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Heterodyne correlation function for a mechanically excited light scattering experiment

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ABSTRACT. A corrected heterodyne correlation function has been calculated for a dynamic light scattering experiment in which the light scattering cell is subjected to an harmonic mechanical force field. In the presence of this external force field the particles, dissolved or suspended in a fluid, suffer sedimentation as an additional effect to the usual diffusion movement. The diffusion and sedimentation velocities can be determined by means of laser Doppler velocimetry. Using this information it is possible to obtain the molecular weight distribution of the sample.

The vibrations of the scattering cell, which produces local sedimentation motions of the particles, appear as oscillations in the measured scattered electric field time correlation function $C(\mathbf{q},t)$. Laplace inversion of the correlation function under the restriction of ill-posedness, yields information on the distribution of sedimentation and diffusion coefficients and consequently on the molecular weight distribution. Two standard samples of polystyrene were used in order to demonstrate the feasibility of this technique.

RESUMEN. Se calcula una función de correlación heterodina para un experimento de dispersión de luz, en el cual la celda de dispersión se sujeta a un campo de fuerzas mecánico externo armónico. En presencia de este campo de fuerzas externo las partículas, ya sea disueltas o suspendidas en un fluido, sufren sedimentación como un efecto adicional al movimiento usual de difusión de las partículas. Las velocidades de difusión y de sedimentación pueden ser determinadas mediante velocimetría Doppler con láser. Usando esta información es posible obtener la distribución de pesos moleculares de la muestra.

Las vibraciones de la celda de dispersión, las cuales producen movimientos de sedimentación locales en las partículas, aparecen como oscilaciones en la función de correlación temporal de campo eléctrico dispersado $C(\mathbf{q},t)$. La transformada inversa de Laplace de la función de correlación con la restricción de mal condicionamiento, proporciona información sobre las distribuciones de los coeficientes de difusión y de sedimentación y, consecuentemente, sobre la distribución de pesos moleculares. Se usaron dos muestras de poliestireno estándar para demostrar la factibilidad de esta técnica.

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1. INTRODUCTION

Photon correlation spectroscopy has been a traditional technique to characterize polymer solutions and colloidal suspension [1-4]. It is based on a Doppler shift in the frequency of the incident light when it is scattered inelastically by a particle which is suffering thermal Brownian motion. In this way, the scattered intensity time correlation function contains information about the motion of the particle, *i.e.*, the diffusion coefficient of the particle.

In the presence of a vibrational force field, which can be achieved by oscillating the light scattering cell, the time correlation function, to the first order in amplitude of the harmonic oscillation, contains the usual diffusive exponential decay term plus an additional contribution consisting of an harmonic term with an amplitude related to the sedimentation coefficient. With this information, and making use of the Svedberg equation, it is possible to determine the molecular weight distribution of the particles under analysis. This approach complements ultracentrifugation in its role as a tool of the molecular weight determination of macromolecules in solution or colloidal particles in suspension [12]. In this case, the kernel of the transformation between the time correlation function and the characteristic linewidth distribution, is no longer the usual Laplace kernel, but it contains the cosine function: this is a Laplace-Fourier type kernel. Due to this the number of eigenvalues that can be recovered is a little larger than the usual for the Laplace inversion, because the Laplace-Fourier kernel decays slower than the Laplace kernel. Under favorable conditions, we were able to recover five independent eigenvalues instead of the usual 3-4 values from Laplace inversion using the Pike-Ostrowski [10] approach.

If the particles under study suffer another kind of movements, it is necessary to obtain the auto-correlation function for heterodyne conditions; this mean to use a local oscillator in order to obtain a scattered electric field auto-correlation function.

In order to probe the correctness of the analytical expression for the time auto-correlation function introduced here, we have obtained polymer molecular weight distributions of two samples, by means of photon correlation spectroscopy and by taking the inverse Laplace transform of the light scattered intensity time correlation function in order to estimate the characteristic linewidth distribution $G(\Gamma)$ [2–5]. It should be noted that the inversion is difficult to perform because the transformation is ill-posed whenever the data is bandwidth limited and contains noise. Different practical approaches to the inversion problem have been reported [6–11]. The Pike-Ostrowski [10] method allows us to carry out the inversion by selecting only those eigenvalues of the Laplace kernel which are above the noise level in the measured time correlation function, and are consistent with the finite bandwidth of the data.

