Discrete scatterers and autocorrelations of multiply scattered light

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The intensity autocorrelation function of light backscattered from the surface of concentrated suspensions of small spheres is studied. In the past, calculations have been based on a model of light diffusing in a continuous medium, which, in order to agree with experiment, relies on rather unphysical, *ad hoc* assumptions about boundary conditions. Here, it is shown that for isotropic scatterers the discrete nature of the scatterers is very important in determining the autocorrelation function, a point that is neglected in the continuum diffusion model. In the case of highly anisotropic scatterers, a one-dimensional diffusion model does not suffice to describe a photon's path, which is characterized both by a slowly changing direction and position. Numerical simulations that take into account the discrete nature of scattering events and the direction and position of scattered photons, give autocorrelation functions that are close to those seen experimentally [D. J. Pine, D. A. Weitz, P. M. Chaikin, and E. Herbolzheimer, Phys. Rev. Lett. **60**, 1134 (1988)]. In addition, various limits of the autocorrelations are examined analytically.

In order to understand the behavior of light scattered from concentrated suspensions of scatterers, one must study multiple-scattering phenomena.[1-4] In contrast with dilute suspensions, where light is likely to be scattered only once as it traverses a sample, the multiple-scattering regime is characterized by a mean free path l which is much smaller than the size of the system. The dynamics of the scatterers, along with the properties of the individual scatterers, determine the temporal autocorrelations of the scattered light. It is hoped that understanding the relation between the observed autocorrelation function of multiply scattered light and the dynamics of simple systems will allow one to use multiple scattering to probe the dynamics of more complex systems.

The model which has generally been used to calculate the autocorrelation function of multiply scattered light assumes that the transport of light in the system is simply diffusive, with a diffusion coefficient determined by a transport mean free path, l^*.[1,3,4] In order to obtain the observed intensity autocorrelation function for a suspension of scatterers, rather unphysical initial conditions for the diffusion equations have been assumed. In this paper we show that accurate predictions can be made using most of the approximations used in the diffusion model, if, however, one in addition takes into account the discrete nature of the scatterers by abandoning the continuum approximation.

For a model of a suspension of spheres, we consider noninteracting elastic scatterers contained in a cell of thickness L, upon which coherent light is incident. The absorption of light by the scatterers is taken to be negligible, as is the case for experiments with submicrometer polystyrene spheres.[1] A detector is used to find the temporal autocorrelation function of the intensity of the light backscattered from the cell. If it is assumed that the mean distance between scatterers is greater than several wavelengths, the propagation of light in the medium can be approximated by ballistic trajectories between scatterers.[2] Since light may reach the detector by many different paths, the electric field at the detector is the sum of the field due to each of these paths. Brownian motion of the scatterers causes the length of each path to vary over time. Because the phase of the field which arrives at the detector due to a particular path depends on the length of that path, this phase evolves in time, giving rise to the dominant time dependence of the autocorrelations.

Let us consider a single path α of a photon with wave vector of magnitude k. This path involves n independently diffusing scatterers. Define q_j^α as the transfer wave vector of the jth collision, $q_j^\alpha = k_j^\alpha - k_{j-1}^\alpha$, with k_j^α being the wave vector after the jth collision, $1 \le j \le n$, $|k_j^\alpha| = k$. The probability distribution for the change in the length of the path during a time t is Gaussian, with mean 0 and variance

$$\sigma_\alpha^2 = Dtk^{-2} \sum_{j=1}^{n} (q_j^\alpha)^2 , \tag{1}$$

where D is the diffusion constant for the scatterers. For paths involving only a few scatterers, this Gaussian form relies on the approximation that the scatterers execute independent random walks. For paths involving many scatterers which undergo more correlated, but isotropic random motion, the same form will be obtained due to the sum over many roughly independent terms, as long as the correlations are of finite range. In this more general case, the effective D can be time dependent.

