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Scattering of Waves by an Ensemble of Fluctuating Potentials

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ABSTRACT

We consider the scattering of waves by a system of potentials with continuously variable scattering amplitudes, which fluctuate about a fixed mean value. The problem is formulated in terms of a generalized correlation function, which combines correlations in position and in scattering amplitude. We use the theory to estimate the shape of maxima which occur in the mobilities of electrons injected into the conduction bands of the condensed rare gases.

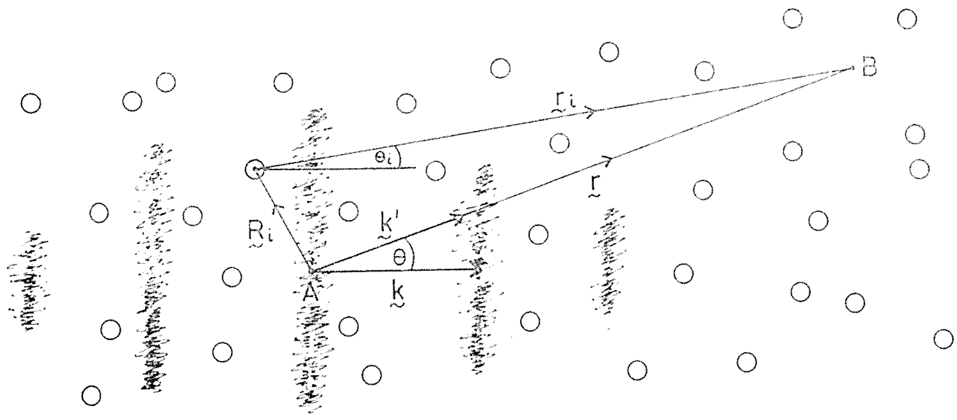
§ 1. INTRODUCTION

IN most physical problems involving the scattering of waves by a system of scatterers, the potentials causing the scattering are either identical, or range over a small number of allowed values. In general the potentials are distributed in the scattering region in a way describable in terms of spatial correlation functions. There are, however, cases where not only the positions but also the magnitudes and shapes of the potentials are variable, and correlated.

Probably the simplest example which illustrates this is the scattering of sound waves propagating through a liquid containing bubbles, where both the bubble sizes and their positions are correlated. A more complicated but more interesting problem is the explanation of the mobility maxima of electrons injected into liquid argon, krypton, and possibly xenon (Schnyders, Rice and Meyer 1966). I have proposed that these maxima are due to the fact that the average scattering length $\langle a \rangle$ of the electron passes through zero at a certain density n_0 (Lekner 1968). At this density the mobility is limited only by the fluctuations in the effective electron–atom potential, and reaches a maximum. One of the purposes of this paper is to give a qualitative description of the shape of this maximum.

§ 2. THE SCATTERING PROBLEM

We shall treat the following problem: the scattering of waves by an ensemble of particles (nuclei, atoms, or bubbles), the potentials at which fluctuate about an average value. The scattering is taken to be weak (as it is near the mobility maximum, where $\langle a \rangle = 0$), and the potentials spherically symmetric. In the space between scatterers the wave propagates as $\exp ikz$, and each scatterer sends out a small proportion of the wave as a radially propagating scattered wave $r^{-1}f(k, \theta) \exp ikr$. Here $f(k, \theta)$ is the scattering amplitude, which in general is a function both of the wave-number k and of the angle of scattering θ. We want to calculate the scattering due to a system of fluctuating potentials. The derivation given below parallels that for the well-known case of identical scatterers (Morse and Feshbach 1953). Consider a wave propagating in the system (figure).



Scattering of a wave by an ensemble of scatterers.

The probability of the wave being scattered from the region about A to the region about B, where B is outside the original path of propagation of the wave at A, is given by calculating the absolute square of the total scattered wave arriving at B. Take $z=0$ at A. Then the phase of the incident wave arriving at the ith scatterer at $\mathbf{R}_i$ is $\exp i\mathbf{k}\cdot\mathbf{R}_i$, and this gives at B the scattered wave:

$$r_i^{-1}f_i(k, \theta_i) \exp i(kr_i + \mathbf{k}\cdot\mathbf{R}_i). \quad \quad (1)$$

The total scattered wave at B is therefore:

$$\psi_s(r, \theta) = \sum_i r_i^{-1}f_i(k, \theta_i) \exp i(kr_i + \mathbf{k}\cdot\mathbf{R}_i). \quad \quad (2)$$

This is equal to:

$$r^{-1} \exp ikr \sum_i \{f_i(k, \theta) \exp i\mathbf{K}\cdot\mathbf{R}_i + \text{terms of order } R_i/r\}. \quad \quad (3)$$

where

$$\mathbf{K} = \mathbf{k} - \mathbf{k}', \quad K = 2k \sin \theta/2. \quad \quad (2)$$

