Dynamic light scattering at low rates of shear
B.J. Ackerson, N.A. Clark

To cite this version:

HAL Id: jpa-00209085
https://hal.archives-ouvertes.fr/jpa-00209085
Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Dynamic light scattering at low rates of shear

B. J. Ackerson
Department of Physics, Oklahoma State University, Stillwater, OK 74078, U.S.A.

and N. A. Clark
Department of Physics, University of Colorado, Boulder, CO 80302, U.S.A.

(Reçu le 4 février 1981, accepté le 9 mars 1981)

Abstract. — Dynamic light scattering as a probe of fluctuations for systems undergoing steady linear shear is examined. Several approximations are made to calculate the intensity correlation function for a dense system of independent particles or fluctuations at low rates of shear. In this limit the intensity correlation function is similar in structure to the equilibrium intensity correlation function; however, the signal to background factor becomes correlation time dependent. The result is tested experimentally by measuring the intensity correlation function for a dilute solution of Brownian particles undergoing shear. The feasibility of using dynamic light scattering as a probe of fluctuations in sheared systems is discussed.

1. Introduction. — Static and dynamic light scattering have been used to probe the structure and fluctuations of a variety of systems in thermodynamic equilibrium [1]. Recently, however, there has been interest in the structure and fluctuations in nonequilibrium steady states, for example in systems undergoing shear. In particular, static light scattering has been used to probe the effect of shear on the spatial structure of fluctuations of binary mixtures near the consolute point [2] and on strongly interacting colloidal particle solutions [3]. The effect of shear on the temporal evolution of fluctuations has been calculated for binary mixtures near the consolute point [4], for solutions of spheroids [5], and for the Brillouin spectra from simple fluids [6]. Presumably dynamic light scattering is capable of probing the temporal evolution of such fluctuations. However, we show that effects accompanying shear may make dynamic light scattering measurements of fluctuations in sheared systems impractical or impossible.

The effect of shear on dynamic light scattering has been considered for laser Doppler velocimetry applications [7, 8]. Here reference beam or heterodyne and crossed beam experimental configurations are considered because velocity estimates are desired and include shear, diffusion, and transit time effects. Fluctuations and the self-beat or homodyne experimental configuration for measuring fluctuations are not emphasized in these analyses.

Because of the current interest in the nature of fluctuations in systems undergoing shear, we analyse the effect of shear on the measurement of fluctuations by dynamic light scattering for a self-beat or homodyne experimental configuration. Several assumptions are made which limit the theoretical result to a dense system of independent particles or fluctuations subjected to a weak shear. Model calculations are made as a function of the scattering volume and photocathode area. The results are compared to experimental data and the feasibility of measuring fluctuations in systems undergoing shear is discussed. It is found that the measured intensity correlation functions will depend
both on scattering volume and photocathode area, with a signal to background factor, $\gamma$, which is dependent on the correlation time $\tau$.

2. Theory. — Dynamic light scattering measures the intensity correlation function averaged over the available photodetector area $A$

$$\langle I(\vec{r}, t) \rangle = \frac{1}{A} \int_A d\vec{r} \int_A d\vec{r}' \langle I(\vec{r}', t) I(\vec{r}, t + \tau) \rangle . \quad (2.1)$$

Here $I(\vec{r}, t)$ is the intensity of light on the photocathode at position $\vec{r}$ at time $t$. The intensity correlation function itself is a time average or ensemble average (for a stationary process).

The intensity at some point on the photocathode may be calculated by considering the scattering of light from particles, atoms or molecules in the scattering volume. The scattering volume is typically determined by the diameter of the illuminating laser beam as well as stops and pinholes in the collection optics.