In our data analysis, we have noted that fewer singular values can be used to model the sedimentation behavior because contributions from the sedimentation amplitudes are relatively small when compared with the total amplitude of the time correlation function. If we try to overspecify the sedimentation behavior, oscillations in the sedimentation amplitudes occur. However, with fewer number of delta functions for the sedimentation contribution, there appears to be a tendency to overestimate the amplitudes.

In Sect. 2 we present the theoretical background which shows a discrepancy in the contribution of the sedimentation effect to the time correlation function when the expression is compared with the one derived by Wada *et al.* [5]. In Sects 3 and 4 we describe the experimental methods and discuss the results, while the conclusion is summarized in Sect. 5.

2. THEORETICAL BACKGROUND

Consider a cell that contains a dilute polymer solution and is oscillating periodically.

The external force which is exerted over a volume occupied by each polymer molecule is $m_0 d^2\mathbf{r}_c/dt^2$, where m_0 is the mass of the *fluid* having the same volume as that of the particle, and $\mathbf{r}_c$ is the position vector of the cell wall. If the particle size is small ($R_p \ll \sqrt{2\eta_0/\omega_0\rho_0}$) and the frequencies are not so high, the friction force between the molecule and the fluid is proportional to the relative velocity between the molecule and the cell wall: $\xi(\mathbf{u} - \mathbf{u}_c)$, where the frictional coefficient $\xi = kT/D$, with D being the translational diffusion coefficient. For large particles and/or high frequencies, the friction force has the form [13]

$$\mathbf{f} = 6\pi\eta_0 R_p \left(1 + \frac{R_p}{\gamma}\right)\mathbf{u} + 3\pi R_p^2 \sqrt{\frac{2\eta_0\rho}{\omega_0}} \left(1 + \frac{2R_p}{9\gamma}\right)\dot{\mathbf{u}},$$

where $\gamma = 2\eta_0/\rho_0\omega_0$, R_p is the particle size and $\mathbf{u}$ is the relative velocity (defined in 2.5). The correction to the Stoke's formula ($\mathbf{f} = 6\pi\eta_0 R_p\mathbf{u}$) begins to be important (about 10%) for particle size larger than 2 microns and frequencies larger than a few KHz. Here, we are going to use the Stokes' formula for the friction force.

In this case, the Langevin equation which describe the dynamic behavior of the polymer molecule, takes on the form

$$m\ddot{\mathbf{u}} = -\xi(\mathbf{u} - \mathbf{u}_c) + m\mathbf{A}(t), \tag{2.1}$$

where m is the polymer molecular mass and $m\mathbf{A}(t)$ is the random force produced by the liquid surrounding the particle. The double dot means the second derivative with respect to the time and $\mathbf{u}$ is the absolute velocity of the particle.

In Eq. (2.1), the relevant variable is not the absolute velocity of the particle, but the relative velocity with respect tot he cell wall. In general, the position of the cell at any instant of time can be written as

$$\mathbf{r}_c = \mathbf{a}_0 e^{i\omega_0 t} + \mathbf{r}_{c0}, \tag{2.2}$$

where $\mathbf{r}_{c0}$ is the equilibrium position of the cell; $\mathbf{a}_0$ and ω_0 are the amplitude and the frequency of oscillation, respectively.

By substituting Eq. (2.2) into Eq. (2.1), the Langevin equation becomes

$$\dot{\mathbf{u}} = \beta\mathbf{u} + \left(\frac{m - m_0}{m}\right)\omega_0^2 \mathbf{a}_0 e^{i\omega_0 t} + \mathbf{A}(t), \tag{2.3}$$

where

$$\beta = \frac{\xi}{m} \tag{2.4}$$

and $\mathbf{u}$ now is the relative velocity:

$$\mathbf{u} \to \mathbf{u} - \mathbf{u}_c. \tag{2.5}$$

The formal solution to Eq. (2.3) is

$$\mathbf{u} = \mathbf{u}_0 e^{-\beta t} + \mathbf{K}(e^{i\omega_0 t} - e^{-\beta t}) + \int_0^t \mathbf{A}(\xi) e^{-\beta(t-\xi)} d\xi, \tag{2.6}$$

where we have defined

$$\mathbf{K} = \frac{(m - m_0)\omega_0^2 \mathbf{a}_0}{m(\beta + i\omega_0)} \tag{2.7}$$

and $\mathbf{u}_0$ is the initial velocity of the particle.