The sum on i should, physically, extend only over atoms which are within the extent of the unscattered wave packet. When there is no long-range order, however, the phases of terms with large R_i's are uncorrelated and these terms cancel. Only the phases of waves scattered from correlated atoms contribute. Therefore, in non-crystalline substances, we can at the same time enlarge the sum to be over all scatterers, and omit the terms of order R_i/AB. The absolute square of (3) then gives the differential scattering cross section per particle:

$$\sigma(k,\theta) = N^{-1}r^2|\psi_s(r,\theta)|^2 = N^{-1}\left|\sum_{i=1}^{N} f_i(k,\theta)\exp i\mathbf{K}\cdot\mathbf{R}_i\right|^2. \tag{5}$$

To calculate physical quantities, for example the attenuation coefficient for sound waves, or the mobility of electrons, we need the ensemble average of (5). This is:

$$\begin{aligned}\langle\sigma(k,\theta)\rangle &= N^{-1}\left\langle \sum_i |f_i(k,\theta)|^2 + \sum_{i\neq j}\sum f_i(k,\theta)f_j^*(k,\theta)\exp i\mathbf{K}\cdot(\mathbf{R}-\mathbf{R}_j)\right\rangle \\ &= \langle|f(k,\theta)|^2\rangle\Big\{1+(N\langle|f(k,\theta)|^2\rangle)^{-1} \\ &\qquad\times\left\langle\sum_{i\neq j}\sum f_i(k,\theta)f_j^*(k,\theta)\exp i\mathbf{K}\cdot(\mathbf{R}-\mathbf{R}_j)\right\rangle\Big\}.\end{aligned} \tag{6}$$

If all the scattering amplitudes $f_i(k,\theta)$ were identical, this ensemble average could be evaluated in terms of the usual pair correlation function:

$$g(\mathbf{r}-\mathbf{r}') \equiv (V/N)^2\left\langle\sum_{i\neq j}\sum \delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j)\right\rangle. \quad . \quad . \quad . \tag{7}$$

By analogy with g, let us therefore define a generalized correlation function G, which includes correlations in both position and scattering amplitude:

$$\begin{aligned}G(\mathbf{r}-\mathbf{r}';\,k,\theta) &\equiv \langle|f(k,\theta)|^2\rangle^{-1}(V/N)^2 \\ &\qquad\times\left\langle\sum_{i\neq j}\sum f_i(k,\theta)f_j^*(k,\theta)\delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j)\right\rangle.\end{aligned} \tag{8}$$

Then the ensemble average scattering cross section can be written:

$$\begin{aligned}\langle\sigma(k,\theta)\rangle &= \langle|f(k,\theta)|^2\rangle\left\{1+\frac{N}{V^2}\int d\mathbf{r}\int d\mathbf{r}'\,G(\mathbf{r}-\mathbf{r}';\,k,\theta)\exp i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}')\right\} \\ &= \langle|f(k,\theta)|^2\rangle\left\{1+\frac{N}{V}\int d\mathbf{R}\,G(\mathbf{R};\,k,\theta)\exp i\mathbf{K}\cdot\mathbf{R}\right\}.\end{aligned} \tag{9}$$

The evaluation of the cross section or attenuation coefficient is thus reduced to the calculation of the Fourier transform of the generalized correlation function defined by (8).

§ 3. The Long-wavelength Limit

As k tends to zero, the scattering amplitude $f(k, \theta)$ generally becomes independent of both k and θ: $f(k, \theta) \to -a$, where a is the scattering length. The formulae of the previous section then simplify considerably:

$$G(R) \equiv G(|\mathbf{r}-\mathbf{r}'|)$$
$$= \langle a^2\rangle^{-1}(V/N)^2 \left\langle \sum_{i\neq j}\sum a_i a_j \delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j)\right\rangle, \qquad (10)$$

$$\langle\sigma(k,\theta)\rangle = \langle a^2\rangle \left\{1 + \frac{N}{V}\int d\mathbf{R}\, G(R) \exp i\mathbf{K}\,.\,\mathbf{R}\right\}. \qquad (11)$$

The generalized correlation function G becomes independent of k and θ, and is a function of scalar R only. $G(R)$ will normally die off rapidly with distance, but in the special cases of vanishing fluctuations, or long-range correlations in fluctuations, $G(\infty)$ may not be zero. In this case the integral in (11) can be written as:

$$(2\pi)^3 G(\infty)\delta(\mathbf{K}) + \int d\mathbf{R}\,(G(R) - G(\infty)) \exp i(\mathbf{K}\,.\,\mathbf{R}). \qquad (12)$$

The delta function term corresponds to pure forward scattering, and does not contribute to attenuation of the wave. Such a term, it if exists, is therefore to be omitted from the cross section (11) (and also from the more general term (9)). Since $G(R) - G(\infty)$ has finite range, in the limit of long waves the cross section is isotropic. The total cross section is therefore:

$$\langle\sigma\rangle = 4\pi\langle a^2\rangle\left\{1 + n\int d\mathbf{R}\,(G(R) - G(\infty))\right\}. \qquad (13)$$

This equation, together with (10), gives a generalization of the well-known scattering law for a fluid of identical scatterers:

$$\langle\sigma\rangle = 4\pi a^2\left\{1 + n\int d\mathbf{R}\,(g(R) - 1)\right\} = 4\pi a^2\,.\,nkT\,\chi_T, \qquad (14)$$

where $n = N/V$, T is the absolute temperature, and χ_T the isothermal compressibility.