Since the intensity is related to the modulus of the electric field, we consider the electric field at the point $\vec{r}'$ on the photocathode, assuming single scattering from $N$ particles in the scattering volume. This may be written as

$$\vec{E}(\vec{r}', t) = \sum_{i=1}^{N} \vec{e}_i(\vec{r}_i(t)) \exp(i \vec{k}(\vec{r}')(\vec{r}(t))). \quad (2.2)$$

The explicit time dependence of $\vec{E}(\vec{r}', t)$ has been omitted for convenience, as it is not present in the corresponding intensity $I(\vec{r}', t)$. The amplitudes $\vec{e}_i$ are determined by the scattering power of the particles, the illumination of the scattering volume, the position of the particles in the volume, and other geometrical factors. Because we limit our calculation to self-beat or homodyne scattering, no reference amplitude is included in equation (2.2). The wave vector $\vec{k}(\vec{r}')$ is given in the Fraunhofer approximation as

$$\vec{k}(\vec{r}') = \frac{\vec{k}_0 - \vec{R}}{R} + \vec{R}_0 \quad \text{where terms which cancel on forming the modulus of $\vec{E}$ are omitted and where}$$

$$\vec{k} = \vec{k}_0 - \frac{\vec{R}}{R} \vec{k}_0 . \quad (2.4)$$

Here $\vec{k}$ is the standard scattered wave vector [1] where $\vec{k}_0$ is the incident wave vector, $\vec{R}$ is a vector from the centre of the scattering volume to the centre of the photocathode, $\vec{R}$ is the magnitude of $\vec{R}$, and $\vec{R}_0$ is the projection of $\vec{r}$ on a plane perpendicular to $\vec{R}$. It is assumed that $R$ is much greater than the maximum dimension of either the scattering volume or the photocathode area.

We now make several assumptions which limit the theoretical result to a dense system of independent particles at low rates of shear. First, because fluctuations in time are of interest, the experimental apparatus must be designed so that the transit time, $\tau_t$, of a particle or fluctuation through the scattering volume is much longer than the decay time, $\tau_d$, of particle correlation or fluctuation. Otherwise, the transit time correlation [7] will suppress the fluctuation correlation. Thus, velocities in the scattering volume must be small. Second, it is assumed that there are a large number of particles or fluctuations in the scattering volume so that Gaussian statistics prevail for the amplitude distribution of $\vec{E}(\vec{r}', t)$. If this is not the case, then number fluctuations [10] complicate the measured spectra. These two assumptions imply that $N$ is large, that the $\vec{e}_i$ are assumed constant and independent of position $(\vec{e}_i(\vec{r}_i, t) = \vec{e}_i)$, and that the intensity correlation function will depend only on the dynamic structure factor [1]. Third, it is assumed that the probability function $P(\vec{r}, \vec{r}_0, \tau)$ which describes the motion of a particle(s) or decay of fluctuations in a shear field has the form:

$$P(\vec{r}, \vec{r}_0, \tau) = P_\lambda(\vec{r} - \vec{r}_0 - \vec{v}_0(\vec{r}_0) \tau, \tau) P_\sigma(\vec{r}_0) . \quad (2.5)$$

Here $\vec{r}$ is the position at time $\tau$ and $\vec{r}_0$ is the initial position. The velocity field $\vec{v}_0(\vec{r}_0)$ is assumed constant in time and is parametrized by the initial coordinate, $\vec{r}_0$. $P_\lambda$ is a conditional probability for $\vec{r}$ given $\vec{r}_0$ at $\tau = 0$; and $P_\sigma$ is the initial distribution. The spatial Fourier transform of $P$ with respect to $\vec{r}$ is given by

$$G(\vec{k}, \vec{r}_0, \tau) = F(\vec{k}, \tau) \exp(i \vec{k} \cdot \vec{v}_0(\vec{r}_0) \tau + i \vec{k} \cdot \vec{r}_0) P_\sigma(\vec{r}_0) . \quad (2.6)$$

Both the studies by Foister and van de Ven [11] on Brownian motion in a linear shear flow and by de Gennes [4] on critical fluctuations of a binary mixture subjected to a linear shear have the forms for $P$ as stated above. Both calculations begin with the Smoluchowski equation suitably generalized to include shear. If the linear shear field is expressed as

$$\vec{v}_0(\vec{r}_0) = z \vec{v}_0 v_x + u_0 \vec{e}_x \quad (2.7)$$

where $z$ is the rate of shear, $u_0$ is the fluid velocity at the centre of the scattering volume and $\vec{e}_x$ is a unit vector in the $x$-direction, then the form for the conditional probability is

