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Diffusing wave spectroscopy of uniform translational motion

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Abstract. Diffusing wave spectroscopy (DWS) is used to investigate the structure and dynamics of opaque (optically dense) media such as colloidal systems. These systems remain fundamentally important from both scientific and industrial viewpoints. Analyses of DWS signals from dense systems subject to flow fields have treated only motions due to velocity fields. Diffusive and other internal effects upon the particle motions are ignored. The present work probes the response of the DWS signal itself by using a model system in which there is no structural dynamics to obscure the motion, in a flow field where velocity gradients are absent. We observe initial, apparently exponential, components on the Gaussian form of the correlation function and compare them to strong localization of light under conditions of diffusive propagation. For dense systems, DWS displays a time dependence, which is governed by the translational motion of the scattering system.

1. Introduction

The structural dynamics of colloidal systems are matters of considerable interest. However, the study of such behaviour is not without its difficulties, particularly when the system under investigation is optically dense, as many are. In such cases the extreme multiple-scattering limit of dynamic light scattering, the so-called diffusing wave spectroscopy (DWS), comes into its own as a probe of these structural dynamics [1]. An illustrative example of what is meant by structural dynamics is the elementary bubble rearrangements, which underlie the evolution of foam. These have been investigated by DWS for static foam as it coarsens [6, 7], and also in foam subject to a flow field, under which conditions the rate of rearrangements is enhanced [2–4]. Similarly, we may consider diffusive Brownian motion of colloidal particles as constituting structural dynamics; as for the previous example, a flow field may affect these motions. Indeed this situation is quite common: we are frequently interested in the response of our system to an applied field.

In thus probing the effect upon the structural dynamics of the system of a flow field, we must consider the response of the DWS probe to that field itself. For instance, in the case of foam rearrangements promoted by a flow field, the DWS signal for constrictive flows was found to exhibit slow decay components [2–4], which were apparently absent in studies involving shear flows [5]. The origin of these slow components was not immediately apparent, and as they did not obscure the effects of interest in that study they were ignored. However, this is somewhat unsatisfactory and full understanding of the whole signal should be sought in such experiments.

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Now theoretical analyses of the DWS signals to be expected from a dense system subject to a flow field have been published [8–10]. It has been usual to treat only motions due to the velocity field, ignoring any diffusive or other 'internal' effects upon the particle motions. These analyses have further been limited to the case where the velocity field is space-varying, as for instance in Poiseuille flow, in which case DWS directly reflects the velocity gradient integrated over all of the optical paths involved in diffusion of the light through the system. However, in such dense systems, flows which show no spatial variations in velocity may well occur: an example is foam in pipe or constrictive flow, where apart from a single layer of bubbles which exhibit stick–slip, the foam moves with unique velocity (plug flow). Despite the absence of velocity gradients we find that the DWS signal reflects the motions involved. This brief paper presents an experimental study of these matters, in a model system, in which there is no structural dynamics to obscure the motion with a unique velocity.

2. Experimental procedure

Our previous studies of foam [2–4] involved two distinct motions: translation of the bulk foam in the plug flow and those bubble motions involved in the dynamical response of the foam to constriction. To clearly separate out the overall translation inherent in plug flow from the structural dynamics, which is of no present concern, we have used a solid scattering object. Any time dependence of the DWS signal can thus only arise from the translational motions. For the scattering system we chose polytetrafluoroethylene (PTFE) tape, $285\pm0.5\ \mu$m thick. It was found that the extreme multiple-scattering limit, essential for the application of DWS concepts, was achieved by using two layers of this tape, which served to completely depolarize the transmitted light, ensuring the diffusive nature of the scattering. It is difficult to know precisely what inhomogeneities in the PTFE scatter the light, but this is of no immediate concern. What matters is that, whatever they are, these inhomogeneities do not move relative to each other but rather move together as a coherent whole throughout the experiment.

Our DWS experiments involved the usual forward-scattering (transmission) geometry [1]. A laser ($\lambda = 633$ nm or 488 nm) beam was incident normally upon the scattering cell in which the PTFE tape was moved with uniform speeds, υ, and a few coherence areas of light forward scattered at 0° were selected for detection by a photomultiplier. Two rather different optical set-ups were used to isolate one (or a few) speckles at the photodetector; they yielded essentially identical time dependences of the DWS signal. Time correlation functions $g(\tau)$ of the scattered light were measured. The data were integrated over varying times, limited in some cases by the translation speeds studied. These speeds ranged over three orders of magnitude, from 0.83 to 900 μm s^{-1}.

