Diffusing-wave spectroscopy and multiple scattering of light in correlated random media

F. C. MacKintosh and Sajeev John
Physics Department, Princeton University, Princeton, New Jersey 08544
and Corporate Research Science Laboratories, Exxon Research and Engineering, Annandale, New Jersey 08801
(Received 20 December 1988)

We discuss the diffusing-wave spectroscopy technique for multiple scattering of light as introduced in recent experiments. This technique has proven to be useful in probing the self-diffusion of scattering particles in suspension by measuring the light-intensity autocorrelation function. We show how the autocorrelation function depends upon the dynamic structure factor of the medium in the presence of correlations between the scattering particles. There is a simple generalization of the result obtained for uncorrelated media to include the dynamic structure factor. Previous theoretical work has employed the *white-noise* model, valid for small uncorrelated scattering centers. The results of this model are valid only so long as the propagation of the light can be regarded as diffusive. On short length scales, however, the propagation becomes increasingly ballistic in nature. We present an exact formal solution of the transport equation capable of describing the crossover from ballistic to diffusive propagation. The resulting transport kernel provides a simple correction to the diffusion approximation for large scattering particles, which substantially improves the agreement with measured autocorrelation functions. We also discuss the polarization dependence of the autocorrelation function for both small as well as large scattering particles.

I. INTRODUCTION

The multiple scattering of light by dense random dielectric materials has received much interest recently. Experimental and theoretical work has been devoted to the nature of fluctuations[1-6] and the coherent backscattering enhancement.[7-14] Most of the theoretical work on light scattering to date has been based on two major assumptions: uncorrelated disorder and the diffusion approximation. In the diffusion approximation one assumes that the propagation of light in a random medium is incoherent and diffusive, which is valid for the transport of light over distances which are large compared with the transport mean free path l^*. Over shorter distances the propagation is increasingly ballistic in nature. The assumption of uncorrelated disorder has also been referred to as the *white-noise* model. This is valid, for example, in media composed of a dense collection of noninteracting scattering particles of size, a, much smaller than the optical wavelength λ. Here the scattering and transport mean free paths are identical: $l = l^*$. In many experimental situations the particle size $a \gtrsim \lambda$. As the correlation length a increases, the scattering becomes nearly ballistic over longer length scales. This leads to a transport mean free path l^* which becomes larger than the extinction length l of the coherent field. Individual scattering events change the direction of propagation only slightly. A complete angular randomization of the wave occurs only over a longer length scale, namely l^*. In this paper we present a detailed theory of the crossover from ballistic propagation to isotropic diffusion, and discuss comparisons to experiments where such a crossover has been observed. As in the field-theoretic analysis of John and Stephen,[15] we find that the scattered intensity due to a plane-wave incident on a disordered medium must be decomposed into an infinite series of spherical harmonic or *angular-momentum* components. The isotropic *s-wave* component corresponds to classical diffusion. In the white-noise model all statistical weight is given to the isotropic part of the intensity, whereas in a realistic medium a summation must be performed to include all higher-angular-momentum components necessary for a proper description of the crossover from ballistic to diffusive propagation.

A departure from the diffusion approximation has been seen in recent measurements of the time autocorrelation function of the speckle pattern of multiply scattered light. This new technique of photon-correlation spectroscopy [known as diffusing-wave spectroscopy (DWS)] relates the measured autocorrelation function to the dynamics of the scattering medium.[2,16,17] This is an extension of single-scattering spectroscopy [quasielastic light scattering (QELS)], which has been useful for some time in studying dynamic structural properties of the scattering medium. Single-scattering spectroscopy relies on the fact that dielectric fluctuations are sufficiently weak that the light scattered by the entire medium can be described within the Born approximation. In dense liquids, colloidal suspensions and other complex fluids, this is no longer true. DWS suggests a new direction in extracting the nature of dynamic correlations within such systems, given a precise theoretical description of the multiple scattering of light in correlated dielectric media. We present a formal theoretical framework, within which this goal may be achieved.

At long times, the decay of the light intensity autocorrelation function for diffusing scatterers is dominated by optical paths of small extent. The departure from the theoretical calculations based upon the diffusion approximation appears at such long times. A proper theoretical treatment of this regime requires that we go beyond the diffusion approximation. In this work we describe an integral equation formalism for dealing with correlations in the scattering medium. With the introduction of a nonzero correlation length we are able to determine the higher-angular-momentum components of the scattered intensity. The resulting description of short paths leads to much better agreement with experiment. The dependence of the autocorrelation function on the dynamic structure factor $S(\mathbf{q},t)$ for interacting particles is discussed as well. Furthermore, the deviation seen in the autocorrelation function suggests that a similar deviation from the diffusion result may be seen at large angles in the coherent backscattering peak. This is due to an analogy that exists between the decay of the autocorrelation function with time and the coherent backscattering peak as a function of angle.[18,19] This analogy is strictly true only for scalar waves, as we shall see below.

We begin Sec. II by reviewing in physical terms the DWS experiments and the origins of the discrepancy between the measurements and the previous theoretical calculations. In Sec. III we discuss the generalization of the DWS techniques for interacting systems. Section IV develops the theoretical framework for dealing with correlations in the medium, while Sec. V is devoted to the example of scattering from large particles. Finally, Sec. VI contains the results of the calculated polarization dependence of the autocorrelation function.

II. THE PHYSICAL PICTURE

Diffusing-wave spectroscopy is an extension of single-scattering techniques to the strongly scattering regime. Quasielastic light scattering has been used to measure the dynamic structure factor $S(q,t)$ of the scattering medium. Since QELS depends only on single scattering, it may be used to probe the motion of scattering particles over distances comparable to the wavelength of light. The multiply scattered light, on the other hand, is sensitive to motion over much smaller distances, due to multiple phase shifts. Maret and Wolf[2] have found that the correlation function for multiply scattered light decays nonexponentially. They demonstrated the existence of multiple time constants, indicative of the differing decay rates of the paths of various lengths. The longest paths decay most rapidly, while the slowest decay rate is that of single scattering (τ_0^{-1}), where τ_0 is the time required for a scatterer to move one optical wavelength. It was subsequently demonstrated for diffusing scatterers, that the experimental correlation functions all decay as exponentials in $\sqrt{t/\tau_0}$ over three decades.[17] Independently, Stephen[20] theoretically demonstrated the dependence of the correlation functions for short times.

For simplicity we shall consider a scalar field $E(\mathbf{x},t)$ which we associate with the electric field of light. We expect that in the multiple-scattering regime the polarization dependence (or vector nature) of the electromagnetic field becomes unimportant (in a sense to be described later), as the scattered light becomes depolarized. So long as the scattering is weak—i.e., provided that the mean free path l is much larger than the wavelength λ of the light—the observed intensity will be an incoherent sum of contributions of light scattered through all possible sequences or paths. Take, for example, a particular sequence of scattering events occurring at points $\mathbf{r}_1,\ldots,\mathbf{r}_n$ for which the scattering wave vectors are $\mathbf{q}_1,\ldots,\mathbf{q}_n$. The field $E(t)$ at the detector will carry a phase

$$E(t)\sim\exp\left[i\sum_j \mathbf{q}_j\cdot\mathbf{r}_j(t)\right] . \tag{2.1}$$

This is the product of scattering amplitudes for identical δ function scatterers at points $\mathbf{r}_1,\ldots,\mathbf{r}_n$. Experiments have measured the correlation between the intensity of the light at different times

$$\langle I(t)I(0)\rangle_c\equiv\langle I(t)I(0)\rangle-\langle I(0)\rangle^2 . \tag{2.2}$$

Here, we denote by $\langle\ \rangle$ the ensemble average over all configurations of the scattering particles. In this case, the fields E may be treated as complex Gaussian random variables, and this correlation of four fields factorizes

$$\langle I(t)I(0)\rangle_c=|\langle E(t)E^*(0)\rangle|^2 . \tag{2.3}$$

In the limit of weak scattering[20] ($\lambda\ll l$) the field $E(t)$ emerging from a sequence of scattering events at $\mathbf{r}_1(t),\ldots,\mathbf{r}_n(t)$ will interfere only with the light $E(0)$ scattered by the same particles in the same order $\mathbf{r}_1(0),\ldots,\mathbf{r}_n(0)$. We thus find the decay of the correlation function obtained by Maret and Wolf[2]

$$\begin{aligned}\langle E(t)E^*(0)\rangle &\propto\left\langle\sum_{\text{paths}}\exp\left[i\sum\mathbf{q}_j\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\right]\right\rangle\\ &\propto\sum_{\text{paths}}e^{-n\langle q^2\rangle\langle r^2\rangle/6} ,\end{aligned} \tag{2.4}$$

where the sums are over all possible paths. Here, $\langle q^2\rangle$ is averaged over the single-particle form factor, and $\langle r^2\rangle\sim 6D_S t$ for simple diffusion of particles with self-diffusion constant D_S. For isotropic scattering the mean-square transfer

$$\langle q^2\rangle=2k_0^2=2\left[\frac{2\pi}{\lambda}\right]^2 .$$

In Eq. (2.4) we have made the assumption that the scattering particles are small and move as if they are independent Gaussian random variables. Hence, the average of the exponential may be replaced by its first cumulant. For interacting particles, this is the leading term in a cumulant expansion which describes interparticle correlations. Such as expansion would be essential in describing the true dynamic structure of a dense or strongly interacting fluid. In addition, we have assumed that the particles scatter light independently. That is to say, the probability distribution for the wave-vector transfers $\mathbf{q}_j$ is independent of the macroscopic arrangement of the scattering centers $\mathbf{r}_j$ but is determined entirely by the structure of individual scattering particles. This is a good approximation when the interparticle distance is very large compared with the optical wavelength. In the case of anisotropic scattering, e.g., from large particles, the form factor becomes q dependent and the scattering is typically confined in the forward direction (small q). We may account for this by noting that the mean-square transfer $\langle q^2\rangle = 2k_0^2 l/l^*$ is reduced by the mean number l^*/l of scattering events required to completely randomize the direction of wave propagation. The number of steps in a path of length s is given simply by $n = s/l$. Thus for a typical path of length s, the loss of coherence with time is proportional to $\exp[-2(t/\tau_0)s/l^*]$, where $\tau_0^{-1} = D_S k_0^2$. The observed intensity is then given by a proper weighting of paths of length s. The weight, or number, of such paths may be characterized by a function $P(s)$, which in turn can be related to the time-dependent intensity of scattered light due to an incident pulse.[2,17]

Having made the above simplifying assumptions concerning the lack of dynamic correlations between the scatterers as well as the statistical independence of the different point scattering events in evaluating the exponential in Eq. (2.4), all remaining information regarding the actual structure of the scattering medium is relegated to the function $P(s)$. If the propagation of light is assumed to be purely classical diffusion on all length scales, then $P(s)$ is given by the probability that a classical random walker will enter and leave the medium at prescribed locations after executing a path of length s. For a point source at $\mathbf{r}'$ and detector at $\mathbf{r}$ ($|\mathbf{r}-\mathbf{r}'| \gg l^*$) in an infinite medium, this is given by

$$P(s) = \left[\frac{c}{4\pi s D}\right]^{3/2} e^{-c|\mathbf{r}-\mathbf{r}'|^2/(4sD)} , \tag{2.5}$$

where $D = cl^*/3$ is the classical diffusion coefficient for light. It follows that

$$\langle E(t)E^*(0)\rangle \propto \int_0^\infty ds P(s) e^{-2ts/(\tau_0 l^*)} = \int_0^\infty ds \left[\frac{c}{4\pi s D}\right]^{3/2} \exp[-c|\mathbf{r}-\mathbf{r}'|^2/(4sD) - 2ts/(\tau_0 l^*)] . \tag{2.6}$$

This integral is dominated by a saddle point at $s_0 = \sqrt{(3\tau_0/8t)}|\mathbf{r}-\mathbf{r}'|$, which maximizes the exponential. At short times ($t \ll \tau_0$) the autocorrelation function is dominated by paths of this length. We may evaluate Eq. (2.6) by expanding the argument

$$f(s) = -c|\mathbf{r}-\mathbf{r}'|^2/(4sD) - 2ts/(\tau_0 l^*) \tag{2.7}$$

about the saddle point, keeping only Gaussian fluctuations

$$\begin{aligned}\langle E(t)E^*(0)\rangle &\propto \int_{-\infty}^\infty dx \left[\frac{c}{4\pi s_0 D}\right]^{3/2} \exp(-\sqrt{6t/\tau_0}|\mathbf{r}-\mathbf{r}'|/l^* - \tfrac{1}{2}\sigma^2 x^2)\\ &\simeq \frac{3}{4\pi l^* |\mathbf{r}-\mathbf{r}'|} e^{-\sqrt{6t/\tau_0}|\mathbf{r}-\mathbf{r}'|/l^*} ,\end{aligned} \tag{2.8}$$

where

$$\sigma^2 = 3\frac{|\mathbf{r}-\mathbf{r}'|^2}{2l^* s_0^3} \tag{2.9}$$

is the second derivative of f with respect to s, and $x = (s - s_0)$ represents the fluctuations about s_0. The experimentally observed square root of time behavior in the exponential is manifest in this simple model for short times, within the diffusion approximation. (As discussed below, the observed autocorrelation function involves a sum of contributions from different initial and final scattering points $\mathbf{r}'$ and $\mathbf{r}$ within the medium.)

Photons in a real physical medium, however, have alternative nondiffusive modes of propagation on short length scales. These correspond to the decomposition of the total incident plane-wave intensity into angular-momentum components for the specific intensity.[15] In a correct treatment of wave propagation, each of these modes must be given the appropriate statistical weight. This weight depends sensitively on the propagation distance. High-angular-momentum components are negligible on long length scales, where propagation becomes isotropic, whereas on short length scales of nearly ballistic propagation, all angular-momentum components must receive significant weight so as to represent a plane wave. The amount of statistical weight given to each mode is determined by the form factor and the instantaneous or static structure factor of the medium. As such, these weight factors provide a spectroscopic probe of the static structure factor within a multiple-scattering medium. In previous first-principles theoretical work, all statistical weight has been given to the diffusion mode, and none to the higher-angular-momentum modes. This is the fundamental origin of certain discrepancies between the white-noise model and experimentally measured correlation functions. The formalism which we present in Sec. IV provides the necessary framework to resolve these discrepancies by incorporating correlations and the resulting nondiffusive modes of optical propagation.

A simple derivation of the intensity autocorrelation has been given by Stephen.[20] This begins with the wave equation satisfied by the (scalar) field $E(\mathbf{x},t)$,

$$\left[\nabla^2 - \frac{1}{c^2}\frac{d^2}{dt^2}[\bar{\epsilon} + \epsilon'(\mathbf{x},t)]\right] E(\mathbf{x},t) = 0 , \tag{2.10}$$

where the light scatters off of the random dielectric fluctuations ϵ' in the medium. (Without loss of generality, it is assumed that the fluctuations have zero mean $\langle \epsilon' \rangle = 0$.) The strength of the fluctuations is characterized by the correlation

$$k_0^4 \langle \epsilon'(\mathbf{x},t_1)\epsilon'(\mathbf{y},t_2)\rangle \equiv B(\mathbf{x}-\mathbf{y},t_1-t_2) . \tag{2.11}$$

For low densities and for noninteracting particles, this correlation is proportional to the density of scattering particles and has a width in $|\mathbf{x}-\mathbf{y}|$, approximately equal to the particle radius. At $t=0$ the Fourier transform $B(\mathbf{q})$ of Eq. (2.11) is proportional to the single-particle form factor. For particles smaller than a wavelength of light, this will have a characteristic width greater than λ^{-1}. In other words, the form factor will be nearly independent of the scattering vector $\mathbf{q}$, and the scattering will be isotropic. This is the essence of the *white-noise* approximation made in Ref. 20. All transfers $\mathbf{q}_j = \mathbf{k}_j - \mathbf{k}_{j-1}$ between wave vectors $\mathbf{k}_j$, which represent physical intermediate states (i.e., $|\mathbf{k}_j| = k_0$), are given equal weight. The transport of the field from one point to another within the medium is given by Green's functions which are solutions to the wave equation. The techniques used to calculate these Green's functions have been described in detail by a number of authors in the context of intensity fluctuations[3,4] and the coherent backscattering of light.[11,13,14] It is not our purpose at present to describe these techniques again, but rather to discuss the physical interpretation of the results obtained to date by these techniques, and to describe recent results which go beyond the diffusion approximation. The result of the calculation of the field-field correlation[20] for backscattering light from a half-space may be expressed by the integral

$$\Gamma_1(t) \equiv \langle E(t)E^*(0)\rangle \sim \int_0^\infty dz\, e^{-z/l}\int_0^\infty dz' e^{-z'/l}\int d^2\rho L(\rho,z,z';\mathbf{k},\mathbf{k}';t) . \tag{2.12}$$

The physical interpretation of this integral is summarized by Fig. 1. The incident light with wave vector $\mathbf{k}'$ enters the medium and is initially scattered at the point $\mathbf{r}'$. The exponential factors denote the attenuation of the coherent field in the medium, while the transport kernel $L(\mathbf{r},\mathbf{r}';\mathbf{k},\mathbf{k}';t) = L(\rho,z,z';\mathbf{k},\mathbf{k}';t)$ describes the specific intensity of light at $\mathbf{r}$ with wave vector $\mathbf{k}$, for multiple scattering of waves from $\mathbf{r}'$ with incident wave vector $\mathbf{k}'$. Here, $\rho=(x,y)$ is the separation between $\mathbf{r}$ and $\mathbf{r}'$ in the plane parallel to the boundary. A precise definition of this function in terms of Green's functions is given in Sec. IV. The integral then adds contributions from all possible initial and final scattering points. For isotropic scattering, L is independent of the initial and final wave vectors $\mathbf{k}'$ and $\mathbf{k}$, since the individual scattering events are independent of the transfers $\mathbf{q}_j$. It is well known that the diffuse intensity ($t=0$) at $\mathbf{r}$ from a source at $\mathbf{r}'$ in an infinite medium varies inversely with separation

$$L(\mathbf{r},\mathbf{r}') = \frac{3}{l^3}\frac{1}{|\mathbf{r}-\mathbf{r}'|} . \tag{2.13}$$

The Green's function techniques are useful in calculating

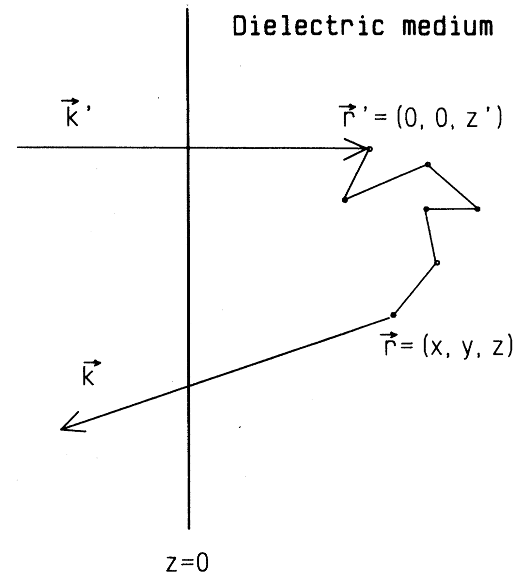

FIG. 1. A typical multiple-scattering path. The incident wave with wave vector $\mathbf{k}'$ begins to scatter at $\mathbf{r}'=(0,0,z')$. The kernel $L(\mathbf{r},\mathbf{r}';\mathbf{k},\mathbf{k}';t)$ describes the transport of the field from $\mathbf{r}'$ to $\mathbf{r}$ within the medium. The coherent field from $\mathbf{r}=(x,y,z)$ is then observed as the reflected light.

the Fourier transform of this function with respect to the separation variable $\mathbf{r}-\mathbf{r}'$:

$$L(\mathbf{K}) = \int d^3r e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}')}L(\mathbf{r}-\mathbf{r}') = \frac{4\pi c}{l^2}\frac{1}{DK^2} , \tag{2.14}$$

where $D=cl/3$ is the diffusion constant of the light in three dimensions.