$$P_\lambda(\vec{r}, \vec{r}_0, \tau) = \exp \left( - \frac{(z - z_0)^2}{4 D t} - \frac{(x - x_0 - v_0 t)^2 + (y - y_0)^2 + (x - x_0 - v_0 t) (y - y_0) \alpha t + \alpha^2 (y - y_0)^2}{12} \right) \quad (2.8)$$
Finally, it is assumed that the particles (or fluctuations) move independently. Thus, \( P \) is a product of \( N \) similar functions like that in equation (2.8) and 
\[
P_{*} = 1/V \text{ where } V \text{ is the scattering volume. When these assumptions are made, the intensity correlation function becomes}
\]
\[
C(\tau) = \frac{1}{2A^2} \left( \frac{\varepsilon}{\mu} \right)^{1/2} \int_{V} \int_{Y} d\bar{r}' \frac{N}{1} \left( \int_{I} d\bar{r}_0 P_{0}(\bar{r}_0) \right) \times 
\sum_{\text{image}} |e_1|^4 \exp(\bar{K}(r').(\bar{r}_1 - \bar{r}_a) - \bar{K}(r').(\bar{r}_0_0 - \bar{r}_p)) = I_0^2(1 + \gamma(\bar{v}_0(r_0), \tau) | P(\bar{K}, \tau) |^2) \tag{2.10}
\]
where \( \varepsilon \) is the permittivity, \( \mu \) the permeability, \( I_0 \) is the average intensity on the photodetector and

\[
\gamma(\bar{v}_0(r_0), \tau) = \frac{1}{A^2 V^2} \int_{V} \int_{A} \exp(ik.(\bar{v}_0(\bar{r}_{10}) - \bar{v}_0(\bar{r}_{20})) \tau + \frac{ik_0}{R}(\bar{r}_p - \bar{r}_0).(\bar{r}_{10} - \bar{r}_{20})) \text{ d}r_{10} \text{ d}r_{20} \text{ d}r' \text{ d}r'' \tag{2.11}
\]

Here quantities which involve \( \left( \frac{k_0 - \bar{k}}{R} \right) \tau \) have been approximated by \( \bar{k} \tau \) since \( | \bar{k} | \) is much larger than \( \left| \frac{k_0 - \bar{k}}{R} \right| \) within our assumptions. This cannot be done for terms which do not contain \( \tau \) as the \( \bar{k} \) terms cancel to lowest order.

The result given in equations (2.10) and (2.11) is very similar to the equilibrium self-beat correlation function. However, there is a signal to background factor \( \gamma \) which depends on \( \tau \) and which reduces to the equilibrium factor when the solvent velocity is uniform or zero. It is important to emphasize that this effect on the correlation function is the result of two different processes. One relates primarily to the size of the scattering volume and the other to the size of the photocathode. First, we consider the scattering volume effect. Brownian particles of a given initial separation in the scattering volume will have a given difference in velocity due to the shear field. Light scattered by these particles, when it mixes on the photocathode, will produce a beat frequency due to the difference in particle velocity. For small scattering volumes the particle separation will be small and so the beat frequency will be small. On the other hand, if the scattering volume is large, two particles at opposite ends of this region will have a large separation and a large velocity difference. They will produce a large beat frequency. The total effect will be a sum over the whole scattering volume of beat frequencies produced by the beating of scattered light by particles with the maximum allowed separation or less. Since large scattering volumes have more high frequency components than do the small, these volumes will produce faster decaying time correlation functions in general.

Now we consider how the size of the photocathode affects the decay rate. Just as the interference pattern produced by light passing through a double slit depends on the slit separation \([12]\), the number of coherence areas on the photocathode is different for particles of different separations. Thus, particles of a given separation will produce a given amplitude photocurrent. Since particles of different separations also have different velocities (and consequently different beat frequencies) the beat frequencies are not all weighted the same on the photocathode. Thus, the effective area and sensitivity variation over the cathode area will influence the measured correlation function of a sheared sample.

