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Diffusion constant in a random system near resonance

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We propose a modification of the traditional Boltzmann equation when scatterers are near resonance conditions. On the basis of this modified equation we find that the diffusion constant is largely renormalized. Our calculated results agree with the recent experimental results of van Albada *et al.* [Phys. Rev. Lett. **66**, 3132 (1991)] for the diffusion of optical waves.

I. INTRODUCTION

Recently, experiments were reported in which the diffusion constant and transport mean-free path for light propagating in a disordered medium were measured independently on the same sample.[1] The medium consisted of dielectric balls situated in air. The unexpected result was that while using the traditional equation $D=vl/3$ which connects the diffusion constant D and mean-free path l, they obtained a value for the velocity v by an order of magnitude smaller than the velocity of light in vacuum. In explaining their results, the authors stressed the role of strong resonance scattering, which is realized in their experiment. Additional insight into the physics of the phenomenon was given in Ref. 2. There it was stressed that a traditional kinetic approach does not take into account the finite duration of the scattering process,[3] the latter being especially large near a resonance. Considering theoretically the influence of this effect on the propagation of electrons in disordered media the authors of Ref. 2 obtained a diffusion constant similar to the experimental results of Ref. 1.

In this paper we propose a simple and physically meaningful modification of the traditional Boltzmann equation to take into account the resonance character of the scattering. We calculate the diffusion constant on the basis of this modified equation. Our results for the case of electrons coincide with the results, postulated in Ref. 2 on the basis of qualitative arguments. Our calculated diffusion constant for the propagation of light is close to the experimental results of Ref. 1.

II. MODIFICATION OF THE BOLTZMANN EQUATION

In any textbook on kinetic theory it is stated that the Boltzmann equation is valid when the time of free flight of the particle between successive acts of scattering is much larger than the duration of the scattering event. The experiments of van Albada *et al.*[1] brought into focus the problem which can be formulated in the following way: how to describe the kinetics of particles when the condition mentioned above does not hold and in addition the scattering by a single scatterer is near resonance. The resonance, as was shown by Wigner,[3] leads not only to large scattering amplitude but also to large scattering delay time. We claim, in line with ideas of Refs. 1 and 2, that we can obtain the physically meaningful approximation for the case of resonance scattering by modifying the traditional kinetic approach, to expand its range of applicability. We take into account only one effect—the aforementioned scattering delay time. That is, we express the kinetic equation for the distribution function $f_k(r,t)$ in the following modified way:

$$\partial f_k(t)/\partial t + v_k \nabla f_k(t) + \sum_{k'} P_{kk'}[f_k(t) - f_{k'}(t-\tau^D_{kk'})] = 0 , \quad (1)$$

where ∇ is the gradient operator, v is the velocity, and the transition probability $P_{kk'}$ is taken from quantum mechanics. We have made a single modification—introduced in the time argument of the input term the delay time $\tau^D_{kk'}$ for the scattering channel $k \rightarrow k'$, similar to the delay time first introduced by Wigner. Our approach though formally different from the approaches of Refs. 1 and 2 gives the results which are very close to those previously obtained and helps to clarify the physics involved.

This modification of the Boltzmann equation reflects also the fact, that in the experimental situation involved (and in many other experimental situations), we measure the intensity of the field (in a direct or indirect way) in vacuum only, i.e., outside scatterers (in recent experiment,[1] outside the dielectric balls). In these cases the equations should be formulated for the free space only, and the region of the scattering potential should be treated as external. According to Eq. (1), in the process of scattering, the particle disappears during the time $\tau^D_{kk'}$ from the scene because it is inside the scattering potential region (inside the dielectric ball) and that is outside of our physical space.