A further integration of the velocity equation (2.6) gives us the relative position of the particle with respect to the cell at any instant of time:

$$\mathbf{R} = \int_0^t \mathbf{u}(t')\, dt' \tag{2.8}$$

$$= \frac{\mathbf{u}_0}{\beta}(1 - e^{-\beta t}) + \mathbf{K}\left(\frac{e^{i\omega_0 t}}{i\omega_0} + \frac{e^{-\beta t} - 1}{\beta}\right) + \int_0^t e^{-\beta t'} dt' \int_0^{t'} e^{\beta\xi} \mathbf{A}(\xi)\, d\xi. \tag{2.9}$$

Due to the stochastic nature of this equation, we can use the Markoff method [14] to obtain the probability distribution function to find the molecule at position $\mathbf{R}$ at time t, if it has an initial velocity $\mathbf{u}_0$ at time zero. With the approximation $\beta \gg \omega_0$, the probability distribution function has the form

$$W(\mathbf{R}, t; \mathbf{u}_0) = \left(\frac{m\beta}{4\pi kTt}\right)^{3/2} \exp\left\{-\frac{m\beta}{4kTt}\left[\mathbf{R} - \frac{\mathbf{u}_0}{\beta} - \mathbf{K}\left(\frac{e^{i\omega_0 t} - 1}{i\omega_0} - \frac{1}{\beta}\right)\right]^2\right\}. \tag{2.10}$$

This conditional probability has to be averaged over all possible values of the initial velocity which will be assumed to follow a Maxwellian distribution function denoted by

$$W(\mathbf{u}_0) = \left(\frac{m}{2\pi kTt}\right)^{3/2} \exp\left\{-\frac{m\mathbf{u}_0^2}{2kT}\right\} \tag{2.11}$$

as the probability distribution function for the initial velocity. Then

$$W(\mathbf{R}, t) = \int W(\mathbf{R}, t, \mathbf{u}_0) W(\mathbf{u}_0)\, d\mathbf{u}_0$$

$$= \left(\frac{m\beta}{4\pi kTt}\right)^{3/2} \exp\left\{-\frac{m\beta}{4kTt}\left[\mathbf{R} - \frac{\mathbf{K}}{\omega_0}\left((i - ie^{i\omega_0 t}) - \frac{\omega_0}{\beta}\right)\right]^2\right\}. \tag{2.12}$$

All ensemble averages will be taken using this probability distribution function. For the center of mass motion of a molecule in solution, the scattered electric field time auto-correlation function is the spatial Fourier transform of this probability distribution function, *i.e.*,

$$C(\mathbf{q},t) = \int W(\mathbf{R},t)e^{i\mathbf{q}\cdot\mathbf{R}}\,d\mathbf{R}, \tag{2.13}$$

where $\mathbf{q}$ is the usual scattering vector whose magnitude is given by $q = (4\pi n_0/\lambda_0)\sin\frac{\Theta}{2}$, with n_0, λ_0 and Θ being the refractive index of the solution, the wavelength of light in vacuum and the scattering angle, respectively.

After having performed the integration over all space as permitted by the molecules in solution, we obtain the (normalized) correlation function in complex space:

$$C(\mathbf{q},t) = \exp\left\{-q^2D|t| + i\mathbf{q}\cdot\frac{\mathbf{K}}{\omega_0}\left[\left(ie^{i\omega_0 t} - i\right) - \frac{\omega_0}{\beta}\right]\right\}, \tag{2.14}$$

where $D = kT/m\beta$ is the translational diffusion coefficient of the polymer molecules.