§ 4. The Shape of the Mobility Maxima

When electrons are injected into the conduction band of the condensed rare gases (solid or liquid), they thermalize at the bottom of the band and move easily under the influence of an electric field. Their mean free paths are large, about 100 Å (Lekner 1967) so that the kinetic picture applies and we can use the Lorentz formula to calculate the mobility:

$$\mu = \tfrac{2}{3}\left\{\frac{2}{\pi m kT}\right\}^{1/2} \frac{e}{n\langle\sigma(k)\rangle}, \qquad (15)$$

where

$$\langle\sigma(k)\rangle = 2\pi\int_0^\pi d\theta \sin\theta(1-\cos\theta)\langle\sigma(k,\theta)\rangle. \qquad (16)$$

Since the electrons are thermalized, their wavelength $2\pi/k$ is long (also about 100 Å) so that only s-wave scattering is important and we may use (13) for the cross section. The integral in (13) can be estimated as follows. Write $a_i = \langle a \rangle + \Delta a_i$ in the definition (10) of $G(R)$:

$$G(R) \equiv G(|\mathbf{r}-\mathbf{r}'|) = \frac{\langle a \rangle^2}{\langle a^2 \rangle}\left(\frac{V}{N}\right)^2 \left\langle \sum_{i \neq j}\sum \delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j) \right\rangle$$

$$+ \frac{\langle a \rangle}{\langle a^2 \rangle}\left(\frac{V}{N}\right)^2 \left\langle \sum_{i \neq j}\sum (\Delta a_i + \Delta a_j)\delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j) \right\rangle$$

$$+ \frac{1}{\langle a^2 \rangle}\left(\frac{V}{N}\right)^2 \left\langle \sum_{i \neq j}\sum \Delta a_i \Delta a_j \delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j) \right\rangle. \quad (17)$$

Referring to (7), we see that the first term is simply $\langle a \rangle^2/\langle a^2 \rangle$ times the pair correlation function $g(R)$, which has the large R limit $g(\infty) = 1$. This first term is a pure spatial correlation function, while the other two contain correlations in both space and the Δa_i. Since Δa_i takes both positive and negative values, we may expect the second two parts of $G(R)$ to have positive and negative regions, and their integrals in (13) to be small because of cancellation. We will therefore approximate $\langle \sigma \rangle$ by:

$$4\pi \langle a^2 \rangle \left\{ 1 + \frac{\langle a \rangle^2}{\langle a^2 \rangle} n \int d\mathbf{R}(g(R)-1) \right\}.$$

Since $n\int d\mathbf{R}(g(R)-1) = nkT\chi_T - 1$, the total cross section becomes:

$$\langle \sigma \rangle \simeq 4\pi\{\langle a^2 \rangle + \langle a \rangle^2 (nkT\chi_T - 1)\}. \quad (18)$$

Now $a_i = \langle a \rangle + \Delta a_i$ and $\langle a^2 \rangle = \langle a \rangle^2 + \langle \Delta a^2 \rangle$. Thus:

$$\langle \sigma \rangle \simeq 4\pi\{\langle \Delta a^2 \rangle + nkT\chi_T \langle a \rangle^2\}. \quad (19)$$

This expression has a simple intuitive interpretation: the total scattering by the system of fluctuating potentials is the sum of scattering by uncorrelated fluctuations, proportional to $\langle \Delta a^2 \rangle$, and correlated average scattering, proportional to $\langle a \rangle^2$. The terms omitted from (19) correspond to interference between the average and the fluctuation scattering, and to correlation between different fluctuations.

We come finally to the shape of the mobility maximum. The maximum occurs at a density n_0 where $\langle a \rangle = 0$. Near n_0 we can therefore write $\langle a \rangle = \gamma(n-n_0)$, where $\gamma = (d\langle a \rangle/dn)_0$. From (15) and (19) we obtain the Lorentzian form:

$$\frac{\mu(n)}{\mu(n_0)} \simeq \frac{\langle \Delta a^2 \rangle}{\langle \Delta a^2 \rangle + nkT\chi_T\gamma^2(n-n_0)^2}. \quad (20)$$

This result has a surprising implication. Since the mean square fluctuation $\langle \Delta a^2 \rangle$ has been estimated (Lekner 1968) to be proportional to $nkT\chi_S$, and since at the critical point χ_T diverges while the adiabatic compressibility χ_S remains finite, the peak may actually be *sharper* if n_0 occurs near the critical point. This may explain why Schnyders, Rice and Meyer did not in fact observe a peak in argon. In any case more detailed experiment is desirable, to test both the predicted variation of $\mu(n_0)$ with the thermodynamic variables, and the predicted shape given above.

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