Both Eqs. (2.13) and (2.14) exhibit poles as $|\mathbf{r}-\mathbf{r}'|\to 0$ and $K^2 \to 0$, respectively. One of these poles is physical, while the other is unphysical and is responsible, in part, for the failure of the diffusion approximation. The divergence of the pole in Eq. (2.14) in the long wavelength limit ($K\to 0$) leads to classical diffusion, described in real space by Eq. (2.13), which is infinite in range as the power-law behavior has no characteristic length scale. In contrast, the nonintegrability of $L(K)$ in dimensions $d \geq 2$ for short wavelengths ($K\to\infty$) leads to the unphysical pole of Eq. (2.13) as the separation from the source becomes small. Equation (2.13) is only valid for $|\mathbf{r}-\mathbf{r}'| \gg l$. This pole overestimates the contribution of shorter paths to the scattered intensity.

If the isotropically scattering particles are themselves diffusing in the medium with self-diffusion coefficient D_S, then the Fourier transform of the dielectric correlation becomes

$$B(\mathbf{q},t) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}}B(\mathbf{r},t) = B(\mathbf{q},0)e^{-q^2D_St} . \tag{2.15}$$

[The precise relationship between $B(q,t)$ and the dynamic structure factor is given in Sec. III.] Physically, the above simply says that large transfers q lead to faster decay of correlations due to the phase factors $e^{i\mathbf{q}\cdot[\mathbf{r}(t)-\mathbf{r}(0)]}$

described above. This leads to[20] an expression for $L(\mathbf{K})$ in which the pole of Eq. (2.14) has been rounded off:

$$L(K,t)=\frac{4\pi c}{l^2}\frac{1}{DK^2+6(t/\tau_0)(c/l)} . \tag{2.16}$$

Here we have made the adiabatic approximation that the velocities of the scattering particles are negligible compared to the speed of light. From this we obtain

$$L(\mathbf{r}-\mathbf{r}',t)=\frac{3}{l^3}\frac{1}{|\mathbf{r}-\mathbf{r}'|}e^{-\sqrt{6t/\tau_0}|\mathbf{r}-\mathbf{r}'|/l} , \tag{2.17}$$

which is simply a statement that longer paths (for which $|\mathbf{r}-\mathbf{r}'|$ is typically larger) lose phase coherence more rapidly. The above is still valid only for $|\mathbf{r}-\mathbf{r}'|\gtrsim l \gg \lambda$, and for isotropic scattering. For anisotropic scattering, l in Eq. (2.17) must be replaced with l^*. This demonstrates the precise equivalence of the simple physical arguments leading to Eq. (2.8) and the formal transport theory within the diffusion approximation. The advantage of the formal theory will become apparent in Sec. IV, where we demonstrate how it may be generalized to incorporate spatial correlations in the disorder and hence nondiffusive propagation. We also show in Sec. VI how this treatment may be generalized to include polarization effects. The expressions above have also assumed an infinite scattering medium. Proper treatment must be given to the effects of boundaries. We shall choose the approximate boundary conditions that the diffuse intensity vanishes at an extrapolation distance $z_b \simeq 0.7l^*$ outside of the medium.[21] This may be accomplished by the method of images. For the case of transmitted light through a slab of width W, it has been shown that the correlation function obtained from Eq. (2.17) is in good agreement with experimental data.[17,20,22] In particular, for thick slabs ($W \gg l^*$), the data asymptotically follows an exponential

$$\Gamma_{\text{trans}} \sim e^{-\sqrt{6t/\tau_0}W/l^*} . \tag{2.18}$$

For backscattered light, however, both of the above treatments fail at long times ($t \sim \tau_0$) for the same reason—they fail to properly treat short paths. It is such short paths which dominate at long times. For isotropic scattering, the diffusion propagator of Eq. (2.17) above leads by the method of images to a correlation function (for small t/τ_0)

$$\Gamma_1(t) \propto \int_0^\infty dz\, e^{-z/l}\int_0^\infty dz' e^{-z'/l}\int d^2\rho \left[\frac{\exp\{-\sqrt{6t/\tau_0}[\rho^2+(z-z')^2]^{1/2}/l\}}{[\rho^2+(z-z')^2]^{1/2}} - \frac{\exp\{-\sqrt{6t/\tau_0}[\rho^2+(z+z'+2z_b)^2]^{1/2}/l\}}{[\rho^2+(z+z'+2z_b)^2]^{1/2}}\right] , \tag{2.19}$$

where we have taken the extrapolation distance $z_b \simeq 0.7l$. We have mentioned an analogy that exists between the decay of the autocorrelation function and the coherent backscattering peak as a function of angle.[18,19] This may be seen beginning with the expression for the coherent backscattering peak

$$C(\theta) \propto \int_0^\infty dz\, e^{-z/l}\int_0^\infty dz' e^{-z'/l}\int d^2\rho \left[\frac{1}{[\rho^2+(z-z')^2]^{1/2}} - \frac{1}{[\rho^2+(z+z'+2z_b)^2]^{1/2}}\right] e^{i\mathbf{q}\cdot\boldsymbol{\rho}} . \tag{2.20}$$

Here $q = k_0 \sin\theta$, and θ is the angle between incident and scattered wave vectors, which is assumed to be small.[14] The integrals over the two-dimensional separation vector $\boldsymbol{\rho}$ may be done analytically.[23] In both of the cases above, this integral may be written as

$$\int d^2\rho \frac{e^{-\eta(\rho^2+a^2)^{1/2}}}{(\rho^2+a^2)^{1/2}}e^{i\mathbf{q}\cdot\boldsymbol{\rho}} = 2\pi\frac{e^{-(q^2+\eta^2)^{1/2}|a|}}{(q^2+\eta^2)^{1/2}} . \tag{2.21}$$

In Eq. (2.19) $\eta=\sqrt{6t/\tau_0}\,l^{-1}$ and $q=0$. In Eq. (2.20) $\eta=0$ and $q = k_0\theta$ for small angles. This leads to an identification of the two-dimensionless parameters

$$(2\pi l/\lambda)\theta \leftrightarrow \sqrt{6t/\tau_0} .$$

In other words, Eqs. (2.19) and (2.20) lead to the same decay of Γ and C when plotted versus $\sqrt{6(t/\tau_0)}$ and $(2\pi l/\lambda)\theta$. This analogy is strictly true only of scalar waves, as the polarization dependence of the coherent backscattering cone is quite different from that of the autocorrelation function. The analogy should be nearly true, however, for highly anisotropic scattering where the polarization dependence is weak. We shall return to this in Sec. VI. The resulting integrals of Eqs. (2.19) and (2.20) are

$$\Gamma_1(t) \sim \frac{1}{(1+\sqrt{6t/\tau_0})^2} \times \left[1+\frac{1}{\sqrt{6t/\tau_0}}\left(1-e^{-(\sqrt{6t/\tau_0})2z_b/l}\right)\right] , \tag{2.22}$$

and

$$C(\theta) \sim \frac{1}{(1+k_0 l\theta)^2}\left[1+\frac{1}{k_0 l\theta}\left(1-e^{-(k_0 l\theta)2z_b/l}\right)\right] . \tag{2.23}$$

The result of Eq. (2.22) is shown in Fig. 2(a). At long times, the calculated correlation function deviates dramatically from the data, which has been shown[17] to follow an exponential in $\sqrt{t/\tau_0}$:

$$\Gamma_1(t) = e^{-\gamma\sqrt{6t/\tau_0}} . \tag{2.24}$$

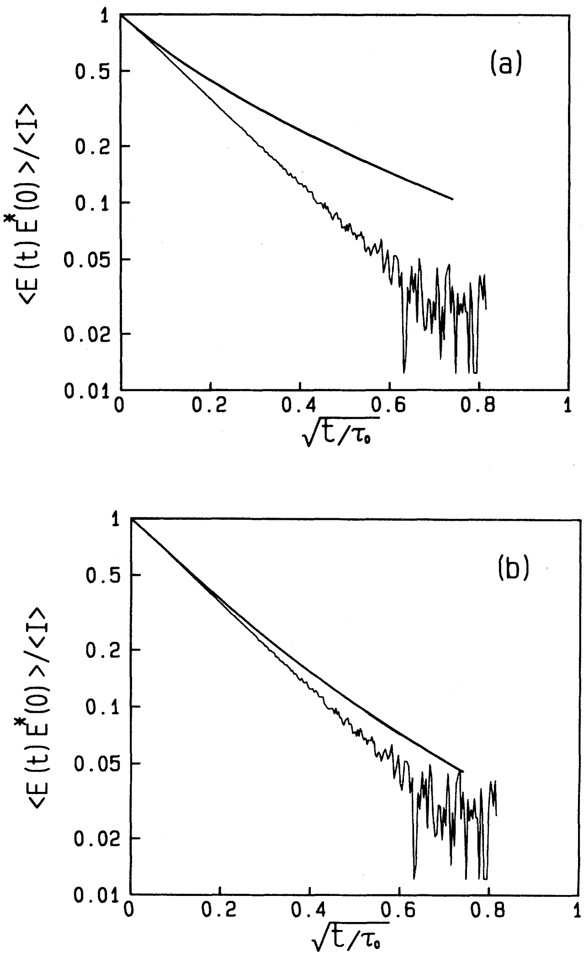

FIG. 2. (a) The autocorrelation function in the scalar white-noise model for isotropic scattering deviates dramatically from the observed nearly straight-line exponential behavior. At long times $t\sim\tau_0$, the overestimate of short paths leads to a much slower decay than is observed. (b) The simple correction derived in Sec. V improves the agreement with the observed exponential behavior. Physically, this is due to a more realistic treatment of short paths.

The deviation is due to the overestimate of the contribution of short paths, which decay very slowly. The treatment summarized by Eq. (2.4) may be improved by cutting off short paths. Within the diffusion approximation, this corresponds to modifying the weight $P(s)$ given to short paths. A fit to the data may also be obtained by forcing the light to begin diffusing from a point approximately l^* within the medium,[17] while retaining the same function $P(s)$. A clear theoretical understanding of the nature of the propagation of light over short, nearly ballistic paths is necessary in order to make this more rigorous. It is the purpose of Secs. IV and V to derive from first principles a physically well-motivated generalization of the diffusion picture, by obtaining the form of the transport kernel L of Eq. (2.12) which is capable of correctly interpolating between ballistic and diffusive propagation.

The parameter γ in Eq. (2.24) is found to be about 2 experimentally. We may define a *slope* (γ) for the decay of the theoretical autocorrelation function by

$$\Gamma_1(t)\sim e^{-\gamma\sqrt{6t/\tau_0}}\sim 1-\gamma\sqrt{6t/\tau_0}\ , \qquad (2.25)$$

for small t. Similarly, we define a slope for the coherent backscattering cone by

$$C(\theta)\sim 1-\gamma k_0 l\theta\ . \qquad (2.26)$$

This slope is simply the inverse of the angular width of the cone in units of $\lambda/(2\pi l)$. By Eqs. (2.22) and (2.23) these slopes are both $\gamma\simeq 2.4$. For anisotropic scatterers, say particles of radius $a\gtrsim\lambda$, the integrals of Eq. (2.12) are modified by simply replacing l by the transport mean free path l^* in the integral over $\boldsymbol{\rho}$. The scattering of the coherent field, however, is still characterized by the mean free path l. In the limit of large l^*/l, the scattering of the coherent field is restricted to the surface of the medium, i.e., $z,z'\ll l^*$. If we choose the approximate boundary condition that the diffuse intensity vanishes at a distance $z_b\simeq 0.7l^*$ outside of the medium,[21] then for example, the coherent backscattering peak is given by

$$C(\theta)\sim 1-\frac{z_b}{l^*}k_0 l^*\theta\ , \qquad (2.27)$$

for small angles. The slope $\gamma\simeq 0.7$ in Eq. (2.27), while a derivation of the coherent backscattering peak from transport theory[24] yields a more realistic slope of 1.7, which is still smaller than the value of about 2 found experimentally.[17] This discrepancy is due to an incorrect treatment of the contribution of short paths, both in Eqs. (2.19), (2.20), and in Ref. 24. Although the *absolute* rate of decay of C and Γ_1 is determined correctly by the diffusion approximation, the overestimate of the intensity contributed by short paths has made the slope γ (or the *relative* decay) too small.

In Sec. VI we derive a simple correction to Eq. (2.17) valid for intermediate distances $|\mathbf{r}-\mathbf{r}'|\sim l^*$ and for $l^*\gg l$. As shown in Fig. 2(b), the resulting expression for the autocorrelation function is in better agreement with the measured autocorrelation function. By the analogy above, we may expect that the similar correction to Eq. (2.20) will account for the coherent backscattering peak at large angles. In addition, the calculated slopes "γ" for $\Gamma(t)$ and $C(\theta)$ are approximately 2, in agreement with experiments.

III. INTERACTING SPHERES

The derivation of Eq. (2.4) assumed that the scattering particles were small and uncorrelated. In reality the amplitude for scattering with wave-vector transfer $\mathbf{q}$ from a point $\mathbf{r}$ within the medium is proportional to the Fourier transform of the dielectric fluctuation. The total scattered field from n scattering events may then be written as

$$E(t)\propto\int_{\{\mathbf{r}_j\}}\prod_{j=1}^{n}\epsilon'(\mathbf{r}_j,t)e^{i\mathbf{r}_j\cdot\mathbf{q}_j}\ , \qquad (3.1)$$

where the integrals over $\mathbf{r}_j$ add contributions of light scattered from all points within the medium. The dependence of E on both static and dynamic correlations within the medium is contained in the fluctuation ϵ', which depends upon the specific configuration of scattering particles. Up to a shift in $\bar{\epsilon}$ in Eq. (2.10), the fluctuation field $\epsilon'(\mathbf{r},t)$ due to N identical particles located at $\mathbf{x}_1(t),\ldots,\mathbf{x}_N(t)$ is

$$\epsilon'(\mathbf{r},t)=\sum_{\alpha=1}^{N} b(\mathbf{r}-\mathbf{x}_\alpha(t)) = \int_{\mathbf{x}} b(\mathbf{r}-\mathbf{x})\sum_{\alpha}\delta(\mathbf{x}-\mathbf{x}_\alpha(t)) , \tag{3.2}$$

where $b(\mathbf{r})$ represents the dielectric constant of an individual particle centered at the origin. For simple spherical particles of radius a, this is given by

$$b(\mathbf{r})=\begin{cases} b_0, & \text{if } r\le a , \\ 0, & \text{otherwise} . \end{cases} \tag{3.3}$$

In the limit that $a\to 0$, $b(\mathbf{r})$ is an approximation to the δ function and Eq. (3.1) reduces to the expression in Eq. (2.1):

$$E(t)\sim \exp\left[i\sum_j \mathbf{q}_j\cdot\mathbf{r}_j(t)\right] , \tag{3.4}$$

where $\mathbf{r}_j$ represent positions of just n of the scattering particles.

In deriving Eq. (2.4) we considered only the interference between scattering paths which involved the same scattering particles and the same transfers $\mathbf{q}_j$, in the same order. Corrections to this (from interference between different scattering paths) are of order $(k_0 l)^{-1}$ and smaller. [This is because the intermediate plane-wave states have wave vectors $\mathbf{k}_j$, which are uncertain by an amount of order l^{-1}. Thus, for example, in paths which differ only by a transposition $\mathbf{q}_j\leftrightarrow\mathbf{q}_{j+1}$, the phase space available to the intermediate state $\mathbf{k}_j$ is restricted to a solid angle of order $(k_0 l)^{-1}$.] In the limit of weak scattering these terms vanish, and the generalization of Eq. (2.4) to include correlations is

$$\langle E(t)E^*(0)\rangle \propto \sum_{n=1}^{\infty}\left\langle\!\!\left\langle \sum_{j=1}^{n}\int_{\mathbf{r}_j,\mathbf{r}'_j}\epsilon'(\mathbf{r}_j,t)\epsilon'(\mathbf{r}'_j,0)e^{i\mathbf{q}_j\cdot(\mathbf{r}_j-\mathbf{r}'_j)}\right\rangle\!\!\right\rangle . \tag{3.5}$$

Here the average $\langle\langle\cdot\rangle\rangle$ denotes the ensemble average $\langle\ \rangle_{\text{ens}}$ over all configurations of ϵ' as well as an average $\langle\ \rangle_q$ over all possible transfers $\{\mathbf{q}_j\}$. For scattering from discrete particles in suspension, the ensemble average assumed in this derivation corresponds to an average of the measured autocorrelation function over all possible configurations of the scattering particles. In colloidal liquids, for example, this ensemble average is equivalent to a time average, since, given sufficient time, each particle will move throughout the liquid and the full configuration space will be spanned. In colloidal glasses, gels, and crystals, the motions of individual particles are restricted about some mean configuration, which is stable.[25] In experiments, the ensemble average may be performed by moving the sample many times, in order to probe various members of the ensemble.[19] This requires that the sample be of linear dimension much larger than the length of correlations within the medium, e.g., for a crystal, the sample must be much larger than the size of an individual grain. We shall also assume Gaussian statistics of the fluctuations ϵ', which allows us to factor the ensemble average of the $2n$-fold product of fields ϵ' in Eq. (3.5) into pair correlations. This is valid when the number of scattering particles is large. With these assumptions, Eq. (3.5) is equivalent to the sum of ladder diagrams (see Sec. IV) for weak scattering ($l\gg\lambda$):

$$\langle E(t)E^*(0)\rangle \propto \sum_{n=1}^{\infty}\left\langle \prod_{1}^{n}\int_{\mathbf{r}_j}\langle\epsilon'(\mathbf{r}_j,t)\epsilon'(0,0)\rangle_{\text{ens}}e^{i\mathbf{q}_j\cdot\mathbf{r}_j}\right\rangle_q . \tag{3.6}$$