In real time space we have

$$C(\mathbf{q},t) = e^{-q^2D|t|}\big[1 + S\omega_0\mathbf{a}_0\cdot\mathbf{q}(\cos\omega_0 t - 1) + \Theta(S^2)\big], \tag{2.15}$$

where we have written terms only to first order in S, with

$$S = \frac{(m - m_0)}{m\beta} \tag{2.16}$$

being the sedimentation coefficient of the polymer molecule. A similar expression for the correlation function it is obtained for electrophoretic mobility of particles under the influence of alternating electric fields [17].

Equation (2.15) represents the correlation function for a collection of identical particles. We can take the polydispersity effect into account by introducing a weighting factor for each particle size/weight which has a diffusion coefficient D and a sedimentation coefficient S. It is important to point out that for homopolymers, once one of the coefficients has been determined (for example D), all other quantities (S and M) are completely specified. However, this statement is no longer applicable for copolymers where, due to the polydispersity in composition, more than one coefficient has to be specified.

On this basis, we can write out the un-normalized scattered electric field time auto correlation function $G^{(1)}(t)$ as

$$G^{(1)}(t) = \int e^{-q^2D|t|}\big[1 + S\omega_0\mathbf{a}_0\cdot\mathbf{q}(\cos\omega_0 t - 1) + \cdots\big]W(S,D)\,dS\,dD, \tag{2.17}$$

where $W(S,D)\,dS\,dD$ is the total intensity scattered by molecules with coefficients $S \in [S, S+dS]$ and $D \in [D, D+dD]$.

The Svedberg equation which relates the coefficients S and D with the molecular weight M at infinite dilution has the form

$$M = \frac{\xi S}{D}, \tag{2.18}$$

where

$$\xi = \frac{kTN_a}{1 - \nu\rho_0}, \tag{2.19}$$

with k being the Boltzman's constant; T, the absolute temperature; N_a, Avogadro's number; ρ_0, the density of the solvent; and ν, the partial specific volume of the polymer.

Based on (2.18), we can write a formal relationship between the molecular weight probability distribution function $W(M)$ and the joint probability $W(S, D)$ [15]

$$W(M) = \int W(S, D)\delta\left(M - \frac{\xi S}{D}\right) dS\, dD. \tag{2.20}$$

As we can see from this expression, once we have obtained $W(S, D)$ using some reasonable model, the distribution $W(M)$ can be calculated. For homopolymers, we have $W(S, D)$ identical to the usual linewidth distribution $G(\Gamma)$. For copolymers we can use as a model the following relationship:

$$W(S, D) = \sum_i P_i \delta(D - D_i)\delta(S - S_i), \tag{2.21}$$

where, due to the properties of the Dirac delta function, P_i denotes the total intensity contributed by fraction i which can be characterized by the couple (S_i, D_i).

With this model, the correlation function for a polydisperse sample can be written as

$$G^{(1)}(t) = \sum_i P_i e^{-q^2 D_i |t|}\left[1 + S_i \omega_0 \mathbf{a}_0 \cdot \mathbf{q}(\cos\omega_0 t - 1) + \cdots\right]. \tag{2.17$'$}$$

On the other hand we know that, in general, the scattered electric field time correlation function can be written as [1,2,18]

$$G^{(1)}(t) \equiv \langle E^*(t')E(t' + t)\rangle = \frac{B\alpha_m^2}{N_a} c \sum_i \left(\frac{c_i}{c}\right) M_i S_{0i}(\mathbf{q}, t), \tag{2.22}$$

where B is a constant which depends on the optical geometry: $B = k_f^4 E_0^2 \mathrm{Vol}/\epsilon^2 R^2$, c is the mass concentration, $c = \sum_i c_i$, M_i is the molecular weight of species i, Vol is the scattering volume and $S_i(\mathbf{q}, t)$ is the dynamic structure factor of species i.

In the limit $t \to 0$, Eq. (2.22) takes on the form, in the continuous case,

$$G^{(1)}(0) = \frac{B\alpha_m^2}{N_a} c \int M f_w(M) S_0(\Theta, M)\, dM, \tag{2.23}$$

where the weight fraction (c_i/c) has been replaced by $f_w(M)\,dM$ in the continuous limit, and $S_0(\Theta, M)$ is the usual static structure factor. By taking the same $t \to 0$ limit in Eq. (2.17), we obtain

$$\int W(S, D)\, dS\, dD = \int M f_w(M) S_0(\Theta, M)\, dM, \tag{2.24}$$

where the multiplicative factor $B\alpha_m^2/N_a$ has been absorbed in the normalization of $f_w(M)$.

