Multiple Scattering Probes of Disordered Materials

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Introduction

A large class of materials of great technological importance and scientific interest are highly disordered on length scales comparable to, or larger than, the wavelength of light. As a consequence of this disorder, these materials are often composed of a large number of regions with different indices of refraction, separated by interfaces that are abrupt on the scale of the wavelength of light. Each of these interfaces refracts or scatters light, making these materials quite opaque optically. Even in the absence of absorption, the strong scattering precludes the direct transmission of light rays through the material. This greatly complicates the study of these materials.

Examples of these disordered materials abound. Many are complex fluids; colloidal suspensions and other dispersions such as foams and emulsions often consist of particles or droplets whose diameters are comparable to the wavelength of light. Unless they are very dilute, these dispersions are typically highly opaque. Other materials consist of solid grains of similar sizes without the surrounding fluid. For example, most ceramics are composed of oxide grains sintered together; the voids between the grains lead to the large number of interfaces, and hence to the strong scattering and opaque appearance commonly associated with these materials. Similarly, many porous materials also possess a high density of voids that scatter light; filters, oxide catalyst supports, and even rocks are all optically opaque because of the strong scattering. Sand and other unconsolidated granular materials are also opaque in part because of the large number of interfaces that scatter light. Finally, there are many important biomaterials that scatter light so strongly as to preclude the use of optical probes of their properties; the most important of these is the human body. These examples of disordered materials that are optically opaque due to the large number of interfaces are representative, but far from all-inclusive.

The first step in the study of any material is to determine its structure; this is followed by a study of its properties. Because the size of the essential structures in this class of disordered materials is comparable to the wavelength of light, optical probes are ideally suited for studying both their structure and their properties; however, precisely because the structures are comparable to the wavelength of light, and thus lead to such strong scattering, the use of optical probes is precluded. Instead, rather specialized techniques must be employed to probe these materials. For example, many materials are dispersions of either solids or droplets of liquids immersed in a fluid; for these dispersions, it is sometimes possible to judiciously choose the fluid to exactly match the indices of refraction of all the components to minimize the scattering and allow direct visualization of the material. Alternatively, modern x-ray tomography techniques can be used to study the structure of small samples of some of these disordered materials; x-rays are prone to strong absorption, but do not scatter as strongly as light. However, despite the advantages of these direct imaging methods, their application is restricted.

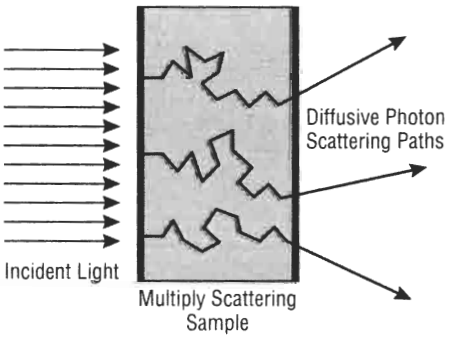

Figure 1. Schematic representation of the random diffusive photon paths that represent the diffusive transport of light through a multiply scattering sample. The light intensity diffuses through the sample, and each path represents the random walk that a photon follows on traversing the sample.

Despite the limitations imposed by the very strong scattering in these materials, optical techniques still possess great potential for studying the properties of these materials. Fortunately, there has been considerable progress in the development of several different optical probes of strongly scattering media. These methods are all based on the recognition that the propagation of light through very strongly scattering media can be well described using the diffusion approximation. This allows the propagation of the light to be described in a simple, statistical fashion. The essential approximation which underlies this diffusion approach is that the phases of all the scattered fields are so randomized that any interference effects within the medium can be neglected. As a result, only the intensity of the light need be considered in the description of the propagation of the light. This intensity propagation can be very well approximated as a diffusive process. Thus, physically, the paths followed by the photons propagating through the medium can be described as diffusion, and hence follow random walks. A physical representation of this is illustrated in Figure 1, where some of the diffusive paths followed by the photons propagating through a strongly scattering medium are illustrated.