The experimental duration ranged up to a few hundred seconds. To ensure a reasonable degree of statistical averaging of the correlation functions over such times requires that we restrict the range of delay times (τ) somewhat. In the present work, we limited τ to a maximum of 10 s. Due to this finite range, the decay of $g(\tau)$ was not fully characterized for the slower translation speeds studied.

3. Results and discussion

Measured correlation functions for several different translation speeds are shown in figure 1(a). They decay with time, reflecting the temporal evolution of the moving speckle pattern. The decay becomes more rapid as the translation speed increases, as would naively be expected.

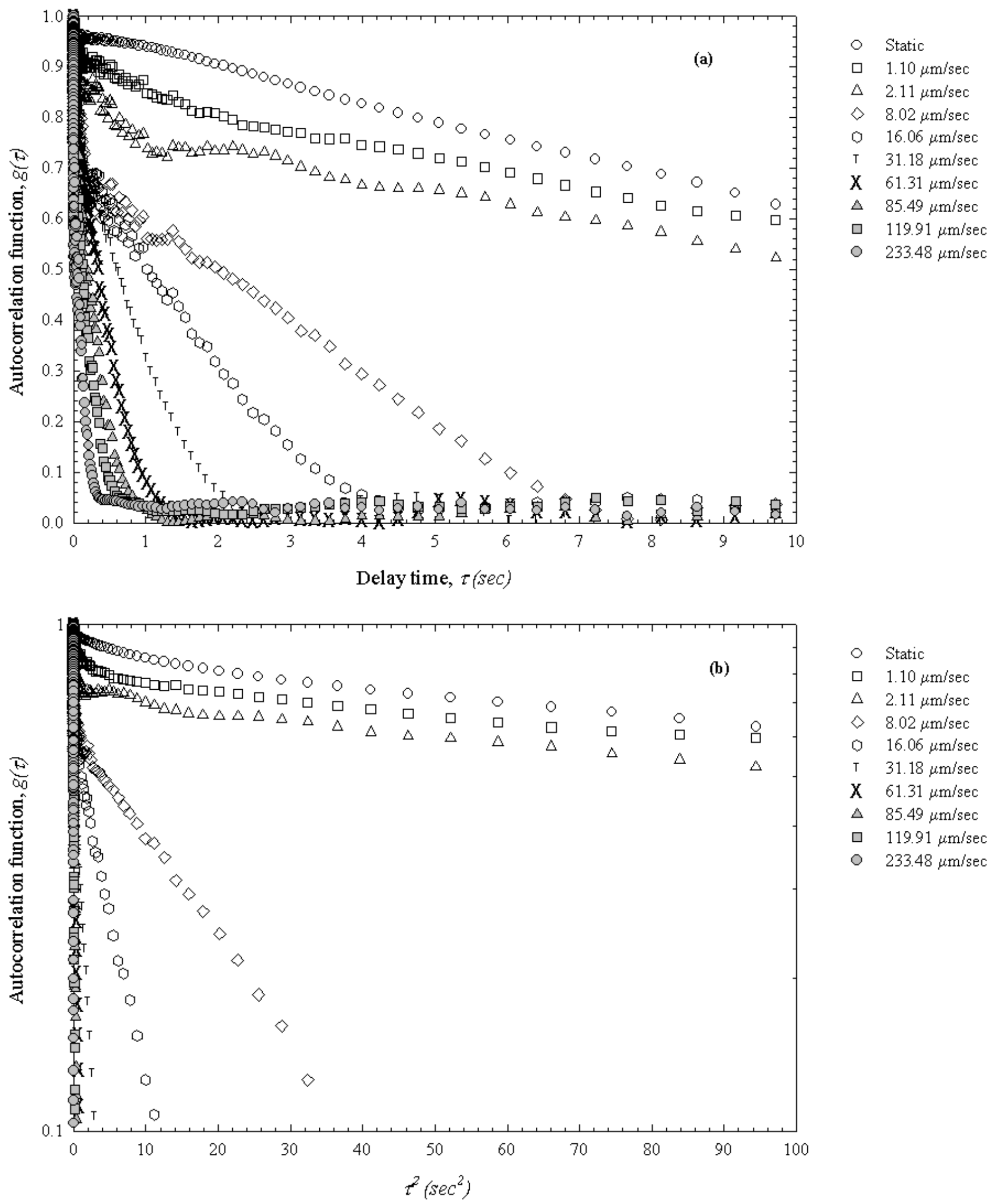

Figure 1. Normalized field autocorrelation functions of PTFE thin solid films, $\sim$570 μm thick, showing: (a) typical correlation functions for various speeds of motion and (b) these functions plotted logarithmically versus τ^2.