Let us analyze the changes caused due to the modification proposed. Consider the case when $\tau^D_{kk'}$ is less than the characteristic scale of the time dependence of the distribution function. In this case Eq. (1) can be rewritten in the form

$$\partial f_k(t)/\partial t + v_k \nabla f_k(t) + \sum_{k'} P_{kk'}[f_k(t) - f_{k'}(t)] + \sum_{k'} P_{kk'}\tau^D_{kk'}\partial f_{k'}(t)/\partial t = 0 . \quad (2)$$

The transition from this modified equation to the diffusion equation is absolutely similar to the case of the traditional Boltzmann equation. We sum Eq. (2) with respect to k and then multiply by v_k and again sum with respect to k. As a result we obtain the diffusion equation

$$\partial I/\partial t - D\Delta I = 0 \ , \tag{3}$$

where

$$D = D_0/(1+X_D) \ , \tag{4}$$

$D_0 = \frac{1}{3}v^2\tau$ is the traditional diffusion constant with the transport relaxation time τ given by the equation

$$\frac{1}{\tau} = \sum_{k'} P_{kk'}[1-\cos(\vartheta_{kk'})] \tag{5}$$

and

$$X_D = \sum_{k'} P_{kk'}\tau^D_{kk'} \ . \tag{6}$$

It is worth noting that we have made a small correction in the scattering term of the Boltzmann equation of the order of $\omega\tau^D$, where ω is the characteristic frequency of distribution function time dependence, but this leads to a much larger correction in the diffusion equation which is of the order of τ^D/τ due to exact cancellation of the zero order contribution from the scattering term in the continuity equation.

It would be convenient to rewrite Eq. (6) in a more explicit way. If we take into account only elastic scattering, the Boltzmann equation can be considered on the isoenergetic shell (i.e., for $E_k = E_{k'}$). Then the scattering probability takes the form

$$P(\vartheta) = n_{\rm sc} v |f(\vartheta)|^2 \ , \tag{7}$$

where $n_{\rm sc}$ is the scatterers concentration and $f(\vartheta)$ is the scattering amplitude (we suppose scattering potential to be isotropic). And instead of Eq. (6) we obtain

$$X_D = 2\pi n_{\rm sc} v \int_0^\pi |f(\vartheta)|^2 \tau^D(\vartheta)\sin(\vartheta) d\vartheta \ . \tag{8}$$

Thus starting from a modified kinetic equation we obtain the renormalization of the diffusion constant. We now apply this approach to the propagation of electrons and light waves.

III. DIFFUSION CONSTANT RENORMALIZATION FOR ELECTRONS

Experiments have not yet been performed for the diffusion of electrons in a random material with high concentration of scatterers near resonance. Nevertheless the predictions for the diffusion constant renormalization for electrons and optical waves are qualitatively and quantitatively different. We hope that future experiments will show these differences. We now discuss the renormalization of the diffusion constant for electrons.

Let us consider a traditional elastic scattering problem for electrons.[4] If the incident wave function is $\Psi_{\rm in} = \exp\{ikz - iEt\}$ the scattered wave function is

$$\Psi_{\rm sc} = \frac{1}{r} f(\vartheta)\exp\{ikr - iEt\} \ . \tag{9}$$

When we are interested in a delay time, instead of s single incident plane wave we must consider a wave packet

$$\Psi_{\rm in} = \int dE\, \Phi(E-E_0)\exp\{iz\sqrt{2E} - iEt\} \ . \tag{10}$$

For simplicity we consider the wave packet which consists of the plane waves with the same direction of the wave vector. $\Phi(E)$ is an arbitrary narrow peaked (near zero) function, which we shall consider to be real. We also use the units in which the electron mass is equal to one. The scattered wave function in this case takes the form

$$\Psi_{\rm sc} = \int dE\, \Phi(E-E_0)\frac{1}{r} f(\vartheta)\exp\{ir\sqrt{2E} - iEt\} \ . \tag{11}$$