The statistics of these random walks are well understood; both the distribution and the length of these paths can be determined through the solution of the diffusion equation for the light. Moreover, since only the diffusing intensity is relevant, each of these diffusive photon paths is statistically uncorrelated with all other paths except with the path itself. Nevertheless, each path still carries some critical phase information; recognition of this fact provided the critical insight that underlies many recent advances. This phase infor-

mation reflects the length of the optical path that the diffusing photons have followed on traversing the medium. It can be determined by the arrival time of the photons if they are incident as a short pulse. Alternatively, it can be determined through interference techniques, using either an independent reference beam, or the light from other, independent diffusive photon paths. Furthermore, despite the relatively small fraction of the light intensity that traverses a very strongly scattering medium, the high photon fluxes easily available with modern lasers, combined with the very high sensitivity of optical detectors, make it possible to measure the transmitted light and determine this phase information. This has led to the development of significantly new optical probes of strongly scattering materials.

The goal of this article is to review some of these new methods and to provide some perspective on their utility and their applications. In particular, we consider two distinct classes of techniques that take two divergent approaches. In the first approach, the consequences of the multiple scattering of the light are minimized. This is typically achieved through time resolution; light which has been more strongly scattered follows a longer path, thereby taking a longer time to traverse the medium. By contrast, light that is unscattered, or scattered only a few times, traverses the medium much faster. Thus, by time resolving the transmitted light, it becomes feasible to restrict the detection to light that is either unscattered or only very weakly scattered, allowing the direct imaging of even very opaque materials.

In the second approach, the strongly scattered light itself is studied, and the diffusion approximation is used to describe its propagation through the medium. In this case, direct imaging of the structure within the medium is rarely achieved; however, significant new information can still be determined based on details of the scattering and propagation of the light. In addition, a great deal of information can be determined about the dynamics of the medium. This is done through the analysis of the temporal fluctuations of the light, which are caused by the dynamics of the scattering medium. The study of the temporal fluctuation of singly scattered light is called dynamic light scattering (DLS); it has become a widely used technique for studying the dynamics of weakly scattering materials that possess structures comparable to the wavelength of light.[1] The analogous study of the dynamics of multiply scattered light is called diffusing wave spectroscopy (DWS); it has become a widely used technique for studying the dynamics of strongly scattering materials.[2,3]

Despite the differences between these two approaches (minimizing consequences of versus studying scattered light), they share many essential features. Both rely on the diffusion approximation to describe the propagation of the light. Both rely on the high flux of modern lasers and the high sensitivity of optical detectors, which enable enormous signal loss to be sustained as the light diffuses through the sample. Both also rely on the fact that optical absorption is often relatively weak in these materials. So, despite the very long paths followed by the photons on traversing the medium, there is often relatively little absorption of the light. Thus, these materials often appear white; this reflects the very strong scattering of the light and the absence of absorption. Moreover, even when the material is colored, the absorption is often limited to a relatively narrow region of the spectrum, with another region accessible to propagation of light with very little absorption. Only those materials that are completely black are clearly restricted from study by diffusive light techniques.

The optical techniques that utilize multiply scattered light can be conveniently divided into two distinct classes, depending on the problem to be studied. In the first case, the techniques entail static methods and their goal is to glean information about the structure of the disordered material. In the second case, the techniques are dynamic methods and their goal is to glean information about the motion and dynamic properties of the disordered material. We consider each class separately in the remainder of this article.

Statics

One of the simplest optical measurements possible is measuring the fraction of light transmitted through a sample of known thickness. Fundamentally, the transmission coefficient measured in this way depends on the amplitude and size of the spatial variations in the dielectric constant (or index of refraction) of the medium. These variations in refractive index are frequently associated with sharp interfaces such as those occurring in foams, emulsions, colloids, or ceramics. In these systems, where the scatterers are essentially a distribution of particles, the transmission coefficient depends on the size, structure, density, and dielectric constant of the scatterers as well as on the spatial correlations between them. It should be possible, therefore, to extract useful information about a material by measuring its optical transmission coefficient. Varying the optical wavelength changes the length scale of the probe and may provide additional information. To make contact between optical measurements and material properties, however, one must be able to describe the transport of light through a multiply scattering sample.