The form of the correlation functions is, however, not as simple as the usual near-exponential functions observed in DWS [1]. In fact the gross shape seems closer to a Gaussian than an exponential. Indeed, as this would suggest, log-linear plots of $g(\tau)$ versus τ^2 (figure 1(b)) are more closely linear than the usual plot as a function of τ. However, it is also apparent that the initial decay of the correlation functions at very short τ departs from this Gaussian form. In fact the initial decay seems more nearly exponential. These initial portions of $g(\tau)$ collapse rather well to a unique function of $\upsilon\tau$ (figure 2). We will return to the origin of these initial portions below.

As already noted, it is qualitatively apparent in figure 1 that the correlation functions decay more rapidly as the speed of movement of the PTFE scattering system is increased. More quantitative data analysis is somewhat inhibited by the mixed nature of $g(\tau)$, part Gaussian and part exponential. We have characterized the gross decay of the correlation functions via their half-widths at half-height (HWHM). Within the scatter of the data this statistic scales quite reasonably as υ^{-1}, as shown in figure 3. Data are not shown for $\upsilon < 8$ μm s^{-1} as under these conditions the Gaussian decay was so slow that the HWHM could not be determined over the limited time span of the measured correlation functions. These HWHMs allow the half-width of the speckles in the moving speckle pattern to be estimated for about 50 μm, independently of υ.

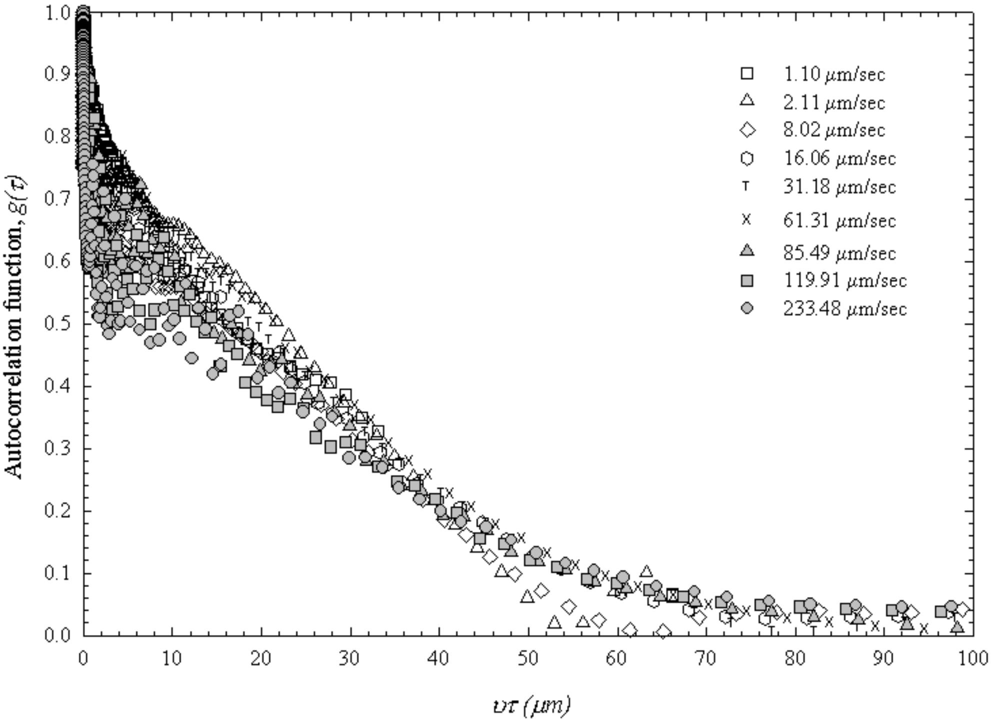

Figure 2. Correlation functions for a range of υ plotted versus $\upsilon\tau$. Note the collapse to a common functional form for $\upsilon\tau$.

