between the scattered particle velocity in a flow and its Doppler frequency was $u/f_D \approx 3 \cdot 10^{-4}$ cm, where $f_D = \omega/2\pi$.

Due to the symmetrical relative position of the channel electrodes and laser beams (Fig. 1), the relationship between the shape of the integral Doppler spectrum of the scatterers, $S(f)$, and their transverse concentration profile in a flow, $w(x)$, is greatly simplified. In this case, eqns. 2 and 3 yield for $D = 0$:

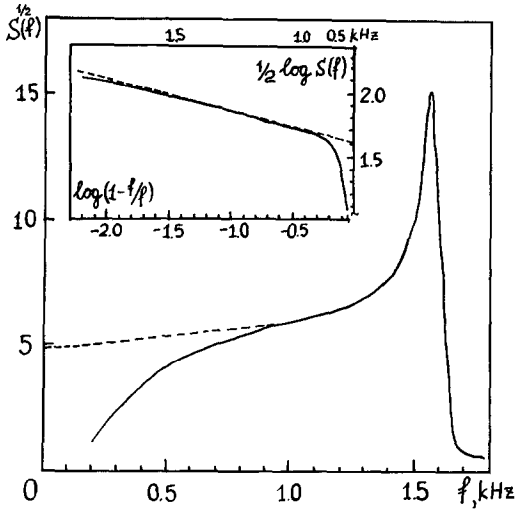
$$S(f) \sim w\left(P_e, \sqrt{1 - \frac{f}{f_0}}\right)\left(1 - \frac{f}{f_0}\right)^{-\frac{1}{2}} \tag{10}$$

Here, $f = \dfrac{q_z u(x)}{2\pi} = \dfrac{q_z u_0}{2\pi}\left(1 - \dfrac{x^2}{h^2}\right)$ is the Doppler frequency of a scatterer, moving in the x channel plane, the flow being characterized by a parabolic velocity profile. Eqn. 10 allows us to find the transverse profile of the scatterer concentration and to observe changes in it under different conditions from the shape of the experimentally measured Doppler spectra.

Recordings of the Doppler spectra amplitudes were carried out in the accumulation mode with averaging of up to 1024 subsequent samplings. Measurements were made at room temperature on a suspension of latex particles in a buffer solution of pH $\approx$ 9.5. The average particle diameter was 1 μm and the volume concentration was 10^5–10^6 cm^{-3}. The flow velocity, averaged over the cross-section of the channel, was 4.5 mm/s.

DISCUSSION

Fig. 2 illustrates a typical integral Doppler spectrum, measured in a flat channel without electrodes. In this case, the latex particles are uniformly distributed across the channel, and it follows from eqn. 10 that $S_{th}(f) \approx (1 - f/f_0)^{-0.5}$. The shape of the spectrum is determined by the parabolic flow velocity profile in a channel. The measured spectrum is well approximated by the dependence $\sqrt{S_{exp}} \approx (1 - f/f_0)^{-0.242}$, where $f_0 = 1.55$ kHz (Fig. 2, insert).



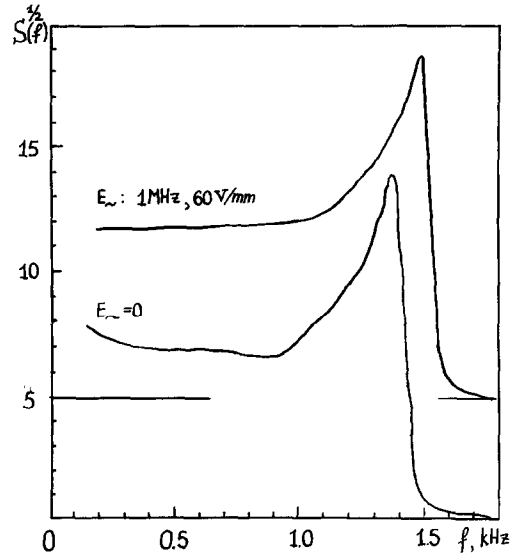


Fig. 2. Integral Doppler spectrum of a latex suspension flow in a flat channel.

Fig. 3. Integral Doppler spectra of a latex suspension, flowing in a flat channel, with electrodes for zero (lower curve) and maximum (upper curve) dielectrophoretic force across the channel.