Here we have used the translation invariance of

$$\langle\epsilon'(\mathbf{r},t)\epsilon'(\mathbf{r}',0)\rangle_{\text{ens}} ,$$

which is ensured by the ensemble average, in order to pick out the only nonzero Wick contractions. The integrals over $\mathbf{r}_j$ simply yield the Fourier transform of the pair correlation, or the dynamic structure factor $S(q,t)$, in the following way. Using Eq. (3.2), the integrals can be evaluated

$$\int_{\mathbf{r},\mathbf{x},\mathbf{x}'} b(\mathbf{r}-\mathbf{x})b(\mathbf{x})\left\langle\sum_{\alpha\beta}\delta(\mathbf{x}-\mathbf{x}_\alpha(t))\delta(\mathbf{x}'-\mathbf{x}_\beta(0))\right\rangle e^{i\mathbf{q}\cdot\mathbf{r}}=N|b(q)|^2\left\langle\frac{1}{N}\sum_{\alpha\beta}e^{i\mathbf{q}[\mathbf{x}_\alpha(t)-\mathbf{x}_\beta(0)]}\right\rangle , \tag{3.7}$$

where we have again used translation invariance. The first term, $|b(q)|^2$, is the form factor (to be derived in Sec. VI) and

$$\left\langle\frac{1}{N}\sum_{\alpha\beta}e^{i\mathbf{q}\cdot[\mathbf{x}_\alpha(t)-\mathbf{x}_\beta(0)]}\right\rangle_{\text{ens}}$$

is the dynamic structure factor $S(q,t)$:

$$B(\mathbf{q},t)\equiv k_0^4\int_{\mathbf{r}}\langle\epsilon'(\mathbf{r},t)\epsilon'(0,0)\rangle e^{i\mathbf{q}\cdot\mathbf{r}} = k_0^4 N|b(q)|^2 S(q,t) . \tag{3.8}$$

With this, Eq. (3.5) becomes

$$\langle E(t)E^*(0)\rangle \propto \sum_n \langle B(\mathbf{q},t)\rangle_q^n . \tag{3.9}$$

The average $\langle\ \rangle_q$ is over all transfers $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ between physical states ($k=k'=k_0$). For large particles, the form factor emphasizes small transfers, so that

$$4\pi\langle B(\mathbf{q},t)\rangle_q=2\pi\int_0^{\pi}\sin\theta\, d\theta\, B(2k_0\sin(\theta/2),t)$$
$$\simeq 2\pi\int_0^{\infty}\theta d\theta B(k_0\theta,t)\ . \tag{3.10}$$

Here we have taken the wave-vector transfers $\mathbf{q}_j$ to be independent of each other. This is true only of long paths. At $t=0$, the product $\prod_j \langle B(\mathbf{q}_j,0)\rangle$ simply gives the weight $P(n)$ of paths of length n contributing to the total scattered intensity. Thus the product

$$\prod_1^n \left[\frac{\langle B(\mathbf{q},t)\rangle}{\langle B(\mathbf{q},0)\rangle}\right]$$

describes the dephasing of the scattered light with time

$$\langle E(t)E^*(0)\rangle \propto \sum_n P(n)\left[\frac{\langle B(\mathbf{q},t)\rangle}{\langle B(\mathbf{q},0)\rangle}\right]^n$$
$$=\sum_n P(n)\exp\left[n\ln\left[\frac{\langle B(\mathbf{q},t)\rangle}{\langle B(\mathbf{q},0)\rangle}\right]\right]\ . \tag{3.11a}$$

This is the generalization of Eq. (2.4), which is valid for large n. When n is large, the ratio

$$\left[\frac{\langle B(\mathbf{q},t)\rangle}{\langle B(\mathbf{q},0)\rangle}\right]$$

must be near unity in order to give an appreciable contribution to the autocorrelation function. An approximation to the logarithm gives

$$\langle E(t)E^*(0)\rangle \propto \sum_n P(n)\exp\left[-n\left[1-\frac{\langle B(\mathbf{q},t)\rangle}{\langle B(\mathbf{q},0)\rangle}\right]\right]\ . \tag{3.11b}$$

This suggests a simple generalization of Eq. (2.4), in which we replace

$$2\frac{tl}{\tau_0 l^*}\rightarrow\left[1-\frac{\langle B(\mathbf{q},t)\rangle}{\langle B(\mathbf{q},0)\rangle}\right]\ . \tag{3.12}$$

Actually, the former expression is just the self-diffusion limit of the latter. Equation (3.11) corresponds to the diffusive mode of propagation of the light, since it exhibits no dependence upon the initial and final wave vectors. In Sec. IV and in Appendix B, we discuss the nondiffusive contributions of the scattered light.

A large body of literature exists on the theoretical and experimental determination of the dynamic structure factor $S(q,t)$ for colloids.[26] The dynamic structure factor $S(q,t)$ is defined by the following sum over all pairs of particles:

$$S(q,t)=\left\langle\frac{1}{N}\sum_{\alpha\beta}e^{i\mathbf{q}\cdot[\mathbf{x}_\alpha(t)-\mathbf{x}_\beta(0)]}\right\rangle_{\text{ens}}\ , \tag{3.13a}$$

while the *single*-particle propagator is the diagonal part of this

$$G(q,t)=\left\langle\frac{1}{N}\sum_{\alpha}e^{i\mathbf{q}\cdot[\mathbf{x}_\alpha(t)-\mathbf{x}_\alpha(0)]}\right\rangle_{\text{ens}}$$
$$\simeq e^{-W(t)q^2}\ . \tag{3.13b}$$

Here $6W(t)=\langle[\mathbf{x}(t)-\mathbf{x}(0)]^2\rangle$ is the mean-square particle displacement as a function of time.[27] (This propagator for motion of individual scattering particles is not to be confused with the single-photon Green's functions discussed above.) We shall presently consider two important limits. First, we consider self-diffusion of the scattering particles. For dilute, noninteracting spheres, the dynamic structure factor may be approximated by the single-particle self-diffusion propagator

$$B(q,t)=k_0^4 N|b(q)|^2 e^{-q^2 D_s t}\ . \tag{3.14}$$

In this case, the small time $[(tl/\tau_0 l^*)\ll 1]$ limit of Eq. (3.11) is precisely Eq. (2.4), where the average $\langle q^2\rangle$ is weighted by the form factor $|b(q)|^2$. The simple results of Sec. II are recovered in this case.

Another important limiting case is that of particles which interact strongly (e.g., via Coulomb repulsion) to form a colloidal glass or crystal. As in solids, the particles will vibrate about their mean positions subject to Brownian motion in the fluid. If the interparticle spacing is large, then the vibrations may be considered to be independent of each other. (In addition, due to the viscosity of the fluid, phononlike modes will be strongly overdamped.) For large transfers q (corresponding to distances smaller than the mean interparticle spacing), only the diagonal terms ($\alpha=\beta$) in Eq. (3.13a) survive. The average over $S(q,t)$ involves an integral in Eq. (3.10) with measure

$$b^2[2\sin(\theta/2)]\sin\theta\, d\theta\ ,$$

which gives weight primarily to transfers $q\sim 1/a$. Thus, if the interparticle spacing is much larger than the wavelength and particle size, we may approximate

$$S(q,t)\simeq G(q,t)\ . \tag{3.15}$$

By Eq. (3.13b) this leads to

$$\langle E(t)E^*(0)\rangle\propto\sum_n P(n)e^{-n\langle q^2\rangle W(t)}\ , \tag{3.16}$$

where the average $\langle q^2\rangle$ is weighted by the form factor. For long paths, the scattered light is still diffusive and hence $P(n)$ may be approximated by Eq. (2.5). The resulting autocorrelation function is then

$$\Gamma_1(t)\simeq e^{-\gamma[6W(t)k_0^2]^{1/2}}\ . \tag{3.17}$$

Thus, in experiments on colloidal glasses or crystals one can measure the mean-square displacement $W(t)$ as a function of time,[19] provided that the interparticle spacing is large.

IV. FORMAL SOLUTION OF THE TRANSPORT EQUATION

In this section we derive from first principles a solution to the transport equation in a random medium with a general correlation function $B(\mathbf{q},t)$ defined in Eq. (2.11). This solution yields a transport kernel $L(\mathbf{r},\mathbf{r}';\mathbf{k},\mathbf{k}';t)$ [see Eq. (2.12)] for the specific intensity of light at $\mathbf{r}$ with wave vector $\mathbf{k}$, given a source at $\mathbf{r}'$ with incident wave vector $\mathbf{k}'$. This leads to a new set of functions $\psi_\alpha(\mathbf{k})$ for $\alpha=0,1,2,3,\ldots$, which describe the spectral content of the wave in the random medium. Each of these functions is highly peaked about $|\mathbf{k}|=k_0$, with characteristic width given by l^{-1}. Here $k_0=(2\pi/\lambda)$, where λ is the wavelength of light. The index α labels the angular-momentum component of the energy density. In general, for an incident plane wave impinging on a dielectric half-space, the specific intensity is decomposed into an infinite series of angular-momentum components with characteristic decay lengths. In the diffusion approximation only the isotropic function $\psi_0(\mathbf{k})$ is retained.

In this section we demonstrate that the crossover from ballistic propagation on short length scales to diffusive propagation on long length scales is obtained by replacing the propagator of Eq. (2.14) by a sum over all the angular-momentum components α:

$$\frac{c\psi_0(\mathbf{k})\psi_0^*(\mathbf{k}')}{l[2(t/\tau_0)+DK^2]}\to\sum_\alpha\frac{\psi_\alpha(\mathbf{k})\psi_\alpha^*(\mathbf{k}')}{\lambda_\alpha(K,t)} . \tag{4.1}$$

Here

$$\lambda_0(K,t)\simeq 2\frac{t}{\tau_0}+\frac{l}{c}DK^2 ,$$

and for $\alpha>0$ and small K,

$$\lambda_\alpha(K,t)\simeq\lambda_\alpha^0+\lambda_\alpha''K^2+\cdots . \tag{4.2}$$

The expansion coefficients define length scales $(\lambda_\alpha''/\lambda_\alpha^0)^{1/2}$ over which the αth angular-momentum component decays exponentially with distance K^{-1}. This result is derived from a linear integral equation which the transport kernel satisfies, without recourse to the field theoretic analysis of Ref. 15. A simple physical interpretation of this result in terms of the photon trajectories is deferred until Sec. V.

The derivation of the diffusion propagator by Green's function techniques in an isotropically scattering medium has been discussed by a number of authors.[11,13,14] The specific intensity $J(\mathbf{R},\mathbf{k})$ of radiation at $\mathbf{R}$ and with wave vector $\mathbf{k}$ can be related to the light $J^0(\mathbf{R},\mathbf{k}')$ incident at $\mathbf{R}'$ with wave vector $\mathbf{k}'$:

$$J(\mathbf{R},\mathbf{k})=\int\Gamma(\mathbf{R}-\mathbf{R}';\mathbf{k},\mathbf{k}')J^0(\mathbf{R}',\mathbf{k}') . \tag{4.3}$$

This expresses the linear response of the scattering medium to incident light with wave vector $\mathbf{k}'$. The response is determined by the averaged two-particle propagator

$$\Gamma(\mathbf{R}-\mathbf{R}';\mathbf{k},\mathbf{k}')=\int_{\mathbf{r},\mathbf{r}'}e^{-i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}'\cdot\mathbf{r}'}\left\langle G^R\left[\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{R}'+\frac{\mathbf{r}'}{2}\right]G^A\left[\mathbf{R}'-\frac{\mathbf{r}'}{2},\mathbf{R}-\frac{\mathbf{r}}{2}\right]\right\rangle . \tag{4.4}$$

An abbreviated notation has been used for the spatial integration: $\int_\mathbf{r}\equiv\int d\mathbf{r}$. Similarly, below we shall abbreviate wave-vector integrals:

$$\int_\mathbf{k}\equiv\int d\mathbf{k}/(2\pi)^3 .$$

The one-particle Green's functions G^R and G^A appearing in Eq. (4.4) are the retarded and advanced exact solutions to the wave equation Eq. (2.10) with a specific configuration of the scattering particles [i.e., a given dielectric fluctuation $\epsilon'(x)$] and a fixed frequency $\omega_0=ck_0/(\bar{\epsilon})^{1/2}$:

$$\{\nabla^2+(\omega_0^2/c^2)[\bar{\epsilon}+\epsilon'(\mathbf{x})]\}G(\mathbf{x},\mathbf{x}')=-\delta(\mathbf{x}-\mathbf{x}') . \tag{4.5}$$

We have neglected the time dependence of the dielectric fluctuations (or, equivalently, the velocities of the scattering particles). This adiabatic approximation is valid for particle velocities much smaller than the wave velocity, c. This is a good approximation for light scattering. The product of Green's functions in Eq. (4.4) is then ensemble averaged over all possible realizations of ϵ'. We will calculate the Fourier transform of Eq. (4.4) with respect to $\mathbf{R}$:

$$\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K})\equiv\int_\mathbf{R}e^{-i\mathbf{K}\cdot\mathbf{R}}\Gamma(\mathbf{R};\mathbf{k},\mathbf{k}') . \tag{4.6}$$

For isotropic scattering, a diffusion approximation may be obtained by summing the ladder diagrams in a perturbation expansion in the scattering potential. In this approximation, the scattered part of Γ is independent of incident and final wave vectors $\mathbf{k}'$ and $\mathbf{k}$, with the result given by Eq. (2.14). This derivation involves an expansion about small K, and is only valid for $Kl\ll1$. From this we obtain a result for Eq. (4.4) which is valid only for $R\gg l$. For anisotropic scattering, the diffusion result is valid over distances R greater than the transport mean free path l^*. We wish to extend Γ to intermediate distances $R\lesssim l^*$, for which Γ must depend upon the wave vectors $\mathbf{k}$ and $\mathbf{k}'$.

The propagator Γ satisfies the Bethe-Salpeter equation

$$\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K})=G^R\left[k+\frac{\mathbf{K}}{2}\right]G^A\left[k-\frac{\mathbf{K}}{2}\right]\times\left[\delta_{\mathbf{k}\mathbf{k}'}+\int_{\mathbf{k}_1}U_{\mathbf{k}\mathbf{k}_1}(\mathbf{K})\Gamma_{\mathbf{k}_1\mathbf{k}'}(\mathbf{K})\right] , \tag{4.7}$$

where $\delta_{\mathbf{k}\mathbf{k}'}\equiv(2\pi)^3\delta(\mathbf{k}-\mathbf{k}')$ and U is the irreducible vertex function. The single-particle Green's functions appearing in Eq. (4.7) are ensemble averaged. This equation is derived in Ref. 28 for electron transport. It may be viewed as a transport equation for the specific intensity, to which the Twersky integral equation is an approximation.[29] The definition of the irreducible vertex function, U, is illustrated diagrammatically in Fig. 3(a). Diagrams of this class cannot be split by cutting a pair of retarded and advanced Green's functions (solid lines). We shall, however, concern ourselves with the weak scattering approximation to this vertex as illustrated in Fig. 3(b), in which (to lowest order in λ/l) we may take

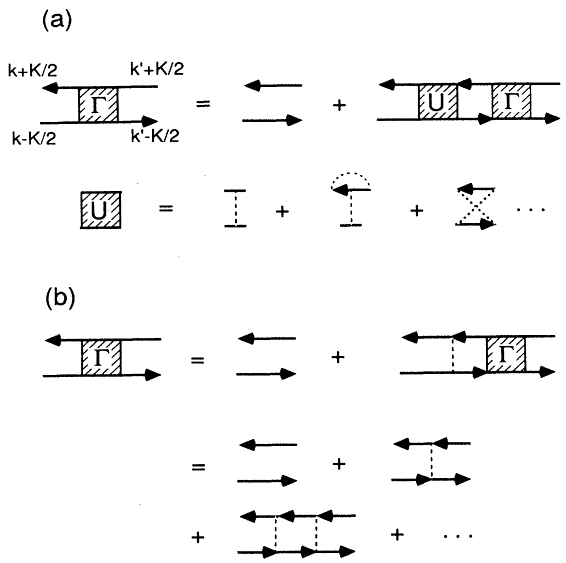

FIG. 3. (a) The Bethe-Salpeter equation is an integral equation relating the transport kernel Γ to the irreducible vertex function U. The irreducible vertex is defined as the sum of all diagrams which do not fall into two distinct parts when a single pair of retarded and advanced propagators (solid lines) are cut. The first few terms in U have been shown. The last of these is one of the "maximally crossed" diagrams. (b) In the weak scattering approximation, only the first term in the expansion of U is included. The Bethe-Salpeter equation then reduces to the sum of ladder diagrams.

$$U_{\mathbf{kk}'}(\mathbf{K}) \simeq k_0^4 \int_{\mathbf{x}} \langle \epsilon'(\mathbf{x},0)\epsilon'(0,0)\rangle e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} \equiv B(\mathbf{k}-\mathbf{k}',0) \ . \tag{4.8}$$

(The next higher correction to this is from the crossed diagrams which describe interference between different diffusion paths. We shall ignore these effects for the present.) In a nondissipative medium we may assume that the dielectric fluctuations are real, as is done in Eq. (4.8). The propagator $\Gamma(\mathbf{R};\mathbf{k},\mathbf{k}')$ in Eq. (4.4) and its Fourier transform satisfying Eq. (4.7) describe the transport of the light at a particular time, and as such involve only equal time correlations of the Green's functions and of ϵ'. More generally, we are interested in the field-field correlation at different times,

$$\langle E(t)E^*(0)\rangle \sim \int \Gamma(\mathbf{R}-\mathbf{R}';\mathbf{k},\mathbf{k}';t)J^0(\mathbf{R}',\mathbf{k}') \ . \tag{4.9}$$

Up to factors describing the decay of the coherent field within the medium, this is the generalization of Eq. (2.12). Here $\Gamma_{\mathbf{kk}'}(\mathbf{K};t)$, obtained as in Eq. (4.6), satisfies

$$\Gamma_{\mathbf{kk}'}(\mathbf{K};t) = G^R\left[k+\frac{\mathbf{K}}{2}\right]G^A\left[k-\frac{\mathbf{K}}{2}\right] \times \left[\delta_{\mathbf{kk}'} + \int_{\mathbf{k}_1} B(\mathbf{k}-\mathbf{k}_1,t)\Gamma_{\mathbf{k}_1\mathbf{k}'}(\mathbf{K};t)\right] \tag{4.10}$$

in the weak scattering limit. Again, we have made an adiabatic approximation. The dielectric fluctuations are assumed to vary slowly with time, and at any instant present a static random potential, which scatters the light. Hence the Green's functions are evaluated at a fixed frequency $\omega_0 = ck_0/(\bar{\epsilon})^{1/2}$. In the coherent potential approximation the single-particle self-energies defined by

$$G^{R/A}(k) = [k_0^2 - k^2 - \Sigma^{R/A}(k)]^{-1} \tag{4.11a}$$

satisfy

$$\mathrm{Im}\Sigma^{R/A}(\mathbf{k}) = \int_{\mathbf{k}'} B(\mathbf{k}-\mathbf{k}',0)\mathrm{Im}G^{R/A}(\mathbf{k}') \ . \tag{4.11b}$$