The diffusion approximation is the most common approach for describing light transport through multiply scattering media. In this approach, photons traversing a sample execute trajectories which are described statistically as random walks, as illustrated schematically in Figure 1. The only important parameter for describing the random walk is the mean step size, l^*, commonly called the transport mean free path. The diffusion approximation relates the transport mean free path to the measured transmission coefficient: $T \approx 5l^*/3L$, where L is the sample thickness.[4] The goal of any useful theory, then, is to relate l^* to the structural properties of the material under study.

Within the diffusion approximation, one assumes that each photon scatters many times and that the total transmitted light intensity is given by the incoherent sum of intensities for all possible photon paths through the sample. The distance between consecutive scattering events is the scattering mean free path, l. If the number density, ρ, of scatterers is small,

$$l = 1/\rho\sigma, \tag{1}$$

where σ is the total scattering cross section. The mean free path is usually smaller than the transport mean free path. This is because materials that multiply scatter light typically consist of particles (or microstructures) whose size is comparable to or larger than the wavelength of light (smaller particles usually do not scatter strongly enough to cause significant multiple scattering). These particles scatter more strongly in the forward direction so that the direction of a photon is not randomized by a single scattering event; the random walk step size is therefore greater than l. The transport mean free path or random walk step size is related to the scattering mean free path by

$$l^* = \frac{l}{1 - \langle\cos\theta\rangle}, \tag{2}$$

where $\langle\cos\theta\rangle$ is the average cosine of the scattering angle for single scattering.[4] Expressions similar to Equation (2) appear in equations for the persistence length of polymers and the resistivity of metals. If there are changes in the size, shape, or spatial distribution of scatterers, $\langle\cos\theta\rangle$ will change. If the number density of scatterers changes, l will change. Equations (1)

and (2) provide us with the starting point we need to relate changes in l^* to changes in the structure of a sample under investigation. We now turn to some examples of how these ideas have been applied to a few different systems.

One particularly simple but elegant application of these ideas has been the use of transmission measurements to follow the time evolution of a water-based foam, namely shaving cream.[5,6] In these experiments, the transmission coefficient of light through shaving cream was observed to increase as the square root of time, indicating that l^* was increasing approximately as $t^{1/2}$. In these foams, the only relevant length scale comparable to or larger than the wavelength of light is the mean bubble size. Each time the light passes through a bubble, its direction is partially randomized. After passing through a few bubbles, the direction of the light is completely randomized; thus, we expect l^* to be proportional to a few bubble diameters, d. More careful estimates and measurements indicate that $l^* \approx 3.5\ d$. Thus, the measurements of the transmission coefficient indicate that the mean bubble diameter of a foam increases approximately as $t^{1/2}$ as the foam ages. A particularly important feature of these measurements is that they probe the structure *inside* the foam, not merely near the foam's surface, even though the foam is optically opaque.

Another group has applied similar techniques to porous rocks and have found a surprising result: The transmission coefficient for light is highly correlated with the permeability of a material.[7] The permeability of a porous material is simply a measure of how easy it is to push a fluid through it. It is therefore related to connectivity of a rock as well as its porosity. Qualitatively, it makes sense that the connectivity of the rock will have a bearing on how well light will be transmitted through a sample; the rock acts as a tortuous wave guide for light. The experimental results and physical picture of light transport in rocks have been borne out by computer simulations as well.

Recent measurements of the wavelength-dependent transmission coefficient of dense colloids have shown that it is possible to measure changes in l^* that arise from changes in the static structure factor $S(q)$, which reflects the correlations in the positions of the particles due to their packing.[8] Equations (1) and (2) can be recast in terms of a wavelength-dependent angular integral over the form factor $F(q,\lambda)$ and $S(q)$, weighted by $1 - \cos\theta$ to properly account for forward scattering. The expression can be rewritten as an integral over the wavevector q:

$$\frac{1}{l^*} = \frac{\pi\rho}{k_0^6}\int_0^{2k_0} F(q,\lambda)S(q)q^3\,dq\,, \qquad (3)$$

where $k_0 = 2\pi/\lambda$, and λ is the wavelength of light.[9] The primary effect of changing the wavelength λ at which l^* is measured is to change the upper limit of the integral in Equation (3), that is, to change the range of q over which the structure factor is probed. By adjusting λ, one can move through the maxima and minima in l^*. With a suitable model, these changes can be identified with the maxima and minima in $S(q)$.