The effect of \( \gamma \) can be observed qualitatively by shearing a solution of sufficiently large particles \((N \geq 1.0 \mu)\). When the system is in equilibrium, a laser beam directed through the sample will produce a changing speckle pattern and a grainy appearance. However, if the sample is subjected to a small shear \((\sim 5/s)\), the laser beam through the sample will appear smooth.

3. Model calculations for linear shear. — In equilibrium dynamic light scattering, the scattering angle is the only geometrical parameter needed to characterize the time decay rate. For sheared suspensions, however, we expect scattering volume size and photocathode area to effect the time decay in general. Other geometrical parameters include the orientation of the shear and velocity fields with respect to the incident and collected light. Thus, there are a variety of possible scattering geometries and a general simple correlation function is unlikely. We now examine a few specific scattering geometries.

When the incident and collected light are arranged such that \( \bar{k} \) is perpendicular to the solvent or particle velocity, then the signal to noise factor, \( \gamma \), is independent of \( \tau \). There will always be some contribution due to the nature of the approximations, but it is minimal as in the equilibrium situation. One would
think this particular geometry could be used to study the effect of shear on the fluctuations of a Brownian particle or critical mixtures since all geometrical effects are minimized. However, $k_x = 0$ for this geometry and the predicted shear-induced effects displayed in equation (2.9) are not visible. However, other low shear systems may exhibit observable effects in this geometry.

Another geometry minimizes the effect of most of the dimensions of the scattering volume and the photocathode. Here the velocity (in the $x$-direction) and the incident wave vector $k_0$ are in the same direction. Scattered light is collected along the same direction as the gradient of the velocity ($y$-direction), and the scattering angle is $90^\circ$. The signal to noise factor is given by

$$\gamma(\tau, \tau_0) = \left\{ \begin{array}{l}
\frac{1}{V^2 b^4} \int_A \int_V \exp \left( \frac{k_0}{R} (x'_0 - x_0) \right) \exp \left( \frac{i k_y}{R} (y'_0 - y_0) \right) \\
\left( \frac{\sin (k_x a c / 2)}{k_x a c / 2} \right)^2 L \right\}
\end{array} \right. \qquad (3.1)$$

where

$$L = \int_{-b/2}^{b/2} dx' \int_{-b/2}^{b/2} dx'' \left( \frac{\sin (k_0 a (x' - x'')/2 R)}{(k_0 a (x' - x'')/2 R)} \right)^2 .$$

The scattering volume is assumed square of side $a$ in the $x$-$z$ plane with a depth $c$ in the $y$-direction. The photocathode is assumed square of side $b$. It is seen that the decay introduced by the geometry dependent term becomes faster as $c$ increases. This effect has been anticipated in section 2.

Finally, a geometry is examined which displays

$$\gamma(\tau, \tau_0) = \left\{ \begin{array}{l}
\frac{1}{V^2 b^4} \int_A \int_V \exp \left( \frac{i k_0}{R} (y'_0 - y_0) \right) \exp \left( \frac{i k_x}{R} (x'_0 - x_0) \right) \\
\left( \frac{\sin (k_x a c / 2)}{k_x a c / 2} \right)^2 L \right\}
\end{array} \right. \qquad (3.2)$$

For simplicity the same assumptions concerning the size and shape of the scattering volume and photocathode have been made as in the previous example. The integral over $w$ is evaluated numerically and results of this calculation are displayed in figure 1. It is seen that there is a significant dependence on geometrical factors.