From this distribution for the change in path length, the autocorrelation function for the electric field at the detector that is due to a single path can be derived.[3]

$$\langle E_\alpha(t) E_\alpha^*(0) \rangle = \exp\left[-Dt \sum_{j=1}^{n} (q_j^\alpha)^2 \right] |E_\alpha(0)|^2 . \tag{2}$$

The form of this expression reflects the Gaussian distribution of the change in the length of the path. If one assumes that the fields due to different paths add incoherently,[2,3] so that interference among different paths gives no significant time dependence, then the autocorrelation function of the total scattered electric field seen by the detector at an angle θ from the incident direction is simply given by

$$\langle E_\theta(t)E_\theta^*(0)\rangle=\int_0^\infty dy\, P_\theta(y)\exp(-Dty)\ , \tag{3}$$

where $P_\theta(y)$ is the probability of a path α leaving the slab at an angle θ from the incident direction and

$$y=\sum_{j=1}^{n}(q_j^\alpha)^2\ . \tag{4}$$

The field autocorrelation functions Eq. (2) for distinct paths are independent if the paths do not overlap. In the limit that the probability that two typical paths which arrive at the detector have a scatterer in common is small, this independence allows the field autocorrelation function to be squared to give $G^{(2)}(\theta,t)$, the intensity autocorrelation function measured at the angle θ. A *sufficient* condition for this approximation to hold in a backscattering experiment is that the width of the incident beam be much greater than the mean free path of the light in the cell.[5]

We can also define an angular average $P_B(y)$ as the sum over all paths with given y, as defined in Eq. (4), and $G_B^{(2)}(t)$ as the intensity autocorrelation function calculated using $P_B(y)$ in place of $P_\theta(y)$ in Eq. (3), which physically corresponds to a detector which collects all of the reflected light. We can similarly define the forward-scattered autocorrelation function $G_F^{(2)}(t)$.

Note that Eq. (3) is very similar to the expression derived elsewhere,[3] but that the integration variable is not the length of the path in the cell, as in Ref. 3, but rather the quantity y. This is because we have *not* assumed here that y is directly proportional to the geometric length of the path, s. The function $P_\theta(y)$ cannot be obtained as the solution of the simple diffusion equation in real space, nor is it simply related to the momentum space kernel. Its relation to a diffusion equation in position and momentum phase space will be discussed later in this paper for the case of predominantly forward scattering.

If the continuum approximation is made that $y\propto s$ and that paths are given by continuous Brownian motion, rather than discrete random walks, then one obtains that $P_\theta(y)$ is independent of θ and is given by the solution to a simple diffusion equation. Specifically, given some initial distribution of light intensity at time $t=0$, $P(y)$ is given by the flux of light at the boundary of the cell at time $t=yl^*/2ck^2$, since $\langle y\rangle=2k^2$ for a path of length the transport mean free path l^*. For forward scattering in a cell with thickness $L\gg l^*$, the assumption that $y\propto s$ is a very good approximation for typical paths since they will involve many scatterings. The resulting predictions of $G_F^{(2)}(t)$ from the diffusion approximation are thus fairly insensitive to the initial distribution chosen for the incident light. By contrast, the choice of the initial distribution of the incoming light in the diffusion approximation is very important for the backscattering problem and the best choice is not *a priori* evident. For initial conditions of the form $\exp(-z/l^*)$, corresponding roughly to an initial light intensity after first scattering that decreases with the distance z into the cell, $G_B^{(2)}(t)$ is found to behave as $t^{-1/2}$ for large t, while an initial condition of the form $\delta(z-\gamma l^*)$, representing all of the initial light intensity concentrated a distance γl^* into the cell, gives $G_B^{(2)}(t)\sim\exp[-\gamma(6t/t_0)^{1/2}]$.[1] Here we have introduced the characteristic time $t_0=(k^2D)^{-1}$ of the autocorrelation function which is the time for the scatterer to diffuse one wavelength of the light.