From Eq.(2.20), we have

$$\int W(M)\, dM = \int W(S, D)\, dS\, dD, \tag{2.25}$$

and with Eqs. (2.24), (2.21) and (2.20) we get the relationship between the probability $W(M)$ and $f_w(M)$, for the model we have used Eq. (2.21); then

$$f_w(M) = \sum_i \frac{P_i \delta(M - M_i)}{M_i S_0(\Theta, M_i)}, \tag{2.26}$$

where

$$M_i = \xi \frac{S_i}{D_i}. \tag{2.27}$$

From Eqs. (2.26) and (2.27) we can see that the weight molecular weight distribution is modeled as a sum of Dirac delta function centered at M_i and with a height given by $(P_i/M_i S_0(\Theta, M_i))$.

3. EXPERIMENTAL METHODS

In order to probe the expressions we have obtained in the last section, two standard samples of polystyrene of high molecular weight was used in a heterodyne dynamic light scattering experiment.

For this experiment an argon ion laser (Spectra Physics, model 165) operating at $\lambda_0 = 448$ nm was used as our light source. We used a piezoelectric stack of 100 ceramic disks, each with a diameter of 0.870″ (±0.005″) and thickness of 0.009″ (±0.001″), as shown in Figs. 1, and 2, operating in parallel in order to oscillate the light scattering cell with sufficient amplitude. A resonant parallel L–C circuit with a variable ferrite coil inductor, as shown in Fig. 3, was used in conjunction with a 60 watt low-noise, wide-band audio

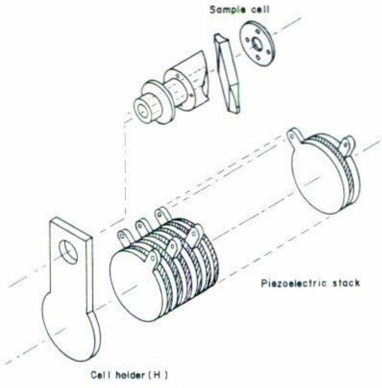

FIGURE 1. The cell holder was supported on a piezo-electric stack; this stack was built up by connecting in parallel a 100 ceramic disk. As can be noted, the cell is not perpendicular to the light beam direction.

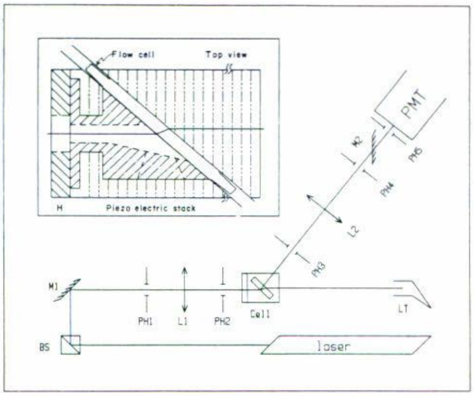

FIGURE 2. A schematic of the whole light scattering apparatus used in this experiment is shown. A detail of the piezo-electric stack and the cell holder is also shown.

amplifier to drive the piezo-electric shaker. A standard function generator was used as a signal source.

A rectangular light scattering cell with inner dimensions of $2 \times 4 \times 20$ mm was supported on the shaker in such a way that the normal direction of the cell surface was at 55 degrees of the direction of the incident beam (see Figs. 1, 2). An apparent scattering angle of 61.5 degrees between the photomultiplier tube (PMT) and the direction of the incident beam was used.