Fig. 3 shows a spectrum measured for the channel with electrodes but without the transverse field. In this case, the experimental spectrum is well described by $\sqrt{S_{\text{exp}}} \approx (1 - f/f_0)^{-0.493}$ for $f/f_0 > 0.7$ and tends to become saturated at lower frequencies. Deviation from the theory developed for the flat channel without any irregularities inside shows that the profile of flow velocities is much more complex in the case of a channel that contains electrodes. Thus, the results presented in Figs. 2 and 3 demonstrate the possibility of experimental determination of the flow velocity profiles in narrow capillaries by means of IDA. As far as the quality of the FFF channel is concerned, the high frequency (HF) electrode system can be mounted outside the channel or deposited as thin strips on the inner surfaces of its windows in order to ensure an appropriate flow velocity profile. In the presence of an inhomogeneous high-frequency electric field applied to the electrodes (Fig. 1), the transverse profile of the particle concentration changes due to the dielectrophoretic force acting on each particle[7]:

$$F_{\text{d.ph.}} = \frac{3V_p}{8\pi} \cdot \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega) + 2\varepsilon_1(\omega)} \cdot \text{grad } E_{\sim}^2 \tag{11}$$

Here V_p is the particle volume, $\varepsilon_2(\omega)$ is the dielectric constant of its substance at the frequency of the applied field (≈ 2.5 for latex), $\varepsilon_1(\omega)$ is the ambient dielectric constant at the same frequency (≈ 80 for water) and $E\sim$ is the local amplitude of the HF field. Thus, for the latex water suspension, $\varepsilon_1 > \varepsilon_2$, and the dielectric forces must expel the latex particles to the region of minimum field inhomogeneity, in particular, to the central region of a channel.

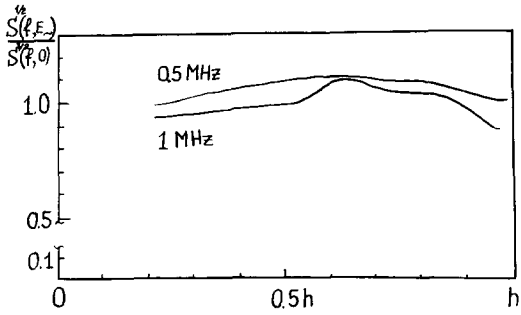


Fig. 4. Transverse profiles of the latex particle concentration in a laminar flow and a transverse dielectrophoretic force field. High-frequency voltage amplitude: 28 V.

For the experimental determination of the inhomogeneous transverse concentration profile, $w(x,E_{\sim})$, it is sufficient as can be seen from eqn. 10, to divide the Doppler spectrum obtained in the presence of the field by that obtained without it, since in the latter case $w(x)$ = constant, as shown above. These calculations are more convenient with the dimensionless term f/f_0, since an increase in f_0 is observed as the amplitude of the HF field grows. This results from the channel-flow velocity increase as a consequence of the high-frequency heating of the suspension and the corresponding decrease in its viscosity.

Fig. 4 presents the results of such measurements and the subsequent data processing for the two values of the HF transverse field. The observed change in the transverse profile of the latex particle concentration is in qualitative agreement with the pattern expected for the geometry of electrode system used and the sign of the dielectrophoretic force (eqn. 11). A comparatively small value of the effect ($\leqslant 10\%$) shows that under experimental conditions the time of particle equilibration in a transverse field, τ_0, substantially exceeds the time, τ_1, of their travelling in a flow to the point of the spectral recording, $z = l$. Indeed, as the estimates show for $V\sim = 30$ V, applied to electrodes spaced by ≈ 500 μm, for the particles of dimension ≈ 1 μm, $h \approx 100$ μm and $l \approx 60$ mm, τ_0 is about 10^2 s and $\tau_1 \approx 10$ s.

CONCLUSIONS

Theoretical considerations and experimental data presented demonstrate the feasibility of IDA, its possible application to flow-profile investigations and to measurements of particle dipole moments in suspension under the conditions of FFF. The possibility, in principle, of particle separation in a flow by this physical parameter, using IDA, has also been demontrated. The experiments show also that for a proper description of the experimental situation when the particle equilibrium in the transverse field force is not quite established, further theoretical investigations of the convective diffusion in such a field will be necessary.

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