More generally, in Ref. 28 is derived the Ward identity relating the self-energies to the irreducible vertex

$$\Delta\Sigma_{\mathbf{k}}(\mathbf{K}) = \int_{\mathbf{k}'} U_{\mathbf{kk}'}(\mathbf{K})\Delta G_{\mathbf{k}'}(\mathbf{K}) \ , \tag{4.12a}$$

where

$$\Delta\Sigma_{\mathbf{k}}(\mathbf{K}) = \Sigma^R\left[\mathbf{k}+\frac{\mathbf{K}}{2}\right] - \Sigma^A\left[\mathbf{k}-\frac{\mathbf{K}}{2}\right] \ , \tag{4.12b}$$

and

$$\Delta G_{\mathbf{k}}(\mathbf{K}) = G^R\left[\mathbf{k}+\frac{\mathbf{K}}{2}\right] - G^A\left[\mathbf{k}-\frac{\mathbf{K}}{2}\right] \ . \tag{4.12c}$$

This is valid for anisotropic as well as isotropic scattering. It is the result of particle number conservation, and thus is true in dissipationless media. With the assumption of weak scattering the integral equation of Eq. (4.10) may be represented diagrammatically as in Fig. 3(b). The scattering events with transfers $\mathbf{q}_i$ are represented by the dashed lines, with which we associate the strength $B(\mathbf{q}_i,t)$. The integral equation (4.10) may be rewritten as

$$\int_{\mathbf{k}_1} [\delta_{\mathbf{kk}_1} - f_{\mathbf{k}}(\mathbf{K})B_{\mathbf{kk}_1}(t)]\Gamma_{\mathbf{k}_1\mathbf{k}'}(\mathbf{K};t) = f_{\mathbf{k}}(\mathbf{K})\delta_{\mathbf{kk}'} \ , \tag{4.13}$$

where

$$f_{\mathbf{k}}(\mathbf{K}) \equiv G^R\left[\mathbf{k}+\frac{\mathbf{K}}{2}\right]G^A\left[\mathbf{k}-\frac{\mathbf{K}}{2}\right] \ . \tag{4.14}$$

Here we have abbreviated $B(\mathbf{k}-\mathbf{k}',t)$ as $B_{\mathbf{kk}'}(t)$. From Eq. (4.13) we see that the propagator Γ may be obtained from the inverse of the operator $(\delta - fB)$, provided that the inverse exists:

$$\Gamma_{\mathbf{kk}'}(\mathbf{K};t) = [\delta - f(\mathbf{K})B(t)]^{-1}_{\mathbf{kk}'} f_{\mathbf{k}'} \ . \tag{4.15}$$

The inverse is defined by

$$\int_{\mathbf{k}_1} [\delta - f(\mathbf{K})B(t)]^{-1}_{\mathbf{kk}_1}[\delta_{\mathbf{k}_1\mathbf{k}'} - f_{\mathbf{k}_1}(\mathbf{K})B_{\mathbf{k}_1\mathbf{k}'}(t)] = \delta_{\mathbf{kk}'} \ . \tag{4.16}$$

The precise relationship between Γ in Eqs. (4.9), (4.10), and the generalization of $L_{\mathbf{kk}'}$ in Eq. (2.12) to anisotropic scattering is that

$$\Gamma_{\mathbf{kk}'}(\mathbf{K};t) = \delta_{\mathbf{kk}'}f_{\mathbf{k}} + f_{\mathbf{k}}L_{\mathbf{kk}'}(\mathbf{K};t)f_{\mathbf{k}'} \ , \tag{4.17}$$

or

$$L_{\mathbf{kk}'}(\mathbf{K};t) = B(\mathbf{k}-\mathbf{k}',t) + \int_{\mathbf{k}_1} B(\mathbf{k}-\mathbf{k}_1,t)f_{\mathbf{k}_1}L_{\mathbf{k}_1\mathbf{k}'}(\mathbf{K},t) \ , \tag{4.18a}$$

$$= B(\mathbf{k}-\mathbf{k}',t) + \int_{\mathbf{k}_1} B(\mathbf{k}-\mathbf{k}_1,t)f_{\mathbf{k}_1}B(\mathbf{k}_1-\mathbf{k}',t) + \cdots \ , \tag{4.18b}$$

$$= \int_{\mathbf{k}_1} B(\mathbf{k}-\mathbf{k}_1,t)[\delta - f(\mathbf{K})B(t)]^{-1}_{\mathbf{k}_1\mathbf{k}'} \ . \tag{4.18c}$$

The transport kernel $L(\mathbf{r},\mathbf{r}';\mathbf{k},\mathbf{k}';t)$ in an infinite medium is obtained by inversion of Eq. (2.14):

$$L(\mathbf{r},\mathbf{r}';\mathbf{k},\mathbf{k}';t)=\int_{\mathbf{K}} e^{i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}')}L_{\mathbf{k}\mathbf{k}'}(\mathbf{K};t) \ . \tag{4.19}$$

An expression similar to Eq. (4.18c), but in terms of the operator $(B^{-1}-f)$, can be found in Ref. 15, and in Appendix A. Formally, the inverse can be expressed as a geometric series

$$(\delta-fB)^{-1}_{\mathbf{k}\mathbf{k}'}=\delta_{\mathbf{k}\mathbf{k}'}+f_{\mathbf{k}}B_{\mathbf{k}\mathbf{k}'}+f_{\mathbf{k}}\int_{\mathbf{k}_1}B_{\mathbf{k}\mathbf{k}_1}f_{\mathbf{k}_1}B_{\mathbf{k}_1\mathbf{k}'}+\cdots \ , \tag{4.20}$$

or by Eq. (4.15):

$$\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K};t)=\delta_{\mathbf{k}\mathbf{k}'}f_{\mathbf{k}'}+f_{\mathbf{k}}B_{\mathbf{k}\mathbf{k}'}f_{\mathbf{k}'} +f_{\mathbf{k}}\int_{\mathbf{k}_1}B_{\mathbf{k}\mathbf{k}_1}f_{\mathbf{k}_1}B_{\mathbf{k}_1\mathbf{k}'}f_{\mathbf{k}'}+\cdots \ . \tag{4.21}$$

The first term $\Gamma^0_{\mathbf{k}\mathbf{k}'}(\mathbf{K},t)\equiv\delta_{\mathbf{k}\mathbf{k}'}f_{\mathbf{k}'}(\mathbf{K})$ represents the coherent (unscattered) field. Subsequent terms represent single- and higher-order scattering. Physically, the reason that all terms must be considered is that, in a scattering medium of dimensions much larger than the mean free path l, very long random walks of the scattered waves are possible. Truncating the series after n terms would correspond to scattering in a medium of linear dimension less than $\sqrt{n}\,l$. This series is none other than the sum of ladder diagrams, which is simple to evaluate only for isotropic scattering, where the integration over the intermediate momenta k_j becomes trivial because B is constant. For anisotropic scattering, Eq. (4.20) no longer represents a practical way to calculate Γ. Equation (4.20) does, however, demonstrate the existence of $(\delta-fB)^{-1}$ for any finite K. It can be shown that the series converges for finite K in the weak scattering limit. Physically, this is apparent since only a finite number of scattering events, and hence only a finite number of terms in Eq. (4.20), can occur in any finite volume. Nonzero K values correspond to probing the system in a finite scattering volume of linear dimension K^{-1}.

We may express the operator $(\delta-fB)^{-1}$ in a special representation in terms of eigenfunctions ψ_α and associated eigenvalues λ_α of the operator $(\delta-fB)$:

$$\int_{\mathbf{k}'}[\delta-f(\mathbf{K})B(t)]_{\mathbf{k}\mathbf{k}'}\psi_\alpha(\mathbf{k}')=\lambda_\alpha(\mathbf{K},t)\psi_\alpha(\mathbf{k}) \ , \tag{4.22}$$

with

$$\lambda_\alpha\geq 0 \ . \tag{4.23}$$

The Ward identity above tells us that $\psi_0(\mathbf{k})\equiv\Delta G_{\mathbf{k}}(0)$ is a zero mode of the operator $[\delta-f(0)B(0)]$:

$$\int_{\mathbf{k}'}[\delta_{\mathbf{k}\mathbf{k}'}-f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(0)]\Delta G_{\mathbf{k}'}(0)=0 \ , \tag{4.24a}$$

since

$$\Delta\Sigma_{\mathbf{k}}(0)=\frac{\Delta G_{\mathbf{k}}(0)}{f_{\mathbf{k}}(0)} \ . \tag{4.24b}$$

We may write $\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K};t)$ in terms of these (normalized) eigenfunctions:

$$\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K};t)=\sum_\alpha\frac{\psi_\alpha(\mathbf{k})\psi^*_\alpha(\mathbf{k}')}{\lambda_\alpha(\mathbf{K},t)}f_{\mathbf{k}'} \ . \tag{4.25}$$

We will concern ourselves primarily with the low-lying eigenvalues $\lambda\ll 1$, for which the eigenfunctions are strongly peaked about $k=k_0$. As $f_{k_0}(K)$ decreases with K, the eigenvalues increase quadratically with K:

$$\lambda_\alpha(K,t)=\lambda^0_\alpha(t)+\lambda''_\alpha K^2+\cdots \ . \tag{4.26}$$

In general, the eigenfunctions $\psi_\alpha(\mathbf{k})$ will depend on $\mathbf{K}$ and t as well. For the present we shall take the eigenfunctions for $K=0$ and $t=0$. [For the case of a Gaussian correlation function $B(\mathbf{x})$ a detailed derivation of the eigenfunctions and eigenvalues is given in Appendix A. More general correlation functions $B(\mathbf{x})$ have been considered in Ref. 15. The eigenfunctions and eigenvalues resemble those of a quantum particle bound in a spherically symmetric δ-shell potential.] The K dependence of the eigenvalues $\lambda_\alpha(K)$ of Eq. (4.26) then leads to an expression for $\Gamma(R;\mathbf{k},\mathbf{k}')$:

$$\Gamma(R;\mathbf{k},\mathbf{k}';t)\simeq\frac{1}{4\pi R}\sum_\alpha\frac{\psi_\alpha(\mathbf{k})\psi^*_\alpha(\mathbf{k}')}{\lambda''_\alpha}e^{-[\lambda^0_\alpha(t)/\lambda''_\alpha]^{1/2}R} \ . \tag{4.27}$$

Here and in Eq. (4.25) the $\alpha=0$ mode corresponds to the diffusion approximation. By the Ward identity, and the spherical symmetry of the eigenfunction $\psi_0(\mathbf{k})=\Delta G(\mathbf{k})$, this term in Eq. (4.25) is independent of $\hat{\mathbf{k}},\hat{\mathbf{k}}'$ and yields

$$\Gamma(\mathbf{K},0)\sim\frac{l}{4\pi}\frac{1}{\lambda''_0K^2} \ , \tag{4.28}$$

which is the diffusion approximation of Eq. (2.14). As discussed in Sec. II, this pole as $K\to 0$ is *physical*, in the sense that the diffusion approximation is good in the long-distance limit. In the short-distance limit $[K\gtrsim(l^*)^{-1}]$, however, the other modes $(\alpha>0)$ will become important, as the eigenvalue $\lambda_0(K)$ increases and becomes comparable to λ_1, λ_2, etc. The diffusion pole, as derived above in Eq. (4.28), is due to the vanishing of $\lambda_0(0,0)$. The other modes $(\alpha>0)$ are not important for large distances R, due to the exponential factors: $\exp[-(\lambda^0_\alpha/\lambda''_\alpha)^{1/2}R]$, where $\lambda^0_\alpha\neq 0$. For the correlation function of Eq. (4.9), the $\alpha=0$ mode of Eq. (4.27) reduces to Eq. (2.17), which describes classical diffusion of light

$$\Gamma(R,t)\sim\frac{l}{(4\pi)^2}\frac{1}{\lambda''_0R}e^{-[\lambda^0_0(t)/\lambda''_0]^{1/2}R} \ , \tag{4.29}$$

where $\lambda^0_0(t)/\lambda''_0=6(t/\tau_0)(l^*)^{-2}$ as we shall see in the next section. The "excited states" with eigenvalues λ_α $(\alpha>0)$ describe the crossover to ballistic propagation on short length scales. The eigenfunctions $\psi_\alpha(\mathbf{k})$ will become increasingly dependent upon the direction $\hat{\mathbf{k}}$, so that the products $\psi_\alpha(\mathbf{k})\psi^*_\alpha(\mathbf{k}')$ will lead to a propagator, $\Gamma(\mathbf{R};\mathbf{k},\mathbf{k}';t)$ in Eq. (4.27), which becomes peaked about $\mathbf{k}=\mathbf{k}'$. This peak becomes more pronounced as R decreases, due to the exponential factors $\exp[-(\lambda^0_\alpha/\lambda''_\alpha)^{1/2}R]$. The wave retains its directional character on length scales shorter than l^*, and only for $R\gg l^*$ does the transport kernel become isotropic, as suggested by the classical diffusion model of Sec. II.

V. SCATTERING FROM LARGE PARTICLES

In this section we consider scattering by particles of radius $a \gtrsim \lambda$. If the particles are uncorrelated (e.g., at low concentrations), the averaged dielectric correlation

$$B(\mathbf{x}-\mathbf{y})=k_0^4\langle \epsilon'(\mathbf{x})\epsilon'(\mathbf{y})\rangle \tag{5.1}$$

will have a characteristic width of approximately a. To be more precise, we shall assume uncorrelated spherical scattering particles at random positions $\mathbf{x}_1,\ldots,\mathbf{x}_N$, and with dielectric constant b_0. The dielectric fluctuation due to a single particle at $\mathbf{x}_j$ is then characterized by

$$\epsilon'(\mathbf{x})=b(\mathbf{x}-\mathbf{x}_j)=\begin{cases} b_0, & \text{if } |\mathbf{x}-\mathbf{x}_j|\le a \ , \\ 0, & \text{otherwise} \ . \end{cases} \tag{5.2a}$$

The ensemble average in Eq. (5.1) then corresponds to an integral over the particle positions $\mathbf{x}_1,\ldots,\mathbf{x}_N$:

$$B(\mathbf{x}-\mathbf{y})=k_0^4\sum_{j=1}^{N}\int_{\mathbf{x}_j} b(\mathbf{x}-\mathbf{x}_j)b(\mathbf{x}_j-\mathbf{y}) \ . \tag{5.2b}$$

The form factor is simply proportional to the Fourier transform of this with respect to the relative coordinate $\mathbf{x}-\mathbf{y}$:

$$\begin{aligned} B(\mathbf{q})&=k_0^4N\int_{\mathbf{x}\mathbf{x}_0} e^{-i\mathbf{q}\cdot\mathbf{x}}b(\mathbf{x}-\mathbf{x}_0)b(\mathbf{x}_0) \\ &=k_0^4Nb^2(q) \ , \end{aligned} \tag{5.3a}$$

where

$$b(\mathbf{q})=\int_{\mathbf{r}} e^{-i\mathbf{q}\cdot\mathbf{r}}b(\mathbf{r})=\frac{4\pi}{3}a^3b_0\left[\frac{3j_1(qa)}{qa}\right] . \tag{5.3b}$$

The function j_1 is the first spherical Bessel function. The form factor $b^2(q)$ is a highly peaked function about $q=0$, with width a^{-1}. Thus for $a>\lambda$, the scattering is predominantly in the forward direction, with mean-square scattering angle [determined by the width of $b^2(q)$] given by $\langle\theta^2\rangle\simeq 2/(k_0a)^2$. As the light is repeatedly scattered in the medium, the direction of the light $\hat{\mathbf{k}}$ executes a random walk on the unit sphere with rms step size $\theta_{\text{rms}}\sim 1/(k_0a)$. The number n_r of such steps required to randomize the light is related to a by

$$n_r\langle\theta^2\rangle\sim 1 \ . \tag{5.4}$$

This number n_r is simply the ratio of the transport mean free path l^* to the scattering mean free path l, where

$$\begin{aligned} l/l^* &\equiv \langle 1-\cos\theta\rangle \\ &=\frac{\int_0^\pi \sin\theta\, d\theta\, B(2k_0\sin(\theta/2))(1-\cos\theta)}{\int_0^\pi \sin\theta\, d\theta\, B(2k_0\sin(\theta/2))} \\ &\simeq \frac{2}{(k_0a)^2} \end{aligned} \tag{5.5}$$

for $a\gtrsim\lambda$. Only over distances R large compared with the transport mean free path l^* will the propagator $\Gamma(\mathbf{R};\mathbf{k},\mathbf{k}')$ become independent of $\mathbf{k}$ and $\mathbf{k}'$, due to the randomization of the intermediate wave-vector directions. For shorter distances $R\lesssim l^*$ it too will be peaked about $\mathbf{k}=\mathbf{k}'$, since short scattering paths are unlikely to have randomized $\mathbf{k}$. This angular dependence arises from the eigenfunctions $\psi_\alpha(\mathbf{k})$ for $\alpha>0$.