To characterize the initial apparently exponential contributions to the decay, we applied the usual cumulants analysis, considering only the first cumulant, Γ_1. Even for the lowest speeds these initial decays could be analysed. As shown in figure 4, we find that within the experimental uncertainties, $\Gamma_1 \propto \upsilon$ over the entire three orders of magnitude in υ. These initial rapidly decaying portions of $g(\tau)$ extend to $\upsilon\tau = 40$ μm (figure 2).

We turn to possible origins of the exponential component, which is superimposed on the broad Gaussian form of the correlation functions. As both characteristic decay rates (HWHM^{-1} and Γ_1) scale linearly with υ, it is apparent that the overall form of $g(\tau)$ must be independent of υ. This form of $g(\tau)$ must reflect the time variation of the detected intensity as individual speckles are moved past the photodetector. The spatial variation of intensity across

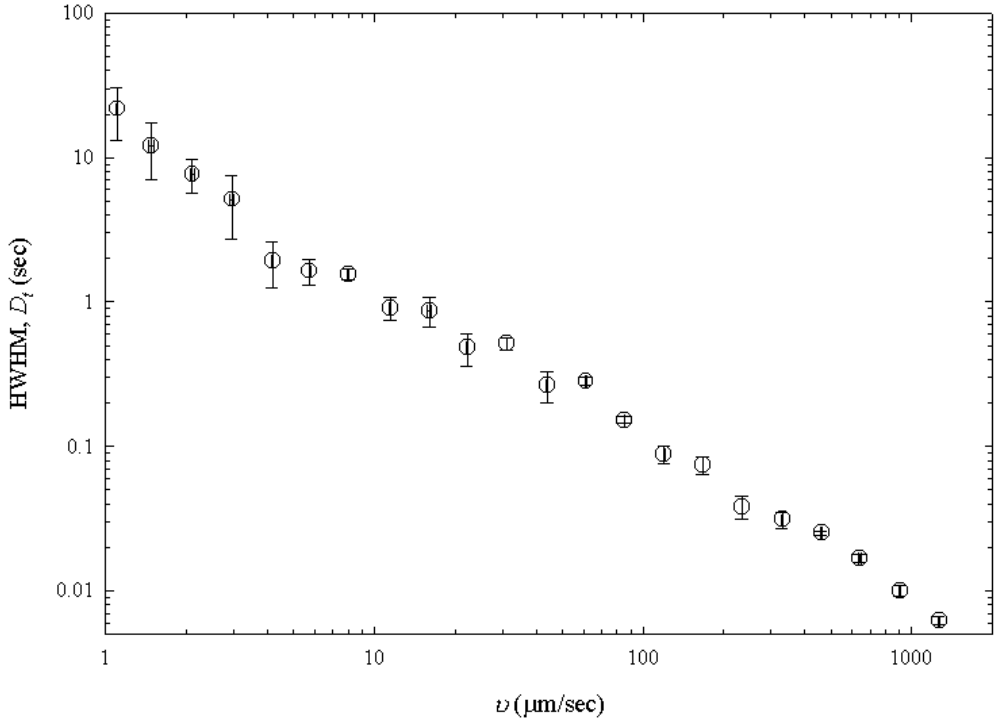

Figure 3. The dependence of the HWHM of the correlation functions upon the translation speed υ. No uncertainties are shown because of the nature of the statistic.

the speckle would be expected to be the Fourier transform of the intensity distribution $I_T(r)$ of the scattered light emanating from the PTFE material [11], which we find to be Gaussian. While the overall Gaussian shape of $g(\tau)$ is thus as expected, it is not so clear why the initial portion is exponential in form instead.

Some novel considerations must come into play. Similar exponential peaks in angular distribution of light scattered from strongly scattering systems are seen in coherent backscatter [12]. In that case they are ascribed to strong localization of light under conditions of diffusive propagation. We know of no reports of such coherent effects in forward scatter. The peak in backscatter is dominated by coherent scattering over long optical paths in the scattering medium, and hence depends on correlations between distant scatterers. While the consequences for forward scattering do not appear to have been explored, it seems possible that such correlations may have an effect here, also. It has been noted that while scatterers which are very far apart do not on *average* cause large interference corrections to the diffusion picture of photon propagation in optically dense media, they may well cause significant fluctuations about the average [13]. DWS, like all dynamic light scattering techniques, probes just such fluctuations. It seems plausible that the initial exponential contribution just reflects the temporal decay of these fluctuations as the sample is moved.