4. Experimental procedure and results. — Dynamic light scattering experiments have been conducted to test the theory presented in previous sections. A typical experimental arrangement is shown in figure 2. Here a helium neon laser beam of diameter 0.78 mm is focused by a lens L1 into the suspension of interest. The suspension is contained in a transparent walled, concentric cylinder, shear cell. The diameter of either cylinder is several times the difference in radii, so that the sheared fluid velocity distribution approximates that obtained between two parallel moving planes. The inner cylinder rotates at 3.6 RPM. The whole cell is immersed in a large radius water bath with the scattering volume in the centre to minimize the refractive bending of light on entering and leaving the shear cell. The suspension consists of DOW 0.489 μm diameter polystyrene latex microspheres in water at a concentration of approximately $10^8$ particles/cc. This size particle is used so that the decay of $F(k, \tau)$ is generally longer than that due to the signal to background integral $\gamma$, so that $\gamma$ may be studied. In figure 2 the scattering angle is $90^\circ$ and the collected light propagates in the same direction as the velocity of the particles in the scattering volume. A lens L2 is used to image the scattering volume onto the stop. The separation between the stop and pinhole is 37 cm while the separation between the pinhole and photocathode is 13 cm. Three stop diameters (1.0 mm, 0.5 mm, 0.1 mm) and three pinhole diameters (1.8 mm, 1.0 mm, 0.41 mm) are used. The beam splitter BS and mirror M arrangement permits heterodyne correlation functions to be measured.
The normalized, time dependent portion of the intensity correlation function, $M(t)/M(0)$, given by equation (2.10) using (3.2), is presented as a function of the correlation delay time. All curves represent a homodyne or self-beat spectrum where $k = 1.87 \times 10^5 /\text{cm}$, $k_0 = 1.32 \times 10^5 /\text{cm}$, $Dk^2 = 520 \text{ cm}^2 /\text{s}$, $R = 50 \text{ cm}$, and the scattering angle is $90^\circ$. In the upper curve $\alpha = 0$. For all other curves $\alpha = 1.8/\text{s}$. The stop width is $0.4 \text{ mm}$ in all cases, while the pinhole width is noted by each curve.

Figure 3 illustrates the variety of intensity correlation functions which one encounters in this type of experiment. The slow decaying correlation function $C$ is the familiar exponential decay for homodyning or self-beating from a non-sheared suspension. The oscillating correlation function $A$ is typical of heterodyning or using a reference beam. The frequency of oscillation is related to the average velocity in the scattering volume [7]. This property has been used to determine the velocity profile in the shear cell, and this profile is displayed in figure 4. It is seen that the velocity profile is not exactly linear due to the finite diameter of the concentric cylinders. This means that $\alpha$ varies over the length of the laser beam. Thus, measurements are restricted to the centre of the beam. This also avoids reflections from the cell walls. The quickly decaying, nonoscillating correlation function $B$ is typical of homodyning from a sheared suspension.

The experimental conditions presented here are not identical to the conditions of the theoretical calculation in section 4. Experimentally the stops, the pinholes, and the beam diameters determine the
size of the scattering volume and effective photocathode area. While the model calculations assume square apertures, the stops and pinholes are round. Also the stops and pinholes are not coincident with the photocathode area or the scattering volume. However, the scattering volume is effectively positioned at the stop, because a lens images this region on the stop. Any magnification of the scattering volume must be accounted for in the effective rate of shear of the sample at the stop. The largest pinhole setting is completely open: no pinhole at all. Only in this case is the size of the photocathode determined by the radius (0.9 mm) of the cathode itself. There is some error in assuming, as we have, that the other pinholes are the effective size of the photocathode at the position of the photocathode. These differences between the theoretical model and the actual experiment produce a discrepancy between the exact shape and rate of decay of the predicted and measured correlation functions. However, the approximations are not severe and the discrepancy is not large.

Because the shape of the theoretical correlation function differs from the measured correlation function, the data is not fit by the theoretical function to determine parameters. A correlation time at half height or \( \text{« half-time »} \) is used to characterize and compare theoretical predictions with experiment. This half-time is determined by finding the correlation delay time where the correlation function is halfway between its initial height and long time constant value.

For the arrangement shown in figure 2 the laser beam diameter in the scattering volume was varied by moving lens L1 or removing it entirely. This produced no significant change in the measured correlation function. Changing the stop or pinhole diameter did produce a significant change in the correlation function. The lower portion of figure 5 illustrates the dependence of the measured half-time on the size of the stop and the photocathode area for the self-beat or homodyne technique. The half-time is given as a function of the stop size. The different symbols indicate data taken for the different pinhole sizes. The effective rate of shear is \( \alpha = 1.8/\text{s} \). The incident wave vector is \( k_0 = 1.32 \times 10^5 \text{cm}/\text{cm} \), the scattered wave vector is \( k = 1.87 \times 10^5 \text{cm}/\text{cm} \), and the component of the wave vector in the direction of the velocity is the same as \( k_0 \). The data was collected at room temperature \( (T = 22^\circ \text{C}) \).