As we have seen in Sec. III, for interacting particles $B(\mathbf{q},t)$ is the product of the form factor and the dynamic structure factor $S(\mathbf{q},t)$ of the medium. For simple Brownian motion of noninteracting particles, the correlation $B(\mathbf{q},t)$ in Eq. (5.3) becomes the product of the form factor with the single-particle self-diffusion propagator

$$B(\mathbf{q},t)=B(\mathbf{q},0)e^{-q^2D_St} \ . \tag{5.6}$$

We wish to find the eigenfunctions and eigenvalues of Eq. (4.25) in the limit that $a\gg\lambda$. In this limit we will be able to make certain simplifying assumptions, which are valid for intermediate distances R. We also wish to consider the weak scattering regime, for which $l\gg\lambda$. Here the function $f_{\mathbf{k}}(0)$ is highly peaked about the energy shell $|\mathbf{k}|=k_0$. The width of $f_{\mathbf{k}}(0)$ is approximately $1/l$, i.e., $f_{\mathbf{k}}(0)$ is small whenever $|k-k_0|>1/l$. Since $f_{\mathbf{k}}(0)$ describes the coherent propagation of plane-wave states with wave vector $\mathbf{k}$ which have a finite lifetime $\tau=l/c$, this is nothing more than the Heisenberg uncertainty principle. From Eq. (4.22) for low-lying states α, with eigenvalues $\lambda_\alpha\ll 1$, the eigenfunctions ψ_α must also be highly peaked about $k=k_0$. In this case, what is important physically is the angular dependence of ψ_α on $\hat{\mathbf{k}}$ near $k\simeq k_0$. As with any quantum-mechanical bound state in a spherically symmetric potential, the wave function factors into a radial eigenfunction and a spherical harmonic (Y) labeled by total angular momentum α and azimuthal quantum number m. It is shown in Appendix A that for $k_0a\gg1$ and $l\gg\lambda$, the radial wave function for all low-lying eigenfunctions becomes independent of α in the classically forbidden region, and may be approximated by the solution for $\alpha=0$. We denote this function by $\psi_0(k)$. We may approximate these low-lying eigenfunctions by

$$\psi_{\alpha,m}(\mathbf{k})\simeq\sqrt{4\pi}\,\psi_0(k)Y_{\alpha,m}(\hat{\mathbf{k}}) \ , \tag{5.7}$$

where the eigenvalues are independent of m, by the spherical symmetry of the operator

$$[\delta_{\mathbf{k}\mathbf{k}'}-f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(0)] \ .$$

We may evaluate the corresponding eigenvalues as follows:

$$\begin{aligned} \lambda_\alpha(0,0)&=\frac{1}{2\alpha+1}\sum_m\int_{\mathbf{k}\mathbf{k}'}\psi^*_{\alpha,m}(\mathbf{k}) \\ &\qquad\times[\delta_{\mathbf{k}\mathbf{k}'}-f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(0)]\psi_{\alpha,m}(\mathbf{k}') \\ &\simeq\int_{\mathbf{k}\mathbf{k}'}\psi_0^*(\mathbf{k})[\delta_{\mathbf{k}\mathbf{k}'}-f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(0)]\psi_0(\mathbf{k}')P_\alpha(x) \ , \end{aligned} \tag{5.8a}$$

where $x=\cos\theta\equiv\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}'$. The eigenfunctions are slowly varying with $\hat{\mathbf{k}}$ over angles small compared to θ_{rms}, provided that $\alpha\ll\theta_{\text{rms}}^{-1}$. Since B weights small angles $\theta\lesssim\theta_{\text{rms}}$, we may approximate the Legendre polynomials in Eq. (5.8a) by

$$P_\alpha(x) \simeq 1 - P'_\alpha(1)(1-x) ,$$

valid near $x=1$. In this case the eigenvalues may be evaluated

$$\lambda_\alpha(0,0) \simeq \int_{\mathbf{kk}'} \psi_0^*(\mathbf{k})[\delta - f(0)B(0)]_{\mathbf{kk}'}\psi_0(\mathbf{k}) + P'_\alpha(1) \times \int_{\mathbf{kk}'} \psi_0^*(\mathbf{k}) f_{\mathbf{k}}(0) B(\mathbf{k}-\mathbf{k}',0)\psi_0(\mathbf{k}')(1-\cos\theta) = \frac{\alpha(\alpha+1)}{2}\frac{l}{l^*} . \quad (5.8b)$$

Here we have used the fact that, in the weak scattering limit, the functions $f_{\mathbf{k}}$ and $\psi_0(\mathbf{k})$ are highly peaked about $k=k_0$. Thus the integrals in Eq. (5.8b) reduce to a single integral over transfers $\mathbf{q}=\mathbf{k}-\mathbf{k}'$, between wave vectors with $k=k'=k_0$. This can be expressed as an integral over the scattering angle θ, as in Eq. (5.5). By the assumption $\alpha \ll \theta_{\rm rms}^{-1}$ made above, these eigenvalues are indeed much smaller than 1. An individual scattering event changes the direction of propagation only by a small angle of order $\theta_{\rm rms}$. Thus, in order to describe propagation of the waves on the short length scale of l, we must consider α of order $1/\theta_{\rm rms}$. Our restriction to small eigenvalues will be sufficient to describe scattering over intermediate scales $l \ll R \lesssim l^*$. The dependence of the eigenvalues for small times t can similarly be evaluated since

$$B(\mathbf{q},t) \simeq B(\mathbf{q},0)(1-q^2 D_S t) = B(\mathbf{q},0)[1-2t/\tau_0(1-\cos\theta)] . \quad (5.9)$$

By "small times t" we mean

$$1 \gg 2t/\tau_0\langle 1-\cos\theta\rangle = \frac{2tl}{\tau_0 l^*} , \quad (5.10)$$

which is valid even for times $t \sim \tau_0$, in the limit that $a \gg \lambda$. Putting Eq. (5.9) into Eq. (5.8a) yields (see Appendix B)

$$\lambda_\alpha(0,t) \simeq \frac{\alpha(\alpha+1)}{2}\frac{l}{l^*} + 2\frac{t}{\tau_0}\frac{l}{l^*} . \quad (5.11)$$

In Appendix B we calculate the shift $\lambda_0'' K^2$ in the eigenvalue λ_0 with small but finite K. For eigenfunctions $\psi_{\alpha,m}(\mathbf{k})$ which vary slowly with direction $\hat{\mathbf{k}}$, we may expect that the shifts $\lambda''_{\alpha,m}K^2$ in $\lambda_{\alpha,m}$ of Eq. (4.22) are nearly independent of α for the low-lying states. With this assumption, the resulting eigenvalues are

$$\lambda_\alpha(K,t) \simeq \frac{\alpha(\alpha+1)}{2}\frac{l}{l^*} + 2\frac{t}{\tau_0}\frac{l}{l^*} + \tfrac{1}{3} l l^* K^2 , \quad (5.12a)$$

or

$$\lambda_\alpha^0(t) \simeq \frac{\alpha(\alpha+1)}{2}\frac{l}{l^*} + 2\frac{t}{\tau_0}\frac{l}{l^*} \quad (5.12b)$$

and

$$\lambda_\alpha'' \simeq \tfrac{1}{3} l l^* . \quad (5.12c)$$

These eigenvalues depend only on the ratio $l/l^* \equiv \langle 1-\cos\theta\rangle$, and not on the specific choice of the form factor $b^2(q)$, so long as it is a highly peaked function about $q=0$ with width $1/a \ll k_0$. Equation (4.27) then becomes

$$\Gamma(R;\mathbf{k},\mathbf{k}';t) \simeq \frac{3\psi_0(\mathbf{k})\psi_0^*(\mathbf{k}')}{4\pi l l^* R}\sum_\alpha \exp\left[-\left[3\frac{\alpha(\alpha+1)}{2}+6\frac{t}{\tau_0}\right]^{1/2} R/l^*\right] 4\pi \sum_{m=-\alpha}^{\alpha} Y_{\alpha,m}(\hat{\mathbf{k}})Y^*_{\alpha,m}(\hat{\mathbf{k}}')$$
$$= \frac{3\psi_0(\mathbf{k})\psi_0^*(\mathbf{k}')}{4\pi l l^* R}\sum_\alpha \exp\left[-\left[3\frac{\alpha(\alpha+1)}{2}+6\frac{t}{\tau_0}\right]^{1/2} R/l^*\right](2\alpha+1)P_\alpha(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}') . \quad (5.13)$$

Here the function ψ_0 is spherically symmetric, and physically just enforces that $k=k'=k_0$. We shall furthermore take the asymptotic expression for the eigenvalues

$$\lambda_\alpha^0(0) \simeq \frac{\alpha^2}{2}\frac{l}{l^*} . \quad (5.14)$$

Consider the specific intensity (at $t=0$), which by Eq. (5.13) may be written as

$$\Gamma(R;\mathbf{k},\mathbf{k}') \simeq \frac{3}{4\pi l l^* R}\sum_\alpha (2\alpha+1)P_\alpha(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')e^{-\alpha R/\xi} . \quad (5.15)$$

Here $l^*\xi^{-1} = \sqrt{3/2}$. For forward scattering

$$\Gamma(R;\mathbf{k},\mathbf{k}) \simeq \frac{3}{4\pi l l^* R}\sum_\alpha (2\alpha+1)e^{-\alpha R/\xi} \simeq \frac{3}{4\pi l l^* R}\frac{1+e^{-R/\xi}}{(1-e^{-R/\xi})^2} , \quad (5.16)$$

while for backward scattering

$$\Gamma(R;\mathbf{k},-\mathbf{k}) \simeq \frac{3}{4\pi l l^* R}\sum_\alpha (-1)^\alpha(2\alpha+1)e^{-\alpha R/\xi} \simeq \frac{3}{4\pi l l^* R}\frac{1-e^{-R/\xi}}{(1+e^{-R/\xi})^2} . \quad (5.17)$$

The physical interpretation of the result in Eq. (5.17) is clear: the unphysical pole as $R \to 0$ in the white-noise model is now rendered finite. This reduces the contribution of short paths to the reflected intensity. The forward scattering result of Eq. (5.16) also has a simple physical interpretation. As $R \to 0$

$$\Gamma(R;\mathbf{k},\mathbf{k}) \simeq \frac{3}{4\pi l l^* R} 2\left[\frac{\xi}{R}\right]^2 . \quad (5.18)$$

For anisotropic scattering on short length scales R, the wave vectors are confined to a small solid angle $\Delta\Omega$ in the forward direction and the intensity falls off with the square of the distance R:

$$I \sim \frac{4\pi}{\Delta\Omega}\frac{1}{R^2} . \tag{5.19}$$

The scattered wave-vector directions $\hat{\mathbf{k}}$ execute a random walk on the unit sphere with small steps $\theta_{\rm rms}$. After a small number $n = R/l$ of such steps, the solid angle grows linearly with n:

$$\Delta\Omega \simeq n\langle\theta^2\rangle \simeq R/l^* . \tag{5.20}$$

Thus the intensity falls off with the cube of R

$$I \sim \frac{4\pi l^*}{R}\frac{1}{R^2} , \tag{5.21}$$

for small R/l^*, as in Eq. (5.18).

The expression for the propagator Γ in Eq. (5.15) is capable of describing the crossover from isotropic diffusion to the nearly ballistic scattering regime for $R \lesssim l^*$. For $R \gg l^*$, only the s-wave term (corresponding to classical diffusion) in the sum survives, due to the exponential suppression of the higher-angular-momentum components. For shorter paths, with $R \lesssim l^*$, these other terms increase the forward scattering. We cannot, however, expect Eq. (5.15) to be valid for very short distances $R \ll l^*$, since we have made several approximations to the eigenfunctions and eigenvalues of Eq. (4.25) which are valid only for intermediate ($R \lesssim l^*$) and longer distances. [Perhaps the most severe approximation is that the eigenfunctions $\psi_{\alpha,m}(\mathbf{k})$ are independent of $\mathbf{K}$.] To describe propagation over very short distances, exact eigenfunctions and eigenvalues would be necessary. For backward scattering we shall approximate the transport kernel $L(\mathbf{R};\mathbf{k},-\mathbf{k};t)$ by the following simple numerical interpolation formula:

$$L(R;\mathbf{k},-\mathbf{k};t) \sim \frac{3}{l^3 R}\left\{\exp\left[-\left[6\frac{t}{\tau_0}\right]^{1/2} R/l^*\right] - \exp\left[-\left[\frac{1}{2}+6\frac{t}{\tau_0}\right]^{1/2} R/l^*\right]\right\} . \tag{5.22}$$

This is chosen because it exhibits the characteristic removal of short paths from the scattered intensity, which we expect on physical grounds, and agrees numerically with Eq. (5.17) for intermediate and longer distances R, where the above treatment is valid. Equation (5.22) is equivalent to a modified weighting factor

$$P(s) = \left[\frac{c}{4\pi s D}\right]^{3/2} e^{-c|\mathbf{r}-\mathbf{r}'|^2/(4sD)}(1-e^{-s/(6l^*)}) \tag{5.23}$$

in Eq. (2.6). [This equivalence may be obtained by a saddle-point approximation, as in Eq. (2.8) or more rigorously, as in Appendix B.] The more general expression in Eq. (4.27) is equivalent to

$$P(s) = \left[\frac{l}{4\pi s}\right]^{3/2} \sum_{\alpha,m} \frac{\psi_{\alpha,m}(\mathbf{k})\psi^*_{\alpha,m}(\mathbf{k}')}{(\lambda''_{\alpha,m})^{3/2}} \exp\left[-\frac{l|\mathbf{r}-\mathbf{r}'|^2}{4s\lambda''_{\alpha,m}} - \frac{\lambda^0_\alpha s}{l}\right] . \tag{5.24}$$

With the substitution of L in Eq. (5.22) into Eq. (2.19), or Eq. (5.23) into Eq. (2.6), we calculate a slope $\gamma \simeq 2$, in the limit of large scattering particles. Furthermore, as can be seen in Fig. 2(b), this more realistic treatment of the short paths yields better agreement with the measured autocorrelation functions. The remaining discrepancy between the observed autocorrelation function and the theory, at long times, is likely to be an artifact of our large particle approximation. It is probably necessary to consider the $\mathbf{K}$ dependence of the eigenfunctions ψ_α, in order to more rigorously treat the crossover to ballistic propagation. Furthermore, it is apparent that the assumption leading to Eq. (5.12c) is not valid for larger α. This is because the saddle point associated with the αth term in Eq. (5.24) corresponds to a characteristic path length

$$s \sim [l^2/(4\lambda''_\alpha\lambda^0_\alpha)]^{1/2}|\mathbf{r}-\mathbf{r}'| ,$$

which must approach $|\mathbf{r}-\mathbf{r}'|$ for increasingly ballistic paths. Here, $\lambda^0_\alpha \sim 1$, and so $\lambda''_\alpha \sim l^2$. We have also implicitly assumed the same boundary conditions for all nondiffusive modes. More precise boundary conditions must be determined before more quantitative comparison with backscattering experiments is possible.

VI. POLARIZATION DEPENDENCE OF THE AUTOCORRELATION FUNCTION

For very short times t, the correlation function $\Gamma_1(t)$ is dominated by long paths for which the observed photons have lost memory of their incident polarization. Thus the correlation functions $\Gamma_\parallel$ and $\Gamma_\perp$ for parallel and perpendicularly polarized light will initially decay with the same *absolute* rate. The two signals will differ, however, due to unequal contributions of short paths. The intensity of the parallel polarized light will be enhanced, relative to the perpendicular intensity, because the short paths tend not to alter the polarization of the incident light. The decay of correlations due to these short paths will be apparent only at longer times. Thus, the difference $\Gamma_\parallel - \Gamma_\perp$ will be independent of time to first order in $(6t/\tau_0)^{1/2}$. Because of the differing contributions due to short paths, the *slopes* (γ) of $\ln\Gamma_\parallel$ and $\ln\Gamma_\perp$ versus $(6t/\tau_0)^{1/2}$ will differ.

The generalization of the Green's function techniques to a vector field such as light has been given by a number of authors in the context of coherent backscattering.[11,13,14] The wave equation for a transverse vector field in the absence of sources is

$$\nabla^2 E_i + \frac{\omega^2}{c^2} D_i = 0 \ , \tag{6.1}$$

subject to $\nabla \cdot \mathbf{E} = 0$. The displacement vector $\mathbf{D}$ is related to $\mathbf{E}$ by the dielectric tensor ϵ:

$$D_i = \epsilon_{ij} E_j \ . \tag{6.2}$$

We shall assume that the scattering of the light is elastic and isotropic. This corresponds to a *real* dielectric tensor which is given by

$$\epsilon_{ij}(\mathbf{x}) = [\bar{\epsilon} + \epsilon'(\mathbf{x})]\delta_{ij} \ , \tag{6.3}$$

where ϵ' fluctuates randomly with zero mean as before. The correlations of the dielectric tensor are characterized by

$$k_0^4 \langle \epsilon'_{ij}(\mathbf{x},t)\epsilon'_{mn}(0,0)\rangle = \delta_{ij}\delta_{mn} B(x,t) \ . \tag{6.4}$$

The averaged one-particle Green's functions are given by

$$G_{ij}^{R/A}(\mathbf{k}) = P_{ij}(\hat{\mathbf{k}}) G^{R/A}(k) \ , \tag{6.5}$$

where $P_{ij}(\hat{\mathbf{k}}) = (\delta_{ij} - \hat{\mathbf{k}}_i \hat{\mathbf{k}}_j)$ reflects the transversality of the wave, and $G^{R/A}$ are the Green's functions for scalar waves. The generalization of Eq. (2.12) becomes

$$\Gamma_{ij}(t) = \langle E_i(t) E_j^*(0)\rangle \propto \int_0^\infty dz\, e^{-z/l} \int_0^\infty dz' e^{-z'/l} \int d^2\rho L_{ijmn}(\rho,z,z';\mathbf{k},\mathbf{k}';t) E_m^0 E_n^{0*} \ , \tag{6.6}$$

where the polarization vector of the incident wave is $\hat{\mathbf{E}}^0$. As before we will calculate the transform of L:

$$L_{ijmn,\mathbf{k}\mathbf{k}'}(\mathbf{K};t) = \int_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} L_{ijmn}(\mathbf{R};\mathbf{k},\mathbf{k}';t) \ , \tag{6.7}$$

which satisfies the integral equation

$$L_{ijmn,\mathbf{k}\mathbf{k}'}(\mathbf{K};t) = B(\mathbf{k}-\mathbf{k}',t)\delta_{im}\delta_{jn} + \int_{\mathbf{k}_1} B(\mathbf{k}-\mathbf{k}_1,t) \sum_{m'n'} P_{im'}(\hat{\mathbf{k}}_1) P_{jn'}(\hat{\mathbf{k}}_1) f_{\mathbf{k}_1}(\mathbf{K}) L_{m'n'mn,\mathbf{k}_1\mathbf{k}'}(\mathbf{K},t) \ . \tag{6.8}$$

We shall consider the white-noise model, in which L is independent of incident and reflected wave vectors. In Appendix C we find that the autocorrelation function for parallel polarized light is

$$\Gamma_{\parallel}(t) \propto I(t,0) + \tfrac{20}{7} I(t,\sqrt{9/7}) \ , \tag{6.9}$$

where for simplicity we have defined

$$I(t,\xi) = \int_0^\infty dz\, e^{-z/l} \int_0^\infty dz' e^{-z'/l} \int d^2\rho \left[\frac{\exp\{-(6t/\tau_0+\xi^2)^{1/2}[\rho^2+(z-z')^2]^{1/2}/l\}}{[\rho^2+(z-z')^2]^{1/2}} - \frac{\exp\{-(6t/\tau_0+\xi^2)^{1/2}[\rho^2+(z+z'+2z_b)^2]^{1/2}/l\}}{[\rho^2+(z+z'+2z_b)^2]^{1/2}} \right] . \tag{6.10}$$

For perpendicularly polarized light

$$\Gamma_{\perp}(t) \propto I(t,0) - I(t,\sqrt{9/7}) \ . \tag{6.11}$$

When $\xi \neq 0$, only short paths ($R \lesssim l^*/\xi$) contribute to the integral in Eq. (6.10). Thus, Eqs. (6.9) and (6.11) exhibit unequal contributions of short paths to the correlation functions. The parallel polarized autocorrelation function is enhanced due to short paths, while the perpendicularly polarized autocorrelation function reflects the removal of certain short paths, which do not depolarize the wave. Substitution of these expressions into Eq. (2.12) yields the following slopes (for small t):

$$\gamma_{\parallel} \simeq 1.6$$

and (6.12)

$$\gamma_{\perp} \simeq 2.7 \ ,$$

which are in good agreement with experimental values[30] of 1.6±0.1 and 2.8±0.2, for scattering of 488 nm light from uncorrelated polystyrene latex spheres of diameter 0.091 μm. For such small particles, the white-noise model is expected to be valid. The autocorrelation function for perpendicularly polarized light has been plotted in Fig. 4. This correlation function more closely follows the