From Eq. (3), it is evident that the long-time behavior of $G_B^{(2)}(t)$ is determined by the paths with small y. Most backscattering paths have a length s on the order of l^*. For such short paths, however, y and s are not in general proportional. In particular, y will not be small for very short paths, which involve only a few scatterers. A path that changes direction in a small number of scatterings must have large momentum transfers q_j, so that y is large. The value of y for backscattered paths will thus be very small only for long paths in which the wave vector changes direction slowly; there are relatively few such paths. As an example of this, we estimate the number of backscattered paths with a particular value of $y\ll k^2$ for the case of isotropic scattering. Since such a backscattering path must have $|\sum q|>2k$, the q_j will typically have magnitude at least $\sim k/n$, where n is the number of scatterers in the path. In order to have $\sum q^2<y$, n must thus be at least k^2/y. The probability of an n-step path satisfying these constraints on the magnitude of the q_j is $\sim(1/n^2)^n$. We must also require that the n-step path not leave the system until the last step. This probability, though, is no smaller than e^{-n} and is thus subdominant for small y. We then have

$$P_B(y)\sim(1/n^2)^n\sim(y^2/dk^4)^{bk^2/y}\ , \tag{5}$$

with dimensionless constants b and d. This probability is extremely small for $y\ll k^2$. For *large* t, the autocorrelation function can be obtained from the Laplace transform of $P_B(y)$ by steepest descents yielding

$$G_B^{(2)}(t)\sim\exp[-4\sqrt{b(t/t_0)\ln(t/t_0)}] \tag{6}$$

for large t. This is to be compared with the diffusion model results already stated, which decay less rapidly with time. The short paths which are responsible for the diffusion model's prediction of a power-law decay of the backscattering autocorrelation function for some apparently reasonable choices of boundary conditions are cutoff in the discrete model, leading to a different functional dependence.

Both the short-time behavior of the backscattering correlations and the forward scattering in a thick slab are determined by the large-y behavior. For $y\gg k^2$, paths involve many scatterers and the q_j^α are not necessarily small, so the constraint that $\sum_j q_j^\alpha$ equal the total momentum transfer $k_n^\alpha - k_0^\alpha(\sim k)$ is unimportant and y will be proportional to s with high probability. The form of the asymptotic behavior of $P_B(y)$ for large y can therefore be found using the continuum approximation, if the initial condition for the density of the diffusing light is taken to fall off sufficiently rapidly with with increasing z. In this case, $P_B(y) \approx a y^{-3/2}$, with a dependent on the boundary conditions used in the continuum approximation. Given this form for $P_B(y)$ for large y and imposing a cutoff for small y, one finds

$$G_B^{(2)}(t) \approx 1 - A(t/t_0)^{1/2} \tag{7}$$

for $(t/t_0) \ll 1$, with $A = 4\sqrt{\pi}\, a$. This agrees with the form given by the diffusion approximation with the δ-function initial condition for the density of diffusing light with the choice $(2\sqrt{6})\gamma = A$. In general, the *form* of the short-time autocorrelations is correctly given by the diffusion approximation, but the coefficient of the $\sqrt{t}$ depends on the details of the initial scatterings.

In order to calculate the full intensity autocorrelation function, the path weight function $P_\theta(y)$ must be found. In the diffusion model, the distribution of path lengths is found simply by solving a one-dimensional diffusion equation with given boundary conditions and the angular dependence is trivial. Unfortunately, with discrete scatterers one cannot find a simple solution for the distribution of paths with a given y and θ analytically. Therefore we have used a Monte Carlo calculation to estimate $P_\theta(y)$. We analyze paths in a three-dimensional system consisting of a slab of thickness L with infinite extent in the other two dimensions. Paths starting at the edge of the slab and initially perpendicular to the slab were sampled by discrete random walks. Sizes of the path steps were chosen from a Poisson distribution with mean free path l. The probability to scatter an angle Ψ at the end of a path step, $S(\Psi)$, was chosen to approximate the intensity of light as given by Mie theory for the scattering of unpolarized light.[6] A probability distribution which fit well to the theoretical intensity and that could be quickly computed was used:

$$S(\Psi) = (1-i)\Psi \exp(-\Psi^2/2w^2)/w^2 + i\sin(\Psi)\ , \tag{8}$$

with the coefficient i giving the probability of s-wave scattering and w giving the width of the forward-scattering peak. The anisotropic part of this distribution is singular at $\Psi = \pi$, but this contribution is very small for the values of w which are appropriate for the experiment.[1] Propagation and scattering for each path were repeated until the path exited the cell. Since the position parallel to the face of the slab is ignored, this calculation gives $P_\theta(y)$ for plane waves incident on the cell. From this approximation to $P_\theta(y)$, the autocorrelation function was found using Eq. (3).