Another exciting recent development has been the use of multiply scattered light for imaging purposes.[10] The goal is to detect objects and structures hidden from direct visual observation inside of optically turbid media. The motivation for much of this work has been medical imaging applications, and a variety of schemes have been developed. A particularly simple scheme conceptually is to launch a very short (picosecond) pulse of light into a sample and to use time gating to detect only the light that is transmitted through the sample without being scattered. The idea is that the propagation delay time for unscattered light, L/c, where c is the speed of light in the sample, is much shorter than the propagation delay time for multiply scattered light, approximately L^2/cl^*. Thus, unscattered light arrives a factor of L/l^* (typically 10 or greater) times earlier than the diffusing light. The image obtained in this way is essentially a shadowgraph of light absorbing objects inside the sample. Experiments have shown that essentially the same kind of image can be obtained from the earliest arriving multiply scattered light, that is, from light which is scattered within only a small forward angle scattering cone so that their paths are essentially ballistic. The advantage, of course, is larger signal levels. A drawback of these gating schemes is that they require costly equipment both to create the pulses and to detect the light with adequate temporal resolution. Moreover, the intensity of unscattered light is attenuated by up to a factor of $\exp(-L/l)$ which is typically 10^{-9} to 10^{-20}. Nevertheless, the technique has been successfully demonstrated in model systems with attenuation factors of 10^{-14}. The reason such high attenuation factors can be tolerated is the high intensity available from modern lasers and the sensitivity of light detectors.

Other imaging schemes utilize rather than discard the highly multiply scattered light. The advantages are a much larger signal and less costly equipment. These advantages are partially offset by decreased spatial resolution. One particularly promising scheme involves using amplitude modulated (AM) continuous-wave laser sources.[11,12] The idea is that light whose *intensity* is modulated at an angular frequency ω and which diffuses with a diffusion coefficient $D = cl^*/3$ in a turbid medium consists of crests and troughs in the light intensity. These crests and troughs are spatially separated by approximately $\sqrt{D/\omega}$, the rms displacement of a photon in one modulation period $2\pi/\omega$. The crests and troughs can be viewed as a damped propagating wave with wavelength of $2\pi\sqrt{D/\omega}$. When such a wave encounters an object with a different value of l^* in the turbid medium, it is refracted since the wavelength of the AM intensity wave is proportional to $\sqrt{l^*}$. By setting up several spatially separated sources and detectors of AM light, one can hope to reconstruct the approximate size and location of the objects which refract the intensity-modulated diffusing light. Preliminary results using schemes of this kind are promising.

Dynamics

Light scattering has long been a very useful probe of the dynamics of systems that possess structures with length scales comparable to the wavelength of light. The most common technique is dynamic light scattering (DLS), which entails an analysis of the temporal fluctuations of the scattered intensity.[1] This technique exploits the coherence of the scattered light; if the incident light is spatially and temporally coherent across the sample volume, the scattered light will consist of a spatially random pattern of intensity maxima, called speckle spots. These speckles represent the diffraction pattern of the light from the whole sample; thus their size is determined by the solid angle subtended by the sample at the detector times the wavelength of the light. The intensity in each speckle spot will fluctuate randomly in time as the scatterers move. The characteristic time scale of these fluctuations is determined by the wavelength of light. Each speckle spot results from the interference of all the light scattered from the sample; therefore the intensity of the speckle spot will change significantly when the relative phase of the light scattered from each point in the sample changes by 2π. This will occur when each scattering region in the sample has moved by roughly q^{-1}, where q is the scattering wave vector. Since $q^{-1} \sim \lambda$, DLS is sensitive to motion or dynamics on a length scale on the order of the wavelength of light.