The solid lines in the lower portion of figure 5 indicate the calculated half-time using equation (3.2) with (2.10) to compute the time dependent part of the intensity correlation function. The edge lengths of the apertures were taken to be the same as the experimental aperture diameters. The diffusion constant is \( D = 1.50 \times 10^{-8} \text{cm}^2/\text{s} \). The separation between the scattering volume and photocathode is \( R = 50 \text{ cm} \). The rate of shear, incident wave vector, and scattered wave vector are the same as the experimental values.

Reasonable quantitative agreement is obtained between the predicted and measured half-times, despite the theoretical approximations which were made. By reducing the value of \( D \) the theoretical lines may be moved up until all data points are below the theory. It is seen that there is a competition between \( F(k, \tau) \) and the geometry dependent term, \( \gamma \). The signal to background term \( \gamma \) dominates for large diameter stops and small diameter pinholes. Conversely, the \( F(k, \tau) \) term dominates for small stops and large diameter pinholes. If the diffusion constant is zero, the time decay of the correlation function is given completely by \( \gamma \). If the diffusion constant is much greater than \( 1.50 \times 10^{-8} \text{cm}^2/\text{s} \), then \( F(k, \tau) \) dominates for the present pinhole and stop diameters.

Data is also presented for the scattering geometry discussed in connection with equation (3.1). Here the shear cell is positioned in the water bath so that the axis of rotation, the stop and the pinhole are collinear. The incident laser beam is directed to intersect this line halfway between the two cylinder walls of the shear cell. The scattering angle is \( 90^\circ \). The shear rate, wave vectors, and diffusion constant are the same as for the lower part of figure 5. The upper portion of figure 5 shows that the measured half-time is independent of stop and photocathode sizes. This is expected from the calculation in section 3. Figure 6 shows the dependence of the measured half-time on the diameter of the incident laser beam in the scattering volume. This width controlled by moving lens L1 or removing it entirely. It is measured directly by using a micrometer. In figure 6 the
Fig. 6. — This graph presents theoretical (line) and experimental (points) half-times as a function of beam diameter for the experimental arrangement discussed in connection with equation (3.1). The theoretical and experimental parameters are the same as for figure 5 and are described in the text.

measured half-time is compared with the half-time predicted by equation (3.1). Here the theoretical width is the width of an assumed rectangular intensity profile for the laser beam. Despite the fact that the experimental beam is round and the theoretical beam is rectangular, the agreement between theory and experiment is good. The theoretical line in figure 6 is nearly the same as that for \( D = 0 \); however, it may be adjusted to lower the half-times by increasing \( D \).

Some data has been taken in the region where \( \vec{K}(r) \) is perpendicular to the fluid velocity. The correlation function decay rate is seen to approach that when the shear is turned off to within 10 \%\). However, no distortion in \( \vec{F}(k, \tau) \) due to shear has yet been observed. Cell redesign is necessary before further measurements in this regime can be made easily.

The precision of the data is indicated by the size of the symbols used in the figures. The precision of the data in figure 4 for the velocity is somewhat better except near the rotating cylinder wall. This wall is out of round by \( \sim 5 \% \) of the radius. The precision of the half-time data in figure 5 is better for small stop and pinhole diameters, where the signal to noise ratio is best. In figure 6 the data is fairly precise but error is introduced by using a micrometer to estimate the beam width. This could introduce a uniform shift of the data left or right.

5. Discussion. — The purpose of this communication is to study and assess dynamic light scattering as a tool for investigating time fluctuations in sheared systems. For equilibrium fluctuations the time decay of the intensity correlation function is independent of many geometrical considerations. When a shear is present, however, there is a time dependent signal to noise factor \( \gamma \). This means that for many geometries dynamic light scattering provides little useful information about the fluctuations in the sample, rather the geometry of the system is being tested.

The factors affecting the intensity correlation function include the rate of shear, the size and shape of the photocathode and stop, the separation of the photocathode and scattering volume, and the orientation of the scattering angle with respect to the velocity and shear in the sample. Other factors, which were not severe in the experiments discussed in this communication, include scattering volume transit time effects and occupation number effects.