For purely *isotropic scattering* with $l = l^*(i=1)$ and $L = 10$, the distribution shown in Fig. 1(a) was derived for backscattered light. The details of $P_\theta(y)$ at small y depend somewhat on the angle θ at which the backscattering is observed, though the form of the large-y behavior is found to be independent of θ, as would be expected for paths which contain many scatterings, since the momentum transfers near the beginning and end of the path make only a small contribution to y in this limit. The shape of the autocorrelation function $G^{(2)}(\theta,t)$ is therefore found to be relatively independent of exit angle θ for $t/t_0 < 1$. The angular integrated autocorrelation function $G_B^{(2)}(t)$ calculated from $P_B(y)$ is shown in Fig. 1(b). For a semi-infinite slab ($L = \infty$), $P_B(y)$ is found to vary as $a y^{-3/2}$ for large y, as expected, with $a = 1.14$. Note that a is the normalization of the large-y behavior of $P(y)$. Although the large-y behavior of $P_B(y)$ determines the short-time behavior of $G_B^{(2)}(t)$, the coefficient is determined by how many "long" paths there are compared with the number of "short" paths and so depends on the behavior of $P(y)$ for small and intermediate values ($y < 60$).

We have also analyzed the transmitted intensity. For $20 < L/l < 75$, the average transmitted intensity can be fit to the form $x/(L/l + g)$, which is the scaling form expected from the diffusion approximation,[2,7] with x determined by these numerical calculations to be 1.60 ± 0.02 and $g = 0.8 \pm 0.2$. In the diffusion approximation, the δ-function initial condition discussed earlier gives $x = \gamma$

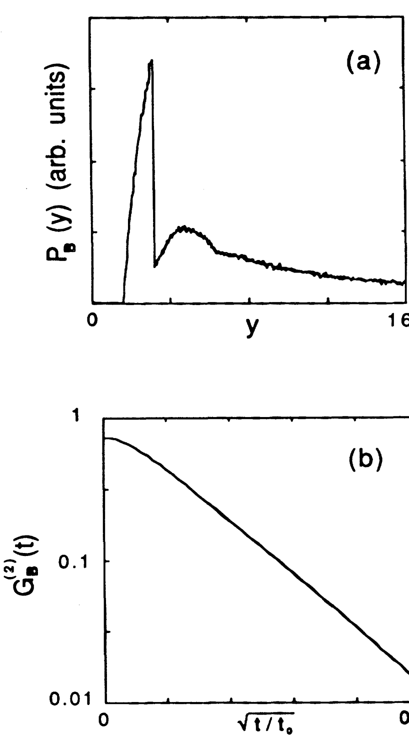

FIG. 1. (a) Distribution of backscattered paths $P_B(y)$ for a suspension of independent particles that scatter isotropically, where y is the sum of the squares of the momentum transfers along the path. Sharp features are due to the discrete nature of the scattering. 10^6 paths were sampled numerically to compute this curve. (b) Logarithmic plot of $G_B^{(2)}(t)$, the autocorrelation function of backscattered light, vs $\sqrt{t/t_0}$ for diffusing isotropic scatterers in a slab of thickness $L/l = 10$. The curve has been scaled by the square of the incident intensity, so the intercept is not 1 at $t = 0$, but rather the square of the reflection coefficient.

and $g=0$.

For the experiments which have been performed,[1-3] scattering is very anisotropic, and the results of the calculation of $P_\theta(y)$ for actual parameters are rather different from those in the isotropic case.[8] For uncharged spherical polystyrene scatterers of 0.5 μm radius and 0.37 μm incident light, Mie theory calculations give $w=0.3$ rad, $i\approx 0.06$, and $l^*/l\approx 7.04$. The calculation of $G^{(2)}(\theta,t)$ is relatively insensitive to the exact value of these parameters as long as L and l^* reflect the experimental values. The distribution $P_B(y)$ calculated with these parameters for $L/l^*=10$ is shown in Fig. 2(a); $P_B(y)$ is much smoother for small y than for the isotropic case, since many more scatterings occur in a typical path.