A typical DLS experiment entails the measurement of the temporal fluctuations of the scattered light intensity within a

single speckle spot. To obtain meaningful data from the random temporal fluctuations, the intensity autocorrelation function is measured. Because the temporal fluctuations are random, the intensity autocorrelation is a decaying function of time difference, and DLS measurements yield the characteristic decay time, τ. To analyze these data, the measured decay time must be related to the dynamics of the scattering system. In general, this involves determining the temporal evolution of the motion of the scatterers; τ is the time required for a typical scatterer to move by q^{-1}. For example, in the simple case of a dilute suspension of small particles undergoing Brownian diffusion, the characteristic decay time is $\tau = 1/q^2D$, where D is the diffusion coefficient of the particles. Thus, to relate the time scale measured experimentally to the motion of the scatterers requires knowledge of a length scale, which is set by q^{-1}. This scattering wave vector is only well-defined in the limit of single scattering, restricting the application of traditional DLS and precluding its use for the study of opaque materials.

While traditional DLS cannot be used to study the dynamics of strongly scattering disordered materials, some DLS techniques can still be employed. If a strongly scattering medium is illuminated with coherent light, the multiply scattered light still exhibits a speckle pattern, and the speckle spots still fluctuate in time due to the dynamics of the scatterers. Moreover, the temporal autocorrelation of these intensity fluctuations still decays with a characteristic time. The challenge is to relate this characteristic decay time to the dynamics of the medium. This can be done, allowing valuable information to be determined about the dynamics of the scattering medium. The resultant light-scattering technique is called diffusing wave spectroscopy (DWS).[2,3] Not only does DWS allow the study of disordered materials that strongly scatter the light, but it specifically exploits the multiple scattering of the light to allow the study of new regimes of dynamics that would not otherwise be accessible.

The central assumption that is made in the analysis of DWS is again that the propagation of the light through the scattering medium can be described by the diffusion approximation. This allows the distribution of diffusing photon paths, and their lengths, to be determined. Moreover, since the contour lengths of the paths are known, the number of scattering events that the photon undergoes can also be determined, provided the transport mean free path, or photon randomization length, is known. The dynamics of the scattering medium will cause the scatterers to move; as a result, the length of each path will change. This corresponds to a change in the relative phase of the path, resulting in temporal fluctuations of the scattered intensity through the interference with light from other paths. Because the paths are uncorrelated, the total autocorrelation function of the temporal fluctuations of the scattered intensity is the sum of the contributions from all the individual paths. However, since the intensity in each speckle spot still reflects the interference of light from the different paths, it will change when the relative phases of the paths vary by 2π, or when the changes in the total length of the paths is on the order of a wavelength of light. This is a critical difference between traditional dynamic light scattering and diffusing wave spectroscopy: in DLS, the dynamics result from the motion of a single scatterer over a distance on the order of a wavelength of light, while in DWS, the dynamics result from the change in the length of a diffusive light path on the order of a wavelength.

Within these approximations, the determination of the total autocorrelation function requires the calculation of the contribution of each of the uncorrelated diffusive light paths. The change in the phase of the full path will reflect the aggregate change in path length due to the motion of all the scatterers that comprise the path. This can be determined by adopting a statistical approach to relate the correlation function of the full path to that of an average over the typical scattering event. Since both the contour length of the path and the scattering length are known, the total number of scattering events that comprise the path can be determined. A long path will consist of a large number of scattering events, each of which is independent. Thus, to a good approximation, the autocorrelation function of the total path will be the product of all the independent correlation functions of the individual scattering events. Moreover, since the total correlation function consists of the contributions of a large number of scattering events, this provides a very effective ensemble average, allowing each of the individual scattering events to be replaced by a single average scattering event, where the averaging reflects the scattering probability of the medium. Then, the total correlation function will be the sum of the individual contributions of all the paths of different lengths, weighted by the probability that the diffusing photons follow that path. Following this scheme, the total autocorrelation function of the scattered intensity fluctuations can be calculated.[13]