The position of the classical particle can be identified with the position of the maximum of the envelope of the wave packet which can be found from the equation

$$\partial(\Psi^*_\vartheta \Psi_\vartheta)/\partial t = 0 \ . \tag{12}$$

Here we must admit that there are alternative ways of obtaining correspondence between the classical particle and wave packet (see all the discussion concerning the problem of tunneling time[5]) but we use the most accepted one. Equation (12) can be rewritten in the form

$$\mathrm{Im}\left\{ \int dE\, EF(E)\Phi(E-E_0) \right. \\ \left. \times \int dE\, F^*(E)\Phi(E-E_0) \right\} = 0 \ , \tag{13}$$

where we have introduced the notation

$$F(E) = f(\vartheta)\exp\{ir\sqrt{2E} - iEt\} \ . \tag{14}$$

Expanding $F(E)$ near E_0 we obtain instead of (13) a simple equation (prime means the derivative with respect to E):

$$\mathrm{Im}[F'(E_0)F^*(E_0)] = 0 \ . \tag{15}$$

It would be also convenient to introduce the notation

$$f = |f|\exp\{i\phi\} \ . \tag{16}$$

Then Eq. (15) yields

$$t - \partial\phi/\partial E = r/\sqrt{2E} \ . \tag{17}$$

We immediately see that $\tau^D = \partial\phi/\partial E$. Hence the delay time can be expressed through the spherical waves phase shifts that are used traditionally in the scattering theory. Using for scattering amplitude the equation

$$f(\vartheta) = \frac{1}{2i(2E)^{1/2}} \sum_{n=0}^{\infty} (2n+1)(\exp\{2i\delta_n\} - 1)P_n(\cos\vartheta) \tag{18}$$

and the obvious identity

$$\partial\phi/dE = \mathrm{Im}[f^*\partial f/\partial E]/|f|^2 \ , \tag{19}$$

we obtain from Eq. (8)

$$X_D = 2\pi n_{\rm sc} v \int_0^\pi \mathrm{Im}[f^*(\vartheta)/\partial E]\sin(\vartheta)d\vartheta \ , \tag{20}$$

which by using Eq. (18) becomes

$$X_D=\frac{2\pi n_{\text{sc}}v}{k^2}\sum_{n=0}^{\infty}\sum_{n'=0}^{\infty}(2n+1)(2n'+1)\frac{\partial\delta_n}{\partial E}\sin\delta_n\sin(2\delta_n-\delta_{n'})\int_0^{\pi}P_n(\cos\vartheta)P_{n'}(\cos\vartheta)\sin\vartheta d\theta\ . \tag{21}$$

Performing the integration we obtain finally

$$X_D=\frac{4\pi n_{\text{sc}}v}{k^2}\sum_{n=0}^{\infty}(2n+1)\frac{\partial\delta_n}{\partial E}\sin^2\delta_n\ . \tag{22}$$

From Eq. (22) it is evident that the diffusion constant renormalization becomes important in the vicinity of resonance due to large values in this field of the multiplier $\partial\delta/\partial E$. It is this multiplier which singles out the correction of the kinetic equation we took into account from all other corrections of the order of n_{sc}. Hence to observe the phenomenon the most favorable is the case when the scattering potential has quasidiscrete levels near the Fermi energy. The application of Eq. (22) to this case will be worked out elsewhere.[6] We should mention that the renormalization of the diffusion constant for electrons coincides with the result obtained in Ref. 2 on the basis of qualitative considerations.

IV. DIFFUSION CONSTANT RENORMALIZATION FOR OPTICAL WAVES

We now show that the renormalization of the diffusion constant for optical waves though formally similar is in fact different from that for electrons.

We start first from the Helmholtz equation:

$$\nabla^2\psi+\frac{\omega^2}{c^2}m(r)\psi=0\ , \tag{23}$$

where $m(r)$ is the coordinate-dependent refraction index. When we consider scattering of light from a dielectric ball, we have $m(r)=m$ inside the ball and $m(r)=1$ outside. We immediately see that Eq. (23) is equivalent to the Schrödinger equation describing the scattering of the electron on a rectangular potential well (spherically symmetrical). The energy of the electron $E=\omega^2/2c^2$, and the potential inside the well $V=-E(m-1)$. This energy dependence of the potential leads to an interesting result. For proper quantum mechanical problems (with energy-independent potential) the derivatives of phase shifts which enter into Eq. (22) can be either positive or negative, yielding a delay time or an advance time.[3] For Eq. (23) all the phase shifts are increasing functions of energy. Therefore the delay time, though first introduced for electron scattering, is more meaningful for the scattering of electromagnetic waves. The energy dependence of the effective scattering potential in the latter case also leads to a more resonant character of the scattering and hence to larger diffusion constant renormalization.