The results of the calculation of the autocorrelation function $G_B^{(2)}(t)$ in the anisotropic case are displayed for various L/l^* in Fig. 2(b). Each curve has been multiplied by the square of the total reflected intensity for clearer comparison with each other and with experimental data, which are normalized to the incident intensity. Since for intermediate values of y the distribution $P(y)$ is roughly independent of L, for $L>l^*$, $G_B^{(2)}(t)$ should be similar at intermediate times $(t/t_0\sim 1)$ for different L, except for the normalization due to the reflected intensity. The dotted lines in Fig. 2(b) show the continuum diffusion approximation prediction given δ-function boundary conditions, the mean free path l^* calculated from single scatterer properties, and a γ of 1.68; this value for γ giving the least-squares fit to the curve as drawn for $L/l^*=10$, over the range of time $\sqrt{t/t_0}<0.5$. Note, though, that the numerical data can be fit quite well if l^* is instead allowed to deviate from its calculated value, as was done in the experimental fits.[1] Figure 2(c) shows the experimental results from Ref. 1 for similar parameters.

In the limit in which the spheres scatter strongly in the forward direction and $L\gg l^*$, there is no dependence on the length scales, so that the autocorrelation function is a function only of t/t_0 and is independent of L, l^*, w, and i. Taking this limit numerically gives the universal dependence shown as the top line in Fig. 2(b). For small t, $G_B^{(2)}(t)\approx 1-A\sqrt{t/t_0}$, with $A=(1.16)4\sqrt{\pi}$. This is close to the value found for isotropic scattering.

In this strongly forward-scattering limit, a two-dimensional diffusion equation can be used which replaces the one-dimensional diffusion approximation. We concentrate on an infinite slab, $L=\infty$. For an incident plane wave, the components of position parallel to the surface of the slab are unimportant. Let z be the distance of the path from the surface of the slab and v be the cosine of the angle that the path direction makes with $\hat{z}$, i.e., the normalized z component of the velocity. Since it takes many scatterings for a path to change direction by a small angle in this limit, y will typically be proportional to s: the sum $\sum q^2$ will have variance $\sum q^2/n$ for n scatterings. This will occur in path length $s=nl$ up to terms of order $1/\sqrt{n}$, and thus with high probability $y=s/2l^*$. The path direction will diffuse over the surface of the unit sphere with diffusion constant c/l^*. This means that a path can be represented as diffusion in the two dimensional space $[0,\infty]\times[-1,1]$ with coordinates