The correlation function of the multiply scattered light measured in a DWS experiment reflects the dynamics of the scattering medium. It involves many of the same quantities as does a correlation function measured in a traditional DLS experiment. The time scale still involves the dynamics of the scatterers, and their motion over the length scale of a wavelength. However, a DWS experiment is sensitive to the aggregate motion of a large number of scatterers that make up each path. Thus each scatterer need move a much smaller distance to make the total path length change by a wavelength. As a consequence, a DWS measurement is sensitive to motion over much smaller length scales than a traditional DLS measurement. The length scale of the motion that is probed by DWS depends on the total length of the scattering paths that contribute, and the number of scattering events in each. For example, if the light is transmitted through a slab of thickness L, the average number of randomization events in the characteristic path is $(L/l^*)^2$. The time scale for the decay of this path is decreased by the inverse of this number; the length scale over which a scatterer must move is decreased by a corresponding amount. This is a primary advantage of DWS; it probes the dynamics of the scattering medium over length scales that are significantly shorter than those probed by traditional DLS. However, because the light is multiply scattered, some information is lost. It is not possible to probe motion at different scattering vectors, as is the case in DLS. Instead, DWS probes an average over all scattering vectors. Moreover, because the diffusion approximation is used to interpret the results, knowledge of l^* is essential to interpret the results. However, l^* can be determined independently through measurements of the total transmission.

Diffusing wave spectroscopy experiments are performed in a fashion very similar to the traditional DLS experiments.[13] The scattered light within a single correlation area or speckle spot is detected and the temporal autocorrelation function of the intensity fluctuations is measured. However, since the light is strongly multiply scattered, it exits the sample in all directions from any given point. Therefore, unlike DLS, the scattering angle is not well-defined. Instead, there are only two useful geometries for DWS experiments, either transmission or backscattering. The essential difference between these two geometries is the distribution of diffusive photon paths that contribute to the auto-

correlation functions. In backscattering, long paths can contribute; however, a significant contribution arises from very short paths, where the light is scattered only a few times and exits the sample from the same side it entered. While the functional form that describes the autocorrelation function in this case is very simple, the contribution of the very short paths can not be correctly described within a diffusion approximation, since the length of these paths is comparable to the transport mean free path, the minimum distance over which a diffusion approach can possibly apply. This complicates the interpretation of the results significantly; as a result, the backscattering geometry has found relatively fewer applications. By contrast, in transmission, the light must traverse through the whole sample; as a result, all of the paths can be well described by the diffusion approximation. There is a characteristic length scale for the paths, L^2/l^*, which can be experimentally controlled by varying the sample thickness. Thus, the exact form of the autocorrelation function measured by DWS depends on the geometry of the experiment.

To illustrate the unique features of DWS, we consider a concentrated suspension of uniformly sized colloidal particles. In this case, the particle motion is simply Brownian diffusion, and the functional forms for the DWS autocorrelation functions can be inverted to determine the root-mean-square (rms) displacement of a particle as a function of time. As an example, we use DWS to probe a suspension of 1.53 μm diameter polystyrene spheres, at a volume fraction of $\phi \approx 0.02$.[14] This is concentrated enough to give the suspension a very milky white appearance, but not so concentrated as to introduce strong interaction effects between the motions and positions of the spheres. We show the measured time evolution of the rms displacement obtained with a DWS measurement in transmission, using a 1 mm thick sample. The data are plotted logarithmically in Figure 2. The resolution of the rms displacement is clearly on the order of a few angstroms! In fact, the resolution of the length and time scales is so good in these measurements that it is possible to resolve deviations from purely diffusive motion at very short times. This is apparent at the earliest times in Figure 2 by the deviation of the data from a slope of 0.5, which is expected for purely diffusive motion, where the mean square displacement grows linearly with time. Instead, the data exhibit a clear curvature and approach a slope of 0.5 only at much larger times. This behavior results from the hydrodynamic interaction of the particles with the surrounding fluid; the wake generated by the motion of the particles causes their velocity correlation function to decay algebraically rather than exponentially, leading to the very slow approach to the asymptotic diffusive form.