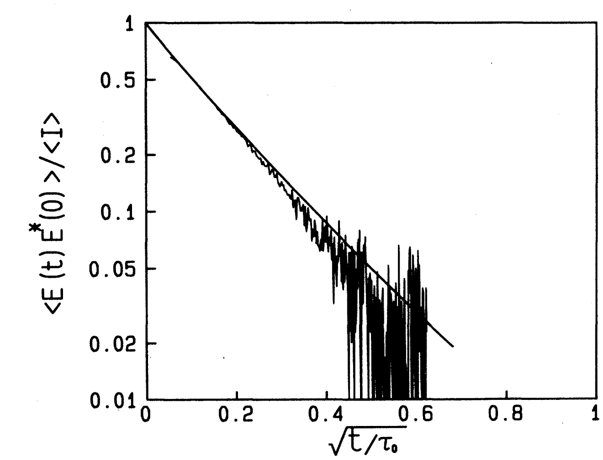

FIG. 4. In the crossed linear polarization channel, the elimination of short scattering paths leads to much better agreement with the observed autocorrelation function. The increased slope in both the observed and calculated correlation functions is due to the fact that short paths, which tend not to flip the polarization, do not contribute in this channel.

experimentally observed exponential decay with $\sqrt{t/\tau_0}$. This demonstrates the importance of properly accounting for the polarization dependence of short paths, even in systems where the white-noise approximation is valid. The improved agreement of the calculation with the data [compared with Fig. 2(a)] is due to the fact that short paths contribute little to the perpendicularly polarized scattered light. Similarly we have calculated the correlation functions for the two circularly polarized channels, which we shall refer to as the *helicity preserving* (incident and observed light of the same circular polarization) and the *opposite helicity* channels. These are obtained in Appendix C:

$$\Gamma_+(t) \propto I(t,0)+\tfrac{1}{2}I(t,\sqrt{9/7})-\tfrac{5}{6}I(\tfrac{5}{9}t,\sqrt{5/3}) , \qquad (6.13)$$

and

$$\Gamma_-(t) \propto I(t,0)+\tfrac{5}{7}I(t,\sqrt{9/7})+\tfrac{5}{3}I(\tfrac{5}{9}t,\sqrt{5/3}) , \qquad (6.14)$$

for the helicity preserving and opposite helicity channels, respectively. The two slopes in these channels are approximately

$$\gamma_+ \simeq 2.4$$

and (6.15)

$$\gamma_- \simeq 1.7 .$$

These results are valid for short times, t, and for isotropic scattering from small particles. For larger particles, the scattering becomes increasingly anisotropic, with the result that the polarization dependence of the autocorrelation functions is reduced. This is because the typical paths involve many scattering events, each of which tends to depolarize the light. This effect has been seen experimentally.[19] For example, the measured slope γ for the decay of the autocorrelation function for parallel (perpendicular) polarized light increases (decreases) monotonically with particle size. (This property has been used to determine the size of unknown but monodisperse particles in suspension at high densities, where QELS is inapplicable.[19]) These two slopes nearly converge as the scattering becomes highly anisotropic. The slopes $\gamma_\perp$ and $\gamma_\parallel$ differ[30] by only 5% for $l^*/l \gtrsim 10$. This is because, for every scattering path which preserves the incident linear polarization, there is an equally probable path which flips the polarization vector. This is true for scattering by large particles, in which case the individual scattering angles θ_j are small. The scattered wave vectors $\mathbf{k}_j$ determine a path on the sphere of radius k_0, as shown in Fig. 5. In the limit of small scattering angles θ_j, we may take this path (C) to be continuous. The polarization vectors are then parallel transported along the path. If this path preserves the incident polarization, then the path C', obtained by azimuthal rotation of the sphere through an angle of 45° about the incident wave vector, will result in a final polarization vector which is perpendicular to the incident polarization. Thus, for scattering from large particles, both parallel and perpendicularly polarized light are equally probable.

There is, however, a striking memory of the incident helicity or *circular* polarization, for paths of length $s \sim l^*$. This is because the wave's helicity is randomized much more slowly than is its direction, which results in a dramatic difference between the slopes γ_+ and γ_- for $l^*/l \gtrsim 3$.[30] For circularly polarized light, the probability of scattering with and without a spin flip depends only on the scattering angles θ_j, and is independent of azimuthal rotations. For example, the scattering from small particles may be characterized within the Born approximation. This yields a simple dependence of the *amplitudes* for scattering through an angle θ with and without spin flip which is given by the overlap of the outgoing circular states $|R'\rangle$ and $|L'\rangle$ with the incident states $|R\rangle$ and $|L\rangle$:

$$\langle L'|R\rangle \propto \frac{1-\cos\theta}{2}, \quad \langle R'|R\rangle \propto \frac{1+\cos\theta}{2} . \qquad (6.16)$$

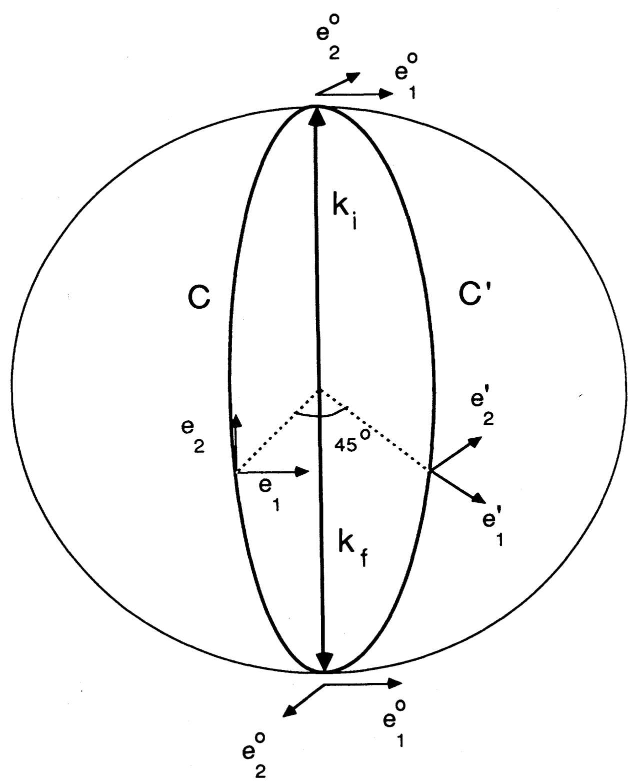

FIG. 5. When the individual scattering angles are small, the wave vectors $\mathbf{k}_j$ define a nearly continuous curve on the sphere of radius k_0. The polarization vector of the wave is parallel transported along this curve. For example, curve C corresponds to a scattering path for light with incident wave vector $\mathbf{k}_i$ and final wave vector $\mathbf{k}_f=-\mathbf{k}_i$. Parallel transport of the unit vectors $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ along path C leads to inversion of $\hat{\mathbf{e}}_2$, while $\hat{\mathbf{e}}_1$ is preserved. Thus, if the polarization of the incident light is directed along either $\hat{\mathbf{e}}_1$ or $\hat{\mathbf{e}}_2$, then path C would lead to observed light polarized along the same direction. Parallel transport along the path C', obtained from C by rotation through 45° about the incident wave vector, would lead to transposition of $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$. This path would contribute to the perpendicular polarization channel, if the incident light is directed along $\hat{\mathbf{e}}_1$ or $\hat{\mathbf{e}}_2$. In general, for any path C contributing to the parallel polarization channel, there is a path C' obtained as above, which contributes to the opposite polarization channel.

Thus, for small scattering angles the probability for spin flip decreases as θ^4, while the degree of randomization of the wave's direction grows as $n\langle\theta^2\rangle$ after n scattering events. For scattering from large particles, the Born approximation is no longer sufficient. The intensities $I^{\pm}(\theta)$ of scattered light without and with spin flip can, however, be calculated from Mie theory.[29,31] For scattering through small angles θ, the calculated dependence of the intensities on θ is qualitatively similar to that of Eq. (6.16). In particular, when the scattering angle is small, the probability for spin flip is quite small. Thus, for highly anisotropic scattering the autocorrelation function (and in fact the intensity itself) in the helicity preserving channel is enhanced, relative to the opposite helicity channel, by the more probable paths which do not result in spin flip. We may represent these probabilities, averaged over all angles, by

$$p_{\pm} \equiv \frac{\int \sin\theta I^{\pm}(\theta) d\theta}{\int \sin\theta [I^{+}(\theta)+I^{-}(\theta)] d\theta} \equiv \tfrac{1}{2}(1\pm A) \tag{6.17a}$$

for scattering without and with spin flip, respectively. The asymmetry factor A is a function of particle size. For isotropic scattering, all scattering angles are equally probable, and there is no asymmetry for an individual scattering event: $A=0$. For large particles, however, the scattering angles are typically very small. This leads to a value of $A \simeq 1$. The probability for scattering n times without a single spin flip is then

$$\prod_{j=1}^{n} p_+ = \left[\frac{1+A}{2}\right]^n , \tag{6.17b}$$

where we have taken the probabilities to be independent of each other. Only paths with an even (odd) number of spin flips will contribute to the helicity preserving (opposite helicity) channel. Thus, the weight factors $P^{\pm}(s)$ for paths which contribute to the two circular polarization channels are

$$P^{\pm}(s) \simeq P(s) \sum_{\{\sigma_j\}}^{\substack{\text{even}\\ \text{odd}}} \prod_{j=1}^{n=s/l} p_{\sigma_j} , \tag{6.18}$$

where $P(s)$ is the scalar weighting function. Here the σ_j are "+" and "−," and the symbols $\sum^{\text{even}}$ and $\sum^{\text{odd}}$ refer to sums with an even and odd number of "−" signs in $\{\sigma_j\}$. Since $p_+ + p_- = 1$,

$$1 = (p_+ + p_-)^n = \sum_{\{\sigma_j\}}^{\text{even}} \prod_{1}^{n} p_{\sigma_j} + \sum_{\{\sigma_j\}}^{\text{odd}} \prod_{1}^{n} p_{\sigma_j} , \tag{6.19}$$

by the binomial expansion. Similarly,

$$A^n = (p_+ - p_-)^n = \sum_{\{\sigma_j\}}^{\text{even}} \prod_{1}^{n} p_{\sigma_j} - \sum_{\{\sigma_j\}}^{\text{odd}} \prod_{1}^{n} p_{\sigma_j} \tag{6.20}$$

follows from the binomial expansion. Thus,

$$P^{\pm}(s) = \tfrac{1}{2} P(s)(1 \pm e^{-s/n'l}) , \tag{6.21}$$

where we have rewritten A in the more suggestive form: $A \equiv e^{-1/n'}$. Physically, n' represents the number of scattering events required to randomize the wave's helicity. For large particles, this number becomes greater than l^*/l, the number of scattering events required to randomize the wave's direction. For example, we find that $n' \sim 50$ for $l^*/l = 10$. This leads to the dramatic difference between the initial slopes

$$\gamma_+ \simeq 1.7$$

and (6.22)

$$\gamma_- \simeq 2.6$$

using Eqs. (6.21) and (5.23) in (2.6).

In Sec. II we discussed an analogy between the decay of the autocorrelation function with time and the coherent backscattering peak as a function of angle, which is strictly true only for scalar waves. The sharp backscattering peak is a consequence of interference between time-reversed paths, and is apparent only in the parallel and helicity preserving channels,[13,14] in which the incident and reflected polarization states are equal. On the other hand, the decay of the autocorrelation function with $\sqrt{t}$ is due to the loss of phase coherence between identical paths separated in time by t, and is manifest in all polarization channels. To be more precise, the vector corrections of Refs. 13 and 14 to the scalar calculation of the backscattering cone differ from those of Appendix C for the autocorrelation function. As in Ref. 14, however, the vector correction in the helicity preserving channel is small. The autocorrelation function and the coherent backscattering cone in this channel more closely resemble scalar results, and hence may be expected to more clearly exhibit the analogy discussed in Sec. II.

There is yet another distinction between the autocorrelation function and the coherent backscattering peak. Single scattering events lead to constructive interference between reversed paths, regardless of the scattering angle. Such events, therefore, contribute only to the incoherent background intensity, and not to the coherent backscattering peak. Only second- and higher-order scattering events contribute to the coherent intensity. This leads to an enhancement factor of approximately 1.85 over the background.[13] For times $t \gtrsim \tau_0$, however, single scattering contributions to the autocorrelation function do decay. The enhancement of $\langle I(t)I(0)\rangle$ at $t=0$ is precisely twice the uncorrelated result: $\langle I\rangle^2$. This will lead to a decay of the coherent backscattering peak at large angles which differs from that of the autocorrelation function at long times, in the parallel polarized channel. In the helicity preserving channel, on the other hand, only second- and higher-order scattering events are present, and the aforementioned vector corrections are small.[14] The analogy, which is strictly true only for scalar waves, should be more apparent in this channel.

VII. DISCUSSION

The essential features of the autocorrelation functions measured in DWS experiments on noninteracting systems can be captured within a simple theoretical framework introduced by Maret and Wolf in Ref. 2. This approach expresses the autocorrelation function as a sum over paths of various lengths s, weighted by the number $P(s)$ of such paths. Having assumed that the scattering centers are pointlike and uncorrelated, self-diffusion of these particles leads to a loss of phase coherence which depends only on the length of the path. This approach is entirely equivalent to the more formal calculation of Ref. 20, using Green's function techniques. The generalization of the more physically transparent result to large scattering particles, for which the transport mean free path $l^* > l$, was obtained by averaging the wave-vector transfers $\mathbf{q}$ over the form factor: $\langle q^2 \rangle = 2k_0^2 l/l^*$. (We have shown in Sec. V that this result is equivalent to the formal solution of the transport equation, within the diffusion approximation.) A simple generalization of this approach, which includes correlations within the medium, has also been derived here. The resulting autocorrelation function depends on the dynamic structure factor $S(q,t)$ only through its average over all transfers $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ between physical intermediate states $(k=k'=k_0)$, weighted by the form factor.

The diffusion approximation corresponds to the weighting factor $P(s)$ in Eq. (2.5) or the equivalent transport kernel $L(R,t)$ in Eq. (2.17), both of which are valid only for paths much longer than l^*. A large portion of the reflected light from a half-space of scattering particles, however, is due to paths of intermediate lengths: $R,s \sim l^*$. It is not surprising, then, at the diffusion approximation leads to rather striking discrepancies between the calculated and measured autocorrelation functions. Physically, the diffusion approximation overestimates the number of short paths, and leads to a much slower than observed decay of the autocorrelation functions at long times. This has been demonstrated by recent numerical studies.[32] On short length scales, the propagation of the light is increasingly ballistic in nature. We have derived a solution for the transport equation, which is capable of describing the crossover from ballistic to diffusive propagation. For large scattering particles, we obtain a transport kernel L in terms of eigenfunctions $\psi_\alpha(\mathbf{k})$, which describe the spectral content of the specific intensity within the medium. For large scattering particles, these functions are part of a spherical harmonic expansion of the specific intensity. Over long length scales, only the spherically symmetric part (corresponding to classical diffusion) is important. Over shorter length scales, increasingly angular dependent terms become significant. As the DWS experiments for backscattering suggest, a more complete understanding of this crossover from ballistic to diffusive propagation is required.

Several experiments are possible which would help to determine the contributions of short, nearly ballistic paths. For example, in Sec. VI we discussed a difference between the autocorrelation functions in the two helicity channels, which is due entirely to short paths. Measuring the difference between these two autocorrelation functions would be an important test of any theory of the crossover region. Furthermore, in the limit of large scattering particles, and provided that precise boundary conditions at the surface of the medium are known, it is possible to "invert" the integral transforms of both Eqs. (2.6) and (2.12) to obtain either the weighting function $P(s)$ or the transport kernel $L(\mathbf{r},\mathbf{r}';t)$ from the measured autocorrelation function. Also, the angular dependence of the spectral modes ψ_α given in Secs. IV and V might allow one to isolate these contributions to the reflected intensity, and thereby measure the eigenvalues λ_α. The angular dependence predicted by the sums in Eqs. (4.27) and (5.13) for backward scattering is, however, quite weak. We have shown in Appendix B that all low-lying eigenvalues depend on the dynamic structure factor in the same way—namely, the aforementioned average. It would be necessary to isolate the contributions of the "highly excited" modes, which might be apparent only near forward scattering, in order to obtain more information about the dynamic structure factor. As the paths length s is reduced, the nature of the measured "average" over $S(q,t)$ is changed. The single scattering limit is that of QELS, where the single transfer $\mathbf{q}$ is precisely known, and $S(q,t)$ may be directly measured. For paths of intermediate length $l \lesssim s \lesssim l^*$, the average of the dynamic structure factor will depend upon the net transfer

$$\mathbf{q}_{\text{net}} = \mathbf{q}_1 + \cdots + \mathbf{q}_n = \mathbf{k} - \mathbf{k}' .$$

The determination of these other moments would allow the study of $S(q,t)$ in the intermediate regime between QELS and DWS.

Within the white-noise model, valid for small uncorrelated scattering particles, the autocorrelation functions differ dramatically in slope for the various polarization channels. This is due entirely to the different numbers of short paths contributing in the various channels. Short scattering paths favor the parallel linear polarized and opposite helicity channels, for backscattering. The slopes in these channels are smaller, due to the slow decay of the short paths. For anisotropic scattering from large particles, the linear polarization dependence is less pronounced. This is because the typical paths contributing to the reflected intensity involve many scattering events, each of which tends to depolarize the wave. There is, however, a high degree of memory of the incident circular polarization over paths of short to intermediate length. This reflects the predominance of forward scattering within the Mie theory.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. DMR 8518163. F.M. wishes to thank P. Chaikin, R. Klein, A. Middleton, S. Milner, D. Pine, D. Weitz, and J. Zhu for helpful discussions.