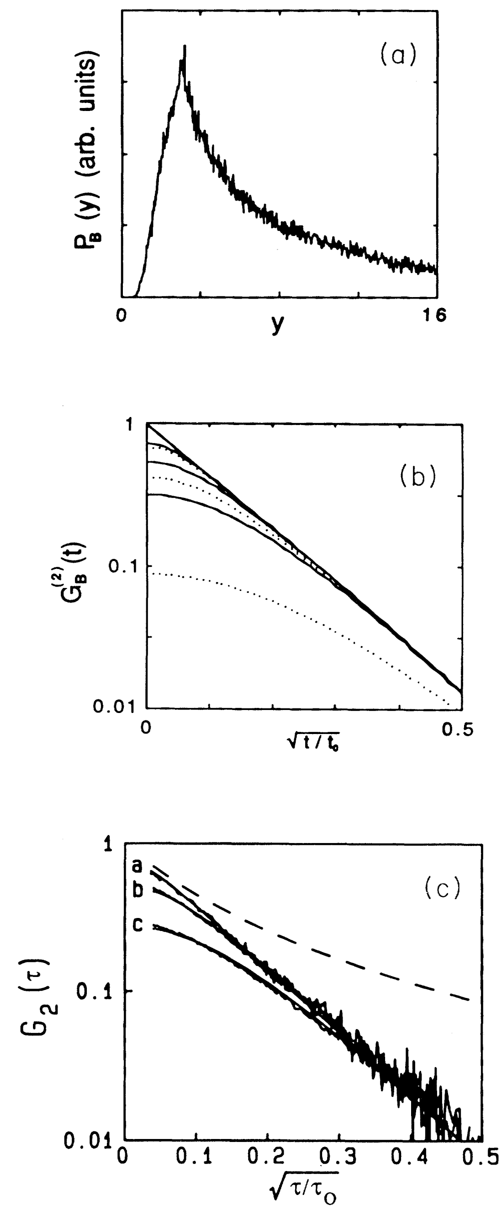

FIG. 2. (a) Distribution of paths $P_B(y)$ for anisotropic scattering with $L/l^*=10$, $w=0.3$ and $i=0.07$, as defined in Eq. (8), corresponding roughly to the experimental parameters of Ref. 1; 10^5 paths were computed. (b) Logarithmic plot of $G_B^{(2)}(t)$ vs $\sqrt{t/t_0}$ for anisotropic scattering with the same parameters and $L/l^*=2.5$, 5, 10, ∞ from bottom to top. The dotted lines show fits to the diffusion approximation using the mean free path l^* computed from the scattering properties of individual particles and a γ of 1.68, which is the best fit for $L/l^*=10$, as discussed in the text. The fit for $L/l^*=\infty$ is indistinguishable from the solid line on this scale, but the fits for the two smaller slabs deviate considerably. (c) Solid lines show the experimental results for $G_B^2(t)$ vs $\sqrt{t/t_0}$ from Ref. 1 for ratios of cell size to mean free path (computed from the single-scattering regime measurements and calculations) of 2.5, 6, and 10. Also shown as the dotted line is the prediction of the diffusion approximation for an exponentially decaying initial distribution of light intensity in the cell, which is a much worse approximation at long times.

$Z=z/l^*$ and v. The light intensity $\rho(T,Z,v)$ at scaled time $T=ct/l^*$, scaled position Z, and direction v obeys the diffusivelike equation

$$\frac{\partial\rho}{\partial T}=(1-v^2)\frac{\partial^2\rho}{\partial v^2}-2v\frac{\partial\rho}{\partial v}-v\frac{\partial\rho}{\partial Z}\ , \qquad (9)$$

where the first two terms on the right-hand side originate from the Laplacian on the unit sphere and the third term is a convective term representing the propagation in Z. For perpendicularly incident light, initial conditions will be $\rho(0,Z,v)=\delta(Z)\delta(v-1)$ and the boundary conditions are $\rho(T,0,v)=0$ for $T>0$, $v>0$, and $\partial\rho/\partial v=0$ for $v=\pm 1$. Given the solution to Eq. (7) with these boundary conditions, the distribution $P(y)$ can be found from the flux through the line segment $Z=0$, $v<0$:

$$P(y)=-\int_{-1}^{0}\rho(2y,0,v)v\,dv\ . \qquad (10)$$

We have not solved Eq. (9) analytically; numerical solutions based upon finite difference methods would be an alternative to the Monte Carlo approach used here for the strongly anisotropic $w\to 0$ limit, although the form of the boundary conditions may present difficulties. We emphasize that Eq. (9) provides an *equivalent* approach to multiple scattering in the strongly anisotropic limit; our Monte Carlo results and asymptotic analysis yield the behavior of the probability $P(y)$ that could, alternatively, have been obtained from this two-dimensional diffusion equation.

In conclusion, the multiple scattering of light from a system of independently diffusing scatterers has been investigated by removing one of the approximations used to derive the diffusion model. A Monte Carlo estimate of the number of paths as a function of the sum of the squared momentum transfer y, which acts as an effective path length, was computed and various limits found analytically. The prediction of the backscattered autocorrelation function $G_B^{(2)}(t)$ as given by this simple model is found to agree well with experiment, and unlike the diffusion model in its simplest form, requires no undetermined parameters. This model could readily be extended to include more complicated effects, such as polarization of the scattered light. Future work on the effects of correlations among the scatterers should be interesting as the experiments progress.

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