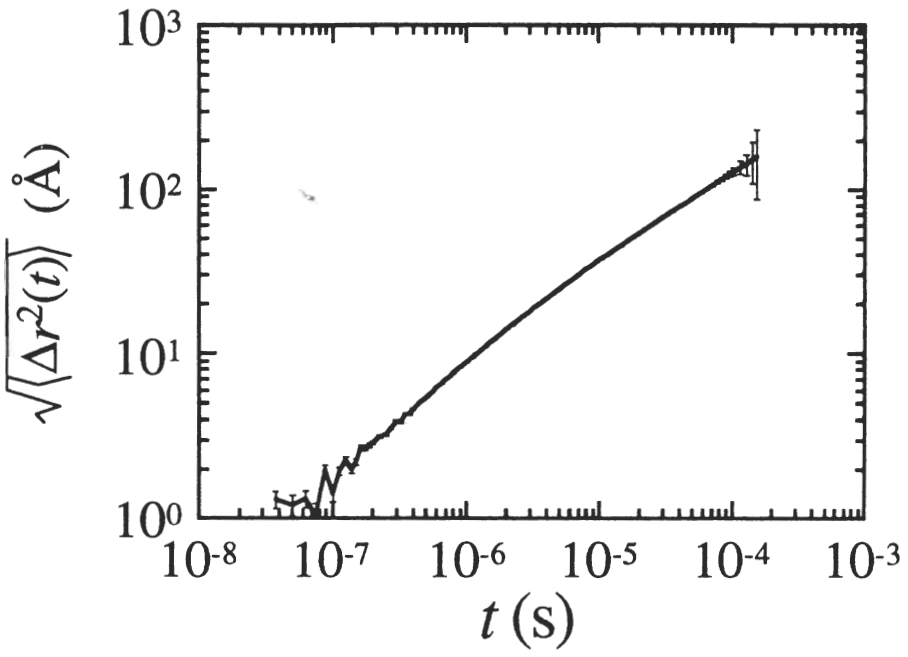

Figure 2. Root-mean-square displacement of a particle as measured with diffusing-wave spectroscopy. The particles are 1.53 μm diameter polystyrene latex spheres, suspended in water at a volume fraction of ~0.02. Motion on length scales as short as a few angstroms can be observed.

These data clearly exhibit the very high resolution of DWS, and its unique ability to probe motion over very short length scales. In fact, the resolution illustrated by this example is not the inherent limitation of DWS; by using a thicker sample, motion over even shorter length scales can be measured. This was done by Kao and collaborators,[15] who used a Michaelson interferometer to measure correlations over even shorter time scales. Using thicker samples, they were able to achieve resolutions on the subangstrom level.

Diffusing wave spectroscopy is ideally suited for applications involving very concentrated suspensions. These are exactly the sort of systems that cannot be studied with traditional DLS because of the problems of multiple scattering; yet these are also the colloidal systems of greatest technological importance. Perhaps one of the most important applications of DWS is for measuring the size and size evolution of colloidal particles in concentrated suspensions without the requirement of dilution needed for traditional DLS. For example, Horne[16] has studied the curdling of milk, which is the precursor to making cheese. In this process, the emulsion droplets of fat that comprise the milk aggregate together and ultimately form a gel network. Using DWS, Horne was able to follow this aggregation and subsequent gelation. These experiments were performed primarily in the backscattering geometry. Other developments of DWS for particle sizing have emphasized the transmission geometry. Van Keuren[17] and collaborators used two-single mode optical fibers immersed directly into the suspension, one for the source and the second for the detector. This provides a simpler functional form for the DWS autocorrelation function, and allows particle sizing measurements to be performed more directly. With continued development, DWS could potentially become an important technique for process monitoring in the manufacture of colloidal particles.

Diffusing wave spectroscopy has also played a role in the study of several important problems in colloid physics. For example, Chaikin[18] and his collaborators have studied the behavior of fluidized beds using DWS. These are suspensions of relatively large colloidal particles; gravitational settling is counteracted by the upward flow of the suspending fluid. Since the particles are undergoing flow, DWS probes the relative velocity differences, or

the shear. In a fluidized bed, the relative velocities are random, so DWS probes the variance in the particle velocities. Chaikin and his collaborators used DWS to measure this variance as the flow rate was varied, and hence the volume fraction of the fluidized bed was changed. The variance was found to decrease with volume fraction, approaching zero near a volume fraction of about 0.4, significantly lower than the volume fractions where the average velocity approaches zero. While DWS is ideally suited to answering some of the important questions in fluidized beds prepared using colloidal suspensions, it may also be used to study the behavior of fluidized beds prepared with granular particles and fluidized by the flow of a gas. The behavior of granular systems such as these is addressed in another article in this issue.[19] The physics of these systems are not well understood, and the application of DWS may help address some of the key problems.