We think the exponential decay at small delay time, τ, results from the direct observation of the spatial coherence function of a speckle since there is no relative motion of the scatterers within our solid sample. The speckle pattern as a whole moves as the sample moves. If we suppose that a point x in a speckle is in the centre of the field of view of a detector at time $t = 0$, at time $t = t_1$ the speckle has moved a distance υt_1 (where υ is the velocity of the sample).

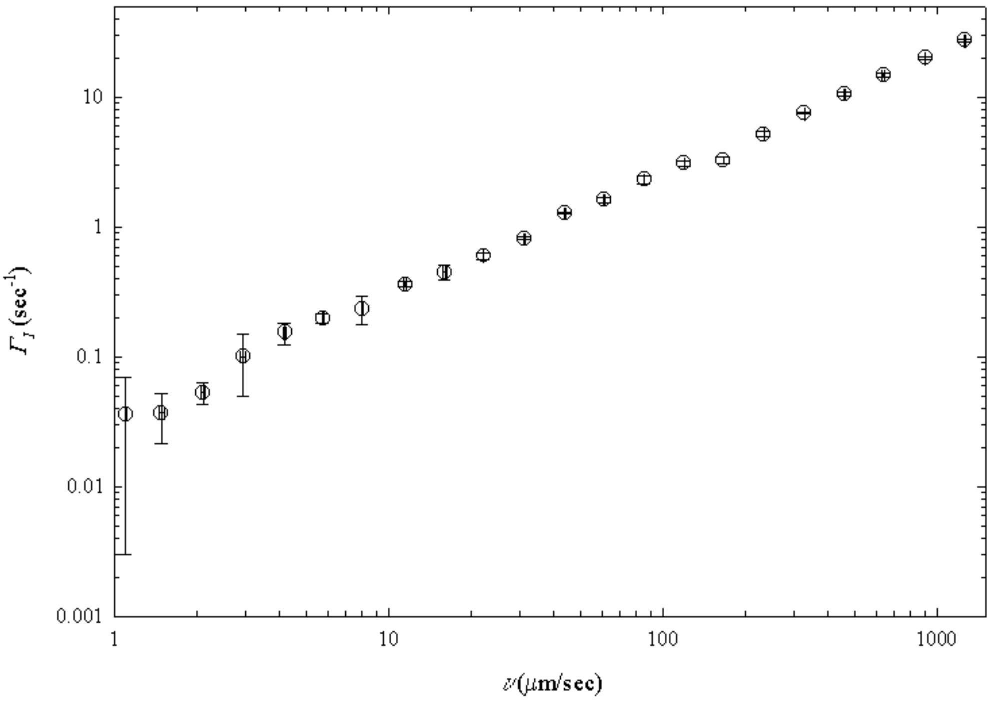

Figure 4. The dependence of the first cumulant Γ_1 of the observed correlation functions upon the translation speed, υ.

So a point $x' = \upsilon t_1$ is now in the centre of the field of view. The intensity correlation between times 0 and t_1 is the spatial intensity correlation between points x and x' in a speckle. The correlation drops to zero, by the time one speckle in the field of view is completely replaced by the next. One expects a Gaussian profile for true DWS time correlation functions. Here the time decay is due to the relative motion of scatterers. There is also a dependence on x squared. This translates into a dependence on t because the random motion is a Brownian motion in which the mean distance squared is proportional to the time. Therefore one gets exponential time decay instead of a Gaussian one. In the present case, there is no Brownian motion or other random motion of the scatterers. The present condition is one of random statistic distribution and results in the $\exp(-ax^2)$ dependence. We feel that the exponential decay at small delay time represents interference effects associated with the speckle. This is the variation with distance of the amplitude of the scattered light wave that results from the superposition of two or more waves having nearly the same frequency. The speckle grains are coherent and their phases are constant, but not their phase difference in positions inside these grains of speckle. In the event of lateral translation, the speckle changes along with the fringe spacing inside the grains. Light can be regarded as propagating by diffusion in our PTFE sample. The speckle is produced by the interference between light following several paths through the material. Fluctuations arising from this interference cause the speckle to flicker leading to spectral broadening of the scattered light. The phase change responsible for a change from constructive to destructive interference is accumulated in events distributed over the entire light path and allows the temporally or spatially rare events to be observed