In a more systematic approach we must start not from Helmholtz equations but from Maxwell equations. In this framework the scattering of electromagnetic radiation from a dielectric sphere is described by Mie theory. Let the plane-wave incident on a dielectric sphere of radius d be described by the equation

$$E=a_x\exp\{-ikz+i\omega t\}\ , \tag{24}$$

where E is the electric field (it is enough for us to keep track only of the electric field) and a_x is the unit vector along x axis. Then the scattered field at large distances from the sphere can be written in the form[7]

$$\begin{aligned}&E_r=0\ ,\\&E_\vartheta=-\frac{i}{kr}\exp\{-ikr+i\omega t\}\cos\varphi S_2(\vartheta)\ ,\\&E_\phi=\frac{i}{kr}\exp\{-ikr+i\omega t\}\sin\varphi S_1(\vartheta)\ ,\end{aligned} \tag{25}$$

where S_1 and S_2 are the so called amplitude functions (see Appendix).

We are interested in scattering of the unpolarized light. It means that we have to consider the incident plane wave as an equipartition sum of plane waves with all possible directions of polarization, the latter being noncoherent. This can be taken into consideration simply by averaging all the equations with respect to φ. As a result we again obtain the traditional Boltzmann equation with the probability of scattering:

$$P(\vartheta)=\tfrac{1}{2}cn_{\text{sc}}[|S_1(\vartheta)|^2+|S_2(\vartheta)|^2]\ . \tag{26}$$

The delay-time calculations in this situation is more complicated. Due to different energy dependences of $S_1(\vartheta)$ and $S_2(\vartheta)$ the state (noncoherent) which is scattered by an angle ϑ is split into two parts; one which was scattered with the probability $cn_{\text{sc}}|S_1(\vartheta)|^2/2$ with the delay time $\partial\phi_1/\partial\omega$ and another, scattered with the probability $cn_{\text{sc}}|S_2(\vartheta)|^2/2$ with the delay time $\partial\phi_2/\partial\omega$, where ϕ_1 and ϕ_2 are, respectively, the phases of S_1 and S_2. So for

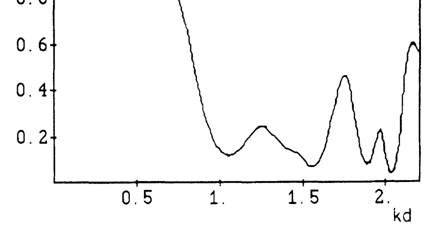

FIG. 1. Diffusion coefficient renormalization for 36 vol% dielectric spheres ($m=2.73$) as a function of size parameter kd.

diffusion coefficient renormalization we have

$$X_D = \pi n_{\mathrm{sc}} c \int_0^{\pi} \sum_{i=1}^{2} \mathrm{Im} \left[S_i^*(\vartheta) \frac{\partial S_i(\vartheta)}{\partial \omega} \right] \sin(\vartheta) d\vartheta \ . \tag{27}$$

Substituting into this equation the results for S_i, which are calculated in the Appendix, and integrating over ϑ we obtain the analog of Eq. (22)

$$X_D = \frac{2\pi n_{\mathrm{sc}} c}{k^2} \sum_{n=1}^{\infty} (2n+1) \left[\frac{\partial \alpha_n}{\partial \omega} \sin^2\alpha_n + \frac{\partial \beta_n}{\partial \omega} \sin^2\beta_n \right] . \tag{28}$$