Another very elegant application of DWS is in the study of electrorheological (ER) suspensions by Ginder.[20] Electrorheological suspensions are dispersions of colloidal particles that are subjected to an electric field, which induces dipole moments in the particles. If the dipole interactions are strong enough, the particles attract one another, forming chainlike structures in a direction parallel to the applied field. These chains can modify the viscosity of the suspension, turning a fluidlike mixture into a solidlike paste. This feature makes ER fluids potentially attractive for applications as electromechanical switches, provided that the response time of the ER fluid of interest is fast enough. Ginder used multiple light scattering techniques to probe the response of an ER fluid to applied electric fields. For example, Ginder found that he could measure the response time of an ER fluid to the sudden application of an electric field by monitoring the increase in intensity of multiply scattered light transmitted through the sample. The increase in transmitted intensity occurs because of the increase in local order between particles induced by the electric field. Ginder also used DWS to monitor the motion of the particles in ER fluids in response to small oscillating electric fields. These fields were kept small enough so as not to change the transmission coefficient of the multiply scattered light; the oscillations he observed in the measured autocorrelation functions arise from temporal phase fluctuations produced by the electrophoretic motion of the suspended particles making up the ER fluid. Ginder concluded from the DWS measurements that electrophoresis does occur in these systems and that it can promote particle aggregation at high applied electric fields.

Although many of the applications of DWS to date have entailed problems involving colloidal suspensions, the measured autocorrelation function will reflect the dynamics of the sample studied. An example of the use of DWS to study a completely different form of dynamics that also highlights another unique feature of the technique is the study of the dynamics within foams.[6] A foam is a dispersion of gas droplets in a fluid. The volume fraction of the gas droplets is typically large, on the order of 0.9 or greater. As a consequence, the droplet shape is considerably deformed from spherical. Thus the droplets do not move any appreciable amount, and a foam is typically a solid, with a finite yield stress. Nevertheless, the foam still possesses internal dynamics. The size of the droplets in the foam are not constant in time; they coarsen due to the diffusion of the gas through the fluid, out of the small droplets and into the larger ones. As this coarsening process evolves, the droplet packing conditions change. This causes stresses to be built up within the foam, which are relieved by the motion of the bubbles rearranging themselves. These rearrangements occur randomly, but relatively rarely, throughout the sample. It is these rearrangements that lead to the fluctuations in the scattered light intensity that cause the decay of the DWS autocorrelation function. This can be understood by recognizing that each rearrangement involves several bubbles, and each bubble is significantly larger than the wavelength. Therefore, each rearrangement entails the motion of the bubble interfaces over length scales that are much greater than the wavelength. Any diffusive light path that passes through one of these rearrangements will have its path length, and hence its phase, changed by a large amount, much greater than the requisite q^{-1}. Thus the DWS autocorrelation function will decay when all of the diffusive light paths have intersected at least one rearrangement. This can be formulated more formally to account for the DWS data from foams. The key parameter that DWS measures is the rate of rearrangement in any volume unit of the foam. These rearrangements can provide new information about the dynamics of foams that lead to their unusual rheological behavior.

Conclusions

While there have been great strides in our understanding of multiply scattered light over the past several years, the application of multiple scattering techniques to probe the structure and dynamics of disordered mesoscopic materials is still in its infancy. Much of the earliest work has centered on basic research studies of colloidal suspensions and other dispersions. The use of multiply scattered light has enabled new physical processes to be studied. Perhaps even more importantly, multiply scattered light is also now beginning to be employed for process control applications. Finally, the most important driving force in the further development of our understanding of the use of multiply scattered light may arise from medical imaging applications. These techniques appear to be extremely promising as a noninvasive probe of the human body, particularly the brain. This may ultimately represent the true embodiment of brain waves.

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