APPENDIX A

A spectral representation of $L_{\mathbf{k}\mathbf{k}'}(\mathbf{K};t)$ in Eq. (4.18) is possible in terms of the operator $(B^{-1}_{\mathbf{k}\mathbf{k}'} - f_{\mathbf{k}}\delta_{\mathbf{k}\mathbf{k}'})$. We may obtain this from Eq. (4.18c), since

$$\begin{aligned} L_{\mathbf{kk}'} &= \int_{\mathbf{k}_1} B_{\mathbf{kk}_1}(\delta - fB)^{-1}_{\mathbf{k}_1\mathbf{k}'} \\ &= [(\delta - fB)B^{-1}]^{-1}_{\mathbf{kk}'} \\ &= (B^{-1} - f)^{-1}_{\mathbf{kk}'} \\ &= \sum_\alpha \frac{v_\alpha(\mathbf{k}) v^*_\alpha(\mathbf{k}')}{\varepsilon_\alpha(K,t)} . \end{aligned} \tag{A1}$$

Here the eigenfunctions v_α and associated eigenvalues ε_α are related by

$$\int_{\mathbf{k}_1} (B^{-1}_{\mathbf{kk}_1} - f_{\mathbf{k}} \delta_{\mathbf{kk}_1}) v_\alpha(\mathbf{k}_1) = \varepsilon_\alpha v_\alpha(\mathbf{k}) , \tag{A2}$$

and B^{-1} is the operator inverse of B:

$$\int_{\mathbf{k}_1} B^{-1}_{\mathbf{kk}_1} B_{\mathbf{k}_1\mathbf{k}'} = \delta_{\mathbf{kk}'} . \tag{A3}$$

Formally the inverse can be expressed as a differential operator[15]

$$B^{-1}_{\mathbf{kk}'} = \delta_{\mathbf{kk}'} \frac{1}{B(i\nabla_{\mathbf{k}'})} , \tag{A4}$$

where B appearing on the right-hand side is the Fourier transform of $B_{\mathbf{kk}'}$

$$B(\mathbf{x}) = k_0^4 \langle \epsilon'(\mathbf{x}) \epsilon'(0) \rangle \tag{A5}$$

with the argument x replaced by the differential $i\nabla_{\mathbf{k}'}$ with respect to $\mathbf{k}'$.

In Sec. V we observed that the eigenvalues of $(\delta - fB)$ did not depend on the specific form factor, but only on the ratio l/l^*. Here we shall use a Gaussian form factor, which closely approximates that of Eq. (5.3b):

$$B(q,0) = B_0 e^{-a^2 q^2/4} . \tag{A6a}$$

By Eqs. (4.11b) and (4.24b):

$$\mathrm{Im}\Sigma^{R/A}_{k_0} \simeq \langle B \rangle \int_{\mathbf{k}} \mathrm{Im} G^{R/A}_{\mathbf{k}} = \langle B \rangle \mathrm{Im}\Sigma^{R/A}_{k_0} \int_{\mathbf{k}} f_{\mathbf{k}}(0) , \tag{A6b}$$

where $\langle B \rangle$ is the average of $B(q,0)$ over transfers $\mathbf{q}$:

$$\begin{aligned} 4\pi \langle B \rangle &= 2\pi B_0 \int_0^\pi \sin\theta \, d\theta \, e^{-a^2 k_0^2 (1-\cos\theta)/2} \\ &= 4\pi B_0 \frac{1 - e^{-a^2 k_0^2}}{a^2 k_0^2} . \end{aligned} \tag{A6c}$$

The inverse in Eq. (A4) can be expressed in a Taylor series for large a:

$$\begin{aligned} B^{-1}_{\mathbf{kk}'} &= \delta_{\mathbf{kk}'} \frac{a^3 \pi^{3/2}}{B_0} \left[1 - \frac{\nabla^2}{a^2} + \cdots \right] \\ &\simeq \delta_{\mathbf{kk}'} \frac{a \pi^{3/2}}{B_0} (a^2 - \nabla^2) , \end{aligned} \tag{A7}$$

where we have neglected terms of order $1/a^2$. [More generally, we could have considered other smooth form factors in (A6a) which allow such an expansion for large a.] For self-diffusion given by Eq. (5.6), $B(q,t)$ is obtained by replacing a^2 by $a^2 + 4D_S t$ in Eq. (A6a). The eigenvalue equation (A2) is then simply a Schrödinger equation

$$\left[-\nabla^2 + a^2 + 4D_S t - \frac{B_0}{a\pi^{3/2}} f_{\mathbf{k}} \right] v_\alpha(\mathbf{k}) = \frac{B_0}{a\pi^{3/2}} \varepsilon_\alpha v_\alpha(\mathbf{k}) , \tag{A8a}$$

with "potential"

$$V(\mathbf{k}) = a^2 + 4D_S t - \frac{B_0}{a\pi^{3/2}} f_{\mathbf{k}} , \tag{A8b}$$

and "energies" ε_α. For $K=0$, the potential is spherically symmetric. Thus the eigenfunctions can be separated into radial and angular variables

$$v_{\alpha,m}(\mathbf{k}) = R_\alpha(k) Y_{\alpha,m}(\hat{\mathbf{k}}) . \tag{A9}$$

The Schrödinger equation then reduces to

$$\left[-\frac{1}{k^2} \frac{d}{dk} \left[k^2 \frac{d}{dk} \right] + a^2 + 4D_S t + \frac{\alpha(\alpha+1)}{k^2} - \frac{B_0}{a\pi^{3/2}} f_k(0) \right] R_\alpha(\mathbf{k}) = \frac{B_0}{a\pi^{3/2}} \varepsilon^0_\alpha(t) R_\alpha(k) . \tag{A10}$$

In the weak scattering limit the potential V is characterized by a deep well near $k = k_0$ due to the highly peaked function $f_k(0)$. The ground-state radial function R_0 and other low-lying states are bound, and are therefore highly concentrated about $k = k_0$. As in Ref. 15, we shall make the δ-shell[33] approximation, in which $f_k(0)$ is approximated by a δ function at $k = k_0$:

$$f_k(0) \simeq \frac{\pi l}{2k_0^2} \delta(k - k_0) . \tag{A11}$$

The low-lying eigenfunctions $R_\alpha(k)$ satisfy the differential equation for the modified spherical Bessel functions away from $k = k_0$:

$$R_\alpha(k) \sim \begin{cases} i_\alpha(ak), & k < k_0 , \\ k_\alpha(ak), & k > k_0 , \end{cases} \tag{A12}$$

where

$$i_\alpha(x) = \sqrt{(\pi/2x)} I_{\alpha+1/2}(x)$$

and

$$k_\alpha(x) = \sqrt{(\pi/2x)} K_{\alpha+1/2}(x) .$$

In the limit of large scattering particles ($ak_0 \gg 1$) and for $\alpha \lesssim k_0 a$, the Bessel functions near $k = k_0$ are well approximated by their asymptotic forms:

$$i_\alpha(x)\sim\frac{e^x}{x}$$

and (A13)

$$k_\alpha(x)\sim\frac{e^{-x}}{x}\ ,$$

which are independent of α. Thus, by Eq. (A10):

$$\frac{B_0}{a^3\pi^{3/2}}\varepsilon_\alpha^0(t)\simeq\frac{\alpha(\alpha+1)}{a^2k_0^2}+4\frac{t}{a^2k_0^2\tau_0}\ . \tag{A14a}$$

In this model with form factor (A6a)

$$\frac{l}{l^*}\equiv\langle 1-\cos\theta\rangle\simeq\frac{2}{a^2k_0^2}\ , \tag{A14b}$$

so that the eigenvalues ε_α of Eq. (A14a) depend only on the ratio l/l^*:

$$\varepsilon_\alpha(0,t)\sim\frac{\alpha(\alpha+1)}{2}\frac{l}{l^*}+2\frac{t}{\tau_0}\frac{l}{l^*}\ . \tag{A14c}$$

Apart from an overall factor, these eigenvalues are the same as those found in Sec. IV. This agreement is due to a relationship between the eigenfunctions ψ_α of $(\delta-fB)$ and v_α of $(B^{-1}-f)$, which is true for low-lying states. In particular, we have observed in Sec. IV that $\psi_0(k)=\Delta G_k(0)$ is (up to normalization) a zero mode of the operator $(\delta-fB)$. Thus

$$v_0(\mathbf{k})=\int_{\mathbf{k}'}B_{\mathbf{kk}'}\psi_0(\mathbf{k}')$$

is the ground state[15] of Eq. (A8a):

$$\begin{aligned}\int_{\mathbf{k}_1}(B^{-1}-f)_{\mathbf{kk}_1}v_0(\mathbf{k}_1)&=\int_{\mathbf{k}_1\mathbf{k}_2}(B^{-1}_{\mathbf{kk}_1}B_{\mathbf{k}_1\mathbf{k}_2}-f_{\mathbf{k}}\delta_{\mathbf{kk}_1}B_{\mathbf{k}_1\mathbf{k}_2})\psi_0(\mathbf{k}_2)\\&=\int_{\mathbf{k}_2}(\delta-fB)_{\mathbf{kk}_2}\psi_0(\mathbf{k}_2)=0\ .\end{aligned} \tag{A15a}$$

Similarly, for the other low-lying modes [see Eq. (A13)],

$$\begin{aligned}v_{\alpha,m}(\mathbf{k})&\simeq Y_{\alpha,m}(\hat{\mathbf{k}})v_0(k)=Y_{\alpha,m}(\hat{\mathbf{k}})\int_{\mathbf{k}_1}B_{\mathbf{kk}_1}\psi_0(k_1)\\&\simeq\int_{\mathbf{k}_1}B_{\mathbf{kk}_1}Y_{\alpha,m}(\hat{\mathbf{k}}_1)\psi_0(\mathbf{k}_1)\ .\end{aligned} \tag{A15b}$$

Here, we have used the fact that the dependence of $Y_{\alpha,m}(\hat{\mathbf{k}})$ is weak on angular scales small compared with $\theta_{\rm rms}$—the width of B. For this reason we obtain the agreement between the low-lying eigenvalues λ_α of $(\delta-fB)$ and ε_α of $(B^{-1}-f)$, as well as the approximation $\psi_{\alpha,m}(\mathbf{k})\simeq Y_{\alpha,m}(\hat{\mathbf{k}})\psi_0(k)$ made in Sec. V—both of which are valid in the limit of large scattering particles ($k_0a\gg1$). The expression for Γ found in Eq. (5.13) can also be obtained as follows. From Eq. (4.17), the kernel $\Gamma_{\mathbf{kk}'}(\mathbf{K};t)$ (excluding the coherent term) can be expressed in terms of the eigenfunctions $v_{\alpha,m}$,

$$\tilde{\Gamma}_{\mathbf{kk}'}(\mathbf{K};t)\equiv\Gamma_{\mathbf{kk}'}(\mathbf{K};t)-\Gamma^0_{\mathbf{kk}'}(\mathbf{K};t)=f_{\mathbf{k}}L_{\mathbf{kk}'}f_{\mathbf{k}'}=\sum_{\alpha,m}\frac{f_{\mathbf{k}}v_{\alpha,m}(\mathbf{k})v^*_{\alpha,m}(\mathbf{k}')f_{\mathbf{k}'}}{\varepsilon_\alpha(K,t)}\ . \tag{A16a}$$

(This function characterizes the scattering portion of the light.) From this we obtain

$$\begin{aligned}\tilde{\Gamma}(R;\mathbf{k},\mathbf{k}';t)&=\frac{1}{4\pi R}\sum_{\alpha,m}\frac{f_{\mathbf{k}}v_{\alpha,m}(\mathbf{k})v^*_{\alpha,m}(\mathbf{k}')f_{\mathbf{k}'}}{\varepsilon''_\alpha}e^{-[\varepsilon^0_\alpha(t)/\varepsilon''_\alpha]^{1/2}R}\\&\simeq\frac{3\psi_0(\mathbf{k})\psi_0^*(\mathbf{k}')}{4\pi ll^*R}\sum_\alpha e^{-[\varepsilon^0_\alpha(t)/\varepsilon''_\alpha]^{1/2}R}4\pi\sum_{m=-\alpha}^{\alpha}Y_{\alpha,m}(\hat{\mathbf{k}})Y^*_{\alpha,m}(\hat{\mathbf{k}}')\ .\end{aligned} \tag{A16b}$$

Here we have used Eqs. (4.12a), (4.24b), and (A15b) to express $v_{\alpha,m}$ in terms of $Y_{\alpha,m}$ and ψ_0,

$$f_{\mathbf{k}}v_{\alpha,m}(\mathbf{k})\propto\psi_0(k)Y_{\alpha,m}(\hat{\mathbf{k}})\ . \tag{A16c}$$

APPENDIX B

The dependence of the eigenvalues λ_α on small K may, in principle, be evaluated from perturbation theory about $K=0$ in the eigenvalue equation (4.22), or in the Schrödinger equation (A11) with perturbing potential

$$V'(\mathbf{k})=B_0^2[f_{\mathbf{k}}(0)-f_{\mathbf{k}}(\mathbf{K})]/(a\pi^{3/2})\ .$$

We shall follow a self-consistent argument given first in Ref. 28 in the context of electron propagation. We begin with the Bethe-Salpeter equation (4.10) in the weak scattering limit. From Eqs. (4.11a) and (4.12c) we have that

$$\Delta G_{\mathbf{k}}(\mathbf{K})=[2\mathbf{k}\cdot\mathbf{K}+\Delta\Sigma_{\mathbf{k}}(\mathbf{K})]f_{\mathbf{k}}(\mathbf{K})\ . \tag{B1}$$

Multiplying both sides of Eq. (4.10) by $(2\mathbf{k}\cdot\mathbf{K}+\Delta\Sigma)$ yields

$$[2\mathbf{k}\cdot\mathbf{K}+\Delta\Sigma_{\mathbf{k}}(\mathbf{K})]\Gamma_{\mathbf{kk}'}(\mathbf{K};t)=\Delta G_{\mathbf{k}}(\mathbf{K})[\delta_{\mathbf{kk}'}+B_{\mathbf{kk}_1}(t)\Gamma_{\mathbf{k}_1\mathbf{k}'}(\mathbf{K};t)]\ , \tag{B2a}$$

where the Ward identity of Eq. (4.12a) becomes

$$\Delta\Sigma_{\mathbf{k}}(\mathbf{K})=B_{\mathbf{kk}_1}(0)\Delta G_{\mathbf{k}_1}(\mathbf{K})\ , \tag{B2b}$$

and integration over $\mathbf{k}_1$ is implied in both equations. Integration of Eq. (B2a) over $\mathbf{k}$ and $\mathbf{k}'$ results in

$$2K\Gamma^c(K;t)=\int_{\mathbf{k}}\Delta G_{\mathbf{k}} + \int_{\mathbf{k}\mathbf{k}_1}[\Delta G_{\mathbf{k}}(\mathbf{K})B_{\mathbf{k}\mathbf{k}_1}(t)\Gamma_{\mathbf{k}_1}(\mathbf{K};t) - \Gamma_{\mathbf{k}}(\mathbf{K};t)B_{\mathbf{k}\mathbf{k}_1}(0)\Delta G_{\mathbf{k}_1}(\mathbf{K})] \ , \tag{B3a}$$

where the current relaxation is defined by

$$\Gamma^c(\mathbf{K};t)=\int_{\mathbf{k}}(\mathbf{k}\cdot\hat{\mathbf{K}})\Gamma_{\mathbf{k}}(\mathbf{K};t) \ , \tag{B3b}$$

and

$$\Gamma_{\mathbf{k}}(\mathbf{K};t)\equiv\int_{\mathbf{k}'}\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K};t) \ . \tag{B3c}$$

Similarly,

$$\Gamma(\mathbf{K};t)\equiv\int_{\mathbf{k}\mathbf{k}'}\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K};t) \ . \tag{B3d}$$

The function $\Gamma_{\mathbf{k}}(\mathbf{K})$ can, by symmetry, be expanded in Legendre polynomials in $\hat{\mathbf{k}}\cdot\hat{\mathbf{K}}$. We shall approximate $\Gamma_{\mathbf{k}}$ as in Ref. 28,

$$\Gamma_{\mathbf{k}}(\mathbf{K};t)\simeq\frac{\Delta G_{\mathbf{k}}}{\int\Delta G}\left[\Gamma(\mathbf{K};t)+d\frac{(\mathbf{k}\cdot\hat{\mathbf{K}})}{k_0^2}\Gamma^c(\mathbf{K};t)\right] \ . \tag{B4}$$

This is valid in the weak scattering limit, where we have seen that $\Gamma_{\mathbf{k}\mathbf{k}'}$ is a sharply peaked function about $k=k_0$. We have approximated this peak by $\Delta G_{\mathbf{k}}$, and we have kept just the first two terms in the expansion of $\Gamma_{\mathbf{k}}$ consistent with definitions (B3b) and (B3d). Higher-angular-momentum dependent terms will not alter our results below in the weak scattering limit. Equation (B3a) now becomes

$$2K\Gamma^c(K;t)=\int\Delta G-\int\Delta G[\langle B(q,0)\rangle - \langle B(q,t)\rangle]\Gamma(K;t) \ , \tag{B5}$$

where we have used the weak scattering approximation

$$\frac{\Delta G_k}{\int\Delta G}\simeq\frac{(2\pi)^3}{4\pi k_0^2}\delta(k-k_0) \ . \tag{B6}$$

Here we have denoted the sum over all transfers $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ between physical states (with $k=k'=k_0$) by $\langle\ \rangle$. Now, if we multiply both sides of Eq. (B2a) by $(\hat{\mathbf{k}}\cdot\hat{\mathbf{K}})$ and integrate we obtain

$$\frac{2Kk_0}{3}\Gamma(K;t)\simeq\int\Delta G\langle B(q,0)\rangle\langle 1-\cos\theta\rangle\Gamma^c(K;t) \ , \tag{B7a}$$

where

$$\frac{l}{l^*}=\langle 1-\cos\theta\rangle\equiv\frac{\int_{\mathbf{k}\mathbf{k}'}(1-\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')B_{\mathbf{k}\mathbf{k}'}(0)}{\int_{\mathbf{k}\mathbf{k}'}B_{\mathbf{k}\mathbf{k}'}(0)} \ . \tag{B7b}$$

Putting Eqs. (B3a) and (B5) together we may solve for Γ:

$$\Gamma(K;t)\simeq\frac{l/(4\pi)}{[1-\langle B(t)\rangle/\langle B(0)\rangle]+\frac{1}{3}ll^*K^2} \ . \tag{B8}$$

Since we have integrated over both $\mathbf{k}$ and $\mathbf{k}'$, this must be identified with the spherically symmetric term in Eq. (5.13). For self-diffusion of scattering particles

$$1-\frac{\langle B(t)\rangle}{\langle B(0)\rangle}\simeq 2\frac{tl}{\tau_0 l^*} \ . \tag{B9}$$

Thus

$$\lambda_0(K,t)=2\frac{tl}{\tau_0 l^*}+\tfrac{1}{3}ll^*K^2 \ , \tag{B10}$$

as in Eq. (5.12).