For a solvent (methyl ethyl ketone (MEK)) with a refractive index of 1.380, the actual scattering angle was 41 degrees. The main reason for choosing this configuration was to

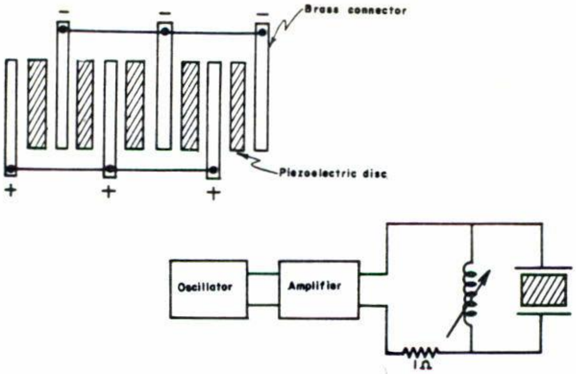

FIGURE 3. In order to increase the amplitude of oscillation of the piezo-electric shaker, and because it has a large capacitive impedance, a resonant L–C circuit with a variable ferrite coil inductor was used.

increase as much as possible the product $\mathbf{a}_0 \cdot \mathbf{q}$ without increasing the scattering angle excessively.

In the detection optics (see Fig. 2) we used a lens (L1) of 25 cm focal length. A real image of the scattering volume was formed on the plane of a horizontal adjustable slit (PH4) by using the lens (L2). The angular divergence of the scattered light was controlled by the slit (PH3) and another pinhole (PH5) of 0.0135″ diameter) appropriately located at a distance 2.35″ away from the slit, resulting in an angular divergence of 2.8 mrad. A movable mirror of the same type used in a single-lens reflex camera, was placed between the adjustable slit (PH4) and pinhole (PH5) such that we could see directly which portion of the scattered light actually reached the PMT.

For measuring the amplitude of oscillation, we built a special device using 19 optical fibers in cylindrical arrangement, as shown in Fig. 4. Six of them (marked by X in the insert) were used to carry white light from a 5-watt halogen lamp. The incident light was reflected by a small mirror mounted on the piezoelectric shaker, as shown in Fig. 5. The reflected light was collected by the remaining fibers and focused on a photo pin diode. The current signal was converted to a voltage signal and a low-noise, high-gain preamplifier (PAR model 113) with a variable band pass filter was used to measure the signal by using a digital voltmeter.

A static calibration curve, as shown schematically in Fig. 5, of the reflected intensity versus the distance between the mirror and the optical fibers probe, was obtained in order to be able to calculate the actual amplitude of oscillation produced by the piezo-electric shaker. With this set up, we could achieve a resolution of 200 Å in the measurement.

The scattered light coming from the illuminated volume was detected by means of fast PMT (EMI MODEL 9893 B/100) whose output was connected to a high bandwidth digital preamplifier amplifier/discriminator (ORTEC models 9301, 9302). The signal was processed by a digital correlator (Brookhaven Instruments model BI 2030).

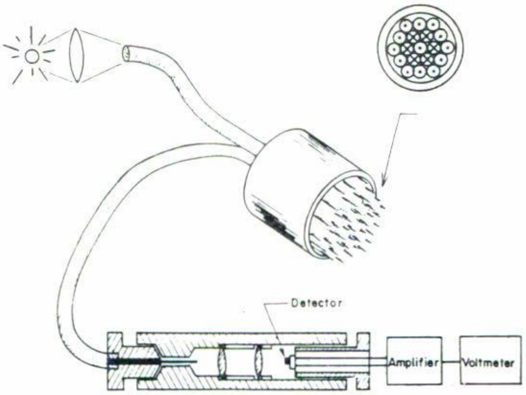

FIGURE 4. An optical fiber device was built up in order to measure the very small displacement of the piezo-electric shaker. Out of 19 optical fibers, 6 were used to carry out white light coming from a 5-Watt halogen lamp. The incident light was reflected on a small mirror mounted on the shaker and collected by the remaining fibers and focused on the detector.

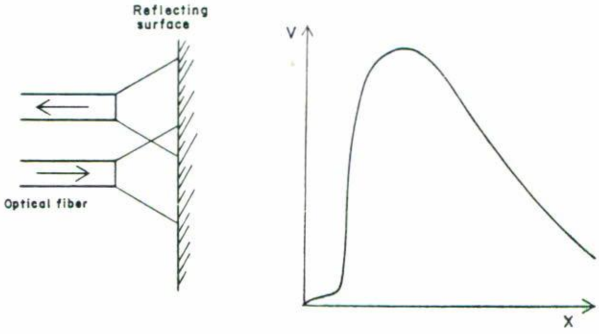

FIGURE 5. The calibration curve for the optical fiber device used for measuring the amplitude of oscillation of the piezo-electric shaker, was made in a static way by using a translational stage, and it is shown in the right hand side of this figure.