Turning to scattering in our sample, we know that the illumination of a stationary rigid scatterer by laser light produces a stationary speckle pattern regardless of whether the scattering is single or multiple. Moving the scatter to a new position results in a different speckle pattern, since a different region is being illuminated. A continuous motion takes the scatterer through a sequence of positions, providing a sequence of speckle patterns. A small detector sees a fluctuating intensity as the speckle moves over it. Doubling the velocity of motion, for example, should give the same sequence of speckles in half the time. All dynamic properties of the scattered light scale as the distance moved, υt. This is shown in figure 2 where all curves are seen to be on top of each other.

The time correlation function in backscattering, associated with Brownian motion of the scattering particles, is of the form $\exp(-at^{1/2})$, where term a is a constant and t is the delay time. Coherent backscattering is a consequence of the fact that for each diffusive path of a photon entering the sample at a given point A and re-emerging from the same face at a point B, there is a time-reversed path which enters at B and exits at A and is identical to the first path in all respects except that it is traced backwards. This produces constructive interference in any other directions. From figure 2, one observes that although $g(\tau)$ scales as υt with all curves lying on top of each other, the scaling does not follow in order of the velocity changes but is almost random as indicated by the shape of the correlation functions. Any forward interference effects are either due to light getting through without being properly randomized or may be the result of some coherence effects associated with the speckle, not predicted by the diffusion approximation. We believe the latter is the case in play here since we know that our sample completely randomizes the transmitted light. Another possibility is that there is some microscopic motion within the scatter, resulting from laser heating or vibrations between the two layers of PTFE becoming slightly separated during motion. Although this would require further work, initial investigation has verified that the speckle pattern from the PTFE sample is stationary when not moving from the moment the laser is switched on. The effect is not large; the initial exponential decay roughly corresponds to a decrease in magnitude of $g(\tau)$ by only $\exp(-0.5)$. Although not directly related, the angular distribution of light transmitted through the PTFE sample has exhibited a forward-directed peak, as in coherent backscatter [12]. However, our measurements of this distribution were too coarse to detect the narrow peak expected (0.4 mrad).

4. Conclusions

The main conclusion of this work is that, even in the absence of any velocity gradients, DWS displays a time dependence, which is governed by the translational motion of the scattering system. In the context of our previous studies of foam in constrictive flow [2–4], it seems likely that we can associate the slow component seen with plug flow of the foam. The Γ_1 values for these slow components were of the right order of magnitude considering the flow speeds used. The correlation of scattered light is used to determine the velocity. This is traditionally known as laser Doppler velocimetry (LDV). The technique of LDV has been applied to gas, liquid and solid flows to measure mean velocity, root mean square turbulence (turbulence intensity) velocity distribution and turbulence frequencies. Reported measurements include those of streaming velocity in plant cells, swimming speed distributions in mobile micro-organisms and studies on jet engines in wind tunnels [14]. Our present work extends speckle velocimetry to optically dense media in the light of research in progress in the areas of particle image and laser speckle velocimetry [11, 15, 16]. Also, this work re-emphasizes that when interpreting DWS signals in terms of the structural dynamics present within the system, all contributions to the correlation functions must be included. However, the present correlation functions decay very slowly, compared to DWS signals seen in systems exhibiting structural dynamics. For example, coarsening in foams leads to values of Γ_1 due to dynamic bubble rearrangements which are typically 25 s^{-1} (this value decreases as the foam coarsens, but for the prototypical shaving foam used in these studies, it only falls to $\approx$1 s^{-1} after 1000 min) [7]. These time constants are markedly increased when the system is subject to strain, as in flowing foam [3, 5]. For even the relatively rapid initial exponential component of $g(\tau)$ to exhibit a time constant Γ_1 of this order of magnitude would require a translation speed of nearly 10 mm s^{-1}. It is thus apparent that the timescales for the two processes are sufficiently well separated that the presence of the slow, plug-flow-associated, contributions will not affect the signal of physical significance.

It may be remarked that the present slow contributions to the observed correlation functions would only be quantifiable when the range of correlator sample times used was such as to span a significant decay of the slow component. Thus when using a correlator, particularly one with only a linear array of sample times, to quantify the faster decays due to structural dynamics the slow component will not be well sampled, and may well be indiscernible.

Acknowledgments

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