For the higher-angular-momentum modes with $\alpha>0$, we may evaluate the eigenvalues as in Eq. (5.8)

$$\begin{aligned}\lambda_\alpha(0,t)&=\frac{1}{2\alpha+1}\sum_m\int_{\mathbf{k}\mathbf{k}'}\psi^*_{\alpha,m}(\mathbf{k})[\delta_{\mathbf{k}\mathbf{k}'}-f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(t)]\psi_{\alpha,m}(\mathbf{k}')\\ &\simeq\int_{\mathbf{k}\mathbf{k}'}\psi^*_0(\mathbf{k})[\delta_{\mathbf{k}\mathbf{k}'}-f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(t)P_\alpha(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')]\psi_0(\mathbf{k}')\\ &\simeq\int_{\mathbf{k}\mathbf{k}'}\psi^*_0(\mathbf{k})[\delta_{\mathbf{k}\mathbf{k}'}-f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(t)]\psi_0(\mathbf{k}')+P'_\alpha(1)\int_{\mathbf{k}\mathbf{k}'}\psi^*_0(\mathbf{k})f_{\mathbf{k}}(0)B_{\mathbf{k}\mathbf{k}'}(0)\psi_0(\mathbf{k}')(1-\cos\theta)\\ &=\left[1-\frac{\langle B(q,t)\rangle}{\langle B(q,0)\rangle}\right]+\frac{\alpha(\alpha+1)}{2}\frac{l}{l^*} \ .\end{aligned} \tag{B11}$$

Here we have used the fact that the functions $f_{\mathbf{k}}(0)$ and $\psi_0(k)$ are highly peaked about the shell $k=k_0$ to replace the integral over $B(\mathbf{k}-\mathbf{k}',t)$ by the average over all transfers $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ between physical states with $k=k'=k_0$. The low-lying eigenvalues depend upon the dynamic structure factor $S(q,t)$ only through this average. This leads to a transport kernel Γ given by Eq. (5.13), in which $6t/\tau_0$ is replaced by $3[1-\langle B(q,t)\rangle/\langle B(q,0)\rangle]$.

The dependence of the scattered light on path length s can be determined from

$$\Gamma(\mathbf{R}-\mathbf{R}';s;\mathbf{k},\mathbf{k}')=\int_{\mathbf{r},\mathbf{r}',\omega}e^{-i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}'\cdot\mathbf{r}'}e^{i\omega s/c}\left\langle G^R\left[\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{R}'+\frac{\mathbf{r}'}{2};\omega_0+\omega/2\right]G^A\left[\mathbf{R}'-\frac{\mathbf{r}'}{2},\mathbf{R}-\frac{\mathbf{r}}{2};\omega_0-\omega/2\right]\right\rangle \ , \tag{B12a}$$

where the Green's functions are now evaluated at different frequencies. The propagator Γ satisfies the modified integral equation

$$\Gamma_{\mathbf{k}\mathbf{k}'}(\mathbf{K};\omega)=G^R\left[k+\frac{\mathbf{K}}{2};\omega_0+\omega/2\right]G^A\left[k-\frac{\mathbf{K}}{2};\omega_0-\omega/2\right]\left[\delta_{\mathbf{k}\mathbf{k}'}+\int_{\mathbf{k}_1}U_{\mathbf{k}\mathbf{k}_1}(\mathbf{K})\Gamma_{\mathbf{k}_1\mathbf{k}'}(\mathbf{K};\omega)\right] \ , \tag{B12b}$$

and the eigenvalues are

$$\lambda_\alpha^0(t;\omega)=\lambda_\alpha^0(t)-i\omega l/c\ , \tag{B12c}$$

from which we obtain Eq. (5.24).

APPENDIX C

The solution of the integral equation (6.8) may be obtained as for Eq. (4.18)

$$L_{ijmn,\mathbf{k}\mathbf{k}'}(K,t)=\int_{\mathbf{k}_1} B(\mathbf{k}-\mathbf{k}_1,t)(1-fB)^{-1}_{ijmn,\mathbf{k}_1\mathbf{k}'}\ , \tag{C1}$$

where

$$\int_{\mathbf{k}_1}[\delta_{im'}\delta_{jn'}\delta_{\mathbf{k}\mathbf{k}_1}-P_{im'}(\hat{\mathbf{k}})P_{jn'}(\hat{\mathbf{k}})f_{\mathbf{k}}(\mathbf{K})B_{\mathbf{k}\mathbf{k}_1}(t)]\times(1-fB)^{-1}_{m'n'mn,\mathbf{k}_1\mathbf{k}'}=\delta_{im}\delta_{jn}\delta_{\mathbf{k}\mathbf{k}}\ . \tag{C2}$$

The white-noise model corresponds to the s wave or spherically symmetric term in Eq. (4.25) for $B(\mathbf{k}-\mathbf{k}',0)=B_0$, a constant. Here L is independent of the incident and scattered wave vectors and Eq. (C1) simplifies to

$$L_{ijmn}(K,t)\simeq B_0(1-fB)^{-1}_{ijmn}\ . \tag{C3}$$

For $t=0$, this inverse was obtained in Refs. 13 and 14 in terms of the eigenvectors $|ij\rangle_\mu$ and associated eigenvalues $\lambda_\mu(K)$ of the matrix

$$Q_{ijmn}(\mathbf{K})=B_0\int_{\mathbf{k}}P_{im}(\hat{\mathbf{k}})P_{jn}(\hat{\mathbf{k}})f_{\mathbf{k}}(\mathbf{K})\simeq\frac{3}{2}\langle P_{im}(\hat{\mathbf{k}})P_{jn}(\hat{\mathbf{k}})(1-\hat{\mathbf{k}}_p\hat{\mathbf{k}}_qK_pK_q)\rangle_{\hat{\mathbf{k}}}\ , \tag{C4}$$

where $\langle\ \rangle_{\hat{\mathbf{k}}}$ refers to an average over $\hat{\mathbf{k}}$ on the unit sphere. The eigenvalues λ_μ of Q are not to be confused with those of Sec. III. Here only the spherically symmetric mode ψ_0 corresponding to the white noise model will be considered. The nine ortho-normal eigenvectors are

$$\begin{aligned}
|mn\rangle_1&=\frac{1}{\sqrt{3}}\delta_{mn}\ ,\\
|mn\rangle_{2,3}&=\frac{1}{\sqrt{3}}\delta_{mn}e^{\pm i(n-1)2\pi/3}\ ,\\
|mn\rangle_{4,5,6}&=\frac{1}{\sqrt{2}}(\delta_{ma}\delta_{nb}+\delta_{mb}\delta_{na})\quad(a\neq b)\ ,\\
|mn\rangle_{7,8,9}&=\frac{1}{\sqrt{2}}(\delta_{ma}\delta_{nb}-\delta_{mb}\delta_{na})\ .
\end{aligned}\tag{C5}$$

For the final six eigenvectors the spatial indices (a,b) take on the values (1,2), (1,3), and (2,3). The eigenvalues $\lambda_\mu(\mu=1,\ldots,9)$ are

$$\begin{aligned}
\lambda_1(K,0)&=1-\tfrac{1}{3}l^2K^2\ ,\\
\lambda_{2,3}(K,0)&=\tfrac{7}{10}-\tfrac{7}{30}l^2K^2\ ,\\
\lambda_{4,5,6}(K,0)&=\tfrac{7}{10}-l^2[\tfrac{23}{70}K^2-\tfrac{10}{70}(K_a^2+K_b^2)]\quad(c\neq a,b)\ ,\\
\lambda_{7,8,9}(K,0)&=\tfrac{1}{2}-l^2[\tfrac{3}{10}K^2-\tfrac{2}{10}(K_a^2+K_b^2)]\ .
\end{aligned}\tag{C6}$$

Here the indices a and b are distinct from each other and from c, which takes on the values 3, 2, and 1. For $t\neq0$, we may obtain these eigenvalues from

$$\lambda_\mu(K,t)=\langle ij|_\mu\psi_0^*(k)P_{im}(\hat{\mathbf{k}})P_{jn}(\hat{\mathbf{k}})f_{\mathbf{k}}(\mathbf{K})\times B_{\mathbf{k}\mathbf{k}'}(t)\psi_0(k')|mn\rangle_\mu\simeq\frac{\langle B(q,t)\rangle}{\langle B(q,0)\rangle}\lambda_\mu(K,0)\ . \tag{C7}$$

For the case of self-diffusion of the scattering particles,

$$\frac{\langle B(q,t)\rangle}{\langle B(q,0)\rangle}\simeq1-2\frac{t}{\tau_0}\ , \tag{C8}$$

and

$$\begin{aligned}
\lambda_1(K,t)&\simeq1-2\frac{t}{\tau_0}-\tfrac{1}{3}l^2K^2\ ,\\
\lambda_{2,3}(K,t)&\simeq\tfrac{7}{10}\left[1-2\frac{t}{\tau_0}\right]-\tfrac{7}{30}l^2K^2\ ,\\
\lambda_{4,5,6}(K,t)&\simeq\tfrac{7}{10}\left[1-2\frac{t}{\tau_0}\right]-l^2[\tfrac{23}{70}K^2-\tfrac{10}{70}(K_a^2+K_b^2)]\quad(c\neq a,b)\ ,\\
\lambda_{7,8,9}(K,t)&\simeq\tfrac{1}{2}\left[1-2\frac{t}{\tau_0}\right]-l^2[\tfrac{3}{10}K^2-\tfrac{2}{10}(K_a^2+K_b^2)]\ .
\end{aligned}\tag{C9}$$

The inverse of $(1-fb)_{ijmn}$ is obtained as in Ref. 14

$$L_{ijmn}(K,t)=B_0\sum_{\mu=1}^{9}|ij\rangle_\mu\frac{1}{1-\lambda_\mu(K,t)}\langle mn|_\mu\ . \tag{C10}$$

The transformed quantity $L_{ijmn}(R,t)$ in Eq. (6.6) may be obtained

$$L_{ijmn}(R,t)=B_0\sum_{\mu=1}^{9}|ij\rangle_\mu D_\mu(R,t)\langle mn|_\mu \tag{C11}$$

from

$$D_\mu(\mathbf{R},t)=\int_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{R}}\left[\frac{1}{1-\lambda_\mu(K,t)}\right]\ . \tag{C12}$$

These functions may be evaluated as in Appendix B of Ref. 14:

$$\begin{aligned}
D_1(\mathbf{R},t)&=\frac{3}{4\pi l^2}\frac{e^{-\sqrt{6t/\tau_0}R/l}}{R}\ ,\\
D_{2,3}(\mathbf{R},t)&=\frac{3}{4\pi l^2}\frac{10}{7}\frac{e^{-\sqrt{6t/\tau_0+9/7}R/l}}{R}\ ,\\
D_{4,5,6}(\mathbf{R},t)&=\frac{3}{4\pi l^2}\frac{70}{39}\frac{\exp\{-\sqrt{99/23(t/\tau_0)+21/23}[R_c^2+\frac{23}{13}(R_a^2+R_b^2)]^{1/2}/l\}}{[R_c^2+\frac{23}{13}(R_a^2+R_b^2)]^{1/2}}\ ,
\end{aligned}\tag{C13}$$

$$D_{7,8,9}(\mathbf{R},t)=\frac{3}{4\pi l^2}\frac{10}{3}\frac{\exp\{-\sqrt{10/3(t/\tau_0)+5/3}[R_c^2+3(R_a^2-R_b^2)]^{1/2}/l\}}{[R_c^2+3(R_a^2+R_b^2)]^{1/2}} .$$

The parallel polarized portion of the autocorrelation function is obtained by choosing the incident and scattered polarization vectors to lie along the same axis (say x). Only the first three modes ($\mu=1,2,3$) contribute

$$L_{\parallel}(R,t)=L_{xxxx}(R,t)=B_0\sum_{1}^{3}|xx\rangle_\mu\langle xx|_\mu D_\mu(R,t)\simeq\frac{3}{l^3R}\left\{\exp\left[-\left[6\frac{t}{\tau_0}\right]R/l\right]+\tfrac{20}{7}\exp\left[-\left[6\frac{t}{\tau_0}+\frac{9}{7}\right]^{1/2}R/l\right]\right\} . \tag{C14}$$

Substitution of this into Eq. (6.6) yields Eq. (6.9). Similarly the perpendicularly polarized autocorrelation function in Eq. (6.11) can be obtained from L_{xxyy} in Eq. (C11). Single scattering events, however, do not contribute in this channel, since such events would leave the incident polarization intact. This is seen by rewriting Eq. (C10), as in Ref. 14:

$$\begin{aligned}L_{ijmn}(K,t)&=B_0\sum_{\mu=1}^{9}|ij\rangle_\mu\frac{1}{1-\lambda_\mu(K,t)}\langle mn|_\mu\\&=B_0\sum_{\mu=1}^{9}|ij\rangle_\mu\left[1+\frac{\lambda_\mu(K,t)}{1-\lambda_\mu(K,t)}\right]\langle mn|_\mu\\&\simeq B_0\delta_{im}\delta_{jn}+B_0\sum_{\mu=1}^{9}|ij\rangle_\mu\frac{\lambda_\mu(0,0)}{1-\lambda_\mu(K,t)}\langle mn|_\mu .\end{aligned} \tag{C15}$$

The first term is just the single scattering term of Eq. (6.8), which vanishes for $i=j=x$ and $m=n=y$. Thus

$$L_{xxyy}(K,t)=B_0\sum_{\mu=1}^{9}|xx\rangle_\mu\frac{\lambda_\mu(0,0)}{1-\lambda_\mu(K,t)}\langle yy|_\mu , \tag{C16}$$

which results in Eq. (6.11).

In Ref. 14 it was shown that

$$P_{ij}^{\pm}(\hat{\mathbf{k}})=\tfrac{1}{2}(\delta_{ij}-\hat{\mathbf{k}}_i\hat{\mathbf{k}}_j\mp ie_{ijl}\hat{\mathbf{k}}_l) \tag{C17}$$

project onto right- and left-hand circularly polarized states with wave vector $\mathbf{k}$. Here e_{ijl} is the antisymmetric tensor. For the helicity preserving channel

$$L_+(K,t)=B_0\sum_{\mu=1}^{9}[P_{ij}^{+}(\hat{\mathbf{k}}_f)]^T|ij\rangle_\mu\frac{\lambda_\mu(0,0)}{1-\lambda_\mu(K,t)}\langle mn|_\mu P_{mn}^{+}(\hat{\mathbf{k}}_i) . \tag{C18}$$

For backscattering the final and incident wave vectors are opposite ($\mathbf{k}_f=-\mathbf{k}_i$), and the single-scattering terms vanish once again, resulting in Eq. (6.13). Similarly, in the opposite helicity channel

$$L_-(K,t)=B_0\sum_{\mu=1}^{9}[P_{ij}^{+}(\hat{\mathbf{k}}_f)]^T|ij\rangle_\mu\frac{1}{1-\lambda_\mu(K,t)}\langle mn|_\mu P_{mn}^{-}(\hat{\mathbf{k}}_i) . \tag{C19}$$

The vector correction for the coherent backscattering peak involves the kernel[14]

$$C_{ijmn}(s)=B_0\sum_{\mu=1}^{9}|in\rangle_\mu\frac{\lambda_\mu(s,0)}{1-\lambda_\mu(s,0)}\langle mj|_\mu , \tag{C20}$$

where $\mathbf{s}\equiv\mathbf{k}_i+\mathbf{k}_f$. Here the presence of λ_μ in the numerator reflects the fact that no single-scattering terms contribute to the coherent intensity. The nature of the time-reversed interference leads to mixing of the polarization of the incident and final states. Only when these two polarization states are equal will the $\mu=0$ mode (corresponding to long diffusion paths) be present.[14]

[1] A. Z. Genack, Phys. Rev. Lett. **58**, 2043 (1987).
[2] G. Maret and P. E. Wolf, Z. Phys. B **65**, 409 (1987).
[3] B. Shapiro, Phys. Rev. Lett. **57**, 2168 (1986).
[4] M. J. Stephen and G. Cwilich, Phys. Rev. Lett. **59**, 285 (1987).
[5] S. Feng, C. Kane, P. A. Lee, and A. D. Stone, Phys. Rev. Lett. **61**, 834 (1988).
[6] I. Freund, M. Rosenbluh, and S. Feng, Phys. Rev. Lett. **61**, 2328 (1988).
[7] Y. Kuga and A. Ishimaru, J. Opt. Soc. Am. **A1**, 831 (1984).
[8] M. P. van Albada and A. Lagendijk, Phys. Rev. Lett. **55**, 2692 (1985).
[9] P. E. Wolf and G. Maret, Phys. Rev. Lett. **55**, 2696 (1985).

[10]S. Etemad, R. Thomson, and M. J. Andrejco, Phys. Rev. Lett. **57**, 575 (1986).

[11]A. A. Golubentzev, Zh. Eksp. Teor. Fiz. **86**, 47 (1984) [Sov. Phys.—JETP **59**, 26 (1984)].

[12]E. Akkermans, P. E. Wolf, and R. Maynard, Phys. Rev. Lett. **56**, 1471 (1986).

[13]M. J. Stephen and G. Cwilich, Phys. Rev. B **34**, 7564 (1986).

[14]F. C. MacKintosh and Sajeev John, Phys. Rev. B **37**, 1884 (1988).

[15]S. John and M. J. Stephen, Phys. Rev. B **28**, 6358 (1983).

[16]I. Freund, M. Kaveh, and M. Rosenbluh, Phys. Rev. Lett. **60**, 1130 (1988).

[17]D. J. Pine, D. A. Weitz, P. M. Chaikin, and E. Herbolzheimer, Phys. Rev. Lett. **60**, 1134 (1988).

[18]G. Maret (private communication).

[19]D. J. Pine, D. A. Weitz, G. Maret, P. E. Wolf, E. Herbolzheimer, and P. M. Chaikin, *Scattering and Localization of Classical Waves in Random Media,* edited by P. Sheng (World Scientific, Singapore, 1989).

[20]M. J. Stephen, Phys. Rev. B **37**, 1 (1988).

[21]S. Glasstone and M. C. Edlund, *The Elements of Nuclear Reactor Theory* (Van Nostrand, New York, 1952).

[22]A. J. Rimberg and R. M. Westervelt, Phys. Rev. B **38**, 5073 (1988).

[23]I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1980), Sec. 6.646.

[24]E. Akkermans, P. E. Wolf, R. Maynard, and G. Maret, J. Phys. (Paris) **49**, 77 (1988).

[25]P. N. Pusey and W. van Megen (unpublished).

[26]*Dynamic Light Scattering,* edited by R. Pecora (Plenum, New York, 1985).

[27]W. Hess and R. Klein, Adv. Phys. **32**, 173 (1983).

[28]D. Vollhardt and P. Wölfle, Phys. Rev. Lett. **45**, 842 (1980); Phys. Rev. B **22**, 4666 (1980).

[29]A. Ishimaru, *Wave Propagation and Scattering in Random Media* (Academic, New York, 1978).

[30]F. C. MacKintosh, J. X. Zhu, D. J. Pine, and D. A. Weitz (unpublished).

[31]M. Kerker, *The Scattering of Light* (Academic, New York, 1969).

[32]A. A. Middleton and D. S. Fisher, Bull. Am. Phys. Soc. **34**, 627 (1989).

[33]K. Gottfried, *Quantum Mechanics* (Benjamin, New York, 1966).