4. RESULTS AND DISCUSSION

Two polystyrene samples of 20×10^6 and 4.48×10^6 daltons nominal molecular weights were used in order to probe the feasibility of the model we have introduced here. These samples were dissolved in methyl ethyl ketone (MEK). MEK was chosen mainly because of the large density difference between the polymer and the solvent. All measurements were performed at room temperature. Data analysis was made following the technique of "decomposition in singular values" [16].

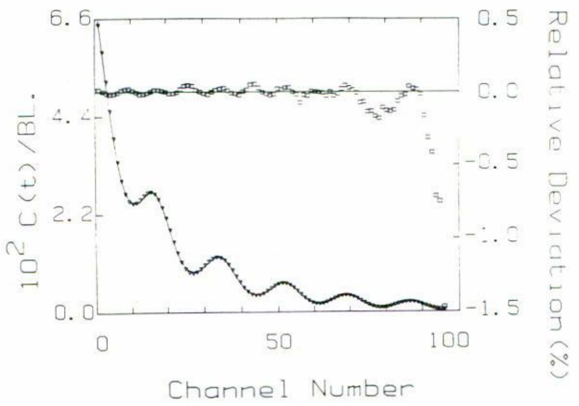

FIGURE 6. This is a typical correlation function which includes the diffusive exponential decay and the contribution of a harmonic term with an amplitude related to the sedimentation coefficient of the particle.

The correlation function (Eq. (2.17′)), as shown in Fig. 6 for one of the samples (20×10^6), can be written, in matrix notation, as

$$\left[\mathbf{C}(t)\right] = \left[e^{-\Gamma t} \mid e^{-\Gamma t} \cos \omega_0 t\right] \begin{bmatrix} \mathbf{A} \\ \mathbf{B} \end{bmatrix}, \tag{4.1}$$

where the vectors **A** and **B** have the components

$$A_i = P_i(1 - S_i \omega_0 \mathbf{a}_0 \cdot \mathbf{q}) \quad (i = 1, \ldots n), \tag{4.2}$$

$$B_i = P_i S_i \omega_0 \mathbf{a}_0 \cdot \mathbf{q} \quad (i = 1, \ldots n), \tag{4.3}$$

the vector $\mathbf{C}(t)$ has as dimensions the number of channels of the correlator (N_0); due to this the matrix $\left[e^{-\Gamma t} | e^{-\Gamma t} \cos \omega_0 t\right]$ has as dimensions $(N_0, 2n)$.

Then the problem consists in getting the inversion of this transformation in order to solve for the extended vector solution $(\mathbf{A}, \mathbf{B})$. Here, we have arbitrarily separated the $\mathbf{A}, \mathbf{B}$, vectors in order to retain the singular-value decomposition technique.

In the usual case (no oscillation: $\omega_0 = 0$ or $\mathbf{a}_0 = 0$) the vector **A** is exactly equal to **P** being defined as the characteristic linewidth distribution vector. In Eq. (4.1), we have the additional **B** vector which is related to the sedimentation coefficient of each fraction P_i. Consequently **A** and **B** allow us to compute directly the molecular weight distribution given by

$$M_i = \frac{\xi q^2}{\omega_0 \mathbf{a}_0 \cdot \mathbf{q}} \left(\frac{B_i}{\Gamma_i (A_i + B_i)} \right) = \frac{\xi S_i}{D_i} \tag{4.4}$$

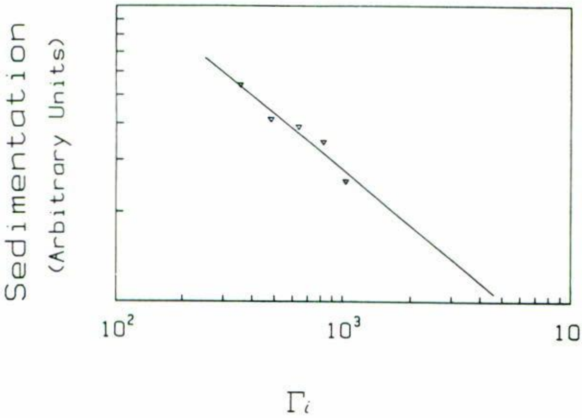

FIGURE 7. This plot allows to generate the complete set of sedimentation coefficients for the sample. With this it is possible to obtain the molecular weight distribution. This data correspond to the sample with a molecular weight of 2×10^7 daltons.