Despite these serious problems there may be ways to circumvent them and to measure the fluctuation information contained in \( \vec{F}(k, \tau) \). One method is to arrange the scattering geometry such that \( \vec{k} \) is perpendicular to the fluid velocity. This would provide a range of scattered wave vectors all perpendicular to the velocity for which \( \vec{F}(k, \tau) \) could be studied. Unfortunately, many shear related effects depend on a scattered wave vector component in the direction of the velocity. If this component is zero, then the corresponding effect is not seen, as in equation (2.9).

For a given geometry one may wish to choose a sample with an intrinsic decay rate sufficiently large that \( \vec{F}(k, \tau) \) dominates \( \gamma \). On the other hand for a given diffusion constant one may minimize the geometry dependent decay by reducing the stop diameter and increasing the pinhole diameter. The shear rate may also be decreased, and the image of the scattering volume on the stop should be magnified. It seems likely that a combination of these adjustments could make shear studies plausible for some systems. However, this is difficult for the suspensions used in the experiments described here, as both terms in the exponent of equation (2.9) which contain \( \alpha \) remain much smaller than the other term, \( Dk^2 \tau \), for several decay times. If \( \alpha \) were increased to compete with the \( Dk^2 \tau \) term, the velocity would be so high that turbulence and transit time problems would be dominant. The situation may be improved by decreasing the diffusion constant. This may be done by increasing the particle size or increasing the viscosity of the solvent. However, this decreases the decay time of \( \vec{F}(k, \tau) \) such that the geometry dependent term again becomes more important. Thus, the geometry dependent time decay term dominates most of the data, but arranging the geometry so that \( k \) is perpendicular to the velocity decreases the contribution of the \( \alpha \) terms drastically.

Possibly the best way to measure \( \vec{F}(k, \tau) \) would be to calibrate the signal to noise factor \( \gamma \) using an appropriate solution of particles and a fixed geometry. Then the solution to be tested, such as a critical binary mixture or another suspension can be introduced into the sample cell with no other changes and measurements made assuming the same form for \( \gamma \). Finally it should be noted that if a nonlinear shear such as Poiseuille flow is used, then the results...
presented in equations (2.10) and (2.11) must be
generalized. Furthermore, it is not clear that the
form for the probability presented in equation (2.5)
is correct for non-linear shear [11] as has been implied
in other calculations [7]. Also, if there are interactions
between the particles [3], the probability does not
factor into dependent parts and the simple results
given here are not applicable. However, in the hydro-
dynamic limit as calculated by de Gennes [4] for
binary mixtures, the results will be valid.

Acknowledgments. — One of the authors (BJA) is
grateful to the Research Corporation for supporting
this research. Heinz Hall and his able staff are com-
mended for their help in constructing the shear cell
and light scattering apparatus.

References

[1] BERN, B. J. and PECORA, R., Dynamic Light Scattering (John
Wiley, New York) 1976;
1974;
371;
CUMMINS, H. Z. and PIKE, E. R., Photon Correlation Spectro-
scopy and Velocimetry (Plenum Press, New York) 1977;
TANFORD, C., Physical Chemistry of Macromolecules (John
Wiley, New York) 1961;
BROWN, J. C., PUKEY, P. N., GOODWIN, J. W. and OTTENWILL,
HILTNER, P. A. and KRIEGER, I. M., J. Phys. Chem. 73
43 (1979) 1253.
1005.
Lett. 42 (1979) 1368;
42 (1979) 287;
KIRKPATRICK, T., COHEN, E.G.D. and DORFMAN, J. R.,
[7] EDWARDS, R. V., ANGUS, J. C., FRENCH, M. J. and DUNNING,
Phys. 44 (1973) 1694;
GOLDSTERN, R. J. and ADRIAN, R. J., Rev. Sci. Instrum. 42
(1971) 1317;
New York) 1964, p. 382.
475.
ian Particles in Shear Flows (PGRL/163, Pulp and Paper
Research Institute of Canada) 1979.
[12] HECHT, E. and ZAJAC, A., Optics (Addison-Wesley, Reading)