Finally for diffusion coefficient renormalization we obtain

$$\frac{D}{D_0} = \left[1 + \frac{3f}{2x^2} \sum_{n=1}^{\infty} (2n+1) \left[\frac{\partial \alpha_n}{\partial x} \sin^2\alpha_n + \frac{\partial \beta_n}{\partial x} \sin^2\beta_n \right] \right]^{-1} , \tag{29}$$

where f is the volume fraction of the Mie spheres, and $x = kd = \omega d / c$ is the size parameter. In Fig. 1 we plot this renormalization coefficient as a function of the size parameter for the external parameters corresponding to the experiment of Ref. 1 ($f = 0.36$ and $m = 2.73$). When we compare our graph with the corresponding graph of Ref. 1 (Fig. 4 of Ref. 1), we see that for our curve the resonance effects are much more explicit. This fact can be seen immediately when comparing our equation (29) and Eq. (12) of Ref. 1. Dividing the expression in large parentheses in (29) in two parts,

$$\frac{\partial \alpha_n}{\partial x} \sin^2\alpha_n + \frac{\partial \alpha_n}{\partial x} \sin^2\beta_n = \frac{1}{2} \left[\frac{\partial \alpha_n}{\partial x} + \frac{\partial \alpha_n}{\partial x} \right] - \frac{1}{2} \left[\frac{\partial \alpha_n}{\partial x} \cos 2\alpha_n + \frac{\partial \beta_n}{\partial x} \cos 2\beta_n \right] , \tag{30}$$

one can easily see that $X_D = \bar{X}_D + X_D^{fl}$, where $\bar{X}_D$ coincides with the result of Ref. 1 and X_D^{fl} is the strongly fluctuating correction to this result.

The exact comparison of our result with the experimentally measured value of the diffusion constant[1] is difficult because of the polydispersive character of the scatterers (in experiment the size parameters of the spheres lie within $x = 0.8$ and $x = 2.5$ and the size parameter distribution function is unknown). But the qualitative conclusion is clear—resonance scattering drastically decreases diffusion constant. One statement concerning the interpretation of the result obtained [Eq. (29)] should be added. Our approach gives the renormalization of the diffusion constant—the quantity which is measured in the experiment. In the case of resonance scattering the simple connection between the velocity and the diffusion constant no longer holds.

V. SUMMARY

We proposed a simple and physically meaningful modification of the traditional kinetic equation for the resonance scattering. This modification is based on the fact that resonance scattering is characterized not only by large scattering amplitude but also by a large delay time. This fact gives us the opportunity to single out the most important corrections to the diffusion constant which is linear with respect to scatterers concentration. We obtained the renormalization of the diffusion constant both for electrons and for light propagation. The results for the light agree with the recent experiments.

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APPENDIX

Here we give the main results of the Mie theory. The amplitude functions are given by the equations

$$\begin{aligned} S_1(\vartheta) &= \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \{ a_n \pi_n(\cos\vartheta) + b_n \tau_n(\cos\vartheta) \} , \\ S_2(\vartheta) &= \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \{ b_n \pi_n(\cos\vartheta) + a_n \tau_n(\cos\vartheta) \} , \end{aligned} \tag{A1}$$

where

$$\begin{aligned} \pi_n(\cos\vartheta) &= \frac{1}{\sin\theta} P_n^1(\cos\vartheta) , \\ \tau_n(\cos\vartheta) &= \frac{d}{d\theta} P_n^1(\cos\vartheta) \end{aligned} \tag{A2}$$

(P_n^1 is the associated Legendre polynomial) and

$$\begin{aligned} a_n &= \tfrac{1}{2}(1 - \exp\{-2i\alpha_n\}) , \\ b_n &= \tfrac{1}{2}(1 - \exp\{-2i\beta_n\}) , \end{aligned} \tag{A3}$$

where α_n and β_n are the so-called phase angles, given by the equations

$$\begin{aligned} \tan\alpha_n &= \frac{\psi_n'(mkd)\psi_n(kd) - m\psi_n(mkd)\psi_n'(kd)}{\psi_n'(mkd)\chi_n(kd) - m\psi_n(mkd)\chi_n'(kd)} , \\ \tan\beta_n &= \frac{m\psi_n'(mkd)\psi_n(kd) - \psi_n(mkd)\psi_n'(kd)}{m\psi_n'(mkd)\chi_n(kd) - \psi_n(mkd)\chi_n'(kd)} , \end{aligned} \tag{A4}$$

where

$$\psi_n(z) = z j_n(z), \quad \chi_n(z) = z n_n(z) , \tag{A5}$$

and j_n and n_n are the spherical Bessel functions.

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