and

$$f_w(M) = \sum_i \left(\frac{A_i + B_i}{M_i}\right) \delta(M - M_i). \tag{4.5}$$

We have $|\mathbf{B}| \ll |\mathbf{A}|$ either because the sedimentation coefficient is very small for low molecular weight particles or because we have to reduce the amplitude of oscillation in order to retain the linear approximation [see Eq. (2.15)] for high molecular weight particles. When the same number of Dirac delta functions is used for both vectors **A** and **B**, some oscillations (instabilities) in the numerical values of the last components of **B** occur. Consequently, we have taken the option to reduce the number of components of the vector **B**. This is equivalent to setting the last (and consequently the small) components of **B** to zero, producing the effect of overestimating the other components. Different procedures may be designed to compensate for this trend.

For each of the few **B** components, we have taken the ratio $B_i/(A_i + B_i)$ which is proportional to the sedimentation coefficient S_i. These values are plotted in a log-log scale versus Γ_i as shown in Fig. 7, resulting in a straight line whose slope is in good agreement with the exponent in the scaling relationship between S and Γ for random coil molecules in a good solvent:

$$S = K_s \Gamma^{-\alpha_s}; \qquad \alpha_s = \frac{2}{3}. \tag{4.6}$$

For the sample No. 1 (polystyrene with $M = 2 \times 10^7$) in MEK, we used a frequency of 2.5 KHz with an amplitude of oscillation of 3.0 microns. The exponent α_s for this sample was 0.59. For sample No. 2 (polystyrene with $M = 4.48 \times 10^6$) in MEK, the frequency

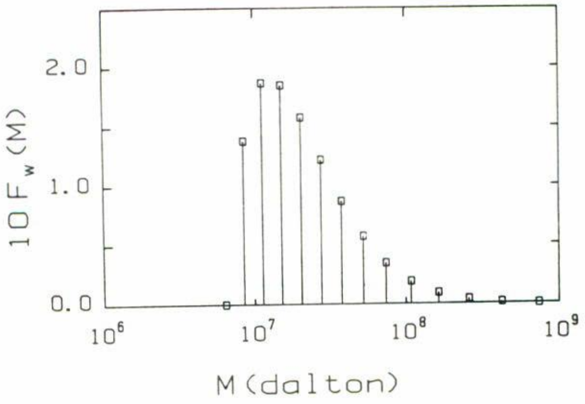

FIGURE 8. **This is the** molecular weight distribution obtained using the diffusion and sedimentation distribution. This distribution corresponds to the sample with molecular weight of 2×10^7 daltons nominal molecular weight.

used was 2.5 KHz with an amplitude of 3.3 microns. In this case, the exponent α_s was 0.68.

It should be noted that the experimental values for the exponent α_s are systematically smaller than the expected value. This trend is due mainly to the fact that the number of B-components is lower than that of the A-components.

By using the slope and the intercept in Fig. 7, we can estimate the remaining components of B needed for computing the molecular weight distribution. We obtained for sample No. 1 a molecular weight of 2.4×10^7 g/mol (see Fig. 8), and for sample No. 2 a molecular weight of 4.8×10^6 g/mol. These results are in good agreement with the nominal values reported for the two standard samples.

5. CONCLUSION

The analytical expression for the electric field time correlation function, which has been demonstrated successfully by using high molecular-weight polymer samples, has the advantage that no additional information (other than ν) is required to determine the molecular weight distribution. It should be particularly useful to characterize complex particle like copolymers where the composition may depend on particle size.

This technique is limited to large particles because our piezoelectric vibrator has limited amplitude of oscillations at high frequencies ($\gtrsim 2$ KHz.). Therefore, it should be particularly useful in determining particle size distribution for large colloidal particles in suspension.

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